

## Effect of dopant atoms on local superexchange in cuprate superconductors: A perturbative treatment

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Recent scanning tunneling spectroscopy experiments have provided evidence that dopant impurities in high- $T_c$  superconductors can strongly modify the electronic structure of the  $\text{CuO}_2$  planes nearby, and possibly influence the pairing. To investigate this connection, we calculate the local magnetic superexchange  $J$  between Cu ions in the presence of dopants within the framework of the three-band Hubbard model, up to fifth order in perturbation theory. We demonstrate that the sign of the change in  $J$  depends on the relative dopant-induced spatial variation of the atomic levels in the  $\text{CuO}_2$  plane, contrary to results obtained within the one-band Hubbard model. We discuss some realistic cases and their relevance for theories of the pairing mechanism in the cuprates.

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### I. INTRODUCTION

Scanning tunneling spectroscopy (STS) experiments on surfaces of several high- $T_c$  materials<sup>1</sup> have discovered a host of fascinating phenomena, including checkerboard local-density-of-states (LDOS) modulations and inhomogeneous superconductivity with enormous gap modulations taking place at the nanoscale.<sup>2-5</sup> Recently, the size of the local gap was found to be positively correlated with simultaneously imaged atomic scale defects, thought to be interstitial oxygen dopants.<sup>6</sup> This is a surprising result since it had been expected that an oxygen, which donates two holes to the  $\text{CuO}_2$  plane, would overdope the system and lead to a smaller gap nearby. The positive correlation between the positions of the oxygen atoms and the gap led Nunner *et al.*<sup>7</sup> to suggest that the dopants might be increasing the pair interaction locally. This could occur if the local electronic structure were altered significantly so as to modify a spin-fluctuation exchange effective interaction, or possibly a local electron-phonon coupling constant. For example, it has been observed that a strong correlation exists between the distance of the apical oxygen from the  $\text{CuO}_2$  plane in high- $T_c$  materials and the critical temperature,<sup>8,9</sup> and it might be imagined that a modulation of this displacement by dopant atoms could change the pairing interaction locally.

Nunner *et al.*<sup>7</sup> did not assume any specific microscopic model, but pointed out simply that the general assumption of dopants modulating the pair interaction could explain a remarkable number of experimental results and correlations. Within a generalized inhomogeneous Bardeen-Cooper-Schrieffer (BCS) pairing model adopted in this work, it correctly reproduces the anticorrelation of coherence peak height and position, the correlation of dopant position with gap size, and the detailed frequency dependence of the O:LDOS ( $\omega$ ) correlation. The theory is still controversial; in almost all treatments of disorder in superconductors, impurities are assumed to simply scatter electrons as a screened Coulomb potential, rather than modulate the pair interaction. There are, however, well-known exceptions,<sup>10</sup> and it is certainly reasonable to expect modulation of the pair interac-

tions to be largest in systems such as the cuprates where the coherence length is small. Strong correlations have not been included systematically in the theory, although some first steps have been made when Zhu showed explicitly using an inhomogeneous slave-boson approach that the proposal of Nunner *et al.* that impurities might modulate the local exchange  $J$  was consistent with the scanning tunneling microscopy (STM) observations.<sup>11</sup>

This scenario was investigated beyond the framework of mean-field theory by Maska *et al.*<sup>12</sup> By assuming that (i) the cuprate superconductors can be described by the  $t$ - $J$  model, with the exchange interaction as the main pairing mechanism,<sup>13,14</sup> and (ii) that the presence of the dopant atoms induces a position-dependent shift of the atomic levels in the  $\text{CuO}_2$  plane, these authors calculated the effective superexchange interaction  $J$  between copper ions in the presence of dopants from a perturbation expansion of the one-band Hubbard Hamiltonian up to second order. They showed that the diagonal disorder in the plane *always* leads to an enhancement of  $J$ ; accordingly, with the assumption that pairing is due to superexchange, the superconducting gap increases in the vicinity of the dopant atoms, in agreement with Ref. 7. If true, this conclusion would provide an important apparently robust way to connect local atomic displacements with the increase in the pairing there, using the results of STS. However, recent results by Johnston *et al.*<sup>15</sup> based on cluster-model calculations for the three-band Hubbard Hamiltonian,<sup>16</sup> which account explicitly for the Cu-O hopping processes, showed instead that electrostatic modifications due to the presence of the oxygen dopant locally suppress  $J$ . They showed, in addition, that electronic coupling to local phonon modes was strongly modified by the dopant, and could enhance  $J$ . This is consistent with the fact that the gap inhomogeneities are strongly (anti)correlated with a local bosonic mode frequency identified in the tunneling conductance by Lee *et al.*,<sup>17</sup> but still in apparent contradiction to the result of Maska *et al.*

In view of the present controversy, we investigate here the possibility that the Maska *et al.* result is an artifact of an oversimplified model of the electronic structure of the  $\text{CuO}_2$

plane, and analyze the effect of a dopant impurity on  $J$  by performing a perturbation expansion on the three-band Hubbard model. As in Ref. 12, we assume initially that the primary effect of the dopant is the shift of the atomic energy levels in the  $\text{CuO}_2$  plane, but account for the shifts in O levels as well as Cu. Our calculations show that the fifth-order contribution is as important as the fourth-order one, in agreement with the results for the pure case.<sup>18</sup> We find that the sign of these contributions is very susceptible to the relative dopant-induced spatial variation of the atomic levels; in contrast to the single-band case, it may be either positive or negative. Finally, we show how the discrepancies between Refs. 12 and 15 may be understood in terms of limiting considerations.

## II. MODEL

Our starting model is the three-band Hubbard Hamiltonian  $H_{\text{Hubb}}$  on the  $\text{CuO}_2$  plane.<sup>16</sup> The three bands arise from the hybridization of: the Cu  $3d_{x^2-y^2}$  orbital and the two degenerate O  $2p$  orbitals, O  $2p_x$  and O  $2p_y$ . In the hole representation,  $H_{\text{Hubb}}$  can be written as

$$H_{\text{Hubb}} = \sum_{i,\sigma} (\varepsilon_d + V_i) d_{i,\sigma}^\dagger d_{i,\sigma} + \sum_{l,\sigma} (\varepsilon_d + \Delta + \delta_l) p_{l,\sigma}^\dagger p_{l,\sigma} + \sum_{\langle i,l \rangle \sigma} t_{pd}^{il} (d_{i,\sigma}^\dagger p_{l,\sigma} + \text{H.c.}) + \sum_{\langle l,n \rangle \sigma} t_{pp}^{ln} (p_{l,\sigma}^\dagger p_{n,\sigma} + \text{H.c.}) + U_d \sum_i d_{i,\uparrow}^\dagger d_{i,\uparrow} d_{i,\downarrow}^\dagger d_{i,\downarrow} + U_p \sum_l p_{l,\uparrow}^\dagger p_{l,\uparrow} p_{l,\downarrow}^\dagger p_{l,\downarrow}. \quad (1)$$

In Eq. (1),  $d_{i,\sigma}^\dagger$  ( $d_{i,\sigma}$ ) creates (annihilates) a hole with spin  $\sigma$  in the  $3d_{x^2-y^2}$  orbital of a Cu atom at site  $i$ . Correspondingly,  $p_{l,\sigma}^\dagger$  ( $p_{l,\sigma}$ ) creates (annihilates) a hole with spin  $\sigma$  in one of the two O  $2p$  orbitals at site  $l$ .  $\varepsilon_d$  is the on-site energy of the Cu  $3d_{x^2-y^2}$  orbital, while  $\Delta$  is the difference between the Cu  $3d_{x^2-y^2}$  and the O  $2p$  energies in the pure system.  $t_{pd}^{il}$  and  $t_{pp}^{ln}$  describe the nearest-neighbor Cu-O and O-O hoppings, respectively. Only hoppings within the  $\text{CuO}_2$  plane are considered. The sign of  $t_{pd}^{il}$  and  $t_{pp}^{ln}$  depends on the relative phase of the overlapping  $3d_{x^2-y^2}$  and  $2p$  orbitals.  $U_d$  ( $U_p$ ) is the on-site Coulomb repulsion for a pair of holes on a Cu (O) atom. The presence of a dopant shifts the atomic Cu and O energy levels in its neighborhood. We denote the energy shift for a Cu at position  $i$  as  $V_i$  and for an O at position  $l$  between Cu ions at positions  $i$  and  $j$  as  $\delta_l = \delta_{ij}$  (see Fig. 1). Besides these shifts, the dopant is expected to cause local lattice distortions, which lead to the modification of the hopping integrals  $t_{pd}^{il}$  and  $t_{pp}^{ln}$ . In the present work we neglect this effect, as in Ref. 12, and concentrate on the effects due to the dopant-induced spatial variation of Cu and O atomic energy levels.

## III. PERTURBATION EXPANSION

The fourth- and fifth-order expressions for the superexchange interaction ( $J^{(4)}$  and  $J^{(5)}$ , respectively) in homogeneous cuprates were derived by Eskes and Jefferson<sup>18</sup> using Rayleigh-Schrödinger perturbation theory,

$$J = J^{(4)} + J^{(5)}, \quad (2)$$

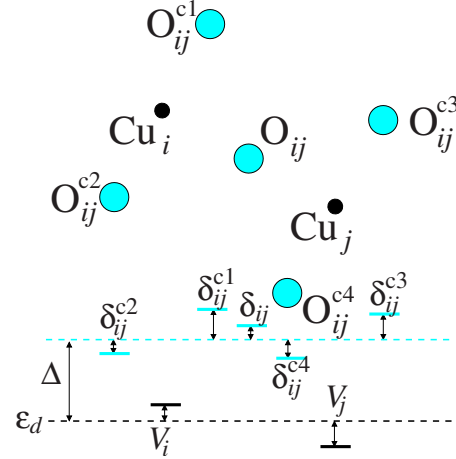


FIG. 1. (Color online) Energy level diagram for a  $\text{Cu}_2\text{O}_5$  cluster illustrating the notation used for the dopant-induced shifts of Cu and O atomic energy levels. Each schematic energy level is located directly beneath its corresponding atom and accordingly colored [black for Cu and cyan (gray) for O levels].

$$J^{(4)} = \frac{4t_{pd}^4}{\Delta^2} \left\{ \frac{1}{U_d} + \frac{2}{2\Delta + U_p} \right\}, \quad (3)$$

$$J^{(5)} = \frac{4t_{pd}^4}{\Delta^2} \left\{ \frac{1}{U_d} \frac{8t_{pp}}{\Delta} + \frac{2}{2\Delta + U_p} \frac{8t_{pp}}{\Delta} + \frac{4t_{pp}}{\Delta^2} \right\}, \quad (4)$$

where we have set to zero the Coulomb repulsion  $U_{pd}$  between a hole on a Cu ion and a hole on the neighboring O ion, which we neglect in our calculations for the sake of simplicity.

We consider now the three-band Hubbard model for the case with an impurity [Eq. (1)] in the regime where  $V_i$ ,  $\delta_l < \Delta$ ,  $U_d$ ,  $U_p$  and apply Rayleigh-Schrödinger perturbation theory. We treat the hopping terms in Eq. (1) as a perturbation  $H_1$ ,

$$H_1 = \sum_{\langle i,l \rangle \sigma} t_{pd}^{il} (d_{i,\sigma}^\dagger p_{l,\sigma} + \text{H.c.}) + \sum_{\langle l,n \rangle \sigma} t_{pp}^{ln} (p_{l,\sigma}^\dagger p_{n,\sigma} + \text{H.c.}). \quad (5)$$

The ground state of the unperturbed Hamiltonian  $H_0$  ( $H_{\text{Hubb}} = H_0 + H_1$ ) corresponds in this case to all Cu atoms occupied by one hole each. This state is  $2^N$ -fold degenerate due to the various possible electron-spin distributions

$$|\sigma_1 \cdots \sigma_N\rangle = \prod_{i=1}^N d_{i,\sigma_i}^\dagger |\text{vac}\rangle, \quad (6)$$

where  $\sigma_1, \dots, \sigma_N = \uparrow$  or  $\downarrow$  and  $i$  runs over Cu sites.

The effective Hamiltonian  $H_{\text{eff}}$  is calculated as a perturbation expansion in powers of  $H_1$ .<sup>19-21</sup> For the set of states (6), we can ignore many terms of the perturbation series by making use of the fact that the terms containing  $PH_1P$ , where the operator  $P$  projects on the ground-state manifold Eq. (6), will all vanish since it is not possible to connect any two states out of the ground-state manifold [Eq. (6)] by a single hopping process. This observation leads to the following expression for  $H_{\text{eff}}$ :

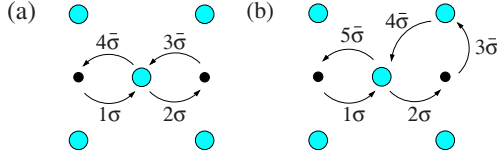


FIG. 2. (Color online) Graphs describing the (a) fourth- and (b) fifth-order hole hopping processes that result in the exchange of spins between two Cu atoms. Black [cyan (gray)] circles represent Cu [O] atoms. Arrows denote hopping processes, with the accompanying number indicating the order, in which the hoppings occur. Symbols  $\sigma$  or  $\bar{\sigma}$  stand for the spin of the hole.

$$\begin{aligned}
H_{\text{eff}} = & E_0 P + PH_1 RH_1 P + PH_1 RH_1 RH_1 P \\
& + PH_1 RH_1 RH_1 RH_1 P \\
& - \frac{1}{2} PH_1 R^2 H_1 PH_1 RH_1 P \\
& - \frac{1}{2} PH_1 RH_1 PH_1 R^2 H_1 P + PH_1 RH_1 RH_1 RH_1 RH_1 P \\
& - \frac{1}{2} PH_1 RH_1 R^2 H_1 PH_1 RH_1 P \\
& - \frac{1}{2} PH_1 RH_1 PH_1 R^2 H_1 RH_1 P \\
& - \frac{1}{2} PH_1 R^2 H_1 RH_1 PH_1 RH_1 P \\
& - \frac{1}{2} PH_1 RH_1 PH_1 RH_1 R^2 H_1 P \\
& - \frac{1}{2} PH_1 R^2 H_1 PH_1 RH_1 RH_1 P \\
& - \frac{1}{2} PH_1 RH_1 RH_1 PH_1 R^2 H_1 P, \tag{7}
\end{aligned}$$

where  $R = (1 - P)/(E_0 - H_0)$  so that, for a state  $|\phi\rangle \notin \{|\sigma_1 \cdots \sigma_N\rangle\}$ ,

$$R|\phi\rangle = \frac{1}{E_0 - E_\phi} |\phi\rangle. \tag{8}$$

$E_0$  is the ground-state energy of  $H_0$  and  $E_\phi = \langle \phi | H_0 | \phi \rangle$ .

Among the terms in  $H_{\text{eff}}$ , Eq. (7), we need only to consider those terms that are of the form

$$\sum_{\langle i,j \rangle, \sigma} d_{i,\sigma}^\dagger d_{j,\bar{\sigma}}^\dagger d_{j,\sigma} d_{i,\bar{\sigma}}, \tag{9}$$

with  $\bar{\sigma} = -\sigma$ , since the corresponding prefactor determines  $J$ . The terms of interest result from calculating the fourth-order term  $PH_1 RH_1 RH_1 RH_1 P$  and the fifth-order term  $PH_1 RH_1 RH_1 RH_1 RH_1 P$  in Eq. (7). All other terms will only add a constant energy term to the effective Hamiltonian.

It is convenient to use graphs for deriving expressions for  $J^{(4)}$  and  $J^{(5)}$ . One has to consider all possible fourth- and fifth-order hopping processes resulting in the exchange of

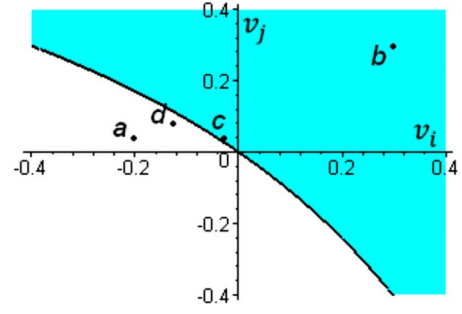


FIG. 3. (Color online) sign ( $\eta_{ij}$ ) diagram for a typical set of the model parameters [ $U_d = 8.8$  eV,  $U_p = 4.1$  eV, and  $\Delta = 2.92$  eV (Ref. 15)] in the space of abscissa  $v_i = V_i - \delta_{ij}$  and ordinate  $v_j = V_j - \delta_{ij}$ . White and cyan (gray) regions indicate negative and positive total fourth-order correction to  $J$ , respectively. Points (a)–(d) denote the values of  $v_i$  and  $v_j$  used for generating diagrams (a)–(d) in Fig. 4.

spins between two Cu atoms and sum up the corresponding  $PH_1 RH_1 RH_1 RH_1 P$  and  $PH_1 RH_1 RH_1 RH_1 RH_1 P$  expressions.

There are in total 12 fourth-order graphs (each of the six topologically distinct graphs has two versions that differ by flipped spins), one of which is shown in Fig. 2(a). In the pure case they reduce to only two terms in  $J^{(4)}$  [Eq. (3)]. In the case of an impurity (dopant-induced spatial variation of Cu and O levels), the terms in the sum for  $J^{(4)}$  corresponding to hoppings that start from the Cu ion at site  $i$  will differ from those corresponding to hoppings that start from a Cu ion at site  $j$  due to the different dopant-induced shifts  $V_i$  and  $V_j$ . With the notation  $t_{pd} = |t_{pd}^{il}|$ ,  $t_{pp} = |t_{pp}^{ln}|$ , the local exchange  $J_{ij}^{(4)}$  to fourth-order is then

$$J_{ij}^{(4)} = \left( \frac{4t_{pd}^4}{\Delta^2} \frac{1}{U_d} + \eta_{ij}^{(1)} \right) + \left( \frac{4t_{pd}^4}{\Delta^2} \frac{2}{2\Delta + U_p} + \eta_{ij}^{(2)} \right), \tag{10}$$

with corrections

$$\eta_{ij}^{(1)} = \frac{4t_{pd}^4}{\Delta^2} \times \frac{1}{U_d (\Delta - v_i)^2 (\Delta - v_j)^2 [U_d^2 - (v_j - v_i)^2]},$$

$$a_0 = (v_j - v_i)^2 (\Delta - v_j)^2 (\Delta - v_i)^2,$$

$$a_1 = \frac{1}{2} (v_j - v_i)^2 [2\Delta - (v_i + v_j)] \Delta^2,$$

$$a_2 = \frac{1}{2} (\Delta - v_j)^2 (2\Delta - v_i) v_i + \frac{1}{2} (\Delta - v_i)^2 (2\Delta - v_j) v_j, \tag{11}$$

and

$$\eta_{ij}^{(2)} = \frac{4t_{pd}^4}{\Delta^2} \frac{2}{2\Delta + U_p} \frac{b_0 + b_1 U_p}{[(2\Delta - v_i - v_j) + U_p] (\Delta - v_j)^2 (\Delta - v_i)^2},$$

$$\begin{aligned}
b_0 = & (\Delta - v_j)^2 [\Delta^2 + \Delta(\Delta - v_i) + (\Delta - v_i)^2] v_i + (\Delta - v_i)^2 \\
& \times (\Delta^2 + \Delta(\Delta - v_j) + (\Delta - v_j)^2) v_j - \frac{1}{2} \Delta^3 (v_j - v_i)^2,
\end{aligned}$$

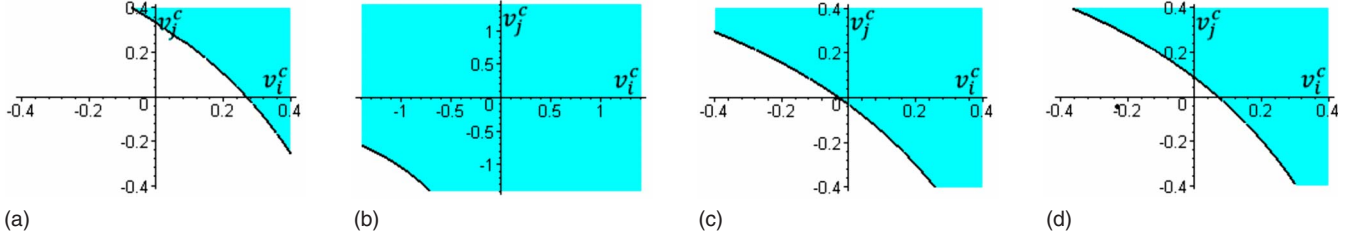


FIG. 4. (Color online)  $\text{sign}(\eta_{ij} + \mu_{ij})$  diagrams in the space of abscissa  $v_i^c$  and ordinate  $v_j^c$ . White and cyan (gray) correspond to negative and positive values of  $\eta_{ij} + \mu_{ij}$ , respectively. The point  $v_i^c = -0.23$  eV,  $v_j^c = -0.05$  eV in diagram (d) corresponds to the energy levels distribution shown in Fig. 2 of Ref. 15.

$$b_1 = \frac{1}{2} [(\Delta - v_j)v_i + (\Delta - v_i)v_j] \times \left[ \Delta \left( \Delta - \frac{v_i + v_j}{2} \right) + (\Delta - v_i)(\Delta - v_j) \right], \quad (12)$$

where we have defined  $v_i = V_i - \delta_{ij}$  and  $v_j = V_j - \delta_{ij}$ . It is easy to check that the correction terms  $\eta_{ij}^{(1)}$  and  $\eta_{ij}^{(2)}$  vanish when the impurity-induced potentials  $v_i$  vanish.

We note that the sign of the total fourth-order correction due to the presence of the dopant,  $\eta_{ij} = \eta_{ij}^{(1)} + \eta_{ij}^{(2)}$ , depends on the sign and the magnitude of  $v_i$  and  $v_j$ , i.e., the actual energy separation between the dopant-shifted Cu and O levels and, in particular, for  $v_i, v_j \ll \Delta$ ,  $\eta_{ij}$  is proportional to  $v_i + v_j$ . In general, this result is shown diagrammatically in Fig. 3 for a typical set of model parameters in the Bi superconductors [ $U_d = 8.8$  eV,  $U_p = 4.1$  eV, and  $\Delta = 2.92$  eV (Ref. 15)]. In the space of  $v_i, v_j$ , negative and positive  $\eta_{ij}$  contributions to  $J$  are shown as white and gray (cyan) areas, respectively. For the parameters considered in the cluster calculation of Ref. 15, the contribution of  $\eta_{ij}$  is negative [black dot (d) in Fig. 3] and therefore the fourth-order correction suppresses  $J$  in that case.

The number of graphs contributing to the fifth-order correction to the superexchange,  $J^{(5)}$ , is 120. They all involve hoppings to one of the four corner O ions [Fig. 2(b)] so that  $J^{(5)}$  will also depend on the corner O atoms energy-level shifts  $\delta_{ij}^{c1}, \delta_{ij}^{c2}, \delta_{ij}^{c3}$ , and  $\delta_{ij}^{c4}$  (Fig. 1). For example, the correction to the first term of  $J^{(5)}$  in Eq. (4) is

$$J_1^{(5)} = 4t_{pd}^4 t_{pp} \times \left( \frac{1}{(\Delta + \delta_{ij} - V_i)^2} \frac{1}{U_d + \{V_j - V_i\}} \left\{ \frac{1}{\Delta + \delta_{ij}^{c1} - V_i} + \frac{1}{\Delta + \delta_{ij}^{c2} - V_i} + \frac{1}{\Delta + \delta_{ij}^{c3} - V_i} + \frac{1}{\Delta + \delta_{ij}^{c4} - V_i} \right\} + \frac{1}{(\Delta + \delta_{ij} - V_j)^2} \frac{1}{U_d - \{V_j - V_i\}} \left\{ \frac{1}{\Delta + \delta_{ij}^{c1} - V_j} + \frac{1}{\Delta + \delta_{ij}^{c2} - V_j} + \frac{1}{\Delta + \delta_{ij}^{c3} - V_j} + \frac{1}{\Delta + \delta_{ij}^{c4} - V_j} \right\} \right). \quad (13)$$

The sign of this term depends on  $v_i, v_j, v_i^{c1} = V_i - \delta_{ij}^{c1}, v_i^{c2} = V_i - \delta_{ij}^{c2}, v_i^{c3} = V_i - \delta_{ij}^{c3}$ , and  $v_i^{c4} = V_i - \delta_{ij}^{c4}$  (alternatively,  $v_j^{c1} = V_j - \delta_{ij}^{c1}, v_j^{c2} = V_j - \delta_{ij}^{c2}, v_j^{c3} = V_j - \delta_{ij}^{c3}$ , and  $v_j^{c4} = V_j - \delta_{ij}^{c4}$  could be considered). These six parameters define the sign of the total fifth-order correction  $\mu_{ij}$  as well.

In order to quantify the effect that hopping to the corner O atoms has on the superexchange  $J$ , we consider the case where  $v_i^{c1} = v_i^{c2} = v_i^c$  and  $v_j^{c3} = v_j^{c4} = v_j^c$  (such a symmetry is realized when the dopant atom is located on the line connecting two Cu atoms<sup>15</sup>). For given  $v_i$  and  $v_j$ , it is then possible to draw a phase diagram of the sign of the total correction,  $\mu_{ij} + \eta_{ij}$ , in the space of  $v_i^c$  and  $v_j^c$ . In Fig. 4, we present, as an example, four such diagrams corresponding to different sets of  $v_i$  and  $v_j$  (four points in Fig. 3). For calculating these diagrams we chose  $t_{pd} = 1.2$  eV and  $t_{pp} = 0.5$  eV as also considered in the cluster calculations Ref. 15. The local Cu and O site energies calculated by Johnston *et al.* correspond to the choice of  $v_i = -0.13$  and  $v_j = 0.08$  eV in Fig. 4(d). It can be concluded from examining the diagrams in Fig. 4 that the parameters  $v_i^{c1}, v_i^{c2}, v_j^{c3}$ , and  $v_j^{c4}$  have to be slightly larger than  $v_i$  and  $v_j$  in order to induce a sign change in the correction to  $J$  as compared to the fourth-order result.

#### IV. ANALYSIS AND DISCUSSION

We are now concerned with trying to answer the following questions. Is the sign of the corrections to  $J$  caused by the impurity uniformly positive, as occurred in the one-band calculation of Ref. 12? For physically reasonable assumptions regarding the magnitude and spatial dependence of the impurity potential for a dopant sitting several Å from the CuO<sub>2</sub> plane, can the modulation of  $J$  be significant at all?

Regarding the first point, there is a simple argument that explains why the superexchange corrections due to doping derived from the three-band model can assume both positive and negative values while from the one-band model one finds that  $J$  is always enhanced. Let us consider what happens between neighboring Cu and O ions when their energy levels shift due to a dopant by  $V$  and  $\delta$ , respectively. The local separation between their energy levels, which we denoted as  $\Delta$  for the homogeneous case, varies as  $\Delta_{\text{loc}} = \Delta - (V - \delta)$ . For  $(V - \delta) > 0$ ,  $\Delta_{\text{loc}}$  decreases compared with  $\Delta$  and vice versa. Expressing  $J$  in terms of  $\Delta_{\text{loc}}$  instead of  $\Delta$ , one sees that for  $V_j - V_i \ll \Delta_{\text{loc}}$  [in this limit  $\Delta$  in Eq. (3) and Eq. (4) can be replaced by  $\Delta_{\text{loc}}$ ] the variation in local Cu and O levels separation  $\Delta_{\text{loc}}$  defines the change of  $J$ : since  $\Delta_{\text{loc}}$  is in the denominator,  $(V - \delta) > 0$  leads to the enhancement of  $J$  and  $(V - \delta) < 0$  leads to the suppression of  $J$ . In Fig. 3, the condition  $V_j - V_i \ll \Delta_{\text{loc}}$  is fulfilled in the vicinity of the  $v_i = v_j$  line (on the line,  $V_j - V_i = 0$ ) and indeed  $J$  is increased in the first quarter and reduced in the third quarter of the dia-



gram. In the second and fourth quarters the relative variation in levels of Cu atoms,  $V_i - V_j$ , becomes equally important. The one-band model excludes completely the O atoms, thus ignoring one of the two microscopic factors (change in the Cu-O energy levels separation and the relative shift of the energy levels of two interacting Cu ions) that govern the variation in the local superexchange coupling  $J$ .

We would like to note that, as shown by Eskes and Jefferson<sup>18</sup> for the homogeneous case, even the fifth-order perturbation expansion for  $J$  is insufficient for quantitative estimates of  $J$  and gives overestimated values compared with the experimental (and cluster-model calculated) values of  $J$ . Such trends, naturally, are also to be expected in the disordered case. We calculate the value of the fourth- and fifth-order superexchange coupling corrections with the same model parameters as used in the cluster-model calculations<sup>15</sup> [Figs. 3 and 4(d)] and find that the sign and the order of magnitude of the correction within our calculation, yielding a suppression of  $J$  by  $\mathcal{O}(5\%)$ , are in good agreement with cluster calculations<sup>15</sup> when no modulation in the hopping integrals is considered, as is the case here. Consideration of other sets of model parameters<sup>22</sup> lead to the same relative correction values.

## V. CONCLUSIONS

The question of the impact of a dopant atom on the local electronic properties in the  $\text{CuO}_2$  plane of the cuprates has been highlighted by STM measurements, indicating that dopants correlate with regions of large gap,<sup>6</sup> and the theoretical proposal that the dopant itself is enhancing the pairing interaction.<sup>7</sup> The appealing argument of Maška *et al.*,<sup>12</sup> based

on a single-band analysis that the perturbation provided by the dopant necessarily enhances the superexchange locally and may therefore enhance pairing, has been shown to be a special result restricted to one-band systems. Within a three-band Hubbard model appropriate to the  $\text{CuO}_2$  plane, we have in this work performed a perturbative calculation to fifth order in the hoppings  $t_{pd}$  and  $t_{pp}$ , and shown that the sign of the correction to  $J$  can be positive or negative depending on the potentials on nearby sites induced by the dopant impurity. The typical modulation is of order  $d\Delta/\Delta$  times the exchange for the homogeneous system, where  $d\Delta$  is a typical dopant-dependent modulation of the local charge-transfer energy between Cu and O, and  $\Delta$  is the homogeneous value of this difference. Using values of these shifts obtained from cluster calculations,<sup>15</sup> we find that a typical modulation due to an O dopant in the Bi-2212 system imaged by STM is of order 5% of the homogeneous value.

It is possible that a more accurate microscopic calculation, accounting for the modulations of the hoppings and the apical oxygen degrees of freedom neglected here, may produce a reliable description of this modulation. Until then, we have shown that the size and sign of this modulation is not universal but depends on details of the impurity and local electronic structure.

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