A new hybrid LDA and Generalized Tight-Binding method for the electronic structure calculations of strongly correlated electron systems

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A novel hybrid scheme is proposed. The \textit{ab initio} LDA calculation is used to construct the Wannier functions and obtain single electron and Coulomb parameters of the multiband Hubbard-type model. In strong correlation regime the electronic structure within multiband Hubbard model is calculated by the Generalized Tight-Binding (GTB) method, that combines the exact diagonalization of the model Hamiltonian for a small cluster (unit cell) with perturbation treatment of the intercluster hopping and interactions. For undoped \textit{La$_2$CuO$_4$} and Nd$_2$CuO$_4$ this scheme results in charge transfer insulators with correct values of gaps and dispersions of bands in agreement to the ARPES data.

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I. INTRODUCTION

A conventional band theory is based on the density functional theory (DFT) and on the Local Density Approximation (LDA) within DFT. In spite of great success of the LDA for conventional metallic systems it appears to be inadequate for strongly correlated electron systems (SCES). For instance, LDA predicts \textit{La$_2$CuO$_4$} to be a metal whereas, in reality, it is an insulator. Several approaches to include strong correlations in the LDA method are known, for example LDA+U and LDA-SIC\cite{3}. Both methods result in the correct antiferromagnetic insulator ground state for \textit{La$_2$CuO$_4$} contrary to LDA, but the origin of the insulating gap is not correct. It is formed by the local single-electron states splitted by spin or orbital polarization. In these approaches the paramagnetic phase of the undoped \textit{La$_2$CuO$_4$} (above the Neel temperature $T_N$) will be metallic in spite of strong correlation regime $U \gg W$, where $U$ is the Hubbard Coulomb parameter and $W$ is a free electron bandwidth. The spectral weight redistribution between Hubbard subbands is very important effect in SCES that is related to the formation of the Mott-Hubbard gap in the paramagnetic phase. This effect is incorporated in the hybrid LDA+dynamical mean field theory (DMFT) (for review see Ref.\cite{4}) and LDA++ approaches.\textsuperscript{4} The electron self-energy in LDA+DMFT approach is calculated by the DMFT theory in the limit of infinite dimension\cite{5},\textsuperscript{5} and is k-independent, $\Sigma_{\mathbf{k}}(E) \rightarrow \Sigma(E)$\textsuperscript{6.7}. That is why the correct band dispersion and the ARPES data for High-$T_c$ compounds cannot be obtained within LDA+DMFT theory. Recent development of the LDA+cluster DMFT method\textsuperscript{8,9} and spectral density functional theory\textsuperscript{10} gives some hopes that non-local corrections may be included in this scheme.

A generalized tight-binding (GTB)\textsuperscript{11} method has been proposed to study the electronic structure of SCES as a generalization of Hubbard ideas for the realistic multi-band Hubbard-like models. The GTB method combines the exact diagonalization of the intracell part of the Hamiltonian, construction of the Hubbard operators on the basis of the exact intracell multielectron eigenstates, and the perturbation treatment of the intercell hoppings and interactions. A similar approach to the 3-band $p-d$ model of cuprates\textsuperscript{10,11} is known as the cell perturbation method.\textsuperscript{12} The practical realization of the GTB method for cuprates required an explicit construction of the Wannier functions to overcome the nonorthogonality of the oxygen molecular orbitals at the neighboring CuO$_6$ cells.\textsuperscript{13} The GTB calculations for undoped and underdoped cuprates are in good agreement with ARPES data both in the dispersion of the valence band and in the spectral intensity.\textsuperscript{14,15} A strong redistribution of spectral weight with hole doping and the formation of the in-gap states have been obtained in these calculations. Similar GTB calculations for the manganites has been done recently.\textsuperscript{16}

As any model Hamiltonian approach the GTB method is not \textit{ab initio}, there are many Hamiltonian parameters like intraatomic energy levels of $p$ and $d$ electrons, various $p-d$ and $p-p$ hopping parameters, Coulomb and exchange interaction parameters. These parameters have been obtained by fitting the set of optical, magnetic\textsuperscript{17} and ARPES data. Generally the question arises how unique the set of parameters is. To overcome this restriction we have proposed in this paper a novel LDA+GTB scheme that allows to calculate the GTB parameters by the \textit{ab initio} LDA approach.

The paper is organized as follows: In Section II the construction of Wannier functions from self-consistent LDA eigenfunctions as well as \textit{ab initio} parameters of the multiband $p-d$ model for \textit{La$_2$CuO$_4$} and \textit{Nd$_2$CuO$_4$} are given. A brief description of the GTB method is done in Section III. Section IV contains the LDA+GTB band structure calculations for \textit{La$_2$CuO$_4$} and \textit{Nd$_2$CuO$_4$}. The effective low-energy $t-J^*$ model with \textit{ab initio} pa-
rameters is presented in Section \[ \textbf{V} \]. Section \[ \textbf{VI} \] is the conclusion.

II. CALCULATION OF AB INITIO PARAMETERS FROM LDA

To obtain hopping integrals for different sets of bands included in consideration we apply projection procedure using Wannier functions (WFs) formalism. WFs were first introduced in 1937 by Wannier, as Fourier transformation of Bloch states $|\psi_{ik}\rangle$:

$$ [W^T] = \frac{1}{\sqrt{N}} \sum_k e^{-i\mathbf{k}\mathbf{T}} |\psi_{ik}\rangle, \quad (1) $$

where $\mathbf{T}$ is lattice translation vector, $N$ is the number of discrete $\mathbf{k}$ points in the first Brillouin zone and $i$ is band index. One major reason why the WFs have been little practical use in solid-state applications is their nonuniqueness since for a certain set of bands any orthonormal linear combination of Bloch functions $|\psi_{ik}\rangle$ can be used in it. Therefore to define them one needs an additional constraint. Among others Marzari and Vanderbilt proposed the condition of maximum localization for WFs, resulting in a variational procedure. To get a good initial guess authors of Ref. proposed to choose a set of localized trial functions $|\phi_n\rangle$ and project them onto the Bloch states $|\psi_{ik}\rangle$. It was found that this starting guess is usually quite good. This fact later led to the simplified calculating scheme where the variational procedure was abandoned as in present work and the result of the aforementioned projection was considered as the final step.

A. Wannier function formalism

To construct the WFs one should to define a set of trial orbitals $|\phi_n\rangle$ and choose the Bloch functions of interest by band indexes $(N_1, \ldots, N_2)$ or by energy interval $(E_1, E_2)$. Non-orthogonalized WFs in reciprocal $|\tilde{W}_{nk}\rangle$ space are then the projection of the set of site-centered atomic-like trial orbitals $|\phi_n\rangle$ on the Bloch functions $|\psi_{ik}\rangle$ of the chosen bands:

$$ |\tilde{W}_{nk}\rangle = \sum_i \langle \psi_{ik}|\psi_{ik}\rangle |\psi_{ik}\rangle |\phi_n\rangle, \quad (2) $$

where $c_i(k)$ is the band dispersion of $i$-th band obtained from self-consistent $ab\initio$ LDA calculation. In present work we use LMT-orbitals as trial functions. The Bloch functions in LMT basis are defined as

$$ |\psi_{ik}\rangle = \sum_{\mu} c^{k,\mu}_{i\mu} |\phi^{k,\mu}_{i\mu}\rangle, \quad (3) $$

where $\mu$ is the combined index representing $qlm$ ($q$ is the atomic number in the unit cell, $l$ and $m$ are orbital and magnetic quantum numbers), $\phi^{k,\mu}_{i\mu}(r)$ are the Bloch sums of the basis orbitals $\phi^{k,\mu}_{i\mu}(r-T)$.

$$ \phi^{k}_{i\mu}(r) = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} e^{i\mathbf{k}\mathbf{T}} \phi^{k}_{i\mu}(r-T), \quad (4) $$

and the coefficients are

$$ c_{i\mu}^{k} = \langle \phi_{i\mu}|\psi_{ik}\rangle. \quad (5) $$

Since in present work $|\phi_n\rangle$ is an orthogonal LMTO basis set orbital (in other words $n$ in $|\phi_n\rangle$ corresponds to the particular $qlm$ combination), then $\langle \psi_{ik}|\phi_n\rangle = c_{ni}^{k}$. Hence

$$ |\tilde{W}_{nk}\rangle = \sum_{i=N_1}^{N_2} |\psi_{ik}\rangle c_{ni}^{k} = \sum_{i=N_1}^{N_2} \sum_{\mu} c_{i\mu}^{k} c_{ni}^{k*} |\phi^{k}_{i\mu}\rangle. \quad (6) $$

In order to orthonormalize the WFs one needs to calculate the overlap matrix $O_{nn'}(k)$

$$ O_{nn'}(k) \equiv \langle \tilde{W}_{nk}|\tilde{W}_{n'k}\rangle = \sum_{i=N_1}^{N_2} c_{ni}^{k} c_{n'i}^{k*}, \quad (7) $$

then its inverse square root $S_{nn'}(k) = O^{-1/2}_{nn'}(k)$ is defined as

$$ S_{nn'}(k) \equiv O_{nn'}^{-1/2}(k). \quad (8) $$

In the derivation of the orthogonality of Bloch states $\langle \psi_{nk}|\psi_{n'k}\rangle = \delta_{nn'}$ was used.

From (6) and (7), the orthonormalized WFs in k-space $|\tilde{W}_{nk}|$ can be obtained as

$$ |\tilde{W}_{nk}\rangle = \sum_{n'} S_{nn'}(k) |\tilde{W}_{n'k}\rangle = \sum_{i=N_1}^{N_2} |\psi_{ik}\rangle c_{ni}^{k*}, \quad (9) $$

Then the matrix element of the Hamiltonian $\tilde{H}^{WF}$ in reciprocal space is

$$ H_{nn'}^{WF}(k) = \langle \tilde{W}_{nk}|\tilde{H}|\tilde{W}_{n'k}\rangle = \sum_{i=N_1}^{N_2} \sum_{k'} c_{ni}^{k*} c_{n'i}^{k} \xi_{i}(k') \langle \psi_{ik'}|\psi_{ik}\rangle \quad (10) $$

Hamiltonian matrix element in real space is

$$ H_{nn'}^{WF}(\mathbf{T}) = \langle \tilde{W}_{nk}^{\mathbf{0}}|\tilde{H}|\tilde{W}_{n'k}^{\mathbf{T}}\rangle = \frac{1}{N} \sum_{k} \sum_{i=N_1}^{N_2} c_{ni}^{k*} c_{n'i}^{k} \xi_{i}(k) e^{-i\mathbf{k}\mathbf{T}}, \quad (11) $$

here atom $n'$ is shifted from its position in the primary unit cell by a translation vector $\mathbf{T}$. For more detailed description of this procedure see [22].
B. LDA band structure, hopping and Coulomb parameters for p- and n-type cuprates

Basically all cuprates have one or more CuO2 planes in their structure, which are separated by layers of other elements (Ba, Nd, La, ...). They provide the carriers in CuO2 plane and according to the type of carriers all cuprates can be divided into two classes: p-type and n-type. In present paper we deal with the simplest representatives of this two classes: La2−xSrxCuO4 (LSCO) and Nd2−xCexCuO4 (NCCO) correspondingly.

LDA band calculation for La2CuO4 and Nd2CuO4 was done within LMTO method using atomic sphere approximation in tight-binding approach (TB-LMTO-ASA). In the case of Nd2CuO4 Nd-4f states were treated as pseudocore states.

La2CuO4 at the low temperature and zero doping has the orthorhombic structure (LTO) with the space group Bmab. The lattice parameters and atomic coordinates at 10 K were taken from Ref.33 to be a=5.3346, b=5.4148 and c=13.1172 Å, La (0, -0.0083, 0.3616), Cu (0, 0, 0), O6 (0.25, 0.25, -0.0084), Oa (0, 0.0404, 0.1837). Here and below O6 denotes in-plane oxygen ions and Oa - apical oxygen ions. In comparison with high temperature tetragonal structure (HTT) orthorhombic La2CuO4 have two formula units per unit cell and the CuO6 octahedra are rotated cooperatively about the [110] axis. As a result O6 ions are slightly moved off the Cu plane and four in-plane La-Oa bond lengths are unequal.

Nd2CuO4 at the room temperature and zero doping has the tetragonal structure with the space group I4/mmm also called T’-structure. The lattice parame-
Cu ions at the 2a site (0, 0, 0) are surrounded by four oxygen ions O1 which occupy 4c position (0, 1/2, 0). The Nd at the 4c site (0, 0, 0.35112) have eight nearest oxygen ions neighbours O2 at 4d position (0, 1/2, 1/4). One can imagine body-centered T'-structure as the HTT structure of La$_2$CuO$_4$ but with two oxygen atoms moved from apices of each octahedron to the face of the cell at the midpoints between two oxygen atoms on the neighbouring CuO$_2$ planes. In other words Nd$_2$CuO$_4$ in T'-structure has no apical oxygen around Cu ion.

The LDA band structure of both compounds along the high-symmetry lines in the Brillouin zone is shown in Figs. 1 and 2 by dotted lines. The coordinates of high-symmetry points in BZ are given on top of each picture. The complex of bands in the energy range (-8, 2.5) eV consists primarily of Cu-3d and O-2p states. The total bandwidths amount 10 eV for La-cuprate and 7 eV for Nd-cuprate. Contribution of Cu-3d and O-2p orbitals to the different bands is displayed by arrows.

One can see that the band crossing $E_F$ have character of Cu-3$d_{x^2-y^2}$ and O$p_{x,y}$ for La$_2$CuO$_4$ and Cu-3$d_{x^2-y^2}$, O1-$p_{x,y}$ in the case of Nd$_2$CuO$_4$. It corresponds to antibonding pd$e$ orbital. So for hoppings calculation the projection on Cu-4$d$ orbitals for La-cuprate and Cu-4$d$ orbitals for Nd-cuprate was done. Such set of orbitals corresponds to the 3-band $p-d$ model. The bands obtained by the described in Sec. II A projection procedure are shown by solid lines in Figs. 1 and 3. It is clearly seen that in case of La$_2$CuO$_4$ 3-band model did not reproduce the band crossing $E_F$ properly (Fig. 1 SR direction).

Since 3-band $p-d$ model didn’t provide proper description of the LDA bands around Fermi level the projection on more complex set of trial orbitals for both compounds was done. The resulting bands are plotted by solid lines in Figs. 2 and 4. Corresponding multiband $p-d$ model contains Cu-3$d_{x^2-y^2}$, Cu-3$d_{z^2-r^2}$, Cu-4$p_{x,y}$, O$p_{x,y}$, O$p_{z}$ states for La$_2$CuO$_4$ and Cu-3$d_{x^2-y^2}$, Cu-3$d_{z^2-r^2}$, O1-$p_{x,y}$, O1-$p_y$ orbitals for Nd$_2$CuO$_4$. The energy range for projection was (-8.4, 2.5) eV and (-8, 2) eV for the case of La-cuprate and Nd-cuprate correspondingly. The main effect of taking into account Cu-3$d_{z^2-r^2}$ and O$p_{z}$ states for La$_2$CuO$_4$ is the proper description of the band structure (in comparison with LDA calculation) at the energies up to 2 eV below Fermi level. From Fig. 3 and 4 one can see that in case of Nd$_2$CuO$_4$ both sets of trial orbitals properly describe the LDA band crossing the Fermi level which has Cu-3$d_{x^2-y^2}$ symmetry. At the same time its bonding part does not agree well with the LDA bands since projection did not include all Cu-3$d$ and O-$p$ orbitals.

The resulting hopping parameters and energy of particular orbitals for two sets of trial orbitals are presented in Tables I and II. The second column contains the connecting vector $T$ between two sites. It is clearly seen that hoppings decay quite rapidly with distance between ions. For the multiband $p-d$ model the values of Coulomb parameters are also required. For Cu in La$_2$CuO$_4$ they were obtained in constrained LDA supercell calculations$^{35}$ to be $U = 10$ eV and $J = 1$ eV$^{36}$. For the Nd$_2$CuO$_4$ we will use the same values of these parameters.

### III. GTB METHOD OVERVIEW

As the starting model that reflects chemical structure of the cuprates it is convenient to use the 3-band $p-d$ model$^{18,19}$ or the multiband $p-d$ model$^{27}$. While the first one is simpler it lacks for some significant features, namely importance of $d_{z^2}$ orbitals on copper and $p_z$ orbitals on apical oxygen. Non-zero occupancy of $d_{z^2}$ orbitals pointed out in XAS and EELS experiments which shows 2-10% occupancy of $d_{z^2}$ orbitals$^{38,39}$ and 15% doping dependent occupancy of $p_z$ orbitals$^{40}$ in all hole doped High-$T_c$ compounds). Henceforth the multiband $p-d$ model will be used.

Let us consider the Hamiltonian with the following general structure:

$$H = \sum_{f,g,\lambda,\lambda'} (\epsilon_\lambda - \mu) n_{f\lambda} + \sum_{f\neq g, \lambda, \lambda'} T^{\lambda \lambda'}_{fg} c_{f\lambda}^{\dagger} c_{g\lambda'} \sigma$$

$$+ \frac{1}{2} \sum_{f,g,\lambda,\lambda',\sigma_{1,2,3,4}} V^{\lambda\lambda'}_{fg} c_{f\lambda\sigma_1}^{\dagger} c_{f\lambda\sigma_2} c_{g\lambda'\sigma_3}^{\dagger} c_{g\lambda'\sigma_4} \sigma \tag{10}$$
TABLE II: Hopping parameters and single electron energies for Nd$_2$CuO$_4$ obtained in WF projection procedure for different sets of trial orbitals (all values in eV). Here $x^2$, $z^2$, $p_x$, $p_y$, $p_z$ denote Cu-$dz^2$-$y^2$, Cu-$dz^2$-$x^2$, O-$p_x$, O-$p_y$, O-$p_z$ orbitals correspondingly. The 3-d and 4-th columns correspond to bases of the $3$-band and the multiband $p-d$ models respectively.

| Hopping       | Connecting vector | Cu-$x^2$, $O_{p_x, p_y}$ | Cu-$z^2$, $O_{p_x, p_y}$ |
|---------------|-------------------|--------------------------|--------------------------|
| $t(x^2,x^2)$  | $(1, 0)$          | 0.01                     | 0.01                     |
| $t'(x^2,x^2)$ | $(1, 1)$          | -0.00                    | -0.00                    |
| $t(z^2,z^2)$  | $(1, 0)$          | 0.01                     | 0.01                     |
| $t'(z^2,z^2)$ | $(1, 1)$          | -0.00                    | -0.00                    |
| $t(x^2,p_x)$  | $(0.5,0)$         | 1.18                     | 1.18                     |
| $t'(x^2,p_x)$ | $(0.5,1)$         | 1.00                     | 0.01                     |
| $t(z^2,p_x)$  | $(0.5,0.771)$     | 0.00                     | 0.67                     |
| $t'(z^2,p_x)$ | $(0.5,0.771)$     | 0.00                     | 0.67                     |
| $t(p_x,p_y)$  | $(0.5,0.5,0.771)$ | 0.00                     | 0.00                     |
| $t'(p_x,p_y)$ | $(0.5,0.5,0.771)$ | 0.00                     | 0.00                     |

where $c_{f\lambda\sigma}$ is the annihilation operator in Wannier representation of the hole at site $f$ at orbital $\lambda$ with spin $\sigma$, $\eta_{f\lambda\sigma} = c_{f\lambda\sigma}^\dagger c_{f\lambda\sigma}$.

In particular case of cuprates and corresponding multiband $p-d$ model, $f$ runs through copper and oxygen sites, index $\lambda$ run through $dz^2$-$y^2$ and $dz^2$-$x^2$ orbitals on copper, $p_x$ and $p_y$ atomic orbitals on the $O_p$-oxygen sites and $p_z$ orbital on the apical $O_a$-oxygen; $\epsilon_{\lambda}$ - single-electron energy of the atomic orbital $\lambda$. $T_{fg\lambda\gamma}$ includes matrix elements of hoppings between copper and oxygen ($t_{pd}$ for hopping $dz^2 \leftrightarrow p_x, p_y$; $t_{pd}/\sqrt{3}$ for $dz^2 \leftrightarrow p_x, p_y$; $t_{pd}'$ for $dz^2 \leftrightarrow p_z$) and between oxygen and oxygen ($t_{pp}$ for hopping $p_x, p_y$; $t_{pp}'$ for hopping $p_x, p_y$). The Coulomb matrix elements $V_{fg\lambda\gamma}$ includes intraatomic Hubbard repulsions of two holes with opposite spins on one copper and oxygen orbital ($U_d$, $U_p$), between different orbitals of copper and oxygen ($V_d$, $V_p$), Hund exchange on copper and oxygen ($J_d$, $J_p$) and the nearest-neighbor copper-oxygen Coulomb repulsion $V_{pd}$.

GTB methods consist of exact diagonalization of intracell part of the multiband Hamiltonian and perturbative account of the intercell part. For La$_2$Sr$_2$CuO$_4$ and Nd$_2$-Ce$_2$CuO$_4$ the unit cells are CuO$_6$ and CuO$_4$ clusters, respectively, and a problem of nonorthogonality of the molecular orbitals of adjacent cells is solved by an explicit fashion using the diagonalization in k-space. In a new symmetric basis the intracell part of the total Hamiltonian is diagonalized, allowing to classify all possible effective quasiparticle excitations in CuO$_2$-plane according to a symmetry. To describe this process the Hubbard X-operators are introduced. Index $m \leftrightarrow (p, q)$ enumerates quasiparticle with energy $\omega_m = \epsilon_p (N+1) - \epsilon_q (N)$, where $\epsilon_p$ is the $p$-th energy level of the N-electron system. There is a correspondence between Hubbard operators and single-electron creation and annihilation operators:

$$c_{f\lambda\sigma} = \sum_m \gamma_{\lambda\sigma} (m) X^m_f,$$

where $\gamma_{\lambda\sigma} (m)$ determines the partial weight of a quasiparticle $m$ with spin $\sigma$ and orbital index $\lambda$. Using this correspondence we rewrite the Hamiltonian

$$H = \sum_{f,p} (\epsilon_p - N\mu) X^p_f + \sum_{f \neq g, m,m'} t_{m'm}^p X^m_f X^{m'}_g.$$

This Hamiltonian, actually, have the form of the multiband Hubbard model.

Diagonalization of the Hamiltonian mentioned above gives energies $\epsilon_p$ and the basis of Hubbard operators $X^m_f$. Values of the hoppings,

$$t_{m'm}^p = \sum_{\sigma,\lambda,\lambda'} T_{fg\lambda\gamma} \gamma_{\lambda\sigma} (m) \gamma_{\lambda'\sigma} (m'),$$

are calculated straightforwardly using the exact diagonalization of the intracell part of the Hamiltonian.

Again, in particular case of multiband $p-d$ model, the essential for cuprates multielectron configurations are $d^{10}p^6$ (vacuum state $|0\rangle$) in a hole representation, single-hole configurations $d^9p^6$, $d^9p^5$, and two-hole configurations $d^8p^6$, $d^8p^5$. In the single-hole sector of the Hilbert space the $b_g$ molecular orbital, that we will denote later as $|\sigma\rangle = \{|\uparrow\rangle, |\downarrow\rangle\}$, has the minimal energy. In the two-hole sector the lowest energy states are singlet state $|S\rangle$ with $^1A_{1g}$ symmetry, that includes Zhang-Rice singlet among other local singlets, and triplet states $|T\rangle = |TM\rangle (M = +1, 0, -1)$ with $^3B_{1g}$ symmetry. All these states form the basis of the Hamiltonian, and they are shown together with quasiparticle excitations between them in the Fig. 3.

In this basis relations between annihilation-creation operators $c_{f\lambda\sigma}$ and Hubbard X-operators $X^m_f$ are

$$c_{f\lambda\sigma} = u X^0_{f\sigma} + 2 \sigma \gamma_{\lambda\sigma} X^S_{f\sigma},$$
$$c_{f\lambda\sigma} = v X^0_{f\sigma} + 2 \sigma \gamma_{\lambda\sigma} X^S_{f\sigma},$$
$$c_{f\lambda\sigma} = \gamma_{\sigma} (\sqrt{2} X^T_{f\sigma} + X^{T2}_{f\sigma}),$$
$$c_{f\lambda\sigma} = \gamma_{\sigma} (\sqrt{2} X^T_{f\sigma} - X^{T2}_{f\sigma}),$$
$$c_{f\lambda\sigma} = \gamma_{\sigma} (\sqrt{2} X^T_{f\sigma} - X^{T2}_{f\sigma}),$$
and the explicit form of the Hamiltonian \([\text{12}]\) is given by

\[
H_{pd} = \sum_{\mathbf{f}} \left[ \varepsilon_1 \sum_{\sigma} X_{\sigma f}^2 + \varepsilon_{25} X_{\sigma f} S_{\sigma f} + \varepsilon_{2T} \sum_{M} X_{\sigma f}^{TM, TM} \right] + \sum_{\mathbf{f} \neq \mathbf{g}, \sigma} \left[ t_{fg}^{00} X_{\sigma f} X_{\sigma g} + t_{fg}^{SS} X_{\sigma f} \bar{\sigma} X_{\sigma g} \bar{\sigma} + 2\sigma \right] + \sum_{\mathbf{f}} \left[ t_{fg}^{ST} \left\{ (\sigma \sqrt{2} X_{\sigma f}^{T0, \bar{\sigma}} - X_{\sigma f}^{T20, \sigma}) (\nu \sigma X_{\sigma f}^{T0, \sigma} + 2\sigma \nu \sigma X_{\sigma f}^{T0, \bar{\sigma}} + h.c.) + t_{fg}^{TT} \left( \sigma \sqrt{2} X_{\sigma f}^{T0, \bar{\sigma}} - X_{\sigma f}^{T20, \sigma} \right) \right\} \right].
\]

Here \(\sigma = -\sigma\). The relation between effective hoppings \([\text{13, 14}]\) in this Hamiltonian and microscopic parameters of the multiband \(p - d\) model is as follows:\n
\[
\begin{align*}
t_{fg}^{00} &= -2t_{pd} \mu_{fg} 2uv - 2t_{pp} \nu_{fg} v^2, \\
t_{fg}^{SS} &= -2t_{pd} \mu_{fg} \gamma_{x, \gamma} \gamma_{b} - 2t_{pp} \nu_{fg} \gamma_{b}, \\
t_{fg}^{OS} &= -2t_{pd} \mu_{fg} (w_{\gamma_{x}} + u_{\gamma_{b}}) - 2t_{pp} \nu_{fg} \gamma_{b}, \\
t_{fg}^{TT} &= \frac{2t_{pd}}{\sqrt{3}} \lambda_{fg} 2\gamma_{x} \gamma_{b} + 2t_{pp} \nu_{fg} \gamma_{b} - 2t'_{pp} \lambda_{fg} 2\gamma_{p} \gamma_{b}, \\
t_{fg}^{ST} &= \frac{2t_{pd}}{\sqrt{3}} \xi_{fg} \gamma_{b} + 2t_{pp} \chi_{fg} \gamma_{b} - 2t'_{pp} \xi_{fg} \gamma_{b}.
\end{align*}
\]

The factors \(\mu, \nu, \lambda, \xi, \chi\) are the coefficients of Wannier transformation made in the GTB method and \(u, v, \gamma_{x}, \gamma_{b}, \gamma_{a}, \gamma_{p}, \gamma_{z}\) are the matrix elements of annihilation-creation operators in the Hubbard \(X\)-operators representation\([\text{35}]\).

Calculations\([\text{23, 24}]\) of the quasiparticle dispersion and spectral intensities in the framework of the multiband \(p - d\) model by the GTB method are in very good agreement to the ARPES data on insulating compound Sr\(_2\)CuO\(_2\)Cl\(_2\)\([\text{45, 46}]\). Other significant results of this method are\([\text{47, 48}]\):

i) pinning of Fermi level in LSCO at low concentrations was obtained in agreement with experiments\([\text{19, 20}]\). This pinning appears due to the in-gap state, spectral weight of this state is proportional to doping concentration \(x\) and when Fermi level comes to this in-gap band then Fermi level “pins” there. The localized in-gap state exist in NCCO also for the same reason as in LSCO, but its energy is determined by the extremum of the band at \((\pi/2, \pi/2)\) point and it appears to be above the bottom of the conductivity band. Thus, the first doped electron goes into the band state at the \((\pi, 0)\) and the chemical potential \(\mu\) for the very small concentration merges into the band. At higher \(x\) it meets the in-gap state with a pinning at \(0.08 < x < 0.18\) and then \(\mu\) again moves into the band. The dependence \(\mu(x)\) for NCCO is quite asymmetrical to the LSCO and also agrees with experimental data\([\text{49}]\).

ii) experimentally observed\([\text{50}]\) evolution of Fermi surface with doping from hole-type (centered at \((\pi, \pi)\)) in the underdoped region to electron-type (centered at \((0, 0)\)) in the overdoped region is qualitatively reproduced:

iii) pseudogap feature for LSCO is obtained as a lowering of density of states between the in-gap state and the states at the top of the valence band.

In all these calculations the set of the microscopic model parameters, obtained by fitting to experimental ARPES data\([\text{45, 50}]\) was used. Hoppings and single-electron energies are listed in Table \([\text{11}]\) values of Coulomb parameters are as follows:

\[
\begin{align*}
U_{d} &= V_{d} = 9, U_{p} = V_{p} = 4, \\
J_{d} &= 1, J_{p} = 0, V_{pd} = 1.5.
\end{align*}
\]
All results above were obtained treating the intercell hopping in the Hubbard-I approximation. The GTB method is not restricted to such a crude approximation. The Fourier transform of the two-time retarded Green function energy representation can be rewritten in terms of matrix Green function $D_{\vec{k}\sigma}^{mn}(E)$:

$$
\left\langle \left( \begin{array}{c} X_{\vec{k}\sigma}^m \\ X_{\vec{k}\sigma}^{m'} \end{array} \right) \rightangle_E = \left( \begin{array}{c} c_{\vec{k}\lambda\sigma} \\ c_{\vec{k}\lambda\sigma}^{*} \end{array} \right) = \sum_{m',m}\gamma_{\lambda\sigma}(m)\gamma_{\lambda\sigma}^{*}(m')D_{\vec{k}\sigma}^{mm'}(E).
$$

The diagram technique for Hubbard X-operators is developed \(^{23,24}\) and the generalized Dyson equation \(^{24}\) reads:

$$
\hat{D}_{\vec{k}\sigma}(E) = \left( \left[ \hat{G}_{\vec{k}\sigma}(0) \right]^{-1} + \hat{\Sigma}_{\vec{k}\sigma}(E) \right)^{-1} \tilde{P}_{\vec{k}\sigma}(E).
$$

Here, $\hat{\Sigma}_{\vec{k}\sigma}(E)$ and $\tilde{P}_{\vec{k}\sigma}(E)$ are the self-energy and the strength operators, respectively. The presence of the strength operator is due to the redistribution of the spectral weight, that is an intrinsic feature of SCES. First time it was introduced in the spin diagram technique and called “a strength operator” \(^{24}\) because the value of $\tilde{P}_{\vec{k}\sigma}(E)$ determines an oscillator strength of excitations.

It is also should be stressed, that $\hat{\Sigma}_{\vec{k}\sigma}(E)$ in Eq. (17) is the self-energy in X-operators representation and therefore it is different from the self-energy entering Dyson equation for the Green function $\left\langle \left( \begin{array}{c} c_{\vec{k}\lambda\sigma} \\ c_{\vec{k}\lambda\sigma}^{*} \end{array} \right) \right\rangle_E$. The Green function $\hat{G}_{\vec{k}\sigma}^{(0)}(E)$ is defined by the formula

$$
\hat{G}_{\vec{k}\sigma}^{(0)}(E) = \left( \hat{G}_{\vec{k}\sigma}(0) \right)^{-1} + \hat{\Sigma}_{\vec{k}\sigma}(E)\tilde{P}_{\vec{k}\sigma}(E)\tilde{t}_{\vec{k}\sigma},
$$

where $\hat{G}_{\vec{k}\sigma}(0)$ is the free propagator and $\tilde{t}_{\vec{k}\sigma}$ is the interaction matrix element (for the Hubbard model, $t_{\vec{k}\sigma}^{mn}\gamma_{\lambda\sigma}(m)\gamma_{\lambda\sigma}^{*}(m')\tilde{t}_{\vec{k}}$, and $G_{\vec{k}\sigma}^{0}(E) = \delta_{mm'}/(iE-\varepsilon_1)$).

In the Hubbard-I approximation at $U \gg W$ the self-energy $\hat{\Sigma}_{\vec{k}\sigma}(E)$ is equal to zero and the strength operator $P_{\vec{k}\sigma}(E)$ is replaced by $P_{\vec{k}\sigma}(E) \rightarrow \tilde{P}_{\vec{k}\sigma} = \delta_{mm}P_{\vec{k}\sigma}^{m}$, where $P_{\vec{k}\sigma} = \left\langle X_{f\sigma}^{m}\right\rangle + \left\langle X_{q\sigma}^{m}\right\rangle$ is the occupation factor.

So, in this approximation the following equation is derived from Eq. (17):

$$
\hat{D}_{\vec{k}\sigma}^{(0)} = \left( \hat{G}_{\vec{k}\sigma}(0) - \tilde{P}_{\vec{k}\sigma}\tilde{t}_{\vec{k}\sigma} \right)^{-1} \bar{P}_{\vec{k}\sigma}.
$$

Using diagram technique for the X-operators it is possible to find solution in the GTB method beyond the Hubbard-I approximation. But such discussion is far from the scope of this paper’s goals.

It should be stressed that the GTB bands are not free electron bands of the conventional band structure, these are the quasiparticle bands with the number of states in each particular band depending on the occupation number of the initial and final multielectron configurations, and thus on the electron occupation. Bands with zero spectral weight or spectral weight proportional to doping value $x$ appear in the GTB approach.

IV. LDA+GTB METHOD: RESULTS AND DISCUSSION

In this Section we will describe the LDA+GTB method itself and some results of this approach.

In LDA+GTB scheme all parameters of the multiband model are calculated within the ab initio LDA (by Wannier function projection technique, see Sec. II A) and constrained LDA method \(^{24}\). Analysis of the LDA band structure gives the minimal model that should be used to describe the physics of system under consideration. Although LDA calculation does not give correct description of the SCES band structure, it gives ab initio parameters and reduced number of essential orbitals or the “minimal reliable model”. Then, the effects of strong electron correlations in the framework of this model with ab initio calculated parameters are explicitly taken into account within the GTB method and the quasiparticle band structure is derived.

In Section IV the ab initio calculations for undoped La$_2$CuO$_4$ and Nd$_2$CuO$_4$ are presented. One can see that in the 3-band model (Figs. 3 and 4) it is possible to describe the top of the valence band but not the lower lying excitations withing 4 eV. The main effect of taking into account Cu-d$_{3z^2-r^2}$ and O$_2$p$_z$ states for La$_2$CuO$_4$ system is the proper description of the band structure (in comparison with LDA calculation) at the energies up to 4 eV below Fermi level (see Fig. 3). Of course, the ab initio LDA band structure is not correct in undoped cuprates, but it gives an indication what orbitals should be included in more appropriate calculations. Therefore if one needs to describe quantitatively the low-energy excitations of La$_{2-x}$Sr$_x$CuO$_4$, the Cu-d$_{3z^2-r^2}$ and O$_2$p$_z$ states should be taken into account and the reliable minimal model is the multiband $p$−$d$ model. In Nd$_2$CuO$_4$ the Cu-d$_{3z^2-r^2}$ and O$_2$p$_z$ states does not contribute significantly to the band structure (compare Figs. 3 and 4) and the minimal model is the 3-band $p$−$d$ model. Nevertheless to treat $p$- and $n$-type cuprates on equal footing later we will use the same multiband $p$−$d$ model for both LSCO and NCCO with different material dependent parameters. Hopping parameters decay rapidly with distance (see Tables II and III) so in GTB calculation we will use only nearest copper-oxygen and oxygen-oxygen hoppings which are listed in Table III.

In Refs. 57, 58 ab initio calculations were done for YBa$_2$Cu$_3$O$_7$ and La$_2$CuO$_4$, and single-electron energy $\varepsilon_{p_z} = 0.9$ eV was obtained. This value is very close to the one presented in Table III. But in Refs. 57, 58 the Cu-s states were taken into account with energy $\varepsilon_s = -6.5$ eV. Our LDA calculations shows that Cu-s bands contributes to the band structure shown in Figs. 2 and 4 at approximately 7 eV below and at 2 eV above Fermi level. Therefore Cu-s states does not contribute significantly to the low-energy physics. But these states can contribute to the effective intraplane hopping parameters $t'$ and $t''$ between the nearest and next-nearest neighboring unit cells. In our LDA+GTB method Cu-s states are
neglected. It could be a reason why for La$_2$CuO$_4$ our $t'/t = -0.137$ (see Table IV) is less then $t'/t = -0.17$ obtained in Ref. SS where influence of Cu-s orbital on hoppings was taken into account.

There is a claim that pd$\pi$-bonds and non-bonding oxygen states are very important in low-energy physics of High-$T_c$ cuprates. To discuss this topic lets start with analysis of ab initio calculations. Present LDA calculations show that anti-bonding bands $\sigma^*$ of $\pi$-bonds (Cu-d+$O$-$p\pi$, see Figs. II and III) situated slightly below $\pi^*$ bands of Cu-d$_{3z^2-r^2}$ origin in La$_2$CuO$_4$ and slightly above anti-bonding $\sigma^*$ bands of Cu-$d_{3z^2-r^2}$ origin in Nd$_2$CuO$_4$ (see Figs. II and III). GTB calculations show that states corresponding to $\sigma^*$ band contributes to the $\sigma_{1g}$ molecular orbital in the single-hole sector of the Hilbert space. This $\sigma_{1g}$ molecular orbital situated about $b_{1g}$ state $|\sigma\rangle = \{|\uparrow\rangle, |\downarrow\rangle\}$ by an energy about 1.2 eV. From the relative position of $\sigma^*$ and $\pi^*$ bands in LDA calculations we conclude that the energy of molecular orbital corresponding to $\sigma^*$ band will be situated around energy of $\sigma_{1g}$ state. Therefore, it will be above $|\sigma\rangle$ state by about 1.0 $\pm$ 1.4 eV. Also, both states corresponding to $\pi^*$ and $\sigma^*$ are empty in undoped compound and spectral weight of quasiparticle excitations to or from these states will be zero. Summarizing, $\pi$-bonds, as well as $\sigma^*$ states, will contribute to the GTB dispersion only upon doping and only in the depth in the valence band below 1 eV from the top. Moreover, since energy difference between triplet $|T\rangle$ and singlet $|S\rangle$ states is about 0.5 eV the contribution from the singlet-triplet excitations will be much more important to the low-energy physics. Although, $\pi$-bonds could be important for explanation of some optical and electron-energy loss spectroscopy experiments, but in description of low-energy physics of interest they could be neglected. The non-bonding oxygen states contribute to the valence band with energy about 2 $\pm$ 3 eV below the top. That is why we will not take $\pi$-bonds and non-bonding oxygen states in our further consideration.

Now we have an idea what model should be used and ab initio microscopic parameters of this model. As described in Section III the GTB method is appropriate method for description of SCES in Mott-Hubbard type insulators and it’s results are in good agreement with experimental data. Then it is natural to use this method to work with the ab initio derived multiband p $-$ d model.

The parameters of the Hamiltonian in the GTB method derived from ab initio one are presented in Tables IV and V for p- and n-type cuprates, respectively. Single-electron energies (in eV) and matrix elements of annihilation-creation operators in the X-operators representation were calculated for both LSCO:

$$
\begin{align*}
\epsilon_1 &= -1.919, \epsilon_{2S} = -2.010, \epsilon_{2T} = -1.300, \\
u &= -0.707, v = -0.708, \gamma_z = -0.619, \\
\gamma_b &= -0.987, \gamma_a = -0.032, \gamma_p = -0.962, \gamma_z = -0.237,
\end{align*}
$$

and NCCO:

$$
\epsilon_1 = -1.660, \epsilon_{2S} = -1.225, \epsilon_{2T} = -0.264, \\
u = -0.756, v = -0.655, \gamma_z = 0.626, \\
\gamma_b = 0.984, \gamma_a = -0.008, \gamma_p = 0.997, \gamma_z = 0.037.
$$

It is known that sign of the hoppings in the $t - t' - t'' - J$ model changes during electron-hole transformation of the operators. Therefore, $t_\rho$ will have different signs in p- and n-type cuprates. In present paper we don’t do electron-hole transformation of the operators and both $t - t' - t'' - J^*$ and singlet-triplet $t - t' - t'' - J^*$ models are written using hole operators. Because of that there is no difference in signs of the hoppings $t_\rho$ for the hole and electron doped systems presented in Tables IV and V.

As the next step we calculate the band structure of the undoped antiferromagnetic (AFM) insulating cuprate within the GTB method. Results for both GTB method with fitting parameters and LDA+GTB method with ab initio parameters (Table III) are presented in the Fig. IV for La$_2$CuO$_4$ and in the Fig. V for Nd$_2$CuO$_4$.

The GTB band structure obtained for both phenomenological and ab initio sets of parameters is almost identical: the valence band, located below 0 eV in figures, and the conductivity band, located above +1.5 eV, divided by the insulator gap of the charge transfer origin $E_{ct} \approx 2$ eV; the undoped La$_2$CuO$_4$ and Nd$_2$CuO$_4$ are insulators in both antiferromagnetic and paramagnetic states. In-gap states at the top of the valence band and about the bottom of the conductivity band are shown by dashed lines. Their spectral weights and dispersions are proportional to doping $x$ and concentration of magnons. Therefore, for undoped compounds, in the Hubbard-I approximation used in GTB method, these states are dispersionless with zero spectral weight.

### Table IV: Parameters of the multiband Hubbard model and exchange integral $J$ for LSCO obtained in the framework of the LDA+GTB method (all values in eV).

| $\rho$ | $t_{10}^{b0}$ | $t_{10}^{bS}$ | $t_{10}^{bS}$ | $t_{10}^{bT}$ | $t_{10}^{bST}$ | $J_\rho$ |
|---|---|---|---|---|---|---|
| (0.1) | 0.453 | 0.679 | 0.560 | 0.004 | -0.086 | 0.157 |
| (1.1) | -0.030 | -0.093 | -0.055 | -0.001 | 0 | 0.001 |
| (0.2) | 0.068 | 0.112 | 0.087 | 0.002 | -0.016 | 0.004 |
| (2.1) | 0.003 | -0.005 | 0 | 0 | -0.002 | 0 |

### Table V: The same as in Table IV but for NCCO. Hoppings giving main contribution to the bottom of the conductivity band are shown by bold type.

| $\rho$ | $t_{10}^{b0}$ | $t_{10}^{bS}$ | $t_{10}^{bS}$ | $t_{10}^{bT}$ | $t_{10}^{bST}$ | $J_\rho$ |
|---|---|---|---|---|---|---|
| (0.1) | 0.410 | 0.645 | -0.523 | 0 | -0.0052 | 0.137 |
| (1.1) | -0.013 | -0.076 | 0.035 | 0 | 0 | 0.001 |
| (0.2) | 0.058 | 0.104 | -0.078 | 0 | -0.0002 | 0.003 |
| (2.1) | 0.005 | -0.002 | -0.003 | 0 | -0.0004 | 0 |
The valence band have bandwidth about 6 eV and consists of a set of very narrow subbands with the highest one at the top of the valence band - the so-called “Zhang-Rice singlet” subband. The dominant spectral weight in the singlet band stems from the oxygen $p$-states, while for the bottom of the empty conductivity band it is from $d_{x^2-y^2}$-states of copper. Both methods give small, less then 0.5 eV, splitting between the $^1A_{1g}$ Zhang-Rice-type singlet band and $^3B_{1g}$ narrow triplet band located below the singlet band (e.g. in the Fig. 6 for Nd$_2$CuO$_4$ it is located at -1.5 eV). The energy of Cu-$d_{x^2-y^2}$ orbital plays the dominant role in this splitting in the GTB method. For La$_2$CuO$_4$ energy $\varepsilon_{d_{x^2-y^2}}$ is smaller then for Nd$_2$CuO$_4$ (see Table III). This results in smaller width of the singlet band for the LSCO compared to the NCCO: about 0.5 eV and 1 eV correspondingly.

However, for La$_2$CuO$_4$ minor discrepancies occurs in the dispersion of the bottom of the conductivity band near $(\pi,0)$ point obtained by GTB with phenomenological set of parameters and by LDA+GTB. This leads to the different character of the optical absorption edge in two presented methods. The absorption edge for the LDA+GTB is formed by the indirect transitions in contrast to the GTB method with phenomenological set of parameters, where the momentum of excited quasiparticle is conserved by optical transition at the absorption edge. For Nd$_2$CuO$_4$ both GTB method with fitting parameters and LDA+GTB result in the conductivity band minima at the $(\pi,0)$ point (see Fig. 7). Also, in the LDA+GTB method the triplet band dispersion and the singlet-triplet hybridization are much smaller then in the GTB method with fitting parameters. This happens mainly due to the smaller values of $t_{pp}'$ used in LDA+GTB method, because it is this microscopic parameter that gives main numerical contribution (see Eqs. (15), (20) and (21)) to the $t_{fG}^{TT}$ and $t_{fG}^{ST}$ - hop-
pings that determines the triplet band dispersion and the singlet-triplet hybridization respectively. So, despite some minor discrepancies, both GTB method with phenomenological parameters and LDA+GTB method without free parameters gives similar band dispersion.

Next topic that we will discuss in connection to the LDA+GTB method is the value of magnetic moment on copper $M_{\text{Cu}}$. From the neutron diffraction studies of $\text{La}_{2}\text{CuO}_{4}$ and $\text{YBa}_{2}\text{Cu}_{3}\text{O}_{6}$ it is known that $M_{\text{Cu}}$ is equal to $0.5\mu_B$ where $\mu_B$ is Bohr magneton. There are two reasons of why $M_{\text{Cu}}$ is different from the free atomic value $1.14\mu_B$ in $S = 1/2 \text{Cu}^{2+}$, namely zero temperature quantum spin fluctuations and the covalent effect. Since each oxygen have two neighboring coppers belonging to different magnetic sublattices the total moment on oxygen is equal to zero. But due to $p-d$ hybridization the $p$-states of oxygen are partially filled so these orbitals could carry non-zero magnetic moment $M_{\text{O}}$, while total moment on oxygen will be equal to zero. Such space distribution of magnetic moment leads to the differences between experimentally observed antiferromagnetic form-factor for $\text{La}_{2}\text{CuO}_{4}$ and the Heisenberg form-factor of $\text{Cu}^{2+}$. In order to take into account covalent effects and zero quantum fluctuations on equal footing we will write down the expression for $M_{\text{Cu}}$:

$$M_{\text{Cu}} = 2.28\mu_B \langle S^z \rangle u^2,$$  \hspace{1cm} (22)

where zero quantum spin fluctuations are contained in $\langle S^z \rangle$ and covalent effects are described by the weight $u^2$ of the $d^9p^6$ configuration. The last quantity is calculated in the framework of the LDA+GTB method and equal to $u^2 = 0.5$. In paper the value $\langle S^z \rangle = 0.3$ was obtained self-consistently in the effective quasi-two-dimensional Heisenberg antiferromagnetic model for typical in $\text{La}_{2}\text{CuO}_{4}$ ratio $10^{-5}$ of the interplane and intraplane exchange parameters. Close value of $\langle S^z \rangle = 0.319$ was obtained in Ref.\cite{67} where also the plaquette ring-exchange was considered in Heisenberg Hamiltonian. Using Eq.\cite{22} and above values of $u^2$ and $\langle S^z \rangle$ we have calculated magnetic moment on copper $M_{\text{Cu}} = 0.4\mu_B$, that is close to the experimentally observed $M_{\text{Cu}} = 0.5\mu_B$.

Summarizing this section, we can conclude that the proposed LDA+GTB scheme works quite well and could be used for quantitative description of the High-$T_c$ cuprates. The LDA+GTB scheme also can be used for wide class of SCES - cuprates, manganites, and other.

V. EFFECTIVE LOW-ENERGY MODEL

When we are interested in the low-energy physics (like e.g. superconductivity) it is useful to reduce the microscopic model to more simpler effective Hamiltonian. For example, the Hubbard model in the regime of strong correlations the effective model is the $t-J^*$ model ($t-J$ model plus 3-centers correlated hoppings $H_3$) obtained by exclusion of the intersubband hoppings perturbatively$^{48,69,70}$. Analysis of the 3-band model results in the effective Hubbard and the $t-J$ model$^{20,22,71,72,73}$. As the next step we will formulate the effective model for the multiband $p-d$ model. Simplest way to do it is to neglect completely contribution of two-particle triplet state $^3B_{1g}$. Then there will be only one low-energy two-particle state - Zhang-Rice-type singlet $^1A_{1g}$ and the effective model will be the usual $t-J^*$ model. But in the multiband $p-d$ model the difference $\varepsilon_T - \varepsilon_S$ between energy of two-particle singlet and two-particle triplet depends strongly on various model parameters, particularly on distance of the apical oxygen from the planar oxygen, energy of the apical oxygen, difference between energy of $d_{x^2-y^2}$-orbitals and $d_{z^2}$-orbitals. For the realistic values of model parameters $\varepsilon_T - \varepsilon_S$ is close to $0.5\ eV^{23,41}$ contrary to the 3-band model with this value being about $2\ eV$. To take into account triplet states we will derive the effective Hamiltonian for multiband $p-d$ model by exclusion of the intersubband hopping between low (LHB) and upper (UHB) Hubbard subbands. These subbands divided by the energy of charge-transfer gap $E_{ct} \approx 2\ eV$ (similar to $U$ in the Hubbard model) and using perturbation theory, similar to Ref.\cite{69} with small parameter $W/U$ we can derive separate effective models for UHB and LHB. This procedure is schematically shown in Fig.\cite{5} And, as one can see, since the UHB and LHB in initial model\cite{14} are formed by different quasiparticles (namely, $\alpha_0$ for LHB and $\alpha_1, \alpha_2, \alpha_3$ for UHB in Fig.\cite{5}), the effective models will be different for upper (valence band, hole doped) and lower (conductivity band, electron doped) subbands.

We write the Hamiltonian in the form $H = H_0 + H_1$, where the excitations via the charge transfer gap $E_{ct}$ are included in $H_1$. Then we define an operator $H(\epsilon) = H_0 + \epsilon H_1$ and make the unitary transformation $\tilde{H}(\epsilon) = \exp (-i\epsilon \hat{S}) H(\epsilon) \exp (i\epsilon \hat{S})$. Vanishing linear in $\epsilon$ component of $\tilde{H}(\epsilon)$ gives the equation for matrix $\hat{S}$:

$$H_1 + i \left[ H_0, \hat{S} \right] = 0.$$  \hspace{1cm} (23)

For the multiband $p-d$ model\cite{14} in case of electron doping we obtain the usual $t-J^*$ model describing conductivity band:

$$H_{1-J^*} = \sum_{f,\sigma} \varepsilon_f X_f^{\sigma,\sigma} + \sum_{f \neq g,\sigma} t_{fg}^{00} X_f^{\sigma,0} X_g^{0,\sigma} + \sum_{f \neq g \neq h,\sigma} H_3 + \sum_{f \neq g} J_{fg} \left( \hat{S}_f \hat{S}_g - \frac{1}{4} n_f n_g \right),$$

here $H_3$ contains three-centers interaction terms given by Eq.\cite{14}, $\hat{S}_f$ are spin operators and $n_f$ are number of particles operators. The $J_{fg} = 2 \left( t_{fg}^{00} \right)^2 / E_{ct}$ is the exchange parameter.

For p-type systems the effective Hamiltonian has the form of the singlet-triplet $t-J^*$ model describing valence
Eq. (A.2). Expressions for $H_{p}$-type systems which is known experimentally. So, we alization of the distance dependence of Wannier functions that determine that fall with distance rapidly, effective model parame-ters from Table IV. The electron Green function (17) corresponding densities of states (DOS) in the coordination spheres (c.s.) in the Fig. 8 we present the calculated for different number of taken into account coordina-tion factors of the single-particle state, $C_{fg} = 2 \langle S_{f}S_{g} \rangle$ are static spin correlation functions which were self-consistently calculated from the spin Green’s functions in the 2D $t – J$ model. As one can easily see from Fig. 5 the dispersion with hoppings only to nearest neighbors (1 c.s.) and to next-nearest neighbors (2 c.s., the so called $t – t’ – J^*$ model) and more coordination spheres taken into account. Recent ARPES experiments show that the Fermi velocity $v_{F} = E_{F}/k_{F}$ is nearly constant for wide range of p-type materials and doping independent within an experimental error of 20%. We have calculated this quantity in the $t – J^*$ model with parameters from Table IV in the approximation described above. In the doping range from $x = 0.03$ to $x = 0.15$ our calculations give very weak doping dependence of the Fermi velocity. Assuming the lattice constant equal to 4Å we have $v_{F}$ varying from 1.6 eVÅ$^{-1}$ to 2.0 eVÅ$^{-1}$. Taking into account experimental error of 20% our results is very close to the experimental one.

VI. CONCLUSION

The approach developed here assumes the multiband Hamiltonian for the real crystal structure and its mapping onto low-energy model. Parameters of the effective model are obtained directly from ab initio multiband model parameters. The sets of parameters for the effective models and are presented in Tables IV and V for p- and n-type cuprates, correspondingly.

The effective low-energy model appears to be the $t – t’ – t'' – J^*$ model for Nd$_2$CuO$_4$ and the singlet-triplet $t – t’ – t'' – J^*$ model for La$_2$CuO$_4$. There is almost no difference in the band dispersion with ad-dition of numerically small hoppings to 4-th, 5-th, etc. neighbors.

Summarizing, we have shown that the hybrid LDA+GTB method incorporate the ab initio calculated parameters of the multiband $p – d$ model and the adequate treatment of strong electron correlations.

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![Graph](https://via.placeholder.com/150)
APPENDIX: EXPRESSIONS FOR 3-CENTERS CORRELATED HOPPINGS IN EFFECTIVE MODELS

In the $t-J^*$ model [24] the 3-centers correlated hopplings are given by:

$$H_3 = \frac{t^{OS}}{E_{ct}} \{ X_f^0 X^\sigma_m X^\sigma_g - X^\sigma_f X^\sigma_m X^\sigma_g \}. \quad (A.1)$$

The three-centers interaction terms $H_{eff3}$ in the effective Hamiltonian are much more complicated then in the $t-J^*$ model due to additional triplet and singlet-triplet contributions:

$$H_{eff3} = \frac{t^{OS}}{E_{ct}} H^{SS}_3 - \frac{t^{OS}}{E_{ct}} H^{ST}_3 + \frac{t^{ST}}{E_{ct}} H^{TT}_3, \quad (A.2)$$

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