Effect of the Cu-Cu superexchange on the stability of Zhang-Rice singlets

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We solve exactly a Cu_4O_8 cluster with four and five holes, for parameters for which the low-energy physics of the three-band Hubbard model can be mapped exactly to a t-J model with J=0. When a Cu-Cu superexchange J is included the mapping is no more exact. We investigate the quality of the mapping and the amount of nonorthogonal Zhang-Rice singlets of each low-energy eigenstate as a function of J. We also explain briefly how to calculate a property of the three-band model (such as the Cu and O photoemission intensity) using the t-J model.

A central problem in the theory of high-T_c cuprates is to find the most appropriate model to describe the low-energy physics and its limits of validity.[1–3] After the proposal[4] that the three-band Hubbard model[2,3] can be reduced to the t-J model, there has been much controversy about it.[5–17] Recently a finite-size scaling study of the t-J model suggests that its ground state (for vanishing hole concentration) is a Fermi liquid,[18] while marginal-Fermi-liquid behavior is obtained in a renormalization-group study of the three-band model for sizeable Cu-O nearest-neighbor Coulomb repulsion U_{pd}.[19] Also, spin-charge separation has been found in an effective field theory constructed starting from the effective Hamiltonian given by Eq. (1).[20]

As in Refs. 5–8, 10, 13, our starting point is the second-order effective Hamiltonian obtained after eliminating the Cu-O hopping t_{pd} by means of a standard canonical transformation, plus the Cu-Cu superexchange. When only up to one hole is added to the undoped system and repulsions at distances larger than the nearest-neighbor Cu-O one are neglected, we can write[13]

$$H_{\rm eff} = J_K \sum_{i\delta} \mathbf{S}_i \cdot \mathbf{S}_{i+\delta} + (t_1+t_2) \sum_{i\delta\neq\delta'\sigma\sigma'} d^\dagger_{i\sigma} d_{i\sigma'} p^\dagger_{i+\delta'\sigma'} p_{i+\delta\sigma} - t_2 \sum_{i\delta\neq\delta'\sigma} p^\dagger_{i+\delta'\sigma} p_{i+\delta\sigma} + \frac{J}{2}\sum_{i\delta}[\mathbf{S}_i\cdot\mathbf{S}_{i+2\delta} - \tfrac{1}{4}]. \quad (1)$$

$d^\dagger_{i\sigma}$ ($p^\dagger_{i+\delta\sigma}$) creates an effective hole on a Cu (O) atom at site i ($i+\delta$). The four vectors connecting a Cu atom with its nearest O (Cu) atoms are labeled by δ (2δ). The expressions of the parameters in terms of those of the three-band model are given in Ref. 13. Equation (1) does not contain a correction to the Cu-Cu superexchange when an O ion is in between.[7] The effect of this correction in the present study would only affect slightly the fraction of states orthogonal to Zhang-Rice singlets in the low-energy eigenstates.

We have shown that, for realistic values of t_{pd}, while the results of a canonical transformation up to order t^4_{pd} are quantitatively incorrect, Eq. (1) is still a good representation of the three-band model if the parameters are renormalized by a simple prescription[21] (a better result for J, also free of finite-size effects can be obtained using a Cu_2O_7 cluster[16,12]). In particular, the photoemission and inverse-photoemission spectra at low energies are well reproduced. For the calculation of these spectra, it is necessary to have the expression of the original operators $\tilde{d}^\dagger_{i\sigma}, \tilde{p}^\dagger_{i+\delta\sigma}$ in terms of the effective ones $d^\dagger_{i\sigma}$, $p^\dagger_{i+\delta\sigma}$. When the appropriate transformation of the operators is considered [Ref. 21 for $H_{\rm eff}$, Eqs. (3), (5), and (6) below for a further reduction to a t-J model, or, for example, Ref. 14 for a reduction to a one-band Hubbard model], the contradiction between the three-band model and its low-energy equivalents mentioned by Meinders *et al.*[15] is resolved. Feiner has recently shown that the correct transfer of spectral weight between low and high energy scales can be understood in terms of an effective single-band model.[22]

O-O hopping t_{pp} can also be included. However, its effects and those of t_1 were already discussed in Ref. 16. Here, we start from the limit $t_{pp} = t_1 = J = 0, J_K = 2t_2$ (the Cu^+ configuration is completely inhibited), in which the mapping to the t-J model is exact[6,10] and study how the mapping deteriorates as J is increased.

Zhang[6] considered the subspace Z of all local Zhang-Rice singlet states for one added hole,

$$|\, A_n\rangle = \psi^\dagger_i \,|\, B_n\rangle, \quad (2)$$

where

$$\psi^\dagger_i = \frac{1}{2\sqrt{2}}\sum_\delta (p^\dagger_{i+\delta\uparrow} d^\dagger_{i\downarrow} - p^\dagger_{i+\delta\downarrow} d^\dagger_{i\uparrow});\ |\, B_n\rangle = \prod_{j\neq i} d^\dagger_{j\sigma_j} \,|\, 0\rangle, \quad (3)$$

and n is a shorthand notation for the set of indices i, σ_j with $j \neq i$. States $|\, A_n\rangle$ which differ in a permutation of the singlet and a nearest-neighbor spin have an overlap of magnitude 1/8. The $|\, A_n\rangle$ have also a finite overlap with local triplet states[7] or states in which the $p^\dagger_{i+\delta\sigma}$ enter into a different linear combination than in $\psi^\dagger_i$. We call P_Z the projector on the subspace Z of Zhang-Rice states. Zhang

has shown that, for $t_1 = J = 0, J_K = 2t_2$,

$$(H_{\text{eff}} + 8t_2) \mid A_n\rangle = \sum_m \alpha_{nm} \mid A_m\rangle;$$
$$H_t \mid B_n\rangle = \sum_m \alpha_{nm} \mid B_m\rangle, \tag{4}$$

where H_t is the Hamiltonian of the infinite-U Hubbard model (or t-J model for $J = 0$) with $t = t_2$. Thus, in spite of the fact that the $\mid B_n\rangle$ are orthogonal while the $\mid A_n\rangle$ are not, the eigenvalue problem of $P_Z H_{\text{eff}} P_Z$ in the basis of the $\mid A_n\rangle$ has the same form as the corresponding problem of H_t in the basis of the $\mid B_n\rangle$. The first line of Eq. (4) implies that the $\mid A_n\rangle$ form an invariant subspace under the action of H_{eff}, i.e., $(1 - P_Z)H_{\text{eff}}P_Z = 0$ and then $P_Z H_{\text{eff}}(1 - P_Z) = 0$. Zhang also has shown that $(1 - P_Z)H_{\text{eff}} = 0$. Thus the spectrum of H_{eff} consists of that of $P_Z H_{\text{eff}} P_Z$ (which is the same as that of $H_{t_2} - 8t_2$) plus a highly degenerate zero eigenvalue. This conclusion has been criticized with the argument that the matrix element of H_{eff} between neighboring triplet and singlet states vanishes only for $t_2 = J = 0$ and $J_K = 2t_1$ and thus the mapping would be exact only in this limit.[7] However, when the eigenvalue problem is formulated in terms of matrix elements (rather than in terms of the expansion coefficients α_{nm}), the overlap matrix enters explicitly and has a different form for the basis of the $\mid A_n\rangle$ extended with triplet states[7] and that of the $\mid B_n\rangle$. Our numerical results for the Cu_4O_8 cluster confirm that the mapping is exact in the Zhang limit $t_1 = J = 0, J_K = 2t_2$.

To complete the description of the mapping, it is necessary to specify how to calculate matrix elements of any operator between any two eigenstates of H_{eff} in terms of eigenstates and eigenenergies of the t-J model. This, together with the transformation of the operators which carries the low-energy part of the three-band model into H_{eff},[21] allows one to calculate low-energy properties of the three-band model using the (eventually extended) t-J model. The matrix elements between eigenstates of $H_{\text{eff}} \mid A_\nu\rangle$ can be expressed in terms of those of the corresponding eigenstates of the one-band model $\mid B_\nu\rangle$, for any number of added holes, using the operator

$$T = \prod_i [(1 - n_i)\psi_i^\dagger + n_i];\ n_i = \sum_\sigma d_{i\sigma}^\dagger d_{i\sigma}, \tag{5}$$

which except for a normalization factor transforms the state $\mid B_\nu\rangle$ into the corresponding one $\mid A_\nu\rangle$ (with the same energy as $\mid B_\nu\rangle$ except for an additive constant):

$$\mid A_\nu\rangle = \frac{T \mid B_\nu\rangle}{(\langle B_\nu \mid T^\dagger T \mid B_\nu\rangle)^{1/2}}. \tag{6}$$

In the following, we take the case of only one added hole and modify only J from the Zhang limit $t_1 = J = 0, J_K = 2t_2$. When J is turned on, the spin-flip part of the last term in Eq. (1) mixes the Zhang-Rice states with local triplet states. Using first-order perturbation theory one can estimate that the amount of triplet states in the low-lying eigenstates is of order $J^2/(8t_2^2)$ and is not negligible for the high values of J used in some numerical calculations.[23] However, since the local singlet and triplet states are not orthogonal, this naive estimate is affected by the superposition of triplet states at different sites, and the wave functions should be multiplied by $1 - P_Z$ to quantify the amount of non-Zhang-Rice states. Since the states $\mid A_n\rangle$ are not orthogonal, it is difficult to define the projector in terms of them, particularly for a large system. In the present case, we can use the important property that for $J = 0$, the spectrum of $P_Z H_{\text{eff}} P_Z$ lies in the range $-12t_2 \le E \le -4t_2$ as can be easily shown using Gerschgorin's theorem.[24] From this and the discussion following Eq. (4), we can write

$$P_Z = \sum_{\nu, E_\nu < 0} \mid \psi_\nu^0\rangle\langle\psi_\nu^0 \mid, \tag{7}$$

where E_ν and $\mid \psi_\nu^0\rangle$ are the eigenenergies and eigenstates of H_{eff} in the Zhang limit and the sum is restricted to the eigenstates of negative energy. As J is turned on, we follow adiabatically each of the eigenstates $\mid \psi_\nu\rangle$, classified according to their symmetry properties,[13,16] and calculate the quantity of non-Zhang-Rice states

$$d_\nu = \langle\psi_\nu \mid 1 - P_Z \mid \psi_\nu\rangle. \tag{8}$$

We also calculate for each value of J the optimum parameters of the modified t-J model $H_{tt't''J}$,[16] which best fit the low-energy spectrum of H_{eff} and the mean square deviation σ of the energy levels defined as in Ref. 16.

The modified t-J Hamiltonian is

$$\begin{aligned} H_{tt't''J} = C &+ \epsilon \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} + t \sum_{i\delta\sigma} c_{i+2\delta\sigma}^\dagger c_{i\sigma} \\ &- t' \sum_{i\gamma\sigma} c_{i+\gamma}^\dagger c_{i\gamma} \\ &- t'' \sum_{i\delta\delta'\sigma} c_{i+2\delta'\sigma}^\dagger c_{i+2\delta\sigma}^\dagger (\tfrac{1}{2} - 2\mathbf{S}_i \cdot \mathbf{S}_{i+2\delta}) \\ &+ \frac{J}{2} \sum_{i\delta\sigma} \mathbf{S}_i \cdot \mathbf{S}_{i+2\delta}. \end{aligned} \tag{9}$$

Here 2δ (γ) are the vectors which connect a point in the square lattice with its first (second) nearest neighbors. The term in t'' is obtained[16] from a canonical transformation of effective one-band Hubbard models[9,14,25] or perturbative calculations[17,26] and improves considerably the fitting of the levels when $t_1 \neq 0$.[16] The fitting of the levels of the undoped system requires that J is the same in H_{eff} and $H_{tt't''J}$.

While the mean square deviation σ and the d_ν defined in Eq. (6) are an inverse measure of the quality of the mapping, the expectation value of the effective spin at the O sites,[5,26] is not. This expectation value is not necessarily zero for linear combinations of the $\mid A_n\rangle$. As an example, one can easily check that, for a completely polarized ferromagnetic background, the linear combination of the $\mid A_n\rangle$ [Eqs. (2) and (3)] with wave vector (π, π) has no component of the effective O spin antiparallel to the background. Thus, this linear combination, although obtained from local singlets, has maximum O effective

TABLE I. Percentage of states orthogonal to Zhang-Rice states $100d_\nu$ [Eq. (8)] as a function of J for each of the low-energy eigenstates of H_{eff} [Eq. (1)] for a Cu_4O_8 cluster with $t_1 = 0$, $J_K = 2$, and $t_2 = 1$, and parameters of the modified t-J model [Eq. (9)] which best fit the corresponding eigenenergies. The eigenstates are characterized by their symmetry (Ref. 29), total spin, and energy of the t-J model for $t = 1, J = 0$ [Eq. (9) with $t = 1$ and other parameters equal to zero].

Eigenstates	$J=0$	$J=0.5$	$J=1$	$J=2$	$J=4$
X_4, 1/2, $-\sqrt{12}$	0	3.4×10^{-2}	0.13	0.66	4.96
Γ_1, 1/2, -2	0	5.8×10^{-2}	0.23	0.88	3.00
M_4, 1/2, -2	0	0.14	0.50	1.59	4.12
Γ_3, 1/2, 2	0	1.14	3.64	9.18	16.88
M_2, 1/2, 2	0	0	0	0	0
X_4, 1/2, $\sqrt{12}$	0	0.31	1.26	5.69	29.67
Γ_3, 3/2, -4	0	2.6×10^{-2}	0.11	0.48	2.39
X_4, 3/2, 0	0	0.23	0.95	4.49	22.03
M_2, 3/2, 4	0	3.18	10.00	22.26	34.20
σ	0	0.101	0.213	0.480	1.086
t	1	0.968	0.922	0.812	0.541
t'	0	8.1×10^{3}	8.0×10^{-3}	1.2×10^{-4}	7.2×10^{-3}
t''	0	-6.4×10^{-3}	-1.2×10^{-2}	-2.0×10^{-2}	-2.9×10^{-2}

spin projection. It is an eigenstate of H_{eff} in the Zhang limit, and is a particular case of the solution of H_{eff} for a completely polarized spin background discussed from opposite points of view by Emery and Reiter[5] and Zhang.[6]

In Table I we represent the quantity $100d_\nu$ of each low-energy eigenstate of H_{eff} for different values of J. We also show the parameters which characterize the fitting of these levels with $H_{tt't''J}$. One can see that the naive perturbative estimate neglecting the overlap between states, $d_\nu = J^2/(8t_2^2)$, is a large overestimation for most of the states. In particular for the state of symmetry M_2 with total spin $S = 1/2$, we obtain $d_\nu = 0$. This state can be described as a combination of eigenstates of the Heisenberg model with $S = 1$ and an effective O hole. For $J < t_2$, the d_ν are approximately proportional to $(J/t_2)^2$, but the coefficient is less than 1/100 for the lower half of the low-energy states. As a consequence, the quality of the fitting with the t-J model is good for $J < t_2$, but it rapidly deteriorates for $J/t_2 > 2$, where the mean square deviation σ becomes of the order of the optimum value of t. The decrease of this value with increasing J is consistent with the increasing amount of non-Zhang-Rice states in the low-energy region, since these states do not propagate [for $J = 0$, $H_{\text{eff}}(1 - P_Z) = 0$.

Since the optimum values of t' and t'' are very small, there is no significant difference between the fitting with the t-J model or the modified version Eq. (9). This fact, together with our previous numerical calculations,[16] suggest that the term in t'' has its origin in the term in t_1 in H_{eff}. This conclusion also agrees with an analytical derivation of a modified t-J model.[27]

Our main conclusion is that the Cu-Cu superexchange interaction J, for realistic values, does not affect sensibly the stability of nonorthogonal Zhang-Rice singlets. We expect a larger effect on orthogonal singlets built using orthogonal O Wannier functions $\alpha_{i\sigma}$ with the same symmetry as the $d_{i\sigma}$ orbitals.[4,12,17] A quantitative study of the stability of these orthogonal singlets in our Cu_4O_8 cluster would be affected by important finite-size effects: the Wannier functions $\alpha_{i\sigma}$ in this cluster look different from those of the infinite system and only three of them are linearly independent. This is because the Fourier transform $\alpha_{k\sigma}$ for wave vector $\mathbf{k} = (\pi, \pi)$ does not exist. To avoid this problem one can first transform the Hamiltonian in terms of O Wannier functions and then take a finite cluster. This study is done elsewhere.[28]

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