Relevance of Cu-3d multiplet structure in models of high Tc cuprates

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We revisit the problem of the spectra of two holes in a CuO$_2$ layer, modeled as a Cu-d$^8$ impurity with full multiplet structure coupled to a full O-2p band as an approximation to the local electronic structure of a hole doped cuprate. Unlike previous studies that treated the O band as a featureless bath, we describe it with a realistic tight binding model. While our results are in qualitative agreement with previous work, we find considerable quantitative changes when using the proper O-2p band structure. We also find (i) that only the ligand O-2p orbitals play an essential role, within this impurity model; (ii) that the three-orbital Emery model provides an accurate description for the subspace with $^1A_1$ symmetry, which includes the ground-state in the relevant region of the phase diagram; (iii) that this ground-state has only $\sim 50\%$ overlap with a Zhang-Rice singlet; (iv) that there are other low-energy states, in subspaces with different symmetries, that are absent from the three-orbital Emery model and its one-band descendants. These states play an important role in describing the elementary excitations of doped cuprates.

I. INTRODUCTION

A central issue still under debate in the study of high-$T_c$ cuprate superconductors is the proper minimal model that correctly captures the low-energy properties, specifically the precise nature of the states closest to the Fermi level. Historically, Anderson proposed that the essential physics can be understood based on the single-band Hubbard model, where the band is identified as the antibonding band of Cu-3d$_z$-$y^2$ band Hubbard model, where the band is identified as the antibonding band of Cu-3d$_z$-$y^2$ and O-2p orbitals$^1$. The even simpler t-J model additionally discards all charge carriers move in a spin background. This has been extensively studied away from half-filling and is believed to provide a good description of the Hubbard model in the strong coupling limit $J/t = 4t/U \ll 1$. However, their common intrinsic assumption is that the cuprate parents compounds, which are known to be effective Mott-Hubbard insulators,$^2$ can instead be modeled as charge transfer insulators,$^2$ and can instead be modeled as charge transfer insulators.$^2$

The need to understand the importance of explicitly including the O ions hosting the doped holes,$^4$ motivated the study of the three-band Emery model$^5$ which includes the Cu d$_{x^2-y^2}$ and the two ligand O-2p$_a$ orbitals in the non-magnetic unit cell. The key idea underlying the expected equivalence of the one- and three-orbital scenarios was proposed by Zhang and Rice, who argued that the doped holes occupy a certain linear combination of O orbitals that is locked into a Zhang-Rice singlet (ZRS) with the hole (spin) residing on the central Cu site. Projecting onto these ZRS then allows one to map the three-band Emery model onto a single-band t-J model$^6$, although a more careful treatment reveals the existence of additional terms ignored by the t-J Hamiltonian.$^5$,

Although various analytical approximations and extensive numerical studies of these model Hamiltonians have revealed many insights in the past decades, the validity of the ZRS concept$^5$ and more generally the equivalence – or lack thereof – between the low-energy properties of one- and three-orbital models are still under debate. On one hand, the existence and stability of states with ZRS-like character have been confirmed in previous photoemission experiments$^9$,$^{10}$ on the other hand, recent calculations contrasting the dynamics of a single doped hole in the one-band vs. the three-band model revealed qualitative differences$^{11}$,$^{12}$ such as the essential vs. the minor role played by the background spin-fluctuations, respectively. Moreover, a recent high-energy optical conductivity study questioned the ZRS argument by revealing a strong mixture of singlet and triplet configurations in the lightly hole-doped Zn-LSCO single crystal.$^6$ Furthermore, this system exhibits strong ferromagnetic correlations between Cu spins near the doped holes, as predicted by the three-band model$^8$.

During the same period when the ZRS was proposed, Eskes et al. carried out a more general study that included the multiplet structure of the Cu, i.e. all singlet and triplet irreducible representations in the $D_{4h}$ point group spanned by two d holes ($d^8$-type configurations) and their corresponding Coulomb and exchange interaction.$^{13}$,$^{14}$ Besides explicitly considering the O band, this was achieved at the cost of simplifying the model to consist of a single Cu impurity hybridizing with a broad O band described in terms of a featureless, semielliptical density of states.

This work confirmed that the first ionization state starting from a Cu-d$^9$ state and a full O-2p band, which ends with the two hole eigenstates involving $d^8$ multiplets and various continuum states, is indeed in the $^1A_1$ symmetry channel consistent with the symmetry of the ZRS, but also found that the energy difference between the lowest ionization states for various symmetry channels is rather small. Moreover, these differences are strongly dependent on the electronic structure, which in turn is likely to depend quite strongly on doping levels. These results cast doubt on whether it suffices to include only the $d_{x^2-y^2}$ orbital instead of the full 3d multiplet structure of the Cu-d$^8$, when modeling these materials.

Most members of our community believe that the Cu-d$_{x^2-y^2}$ orbital is the only d-orbital needed to account for
the essential physics of cuprates, explaining why there are so few studies on the effects of the multiplet structure, compared to the very extensive investigations of the one- and three-band models involving only Cu $d_{x^2-y^2}$ orbital and/or its ZRS daughter. However, there are both theoretical and experimental results pointing out the importance of non-planar orbitals like Cu-$3d_{3z^2-r^2}$ and/or O-$2p_z$. In particular, the importance of Cu-$3d_{3z^2-r^2}$ is revealed by the recent discovery of the cuprate superconductor Ba$_2$CuO$_4\delta$ with critical temperature $T_c \sim 70$ K, where based on the compressed c-axis bond length, it is claimed that some doped holes are likely in the $d_{3z^2-r^2}$ orbital. Early Auger spectroscopic experiments clearly demonstrated strong multiplet effects ranging over a large energy scale in Cu compounds such as CuO and Cu$_2$O. In fact, in Cu$_2$O the lowest energy Cu $d^8$ state is a triplet state consistent with the Hund’s rule expectations. As pointed out by Eskes, the crossing of the singlet and triplet states in the cuprate parent compounds is a result of the strong O character in these states due to the strong Cu-O hybridization and the fact that the Cu $d^8$ states are pushed out of the top of the O 2p band, resulting in the lowest energy singlet bound state.

Also important evidence for the significant role of the multiplets comes from X-ray absorption (XAS) experiments that have shown, upon increased doping, a strong change from purely $x, y$ polarized absorption to one including a large contribution of $z$ polarized intensity for the O and Cu core-to-valence transition. This implies that there are doped holes whose wavefunctions have a considerable component in the Cu-$d_{3z^2-r^2}$ or O-$p_z$ orbitals. These results point to the breakdown of the single-band or even three-band (Cu-$d_{x^2-y^2}$ based) approaches to the description of the phase diagram of cuprate superconductors.

This motivates us to revisit the importance of the full Cu-$3d$ multiplet structure and explore its effects on the low-energy properties of cuprate models. In order to obtain numerically exact results, we follow Eskes et al. and study a single Cu impurity with all its 3d orbitals included. In contrast to this earlier work, however, we properly embed this Cu impurity in a square lattice of O 2p orbitals, with a realistic band-structure. This allows us to contrast models containing only the O-2p ligand orbitals vs. those also including the other in-plane orbital, and also the $p_z$ orbital. The results reveal the importance of the realistic modeling of the O bath, and which O-2p orbitals play an essential role. It is important to note that the linear combination of O 2p orbitals that hybridize with the various Cu 3d states live in different energy regions of the O 2p band structure and this strongly influences the importance of this hybridization. For example, the $d_{x^2}$ orbital hybridizes with the O-$p_z$ and $p_x \pi$-bonding orbitals while the $d_{x^2-y^2}$ orbital hybridizes with the O-2p $\sigma$-bonding orbitals. Besides, the linear combination of the O-2p orbitals that hybridize with $d_{x^2-y^2}$ orbital is different in their relative phases than with the $d_{3z^2-r^2}$ orbital. We will see below how this strongly influences the appearance and relative energies of bound states pushed out of the O band for the various symmetries. Furthermore, by calculating the Cu-3d electron removal spectra in various symmetry channels of the $D_{4h}$ point group, we are able to identify the character (symmetry, spin, and orbital composition) of the first ionization state, and to gauge its similarity to a ZRS. Finally, our results reveal strong similarities between the model including all multiplets and the conventional three-orbital Emery model if we restrict ourselves to the lowest energy electron removal states, although open issues still remain. However, if one wants to describe the spectroscopies like ARPES going up to one or more eV below the Fermi energy as, for example, in descriptions of the so called “waterfall” feature, it is essential to include all of the multiplets since they all have appreciable spectral weights extending to energies well above 1 eV.

This paper is organized as follows. In Sec. II, we define our model and the variational method employed to study its single-doped hole eigenstates. Sec. III discusses the resulting spectra for various cases considered. The summary and future issues to be addressed are presented in Sec. IV.

II. MODELS AND METHODS

A. Multi-orbital models with a single Cu impurity

We simplify the description of a CuO$_2$ plane by replacing the Cu lattice with a single Cu impurity properly embedded in a square lattice of O orbitals; the resulting problem can be solved exactly, unlike the corresponding one for the full CuO$_2$ lattice. The central part of the system, consisting of the Cu impurity and its 4 nearest neighbor (NN) O ions, is depicted in Fig. 1.

The Hamiltonian describing this system is

$$H = E_s + K_{pd} + K_{pp} + V_{dd} + V_{pp}$$

$$E_s = \sum_{m\sigma} \epsilon_d(m)d_{m\sigma}d_{m\sigma} + \sum_{j\sigma} \epsilon_p p_{j\sigma}p_{j\sigma}$$

$$K_{pd} = \sum_{\langle i,j \rangle m\sigma} (T_{pp}^{pd})_{m\sigma}p_{j\sigma} + h.c.$$  

$$K_{pp} = \sum_{\langle i,j \rangle m\sigma} (T_{pp}^{pp})_{m\sigma}p_{j\sigma}p_{j\sigma} + h.c.$$  

$$V_{dd} = \sum_{\bar{m}\bar{n}} U(m_1m_2m_3m_4)d_{m_1\bar{m}}d_{m_2\bar{m}}d_{m_3\bar{m}}d_{m_4}$$  \hspace{1cm} (1)$$

Here, the simplified notation $\bar{m} = m + \sigma s_\sigma$ in $V_{dd}$ with $x = 1, 2, 3, 4$ denote the spin-orbital. The $E_s$ represents the onsite energies, where $d_{m\sigma}^\dagger (d_{m\sigma})$ creates (destroys) a hole in the Cu-3d orbital $m$ with on-site energy $\epsilon_d(m)$ and spin $\sigma$, while $p_{j\sigma}^\dagger (p_{j\sigma})$ creates (destroys) a hole at the O lattice site $j$, in its 2p orbital $n$ with energy $\epsilon_p$. The term $K_{pd}$ is the hopping between d and p orbitals, while $K_{pp}$ is the hopping between two p orbitals, with the Coulomb term $V_{dd}$ representing the interaction between d and p orbitals. The parameters $T_{pp}^{pd}$ and $T_{pp}^{pp}$ in $K_{pd}$ and $K_{pp}$ respectively, are given by the hopping integrals between the respective orbitals.

In Eq. (1), $U(m_1m_2m_3m_4)$ is the on-site interaction between the d orbitals, where $U(m_1m_2m_3m_4)$ represents the Coulomb repulsion between the d orbitals at different sites. The $V_{dd}$ term is crucial in describing the Coulomb interaction between the d orbitals, which plays a significant role in determining the d band structure and the resulting electronic properties of the system.
that the parameters. Finally, the onsite d-hole energies \(\epsilon_d(m) = 0\) are assumed to be independent of \(m\), thus omitting the point-charge crystal splitting. This is expected to be a good approximation because it is the hybridization with the O orbitals, included in our model, that accounts for most of the difference between the effective on-site energies of the 3d levels. As a result, the charge-transfer energy \(\Delta = \epsilon_p\).

\(K_{pd}\) and \(K_{pp}\) describe the Cu-O and O-O hoppings, respectively. The labels \(j, j'\) run over the positions of the O atoms, \((j, j')\) is a sum over the four O adjacent to the \(j^{th}\) Cu site, and only NN \(pp\) hopping is included. Following Slater and Koster,\(^{33}\) the Cu-O and O-O hopping integrals \(T_{mn}^{pd}\) and \(T_{nn'}^{pp}\), are listed in Table I. Throughout the paper, energies are measured in eV.

In the following we focus on four possible models: (i) N3, where \(m = b_1\) and \(n \in \{p_{x_1}, p_{y_1}\}\), i.e. the usual three-band Emery model where only the ligand orbital is kept for each O; (ii) N7, where \(m \in \{a_1, b_1, b_2, e_x, e_y\}\) and \(n \in \{p_{x_1}, p_{y_1}\}\), i.e. multiplet-like physics is added to the Emery model; and (iii) N9, where \(m \in \{a_1, b_1, b_2, e_x, e_y\}\) and \(n \in \{p_{x_1}, p_{y_1}, p_{x_2}, p_{y_2}\}\), i.e. for each O we keep both in-plane 2p orbitals; and (iv) N11, where \(m \in \{a_1, b_1, b_2, e_x, e_y\}\) and \(n \in \{p_{x_1}, p_{y_1}, p_{x_2}, p_{y_2}\}\), i.e. for each O we keep all three O-2p orbitals.

For the N9 and N11 models we use \(T_{b_2}^{pd} = T_{b_1}^{pd}/2\), so that \(t_{pd\sigma} = \sqrt{3}t_{pd\sigma}/4\). We emphasize that all the Cu-O hybridization parameters \(t_{pd}, t_{pp}, t_{pd\sigma}, t_{pdx}, t_{pp\sigma}\) are taken to be positive, and the signs due to the orbitals’ overlap (see Fig. 1) are explicitly indicated in Table I.

In this impurity model, the single electron removal states of the undoped Cu-d\(^{10}\) system are due to the hybridization of various Cu-d\(^9\) configurations with the full O band 2p\(^8\), in other words there is a single hole in the system and the problem can be solved trivially. As expected, if the bottom of the oxygen band at \(\Delta - 4t_{pp} > \epsilon_d\), then the system lies in the positive charge-transfer regime, where the lowest energy electron removal state is dominated by an (antibonding) orbital of \(b_1\) symmetry that has predominantly Cu-d\(^9\) character; this is mixed with a ligand hole d\(^{10}\)LL states which have a low amplitude of probability. This confirms that if there is a single hole in the system, it is indeed located primarily on the Cu as in the ground state of the undoped cuprates.

Photoemission or doping of the system with one hole from its ground state of mainly d\(^9\) character removes another electron. The resulting two-hole problem is exactly soluble using the Cini-Sawatzky method.\(^{34}\) The two-hole problem requires taking into account the d-d Coulomb and exchange interactions \(U(mn'm'n')\) described by \(V_{dd}\). These are listed in Table I, which contains the interaction matrices for all singlet/triplet irreducible representations of the \(D_{4h}\) point group spanned by two d holes, in terms of the Racah parameters \(A, B, C\). Throughout the paper, the free-ion values \(B = 0.15\) eV, \(C = 0.58\) eV are adopted and \(A\) is treated as a variable.

If we chose to focus on relevance to experiments, we would need to calculate the d-electron removal spectrum \(A_{d}^{T}(\omega)\) which can be compared to photoemission experiments, and the d\(^8\) partial density of states (PDOS) for the various two-hole irreducible representations (symmetry channels) \(A_{d}^{T}(\omega)\), linked to the resonant

| TABLE I: The Cu-O and O-O hopping integrals \(T_{mn}^{pd}\) and \(T_{nn'}^{pp}\) with \(m \in \{b_1(d_{x^2-y^2}), a_1(d_{3z^2-r^2}), b_2(d_{xy}), e_x(d_{xz}), e_y(d_{yz})\}\) for various models. The hoppings involving \(p_{x_1}, p_{y_1}, p_{x_2}, p_{y_2}\) follow the sign convention in Fig. 1. |
|---|---|---|---|---|---|---|---|
| | N3 | N7 | N9 |
| ---|---|---|---|---|---|---|---|
| \(m\) | \(T_{b_1}^{pd}\) | \(T_{pp}\) | \(T_{pp}\) | \(T_{pp}\) | \(T_{pp}\) | \(T_{pp}\) | \(T_{pp}\) |
| \(a_1\) |-t\(_{pd}\) | t\(_{pd}\) | -t\(_{pd}\) | t\(_{pd}\) | -t\(_{pd}\) | t\(_{pd}\) | 0 |
| \(b_2\) | -t\(_{pd}\) | t\(_{pd}/\sqrt{3}\) | -t\(_{pd}/\sqrt{3}\) | t\(_{pd}/\sqrt{3}\) | -t\(_{pd}/\sqrt{3}\) | t\(_{pd}/\sqrt{3}\) | 0 |
| \(e_x\) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| \(e_y\) | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| N9/N7 | \(2T_{pp}^{T_{b_1}^{pd}}\) | \(2T_{pp}^{T_{b_1}^{pd}}\) | \(2T_{pp}^{T_{b_1}^{pd}}\) | \(2T_{pp}^{T_{b_1}^{pd}}\) | \(2T_{pp}^{T_{b_1}^{pd}}\) | \(2T_{pp}^{T_{b_1}^{pd}}\) | \(2T_{pp}^{T_{b_1}^{pd}}\) |
| \(t_{pp}\) | \(t_{pp} - t_{pp}\) | \(t_{pp} - t_{pp}\) | \(t_{pp} - t_{pp}\) | \(t_{pp} - t_{pp}\) | \(t_{pp} - t_{pp}\) | \(t_{pp} - t_{pp}\) | \(t_{pp} - t_{pp}\) |

FIG. 1: Schematic view of the orbitals involved in our model calculations, adapted from Eskes’s previous related work.\(^{33}\) The Cu \(d_{x^2}, d_{yz}\) and the O \(p_\sigma\) orbitals are not shown. Note that only the four O that are adjacent to the Cu impurity are depicted, however we consider the full O square lattice.
TABLE II: Irreducible representations spanned by two d holes (d^2) and corresponding Coulomb and exchange matrix elements in terms of Racah parameters A, B, C. The basis functions are based on the single hole irreducible representations: b1(d_x^2d_y^2), a1(d_x^2d_z^2), b2(d_xy), e_x(d_zx), e_y(d_yz). Throughout the paper, the free-ion values B = 0.15 eV, C = 0.58 eV are adopted and A as a variable is also often refereed to as Hubbard U, whose value varies in different materials.

| Irreducible Representation | a1^2 | b1^2 | b2^2 | (e^2 + e^2)/\sqrt{2} |
|---------------------------|------|------|------|----------------------|
| G                        | 4B + C | 4B + C | 4B + C | \sqrt{2}(B + C) |
| G                        | 4B + C | 4B + C | 4B + C | \sqrt{2}(3B + C) |
| (e^2 + e^2)/\sqrt{2}     | \sqrt{2}(B + C) | \sqrt{2}(3B + C) | \sqrt{2}(3B + C) | \sqrt{2}(3B + C) |

TABLE III: Irreducible representations spanned by two d holes (d^2) and corresponding Coulomb and exchange matrix elements in terms of Racah parameters A, B, C. The basis functions are based on the single hole irreducible representations: b1(d_x^2d_y^2), a1(d_x^2d_z^2), b2(d_xy), e_x(d_zx), e_y(d_yz). Throughout the paper, the free-ion values B = 0.15 eV, C = 0.58 eV are adopted and A as a variable is also often refereed to as Hubbard U, whose value varies in different materials.

| Irreducible Representation | a1^2 | b1^2 | b2^2 | (e^2 + e^2)/\sqrt{2} |
|---------------------------|------|------|------|----------------------|
| G                        | 4B + C | 4B + C | 4B + C | \sqrt{2}(B + C) |
| G                        | 4B + C | 4B + C | 4B + C | \sqrt{2}(3B + C) |
| (e^2 + e^2)/\sqrt{2}     | \sqrt{2}(B + C) | \sqrt{2}(3B + C) | \sqrt{2}(3B + C) | \sqrt{2}(3B + C) |

\section*{B. Variational exact diagonalization}

We use variational exact diagonalization to calculate the propagator \( G_d(m, z; \Gamma) \). The two-hole states in the variational space are of three possible types: (a) both holes are on the Cu; (b) one hole is on the Cu and one on an O; and (c) both holes are on O sites. All states in (a) are included in the variational space. For the (b) and (c) states, we impose a cutoff \( R_c \) between the O hosting the hole(s) and the Cu. Obviously, \( R_c \to \infty \) recovers the full Hilbert space. We typically set \( R_c = 20 \) for the results shown below. This suffices for convergence to be reached for all the bound states. Unless we use a very large \( \eta \), the continua are not yet fully converged for this \( R_c \), instead they look like a collection of peaks whose number increases with \( R_c \). The upper and lower bandedges are already converged, however, and that is all the information relevant for our analysis.

Within this variational space, we set up the Hamiltonian matrix for each irreducible representation and use standard exact diagonalization to calculate the corresponding propagators via Lanczos diagonalization.

\section*{III. RESULTS}

Before proceeding, we remark that throughout the paper, we adopt the usual convention of photoemission spectroscopies that the electron removal energy, or the
hole energy, increases to the left while the energy of the electron addition states increases to the right. The chemical potential, taken to be the zero energy, is chosen at the lowest energy of the two-hole state.

Figure 2 illustrates the two-hole spectra $A^\Gamma(\omega)$ for various irreducible representations $\Gamma$ in the seven-orbital (N7) model in the cases of (a) single Cu-$d^9$ ion with onsite energies $\epsilon_d(m) = 0$, (b) single Cu-$d^8$ ion including the additional ligand field splitting and single Cu impurity in a lattice of oxygen with finite Cu-O hybridization corresponding to two characteristic cases with differing two-hole ground state of $^1A_1$ (c) and $^3B_1$ (d) symmetry respectively. The parameters are (c) $\Delta = 2.75$ eV, $A = 6.5$ eV and (d) $\Delta = 6.5$ eV, $A = 2.5$ eV with $t_{pd} = 1.5$ eV, $t_{pp} = 0.55$ eV. The chemical potential, taken to be zero energy, is chosen as the lowest energy of two-hole state.

From now on we focus on the case where the lowest energy two-hole ground state is of $^1A_1$ symmetry, as illustrated in Fig. 2(c). There is a clearly visible low-energy discrete peak, proving that for these parameters the two holes form a bound state which is a linear combination of two holes on Cu, one hole on Cu and the other on O, and two holes on O, i.e. the configurations of $d_8^2, d_8^1L$ and $d_{10}^2L^2$. The lowest energy state for adding one hole to a Cu $d^9$ state as in the hole doped cuprates would be a bound state of $^1A_1$ symmetry similar to the ZRS as the lowest energy state. According to the Fig. 2 this bound state would be separated from a continuum corresponding to the doped hole in an O-2p band by about 1 eV, which is indeed close to what is observed in ARPES experiments of the cuprates. In addition to the broadening and appearance of bound states beyond the continua, the hybridization also introduces the ligand field like splittings which will mix the various atomic multiplets. Note that for these parameter values, only the $^1A_1$ peak is clearly below the corresponding continuum, and thus a truly bound state; the other peaks are inside the lower edge of their continua. At even higher energies lies the two hole continuum, where both holes move freely in the O lattice and the Cu is in a $d_{10}$ state; this is superimposed over strong resonances where Cu multiplet lines hybridize with (and are shifted around by) this continuum. All this forms a very broad structure with mixed character and is basically the origin of the so called “waterfall”, a name coined by Lanzara et al [12].

Of most interest are three lowest peaks, of which the lowest one, with $^1A_1$ symmetry, is the first ionization...
state starting from Cu-d³. Its eigenstate is
\[
|\psi\rangle = \sqrt{0.072}|b_1b_1\rangle + \sqrt{0.549}|b_1L_{b_1}\rangle + \sqrt{0.054}|b_1L'_{b_1}\rangle
+ \sqrt{0.275}|d^{10}L^2\rangle + \ldots
\]
where \ldots represents states having \(a_1a_1, b_2b_2, ee\) characters, whose probabilities add up to less than 1%. Here \(L_{b_1}\) denotes one hole in a linear combination of O orbitals nearest to the Cu impurity, with overall \(b_1\) symmetry. We emphasize that this weight distribution is almost independent on the number of orbitals considered, whether the N3, N7, N9, or N11 models. This shows that the ground-state is only about 55% ZRS-like, i.e. \(|b_1L_{b_1}\rangle, L'_{b_1}\) denotes the configurations where the hole is on the second, third, etc. rings of O ions, which strictly speaking are discarded by the ZRS. The strong mixing of the ground state with the \(d^{10}L^2\) state is the reason for the strong antiferromagnetic exchange interaction which stabilizes the singlet. It is worth noting that this strong wave function mixing is strongly dependent on \(t_{pd}\), which in turn is strongly dependent on the interatomic distance between Cu and the nearest-neighbor O. This is the origin of a possibly strong electron-phonon and magnon-phonon coupling.

The second and third lowest peaks are the high spin \(3B_1\) state and the singlet \(1B_1\) state respectively. All these results are qualitatively similar to those reported in previous work by Eskes et al.\(^{13,14}\). The quantitative differences, especially the differences in the weights of various continua, are due to how the O band is modelled (realistic tight-binding model in our work, vs. featureless semi-elliptical DOS in theirs).

Next we elaborate on the case where the lowest energy two-hole ground state is of \(3B_1\) symmetry, as illustrated in Fig. 2(d). To obtain this we adopted \(A - \Delta = -4\) eV, which puts the system well into the Mott Hubbard rather than charge transfer gap of the ZSA classification scheme. The major difference from the case shown in Fig. 2(c) is the order of lowest peaks, which changed to be of \(2A_1, 2E, 3A_2\) symmetries from those of \(1A_1, 3B_1, 1B_1\) symmetries. Furthermore, it is clear that the conventional three-orbital (N3) model cannot capture the lowest bound state any more due to the lack of the involvement of the \(a_1(d_{z^2-\rho^2})\) orbital.

To investigate the effects of including more Cu-3d and/or O-2p orbitals in the model Hamiltonians, Figure 3 compares the two-hole spectra \(A(\omega)\) calculated for the (a,d) seven-orbital (N7), (b,e) nine-orbital (N9), and (c,f) eleven-orbital (N11) models for two characteristic parameter sets corresponding to the low spin (singlet) (a-c) and high spin triplet (d-f) cases. The comparison between N7 and N9/N11 models illustrates the impact of including additional \(\pi\)-bonding oxygen orbitals. The additional hybridization with Cu-b_{2g}(d_{xy}) orbital extends the continua to lower energies for all the symmetries, which causes a much smaller difference between the continuum bottom of various A and B types of symmetries. This clearly demonstrates the importance of having all the continua in place correctly in order to decide which is the lowest energy state. For example, if the \(1A_1\) continuum would also be involved in the hybridization with the \(3B_1\) or \(1B_1\) state, these states would be appreciably closer to the \(1A_1\) lowest energy state and even cross it. This could happen if we could take into account the full lattice of Cu-d³ states in the starting configuration, for example, as done in the exact diagonalization study of the large cluster with 32 Cu sites and 64 O sites by Lau et al.\(^{12}\). It is important to note that Lau indeed found a very strong ferromagnetic coupling between the Cu sandwiching an O hole, which indicates that our impurity limit could be different from what happens in the actual crystal although the experiments of cuprates did agree with our classification for the undoped system. Strong hole doping however could strongly modify these conclusions. This also questions the use of single site DMFT or single orbital cluster DMFT results with regard to the relevance for the full problem which includes both O and Cu states explicitly in the cluster.

In the isolated Cu atom, the two-hole ground-state has \(3B_1\) symmetry (Hund’s rule), while, as shown in Fig. 2(c), a strong enough hybridization with the O bands favors a ground-state with \(1A_1\) symmetry, i.e. there is a high spin to low spin transition. To fully characterize the various possible symmetries of the ground-state, in Figure 3 we show phase diagrams in the full parameter space. In panel (a), we plot a \(A - \Delta\) vs. \(2t_{pd}\) phase diagram, which can be directly compared against that shown in Ref. 13. It shows the phase boundaries for obtaining the lowest peak with \(1A_1\) (blue curve) and with \(3B_1\) (red curve) symmetries, respectively, for an O bandwidth \(W = 4.4\) eV \((t_{pp} = 0.55\) eV). Furthermore, the green curve shows the phase boundary separating the ground state of \(1A_1\) (low spin) and \(3B_1\) (high spin) character. The three different types of ground-states are filled by different colors: region I denotes the absence of a bound ground-state state, i.e. the doped hole moves freely in the O lattice instead of being bound to the Cu hole. In regions II and III there is a bound ground state with \(3B_1\) and \(1A_1\) symmetry, respectively. Clearly, region III is physically relevant to cuprates.

While this phase diagram is qualitatively similar with Eskes’ corresponding phase diagram\(^{13}\) there are again quantitative differences between the two. There is a shift of the critical value of the \(pd\) hybridization needed to obtain a bound state with \(1A_1\) symmetry from their value \(T(B_{1g}) = 2t_{pd} \approx 1.6\) eV to our value of \(\approx 1.0\) eV. In addition, the lines separating the various regions have quite different slopes. These non-trivial quantitative differences are due to the difference in how the O bath is modeled. One of the main reasons for this difference is that in the Eskes approach the ligand hole states are all spread equally over the hemispherical band while in our tight-binding band structure the \(b_1\) symmetry hole states are concentrated at the bottom of the hole density of states making the appearance of a two-hole \(1A_1\) bound
FIG. 3: (Color online) The comparison of two-hole spectra \(A^f(\omega)\) calculated for various irreducible representations \(\Gamma\) in the (a,d) seven-orbital (N7), (b,e) nine-orbital (N9), and (c,f) eleven-orbital (N11) models for two characteristic parameter sets corresponding to the low spin (singlet) (a-c) and high spin triplet (d-f) cases. The spectra of N3 model (black curve) is plotted for comparison as well. The parameters are (a-c) \(\Delta = 2.75\) eV, \(A = 6.5\) eV and (d-f) \(\Delta = 6.5\) eV, \(A = 2.5\) eV with (a, d) \(t_{pd} = 1.5\) eV, \(t_{pp} = 0.55\) eV and (b-c, e-f) \(t_{pd\sigma} = \sqrt{3}\) eV, \(t_{pd\pi} = 0.75\) eV, \(t_{pp\sigma} = 0.9\) eV, \(t_{pp\pi} = 0.2\) eV. For the N3 model, we use \(U_{dd} = A + 4B + 3C\), \(t_{pp} = 0.55\) eV.

state possible at even lower \(t_{pd}\). Another important difference caused by the same effect is that in our case the splitting between the \(1^A_1\) and the \(3^B_1\) peaks is larger than that in the Eskes picture (it is even larger for the \(3^B_1\) case). This results in a stabilization of the \(1^A_1\) state to even more negative \(A - \Delta\) or extending even further into the Mott Hubbard regime of the ZSA classification scheme.

Figure 4(b) illustrates the impact on the phase boundaries of the number of O-2p orbitals kept in the model: full/dashed lines are for the N7/N9 model. The conventional relations \(t_{pd} \approx \sqrt{3}t_{pd\pi}/2 = 2t_{pd\pi}\) and \(t_{pp\sigma} = 0.9\) eV, \(t_{pp\pi} = 0.2\) eV are used for the N9 model. Clearly, adding the second in-plane O-2p orbital in the model does not have significant effects on the phase boundaries, except to slightly shift the I-III boundary. The same is true if the \(p_z\) orbitals are also included, in N11 (not shown). For comparison, the black line denotes the critical \(A - \Delta\) for the appearance of low-energy bound state of Zhang-Rice singlet nature in the N3 model. At larger \(t_{pd}\) this agrees well with the \(1^A_1\) boundary for N7 model, suggesting minor differences there between the N3 and N7 models.

Two-dimensional phase diagrams like those of Figure 4 may be expected to change depending on whether the \(A - \Delta\) axis is spanned by changing \(A\) while keeping \(\Delta\) constant, or by changing \(\Delta\) while keeping \(A\) constant, or by some other protocol. In Fig. 5 we show how the phase diagram evolves with the charge transfer energy \(\Delta\). The rather weak dependence of the \(A - \Delta\) vs. \(t_{pd}\) phase boundaries upon \(\Delta\) confirms the importance of the energy separation between \(A\) and \(\Delta\). Specifically, as \(\Delta\) governs the energy difference between the \(d^9\) and \(d^{10}L\) state, \(A - \Delta\) governs the average energy difference.
between $d^8$ and $d^9L$. If $A$ is less than $\Delta$, we are closer to a Mott-Hubbard limit than a charge-transfer gap limit. In that case, the $d^8$ triplet is the lowest energy electron removal state as clearly seen in Fig. 4(b), although the singlet lowest energy state extends well into this negative $A-\Delta$ region.

To further characterize the evolution of the ground state from region II ($^3B_1$) to III ($^1A_1$), Fig. 6 plots how the weights of the dominant components to the ground state change with $A$, for realistic values of $t_{pd} = 1.3$ eV, $\Delta = 3.5$ eV. As expected (see also Eq. [5]), in region III the ground state is dominated by the $b_1Lb_1$ singlet, which is the equivalent of the ZRS. In region II, the high spin ground state is dominated by the $a_1b_1$ triplet. However, in both cases there are significant contributions from other configurations with the correct symmetry. This shows that overly simplistic models, which project out everything but the largest probability component, may be qualitatively correct but will certainly not be quantitatively accurate for realistic values of the parameters.

Finally, we compare the results of the conventional three-orbital Emery model (N3 in our notation) against the N7 and N9 results, to see if the multiplet physics plays any essential role at values of the parameters believed to be reasonable for cuprates. To achieve this, we performed the N3 calculation with the same Cu-O hybridization, O-2p hopping integrals, and charge transfer energy $\Delta$ in region III of the phase diagram as in the N7 model, but keeping only the $b_1(d_{x^2-y^2})$ orbital with a Hubbard-like $U_{dd} = A + 4B + 3C$ (see Table I).

Figure 7(a) compares the spectral weight with $^1A_1$ symmetry for the three models. Clearly, the ground-state peak and the intermediate energy continua due to Cu-O hybridization are in good agreement. However, the high energy regions ($\omega \approx 10.0$ eV) of the N7 and N9 models...
As a final note, we remark again about the potential importance of including more than one Cu atoms in addition to explicitly including the O states, as done in Lau’s previous calculation\cite{Lau}. This might lead to very different conclusions especially when considering the effects of doping to a level where the ZR like states strongly overlap, which already occurs at less than 10% doping.

IV. CONCLUSION

In summary, we used variational exact diagonalization to revisit the problem of the spectra of two holes doped into an otherwise full CuO$_2$ layer, modelled as a Cu-d$^{10}$ impurity properly embedded into a square lattice of O-2p\cite{Lau}. While the relevance of the full Cu multiplet structure was considered before, with results in qualitative agreement with ours, the novelty here is that we use a realistic tight binding band structure for the O band and consider the implications of adding non-ligand 2p orbitals, as well.

We find that using a realistic O-2p band structure does not change qualitatively the two-hole spectra in the various symmetry channels, when compared against those obtained using a featureless, semicircular band structure. However, there are significant quantitative changes. For example, the region in the phase diagram favoring a bound ground-state with $^1A_1$ symmetry is enlarged significantly and extends well into the Mott Hubbard region of the ZSA classification scheme. This proves that using a realistic band-structure has non-trivial quantitative consequences, that are important if detailed modelling and comparison to experiments is desired. This is an important lesson for any impurity-type calculations, including for the use of the dynamical mean-field theory (DMFT) approximations. In particular, it is important to include the O-2p states explicitly in the impurity Hamiltonian together with the full multiplet structure, rather than restricting to coupling to a bath of Cu or effective Cu 3d states.

Speaking of approximations, our results also caution against the approach of using Wannier functions together with $A,B,C$ Racah parameters renormalized so as to obtain an atomic limit multiplet similar to the one produced by the strong hybridization. As discussed when analyzing the results from Fig. 2(a), the two have very different splittings and even ordering of the peaks in the various symmetry channels. For example, in order to get the singlet-triplet crossing within an atomic multiplet approach, one would need to have a Hund’s rule $J_d < 0$, which is not reasonable. In the original papers describing the effective screening of $U$, the lack of screening of $J_h$ and other Hund’s rule interactions were obtained with the assumption that the covalency and transition metal to oxygen hybridization would be explicitly included in the model Hamiltonians. This is very different from trying to account for the effects of hybridization through...
the use of Wannier functions.

Furthermore, we find that the three-orbital Emery model reproduces well the low-energy results obtained in the \(1A_1\) symmetry channel of the N7 and N9 models. In particular, its ground-state is consistent with the ZRS, but the overlap with the ZRS wavefunction is only around 50% for reasonable values of the parameters. This raises questions about the accuracy of projecting the Emery model onto ZRS, to obtain simple one-band Hamiltonians.\(^\text{12}\) We point out again the importance of including all the multiplets when discussing energy scales larger than about 1eV as in many of the optical and photoemission spectroscopies. An obvious example is the appearance of the so-called “waterfall” feature\(^\text{12}\) at energies of about 1eV above the lowest energy electron removal state. This can trivially be explained by taking into account all the multiplets and their hybridization with the oxygen bands, forming a broad region in energy where a huge number of bands cross and overlap so that a broad continuum sets in a momentum distribution plot.

The lower symmetry of the lattice (as opposed to an impurity) may also explain how the z-axis polarization, discussed in the introduction, may be accounted for. The \(d_{3z^2-r^2}, d_{xz}\) and \(d_{yz}\) orbitals have very little contribution to the \(1A_1\) ground-state, but they contribute significantly to the low-energy peaks in the other symmetry channels. A lattice calculation that breaks the \(D_{4h}\) point group symmetry may boost not only their contribution to the ground-state, but also the importance of the O-2p\(_z\) orbitals that mostly hybridize with them.

To settle these questions, calculations for the lattice equivalent of the N7 model are needed. Needless to say, an exact solution is a very hard challenge. Instead, it may be possible to obtain accurate results using variational approximations similar to those used here, but extended to a full Cu lattice. We will investigate this next.

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