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A d-wave pairing state in terms of the Zhang–Rice singlets

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Abstract

In cuprate superconductors doping is believed to create holes on the O-sites, which couple antiferromagnetically with holes on the Cu-sites to form the so-called Zhang–Rice singlets. Here we study a d-wave pairing state based on the Zhang–Rice singlet states. Upper and lower bounds of an off-diagonal long-range order parameter with d-wave symmetry for this state are estimated. We also introduce a concrete model with on-site Coulomb repulsion and kinds of antiferromagnetic interactions whose ground state is this d-wave pairing state.

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1. Introduction

The mechanism of high-T_c cuprate superconductivity has been attracting much interest since it was discovered in 1986 [1]. In cuprate superconductors, electrons (or holes) in the CuO_2 planes play major roles, and the importance of the Coulomb repulsion at the Cu-sites is emphasized from the beginning [2–4]. However, theoretical understanding of its effects on the superconductivity is still limited and is a challenging problem in condensed matter physics.

Most theories which start with viewing cuprate superconductors as doped Mott insulators are based on the so-called Zhang–Rice singlet states [5]. In the undoped case, where there is one hole per Cu-site in CuO_2 planes, the cuprates exhibit insulating antiferromagnetism due to the strong Coulomb repulsion at the Cu-sites. When the system is doped, additional holes are created on the O-sites. Because of a superexchange antiferromagnetic interaction, each of the holes occupies a quasi-localized state on the four nearest-neighbour O-sites around a Cu-site, forming a local spin-singlet with the hole on the central Cu-site. This singlet is now referred to as Zhang–Rice singlet. The Zhang–Rice singlets become charge carriers moving through the CuO_2 plane and condense into a superconducting state.

This scenario is usually examined by using the t–J model which is a single-band effective Hamiltonian with antiferromagnetic interactions between nearest-neighbour holes on the Cu-sites [5]. Despite its simple form, however, it is a formidably difficult task to rigorously analyse the t–J model, and whether the model really describes the cuprate superconductivity has not yet been clarified. In the current situation, we think that a rigorous establishment of occurrence of a superconducting state based on the Zhang–Rice singlets in a model with the Coulomb repulsion and antiferromagnetic interactions, even if it is apart from the t–J model, certainly gives us an important step towards understanding of the cuprates superconductivity.

In this paper, we study a simple d-wave pairing state expanded in terms of the Zhang–Rice singlet states. It is shown that the pairing state is regarded as a condensed state of the Zhang–Rice singlets in the background of a resonating-valence-bond state consisting of holes at the Cu-sites. We estimate an upper bound on an off-diagonal long-range order (ODLRO) parameter with d-wave symmetry for the pairing state as a function of doping concentration $0 \leqslant \delta \leqslant 1$. It is found that an upper bound has a dome structure with a maximum at $\delta = 0.5$ and becomes zero at $\delta = 0, 1$. We also estimate a lower bound on the ODLRO parameter and show that ODLRO exists for sufficiently large doping concentrations. We then introduce a model with on-site repulsion and kinds of antiferromagnetic interactions, and show that the pairing state is a ground state of this model. A related model with infinitely large on-site repulsion at the Cu-site is analysed in [6]. This model, however, has following disadvantages: the Hamiltonian does not have spin rotational symmetry, and its exact pairing ground state has less relevance to the Zhang–Rice singlets. Although the present model has still somewhat artificial aspects, it is for the first time that the pairing state with d-wave symmetry which is written explicitly in terms of the Zhang–Rice singlet states is realized as a ground state of the concrete Hamiltonian.

This paper is organized as follows. In the next section, we prepare some notation and give a definition of the Zhang–Rice singlet states. In section 3, we introduce a two-electron state with d-wave symmetry, and, on the basis of the Zhang–Rice singlet states, we construct a pairing state in which many electrons condense into this two-electron state. In section 4, we discuss an expectation value of an order parameter with d-wave symmetry for the pairing state. An upper bound for the order parameter is obtained in this section and a lower bound, whose estimation needs somewhat technical calculations, is obtained in section 6. In section 5, we introduce a Hamiltonian whose ground state is the pairing state which we construct. In the final section, a summary and some remarks are given. In the appendix, we show that the pairing state is non-vanishing.

2. Zhang–Rice singlet states

We start with the definition of a lattice. With even integers L_1 and L_2, let

$$D = ([1, L_1] \times [1, L_2]) \cap \mathbf{Z}^2, \tag{2.1}$$

which represents a collection of the Cu-sites. Let $\delta^1 = (1, 0)$ and $\delta^2 = (0, 1)$. We define

$$P = \{u | u = x + \delta^l/2, l = 1, 2, x \in D\}, \tag{2.2}$$

which is the collection of the mid-points of the nearest-neighbour bonds in D and corresponds to the O-sites. Then we consider the lattice $\Lambda = D \cup P$, which mimics the CuO_2 plane. (See figure 1.) For a technical reason, we impose periodic boundary conditions on Λ. For later use, we introduce further the following sublattices of D:

$$D_o = \{x | x = (x_1, x_2) \in D \text{ with } x_1 + x_2 \text{ being odd}\}, \tag{2.3}$$

$$D_e = \{x | x = (x_1, x_2) \in D \text{ with } x_1 + x_2 \text{ being even}\}. \tag{2.4}$$

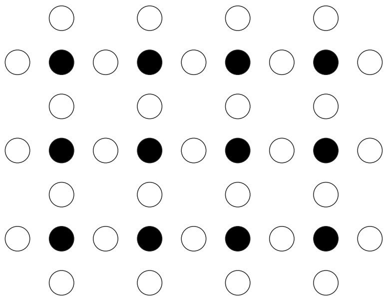

Figure 1. The lattice structure. The solid and open circles indicate the Cu- and O-sites, respectively.

Next we introduce fermion operators which annihilate or create *holes* with spin $\sigma =\uparrow, \downarrow$ at sites in Λ. Any states with the number $N_{\rm h}$ of holes can be constructed by operating these operators on a state Φ_0 with no holes on Λ. By $d_{x,\sigma}\left(d^{\dagger}_{x,\sigma}\right)$ and $p_{u,\sigma}\left(p^{\dagger}_{u,\sigma}\right)$, we denote the annihilation(creation) operators of holes at $x \in D$ and $u \in P$, respectively. As mentioned in section 1, each hole additionally induced in a CuO_2 plane with 1 hole per Cu is considered to localize well at the four nearest O-sites of a Cu-site because of the antiferromagnetic superexchange interactions between Cu- and O-sites. To describe this localized state on the O-sites we introduce the following operators for each $x \in D$:[1]

$$f_{x,\sigma} = \frac{1}{2} \sum_{u \in P; |u-x|=1/2} p_{u,\sigma}. \tag{2.5}$$

As is easily seen, the annihilation operator $f_{x,\sigma}$ and the creation operator $f^{\dagger}_{x'}$ defined by (2.5) do not anticommute when $|x - x'| = 1$, implying that the single-electron states corresponding to (2.5) are not orthogonal. To avoid technical complexities arising from this fact, we consider corresponding Wannier states. To do so, we introduce the fermion operator $f^1_\sigma = (1/\sqrt{D}) \sum_{x \in D} \mathrm{e}^{\mathrm{i}\pi\delta^1 \cdot x} p_{x+\delta^1/2,\sigma}$ and the reciprocal lattice

$$\mathcal{K} = \left\{ \left(\frac{2\pi}{L_1} n_1, \frac{2\pi}{L_2} n_2 \right) | n_l \in \mathbf{Z}, -L_l/2 < n_l \leqslant L_l/2 \quad \text{with} \quad l = 1, 2 \right\}, \tag{2.6}$$

and then define $\hat{f}_{k,\sigma} = (1/\sqrt{|D|}) \sum_{x \in D} f_{x,\sigma} \mathrm{e}^{-\mathrm{i}k \cdot x}$ for $k \in \mathcal{K} \backslash \{(\pi, \pi)\}$ and $\hat{f}_{(\pi,\pi),\sigma} = f^1_\sigma$. We normalize the $\hat{f}$-operators as $\hat{a}_{k,\sigma} = \hat{f}_{k,\sigma} / \|f_k\|$, where the normalization factors are given by

$$\|f_k\| = \begin{cases} 1 & \text{if} \quad k = (\pi, \pi), \\ \sqrt{1 + \frac{1}{2}(\cos k_1 + \cos k_2)} & \text{otherwise.} \end{cases} \tag{2.7}$$

The fermion operators corresponding to the Wannier states are defined by

$$a_{x,\sigma} = \frac{1}{\sqrt{|D|}} \sum_{k \in \mathcal{K}} \hat{a}_{k,\sigma} \mathrm{e}^{\mathrm{i}k \cdot x}. \tag{2.8}$$

The a-operators defined as above approximate the f-operators well, and satisfy the canonical fermion anticommutation relations $\left\{a^{\dagger}_{x,\sigma}, a^{\dagger}_{y,\tau}\right\} = \{a_{x,\sigma}, a_{y,\tau}\} = 0$ and $\left\{a^{\dagger}_{x,\sigma}, a_{y,\tau}\right\} = \delta_{\sigma,\tau}\delta_{x,y}$ for $\sigma, \tau =\uparrow, \downarrow$ and $x, y \in D$. In the rest of this paper, we consider the Zhang–Rice singlets by using the a-operators, instead of the f-operators.

[1] Here $|\cdot|$ represents the Euclidean norm. The same symbol $|X|$ is used to denote the number of elements in a set X.

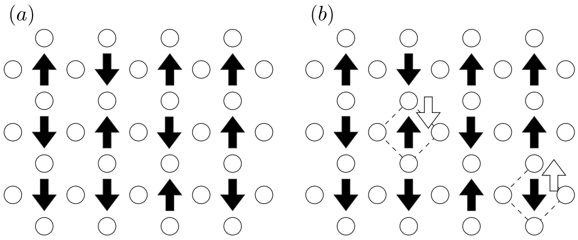

Figure 2. The solid and open arrows indicate spins of the holes on the Cu- and O-sites, respectively. (*a*) In the case of $N_\mathrm{h} = |D|$, every Cu-site is occupied by one hole. (*b*) When N_h is greater than $|D|$, every Cu-site remains to be occupied by one hole, and additional holes are created on the O-sites. Each hole on the O-sites occupies a quasi-localized state, which is indicated by dot lines, and couples to the hole at the central Cu-site to form the Zhang–Rice singlet.

The Zhang–Rice singlet around a Cu-site x is formed by holes occupying $a^\dagger_{x,\sigma}$ and $d^\dagger_{x,\tau}$. This singlet is represented by the two-hole creation operator

$$\psi^\dagger_x = d^\dagger_{x,\uparrow} a^\dagger_{x,\downarrow} + a^\dagger_{x,\uparrow} d^\dagger_{x,\downarrow}. \tag{2.9}$$

We assume that, in the case where the hole number is $|D|$, each hole occupies a Cu-site. Any $|D|$-hole state is then expressed by a linear combination of $\prod_{x\in D} d^\dagger_{x,\sigma_x}\Phi_0$ with $\sigma_x = \uparrow, \downarrow$ (figure 2(*a*)). We furthermore assume that N holes added in this state form Zhang–Rice singlets. Then a $(|D| + N)$-hole state with $0 < N \leqslant |D|$ is written by using a set of states

$$\left(\prod_{x\in A} d^\dagger_{x,\sigma_x}\right)\left(\prod_{y\in D\setminus A} \psi^\dagger_y\right)\Phi_0, \tag{2.10}$$

where A is a subset of D with $|A| = |D| - N$ and its compliment $D\setminus A$ is a collection of sites where the Zhang–Rice singlets are formed (figure 2(*b*)). Noting the relation

$$d^\dagger_{x,\sigma}\Phi_0 = -\mathbf{sgn}[\sigma] a_{x,-\sigma}\psi^\dagger_x\Phi_0 \tag{2.11}$$

where $\mathbf{sgn}[\sigma] = +$ if $\sigma = \uparrow$ and $\mathbf{sgn}[\sigma] = -$ if $\sigma = \downarrow$, we find that (2.10) is rewritten as

$$\left(\prod_{x\in A} a_{x,-\sigma_x}\right)\Psi_0 = \Psi_{A,\boldsymbol{\sigma}_A}, \tag{2.12}$$

with

$$\Psi_0 = \left(\prod_{y\in D}\psi^\dagger_y\right)\Phi_0 \tag{2.13}$$

up to a sign factor. Here $\boldsymbol{\sigma}_A$ is a short hand for a spin configuration $(\sigma_x)_{x\in A}$. We write $\mathcal{S}_A$ for the collection of spin configurations $\{(\sigma_x)_{x\in A} | \sigma_x = \uparrow, \downarrow, x \in A\}$. It is easy to see that $\langle \Psi_{A,\boldsymbol{\sigma}_A}, \Psi_{B,\boldsymbol{\tau}_B}\rangle = 2^{|D|-|A|}\chi[A = B]\chi[\boldsymbol{\sigma}_A = \boldsymbol{\tau}_B]$, where $\chi[\text{event}] = 1$ if 'event' is true and 0 otherwise. Thus the collection of states

$$\left\{\Psi_{A,\boldsymbol{\sigma}_A} | A \subset D, \boldsymbol{\sigma}_A \in \mathcal{S}_A\right\} \tag{2.14}$$

is orthogonal. For $|D| < N_\mathrm{h} \leqslant 2|D|$, let $\mathbf{H}^{N_\mathrm{h}}_{\mathrm{ZRS}}$ be the Hilbert space spanned by the basis states $\{\Psi_{A,\boldsymbol{\sigma}_A}\}$ with $|A| = 2|D| - N_\mathrm{h}$. The Zhang–Rice singlet states are defined to be states in $\mathbf{H}^{N_\mathrm{h}}_{\mathrm{ZRS}}$.

3. d-wave pairing state

Assuming that N_h takes an even number in $|D| < N_\mathrm{h} \leqslant 2|D|$, we consider a d-wave pairing state in the Hilbert space $\mathbf{H}_{\mathrm{ZRS}}^{N_\mathrm{h}}$. Let us define a pair operator ζ by

$$\zeta = \sum_{k=(k_1,k_2)\in\mathcal{K}} (\cos k_1 - \cos k_2)\hat{a}_{-k,\downarrow}\hat{a}_{k,\uparrow}. \tag{3.1}$$

Recall that $\hat{a}_{k,\sigma} = (1/\sqrt{|D|})\sum_{x\in D} a_{x,\sigma}\,\mathrm{e}^{-\mathrm{i}k\cdot x}$ are the Fourier transforms of $a_{x,\sigma}$. This operator *creates* an *electron* pair with d-wave symmetry. For the hole number $N_\mathrm{h} = |D| + N$ with a positive even integer N, one of the simplest d-wave pairing states in $\mathbf{H}_{\mathrm{ZRS}}^{N_\mathrm{h}}$ is given by

$$\Phi_\mathrm{p} = (\zeta)^{N_\mathrm{p}}\Psi_0 \tag{3.2}$$

with the number of pairs $N_\mathrm{p} = (|D| - N)/2$. Here we note that

$$a_{x,\downarrow}a_{x,\uparrow}\Psi_0 = 0 \tag{3.3}$$

since $\left[a_{x,\downarrow}a_{x,\uparrow}, \psi_x^\dagger\right] = -d_{x,\uparrow}^\dagger a_{x,\uparrow} - d_{x,\downarrow}^\dagger a_{x,\downarrow}$, so that Φ_p is actually expanded in terms of (2.12). In the appendix, we show that Φ_p is non-vanishing.

In order to see the real space representations of ζ and Φ_p, we define the following operators: for $x \in D$

$$b_{x,\sigma} = \frac{1}{2}\sum_{y\in D;|x-y|=1} a_{y,\sigma}\,\mathrm{e}^{\mathrm{i}\pi\delta^2\cdot(x-y)}, \tag{3.4}$$

and for $x, y \in D$

$$\phi^a_{\{x,y\}} = \tfrac{1}{2}\,\mathrm{e}^{\mathrm{i}\pi\delta^2\cdot(x-y)}(a_{x,\downarrow}a_{y,\uparrow} + a_{y,\downarrow}a_{x,\uparrow}). \tag{3.5}$$

The operator $\phi^a_{\{x,y\}}$ corresponds to a two-electron singlet state formed by electrons on the O-sites around Cu-sites x and y. By using these operators we can write ζ as

$$\zeta = \sum_{x\in D} a_{x,\downarrow}b_{x,\uparrow} = \sum_{x\in D} b_{x,\downarrow}a_{x,\uparrow} \tag{3.6}$$

or

$$\zeta = \sum_{\{x,y\}\in\mathcal{B}} \phi^a_{\{x,y\}}, \tag{3.7}$$

where

$$\mathcal{B} = \{\{x,y\} | x, y \in D, |x-y| = 1\} \tag{3.8}$$

is the collection of bonds in D (we assume that $\{x,y\} = \{y,x\}$). Let $C(\mathcal{B})$ be the collection of subsets B of $\mathcal{B}$ such that no two elements in B share the same site. Substituting (3.7) into (3.2), and noting the relation (3.3), we obtain

$$\Phi_\mathrm{p} = N_\mathrm{p}! \sum_{B\in C(\mathcal{B});|B|=N_\mathrm{p}} \prod_{\{x,y\}\in B} \phi^a_{\{x,y\}}\Psi_0. \tag{3.9}$$

Therefore, the pairing state Φ_p is regarded as a nearest-neighbour resonating-valence-bond state (which is a linear combination of products of two-electron singlets) consisting of electrons on O-sites with the background of the fully-filled Zhang–Rice singlets.

Finally let us see the form of Φ_p in terms of the hole creation operators. Let $n^d_{x,\sigma} = d^\dagger_{x,\sigma}d_{x,\sigma}$ and define $\mathcal{P}_D = \prod_{x\in D}\left(1 - n^d_{x,\uparrow}n^d_{x,\downarrow}\right)$, which is the projection operator onto the space without double occupancies of holes at the Cu-sites. By using this projection operator we can rewrite Ψ_0 as

$$\Psi_0 = \frac{1}{|D|!}\mathcal{P}_D\left(\sum_{x\in D}\psi_x^\dagger\right)^{|D|}\Phi_0 = \frac{1}{|D|!}\mathcal{P}_D\left(\sum_{k\in\mathcal{K}}\left(\hat{d}^\dagger_{k,\uparrow}\hat{a}^\dagger_{-k,\downarrow} + \hat{a}^\dagger_{k,\uparrow}\hat{d}^\dagger_{-k,\downarrow}\right)\right)^{|D|}\Phi_0, \tag{3.10}$$

where $\hat{d}_{k,\sigma} = (1/\sqrt{|D|})\sum_{x\in D} d_{x,\sigma}\,\mathrm{e}^{-\mathrm{i}k\cdot x}$. Then, noting two commutation relations

$$\left[\hat{a}_{-k,\downarrow}\hat{a}_{k,\uparrow},\left(\sum_{p\in\mathcal{K}}(\hat{d}^\dagger_{p,\uparrow}\hat{a}^\dagger_{-p,\downarrow}+\hat{a}^\dagger_{p,\uparrow}\hat{d}^\dagger_{-p,\downarrow})\right)\right] = -(\hat{d}^\dagger_{k,\uparrow}\hat{a}_{k,\uparrow}+\hat{d}^\dagger_{-k,\downarrow}\hat{a}_{-k,\downarrow}) \tag{3.11}$$

and

$$\left[-(\hat{d}^\dagger_{k,\uparrow}\hat{a}_{k,\uparrow}+\hat{d}^\dagger_{-k,\downarrow}\hat{a}_{-k,\downarrow}),\left(\sum_{p\in\mathcal{K}}(\hat{d}^\dagger_{p,\uparrow}\hat{a}^\dagger_{-p,\downarrow}+\hat{a}^\dagger_{p,\uparrow}\hat{d}^\dagger_{-p,\downarrow})\right)\right] = -2\hat{d}^\dagger_{k,\uparrow}\hat{d}^\dagger_{-k,\downarrow}, \tag{3.12}$$

we obtain

$$\begin{aligned}\Phi_{\mathrm{p}} &= \frac{1}{N!}\mathcal{P}_D\left(\sum_{k\in\mathcal{K}}(\cos k_2-\cos k_1)\hat{d}^\dagger_{k,\uparrow}\hat{d}^\dagger_{-k,\downarrow}\right)^{N_{\mathrm{p}}}\left(\sum_{x\in D}\psi^\dagger_x\right)^N\Phi_0\\ &= \frac{N_{\mathrm{p}}!}{N!}\mathcal{P}_D\left(\sum_{B\in C(\mathcal{B})\mathcal{B};|B|=N_{\mathrm{p}}}\ \prod_{\{x,y\}\in B}(\phi^d_{\{x,y\}})^\dagger\right)\left(\sum_{x\in D}\psi^\dagger_x\right)^N\Phi_0\end{aligned} \tag{3.13}$$

with

$$\left(\phi^d_{\{x,y\}}\right)^\dagger = \tfrac{1}{2}\mathrm{e}^{-\mathrm{i}\pi\delta^1\cdot(x-y)}\left(d^\dagger_{x,\uparrow}d^\dagger_{y,\downarrow}+d^\dagger_{y,\uparrow}d^\dagger_{x,\downarrow}\right). \tag{3.14}$$

To get the second line in (3.13) we used $\mathcal{P}_D d^\dagger_{x,\uparrow}d^\dagger_{x,\downarrow}=0$. The operator $\left(\phi^d_{\{x,y\}}\right)^\dagger$ corresponds to a two-hole singlet state formed by holes at the Cu-sites. From expression (3.13) we find that the state Φ_{p} can be regarded also as a projected state in which the Zhang–Rice singlets condense and the remaining holes at the Cu-sites are forming nearest-neighbour singlet states.

Here it should be noted that, despite the form (3.13), Φ_{p} does not exhibit long-range order associated with the Zhang–Rice singlets. In fact, it is easy to see that

$$\langle\Phi_{\mathrm{p}},\psi^\dagger_x\psi_y\Phi_{\mathrm{p}}\rangle = 0 \tag{3.15}$$

for $x\neq y$, since there is no charge fluctuation on the Cu-sites. It is important to consider long-range order associated with movable holes on the O-sites, which we discuss in the next section.

4. Order parameter

In this section, we estimate the value of a d-wave order parameter for the state (3.2). Let

$$\Delta = \frac{1}{|D|}\sum_{\{x,y\}\in\mathcal{B}}\phi^a_{\{x,y\}} = \frac{1}{|D|}\zeta. \tag{4.1}$$

We then define

$$\mu_{\Lambda,N} = \sqrt{\frac{\langle\Phi_{\mathrm{p}},\Delta^\dagger\Delta\Phi_{\mathrm{p}}\rangle}{\langle\Phi_{\mathrm{p}},\Phi_{\mathrm{p}}\rangle}}, \tag{4.2}$$

$$\mu_\delta = \lim_{\substack{|D|,N\to\infty\\ N/|D|=\delta}}\mu_{\Lambda,N}, \tag{4.3}$$

where the limit is taken with $N/|D|$ kept fixed to δ. This order parameter measures a long range correlation between spin-singlet pairs corresponding $\phi^a_{\{x,y\}}$.

We firstly show that

$$\langle\Phi_{\mathrm{p}},\Delta^\dagger\Delta\Phi_{\mathrm{p}}\rangle = \frac{N_{\mathrm{p}}+1}{2|D|^2}\sum_{x\in D}\sum_{\sigma=\uparrow,\downarrow}\left\langle\Phi_{\mathrm{p}},a^\dagger_{x,\sigma}a_{x,\sigma}b^\dagger_{x,-\sigma}b_{x,-\sigma}\Phi_{\mathrm{p}}\right\rangle \tag{4.4}$$

which is crucial for our estimation of μ_δ (recall $N_{\rm p} = (|D| - N)/2$). To see this, we observe that

$$\begin{aligned}\left\langle(\zeta)^{N_{\rm p}}\Psi_0, a^\dagger_{x,\uparrow}b^\dagger_{x,\downarrow}(\zeta)^{N_{\rm p}+1}\Psi_0\right\rangle &= \left\langle(\zeta)^{N_{\rm p}}d^\dagger_{x,\downarrow}\prod_{y\in D\backslash\{x\}}\psi^\dagger_y\Phi_0, b^\dagger_{x,\downarrow}(\zeta)^{N_{\rm p}+1}\Psi_0\right\rangle\\ &= (N_{\rm p}+1)\left\langle(\zeta)^{N_{\rm p}}d^\dagger_{x,\downarrow}\prod_{y\in D\backslash\{x\}}\psi^\dagger_y\Phi_0, b^\dagger_{x,\downarrow}b_{x,\downarrow}(\zeta)^{N_{\rm p}}d^\dagger_{x,\downarrow}\prod_{y\in D\backslash\{x\}}\psi^\dagger_y\Phi_0\right\rangle\\ &= (N_{\rm p}+1)\left\langle(\zeta)^{N_{\rm p}}\Psi_0, a^\dagger_{x,\uparrow}a_{x,\uparrow}b^\dagger_{x,\downarrow}b_{x,\downarrow}(\zeta)^{N_{\rm p}}\Psi_0\right\rangle. \end{aligned} \tag{4.5}$$

To get the second line we used the commutation relation

$$\left[\zeta a^\dagger_{x,\sigma}, a^\dagger_{x,\sigma}\zeta\right] = \mathbf{sgn}[\sigma]b_{x,-\sigma}, \tag{4.6}$$

which immediately follows from the real space representation (3.6) of ζ. Then, by using the spin-rotation symmetry for $\Phi_{\rm p}$, (4.4) follows from (4.1) and (4.5).

By noting the inequality

$$\begin{aligned}\left\langle\Phi_{\rm p}, a^\dagger_{x,\sigma}a_{x,\sigma}b^\dagger_{x,-\sigma}b_{x,-\sigma}\Phi_{\rm p}\right\rangle &= \left\langle\Phi_{\rm p}, a^\dagger_{x,\sigma}a_{x,\sigma}\left(1 - b_{x,-\sigma}b^\dagger_{x,-\sigma}\right)\Phi_{\rm p}\right\rangle\\ &\leqslant \left\langle\Phi_{\rm p}, a^\dagger_{x,\sigma}a_{x,\sigma}\Phi_{\rm p}\right\rangle\end{aligned} \tag{4.7}$$

and the fact that the number of a-holes (which are holes in the state corresponding to the a-operators) is exactly N for $\Phi_{\rm p}$, we find that $\mu_{\Lambda,N}$ is bounded from above as

$$\mu_{\Lambda,N} \leqslant \sqrt{\left(\frac{N_{\rm p}+1}{|D|}\right)\left(\frac{N}{2|D|}\right)}. \tag{4.8}$$

The limit is thus bounded from above as

$$\mu_\delta \leqslant \tfrac{1}{2}\sqrt{\delta(1-\delta)}. \tag{4.9}$$

As for a lower bound for μ_δ we have the following result. Let $\frac{8}{9} \leqslant \delta \leqslant 1$. Then we have that

$$\mu_\delta \geqslant \tfrac{1}{2}\sqrt{\gamma_\delta I(\delta)(1-\delta)}, \tag{4.10}$$

where $\gamma_\delta = \frac{9\delta-8}{2(8\delta-7)}$ and

$$I(\delta) = \frac{2}{(2\pi)^2}\int_{|k_i|\leqslant\pi}\epsilon_b(k)\chi[\epsilon_b(k)\leqslant\epsilon_\delta]\,{\rm d}k \tag{4.11}$$

with $\epsilon_b(k) = (\cos k_1 - \cos k_2)^2$. Here ϵ_δ is determined by

$$\delta = \frac{2}{(2\pi)^2}\int_{|k_i|\leqslant\pi}\chi[\epsilon_b(k)\leqslant\epsilon_\delta]\,{\rm d}k. \tag{4.12}$$

The inequality (4.10) means that the state $\Phi_{\rm p}$ exhibits ODLRO with d-wave symmetry for $\frac{8}{9} < \delta < 1$. The calculation for this bound is somewhat complicated and technical. We defer the proof to section 6. It should be noted that the above lower bound is not optimal at all and never means that there is no d-wave pairing order in a low density region of holes. It is desirable to obtain an improved bound in the future.

5. Hamiltonian with ground state Φ_p

So far we have constructed the pairing state Φ_p with d-wave symmetry and studied its properties. In this section we propose a Hamiltonian H on Λ whose ground state is given by Φ_p.

Let us define the number operator $n^a_{x,\sigma}$, with $\sigma = \uparrow, \downarrow$, and the spin operators $S^a_{x,\alpha}$, with $\alpha = 1, 2, 3$, corresponding to the a-operators by

$$n^a_{x,\sigma} = a^\dagger_{x,\sigma} a_{x,\sigma}, \tag{5.1}$$

$$S^a_{x,1} = \tfrac{1}{2}\left(a^\dagger_{x,\uparrow} a_{x,\downarrow} + a^\dagger_{x,\downarrow} a_{x,\uparrow}\right), \tag{5.2}$$

$$S^a_{x,2} = \tfrac{1}{2\mathrm{i}}\left(a^\dagger_{x,\uparrow} a_{x,\downarrow} - a^\dagger_{x,\downarrow} a_{x,\uparrow}\right), \tag{5.3}$$

$$S^a_{x,3} = \tfrac{1}{2}\left(a^\dagger_{x,\uparrow} a_{x,\uparrow} - a^\dagger_{x,\downarrow} a_{x,\downarrow}\right). \tag{5.4}$$

We also define

$$n^a_x = n^a_{x,\uparrow} + n^a_{x,\downarrow}. \tag{5.5}$$

The number and the spin operators for the b- and the d-operators are defined similarly. By using these operators, the Hamiltonian H is defined as follows:

$$H = H_0 + H_1 \tag{5.6}$$

with

$$H_0 = -\varepsilon_d \sum_{x\in D} n^d_x + U \sum_{x\in D} n^d_{x,\uparrow} n^d_{x,\downarrow} + J_0 \sum_{x\in D} \boldsymbol{S}^a_x \cdot \boldsymbol{S}^d_x, \tag{5.7}$$

$$\begin{aligned} H_1 = \frac{3}{4} J_1 \sum_{x\in D} \sum_{\sigma=\uparrow,\downarrow} &\left(a^\dagger_{x,\sigma} a_{x,\sigma} + b^\dagger_{x,\sigma} b_{x,\sigma}\right) \\ &+ J_1 \sum_{x\in D} \left(\boldsymbol{S}^a_x \cdot \boldsymbol{S}^d_x + \boldsymbol{S}^b_x \cdot \boldsymbol{S}^d_x + \boldsymbol{S}^a_x \cdot \boldsymbol{S}^b_x - \frac{3}{4} n^a_x \cdot n^b_x \right). \end{aligned} \tag{5.8}$$

Here, all the parameters, ε_d, U, J_0 and J_1, are positive, and ε_d is assumed to take values in $\frac{3}{4}J_0 < \varepsilon_d < \frac{3}{4}J_0 + U$. It should be noted that one can rewrite H by using the d- and the p-operators, although it has a somewhat complicated form. It is also noted that we do not take any peculiar limit, such as $U \to \infty$ and $J_0 \to \infty$, and thus H acts on a whole Hilbert space constructed by the d- and the p-operators.

We shall show that the lowest energy of H_0 for the hole number $N_\mathrm{h} = |D| + N$ with $0 < N \leqslant |D|$ is $\varepsilon_0 = -\varepsilon_d|D| - \frac{3}{4}J_0 N$, which is attained by the Zhang–Rice singlet states in $\mathbf{H}^{N_\mathrm{h}}_{\mathrm{ZRS}}$.

Let N^d_h be the eigenvalue of $\sum_{x\in D} n^d_x$, the number of d-holes. Since N^d_h is a conserved quantity for H_0, it is convenient to decompose the N_h-hole Hilbert space into the subspaces with fixed N^d_h. We denoted by $\mathbf{H}^{N_\mathrm{h}}_{N^d_\mathrm{h}}$ the subspace with fixed N^d_h and by $E\left(N^d_\mathrm{h}\right)$ the lowest energy of H_0 for the states in $\mathbf{H}^{N_\mathrm{h}}_{N^d_\mathrm{h}}$.

Let us examine each term in H_0. The eigenvalue of the first sum in H_0 is $-\varepsilon_d N^d_\mathrm{h}$ for the states in $\mathbf{H}^{N_\mathrm{h}}_{N^d_\mathrm{h}}$. The lowest eigenvalue for the second sum is zero which is attained by the states without doubly occupied d-states. The eigenvalues of $J_0\boldsymbol{S}^a_x \cdot \boldsymbol{S}^d_x$ are $-\frac{3}{4}J_0$, 0 and $\frac{1}{4}J_0$. We have eigenvalue $-\frac{3}{4}J_0$ when each of the d-state and the a-state at site x is occupied by one hole and furthermore the two holes in these states form the spin-singlet state.

It immediately follows from the above observation that $E(|D|) = \varepsilon_0$, which is attained by the states in $\mathbf{H}_{\mathrm{ZRS}}^{N_\mathrm{h}} \subset \mathbf{H}_{|D|}^{N_\mathrm{h}}$. In the case $0 \leqslant N_\mathrm{h}^d < |D|$, noting that there are $N_\mathrm{h}^p = |D| + N - N_\mathrm{h}^d$ holes on the O-sites, we have

$$\begin{aligned} E\left(N_\mathrm{h}^d\right) &= -\varepsilon_d N_\mathrm{h}^d - \tfrac{3}{4} J_0 \min\left(N_\mathrm{h}^d, N_\mathrm{h}^p\right) \\ &> \varepsilon_0 + \tfrac{3}{4} J_0 \left\{N_\mathrm{h}^p - \min\left(N_\mathrm{h}^d, N_\mathrm{h}^p\right)\right\} \\ &\geqslant \varepsilon_0. \end{aligned} \tag{5.9}$$

Here the second line follows from the assumptions $0 < \frac{3}{4} J_0 < \varepsilon_d$ and $N_\mathrm{h}^d < |D|$(or $N < N_\mathrm{h}^p$), and the third line follows from $N_\mathrm{h}^p \geqslant \min\left(N_\mathrm{h}^d, N_\mathrm{h}^p\right)$. In the case $|D| < N_\mathrm{h}^d \leqslant |D| + N$, noting that there are, at least, $\left(N_\mathrm{h}^d - |D|\right)$ doubly occupied d-states, we have

$$\begin{aligned} E\left(N_\mathrm{h}^d\right) &= -\varepsilon_d N_\mathrm{h}^d + U\left(N_\mathrm{h}^d - |D|\right) - \tfrac{3}{4} J_0 N_\mathrm{h}^p \\ &= \varepsilon_0 + \left(\tfrac{3}{4} J_0 + U - \varepsilon_d\right)\left(N_\mathrm{h}^d - |D|\right) \\ &> \varepsilon_0. \end{aligned} \tag{5.10}$$

Here the final inequality follows from the assumptions $\varepsilon_d < \frac{3}{4} J_0 + U$ and $|D| < N_\mathrm{h}^d$. As a result, we have $E\left(N_\mathrm{h}^d\right) > \varepsilon_0$ for $N_\mathrm{h}^d \neq |D|$, which proves the claim.

We have shown that the lowest-energy states of H_0 are the Zhang–Rice singlet states in $\mathbf{H}_{\mathrm{ZRS}}^{N_\mathrm{h}}$. In the following, we shall show that H_1 is positive semi-definite and Φ_p in $\mathbf{H}_{\mathrm{ZRS}}^{N_\mathrm{h}}$ is its zero energy state. This implies $H = H_0 + H_1 \geqslant \varepsilon_0$ and $H\Phi_\mathrm{p} = \varepsilon_0 \Phi_\mathrm{p}$. We thus conclude that Φ_p is a ground state of H.

By a straightforward but somewhat lengthy calculation, one finds that H_1 is rewritten as

$$H_1 = \frac{3}{8} J_1 \sum_{x \in D} \sum_{m=1}^{2} \sum_{l=1}^{4} \left[\left(K_{x,l}^m\right)^\dagger K_{x,l}^m + K_{x,l}^m \left(K_{x,l}^m\right)^\dagger\right] \tag{5.11}$$

with

$$K_{x,1}^1 = b_{x,\uparrow}^\dagger a_{x,\downarrow} d_{x,\downarrow}, \tag{5.12}$$

$$K_{x,2}^1 = \tfrac{1}{\sqrt{3}}\left(b_{x,\uparrow}^\dagger a_{x,\downarrow} d_{x,\uparrow} + b_{x,\uparrow}^\dagger a_{x,\uparrow} d_{x,\downarrow} - b_{x,\downarrow}^\dagger a_{x,\downarrow} d_{x,\downarrow}\right), \tag{5.13}$$

$$K_{x,3}^1 = \tfrac{1}{\sqrt{3}}\left(b_{x,\uparrow}^\dagger a_{x,\uparrow} d_{x,\uparrow} - b_{x,\downarrow}^\dagger a_{x,\downarrow} d_{x,\uparrow} - b_{x,\downarrow}^\dagger a_{x,\uparrow} d_{x,\downarrow}\right), \tag{5.14}$$

$$K_{x,4}^1 = -b_{x,\downarrow}^\dagger a_{x,\uparrow} d_{x,\uparrow}, \tag{5.15}$$

and

$$K_{x,1}^2 = a_{x,\uparrow}^\dagger b_{x,\downarrow} d_{x,\downarrow}, \tag{5.16}$$

$$K_{x,2}^2 = \tfrac{1}{\sqrt{3}}\left(a_{x,\uparrow}^\dagger b_{x,\downarrow} d_{x,\uparrow} + a_{x,\uparrow}^\dagger b_{x,\uparrow} d_{x,\downarrow} - a_{x,\downarrow}^\dagger b_{x,\downarrow} d_{x,\downarrow}\right), \tag{5.17}$$

$$K_{x,3}^2 = \tfrac{1}{\sqrt{3}}\left(a_{x,\uparrow}^\dagger b_{x,\uparrow} d_{x,\uparrow} - a_{x,\downarrow}^\dagger b_{x,\downarrow} d_{x,\uparrow} - a_{x,\downarrow}^\dagger b_{x,\uparrow} d_{x,\downarrow}\right), \tag{5.18}$$

$$K_{x,4}^2 = -a_{x,\downarrow}^\dagger b_{x,\uparrow} d_{x,\uparrow}. \tag{5.19}$$

It follows from this representation that H_1 is positive semi-definite. Therefore, the lowest energy of H_1 is greater than or equal to zero, and any zero energy state Φ of H_1, if it exists, must satisfy $\left(K_{x,l}^m\right)^\dagger \Phi = 0$ and $K_{x,l}^m \Phi = 0$ for all $m = 1, 2$, $l = 1, \ldots, 4$ and $x \in D$. We shall prove that Φ_p indeed satisfies these conditions.

We start with the case of $m = 1$ and $l = 1$. By using the commutation relation (4.6), we have

$$\left(K^1_{x,1}\right)^\dagger \zeta = d^\dagger_{x,\downarrow} a^\dagger_{x,\downarrow} b_{x,\uparrow} \zeta = d^\dagger_{x,\downarrow} (b_{x,\uparrow})^2 + \zeta d^\dagger_{x,\downarrow} a^\dagger_{x,\downarrow} b_{x,\uparrow} = \zeta \left(K^1_{x,1}\right)^\dagger. \quad (5.20)$$

This together with $\left(K^1_{x,1}\right)^\dagger \psi^\dagger_x = 0$, which follows from $\left(a^\dagger_{x,\sigma}\right)^2 = \left(d^\dagger_{x,\sigma}\right)^2 = 0$, leads to

$$\left(K^1_{x,1}\right)^\dagger (\zeta)^{N_{\rm p}} \Psi_0 = (\zeta)^{N_{\rm p}} \left(K^1_{x,1}\right)^\dagger \Psi_0 = 0. \quad (5.21)$$

From $a_{x,\downarrow} d_{x,\downarrow} \psi^\dagger_x = -d_{x,\downarrow} a^\dagger_{x,\uparrow} d^\dagger_{x,\downarrow} a_{x,\downarrow} + a_{x,\downarrow} d^\dagger_{x,\uparrow} a^\dagger_{x,\downarrow} d_{x,\downarrow}$ we immediately obtain

$$K^1_{x,1} (\zeta)^{N_{\rm p}} \Psi_0 = b^\dagger_{x,\uparrow} (\zeta)^{N_{\rm p}} a_{x,\downarrow} d_{x,\downarrow} \Psi_0 = 0. \quad (5.22)$$

We thus conclude $\left(K^1_{x,1}\right)^\dagger \Phi_{\rm p} = K^1_{x,1} \Phi_{\rm p} = 0$ for all x in D.

Let us consider the cases of $m = 1$ and $l = 2, 3, 4$. Define spin-lowering and raising operators as

$$S^- = \sum_{x \in D} \left(a^\dagger_{x,\downarrow} a_{x,\uparrow} + d^\dagger_{x,\downarrow} d_{x,\uparrow}\right), \quad (5.23)$$

$$S^+ = \sum_{x \in D} \left(a^\dagger_{x,\uparrow} a_{x,\downarrow} + d^\dagger_{x,\uparrow} d_{x,\downarrow}\right). \quad (5.24)$$

From the results for $l = 1$ we have $S^+ \left(K^1_{x,1}\right)^\dagger \Phi_{\rm p} = 0$. It is easy to see that $S^+ \left(K^1_{x,1}\right)^\dagger = \sqrt{3} \left(K^1_{x,2}\right)^\dagger + \left(K^1_{x,1}\right)^\dagger S^+$, $S^+ \left(K^1_{x,2}\right)^\dagger = 2 \left(K^1_{x,3}\right)^\dagger + \left(K^1_{x,2}\right)^\dagger S^+$, and $S^+ \left(K^1_{x,3}\right)^\dagger = \sqrt{3} \left(K^1_{x,4}\right)^\dagger + \left(K^1_{x,3}\right)^\dagger S^+$. Substituting the first relation into $S^+ \left(K^1_{x,1}\right)^\dagger \Phi_{\rm p} = 0$ and noting $S^+ \Phi_{\rm p} = 0$, we find $\left(K^1_{x,2}\right)^\dagger \Phi_{\rm p} = 0$. Repeating the same argument, we have $\left(K^1_{x,3}\right)^\dagger \Phi_{\rm p} = \left(K^1_{x,4}\right)^\dagger \Phi_{\rm p} = 0$. By using $S^- K^1_{x,1} \Phi_{\rm p} = 0$, $S^- K^1_{x,1} = -\sqrt{3} K^1_{x,2} + K^1_{x,1} S^-$, $S^- K^1_{x,2} = -2 K^1_{x,3} + K^1_{x,2} S^-$, $S^- K^1_{x,3} = -\sqrt{3} K^1_{x,4} + K^1_{x,3} S^-$, and $S^- \Phi_{\rm p} = 0$, we similarly obtain $K^1_{x,l} \Phi_{\rm p} = 0$ for $l = 2, 3, 4$.

Proceeding in the same way, we obtain $\left(K^2_{x,l}\right)^\dagger \Phi = K^2_{x,l} \Phi = 0$ for $l = 1, \ldots, 4$ and $x \in D$. This completes the proof of the claim.

We remark that the uniqueness of the ground state of H for each hole number is not proved at present. We hope that this will be clarified in a future study.

6. Estimation of a lower bound for μ_δ

In this section we estimate a lower bound for μ_δ. We will show later that

$$\frac{\left\langle \Phi_{\rm p}, a^\dagger_{x,\sigma} a_{x,\sigma} b^\dagger_{x,-\sigma} b_{x,-\sigma} \Phi_{\rm p} \right\rangle}{\left\langle \Phi_{\rm p}, b^\dagger_{x,-\sigma} b_{x,-\sigma} \Phi_{\rm p} \right\rangle} \geqslant \gamma_{\Lambda,N}, \quad (6.1)$$

with $\gamma_{\Lambda,N} = \frac{9N - 8|D|}{2(8N - 7|D|)}$, for $N \geqslant (8|D|)/9$. It follows from this inequality that

$$\mu_{\Lambda,N} \geqslant \sqrt{\gamma_{\Lambda,N} \frac{N_{\rm p} + 1}{2|D|^2} \frac{\sum_{x,\sigma} \left\langle \Phi_{\rm p}, b^\dagger_{x,\sigma} b_{x,\sigma} \Phi_{\rm p} \right\rangle}{\langle \Phi_{\rm p}, \Phi_{\rm p} \rangle}}. \quad (6.2)$$

Here, we have that

$$\sum_{x \in D} \sum_{\sigma = \uparrow,\downarrow} \left\langle \Phi_{\rm p}, b^\dagger_{x,\sigma} b_{x,\sigma} \Phi_{\rm p} \right\rangle = \sum_{k \in \mathcal{K}} \sum_{\sigma = \uparrow,\downarrow} \left\langle \Phi_{\rm p}, \epsilon_b(k) \hat{a}^\dagger_{k,\sigma} \hat{a}_{k,\sigma} \Phi_{\rm p} \right\rangle, \quad (6.3)$$

and it is easy to find that the right-hand side is bounded from below by

$$2\sum_{l=1}^{N/2}\epsilon_b(k^{(l)})\langle\Phi_{\mathrm{p}},\Phi_{\mathrm{p}}\rangle, \tag{6.4}$$

where $\epsilon_b(k^{(1)}) \leqslant \epsilon_b(k^{(2)}) \ldots \leqslant \epsilon_b(k^{(|D|)})$ is an arrangement of $\epsilon_b(k)$ with $k \in \mathcal{K}$ in ascending order. Substituting this lower bound into (6.2) and taking the limit, we obtain (4.10).

In what follows, we prove inequality (6.1). By the spin-rotation symmetry for Φ_{p}, it suffices to consider the case of $\sigma = \uparrow$. By the translation symmetry, we can also assume $x \in D_{\mathrm{e}}$ without loss of generality . We first show that the left-hand side of (6.1) with $\sigma = \uparrow$ is rewritten as

$$\frac{\sum_{S\subset D_{\mathrm{e}};x\notin S,|S|=N_{\mathrm{p}}} W_x(S)}{2\sum_{S\subset D_{\mathrm{e}};|S|=N_{\mathrm{p}}} W_x(S)} = \frac{\sum_{S\subset D_{\mathrm{e}};x\notin S,|S|=N_{\mathrm{p}}} W_x(S)}{2(\sum_{S\subset D_{\mathrm{e}};x\notin S,|S|=N_{\mathrm{p}}} W_x(S) + \sum_{S\subset D_{\mathrm{e}};x\in S,|S|=N_{\mathrm{p}}} W_x(S))} \tag{6.5}$$

with the nonnegative weights

$$W_x(S) = \left\langle\left(\prod_{z\in S}\tilde{\phi}_z\right)\Psi_0, b^\dagger_{x,\downarrow}b_{x,\downarrow}\left(\prod_{z\in S}\tilde{\phi}_z\right)\Psi_0\right\rangle, \tag{6.6}$$

where $\tilde{\phi}_z = (b_{z,\downarrow}a_{z,\uparrow} + a_{z,\downarrow}b_{z,\uparrow})$. To see this, note that

$$\zeta = \sum_{z\in D_{\mathrm{e}}} b_{z,\downarrow}a_{z,\uparrow} + \sum_{z\in D_{\mathrm{o}}} b_{z,\downarrow}a_{z,\uparrow} = \sum_{z\in D_{\mathrm{e}}}(b_{z,\downarrow}a_{z,\uparrow} + a_{z,\downarrow}b_{z,\uparrow}) = \sum_{z\in D_{\mathrm{e}}}\tilde{\phi}_z. \tag{6.7}$$

Then, since $(\tilde{\phi}_z)^2\Psi_0 = 0$ (which follows from $a_{z,\downarrow}a_{z,\uparrow}\Psi_0 = 0$), Φ_{p} is expanded as

$$\Phi_{\mathrm{p}} = N_{\mathrm{p}}!\sum_{\substack{S\subset D_{\mathrm{e}}\\ |S|=N_{\mathrm{p}}}}\left(\prod_{z\in S}\tilde{\phi}_z\right)\Psi_0. \tag{6.8}$$

Since $a_{x,\uparrow}\left(\prod_{z\in S}\tilde{\phi}_z\right)\Psi_0 = 0$ for $x \in S$ (which again follows from $a_{z,\downarrow}a_{z,\uparrow}\Psi_0 = 0$), and

$$\left\langle\left(\prod_{z\in S'}\tilde{\phi}_z\right)\Psi_0, a^\dagger_{x,\uparrow}a_{x,\uparrow}b^\dagger_{x,\downarrow}b_{x,\downarrow}\left(\prod_{z\in S}\tilde{\phi}_z\right)\Psi_0\right\rangle = 0 \qquad \text{for} \quad S' \neq S, \tag{6.9}$$

we have that

$$\begin{aligned}\left\langle\Phi_{\mathrm{p}}, a^\dagger_{x,\uparrow}a_{x,\uparrow}b^\dagger_{x,\downarrow}b_{x,\downarrow}\Phi_{\mathrm{p}}\right\rangle &= (N_{\mathrm{p}}!)^2\sum_{\substack{S\subset D_{\mathrm{e}}\\ x\notin S,|S|=N_{\mathrm{p}}}}\left\langle\left(\prod_{z\in S}\tilde{\phi}_z\right)\Psi_0, a^\dagger_{x,\uparrow}a_{x,\uparrow}b^\dagger_{x,\downarrow}b_{x,\downarrow}\left(\prod_{z\in S}\tilde{\phi}_z\right)\Psi_0\right\rangle.\\ &= \frac{1}{2}(N_{\mathrm{p}}!)^2\sum_{\substack{S\subset D_{\mathrm{e}}\\ x\notin S,|S|=N_{\mathrm{p}}}} W_x(S).\end{aligned} \tag{6.10}$$

To get the second line we used

$$\left\langle\psi^\dagger_x\Phi_0, a^\dagger_{x,\uparrow}a_{x,\uparrow}\psi^\dagger_x\Phi_0\right\rangle = 1 = \left\langle\psi^\dagger_x\Phi_0, \psi^\dagger_x\Phi_0\right\rangle/2. \tag{6.11}$$

Likewise, we have that

$$\left\langle\Phi_{\mathrm{p}}, b^\dagger_{x,\downarrow}b_{x,\downarrow}\Phi_{\mathrm{p}}\right\rangle = (N_{\mathrm{p}}!)^2\sum_{S\subset D_{\mathrm{e}};|S|=N_{\mathrm{p}}} W_x(S), \tag{6.12}$$

which together with (6.10) leads to (6.5).

Before proceeding, we need to introduce some notation. For each $z \in D_{\mathrm{e}}$, define $D_{\mathrm{o},z} = \{y||y-z| = 1, y \in D_{\mathrm{o}}\}$, which is the collection of the nearest-neighbour sites of z.

We say that z and z' in D_e are connected if $D_{o,z} \cap D_{o,z'} \neq \emptyset$. For $S \subset D_e$ which does not contain x, we call z an isolated point in S if z is not connected any other sites in $S \cup \{x\}$, and write $D_x(S)$ for the collection of these isolated points in S. It is noted that, if $y \in D_x(S' \cup \{y\})$, the weight $W_x(S' \cup \{y\})$ is reduced as

$$W_x(S' \cup \{y\}) = \tfrac{1}{2} W_x(S'), \tag{6.13}$$

since $a^\dagger_{y',\sigma}$ with $|y'-y| \leqslant 1$ commutes with $b^\dagger_{x,\downarrow} b_{x,\downarrow} \prod_{z\in S'} \tilde{\phi}_z$ and thus

$$\left\langle \Psi_0, \tilde{\phi}^\dagger_y \tilde{\phi}_y \Psi_0 \right\rangle = \frac{1}{4} \sum_{\substack{y'\in D_o \\ |y'-y|=1}} \sum_{\sigma=\uparrow,\downarrow} \left\langle \Psi_0, a^\dagger_{y,\sigma} a^\dagger_{y',-\sigma} a_{y',-\sigma} a_{y,\sigma} \Psi_0 \right\rangle = \tfrac{1}{2} \left\langle \Psi_0, \Psi_0 \right\rangle . \tag{6.14}$$

(Recall (6.11).) We denote by $\mathcal{D}_x(N_p, l)$ the collection of subsets S of D_e such that $x \notin S$, $|S| = N_p$ and $|D_x(S)| = l$.

Since the value of $|D_x(S)|$ is determined for each $S \subset D_e$, we have

$$\sum_{\substack{S\subset D_e \\ x\notin S, |S|=N_p}} W_x(S) = \sum_{l=0}^{N_p} \sum_{S\in\mathcal{D}_x(N_p,l)} W_x(S) \geqslant \sum_{l=1}^{N_p} \sum_{S\in\mathcal{D}_x(N_p,l)} W_x(S). \tag{6.15}$$

Now fix $l \geqslant 1$. Noting that there are l isolated sites in $S \in \mathcal{D}_x(N_p, l)$, we find

$$\begin{aligned} \sum_{S\in\mathcal{D}_x(N_p,l)} W_x(S) &= \frac{1}{l} \sum_{S\in\mathcal{D}_x(N_p,l)} \sum_{y\in D_e} W_x(S) \chi[y \in D_x(S)] \\ &= \frac{1}{l} \sum_{S\in\mathcal{D}_x(N_p,l)} \sum_{y\in D_e} \sum_{S'\in\mathcal{D}_x(N_p-1,l-1)} W_x(S)\chi[y\in D_x(S)]\chi[S' = S\backslash\{y\}] \\ &= \frac{1}{2l} \sum_{S'\in\mathcal{D}_x(N_p-1,l-1)} W_x(S') \sum_{S\in\mathcal{D}_x(N_p,l)} \sum_{y\in D_e} \chi[y\in D_x(S)]\chi[S = S'\cup\{y\}] \\ &\geqslant \frac{1}{2N_p} \left(\frac{|D|}{2} - 9N_p \right) \sum_{S'\in\mathcal{D}_x(N_p-1,l-1)} W_x(S'). \end{aligned} \tag{6.16}$$

To get the second line, note that removing an isolated point in $S \in \mathcal{D}_x(N_p, l)$ yields an element in $\mathcal{D}_x(N_p - 1, l - 1)$. The third line follows from (6.13). The last inequality is obtained as follows. Each site z in D_e has eight connected sites. Therefore, for every $S' \in \mathcal{D}_x(N_p-1, l-1)$, there exist at least $|D_e| - 9N_p$ sites, y, such that y is an isolated point in $S' \cup \{y\}$, and $S' \cup \{y\}$ becomes an element in $\mathcal{D}_x(N_p, l)$. Note that $|D_e| - 9N_p$ is a positive number by the assumption. Then, by using $l \leqslant N_p$, we get the last inequality.

From (6.15) and (6.16) we get

$$\sum_{\substack{S\subset D_e \\ x\notin S, |S|=N_p}} W_x(S) \geqslant \frac{1}{2N_p} \left(\frac{|D|}{2} - 9N_p \right) \sum_{l=0}^{N_p-1} \sum_{S\in\mathcal{D}_x(N_p-1,l)} W_x(S). \tag{6.17}$$

Here, for $x \notin S$, we have

$$\begin{aligned} W_x(S \cup \{x\}) &= \left\langle \left(\prod_{z\in S} \tilde{\phi}_z \right) \Psi_0, a^\dagger_{x,\downarrow} a_{x,\downarrow} b^\dagger_{x,\uparrow} b_{x,\uparrow} b^\dagger_{x,\downarrow} b_{x,\downarrow} \left(\prod_{z\in S} \tilde{\phi}_z \right) \Psi_0 \right\rangle \\ &= \frac{1}{2} \left\langle \left(\prod_{z\in S} \tilde{\phi}_z \right) \Psi_0, (1 - b_{x,\uparrow} b^\dagger_{x,\uparrow}) b^\dagger_{x,\downarrow} b_{x,\downarrow} \left(\prod_{z\in S} \tilde{\phi}_z \right) \Psi_0 \right\rangle \\ &\leqslant \frac{1}{2} W_x(S). \end{aligned} \tag{6.18}$$

It follows from this inequality and (6.17) that

$$\sum_{\substack{S\subset D_{\mathrm{e}}\\ x\notin S,|S|=N_{\mathrm{p}}}} W_x(S) \geqslant \frac{1}{N_{\mathrm{p}}}\left(\frac{|D|}{2}-9N_{\mathrm{p}}\right)\sum_{l=0}^{N_{\mathrm{p}}-1}\sum_{S\in\mathcal{D}_x(N_{\mathrm{p}}-1,l)} W_x(S\cup\{x\})$$
$$=\left(\frac{|D|}{2N_{\mathrm{p}}}-9\right)\sum_{\substack{S\subset D_{\mathrm{e}}\\ x\in S,|S|=N_{\mathrm{p}}}} W_x(S). \tag{6.19}$$

From (6.5) and (6.19) we obtain the desired inequality (6.1).

7. Summary and remarks

In this paper, for the even numbers N_{h} of holes in $|D| < N_{\mathrm{h}} \leqslant 2|D|$, we have constructed a pairing state Φ_{p} with d-wave symmetry which is expanded in terms of the Zhang–Rice singlet states. We have calculated upper and lower bounds of the ODLRO parameter for Φ_{p} as a function of the doping concentration. We have also presented the concrete Hamiltonian $H = H_0 + H_1$ (5.6) on the CuO_2 plain which has Φ_{p} as its ground state. We have proved that the lowest energy states of H_0 (5.7) are the Zhang–Rice singlet states and then have shown that, by using the positive-semidefiniteness of H_1 (5.11), the pairing state Φ_{p} consisting of the Zhang–Rice singlet states attains the ground state energy of the whole Hamiltonian H. The uniqueness of the ground state is not proved at present, and we leave this as a problem in a future study.

It is noted that H_0 with $J_0 = 0$ becomes the Hamiltonian of the d–p (or 3-band) model in the atomic limit [3–5], and H_0 with $J_0 \neq 0$ is essentially the same as the effective Hamiltonian derived by taking into account the hopping terms between Cu- and O-sites as a perturbation in the limit [5]. The idea of the Zhang–Rice singlet is based on this effective Hamiltonian, and the t–J model is obtained by furthermore considering the motion of the Zhang–Rice singlets perturbatively with the inclusion of the antiferromagnetic interactions between Cu-holes

$$H_2 = J_2 \sum_{x,y\in D;|x-y|=1} \boldsymbol{S}_x^d \cdot \boldsymbol{S}_y^d, \tag{7.1}$$

which is the effective interaction due to the hopping process between neighbouring Cu-sites [5].

In the $|D|$-hole case, the present Hamiltonian has degenerate paramagnetic ground states with one hole per Cu-site and does not exhibit antiferromagnetism which is essential to high-T_{c} cuprates. This will be improved if we consider the modified Hamiltonian $H_0 + H_1 + H_2$. This Hamiltonian or more generally the d–p Hamiltonian with H_1 may be able to reproduce the essential features of high-T_{c} cuprates, such as antiferromagnetism at low doping concentrations and charge density order (or a stripe structure) between the antiferromagnetic and the superconducting states. We believe that further investigations about modified models based on our Hamiltonian which is now shown to exhibit ODRLO with d-wave symmetry will contribute the understanding of high-T_{c} cuprate superconductivity.

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Appendix

In this appendix, we shall show that the pairing state $\Phi_{\rm p}$ is non-vanishing when the number of holes, $N_{\rm h} = |D| + N$, satisfies $N = |D| - 2l_2L_1$ with some integer $0 \leqslant l_2 \leqslant (L_2 - 2)/2$. A similar argument will show that $\Phi_{\rm p}$ is non-vanishing for $2L_1 \leqslant N \leqslant |D|$.

It is easy to see that the collection of the states on the right-hand side of (6.8) is orthogonal. So $\Phi_{\rm p}$ is non-vanishing if one of those terms is non-vanishing. We shall show that this is the case. Let

$$A_1 = \{x = (x_1, x_2) \mid 1 \leqslant x_1 \leqslant L_1, 1 \leqslant x_2 \leqslant 2l_2,\ x_2 \text{ is odd}\} \tag{A.1}$$

and

$$A_2 = \{x = (x_1, x_2) \mid 1 \leqslant x_1 \leqslant L_1, 1 \leqslant x_2 \leqslant 2l_2,\ x_2 \text{ is even}\}. \tag{A.2}$$

Now we pick up the state in (6.8) corresponding to the subset $S_0 = (A_1 \cup A_2) \cap D_{\rm e}$. Substituting $\tilde{\phi}_z = a_{z,\downarrow} b_{z,\uparrow} + b_{z,\downarrow} a_{z,\uparrow}$ into this state, we obtain

$$\prod_{z\in S_0} (a_{z,\downarrow} b_{z,\uparrow} + b_{z,\downarrow} a_{z,\uparrow}) \Psi_0 = \sum_{T\subset S_0} \left(\prod_{z\in T} a_{z,\downarrow} b_{z,\uparrow} \right) \left(\prod_{z\in S_0\setminus T} b_{z,\downarrow} a_{z,\uparrow} \right) \Psi_0. \tag{A.3}$$

The collection of the states on the right-hand side of the above expression is again orthogonal. Let $S_1 = A_1 \cap D_{\rm e}$. Then it is easy to see that

$$\left\langle \left(\prod_{z\in A_1} a_{z,\downarrow} \right) \left(\prod_{z\in A_2} a_{z,\uparrow} \right) \Psi_0, \left(\prod_{z\in S_1} a_{z,\downarrow} b_{z,\uparrow} \right) \left(\prod_{z\in S_0\setminus S_1} a_{z,\uparrow} b_{z,\downarrow} \right) \Psi_0 \right\rangle \tag{A.4}$$

is nonzero. This implies that the term in (A.3) with $T = S_1$ (and thus the term with $S = S_0$ in (A.3)) is non-vanishing, which concludes that $\Phi_{\rm p}$ is non-vanishing.

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