Comment on "Relevance of Cu-3*d* multiplet structure in models of high-T_c cuprates"

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In a recent work [Jiang *et al.*, Phys. Rev. B **101**, 035151 (2020)], the authors solved a model with a Cu impurity in an O-2*p* band as an approximation to the local electronic structure of a hole doped cuprate. One of their conclusions is that the ground state has only ≈50% overlap with a Zhang-Rice singlet (ZRS). This claim is based on the definition of the ZRS in a different representation, in which the charge fluctuations at the Cu site have been eliminated by a canonical transformation. The correct interpretation of the results, based on known low-energy reduction procedures for a multiband model including $3d^8$ and $3d^{10}$ configurations of Cu, indicates that this overlap is near 94%.

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Three decades after their discovery of high-T_c cuprate superconductors, the issue of the appropriate minimal model that correctly describes the low-energy physics is still debated, as stated by Jiang *et al.* [1]. In particular, the relevance of the Zhang-Rice singlets (ZRSs) at low energies is crucial for the debate [1–8]. Recent papers were published with opposite views about the role of the Zhang-Rice singlets (ZRSs) in tetragonal CuO [9,10].

While the models used to describe the cuprates are periodic and include usually only one Cu *d* orbital, Jiang *et al.* considered an impurity model with only one Cu site embedded in an O band, but included the full structure of the 3*d* Cu shell. This study is relevant, because to explain some Raman and photoemission experiments at excitation energies of order of 1 eV or higher, more than one *d* orbital should be included [1,11,12]. They calculate, in particular, the ground state for two holes, as discussed in more detail below.

The most widely used models used to describe the cuprates can be classified in the following four types in decreasing order of number of degrees of freedom:

(1) The three-band Hubbard model H_{3b} [13,14], which contains the *d* orbital of Cu of b_1 symmetry (x^2-y^2) and the *p* orbitals of O aligned in the direction of the nearest Cu atoms. Usually it includes on-site repulsions at Cu (U_d) and O (U_p), Cu and O interatomic repulsion U_{pd}, in addition to the one-particle terms (described in Ref. [1]): On-site Cu (ϵ_{Cu}) and O (ϵ_O) energies, nearest-neighbor Cu-O hopping t_{pd}, and O-O hopping t_{pp}. The other models are derived from H_{3b}.

(2) the spin-fermion model H_{sf} [3,15], obtained from H_{3b} after eliminating the Cu-O hopping term t_{pd} by means of a canonical transformation. Only the d^9 configuration of Cu is retained, represented by a spin-1/2, which interacts with the fermions of two O bands.[1] An extension of this model to tetragonal CuO was used in Ref. [9].

(3) The one-band Hubbard-like model H_{1b} [8,16,17], derived from H_{3b} using the cell-perturbation method [6,8].

(4) The generalized $t-J$ model H_{GtJ} [2,7], which consists of holes moving in a background of Cu spins-1/2 with antiferromagnetic exchange J, nearest-neighbor hopping t, and additional terms of smaller magnitude. This model is derived as a low-energy effective one for the others [6–8,10].

In the derivation of the last two models, an essential role is played by local ZRSs.

To define properly the ZRSs, it is important to realize that, as for any state or operator, while the *physical meaning* of the states should be the same for all effective Hamiltonians $H_{\rm eff}$ used to describe the cuprates, the*form* depends on $H_{\rm eff}$. In order to give an example with a familiar case, let us consider the simplest half filled Hubbard model $H_{\rm Hubb} = -t\sum_{i\delta} c^\dagger_{i\sigma}c_{i+\delta\sigma} + U\sum_i n_{i\uparrow}n_{i\downarrow}$, where $i+\delta$ denotes the nearest neighbors of site i and $n_{i\sigma} = c^\dagger_{i\sigma}c_{i\sigma}$. It is well known that a canonical transformation that eliminates the hopping term to second order in t leads to the effective Heisenberg Hamiltonian $H_{\rm Heiss} = J\sum_{\langle ij\rangle}\mathbf{S}_i\cdot\mathbf{S}_j$, with $J = 4t^2/U$. This Hamiltonian does not contain double occupied sites. Of course, this does not mean that the original Hamiltonian does not contain double occupied sites. In fact, by performing the same canonical transformation to $n_{i\uparrow}n_{i\downarrow}$, one obtains (see, for example, Ref. [18] for the procedure)

$$(n_{i\uparrow}n_{i\downarrow})_{\rm Hubb} = (t/U)^2\sum_\delta\left[\frac{1}{2} - 2(\mathbf{S}_i\cdot\mathbf{S}_{i+\delta})_{\rm Heiss}\right]. \quad (1)$$

Therefore, as expected, unless all nearest neighbors of site i are ferromagnetically correlated with site i, there is a finite double occupancy at this site that can be calculated with $H_{\rm Heiss}$. In fact, although $H_{\rm Heiss}$ is a pure spin model, it has been used to calculate charge-charge and bond-bond correlation functions in a modified Hubbard model with alternating on-site energies [18].

[1]The parameters obtained from a canonical transformation in second order in t_{pd} are not accurate because t_{pd} is not small enough. Improved parameters of H_{sf} were obtained fitting the lowest singlet and triplet states of a CuO_4 cluster described by H_{3b} and the resulting low-energy model H_{sf} was used to calculate Cu and O photoemission spectrum of a Cu_4O_8 cluster, obtaining very good agreement with previous results for H_{3b} in the same cluster [15].

For H_{3b}, the ZRS was defined as the lowest two-hole state of a cell composed of a d orbital of Cu of b_1 symmetry at a site and the Wannier function w of the O p orbitals at the same site Cu site and with the same symmetry [8]. w has 92% overlap [see Eq. (5)] with the linear combination of $2p$ orbitals involving only the O atoms nearest to the Cu site, which we denote as L_{b_1}, following the notation of Ref. [1]. The rest of the Wannier function extends to more distant O sites with decreasing amplitude. Therefore, the ZRS has basically the same form as the ground state for two holes found by Jiang *et al.* in their impurity Hamiltonian for realistic parameters [1]. This state (Eq. (5) of Ref. [1]) is

$$|\psi\rangle = a|b_1b_1\rangle + b|b_1L_{b_1}\rangle + c|b_1L'_{b_1}\rangle + d|d^{10}L^2\rangle + \cdots, \tag{2}$$

where $|b_1b_1\rangle$ represents the state with two d b_1 holes, $|b_1L_{b_1}\rangle$ corresponds to the singlet between a d b_1 hole, L_{b_1}, $|b_1L'_{b_1}\rangle$ is the same for more distant O sites, $|d^{10}L^2\rangle$ corresponds to the state with two O holes, and an ellipsis denotes states which are not included in H_{3b}. It is not expressed how much of the state $|d^{10}L^2\rangle$ corresponds to double occupancy of L_{b_1} (this state, which we denote as $|L^2_{b_1}\rangle$, is the only one included in H_{3b}) but from statements in Ref. [1], I infer that $|d^{10}L^2\rangle \approx |L^2_{b_1}\rangle$. The reported coefficients (except for a phase) are

$$|a|^2 = 0.072,\ |b|^2 = 0.549,\ |c|^2 = 0.054,\ |d|^2 = 0.275. \tag{3}$$

Adding these numbers, one concludes that 95% of $|\psi\rangle$ is consistent with a ZRS and the rest correspond to states not included in H_{3b}.

The representation of the ZRS in H_{sf} corresponds to a singlet between a Cu spin and a hole occupying w at the same site [2]. This was the original definition of the ZRS by Zhang and Rice *because they were using H_{sf} as the original model* [2]. Depending on details of the low-energy reduction procedure, the singlet can also be formed using L_{b_1} instead of the O Wannier function [2,7].[2] The representation of the ZRS in H_{1b} is $|b_1b_1\rangle$ and in H_{GtJ} is a hole. I stress that all representations correspond to the same physical state.

Based on the weight of $|b_1L_{b_1}\rangle$ in $|\psi\rangle$, specifically the value $|b|^2 = 0.549$, Jiang *et al.* [1] conclude that $|\psi\rangle$ "has only about 50% overlap with a ZRS." As explained above, this corresponds to one of the two choices of a ZRS for H_{sf} but not for H_{3b} or a model with more degrees of freedom. However, to calculate an overlap between two states, both should be written in the same representation. In fact, it is easy to realize that a calculation similar to that leading to Eq. (1) can be done using the canonical transformation that maps the low-energy part of H_{3b} to H_{sf}, to show that antiferromagnetic correlations between a Cu spin and the spin of a nearest-neighbor O atom implies both a contribution to the double-hole occupancy of Cu ($|b_1b_1\rangle$ state) of the order of $t^2_{pd}/(U_d - \Delta)$ and to double-hole occupancy of the O atom (part of $|L^2_{b_1}\rangle$) of the order of t^2_{pd}/Δ, for $U_p = U_{pd} = 0$, where $\Delta = \epsilon_O - \epsilon_{Cu}$ [15]. These contributions are not small, since t_{pd} is smaller but of the order of magnitude of the denominators Δ and $U_d - \Delta$.[1]

This is of course expected since $|b_1L_{b_1}\rangle$ in H_{sf} is the representation of the part of $|\psi\rangle$ which contains states included in H_{3b} and in the first O shell around the Cu impurity. It is also natural that experiments in the cuprates identify the ZRS as a mixture of double-hole states d^9L, d^8, and $d^{10}L^2$, and not just d^9L [19].

In the remainder of this work, I made a quantitative comparison of the ZRS obtained using the cell-perturbation method [8] and Eqs. (2) and (3). This comparison is in principle expected to be only semiquantitative, because H_{3b} is a periodic model and in the model of Jiang *et al.* there is only one Cu atom. Therefore, while in H_{3b} the O orbitals tend to form singlets with their nearest neighbor Cu atoms, in the impurity model all O orbitals interact with only one Cu atom. Considering this point, to study the effect of all the Cu d orbitals in the cuprates, it would be probably more realistic to add them to a localized cell including the full d shell at a Cu site and the O Wannier function w at that site than to consider an impurity model.

For $U_p = U_{pd} = 0$, following Ref. [8], the ZRS is obtained as the ground state of the following matrix involving the states $|b_1b_1\rangle$, the singlet between b_1 and the Wannier function $|b_1w\rangle$, and the doubly occupied Wannier function $|w^2\rangle$:

$$\begin{pmatrix} U_d & V & 0 \\ V & \Delta' & V \\ 0 & V & 2\Delta' \end{pmatrix},$$
$$\Delta' = \Delta - 1.4536t_{pp},\ V = 2.7099t_{pd}. \tag{4}$$

Using $U_d = 8.84$, $\Delta = 2.75$, $t_{pd} = 1.5$, $t_{pp} = 0.55$ from Ref. [1] and (see Refs. [6,8])

$$|\langle w|L_{b_1}\rangle|^2 = 0.9180,\ |\langle w|L'_{b_1}\rangle|^2 = 1 - |\langle w|L_{b_1}\rangle|^2, \tag{5}$$

the ground state of the matrix Eq. (4) can be written in the form

$$|\mathrm{ZRS}\rangle = a'|b_1b_1\rangle + b'|b_1L_{b_1}\rangle + c'|b_1L'_{b_1}\rangle + d'|L^2_{b_1}\rangle,$$
$$|a'|^2 = 0.086,\ |b'|^2 = 0.583,\ |c'|^2 = 0.052,$$
$$|d'|^2 = 0.279. \tag{6}$$

Taking into account the difference between the models explained above, the agreement with Eqs. (2) and (3) is remarkable. Assuming $|d^{10}L^2\rangle = |L^2_{b_1}\rangle$, the overlap is $|\langle\psi|\mathrm{ZRS}\rangle|^2 = 0.942$. In an impurity model, the O shells that have a hopping with the Wannier function w reduce its effective energy, increasing its occupancy and decreasing that of b_1, improving the agreement.

In conclusion, the results of Jiang *et al.* [1], interpreted correctly on the basis of existing low-energy reduction procedures from the three-band Hubbard model, support the validity of generalized Hubbard and $t - J$ models based on Zhang-Rice singlets at low energies, even when the full Cu-3d multiplet structure (and not just the x^2-y^2 orbital) is included.

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