
**MAGNETIC MECHANISMS
OF SUPERCONDUCTIVITY**

Ab initio Calculation of the Parameters and Band Structure of the Multiband p - d Model for La_2CuO_4 ¹

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Abstract—In this paper, we proposed *ab initio* calculation of hopping parameters for La_2CuO_4 . The Wannier-function projection procedure of obtaining a small Hamiltonian in real space for different sets of bands of interest was used. The importance of taking into account $\text{Cu } d_{3z^2-r^2}$ and apical $\text{O}_a p_z$ orbitals is shown. The parameters obtained are used to calculate the band structure of undoped La_2CuO_4 in the framework of the multiband p - d model in the regime of strong electron correlations.

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Since the high- T_c superconducting cuprates (HTSCs) belong to the class of substances in which strong electron correlations are important, it is the model approach that is most frequently used for theoretical investigations of HTSCs. The effective models of HTSC (e.g., the t - J model) usually contain free parameters. They can be determined by fitting to the experimental data or by *ab initio* calculations. The *ab initio* (e.g., LDA) band structure is incorrect in the low-doping region where correlations are most significant. But it is well known that the Fermi surface obtained in LDA (local density approximation) is in very good agreement with experiments. So, values of hoppings can be properly estimated by LDA calculations.

To obtain hopping integrals for different sets of bands under consideration, we apply the projection procedure using the formalism of Wannier functions (WFs). Since WFs are nonunique, to define them one needs an additional restriction to be imposed on their properties. Among others, Marzari and Vanderbilt [1] proposed the condition of maximum localization for WFs, resulting in a variational procedure. To start from appropriate values, the authors of [1] suggested choosing a set of localized trial orbitals $|\phi_n\rangle$ and projecting them onto the Bloch functions $|\psi_{\mathbf{k}}\rangle$. It was found that this starting guess is usually quite good. This fact later led to a simplified calculation scheme proposed in [2] where the variational procedure was abandoned and the result of the aforementioned projecting was considered as the final step.

In this paper, we also ignore the variational procedure. We define a set of trial orbitals $|\phi_n\rangle$ and choose the Bloch bands in the energy interval (E_1, E_2) to construct the WFs. The nonorthogonalized WFs in reciprocal $|\tilde{W}_{n\mathbf{k}}\rangle$ space are defined as a projection of the set of site-centered atomic-like trial LMT orbitals [3] $|\phi_n\rangle$ on the subspace defined by the Bloch functions $|\psi_{\mathbf{k}}\rangle$ from the chosen bands:

$$|\tilde{W}_{n\mathbf{k}}\rangle \equiv \sum_{i(E_1 \leq \epsilon_i(\mathbf{k}) \leq E_2)} |\psi_{i\mathbf{k}}\rangle \langle \psi_{i\mathbf{k}} | \phi_n \rangle. \quad (1)$$

Since $|\phi_n\rangle$ is an orthogonal LMTO basis-set orbital, we have $\langle \psi_{i\mathbf{k}} | \phi_n \rangle = c_{ni}^*(\mathbf{k})$ and, hence,

$$|\tilde{W}_{n\mathbf{k}}\rangle \equiv \sum_i |\psi_{i\mathbf{k}}\rangle c_{ni}^*(\mathbf{k}). \quad (2)$$

For a more detailed description of this procedure, see [4]. Then, the hopping integrals between two sites connected by a translation vector \mathbf{T} are

$$\langle W_n^0 | \hat{H} | W_m^T \rangle = \frac{1}{N} \sum_{\mathbf{k}, i} \bar{c}_{n,i}(\mathbf{k}) \bar{c}_{mi}^*(\mathbf{k}) \epsilon_i(\mathbf{k}) e^{-i\mathbf{k}\mathbf{T}}, \quad (3)$$

where $|W_{n\mathbf{k}}\rangle$ are the orthonormalized WFs, N is the number of discrete \mathbf{k} points in the first BZ, $\epsilon_i(\mathbf{k})$ is the eigenvalue for a particular band, and the coefficients $\bar{c}_{ni}(\mathbf{k})$ are $c_{ni}(\mathbf{k})$ modified by the orthonormalization of $|\tilde{W}_{n\mathbf{k}}\rangle$.

La_2CuO_4 at a low temperature and zero doping has an orthorhombic structure (space group $Bmab$) [5]. We use the linearized muffin-tin orbital method [3] in the

¹ The text was submitted by the authors in English.

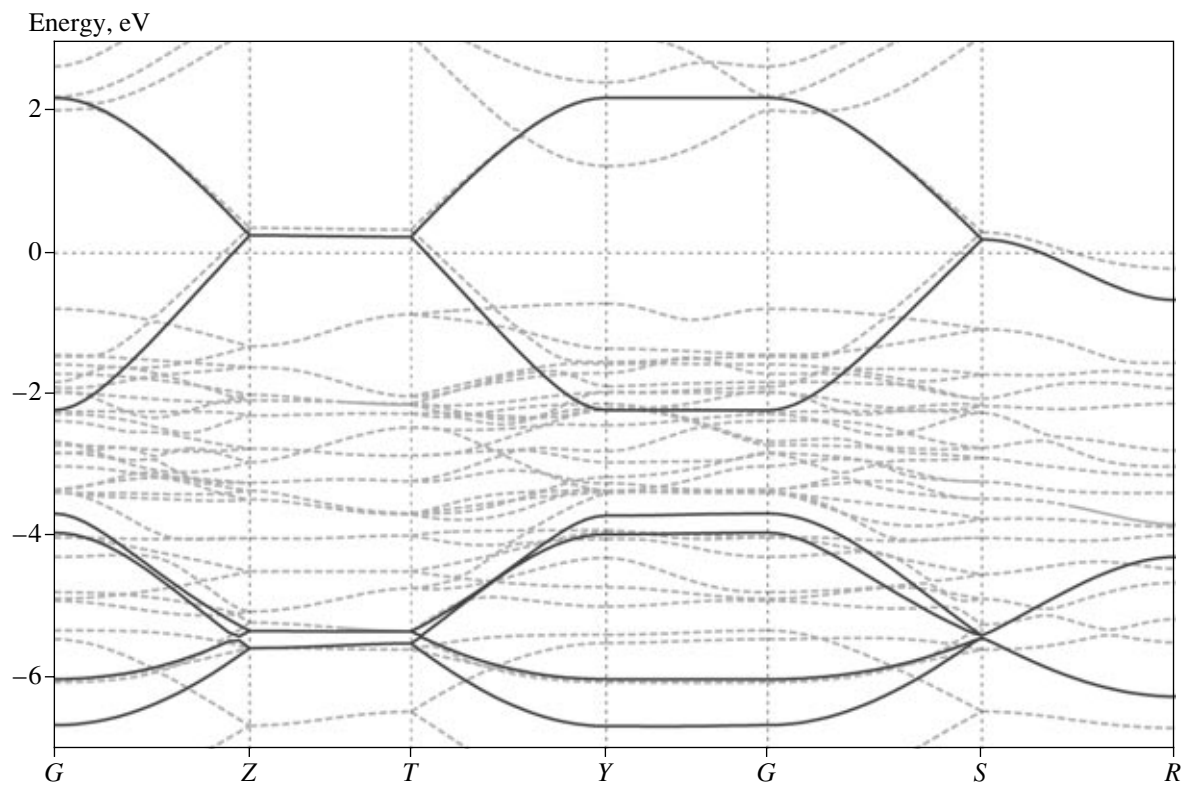


Fig. 1. Comparison of the band structure of La₂CuO₄ obtained from LDA calculations (dashed lines) and from the projection on the set of Cu $d_{x^2-y^2}$, $O_p p_x$, and $O_p p_y$ orbitals (solid lines). Fermi level corresponds to zero energy.

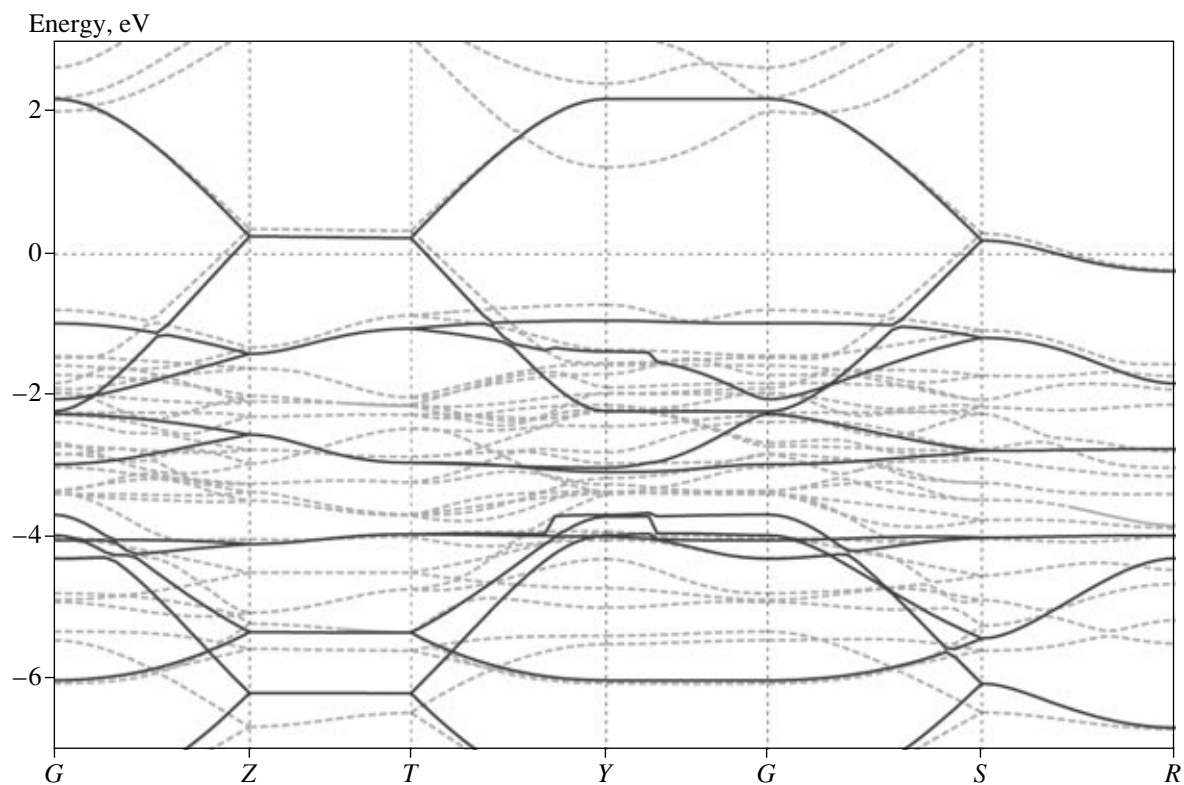


Fig. 2. Comparison of the band structure of La₂CuO₄ obtained from LDA calculations (dashed lines) and from the projection on the set of Cu $d_{x^2-y^2}$, Cu $d_{3z^2-r^2}$, $O_p p_x$, $O_p p_y$, and $O_a p_z$ orbitals (solid lines). Fermi level corresponds to zero energy.

tight-binding approach [6] (TB-LMTO) within the LDA to calculate the band structure of La_2CuO_4 . The comparison of the LDA band structure (dashed lines) and bands obtained by the above-described projection method (solid lines) for two different sets of orbitals (Cu $d_{x^2-y^2}$, $O_p p_x$, $O_p p_y$; and Cu $d_{x^2-y^2}$, Cu $d_{3z^2-r^2}$, $O_p p_x$, $O_p p_y$, $O_a p_z$) is shown in Figs. 1 and 2, respectively. Here, O_p denotes oxygens in the ab plane, and O_a denotes the apical oxygen ions. The energy range for the projection was $(-8.4, 2.5)$ eV in both cases. The main effect of taking into account the Cu $d_{3z^2-r^2}$ and $O_a p_z$ states is the proper description of the band structure (in comparison with the LDA calculation) at the energies up to 2 eV below the Fermi level. Therefore, if one needs to quantitatively describe the low-energy excitations of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ within 2 eV, the Cu $d_{3z^2-r^2}$ and $O_a p_z$ orbitals should be taken into account. The resulting hopping parameters for these two sets of trial orbitals are presented in Table 1. The second column contains the connecting vector \mathbf{T} between two sites. It is clearly seen that hoppings decay quite rapidly with distance between ions.

We use generalized tight-binding method (GTBM) [7] to calculate the band structure of the parent HTSC material La_2CuO_4 in the AFM phase, since this method explicitly takes into account strong electron correlations [8]. However, the GTBM generally uses a set of phenomenological parameters which are extracted from the most informative experiments, e.g., from ARPES. To compare the parameters obtained in the GTBM and in the LDA (Table 2), quasiparticle spectra for the AFM phase of La_2CuO_4 were calculated for both cases (Figs. 3a, 3b). The results obtained are almost identical for the top of the valence band. Some discrepancies concern the behavior of the dispersion near the $\mathbf{k} = (\pi, 0)$ point, where the results gained for the phenomenological set correspond better to the ARPES results. The width of the first valence band is almost the same, ~ 0.4 eV. Moreover, both sets give small (~ 0.5 eV) splitting between the singlet Zhang–Rice state and the ${}^3B_{1g}$ triplet state. The large energy of the apical orbital plays the dominant role in this splitting for the *ab initio* set of parameters. However, these two sets of parameters indicate the different mechanism of formation of the optical absorption edge. The absorption edge for the *ab initio* set is formed by the indirect transitions in contrast to the phenomenological set, where the momentum of an excited quasiparticle is unchanged upon the optical transition at the absorption edge.

To summarize the paper, we performed *ab initio* calculations of the hopping parameters for the multiband p – d model of La_2CuO_4 using the Wannier-function projection procedure. The set of the parameters obtained is close to the one extracted from the experiment [8]. The band structure of undoped La_2CuO_4 is calculated within the multiband p – d model in the generalized tight-bind-

Table 1. Hopping parameters for orthorhombic La_2CuO_4 obtained using the WF projection procedure for different sets of trial orbitals (eV). Here, x^2, z^2, p_x, p_y, p_z denote Cu $d_{x^2-y^2}$, Cu $d_{3z^2-r^2}$, $O_p p_x$, $O_p p_y$, and $O_a p_z$ orbitals, respectively

| Hopping | Direction | Cu x^2 $O p_x, p_y$ | Cu x^2, z^2 $O p_x, p_y, p_z$ |
|--------------------|-------------------------|--------------------------|------------------------------------|
| $t(x^2, x^2)$ | (−0.493, −0.5) | −0.188 | −0.188 |
| $t^0(x^2, x^2)$ | (−0.985, 0.0) | 0.001 | 0.002 |
| $t(z^2, z^2)$ | (−0.493, −0.5) | | 0.054 |
| $t^0(z^2, z^2)$ | (−0.985, 0.0) | | −0.001 |
| $t(x^2, p_x)$ | (0.246, 0.25, −0.02) | 1.357 | 1.335 |
| $t^0(x^2, p_x)$ | (−0.739, 0.25, −0.02) | −0.022 | −0.020 |
| $t(z^2, p_x)$ | (0.246, 0.25, −0.02) | | −0.556 |
| $t^0(z^2, p_x)$ | (−0.739, 0.25, −0.02) | | −0.028 |
| $t(z^2, p_z)$ | (0, 0.04, 0.445) | | 0.773 |
| $t^0(z^2, p_z)$ | (−0.493, −0.46, −0.445) | | −0.011 |
| $t(p_x, p_y)$ | (0.493, 0.0) | −0.841 | −0.858 |
| $t^0(p_x, p_y)$ | (0, 0.5, 0.041) | 0.775 | 0.793 |
| $t^{00}(p_x, p_y)$ | (0.985, 0.5, 0.041) | −0.001 | −0.001 |
| $t(p_x, p_z)$ | (−0.246, −0.21, 0.465) | | −0.391 |
| $t^0(p_x, p_z)$ | (0.246, 0.29, −0.425) | | −0.377 |
| $t^{00}(p_x, p_z)$ | (0.246, −0.21, −0.746) | | 0.018 |

Table 2. Hopping (in t_{pd}) and one-electron energy (in eV) parameters obtained in *ab initio* and in GTBM approaches

| <i>Ab initio</i> hoppings | GTBM hoppings |
|--|----------------------------|
| $t_{pd} = 1$ | $t_{pd} = 1$ |
| $t_{pd}^0 = 0:57$ | $t_{pd}^0 = 0:41$ |
| $t_{pp} = 0:63$ | $t_{pp} = 0:46$ |
| $t_{pp}^0 = 0:29$ | $t_{pp}^0 = 0:42$ |
| <i>Ab initio</i> one-electron energies | GTBM one-electron energies |
| " $d_{x^2} = 0$ | " $d_{x^2} = 0$ |
| " $d_{z^2} = 0:14$ | " $d_{z^2} = 0:2$ |
| " $p_x = 0:91$ | " $p_x = 1:5$ |
| " $p_z = 0:18$ | " $p_z = 0:45$ |

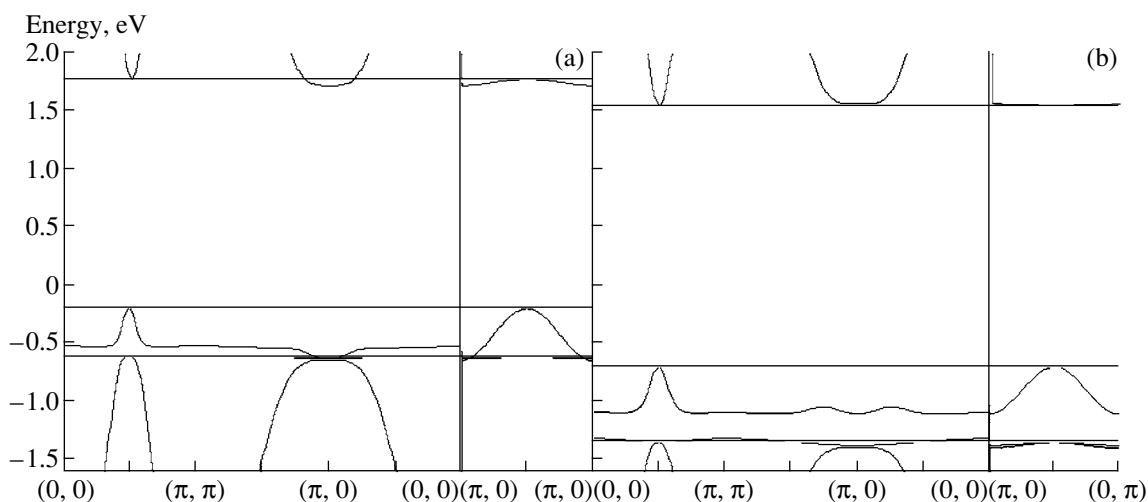


Fig. 3. The AFM band structure of La_2CuO_4 obtained by GTBM calculations for (a) the *ab initio* and (b) phenomenological sets of parameters.

ing method [7] that explicitly takes into account strong electron correlations. A comparison of the GTBM results for these two sets of microscopic parameters shows that they give a similar band dispersion at the top of the valence band.

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