

## Canonical perturbation theory and the two-band model for high- $T_c$ superconductors

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We analyze in more detail a model which describes spins localized on the Cu sites and carriers of oxygen character which has been proposed for high-temperature superconducting oxides by, among others, Emery and Hirsch. This model is discussed in a more general framework of the electronic structure of transition-metal compounds as has emerged from detailed electron-spectroscopy studies. We argue that the Emery model corresponds with the charge-transfer semiconductor in this electronic picture. Using canonical perturbation theory we analyze systematically the near-ground-state physics when holes are introduced into such a system. We derive explicit expressions for the carrier-spin, spin-spin, and carrier-carrier interactions which turn out to depend in a nontrivial way on the electronic parameters, thereby creating a link between the high-energy data and the macroscopic physics in these systems. We find that the dominant interactions are the Kondo-like spin-carrier interactions which give rise to the well-known magnetic semiconductor physics characterized by ferromagnetic correlations (spin polarons, double exchange). Using some simple finite models we discuss then the pairing mechanisms as proposed by Emery and Hirsch. We show that both of them are based on fourth-order attractive interactions. These are, however, overruled by the second-order processes which favor the opposite behavior and suppress the pairing. Our conclusion is that the charge degrees of freedom are essential in the real high-temperature superconductors and we supply further evidence in favor of their mixed-valence behavior.

### I. INTRODUCTION

Since the discovery<sup>1,2</sup> of the high- $T_c$  superconducting oxides (HTSO) the suspicion has been growing that a new pairing mechanism of electronic rather than of phonon nature is at work. At the same time there are many indications pointing at rather strong electronic correlations in these materials. For instance, it is well established that the ground state of slightly oxygen-deficient  $\text{La}_2\text{CuO}_{4-\delta}$  is antiferromagnetic,<sup>3</sup> while in the local density (LD) band-structure picture the system is far from being magnetic.<sup>4</sup> Maybe the most direct evidence in favor of the correlated nature of these compounds is the observation of large core-line and valence-band satellites in the photoemission spectra.<sup>5,6</sup> The magnitude of those is unprecedented for metallic transition-metal compounds. It is generally accepted that these satellites originate from strong repulsive Coulomb interactions between the "bare" electrons. However, an exciting possibility is that these repulsive interactions renormalize into attractive quasiparticle interactions, which in turn are responsible for the superconductivity.

Very recently several models have been proposed which are suggestive in this respect. The resonating-valence-bond (RVB) model of Anderson and co-workers<sup>7</sup> is the most famous one. It is assumed in this model, as well as several related models,<sup>8-12</sup> that the electronic degrees of freedom can be described by the one-band Hubbard Hamiltonian. However, in the conventional Hubbard model

only the  $d$  degrees of freedom are taken into account. It is then assumed that the other electronic degrees of freedom (O  $2p$ , TM  $4s$ , where TM stands for a transition-metal element) are at much higher energy and therefore can be projected out.<sup>9,13</sup> However, recent studies have shown that this is, in general, not a good assumption for late  $3d$  compounds.<sup>14</sup> These studies are based on photoemission<sup>15</sup> (PES) and inverse photoemission<sup>16</sup> (IPES), core photoemission,<sup>17</sup> x-ray absorption spectroscopy<sup>18</sup> (XAS), and ultraviolet (uv) optical<sup>14</sup> data, which all probe the electronic structure in a more or less direct way. It has been shown that this information can be understood in surprising detail, thereby quantifying our understanding of the electronic structure of  $3d$  compounds. The cornerstones of this interpretational framework are on the one hand the reasonable description derived from LD theory of many facets of the electronic structure of these materials. On the other hand, this scheme fails with respect to the description of  $d$  or  $f$  electrons. It is known that this can be improved by treating these electrons on a quasiatomic footing, including multiplet interactions and a screened atomic on-site Coulomb interaction  $U$ . These electrons behave then as localized in contrast to the other charge degrees of freedom which behave bandlike. This physical situation is, in general, described by the Anderson-lattice Hamiltonian. Following the LD band-structure results for the HTSO,<sup>19</sup> we may assume that only the Cu  $3d_{x^2-y^2}$  and O  $2p_{x(y)}$  degrees of freedom are of relevance for the low-energy properties of these systems. In the spirit of the

preceding discussion, a realistic electronic model of the HTSO would be<sup>20-23</sup>

$$\begin{aligned}
 H &= H_0 + H_1, \\
 H_0 &= \sum_{i\sigma} (\varepsilon_d n_{di\sigma} + \frac{1}{2} U n_{di\uparrow} n_{di\downarrow}) + \sum_{j\sigma} \varepsilon_L n_{j\sigma} \\
 &\quad + \sum_{j \neq j' \sigma} t_{jj'} c_{j\sigma}^\dagger c_{j'\sigma}, \\
 H_1 &= \sum_{ij\sigma} V_{ij} (d_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}).
 \end{aligned}
 \tag{1.1}$$

The operators  $d_{i\sigma}^\dagger$  and  $c_{j\sigma}^\dagger$  create holes in a  $d_{x^2-y^2}$  orbital on Cu site  $i$  and in a  $p_{x(y)}$  orbital on O site  $j$ , respectively. We include in (1.1) the  $d$ - $p$  ( $V_{ij}$ ) and  $p$ - $p$  ( $t_{jj'}$ ) hopping as suggested by the band structure,<sup>4,19</sup> and in addition to that we include a term describing the on-site repulsion  $U$  between the  $d$  electrons. This Hamiltonian is just a tight-binding formulation of the spin-degenerate Anderson lattice Hamiltonian.

Under the neglect of the  $d$ -dispersional width (impurity model), the physics contained in the Hamiltonian (1.1) for arbitrary degeneracy has been systemized recently.<sup>24</sup> The key parameters are the Coulomb interaction  $U$  and the charge-transfer energy  $\Delta = \varepsilon_L - \varepsilon_d$ . The latter is the energy cost of transferring a hole from the Cu site to the O site ( $d^9 \rightarrow d^{10}\underline{L}$ ). As a function of  $U$  and  $\Delta$  we encounter a number of different situations (see Fig. 1). If  $\Delta \gg U$ , the  $2p$  degrees of freedom can be projected out and it can be shown that we end up with an effective one-band Hubbard Hamiltonian with transfer integrals of  $\sim V^2/\Delta$ . On the other hand, if  $\Delta \ll U$ , the conduction band still corresponds to the upper Hubbard band but the valence band is of O  $2p$  character while the lower Hubbard band is lying below the bottom of this valence band (see Fig. 2). In this case we have a charge-transfer correlation gap of magnitude proportional to  $\Delta$  (i.e., charge-transfer semiconductor). For  $\Delta \approx U$  the situation is more complicated

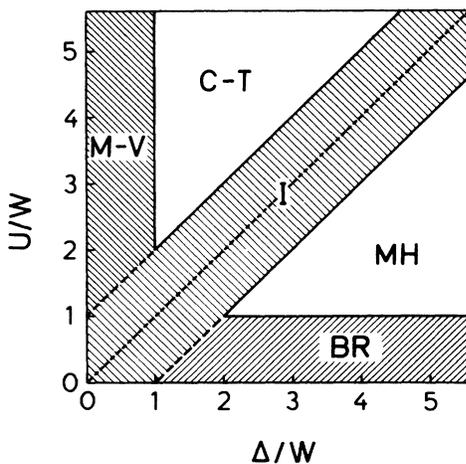


FIG. 1. Schematic phase diagram for transition-metal compounds, indicating the various sorts of metals [mixed-valence (MV) and Brinkman-Rice (BR)] and insulators [charge-transfer (CT) and Mott-Hubbard (MH)]. The canonical perturbation theory may be used in CT and MH regimes, while it breaks down in the intermediate (I) regime.

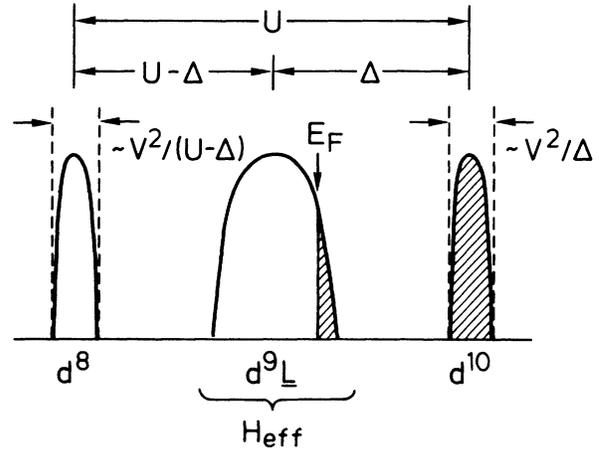


FIG. 2. Schematic representation of the various subbands in a doped charge-transfer semiconductor. A partial filling of the  $d^9\underline{L}$  subband up to the Fermi energy  $E_F$  is assumed.

because the lower Hubbard band and the  $p$  band are strongly mixed (intermediate regime). Finally, if  $\Delta$  (in case of  $U > \Delta$ ) or  $U$  (for  $U < \Delta$ ) becomes of the order of the relevant bandwidth, we enter metallic regimes of either mixed-valence (small  $\Delta$ ) or Brinkman-Rice<sup>25</sup> (small  $U$ ) nature.

By analyzing the accessible spectroscopic data of the HTSO, Fuggle *et al.*<sup>26</sup> came to the conclusion that these compounds are, in any case, in the regime of  $U > \Delta$  (see also Ref. 27). Maybe the most straightforward evidence for this are the resonant photoemission data of Kurtz *et al.*,<sup>28</sup> where a satellite feature is resolved well below the bottom of the valence band showing clearly the resonant behavior of a multiplet split  $d^8$  (lower Hubbard) band. In this way the direct use of the Hubbard Hamiltonian is excluded. We then have two possibilities for the general nature of the electronic structure of the HTSO's. Either they have a correlation gap and they belong to the class of charge-transfer semiconductors, or  $\Delta$  is too small and we are dealing with mixed-valence itinerant systems.

Because the  $d$ -charge degrees of freedom are frozen in if we consider the valence band of the charge-transfer semiconductor, it is clear that this system can be described effectively as having localized spins at the Cu sites and  $p$  hole (resulting, e.g., from doping of  $\text{La}_2\text{CuO}_4$  with Sr). Recently, there have been proposals by Emery<sup>20</sup> and Hirsch<sup>21</sup> for electronic pairing mechanisms within this picture. However, there is no systematic attempt in these papers to distangle the various interactions and their relative magnitude starting from an electronic Hamiltonian like (1.1). This question is, in fact, of crucial importance for the validity of the proposed pairing mechanisms and is addressed in this paper. For that purpose we generalize the canonical perturbation theory (CPT) of Chao, Spalek, and Oleś (CSO),<sup>29,30</sup> which has been developed for the Hubbard Hamiltonian, to the Anderson lattice (Sec. II). We note that with the CSO method the RVB Hamiltonian<sup>7,31</sup> was derived from the Hubbard Hamiltonian.<sup>29</sup>

In Sec. III we analyze the second-order (in  $V_{ij}$ ) contributions and we show that these terms produce an  $s$ - $d$ -like

Hamiltonian. However, it turns out that this Hamiltonian has a richer physical content than the phenomenological Hamiltonians usually used in the studies of magnetic semiconductors and, in fact, these results are more in line with the picture obtained from the Anderson impurity Hamiltonian. In Sec. IV we derive explicit expressions for Emery's<sup>20</sup> fourth-order carrier-carrier interactions. These are indeed attractive but we show that they give only a minor correction in the whole parameter range to the repulsive interactions originating from the second-order terms which are overlooked by Emery. In Sec. V we derive a new expression for the spin-spin (superexchange) interaction and we show that this is always considerably smaller than the second-order spin-carrier interactions, thereby excluding Hirsch's mechanism.<sup>21</sup>

From these findings we conclude (in Sec. VI) that a charge-transfer (or magnetic) semiconductor is not a very likely environment for superconducting correlations, and we give some other arguments in favor of the mixed-valence picture.

## II. CANONICAL PERTURBATION THEORY: FORMALISM

From the preceding discussion it may be clear that the electronic Hamiltonian (1.1) can be simplified using perturbation theory as long as the following conditions hold:

$$\frac{V}{\Delta} \ll 1, \quad \frac{V}{U} \ll 1, \quad \frac{V}{U-\Delta} \ll 1. \quad (2.1)$$

The first two criteria are equivalent to having a correlation gap while the third criterion shows that the perturbation theory cannot be carried through in the intermediate regime. The Hamiltonian (1.1) is nothing else than the spin-degenerate Anderson lattice Hamiltonian in a tight-binding formulation, and the perturbation theory we look for is just the lattice generalization of the Schrieffer-Wolff transformation.<sup>32</sup> Although we are not aware of any attempt into this direction in the literature, this task is easily accomplished by using the formalism developed by CSO for the Hubbard Hamiltonian<sup>29,30</sup> some time ago.

In the method of CSO one introduces projection operators which project on the different degenerate subbands, in the case of the Hubbard Hamiltonian having no, one, two, etc., doubly occupied sites at energies 0,  $U$ ,  $2U$ , etc. The Hamiltonian describing these projected subbands acts as zeroth order, including intrasubband hopping, and the intersubband hopping is then treated in perturbation theory. It has been shown<sup>30</sup> that by neglecting the width of the subbands compared to the intersubband splitting ( $U$ ), the formalism is greatly simplified ending up with a perturbation expansion which is basically similar to the single-impurity canonical transformation.<sup>32</sup>

Our goal is to derive an effective Hamiltonian from Eq. (1.1) which describes the physics of the doped charge-transfer semiconductor (see Fig. 2). The only accessible charge degrees of freedom are the ligand holes while in zeroth order the  $d$  holes are frozen. We therefore introduce the projection operator

$$P_1 = \prod_i \hat{n}_{di} \quad (2.2)$$

with  $\hat{n}_{di} = n_{di\uparrow} + n_{di\downarrow} - 2n_{di\uparrow}n_{di\downarrow}$ , which projects on the subspace with one hole located on each Cu site ( $i$ ). In zeroth order the charge-transfer subband refers to the noninteracting ligand holes

$$H_{\text{eff}}^{(0)} = P_1 H P_1 = \epsilon_L \sum_{j\sigma} n_{j\sigma} + \sum_{j \neq j', \sigma} t_{jj'} c_{j\sigma}^\dagger c_{j'\sigma}. \quad (2.3)$$

We note that  $P_1$  (and the projections which follow) does not refer to the number of ligand holes present, and as such it describes both the ground state and the system with an arbitrary number of holes.

The next subbands of interest are the "lower" ( $d^n \rightarrow d^{n-1}$ ) and "upper" ( $d^n \rightarrow d^{n+1}$ ) Hubbard bands (see Fig. 2). These refer to situations with one doubly occupied (with holes) Cu site and to one unoccupied Cu site, respectively, with all the other Cu sites being singly occupied. The relevant projection operators are

$$P_0 = \sum_{i'} \left[ \prod_{i \neq i'} \hat{n}_{di} \right] \bar{n}_{di'}, \quad (2.4)$$

$$P_2 = \sum_{i'} \left[ \prod_{i \neq i'} \hat{n}_{di} \right] n_{di'\uparrow} n_{di'\downarrow}$$

with  $\bar{n}_{di} = (1 - n_{di\uparrow})(1 - n_{di\downarrow})$ .  $P_0$  describes the  $d^n \rightarrow d^{n+1}$  higher-energy subband at  $E_0 = \Delta$ , and  $P_2$  describes the lower-energy subband at  $E_2 = U - \Delta$  (see Fig. 2).

It is clear that the  $P_1$  band is connected to the  $P_0$  as well as to the  $P_2$  band by a single  $d$ - $p$  hopping process. In this situation one may use Eq. (25) of CSO,<sup>30</sup> and one finds for the second-order contribution

$$H_{\text{eff}}^{(2)} = -\frac{1}{\Delta} P_1 H_1 P_0 H_1 P_1 - \frac{1}{U-\Delta} P_1 H_1 P_2 H_1 P_1. \quad (2.5)$$

We will show explicitly in the next section how  $H_{\text{eff}}^{(2)}$  describes the interaction between the localized Cu spins and the ligand holes. As for the single impurity<sup>32</sup> this interac-

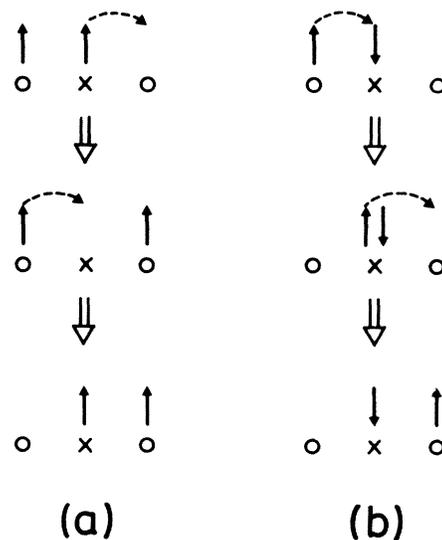


FIG. 3. The two channels leading to the dynamics of carriers by its coupling to local spins: (a)  $1/\Delta$  process; (b)  $1/(U-\Delta)$  process. Crosses and circles stand for Cu and O atoms, respectively. Only the carrier-spin conserving processes are indicated.

tion can arise through an intermediate state of a Cu site being either empty (first term, “ $1/\Delta$  process”) or doubly occupied [second term, “ $1/(U-\Delta)$  process”], as shown schematically in Fig. 3. We note that the assumption crucial to the use of CSO perturbation theory is the narrowness of the  $d^{n-1}$  and  $d^{n+1}$  subbands [with widths of  $\sim V^2/(U-\Delta)$  and  $\sim V^2/\Delta$ ] compared to the intersubband splittings (being  $U-\Delta$  and  $\Delta$ , respectively). For the next relevant (fourth) order we have to introduce additional subbands

$$P_{00} = \sum_{i' \neq i''} \left( \prod_{i \neq i', i''} \hat{n}_{di} \right) \bar{n}_{di'} \bar{n}_{di''}, \quad P_{02} = \sum_{i' \neq i''} \left( \prod_{i \neq i', i''} \hat{n}_{di} \right) \bar{n}_{di'} n_{di''} \uparrow n_{di''} \downarrow, \quad P_{22} = \sum_{i' \neq i''} \left( \prod_{i \neq i', i''} \hat{n}_{di} \right) n_{di'} \uparrow n_{di'} \downarrow n_{di''} \uparrow n_{di''} \downarrow, \quad (2.6)$$

where  $P_{00}$  refers to having two unoccupied Cu sites (at  $E_{00} = 2\Delta$ ),  $P_{02}$  to one unoccupied and one doubly occupied Cu site (at  $E_{02} = U$ ), and  $P_{22}$  to two doubly occupied Cu sites [at  $E_{22} = 2(U-\Delta)$ ]. Using again Eq. (25) of Ref. 30, we find then the fourth-order contributions

$$H_{\text{eff}}^{(4)} = H_{\text{CC}}^{(4)} + H_{\text{SS}}^{(4)} + H_{\text{SC}}^{(4)}, \quad (2.7)$$

with

$$H_{\text{CC}}^{(4)} = \frac{1}{\Delta^3} P_1 H_1 P_0 H_1 P_1 H_1 P_0 H_1 P_1 + \frac{1}{2} \frac{U}{(U-\Delta)^2 \Delta^2} (P_1 H_1 P_0 H_1 P_1 H_1 P_2 H_1 P_1 + P_1 H_1 P_2 H_1 P_1 H_1 P_0 H_1 P_1) + \frac{1}{(U-\Delta)^3} P_1 H_1 P_2 H_1 P_1 H_1 P_2 H_1 P_1, \quad (2.8)$$

$$H_{\text{SS}}^{(4)} = -\frac{1}{2} \frac{1}{\Delta^3} P_1 H_1 P_0 H_1 P_0 H_1 P_0 H_1 P_1 - \frac{1}{4} \frac{3U-4\Delta}{\Delta^2 (U-\Delta)^2} P_1 H_1 P_0 H_1 P_0 H_1 P_0 H_1 P_1, \quad (2.9)$$

and

$$H_{\text{SC}}^{(4)} = \frac{1}{4} \frac{4\Delta-U}{\Delta^2 (U-\Delta)^2} P_1 H_1 P_2 H_1 P_0 H_1 P_2 H_1 P_1 - \frac{1}{4} \frac{U}{\Delta^2 (U-\Delta)^2} (P_1 H_1 P_0 H_1 P_0 H_1 P_2 H_1 P_1 + P_1 H_1 P_2 H_1 P_0 H_1 P_0 H_1 P_1) - \frac{1}{2} \frac{1}{(U-\Delta)^3} P_1 H_1 P_2 H_1 P_2 H_1 P_2 H_1 P_1. \quad (2.10)$$

In Eq. (2.6) we separated the fourth-order contributions in three different groups. As we will show in Sec. IV, the terms gathered in  $H_{\text{CC}}^{(4)}$  will give rise, among others, to the spin-mediated carrier-carrier interactions as postulated by Emery.<sup>20</sup>  $H_{\text{SS}}^{(4)}$  will be shown in Sec. V to give rise to the spin-spin (superexchange) interactions, at least in the absence of carriers. The remaining term,  $H_{\text{SC}}^{(4)}$ , stands for different kinds of coupling between the carriers and localized spins which do not reduce to the former ones. We give in the Appendix general expressions for all the interactions contained in Eqs. (2.8)–(2.10) in terms of  $p$  holes and  $d$  pseudofermions.

### III. SECOND-ORDER INTERACTIONS: SPIN CARRIER

From the analogy with the single-impurity problem it can be directly inferred that the second-order correction to  $H_{\text{eff}}^{(0)}$  will lead to effective spin-carrier interactions. As can be seen from Eq. (2.4) and Fig. 3, these interactions are driven by two qualitatively different channels. In the first, the Cu spin hops away to an O site ( $P_0$ ) and the Cu site is subsequently refilled by either the same hole which renormalizes the ground-state energy, or, by a different hole giving rise to a spin-carrier interaction [Fig. 3(a)]. The probability of this process is inversely proportional to the charge-transfer energy  $\Delta$ . Hence we call these processes  $1/\Delta$  ones. On the other hand, we have the process indicated in Fig. 3(b), where the carrier hops onto an already occupied Cu site and generates a doubly occupied intermediate state ( $P_2$ ) at energy  $U-\Delta$ . The latter process will be called  $1/(U-\Delta)$ . It is rather straightforward to get an explicit form of Eq. (2.5) which is

$$H_{\text{eff}}^{(2)} = -\sum_{ij} \frac{V_{ij} V_{ji}}{\Delta} + \sum_{ijj'} \left( \frac{1}{\Delta} + \frac{1}{U-\Delta} \right) V_{ji} V_{ij'} [S_i^z (c_{j'}^\dagger c_{j\uparrow} - c_{j\downarrow}^\dagger c_{j'\downarrow}) + S_i^+ c_{j\downarrow}^\dagger c_{j'\uparrow} + S_i^- c_{j\uparrow}^\dagger c_{j'\downarrow}] + \sum_{ijj'\sigma} \frac{1}{2} \left( \frac{1}{\Delta} - \frac{1}{U-\Delta} \right) V_{ji} V_{ij'} c_{j\sigma}^\dagger c_{j'\sigma}. \quad (3.1)$$

The first term in Eq. (3.1) refers to the (irrelevant) renormalization of the ground state, the second term is a tight-binding formulation of the Kondo-lattice Hamiltonian, and, finally, we have an additional spin-independent  $p$ - $p$  hopping term. It is of interest to observe that the Kondo term in Eq. (3.1) involves the sum, while the hopping term involves the difference between  $1/\Delta$  and  $1/(U-\Delta)$ . In order to understand the significance of this, it is instructive to rewrite Eq. (3.1) in terms of particle operators

$$H_{\text{eff}}^{(2)} = -\frac{1}{\Delta} \sum_{ij\sigma} V_{ij} V_{ji} \tilde{n}_{di\sigma} + \frac{1}{\Delta} \sum_{ijj'} V_{ji} V_{ij'} (\tilde{n}_{di\uparrow} c_{j\uparrow}^\dagger c_{j'\uparrow} + \tilde{n}_{di\downarrow} c_{j\downarrow}^\dagger c_{j'\downarrow} + S_i^+ c_{j\uparrow}^\dagger c_{j'\uparrow} + S_i^- c_{j\downarrow}^\dagger c_{j'\downarrow}) \\ + \frac{1}{U-\Delta} \sum_{ijj'} V_{ji} V_{ij'} (-\tilde{n}_{di\downarrow} c_{j\uparrow}^\dagger c_{j'\uparrow} - \tilde{n}_{di\uparrow} c_{j\downarrow}^\dagger c_{j'\downarrow} + S_i^+ c_{j\uparrow}^\dagger c_{j'\uparrow} + S_i^- c_{j\downarrow}^\dagger c_{j'\downarrow}), \quad (3.2)$$

where  $\tilde{n}_{di\sigma} = (1 - n_{di-\sigma}) n_{di\sigma}$ . From this expression it can be seen that although both channels give the same result for the spin-flip terms, this is not true for the carrier-spin conserving terms. One observes that the  $1/\Delta$  process is only possible for aligned carrier spin and localized spin, while for the  $1/(U-\Delta)$  process an antiparallel alignment is required. This is evident from Fig. 3. For non-spin-flip processes it is required that the "initial" and "final" carrier spins are the same and the only possibilities are then the ones indicated in the figure. The negative sign of the  $1/(U-\Delta)$  term follows from the Fermi statistics due to the reversed order of holes in the lattice after the considered second-order process.

In the study of magnetic semiconductors such as the Eu chalcogenides<sup>33</sup> or semimagnetic semiconductors,<sup>34</sup> one usually assumes a Hamiltonian of a similar form to that given by Eqs. (3.1) and (3.2). However, our results suggest that the description of these systems may be considerably refined. First, we note that a tight-binding description is more appropriate for relatively ionic systems. This introduces a strong  $\mathbf{k}$  dependence of the coupling constants as can be inferred from Eqs. (3.1) and (3.2). This  $\mathbf{k}$  dependence is a natural consequence of the exchange interaction taking place between the localized spins and the Bloch waves in a crystal and not with the plane-wave-like

electronic states.<sup>35</sup> Second, the scattering is found to be different for the parallel and antiparallel alignment of carrier and local spin for the considered kinetic exchange mechanism, as is particularly evident from Eq. (3.2). We expect that these points are of a more general significance. Strictly speaking, the exchange we find is antiferromagnetic (AF) [Eq. (3.1)]. This is characteristic of the spin-degenerate case we study here and is not in conflict with the ferromagnetic exchange found in, e.g., the Eu chalcogenides.<sup>33,36</sup> Besides the exclusively ferromagnetic direct  $p$ - $d$  (or  $d$ - $f$ ) exchange which is expected to be relatively important in  $4f$  systems, it is very possible that the kinetic exchange mechanism gives rise to a ferromagnetic coupling if we consider higher degeneracies.<sup>37</sup> This is currently under investigation.

In order to gain some more insight into the nature of the electronic states which follow from  $H_{\text{eff}}^{(2)}$ , we have considered a simple linear chain consisting of alternating  $p$  orbitals and spins localized in  $d$  orbitals (see Fig. 4). In  $H_{\text{eff}}^{(0)}$  we include nearest-neighbor  $p$ - $p$  hopping of magnitude  $t$  which gives the dispersion of the carrier states  $\varepsilon_k$ . The  $p$  and  $d$  states interact due to the nearest-neighbor hybridization  $V$  [see Eq. (1.1)]. The resulting effective Hamiltonian may be written as follows:

$$H_{\text{eff}} = H_{\text{eff}}^{(0)} + H_{\text{eff}}^{(2)} = \sum_{k\sigma} \varepsilon_k n_{k\sigma} - 2 \frac{NV^2}{\Delta} + \sum_{kq} J(\Delta; k, q) (\tilde{n}_{dq\uparrow} c_{k\uparrow}^\dagger c_{k+q\uparrow} + \tilde{n}_{dq\downarrow} c_{k\downarrow}^\dagger c_{k+q\downarrow} + S_q^+ c_{k\uparrow}^\dagger c_{k+q\uparrow} + S_q^- c_{k\downarrow}^\dagger c_{k+q\downarrow}) \\ + \sum_{kq} J(U-\Delta; k, q) (-\tilde{n}_{dq\downarrow} c_{k\uparrow}^\dagger c_{k+q\uparrow} - \tilde{n}_{dq\uparrow} c_{k\downarrow}^\dagger c_{k+q\downarrow} + S_q^+ c_{k\downarrow}^\dagger c_{k+q\downarrow} + S_q^- c_{k\uparrow}^\dagger c_{k+q\uparrow}), \quad (3.3)$$

where we defined

$$\varepsilon_k = -2t \cos k, \\ \tilde{n}_{dq\sigma} = \frac{1}{N} \sum_n \tilde{n}_{dn\sigma} e^{-iq \cdot \mathbf{n}}, \\ S_q^a = \frac{1}{N} \sum_n S_n^a e^{-iq \cdot \mathbf{n}}, \quad a = +, -, \\ J(D; k, q) = \frac{V^2}{D} [1 - e^{-ik} + e^{iq}(1 - e^{ik})]. \quad (3.4)$$

The first approximation to the solution of Eq. (3.3) is the mean-field (or Zener) approximation where one neglects the spin-flip terms. This is expected to be a good approximation in the weak-coupling regime ( $t \gg J$ ).<sup>33,36</sup> Assuming a ferromagnetic alignment for the localized spins, we have only to consider  $q=0$  and it follows ( $\tilde{n}_{dq=0\uparrow} = 1$ ,  $\tilde{n}_{dq=0\downarrow} = 0$ )

$$H_{\text{eff}}(F) = \sum_k [E_F(k, \uparrow) n_{k\uparrow} + E_F(k, \downarrow) n_{k\downarrow}] - 2 \frac{NV^2}{\Delta} \quad (3.5)$$

with the dispersion relations for the two spin directions

given by

$$E_F(k, \uparrow) = \frac{2V^2}{\Delta} (1 - \cos k) - 2t \cos k, \\ E_F(k, \downarrow) = -\frac{2V^2}{U-\Delta} (1 - \cos k) - 2t \cos k. \quad (3.6)$$

These carrier subbands are presented in Fig. 4(a) for  $t=0$ . In this case we have a majority spin band of antibonding character (with respect to holes) and of width equal to  $4V^2/\Delta$ . On the other hand, the minority spin band disperses downwards and has a width of  $4V^2/(U-\Delta)$ . The one-particle calculation is exact for the majority spin band, and it is easy to see that this band coincides in our calculation with the antibonding band found if (1.1) is treated up to second order in  $V$  for  $U=0$ . On the other hand, the down-curving  $U-\Delta$  band is a many-body feature. This is the lattice generalization of the bound state appearing below the ligand band if  $U$  was lowered with respect to  $\Delta$  in the impurity theory for transition-metal compounds.<sup>24</sup> Although our mean-field approximation gives only qualitative information about electronic states, it is expected that the general features

will survive if the spin-flip terms are included (see, e.g., Ref. 38). However, we see that the asymmetry between the minority and majority bands is certainly beyond the reach of the usual magnetic semiconductor models where a single (in our case AF) spin-carrier coupling constant is assumed.<sup>39</sup> For comparison we show as well the bands obtained at the presence of large hopping  $t$  in Fig. 4(b). As can be seen, in this specific case the free-carrier dispersion simply adds to the dispersions shown in Fig. 4(a) and the qualitative picture remains similar.

Another interesting case to consider is the one with antiferromagnetically ordered local spins. Taking  $q = \pi/2$  ( $\bar{n}_{dq = \pi/2, \sigma} = \frac{1}{2}$ ), we find

$$H_{\text{eff}}(\text{AF}) = \sum_{k\sigma} [E_{\text{AF}}(+, k) + E_{\text{AF}}(-, k)] n_{k\sigma} - \frac{N_A V^2}{\Delta} \quad (3.7)$$

with  $N_A$  referring to the number of AF unit cells,  $k$  defined in the AF Brillouin zone, and

$$E_{\text{AF}}(\pm, k) = V^2 \left[ \frac{1}{\Delta} - \frac{1}{U-\Delta} \right] \pm \left\{ \left[ V^2 \left( \frac{e^{ik}}{\Delta} - \frac{1}{U-\Delta} \right) + 2t \cos \left( \frac{k}{2} \right) \right] \left[ V^2 \left( \frac{e^{-ik}}{\Delta} - \frac{1}{U-\Delta} \right) + 2t \cos \left( \frac{k}{2} \right) \right] \right\}^{1/2}. \quad (3.8)$$

This result may be again interpreted by first neglecting  $t$ , in which case Eq. (3.8) reduces to

$$E_{\text{AF}}(\pm, k) = V^2 \left[ \frac{1}{\Delta} - \frac{1}{U-\Delta} \right] \pm V^2 \left[ \left( \frac{1}{\Delta} \right)^2 + \left( \frac{1}{U-\Delta} \right)^2 - \frac{2 \cos k}{\Delta(U-\Delta)} \right]^{1/2}. \quad (3.9)$$

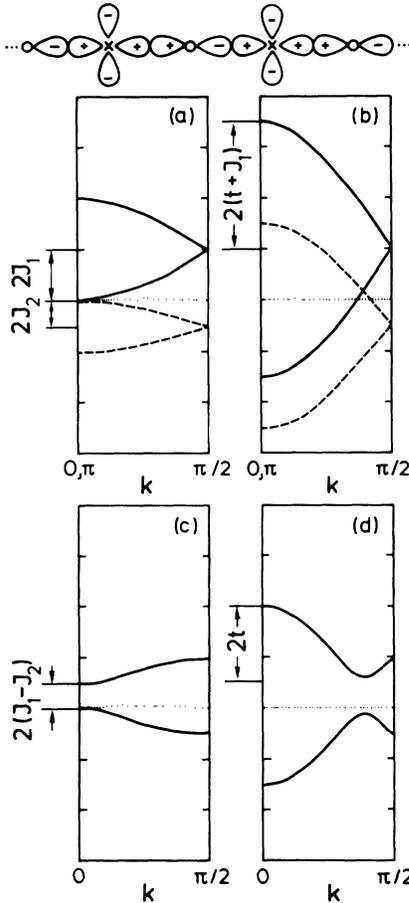


FIG. 4. Bands obtained in the mean-field approximation for the spin-carrier interaction in the indicated one-dimensional Cu-O model. Upper part assuming a ferromagnetic spin-lattice: (a) without and (b) with direct  $p$ - $p$  overlap  $t$ , respectively. Solid (dashed) lines represent majority (minority) spin in a folded Brillouin zone. (c) and (d) the same for the antiferromagnet. Dotted lines indicate the reference energy and  $J_1 = V^2/\Delta$ ,  $J_2 = V^2/(U-\Delta)$ .

If either  $V/\Delta$  or  $V/(U-\Delta)$  goes to zero, two dispersionless bands are found at 0 and  $-2V^2/(U-\Delta)$  or  $2V^2/\Delta$ , respectively. The reason for this localization is immediately clear from Eq. (3.2). If the carrier spin has the proper orientation to hop over a particular spin, the neighboring spins have the opposite orientation and, therefore, the carrier is trapped between them. If, however, both  $V/\Delta$  and  $V/(U-\Delta)$  are finite, the carrier is propagating and the dispersions of the two bands are indicated in Fig. 4(c). We see that the bottom of the band is located at  $-2V^2/(U-\Delta)$ , while for the ferromagnet we found this quantity to be  $-4V^2/(U-\Delta)$ . We see that on the mean-field level the carrier can decrease its energy considerably by polarizing the spin lattice ferromagnetically. Therefore, despite the complications arising from the two types of processes and the  $k$  dependences, the cornerstones of the magnetic semiconductor picture, namely spin polarons<sup>40</sup> and double exchange in antiferromagnets,<sup>41</sup> are unaltered in the mean-field picture.

In Fig. 4(d) we show a more relativistic example using a large, positive  $t$ . From this figure we can get some impression about the complexities arising from a  $k$ -dependent  $J$ . As can be inferred from Eq. (3.8), the bottom of the band moves in any case from the  $X$  to the  $\Gamma$  point if  $2t > V^2[1/\Delta - 1/(U-\Delta)]$ . We find that the lowest energy state for the carrier is now at  $V^2[-1/\Delta + 1/(U-\Delta)] - 2t$ . This means that for  $1/\Delta > 3/(U-\Delta)$  one finds even AF double exchange, at least on the mean-field level.

It is expected that the influence of spin-flip processes (quantum fluctuations) is particularly significant for small spin. Zhang and Rice<sup>42</sup> suggested recently a one-step renormalization procedure by which the Hamiltonian Eq. (3.1) may be mapped on a RVB (Hubbard) Hamiltonian. In the first step of this procedure one constructs (nonorthogonal) Wannier orbitals out of the  $p$  states which are largely localized on the four oxygen ions surrounding each copper ion. Solving Eq. (3.1) for an oxygen hole localized in this way, coupled to a Cu spin, one

finds a singlet ground state and triplet and nonbonding excited states. Zhang and Rice show then that the splittings between these localized states are much larger than the matrix elements connecting such states on different sites. This finding suggests that the internal electronic structure of the  $\text{CuO}_4$  squares can be neglected. One associates a local singlet state with each oxygen hole and this singlet hops around in the lattice formed by the Cu spins, as described by the RVB Hamiltonian.

These ideas can be illustrated using the small cluster indicated in Fig. 5, which can be easily solved exactly. For the localized spins we introduce the basis

$$\begin{aligned} |S\rangle &= (|1^+2^- \rangle - |1^-2^+ \rangle) / \sqrt{2}, \\ |T_0\rangle &= (|1^+2^- \rangle + |1^-2^+ \rangle) / \sqrt{2}, \text{ etc.} \end{aligned} \quad (3.10)$$

The carrier wave functions for the considered cluster are ( $k=0, \pi$ )

$$c_{0\sigma}^\dagger = (c_{1\sigma}^\dagger + c_{2\sigma}^\dagger) / \sqrt{2}, \quad c_{\pi\sigma}^\dagger = (c_{1\sigma}^\dagger - c_{2\sigma}^\dagger) / \sqrt{2}. \quad (3.11)$$

Inserting Eqs. (3.10)–(3.11) into Eqs. (3.3)–(3.4), it is found that the  $k=0$  carrier is nonbonding with respect to the spin system and we end up with a Hamiltonian which can be solved easily. The energies of the cluster with one charge carrier are shown schematically in Fig. 5. Besides the eightfold degenerate  $k=0$  state, we have the quartet ( $Q$ ) and doublet ( $D_n$ ) eigenstates

$$\begin{aligned} |Q\rangle &\approx |T_1; \pi \uparrow\rangle, \\ |D_1\rangle &\approx (\sqrt{2} |T_1; \pi \downarrow\rangle - |T_0; \pi \uparrow\rangle) / \sqrt{3}, \\ |D_2\rangle &\approx |S; \pi \uparrow\rangle, \end{aligned} \quad (3.12)$$

with energies

$$\begin{aligned} E(Q) &= \frac{4V^2}{\Delta}, \\ E(D_1) &= \frac{-6V^2}{U-\Delta} - \frac{2V^2}{\Delta}, \\ E(D_2) &= 2V^2 \left[ \frac{1}{\Delta} - \frac{1}{U-\Delta} \right]. \end{aligned} \quad (3.13)$$

In the mean-field model we found

$$\begin{aligned} E_{\text{MF}}(|1^+2^+; \pi \uparrow\rangle) &= \frac{4V^2}{\Delta}, \\ E_{\text{MF}}(|1^+2^+; \pi \downarrow\rangle) &= -\frac{4V^2}{U-\Delta}, \\ E_{\text{MF}}(|1^+2^-; \pi \uparrow\rangle) &= 2V^2 \left[ \frac{1}{\Delta} - \frac{1}{U-\Delta} \right]. \end{aligned} \quad (3.14)$$

From comparing Eqs. (3.13)–(3.14) it is seen that the ground-state energy is considerably lowered by the inclusion of the transverse spin fluctuations. Further, from Eq. (3.12) it is found that the local spin correlation  $\langle S_{z1} S_{z2} \rangle$  is lowered from  $\frac{1}{4}$  in the mean-field ground state to  $\frac{1}{6}$  in the  $|D_1\rangle$  wave function. This can be understood to be a consequence of the local singlet formation. In fact, the Zhang-Rice construction turns out to be exact for this

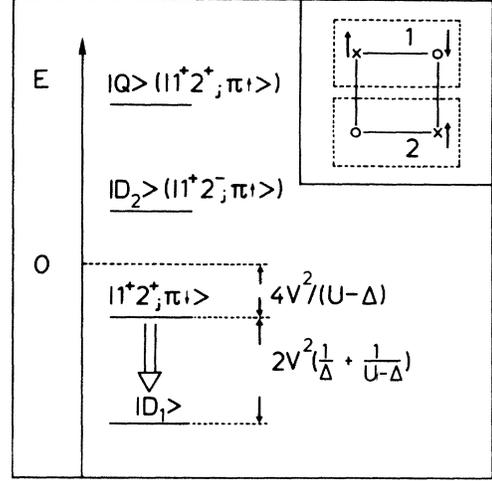


FIG. 5. Energy levels for the cluster consisting of two unit cells, indicated in the inset. Exact eigenstates are compared with the mean-field results.

case, which is an artifact of this cluster. For the local singlet wave functions we write

$$|\phi_{S1}\rangle = \frac{1}{\sqrt{2}} (|1^+ \pi \downarrow\rangle - |1^- \pi \uparrow\rangle), \quad (3.15)$$

$$|\phi_{S2}\rangle = \frac{1}{\sqrt{2}} (|2^+ \pi \downarrow\rangle - |2^- \pi \uparrow\rangle),$$

and the linear combination

$$|\phi^+\rangle = \frac{1}{\sqrt{3}} (-|\phi_{S1} 2^+\rangle + |1^+ \phi_{S2}\rangle) \quad (3.16)$$

gives just  $|D_1\rangle$ .

Despite its elegance this quasiparticle concept may be to a certain extent misleading. A first criticism relates to the neglect of the  $p$ - $p$  hopping ( $t$ ). As we pointed out, if the intrinsic oxygen bandwidth is much larger than the spin-carrier interactions, the mean-field picture should be essentially correct. There is abundant evidence that local-density calculations yield good estimates for transfer integrals. According to tight-binding fits to the linear augmented-plane-wave (LAPW) bands,<sup>40</sup> as well as results of first-principle tight-binding linear muffin-tin-orbital (LMTO) calculations,<sup>41</sup>  $V \approx 1.2$  eV and  $t \approx 0.5$  eV. Observing that each oxygen has two Cu atoms as nearest neighbors and four O atoms as next-nearest neighbors, as well as taking into account the condition that  $V^2/\Delta$ , etc.,  $< 1$  eV, which has to be satisfied in order to have a meaningful localized picture, it is expected that the real systems are closer to the mean-field picture than to the limit considered by Zhang and Rice.<sup>42</sup>

A second criticism relates to the Zhang-Rice procedure itself. Although it is true that the local splittings are much larger than the matrix elements for intercluster excitation, there is a very large phase space for the latter. Although each excitation separately can be handled by perturbation theory, all these separate contributions can add up to quite a large correction. This is a known caveat of real-space renormalization-group techniques and pre-

liminary calculations indicate that the Zhang-Rice construction is also troubled in this way. Calculations along these lines are in progress.

#### IV. FOURTH ORDER: CARRIER-CARRIER INTERACTIONS OF EMERY'S MECHANISM

Very recently, Emery<sup>20</sup> pointed out that effective attractive interactions arise between the carriers in fourth order in  $V$ . In this section we will quantify these interactions using the canonical perturbation theory, and subsequently show that these interactions are small (fourth-order) corrections to the strongly repulsive carrier-carrier interactions arising from the second-order terms. The physical origin of these fourth-order interactions is analogous to the origin of spin-spin superexchange (see also, the next section), i.e., it is a kinetic mechanism. This is illustrated in Fig. 6, where it is seen that the wave function of two carriers can spread out further for antiparallel-aligned carrier spins than when the spins are aligned in parallel. This gives rise to the energy lowering of the former state as compared to the latter.

From the figure it may be clear that this interaction can arise only when a single local spin site is involved. This implies that we can limit the search for these interactions to the terms collected in  $H_{CC}$  [Eq. (2.8)] containing only a single local spin site. Consequently, we write Eqs. (A1)–(A3) for  $i=i'$ . As a result, we find Kondo-like terms (spin-carrier), carrier-carrier terms, and spin-carrier-carrier ones. The carrier-carrier terms may be written as follows:

$$\begin{aligned} \tilde{H}_{CC}^{(4)} = & -\tilde{J}_{CC} \left[ \sum_{ij} (V_{ji}V_{ij})^2 n_{j\uparrow} n_{j\downarrow} + \sum_{i,j \neq j'} V_{ji}V_{ij}V_{j'i}V_{ij'} (n_{j\uparrow} n_{j'\downarrow} + c_{j\downarrow}^\dagger c_{j'\uparrow}^\dagger c_{j\uparrow} c_{j'\downarrow} + c_{j\downarrow}^\dagger c_{j'\uparrow}^\dagger c_{j\uparrow} c_{j'\downarrow}) \right. \\ & + \sum_{i,j \neq j' \neq j''} V_{ji}V_{ij}V_{j'i}V_{ij''} (n_{j\uparrow} c_{j'\downarrow}^\dagger c_{j''\downarrow} + n_{j\downarrow} c_{j'\uparrow}^\dagger c_{j''\uparrow} + c_{j\downarrow}^\dagger c_{j'\uparrow}^\dagger c_{j\uparrow} c_{j''\downarrow} + c_{j\downarrow}^\dagger c_{j'\uparrow}^\dagger c_{j\uparrow} c_{j''\uparrow} \\ & \left. + c_{j\downarrow}^\dagger c_{j'\uparrow}^\dagger c_{j\uparrow} c_{j''\downarrow} + c_{j\downarrow}^\dagger c_{j'\uparrow}^\dagger c_{j\uparrow} c_{j''\uparrow}) \right], \end{aligned} \quad (4.1)$$

with

$$\tilde{J}_{CC} = \left( \frac{1}{U-\Delta} \right)^3 + \frac{2}{\Delta(U-\Delta)^2} + \frac{2}{\Delta^2(U-\Delta)} + \left( \frac{1}{\Delta} \right)^3. \quad (4.2)$$

As it may be seen, attractive interactions between the carriers are found. These interactions are taking place either on one site or they couple two or three (nearest-neighbor) sites (keeping all four sites different produces three-body terms). We also notice that their strength ( $J_{CC}$ ) is dependent in a symmetric way on  $U-\Delta$  and  $\Delta$ , indicating that the two involved processes are contributing to the carrier-carrier interactions in a similar way.

Let us consider as an example a linear chain with nearest-neighbor  $p$ - $d$  hopping introduced in the preceding section. One obtains then for the interactions in  $k$  space ( $J_{CC} = \tilde{J}_{CC} V^4$ )

$$\tilde{H}_{CC}^{(4)} = -2J_{CC} \frac{1}{N} \sum_{kk'q} \{ [1 + \cos(q)] c_{k\uparrow}^\dagger c_{k'\downarrow}^\dagger c_{k'+q\downarrow} c_{k-q\uparrow} + \cos(q) c_{k\uparrow}^\dagger c_{k'\downarrow}^\dagger c_{k+q\downarrow} c_{k'-q\uparrow} + \cos(k-k') c_{k\uparrow}^\dagger c_{-k'\downarrow}^\dagger c_{-k'+q\downarrow} c_{k-q\uparrow} \}. \quad (4.3)$$

This would correspond to a  $k$ -dependent pairing interaction of the form

$$\begin{aligned} \tilde{H}_{\text{pair}}^{(4)} = & -4J_{CC} \frac{1}{N} \sum_{kk'} [1 + \cos(k)\cos(k')] \\ & \times c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger c_{-k'\downarrow} c_{k'\uparrow}. \end{aligned} \quad (4.4)$$

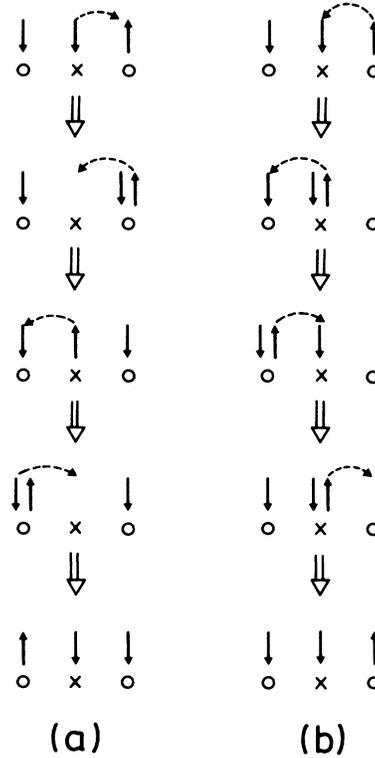


FIG. 6. Examples of processes giving rise to local, spin-mediated carrier-carrier interactions in fourth-order CPT originating from the (a)  $1/\Delta$  and (b)  $1/(U-\Delta)$  mechanism.

Assuming now, as Emery does,<sup>20</sup> that the second-order terms produce just a single-particle band with a renormalized width, one would indeed get a high- $T_c$  superconductor. However, we have seen in the preceding section that these second-order interactions do not reduce to a simple band renormalization but, in fact, produce complicated

dynamics. It is important to note that in the regime of validity of the perturbation theory, the fourth-order terms are going to be overruled by the second-order ones. From the discussion in the preceding section it is clear that the second-order spin-carrier interactions suppress strongly on site singlet correlations between the carriers.

In order to demonstrate this point in more detail, let us consider the finite-size ring introduced in Sec. III. From Eqs. (4.4) and (3.11) it follows that

$$\tilde{H}_{CC}^{(4)} = -4J_{CC}(n_{0\uparrow}n_{0\downarrow} + n_{\pi\uparrow}n_{\pi\downarrow}) . \quad (4.5)$$

The presence of a short-range attractive interaction between the carriers may be tested with the quantity

$$E_{CC} = E_0(2) - 2E_0(1) , \quad (4.6)$$

where  $E_0(1)$  and  $E_0(2)$  are the ground-state energies of the cluster containing one and two carriers, respectively. If  $E_{CC}$  becomes negative, attractive carrier-carrier interaction is present. According to Eq. (3.14),  $E_0(1) = E(D_1)$ . With two carriers in a single cluster one has states  $|0, \pi\rangle$  which are at the same energy as the single-carrier states with only a  $\pi$  electron, and we will therefore find  $E_{CC}(0, \pi) > 0$ . Furthermore, we have the states with two 0 or two  $\pi$  electrons, and these have the energies

$$E(|\text{spin}; 0\uparrow 0\downarrow\rangle) = -4J_{CC} , \quad (4.7)$$

$$E(|\text{spin}; \pi\uparrow \pi\downarrow\rangle) = 4V^2 \left[ \frac{1}{\Delta} - \frac{1}{U-\Delta} \right] - 4J_{CC} .$$

As a result, we end up with

$$E_{CC} = \begin{cases} 4 \left[ V^2 \left( \frac{3}{U-\Delta} + \frac{1}{\Delta} \right) - J_{CC} \right] , & \text{if } U > 2\Delta , \\ 4 \left[ 2V^2 \left( \frac{1}{U-\Delta} + \frac{1}{\Delta} \right) - J_{CC} \right] , & \text{otherwise .} \end{cases} \quad (4.8)$$

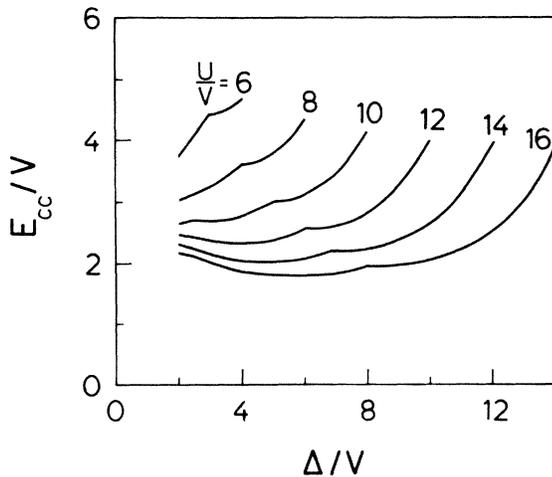


FIG. 7. Effective carrier-carrier repulsion energy  $E_{CC}/V$  in a small cluster including the second-order terms and Emery's interactions.

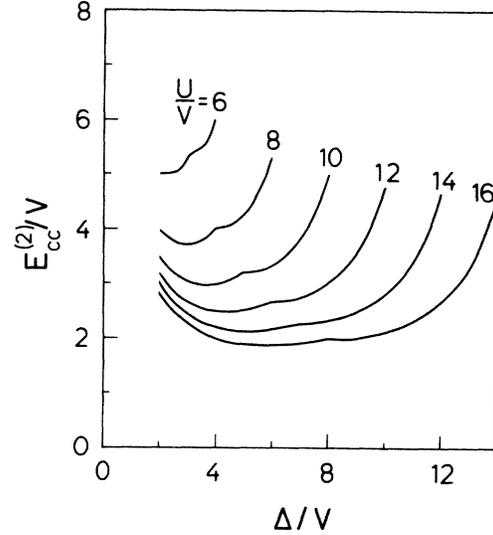


FIG. 8. The same as in Fig. 7, but now showing only the effect of the second-order terms  $E_{CC}^{(2)}/V$ .

In order to have a reasonably well converged result we should require  $\Delta/V \geq 3$  and  $(U-\Delta)/V \geq 3$  (see also the next section). The results for  $E_{CC}$  in this parameter range are presented in Fig. 7. It is found that  $E_{CC}$  is positive for all values of  $U$  and  $\Delta$ , which indicates that the carriers always repel each other. In Fig. 8 we show the quantity  $E_{CC}^{(2)}$  where we only take into account the second-order contributions contained in Eq. (4.8). The comparison of these figures shows that the fourth-order contributions are of minor importance in the regime where the expansion is expected to be well behaved.

The underlying physical picture is straightforward. On the mean-field level, each carrier on its own causes a ferromagnetic polarization cloud in the spin lattice. If the carriers have opposite spins, these polarization clouds have opposite polarizations, which results in a strong short-range repulsive interaction. This interaction is further increased by the transverse spin fluctuation because the carriers restrict each other's fluctuation phase space. The terms such as (4.1) are then a small correction to the leading contributions.

In conclusion, we have shown in this section that Emery's proposal<sup>20</sup> is characterized by the same pathology<sup>43</sup> as many of the proposals based on the Hubbard Hamiltonian.<sup>8-11,44</sup> By making a mean-field approximation in the leading order, one masks strong nearest-neighbor repulsive interactions. The higher-order attractive processes are only a correction to those, and cannot be thus responsible for the pairing.

## V. SPIN-SPIN INTERACTIONS AND HIRSCH'S MECHANISM

It is a well-established fact that the low-temperature properties of magnetic insulators can be described by a spin-only (Heisenberg) Hamiltonian in the absence of carriers. The spin-spin interaction is usually AF, and An-

person already showed long ago<sup>41,45</sup> that this interaction has a kinetic origin (superexchange). By considering a three-site cluster he derived the famous expression  $J_{SS} = -2b^2/U$  with (in our notation)  $b = V^2/\Delta$ . However, this expression is only valid in the ‘‘Mott-Hubbard’’ (MH) regime (i.e., if  $\Delta \gg U$ , as shown in Fig. 1), and only much later Anderson’s procedure was generalized to include also the charge-transfer and intermediate regimes.<sup>46</sup> For the spin-degenerate Anderson lattice it is then found that

$$H = 2J_{SS}(C1) \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1},$$

with

$$J_{SS}(C1) = \frac{V^4}{\Delta^2} \left( \frac{2}{\Delta} + \frac{2}{U} \right). \quad (5.1)$$

Using this formula together with estimates for  $V$ ,  $\Delta$ , and  $U$  derived from spectroscopic data, Zaanen and Sawatzky<sup>47</sup> showed that the trends in the Néel temperatures of the 3d monoxides can be fully reproduced, thereby solving a long-standing quantitative problem with Anderson’s theory.

CSO already showed for the Hubbard Hamiltonian and Anderson’s superexchange, that the canonical perturbation theory can be used to derive the spin-spin Hamiltonian in an elegant way.<sup>29</sup> In this section we will derive an expression for the spin-only interactions valid for (undoped) charge-transfer semiconductors.

It is obvious that the spin-spin interactions arise for the first time in fourth order, and in the absence of carriers only two processes are relevant. They are indicated in Figs. 9(a) and 9(b) as corresponding to the first and second terms in Eq. (2.8). We note that the first process is present independently of the value of  $U$ , while the second one vanishes for  $U - \Delta \rightarrow \infty$  [see also Eq. (5.1)].

In the absence of carriers we find from Eqs. (2.8), (A6), and (A7)

$$H_{SS}^{(4)} = \tilde{H}_{00}^{(4)} + \tilde{H}_{SS}^{(4)},$$

$$\begin{aligned} \tilde{H}_{00}^{(4)} = & -\frac{1}{2} \frac{1}{\Delta^3} \sum_{ii'jj'} V_{ij} V_{ji} V_{i'j'} V_{j'i'} \\ & + \frac{1}{4} \left[ \frac{2}{\Delta^3} - \frac{1}{2} \frac{3U-4\Delta}{\Delta^2(U-\Delta)^2} \right] \sum_{ijj'i'} V_{ij} V_{ji} V_{i'j'} V_{j'i'}, \end{aligned}$$

$$\tilde{H}_{SS}^{(4)} = 2\tilde{J}_{SS}(\text{CPT}) \sum_{ijj'i'} V_{ij} V_{ji} V_{i'j'} V_{j'i'} \mathbf{S}_i \cdot \mathbf{S}_{i'},$$

with

$$\tilde{J}_{SS}(\text{CPT}) = \frac{1}{2\Delta^2} \left( \frac{2}{\Delta} + \frac{1}{2} \frac{3U-4\Delta}{(U-\Delta)^2} \right). \quad (5.2)$$

In this expression,  $\tilde{H}_{00}^{(4)}$  gives an (irrelevant) spin-independent correction to the ground-state energy while in  $\tilde{H}_{SS}^{(4)}$  we recognize the Heisenberg Hamiltonian. If we consider only nearest-neighbor hopping via a single ligand we find

$$\tilde{H}_{SS}^{(4)} = 2J_{SS}(\text{CPT}) \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1},$$

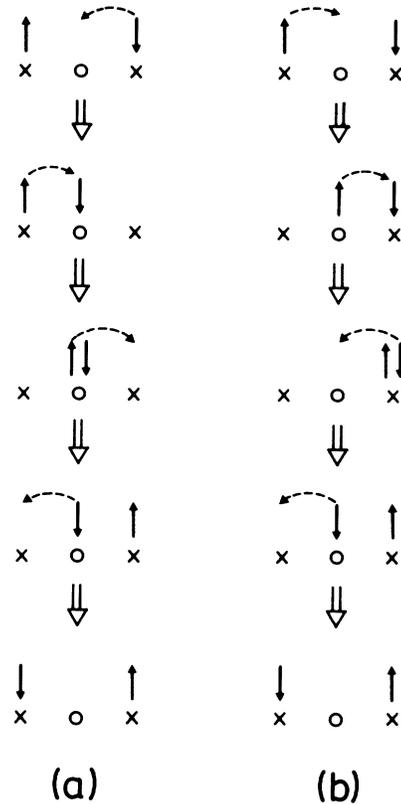


FIG. 9. The two fourth-order channels giving rise to spin-spin superexchange in CPT: (a) charge transfer only ( $1/\Delta$ ); (b) charge-transfer ( $1/\Delta$ ) and  $1/(U-\Delta)$  processes.

with

$$J_{SS}(\text{CPT}) = \frac{V^4}{\Delta^2} \left( \frac{2}{\Delta} + \frac{1}{2} \frac{3U-4\Delta}{(U-\Delta)^2} \right). \quad (5.3)$$

Comparing Eqs. (5.3) and (5.1), it is seen that the exchange constant found from CPT is quite different from the one derived using a Rayleigh-Schrödinger expansion for a three-site cluster. In order to quantify matters we compare in Fig. 10 the singlet-triplet splitting  $E_{ST}$  for two spins, derived from Eqs. (5.1) and (5.3), with the result of the exact electronic calculation for the three-site cluster. As it may be seen in Fig. 10, the  $J_{SS}(C1)$  and  $J_{SS}(\text{CPT})$  behave very similarly as long as  $U-\Delta$  is large. If  $U-\Delta$  becomes small, however, the CPT starts to break down. This is, of course, not surprising and the Rayleigh-Schrödinger expansion is in this respect superior.

A second pairing mechanism in the (localized) two-band framework has been proposed by Hirsch.<sup>21</sup> In contrast to Emery,<sup>20</sup> Hirsch emphasizes the spin-carrier interactions and speculates that these interactions, together with the spin-spin interactions, could give rise to tightly bound singlet pairs of carriers. This picture is based on a few assumptions. The first of them is that the carrier can only pass a Cu ion if it flips the localized (and its own) spin, i.e., only the spin-flip terms in Eq. (3.1) are taken into account. Second, Hirsch assumes<sup>21</sup> that the spins are coupled by an AF superexchange interaction which is

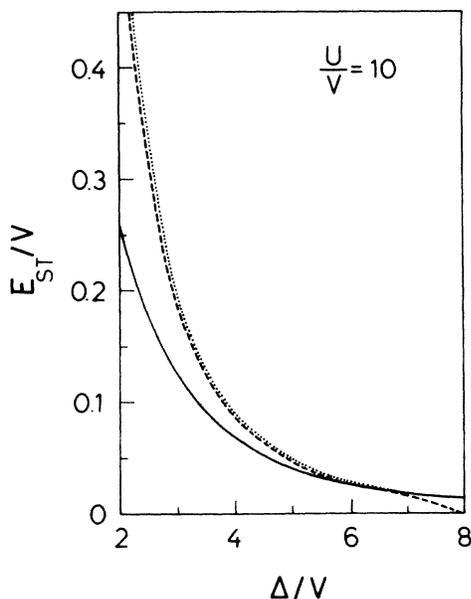


FIG. 10. Comparison of the exact singlet-triplet splitting  $E_{St}$  in a three-site cluster with two holes (solid line) with the CPT (dashed line) and with the Rayleigh-Schrödinger (dotted line) result for different values of  $\Delta/V$ .

much stronger than the spin-carrier interaction. Finally, strong anisotropy effects are assumed which reduce the spin-only problem to the Ising one. Under these assumptions Hirsch argues that a single carrier will become trapped in a two-dimensional lattice (this has been questioned recently<sup>48</sup>) while a pair of carriers with opposite spins is mobile because the second carrier is able to repair the damage in the spin lattice, created by the first one. The respective gain in kinetic energy then stabilizes this singlet spin bipolaron.

There are a couple of reasons why the above-described physical picture is rather unlikely. A first objection to Hirsch's mechanism could be that strong anisotropy effects are not expected in these systems. However, from the results obtained by us so far, more arguments against this mechanism may be extracted. From Eq. (3.1) it is immediately seen that there is no reason to neglect the local spin conserving terms in the carrier-spin interaction. They are, in fact, of equal importance as the spin-flip terms. Finally, the most straightforward argument we can put forward is related to the relative strength of the spin-spin and spin-carrier interaction. It is of similar nature to that used in Sec. IV. Both interactions have the same (kinetic) origin but the former is of higher order than the latter and is, therefore, of relatively minor importance if a truly localized limit is considered and the presented CPT applies.

In order to get some quantitative insight into the pairing mechanism proposed by Hirsch, let us again consider the small ring of Secs. III and IV. In order to describe the magnetic energy and to mimic Hirsch's two-dimensional system, we attach to each spin site three additional local spins. We assume an Ising-type spin-spin interaction with a magnitude given by Eq. (5.3). We notice that in this

way the spin-spin interactions are overemphasized, compared to the carrier-spin interactions. An estimate of the relative importance of these interactions, in the spirit of Hirsch,<sup>21</sup> can be obtained by considering, on the one hand, the ground-state energy of the cluster with a single carrier and all the local spins, including the ring spins, aligned antiferromagnetically. One finds

$$E_0(\text{AF}) = E_{SC}(\text{AF}) + E_{SS}(\text{AF}),$$

$$E_{SC}(\text{AF}) = \begin{cases} 0, & \text{if } U > 2\Delta, \\ 2V^2 \left[ \frac{1}{\Delta} - \frac{1}{U-\Delta} \right], & \text{otherwise,} \end{cases} \quad (5.4)$$

$$E_{SS}(\text{AF}) = -\frac{6V^4}{\Delta^2} \left[ \frac{2}{\Delta} + \frac{1}{2} \frac{3U-4\Delta}{(U-\Delta)^2} \right].$$

It has been assumed that the presence of the carrier on the intermediate ligand ion will break up the spin-spin coupling. This feature follows from the general expressions for the superexchange terms (A6)-(A7) which includes also spin-spin-carrier interactions. On the other hand, we consider the state with the ring spins in a  $|T_1\rangle$  or  $|T_0\rangle$  state [Eq. (3.10)], keeping the other spins fixed. We find then for the ground-state energy

$$E_0(F) = E_{SC}(F) = -2V^2 \left[ \frac{3}{U-\Delta} + \frac{1}{\Delta} \right]. \quad (5.5)$$

The quantity  $E_{SS}/E_{SC} = E_{SS}(\text{AF})/[E_{SC}(F) - E_{SC}(\text{AF})]$  may now be considered as a rough measure of the importance of the spin-spin coupling compared to the spin-carrier interaction. This quantity is presented in Fig. 11 for representative parameter values, and it is seen that the

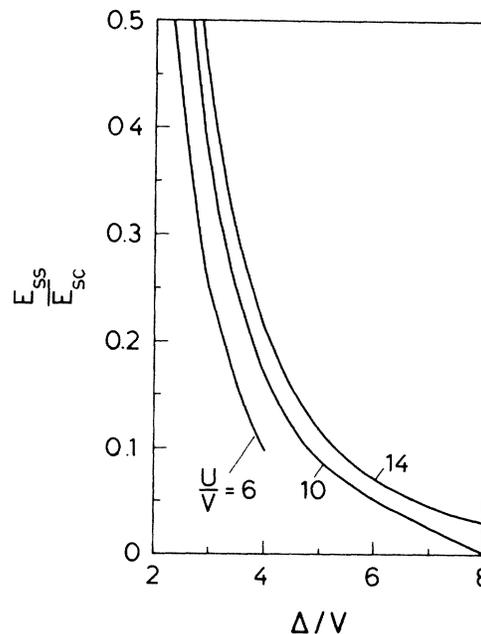


FIG. 11. Ratio of the spin-spin to the spin-carrier energy  $E_{SS}/E_{SC}$  as a function of the charge transfer energy  $\Delta/V$  in a model inspired on Hirsch's proposal.

spin-spin energy is always smaller than the spin-carrier energy in the range of validity of our expansion (see, e.g., Fig. 10), even in this overoptimistic estimation. We expect therefore that Hirsch's pairing mechanism does not exist in a real (change-transfer) semiconductor, and, instead, the usual spin-polaron picture seems to be more appropriate.

In another respect, Fig. 11 is also quite interesting. As can be seen, the importance of the superexchange relative to the spin-carrier exchange is strongly parameter dependent. The reason is that the superexchange is always limited by  $V^3/\Delta^2$ , and is therefore small for large  $\Delta$ , while the latter quantity remains proportional to  $V^2/(U-\Delta)$ . It is therefore expected that the spin polaron in an extreme charge-transfer material ( $U \gg \Delta$ ) is a relatively compact object, while its size grows with increasing  $\Delta$  (or decreasing  $U$ ). It would be interesting to see if this trend can be confirmed by experiment. Systems to search for this trend are possibly the Ni dihalides.<sup>17,18</sup>

## VI. DISCUSSION

In the preceding sections we have systematically explored the physics of the two-band model in the charge-transfer semiconductor regime, i.e., under the assumption of a well-developed  $p$ - $d$  correlation gap. The basic picture we have obtained is not new, but, instead, confirms the common understanding of magnetic semiconductors.<sup>33</sup> At least for low doping concentrations only the Kondo-like spin-carrier interaction and the superexchange between the spins are of relevance on top of the one-particle aspects of the  $p$  band. The former is important because its coupling constant is relatively large, while the spin-spin interaction cannot be neglected because there are many (weakly interacting) spins per carrier.

The new aspects in our work is the explicit connection between the electronic Hamiltonian and the effective description of the near-ground-state physics at low carrier concentrations. In this way we have shown how to bridge, in principle, the gap between, on the one hand, information obtained from the electron spectroscopies and, on the other hand, near-ground-state properties such as transport, magnetic, and thermodynamic ones. We have shown that this relationship is not straightforward. The spin-carrier interactions and the superexchange depend in an intricate and different way on the electronic parameters ( $U$ ,  $\Delta$ ,  $V$ ), suggesting a strong variation of the near-ground-state properties as a function of transition-metal and ligand ion. For instance, we predict that the spin polaron is a relatively compact object for small  $\Delta$  and large  $U$ , while its size will increase with decreasing  $U$  (see Sec. V). We hope that this work will inspire experimentalists to pick up the lead again<sup>49</sup> in the field of concentrated, strongly coupled antiferromagnetic semiconductors.

Among the promising theories the RVB concept of Anderson and co-workers<sup>7</sup> is prominent. An important problem is to bridge the gap between the two-band-like "bare" Hamiltonian and the one-band "generic" Hamiltonian used by Anderson. As we pointed out, one can have strong doubts if this is possible in the regime where the  $d$  degrees of freedom are frozen in. In fact, we expect that

the more conventional ferromagnetic spin-polaron physics is closer to reality. We also showed that the proposals of Hirsch<sup>21</sup> and Emery<sup>20</sup> for two-band superconductors are misleading. Both of these proposals rely on short-range (nearest-neighbor) hole-hole attractions. As pointed out very clearly by Stollhoff,<sup>43</sup> this assumption is unphysical for the single-band Hamiltonian. The strong on-site repulsion tends to reduce considerably the hopping phase space of the carriers if they approach each other, leading to a net repulsion. In the two-band situation the on-site repulsive interaction is "diluted" because of the neglect of  $p$ - $p$  Coulomb interactions and it is natural to discuss the physics in terms of "holes" and "spins." However, the basic effect that the carriers tend to avoid each other on small distance scales is the same. As we showed explicitly, this point is missed both by Hirsch and Emery. They both consider the fourth-order terms to be dominant, overlooking the repulsive effects arising in leading (second) order to which fourth-order terms are merely small corrections.

In our opinion, these findings give reason to be pessimistic about the localized two-band model being the right large-energy scale framework for the high- $T_c$  superconductors. In fact, there are direct indications that a well-developed correlation gap is absent. For instance, transport measurements have shown that both  $n$ - and  $p$ -type carriers are present in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ ,<sup>50</sup> while the transport in the presence of the gap would be exclusively  $p$  type. Also the photoemission data seem to argue against the localized picture. Although, at least for  $\text{La}_2\text{CuO}_{4-\delta}$ , a gap seems to be observed,<sup>5,51</sup> this does not necessarily mean that a localized description makes sense. A much better criterion is the presence of a narrow  $d^n \rightarrow d^{n+1}$  band above the Fermi level (see Sec. II), which is seen clearly in the inverse photoemission of  $\text{CuO}$  (Ref. 5) and also  $\text{NiO}$  (Ref. 16). This feature is missing in the inverse photoemission of the HTSO's and instead a broad band is observed.

From these arguments it may be clear that the charge degrees of freedom of the  $d$  electrons cannot be neglected and the HTSO's should be placed in the mixed-valence regime (MV) of the phase diagram presented in Fig. 1 (see also Refs. 52 and 53). This is also expected when we consider the results of the LD band-structure calculations.<sup>19</sup> These calculations show that the  $p$ - $d$  bands which cross the Fermi energy are unusually wide while the  $d$ -hole count  $n_d$  is rather low [ $n_d \approx 0.5$ , in agreement with core x-ray photoemission spectroscopy data, suggesting  $n_d \approx 0.5$  (Ref. 6) – 0.7 (Ref. 52)]. In this situation we can again use the CPT to project out only the doubly occupied (with holes)  $d$  states, which results in an effective Hamiltonian (up to second order)

$$\begin{aligned}
 H_{\text{MV}}^{(0+2)} = & \sum_{i\sigma} \varepsilon_d n_{di\sigma} + \sum_{j\sigma} \varepsilon_L n_{j\sigma} + \sum_{j \neq j'\sigma} t_{jj'} c_{j\sigma}^\dagger c_{j'\sigma} \\
 & + \sum_{ij\sigma} V_{ij} (\tilde{d}_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger \tilde{d}_{i\sigma}) \\
 & + \frac{1}{U-\Delta} \sum_{ijj'\sigma} V_{ji} V_{ij'} (\tilde{d}_{i\sigma}^\dagger c_{j'-\sigma}^\dagger \tilde{d}_{i\sigma} c_{j'-\sigma} \\
 & - d_{i\sigma}^\dagger c_{j'-\sigma}^\dagger \tilde{d}_{i-\sigma} c_{j'\sigma}) .
 \end{aligned} \tag{6.1}$$

Here we have introduced the pseudofermion operator  $\tilde{d}_{i\sigma}^\dagger = (1 - n_{di-\sigma})d_{i\sigma}^\dagger$ .

Starting from Eq. (6.1), we could, in principle, construct a Bardeen-Cooper-Schrieffer (BCS) -like Hamiltonian by factorizing the hopping term in the spirit of the Gutzwiller approximation<sup>54</sup> and the  $1/U$  term in the usual BCS way. It is easy to show that a pairing theory is then constructed.<sup>37</sup> In fact, such a construction was already proposed by Newns,<sup>23</sup> who used an extension of the slave boson technique to achieve very much the same goal. However, it is rather straightforward to realize that this procedure is a simple extension of the superexchange mechanism for the Hubbard Hamiltonian.<sup>8,9</sup> It thus seems rather unlikely that this mechanism may become effective in HTSO's.

Despite all the negative findings presented in this paper, we are not of the opinion that the search for electronic pairing is hopeless. We have merely shown that superconductivity is unlikely in the (localized) charge-transfer regime, and we have provided additional evidence in favor of the absence of a correlation gap in these materials. To us it then seems more promising to investigate the mixed-valence system [Eq. (6.1)]. In this respect some observations can be made.

The controlling quantity here is the  $d$ -hole count, more than  $U/W$ . Assuming that  $\langle n_d \rangle \approx 0.5$  it is expected that an itinerant picture is somehow more adequate than a localized picture. For instance, either from the Gutzwiller or from the  $T$  matrix approximation an electronic mass enhancement of the order of two is expected which places the HTSO's in the same class as Ni metal, which is clearly an itinerant system. The presence of antiferromagnetism<sup>55</sup> and a gap in the half-filled systems  $\text{La}_2\text{CuO}_4$  and

$\text{YBa}_2\text{Cu}_3\text{O}_6$  is then a problem. However, both in the Rice-Ueda Gutzwiller framework<sup>54</sup> as well as in the Hartree-Fock framework (including self-energy corrections on the one-loop level<sup>56</sup>) one can well account for this AF, including its breakdown. Both these approaches suggest that, upon doping, the normal paramagnetic metallic state is realized, suggesting that the AF gap is nonlocal (i.e., coupled to the order parameter). The question which then remains is if the antiferromagnetic fluctuations in the metallic state are strong enough to give rise to the spin bags as proposed by Schrieffer, Wen, and Zhang.<sup>57</sup>

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#### APPENDIX: FOURTH-ORDER CONTRIBUTIONS IN THE EFFECTIVE HAMILTONIAN

Here we present the general expressions for the fourth-order processes  $H_{\text{eff}}^{(4)}$  as derived from the Hamiltonian (1.1) in the limit of  $V \ll \Delta$  and  $V \ll U - \Delta$ .

The carrier-carrier terms  $H_{\text{CC}}^{(4)}$  (2.8) are

$$\begin{aligned}
P_1 H_1 P_0 H_1 P_1 H_1 P_0 H_1 P_1 = & - \sum_{j_n \sigma_n} \sum_{i \neq i'} [V_{ij_1} V_{ij_2} V_{i'j_3} V_{i'j_4} \tilde{d}_{i\sigma_1}^\dagger \tilde{d}_{i\sigma_2} \tilde{d}_{i'\sigma_3}^\dagger \tilde{d}_{i'\sigma_4} (c_{j_4\sigma_4}^\dagger c_{j_1\sigma_1} - \delta_{j_1j_4} \delta_{\sigma_1\sigma_4}) c_{j_3\sigma_3} \\
& + \delta_{j_3j_4} V_{ij_1} V_{ij_2} V_{i'j_3}^2 \tilde{d}_{i\sigma_1}^\dagger \tilde{d}_{i\sigma_2} \tilde{n}_{di\sigma_3} c_{j_2\sigma_2} c_{j_1\sigma_1}] \\
& - \sum_{j_n} \sum_{i\sigma\sigma'} \{V_{ij_1} V_{ij_2} V_{ij_3} V_{ij_4} [\tilde{n}_{di\sigma} c_{j_2\sigma'}^\dagger (c_{j_4\sigma}^\dagger c_{j_1\sigma} - \delta_{j_1j_4}) c_{j_3\sigma'} + d_{i\sigma}^\dagger d_{i-\sigma} c_{j_2\sigma}^\dagger c_{j_4-\sigma}^\dagger c_{j_1\sigma} c_{j_3\sigma'}] \\
& + \delta_{j_3j_4} V_{ij_1} V_{ij_2} V_{ij_3}^2 (\tilde{n}_{di\sigma} c_{j_2\sigma}^\dagger c_{j_1\sigma} + d_{i\sigma}^\dagger d_{i-\sigma} c_{j_2-\sigma}^\dagger c_{j_1\sigma}) \}, \quad (A1)
\end{aligned}$$

$$\begin{aligned}
P_1 H_1 P_0 H_1 P_1 H_1 P_2 H_1 P_1 + P_1 H_1 P_2 H_1 P_1 H_1 P_0 H_1 P_1 = & - \sum_{j_n \sigma_n} \sum_{i \neq i'} V_{ij_1} V_{ij_2} V_{i'j_3} V_{i'j_4} (\tilde{d}_{i\sigma_1}^\dagger \tilde{d}_{i\sigma_2} \hat{d}_{i'\sigma_3}^\dagger \hat{d}_{i'\sigma_4} + \hat{d}_{i\sigma_1} \hat{d}_{i\sigma_2} \tilde{d}_{i'\sigma_3}^\dagger \tilde{d}_{i'\sigma_4}) c_{j_2\sigma_2}^\dagger (c_{i_4\sigma_4}^\dagger c_{j_1\sigma_1} - \delta_{j_1j_4} \delta_{\sigma_1\sigma_4}) c_{j_3\sigma_3} \\
& + \sum_{j_n \sigma_1 \sigma_2 \sigma_3} \sum_{i \neq i'} V_{ij_1} V_{ij_2} V_{i'j_3} V_{i'j_4} \tilde{d}_{i\sigma_1}^\dagger \tilde{d}_{i\sigma_2} \tilde{n}_{di\sigma_3} (c_{j_2\sigma_2}^\dagger c_{j_4\sigma_3}^\dagger c_{j_1\sigma_1} c_{j_3\sigma_3} + c_{j_2\sigma_3}^\dagger c_{j_4\sigma_2}^\dagger c_{j_1\sigma_3} c_{j_3\sigma_1} - \delta_{j_1j_4} \delta_{\sigma_1\sigma_3} c_{j_2\sigma_2}^\dagger c_{j_3\sigma_1} - \delta_{j_1j_4} \delta_{\sigma_2\sigma_3} c_{j_2\sigma_2}^\dagger c_{j_3\sigma_1}) \\
& + 2 \sum_{j_n} \sum_{i\sigma} V_{ij_1} V_{ij_2} V_{ij_3} V_{ij_4} [\tilde{n}_{di\sigma} (c_{j_2\sigma}^\dagger c_{j_4-\sigma}^\dagger c_{j_1\sigma} c_{j_3-\sigma} - c_{j_2-\sigma}^\dagger c_{j_4\sigma}^\dagger c_{j_1\sigma} c_{j_3-\sigma}) \\
& + d_{i\sigma}^\dagger d_{i-\sigma} (c_{j_2-\sigma}^\dagger c_{j_4\sigma}^\dagger c_{j_1\sigma} c_{j_3\sigma} - c_{j_2\sigma}^\dagger c_{j_4-\sigma}^\dagger c_{j_1\sigma} c_{j_3\sigma})] \\
& + 4 \sum_{j_1 j_2 j_3} \sum_{i\sigma} V_{ij_1} V_{ij_2} V_{ij_3}^2 (\tilde{n}_{di\sigma} c_{j_2-\sigma}^\dagger c_{j_1-\sigma}^\dagger - d_{i\sigma}^\dagger d_{i-\sigma} c_{j_2-\sigma}^\dagger c_{j_1\sigma}) , \quad (A2)
\end{aligned}$$

$$\begin{aligned}
P_1 H_1 P_2 H_1 P_1 H_1 P_2 H_1 P_1 = & - \sum_{j_n \sigma_n} \sum_{i \neq i'} V_{ij_1} V_{ij_2} V_{i'j_3} V_{i'j_4} [\hat{d}_{i\sigma_1}^\dagger \hat{d}_{i\sigma_2} \hat{d}_{i'\sigma_3}^\dagger \hat{d}_{i'\sigma_4} c_{j_2\sigma_2}^\dagger (c_{j_4\sigma_4}^\dagger c_{j_1\sigma_1} - \delta_{j_1j_4} \delta_{\sigma_1\sigma_4}) c_{j_3\sigma_3} \\
& - \delta_{\sigma_3\sigma_4} d_{i\sigma_1}^\dagger d_{i\sigma_2} \tilde{n}_{di' - \sigma_3} (c_{j_2\sigma_2}^\dagger c_{j_4\sigma_3}^\dagger c_{j_1\sigma_1} c_{j_3\sigma_3} + c_{j_4\sigma_3}^\dagger c_{j_2\sigma_2}^\dagger c_{j_3\sigma_3} c_{j_1\sigma_1} \\
& - \delta_{j_1j_4} \delta_{\sigma_1\sigma_3} c_{j_2\sigma_2}^\dagger c_{j_3\sigma_1} - \delta_{j_2j_3} \delta_{\sigma_2\sigma_3} c_{j_4\sigma_2}^\dagger c_{j_1\sigma_1})] \\
& - \sum_{j_n, \sigma, \sigma'} \sum_{i \neq i'} V_{ij_1} V_{ij_2} V_{i'j_3} V_{i'j_4} \tilde{n}_{di - \sigma} \tilde{n}_{di' - \sigma'} c_{j_2\sigma}^\dagger (c_{j_4\sigma'} c_{j_1\sigma} - \delta_{j_1j_4} \delta_{\sigma\sigma'}) c_{j_3\sigma'} \\
& - \sum_{j_n} \sum_{i\sigma\sigma'} V_{ij_1} V_{ij_2} V_{ij_3} V_{ij_4} (\tilde{n}_{di\sigma} c_{j_2 - \sigma}^\dagger c_{j_4\sigma'}^\dagger c_{j_1\sigma'} c_{j_3 - \sigma} - d_{i\sigma}^\dagger d_{i - \sigma} c_{j_2 - \sigma}^\dagger c_{j_4\sigma'}^\dagger c_{j_1\sigma'} c_{j_3\sigma} \\
& - \tilde{n}_{di\sigma} c_{j_2 - \sigma}^\dagger c_{j_3 - \sigma} + d_{i\sigma}^\dagger d_{i - \sigma} c_{j_2 - \sigma}^\dagger c_{j_3\sigma}) , \tag{A3}
\end{aligned}$$

where we have used

$$\sum_{j_n} \dots = \sum_{j_1, j_2, j_3, j_4} \dots, \quad \sum_{\sigma_n} \dots = \sum_{\sigma_1, \sigma_2, \sigma_3, \sigma_4} \dots, \tag{A4}$$

and the operators  $\tilde{d}_{i\sigma}$ ,  $\hat{d}_{i\sigma}$  which are defined as follows:

$$\tilde{d}_{i\sigma} = d_{i\sigma} (1 - n_{i-\sigma}), \quad \hat{d}_{i\sigma} = d_{i\sigma} n_{di-\sigma}. \tag{A5}$$

The above terms describe the interactions between two carriers in the presence of the spin subsystem, as well as between one carrier and the spins. The latter processes renormalize those derived in second order (see Sec. III). Pure carrier-carrier interactions resulting from the above terms are discussed in Sec. IV.

The superexchange terms  $H_{SS}^{(4)}$  (2.9) are of the form

$$P_1 H_1 P_0 H_1 P_0 H_1 P_0 H_1 P_1$$

$$\begin{aligned}
= & - \sum_{j_n} \sum_{ii'\sigma\sigma'} V_{ij_1} V_{ij_2} V_{ij_3} V_{ij_4} [\tilde{n}_{di\sigma} \tilde{n}_{di'\sigma'} c_{j_4\sigma}^\dagger c_{j_3\sigma'}^\dagger c_{j_1\sigma} c_{j_2\sigma'} + \tilde{n}_{di\sigma} d_{i'\sigma'}^\dagger d_{i-\sigma} c_{i_4\sigma}^\dagger c_{j_3\sigma'}^\dagger c_{j_1\sigma} c_{j_2\sigma'} \\
& + d_{i\sigma}^\dagger d_{i-\sigma} \tilde{n}_{di'\sigma'} c_{j_4-\sigma}^\dagger d_{j_3\sigma'}^\dagger c_{j_1\sigma} c_{j_2\sigma'} + d_{i\sigma}^\dagger d_{i-\sigma} d_{i'\sigma'}^\dagger d_{i-\sigma} c_{j_4-\sigma}^\dagger c_{j_3-\sigma}^\dagger c_{j_1\sigma} c_{j_2\sigma'} \\
& - \delta_{j_1j_3} \delta_{\sigma\sigma'} (\tilde{n}_{di\sigma} \tilde{n}_{di'\sigma'} c_{j_4\sigma}^\dagger c_{j_2\sigma'} + d_{i\sigma}^\dagger d_{i-\sigma} \tilde{n}_{di'\sigma'} c_{j_4-\sigma}^\dagger c_{j_2\sigma'}) \\
& - \delta_{j_1j_3} \delta_{\sigma, -\sigma'} (\tilde{n}_{di\sigma} d_{i'\sigma'}^\dagger d_{i-\sigma} c_{j_4\sigma}^\dagger c_{j_2-\sigma} + d_{i\sigma}^\dagger d_{i-\sigma} d_{i'\sigma}^\dagger d_{i-\sigma} c_{j_4-\sigma}^\dagger c_{j_2-\sigma})] \\
& + \sum_{j_1j_2j_3} \sum_{ii'\sigma} V_{ij_1} V_{i'j_2} V_{i'j_3} V_{ij_4} (\frac{1}{2} + 2\mathbf{S}_i \cdot \mathbf{S}_{i'}) c_{j_3\sigma}^\dagger c_{j_1\sigma} + \sum_{j_1j_2j_3} \sum_{ii'\sigma} (V_{ij_1} V_{i'j_3} - V_{i'j_1} V_{ij_3}) V_{i'j_2} V_{ij_4} \tilde{n}_{di' - \sigma} d_{i - \sigma} c_{j_3 - \sigma}^\dagger c_{j_1} \\
& + \sum_{ii'jj'} V_{ij}^2 V_{i'j'}^2 - \sum_{ii'jj'} V_{ij} V_{ij'} V_{i'j} V_{i'j'} (\frac{1}{2} + 2\mathbf{S}_i \cdot \mathbf{S}_{i'}) , \tag{A6}
\end{aligned}$$

$$P_1 H_1 P_0 H_1 P_0 H_1 P_0 H_1 P_1$$

$$\begin{aligned}
= & - \sum_{j_n} \sum_{ii'\sigma\sigma'} V_{ij_1} V_{i'j_2} V_{i'j_3} V_{ij_4} [\tilde{n}_{di\sigma} \tilde{n}_{di'\sigma'} c_{j_2 - \sigma}^\dagger c_{j_4\sigma}^\dagger c_{j_1\sigma} c_{j_3 - \sigma'} - \tilde{n}_{di\sigma} d_{i'\sigma'}^\dagger d_{i-\sigma} c_{j_2\sigma'}^\dagger c_{j_4\sigma}^\dagger c_{j_1\sigma} c_{j_3 - \sigma'} \\
& + d_{i\sigma}^\dagger d_{i-\sigma} \tilde{n}_{di'\sigma'} c_{j_2 - \sigma}^\dagger c_{j_4 - \sigma}^\dagger c_{j_1\sigma} c_{j_3 - \sigma'} - d_{i\sigma}^\dagger d_{i-\sigma} d_{i'\sigma'}^\dagger d_{i-\sigma} c_{j_2\sigma'}^\dagger c_{j_4 - \sigma}^\dagger c_{j_1\sigma} c_{j_3 - \sigma'} \\
& - \delta_{j_1j_4} \tilde{n}_{di\sigma} (\tilde{n}_{di'\sigma'} c_{j_2\sigma'}^\dagger c_{j_3\sigma'} - d_{i'\sigma'}^\dagger d_{i-\sigma} c_{j_2\sigma'}^\dagger c_{j_3 - \sigma'})] \\
& - \sum_{j_1j_2j_3} \sum_{ii'\sigma} V_{ij_1} V_{i'j_2} V_{i'j_3} V_{ij_4} (2\mathbf{S}_i \cdot \mathbf{S}_{i'} - \frac{1}{2}) c_{j_2\sigma}^\dagger c_{j_1\sigma} - \sum_{ii'jj'} V_{ij} V_{i'j} V_{i'j'} V_{ij'} (2\mathbf{S}_i \cdot \mathbf{S}_{i'} - \frac{1}{2}) . \tag{A7}
\end{aligned}$$

The first sums in Eqs. (A6) and (A7) describe the dynamics of carriers interacting with the spins. The spin-spin interactions standing as the last sum in Eqs. (A6) and (A7), respectively, are the superexchange ones as discussed in Sec. V. They are suppressed if a carrier is present at the O atom which is located between the two Cu spins (Fig. 9).

Finally, the remaining spin-carrier interactions  $H_{SC}^{(4)}$  [Eq. (2.10)] have the following contributions:

$$P_1 H_1 P_2 H_1 P_0 H_1 P_2 H_1 P_1$$

$$\begin{aligned}
= & - 2 \sum_{j_n} \sum_{ii'\sigma\sigma'} V_{ij_1} V_{i'j_2} V_{i'j_3} V_{ij_4} (\tilde{n}_{di\sigma} \tilde{n}_{di'\sigma'} c_{j_1 - \sigma}^\dagger c_{j_2 - \sigma}^\dagger c_{j_3 - \sigma} c_{j_4 - \sigma} + \tilde{n}_{di\sigma} d_{i'\sigma'}^\dagger d_{i-\sigma} c_{j_1 - \sigma}^\dagger c_{j_2 - \sigma}^\dagger c_{j_3\sigma'} c_{j_4 - \sigma} \\
& - d_{i\sigma}^\dagger d_{i-\sigma} \tilde{n}_{di'\sigma'} c_{j_1 - \sigma}^\dagger c_{j_2 - \sigma}^\dagger c_{j_3 - \sigma} c_{j_4\sigma} + d_{i\sigma}^\dagger d_{i-\sigma} d_{i'\sigma'}^\dagger d_{i-\sigma} c_{j_1 - \sigma}^\dagger c_{j_2 - \sigma}^\dagger c_{j_3\sigma'} c_{j_4\sigma}) , \tag{A8}
\end{aligned}$$

$$\begin{aligned}
& P_1 H_1 P_0 H_1 P_0 H_1 P_2 H_1 P_1 + P_1 H_1 P_2 H_1 P_0 H_1 P_0 H_1 P_1 \\
&= -2 \sum_{j_n} \sum_{i i' \sigma \sigma'} V_{ij_1} V_{i'j_2} V_{i'j_3} V_{ij_4} (\tilde{n}_{di\sigma} \tilde{n}_{d'i'\sigma} c_{j_1-\sigma}^\dagger c_{j_3\sigma}^\dagger c_{j_2\sigma} c_{j_4-\sigma} \\
&\quad + \tilde{n}_{di\sigma} d_{i'\sigma}^\dagger d_{i'-\sigma} c_{j_1-\sigma}^\dagger c_{j_3-\sigma}^\dagger c_{j_2\sigma} c_{j_4-\sigma} - d_{i\sigma}^\dagger d_{i-\sigma} \tilde{n}_{d'i'\sigma} c_{j_1-\sigma}^\dagger c_{j_3\sigma}^\dagger c_{j_2\sigma} c_{j_4\sigma} \\
&\quad - d_{i\sigma}^\dagger d_{i-\sigma} d_{i'\sigma}^\dagger d_{i'-\sigma} c_{j_1-\sigma}^\dagger c_{j_3-\sigma}^\dagger c_{j_2\sigma} c_{j_4\sigma}) \\
&+ \sum_{j_1 j_2 j_3 i i' \sigma} (V_{ij_1} V_{i'j_2} + V_{i'j_1} V_{ij_2}) V_{ij_3} V_{i'j_3} (\tilde{n}_{di\sigma} \tilde{n}_{d'i'\sigma} - d_{i\sigma}^\dagger d_{i-\sigma} d_{i'\sigma}^\dagger d_{i'-\sigma}) c_{j_1\sigma}^\dagger c_{j_2\sigma} \\
&+ 2 \sum_{j_1 j_2 j_3 i i' \sigma} V_{ij_1} V_{i'j_2}^2 V_{ij_3} (\tilde{n}_{di\sigma} c_{j_1-\sigma}^\dagger c_{j_3-\sigma} - d_{i\sigma}^\dagger d_{i-\sigma} c_{j_1-\sigma}^\dagger c_{j_3\sigma}) , \tag{A9}
\end{aligned}$$

$$\begin{aligned}
& P_1 H_1 P_2 H_1 P_2 H_1 P_2 H_1 P_1 \\
&= - \sum_{j_n \sigma \sigma' i \neq i'} \sum V_{ij_1} V_{i'j_2} V_{i'j_3} V_{ij_4} (\tilde{n}_{di\sigma} \tilde{n}_{d'i'\sigma} c_{j_1-\sigma}^\dagger c_{j_3\sigma}^\dagger c_{j_2\sigma} c_{j_4-\sigma} + \tilde{n}_{di\sigma} d_{i'\sigma}^\dagger d_{i'-\sigma} c_{j_1-\sigma}^\dagger c_{j_3-\sigma}^\dagger c_{j_2\sigma} c_{j_4-\sigma} \\
&\quad - d_{i\sigma}^\dagger d_{i-\sigma} \tilde{n}_{d'i'\sigma} c_{j_1-\sigma}^\dagger c_{j_3\sigma}^\dagger c_{j_2\sigma} c_{j_4\sigma} - d_{i\sigma}^\dagger d_{i-\sigma} d_{i'\sigma}^\dagger d_{i'-\sigma} c_{j_1-\sigma}^\dagger c_{j_3-\sigma}^\dagger c_{j_2\sigma} c_{j_4\sigma}) \\
&- \sum_{j_1 j_2 j_3 i \neq i', \sigma} V_{ij_1} V_{i'j_2}^2 V_{ij_3} (\tilde{n}_{di\sigma} c_{j_1-\sigma}^\dagger c_{j_3-\sigma} - d_{i\sigma}^\dagger d_{i-\sigma} c_{j_1-\sigma}^\dagger c_{j_3\sigma}) . \tag{A10}
\end{aligned}$$

The latter contributions (A8)–(A10) are nonzero only if the carriers are present in the system. They describe dynamics of carriers due to their coupling to the spin subsystem.

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