

## Theory of superexchange in CuO<sub>2</sub>

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The limit method allows exact analysis of low-lying electronic states in a strong-coupling model CuO<sub>2</sub> plane. We extend it to *nonorthogonal* orbitals and fit to a  $t$ - $t'$ - $J$  model. The superexchange parameter is  $J = g_3^2 t^*$ , with  $t^*$  the unit of energy and  $g_3$  a lumped parameter.

**Introduction.** Charge carriers in CuO<sub>2</sub> planes are composite entities subject to numerous nontrivial interactions. As these are basic ingredients in high-temperature superconductors (HTS) it is necessary to understand their physics on a microscopic level. Only in this way could it be determined whether HTS is unique to copper-oxide planes, could be optimized, and might be manifest in other compounds. The most peculiar of the interactions is *superexchange*, the subject of the present paper. It is specific to oxides<sup>1</sup> and generally unavailable in conventional, low-temperature superconductors. Responsible for antiferromagnetism in the insulator, this same mechanism favors Cooper pairing, hence superconductivity, in the metal. We obtain its parameter  $J$  in the strong-coupling limit<sup>2</sup> by introducing *nonorthogonality* into a three-band model of copper and oxygen atomic orbitals.

For the purpose of this study we retain as basis functions one copper and two oxygen orbitals *per* cell, and use the smallest number of independent physical parameters. They are  $e_d$ , the energy of the copper  $d$  orbitals and  $U_{dd}$ , the strength of the two-body Coulomb repulsion on this orbital; the matrix element  $t_{pd}$  connecting an oxygen orbital to that of an adjacent copper, and a *quasi-infinitesimal* overlap parameter  $\lambda_{pd}$  characterizing the lack of orthogonality of these two atomic functions. With *just these parameters* we provide a microscopic derivation of the  $t$ - $t'$ - $J$  model for the low-lying states and find  $|J/t|$  can be as large as one wishes, while  $t'/t$  remains fixed at the near-optimal value,  $-0.168$ .

The largest energies in the problem are  $U$  and  $|e_d|$ . Next in magnitude is  $t_{pd}$  followed by  $t^* \equiv t_{pd}^2/U_{dd}$  which is kept *finite* in the strong-coupling limit  $t_{pd} \propto U_{dd}^{1/2} \rightarrow \infty$  and sets the energy scale of the low-lying states and of their dispersion.<sup>2</sup> We define two finite, dimensionless coupling constants: a very small one  $g_1$  ( $g_1^2 \ll 1$ ) where  $e_d \equiv -(g_1 + 1)(U_{dd}/2)$ , and  $g_2$  with which to measure the nonorthogonality,  $\lambda_{pd} \equiv g_2(t_{pd}/U_{dd})^{1/2}$ . Ultimately we obtain  $J g_1^2 g_2^4 t^* \rightarrow g_3^2 t^*$  with  $g_3 \equiv g_1 g_2^2$  an unconstrained parameter.

If, in strong-coupling, one did not proceed to "the limit" countless additional small terms of  $O(t_{pd}^3/U_{dd}^2)$  or even smaller terms  $O(t_{pd}^4/U_{dd}^3)$ ,<sup>3</sup> would enter into every calculation including that of  $J$ . To our knowledge there does not exist any systematic many-body strong-coupling expansion in powers of  $1/U$ . This makes it difficult to rely on any theory which predicts  $J \propto O(t_{pd}^4/U_{dd}^3)$ , however reasonable it may seem, as this quantity is *zero* in strong-coupling limit.<sup>4</sup> Even with realistic energies, Anderson<sup>1</sup> found long ago that

in *small clusters* nonorthogonality contributed more to superexchange than did high-order terms in  $1/U$ . It is our finding as well, that for an infinite array of copper oxide in the strong-coupling limit nonorthogonality becomes the *only* vehicle for superexchange.

Copper ions are physically disposed on a  $sq$  lattice with oxygen ions on the links. The *atomic orbitals* are  $D(\mathbf{r}-\mathbf{R}_i)$ , a *normalized*  $d(x^2-y^2)$  function on the  $i$ th copper ion,  $p_x[\mathbf{r}-\mathbf{R}_i \pm (a,0)/2]$  a *normalized* horizontal ligand oxygen  $p(x)$  orbital and  $p_y[\mathbf{r}-\mathbf{R}_i \pm (0,a)/2]$  the corresponding vertical ligand. The zero of energy is set at the  $p$  orbitals' energy,  $e_p \equiv 0$ . Copper ions have valency  $2+$  and spin  $1/2$ . We assign to the  $d$  orbital an energy<sup>5</sup>  $e_d < 0$  which disfavors  $3+$  relative to  $2+$ . Valency  $1+$  is discouraged by the two-body Coulomb repulsion parameter<sup>5</sup>  $U_{dd}$ . We adopt the simplest sign convention for the orbitals: (+) lobes on the oxygens facing (+) lobes on a copper, and (-) facing (-). In this gauge,

$$t_{pd} = \int d\mathbf{r} D^*(\mathbf{r}) H_0 p_{x \text{ or } y}(\mathbf{r})$$

and

$$\lambda_{pd} = \int d\mathbf{r} D^*(\mathbf{r}) p_{x \text{ or } y}(\mathbf{r}), \quad (1)$$

where  $H_0$  is the one-particle Hamiltonian. Only nearest-neighbors<sup>6</sup> overlap; all *non-nearest-neighbor* overlaps and hopping matrix elements are taken to be zero, including the direct  $p_x$ ,  $p_y$  overlap and corresponding matrix elements. One-body energies are as follows:

$$\begin{aligned} & \int d\mathbf{r} p_x^*[\mathbf{r}-\mathbf{R}_i - \frac{1}{2}(a,0)] H_0 p_x[\mathbf{r}-\mathbf{R}_j - \frac{1}{2}(a,0)] \\ &= \int d\mathbf{r} p_y^*[\mathbf{r}-\mathbf{R}_i - \frac{1}{2}(0,a)] H_0 p_y[\mathbf{r}-\mathbf{R}_j - \frac{1}{2}(0,a)] \\ &\equiv e_p \delta_{i,j} = 0 \end{aligned} \quad (2)$$

and

$$\int d\mathbf{r} D^*(\mathbf{r}-\mathbf{R}_i) H_0 D(\mathbf{r}-\mathbf{R}_j) \equiv e_d \delta_{i,j}. \quad (3)$$

The *only* nonvanishing two-body interactions retained are the one-center, two-electron, Coulomb repulsion on each copper ion. For example, for the  $l$ th copper ion,

$$\int \int d\mathbf{r} d\mathbf{r}' D^*(\mathbf{r}-\mathbf{R}_1) D^*(\mathbf{r}'-\mathbf{R}_2) U_i(r, r') \times D(\mathbf{r}'-\mathbf{R}_3) D(\mathbf{r}-\mathbf{R}_4) \equiv U_{dd} \prod_{i=1}^4 \delta_{i,l}. \quad (4)$$

Additional four-point functions involving atomic orbitals on two or more distinct centers are set zero. The small set of parameters<sup>7</sup> in Eqs. (1)–(4) is actually quite sufficient.<sup>8</sup> While it would not be difficult to augment it for better fit to transport, optical absorption, photoemission, and even superconductivity data, none of this is required in the derivation of the many-body superexchange mechanism which follows.

*Transformation to orthonormal representation.* The first step is a Fourier transform:

$$D_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_j e^{-i\mathbf{k}\cdot\mathbf{R}_j} D(\mathbf{r}-\mathbf{R}_j), \quad (5)$$

$$p_{\mathbf{k},x}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_j e^{-i\mathbf{k}\cdot\mathbf{R}_j} p_x[\mathbf{r}-\mathbf{R}_j - \frac{1}{2}(a, 0)]$$

and

$$p_{\mathbf{k},y}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_j e^{-i\mathbf{k}\cdot\mathbf{R}_j} p_y[\mathbf{r}-\mathbf{R}_j - \frac{1}{2}(0, a)], \quad (6)$$

then we combine these last into two, symmetry-adapted functions,

$$\beta_{\mathbf{k}}(\mathbf{r}) = \frac{2}{\omega(k)} \left[ \cos \frac{k_y}{2} p_{\mathbf{k},x}(\mathbf{r}) - \cos \frac{k_x}{2} p_{\mathbf{k},y}(\mathbf{r}) \right] \quad (7)$$

and

$$\Phi_{\mathbf{k}}(\mathbf{r}) = \frac{2}{\omega(k)} \left[ \cos \frac{k_x}{2} p_{\mathbf{k},x}(\mathbf{r}) + \cos \frac{k_y}{2} p_{\mathbf{k},y}(\mathbf{r}) \right]. \quad (8)$$

The normalization parameter is  $\omega(k) = 2\sqrt{\cos^2(k_x/2) + \cos^2(k_y/2)}$ . Each of the functions defined in (5), (7), and (8) is normalized. But while  $\beta_{\mathbf{k}}(\mathbf{r})$  is orthogonal to all  $D_{\mathbf{k}}(\mathbf{r})$  and  $\Phi_{\mathbf{k}}(\mathbf{r})$ , the others still fail to be orthogonal to each other. Using (1) we note

$$\int d\mathbf{r} D_{\mathbf{k}}^*(\mathbf{r}) H_0 \Phi_{\mathbf{k}}(\mathbf{r}) = t_{pd} \omega(k)$$

and

$$\int d\mathbf{r} D_{\mathbf{k}}^*(\mathbf{r}) \Phi_{\mathbf{k}}(\mathbf{r}) = \lambda_{pd} \omega(k) \equiv \lambda_k. \quad (9)$$

Next, construct a normalized Bloch function  $\Psi$  orthogonal to (7) and (8),

$$\Psi_{\mathbf{k}}(\mathbf{r}) \equiv \frac{D_{\mathbf{k}}(\mathbf{r}) - \lambda_k \Phi_{\mathbf{k}}(\mathbf{r})}{\sqrt{1 - \lambda_k^2}}. \quad (10)$$

The site-centered Wannier functions corresponding to (8) and (10) are<sup>9</sup>

$$\Phi(\mathbf{r}-\mathbf{R}_j) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in \text{BZ}} e^{i\mathbf{k}\cdot\mathbf{R}_j} \Phi_{\mathbf{k}}(\mathbf{r}),$$

$$\Psi(\mathbf{r}-\mathbf{R}_j) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in \text{BZ}} e^{i\mathbf{k}\cdot\mathbf{R}_j} \Psi_{\mathbf{k}}(\mathbf{r}), \quad (11)$$

somewhat less localized than the originals. In general, their spread is measured by four lattice Green functions:  $G(R) = (1/N) \sum_{\mathbf{k} \in \text{BZ}} [\cos \mathbf{k}\cdot\mathbf{R} / (1 - \lambda_{\mathbf{k}}^2)]$ ,  $K(R) = (1/N) \sum_{\mathbf{k} \in \text{BZ}} \times [\omega^2(\mathbf{k}) \cos \mathbf{k}\cdot\mathbf{R} / (1 - \lambda_{\mathbf{k}}^2)]$ ,  $T(R) = (1/N) \sum_{\mathbf{k} \in \text{BZ}} \times [\omega(\mathbf{k}) \cos \mathbf{k}\cdot\mathbf{R} / (\sqrt{1 - \lambda_{\mathbf{k}}^2})]$  and  $M(R) = (1/N) \sum_{\mathbf{k} \in \text{BZ}} \times [\cos \mathbf{k}\cdot\mathbf{R} / (\sqrt{1 - \lambda_{\mathbf{k}}^2})]$  which fall off with distance and are related by  $G(\mathbf{R}_{ij}) = \sum_{\mathbf{R}} M(\mathbf{R}_i - \mathbf{R}) M(\mathbf{R}_j - \mathbf{R})$ , and  $K(\mathbf{R}_{ij}) = \sum_{\mathbf{R}} T(\mathbf{R}_i - \mathbf{R}) T(\mathbf{R}_j - \mathbf{R})$ . While generally such functions need to be evaluated numerically, they are also quite easily expanded to leading order in the small parameter, e.g.,  $G(0) = 1 + 4\lambda_{pd}^2$ ,  $K(0) = 4(1 + 5\lambda_{pd}^2)$ ,  $G(\delta) = \lambda_{pd}^2$ , ( $\delta$  = nearest-neighbor vector), etc. We next construct an Hamiltonian in the basis of the orthonormal functions (11).

*The Hamiltonian.* The Hamiltonian operator  $\mathcal{H}$  will contain terms quadratic and quartic in field operators. In the notation of Ref. 2, field operators denoted  $\alpha_{i,\sigma}$  and  $\alpha_{i,\sigma}^*$  accompany the functions  $\Phi_i$  and  $\Phi_i^*$ , while  $c_{i,\sigma}$  and  $c_{i,\sigma}^*$  accompany the  $\Psi_i$  and  $\Psi_i^*$ . The symbol  $\sigma$  labels the spin degree of freedom of the electrons. For example, the coefficient of  $c_{i,\sigma}^* c_{j,\sigma}$  in  $\mathcal{H}$  is found, after a little algebra, to be

$$\int d\mathbf{r} \Psi^*(\mathbf{r}-\mathbf{R}_i) H_0 \Psi(\mathbf{r}-\mathbf{R}_j) = e_d G(R_{ij}) - 2t_{pd} \lambda_{pd} K(R_{ij}). \quad (12)$$

Unlike the equivalent integral in Eq. (3), (12) is not limited to just  $i=j$  [although the dropoff in (12) is exponential].<sup>10</sup> The coefficient of  $\alpha_{i,\sigma}^* \alpha_{j,\sigma}$  remains, just as in Eq. (2), zero for all  $i, j$ . The coefficient of the cross term ( $c_{i,\sigma}^* \alpha_{j,\sigma} + \text{H.c.}$ ) is

$$\int d\mathbf{r} \Psi^*(\mathbf{r}-\mathbf{R}_i) H_0 \Phi(\mathbf{r}-\mathbf{R}_j) = t_{pd} T(R_{ij}) \quad (13)$$

Copper Coulomb integrals which accompany  $c_{i,\sigma}^* c_{j,\sigma}^* c_{n,\sigma} c_{m,\sigma}$  are no longer *strictly* confined to individual centers:

$$\sum_j \int \int d\mathbf{r} d\mathbf{r}' \Psi^*(\mathbf{r}-\mathbf{R}_i) \Psi^*(\mathbf{r}'-\mathbf{R}_j) U_i(r, r')$$

$$\times \Psi(\mathbf{r}'-\mathbf{R}_n) \Psi(\mathbf{r}-\mathbf{R}_m)$$

$$= U_{dd} \sum_{\mathbf{R}} M(\mathbf{R}_i - \mathbf{R}) M(\mathbf{R}_j - \mathbf{R}) M(\mathbf{R}_n - \mathbf{R}) M(\mathbf{R}_m - \mathbf{R}). \quad (14)$$

However there still are no quartic terms in *any* oxygen-related operators  $\alpha_{i,\sigma}$  or  $\alpha_{i,\sigma}^*$ . Thus Eq. (14), with its huge number of terms, completes the list. There results a Hamiltonian of the following form:

$$\begin{aligned}
\mathcal{H} = & \sum_{i,j} \sum_{\sigma} [e_d G(R_{ij}) - 2t_{pd} \lambda_{pd} K(R_{ij})] c_{i,\sigma}^* c_{j,\sigma} \\
& + t_{pd} \sum_{i,j} \sum_{\sigma} T(R_{ij}) (c_{i,\sigma}^* \alpha_{j,\sigma} + \text{H.c.}) \\
& + U_{dd} \sum_{i,j,n,m} \left\{ \sum_l M(R_{il}) M(R_{jl}) M(R_{ln}) M(R_{lm}) \right\} \\
& \times \sum_{\sigma,\sigma'} c_{i,\sigma}^* c_{j,\sigma'}^* c_{n,\sigma'} c_{m,\sigma}. \quad (15)
\end{aligned}$$

Because the  $\beta$  states do not explicitly appear in  $\mathcal{H}$  we infer the existence of an energy band of zero width at energy  $e_p=0$ . Once the Fermi level is positioned at  $\mu>0$  two  $\beta$  electrons permanently occupy each  $\text{CuO}_2$  cell. We now deal with the remainder.

*Limit model values.* We decompose  $\mathcal{H}$  into parts:  $\mathcal{H}_1$  which involves individual sites only,  $\mathcal{H}_2$  which involves pairs of distinct sites (and similarly  $\mathcal{H}_3$  and  $\mathcal{H}_4$ , although in the limit, these do not contribute to the interactions we seek to study). We examine the first two in detail. Let  $\mathcal{H}_1 = \sum_i H_i$  where the Hamiltonian of the  $i$ th site is

$$\begin{aligned}
H_i = & [e_d G(0) - 2t_{pd} \lambda_{pd} K(0)] \sum_{\sigma} n_{i,\sigma} + t_{pd} T(0) \\
& \times \sum_{\sigma} (c_{i,\sigma}^* \alpha_{i,\sigma} + \text{H.c.}) + U_{dd} \left[ \sum_{\mathbf{R}} M^4(\mathbf{R}) \right] n_{i,\uparrow} n_{i,\downarrow}, \quad (16)
\end{aligned}$$

where  $n_{i,\sigma} \equiv c_{i,\sigma}^* c_{i,\sigma}$  and, we recall,  $e_d = -(1+g_1)U_{dd}/2$ . Next,  $\mathcal{H}_2 = \sum_{(ij)} H_{ij}$  [with  $(i,j)$  = any distinguishable pair of sites,  $R_{ij} \neq 0$ ]. We split up  $H_{ij} = H_{ij}^{(1)} + H_{ij}^{(2)} + H_{ij}^{(3)}$  as follows:

$$H_{ij}^{(1)} = t_{pd} T(R_{ij}) \sum_{\sigma} (c_{i,\sigma}^* \alpha_{i,\sigma} + \text{H.c.}), \quad (17a)$$

$$H_{ij}^{(2)} = U_{dd} \left[ \sum_{\mathbf{R}} M^2(\mathbf{R}) M^2(\mathbf{R} + \mathbf{R}_{ij}) \right] n_i n_j, \quad (17b)$$

where<sup>7</sup>  $n_i = \sum_{\sigma} n_{i,\sigma}$ , and

$$\begin{aligned}
H_{ij}^{(3)} = & \sum_{\sigma} \left\{ e_d G(R_{ij}) - 2t_{pd} \lambda_{pd} K(R_{ij}) \right. \\
& + U_{dd} \left[ \sum_{\mathbf{R}} M^3(\mathbf{R}) M(\mathbf{R} + \mathbf{R}_{ij}) \right] n_{i,-\sigma} \left. \right\} c_{i,\sigma}^* c_{j,\sigma} \\
& + \sum_{\sigma} \left\{ e_d G(R_{ij}) - 2t_{pd} \lambda_{pd} K(R_{ij}) \right. \\
& + U_{dd} \left[ \sum_{\mathbf{R}} M^3(\mathbf{R}) M(\mathbf{R} + \mathbf{R}_{ji}) \right] n_{j,-\sigma} \left. \right\} c_{j,\sigma}^* c_{i,\sigma}, \quad (17c)
\end{aligned}$$

Up to this point *all* the results have been obtained without approximation. We now pass to the strong-coupling limit. The coefficients in  $H_i$  simplify as follows:  $e_d G(0) - 2t_{pd} \lambda_{pd} K(0) \rightarrow e_d(1 + 4\lambda_{pd}^2) - 8t_{pd} \lambda_{pd}(1 + 5\lambda_{pd}^2) \rightarrow e_d$

and similarly,  $T(0)t_{pd} = \langle \omega(k) + \frac{1}{2}\lambda_{pd}^2 \omega^3(k) \rangle_{\text{BZ}} t_{pd} \rightarrow 1.91618\dots t_{pd}$  and  $\sum_{\mathbf{R}} M^4(\mathbf{R}) = 1 + 8\lambda_{pd}^2 + \dots \rightarrow 1$ .

The coefficients in  $H_{ij}$  are similarly simplified. While Eq. (17a) contributes only to charge transport (“hopping”), (17b) is *both* spin-independent *and* irrelevant to charge transport, and is essentially constant.<sup>7</sup> It is only (17c) which is sensitive to the relative spins in neighboring cells. In strong-coupling, for adjacent sites  $(i,j)$  the first part of (17c) is  $\{e_d G(R_{ij}) - 2t_{pd} \lambda_{pd} K(R_{ij}) + U[\sum_{\mathbf{R}} M^3(\mathbf{R}) M(\mathbf{R} + \mathbf{R}_{ij})] n_{i,-\sigma}\} c_{i,\sigma}^* c_{j,\sigma} \rightarrow -(U/2)g_1 \lambda_{pd}^2 c_{i,\sigma}^* c_{j,\sigma}$ . More distant sites carry higher powers of  $\lambda_{pd}^2$  and do not contribute in the limit. The replacement  $n_{i,-\sigma} c_{i,\sigma}^* \rightarrow n_i c_{i,\sigma}^* \rightarrow c_{i,\sigma}^*$  which is used is exact in the strong-coupling limit.<sup>7</sup> Finally, the second part of (17c) provides the Hermitean conjugate of the first.

*Superexchange.* The operators in  $H_{ij}$  provide the matrix elements connecting any of the 64 conjoint low-lying states of any pair of cells  $(i,j)$ . Superexchange, from (17c), only comes into play when adjacent sites are each occupied by a spin 1/2 doublet of the type,<sup>2</sup>

$$|5\sigma\rangle_i = \frac{c_{i,\sigma}^* \alpha_{i,-\sigma}^* + \zeta c_{i,\sigma}^* c_{i,-\sigma}^* \alpha_{i,\sigma}^*}{\sqrt{1+\zeta^2}} \beta_{i,\uparrow}^* \beta_{i,\downarrow}^* |0\rangle.$$

The effective spin-dependent interaction is found to take the form  $J(\sigma_i \cdot \sigma_j - 1/4)$ . For *non*-nearest-neighbor sites, (17c) is proportional to higher powers of  $\lambda_{pd}^2$  and vanishes in the limit. The nearest-neighbor superexchange parameter  $J$  is given by the following formula:

$$\begin{aligned}
J = & 2 \frac{[(U/2)g_1 \lambda_{pd}^2]^2}{U} \langle 5\uparrow |_i \otimes \langle 5\downarrow |_j \left( \sum_{\sigma} c_{i,\sigma}^* c_{j,\sigma} + \text{H.c.} \right)^2 \\
& \times |5\downarrow\rangle_j \otimes |5\uparrow\rangle_i = g_1^2 g_2^4 t^* \quad (18)
\end{aligned}$$

There are no additional contributions to the superexchange. Once we have proceeded to the limit, the magnitude of  $g_2$  is not constrained. We can therefore define a third coupling constant  $g_3 \equiv g_2^2 g_1$ . While holding  $g_3$  constant we set  $g_1$  at some arbitrarily small value  $|g_1| \ll 1$  [so as to retain the advantageous SO(4) symmetry of the earlier model<sup>2</sup>] and set  $g_2 = (g_3/g_1)^{1/2}$ . This *double*-limiting procedure results in  $J = g_3^2 t^*$  with  $g_3$  essentially arbitrary.

*Charge transport.* When the antiferromagnet is hole doped, the occupation number of some cells must drop to less than 5. Cells containing four particles in a singlet state labeled  $|4\rangle_i$ , known as “Zhang-Rice singlets,” are the most stable:

$$|4\rangle_i = \frac{c_{i,\uparrow}^* \alpha_{i,\downarrow}^* + \alpha_{i,\uparrow}^* c_{i,\downarrow}^0 + \zeta_4^- c_{i,\uparrow}^* c_{i,\downarrow}^* + \zeta_4^+ \alpha_{i,\uparrow}^* \alpha_{i,\downarrow}^*}{\sqrt{2 + \zeta_4^{+2} + \zeta_4^{-2}}} \beta_{i,\uparrow}^* \beta_{i,\downarrow}^* |0\rangle. \quad (19)$$

With  $g_1 \rightarrow 0$ , the number of 4’s and of 5’s are separately conserved quantities. A  $|4\rangle_i$  configuration at  $R_i$  can be permuted with a  $|5\rangle_j$  at  $R_j$ , resulting in an effective matrix element for charge transport and procuring a width to a conduction band. The operator for such a process is found in (17a) and its matrix element is

$$t_{\text{eff}}(R_{ij}) = \langle 5\uparrow |_i \otimes \langle 4 |_j \{ t_{pd} T(R_{ij}) (c_{i,\uparrow}^* \alpha_{j,\uparrow} + \alpha_{i,\uparrow}^* c_{j,\uparrow}) \} \\ \times | 5\uparrow \rangle_j \otimes | 4 \rangle_i \\ = 6t^* T(0) T(R_{ij}) \frac{1+g_1/3}{1-g_1^2} \rightarrow 6t^* T(0) T(R_{ij}) \quad (20)$$

becoming identical with Ref. 2 after we proceed to the double limit.

$T(R_{ij})$ , a Green function defined following Eq. (11), decreases with distance and oscillates in sign. With  $\delta = (\pm 1, 0)$  or  $(0, \pm 1)$  a *nearest-neighbor* vector and  $\delta' = (\pm 1, \pm 1)$  a *next-nearest neighbor* vector, define  $t = t_{\text{eff}}(\delta)$ ,  $t' = t_{\text{eff}}(\delta')$ . We use known<sup>2</sup> values of  $T(R)$  to obtain the figure of merit in the  $t$ - $J$  model,<sup>11</sup>  $J/t = 1.8626g_3^2$ . It depends only on the arbitrary value assigned to  $g_3$ .

In the extended model there exists a second ratio or figure of merit,  $t'/t$ . For optimum fit to a number of experiments,

Dagotto<sup>11</sup> estimates this ratio to be in the range  $-0.3$  to  $-0.4$ . An independent fit by Fehrenbacher and Norman<sup>12</sup> estimates this same ratio to be  $-0.275$ . Unlike the value of  $J$  which remains arbitrary (albeit positive and restricted to nearest neighbors), the band structure is uniquely determined in our model. Using Eq. (20) we find  $t'/t = -0.168$ . This should be considered good agreement—any small amount of  $p$ - $p$  overlap easily brings it into compliance with either experimental estimate. Finally, as no two configurations can share the same cell, there comes into play an effective “hard-core” repulsion which is one of the principal attributes of the  $t$ - $J$  and  $t$ - $t'$ - $J$  models.

*Conclusion.* We derived a  $t$ - $t'$ - $J$  model from microscopic first principles in the strong-coupling limit. We find  $J > 0$ , that it is restricted to nearest-neighbor sites, its magnitude being a sensitive blend of overlap and energy parameters best obtained from experiment.<sup>1,11</sup>

<sup>1</sup>P. W. Anderson, Phys. Rev. **115**, 2 (1959); N. L. Huang and R. Orbach, *ibid.* **154**, 487 (1967); D. E. Rimmer, J. Phys. C **2**, 329 (1969).

<sup>2</sup>D. C. Mattis, Mod. Phys. Lett. B **8**, 1387 (1994); Phys. Rev. Lett. **74**, 3676 (1995).

<sup>3</sup>Or  $O(t_{pd}^4 / |e_d|^a U_{dd}^{3-a})$  with  $a = 0, 1, 2, 3$  which are all equivalent in our model.

<sup>4</sup>It must be remarked that *if* in leading order there were found some essential or accidental degeneracies, such degeneracies *could* be lifted even by nominally small, higher-order terms. But there are no such degeneracies among the low-lying states, therefore calculations based on the limit model are qualitatively correct (and perhaps even quantitatively accurate) provided only that  $U_{dd} \gg t_{pd} \gg t^*$ .

<sup>5</sup>In the free atom (ion), the ionization potential of  $\text{Cu}^{2+}$  (roughly corresponding to  $-e_d$ ) is 36.8 eV and  $U_{dd} = 16.5$  eV, but the former is reduced by an order of magnitude in the oxide, while the latter is often estimated to lie in the range  $O(5$  eV).

<sup>6</sup>Because these are two-center integrals, they do not automatically vanish despite the differing symmetries of the two orbitals.

<sup>7</sup>With these parameters, in the limit the occupation number of each  $d$  orbital is quite close to 1,  $\langle n_i \rangle = 1 \pm \epsilon$ . There are two sources for the small quantity  $\epsilon$ : virtual excitations yield  $O(t_{pd}^2 / U_{dd}^2)$ , and nonorthogonality  $O[g_2^2 (|t_{pd}| / U_{dd})]$ . Thus, in effect the operator  $n_i = 1$  in the limit.

<sup>8</sup>Some knowledgeable readers may object to the neglect of their favorite matrix elements such as  $p_x$ - $p_y$  overlap, two- and three-center integrals including  $U_{pd}, U_{pp'}, \dots$  etc. None of these are

necessary for the generic arguments in the present paper and their inclusion only results in bogging down the presentation. In a forthcoming publication [J. M. Wheatley and D. C. Mattis (unpublished)], we present a more complete exposition in which we show that it is possible to flesh out the bare-bones model by including numerous additional orbitals and interaction parameters, using extensive computer programming adapted to the limit model. With such computer assistance one hopes to fit the documented properties of any specific HTS perovskite in some detail.

<sup>9</sup>For present purposes it is not necessary to know the Wannier functions for the nonbonding  $\beta_k$  band. With the choice of parameters in our model the coefficients of *any* operators which relate to the  $\beta_k$  band are  $\equiv 0$  in the Hamiltonian and therefore they disappear from the present analysis, reappearing only when one computes interactions with the electromagnetic field such as in optical absorption [D. C. Mattis and J. M. Wheatley (unpublished)] or when  $p$ - $p$  interactions are introduced into the model.

<sup>10</sup>With characteristic length  $\xi \propto (\ln 1/\lambda_{pd}^2)^{-1}$ .

<sup>11</sup>See reviews by E. Dagotto, Rev. Mod. Phys. **66**, 763 (1994) and W. Brenig, Phys. Rep. **253**, 155 (1995) for surveys and comparisons with experiment of the parameters in  $t$ - $J$  and  $t$ - $t'$ - $J$  models.

<sup>12</sup>R. Fehrenbacher and M. R. Norman [Phys. Rev. Lett. **74**, 3884 (1995)] fit parameters of band structure and of a structured attractive short-range potential, to observed superconducting properties.