

# Superexchange, hole-hole interactions, and oxygen spin dynamics in high- $T_c$ superconductors

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A contribution to superexchange coming from empty oxygen orbitals is pointed out. We also estimate the small anisotropy of the in-plane superexchange, as well as the superexchange between two adjacent layers in the specific  $\text{YBa}_2\text{Cu}_3\text{O}_6$  compound. In doped compounds, we improve the description of the transport properties of Zhang-Rice singlets over the simple  $t$ - $J$  model. Particularly important for the bandwidth is the role of what we call  $t'_{\text{unequal spins}}$  and  $t''_{\text{unequal spins}}$ . When more than one doped hole is present in the system, the interaction between holes becomes rapidly non-negligible: two Zhang-Rice singlets placed on neighboring cells highly *repel* each other. Some aspects of oxygen spin dynamics are discussed, in connection with NMR experiments.

## I. INTRODUCTION

The electronic structure of high- $T_c$  superconductors has been the subject of considerable scrutiny in the past few years. High-energy spectroscopies, in particular, have provided meaningful estimates for the majority of relevant quantum chemical parameters.<sup>1</sup>

Among these, the three most important ones are  $(E_p - E_d)$  (within rigorous configuration-interaction notations,  $E_{|\text{Cu } 3d^{10} \text{ O } 2p^5\rangle} - E_{|\text{Cu } 3d^9 \text{ O } 2p^6\rangle}$ ),  $t_{pd}$ , and  $U_d$ , which correspond, respectively, to the difference in energy between oxygen and copper orbitals, covalency, and on-site copper repulsion. Roughly speaking, such stoichiometric compounds as  $\text{CuO}$ ,  $\text{La}_2\text{CuO}_4$ , and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.0}$  are called charge-transfer insulators<sup>2</sup> because  $(E_p - E_d)$  and  $t_{pd}$  are found to be significantly lower than  $U_d$ . Considering covalency (related to  $t_{pd}$ ) provides further understanding:  $t_{pd}$  determines the hole symmetry ( $x^2 - y^2$ ) in the insulator. Doped holes couple with copper spins to form Zhang-Rice singlets,<sup>3</sup> which also possess ( $x^2 - y^2$ ) symmetry.

A good quantitative estimate of covalency is provided by the spectral weight of  $d^9\bar{L}$  peaks in x-ray photoelectron spectroscopy (XPS) valence-band spectra.<sup>4</sup> Some neutron measurements have been used to support the idea that  $t_{pd}$  is negligible in high- $T_c$  compounds.<sup>5</sup> This misinterpretation is, at least partially, due to an incorrect use of data taken on  $\text{K}_2\text{CuF}_4$ .

Of course, many parameters other than  $(E_p - E_d)$ ,  $t_{pd}$ , and  $U_d$  also play a role in high- $T_c$  superconductors. Not all of them have been examined with sufficient care so far. This is at least the case for oxygen empty orbitals ( $3s$ ,  $3p$ ,  $3d$ , etc). We show in Sec. II that their contribution to superexchange is significant. In spite of forty years of improvements on the original superexchange theory of Anderson,<sup>6</sup> this contribution had remained unnoticed so far to our knowledge.

The most popular model studied in connection with high- $T_c$  superconductors is the so-called  $t$ -( $t'$ )- $J$  model.<sup>3,7</sup> The superexchange contribution that we derive simply

acts to renormalize the value of  $J$ . The  $t$ - $t'$ - $J$  model, however, does not take interactions between doped holes into account. On-site Coulomb interaction on oxygen sites is trivially responsible for significant repulsion between two neighboring Zhang-Rice singlets. It is less trivial to understand that this Coulomb interaction also increases the kinetic energy of two neighboring Zhang-Rice Wannier states. The overall contribution of  $U_p$  to hole-hole interactions is considered in Sec. III.

The  $t$ - $t'$ - $J$  model also encounters serious difficulties for describing the oxygen spin dynamics.<sup>8</sup> This point is of some importance, not only for the understanding of the  $t$ - $t'$ - $J$  model, but also for the description of oxygen and yttrium NMR data, which have revealed very unusual behavior,<sup>9-11</sup> especially concerning the anisotropy of the oxygen hyperfine field is presented in Sec. IV. A more elaborate discussion of oxygen spin dynamics follows in Sec. V, which resorts to the use of nonorthogonal  $\text{CuO}_4$ -based Zhang-Rice singlets. A better understanding of the role of triplet states as a function of doping is needed for the future.

## II. SUPEREXCHANGE

### A. All contributions

Among the most recent works dealing with superexchange is one by Eskes and Jefferson.<sup>12</sup> These authors show that, although the simplest Rayleigh-Schrödinger perturbation approach provides very poor quantitative results, it is a very useful technique for visualizing all the different contributions involved in the superexchange mechanism. This remark happens to be valid for our contribution also. We therefore keep in the same track as Eskes and Jefferson. Defining the Heisenberg-like (isotropic) term in superexchange by the Hamiltonian

$$H = JS_i \cdot S_j, \quad (1)$$

four relevant mechanisms were distinguished by these authors, providing the following contributions.

(i) A “double hopping” ferromagnetic contribution:<sup>13</sup>

$$J_{\text{ferro}} = \frac{4t_{pd}^2 K_{pd(\text{double hopping})}}{\Delta^2}. \quad (2)$$

$K_{pd(\text{double hopping})}$  is a copper-oxygen exchange integral,<sup>13</sup>  $t_{pd}$  is the transfer between Cu  $3d_{(x^2-y^2)}$  and O  $2p\sigma$ , and  $\Delta = (E_p - E_d - 2t_{pp})$ .

(ii) The Anderson<sup>6</sup> contribution, involving double occupancy of a copper atom:

$$J_{\text{Anderson}} = \frac{4t_{pd}^4}{(\Delta + U_{pd})^2} \frac{1}{U_d} \left[ 1 + \frac{4t_{pp}}{\Delta + U_{pd}} + \frac{4t_{pp}}{\Delta + 2U_{pd}} \right]. \quad (3)$$

(iii) The Geertsma<sup>14</sup> contribution, involving double occupancy on oxygen:

$$J_{\text{Geertsma}} = \frac{8t_{pd}^4}{(\Delta + U_{pd})^2} \frac{1}{(2\Delta + U_p)} \times \left[ 1 + \frac{4t_{pp}}{\Delta + U_{pd}} + \frac{8t_{pp}}{2\Delta + U_{pd}} \right]. \quad (4)$$

(iv) A topological contribution allowed by oxygen-oxygen transfer ( $t_{pp}$ ), and which does not involve any doubly occupied state:

$$J_{\text{topological}} = \frac{32t_{pd}^4 t_{pp}}{(\Delta + U_{pd})^2 (\Delta + 2U_{pd}) (2\Delta + U_{pd})}. \quad (5)$$

We now add our contribution, which is a fourth-order process involving empty oxygen orbitals. For the oxygen 3s orbital, in particular, the calculation provides

$$J_{O\ 3s} = \frac{4t_{pd}^2 t_{Cu\ 3d/O\ 3s}}{(\Delta + U_{pd})^2 (E_{O\ 3s} - E_{O\ 2p})}. \quad (6)$$

$t_{Cu\ 3d/O\ 3s}$  represents the transfer integral from copper 3d to oxygen 3s orbitals, whereas  $(E_{O\ 3s} - E_{O\ 2p})$  is the energy that is needed to promote an electron from O 2p to O 3s, the formal valency of oxygen remaining O<sup>2-</sup>. The different steps involved in the perturbation are represented in Fig. 1.

It might seem strange that a nearly empty oxygen orbital (in first approximation spinless) would contribute to superexchange at all. The effect calculated here does not require the double occupancy of any particular orbital; it is a pure result of orbital symmetries, as represented in Fig. 1. In that sense, it might be called “topological,” just as well as the preceding effect in Eq. (5). This effect is not restricted to O 3s: all unoccupied oxygen orbitals hybridizing with copper ( $3d_{x^2-y^2}$ ) provide an antiferromagnetic contribution to superexchange if they possess an even symmetry along the Cu-O-Cu axis, and a ferromagnetic contribution if their symmetry is odd. This might be considered as a sort of extended Hund’s rule.<sup>15</sup> For instance, there also exists an antiferromagnetic contribution coming from oxygen 3d orbitals. In contrast, oxygen 3p orbitals provide a ferromagnetic contribution.

To estimate the order of magnitude of our contribution for O 3s orbitals, we take  $t_{Cu\ 3d/O\ 3s} = t_{pd} = 1.3$  eV,

$(E_{O\ 3s} - E_{O\ 2p}) = 30$  eV,<sup>16</sup> and the set of parameters provided in Table I. Equation (6) then gives

$$J_{O\ 3s} = 0.031 \text{ eV}. \quad (7)$$

This amounts to ~25% of the experimentally determined superexchange. Indeed, the process well deserves some considerations. It is a fourth-order process, just like the Anderson and Geertsma terms. This is to be contrasted with the contribution of empty orbitals on copper, such as Cu 4s, which is at best of fifth order, and which with reasonable parameters does not exceed  $-0.01$  eV. Unfortunately, the contributions of all unoccupied oxygen orbitals would have to be summed up in order to obtain the correct overall estimate. The sum is probably only slowly convergent. We guess that the total contribution is antiferromagnetic because oxygen 3s orbitals are the lowest in energy.

We may try to apply our decomposition technique to the intralayer antiferromagnetism in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.0</sub>. It seems reasonable to suppose that the oxygen-oxygen transfer is the only relevant coupling between the planes of a single bilayer (cf. Fig. 2). Under such conditions, the contribution of empty oxygen orbitals becomes irrelevant, and the ferromagnetic mechanism of Eq. (2), as well as the Geertsma mechanism of Eq. (4), provide an average contribution to the antiferromagnetism between layers which is zero (cf. Fig. 2). Only the Anderson and the Eskes-Jefferson topological mechanisms contribute to the overall intralayer antiferromagnetic coupling, where the second term actually dominates:

$$J_{\text{intralayer (effective)}} = \frac{48t_{pd}^4 t_{pp}^2 \text{ interplane}}{\Delta^4 U_d} + \frac{96t_{pd}^4 t_{pp}^2 \text{ interplane}}{\Delta^5}. \quad (8)$$

Taking  $t_{pp \text{ interplane}} \simeq pp\pi$  (the in-plane nearest-neighbor oxygen-oxygen distance differs by less than 2% from the interlayer nearest-neighbor oxygen-oxygen distance), and the parameters for  $pp\pi$ ,  $t_{pd}$ ,  $\Delta$ , and  $U_d$  provided in Table I, we obtain

TABLE I. The standard parameter set. All energies in eV. The bare crystal-field splittings that we use in Sec. II B are taken from Ref. 17, case II, and are not reproduced in the table. In all our numerical applications using perturbation theory, we actually use  $\Delta = (E_p - E_d - 2t_{pp}) = 3.5$  instead of 2.2, thus neglecting the role of  $t_{pp}$ .

$\epsilon_d$	0	A	6.5	$U_d = A + 4B + 3C = 8.8$
$\epsilon_p$	3.5	B	0.15	$U_p = F_0 + 0.16F_2 = 6.0$
$pd\sigma$	1.5	C	0.58	
$pd\pi$	-0.7	$F_0$	5	$t_{pd} = \frac{1}{2}\sqrt{3}pd\sigma = 1.3$
$pp\sigma$	-1.0	$F_2$	6	$t_{pp} = \frac{1}{2}(pp\pi - pp\sigma) = 0.65$
$pp\pi$	0.3	$U_{pd}$	0	$t_{pp \text{ interplane}} \simeq pp\pi$
Correlated hoppings				
$pd\sigma_{CuCu/Cu-O}$	$pd\sigma_{Cu-O/OO}$			$pp\sigma_{O-O/OO} = -0.2$
$pd\pi_{CuCu/Cu-O}$	$pd\pi_{Cu-O/OO}$			$pp\pi_{O-O/OO} = 0.06$

$$J_{\text{intra bilayer}}^{\text{(effective)}} = 5.6 \times 10^{-2} \text{ eV}, \quad (9)$$

which is not so small compared to  $J_{\text{in plane}}$ . The measurement of  $J_{\text{intra bilayer}}$  might serve as a test for the value of  $t_{pp}$  interplane, also.

### B. Cluster calculations

Some cluster calculations using standard quantum chemical parameters already provide a value for superexchange which is twice as large as that measured experimentally,<sup>12</sup> without including empty oxygen orbitals.

Our superexchange mechanism does not improve the situation in that respect.

As far as the (too high) value of superexchange obtained by these cluster calculations is concerned, we think that two explanations are possible.

(i) First, it is very difficult to know quite accurately, among other things, the ferromagnetic contribution [Eq. (1)] studied by Stechel and Jennison.<sup>13</sup> If this contribution were larger than usually estimated (i.e.,  $\sim -0.1$  instead of  $\sim -0.04$  eV), the discrepancy between theory and experiment would simply disappear.

(ii) Second, the cluster calculations that we mentioned

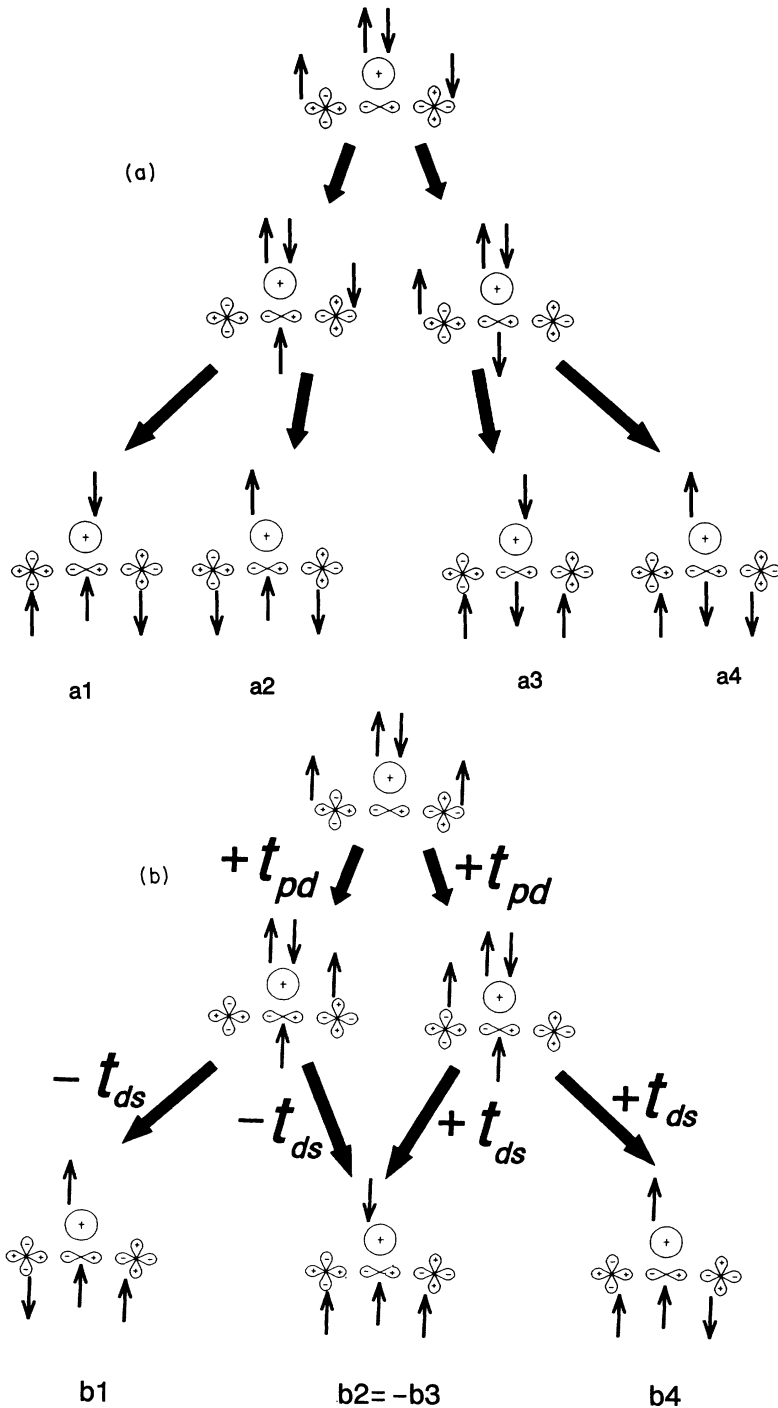


FIG. 1. Successive steps in the perturbation involving O 3s orbitals, in the hole representation. In (a), the total spin is zero. We start from the state  $\text{Cu}\uparrow\text{Cu}\downarrow$ , which is half of a triplet and half of a singlet. Starting from a singlet would build up more coherence, because  $a2$  and  $a3$  are reachable from  $\text{Cu}\downarrow\text{Cu}\uparrow$ . In (b), we have a ferromagnetic configuration,  $b2$  and  $b3$  cancel each other because of the Pauli principle.

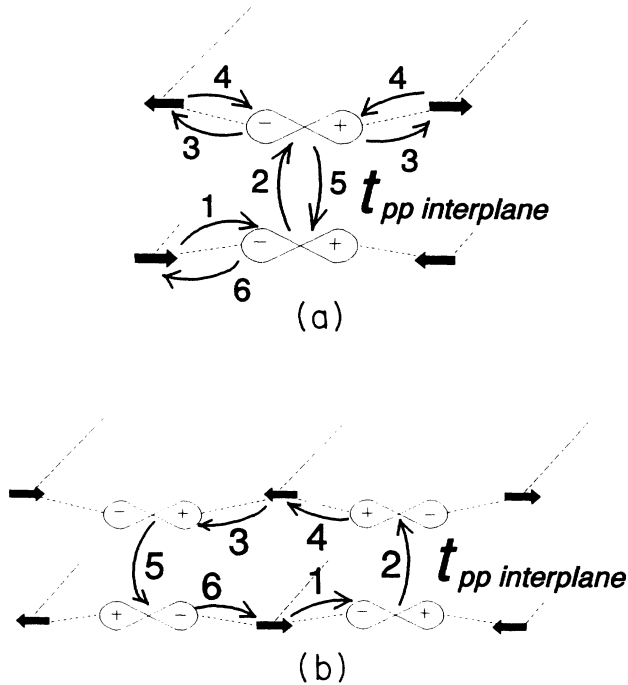


FIG. 2. (a) Schematic representation of the copper double-occupation effect (Anderson  $U_d$  mechanism) contributing to  $J_{\text{intrabilayer}}$ . The average effect of  $U_d$  (for the effective  $J_{\text{intrabilayer}}$ ) between all possible spin pairs is not zero due to the coherent enhancement of  $J$  for copper pairs aligned along the  $c$  axis. The absence of such enhancement for  $K_{pd}(\text{double hopping})$  and  $U_p$  makes the ferromagnetic and Geertsma contributions to  $J_{\text{intrabilayer}}$  zero on the average. (b) One of the possible paths for the Eske-Jefferson topological contribution to  $J_{\text{intrabilayer}}$ .

have neglected the effect of bare crystal-field splittings (i.e., the energy splittings among all five Cu  $3d$  orbitals, and among all three O  $2p$  orbitals). Including these in the calculations would enhance the energy difference between Cu  $3d_{(x^2-y^2)}$  and O  $2p\sigma$  orbitals, while reducing some others. Naturally, the superexchange value would be reduced in the process.

In order to get more insight into the crystal-field problem, we have carried out some numerical cluster simulations of XPS spectra which are similar to those presented before by one of us,<sup>4</sup> except that the copper and oxygen crystal-field splittings have been included in the bare on-site energies of the corresponding orbitals. We have taken the bare crystal-field splittings calculated by McMahan, Annett, and Martin.<sup>17,42</sup> Such an exploration of the role of crystal-field splittings actually does not deserve much approval, because we are led to compare our numerical results with some XPS data taken on CuO,<sup>16</sup> whereas the crystal-field splittings calculated by McMahan, Annett, and Martin are supposed to be valid for La<sub>2</sub>CuO<sub>4</sub> only. It is likely that the bare crystal-field splittings in CuO and La<sub>2</sub>CuO<sub>4</sub> are quite different, at least for the oxygen sites. Nevertheless, our study provides us with the occasion to consider some physical issues which are of more than pedagogical interest. "Reasonable spectra" (Fig. 3) could be obtained under two conditions.

(i) First, the average energy difference between copper and oxygen orbitals should remain unchanged (this was necessary in order to maintain the good intensity of the high-energy Cu  $3d^8$  satellite).

(ii) Second, a correlated hopping<sup>18</sup> between Cu  $3d_{(x^2-y^2)}$  and O  $2p\sigma$  orbitals had to be added in the Hamiltonian:

$$H_{\text{correlated hopping}} = t_1 (c_{\text{Cu}(x^2-y^2),\sigma}^\dagger c_{\text{O}(2p\sigma),\sigma} + \text{H.c.}) n_{\text{Cu}(x^2-y^2),-\sigma} + t_2 (c_{\text{Cu}(x^2-y^2),\sigma}^\dagger c_{\text{O}(2p\sigma),-\sigma} + \text{H.c.}) n_{\text{O}(2p\sigma),-\sigma} \quad (10)$$

Let us briefly comment on the physics of  $H_{\text{correlated hopping}}$ . This term originates from the Coulombic interaction between a hole on copper and a hole on oxygen. Such interaction gives rise to some repulsion ( $U_{pd}$ ), but also to transfer. A simple order of magnitude for  $t_1$  and  $t_2$  should be given by

$$sU_{pd} \leq t_1 \leq sU_d, \quad (11)$$

and

$$sU_{pd} \leq t_2 \leq sU_p, \quad (12)$$

where  $s$  is the overlap between Cu  $3d_{(x^2-y^2)}$  and O  $2p\sigma$  orbitals.

These approximations are obtained from the formal relations

$$\langle 1,1|H|1,2\rangle \simeq \langle 1|2\rangle \langle 1,2|H|1,2\rangle,$$

and also

$$\langle 1,1|H|1,2\rangle \simeq \langle 1|2\rangle \langle 1,1|H|1,1\rangle,$$

$|1\rangle$  and  $|2\rangle$  being the copper and oxygen orbitals.  $s \sim 0.1$  and thus  $sU_d \sim 0.8$  eV. Because  $t_{pd} \sim 1.3$  eV, we see that the upper estimate for  $t_1$  is of order  $0.6t_{pd}$ , which is quite significant. However, the actual value of  $t_1$  and  $t_2$  is probably much smaller than the upper limit 0.8 eV. A value of  $t_1 = t_2 = 0.2t_{pd}$  has been empirically chosen for the cluster calculation (cf. Table I).

One effect of such correlated hoppings has already been considered some time ago in a realistic context for the comparison of some XPS and x-ray absorption spectroscopy (XAS) results in transition-metal oxides.<sup>19</sup> Interestingly,  $H_{\text{correlated hopping}}$  is somewhat attractive for holes,<sup>18</sup> in the sense that the noncorrelated transfer is enhanced. In contrast, the equivalent correlated hopping would be repulsive for real electrons, since correlated and noncorrelated transfers would bear opposite signs in this case. It is our opinion, however, that the  $H_{\text{correlated hopping}}$

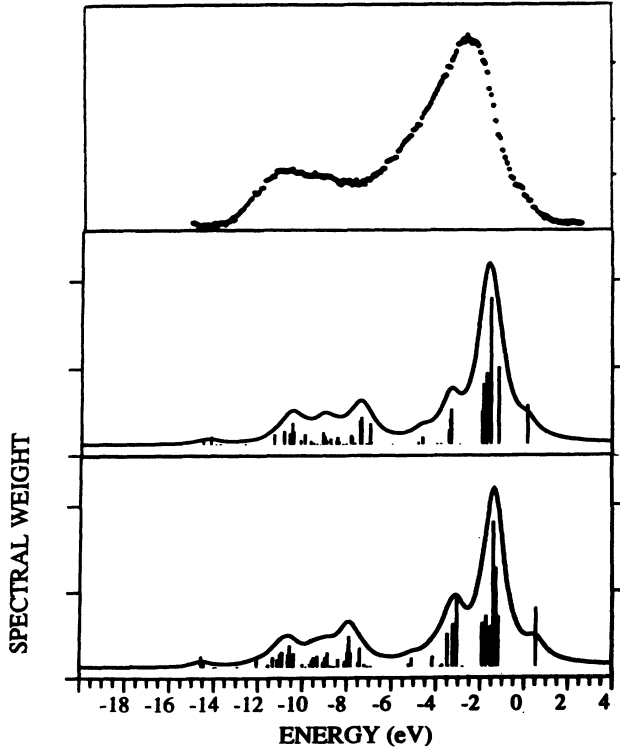


FIG. 3. Top panel: experimental spectrum of valence-band XPS in CuO, taken from Ref. 16.  $h\nu=1486$  eV. Middle panel: cluster calculation without bare crystal-field splittings (cf. Ref. 4). Bottom panel: cluster calculation including the bare crystal-field splittings of McMahan, Annett, and Martin (Ref. 17, case II) and correlated hopping (taken to be 20% of the normal hopping), all other parameters being the same as in Ref. 4. A Lorentzian broadening of 1 eV has been applied in both cases.

of Eq. (10) does not play any crucial role in the superconductivity of the cuprates, because its existence depends on the presence of some much stronger on-site repulsions. The reason we introduced it in our XPS simulations is that  $H_{\text{correlated hopping}}$  proves very useful to stabilize the Zhang-Rice singlet against oxygen planar  $\pi$  states. In this sense,  $H_{\text{correlated hopping}}$  compensates somehow the effect of bare crystal-field splittings in the ground state. However, taking a value bigger than  $0.5t_{pd}$  for the correlated hopping leads to XPS simulation spectra which cannot fit the experimental data properly any more. This puts some limitations on the physical effects that might be expected from correlated hopping (although another kind of correlated hopping between quasiparticles, due to  $U_p$ , is introduced in Sec. II B).

The general conclusion that we get concerning XPS is that the shape of the spectrum is very little affected by bare crystal-field splittings (as long as they remain of the order of 1 eV).

### C. Anisotropy

Trying to adjust our parameters in order to obtain a superexchange value in perfect agreement with experiment<sup>20</sup> appears to be a useless exercise, because of the number of contributions involved. Trying to estimate the anisotropy of superexchange is actually somewhat more rewarding, because the only process which is important in this case is a modification of the Anderson contribution (involving double occupation of one copper site). We define the in-plane anisotropy of superexchange by the Hamiltonian

$$H = \sum_{i,j} J(S_i^a S_j^a + S_i^b S_j^b + S_i^c S_j^c) + J_{\text{in plane } c \text{ direction}} S_i^c S_j^c. \quad (13)$$

Using the same perturbation theory formalism as before, we obtain

$$J_{\text{in plane } c \text{ direction}} = \frac{-8\lambda^2 t_{pd}^4}{E_{xy}^2 (\Delta + E_{xy})^2} \left[ \frac{1}{E_{xy} + A + 4B} - \frac{1}{E_{xy} + A + 4B + 2C} \right] + \frac{2\lambda^2 t_{pd}^4}{E_{xz}^2 (\Delta + E_{xz})^2} \left[ \frac{1}{E_{xz} + A - 5B} - \frac{1}{E_z + A + 4B + 2C} \right]. \quad (14)$$

In Eq. (14),  $E_{xy}$  and  $E_{xz}$  represent the crystal-field splittings on copper,  $\lambda$  the copper spin-orbit coupling,  $\Delta$  is equal to  $(E_p - E_d - 2t_{pp})$ , and  $A$ ,  $B$ , and  $C$  are the Racah parameters on copper. ( $U_{pd}$  and the correlated transfer have been neglected here.) All successive steps in the perturbation are represented in Fig. 4. Incidentally, we note that Eq. (14) provides a quite different (and much smaller) result in comparison with the  $(\delta g/g)^2 J$  estimate which is often quoted in the literature.

Because of the strong covalency in the cuprates, Eq. (12) can still be significantly improved. We may proceed as follows.

(i) On the site where spin-orbit coupling operates, we now consider that  $E_{xy}$  and  $E_{xz}$  correspond to the energies of optically forbidden  $d-d$  transitions, instead of the bare crystal-field splittings. Assuming that covalency reduces the hole occupation of Cu  $3d_{(x^2-y^2)}$  orbitals by 30%,<sup>1</sup> we further multiply Eq. (14) by the factor 0.7.

(ii) On the site where spin-orbit coupling does not operate, strong covalency is treated by replacing the factors

$$\frac{t_{pd}^4}{(\Delta + E_{xy})^2} \quad (15)$$

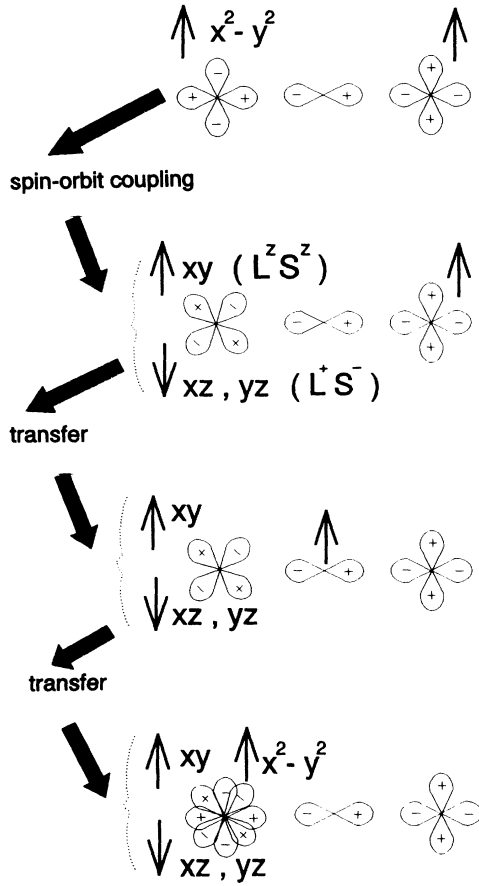


FIG. 4. Successive steps in the perturbation used for calculating the anisotropy of the in-plane superexchange in high- $T_c$  superconductors.

and

$$\frac{t_{pd}^4}{(\Delta + E_{xz})^2} \quad (16)$$

by, respectively,

$$t_{pd}^2 \left[ \frac{t_{pd}^2 \cos^2 \theta}{(\Delta + E_{xy})^2} + \sin^2 \theta \right] \quad (17)$$

and

$$t_{pd}^2 \left[ \frac{t_{pd}^2 \cos^2 \theta}{(\Delta + E_{xz})^2} + \sin^2 \theta \right] \quad (18)$$

with

$$\tan 2\theta = -\frac{2t_{pd}}{\Delta}. \quad (19)$$

$\sin \theta$  corresponds to the amplitude of a hole on an O  $2p\sigma$  orbital. On this second copper site, the improvement comes from the exact treatment of copper-oxygen covalency. This trick was introduced by Jefferson, Eskes, and Feiner in their so-called cell-perturbation approach.<sup>7</sup>

A last significant improvement can be obtained by including the contribution of copper  $3z^2-r^2$  orbitals, which adds three more terms to Eq. (14), the last one originating in a coherent effect between  $x^2-y^2$  and  $3z^2-r^2$  orbitals: in Eq. (14) as in Fig. 4, only the on-site combinations  $\text{Cu}(xy)\text{Cu}(x^2-y^2)$ ,  $\text{Cu}(xz)\text{Cu}(x^2-y^2)$ , and  $\text{Cu}(yz)\text{Cu}(x^2-y^2)$  were represented, whereas the combinations  $\text{Cu}(xy)\text{Cu}(3z^2-r^2)$ ,  $\text{Cu}(xz)\text{Cu}(3z^2-r^2)$ , and  $\text{Cu}(yz)\text{Cu}(3z^2-r^2)$  also contribute to the anisotropy of  $J$ .

Our final value for  $J_{\text{in plane}, c}$  direction is thus

$$\begin{aligned}
 J_{\text{in plane}, c} = & \frac{-0.7 \times 8 \lambda^2 t_{pd}^2}{E_{xy}^2} \left[ \frac{t_{pd}^2 \cos^2 \theta}{(\Delta + E_{xy})^2} + \sin^2 \theta \right] \left[ \frac{1}{E_{xy} + A + 4B} - \frac{1}{E_{xy} + A + 4B + 2C} \right] \\
 & + \frac{0.7 \times 2 \lambda^2 t_{pd}^2}{E_{xz}^2} \left[ \frac{t_{pd}^2 \cos^2 \theta}{(\Delta + E_{xz})^2} + \sin^2 \theta \right] \left[ \frac{1}{E_{xz} + A - 5B} - \frac{1}{E_{xz} + A + 4B + 2C} \right] \\
 & + \frac{-0.7 \times 8 \lambda^2 t_{pd}^2}{3E_{xy}^2} \left[ \frac{t_{pd}^2 \cos^2 \theta}{(\Delta + E_{xy})^2} + \sin^2 \theta \right] \left[ \frac{1}{E_{xy} + A - 8B} - \frac{1}{E_{xy} + A + 2C} \right] \\
 & + \frac{0.7 \times 2 \lambda^2 t_{pd}^2}{3E_{xz}^2} \left[ \frac{t_{pd}^2 \cos^2 \theta}{(\Delta + E_{xz})^2} + \sin^2 \theta \right] \left[ \frac{1}{E_{xz} + A + B + 2C} - \frac{1}{E_{xz} + A + 3B + 2C} \right] \\
 & + \frac{-0.7 \times 4 \lambda^2 t_{pd}^2}{\sqrt{3}E_{xz}^2} \left[ \frac{t_{pd}^2 \cos^2 \theta}{(\Delta + E_{xz})^2} + \sin^2 \theta \right] \\
 & \times \left[ \frac{3\sqrt{3}B}{(E_{xz} + A - 5B)(E_{xz} + A + B)} - \frac{\sqrt{3}B}{(E_{xz} + A + B + 2C)(E_{xz} + A + 3B + 2C)} \right]. \quad (20)
 \end{aligned}$$

Taking  $\lambda = 0.1$  eV,<sup>21</sup>  $E_{xy} = E_{xz} = 1.3$  eV,<sup>1</sup> and the set of parameters provided in Table I, we get

$$J_{\text{in plane}} = -1.23 \times 10^{-4} \text{ eV} . \quad (21)$$

c direction

The result of Eq. (20) depends strongly on the values taken by the ratios  $B/A$  and  $C/A$ , as well as on the energies of optically forbidden  $d-d$  transitions. Our numerical value is ten times larger than what was originally extracted from neutron experiments on  $\text{YBa}_2\text{Cu}_3\text{O}_{6.0}$ , which was<sup>22</sup>

$$J_{\text{in plane}} \simeq -1.3 \times 10^{-5} \text{ eV} . \quad (22)$$

c direction experimental

The experimental value extended from  $\text{La}_2\text{CuO}_4$  was found to be of comparable magnitude.<sup>23</sup> Recent progress<sup>24</sup> in the understanding of Dzyaloshinskii-Moriya interactions suggests that the interpretation of all the experimental data should be revised. We do not consider dipolar interactions in this article. What remains totally unexplained so far is why the spin orientations in the planes of  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$  are different.

### III. HOLE TRANSFER AND HOLE-HOLE INTERACTIONS: FROM A $t$ - $J$ TO A $t$ - $J$ - $R$ MODEL WITH $t \simeq -0.5$ eV, $J \simeq 0.1$ eV, AND $R \simeq 0.3$ eV

Let us now turn to the problem of holes in doped cuprates. To describe these, the  $t$ -( $t'$ )- $J$  model has received the strongest support. In this model, doped holes are described as Zhang-Rice singlets hopping in a square lattice of copper spins.<sup>3,7</sup>

Zhang-Rice singlets are usually constructed from oxygen Wannier states, which serve to eliminate orthogonality problems. These Wannier states give rise to a lot of small long-range interactions, which are of course usually

neglected. More problematic, however, is the neglect of triplet states,<sup>8</sup> some aspects of which are discussed in Sec. V.

#### A. Hole motion

In this subsection, we suppose that all the dynamics can be described in the Zhang-Rice-singlet picture. We concentrate on the motion of a single Zhang-Rice singlet, by supposing that  $t_{pd} \ll \Delta$  and  $t_{pd} \ll (U_d - \Delta)$ , in order to use the simplest analytic expressions. Hopping parameters to nearest neighbor ( $t$ ) and second-nearest neighbor ( $t'$ ) are readily estimated (all numerical coefficients are approximated by the simplest fractional values):

$$t \simeq -\frac{t_{pp}}{4} - \frac{t_{pd}^2}{2\Delta} - \frac{t_{pd}^2}{2(U_d - \Delta)} , \quad (23)$$

$$t' \simeq \frac{t_{pp}}{10} - \frac{t_{pd}^2}{11\Delta} - \frac{t_{pd}^2}{11(U_d - \Delta)} . \quad (24)$$

It is interesting to note that empty oxygen orbitals, which have been shown to play an important role for superexchange in Sec. II A, do not seem to be relevant for the transfer of Zhang-Rice singlets. To the same order in perturbation, many other terms are obtained, which go beyond the  $t$ - $t'$ - $J$  model.

(i) We obtain a second-nearest-neighbor transfer with equal initial spins on first- and second-nearest neighbors (Fig. 5), which we name  $t'_{\text{equal spins}}$ :

$$t'_{\text{equal spins}} \simeq \frac{t_{pd}^2}{16(U_d - \Delta)} . \quad (25)$$

(ii) There is a second-nearest-neighbor transfer with unequal spins on first- and second-nearest neighbors (Fig. 5), which we name  $t'_{\text{unequal spins}}$ :

$$t'_{\text{unequal spins}} \simeq -\frac{t_{pd}^2}{16} \frac{1}{(\Delta + 8t_{pd}^2/\Delta) - [6t_{pd}^2/\Delta + 2t_{pd}^2/(U_p + \Delta) + 8t_{pd}^2/(U_d - \Delta)]} . \quad (26)$$

The denominator

$$\left[ \Delta + \frac{8t_{pd}^2}{\Delta} \right] - \left[ \frac{6t_{pd}^2}{\Delta} + \frac{2t_{pd}^2}{(U_p + \Delta)} + \frac{8t_{pd}^2}{(U_d - \Delta)} \right] \quad (27)$$

found in Eq. (26) is precisely equal to the charge-transfer optical gap in the insulator, plus the coherent energy of a local Wannier Zhang-Rice singlet. Basically, starting from one Zhang-Rice singlet, we form an intermediate excited state with two Zhang-Rice singlets, which relaxes again into a single Zhang-Rice singlet located somewhere else in the lattice.

(iii) We also obtain a second-nearest-neighbor transfer involving spin flips, which we name  $t'_{\text{spin flip}}$ :

$$t'_{\text{spin flip}} \simeq -\frac{+t_{pd}^2}{16(U_d - \Delta)} + \frac{t_{pd}^2}{16} \frac{1}{(\Delta + 8t_{pd}^2/\Delta) - [6t_{pd}^2/\Delta + 2t_{pd}^2/(U_p + \Delta) + 8t_{pd}^2/(U_d - \Delta)]} . \quad (28)$$

(iv) There is a third-nearest-neighbor transfer, which we name  $t''$ :

$$t'' \simeq -\frac{t_{pd}^2}{15\Delta} - \frac{t_{pd}^2}{15(U_d - \Delta)} - \frac{t_{pp}}{13} . \quad (29)$$

(v) There is a third-nearest-neighbor transfer with equal initial spins on first- and third-nearest neighbors, which we

name  $t''_{\text{equal spins}}$ :

$$t''_{\text{equal spins}} \simeq \frac{t_{pd}^2}{32(U_d - \Delta)} . \quad (30)$$

(vi) We find also a third-nearest-neighbor transfer with unequal initial spins on first- and third-nearest neighbors, which we name  $t''_{\text{unequal spins}}$ :

$$t''_{\text{unequal spins}} \simeq -\frac{t_{pd}^2}{32} \frac{1}{(\Delta + 8t_{pd}^2/\Delta) - [6t_{pd}^2/\Delta + 2t_{pd}^2/(U_p + \Delta) + 8t_{pd}^2/(U_d - \Delta)]} . \quad (31)$$

(vii) Finally, there is a third-nearest-neighbor transfer involving spin flips, which we name  $t''_{\text{spin flip}}$ :

$$t''_{\text{spin flip}} \simeq +\frac{t_{pd}^2}{32(U_d - \Delta)} + \frac{t_{pd}^2}{32} \frac{1}{(\Delta + 8t_{pd}^2/\Delta) - [6t_{pd}^2/\Delta + 2t_{pd}^2/(U_p + \Delta) + 8t_{pd}^2/(U_d - \Delta)]} . \quad (32)$$

From exact calculations on a  $\text{Cu}_4\text{O}_8$  cluster with five holes, Batista and Aligia<sup>25</sup> independently decided on the necessity of adding another term to the  $t$ - $J$  Hamiltonian. Their supplementary term can be formally related to a certain combination of the factors calculated above.

Using the parameter estimates of Table I, we find that all transfer-parameter values are, in order of importance,

$$t = 0.56 \text{ eV}, \quad t'' = -0.1 \text{ eV},$$

$$t'_{\text{spin flip}} = 0.085 \text{ eV},$$

$$t'_{\text{unequal spins}} = -0.065 \text{ eV},$$

$$t''_{\text{spin flip}} = 0.04 \text{ eV},$$

$$t''_{\text{unequal spins}} = -0.03 \text{ eV},$$

$$t'_{\text{equal spins}} = 0.02 \text{ eV},$$

$$t''_{\text{equal spins}} = 0.01 \text{ eV}, \quad t' = 0.008 \text{ eV} .$$

All transitions via triplet states have been neglected, and also a few very small terms due to  $U_p$ .

For the  $t$ - $J$  model with one doped hole, the ground state has the wave vector  $(\pi/2, \pi/2)$  and the coherent bandwidth is approximately  $2J$ .<sup>26</sup> The terms in  $t_{pd}^2/\Delta$  found in  $t'$ ,  $t'_{\text{unequal spins}}$ ,  $t''$ , and  $t''_{\text{unequal spins}}$  would all significantly enlarge the bandwidth. The influence of  $t_{pp}$  makes the picture even more complicated, because in the  $t$ - $t'$ - $J$  model with  $t \simeq 0$ ,  $t' \gg J$  ( $t' > 0$ ), the wave vector of the ground state can be expected to be in the neighborhood of  $(0, 0)$ ,  $(0, \pm\pi)$ ,  $(\pm\pi, 0)$ ,  $(\pm\pi, \pm\pi)$ , and the width of the band is, tentatively,  $8t'$ . As far as the propagation of holes is concerned, the difference between the  $t$ - $J$  model and some more elaborate versions which include second- and third-nearest-neighbor hopping is rather drastic.

We may actually wonder if the reentrant behavior of the antiferromagnetic order parameter  $\langle M \rangle$  measured in neutron scattering as a function of temperature at low doping,<sup>27,28</sup> and which has been related to charge localization, is not attributable to a coherent bandwidth which

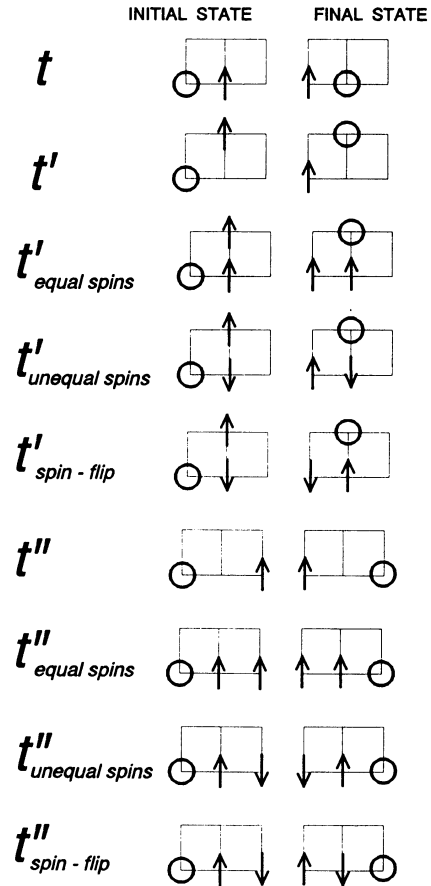


FIG. 5. Transfer processes of a Zhang-Rice singlet (in the Wannier representation) which improve over the simpler  $t$ - $J$  version. In Eqs. (25)–(32), we have adopted the conventions  $t'_{\text{equal spins}} = 2t''_{\text{equal spins}}$ ,  $t'_{\text{unequal spins}} = 2t''_{\text{unequal spins}}$ , and  $t'_{\text{spin flip}} = t''_{\text{spin flip}}$ , whereas from the conventions of the figure we would rather get  $t'_{\text{equal spins}} = t''_{\text{equal spins}}$ ,  $t'_{\text{unequal spins}} = t''_{\text{unequal spins}}$ , and  $t'_{\text{spin flip}} = t''_{\text{spin flip}}$ . The conventions of Eqs. (25)–(32), which may not be the best, reflect the potential overall physical importance of the different processes.



is significantly larger than  $2J$ . It seems very improbable that localization may act to destroy antiferromagnetic long-range correlations in the simple  $t$ - $J$  model (in the  $t$ - $J$  model, the motion of holes destroys the antiferromagnetic background).

### B. Hole-hole interactions

We now come to hole-hole interactions. Let us first consider two Zhang-Rice singlets based on two neighboring  $\text{CuO}_4$  units (Fig. 6). For the moment, the Zhang-Rice singlets are not constructed as Wannier states. They have to share a common oxygen orbital, which has a probability of around  $\frac{1}{4}$  to be occupied by each singlet (neglecting the difference between the amplitudes of Cu  $3d^{10}$  and Cu  $3d^8$  in the Zhang-Rice singlet wave function). A crude estimate for nearest-neighbor repulsion between the two singlets might thus seem to be

$$R = \frac{U_p}{16} . \quad (33)$$

This is, however, incorrect because the common oxygen orbital cannot be occupied simultaneously by two holes of the same spin. Considering that this spin constraint transforms each  $\text{CuO}_4$  singlet into a mixture of  $\text{CuO}_3$ -based and  $\text{CuO}_4$ -based compositions, the correct estimate for nearest-neighbor repulsion is

$$R \approx \frac{U_p}{32} + (1 - \frac{7}{8}) \frac{2t_{pd}^2}{\Delta} . \quad (34)$$

With the parameters of Table I, this gives

$$R \approx 0.31 \text{ eV} . \quad (35)$$

If the Zhang-Rice singlets are built out of Wannier states, the nearest-neighbor correlation due to  $U_p$  is significantly different. The fact that Wannier states are orthogonal eliminates the problem related to the non-double-occupancy of an oxygen orbital by two holes of the same spin. A good estimate for nearest-neighbor repulsion is thus

$$R_{\text{first-nearest neighbors Wannier states}} \approx \frac{U_p}{32} \approx 0.19 \text{ eV} . \quad (36)$$

In Eq. (36), the repulsion  $R$  is smaller than estimated for nonorthogonal Zhang-Rice singlets. This is partly compensated by the fact that a repulsion at longer dis-

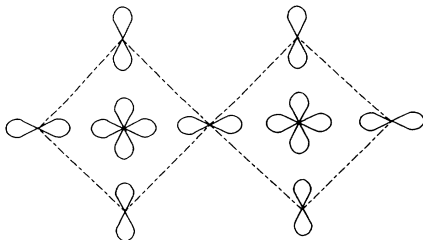


FIG. 6. Two neighboring Zhang-Rice singlets have to share a common oxygen orbital.

tances also exists for Wannier states, which we estimate as

$$R_{\text{second-nearest neighbors Wannier states}} \approx \frac{U_p}{760} \approx 0.008 \text{ eV} , \quad (37)$$

$$R_{\text{third-nearest neighbors Wannier states}} \approx \frac{U_p}{960} \approx 0.006 \text{ eV} , \quad (38)$$

$$R_{\text{fourth-nearest neighbors Wannier states}} \approx 0.001 \text{ eV} . \quad (39)$$

There is another very interesting effect of  $U_p$ , which is correlated hopping for Wannier states. Let us consider the hole configuration represented in Fig. 7. The Zhang-Rice Wannier state located on the right side of the figure can hop to three other sites (including the one situated on the left, by crossing over the other singlet) because of  $U_p$ . The matrix element for such hopping is

$$t_{\text{correlated hopping}} \approx \frac{2}{6} \frac{U_p}{64} \approx 0.03 \text{ eV} . \quad (40)$$

Because of its sign, it is preferable for  $t_{\text{correlated hopping}}$  to form a local Cooper pair with  $s$ -wave symmetry. Unfortunately, this gain in kinetic energy cannot balance the loss in potential energy. The overall effect of  $U_p$  is definitely repulsive. On a cluster made of five copper atoms (Fig. 8),  $U_p$  would enhance the energy of an  $s$ -wave Cooper pair of Wannier states by approximately

$$E_{\text{local pair of } s\text{-wave symmetry}} = E_{\text{potential}} + E_{\text{kinetic, } s \text{ wave}} \quad (41)$$

with

$$E_{\text{potential}} \approx \frac{U_p}{32} \approx 0.19 \text{ eV} \quad (42)$$

and

$$E_{\text{kinetic, } s \text{ wave}} \approx -\frac{U_p}{64} \approx -0.09 \text{ eV} . \quad (43)$$

The energy of a  $d$ -wave Cooper pair would be enhanced by

$$E_{\text{local pair of } d\text{-wave symmetry}} = E_{\text{potential}} + E_{\text{kinetic } d, \text{ wave}} \quad (44)$$

with

$$E_{\text{kinetic, } d \text{ wave}} \approx \frac{1}{3} \frac{U_p}{64} \approx +0.03 \text{ eV} . \quad (45)$$

Accordingly, the difference between  $s$ -wave and  $d$ -wave

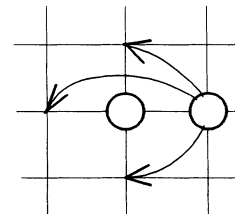


FIG. 7. Schematic view of correlated hopping due to the interaction of two Zhang-Rice singlets (Wannier states) via  $U_p$ .

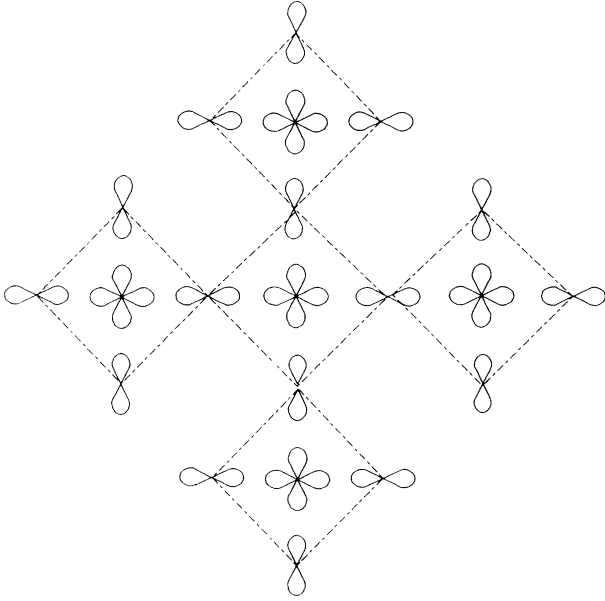


FIG. 8.  $\text{Cu}_5\text{O}_{16}$  cluster used to estimate the energies  $s$ - and  $d$ -wave symmetry states for two Zhang-Rice singlets (total doping five holes with spin up and two holes with spin down). We argue that, partly because of correlated transfer due to  $U_p$ , and partly because of a reduction of the roles of  $t'_{\text{unequal spins}}$  and  $t''_{\text{unequal spins}}$ , the one-hole quasiparticle wave function in the ground state possesses  $s$ -wave symmetry. The quasiparticles which are situated around  $[\pi-x, x]$ ,  $[-x, \pi-x]$ ,  $[-x, -\pi+x]$ , and  $[\pi-x, -x]$  in the Brillouin zone naturally generate a  $d$ -wave local symmetry, which is why we eventually model such symmetry effects by simply increasing the effective value of  $R$  (nearest-neighbor repulsion between two Zhang-Rice singlets).

symmetries is more than 0.1 eV.

Our description of hole-hole interactions is not yet complete. For two nearest-neighbor Zhang-Rice singlets placed in an antiferromagnetic background, half of what we called  $t'_{\text{unequal spins}}$  and all of  $t''_{\text{unequal spins}}$  (cf. Fig. 5) disappear in the cluster of Fig. 8. Once more, it is an  $s$ -wave Cooper pair which is advantaged by this gain in kinetic energy (in the most favorable case, this may be considered as a gain because the contributions of  $t_{pp}$  in  $t'$  [cf. Eq. (24)] and the contribution of  $t_{pd}^2/\Delta$  in  $t'_{\text{unequal spins}}$  [cf. Eq. (26)] are of opposite sign; by suppressing part of  $t'_{\text{unequal spins}}$  we reinforce the effect of  $t_{pp}$ , thus possibly acquiring some supplementary kinetic energy). The gain for a  $\text{Cu}_5\text{O}_{16}$  cluster (Fig. 8) is this time

$$E_{\text{kinetic, } s \text{ wave}} \simeq 3t''_{\text{unequal spins}} \quad (46)$$

$3t''_{\text{unequal spins}}$  is of the order of  $-0.15$  eV. At first sight, this gain in kinetic energy might seem large enough to exceed the overall repulsion due to  $U_p$ . However, bound pairs of  $s$ -wave symmetry do not seem to have a chance to exist, because when two Zhang-Rice singlets are

placed on neighboring sites they each constitute an obstacle for the motion of the other. This is a kind of effective repulsion which is of order  $t$  for a pair; thus 0.5 eV.

If bound states of  $s$ -wave symmetry do not exist, then *a fortiori* the nearest-neighbor repulsion between Zhang-Rice singlets is quite significant (at least of order 0.2 or 0.3 eV). This, in turn, leads us to make a few hypotheses.

Supposing that the spin background is nearly antiferromagnetic and that Cooper pairs are made of two oxygen holes, one with a spin up and one with a spin down (for which there seems to be considerable NMR evidence: all the Knight shifts are close to zero in the superconducting state at zero kelvin), the closest possible hole-hole distances are only equal to

$$a, \sqrt{5}a, 3a, \quad (47)$$

$a$  being the copper-copper distance. Supposing that this small distance  $a$  is discarded because of the repulsion due to  $U_p$ , only the next candidates remain, which are of order 8–10 Å. If the motion of one hole around the other retains some memory of the Fermi surface, which is around  $[\pi-x, x]$ ,  $[-x, \pi-x]$ ,  $[-x, -\pi+x]$ , and  $[\pi-x, -x]$ ,<sup>29</sup> then Cooper pairs possess  $g$ -wave symmetry (Fig. 9). Of course, this is only speculation.

Another consequence of first-nearest-neighbor repulsion can be seen as follows. Supposing that this repulsion is infinite, each Zhang-Rice singlet occupies *de facto* five copper sites in the square lattice. A doping of 15% is thus equivalent to 75% phase-space occupation. This makes the phase-separation scheme advocated by Emery and Kivelson<sup>30</sup> very unlikely.

It is intuitively appealing to remember that, if doped holes in high- $T_c$  superconductors are placed in a crystalline electronic square lattice of constant  $3a$ , the doping is equal to  $\frac{1}{3} = 14\%$ . This (frozen) electronic crystal is quite

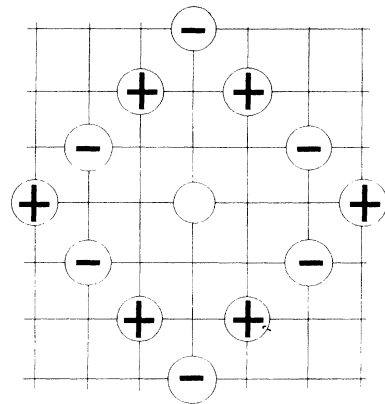


FIG. 9. A naive representation of what looks like  $g$ -wave symmetry for a hole pair in real space. The  $g$ -wave symmetry is simply generated by the position of only *one* quasiparticle located anywhere on the Fermi surface (thus close to  $[\pi-x, x]$ ,  $[x, \pi-x]$ ,  $[-x, -\pi+x]$ , or  $[\pi-x, -x]$ ), and is not necessarily connected to the symmetry of any hypothetical order parameter for a *pair* of particles. Trying to guess the symmetry of such a pair potential is certainly not trivial.

efficient to circumvent the repulsion between Zhang-Rice singlets. Of course, real holes are mobile (also, long-range antiferromagnetic order does not exist). However, the first- (as well as second- and third-) nearest-neighbor

repulsions between singlets are likely to favor an overall hole repartition in the lattice which is nearly crystal-like. Accordingly, a very nice speculation that can be made is that the hole-hole correlation functions

$$F_{\text{in plane}}^{(3a,0)}[R=(x,y),\omega]=\int dt e^{-i\omega t}\langle C_{(x+3a,y,t)\uparrow}^\dagger C_{(x,y,t)\downarrow}^\dagger C_{(3a,0,0)\uparrow} C_{(0,0,0)\downarrow} \rangle \quad (48)$$

and

$$F_{\text{in plane}}^{(2a,a)}[R=(x,y),\omega]=\int dt e^{-i\omega t}\langle C_{(x+2a,y+a,t)\uparrow}^\dagger C_{(x,y,t)\downarrow}^\dagger C_{(2a,a,0)\uparrow} C_{(0,0,0)\downarrow} \rangle \quad (49)$$

possess a tail at quite low frequencies, which does not exist in a normal liquid [in Eqs. (48) and (49), the creation and annihilation operators are based on oxygen orbitals]. If this is the case, correlations of two  $F_{\text{in plane}}$  functions between different planes might follow.

#### IV. OXYGEN HYPERFINE COUPLING

The use of oxygen hyperfine coupling that we make in Sec. V, which is devoted to oxygen spin dynamics, is particularly difficult, so that it appears useful to analyze the quantum chemical origin of this hyperfine coupling in some detail. Let us first recall some fundamental properties of hyperfine couplings. Any NMR frequency shift can be decomposed into an orbital and a spin shift:

$$K=K_{\text{orb}}+K_{\text{spin}}(\%). \quad (50)$$

$K_{\text{orb}}$  is often designated as the "chemical shift," which, in the case of strong Landau diamagnetism for some metals, is inappropriate. When only one orbital contributes to the Knight shift,  $K_{\text{spin}}$  can be written

$$K_{\text{spin}}=Af\chi^{\text{spin}}, \quad (51)$$

where  $\chi$  is a spin susceptibility,  $f$  a fractional spin occupancy, and  $A$  the hyperfine interaction. When several orbitals are contributing simultaneously, the expression for  $K_{\text{spin}}$  is more complicated, due to coherence effects between all the orbitals.  $K_{\text{spin}}$  can always be decomposed into an isotropic part  $K_{\text{spin iso}}$ , and an anisotropic, traceless part  $K_{\text{spin aniso}}$ :

$$K_{\text{spin}}=K_{\text{spin iso}}+K_{\text{spin aniso}}. \quad (52)$$

##### A. The isotropic part of the hyperfine field

$K_{\text{spin iso}}$  comes essentially from the polarization of  $s$  orbitals. The first mechanism that contributes to this polarization is the hole transfer from Cu  $3d$  to O  $2s$  and O  $1s$ , as well as the electron transfer from Cu  $3d$  to O  $3s$ .

(i) The energy of O  $1s$  orbitals, as measured by XPS, is approximately  $-530$  eV. The transfer integral  $t_{\text{Cu } 3d/\text{O } 3s}$  is quite small (a precise estimation of this transfer integral seems to go beyond the present knowledge of quantum chemistry), so that the polarization of O  $1s$  is extremely small. However, the hyperfine interaction of O  $1s$  with the  $^{17}\text{O}$  nucleus is huge, so that the contribution of O  $1s$  to  $K_{\text{spin iso}}$  cannot be neglected in principle.<sup>31</sup>

(ii) The energy of O  $2s$  orbitals, as measured by XPS, is located around  $-20$  eV.<sup>32</sup> The transfer integral  $t_{\text{Cu } 3d/\text{O } 3s}$  is presumably of order  $0.5-1$  eV. The hyperfine interaction of the O  $2s$  orbital with the  $^{17}\text{O}$  nucleus has been estimated by Morton and Preston.<sup>33</sup>

(iii) The energy of O  $3s$  orbitals, as measured by inverse photoemission spectroscopy,<sup>16</sup> is located around  $30$  eV. Because the O  $3s$  orbital is quite extended, the transfer integral  $t_{\text{Cu } 3d/\text{O } 3s}$  is presumably large, but the hyperfine interaction of O  $3s$  with the  $^{17}\text{O}$  nucleus is small.

It is known that the contribution of all the transfers from copper  $3d$  to oxygen  $1s$ ,  $2s$ , and  $3s$  orbitals must be taken as a whole to calculate  $K_{\text{spin iso}}$ , because of a coherence effect. Essential to this coherence is the fact that the sign of the O  $2s$  orbital is opposite to that of the O  $1s$  and O  $3s$  orbitals on the nucleus, if we take the convention that the tails of all orbitals possess the same sign.

A lot of effort has been devoted in the years 1950-1970 to understand all these details. Some aqueous complexes of copper, namely the Tutton salts, were thoroughly studied in this time. The oxygen hyperfine field was measured rather recently (due to the problem of isotropic doping) by Getz and Silver using electron paramagnetic resonance (EPR).<sup>31</sup> The copper-oxygen covalency of the tetra-valent Tutton salts may be considered to be similar to the covalency in high- $T_c$  cuprates. For the Tutton salts, it has been concluded that the O  $2s$  orbital provides the most important contribution to  $K_{\text{spin iso}}$ , but that the coherent term between O  $1s$  and O  $2s$  orbitals cannot be neglected. A fractional hole occupation of slightly more than 1% was generally deduced for the O  $2s$  orbitals.

If we try to estimate the fractional hole occupancy numerically, writing the ground-state wave function for a  $\text{CuO}_4$  cluster in the insulator as

$$\begin{aligned} \Psi_{\text{ground state}} = & \sqrt{f_{\text{Cu } 3d}} |\text{Cu } 3d^9 \text{O } 2p\sigma^6 \text{O } 2s^2\rangle \\ & + \sqrt{f_{\text{O } 2p\sigma}} |\text{Cu } 3d^{10} \text{O } 2p\sigma^5 \text{O } 2s^2\rangle \\ & + \sqrt{f_{\text{O } 2s}} |\text{Cu } 3d^{10} \text{O } 2p\sigma^6 \text{O } 2s^1\rangle \end{aligned} \quad (53)$$

and taking  $t_{\text{Cu } 3d/\text{O } 2s} = 1 \text{ eV}$  and

$$(E_{|\text{Cu } 3d^9 \text{O } 2s^2\rangle} - E_{|\text{Cu } 3d^{10} \text{O } 2s^1\rangle}) = 20 \text{ eV},$$

we get

$$\begin{aligned} f_{\text{O } 2s} = & \frac{t_{\text{Cu } 3d/\text{O } 2s}}{(E_{|\text{Cu } 3d^9 \text{O } 2s^2\rangle} - E_{|\text{Cu } 3d^{10} \text{O } 2s^1\rangle})^2} \\ \simeq & 0.25\% . \end{aligned} \quad (54)$$

This result is five times smaller than the NMR value. Of course, our estimate for the quantity

$$(E_{|\text{Cu } 3d^9 \text{O } 2s^2\rangle} - E_{|\text{Cu } 3d^{10} \text{O } 2s^1\rangle})$$

relies on XPS data, for which the number of electrons is not conserved. A slightly smaller value than 20 eV might have to be used in Eq. (54), due to the Cu  $3d$ -O  $2s$  Coulomb interaction. However, the distinction is completely academic in our case. On the other hand, the estimate  $t_{\text{Cu } 3d/\text{O } 2s} = 1 \text{ eV}$  must be considered as an upper limit (the transfer from Cu  $3d$  to O  $2p\sigma$  orbitals is known to be close to 1.3 eV; the transfer from Cu  $3d$  to O  $2s$  is naturally smaller).

On the whole, it would seem that a fractional occupancy  $f_{\text{O } 2s} \sim 0.25\%$  would be quite reasonable. How can we reconcile this very small value with the result of NMR experiments? The boldest way to do that is to reevaluate the theoretical value of  $A_{\text{O } 2s}$ ,<sup>33</sup> the hyperfine coupling of  $2s$  orbitals, at least by a factor of 5. As a matter of fact, during the hole transfer from Cu  $3d$  to O  $2s$ , the oxygen orbital is occupied by only one electron and not two. The radius of the O  $2s$  orbital is thus reduced. An overestimate of the enhancement can be obtained by comparing the value of  $\Psi^2(0)$  for oxygen and fluorine atoms, as given in Ref. 33. We find that the enhancement of the density at the nucleus might be as large as 40%.

It is worth looking for supplementary physical insight into that problem. The hole transfer from Cu  $3d$  to O  $2s$  is viewed as a transition from  $|\text{Cu } 3d^9 \text{O } 2s^2\rangle$  to  $|\text{Cu } 3d^{10} \text{O } 2s^1\rangle$ . We feel it necessary to attribute a different radius to  $|\text{O } 2s^2\rangle$  and  $|\text{O } 2s^1\rangle$ . There is indeed a well-known quantum chemical approach, which can be viewed as a variant of the original configuration-interaction scheme, and which defines "orbitals" by a fixed set of energies and transfer integrals only. Orbital radii are considered as adjustable *dynamical* quantities. This method, which is not easily implemented on *ab initio* numerical approaches, is, however, perfectly suited to the interpretation of high-energy spectroscopic data. Nonconstant orbital radii, which influence the details of hyperfine couplings, also account for some subtle changes in the cross sections of high-energy spectroscopies.

There is, however, a difficult part in this dynamical radii scheme in our case, which concerns the density of the Cu  $3d_{x^2-y^2}$  orbital itself on the oxygen nucleus. This

density is much bigger than what would be expected from the small extension of a purely atomic Cu  $3d$  orbital. In other words, the wave function  $|\text{Cu } 3d^9 \text{O } 2s^2\rangle$  possesses a significant nonzero average spin density on the oxygen nucleus. Indeed, a somewhat related term has already been derived many times by using simple orthogonality considerations;<sup>34</sup> the contribution of what could be assimilated with  $|\text{Cu } 3d^9 \text{O } 2s^2\rangle$  to the hyperfine field was estimated to be of order  $s^2 A_{|\text{O } 2s\rangle}$  (cf. Ref. 34; actually the coherence between  $|\text{Cu } 3d^9 \text{O } 2s^2\rangle$  and  $|\text{Cu } 3d^{10} \text{O } 2s^1\rangle$  makes the comparison between our highly correlated formalism and the molecular-orbital theory employed in Ref. 34 rather awkward),  $s$  being the overlap between Cu  $3d$  and O  $2s$ . In the dynamical scheme that we follow, it is no longer trivial to calculate the orthogonality properties of many-body wave functions.

It seems clear that the large value of  $K_{\text{spin iso}}$  can be mainly attributed to unexpectedly high spin density of  $|\text{Cu } 3d^9 \text{O } 2s^2\rangle$  on the oxygen nucleus, and also partly to the small radius of the O  $2s$  orbital in  $|\text{Cu } 3d^{10} \text{O } 2s^1\rangle$ . We thus reconcile the NMR and XPS data.

The last contribution which is usually considered for  $K_{\text{spin iso}}$  is the core polarization of oxygen  $s$  orbitals ( $1s$ ,  $2s$ ,  $3s$ , etc.) by oxygen  $2p$  orbitals. This core polarization has been estimated very precisely by Harvey in the triplet state of atomic oxygen.<sup>35</sup> In the experiment of Harvey, the valency of oxygen was neutral. In the insulating state of high- $T_c$  superconductors, the valency of oxygen which should be relevant for core polarization is  $\text{O}^{1-}$ , which makes the O  $2p\sigma$  orbital more elongated than in the atom. Crystal fields also act in the same way. This, in turn, lowers the exchange integral between O  $2p$  and O  $s$  states, and thus the core polarization itself. Moreover, if we wanted to calculate the core polarization perturbatively in the insulating case, by considering the transition from O  $2s$  to O  $3s$ , for instance, we would have to include the factor

$$(E_{|\text{Cu } 3d^{10} \text{O } 2s^1 \text{O } 3s^1\rangle} - E_{|\text{Cu } 3d^{10} \text{O } 2s^2 \text{O } 3s^0\rangle} + \Delta)$$

in the denominator, where  $\Delta$  is the charge transfer from Cu  $3d$  to O  $2p$ . In the atom, for the same contribution to core polarization, the energy  $\Delta$  would be absent. All this indicates that the oxygen core polarization in high- $T_c$  superconductors is, if anything, smaller than in the atom. Because the atomic core polarization is already small, we feel it justified (as has been done extensively in the literature) to neglect  $K_{\text{core polarization, iso}}$  completely in the solid.

### B. The anisotropic part of the hyperfine field

Now we come to  $K_{\text{spin aniso}}$ . The biggest contribution to this term originates naturally from the O  $2p\sigma$  orbitals themselves. The fractional hole occupancy (per copper) of the O  $2p\sigma$  orbitals that can be deduced from XPS data is

$$\begin{aligned} f_{\text{O } 2p\sigma} = & \frac{t_{\text{Cu } 3d/\text{O } 2p\sigma}^2}{(E_{|\text{Cu } 3d^9 \text{O } 2p\sigma^6\rangle} - E_{|\text{Cu } 3d^{10} \text{O } 2p\sigma^5\rangle})^2} \\ \simeq & 8\% , \end{aligned} \quad (55)$$

which is, this time, in very good agreement with NMR estimations.<sup>36</sup>

The next contribution to  $K_{\text{spin aniso}}$  originates from the term  $|\text{Cu } 3d^9 \text{ O } 2p\sigma^2\rangle$  itself, via long-range dipolar interactions and also via the nonorthogonality of Cu  $3d$  with O  $2p\sigma$ . It has been quite roughly estimated that<sup>36</sup>

$$K_{\text{spin aniso}}(\text{Cu } 3d) \approx \frac{1}{5} K_{\text{spin aniso}}(\text{O } 2p\sigma). \quad (56)$$

The orthogonality problem between Cu  $3d$  and O  $2p$ , which was not considered in Ref. 36, makes the contribution  $|\text{Cu } 3d^9 \text{ O } 2p\sigma^2\rangle$  even bigger. *A priori*, it is thus not possible to neglect the  $|\text{Cu } 3d^9 \text{ O } 2p\sigma^2\rangle$  term, although this approximation is often done in practice for simplicity. We make the same approximation in the next section. There are other contributions to  $K_{\text{spin aniso}}$  which we also want to discuss.

(i) Because of the canting of the Cu-O-Cu bonds, the O  $2p\pi$  orbitals which point out of the  $\text{CuO}_2$  planes are slightly occupied. The Cu-O-Cu angle is such, however, that this contribution is completely negligible.

(ii) The in-plane O  $2p\pi$  orbitals are also slightly occupied, due to O  $2p\sigma$ -O  $2p\pi$  transfer (Fig. 10). In the insulating phase, we can estimate the ratio

$$\frac{f_{\text{O } 2p\pi}}{f_{\text{O } 2p\sigma}} = \frac{2t_{pp\perp}^2}{\Delta^2}, \quad (57)$$

which gives

$$\frac{f_{\text{O } 2p\pi}}{f_{\text{O } 2p\sigma}} \approx \frac{2 \times 0.35^2}{3.5^2} \approx 0.02. \quad (58)$$

The corresponding contribution to the oxygen Knight shift is thus, again, quite negligible. Actually, this fractional occupancy of O  $2p\pi$  orbitals is also responsible for a positive contribution to the  $^{89}\text{Y}$  Knight shift in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . The fact that the experimental value is negative confirms our opinion that the fractional occupancy of O  $2p\pi$  in-plane orbitals is very small, at least in undoped compounds.<sup>37</sup>

(iii) Another mechanism which contributes to  $K_{\text{spin aniso}}$  on the oxygen is the spin-orbit coupling on copper (the spin-orbit coupling on oxygen is negligible in this case).

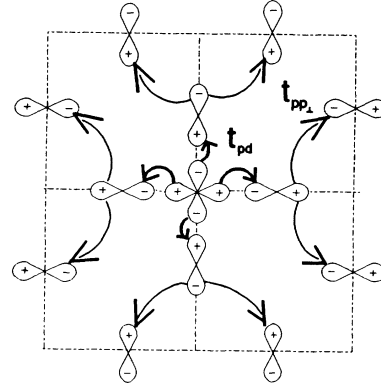


FIG. 10. Hole occupation of O  $2p\pi$  orbitals in the insulator.

The spin-orbit contribution to the hyperfine coupling on copper itself is already known,<sup>38</sup> but the corresponding contribution on the ligand seems never to have been studied. Just as for the copper hyperfine field, all the optically forbidden  $d-d$  transition states contribute. Unfortunately, the expected precision of the calculation in the case of oxygen is very low because we have to know the copper-oxygen covalency in the ground state, as well as in all the excited states of  $xy$ ,  $xz$ , and  $yz$  symmetry (for each symmetry, there are two relevant excited states, one mainly based on copper, and one mainly on oxygen; these states are conveniently calculated on a  $\text{CuO}_4$  cluster<sup>1</sup>). Because of the low covalency in the excited states, the precision of the calculation is also low (in the case of copper, in contrast, it is a good approximation to suppose that the covalency of all excited  $xy$ ,  $xz$ , and  $yz$  states is simply zero). We have decided to neglect the effect of the excited states which are based essentially on oxygen in the following formulas (this approximation leads to an overestimate of the exact result of about 20%). Both the orbital and dipolar hyperfine coupling on oxygen combine with the copper spin-orbit coupling, just as in the case of copper.<sup>38</sup> The result for oxygen is

$$K_{\text{spin orbit}}^{\parallel} = -\lambda\gamma_e \hbar\alpha_{x^2-y^2} \beta_{x^2-y^2} \left[ \frac{12\alpha_{xy}\beta_{xy}}{5E_{xy}} + \frac{6\alpha_{xz}\beta_{xz}}{5E_{xz}} \right] \left\langle \frac{1}{r^3} \right\rangle_{\text{dip}}, \quad (59)$$

$$K_{\text{spin orbit}}^{\perp} = -\frac{2\lambda\gamma_e \hbar\alpha_{x^2-y^2} \beta_{x^2-y^2} \alpha_{xz} \beta_{xz}}{E_{xz}} \left\langle \frac{1}{r^3} \right\rangle_{\text{orb}} - \frac{8\lambda\gamma_e \hbar\alpha_{x^2-y^2} \beta_{x^2-y^2} \alpha_{xy} \beta_{xy}}{5E_{xy}} \left\langle \frac{1}{r^3} \right\rangle_{\text{dip}}, \quad (60)$$

$$K_{\text{spin orbit}}^c = -\frac{4\lambda\gamma_e \hbar\alpha_{x^2-y^2} \beta_{x^2-y^2} \alpha_{xz} \beta_{xz}}{E_{xz}} \left\langle \frac{1}{r^3} \right\rangle_{\text{orb}} - \frac{4\lambda\gamma_e \hbar\alpha_{x^2-y^2} \beta_{x^2-y^2} \alpha_{xz} \beta_{xz}}{5E_{xz}} \left\langle \frac{1}{r^3} \right\rangle_{\text{dip}}. \quad (61)$$

The convention for the directions of  $K^{\parallel}$ ,  $K^{\perp}$ , and  $K^c$  is the one which is usually found in the literature.<sup>9</sup> An interesting effect of the copper-oxygen covalency is that it acts as a "gear": when the copper  $3d$  orbital turns clock-

wise (from  $x^2-y^2$  to  $xy$ , for instance), the oxygen  $2p$  orbital turns anticlockwise (from  $2p\sigma$  to  $2p\pi$ ), as illustrated in Fig. 11. This is why the spin-orbit contributions to the copper and oxygen hyperfine fields possess opposite signs.

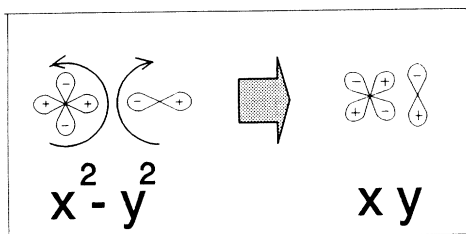


FIG. 11. Effect of the combined rotation of copper and oxygen orbitals.

In order to obtain numerical values, we use some simplified covalency estimates derived from Ref. 1 (cf. Fig. 12). Taking  $\langle 1/r^3 \rangle_{\text{orb}} = \langle 1/r^3 \rangle_{\text{dip}}$ ,  $\lambda = 0.1$  eV, and  $E_{xy} = E_{xz} = 1.3$  eV, we are able to compare the well-known O  $2p\sigma$  dipolar contribution with the spin-orbit contribution, and we get

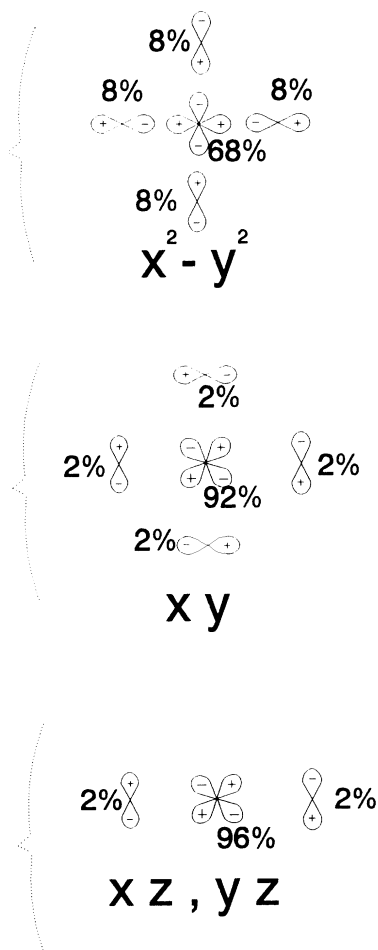


FIG. 12. Covalency estimates for one hole in a  $\text{CuO}_4$  cluster: lowest energy states of  $x^2-y^2$ ,  $xy$ ,  $xz$ , and  $yz$  symmetry. In the notations of Eqs. (59)–(61), we have  $\alpha_{x^2-y^2} = \sqrt{0.68}$ ,  $\beta_{x^2-y^2} = \sqrt{0.08}$ ,  $\alpha_{xy} = \sqrt{0.92}$ ,  $\beta_{xy} = \sqrt{0.02}$ ,  $\alpha_{xz} = \alpha_{yz} = \sqrt{0.96}$ , and  $\beta_{xz} = \beta_{yz} = \sqrt{0.02}$ .

$$\begin{pmatrix} A_{\parallel} \\ A_{\perp} \\ A_c \end{pmatrix} \propto \begin{pmatrix} 2 \\ -1 \\ -1 \end{pmatrix} + \begin{pmatrix} -0.18 \\ -0.18 \\ -0.24 \end{pmatrix}. \quad (62)$$

The first term in Eq. (62) is the O  $2p\sigma$  dipolar contribution, and the second term is the spin-orbit contribution (which is actually more isotropic than anisotropic).

(iv) Another contribution to  $K_{\text{spin aniso}}$  comes from the polarization of O  $2p\pi$  orbitals by O  $2p\sigma$  orbitals. Such an anisotropic core polarization mechanism is known to be important in atomic quantum chemistry<sup>39</sup> generally. It is indeed responsible for the negative Knight shift of  $^{89}\text{Y}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . Such core polarization preserves the axial symmetry around the Cu-O-Cu axis in first order. Anisotropy due to neighboring  $\text{Y}^{3+}$  and  $\text{Ba}^{2+}$  atoms appears on a higher level of perturbation only. The anisotropic core polarization, therefore, only acts to reduce the contribution of O  $2p\pi$  orbitals to  $K_{\text{spin aniso}}$ , thus lowering the effective value of  $\langle 1/r^3 \rangle_{\text{dip}}$ . Such an effect is already present in atomic oxygen.

(v) The last contribution in  $K_{\text{spin aniso}}$  is due to the transfer of electrons from Cu  $3d$  to oxygen  $3d$  orbitals (and other anisotropic orbitals of higher energies). This contribution was suggested to induce some anisotropy perpendicular to the Cu-O axis in a Tutton salt,<sup>31</sup> due to the presence of hydrogen orbitals close to the oxygen. It seems to us rather improbable that the unoccupied oxygen orbitals provide the correct order of magnitude for such an effect. The contribution of O  $3d$  orbitals, for instance, is small, and it preserves mainly the Cu-O-Cu axial symmetry. We would rather attribute the anisotropy of  $K_{\text{spin}}$  perpendicularly to the Cu-O axis to the copper spin-orbit coupling only, as was shown in Eqs. (60) and (61). This is an interesting remark, because it could help us to believe that the anisotropy of  $K_{\text{spin}}$  measured in Ref. 31 and that of high- $T_c$  superconductors are very close to each other. This would be quite valuable for the interpretation of experimental data.

Except for the (quite small) correction due to the copper spin-orbit coupling, a correct approximation to  $K_{\text{spin}}$  in the insulating phase should thus be

$$\begin{pmatrix} K_{\parallel} \\ K_{\perp} \\ K_c \end{pmatrix} = \begin{pmatrix} a + 2b \\ a - b \\ 1.2(a - b) \end{pmatrix}, \quad (63)$$

and for the anisotropy of  $1/T_1$  on oxygen

$$\begin{pmatrix} \frac{1}{T_{\parallel}} \\ \frac{1}{T_{\perp}} \\ \frac{1}{T_c} \end{pmatrix} \propto \begin{pmatrix} 2(a-b)^2 \\ (1+2b)^2 + (a-b)^2 \\ (a+2b)^2 + (a-b)^2 \end{pmatrix}, \quad (64)$$

where  $a$  and  $b$  correspond, respectively, to the contact and dipolar interactions. The precise values for  $a$  and  $b$  are provided by experiment.<sup>31</sup> The factor 1.2 (1.15 might

be better) which has been introduced in  $K_c$  reflects the anisotropy of the  $g$  factor, for which a reasonable (but not exact) approximation should be

$$(g_a, g_b, g_c) \simeq (2, 2, 2.4). \quad (65)$$

It is not possible to know  $g$  exactly unless it is measured by EPR, or as long as optically forbidden  $d-d$  transitions remain undetected.

The anisotropy of  $g$  does not play a role in the  $1/T_1$  anisotropy. The  $a$  and  $b$  terms are included coherently in Eq. (64), in contrast with what one of the authors presented earlier.<sup>40</sup> The coherence effects in the doped phase are considered in the next section.  $K_{\text{orb}}$  should necessarily account for the rest of the observed NMR shift on oxygen, which puts a strong constraint upon its anisotropy perpendicular to the Cu-O-Cu axis.  $K_{\text{orb}}$  is partly due to the Van Vleck susceptibility of copper holes, and partly to the Van Vleck susceptibility of  $\text{La}^{3+}$ ,  $\text{Y}^{3+}$ , or  $\text{Ba}^{2+}$  holes. We will not discuss  $K_{\text{orb}}$  quantitatively in this paper.

## V. THE OXYGEN SPIN PROBLEM

In the original paper of Zhang and Rice,<sup>3</sup> Zhang-Rice singlets were considered as true singlets. Emery and Reiter<sup>8</sup> have shown, however, that true quasiparticles do possess a spin. The essence of Emery and Reiter's argument can be understood easily by considering a simple  $\text{Cu}_2\text{O}$  molecule with three holes, one of which has spin up. Neglecting normalization, the ground state is a "bonding" superposition of two Zhang-Rice singlets based on each copper atom:

$$\begin{aligned} |g.s.\rangle &\simeq (\text{Cu}\downarrow\text{O}\uparrow - \text{Cu}\uparrow\text{O}\downarrow)\text{Cu}\downarrow - \text{Cu}\downarrow(\text{O}\downarrow\text{Cu}\uparrow - \text{O}\uparrow\text{Cu}\downarrow) \\ &= 2(\text{Cu}\downarrow\text{O}\uparrow\text{Cu}\downarrow) - (\text{Cu}\uparrow\text{O}\downarrow\text{Cu}\downarrow) - (\text{Cu}\downarrow\text{O}\downarrow\text{Cu}\uparrow). \end{aligned} \quad (66)$$

Because of coherence,  $|g.s.\rangle$  has an oxygen spin of  $\frac{1}{3}$  (using the same definition of spin as Emery and Reiter). The first excited state is the "antibonding" combination of the same Zhang-Rice singlets:

$$\begin{aligned} |1\rangle &\simeq (\text{Cu}\downarrow\text{O}\uparrow - \text{Cu}\uparrow\text{O}\downarrow)\text{Cu}\downarrow + \text{Cu}\downarrow(\text{O}\downarrow\text{Cu}\uparrow - \text{O}\uparrow\text{Cu}\downarrow) \\ &= -(\text{Cu}\uparrow\text{O}\downarrow\text{Cu}\downarrow) + (\text{Cu}\downarrow\text{O}\downarrow\text{Cu}\uparrow). \end{aligned} \quad (67)$$

Only the down spin appears on the oxygen in the excited state, which thus has an oxygen spin of 1. The presence of a spin on oxygen shows that Zhang-Rice triplets, which were originally projected out by Zhang and Rice, are in fact significantly occupied. Indeed, a Zhang-Rice singlet can always hop to a nearest-neighbor copper spin by forming a triplet, and it can do so in two ways by choosing among the three triplet states with  $m = -1, 0$ , or  $+1$  (moreover, triplet states of  $x^2 - y^2$  are not the only ones to contribute;  $x^2 + y^2$ , i.e.,  $a_1$  in  $D_{4h}$  symmetry, also intervenes). The hopping matrix between a singlet and a triplet is some fraction of  $t_{pd}^2/\Delta$ , whereas the smallest difference in energy between a singlet and a triplet is about

$$(6t_{pd}^2/\Delta + 2t_{pd}^2/(U_p + \Delta) + 8t_{pd}^2/(U_d - \Delta)).$$

The occupancy ratio between singlet and triplet states thus appears to be independent of  $t_{pd}$  and  $\Delta$  in first order (which suggests the breakdown of a perturbation approach).

The exact result of Emery and Reiter indeed confirms that, for a ferromagnetic lattice, the occupancy of triplet states is independent of the ratio  $t_{pd}/\Delta$ . The fact that the spin on oxygen is one-third in the ground state of the Emery and Reiter model<sup>8</sup> (just as in our  $\text{Cu}_2\text{O}$  molecule) is perhaps acceptable. The fact that the spin on oxygen is equal to 1 at the top of the band<sup>8</sup> (again, just as in our  $\text{Cu}_2\text{O}$  molecule) is more problematic. It is legitimate to question the validity of the  $t-t'-J-R$  model at high doping. The question is to know at what doping triplet states really start to become important. Are high- $T_c$  superconductors highly doped materials in that respect? We do not know the answer to this question for the moment. Encouraged by the fact that hyperfine couplings are very little sensitive to doping in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ,<sup>11</sup> we may speculate that the dynamics of triplet states are not crucial in high- $T_c$  superconductors, i.e., up to the dopings for which  $T_c$  is at its maximum.

However, whatever the doping, Zhang-Rice triplets introduce a new spin degree of freedom in the Hamiltonian, as was correctly pointed out by Emery and Reiter.<sup>8</sup> The example of the simple  $\text{Cu}_2\text{O}$  molecule suggests that a convenient way of exhibiting the spin on oxygen is just to superpose nonorthogonal,  $\text{CuO}_4$ -based Zhang-Rice singlets. This avoids the difficulty of describing rigorously Zhang-Rice triplets (which are numerous). Such a crucial assumption is nontrivial, and its validity depends upon doping. Notwithstanding, we shall omit any further rigorous examination of it. Even if approximate, our approach provides much insight concerning spin dynamics.

We first consider briefly the antiferromagnetic dynamics of copper spins. If we suppose that the  $\text{CuO}_4$ -based Zhang-Rice singlets are completely localized in the lattice, the only dynamics come from the spins of singly occupied sites, just as in a randomly frustrated antiferromagnet. For 15% hole doping, around 30% of the oxygen atoms are situated between a Zhang-Rice singlet and a copper spin. For these oxygen sites, the so-called magnetic form factor does not filter the antiferromagnetic fluctuations at all. Thus all the formal justifications that have been given in the literature for this oxygen form factor are questionable. The huge difference between copper and oxygen NMR relaxation rates which is observed experimentally can only be understood if the holes are mobile, thus motionally destroying the local fields of antiferromagnetic spin waves on oxygen (which is nearly paradoxical because the motion of the holes destroys the antiferromagnetic spin ordering).

Let us now consider the properties of added spins. It is relatively easy to see that, within a first approximation, a single hole in a nearly antiferromagnetic lattice possesses  $\frac{1}{6}$  of an up spin on half of the oxygen sites, and  $\frac{1}{6}$  of a down spin on the other oxygen sites (if  $t \gg J$  in the  $t-J$  model). Contrary to what happens in the ferromagnetic

case, the average polarization on oxygen is nearly zero. This might well explain why  $^{89}\text{Y}$  NMR hyperfine fields remain nearly constant as a function of doping in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ .

What about dynamic response functions? Let us still suppose that we have a nearly antiferromagnetic spin background. The initial state is represented in Fig. 13(a). The doped hole has spin up. If we apply a lowering spin operator on the doped hole, we obtain the state represented in Fig. 13(b). In the Zhang and Rice Wannier-states philosophy, the new state is a triplet, the energy of which is high. No interesting low-energy-scale spin fluctuations appear. In the nonorthogonal-singlets picture, on the contrary, the new down spin is nonorthogonal to neighboring nonorthogonal singlets. This final state is a rather extended object, so that we have to be careful about the dispersion of the singlets. Angle-resolved photoemission studies tell us that Fermi level states can be found in the neighborhood of the four diagonals  $[\pi-x, x]$ ,  $[-x, \pi-x]$ ,  $[-x, -\pi+x]$ , and  $[\pi-x, -x]$  in the reciprocal.<sup>29</sup> The overlap of our final state with Fermi level states is thus zero. Had we taken the dispersion of the initial hole into account, the result would still be zero.

Following the same lines of reasoning, we could modify

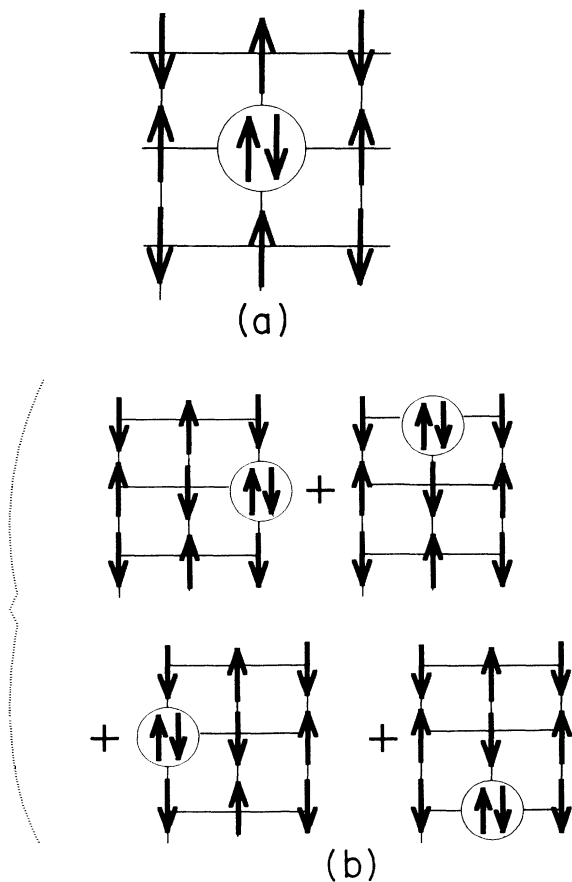


FIG. 13. (a) Initial state: a Zhang-Rice singlet (non-Wannier-like) in an antiferromagnetic background. (b) Final state: after a lowering spin operator is applied on the spin of the doped hole.

our response function to discuss the observability of such fluctuations by neutron scattering experiments. In this paper, we choose to concentrate on oxygen NMR experiments, since it has already been suggested that such fluctuations might be of importance to understand some of the data.<sup>9</sup> In the original paper of Barriquand, Odier, and Jerome,<sup>9</sup> doped holes were assumed to be located in O  $2p\sigma$  orbitals only, and the occupation of O  $2s$  orbitals by doped holes was neglected, so that the hyperfine coupling of doped holes on oxygen was purely dipolar. This is, however, incorrect. In the insulator,  $K_{\text{iso}}$  is bigger than  $K_{\text{aniso}}$ , so that for doped holes the isotropic and anisotropic contributions to the hyperfine field are comparable. Let us consider a Zhang-Rice singlet, whose wave function is known to be approximately<sup>1</sup>

$$|\text{ZR}\rangle = \frac{1}{\sqrt{2}} \left( \sqrt{0.7} (\text{Cu}\uparrow L\downarrow - \text{Cu}\downarrow L\uparrow) + \sqrt{0.1} (\text{Cu}\uparrow \text{Cu}\downarrow) + \sqrt{0.2} (L\uparrow L\downarrow) \right), \quad (68)$$

which can be drastically simplified into

$$|\text{ZR}\rangle \simeq \frac{1}{\sqrt{2}} (\text{Cu}\uparrow L\downarrow - \text{Cu}\downarrow L\uparrow). \quad (69)$$

According to our discussion in Sec. IV A, the nonorthogonality of Cu  $3d$  and O  $2s$  orbitals is possibly responsible for the main part of  $K_{\text{iso}}$  in the insulator. The same process might thus also account for the main part of the isotropic coupling between a Zhang-Rice singlet and the  $^{17}\text{O}$  nucleus. NMR is a clumsy tool to discriminate between transfer and orthogonality contributions, however, so that we find it most convenient to suppose that only the transfer contribution exists in the rest of our discussion. Including O  $2s$  orbitals in the simplified Zhang-Rice wave function of Eq. (65) then gives

$$|\text{ZR}\rangle \simeq \frac{1}{\sqrt{2}} (\text{Cu}\uparrow L_{O\ 2p}\downarrow - \text{Cu}\downarrow L_{O\ 2p}\uparrow) + \left[ \frac{f_{O\ 2s}}{2} \right]^{1/2} (L_{O\ 2s}\uparrow L_{O\ 2p}\downarrow - L_{O\ 2s}\downarrow L_{O\ 2p}\uparrow). \quad (70)$$

The functions  $|L_{O\ 2s}\rangle$  and  $|L_{O\ 2p}\rangle$  are represented in

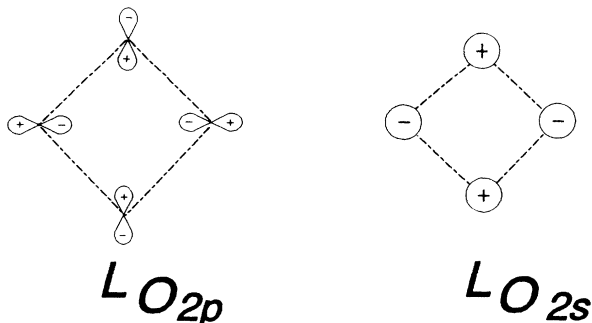


FIG. 14. Ligand wave functions  $L_{O\ 2p}$  and  $L_{O\ 2s}$ .



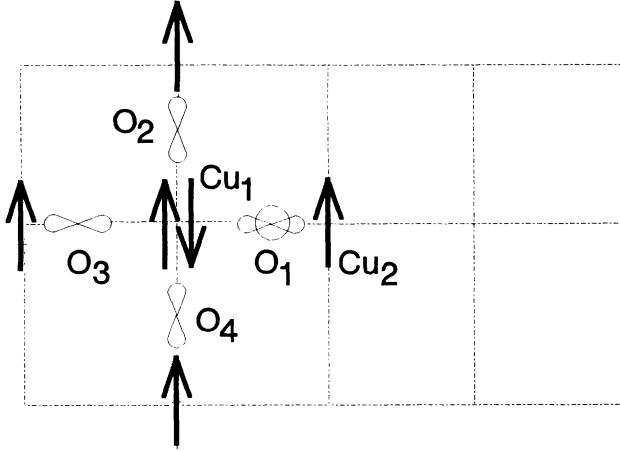


FIG. 15. Initial state: a Zhang-Rice singlet (non-Wannier-like) in an antiferromagnetic background. In contrast with Fig. 13(a), the spin lowering operator acts only “locally” on the O 2p and O 2s orbitals of oxygen 1.

$$\begin{aligned}
 |g.s.\rangle = & -\frac{1}{\sqrt{8}}(Cu_1\downarrow O_{1\ 2p}\uparrow Cu_2\uparrow) \\
 & +(\sqrt{f_{O\ 2s}}O_{1\ 2s}\uparrow + \sqrt{f_{O\ 2p}}O_{1\ 2p}\uparrow) \left[ \frac{1}{\sqrt{8}}(O_{1\ 2p}\downarrow - O_{2\ 2p}\downarrow + O_{3\ 2p}\downarrow - O_{4\ 2p}\downarrow) \right] Cu_2\uparrow \\
 & - \left[ \frac{f_{O\ 2s}}{8} \right]^{1/2} (Cu_1\downarrow O_{1\ 2p}\uparrow O_{1\ 2s}\uparrow). \tag{71}
 \end{aligned}$$

Again, the final state is an extended object, so that we have to be careful about the dispersion of Zhang-Rice singlets. Assuming that Fermi level states can be found in the neighborhood of the four diagonals  $(\pi-x, x)$ ,  $(-x, \pi-x)$ ,  $(-x, -\pi+x)$ , and  $(\pi-x, -x)$  of the reciprocal space, only the first and the last (third) terms of Eq. (71) contribute to the overlap of the final state with Fermi level states.

The relevant part of the final state is thus

$$\begin{aligned}
 |F\rangle = & -\frac{A_p}{\sqrt{8}}(Cu_1\downarrow O_{1\ 2p}\downarrow Cu_2\uparrow) \\
 & - A_{2s} \frac{\sqrt{f_{O\ 2s}}}{\sqrt{8}}(Cu_1\downarrow O_{1\ 2p}\uparrow O_{1\ 2s}\downarrow). \tag{72}
 \end{aligned}$$

Coming back to our notation of Sec. IV (Eq. 64), we now find

$$\begin{aligned}
 \begin{pmatrix} \frac{1}{T_{\parallel}} \\ \frac{1}{T_{\perp}^1} \\ \frac{1}{T_{\perp}^c} \end{pmatrix} \propto & \begin{pmatrix} 2(af_{O\ 2p} + b)^2 \\ (af_{O\ 2p} - 2b)^2 + (af_{O\ 2p} + b)^2 \\ (af_{O\ 2p} - 2b)^2 + (af_{O\ 2p} + b)^2 \end{pmatrix}. \tag{73}
 \end{aligned}$$

Fig. 14. In Eq. (70), the probability that a copper hole hops into the O 2s orbital does not depend on the hole occupation of the O 2p orbital. The parameter  $f_{O\ 2s}$  is the same as considered in Sec. IV for the insulator ( $f_{O\ 2s} \simeq 1.5\%$ ). This is not a bad approximation as long as the on-site Coulomb repulsion  $U_{O\ 2s/O\ 2p}$  between a hole in O 2s and a hole in O 2p (which we guess is of order  $U_{O\ 2s/O\ 2p} \simeq 10$  eV) is smaller than the energy difference between Cu 3d and O 2p orbitals (which is of order 20 eV). Even if  $U_{O\ 2s/O\ 2p}$  is big, the correlated transfer from Cu 3d to O 2s due to a hole in O 2p acts in the opposite way to  $U_{O\ 2s/O\ 2p}$ , so that it is difficult to decide which process dominates the modification of the O 2s hole occupancy with respect to the insulator.

If we now want to apply the operator  $(A_{2s}S_{O\ 2s}^- + A_{2p}S_{O\ 2p}^-)$  on the oxygen 1 represented in Fig. 15, the part of the initial wave function which is interesting possesses at least one up spin on oxygen 1, and can be decomposed into

The signs in Eq. (73) come from the correlated nature of Zhang-Rice singlets. Taking  $f_{O\ 2p} = 0.08$ ,  $a/b = 5.4$ , we get

$$\begin{pmatrix} \frac{1}{T_{\parallel}} \\ \frac{1}{T_{\perp}^1} \\ \frac{1}{T_{\perp}^c} \end{pmatrix} \approx \begin{pmatrix} 1 \\ 1.1 \\ 1.1 \end{pmatrix}. \tag{74}$$

There exist many possible reasons which would make the numerical result of Eq. (74) imprecise. The point is that the anisotropy is completely different (and more isotropic) than in the insulator.

It is tempting to interpret the experimental data of  $^{17}O$  NMR within our framework. Because of the strange anisotropy measured for the  $1/T_1$  of  $YBa_2Cu_3O_{6.5}$  (Refs. 9,10) [and not  $YBa_2Cu_3O_{7.0}$  (Ref. 10)], the spin fluctuations of doped holes seem to become significant in  $YBa_2Cu_3O_{6.5}$  at temperatures not too far from  $T_c$  (our interpretation is thus reversed if compared with that of Ref. 9). This strange behavior as a function of doping and temperature is not well understood at present.

An intuitive way of looking at these spin fluctuations is the following. Supposing that we want to introduce a

hole in a Néel-ordered spin lattice, we have to choose whether this hole possesses up spin or down spin. If the spin is up, it will bind with a down spin to form a Zhang-Rice singlet, and vice versa. When we add more holes, we still have to choose their spin. Obviously, it is preferable for the system to have the same number of up and down spins (at least if some symmetry is not broken), because up spins have to share the same phase space, and down spins occupy another phase space. It is then natural to associate a response function with the spin fluctuations between the two phase spaces. This is more or less what we have done for the oxygen relaxation rate.

*A priori*, there seems to be a way of extracting this oxygen NMR response function from the  $t$ - $t'$ - $J$ - $R$  model: by moving a Zhang-Rice singlet from one site to the other, while reversing the spin which moves in the other direction (Fig. 16). It might appear surprising that the  $t$ - $t'$ - $J$ - $R$  model can simulate the fluctuations of a spin degree of freedom which is supposed not to exist. It is suggestive to remember that, within an antiferromagnetic lattice, a Zhang-Rice singlet hops coherently from one site to all second neighbors only (and not to first-nearest-neighbor sites); this is reminiscent of the existence of the two phase spaces for up and down spins that we have considered above.

One might wonder if the  $^{89}\text{Y}$  NMR in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  would allow one to observe the hole spin fluctuations as well as the oxygen NMR does. The coherent core polarization  $\text{O } 2p\sigma - \text{O } 2p\pi$  of all the oxygen orbitals of one plane which are situated in the neighborhood of an  $^{89}\text{Y}$  nucleus makes the contribution of doped hole spins to the  $^{89}\text{Y}$   $1/T_1$  four times smaller than what would be guessed by comparing the hyperfine fields of  $^{89}\text{Y}$  and  $^{17}\text{O}$  in the insulator. Just for the same reason, if the spins of doped holes contributed to the  $^{17}\text{O}$  and  $^{89}\text{Y}$  Knight shifts, which they do not seem to do, their contribution to the  $^{89}\text{Y}$  Knight shift would be twice as small than expected from their contribution to the  $^{17}\text{O}$  Knight shift. This all comes from the difference between the core polarization of two  $\text{O } 2p\pi$  orbitals in the insulator, and the core polarization of four  $\text{O } 2p\pi$  orbitals by doped holes. For  $^{89}\text{Y}$ , the coupling between planes makes the situation possibly even more complex, which goes outside the scope of our article.

Our last remark concerns the apical oxygens in  $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$ . The relaxation rate of these sites is surprisingly much smaller than the relaxation rate of the chain oxygen sites. The Zhang-Rice singlets in the chains (which are formed with chain and apical oxygen sites) do



delocalization + spin - flip

FIG. 16. The response function of the  $t$ - $t'$ - $J$ - $R$  model that may account for the spin dynamics of doped holes is a combination of (effective) charge transfer and spin flip.

not encounter any orthogonality problem on the apical oxygen sites, in contrast with what happens with the chain sites. Should that not explain the experimental result? The real picture is probably more complex, because the doping of the chains in  $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$  is about 70% (which is indeed quite high), and we do not know what happens to the remaining 30% copper sites, except that there is no filtering form factor on the corresponding apical sites. The chains in  $\text{YBa}_2\text{Cu}_3\text{O}_{7.0}$  are certainly highly correlated.

## VI. CONCLUSIONS

Our study of superexchange in Sec. II has clarified the role of some of the quantum chemical parameters involved. It approaches the limit of what can be obtained from a purely analytical analysis, although a much more detailed understanding of spin waves (including spin gaps) can be expected for the future.

The study of the doped phase is much more open. One of the conclusions that we draw in Sec. III, namely, that the repulsion between nearest-neighbor Zhang-Rice singlets is a very important process, should receive strong consideration, especially as it leads us to speculate on the existence of liquid-crystal-like (Wigner) correlations between Zhang-Rice singlets. It is a common opinion that some kind of interplanar coupling is essential to superconductivity in the high- $T_c$  cuprates. So far, three such interplanar mechanisms have been proposed; namely, a phonon-assisted coupling, a Coulombic coupling between quasi-phase-separated droplets,<sup>30</sup> and the Josephson delocalization process of Anderson.<sup>41</sup>

It seems that our liquid-crystal correlations give rise to a fourth alternative. Such a scenario is in some ways similar and in some ways completely opposite to the phase-separation picture.

From the study of the oxygen hyperfine coupling, we have clarified the impact of some nonorthogonality contributions within a highly correlated formalism and the effect of the copper spin-orbit coupling on the oxygen hyperfine field.

The study of spin fluctuations in the doped phase remains also a quite open subject. The biggest spin fluctuations are essentially antiferromagnetic, as can be seen from neutron scattering or copper NMR data, but even the behavior of such antiferromagnetic fluctuations is not well understood. We have concentrated in this paper on a different issue, which is the NMR on oxygen, and the anisotropy thereof. It is clear that none of our results could be obtained in a noncorrelated electronic picture (i.e., without some understanding of what a Zhang-Rice singlet represents). One of the simplest questions, which is why the oxygen and copper NMR relaxation rates are so different, remains unanswered however.

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- <sup>1</sup>H. Eskes and G. A. Sawatzky, in *Electronic Properties of High- $T_c$  Superconductors and Related Compounds*, edited by H. Kuzmany, M. Mehring, and J. Fink, Springer Series in Solid State Sciences Vol. 99 (Springer-Verlag, Berlin, 1990), p. 127.
- <sup>2</sup>J. Zaanen, G. A. Sawatzky, and J. W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985).
- <sup>3</sup>F. C. Zhang and T. M. Rice, *Phys. Rev. B* **37**, 3759 (1988).
- <sup>4</sup>H. Eskes and G. A. Sawatzky, *Phys. Rev. B* **43**, 119 (1991).
- <sup>5</sup>J. Akimitsu and Y. Ito [*J. Phys. Soc. Jpn.* **40**, 1621 (1976), Fig. 6] show that, already for the (0,0,2) peak, the reduction in the form factor to covalency is significant. The experimental data in high- $T_c$  compounds should be divided by approximately 0.94 [which is the value plotted in Fig. 6 of this reference for a wavelength close to (0,0,2) without covalency] instead of 0.84 (which corresponds to the same value with covalency included). Otherwise, the reduction due to covalency is more or less counted twice. It is also interesting to note that the antiferromagnetic cancellation on oxygen is no longer perfect when oxygen  $s$  orbitals are considered together with O  $2p\sigma$  because of a kind of  $s$ - $p$  hybridization.
- <sup>6</sup>P. W. Anderson, *Phys. Rev.* **79**, 705 (1950).
- <sup>7</sup>J. H. Jefferson, H. Eskes, and L. F. Feiner, *Phys. Rev. B* **45**, 7959 (1992).
- <sup>8</sup>V. J. Emery and G. Reiter, *Phys. Rev. B* **38**, 11 938 (1988).
- <sup>9</sup>F. Barriquand, P. Odier, and D. Jerome, *Physica C* **177**, 230 (1991).
- <sup>10</sup>M. Horvatic, T. Auler, C. Berthier, P. Butaud, W. G. Clark, J. A. Gillet, and P. Segransan, *Phys. Rev. B* **47**, 3461 (1993).
- <sup>11</sup>H. Alloul, A. Mahajan, H. Casalta, and O. Klein, *Phys. Rev. Lett.* **70**, 1171 (1993).
- <sup>12</sup>H. Eskes and J. H. Jefferson, *Phys. Rev. B* **48**, 9788 (1993).
- <sup>13</sup>E. B. Stechel and D. R. Jennison, *Phys. Rev. B* **38**, 4632 (1988).
- <sup>14</sup>W. Geertsma, *Physica B* **164**, 241 (1990).
- <sup>15</sup>H. Eskes, Ph.D. thesis, University of Groningen, 1992.
- <sup>16</sup>J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G. A. Sawatzky, and M. T. Czyżyk, *Phys. Rev. B* **38**, 11 322 (1988).
- <sup>17</sup>A. K. McMahan, J. F. Annett, and R. M. Martin, *Phys. Rev. B* **42**, 6268 (1990).
- <sup>18</sup>F. Marsiglio and J. E. Hirsch, *Phys. Rev. B* **41**, 6435 (1990); J. E. Hirsch, *ibid.* **47**, 5351 (1993).
- <sup>19</sup>J. Zaanen, C. Westra, and G. A. Sawatzky, *Phys. Rev. B* **33**, 8060 (1986).
- <sup>20</sup>S. M. Hayden, G. Aeppli, R. Osborn, A. D. Taylor, T. G. Per-ring, S-W. Cheong, and Z. Fisk, *Phys. Rev. Lett.* **67**, 3622 (1991).
- <sup>21</sup>H. J. Zeiger and G. W. Pratt, *Magnetic Interactions in Solids* (Clarendon, Oxford, 1973), Table 3.4.
- <sup>22</sup>J. Rossat Mignod, L. P. Regnault, C. Vettier, P. Bourges, P. Burllet, J. Bossy, J. Y. Henry, and G. Lapertot, *Physica B* **180**, 383 (1992).
- <sup>23</sup>C. J. Peters, R. J. Birgeneau, M. A. Kastner, H. Yoshizawa, Y. Endoh, J. Tranquada, G. Shirane, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, *Phys. Rev. B* **37**, 9761 (1988).
- <sup>24</sup>N. E. Bonesteel, *Phys. Rev. B* **47**, 11 302 (1993).
- <sup>25</sup>C. D. Batista and A. A. Aligia, *Phys. Rev. B* **47**, 8929 (1993).
- <sup>26</sup>D. Poilblanc, H. J. Schulz, and T. Ziman, *Phys. Rev. B* **47**, 3268 (1993).
- <sup>27</sup>J. Rossat Mignod *et al.* (unpublished).
- <sup>28</sup>B. Keimer, N. Belk, R. Birgeneau, A. Cassanho, C. Y. Chen, M. Greven, M. A. Kastner, A. Aharony, Y. Endoh, R. W. Erwin, and G. Shirane, *Phys. Rev. B* **46**, 14 034 (1992).
- <sup>29</sup>Z. X. Shen, D. S. Dessau, B. O. Wells, D. M. King, W. E. Spicer, A. J. Arko, D. Marshall, L. W. Lombardo, A. Kapitlnik, P. Dickinson, S. Doniach, J. DiCarlo, A. G. Loeser, and C. H. Park, *Phys. Rev. Lett.* **70**, 1553 (1993).
- <sup>30</sup>V. J. Emery and S. A. Kivelson, *Physica C* **209**, 597 (1993).
- <sup>31</sup>D. Getz and B. Silver, *J. Chem. Phys.* **61**, 630 (1974).
- <sup>32</sup>S. Hufner and G. K. Wertheim, *Phys. Rev. B* **8**, 4857 (1973).
- <sup>33</sup>J. R. Morton and K. F. Preston, *J. Magn. Reson.* **30**, 517 (1978).
- <sup>34</sup>P. W. Anderson, in *Solid State Physics, Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 14.
- <sup>35</sup>J. S. M. Harvey, *Proc. R. Soc. London Ser. A* **285**, 581 (1965).
- <sup>36</sup>M. Takigawa, P. C. Hammel, R. H. Heffner, Z. Fisk, K. C. Ott, and J. D. Thompson, *Phys. Rev. Lett.* **63**, 1865 (1989). Hyperfine fields in the doped phase have since been shown to be nearly independent of doping, for instance, by Y. Yoshinari, H. Yasuoka, Y. Ueda, K. Koga, and K. Kosuge, *J. Phys. Soc. Jpn.* **59**, 3698 (1990).
- <sup>37</sup>H. Alloul, *Phys. Rev. Lett.* **63**, 689 (1989).
- <sup>38</sup>B. Bleaney, K. D. Bowers, and D. J. E. Ingram, *Proc. R. Soc. London Ser. A* **228**, 147 (1955).
- <sup>39</sup>*Atomic Many Body Theory*, edited by I. Lindgren and J. Morrison (Springer-Verlag, Berlin, 1982).
- <sup>40</sup>We thank C. Berthier for repeatedly criticizing the treatment of coherence effects proposed in Ref. 9.
- <sup>41</sup>P. W. Anderson, in *Proceedings of the International Conference on Materials and Mechanisms of Superconductivity, Kanazawa, Japan* [*Physica C* **185**, 11 (1991)].
- <sup>42</sup>A. K. McMahan, R. M. Martin, and S. Satpathy, *Phys. Rev. B* **38**, 6650 (1988).

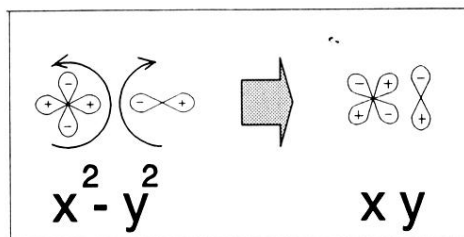
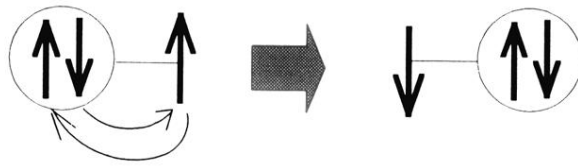


FIG. 11. Effect of the combined rotation of copper and oxygen orbitals.



delocalization + spin - flip

FIG. 16. The response function of the  $t$ - $t'$ - $J$ - $R$  model that may account for the spin dynamics of doped holes is a combination of (effective) charge transfer and spin flip.