A novel first-principles approach to effective Hamiltonians for high $T_c$ superconducting cuprates

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Abstract. We report our recent progress of deriving the low-energy effective one-band Hamiltonians for the prototypical cuprate superconductor Ca$_2$CuO$_2$Cl$_2$, based on a newly developed first-principles Wannier-states approach that takes into account large on-site Coulomb repulsion. The apical atom $p_z$ state is found to affect the general properties of the low-energy hole state, namely the Zhang-Rice singlet, via additional intra-sublattice hoppings, nearest-neighbor “super-repulsion,” and other microscopic many-body processes.

1. Introduction

High critical temperature ($T_c$) superconductivity (HTSC) takes place in a number of layer-structured copper oxides when they are doped away from the antiferromagnetic Mott insulating phase by introducing extra electrons or holes into the CuO$_2$ plane. Its origin remains unresolved, despite extensive and intensive studies for two decades. One of the main challenges is attributed to the proximity of competing orders due to strong electron correlation, making the ground state and phase diagram unusually sensitive to small changes in various parameters. Therefore, it is crucial to establish the realistic microscopic models for HTSC and to identify the factors that substantially affect the model parameters. Especially, since the highly correlated nature makes it difficult to unambiguously justify the cuprate model by fitting to limited experiments (see Fig. 2), a first-principles approach is desirable. This topic has long been intriguing and challenging for strongly correlated electronic materials [1, 2, 3, 4].

The CuO$_2$ plane constitutes a typical charge-transfer system, exhibiting strong electron-hole asymmetry: doped electrons occupy the copper $3d_{x^2−y^2}$-derived upper Hubbard band, while doped holes reside in an oxygen $2p_o$-derived band. This renders a $d$-$p$ complexity. Nevertheless, to date, the most studied model Hamiltonian for HTSC is the effective one-band $t$-$U$ or $t$-$J$ model (here $t$ is the nearest-neighbor hopping integral, $U$ the Hubbard repulsion, and $J$ the spin superexchange constant) [5]. Yet, there is considerable skepticism in the adequacy of the “bare” $t$-$U$ or $t$-$J$ model, as unbiased numerical results generally do not support a robust superconducting pairing in these models for realistic $J/t < 0.5$ [6, 7, 8, 9]. Recently, the idea of introducing longer range hoppings in the CuO$_2$ plane has become popular, as $t'$ and $t''$ (the second- and third-neighbor hoppings) are found necessary to the explanation of electron-hole asymmetry [10] and angle-resolved photoemission spectroscopy (ARPES) [11, 12, 13, 14]. Previous theoretical analyses of the ARPES data lead to $-t'/t ∼ 0.15$ for La$_2$CuO$_4$ [15, 16] and $t''/t ∼ 0.3$ for both Ca$_2$CuO$_2$Cl$_2$ [14, 17, 18] and Bi$_2$Sr$_2$CaCu$_2$O$_8$ [13, 19], consistent with the diamond-like Fermi surface in La$_2$CuO$_4$ and square-like ones in the other two. The effect of $t'$ on superconducting instability is still an open question [20, 21, 22, 23].
Recently, Pavarini et al. [24] proposed that the effective orbital in the $t$-$U$ model could be obtained within the local density approximation (LDA) of density functional theory by downfolding the LDA bands near the Fermi level to one Cu $d_{x^2−y^2}$-like orbital per CuO$_2$ unit. Regarding the hopping parameters in this orbital (referred to as $t^\prime_{\text{LDA}}$, $t_\text{LDA}'$, $t^{\prime\prime}_{\text{LDA}}$, etc.), they showed that for a large number of hole-doped high temperature superconductors, $−t^\prime_{\text{LDA}} ≈ 2t^{\prime\prime}_{\text{LDA}}$ is controlled by the axial orbitals and $T_c^{\text{max}}$ ($T_c$ at optimal doping) appears to positively correlate with $−t^\prime_{\text{LDA}}/t_{\text{LDA}}$; for instance, $−t^\prime_{\text{LDA}}/t_{\text{LDA}} \sim 0.18$ for La$_2$CuO$_4$ ($T_c^{\text{max}}$=42 K) and $\sim 0.12$ for Ca$_2$CuO$_2$Cl$_2$ ($T_c^{\text{max}}$=28 K).

In literature, the $t^\prime_{\text{LDA}}$’s have been often inadvertently treated as the $t$’s in the extended $t$-$U$ or $t$-$J$ model [16, 24]. Hence, on the one hand, the LDA results seem to confirm earlier predictions [25]. On the other hand, it is confusing that $−t^\prime_{\text{LDA}}/t_{\text{LDA}}$ for Ca$_2$CuO$_2$Cl$_2$ are much smaller than $−t^\prime/\bar{t}$ suggested by the ARPES community. In addition, it remains unclear that the role of the apical oxygen atoms is constructive [26, 27] or destructive [28] to superconductivity in the $t$-$U$ or $t$-$J$ model. Actually, simply treating $t^\prime_{\text{LDA}}$’s as $t$’s is essentially incorrect: The effective upper and lower Hubbard bands (UHB and LHB) associated with $t^\prime_{\text{LDA}}$’s have the same band character, whereas in the cuprate-$t$-$U$ model the UHB and LHB mainly have Cu 3$d$ and O 2$p$ band characters, respectively, and the t’s stand for the intersite exchange of the one-hole Cu $d_{x^2−y^2}$-derived state and the Zhang-Rice singlet (ZRS, the lowest-energy local two-hole multiplet) [29]. It is known that the multiplet structure due to strong electronic correlation is beyond LDA. The LDA ground state of the undoped cuprates is even unfavorably paramagnetic—metallic—the Mott physics is absent in LDA because of a serious self-interaction problem for strongly localized orbitals, such as Cu 3$d$ states in the present case. Thus, it is important to examine the material dependence of general electron behavior in the CuO$_2$ plane by deriving an effective interacting Hamiltonian with a first-principles approach that takes into account, from the beginning, large Coulomb repulsion on the Cu sites. Such studies would not only produce a more appropriate character of low-energy states, but also reveal new material-dependent physical effects derived from the complexity of strong electronic correlation and the charge-transfer nature.

The purpose of this article is to move one step forward in deriving effective Hamiltonians for the cuprates by using a novel first-principles Wannier states (WSs) analysis of the LDA+$U$ band structure [30]. The presentation will be focused on the prototypical cuprate Ca$_2$CuO$_2$Cl$_2$. We provide quantitative evidence that the apical oxygen atoms are crucial in tuning $t^\prime$ and $t^{\prime\prime}$. The proximity of $\varepsilon_{p_z}$, the energy of the apical (out-of-plane) atom $p_z$ state [31], to the Fermi level is found to suppress $|t^\prime/\bar{t}|$ of ZRS, in agreement with the ARPES measurements on La$_2$CuO$_4$ and Ca$_2$CuO$_2$Cl$_2$. In addition, our results reveal that $|t^{\prime\prime}|$ can be larger than $|t^\prime|$, and the shape of the quasiparticle band dispersion is much more sensitive to $t^{\prime\prime}$ than to $t^\prime$. More interestingly, this proximity generates several crucial many-body effects, including local site-dependent potentials and a novel inter-site “super-repulsion” between the doped holes. These findings would shed new light on the general material dependence and microscopic understanding of HTSC.

2. Methods And Results

A three-step approach is used to reduce systematically the energy scale of the relevant Hilbert space:

(i) The full-energy electronic structures are obtained within the LDA+$U$ method [32] known as a state-of-the-art generalization of LDA to include strong local interaction. Indeed, the ground state of the undoped cuprate is correctly predicted to be a charge-transfer insulator, as opposed to a metallic state produced in LDA.

(ii) At the intermediate-energy scale (~ 10 eV covering relevant Cu 3$d$, O 2$p$, and apical orbitals), an effective Hubbard-like five-band interacting Hamiltonian, $H^{5b}$, is derived via the WSs analysis of the LDA+$U$ results [30].

One particular state-of-art technique employed here is the Wannier states analysis where the orthogonal Wannier functions (WFs) are constructed by maximizing the weights of certain symmetry inside some atomic spheres. Therefore, in the Wannier representation the LDA+$U$ [32] one-particle
Hamiltonian $H_{\text{LDA+U}}$ can be calculated out, which directly gives all the hopping integrals

$$T_{ij}^{m'n'} = H_{\text{LDA+U}}^{im\sigma; jm'n'\sigma},$$  \hspace{5cm} (1)

To compare, the usual way of fitting the hopping parameters to the band structure is not well-controlled, for example, the direct in-plane O-O hopping $t_{pp}$—which controls the value of $t'$—was reported to vary from 0.04 eV to 0.65 eV [33]. Large $t_{pp}$ means that the O $p$ orbitals are quite extended, and thus the effects of Coulomb interaction in the oxygen orbitals may be insignificant. Here we confirm that $t_{pp} \approx 0.65$ eV. To investigate the effects of strong electron correlation and strong $d-p$ hybridization on the local multiplets, it is convenient to construct the WFs to center at the copper site—for example, the locally $b_1$-symmetrized combination of the planar oxygen $p_x$ orbitals results in an oxygen Wannier state (referred to as $P_s$, see Fig. 1), which strongly hybridizes with the central copper $d_{x^2-y^2}$ orbital. In this representation, the decorated CuO$_2$ plane reduces to a regular simple square lattice.

Based on the LDA+U electronic structures of a number of cuprate superconductors, the $b_1$ Wannier orbitals (Cu $3d_{x^2-y^2}$ and O $P_s$) are the most relevant. As shown in Fig. 3, the Cu $3d_{x^2-y^2}$ band is split to the spin-majority lower Hubbard band (LHB) and spin-minority upper Hubbard band (UHB), both strongly hybridized with the O $P_s$ orbital. Clearly, the undoped system has an intrinsic hole (with respect to the Cu $3d^{10}$ O $2p^6$ full shell configuration) in the spin-minority anti-bonding orbital, which is mainly of Cu $3d_{x^2-y^2}$ character. An additional hole will be doped into the spin-majority anti-bonding orbital, which is mainly of O $P_s$ character. Upon switching on the local electron correlation neglected in the LDA+U approach, the two holes will form a local spin singlet, i.e., ZRS [29].

**Figure 1.** (Color online) (a) Wannier functions centered at Cu sites for $H^{b_1}$: O $P_s$ and $P_a$ are constructed by maximizing the weight of the $b_1$- and $a_1$-symmetrized combinations of four neighboring planar O $p_x$ orbitals, respectively; $P_z$ is the $a_1$-symmetrized combination of two apical $p_z$ orbitals. (b) Left panel: Band structures of Ca$_2$CuO$_2$Cl$_2$ from LDA+U calculations (dots) and Wannier states analysis (lines). $\Gamma=(0,0,0)$, $X=(\pi,0,0)$, $M=(\frac{\pi}{2},\frac{\pi}{2},0)$. Right panel: Corresponding local energy level splitting due to interactions and $d-p$ hybridization, filled with electrons (solid arrows) or holes (dashed arrows). $P_z$ are derived from two highest $a_1$ hybrids. EUHB (ELHB) means the effective upper (lower) Hubbard band.
Table 1. Parameters in Eq. (2) obtained from the Wannier states analysis of the LDA+U ground state electron structures of Ca$_2$CuO$_2$Cl$_2$. $D_z$ stands for $d_{x^2-y^2}$ and $D_z$ for $d_{3z^2-r^2}$. The unit is eV.

|     | on-site | 1st n.n. | 2nd n.n. | 3rd n.n. |
|-----|---------|----------|----------|----------|
| $U_{\text{eff}}$ | 9.625   | 0.388    | -0.034   | 0.092    |
| $U_1$ | 6.754   | 0.288    | -0.185   | 0.076    |
| $J_{\text{eff}}$ | 0.706   | -0.032   | 0.003    | -0.002   |
| $\epsilon_d$ | -0.964  | -0.129   | -0.029   |          |
| $\epsilon_{P_s}$ | 2.003   | 0.130    | 0.030    |          |
| $\epsilon_{P_a}$ | 4.111   | -0.065   | -0.003   |          |
| $\epsilon_{P_z}$ | 2.812   | -0.026   | -0.006   |          |
| $T_{P_sD_x}$ | -2.351  | -0.034   | -0.003   |          |
| $T_{P_aD_x}$ | -0.845  | 0.354    | 0.084    |          |
| $T_{P_zD_z}$ | 0.778   | 0.951    |          |          |

Next, a high-energy interacting multi-band Hubbard Hamiltonian $H$ is derived from $H^LDA+U$. Since LDA+U treats the interaction in the localized orbitals in an effective Hartree-Fock (HF) approach, a clear mapping can be achieved by matching the low-energy $H^LDA+U$ to the self-consistent HF expression of $H$. This scheme is well controlled and has been shown to work well for manganites [30]. To also investigate the role of the apical atoms, three more orbitals are included: the $a_1$-symmetrized apical atom $p_z$ Wannier state (referred to as $P_z$), the center copper $d_{3z^2-r^2}$, and locally $a_1$-symmetrized combination of the planar oxygen $p_{o}$ orbitals (referred to as $P_o$); they are mutually hybridized. Therefore, the essential low-energy physics in high $T_c$ superconductors can be captured by a five-band $d - p$ model:

\[
H = \sum_{i,j,m,n} \langle \hat{t}_{ij} \rangle C_{i\sigma}^\dagger C_{j\sigma'} + H.c.) + \sum_{i,m} \epsilon_m n_{i\sigma} + U_{\text{eff}} \sum_{i,m=1}^n \sum_{\sigma,\sigma'} n_{i\sigma} n_{i\sigma'} + J_{\text{eff}} \sum_{\sigma,\sigma'} C_{i\sigma}^\dagger C_{i\sigma} C_{i\sigma'}^\dagger C_{i\sigma'},
\]

where $C_{i\sigma}$ annihilates an electron with spin $\sigma$ in the $m$-th Wannier state at site $i$. Here $m = 1, 2, \ldots$, 5 stand for Cu $d_{x^2-y^2}$, Cu $d_{3z^2-r^2}$, planar O $P_s$, planar O $P_a$, and apical O $P_z$ Wannier orbitals, respectively. In our approach, all model parameters can be calculated out as follows: (i) All the hopping integrals $\hat{t}_{ij}^{m,n}$ are given by Eq. (1). (ii) The site energy of the oxygen Wannier states $\epsilon_m = H_{\text{LDA+U}}^{\text{LDA+U}}$ for $m = 3, 4, 5$ are given by Eq. (1), too. (iii) The remaining four matrix elements $H_{\text{LDA+U}}^{\text{LDA+U}}$ for $m = 1, 2$ and both the spin-majority and spin-minority sites are used to determine $U_{\text{eff}}, U_{1}, J_{\text{eff}}$, and $\epsilon_d = \epsilon_1 = \epsilon_2$ in self-consistent Hartree-Fock theory with diagonal mean fields $\langle n_{i\sigma} \rangle$ known from the LDA+U density matrix, which also reveals that other mean fields are negligible.

The results for Ca$_2$CuO$_2$Cl$_2$—except for the less important $T_{ij}^{m,n}$ among the $a_1$ orbitals ($d_{3z^2-r^2}$, $P_a$ and $P_z$)—are presented in Table 1. Note that nearest-neighbor $T_{ij}^{D,D_s} = 0.39$ eV and $T_{ij}^{D_s,P_s} = 0.35$ eV are similar, substantively different from $T_{ij}^{D_s,P_s} = 0.36$ eV and $T_{ij}^{D_s,P_a} = 0$ eV derived in the formalism used in previous studies [4, 29]. The present numbers confirm that overall, the Wannier functions constructed in our approach are more localized.

(iii) At the low-energy scale ($\sim 1$ eV), an effective one-band Hamiltonian, $H^{1b}$, is derived from canonical transformation (CT) of $H$ to the second order [4, 29, 34].
To reduce the multiband Hubbard model to a one-band model, we follow Hubbard’s atomic representation approach [34, 35, 36, 37, 38], in which \( H \) is rewritten in terms of the multiplets of its one-unit-cell part solved by exact diagonalization. For \( \text{Ca}_2\text{CuO}_2\text{Cl}_2 \), the local one-hole ground state (referred to as \(|\sigma\rangle\)) with energy \( E_1 = -2.26 \text{ eV} \) is a hybrid of \( d_{x^2-y^2} \) (76\%) and \( P_s \) (24\%), and the first-excited one-hole state with energy \(-1.38 \text{ eV}\) is a hybrid of \( d_{3z^2-r^2} \) (91\%), \( P_n \) (6\%) and \( P_z \) (3\%); thus, the local \( d_{x^2-y^2} \rightarrow d_{3z^2-r^2} \) excitation energy (\( \Delta_1 \)) is 0.88 eV. The local two-hole ground state is the ZRS of two \( b_1 \) holes (referred to as \(|\text{ZRS}\rangle\)) with energy \( E_2 = -1.96 \text{ eV} \), and the first excited two-hole state is a spin-triplet (referred to as \(|\text{axial}\rangle\)) of one \( b_1 \) hole and the other in the \( a_1 \) states; the \(|\text{ZRS}\rangle \rightarrow |\text{axial}\rangle \) excitation energy (\( \Delta_2 \)) is 0.81 eV. In addition, the spin-triplet state of two \( b_1 \) holes (the Emery-Reiter triplet) is 3.3 eV higher than the ZRS. Therefore, it may be appropriate to keep in the low-energy space only \(|\sigma\rangle, |\text{ZRS}\rangle\) and integrate out all the other states by canonical transformation [34] or perturbation to the second order [38]: Suppose \( H = H_0 + H_1 \), and define \( H(\lambda) = H_0 + \lambda H_1 \). Then, the transformed Hamiltonian is

\[
H_S(\lambda) = e^{-\lambda S} He^{\lambda S} \simeq H_0 + \frac{\lambda^2}{2!}[H_1, S],
\]

after removing the terms linear with respect to \( \lambda \) following

\[
\lambda H_1 + [H_0, \lambda S] = 0. \tag{4}
\]

Let us apply the above canonical transformation to Eq. (2). First define the projection operator

\[
P_0 = \prod_i \sum_{p \in \text{g.s.}} X_{pp}^i, \quad P_1 = 1 - P_0, \tag{5}
\]

where g.s. means the ground state multiplets (the states we want to keep). Then, \( H_0 \) and \( H_1 \) may be defined by

\[
H_0 = P_0 HP_0 + P_1 HP_1 = \sum_i \sum_p \epsilon_{ip} X_{pp}^i + P_0 \sum_{i<j} \sum_{rr'<ss'} (V_{ij}^{rr',ss'} X_{i}^{rr'} X_{j}^{ss'} + H.c.) P_0 + P_1 \sum_{i<j} \sum_{rr's's'} (V_{ij}^{rr',ss'} X_{i}^{rr'} X_{j}^{ss'} + H.c.) P_1, \tag{6}
\]

and

\[
H_1 = P_0 HP_1 + P_1 HP_0 = P_0 \sum_{i<j} \sum_{rr's's'} (V_{ij}^{rr',ss'} X_{i}^{rr'} X_{j}^{ss'} + H.c.) P_1 + P_1 \sum_{i<j} \sum_{rr's's'} (V_{ij}^{rr',ss'} X_{i}^{rr'} X_{j}^{ss'} + H.c.) P_0. \tag{7}
\]

From Eq. (4) on the condition we neglect the intersite terms,

\[
S \simeq P_0 \sum_{i<j} \sum_{rr's's'} (A_{ij}^{rr',ss'} X_{i}^{rr'} X_{j}^{ss'} - H.c.) P_1 + P_1 \sum_{i<j} \sum_{rr's's'} (A_{ij}^{rr',ss'} X_{i}^{rr'} X_{j}^{ss'} - H.c.) P_0, \tag{8}
\]
where

\[ A_{ij}^{rr',ss'} = \frac{V_{ij}^{rr',ss'}}{\epsilon_{r'} + \epsilon_{s'} - \epsilon_r - \epsilon_s}. \] (9)

This gives rise to the one-band \( t-J \)-type Hamiltonian, or \( t-U \) Hamiltonian with effective \( U = E_2 - 2E_1 = 2.56 \) eV when the no-hole vacuum state \( |0\rangle \) is also retained. Here the \( t \)'s stand for the intersite exchange of the \( |ZRS\rangle \) and \( |\sigma\rangle \) states [29].

\[
H^{1b} = -\sum_{ij\sigma} t_{ij} (\tilde{c}_{i\sigma}^\dagger \tilde{c}_{j\sigma} + H.c.) + J \sum_{\langle ij \rangle} (\vec{S}_i \cdot \vec{S}_j - \frac{n_i n_j}{4})
+ \frac{J}{4} \sum_{\langle ijk \rangle \sigma} (\tilde{c}_{i\sigma}^\dagger \tilde{c}_{j\sigma} \tilde{c}_{j\sigma} \tilde{c}_{k\sigma} - \tilde{c}_{i\sigma} n_{j\sigma} \tilde{c}_{j\sigma} \tilde{c}_{k\sigma} + H.c.)
+ \sum_{\langle ij \rangle} V_{ij} n_i n_j + \sum_{i} \mu_i n_i + \sum_{\langle ij \rangle} \varepsilon_{ij}, \tag{10}
\]

where the notation follows the standard \( t-J \) model [29, 39] and \( t_{ij} \) extends to the third nearest neighbors (\( t'' \)). Tiny corrections of three-site hopping terms including \( \tilde{c}_{i\sigma}^\dagger (1 - n_j) \tilde{c}_{k\sigma} \) have been neglected. The first two lines of Eq. (10) resemble the \( t-J \) model mapped from the one-band Hubbard model and have been extensively studied [39]. The other terms include locally \( \varepsilon_{p_z} \)-dependent “super-repulsion” \( V_{ij} \), site potential \( \mu_i \), and energy “constant” \( \varepsilon_{ij} \) (only relevant to equilibrating apical atoms).

If the effects of the other multiplets can be neglected, the “unrenormalized” \( t \)'s of the resulting one-band \( t-U \) or \( t-J \) model are [34, 35, 37, 38],

\[
t_{ij} = \sum_{mm'} T_{ij}^{m'm'} \langle i\sigma | C_{im\sigma}^\dagger | j, ZRS \rangle \langle j, ZRS | C_{jm'\sigma} | j\sigma \rangle, \tag{11}
\]

where only \( m \) and \( m' \) belonging to the \( b_1 \) orbital space have contribution. Otherwise, virtual nearest-neighbor hopping to the integrated out states will renormalize \( t' \) by \(-2|t_{ijk}^{(1)}|\) and \( t'' \) by \(|t_{ijk}^{(1)}|\) [38]; obviously, hopping through [axial] is the most significant. The results for hole-doped \( \text{Ca}_2\text{CuO}_2\text{Cl}_2 \) are: \( t = 0.46 \) eV, \( t'/t = -0.32 \), and \( t''/t = 0.23 \) (unrenormalized \( t'/t = -0.19 \) and \( t''/t = 0.16 \)), as shown in Table 2. The apical atom \( p_z \) state is thus found to affect quite significantly the general properties of the low-energy hole state.

The justification of our resulting Hamiltonian can be made by comparing the (approximate) solution with known experimental data. For the cuprates, much attention has been paid to the angle-resolved photoemission spectroscopy (ARPES) on undoped \( \text{A}_2\text{CuO}_2\text{Cl}_2 \) (A=Ca, Sr), since they correspond to the single doped hole case, for which we have sofar the cleanest theory in the context of a doped Mott insulator. Compared with the generally known results extrapolated from ARPES on \( \text{A}_2\text{CuO}_2\text{Cl}_2 \) [11, 14, 17], \( t''/t \) agrees well but \( t'/t \) is smaller by half. Thus, we are motivated to reexamine the single-hole dynamics within the self-consistent Born approximation (SCBA) of the spin-polaron picture [13, 40], whose accuracy for the single-hole problem has been verified by small cluster exact diagonalization [41]. As shown in Fig. 2, the hole quasiparticle dispersion is surprisingly insensitive to

Table 2. Parameters of Eq. (10) for the prototypical cuprate \( \text{Ca}_2\text{CuO}_2\text{Cl}_2 \). Inside the parentheses are contributions purely from the \( b_1 \) orbitals. The energy unit is meV.

| \( J/2 \) | \( t \) | \( t'/|t| \) | \( t''/|t| \) | \( V_{ij} \) | \( \mu_i \) | \( \varepsilon_{ij} \) |
|---|---|---|---|---|---|---|
| 131 (131) | 459 (459) | -0.19 (-0.32) | 0.16 (0.23) | 54 (30) | -295 (-412) | -133 (-17) |
Figure 2. Single-hole quasiparticle dispersion in the self-consistent Born approximation (SCBA) for the $t$-$t'$-$t''$-$J$ models with $t = 0.5$ eV (solid lines), compared with the ARPES results for Sr$_2$CuO$_2$Cl$_2$ [11] (circles) and the SCBA result for Eq. (2) (dotted line).

Figure 3. Schematics of virtual kinematical processes (dashed lines) and corresponding effective one-band interactions for (a) Heisenberg superexchange within a one-orbital system and (b)-(d) additional “vacuum fluctuations” in a two-orbital system. Electrons (solid arrows) in the targeted and projected out orbitals are black and gray, respectively.

t', given $t''/t = 0.2$ [42]. That is, our present results can accurately reproduce the ARPES data. It is known that the three-site hopping terms can improve the agreement with ARPES [43, 44]. It is worth mentioning that the main role of the three-site hopping terms is to suppress $t'$ by $J/2$ and enhance $t''$ by $J/4$; therefore, the fitted values of $t'$ and $t''$ depend sensitively on inclusion of the three-site hopping terms [42]. Our first-principles derived Hamiltonian finally provides an unambiguous benchmark of these material-dependent parameters.
kinematical processes as demonstrated in Fig. 3. For a purely one-band system in the large on-site repulsion limit [Fig. 3(a)], the virtual hoppings between two singly-occupied neighboring sites generate the well-known superexchange effect $-\frac{1}{2}n_{i\sigma}n_{j\tilde{\sigma}}$. Given an extra fully-occupied orbital to be projected out ($P_z$ in the present work), additional virtual kinematical processes give rise to three new spin-independent terms $[\propto v_{00}, v_{10}$, and $v_{11}$, see Fig. 3(b)-(d)] to the targeted one-band Hamiltonian, leading to $V_{ij} = 2v_{00} - v_{01} - v_{11}$, $\mu_i = 4v_{00} - v_{10}$ and $\varepsilon_{ij} = -v_{00}$. Clearly, this new effective repulsion—named super-repulsion in analog to superexchange—is to be distinguished from direct Coulomb interaction: Not only is $V_{ij}$ controlled by $\varepsilon_{P_z}$, but also its virtual kinematical origin makes it less subject to electronic screening.

In summary, we have presented a novel general first-principles Wannier state approach to effective Hamiltonians for the HTSC cuprates and illustrated it with Ca$_2$CuO$_2$Cl$_2$. We provide quantitative evidence that the apical oxygen atoms are crucial in tuning $t'$ and $t''$, super-repulsion, and chemical potential. The proximity of $\varepsilon_{P_z}$, the energy of the apical (out-of-plane) atom $p_z$ state [31], to the Fermi level is found to suppress $|t'/t|$ of ZRS, in agreement with the ARPES measurements on La$_2$CuO$_4$ and Ca$_2$CuO$_2$Cl$_2$. In addition, our results reveal that $|t''|/|t'|$ can be larger than $|t'|$, and the shape of the quasiparticle band dispersion is much more sensitive to $t''$ than to $t'$. These findings would shed new light on the general material dependence and microscopic understanding of HTSC.

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