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THE CELL REPRESENTATION
OF THE THREE-BAND HUBBARD MODEL

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The d-p model of oxide superconductors, which includes the $3d_{x^2-y^2}$ orbitals of copper and the $\sigma - 2p_x/2p_y$ orbitals of oxygen, is reformulated by using the orthogonalized Wannier orbitals centred on the copper lattice sites. Only the nearest-neighbor Cu-O and O-O hopping terms are included together with the on-site Coulomb terms for Cu and O. We diagonalize firstly the O-O hopping term by introducing *diagonalizing fermions* $a_{i\sigma}$ and $b_{i\sigma}$ with two local energies e_a and e_b which cosiderably differ from local oxygen ion energy ϵ_p. The diagonalization is made before the Wannier orthogonalization of the orbitals is done. In our cell representation the Hamiltonian is the sum of different contributions which contain three orthogonalized operators: $d_{i\sigma}$, $a_{i\sigma}$, and $b_{i\sigma}$. The main part of it is the local one. There are also the perturbative delocalizing contributions. The detailed investigation of the eigenvalue problem of the local Hamiltonian has been done by using the S-matrix method, elaborated by us. The energy spectrum of the local Hamiltonian depends on such quantum numbers as the full number N of a, b and d particles of the state, their full spin S and its z projection. All the renormalized states with $N = 0, 1, 2..., 6$ have been analyzed. When $N = 2$ and $S = 0$, there are six singlet states and the lowest from them is Zhang–Rice one. The diagonalizing process lowers the energy of this state considerably. In the local approximation the chemical potential dependence on the temperature and hole numbers has been also established.

Гамильтониан d-p-модели переписан в представлении ортогонализованных ванье-орбиталей меди и кислорода. В данной работе, в отличие от других, выполнен точный учет гибридизации

дырок на ионах кислорода. С этой целью используются две диагонализованные фермионные ячеечные моды кислородных дырок, наряду с модой медных дырок. Эти диагонализованные моды обладают существенно различными локальными энергиями, что заметно сказывается на результатах теории. Отмечена некоммутируемость операции диагонализации кислородного гамильтониана и ортогонализации орбиталей Ванье по узлам медной решетки. Ячеечная орбиталь кислородных дырок, принадлежащих ионному комплексу CuO_4, оказывается в нашем подходе суперпозицией этих двух диагонализованных орбиталей. Полученный гамильтониан имеет вид суммы слагаемых, члены которых имеют различное число индексов узлов решетки меди. Наибольшим является локальное слагаемое. Определены все главные состояния кластерного представления и детально проанализирован спектр элементарных возбуждений локальной модели. В локальном приближении определен химический потенциал системы и его зависимость от числа дырок и температуры. Показано, что процесс перенормировки кислородных дырок существенно влияет на низкоэнергетическую часть спектра системы и, в частности, на энергию синглета Жанга и Райса, приводя к значительному ее понижению.

INTRODUCTION

Since the discovery of high-T_c superconductivity, there have been made great efforts to obtain a simple theoretical model suitable to describe the main peculiarities of this phenomenon. We start with a tight-binding model for the Cu-O planes of high-temperature superconductors, which includes orbitals of both Cu and O ions. Only the nearest-neighbor Cu-O and O-O hopping terms are included together with the on-site Coulomb terms U_d and U_p for holes on Cu and O, respectively. In addition we take the Coulomb interaction U_{dp} into account. With respect to orbitals we consider only $3d_{x^2-y^2}$ of Cu and σ-$2p_x/2p_y$ of O. The vacuum state corresponds to the filled $3d$ and $2p$ shells ($3d^{10}2p^6$). Therefore there are 3 orbitals per unit cell.

This kind of model Hamiltonian for the motion of holes in the Cu-O planes has been proposed, for example, in [1–3]. As mentioned above, the elementary cell for the CuO_2 plane includes only the orbitals $d_{\mathbf{i},\,x^2-y^2}$ and $p_{\mathbf{l}}^{x,y}$, where $\mathbf{i}$, $\mathbf{l}$ are the site indices of Cu and O, respectively, with $\mathbf{l} = \mathbf{i} \pm \dfrac{a}{2}\widehat{x}$ and $\mathbf{l} = \mathbf{i} \pm \dfrac{a}{2}\widehat{y}$; $\widehat{x}$ and $\widehat{y}$ being unit vectors in x and y direction, respectively. The p-d Hamiltonian is then of the form

$$H = H_d + H_p + H_{d-p}, \tag{1}$$

where

$$H_d = \epsilon_d \sum_{i,\sigma} n_{i\sigma}^d + U_d \sum_i n_{i\uparrow}^d n_{i\downarrow}^d,$$

$$H_p = \epsilon_p \sum_{l,\sigma} n_{l\sigma}^p + t_{pp} \sum_{\langle l,l'\rangle,\sigma} p_{l,\sigma}^+ p_{l',\sigma} S_{ll'} + U_p \sum_l n_{l\uparrow}^p n_{l\downarrow}^p, \tag{2}$$

$$H_{d-p} = t_{dp} \sum_{\langle i,l\rangle,\sigma} \left(d_{i,\sigma}^+ p_{l,\sigma} + \text{H.C.} \right) S_{il} + U_{dp} \sum_{\langle i,l\rangle} n_i^d n_l^p.$$

Here $d_{i\sigma}$ $(d_{i\sigma}^{+})$ and $p_{l\sigma}$ $(p_{l\sigma}^{+})$ are annihilation (creation) operators of d and p holes of spin σ at the lattice sites i and l with corresponding hole densities $n_i^d = n_{i\uparrow}^d + n_{i\downarrow}^d$, $n_{l\sigma}^p = p_{l\sigma}^{+} p_{l\sigma}$, $n_l^p = n_{l\uparrow}^p + n_{l\downarrow}^p$; $\epsilon_d = \overline{\epsilon}_d - \mu$ and $\epsilon_p = \overline{\epsilon}_p - \mu$ are the local energies of holes with respect to the chemical potential. The quantities $t_{pp} S_{ll'} = \pm t_{pp}$ and $t_{dp} S_{il} = \pm t_{dp}$ are the nearest neighbor O-O and Cu-O transfer terms with corresponding phase factors $S_{ll'}$ and S_{il} which originate from inversion symmetry of the orbitals. Our choice for these factors agrees with that used in Refs. 4, 6–14. Other choices for the orbital signs will change the phase factors but not the physical results [15–19].

With this choice in mind we rewrite the d-p hybridization term in Eq. (2) in the form of an interaction between the $d_{i\sigma}$ orbital and the oxygen cluster $\beta_{i\sigma}$ of holes surrounding the central Cu ion at site i,

$$2t_{dp} \sum_{i,\sigma} \left(d_{i,\sigma}^{+} \beta_{i,\sigma} + \beta_{i,\sigma}^{+} d_{i,\sigma} \right), \tag{3}$$

where the cluster or cell annihilation operator is

$$\beta_{i,\sigma} = \frac{1}{2} \left(p_{\mathbf{i}+\frac{a}{2}\widehat{x},\sigma}^x - p_{\mathbf{i}+\frac{a}{2}\widehat{y},\sigma}^y - p_{\mathbf{i}-\frac{a}{2}\widehat{x},\sigma}^x + p_{\mathbf{i}-\frac{a}{2}\widehat{y},\sigma}^y \right). \tag{4}$$

This reflects the local D_{4h} symmetry of the CuO_2 plane with the corresponding b_1 transformation representation of the symmetry group. This orbital was first introduced by Zhang and Rice [4] pointing out that essential physics is connected with the formation of singlet and triplet states between the Cu and the cluster orbitals. As discussed below, it will actually be more convenient to transform the orbital $\beta_{i\sigma}$ with the help of Wannier functions being orthogonal on site i (when centred on neighboring sites i and j) by using the *canonical fermions* of Shastry [7].

On the basis of the singlet model Zhang and Rice have shown that the corresponding one-band model accurately describes the low-energy physics of the d-p model. Their method resembles the derivation of the t-J model from the one-band Hubbard Hamiltonian in the case of strong correlations [5]. The concept of Zhang and Rice has been discussed in Refs. 6–14, further exploration of this model in [15–32], and slightly different treatments can be found in [33–44].

The main stages of investigations based on the Zhang–Rice model (see papers cited above) are the following ones. The first is to introduce cluster oxygen orbitals centred on the Cu ions, which take into account the local symmetry of it. The second stage is the Wannier orthogonalization of them and obtaining of the Hamiltonian. At the last stage there is the projection of this Hamiltonian on the low energy Hilbert subspace and the definition of the dynamical properties of the system.

Now we come back to the Hamiltonian and discuss its part H_p^0 which is connected with the oxygen holes movement

$$H_p^0 = \epsilon_p \sum_{l,\sigma} p_{l,\sigma}^+ p_{l,\sigma} + t_{pp} \sum_{\langle l,l'\rangle,\sigma} p_{l,\sigma}^+ p_{l',\sigma} S_{l,l'}. \tag{5}$$

The last term of this equation is the contribution of the O-O tunneling process. By taking into account the phase factors $S_{ll'}$ we obtain

$$
\begin{aligned}
t_{pp} \sum_{\langle l,l'\rangle,\sigma} p_{l,\sigma}^+ p_{l',\sigma} S_{l,l'} = \frac{1}{2} \sum_{l,\sigma} \Big\{ & p_{\mathbf{i}+\frac{a}{2}\widehat{x},\sigma}^{x+} \Big[-p_{\mathbf{i}+a\widehat{x}+\frac{a}{2}\widehat{y},\sigma}^{y} + \\
& + p_{\mathbf{i}+\frac{a}{2}\widehat{y},\sigma}^{y} - p_{\mathbf{i}-\frac{a}{2}\widehat{y},\sigma}^{y} + p_{\mathbf{i}+a\widehat{x}-\frac{a}{2}\widehat{y},\sigma}^{y} \Big] + \\
+ p_{\mathbf{i}+\frac{a}{2}\widehat{y},\sigma}^{y+} & \Big[-p_{\mathbf{i}+\frac{a}{2}\widehat{x}+a\widehat{y},\sigma}^{x} + p_{\mathbf{i}-\frac{a}{2}\widehat{x}+a\widehat{y},\sigma}^{x} - p_{\mathbf{i}-\frac{a}{2}\widehat{x},\sigma}^{x} + p_{\mathbf{i}+\frac{a}{2}\widehat{x},\sigma}^{x} \Big] + \\
+ p_{\mathbf{i}-\frac{a}{2}\widehat{x},\sigma}^{x+} & \Big[-p_{\mathbf{i}+\frac{a}{2}\widehat{y},\sigma}^{y} + p_{\mathbf{i}-a\widehat{x}+\frac{a}{2}\widehat{y},\sigma}^{y} - p_{\mathbf{i}-a\widehat{x}-\frac{a}{2}\widehat{y},\sigma}^{y} + p_{\mathbf{i}-\frac{a}{2}\widehat{y},\sigma}^{y} \Big] + \\
+ p_{\mathbf{i}-\frac{a}{2}\widehat{y},\sigma}^{y+} & \Big[-p_{\mathbf{i}+\frac{a}{2}\widehat{x},\sigma}^{x} + p_{\mathbf{i}-\frac{a}{2}\widehat{x},\sigma}^{x} - p_{\mathbf{i}-\frac{a}{2}\widehat{x}-a\widehat{y},\sigma}^{x} + p_{\mathbf{i}+\frac{a}{2}\widehat{x}-a\widehat{y},\sigma}^{x} \Big] \Big\}. \tag{6}
\end{aligned}
$$

Let us introduce now the Fourier representation of the oxygen operators p^x and p^y by using the Brillouine zone of the copper ions:

$$
\begin{aligned}
p_{\mathbf{i}\pm\frac{a}{2}\widehat{x},\sigma}^x &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\left(\mathbf{R}_i\pm\frac{a}{2}\widehat{x}\right)} p_{\mathbf{k},\sigma}^x, \\
p_{\mathbf{i}\pm\frac{a}{2}\widehat{y},\sigma}^y &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\left(\mathbf{R}_i\pm\frac{a}{2}\widehat{y}\right)} p_{\mathbf{k},\sigma}^y.
\end{aligned}
\tag{7}
$$

Here N is the number of copper ions; $\mathbf{k}_x$, $\mathbf{k}_y$ are changing in the limits $\left(-\dfrac{\pi}{a}, \dfrac{\pi}{a}\right)$. In the $\mathbf{k}$ representation the oxygen cluster operator $\beta_{\mathbf{i},\sigma}$ has the form

$$\beta_{i,\sigma} = \frac{i}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_i} \left(-p_{\mathbf{k},\sigma}^x S_x(\mathbf{k}) + p_{\mathbf{k},\sigma}^y S_y(\mathbf{k}) \right), \tag{8}$$

where $S_x(\mathbf{k}) = \sin\left(\dfrac{\mathbf{k}_x a}{2}\right)$ and $S_y(\mathbf{k}) = \sin\left(\dfrac{\mathbf{k}_y a}{2}\right)$. This equation suggests the proper introduction of the two Shastry canonical fermion operators

$$
\begin{aligned}
P_{\mathbf{k},\sigma} &= \frac{i}{S(\mathbf{k})} \left[-S_x(\mathbf{k}) p_{\mathbf{k},\sigma}^x + S_y(\mathbf{k}) p_{\mathbf{k},\sigma}^y \right], \\
Q_{\mathbf{k},\sigma} &= \frac{i\varepsilon(\mathbf{k})}{S(\mathbf{k})} \left[S_y(\mathbf{k}) p_{\mathbf{k},\sigma}^x + S_x(\mathbf{k}) p_{\mathbf{k},\sigma}^y \right],
\end{aligned}
\tag{9}
$$

where

$$S(\mathbf{k}) = \sqrt{S_x^2(\mathbf{k}) + S_y^2(\mathbf{k})} = \left[1 - \frac{1}{2} \left(\cos(\mathbf{k}_x a) + \cos(\mathbf{k}_y a) \right) \right]^{\frac{1}{2}},$$

$$\varepsilon(\mathbf{k}) = \mathrm{sgn}\,(S_x S_y).$$

The sign function $\varepsilon(\mathbf{k})$ was introduced in paper [23]. By using the new canonical fermion operators we obtain:

$$p_{\mathbf{k},\sigma}^x = \frac{i}{S(\mathbf{k})} \left[S_x P_{\mathbf{k},\sigma} - \epsilon(\mathbf{k}) S_y Q_{\mathbf{k},\sigma} \right],$$

$$p_{\mathbf{k},\sigma}^y = \frac{-i}{S(\mathbf{k})} \left[S_y P_{\mathbf{k},\sigma} + \epsilon(\mathbf{k}) S_x Q_{\mathbf{k},\sigma} \right]. \tag{10}$$

On the basis of Eq. (9) we obtain, for the cluster operator $\beta_{\mathbf{i},\sigma}$, the equation

$$\beta_{i,\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \mathrm{e}^{-i\mathbf{k}\mathbf{R}_i} S(\mathbf{k}) P_{\mathbf{k},\sigma}. \tag{11}$$

As we can see from Eqs. (3) and (11), the copper orbital $d_{i\sigma}$ interacts only with one of two oxygen cluster orbitals, namely with $P_{\mathbf{k},\sigma}$. We shall introduce now the orthogonalized on copper sites «canonical operators»

$$P_{i,\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} P_{\mathbf{k},\sigma}\, \mathrm{e}^{-i\mathbf{k}\mathbf{R}_i},$$

$$Q_{i,\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} Q_{\mathbf{k},\sigma}\, \mathrm{e}^{-i\mathbf{k}\mathbf{R}_i}. \tag{12}$$

By using such equations, we have

$$\beta_{i,\sigma} = \sum_j P_{j,\sigma} \lambda(i-j), \quad \lambda(R) = \frac{1}{N} \sum_{\mathbf{k}} S(\mathbf{k})\, \mathrm{e}^{-i\mathbf{k}\mathbf{R}}, \tag{13}$$

and, as the consequence, the d-p hybridization term of Hamiltonian (3) has the form

$$2t_{dp} \sum_{i,j} \left(d_{i\sigma}^+ P_{j,\sigma} \lambda(i-j) + \mathrm{H.C.} \right) = 2t_{dp}\lambda(0) \sum_i \left(d_{i\sigma}^+ P_{i,\sigma} + P_{i,\sigma}^+ d_{i\sigma} \right) +$$

$$+ 2t_{dp} \sum_{\substack{i,j \\ i \neq j}} \left(d_{i\sigma}^+ P_{j,\sigma} \lambda(i-j) + \mathrm{H.C.} \right). \tag{14}$$

The quantity $\lambda(x, y)$ has been calculated in [16, 22]. It decreases rather quickly with the distance

$$\lambda(0,0) = 0.95, \quad \lambda(\pm a, 0) = \lambda(0, \pm a) = -0.14, \quad \lambda(\pm a, \pm a) = -0.02. \quad (15)$$

Both the terms of kinetic energy (5) of oxygen holes in **k** representation have the form

$$\epsilon_p \sum_{l,\sigma} p^+_{l,\sigma} p_{l,\sigma} = \epsilon_p \sum_{\mathbf{k},\sigma} \left(p^{x+}_{\mathbf{k},\sigma} p^x_{\mathbf{k},\sigma} + p^{y+}_{\mathbf{k},\sigma} p^y_{\mathbf{k},\sigma} \right), \quad (16)$$

$$t_{pp} \sum_{\langle l,l'\rangle,\sigma} p^+_{l,\sigma} p_{l',\sigma} S_{l,l'} = 4t_{pp} \sum_{\mathbf{k},\sigma} S_x S_y \left(p^{x+}_{\mathbf{k},\sigma} p^y_{\mathbf{k},\sigma} + p^{y+}_{\mathbf{k},\sigma} p^x_{\mathbf{k},\sigma} \right). \quad (17)$$

By using Eq. (10) we obtain the following result:

$$H^0_p = \epsilon_p \sum_{\mathbf{k},\sigma} \left(P^+_{\mathbf{k},\sigma} P_{\mathbf{k},\sigma} + Q^+_{\mathbf{k},\sigma} Q_{\mathbf{k},\sigma} \right) -$$

$$- 4t_{pp} \sum_{\mathbf{k},\sigma} S_x S_y \left[2 S_x S_y \left(P^+_{\mathbf{k},\sigma} P_{\mathbf{k},\sigma} - Q^+_{\mathbf{k},\sigma} Q_{\mathbf{k},\sigma} \right) + \right.$$

$$\left. + \varepsilon(\mathbf{k}) \left(S^2_x - S^2_y \right) \left(P^+_{\mathbf{k},\sigma} Q_{\mathbf{k},\sigma} + Q^+_{\mathbf{k},\sigma} P_{\mathbf{k},\sigma} \right) \right]. \quad (18)$$

The final representation of (18) is

$$H^0_p = \epsilon_p \sum_{j,\sigma} \left(P^+_{j,\sigma} P_{j,\sigma} + Q^+_{j,\sigma} Q_{j,\sigma} \right) -$$

$$- 4t_{pp} \sum_{j,j'} \left\{ \left(P^+_{j,\sigma} P_{j',\sigma} - Q^+_{j,\sigma} Q_{j',\sigma} \right) \frac{1}{N} \sum_{\mathbf{k}} 2 S^2_x S^2_y \, e^{-i\mathbf{k}\left(\mathbf{R}_j - \mathbf{R}_{j'}\right)} + \right.$$

$$\left. + \left(P^+_{j,\sigma} Q_{j',\sigma} + Q^+_{j,\sigma} P_{j',\sigma} \right) \frac{1}{N} \sum_{\mathbf{k}} |S_x S_y| \left(S^2_x - S^2_y \right) e^{-i\mathbf{k}\left(\mathbf{R}_j - \mathbf{R}_{j'}\right)} \right\}. \quad (19)$$

To find the local contribution of this term it is necessary to put $j = j'$. We observe that two quantities:

$$\frac{1}{N} \sum_{\mathbf{k}} 2 S^2_x S^2_y \, e^{-i\mathbf{k}\mathbf{R}}, \quad \frac{1}{N} \sum_{\mathbf{k}} |S_x S_y| \, e^{-i\mathbf{k}\mathbf{R}} (S^2_x - S^2_y) \quad (20)$$

manifest quite different behaviour for $\mathbf{R} = 0$. The first quantity of them is nonzero, but the second is just zero. We can see that the most important local

contribution from (19) doesn't contain the mixed $P_{\mathbf{k},\sigma}$ and $Q_{\mathbf{k},\sigma}$ terms and therefore these two orbitals are not connected in between and have the independent contributions for the oxygen holes movement. Because the hybridization contribution (14) is also independent of $Q_{\mathbf{k},\sigma}$ orbitals, the authors of all cited above papers devoted to the cluster representation of d-p model, drew the conclusion that it is possible to exclude completely the $Q_{\mathbf{k},\sigma}$ orbital from the next investigation. In such a way the d-p model turned out to be equivalent to the two-cluster model of $d_{i\sigma}$, $P_{i,\sigma}$ orbitals. Because the quantities (20) for $\mathbf{R} \neq 0$ decrease quickly with the distance, and the hybridization energy of the oxygen holes is not large, the last term of (19) has been considered as nonimportant for the dynamics of the oxygen holes. The same conclusion was made about the Coulomb interaction terms of (1) relevant to oxygen holes and was interpreted as a real isolation of the $Q_{i,\sigma}$ cluster fermions in some independent subsystem, the presence of which was neglected completely in the next analysis. So the cluster description of the oxygen holes behavior in CuO_2 plane results in the fact that three-band $d_{i,\sigma}$, $p_{i,\sigma}^x$, $p_{i,\sigma}^y$ model of the holes on two sublattices of copper and oxygen ions has been reduced to two-band $d_{i,\sigma}$ and $P_{i,\sigma}^x$ model only on the copper sites lattice.

Our point of view on this problem is different. We consider that there are several objections to previous approach. The first of them is connected with the transition from the momentum representation (18) to orthogonalized Wannier representation (19). Our approach to this problem is to do firstly the diagonalization of oxygen operator H_p^0 and only after that to use the orthogonalized representation. These two operations are not commutative and the results are quite different. This diagonalization doesn't depend, as we can see below, on the values of t_{pp} matrix elements and it is not a small effect, as was supposed in previous papers. In such a way, we firstly make the canonical transformation of the H_p^0 operator and only then introduce the orthogonalized Wannier orbitals. This approach renormalizes the energy spectrum of the oxygen bands and significantly changes the charge-transfer energy $\epsilon_p - \epsilon_d$ between oxygen and copper ions. As is well known, in the case when $\epsilon_p - \epsilon_d + 2U_{dp} < U_d$, the doped holes are settled on the oxygen ions and fill in the lowest energy levels of their collective motion, when their concentration is little. But if their concentration is high enough, the knowledge (besides of the low part) also of all the energy spectrum is important. This is our second reason to make this investigation. Our last reason is connected with the existence of additional interaction between collective oxygen modes, conditioned by the Coulomb repulsion of the holes situated on oxygen ions and their interaction when they are situated on the nearest Cu and O ions. Such additional interaction will be demonstrated below. It can be also proved that the interaction of the holes with phonons gives the additional mechanism of interaction between two oxygen collective modes and that the supposed, by previous authors, separation of one of two collective oxygen modes is not realized. These our considerations initiate this investigation. It takes into account

more correctly the oxygen–oxygen hybridization, introduces the notion of the diagonalizing oxygen fermions and proves the existence of interaction between them. The Wannier orthogonalization is done after the diagonalization and the contributions to the local cell Hamiltonian and its delocalizing perturbation are established. This program is realized in Sec. 1.

The detailed investigation of the renormalized states and their energies is done in Sec. 2, and in Sec. 3 we discuss the obtained results.

1. THE CELL REPRESENTATION OF THE HAMILTONIAN

We take into account the contribution of O-O tunneling to the oxygen Hamiltonian H_p^0

$$H_p^0 = \sum_{\mathbf{k},\sigma} \left\{ \epsilon_p \left(p_{\mathbf{k},\sigma}^{x+} p_{\mathbf{k},\sigma}^{x} + p_{\mathbf{k},\sigma}^{y+} p_{\mathbf{k},\sigma}^{y} \right) - \right.$$
$$\left. -4t_{pp} S_x S_y \left(p_{\mathbf{k},\sigma}^{x+} p_{\mathbf{k},\sigma}^{y} + p_{\mathbf{k},\sigma}^{y+} p_{\mathbf{k},\sigma}^{x} \right) \right\}, \quad (21)$$

and make the canonical transformation of it by introducing two new, diagonalizing $a_{\mathbf{k},\sigma}$ and $b_{\mathbf{k},\sigma}$ oxygen holes, operators:

$$p_{\mathbf{k},\sigma}^{x} = u(\mathbf{k})a_{\mathbf{k},\sigma} + v(\mathbf{k})b_{\mathbf{k},\sigma},$$
$$p_{\mathbf{k},\sigma}^{y} = -v^*(\mathbf{k})a_{\mathbf{k},\sigma} + u^*(\mathbf{k})b_{\mathbf{k},\sigma}. \quad (22)$$

The coefficients of this transformation are subjected to the next conditions:

$$|u(\mathbf{k})|^2 + |v(\mathbf{k})|^2 = 1, \quad (u^*(\mathbf{k}))^2 = (v(\mathbf{k}))^2. \quad (23)$$

The second condition (23) ensures the diagonalization of the second term of operator (21). These coefficients are independent of the values of matrix elements t_{pp}, as we mentioned above. By using the oxygen diagonalizing operators $a_{\mathbf{k},\sigma}$ and $b_{\mathbf{k},\sigma}$, we obtain for (21) the next form:

$$H_p^0 = \sum_{\mathbf{k},\sigma} \{ \epsilon_p (a_{\mathbf{k},\sigma}^+ a_{\mathbf{k},\sigma} + b_{\mathbf{k},\sigma}^+ b_{\mathbf{k},\sigma}) +$$
$$+ 4t_{pp} S_x S_y (u(\mathbf{k})v(\mathbf{k}) + u^*(\mathbf{k})v^*(\mathbf{k}))(b_{\mathbf{k},\sigma}^+ b_{\mathbf{k},\sigma} - a_{\mathbf{k},\sigma}^+ a_{\mathbf{k},\sigma}) \}. \quad (24)$$

The conditions (23) determine the module of our coefficients: $|u(\mathbf{k})| = |v(\mathbf{k})| = 1/\sqrt{2}$, but not their phases. Our next restriction is ($t_{pp} > 0$):

$$uv + u^*v^* = \text{sgn}(S_x S_y). \quad (25)$$

As a result of this last condition we have

$$H_p^0 = \sum_{\mathbf{k},\sigma} \left\{ \epsilon_a(\mathbf{k}) a_{\mathbf{k},\sigma}^+ a_{\mathbf{k},\sigma} + \epsilon_b(\mathbf{k}) b_{\mathbf{k},\sigma}^+ b_{\mathbf{k},\sigma} \right\},$$

$$\epsilon_{a,b}(\mathbf{k}) = \epsilon_p \mp 4t_{pp}|S_x(\mathbf{k})S_y(\mathbf{k})|. \tag{26}$$

Thus the hybridization of the oxygen holes results in the appearance of two subbands one of which, $\epsilon_a(\mathbf{k})$, is lower and the second, $\epsilon_b(\mathbf{k})$, is above the local oxygen energy ϵ_p. The conditions (23) and (25) for our coefficients admit some else arbitraryness of their phases. This arbitraryness will be used by us to establish the most convenient relation between canonical $P_{\mathbf{k},\sigma}$, $Q_{\mathbf{k},\sigma}$ and diagonalizing $a_{\mathbf{k},\sigma}$, $b_{\mathbf{k},\sigma}$ fermions. The relation between two groups of fermions is the following

$$P_{\mathbf{k},\sigma} = \frac{i}{S(\mathbf{k})} \{ -a_{\mathbf{k},\sigma}[S_x(\mathbf{k})u(\mathbf{k}) + S_y(\mathbf{k})v^*(\mathbf{k})] +$$

$$+ b_{\mathbf{k},\sigma}[S_y(\mathbf{k})u^*(\mathbf{k}) - S_x(\mathbf{k})v(\mathbf{k})] \},$$

$$Q_{\mathbf{k},\sigma} = \frac{i\epsilon(\mathbf{k})}{S(\mathbf{k})} \{ a_{\mathbf{k},\sigma}[S_y(\mathbf{k})u(\mathbf{k}) - S_x(\mathbf{k})v^*(\mathbf{k})] + \tag{27}$$

$$+ b_{\mathbf{k},\sigma}[S_x(\mathbf{k})u^*(\mathbf{k}) + S_y(\mathbf{k})v(\mathbf{k})] \}.$$

We define finally the coefficients $u(\mathbf{k})$ and $v(\mathbf{k})$ from the condition that the orbitals $P_{\mathbf{k},\sigma}$ and $a_{\mathbf{k},\sigma}$ are like as much as possible

$$u(\mathbf{k}) = \frac{i}{\sqrt{2}} \operatorname{sgn}(S_x(\mathbf{k})), \qquad v(\mathbf{k}) = -\frac{i}{\sqrt{2}} \operatorname{sgn}(S_y(\mathbf{k})). \tag{28}$$

This choice agrees with all the previous restrictions for them.

As a result, we can rewrite the equations (27) in the form

$$P_{\mathbf{k},\sigma} = a_{\mathbf{k},\sigma} \frac{|S_x| + |S_y|}{\sqrt{2}S(\mathbf{k})} + b_{\mathbf{k},\sigma} \operatorname{sgn}(S_x S_y) \frac{|S_y| - |S_x|}{\sqrt{2}S(\mathbf{k})},$$

$$Q_{\mathbf{k},\sigma} = -a_{\mathbf{k},\sigma} \frac{|S_y| - |S_x|}{\sqrt{2}S(\mathbf{k})} + b_{\mathbf{k},\sigma} \operatorname{sgn}(S_x S_y) \frac{|S_x| + |S_y|}{\sqrt{2}S(\mathbf{k})}. \tag{29}$$

According to these equations the canonical amplitudes (P, Q) are the superpositions of diagonalizing amplitudes (a, b) with corresponding probabilities.

Now we shall introduce the Wannier amplitudes for diagonalizing fermions

$$a_{i,\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} a_{\mathbf{k},\sigma}\, \mathrm{e}^{-i\mathbf{k}\mathbf{R}_i},$$

$$b_{i,\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} b_{\mathbf{k},\sigma}\, \mathrm{e}^{-i\mathbf{k}\mathbf{R}_i}. \tag{30}$$

We can establish the linear relations between cluster Wannier amplitudes $P_{\mathbf{i},\sigma}$, $Q_{\mathbf{i},\sigma}$ and diagonalizing Wannier amplitudes $a_{\mathbf{i},\sigma}$, $b_{\mathbf{i},\sigma}$ with the coefficients of proportionality which are less than one. Therefore all the local contributions to the dynamical quantities expressed in terms of $a_{\mathbf{i},\sigma}$ amplitudes will be less than the corresponding contributions expressed through $P_{\mathbf{i},\sigma}$ amplitudes. This difference is essential and can be demonstrated already for the case of d-p hybridization. We want to underline that these differences are not at all connected with the value of the matrix element t_{pp}. The cluster amplitude $\beta_{\mathbf{i},\sigma}$ can be expressed in the form

$$\beta_{i\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_i} \left[a_{\mathbf{k},\sigma} \frac{|S_x| + |S_y|}{\sqrt{2}} + \right.$$
$$\left. + b_{\mathbf{k},\sigma} \operatorname{sgn}(S_x S_y) \frac{|S_y| - |S_x|}{\sqrt{2}} \right] = \sum_j [\lambda_a(i-j) a_{j,\sigma} +$$
$$+ \lambda_b(i-j) b_{j,\sigma}] = \sum_j \lambda(i-j) P_{j,\sigma}, \quad (31)$$

where

$$\lambda_a(\mathbf{R}) = \frac{1}{N} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}} \frac{|S_x| + |S_y|}{\sqrt{2}} =$$

$$= \frac{1}{2\sqrt{2}\pi} \left[\frac{\delta_{y,0}}{\frac{1}{4} - \left(\frac{x}{a}\right)^2} + \frac{\delta_{x,0}}{\frac{1}{4} - \left(\frac{y}{a}\right)^2} \right],$$

$$\lambda_b(\mathbf{R}) = \frac{1}{N} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}} \operatorname{sgn}(S_x S_y) \frac{|S_y| - |S_x|}{\sqrt{2}} = \quad (32)$$

$$= \frac{1}{\pi^2} \left[\frac{\left(1 - \cos \pi \frac{x}{a}\right) \frac{y}{a} \cos \pi \frac{y}{a}}{\frac{x}{a} \left[\left(\frac{y}{a}\right)^2 - \frac{1}{4}\right]} - \frac{\left(1 - \cos \pi \frac{y}{a}\right) \frac{x}{a} \cos \pi \frac{x}{a}}{\frac{y}{a} \left[\left(\frac{x}{a}\right)^2 - \frac{1}{4}\right]} \right],$$

$$\lambda(\mathbf{R}) = \frac{1}{N} \sum_{\mathbf{k}} S(\mathbf{k}) e^{-i\mathbf{k}\mathbf{R}}.$$

Here $\mathbf{R} = (x, y)$ is the distance between the copper ions, and therefore the quantities x/a and y/a are the positive or negative integer numbers. Equation (32) gives us the next values $\lambda_a(0) = \frac{2\sqrt{2}}{\pi} \simeq 0.900$, $\lambda_b(0) = 0$. In papers [16, 19, 20] we can find the value $\lambda(0) = 0.958$ which is analogous to our $\lambda_a(0)$ and exceeds

the last one, as it was expected. On the basis of equation (31), the d-p-hybridization term of the Hamiltonian can be rewritten in the form

$$H_{dp} = 2t_{dp}\lambda_a(0) \sum_i \left(d_{i\sigma}^+ a_{i\sigma} + a_{i\sigma}^+ d_{i\sigma}\right) +$$

$$+ 2t_{dp} \sum_{\substack{i,j \\ j \neq i}} \left(d_{i\sigma}^+ [\lambda_a(i-j)a_{j\sigma} + \lambda_b(i-j)b_{j\sigma}] + \text{H.C.}\right). \quad (33)$$

The first term of the right-hand part of equation (33) is the main local approximation of the Hamiltonian. The second term determines the holes delocalization processes. This term is not concerned only with the nearest-neighbour sites as it was in the initial Hamiltonian (1). This enlargement of the space is rather artificial and is the result of the orthogonalization procedure. On the basis of equations (32) $(\varepsilon_1, \varepsilon_2 = \pm 1)$ we have

$$\lambda_a(x = \varepsilon_1 a, y = 0) = \lambda_a(x = 0, y = \varepsilon_2 a) = -\lambda_a(0,0)/6,$$

$$\lambda_a(x = 2\varepsilon_1 a, y = 0) = \lambda_a(x = 0, y = 2\varepsilon_2 a) = -\lambda_a(0,0)/30,$$

$$\lambda_b(x = \varepsilon_1 a, y = 0) = \lambda_b(x = 0, y = \varepsilon_2 a) = \lambda_b(x = \varepsilon_1 a, y = \varepsilon_2 a) = 0,$$

$$\lambda_b(x = \varepsilon_1 a, y = 2\varepsilon_2 a) = -\lambda_b(x = 2\varepsilon_1 a, y = \varepsilon_1 a) = (\varepsilon_2/\varepsilon_1)\lambda_a(0,0)4\sqrt{2}/(15\pi),$$

$$\lambda_b(x = \varepsilon_1 a, y = 3\varepsilon_2 a) = (\varepsilon_2/\varepsilon_1)\lambda_a(0,0)16\sqrt{2}/(315\pi) = \lambda_b(x = 3\varepsilon_1 a, y = \varepsilon_2 a).$$

The function $\lambda_a(x,y)$ differs from zero both on the central and on the nearest neighbour (n.n.) ion sites and quickly diminishes on the next n.n. (n.n.n.) sites. The function $\lambda_b(x,y)$ is zero on central and n.n. sites but is different from zero and small on the n.n.n. sites. Therefore there are two channels of delocalization of the copper holes, just by their hybridization both with $a_{\mathbf{i},\sigma}$ and $b_{\mathbf{i},\sigma}$ oxygen orbitals.

Now the Hamiltonian (26) of the free oxygen holes can be rewritten in the cell representation

$$H_p^0 = \sum_{j,j',\sigma} \left(t_a(j-j')a_{j,\sigma}^+ a_{j',\sigma} + t_b(j-j')b_{j,\sigma}^+ b_{j',\sigma}\right), \quad (34)$$

where

$$t_{a,b}(\mathbf{R}) = \frac{1}{N}\sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}}\epsilon_{a,b}(\mathbf{k}) = \epsilon_p\delta_{\mathbf{R},0} \mp 4t_{pp}\tau(\mathbf{R}),$$

$$\tau(\mathbf{R}) = \frac{1}{N}\sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}}|S_x S_y| = \frac{1}{(2\pi)^2\left[\frac{1}{4} - \left(\frac{x}{a}\right)^2\right]\left[\frac{1}{4} - \left(\frac{y}{a}\right)^2\right]}. \quad (35)$$

From this equation we obtain the following values

$$\tau(0) = \left(\frac{2}{\pi}\right)^2 = 0.4045, \quad \epsilon_{a,b} \equiv \epsilon_p \mp 4t_{pp}\tau(0).$$

Equation (34) can be rewritten in the form

$$H_p^0 = \sum_{j,\sigma}(\epsilon_a a_{j,\sigma}^+ a_{j,\sigma} + \epsilon_b b_{j,\sigma}^+ b_{j,\sigma}) -$$

$$- 4t_{pp}\sum_{j\neq j',\sigma}(a_{j,\sigma}^+ a_{j',\sigma} - b_{j,\sigma}^+ b_{j',\sigma})\tau(j - j'). \quad (36)$$

The properties of the function $\tau(x,y)$ of this equation are demonstrated here

$$\tau(\pm a, 0) = \tau(0, \pm a) = -\frac{\tau(0,0)}{3}, \quad \tau(\pm a, \pm a) = \frac{\tau(0,0)}{9}.$$

The first term of the right-hand part of (36) is the main local contribution of the oxygen holes to the Hamiltonian while the second one is its delocalizing perturbation. To have the possibility of carrying out the cell representation of other terms of the initial Hamiltonian (1), we firstly make such a representation for the oxygen-holes operators

$$p_{\mathbf{i}\pm a/2\hat{x},\sigma}^x = \sum_{\mathbf{j}}\left[a_{\mathbf{j},\sigma}\mu_a^{\pm x}(\mathbf{R}_i - \mathbf{R}_j) + b_{\mathbf{j},\sigma}\mu_b^{\pm x}(\mathbf{R}_i - \mathbf{R}_j)\right],$$

$$p_{\mathbf{i}\pm a/2\hat{y},\sigma}^y = \sum_{j}\left[a_{\mathbf{j},\sigma}\mu_a^{\pm y}(\mathbf{R}_i - \mathbf{R}_j) + b_{\mathbf{j},\sigma}\mu_b^{\pm y}(\mathbf{R}_i - \mathbf{R}_j)\right], \quad (37)$$

where

$$\mu_a^{\pm x}(\mathbf{R}) = \frac{1}{N}\sum_{\mathbf{k}}e^{-i\mathbf{kR}}u(\mathbf{k})e^{\mp ik_x\frac{a}{2}} = \frac{\delta_{y,0}}{\sqrt{2}\pi\left(\frac{x}{a}\pm\frac{1}{2}\right)},$$

$$\mu_b^{\pm x}(\mathbf{R}) = \frac{1}{N}\sum_{\mathbf{k}}e^{-i\mathbf{kR}}v(\mathbf{k})e^{\mp ik_x\frac{a}{2}} = \frac{\mp\cos\frac{\pi x}{a}\left(1 - \cos\frac{\pi y}{a}\right)}{\sqrt{2}\pi^2\left(\frac{x}{a}\pm\frac{1}{2}\right)\left(\frac{y}{a}\right)},$$

$$\mu_a^{\pm y}(\mathbf{R}) = -\frac{1}{N}\sum_{\mathbf{k}}e^{-i\mathbf{kR}}v^*(\mathbf{k})e^{\mp ik_y a/2} = -\frac{\delta_{x,0}}{\sqrt{2}\pi\left(\frac{y}{a}\pm\frac{1}{2}\right)},$$

$$\mu_b^{\pm y}(\mathbf{R}) = \frac{1}{N}\sum_{\mathbf{k}}e^{-i\mathbf{kR}}u^*(\mathbf{k})e^{\mp ik_y a/2} = \frac{\mp\cos\frac{\pi y}{a}\left(1 - \cos\frac{\pi x}{a}\right)}{\sqrt{2}\pi^2\left(\frac{y}{a}\pm\frac{1}{2}\right)\left(\frac{x}{a}\right)}.$$

(38)

To realize the next step of this program, we shall discuss firstly the Coulomb repulsion of the oxygen holes. This Hamiltonian has the form

$$H_p^c = U_p \sum_{\mathbf{i}} \left[p_{x\uparrow}^+ p_{x\uparrow} p_{x\downarrow}^+ p_{x\downarrow} + p_{y\uparrow}^+ p_{y\uparrow} p_{y\downarrow}^+ p_{y\downarrow} \right], \tag{39}$$

where, for shortness, we use the notations $p_x = p_{\mathbf{i}+a/2\widehat{x}}$, $p_y = p_{\mathbf{i}+a/2\widehat{y}}$, $\widehat{x}$ and $\widehat{y}$ are unit vectors in the two main directions.

On the basis of equations (37) and (39) we have

$$H_p^c = U_p \sum_{\mathbf{i}} \sum_{j_1,j_2,j_3,j_4} \{[a_{j_1\uparrow}^+ \mu_a^{x*}(\mathbf{R}_i - \mathbf{R}_{j_1}) + b_{j_1\uparrow}^+ \mu_b^{x*}(\mathbf{R}_i - \mathbf{R}_{j_1})] \times$$

$$\times [a_{j_2\uparrow} \mu_a^x(\mathbf{R}_i - \mathbf{R}_{j_2}) + b_{j_2\uparrow} \mu_b^x(\mathbf{R}_i - \mathbf{R}_{j_2})] \times$$

$$\times [a_{j_3\downarrow}^+ \mu_a^{x*}(\mathbf{R}_i - \mathbf{R}_{j_3}) + b_{j_3\downarrow}^+ \mu_b^{x*}(\mathbf{R}_i - \mathbf{R}_{j_3})] \times$$

$$\times [a_{j_4\downarrow} \mu_a^x(\mathbf{R}_i - \mathbf{R}_{j_4}) + b_{j_4\downarrow} \mu_b^x(\mathbf{R}_i - \mathbf{R}_{j_4})] +$$

$$+ [a_{j_1\uparrow}^+ \mu_a^{y*}(\mathbf{R}_i - \mathbf{R}_{j_1}) + b_{j_1\uparrow}^+ \mu_b^{y*}(\mathbf{R}_i - \mathbf{R}_{j_1})] \times$$

$$\times [a_{j_2\uparrow} \mu_a^y(\mathbf{R}_i - \mathbf{R}_{j_2}) + b_{j_2\uparrow} \mu_b^y(\mathbf{R}_i - \mathbf{R}_{j_2})] \times$$

$$\times [a_{j_3\downarrow}^+ \mu_a^{y*}(\mathbf{R}_i - \mathbf{R}_{j_3}) + b_{j_3\downarrow}^+ \mu_b^{y*}(\mathbf{R}_i - \mathbf{R}_{j_3})] +$$

$$+ [a_{j_4\downarrow} \mu_a^y(\mathbf{R}_i - \mathbf{R}_{j_4}) + b_{j_4\downarrow} \mu_b^y(\mathbf{R}_i - \mathbf{R}_{j_4})]\}. \tag{40}$$

Now we have carried out the summing by index $\mathbf{i}$ of copper ion sites and after some transformations obtained the rather complicated Coulomb contribution H_p^c, which contains 16 terms. We shall take into account only those of them the coefficients of which are not equal to zero in the local case

$$H_p^c = U_p \sum_{j_1,j_2,j_3,j_4} \{a_{j_1\uparrow}^+ a_{j_2\uparrow} a_{j_3\downarrow}^+ a_{j_4\downarrow} \times$$

$$\times \Psi^{aaaa}(\mathbf{R}_{j_1} - \mathbf{R}_{j_2}, \mathbf{R}_{j_3} - \mathbf{R}_{j_4}, \mathbf{R}_{j_2} - \mathbf{R}_{j_4}) +$$

$$+ b_{j_1\uparrow}^+ b_{j_2\uparrow} b_{j_3\downarrow}^+ b_{j_4\downarrow} \Psi^{bbbb}(\mathbf{R}_{j_1} - \mathbf{R}_{j_2}, \mathbf{R}_{j_3} - \mathbf{R}_{j_4}, \mathbf{R}_{j_2} - \mathbf{R}_{j_4}) +$$

$$+ a_{j_1\uparrow}^+ a_{j_2\uparrow} b_{j_3\downarrow}^+ b_{j_4\downarrow} \Psi^{aabb}(\mathbf{R}_{j_1} - \mathbf{R}_{j_2}, \mathbf{R}_{j_3} - \mathbf{R}_{j_4}, \mathbf{R}_{j_2} - \mathbf{R}_{j_4}) +$$

$$+ b_{j_1\uparrow}^+ b_{j_2\uparrow} a_{j_3\downarrow}^+ a_{j_4\downarrow} \Psi^{bbaa}(\mathbf{R}_{j_1} - \mathbf{R}_{j_2}, \mathbf{R}_{j_3} - \mathbf{R}_{j_4}, \mathbf{R}_{j_2} - \mathbf{R}_{j_4}) +$$

$$+ a_{j_1\uparrow}^+ b_{j_2\uparrow} b_{j_3\downarrow}^+ a_{j_4\downarrow} \Psi^{abba}(\mathbf{R}_{j_1} - \mathbf{R}_{j_4}, \mathbf{R}_{j_3} - \mathbf{R}_{j_2}, \mathbf{R}_{j_4} - \mathbf{R}_{j_2}) +$$

$$+ b_{j_1\uparrow}^+ a_{j_2\uparrow} a_{j_3\downarrow}^+ b_{j_4\downarrow} \Psi^{baab}(\mathbf{R}_{j_1} - \mathbf{R}_{j_4}, \mathbf{R}_{j_3} - \mathbf{R}_{j_2}, \mathbf{R}_{j_4} - \mathbf{R}_{j_2})\}, \tag{41}$$

where

$$\Psi^{aaaa}\left(\mathbf{R}_{j_1}-\mathbf{R}_{j_2},\mathbf{R}_{j_3}-\mathbf{R}_{j_4},\mathbf{R}_{j_2}-\mathbf{R}_{j_4}\right)=\frac{1}{N^3}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}}\mathrm{e}^{-i\mathbf{k}(\mathbf{R}_{j_1}-\mathbf{R}_{j_2})}\times$$

$$\times\,\mathrm{e}^{-i\mathbf{k}'(\mathbf{R}_{j_3}-\mathbf{R}_{j_4})+i\mathbf{q}(\mathbf{R}_{j_2}-\mathbf{R}_{j_4})}\left[\overset{*}{u}(\mathbf{k})u(\mathbf{k}+\mathbf{q})\overset{*}{u}(\mathbf{k}')u(\mathbf{k}'-\mathbf{q})+\right.$$

$$\left.+\,v(\mathbf{k})\overset{*}{v}(\mathbf{k}+\mathbf{q})v(\mathbf{k}')\overset{*}{v}(\mathbf{k}'-\mathbf{q})\right],$$

$$\Psi^{aabb}\left(\mathbf{R}_{j_1}-\mathbf{R}_{j_2},\mathbf{R}_{j_3}-\mathbf{R}_{j_4},\mathbf{R}_{j_2}-\mathbf{R}_{j_4}\right)=\frac{1}{N^3}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}}\mathrm{e}^{-i\mathbf{k}(\mathbf{R}_{j_1}-\mathbf{R}_{j_2})}\times$$

$$\times\,\mathrm{e}^{-i\mathbf{k}'(\mathbf{R}_{j_3}-\mathbf{R}_{j_4})+i\mathbf{q}(\mathbf{R}_{j_2}-\mathbf{R}_{j_4})}\left[\overset{*}{u}(\mathbf{k})u(\mathbf{k}+\mathbf{q})\overset{*}{v}(\mathbf{k}')v(\mathbf{k}'-\mathbf{q})+\right.$$

$$\left.+\,v(\mathbf{k})\overset{*}{v}(\mathbf{k}+\mathbf{q})u(\mathbf{k}')\overset{*}{u}(\mathbf{k}'-\mathbf{q})\right]. \tag{42}$$

The other coefficients of interest differ from the written ones by changing the indices a and b and corresponding functions $u(\mathbf{k})$ and $v(\mathbf{k})$ between them. By using (28) we obtain

$$\frac{1}{N^3}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}}\overset{*}{u}(\mathbf{k})u(\mathbf{k}+\mathbf{q})\overset{*}{u}(\mathbf{k}')u(\mathbf{k}'-\mathbf{q})=\frac{1}{12},$$

$$\frac{1}{N^3}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}}\overset{*}{u}(\mathbf{k})u(\mathbf{k}+\mathbf{q})\overset{*}{v}(\mathbf{k}')v(\mathbf{k}'-\mathbf{q})=\frac{1}{16}. \tag{43}$$

Equations (42) and (43) give us the following values of the coefficients

$$\Psi^{aaaa}\left(0,0,0\right)=\Psi^{bbbb}\left(0,0,0\right)=\frac{1}{6},$$

$$\Psi^{aabb}\left(0,0,0\right)=\Psi^{bbaa}\left(0,0,0\right)=\Psi^{abba}\left(0,0,0\right)=\Psi^{baab}\left(0,0,0\right)=\frac{1}{8}. \tag{44}$$

As a result of these calculations we obtain the following local contribution from the Coulomb repulsion of the oxygen holes

$$H_p^c\simeq U_a\sum_j n_{j\uparrow}^a n_{j\downarrow}^a + U_b\sum_j n_{j\uparrow}^b n_{j\downarrow}^b +$$

$$+\,U_{ab}\sum_j\left(n_{j\uparrow}^a n_{j\downarrow}^b + n_{j\uparrow}^b n_{j\downarrow}^a - S_{j+}^a S_{j-}^b - S_{j-}^a S_{j+}^b\right), \tag{45}$$

where the renormalized Coulomb constants of this Hamiltonian are $U_a=U_b=U_p/6$ and $U_{ab}=U_p/8$. In equation (45) the following definitions were used $(c=a,b)$

$$n_{j\sigma}^c=c_{j\sigma}^+ c_{j\sigma},\quad S_{j+}^c=c_{j\uparrow}^+ c_{j\downarrow},\quad S_{j-}^c=c_{j\downarrow}^+ c_{j\uparrow}. \tag{46}$$

The last term of (45) can be rewritten in more simple form

$$U_{ab} \sum_j \left(a_{j\uparrow}^+ b_{j\downarrow}^+ - a_{j\downarrow}^+ b_{j\uparrow}^+ \right) (b_{j\downarrow} a_{j\uparrow} - b_{j\uparrow} a_{j\downarrow}), \tag{47}$$

which can be interpreted as the interaction of the (a, b) singlet pairs.

The Hamiltonian (39) and its cell local representation (45) commutes with the spin operator $\mathbf{S}$ of the oxygen holes and its square S^2 both in the ionic initial and in the cell final representations. In the cell representation the operator $\mathbf{S}$ has the form

$$\mathbf{S}^{ab} = \sum_j \left(\mathbf{S}_j^a + \mathbf{S}_j^b \right) \tag{48}$$

$(c = a, b)$,

$$S_{jx}^c = \frac{1}{2}(S_{j+}^c + S_{j-}^c), \quad S_{jy}^c = \frac{1}{2i}(S_{j+}^c - S_{j-}^c), \quad S_{jz}^c = \frac{1}{2}(n_{j\uparrow}^c - n_{j\downarrow}^c). \tag{49}$$

The renormalized Coulomb repulsions U_a and U_{ab} of the diagonalizing fermions are essentially less than the initial repulsion of the holes on oxygen ions. The decrease of the constant U_a in our case is more considerable than the value $0.211 U_p$ obtained in previous papers (see for example [22]).

In the next part of the paper we shall use the following standard set of the theory parameters

$$t_{dp} = 1.3 \text{ eV}, \quad \frac{\epsilon_p - \epsilon_d}{t_{dp}} = 2.7, \quad \frac{t_{pp}}{t_{dp}} = 0.5,$$

$$\frac{U_d}{t_{dp}} = 7, \quad \frac{U_p}{t_{dp}} = 3, \quad \frac{U_{dp}}{t_{dp}} = 1. \tag{50}$$

Because in this set of parameters $U_a = t_{pp}$ and $U_{ab} = \frac{3}{4} t_{pp}$, both the effects of O-O tunneling and Coulomb repulsion of the holes on the oxygen ions have to be discussed together. The Hamiltonian (41), besides the local part (45), contains also the intercell transitions of the Wannier fermions. These last terms have the nonequal site indices and are several times less than local ones. In the next part of the paper these nonlocal contributions will be omitted. We shall omit also the nonlocal part of the kinetic energy of the oxygen holes (36).

Now we shall discuss the cell transformation of the Coulomb repulsion term H_{dp}^c of our initial Hamiltonian (1). It has the form

$$H_{dp}^c = U_{dp} \sum_{i,\sigma,\sigma'} d_{i,\sigma}^+ d_{i,\sigma} (p_{x,\sigma'}^+ p_{x,\sigma'} + p_{-x,\sigma'}^+ p_{-x,\sigma'} +$$

$$+ p_{y,\sigma'}^+ p_{y,\sigma'} + p_{-y,\sigma'}^+ p_{-y,\sigma'}). \tag{51}$$

Here, as in equation (39), we use our previous notations for $p_{x,\sigma}$ and $p_{y,\sigma}$. On the basis of (37) and (51) we obtain the new equations which contain only Wannier orbitals centred on the copper lattice sites of the form

$$
H_{dp}^c = U_{dp} \sum_{i,j,j'} \sum_{\sigma,\sigma'} n_{i\sigma}^d [\phi^{aa}\left(\mathbf{R}_i - \mathbf{R}_j; \mathbf{R}_i - \mathbf{R}_{j'}\right) a_{j\sigma'}^+ a_{j'\sigma'} +
$$
$$
+ \phi^{ab}\left(\mathbf{R}_i - \mathbf{R}_j; \mathbf{R}_i - \mathbf{R}_{j'}\right) a_{j\sigma'}^+ b_{j'\sigma'} + \phi^{ba}\left(\mathbf{R}_i - \mathbf{R}_j; \mathbf{R}_i - \mathbf{R}_{j'}\right) b_{j\sigma'}^+ a_{j'\sigma'} +
$$
$$
+ \phi^{bb}(\mathbf{R}_i - \mathbf{R}_j; \mathbf{R}_i - \mathbf{R}_{j'}) b_{j\sigma'}^+ b_{j'\sigma'}]. \quad (52)
$$

The coefficients of this equation are equal to

$$
\phi^{aa}(\mathbf{R}_i - \mathbf{R}_j; \mathbf{R}_i - \mathbf{R}_{j'}) = \frac{1}{N^2} \sum_{\mathbf{k},\mathbf{k}'} \exp\left(i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j) - i\mathbf{k}'(\mathbf{R}_i - \mathbf{R}_{j'})\right) \times
$$
$$
\times \left[2\cos\frac{(k_x - k_x')a}{2} \overset{*}{u}(\mathbf{k})u(\mathbf{k}') + 2\cos\frac{(k_y - k_y')a}{2}v(\mathbf{k})\overset{*}{v}(\mathbf{k}')\right],
$$

$$
\phi^{ab}(\mathbf{R}_i - \mathbf{R}_j; \mathbf{R}_i - \mathbf{R}_{j'}) = \frac{1}{N^2} \sum_{\mathbf{k},\mathbf{k}'} \exp\left(i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j) - i\mathbf{k}'(\mathbf{R}_i - \mathbf{R}_{j'})\right) \times
$$
$$
\times \left[2\cos\frac{(k_x - k_x')a}{2} \overset{*}{u}(\mathbf{k})v(\mathbf{k}') - 2\cos\frac{(k_y - k_y')a}{2}v(\mathbf{k})\overset{*}{u}(\mathbf{k}')\right], \quad (53)
$$

$$
\phi^{bb}(\mathbf{R}_i - \mathbf{R}_j; \mathbf{R}_i - \mathbf{R}_{j'}) = \frac{1}{N^2} \sum_{\mathbf{k},\mathbf{k}'} \exp\left(i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j) - i\mathbf{k}'(\mathbf{R}_i - \mathbf{R}_{j'})\right) \times
$$
$$
\times \left[2\cos\frac{(k_x - k_x')a}{2} \overset{*}{v}(\mathbf{k})v(\mathbf{k}') + 2\cos\frac{(k_y - k_y')a}{2}u(\mathbf{k})\overset{*}{u}(\mathbf{k}')\right],
$$

$$
\phi^{ba}(\mathbf{R}_i - \mathbf{R}_j; \mathbf{R}_i - \mathbf{R}_{j'}) = (\phi^{ab}(\mathbf{R}_i - \mathbf{R}_{j'}; \mathbf{R}_i - \mathbf{R}_j))^*.
$$

In the local case, when $i = j = j'$ among the four coefficients (53) only the first is different from zero and has the value

$$
\phi^{aa} = \phi^{aa}(0,0) = \frac{8}{\pi^2} \simeq 0.811. \quad (54)
$$

Therefore in the local limit only Coulomb interaction between $a_{\mathbf{i},\sigma}$ localizing fermions and $d_{\mathbf{i},\sigma}$ holes is manifested:

$$
H_{ad}^c = U_{ad} \sum_i n_i^d n_i^a,
$$
$$
U_{ad} = U_{dp}\phi^{aa} = \frac{8U_{dp}}{\pi^2}, \quad n_i^\alpha = \sum_\sigma n_{i\sigma}^\alpha, \quad \alpha = a, d. \quad (55)
$$

The effective repulsion constant which was obtained in paper [22] is $0.918 U_{dp}$ in comparision with our value $0.812 U_{dp}$. The coefficients of equation (53) are equal to

$$\varphi^{aa}(\mathbf{R}, \mathbf{R}') = \frac{1}{\pi^2} \left\{ \frac{\delta_{x,0} \delta_{x',0} \left(\dfrac{y}{a} \dfrac{y'}{a} + \dfrac{1}{4} \right)}{\left[\left(\dfrac{y}{a} \right)^2 - \dfrac{1}{4} \right] \left[\left(\dfrac{y'}{a} \right)^2 - \dfrac{1}{4} \right]} + \begin{pmatrix} x \to y \\ x' \to y' \end{pmatrix} \right\},$$

$$\varphi^{ab}(\mathbf{R}, \mathbf{R}') = \frac{-1}{2\pi^3} \left\{ \frac{\delta_{x,0} \left[1 - \cos \left(\dfrac{\pi x'}{a} \right) \right] \cos \left(\dfrac{\pi y'}{a} \right) \left(\dfrac{y}{a} + \dfrac{y'}{a} \right)}{\left(\dfrac{x'}{a} \right) \left[\left(\dfrac{y}{a} \right)^2 - \dfrac{1}{4} \right] \left[\left(\dfrac{y'}{a} \right)^2 - \dfrac{1}{4} \right]} - \begin{pmatrix} x \to y \\ x' \to y' \end{pmatrix} \right\},$$

(56)

$$\varphi^{bb}(\mathbf{R}, \mathbf{R}') = \frac{1}{\pi^4} \left\{ \frac{\left[1 - \cos \left(\dfrac{\pi x'}{a} \right) \right] \left[1 - \cos \left(\dfrac{\pi x}{a} \right) \right] \cos \left(\dfrac{\pi y}{a} \right) \cos \left(\dfrac{\pi y'}{a} \right)}{\left(\dfrac{x}{a} \right) \left(\dfrac{x'}{a} \right) \left[\left(\dfrac{y}{a} \right)^2 - \dfrac{1}{4} \right] \left[\left(\dfrac{y'}{a} \right)^2 - \dfrac{1}{4} \right]} \times \right.$$

$$\left. \times \left(\frac{y}{a} \frac{y'}{a} + \frac{1}{4} \right) - \begin{pmatrix} x \to y \\ x' \to y' \end{pmatrix} \right\}.$$

Here $x(x')$ and $y(y')$ are the projections of the vectors $\mathbf{R}(\mathbf{R}')$ which are the integer multiples of lattice constant a. In such a way, this Coulomb interaction was not changed considerably, in comparison with its initial value, after the cell transformation. The operator (52) can be presented as the sum of the main local and its perturbation contributions

$$H^c_{dp} = H^c_{ad} + H'_{dp}, \tag{57}$$

where H'_{dp} is obtained from (52) by omitting all the local terms.

Thus we have finished the transformation to the cell representation of all the terms of Hamiltonian (1), which contain clusters of oxygen holes. We have separated the local one-cell part from the intercell contributions. The first of them H^0 is the main contribution of the orthogonalized Wannier fermions and the second H' is considered as a perturbation. In the final form our Hamiltonian is

$$H = H^0 + H', \quad H^0 = \sum_i H^0_i, \tag{58}$$

where the one-cell local contribution is the following

$$H^0 = \epsilon_d \sum_\sigma n_\sigma^d + U_d n_\uparrow^d n_\downarrow^d + \epsilon_a \sum_\sigma n_\sigma^a + U_a n_\uparrow^a n_\downarrow^a + \epsilon_b \sum_\sigma n_\sigma^b + U_b n_\uparrow^b n_\downarrow^b +$$
$$+ t_{ad} \sum_\sigma \left(d_\sigma^+ a_\sigma + a_\sigma^+ d_\sigma \right) + U_{ad} n^d n^a +$$
$$+ U_{ab} \left(n_\uparrow^a n_\downarrow^b + n_\downarrow^a n_\uparrow^b - S_+^a S_-^b - S_-^a S_+^b \right). \quad (59)$$

Here, for simlicity, we have omitted the index $\mathbf{i}$ of the copper site and supposed the equalities $U_b = U_a$, $U_{ab} = 3/4 U_a$ and used the definitions $\epsilon_{a,b} = \epsilon_p \mp 4 t_{pp} \tau(0)$. The perturbative term has rather complicated form, because it contains a lot of intercell contributions from $d_{\mathbf{i}\sigma}$, $a_{\mathbf{i}\sigma}$ and $b_{\mathbf{i}\sigma}$ orthogonalized fermions. We consider that the most important perturbations are the following

$$H' = 2 t_{dp} \sum_{j \neq i} \left[d_{i\sigma}^+ \left(\lambda_a(\mathbf{R}_i - \mathbf{R}_j) a_{j\sigma} + \lambda_b(\mathbf{R}_i - \mathbf{R}_j) b_{j\sigma} \right) + \mathrm{H.\,C.} \right] +$$
$$+ U_{dp} \sum_{i,j,j'}' \sum_\sigma n_i^d [\phi^{aa}(\mathbf{R}_i - \mathbf{R}_j, \mathbf{R}_i - \mathbf{R}_{j'}) a_{j\sigma}^+ a_{j'\sigma} +$$
$$+ \phi^{ab}(\mathbf{R}_i - \mathbf{R}_j, \mathbf{R}_i - \mathbf{R}_{j'}) a_{j\sigma b}^+ b_{j'\sigma} + \phi^{ba}(\mathbf{R}_i - \mathbf{R}_j, \mathbf{R}_i - \mathbf{R}_{j'}) b_{j\sigma a}^+ a_{j'\sigma} +$$
$$+ \phi^{bb}(\mathbf{R}_i - \mathbf{R}_j, \mathbf{R}_i - \mathbf{R}_{j'}) b_{j\sigma b}^+ b_{j'\sigma}]. \quad (60)$$

Here the sum index with prime means the absence of contributions with the equality $i = j = j'$ of copper site indices. In (60) we have omitted the contributions proportional to t_{pp} and U_p in conformity with the previous explanation.

2. THE DIAGONALIZATION OF THE CELL HAMILTONIAN

As we can see from equation (59), in every cell centred on Cu site, there are three kinds of strongly correlated fermions. Namely there are $d_{\mathbf{i},\sigma}$ holes on the copper ions and two diagonalizing fermions $a_{\mathbf{i},\sigma}$ and $b_{\mathbf{i},\sigma}$ which describe the movement of the oxygen holes in CuO_2 plane. Every one of these three kinds of particles, if they are considered as independent, has four quantum states $|0\rangle$, $|\uparrow\rangle$, $|\downarrow\rangle$, $|\uparrow\downarrow\rangle$, with the energies $E_0^\alpha = 0$, $E_\sigma^\alpha = \epsilon_\alpha$, $E_2^\alpha = 2\epsilon_\alpha + U_\alpha$ $\alpha = a, b, d$. Therefore the full number of the states for one cell is equal to $4^3 = 64$. The matrix of the local Hamiltonian (59) calculated on the basis of the cell functions ψ_A is a rather complicated one being of 64×64 rank. Really this matrix is quasi-diagonal containing the submatrices with maximal rank equal to four. The index A of the cell quantum functions contains the N_a, N_b, and N_d numbers of our particles and also their spin quantum numbers. But the renormalized quantum states $|E_\lambda\rangle$ of this Hamiltonian don't conserve the individual numbers of our

Table 1. **The distribution of states number N_s by quantum numbers**

N	S	S_z	N_s	N	S	S_z	N_s	N	S	S_z	N_s
0	0	0	1	3	1/2	+1/2	8	4	0	0	6
1	1/2	+1/2	3			-1/2	8		1	1	3
		-1/2	3		3/2	+3/2	1			0	3
2	0	0	6			+1/2	1			-1	3
	1	-1	3			-1/2	1	5	1/2	+1/2	3
		0	3			-3/2	1			-1/2	3
		1	3					6	0	0	1

fermions and therefore we use as the real quantum numbers the full numbers of particles $N = N_a + N_b + N_d$ (this number has not to be confused with N — the number of copper ion sites, which was used in previous part of the paper), the full spin S and its projection S_z. Some additional inner quantum numbers will be used also. The renormalized functions $|E_\lambda\rangle$ are the linear superpositions of the cell functions ψ_A and the coefficients of proportionality are determined by the elements of the S matrix which realizes the transformation from the initial cell representation to the final renormalized one.

The S-matrix method has been firstly elaborated by us [44–47] for discussing the properties of atomic limit of the periodic Anderson model. N_s is the number of the renormalized quantum states which depends of the main three quantum numbers N, S, and S_z. The full number of these states is 64. The distribution of N_s is demonstrated in Table 1.

To have some notion about our S-matrix method we present here a brief information about it. This method is based on the existence of a full system of orthonormalized functions $\Phi_n(E_\lambda)$ which are determined from the matrix equation

$$\left(\widehat{H}^0 - E\lambda\widehat{I}\right) \begin{pmatrix} \Phi_1(E_\lambda) \\ : \\ \Phi_n(E_\lambda) \end{pmatrix} = 0, \tag{61}$$

with the following conditions of orthonormalization

$$\sum_\lambda \Phi_n^*(E_\lambda)\Phi_m(E_\lambda) = \delta_{nm},$$

$$\sum_n \Phi_n^*(E_\lambda)\Phi_n(E_{\lambda'}) = \delta_{\lambda\lambda'}. \tag{62}$$

$\widehat{H}^0$ is the matrix of the Hamiltonian, calculated on the basis of the initial particle functions ψ_A, and $\widehat{I}$ is the unit matrix. The knowledge of the new functions

$\Phi_n(E_\lambda)$ permits us to construct the S matrix

$$\widehat{S} = \begin{pmatrix} \Phi_1(E_1)...\Phi_1(E_n) \\ \vdots \qquad \vdots \\ \Phi_n(E_1)...\Phi_n(E_n) \end{pmatrix}. \qquad (63)$$

The relation between initial Ψ_n and final renormalized $|E_\lambda\rangle$ functions is

$$\Psi_n = \sum_\lambda \Phi_n(E_\lambda)|E_\lambda\rangle, \quad |E_\lambda\rangle = \sum_n \Phi_n^*(E_\lambda)\Psi_n. \qquad (64)$$

Let us begin now the detailed analysis of eigenvalues and eigenfunctions renormalization of the local Hamiltonian (59). It is obvious that the vacuum state with $N = 0$ remains unrenormalized. The first nontrivial case is that with $N = 1$. The full number of states is $N_s = 6$. The spin of these states is $S = 1/2$. Three of them have the value S_z equal to 1/2; and others to 1/2. The initial nonrenormalized functions with $S_z = 1/2$ are

$$\Psi_1 = d_\uparrow^+|0\rangle, \quad \Psi_2 = a_\uparrow^+|0\rangle, \quad \Psi_3 = b_\uparrow^+|0\rangle. \qquad (65)$$

It is easy to find the following equations

$$H^0\Psi_1 = \epsilon_d\Psi_1 + V\Psi_2, \quad H^0\Psi_2 = \epsilon_a\Psi_2 + V\Psi_1, \quad H^0\Psi_3 = \epsilon_b\Psi_3. \qquad (66)$$

Here $V = t_{ad}$. The corresponding submatrix of the second rank constructed in the subspace of the functions Ψ_1 and Ψ_2 has the form

$$\begin{pmatrix} \epsilon_d - E & V \\ V & \epsilon_a - E \end{pmatrix}. \qquad (67)$$

Here and below the matrix $\widehat{H}^0 - E\widehat{I}$ is used. From the condition that the determinant of this matrix is zero, we obtain two renormalized energy values, which belong to doublet states

$$E_{1,2}\,(N = 1, S = 1/2) = E_{1,2} = \frac{1}{2}\left[\epsilon_a + \epsilon_d \mp \sqrt{(\epsilon_a - \epsilon_d)^2 + 4V^2}\right]. \qquad (68)$$

On the basis of (67) we determine two orthonormalized functions $\Phi_1(E_\lambda)$ and $\Phi_2(E_\lambda)$ in the form

$$\Phi_2(E_\lambda) = \frac{E_\lambda - \epsilon_d}{V}\Phi_1(E_\lambda),$$

$$\Phi_1(E_{1,2}) = \frac{1}{\sqrt{2}}\left[1 \mp \frac{\epsilon_a - \epsilon_d}{\sqrt{(\epsilon_a - \epsilon_d)^2 + 4V^2}}\right]^{1/2}. \qquad (69)$$

By using these results, we obtain

$$|E_1\rangle = \Phi_1(E_1) \left[\Psi_1 + \frac{E_1 - \epsilon_d}{V} \Psi_2 \right],$$

$$|E_2\rangle = \Phi_1(E_2) \left[\Psi_1 + \frac{E_2 - \epsilon_d}{V} \Psi_2 \right]. \tag{70}$$

Here and below, for shortness, we omit the values of quantum numbers and consider the Φ functions to be real. The third function Ψ_3 is the eigenfunction of our Hamiltonian and consequently $E_3 = \epsilon_b, |E_3\rangle = \Psi_3$, and $\Phi_3(E_3) = 1$. Other three functions Ψ_4, Ψ_5, and Ψ_6 differ from the previous three only by the direction of spin, and the renormalization of them is the same as for the first group. We have $E_{4,5} = E_{1,2}$, $E_6 = E_3$, $\Phi_{4,5} = \Phi_{1,2}$, and $\Phi_6 = \Phi_3$. More interesting case is that of two particles $N = 2$ with two possible values of full spin $S = 0$ and $S = 1$. For $S = 0$ there are six initial singlet states ψ_A. They are enumerated below

$$\Psi_1 = \frac{1}{\sqrt{2}} \left(d_\uparrow^+ a_\downarrow^+ - d_\downarrow^+ a_\uparrow^+ \right) |0\rangle, \quad \Psi_2 = a_\uparrow^+ a_\downarrow^+ |0\rangle,$$

$$\Psi_3 = d_\uparrow^+ d_\downarrow^+ |0\rangle, \quad \Psi_4 = \frac{1}{\sqrt{2}} \left(d_\uparrow^+ b_\downarrow^+ - d_\downarrow^+ b_\uparrow^+ \right) |0\rangle, \tag{71}$$

$$\Psi_5 = \frac{1}{\sqrt{2}} \left(a_\uparrow^+ b_\downarrow^+ - a_\downarrow^+ b_\uparrow^+ \right) |0\rangle, \quad \Psi_6 = b_\uparrow^+ b_\downarrow^+ |0\rangle.$$

The action of Hamiltonian (59) on them results in

$$H^0 \Psi_1 = (\epsilon_a + \epsilon_d + G) \Psi_1 + \sqrt{2} V \Psi_2 + \sqrt{2} V \Psi_3,$$

$$H^0 \Psi_2 = (2\epsilon_a + U_a) \Psi_2 + \sqrt{2} V \Psi_1,$$

$$H^0 \Psi_3 = (2\epsilon_d + U_d) \Psi_3 + \sqrt{2} V \Psi_1, \quad H^0 \Psi_4 = (\epsilon_d + \epsilon_b) \Psi_4 + V \Psi_5, \tag{72}$$

$$H^0 \Psi_5 = (\epsilon_a + \epsilon_b + 2U_{ab}) \Psi_5 + V \Psi_4, \quad H^0 \Psi_6 = (2\epsilon_b + U_b) \Psi_6.$$

The first three functions form a trio of (a, d) singlets with the following submatrix

$$\begin{pmatrix} \epsilon_a + \epsilon_d + G - E & \sqrt{2} V & \sqrt{2} V \\ \sqrt{2} V & 2\epsilon_a + U_a - E & 0 \\ \sqrt{2} V & 0 & 2\epsilon_d + U_d - E \end{pmatrix}. \tag{73}$$

Here the quantity G means $G = U_{ad}$. The renormalized energies of this trio of states are determined from the equation of the third degree:

$$(2\epsilon_a + U_a - E)(2\epsilon_d + U_d - E)(\epsilon_a + \epsilon_d + G - E) -$$
$$- 2V^2 (2\epsilon_a + U_a + 2\epsilon_d + U_d - 2E) = 0. \tag{74}$$

The state with the lowest energy, from this trio, is the Zhang–Rice singlet. To obtain the approximate values of these eigenenergies E_1, E_2, E_3 we use the series expansions by $\dfrac{1}{U_d}$. In this case we have

$$E_{1,2}(2,0) \simeq 2\epsilon_a + \frac{1}{2}\left[\epsilon_d - \epsilon_a + G + U_a \mp \sqrt{(\epsilon_d - \epsilon_a + G - U_a)^2 + 8V^2} \times\right.$$

$$\left. \times \left[1 \pm \frac{2V^2}{U_d\sqrt{(\epsilon_d - \epsilon_a + G - U_a)^2 + 8V^2}}\right]\right], \quad (75)$$

$$E_3(2,0) \simeq 2\epsilon_d + U_d + \frac{2V^2}{U_d}.$$

In this equation the index $1(2)$ refers to the up(down) sign of the right-hand part of it. The functions $\Phi_n(E_\lambda)$ are equal to

$$\Phi_2(E_\lambda) = -\frac{\sqrt{2}V\Phi_1(E_\lambda)}{2\epsilon_a + U_a - E_\lambda}, \quad \Phi_3(E_\lambda) = -\frac{\sqrt{2}V\Phi_1(E_\lambda)}{2\epsilon_d + U_d - E_\lambda},$$

$$\Phi_1(E_\lambda) = \left(1 + \frac{2V^2}{(2\epsilon_a + U_a - E_\lambda)^2} + \frac{2V^2}{(2\epsilon_d + U_d - E_\lambda)^2}\right)^{1/2}, \quad (76)$$

and as a result we obtain the following renormalized eigenfunctions $(\lambda = 1, 2, 3)$

$$|E_\lambda\rangle = \frac{\Phi_1(E_\lambda)}{\sqrt{2}} \times$$

$$\times \left[d^+_\uparrow a^+_\downarrow - d^+_\downarrow a^+_\uparrow - \frac{2Va^+_\uparrow a^+_\downarrow}{2\epsilon_a + U_a - E_\lambda} - \frac{2Vd^+_\uparrow d^+_\downarrow}{2\epsilon_d + U_d - E_\lambda}\right]|0\rangle. \quad (77)$$

The two functions Ψ_4 and Ψ_5 form a doublet of singlet states with corresponding submatrix

$$\begin{pmatrix} \epsilon_d + \epsilon_b - E & V \\ V & \epsilon_a + \epsilon_b + 2U_{ab} - E \end{pmatrix}. \quad (78)$$

Two values for renormalized energies of (d, b) and (a, b) singlets are

$$E_{4,5}(2,0) = \epsilon_b + \frac{1}{2}\left[\epsilon_a + \epsilon_d + 2U_{ab} \mp \sqrt{(\epsilon_d - \epsilon_a - 2U_{ab})^2 + 4V^2}\right]. \quad (79)$$

These values correspond to the energies of the (a, d) doublet (68) in the presence of additional b fermion. This presence changes the value of energy ϵ_a to $\epsilon_a + 2U_{ab}$. The functions $\Phi_n(E_\lambda)$ with $n = 4, 5$ are the following:

$$\Phi_5(E_\lambda) = \frac{(E_\lambda - \epsilon_d - \epsilon_b)}{V} \Phi_4(E_\lambda),$$

$$\Phi_4(E_{4,5}) = \frac{1}{2} \left[1 \pm \frac{\epsilon_a + 2U_{ab} - \epsilon_d}{\sqrt{(\epsilon_a + 2U_{ab} - \epsilon_d)^2 + 4V^2}} \right]^{1/2}. \tag{80}$$

As a result we have

$$|E_{4,5}\rangle = \Phi_4(E_{4,5}) \left[\Psi_4 + \frac{E_{4,5} - \epsilon_d - \epsilon_b}{V} \Psi_5 \right]. \tag{81}$$

The last singlet state Ψ_6 from this group is a doublon of b fermions. It remains unrenormalized with the energy value $E_6 = 2\epsilon_b + U_b$ and unrenormalized eigenfunction $|E_6\rangle = \Psi_6$. Now we shall examine the triplet ($N = 2$, $S = 1$) subspace of states. For each projection of spin $S_z = 1, 0$, there are three degenerate states. They are

$$\Psi_7 = \frac{1}{\sqrt{2}} \left(d_\uparrow^+ a_\downarrow^+ + d_\downarrow^+ a_\uparrow^+ \right) |0\rangle, \quad \Psi_8 = \frac{1}{\sqrt{2}} \left(d_\uparrow^+ b_\downarrow^+ + d_\downarrow^+ b_\uparrow^+ \right) |0\rangle,$$

$$\Psi_9 = \frac{1}{\sqrt{2}} \left(a_\uparrow^+ b_\downarrow^+ + a_\downarrow^+ b_\uparrow^+ \right) |0\rangle, \quad \Psi_{10} = d_\uparrow^+ a_\uparrow^+ |0\rangle, \quad \Psi_{11} = d_\uparrow^+ b_\uparrow^+ |0\rangle, \tag{82}$$

$$\Psi_{12} = a_\uparrow^+ b_\uparrow^+ |0\rangle, \quad \Psi_{13} = d_\downarrow^+ a_\downarrow^+ |0\rangle, \quad \Psi_{14} = d_\downarrow^+ b_\downarrow^+ |0\rangle, \quad \Psi_{15} = a_\downarrow^+ b_\downarrow^+ |0\rangle.$$

The action of the Hamiltonian (59) on them gives the results:

$$H^0 \Psi_7 = (\epsilon_a + \epsilon_d + G) \Psi_7, \quad H^0 \Psi_8 = (\epsilon_d + \epsilon_b) \Psi_8 + V \Psi_9,$$

$$H^0 \Psi_9 = (\epsilon_a + \epsilon_b) \Psi_9 + V \Psi_8, \quad H^0 \Psi_{10} = (\epsilon_a + \epsilon_d + G) \Psi_{10}, \tag{83}$$

$$H^0 \Psi_{11} = (\epsilon d + \epsilon_b) \Psi_{11} + V \Psi_{12}, \quad H^0 \Psi_{12} = (\epsilon_a + \epsilon_b) \Psi_{12} + V \Psi_{11}.$$

The equations for other three functions Ψ_{13}, Ψ_{14}, and Ψ_{15} are similar to those for Ψ_{10}, Ψ_{11}, and Ψ_{12} correspondingly. The triplet states Ψ_7, Ψ_{10}, and Ψ_{13} remain unrenormalized with the energy value $E_7 = E_{10} = E_{13} = \epsilon_a + \epsilon_d + G$. Their eigenfunctions also remain unrenormalized ($\lambda = 7, 10, 13$) : $|E_\lambda\rangle = \Psi_\lambda$. Then, we have a doublet of states Ψ_8 and Ψ_9 with a submatrix

$$\begin{pmatrix} \epsilon_d + \epsilon_b - E & V \\ V & \epsilon_a + \epsilon_b - E \end{pmatrix}. \tag{84}$$

From it we obtain two values of renormalized energies

$$E_{8,9} = \epsilon_b + \frac{1}{2}\left[\epsilon_a + \epsilon_d \mp \sqrt{(\epsilon_a - \epsilon_d)^2 + 4V^2}\right]. \qquad (85)$$

These values correspond to those of the (a, d) doublet in the presence of b fermion. The functions Φ_8 and Φ_9 are equal to

$$\Phi_9(E_\lambda) = \frac{E_\lambda - \epsilon_d - \epsilon_b}{\epsilon_d + \epsilon_b}\Phi_8(E_\lambda), \quad \lambda = 8, 9,$$

$$\Phi_8(E_{8,9}) = \left[1 \pm \frac{\epsilon_a - \epsilon_d}{\sqrt{(\epsilon_a - \epsilon_d)^2 + 4V^2}}\right]^{1/2}, \qquad (86)$$

and, as a result, we obtain the renormalized eigenfunctions

$$|E_8\rangle = \Phi_8(E_8)\left[\Psi_8 + \frac{E_8 - \epsilon_d - \epsilon_b}{V}\Psi_9\right],$$

$$|E_9\rangle = \Phi_8(E_9)\left[\Psi_8 + \frac{E_9 - \epsilon_d - \epsilon_b}{V}\Psi_9\right]. \qquad (87)$$

It is easy to see that for two other doublets (Ψ_{11}, Ψ_{12}) and (Ψ_{14}, Ψ_{15}) composed of our triplet states we shall obtain the same results. Thus we have $E_8 = E_{11} = E_{14}$ and $E_9 = E_{12} = E_{15}$.

Now we shall discuss the situation when the number of particles is three $(N = 3)$, and there are two spin values $S = 1/2$ and $S = 3/2$. First of all, it is necessary to analyse the spin structure of our initial cell functions. In order to do that, we shall examine the next three functions

$$\chi_1 = d_\uparrow^+ a_\downarrow^+ b_\uparrow^+ |0\rangle, \quad \chi_2 = d_\downarrow^+ a_\uparrow^+ b_\uparrow^+ |0\rangle, \quad \chi_3 = d_\uparrow^+ a_\uparrow^+ b_\downarrow^+ |0\rangle, \qquad (88)$$

and will act on them with the operator S^2, where $\mathbf{S}$ is the spin operator of three particles

$$\mathbf{S} = \mathbf{S}^a + \mathbf{S}^b + \mathbf{S}^d,$$

$$(\mathbf{S})^2 = 3\left[(S_z^a)^2 + (S_z^b)^2 + (S_z^d)^2\right] + 2\left[S_z^a S_z^b + S_z^a S_z^d + S_z^b S_z^d\right] + \qquad (89)$$

$$+ S_-^a S_+^b + S_+^a S_-^b + S_-^a S_+^d + S_+^a S_-^d + S_-^b S_+^d + S_+^b S_-^d,$$

where

$$S_z^c = \frac{1}{2}\left(n_\uparrow^c - n_\downarrow^c\right), \quad S_+^c = c_\uparrow^+ c_\downarrow, \quad S_-^c = c_\downarrow^+ c_\uparrow, \quad c = a, b, d.$$

As a result, we have

$$(\mathbf{S})^2 \chi_1 = \frac{7}{4}\chi_1 + \chi_2 + \chi_3, \quad (\mathbf{S})^2 \chi_2 = \chi_1 + \frac{7}{4}\chi_2 + \chi_3,$$

$$(\mathbf{S})^2 \chi_3 = \chi_1 + \chi_2 + \frac{7}{4}\chi_3. \tag{90}$$

These results suggest the necessity of introducing the new orthonormalized cell functions which are the eigenfunctions of the operator (89). We shall form two new linear superpositions Ψ_1 and Ψ_2 from initial three functions (88) and add to them two other functions Ψ_3 and Ψ_4 which are listed below

$$\Psi_1 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2), \quad \Psi_2 = \frac{1}{\sqrt{6}}(\chi_1 + \chi_2 - 2\chi_3),$$

$$\Psi_3 = a_\uparrow^+ a_\downarrow^+ b_\uparrow^+ |0\rangle, \quad \Psi_4 = d_\uparrow^+ d_\downarrow^+ b_\uparrow^+ |0\rangle. \tag{91}$$

These four functions are the components of one quartet with the spin $S = 1/2$ and its projection equal to 1/2. The third linear combination $\chi_1 + \chi_2 + \chi_3$ of the functions (88) has the spin $S = 3/2$ and will be discussed below together with other functions with such spin value. The quartet functions fulfill the following system of equations

$$H^0 \Psi_1 = \left(\epsilon_a + \epsilon_b + \epsilon_d + G + \frac{U_{ab}}{2}\right)\Psi_1 + \frac{\sqrt{3}}{2}U_{ab}\Psi_2 + \sqrt{2}V(\Psi_3 + \Psi_4),$$

$$H^0 \Psi_2 = \left(\epsilon_a + \epsilon_b + \epsilon_d + G + \frac{3U_{ab}}{2}\right)\Psi_2 + \frac{\sqrt{3}}{2}U_{ab}\Psi_1,$$

$$H^0 \Psi_3 = (2\epsilon_a + U_a + \epsilon_b + U_{ab})\Psi_3 + \sqrt{2}V\Psi_1,$$

$$H^0 \Psi_4 = (2\epsilon_d + U_d + \epsilon_b)\Psi_4 + \sqrt{2}V\Psi_1, \tag{92}$$

with the submatrix of the form

$$\begin{pmatrix} \epsilon_a + \epsilon_b + \epsilon_d + \\ +G + \dfrac{U_{ab}}{2} - E & \dfrac{\sqrt{3}}{2}U_{ab} & \sqrt{2}V & \sqrt{2}V \\ \dfrac{\sqrt{3}}{2}U_{ab} & \begin{matrix} \epsilon_a + \epsilon_b + \epsilon_d + \\ +G + \dfrac{3U_{ab}}{2} - E \end{matrix} & 0 & 0 \\ \sqrt{2}V & 0 & \begin{matrix} 2\epsilon_a + U_a + \epsilon_b + \\ +U_{ab} - E \end{matrix} & 0 \\ \sqrt{2}V & 0 & 0 & \begin{matrix} 2\epsilon_d + U_d + \\ +\epsilon_b - E \end{matrix} \end{pmatrix}. \tag{93}$$

The renormalized energy values are the solutions of the following equation of the fourth order:

$$\left(\epsilon_a + \epsilon_d + \overline{G} - E'\right)^2 \left(2\epsilon_a + \overline{U}_a - E'\right)\left(2\epsilon_d + U_d - E'\right) -$$
$$- 2V^2 \left(\epsilon_a + \epsilon_d + \overline{G} + \frac{U_{ab}}{2} - E'\right)\left(2\epsilon_d + U_d + 2\epsilon_a + \overline{U}_a - 2E'\right) -$$
$$- U_{ab}^2 \left(2\epsilon_a + \overline{U}_a - E'\right)\left(2\epsilon_d + U_d - E'\right) = 0, \quad (94)$$

where

$$E' = E - \epsilon_b, \quad \overline{G} = G + U_{ab}, \quad \overline{U}_a = U_a + U_{ab}.$$

Four solutions of this equations E'_n, $n = 1, 2, 3, 4$ must be subjected to the condition:

$$4\left(\epsilon_a + \epsilon_b + \epsilon_d\right) + 2G + 3U_{ab} + U_a + U_d = \sum_n E'_n.$$

For the large values of Coulomb repulsion U_d one of the energy values is

$$E \simeq U_d + 2\epsilon_d + \epsilon_b + \frac{2V^2}{U_d}, \quad (95)$$

the other three solutions can be presented in the approximate form

$$E \simeq E'_0 + \epsilon_b + E'_1, \quad (96)$$

where the quantity E'_0 is the solution of the following equation of the third order

$$\left(\epsilon_a + \epsilon_d + \overline{G} - E'_0\right)^2 \left(2\epsilon_a + U_a - E'_0\right) -$$
$$- 2V^2 \left(\epsilon_a + \epsilon_d + \overline{G} + \frac{U_{ab}}{2} - E'_0\right) - U_{ab}^2 \left(2\epsilon_a + \overline{U}_a - E'_0\right) = 0. \quad (97)$$

The energy correction E'_1, which is proportional to the small value U_d^{-1} is determined by the equation:

$$E'_1 = \frac{1}{U_d} \left\{ 2V^2 \left(\epsilon_a + \epsilon_d + \overline{G} + \frac{U_{ab}}{2} - E'_0\right)\left(2\epsilon_a + \overline{U}_a + 2\epsilon_d - 2E'_0\right) - \right.$$
$$\left. - (2\epsilon_d - E'_0)\left(2\epsilon_a + \overline{U}_a - E'_0\right)\left[\left(\epsilon_a + \epsilon_d + \overline{G} - E'_0\right)^2 - U_{ab}^2\right]\right\} \times$$
$$\times \left\{U_{ab}^2 + 2V^2 - \left(\epsilon_a + \epsilon_d + \overline{G} - E'_0\right)\left(5\epsilon_a + \epsilon_d + \overline{G} + 2\overline{U}_a - 3E'_0\right)\right\}^{-1}. \quad (98)$$

To obtain the renormalized functions $|E_\lambda\rangle$, we shall use the following values of the Φ_1, Φ_2, Φ_3 and Φ_4 eigenfunctions of the matrix (93):

$$\Phi_2(E_\lambda) = -\frac{\sqrt{3}}{2}\frac{U_{ab}\Phi_1(E_\lambda)}{\left(\epsilon_a + \epsilon_d + \overline{G} + \dfrac{U_{ab}}{2} - E'_\lambda\right)},$$

$$\Phi_3(E_\lambda) = -\frac{\sqrt{2}V\Phi_1(E_\lambda)}{\left(2\epsilon_a + \overline{\overline{U}}_a - E'_\lambda\right)}, \quad \Phi_4(E_\lambda) = -\frac{\sqrt{2}V\Phi_1(E_\lambda)}{\left(2\epsilon_d + U_d - E'_\lambda\right)},$$

$$\Phi_1(E_\lambda) = \left\{ 1 + \frac{3}{4}\frac{U_{ab}^2}{\left(\epsilon_a + \epsilon_d + \overline{G} + \dfrac{U_{ab}}{2} - E'_\lambda\right)^2} + \right. \tag{99}$$

$$\left. + \frac{2V^2}{\left(2\epsilon_a + \overline{U}_a - E'_\lambda\right)^2} + \frac{2V^2}{\left(2\epsilon_d + U_d - E'_\lambda\right)^2} \right\}^{-1/2}.$$

Consequently the four renormalized eigenfunctions $|E_\lambda\rangle$ have the form ($\lambda = 1, 2, 3, 4$)

$$|E_\lambda\rangle = \Phi_1(E_\lambda)\left[\Psi_1 - \frac{\sqrt{3}}{2}\frac{U_{ab}\Psi_2}{\left(\epsilon_a + \epsilon_d + \overline{G} + \dfrac{U_{ab}}{2} - E'_\lambda\right)} - \right.$$

$$\left. - \frac{\sqrt{2}V\Psi_3}{\left(2\epsilon_a + \overline{U}_a - E'_\lambda\right)} - \frac{\sqrt{2}V\Psi_4}{\left(2\epsilon_d + U_d - E'_\lambda\right)}\right]. \tag{100}$$

Let us now discuss the next four states $\Psi_5, ..., \Psi_8$ with $S = 1/2$ and $S_z = 1/2$:

$$\Psi_5 = b_\uparrow^+ b_\downarrow^+ d_\uparrow^+ |0\rangle, \quad \Psi_6 = b_\uparrow^+ b_\downarrow^+ a_\uparrow^+ |0\rangle,$$

$$\Psi_7 = a_\uparrow^+ a_\downarrow^+ d_\uparrow^+ |0\rangle, \quad \Psi_8 = d_\uparrow^+ d_\downarrow^+ a_\uparrow^+ |0\rangle. \tag{101}$$

We can form from them two doublet groups (Ψ_5, Ψ_6) and (Ψ_7, Ψ_8). For the first doublet we have the equations

$$H^0\Psi_5 = (2\epsilon_b + U_b + \epsilon_d)\Psi_5 + V\Psi_6,$$

$$H^0\Psi_6 = (2\epsilon_b + U_b + \epsilon_a + U_{ab})\Psi_6 + V\Psi_5. \tag{102}$$

In this subspace of functions, we have the following submatrix

$$\begin{pmatrix} 2\epsilon_b + U_b + \epsilon_d - E & V \\ V & 2\epsilon_b + U_b + \epsilon_a + U_{ab} - E \end{pmatrix}. \tag{103}$$

By using this matrix, we obtain two branches of energy spectrum

$$E_{5,6} = 2\epsilon_b + U_b + E'_{5,6}, \tag{104}$$

$$E'_{5,6} = \frac{1}{2}\left[\epsilon_a + \epsilon_d + U_{ab} \mp \sqrt{(\epsilon_a - \epsilon_d + U_{ab})^2 + 4V^2}\right].$$

These values correspond to ones of the doublet state with $N = 1$ in the presence of b-particles doublon. Here the repulsion U_{ab} between a and b fermions is taken into account. The eigenfunctions of the submatrix (103) have the values:

$$\Phi_6(E_\lambda) = -\frac{(\epsilon_d - E'_\lambda)}{V}\Phi_5(E_\lambda), \qquad \lambda = 5, 6, \tag{105}$$

$$\Phi_5(E_{5,6}) = \frac{1}{\sqrt{2}}\left[1 \pm \frac{\epsilon_a - \epsilon_d + U_{ab}}{\sqrt{(\epsilon_a - \epsilon_d + U_{ab})^2 + 4V^2}}\right]^{1/2}.$$

The knowledge of them permits us to obtain the corresponding renormalized functions $|E_\lambda\rangle$, $(\lambda = 5, 6)$:

$$|E_\lambda\rangle = \Phi_5(E_\lambda)\left[\Psi_5 - \frac{(\epsilon_d - E'_\lambda)}{V}\Psi_6\right]. \tag{106}$$

Let us now discuss the properties of the second doublet of states (Ψ_7, Ψ_8). The following system of equations exists for them:

$$H^0\Psi_7 = (2\epsilon_a + U_b + \epsilon_d + 2G)\Psi_7 - V\Psi_8, \tag{107}$$
$$H^0\Psi_8 = (2\epsilon_d + U_d + \epsilon_a + 2G)\Psi_8 - V\Psi_7,$$

with corresponding submatrix

$$\begin{pmatrix} 2\epsilon_a + U_a + \epsilon_d + 2G - E & -V \\ -V & 2\epsilon_d + U_d + \epsilon_a + 2G - E \end{pmatrix}, \tag{108}$$

which permits us to obtain the two branches of the energy spectrum

$$E_{7,8} = \epsilon_a + \epsilon_d + 2G + E'_{7,8}, \tag{109}$$

$$E'_{7,8} = \frac{1}{2}\left[\epsilon_a + U_a + \epsilon_d + U_d \mp \sqrt{(\epsilon_a + U_a - \epsilon_d - U_d)^2 + 4V^2}\right].$$

The functions Φ_7 and Φ_8 have the values:

$$\Phi_8(E_\lambda) = -\frac{(\epsilon_a + U_a - E'_\lambda)}{V}\Phi_7(E_\lambda),$$

$$\Phi_7(E_{7,8}) = \frac{1}{\sqrt{2}}\left[1 \mp \frac{\epsilon_a + U_a - \epsilon_d - U_d}{\sqrt{(\epsilon_a + U_a - \epsilon_d - U_d)^2 + 4V^2}}\right]^{1/2}.$$

(110)

The renormalized eigenfunctions have the form

$$|E_{7,8}\rangle = \Phi_7(E_{7,8})\left[\Psi_7 + \frac{(\epsilon_a + U_a - E'_{7,8})}{V}\Psi_8\right]. \tag{111}$$

Besides these eight states with the spin projection $S_z = 1/2$ there are other eight states $\Psi_9,...,\Psi_{16}$ with opposite spin projection. These last functions are analogous to eight functions of the first group and their renormalization is the same. Thus we have eight double degenerate renormalized states. These 16 functions exhaust the group of states with the spin equal to 1/2. Besides them there are four states with the spin equal to 3/2 and spin projection values $S_z = \pm 3/2, \pm 1/2$. Now we shall take into account the linear combination $\chi_1 + \chi_2 + \chi_3$ which was not used untill now. The four orthonormalized functions with this value of spin are equal to

$$\Psi_{17} = d^+_\uparrow a^+_\uparrow b^+_\uparrow |0\rangle, \quad \Psi_{18} = \frac{1}{\sqrt{3}}(\chi_1 + \chi_2 + \chi_3) =$$

$$= \frac{1}{\sqrt{3}}\left(d^+_\uparrow a^+_\downarrow b^+_\uparrow + d^+_\downarrow a^+_\uparrow b^+_\uparrow + d^+_\uparrow a^+_\uparrow b^+_\downarrow\right)|0\rangle, \tag{112}$$

$$\Psi_{19} = \frac{1}{\sqrt{3}}\left(d^+_\uparrow a^+_\downarrow b^+_\downarrow + d^+_\downarrow a^+_\uparrow b^+_\downarrow + d^+_\downarrow a^+_\downarrow b^+_\uparrow\right)|0\rangle, \quad \Psi_{20} = d^+_\downarrow a^+_\downarrow b^+_\downarrow |0\rangle.$$

It is easy to see that all of them are the eigenfunctions of the local Hamiltonian (59) with the energy value

$$E_\lambda = \epsilon_a + \epsilon_b + \epsilon_d + G, \quad \lambda = 17,...,20. \tag{113}$$

Let us now discuss the process of renormalization of the states with four particles $(N = 4)$ and two possible values of spin $S = 0$ and $S = 1$. The full number of states is 15 and among them 6 are singlet and 9 are triplet states.

Firstly we shall consider a group of three singlet states

$$\Psi_1 = \frac{\left(d_\uparrow^+ a_\downarrow^+ - d_\downarrow^+ a_\uparrow^+\right)}{\sqrt{2}} b_\uparrow^+ b_\downarrow^+ |0\rangle,$$

$$\Psi_2 = a_\uparrow^+ a_\downarrow^+ b_\uparrow^+ b_\downarrow^+ |0\rangle, \tag{114}$$

$$\Psi_3 = d_\uparrow^+ d_\downarrow^+ b_\uparrow^+ b_\downarrow^+ |0\rangle.$$

The action of the local Hamiltonian on them gives the equations

$$H^0 \Psi_1 = (\epsilon_a + 2\epsilon_b + \epsilon_d + U_b + G + U_{ab}) \Psi_1 + \sqrt{2} V \Psi_2 + \sqrt{2} V \Psi_3,$$

$$H^0 \Psi_2 = (2\epsilon_a + 2\epsilon_b + U_a + U_b) \Psi_2 + \sqrt{2} V \Psi_1, \tag{115}$$

$$H^0 \Psi_3 = (2\epsilon_d + 2\epsilon_b + U_d + U_b) \Psi_3 + \sqrt{2} V \Psi_1.$$

The submatrix of the third rank in this subspace of states has the form

$$\begin{pmatrix} \epsilon_a + 2\epsilon_b + \epsilon_d + \\ +U_b + G + U_{ab} - E & \sqrt{2}V & \sqrt{2}V \\ \sqrt{2}V & \begin{matrix} 2\epsilon_a + 2\epsilon_b + U_a + \\ +U_b - E \end{matrix} & 0 \\ \sqrt{2}V & 0 & \begin{matrix} 2\epsilon_d + 2\epsilon_b + U_d + \\ +U_b - E \end{matrix} \end{pmatrix}. \tag{116}$$

The energy spectrum of this trio of singlets is determined from the equation of the third degree formulated for the energy E_λ' which differs from the enegy E_λ by the energy of b doublon $E_\lambda' = E_\lambda - (2\epsilon_b + U_b)$:

$$(\epsilon_a + \epsilon_d + U_{ab} + G - E') (2\epsilon_a + U_a - E') (2\epsilon_d + U_d - E') -$$
$$- 2V^2 (2\epsilon_a + 2\epsilon_d + U_a + U_d - 2E') = 0. \tag{117}$$

This equation is analogous to that for two-particle singlets with the difference that here the repulsion between a and b fermions is additionally taken into account. The investigation of this equation can be done in the same way as in the case of two particles ($N = 2$). The submatrix (116) determines three functions $\Phi_n(E_\lambda)$ with $n = 1, 2, 3$:

$$\Phi_2(E) = -\frac{\sqrt{2}V \Phi_1(E)}{2\epsilon_a + U_a - E'}, \quad \Phi_3(E) = -\frac{\sqrt{2}V \Phi_1(E)}{2\epsilon_d + U_d - E'},$$

$$\Phi_1(E) = \left[1 + \frac{2V^2}{(2\epsilon_a + U_a - E')^2} + \frac{2V^2}{(2\epsilon_d + U_d - E')^2}\right]^{-1/2}. \tag{118}$$

By using these results, we obtain the following renormalized functions

$$|E_\lambda\rangle = \Phi_1(E_\lambda) \left[\Psi_1 - \frac{\sqrt{2}V}{2\epsilon_a + U_a - E'}\Psi_2 - \frac{\sqrt{2}V}{2\epsilon_d + U_d - E'}\Psi_3 \right]. \qquad (119)$$

There are three else singlet four-particle states of the form:

$$\Psi_4 = d_\uparrow^+ d_\downarrow^+ a_\uparrow^+ a_\downarrow^+ |0\rangle,$$

$$\Psi_5 = \frac{\left(d_\uparrow^+ b_\downarrow^+ - d_\downarrow^+ b_\uparrow^+\right)}{\sqrt{2}} a_\uparrow^+ a_\downarrow^+ |0\rangle. \qquad (120)$$

$$\Psi_6 = \frac{\left(a_\uparrow^+ b_\downarrow^+ - a_\downarrow^+ b_\uparrow^+\right)}{\sqrt{2}} d_\uparrow^+ d_\downarrow^+ |0\rangle.$$

The function Ψ_4 is the eigenfunction of the local Hamiltonian with the eigenvalue

$$E_4 = 2\epsilon_d + U_d + 2\epsilon_a + U_a + 4G, \qquad (121)$$

and as the consequence $\Phi_4 = 1$ and $|E_4\rangle = \Psi_4$. The functions Ψ_5 and Ψ_6 form one doublet of states with the following system of equations

$$H^0 \Psi_5 = (2\epsilon_a + U_a + \epsilon_d + \epsilon_b + 2G + U_{ab}) \Psi_5 - V\Psi_6,$$
$$H^0 \Psi_6 = (2\epsilon_d + U_d + \epsilon_a + \epsilon_b + 2G + 2U_{ab}) \Psi_6 - V\Psi_5. \qquad (122)$$

These equations determine the submatrix

$$\begin{pmatrix} 2\epsilon_a + U_a + \epsilon_d + \epsilon_b + \\ +2G + U_{ab} - E & -V \\ \\ -V & 2\epsilon_d + U_d + \epsilon_a + \epsilon_b + \\ +2G + 2U_{ab} - E \end{pmatrix}. \qquad (123)$$

By using it we obtain the following two branches of the renormalized energy spectrum

$$E_{5,6} = \epsilon_a + \epsilon_b + \epsilon_d + 2G + 2U_{ab} + E'_{5,6},$$

$$E'_{5,6} = \frac{1}{\sqrt{2}} \left[\epsilon_a + U_a + \epsilon_d + U_d + U_{ab} \mp \qquad (124) \right.$$

$$\left. \mp \sqrt{(\epsilon_a + U_a - \epsilon_d - U_d - U_{ab})^2 + 4V^2} \right],$$

and also the values of two functions Φ_5 and Φ_6

$$\Phi_6(E_{5,6}) = \frac{\left(\epsilon_a + U_a - E'_{5,6}\right)}{V}\Phi_5(E_{5,6})\,,$$

$$\Phi_5(E_{5,6}) = \frac{1}{\sqrt{2}}\left[1 \mp \frac{\epsilon_a + U_a - \epsilon_d - U_d - U_{ab}}{\sqrt{\left(\epsilon_a + U_a - \epsilon_d - U_d - U_{ab}\right)^2 + 4V^2}}\right]\,. \tag{125}$$

The renormalized quantum states $|E_\lambda\rangle$ with $\lambda = 5, 6$ have the form

$$|E_{5,6}\rangle = \Phi_5(E_{5,6})\left(\Psi_5 + \frac{\epsilon_a + U_a - E'_{5,6}}{V}\Psi_6\right)\,. \tag{126}$$

Now we shall investigate the properties of nine states with the full spin $S = 1$ and with three values of its projection S_z. Three functions Ψ_7, Ψ_8, and Ψ_9 with $S_z = 1$ are

$$\Psi_7 = d_\uparrow^+ b_\uparrow^+ a_\uparrow^+ a_\downarrow^+ |0\rangle, \quad \Psi_8 = a_\uparrow^+ b_\uparrow^+ d_\uparrow^+ d_\downarrow^+ |0\rangle, \quad \Psi_9 = d_\uparrow^+ a_\uparrow^+ b_\uparrow^+ b_\downarrow^+ |0\rangle. \tag{127}$$

The action of the local Hamiltonian on them gives the system of equations

$$H^0\Psi_7 = \left(2\epsilon_a + U_a + \epsilon_b + \epsilon_d + 2G + U_{ab}\right)\Psi_7 - V\Psi_8,$$

$$H^0\Psi_8 = \left(2\epsilon_d + U_d + \epsilon_a + \epsilon_b + 2G\right)\Psi_8 - V\Psi_7, \tag{128}$$

and the corresponding submatrix has the form

$$\begin{pmatrix} 2\epsilon_a + U_a + \epsilon_b + \epsilon_d + \\ +2G + U_{ab} - E & -V \\ \\ -V & 2\epsilon_d + U_d + \epsilon_a + \epsilon_b + \\ +2G - E \end{pmatrix}\,. \tag{129}$$

Two branches of renormalized energy spectrum for this doublet of states are:

$$E_{7,8} = \epsilon_a + \epsilon_b + \epsilon_d + 2G + E'_{7,8},$$

$$E'_{7,8} = \frac{1}{2}\left[\epsilon_a + U_a + U_{ab} + \epsilon_d + U_d \mp \right.$$

$$\left. \mp \sqrt{\left(\epsilon_a + U_a - \epsilon_d - U_d + U_{ab}\right)^2 + 4V^2}\right]\,. \tag{130}$$

The functions Φ_7 and Φ_8 have the values

$$\Phi_8(E) = \frac{\left(\epsilon_a + U_a + U_{ab} - E'\right)}{V}\Phi_7(E),$$

$$\Phi_7(E_{7,8}) = \frac{1}{\sqrt{2}}\left[1 \mp \frac{\epsilon_a + U_a - \epsilon_d - U_d + U_{ab}}{\sqrt{\left(\epsilon_a + U_a - \epsilon_d - U_d + U_{ab}\right)^2 + 4V^2}}\right]^{1/2}\,. \tag{131}$$

By using these results we obtain the renormalized eigenfunctions $|E_{7,8}\rangle$

$$|E_{7,8}\rangle = \Phi_7(E_{7,8}) \left[\psi_7 + \frac{(\epsilon_a + U_a + U_{ab} - E'_{7,8})}{V} \Psi_8 \right]. \tag{132}$$

The function Ψ_9 is the eigenfunction of the local Hamiltonian with the energy eigenvalue

$$E_9 = 2\epsilon_b + U_b + \epsilon_a + \epsilon_d + G + U_{ab}. \tag{133}$$

Now we shall discuss three triplet states with projection $S_z = 0$:

$$\Psi_{10} = \frac{\left(d_\uparrow^+ a_\downarrow^+ + d_\downarrow^+ a_\uparrow^+ \right)}{\sqrt{2}} b_\uparrow^+ b_\downarrow^+ |0\rangle,$$

$$\Psi_{11} = \frac{\left(d_\uparrow^+ b_\downarrow^+ + d_\downarrow^+ b_\uparrow^+ \right)}{\sqrt{2}} a_\uparrow^+ a_\downarrow^+ |0\rangle, \tag{134}$$

$$\Psi_{12} = \frac{\left(a_\uparrow^+ b_\downarrow^+ + a_\downarrow^+ b_\uparrow^+ \right)}{\sqrt{2}} d_\uparrow^+ d_\downarrow^+ |0\rangle.$$

The state Ψ_{10} is the eigenfunction of the cell Hamiltonian with the value of energy $E_{10} = E_9$. We have also $|E_{10}\rangle = \Psi_{10}$. The functions Ψ_{11} and Ψ_{12} form a doublet with the system of equations

$$H^0 \Psi_{11} = (2\epsilon_a + U_a + \epsilon_d + \epsilon_b + 2G + U_{ab}) \Psi_{11} - V \Psi_{12},$$

$$H^0 \Psi_{12} = (2\epsilon_d + U_d + \epsilon_a + \epsilon_b + 2G) \Psi_{12} - V \Psi_{11}. \tag{135}$$

This system coincides with the corresponding system for the doublet of functions (Ψ_7, Ψ_8) and we can use the previous results:

$$E_{11,12} = E_{7,8}; \quad \Phi_{11} = \Phi_7, \quad \Phi_{12} = \Phi_8,$$

$$|E_{11,12}\rangle = \Phi_{11}(E_{11,12}) \left[\Psi_{11} + \frac{\epsilon_a + U_a + U_{ab} - E'_{11,12}}{V} \Psi_{12} \right]. \tag{136}$$

At last, there are three states with spin projection $S_z = -1$:

$$\Psi_{13} = d_\downarrow^+ b_\downarrow^+ a_\uparrow^+ a_\downarrow^+ |0\rangle, \quad \Psi_{14} = a_\downarrow^+ b_\downarrow^+ d_\uparrow^+ d_\downarrow^+ |0\rangle, \quad \Psi_{15} = d_\downarrow^+ a_\downarrow^+ b_\uparrow^+ b_\downarrow^+ |0\rangle. \tag{137}$$

The functions Ψ_{13} and Ψ_{14} repeat the properties of the functions Ψ_7 and Ψ_8; and the function Ψ_{15}, that of Ψ_9. On the basis of previous results, we have

$$E_{13,14} = E_{7,8}, \quad E_{15} = E_9, \quad \Phi_{13,14} = \Phi_{7,8}, \quad \Phi_{15} = 1,$$

$$|E_{13,14}\rangle = \Phi_{13}(E_{11,12}) \left[\Psi_{13} + \frac{\epsilon_a + U_a + U_{ab} - E'_{13,14}}{V} \Psi_{14} \right], \quad |E_{15}\rangle = \Psi_{15}. \tag{138}$$

Let us now discuss the properties of the local Hamiltonian states with $N = 5$, $S = 1/2$, and $S_z = \pm 1/2$. The full number of states is six and one half of them have spin up and others spin down. There are only three energy levels two-fold times degenerate. Three states with spin up are:

$$\Psi_1 = a_\uparrow^+ a_\downarrow^+ b_\uparrow^+ b_\downarrow^+ d_\uparrow^+ |0\rangle, \quad \Psi_2 = b_\uparrow^+ b_\downarrow^+ d_\uparrow^+ d_\downarrow^+ a_\uparrow^+ |0\rangle,$$

$$\Psi_3 = a_\uparrow^+ a_\downarrow^+ d_\uparrow^+ d_\downarrow^+ b_\uparrow^+ |0\rangle,$$

(139)

and they undergo the following equations of motion

$$H^0 \Psi_1 = (2\epsilon_a + U_a + 2\epsilon_b + U_b + \epsilon_d + 2G + 2U_{ab}) \Psi_1 - V\Psi_2,$$

$$H^0 \Psi_2 = (2\epsilon_b + U_b + 2\epsilon_d + U_d + \epsilon_a + 2G + U_{ab}) \Psi_2 - V\Psi_1,$$

(140)

$$H^0 \Psi_3 = (2\epsilon_a + U_a + 2\epsilon_d + U_d + \epsilon_b + 4G + U_{ab}) \Psi_3.$$

Two first states (139) form a doublet and the corresponding submatrix has a form

$$\begin{pmatrix} 2\epsilon_a + U_a + 2\epsilon_b + U_b + \epsilon_d+ \\ +2G + 2U_{ab} - E \end{pmatrix} \quad \begin{matrix} -V \\ \\ 2\epsilon_b + U_b + 2\epsilon_d + U_d + \epsilon_a+ \\ +2G + U_{ab} - E \end{matrix} \bigg).$$

(141)

Two renormalized values of energy are

$$E_{1,2} = 2\epsilon_b + U_b + \epsilon_a + \epsilon_d + 2G + U_{ab} + E'_{1,2},$$

$$E'_{1,2} = \frac{1}{2} \bigg[\epsilon_a + U_a + \epsilon_d + U_d + U_{ab} \mp$$

(142)

$$\mp \sqrt{(\epsilon_a + U_a - \epsilon_d - U_d + U_{ab})^2 + 4V^2} \bigg].$$

The eigenfunctions of this matrix have the values

$$\Phi_2(E_{1,2}) = \frac{1}{V} (\epsilon_a + U_a + U_{ab} - E'_{1,2}) \Phi_1(E_{1,2}),$$

(143)

$$\Phi_1(E_{1,2}) = \frac{1}{\sqrt{2}} \left[1 \mp \frac{\epsilon_a + U_a - \epsilon_d - U_d + U_{ab}}{\sqrt{(\epsilon_a + U_a - \epsilon_d - U_d + U_{ab})^2 + 4V^2}} \right]^{1/2}.$$

The renormalized eigenfunctions $|E_{1,2}\rangle$ have the form

$$|E_{1,2}\rangle = \Phi_1(E_{1,2}) \left[\Psi_1 + \frac{\epsilon_a + U_a + U_{ab} - E'_{1,2}}{V} \Psi_2 \right].$$

(144)

The function Ψ_3 is the eigenfunction of the local Hamiltonian with the self-energy

$$E_3 = \epsilon_b + 2\epsilon_a + U_a + 2\epsilon_d + U_d + 4G + U_{ab}. \tag{145}$$

The other three states

$$\Psi_4 = a_\uparrow^+ a_\downarrow^+ b_\uparrow^+ b_\downarrow^+ d_\downarrow^+ |0\rangle, \quad \Psi_5 = b_\uparrow^+ b_\downarrow^+ d_\uparrow^+ d_\downarrow^+ a_\downarrow^+ |0\rangle,$$
$$\Psi_6 = a_\uparrow^+ a_\downarrow^+ d_\uparrow^+ d_\downarrow^+ b_\downarrow^+ |0\rangle, \tag{146}$$

have the spin down and their properties repeat those with spin up. Thus we have:

$$E_{4,5} = E_{1,2}, \quad E_6 = E_3, \quad \Phi_4 = \Phi_{1,2}, \quad \Phi_6 = 1,$$
$$|E_{4,5}\rangle = \Phi_4(E_{4,5}) \left[\Psi_4 + \frac{\epsilon_a + U_a + U_{ab} - E'_{4,5}}{V} \Psi_5 \right], \quad |E_6\rangle = \Psi_6. \tag{147}$$

Finally, there is one unrenormalized state with six particles and spin equal to zero. It is the state composed of a, b, and d doublons

$$\Psi = a_\uparrow^+ a_\downarrow^+ b_\uparrow^+ b_\downarrow^+ d_\uparrow^+ d_\downarrow^+ |0\rangle \tag{148}$$

with the energy

$$E = 2\epsilon_a + U_a + 2\epsilon_b + U_b + 2\epsilon_d + U_d + 4G + 2U_{ab}. \tag{149}$$

3. DISCUSSION

The cell representation for the copper oxide Hamiltonian has been established in this paper. The new element of our investigation is the conception of diagonalizing $a_{\mathbf{k},\sigma}$ and $b_{\mathbf{k},\sigma}$ fermions for which the relations with canonical fermions $P_{\mathbf{k},\sigma}$ and $Q_{\mathbf{k},\sigma}$ have been formulated. This conception has permitted us to precise the value of charge transfer energy and to take into account correctly both the kinetic energy and the Coulomb interaction of the oxygen holes. On such a basis we have proved the new form of the local part of the cell Hamiltonian with three kinds of Wannier fermions and have selected the main delocalizing processes. The detailed analysis of the renormalization of the energy spectrum and of the wave functions of the elementary excitations has been done. These results can be demonstrated by using the standard system of parameters (50).

For example, in the case when $N = 1$ the lowest energy level E_1 (68) contains the energy gain

$$E_1 = \epsilon_d - 1.088 t_{dp} = \epsilon_d - 1.414 \text{ eV}. \tag{150}$$

The second energy level of this doublet has considerably higher energy:

$$E_2 = \epsilon_d + 2.978t_{dp} = \epsilon_d + 3.871 \text{ eV}. \tag{151}$$

These values can be compared with the energy of one b fermion

$$E_3 = \epsilon_d + 3.510t_{dp} = \epsilon_d + 4.563 \text{ eV}. \tag{152}$$

This energy is higher than doublet energies. The energy of one a fermion $\epsilon_a = \epsilon_d + 1.890t_{dp} = \epsilon_d + 2.457$ eV is considerably lower than that for b diagonalizing fermion.

For the case $N = 2$ three singlet states composed of a and d fermions have the energies determined by equation (74). In our system of parameters (50), equation (74) and his three solutions have the form

$$
\begin{aligned}
E_n &= 2\epsilon_d + e_n t_{dp}, \\
(7 - e)&(4.280 - e)(2.701 - e) - 6.48(11.280 - 2e) = 0, \\
e_1 &= 0.174, \quad e_2 = 5.294, \quad e_3 = 8.513, \\
E_1 &= 2\epsilon_d + 0.174t_{dp} = 2\epsilon_d + 0.226 \text{ eV}, \\
E_2 &= 2\epsilon_d + 5.294t_{dp} = 2\epsilon_d + 6.882 \text{ eV}, \\
E_3 &= 2\epsilon_d + 8.513t_{dp} = 2\epsilon_d + 11.067 \text{ eV}.
\end{aligned}
\tag{153}
$$

The lowest of them is Zhang–Rice singlet.

Besides these singlets, there are also two other singlets (79) of (d, b) and (a, b) kind and one additional (b, b) singlet with the energy

$$E_6 = 2\epsilon_d + 2(\epsilon_b - \epsilon_d) + U_b.$$

The numerical values of them are:

$$
\begin{aligned}
E_4 &= 2\epsilon_d + 2.598t_{dp} = 2\epsilon_d + 3.377 \text{ eV}, \\
E_5 &= 2\epsilon_d + 7.062t_{dp} = 2\epsilon_d + 9.181 \text{ eV}, \\
E_6 &= 2\epsilon_d + 7.520t_{dp} = 2\epsilon_d + 9.776 \text{ eV}.
\end{aligned}
\tag{154}
$$

The triplet energy levels are three-fold degenerate. Their numerical values are the following:

$$
\begin{aligned}
E_7 &= 2\epsilon_d + 2.701t_{dp} = 2\epsilon_d + 3.511 \text{ eV}, \\
E_8 &= 2\epsilon_d + 2.422t_{dp} = 2\epsilon_d + 3.149 \text{ eV}, \\
E_9 &= 2\epsilon_d + 6.488t_{dp} = 2\epsilon_d + 8.434 \text{ eV}.
\end{aligned}
\tag{155}
$$

These triplets are composed of (a, d), (d, b) and (a, b) fermions correspondingly. Thus among 15 states with two particles, one, just Zhang–Rice singlet, has the

lowest energy E_1. Three levels E_4, E_7, and E_8 have the moderate values, and the group of levels E_2, E_3, E_5, E_6, E_9 has high values.

Among 20 states with $N = 3$ we shall distinguish a quartet of states with $S = 1/2$ and $S_z = 1/2$, the energy spectrum of which is determined firstly by the equation (94). For our system of parameters this equation and his solutions are ($t_{dp} = 1.3$ eV)

$$E_n = 3\epsilon_d + (\epsilon_b - \epsilon_d) + e_n t_{dp},$$
$$(7 - e)(4.655 - e)(3.076 - e)^2 - 6.48(3.263 - e) \times$$
$$\times (11.655 - 2e) - 0.141(4.655 - e)(7 - e) = 0,$$
$$e_1 = 0.365, \quad e_2 = 3.279, \quad e_3 = 5.563, \quad e_4 = 8.600,$$
$$E_1 = 3\epsilon_d + (\epsilon_b - \epsilon_d) + 0.365 t_{dp} = 3\epsilon_d + 3.875 t_{dp},$$
$$E_2 = 3\epsilon_d + (\epsilon_b - \epsilon_d) + 3.279 t_{dp} = 3\epsilon_d + 6.789 t_{dp},$$
$$E_3 = 3\epsilon_d + (\epsilon_b - \epsilon_d) + 5.563 t_{dp} = 3\epsilon_d + 9.073 t_{dp},$$
$$E_4 = 3\epsilon_d + (\epsilon_b - \epsilon_d) + 8.600 t_{dp} = 3\epsilon_d + 12.110 t_{dp}.$$

$$(156)$$

Besides them, there are two energies $E_{5,6}$ (104) which belong to the (a, d) doublet in the presence of the b doublon:

$$E_{5,6} = 3\epsilon_d + [2(\epsilon_b - \epsilon_d) + U_b] +$$
$$+ \frac{1}{2}\left[\epsilon_a + U_{ab} - \epsilon_d \mp \sqrt{(\epsilon_a + U_{ab} - \epsilon_d)^2 + 4V^2}\right],$$
$$E_5 = 3\epsilon_d + 6.526 t_{dp}, \quad E_6 = 3\epsilon_d + 10.779 t_{dp}.$$

$$(157)$$

In the case when this doublet exists in the presence of the doublons a or d the energy levels are determined by the equation (109):

$$E_{7,8} = 3\epsilon_d + (\epsilon_a - \epsilon_d) + 2G +$$
$$+ \frac{1}{2}\left[\epsilon_a + U_a - \epsilon_d + U_d \mp \sqrt{(\epsilon_a + U_a - \epsilon_d - U_d)^2 + 4V^2}\right],$$
$$E_7 = 3\epsilon_d + 5.282 t_{dp}, \quad E_8 = 3\epsilon_d + 11.131 t_{dp}.$$

$$(158)$$

All the energy values, listed above, are independent of the spin projection value, therefore the energy levels for other 8 states with opposite spin direction are the same. When the spin value is $S = 3/2$, one four-fold degenerate energy level exists with the value:

$$E_{17} = 3\epsilon_d + (\epsilon_a - \epsilon_d) + (\epsilon_b - \epsilon_d) + G = 3\epsilon_d + 6.211 t_{dp}. \qquad (159)$$

Our analysis of the properties of three-particle renormalized cell states reveals the peculiarities connected with the presence of the b fermion, its influence on the spin structure of the states and its interaction with other two particles.

For completeness, we shall enumerate here the numerical values of renormalized energy levels of the states with $N = 4, 5, 6$. The energy values, as we have demonstrated above for the case $N = 1, 2, 3$, can be presented in the general form $E(N, S, n) = N\epsilon_d + F_n(N, S)$. We shall enumerate below only these F_n values, omitting also, for simplicity, the main quantum numbers.

For example, for $N = 4$ and $S = 0$, six singlet states exist. The first three values have been obtained from equation (117). In our system of parameters (50) this equation and its solutions have the form

$$
\begin{aligned}
E_n &= 4\epsilon_d + 2(\epsilon_b - \epsilon_d) + U_a + e_n t_{dp}, \\
(7 - e)&(4.280 - e)(3.076 - e) - 12.96(5.640 - e) = 0, \\
e_1 &= 0.415, \quad e_2 = 5.334, \quad e_3 = 8.607, \\
F_1 &= 7.935 t_{dp}, \quad F_2 = 12.854 t_{dp}, \quad F_3 = 16.127 t_{dp}.
\end{aligned}
\tag{160}
$$

There are three else singlet solutions

$$
F_4 = 14.524 t_{dp}, \quad F_5 = 9.580 t_{dp}, \quad F_6 = 15.729 t_{dp}.
$$

The first of them is obtained from equation (121); and the last two, from (124). There are also three triplet levels (see equations (130) and (133)) with energy values:

$$
F_7 = 9.125 t_{dp}, \quad F_8 = 14.683 t_{dp}, \quad F_9 = 10.596 t_{dp}.
\tag{161}
$$

In the case $N = 5$ and $S = 1/2$, there are three energy levels

$$
F_1 = 13.510 t_{dp}, \quad F_2 = 19.068 t_{dp}, \quad F_3 = 18.409 t_{dp}.
\tag{162}
$$

Finally, for $N = 6$, we have:

$$
F = 22.794 t_{dp}.
\tag{163}
$$

The comparison between the renormalized energy spectrum in the presence and the absence of diagonalizing fermions can help us to understand the necessity of their using. We shall make this comparison for the simplest states with $N = 1$ and $N = 2$. In the absence of the diagonalizing fermions instead of two local energies ϵ_a and ϵ_b we must use the initial local oxygen ion value $\epsilon_p = \epsilon_d + 2.700 t_{dp}$. Such parameters, of our theory, as $V = 1.800 t_{dp}$, $G = 0.811 t_{dp}$, and $U_a = 0.500 t_{dp}$ have to be changed. Their new values will be $\bar{V} = 1.916 t_{dp}$, $\bar{G} = 0.918 t_{dp}$, and $\bar{U}_a = 0.633 t_{dp}$. Now we shall introduce in our previous equations (150)–(152) the new values of the parameters and obtain the following results ($N = 1$)

$$
\begin{aligned}
\bar{E}_1 &= \epsilon_d - 0.994 t_{dp} = \epsilon_d - 1.292 \text{ eV}, \\
\bar{E}_2 &= \epsilon_d + 3.694 t_{dp} = \epsilon_d + 4.802 \text{ eV}, \\
\bar{E}_3 &= \epsilon_d + 2.700 t_{dp} = \epsilon_d + 3.510 \text{ eV}.
\end{aligned}
\tag{164}
$$

Thus, in the absence of diagonalizing process, the lowest level of doublet $\bar{E}_1$ is found to be situated higher at 0.122 eV than the value E_1 (150), obtained by us in the presence of the diagonalizing fermions. Now we shall discuss the case $N = 2$ and $S = 0$. The energy levels of singlet states (153) have been obtained in the presence of diagonalizing fermions. Now, if we use the unrenormalized parameters $\epsilon_p, \bar{V}, \bar{G}$, and $\bar{U}_a$ we obtain the new equation for three values of singlet energy, instead of (153):

$$(7 - \bar{e})(3.618 - \bar{e})(6.033 - \bar{e}) - 7.342(13.033 - 2\bar{e}) = 0. \qquad (165)$$

This last equation gives us the following results $\bar{E}_n = 2\epsilon_d + \bar{e}_n t_{dp}$:

$$\begin{aligned}
\bar{E}_1 &= 2\epsilon_d + 0.957 t_{dp} = 2\epsilon_d + 1.244 \text{ eV}, \\
\bar{E}_2 &= 2\epsilon_d + 6.471 t_{dp} = 2\epsilon_d + 8.412 \text{ eV}, \qquad (166) \\
\bar{E}_3 &= 2\epsilon_d + 9.223 t_{dp} = 2\epsilon_d + 11.990 \text{ eV}.
\end{aligned}$$

The comparison of these results with the values (153) demonstrates that the diagonalizing process lowers the energy levels of all three singlet states. The energy level of the singlet Zhang–Rice is lower in our case by 1.018 eV.

The numerical analysis of the energy spectrum of the cell Hamiltonian, given above, permits us to consider that, for every value of the particle number N, only one lowest energy level exists and that the distance ΔE between it and all other higher levels is not less than 1.5 eV. Because the temperature T of interest is about T_c — the critical temperature of oxides superconductors — we can consider that the quantity $\beta \Delta E$ is higher than 100, where $\beta = (k_B T)^{-1}$. Therefore we can take into account only the lowest level (for every N) in our thermodynamical investigation. On the basis of such arguments, we obtain the following approximate equation for mean number of holes n_h with both directions of the spin, attributed to one copper site:

$$\begin{aligned}
n_h = 2 &\left[e^{-\beta(\epsilon_d + F_1)} + e^{-\beta(2\epsilon_d + F_2)} + 3 e^{-\beta(3\epsilon_d + F_3)} + \right. \\
&\left. + 2 e^{-\beta(4\epsilon_d + F_4)} + 5 e^{-\beta(5\epsilon_d + F_5)} + 3 e^{-\beta(6\epsilon_d + F_6)} \right] \times \\
\times &\left[1 + 2 e^{-\beta(\epsilon_d + F_1)} + e^{-\beta(2\epsilon_d + F_2)} + 2 e^{-\beta(3\epsilon_d + F_3)} + e^{-\beta(4\epsilon_d + F_4)} + \right. \\
&\left. + 2 e^{-\beta(5\epsilon_d + F_5)} + e^{-\beta(6\epsilon_d + F_6)} \right]^{-1}. \quad (167)
\end{aligned}$$

Here the contribution F_N corresponds to the lowest energy value, with fixed N. For example, F_1 is the second contribution of the right-hand part of (150), F_2 can be found in the fourth line of (153); F_3, in (156) and so on. The chemical potential μ is contained only in the energy $\epsilon_d = \bar{\epsilon}_d - \mu$. The quantity ϵ_d is positive

and has a large value when the number of holes is very small. But this quantity becomes negative when the hole number increases. The number of holes can change from zero to six. The corresponding changing of μ will be from minus to plus infinity. We propose a simple equation, which describes the dependence of the chemical potential, or ϵ_d, on the number of holes $0 < n_h < 1$:

$$\epsilon_d = -F_1 + y, \quad \beta y = \ln m, \quad y \ll |F_1|,$$

$$n_h = \frac{2}{2+m} + \frac{2(m+1)}{(2+m)^2}\, e^{-\beta(F_2 - F_1)}. \tag{168}$$

As we can see from this equation, the number n_h is equal to 2/3 when m is equal to one and is more(less) than 2/3 when m is less(more) than one.

In this investigation we didn't take into account the delocalization processes, which can change radically the physics of this problem. This question needs a special investigation.

REFERENCES

1. *Emery V. J.* // Phys. Rev. Lett. 1987. V. 58. P. 2794.

2. *Varma C. M., Schmitt-Rink S., Abrahams E.* // Solid State Commun. 1987. V. 62. P. 681.

3. *Gaididei Yu. B., Loktev V. M.* // phys. status solidi B. 1988. V. 147. P. 307.

4. *Zhang F. C., Rice T. M.* // Phys. Rev. B. 1988. V. 37. P. 3759.

5. *Anderson P. W.* // Science. 1987. V. 235. P. 1196.

6. *Emery V. J., Reiter G.* // Phys. Rev. B. 1988. V. 38. P. 4547.

7. *Shastry B. S.* // Phys. Rev. Lett. 1989. V. 63. P. 1288.

8. *Zhang F. C.* // Phys. Rev. B. 1989. V. 39. P. 7375.

9. *Frenkel D. M. et al.* // Phys. Rev. B. 1990. V. 41. P. 350.

10. *Shen J. L., Ting C. S.* // Ibid. P. 1969.

11. *Pang H. B. et al.* // Ibid. P. 7209.

12. *Zhang F. C., Rice T. M.* // Ibid. P. 7243.

13. *Emery V. J., Reiter G.* // Ibid. P. 7247.

14. *Shen J. L. et al.* // Ibid. P. 8728.

15. *Lovtsov S. V., Yushankhai V. Yu.* // Physica C. 1991. V. 179. P. 159.

16. *Lovtsov S. V., Yushankhai V. Yu.* // phys. status solidi B. 1991. V. 166. P. 209.

17. *Hayn R., Yushankhai V. Yu., Lovtsov S. V.* // Phys. Rev. B. 1993. V. 47. P. 5253.

18. *Yushankhai V. Yu., Ovdovenko V. S., Hayn R.* // Phys. Rev. B. 1997. V. 55. P. 15562.

19. *Yushankhai B. Yu.* Thesis. Dubna, 1999.

20. *Jefferson J. H.* // Physica B. 1990. V. 165–166. P. 1013.

21. *Jefferson J. H., Eskes H., Feiner L. F.* // Phys. Rev. B. 1992. V. 45. P. 7959.

22. *Feiner L. F., Jefferson J. H., Raimondi R.* // Phys. Rev. B. 1996. V. 53. P. 8751.

23. *Raimondi R., Jefferson J. H., Feiner L. F.* // Ibid. P. 8774.

24. *Schüttler H.-B., Fedro A. J.* // Phys. Rev. B. 1992. V. 45. P. 7588.

25. *Belinicher V. I., Chernyshev A. L.* // Phys. Rev. B. 1993. V. 47. P. 390.

26. *Belinicher V. I., Chernyshev A. L.* // Physica C. 1993. V. 213. P. 298.

27. *Belinicher V. I., Chernyshev A. L.* // Phys. Rev. B. 1994. V. 49. P. 9746.

28. *Belinicher V. I., Chernyshev A. L., Popovici L. V.* // Ibid. P. 13768.

29. *Belinicher V. I., Chernyshev A. L., Popovici L. V.* // Phys. Rev. B. 1996. V. 53. P. 335.

30. *Lovtsov S. V., Plakida N. M., Yushankhai V. Yu.* // Physica B. 1990. V. 165–166. P. 1007.

31. *Plakida N. M., Hayn R., Richard J.-L.* // Phys. Rev. B. 1995. V. 51. P. 16599.

32. *Plakida N. M.* // Physica C. 1997. V. 282–287. P. 1737.

33. *Fujimori A., Minami F.* // Phys. Rev. B. 1984. V. 30. P. 957.

34. *Sawatzky G. A., Allen J. M.* // Phys. Rev. Lett. 1984. V. 53. P. 2339.

35. *Zaanen J., Sawatzky G. A., Allen J. M.* // Phys. Rev. Lett. 1985. V. 55. P. 418.

36. *Mila F.* // Phys. Rev. B. 1988. V. 38. P. 11358.

37. *Fujimori A.* // Phys. Rev. B. 1989. V. 39. P. 793.

38. *Eskes H., Sawatzky G. A., Feiner L. F.* // Physica C. 1989. V. 160. P. 424.

39. *Eskes H., Tjeng L. H., Sawatzky G. A.* // Phys. Rev. B. 1990. V. 41. P. 288.

40. *Mattis D. C.* // Mod. Phys. Lett. B. 1994. V. 8. P. 1387.

41. *Mattis D. C., Wheatley J. M.* // Mod. Phys. Lett. 1995. V. 9. P. 1107.

42. *Mattis D. C., Wheatley J. M.* // Phys. Rev. B. 1995. V. 52. P. 15103.

43. *Mattis D. C.* // Phys. Rev. Lett. 1995. V. 74. P. 3676.

44. *Mattis D. C.* // Phys. Rev. B. 1999. V. 59. P. 7166.

45. *Moskalenko V. A., Perkins N. B.* // Theor. Math. Phys. 1999. V. 121. P. 1654.

46. *Moskalenko V. A. et al.* // Phys. Rev. B. 2001. V. 63. P. 245119.

47. *Digor D. F. et al.* // Theor. Math. Phys. 2001. V. 127, No. 2. P. 664.