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Spin Hamiltonian and hole excitations in the Emery model

M Ya Ovchinnikova

Institute of Chemical Physics, ulitsa Kosygina 4, Moscow 117977, Russia

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Abstract. Extra hole and electron excitations are studied for the simplified Emery model on the basis of the perturbation expansion in the intercluster interaction. The undoped system is described by the hard antiferromagnetic state with localization of holes on the lower hybrid orbitals of clusters. An admixture of the triplet double-hole states of clusters in the lower excitation band of singlet nature indicates the limitation of the single-band mapping of the correlated Emery model excited states.

One of the methods for the description of the electronic structure of HTSCs, as strongly correlated systems, is based on the t–J approach for the Hubbard models [1–4] or for the more realistic Emery models [5–10]. The Hamiltonian for the model of the CuO_2 plane of an HTSC is derived in lower orders of the perturbation theory in t/U and $t/\delta\varepsilon$. Here t is the p–d hopping, $\delta\varepsilon = \varepsilon_p - \varepsilon_d$ is the energy difference between the p and d orbitals and U is the on-centre Coulomb interaction on the Cu site. For an undoped system with one hole per unit cell the ground state (GS) of the CuO_2 plane is presented [5–10] as an aggregate of holes (spins) localized on the d orbitals and described by a spin Hamiltonian. The extra holes of the oxygen system are considered to form a sort of polaron together with the copper spin (the Zhang–Rice [5] singlet or similar polaron states [6–11]).

Practically, the parameters of the above perturbation expansion $4t/U$ and $4t/\delta\varepsilon$ are not small. This means that the strong covalency of the p–d bonds must be taken into account already in the zero order GS of the undoped system. This conclusion follows from various cluster-band models [12–14] which have reproduced many important features of the photoelectron spectra [15].

Recently an improved expansion has been proposed [16, 17] which is convergent even at $\delta\varepsilon \to 0$. It is based on the cluster perturbation method in the intercluster part of the p–d and p–p bond interactions. Each of the non-overlapping clusters (or cells) consists of the d orbital of Cu and the corresponding Wannier combination [18] of the oxygen p orbitals. The zero-approximation basis includes the singly occupied hybrid orbitals of the clusters for undoped systems and the additional lowest singlet states of clusters with the double-hole states in the case of some doping. The largest part of the p–d bond interaction, the intracluster part, has already been taken into account in the zero approximation. For low-energy physics it is important to know the accuracy of the single-band mapping of the problem, that is whether the lower single-hole states of clusters and the lowest singlet double-hole states of clusters are sufficient to describe the excitations in the system. In the present paper we try to answer this question by studying the excitations in the simplest Emery model on the background of the hard antiferromagnetic (AF) state of the undoped system.

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The GS and the spin-wave excitations of the undoped system are described by the effective spin Hamiltonian, deduced by the cluster perturbation method [16, 17]. The extra hole excitations, however, can form polarons with a more complicated structure. In the simplest way their structure can be studied by non-perturbative expansion of the polaron wavefunction over a more complete local basis of the cluster with an extra hole. Making some assumption about the GS one can obtain the extra hole excitation energy in a variational way. This consideration allows one to verify the correctness of the one-band mapping for the charge polaron states.

The original model is formulated in terms of the $d_{x^2-y^2}$ orbitals of Cu and p_x and p_y orbitals of oxygen and is parametrized by $\delta\varepsilon = \varepsilon_p - \varepsilon_d$, the p–d hopping t and the on-site Coulomb interaction $U = U_d$ on Cu only. According to [16, 17] the cluster basis $\{d_n a_n c_n\}$ contains the symmetry-adopted local orbitals [18]:

$$\ddagger{a}_{n\sigma} = N^{-1/2}\sum_k \exp(-ikn)\ddagger{a}_{k\sigma} \qquad \ddagger{c}_{n\sigma} = N^{-1/2}\sum_k \exp(-ikn)\ddagger{c}_{k\sigma}. \tag{1}$$

Here a_k and c_k refer to the states which participate in the bonding and antibonding solutions $\cos\gamma_k d_k + \sin\gamma_k a_k$ and $\sin\gamma_k d_k - \cos\gamma_k a_k$ of the linearized Emery problem and c_k refers to the orthogonal combination corresponding to the non-bonding p band which is separated from the (a, d) band:

$$\ddagger{a}_{k\sigma} = (-e_x s_x \ddagger{x}_{k\sigma} + e_y s_y \ddagger{y}_{k\sigma})/f_k \qquad \ddagger{c}_{k\sigma} = (e_x s_y \ddagger{x}_{k\sigma} + e_y s_x \ddagger{y}_{k\sigma})/f_k \tag{2}$$

$$\begin{aligned} &e_{x(y)} = \mathrm{i}\exp(\mathrm{i}k_{x(y)}/2) \qquad s_{x(y)} = \sin(k_{x(y)}/2) \\ &\tan(2\gamma_k) = \delta\varepsilon/4tf_k \qquad f_k = (s_x^2 + s_y^2)^{1/2}. \end{aligned} \tag{3}$$

Four p orbitals of the first coordination sphere with appropriate signs give the main contribution of about 0.918 to the norm of the orbital a_n.

In the basis $\{d_n a_n c_n\}$ the Hamiltonian of the system is

$$H = H_0 + V \tag{4}$$

$$H_0 = \sum_n h_n = \sum_{n,\sigma}[\varepsilon_d n^d_{n\sigma} + \varepsilon_p(n^a_{n\sigma} + n^c_{n\sigma}) + \tfrac{1}{2}U_d n^d_{n\sigma} n^d_{n-\sigma} + 2t(\ddagger{d}_{n\sigma}a_{n\sigma} + \mathrm{HC})] \tag{5}$$

$$V = \sum_{n\neq m} V_{nm} = 2t\sum_{n\neq m}\sum_\sigma F_{n-m}(\ddagger{d}_{n\sigma}a_{m\sigma} + \mathrm{HC}) \tag{6}$$

$$F_l = N^{-1}\sum_k \exp(\mathrm{i}kl) f_k. \tag{7}$$

The zero-order functions of the undoped system assume the form

$$\Psi_{\mathrm{Loc}}(\{\sigma_n\}) = \prod_n \ddagger{b}_{n,\sigma_n}|0\rangle \qquad b_{n\sigma} = s_\alpha d_{n\sigma} + c_\alpha a_{n\sigma} \tag{8}$$

$$c_\alpha = \cos\alpha \qquad s_\alpha = \sin\alpha \qquad \tan(2\alpha) = 4tF_0/\delta\varepsilon. \tag{9}$$

Functions (8) correspond to localization of the holes on the lower hybrid orbitals of clusters. This differs from the zero approximation assuming the localization on the d orbitals only [5–10].

The zero-order energy corresponding to localized state (8) is

$$\langle H\rangle = NE_b \qquad E_b = \tfrac{1}{2}(\varepsilon_d + \varepsilon_p) - [(\tfrac{1}{2}\delta\varepsilon)^2 + 4t^2F_0^2]^{1/2}. \tag{10}$$

Here $F_0^2 = 0.918$ and the energy E_b of the lowest hybrid orbital b_n of the cluster $(d_n a_n c_n)$ is lower than the energy of the lowest hybrid orbital of the linear cluster O–Cu–O [12–14] which is given by equation (10) on replacing F_0^2 by the value 0.5. This provides one of the advantages of the choice of the symmetric clusters $(d_n a_n c_n)$ instead of the linear three-atomic clusters of x and y orientation.

In the improved perturbation expansion [16, 17] the energy (10) of the zero-order state (8) is considerably lower than the mean energy $\langle H\rangle^d/N = \varepsilon_d$ for the states $\Psi^d_{Loc} = \prod_n \hat{d}^{\dagger}_{n,\sigma_n}|0\rangle$ with localization of holes on the d orbitals only. Since each cluster (d_n, a_n) contains only one Cu site, the single occupation of its hybrid orbital b_n excludes automatically the configurations with the double occupation of the d orbitals also.

The terms of second order in V lead to the effective spin Hamiltonian of the undoped system:

$$H = N(E_b + \delta E) + \sum_{m\neq n} G(m-n)(S_nS_m - \tfrac{1}{4}) \tag{11}$$

$$\delta E = B\sum_{l\neq 0} F_l^2 \qquad G(l) = (B-A)F_l^2. \tag{12}$$

The terms A and B correspond to the contributions of the intermediate singlet and triplet double-hole states in the second-order correction to the energy:

$$A = 4t^2\sum_{\lambda}[(S_{1\lambda} + S_{3\lambda})\sin(2\alpha) + \sqrt{2}S_{2\lambda}]^2(2E_b - E_\lambda)^{-1} \tag{13}$$

$$B = 4t^2\cos^2(2\alpha)(2E_b - \varepsilon_d - \varepsilon_p)^{-1} \tag{14}$$

where E_λ and $S_{i\lambda}$ are the eigenvalues and eigenvectors of the cluster Hamiltonian:

$$(h_n)_{ij}S_{j\lambda} = S_{i\lambda}E_\lambda \qquad (h_n)_{ij} = 2\bar{\varepsilon}\delta_{ij} + \begin{bmatrix} \varepsilon & w & 0 \\ w & 0 & w \\ 0 & w & -\delta\varepsilon + U \end{bmatrix}_{ij} \tag{15}$$

in the basis of the double-hole singlet configurations of the cluster:

$$\phi_{in} = \{\hat{d}^{\dagger}_{n\uparrow}\hat{d}^{\dagger}_{n\downarrow}, (\hat{d}^{\dagger}_{n\uparrow}\hat{d}^{\dagger}_{n\downarrow} + \hat{d}^{\dagger}_{n\uparrow}\hat{d}^{\dagger}_{n\downarrow})/\sqrt{2}, \hat{d}^{\dagger}_{n\uparrow}\hat{d}^{\dagger}_{n\downarrow}\}_i \qquad i = 1\text{–}3. \tag{16}$$

Here $\bar{\varepsilon} = \frac{1}{2}(\varepsilon_d + \varepsilon_p)$, $w = 2tF_0$, and F_l and α are determined by equations (7) and (9). At large l the coefficients F_l decrease as $1/2\pi l^3$. The first values are $F_l = 0.958, 0.140, 0.0235, 0.0014$, etc, at $l = (0,0), (1,0), (1,1), (2,0)$, etc. So it is sufficient to take into account the exchange interaction of spins of the neighbouring clusters only since $G(l) \simeq |l|^{-6}$ at large $|l|$ and $G(1,1)/G(1,0) = 0.028$.

For the reasonable parameters $|\delta\varepsilon/2t| = 1$ and $U/t = 7$, the second-order correction to the energy is smaller than the energy gain $\Delta E_0 = E_b - \varepsilon_d$ (per unit cell) owing to the exact incorporation of the intracluster part of the p–d bond energy. For the hard ferromagnetic (F) and AF spin configurations these corrections to the energies and ΔE_0 are

$$\delta E^F = -0.032t \qquad \delta E^{AF} = -0.330t \qquad \Delta E_0 = 1.16t.$$

Values of δE remain small even at $\delta\varepsilon \to 0$. For example, at $U = \infty$, $\delta\varepsilon = 0$, one obtains $\delta E^{\mathrm{F}} = 0$ and $\delta E^{\mathrm{AF}} = -0.204t$.

It should be stressed that S_n in (11) is the total spin of the hole localized on the cluster and the spin density $\langle S_z^{\mathrm{d}}\rangle = c_\alpha^2\langle S_z\rangle$ on the Cu site is smaller than $\langle S_z\rangle$ predicted by the 2D Heisenberg model (11).

The spectrum and structure of the elementary electron or hole excitations in the system depend on the magnetic order in the system. We study them assuming the hard AF GS (8) of the undoped system. For this state the hopping of the extra hole or electron between clusters is possible even in the first order in the intercluster part $V(\simeq t/4)$ of the kinetic energy. Note that in the previous t–J models [5–10] in which spins are localized on the Cu sites in the zero-order GS the hopping of the oxygen holes was possible only in the second order in t.

In the first order in the intercluster interaction V the state of the extra electron with the momentum k and spin projection $\sigma = -\frac{1}{2}$ on the background of the hard AF GS is described by the simplest function

$$\Psi_k^{\mathrm{e}} = \frac{1}{2}\left(\frac{2}{N}\right)^{1/2}\sum_n \exp(\mathrm{i}kn)(1+\zeta_n)\Psi_{n\sigma}^{\mathrm{e}} \tag{17}$$

$$\Psi_{n\sigma}^{\mathrm{e}} = b_{n\sigma}\prod_m \overset{+}{b}_{m\sigma_m}|0\rangle \tag{18}$$

$$\zeta_n = (-1)^{n_x+n_y} \qquad \sigma_n = \tfrac{1}{2}\zeta_n.$$

The corresponding energy is

$$\begin{aligned} E_k^{\mathrm{e}} &= \langle\Psi_k|H|\Psi_k\rangle - \langle\Psi_0|H|\Psi_0\rangle = -E_a - \kappa(f_k + f_{\tilde{k}} - 2F_0) \\ \kappa &= 2t^2F_0[\tfrac{1}{4}\delta\varepsilon^2 + (2tF_0)^2]^{-1/2}. \end{aligned} \tag{19}$$

Here $\tilde{k} = (\pi,\pi) - k$, the function f_k and constant F_0 are determined from equations (3) and (7). Thus the band of the extra electrons has a minimum on the boundary of the magnetic Brillouin zone $|k_x \pm k_y| = \pi$ and the dispersion $\Delta E = 0.586\kappa \simeq 0.5t$ of this electron band is sufficiently large. For example, at $\delta\varepsilon = -2t$ and $U = 7t$, one obtains $\Delta E = 0.52t$.

To the same first order in V the state of the extra hole with momentum k and spin $\sigma = -\frac{1}{2}$ (for example) on the background of the hard AF GS is sought in the form

$$\Psi_k^{\mathrm{h}} = \left(\frac{2}{N}\right)^{1/2}\sum_n \exp(\mathrm{i}kn)\left(\tfrac{1}{2}(1+\zeta_n)\sum_{i=1}^{4}\gamma_i\phi_{in} + \tfrac{1}{2}(1-\zeta_n)\gamma_5\overset{+}{d}_n\overset{+}{a}_n\right)|\Psi_{n\sigma}^{\mathrm{e}}\rangle. \tag{20}$$

The function $\Psi_{n\sigma}^{\mathrm{e}}$ is determined from equation (18). For the even cluster ($\zeta_n = 1$; $\sigma_n = \frac{1}{2}$) the double-hole state of the cluster is expanded in the basis of three possible singlet configurations (16) and the triplet state $\phi_{4n} = (\overset{+}{d}_n\overset{+}{a}_n - \overset{+}{a}_n\overset{+}{d}_n)/\sqrt{2}$ with $S_z = 0$. The normalization condition for the wavefunction (20) is

$$\sum_{i=1}^{5}|\gamma_i|^2 = 1.$$

The average energy $\langle H\rangle_k$ for the state (20) after subtraction of the GS energy is

$$\langle H\rangle_k - \langle H\rangle_0 = \sum_{i,j}[(\varepsilon_{\mathrm{p}} + \varepsilon_{\mathrm{d}} - 2E_{\mathrm{a}})\delta_{ij} + \mathsf{H}_{ij}]\gamma_i\gamma_j. \tag{21}$$

The non-zero elements of the matrix $\mathbf{H}_{ij}$ are

$$\mathbf{H}_{ij} = \{\delta\varepsilon,\ Qc_\alpha s_\alpha,\ -\delta\varepsilon + U,\ -Qc_\alpha s_\alpha,\ -2Qc_\alpha s_\alpha\}_i \qquad i = 1\text{–}5$$

$$\mathbf{H}_{1j} = \{R + \tilde{Q}c_\alpha^2,\ Qc_\alpha s_\alpha,\ -\tilde{Q}c_\alpha^2,\ -Gc_\alpha^2\}_j \qquad j = 2\text{–}5$$

$$\mathbf{H}_{23} = R + \tilde{Q}s_\alpha^2 \qquad \mathbf{H}_{34} = \tilde{Q}s_\alpha^2 \qquad \mathbf{H}_{35} = Gs_\alpha^2 \qquad \mathbf{H}_{45} = -2^{1/2}Gs_\alpha c_\alpha$$

$$R = 2^{3/2}F_0 t \qquad Q = 2t(f_k + f_{\tilde{k}} - 2F_0) \qquad \tilde{Q} = 2^{-1/2}Q \qquad G = t(f_k - f_{\tilde{k}}).$$

Here $\tilde{k}$, f_k, F_l are the same as in equations (3), (7) and (19).

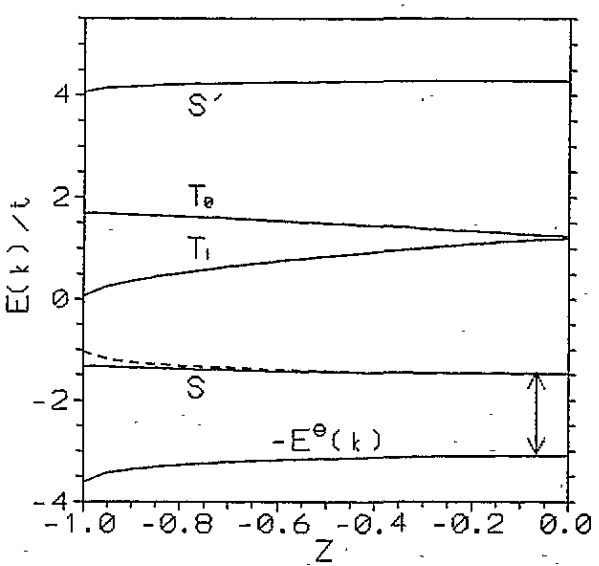

Figure 1. The z-dependences of the bands E_k of the elementary hole excitations for model corresponding to $(\varepsilon_p - \varepsilon_d)/t = 2$, and $U/t = 7$. The letters S, S', T_1 and T_0 near the curves show the preferential characters of states. The broken curve is the singlet band calculated in the single-band approach [17] which takes into account only the lowest singlet configurations of the double-hole clusters. The lowest curve $(-E_k^e)$ is the electron band with the opposite sign. The arrow demonstrates the value of the dielectric gap.

The eigenvalues E_k of equation (21) depend on $z = s_x^2 + s_y^2 - 1$ since $f_k = (1+z)^{1/2}$, $f_{\tilde{k}} = (1-z)^{1/2}$. Figure 1 presents the z-dependences of the bands E_k of elementary hole excitations for the model corresponding to $(\varepsilon_p - \varepsilon_d)/t = 2$ and $U/t = 7$. The letters S, S', T_1 and T_0 near the curves show the preferential characters of states. The main contributions to the corresponding wavefunctions are the singlet double-hole cluster states of bonding (S) or antibonding (S') types, or triplet states T_1 and T_0 of odd or even clusters with the spin projections -1 or 0, respectively. A third singlet band at $E_k \simeq 7.6t$ corresponding to the doubly occupied d orbital is not presented in figure 1. The lower singlet band is an analogue of the Zhang–Rice [5] singlet or similar polaron states in the early work [6–11]. As in [6–10] the energy E_k of this band has a minimum at the boundary $k = k_F$ of the magnetic Brillouin zone. The types of band are seen from the values of the coefficients γ_i in

the extra hole wavefunction (20). For example, for the lower singlet band these coefficients are

$$\gamma_i(S) = (0.490, -0.821, 0.292, 0.010, 0.000)_i \qquad \text{at } k = 0$$

$$\gamma_i(S) = (0.475, -0.711, 0.274, 0.215, 0.384)_i \qquad \text{at } k = k_F.$$

It is seen that at $k \simeq k_F$ there is a considerable admixture of the triplet double-hole configurations; their weights are determined by γ_4 and γ_5, but this admixture of triplets cannot be described in the single-band approximation [17].

The dispersions $\Delta E = E(k = 0) - E(k_F)$ of the bands S, T_1, T_0 and S′ (see figure 1) are $\Delta E/t = 0.15, -0.59, 0.45$ and -0.22. Taking into account the triplet configurations results in a decrease of about three times in the lower singlet bandwidth. The broken curve in figure 1 presents the corresponding energy E_k of this band calculated in the single-band approximation [17], i.e. taking into account only the lowest singlet double-hole configurations of the clusters. The corresponding value of ΔE is $0.44t$ in comparison with $0.15t$ in the complete calculation.

Slight k-dependences of the coefficients γ_1 and γ_2 in the singlet lowest band function (20) mean a high degree of localization of the extra hole $\sigma = -\frac{1}{2}$ inside one cluster with opposite spin projection, mainly on four p orbitals of oxygen surrounding the corresponding Cu site. Such a Zhang–Rice singlet is accompanied by the admixture of triplet states on the odd neighbouring clusters. The arrow in figure 1 demonstrates the value of the dielectric gap. For a hard AF undoped GS the gap given by

$$\text{gap} = E_k(S) - [-E_k^e] \qquad \text{at } k = k_F$$

is determined by the lower hole band S and the electron band E_k^e. At $|\delta\varepsilon/2t| = 1$ and $U/t = 7$, one obtains a gap of $1.80t$. This value is close to the gap value of $1.52t$ obtained in [19] for the variational correlated AF state with the spin density of 0.43 instead of 0.5 for hard AF state suggested here.

Thus the single-band approximation [16, 17] is insufficient for the description of the extra hole excitations, and incorporation of the triplet configurations of clusters may be needed to understand the low-energy physics in doped systems.

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