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 formidable 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 $0 \leq \delta \leq 1$. 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

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

(2.1)

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

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

(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 $\Lambda$. For later use, we introduce further the following sublattices of $D$:

$$D_0 = \{x | x = (x_1, x_2) \in D \text{ with } x_1 + x_2 \text{ being odd}\},$$

(2.3)

$$D_\varepsilon = \{x | x = (x_1, x_2) \in D \text{ with } x_1 + x_2 \text{ being even}\}.$$
Next we introduce fermion operators which annihilate or create holes with spin $\sigma = \uparrow, \downarrow$ at sites in $\Lambda$. Any states with the number $N_h$ of holes can be constructed by operating these operators on a state $\Phi_0$ with no holes on $\Lambda$. By $d_{i,\sigma}(\bar{d}_{i,\sigma})$ and $p_{u,\sigma}(\bar{p}_{u,\sigma})$, 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 $x \in D$:

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

As is easily seen, the annihilation operator $f_{x,\sigma}$ and the creation operator $\bar{f}_{x,\sigma}$ 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 $f_{1,\sigma} = (1/\sqrt{|D|}) \sum_{x \in D} f_{x,\sigma} e^{-i k \cdot x}$ for $k \in \mathcal{K} = \left\{ \left( \frac{2\pi}{L_1} n_1, \frac{2\pi}{L_2} n_2 \right) | n_1, n_2 \in \mathbb{Z}, -L_l/2 < n_l \leq L_l/2 \text{ with } l = 1, 2 \right\}$, and then define $f_k,\sigma = f_{k,\sigma}/\|f_k\|$, where the normalization factors are given by

$$\|f_k\| = \begin{cases} \frac{1}{\sqrt{1 + \frac{1}{2} \cos k_1 + \cos k_2}} & \text{if } k = (\pi, \pi), \\ \sqrt{|D|} \sum_{k \in K} \bar{a}_{k,\sigma} e^{i k \cdot x}. \quad (2.8)$$

The $a$-operators defined as above approximate the $f$-operators well, and satisfy the canonical fermion anticommutation relations $\{a_{x,\sigma}, a_{y,\tau}^\dagger\} = 0$ and $\{a_{x,\sigma}, a_{y,\tau}\} = \delta_{\sigma,\tau} \delta_{x,y}$ 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 $X$. 

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

$$\Psi^\dagger = d^\dagger_{x,\uparrow} a^\dagger_{x,\downarrow} + a^\dagger_{x,\uparrow} d^\dagger_{x,\downarrow}.$$  \hfill (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 $\prod_{x \in D} d^\dagger_{x,\sigma} \Phi_0$ with $\sigma_x = \uparrow, \downarrow$ (figure 2(a)). We furthermore assume that $N_h$ holes added in this state form Zhang–Rice singlets. Then a $(|D| + N_h)$-hole state with $0 < N_h \leq |D|$ is written by using a set of states $\prod_{x \in A} a^\dagger_{x,-\sigma_x} \Psi^\dagger \Phi_0$, \hfill (2.10)

where $A$ is a subset of $D$ with $|A| = |D| - N_h$ and its compliment $D \setminus A$ is a collection of sites where the Zhang–Rice singlets are formed (figure 2(b)). Noting the relation $d^\dagger_{x,\sigma} \Phi_0 = -\text{sgn}[\sigma] a^\dagger_{x,-\sigma} \Psi^\dagger \Phi_0$ \hfill (2.11)

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

$$\prod_{x \in A} \alpha^\dagger_{x,-\sigma_x} \Psi_0 = \Psi_{A,\sigma_A},$$  \hfill (2.12)

with

$$\Psi_0 = \left(\prod_{y \in D} \Psi^\dagger\right) \Phi_0 \hfill (2.13)$$

up to a sign factor. Here $\sigma_A$ is a short hand for a spin configuration $(\sigma_x)_{x \in A}$. We write $S_A$ for the collection of spin configurations $((\sigma_x)_{x \in A}|\sigma_x = \uparrow, \downarrow, x \in A)$. It is easy to see that $\langle \Psi_{A,\sigma_A}, \Psi_{B,\tau_B} \rangle = 2^{(|D| - |A|)}\chi[A = B]\chi[\sigma_A = \tau_B]$, where $\chi[\text{event}] = 1$ if ‘event’ is true and 0 otherwise. Thus the collection of states $\{\Psi_{A,\sigma_A}|A \subset D, \sigma_A \in S_A\}$ \hfill (2.14)

is orthogonal. For $|D| < N_h \leq 2|D|$, let $H_{ZRS}^{N_h}$ be the Hilbert space spanned by the basis states $\{\Psi_{A,\sigma_A}|A = 2|D| - N_h\}$. The Zhang–Rice singlet states are defined to be states in $H_{ZRS}^{N_h}$.

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**Figure 2.** The solid and open arrows indicate spins of the holes on the Cu- and O-sites, respectively. 
(a) In the case of $N_h = |D|$, 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.
3. d-wave pairing state

Assuming that \( N_h \) takes an even number in \(|D| < N_h \leq 2|D|\), we consider a d-wave pairing state in the Hilbert space \( \mathbb{H}^{N_h}_{ZRS} \). Let us define a pair operator \( \zeta \) by

\[
\zeta = \sum_{k=(k_1, k_2) \in \mathcal{K}} (\cos k_1 - \cos k_2) \hat{a}_{-k, \uparrow} \hat{a}_{k, \uparrow}.
\]  

(3.1)

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

\[
\Phi_p = (\zeta)^N \Psi_0
\]  

(3.2)

with the number of pairs \( N_p = (|D| - N)/2 \). Here we note that

\[
a_{x, \downarrow} a_{x, \uparrow} \Psi_0 = 0
\]  

(3.3)

since \( [a_{x, \downarrow} a_{x, \uparrow}, \psi]\| = -d_{x, \downarrow}^\dagger a_{x, \downarrow} - d_{x, \uparrow}^\dagger a_{x, \downarrow} \), so that \( \Phi_p \) is actually expanded in terms of (2.12).

In the appendix, we show that \( \Phi_p \) is non-vanishing.

In order to see the real space representations of \( \zeta \) and \( \Phi_p \), we define the following operators: for \( x \in D \)

\[
b_{x, \sigma} = \frac{1}{2} \sum_{y \in D, |x-y|=1} a_{y, \sigma} e^{i \pi \delta^2(x-y)},
\]  

(3.4)

and for \( x, y \in D \)

\[
\phi^a_{(x, y)} = \frac{1}{2} e^{i \pi \delta^2(x-y)} (a_{x, \downarrow} a_{y, \uparrow} + a_{y, \downarrow} a_{x, \uparrow}).
\]  

(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 \( \zeta \) as

\[
\zeta = \sum_{x \in D} a_{x, \downarrow} b_{x, \uparrow} = \sum_{x \in D} b_{x, \downarrow} a_{x, \uparrow}
\]  

(3.6)

or

\[
\zeta = \sum_{(x, y) \in B} \phi^a_{(x, y)},
\]  

(3.7)

where

\[
B = \{(x, y) | x, y \in D, |x - y| = 1\}
\]  

(3.8)

is the collection of bonds in \( D \) (we assume that \( \{x, y\} = \{y, x\} \)). Let \( C(B) \) be the collection of subsets \( B \) of \( B \) 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

\[
\Phi_p = N_p! \sum_{B \in C(B) : |B| = N_p, \{x, y\} \in B} \prod_{(x, y) \in B} \phi^a_{(x, y)} \psi_0.
\]  

(3.9)

Therefore, the pairing state \( \Phi_p \) 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 \( \Phi_p \) in terms of the hole creation operators. Let \( n_{x, \sigma}^d = d_{x, \sigma}^\dagger d_{x, \sigma} \) and define \( \mathcal{P}_D = \prod_{x \in D} (1 - n_{x, \uparrow}^d, n_{x, \downarrow}^d) \), 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 \( \psi_0 \) as

\[
\psi_0 = \frac{1}{|D|!} \mathcal{P}_D \left( \sum_{x \in D} \psi_x \right)^{|D|} \Phi_0 = \frac{1}{|D|!} \mathcal{P}_D \left( \sum_{k \in \mathcal{K}} (\hat{a}_{k, \uparrow}^\dagger \hat{a}_{-k, \downarrow} + \hat{a}_{k, \downarrow} \hat{a}_{-k, \uparrow}) \right)^{|D|} \Phi_0,
\]  

(3.10)
where \( d_{k,\sigma} = (1/\sqrt{|D|}) \sum_{x \in D} d_{k,\sigma} e^{-i k \cdot x} \). Then, noting two commutation relations

\[
\left[ \hat{a}_{-k,\downarrow} \hat{a}_{k,\uparrow}, \left( \sum_{p \in k} (\hat{d}_{p,\uparrow}^{\dagger} \hat{a}_{p,\downarrow}^{\dagger} + \hat{a}_{p,\downarrow}^{\dagger} \hat{d}_{p,\uparrow}^{\dagger}) \right) \right] = - (\hat{d}_{k,\uparrow}^{\dagger} \hat{a}_{k,\uparrow}^{\dagger} + \hat{a}_{k,\downarrow}^{\dagger} \hat{a}_{k,\downarrow}^{\dagger})
\]

(3.11)

and

\[
\left[ - (\hat{d}_{k,\uparrow}^{\dagger} \hat{a}_{k,\uparrow}^{\dagger} + \hat{d}_{-k,\downarrow}^{\dagger} \hat{a}_{-k,\downarrow}^{\dagger}), \left( \sum_{p \in k} (\hat{d}_{p,\uparrow}^{\dagger} \hat{a}_{p,\downarrow}^{\dagger} + \hat{a}_{p,\downarrow}^{\dagger} \hat{d}_{p,\uparrow}^{\dagger}) \right) \right] = -2 \hat{d}_{k,\uparrow}^{\dagger} \hat{d}_{k,\downarrow}^{\dagger}
\]

(3.12)

we obtain

\[
\Phi_{p} = \frac{1}{N!} \mathcal{P}_{D} \left( \sum_{x \in k} (\cos k_{2} - \cos k_{1}) \hat{d}_{k,\downarrow}^{\dagger} \hat{d}_{k,\uparrow}^{\dagger} \right) \left( \sum_{x \in \beta} \psi_{x}^{\dagger} \right)^{N} \Phi_{0}
\]

\[
= \frac{N_{p}}{N!} \mathcal{P}_{D} \left( \sum_{B \subseteq C \in \beta|B|=N_{p}} \prod_{x \in \beta} (\phi_{x}^{d}) \right) \left( \sum_{x \in \beta} \psi_{x}^{\dagger} \right)^{N} \Phi_{0}
\]

(3.13)

with

\[
(\phi_{x,y}^{d}) = \frac{1}{2} e^{-i \pi \delta} \delta_{x-y} (d_{x,\uparrow}^{\dagger} d_{x,\downarrow}^{\dagger} + d_{x,\downarrow}^{\dagger} d_{x,\uparrow}^{\dagger})
\]

(3.14)

To get the second line in (3.13) we used \( \mathcal{P}_{D} \hat{d}_{k,\uparrow}^{\dagger} \hat{d}_{k,\downarrow}^{\dagger} \hat{d}_{k,\downarrow}^{\dagger} \hat{d}_{k,\uparrow}^{\dagger} = 0 \). The operator \( (\phi_{x,y}^{d})^{\dagger} \) corresponds to a two-hole singlet state formed by holes on the Cu-sites. From expression (3.13) we find that the state \( \Phi_{p} \) 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), \( \Phi_{p} \) does not exhibit long-range order associated with the Zhang–Rice singlets. In fact, it is easy to see that

\[
\langle \Phi_{p}, \psi_{x}^{\dagger} \psi_{y} \Phi_{p} \rangle = 0
\]

(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

\[
\Delta = \frac{1}{|D|} \sum_{(x,y) \in \beta} \phi_{x,y}^{d} = \frac{1}{|D|} \zeta.
\]

(4.1)

We then define

\[
\mu_{\Delta,N} = \sqrt{\frac{\langle \Phi_{p}, \Delta^{\dagger} \Delta \Phi_{p} \rangle}{\langle \Phi_{p}, \Phi_{p} \rangle}},
\]

\[
\mu_{\delta} = \lim_{|D|N \rightarrow \infty, N/|D| \rightarrow \delta} \mu_{\Delta,N}
\]

(4.2)

(4.3)

where the limit is taken with \( N/|D| \) kept fixed to \( \delta \). This order parameter measures a long range correlation between spin-singlet pairs corresponding \( \phi_{x,y}^{d} \).

We firstly show that

\[
\langle \Phi_{p}, \Delta^{\dagger} \Delta \Phi_{p} \rangle = \frac{N_{p}}{2|D|^{2}} \sum_{x \in \beta} \sum_{\sigma = \uparrow, \downarrow} \langle \Phi_{p}, a_{x,\sigma}^{\dagger} a_{x,\sigma} b_{x,\sigma}^{\dagger} b_{x,\sigma} \Phi_{p} \rangle
\]

(4.4)
which is crucial for our estimation of $\mu_\delta$ (recall $N_p = (|D| - N)/2$). To see this, we observe that

\[
\langle (\zeta)^N \Psi_0, a^d_{x,\downarrow} (\zeta)^N \Psi_0 \rangle = \langle (\zeta)^N \Psi_0, b^d_{x,\downarrow} (\zeta)^N \Psi_0 \rangle
\]

\[
= (N_p + 1) \langle (\zeta)^N \Psi_0, a^d_{x,\downarrow} a^\uparrow_{x,\uparrow} b^d_{x,\downarrow} (\zeta)^N \Psi_0 \rangle
\]

\[
= (N_p + 1) \langle (\zeta)^N \Psi_0, a^d_{x,\downarrow} a^\uparrow_{x,\uparrow} b^d_{x,\downarrow} (\zeta)^N \Psi_0 \rangle.
\]

(4.5)

To get the second line we used the commutation relation

\[
[\zeta a^d_{x,\sigma}, a^d_{x,\sigma} \zeta] = \text{sgn} [\sigma] b_{x,-\sigma},
\]

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

By noting the inequality

\[
\langle \Phi_\delta, a^d_{x,\sigma} a^\uparrow_{x,\uparrow} b^d_{x,\downarrow} b^\downarrow_{x,-\sigma} \Phi_\delta \rangle = \langle \Phi_\delta, a^d_{x,\sigma} a^\uparrow_{x,\uparrow} (1 - b^d_{x,-\sigma} b^\downarrow_{x,-\sigma}) \Phi_\delta \rangle
\]

\[
\leq \langle \Phi_\delta, a^d_{x,\sigma} a^\uparrow_{x,\uparrow} \Phi_\delta \rangle
\]

(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 $\Phi_\delta$, we find that $\mu_{\Lambda,N}$ is bounded from above as

\[
\mu_{\Lambda,N} \leq \sqrt{\frac{(N_p + 1)}{|D|} \left( \frac{N}{2|D|} \right)}.
\]

(4.8)

The limit is thus bounded from above as

\[
\mu_\delta \leq \frac{1}{2} \sqrt{\delta (1 - \delta)}.
\]

(4.9)

As for a lower bound for $\mu_\delta$ we have the following result. Let $\frac{5}{6} \leq \delta \leq 1$. Then we have that

\[
\mu_\delta \geq \frac{1}{2} \sqrt{\gamma_\delta I(\delta)(1 - \delta)},
\]

(4.10)

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

\[
I(\delta) = \frac{2}{(2\pi)^2} \int_{|k| \leq \pi} \epsilon_\delta(k) \chi[\epsilon_\delta(k) \leq \epsilon_3] \, dk
\]

(4.11)

with $\epsilon_\delta(k) = (\cos k_1 - \cos k_2)^2$. Here $\epsilon_3$ is determined by

\[
\delta = \frac{2}{(2\pi)^2} \int_{|k| \leq \pi} \chi[\epsilon_\delta(k) \leq \epsilon_3] \, dk.
\]

(4.12)

The inequality (4.10) means that the state $\Phi_\delta$ exhibits ODLRO with d-wave symmetry for $\frac{5}{6} < \delta < 1$. 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 Φₚ

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

Let us define the number operator \( n_{x,\sigma}^a \), with \( \sigma = \uparrow, \downarrow \), and the spin operators \( S_{x,\alpha}^a \), with \( \alpha = 1, 2, 3 \), corresponding to the \( a \)-operators by

\[
n_{x,\sigma}^a = a_{x,\sigma}^\dagger a_{x,\sigma}, \tag{5.1}
\]

\[
S_{x,1}^a = \frac{i}{2} (a_{x,\uparrow}^\dagger a_{x,\downarrow} + a_{x,\downarrow}^\dagger a_{x,\uparrow}), \tag{5.2}
\]

\[
S_{x,2}^a = \frac{i}{2i} (a_{x,\uparrow}^\dagger a_{x,\uparrow} - a_{x,\downarrow}^\dagger a_{x,\downarrow}), \tag{5.3}
\]

\[
S_{x,3}^a = \frac{i}{2} (a_{x,\downarrow}^\dagger a_{x,\uparrow} - a_{x,\uparrow}^\dagger a_{x,\downarrow}). \tag{5.4}
\]

We also define

\[
n_x^a = n_{x,\uparrow}^a + n_{x,\downarrow}^a. \tag{5.5}
\]

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

\[
H_0 = -\varepsilon_d \sum_{x \in D} n_x^d + U \sum_{x \in D} n_{x,\uparrow}^d n_{x,\downarrow}^d + J_0 \sum_{x \in D} S_x^a \cdot S_x^d, \tag{5.7}
\]

\[
H_1 = \frac{3}{4} J_1 \sum_{x \in D} \sum_{\sigma = \uparrow, \downarrow} \left( a_{x,\sigma}^\dagger a_{x,\sigma} + b_{x,\sigma}^\dagger b_{x,\sigma} \right)
+ J_1 \sum_{x \in D} \left( S_x^a \cdot S_x^a + S_x^b \cdot S_x^b + S_x^d \cdot S_x^d - \frac{3}{4} n_x^a \cdot n_x^b \right). \tag{5.8}
\]

Here, all the parameters, \( \varepsilon_d, U, J_0 \) and \( J_1 \), are positive, and \( \varepsilon_d \) is assumed to take values in \( \frac{3}{2} J_0 < \varepsilon_d < \frac{5}{2} J_0 + U \). 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 \( N_h = |D| \) with \( 0 < N \leq |D| \) is \( \varepsilon_0 = -\varepsilon_d |D| - \frac{3}{2} J_0 N \), which is attained by the Zhang–Rice singlet states in \( \mathbf{H}^{N_h}_{ZRS} \).

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

Let us examine each term in \( H_0 \). The eigenvalue of the first sum in \( H_0 \) is \( -\varepsilon_d N_h^d \) for the states in \( \mathbf{H}_{N_h^d}^{N_h} \). The lowest eigenvalue for the second sum is zero which is attained by the states without doubly occupied \( d \)-states. The eigenvalues of \( J_0 S_x^a \cdot S_x^d \) are \( -\frac{3}{2} J_0, 0 \) and \( \frac{1}{2} J_0 \). We have eigenvalue \( -\frac{3}{2} J_0 \) 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 $E(|D|) = \epsilon_0$, which is attained by the states in $H_{\text{ZRS}}^{N_d} \subset H_{\Phi_1}$. In the case $0 \leq N^d < |D|$, noting that there are $N^d = |D| + N - N^d$ holes on the O-sites, we have

$$E(N^d) = -\epsilon_d N^d - \frac{1}{2} J_0 \min\{N^d_p, N^d_p\}$$

$$> \epsilon_0 + \frac{1}{2} J_0 \left\{ N^d_p - \min\{N^d_p, N^d_p\} \right\}$$

$$\geq \epsilon_0. \quad (5.9)$$

Here the second line follows from the assumptions $0 < \frac{3}{4} J_0 < \epsilon_d$ and $N^d < |D|$ (or $N < N^d$), and the third line follows from $N^d_p \geq \min\{N^d_p, N^d_p\}$. In the case $|D| < N^d \leq |D| + N$, noting that there are, at least, $(N^d - |D|)$ doubly occupied $d$-states, we have

$$E(N^d) = -\epsilon_d N^d + U (N^d - |D|) - \frac{1}{2} J_0 N^d$$

$$= \epsilon_0 + \left( \frac{1}{2} J_0 + U - \epsilon_d \right) (N^d - |D|)$$

$$\geq \epsilon_0. \quad (5.10)$$

Here the final inequality follows from the assumptions $\epsilon_d < \frac{3}{4} J_0 + U$ and $|D| < N^d$. As a result, we have $E(N^d) > \epsilon_0$ for $N^d = |D|$, which proves the claim.

We have shown that the lowest-energy states of $H_0$ are the Zhang–Rice singlet states in $H_{\text{ZRS}}^{N_d}$. In the following, we shall show that $H_1$ is positive semi-definite and $\Phi_0$ in $H_{\text{ZRS}}^{N_d}$ is its zero energy state. This implies $H = H_0 + H_1 \geq \epsilon_0$ and $H \Phi_0 = \epsilon_0 \Phi_0$. We thus conclude that $\Phi_0$ is a ground state of $H$.

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

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

with

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

$$K_{x,2}^{1} = \frac{1}{\sqrt{2}} (b_{x,\uparrow}^\dagger a_{x,\downarrow} d_{x,\downarrow} + b_{x,\downarrow}^\dagger a_{x,\uparrow} d_{x,\downarrow} - b_{x,\downarrow}^\dagger a_{x,\downarrow} d_{x,\downarrow} - b_{x,\downarrow}^\dagger a_{x,\downarrow} d_{x,\downarrow}). \quad (5.13)$$

$$K_{x,3}^{1} = \frac{1}{\sqrt{2}} (b_{x,\uparrow}^\dagger a_{x,\uparrow} d_{x,\downarrow} - b_{x,\uparrow}^\dagger a_{x,\downarrow} d_{x,\downarrow} - b_{x,\downarrow}^\dagger a_{x,\downarrow} d_{x,\downarrow} - b_{x,\downarrow}^\dagger a_{x,\downarrow} d_{x,\downarrow}). \quad (5.14)$$

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

and

$$K_{x,1}^{2} = a_{x,\uparrow} b_{x,\downarrow} d_{x,\downarrow}, \quad (5.16)$$

$$K_{x,2}^{2} = \frac{1}{\sqrt{2}} (a_{x,\uparrow} b_{x,\downarrow} d_{x,\downarrow} + a_{x,\uparrow} b_{x,\downarrow} d_{x,\downarrow} - a_{x,\downarrow} b_{x,\downarrow} d_{x,\downarrow} - a_{x,\downarrow} b_{x,\downarrow} d_{x,\downarrow}). \quad (5.17)$$

$$K_{x,3}^{2} = \frac{1}{\sqrt{2}} (a_{x,\uparrow} b_{x,\downarrow} d_{x,\downarrow} - a_{x,\downarrow} b_{x,\downarrow} d_{x,\downarrow} - a_{x,\downarrow} b_{x,\downarrow} d_{x,\downarrow} - a_{x,\downarrow} b_{x,\downarrow} d_{x,\downarrow}). \quad (5.18)$$

$$K_{x,4}^{2} = -a_{x,\downarrow} b_{x,\downarrow} d_{x,\downarrow}. \quad (5.19)$$

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 $\Phi$ of $H_1$, if it exists, must satisfy $(K_{x,l}^{m})^\dagger \Phi = 0$ and $K_{x,l}^{m} \Phi = 0$ for all $m = 1, 2, l = 1, \ldots, 4$ and $x \in D$. We shall prove that $\Phi_0$ indeed satisfies these conditions.
We start with the case of \( m = 1 \) and \( l = 1 \). By using the commutation relation (4.6), we have
\[
(K_{x,1}^\dagger)^\dagger \zeta = d_{x,1}^\dagger a_{x,1}^\dagger b_{x,\gamma} \zeta = d_{x,1}^\dagger (b_{x,\gamma})^2 + \zeta d_{x,1}^\dagger a_{x,1}^\dagger b_{x,\gamma} = \zeta (K_{x,1})^\dagger.
\] (5.20)
This together with \((K_{x,1}^\dagger)^\dagger \psi_\zeta = 0\), which follows from \((a_{x,\sigma})^2 = (d_{x,\sigma})^2 = 0\), leads to
\[
(K_{x,1}^\dagger)^\dagger (\zeta)_{\Phi_0} = (\zeta)_{\Phi_0} (K_{x,1}^\dagger)^\dagger \psi_0 = 0.
\] (5.21)
From \(a_{x,\dagger} d_{x,\dagger} \psi_\zeta = -d_{x,\dagger} a_{x,\dagger}^\dagger a_{x,\dagger} + a_{x,\dagger} d_{x,\dagger} a_{x,\dagger}^\dagger\), we immediately obtain
\[
K_{x,1}^\dagger (\zeta)_{\Phi_0} = b_{x,\dagger} (\zeta)_{\Phi_0} a_{x,\dagger} d_{x,\dagger} \psi_0 = 0.
\] (5.22)
We thus conclude \((K_{x,1}^\dagger)^\dagger \Phi_p = K_{x,1}^\dagger \Phi_p = 0\) 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
\[
S^- = \sum_{x \in D} (a_{x,\dagger}^\dagger a_{x,\dagger} + d_{x,\dagger}^\dagger d_{x,\dagger}),
\] (5.23)
\[
S^+ = \sum_{x \in D} (a_{x,\dagger}^\dagger a_{x,\dagger} + d_{x,\dagger}^\dagger d_{x,\dagger}).
\] (5.24)
From the results for \( l = 1 \) we have \( S^+ (K_{x,1}^\dagger)^\dagger \Phi_p = 0 \). It is easy to see that \( S^+ (K_{x,1}^\dagger)^\dagger \Phi_p = \sqrt{3} (K_{x,1}^\dagger)^\dagger + (K_{x,1}^\dagger)^\dagger S^+ \Phi_p = 2 (K_{x,1})^\dagger + (K_{x,1}^\dagger)^\dagger S^+ \Phi_p = \sqrt{3} (K_{x,1})^\dagger + (K_{x,1}^\dagger)^\dagger S^+. \) Substituting the first relation into \( S^+ (K_{x,1}^\dagger)^\dagger \Phi_p = 0 \) and noting \( S^+ \Phi_p = 0 \), we find \((K_{x,1}^\dagger)^\dagger \Phi_p = 0 \). Proceeding in the same way, we have \((K_{x,1}^\dagger)^\dagger \Phi_p = 0 \). By using \( S^- (K_{x,1}^\dagger)^\dagger \Phi_p = 0 \), we similarly obtain \( K_{x,1}^\dagger \Phi_p = 0 \) for \( l = 2, 3, 4 \).

Proceeding in the same way, we obtain \((K_{x,2}^\dagger)^\dagger \Phi = K_{x,2}^\dagger \Phi = 0 \) 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 \( \mu_\delta \)

In this section we estimate a lower bound for \( \mu_\delta \). We will show later that
\[
\frac{\langle \Phi_p, a_{x,\sigma}^\dagger a_{x,\sigma} b_{x,\sigma}^\dagger b_{x,\sigma} \Phi_p \rangle}{\langle \Phi_p, b_{x,\sigma}^\dagger b_{x,\sigma} \Phi_p \rangle} \geq \gamma_{\Lambda, N},
\] (6.1)
with \( \gamma_{\Lambda, N} = \frac{9N - 8|D|}{20N - 9|D|} \), for \( N \geq (8|D|)/9 \). It follows from this inequality that
\[
\mu_{\Lambda, N} \geq \sqrt{\gamma_{\Lambda, N} N_p + \frac{1}{2|D|^2} \sum_{x,\sigma} \langle \Phi_p, b_{x,\sigma}^\dagger b_{x,\sigma} \Phi_p \rangle \langle \Phi_p, \Phi_p \rangle}.
\] (6.2)
Here, we have that
\[
\sum_{x \in D} \sum_{\sigma = \uparrow, \downarrow} \langle \Phi_p, b_{x,\sigma}^\dagger b_{x,\sigma} \Phi_p \rangle = \sum_{k \in \Gamma} \sum_{\sigma = \uparrow, \downarrow} \langle \Phi_p, \epsilon_{\delta}(k) \hat{a}_{k,\sigma}^\dagger \hat{a}_{k,\sigma} \Phi_p \rangle.
\] (6.3)
and it is easy to find that the right-hand side is bounded from below by

\[ 2 \sum_{l=1}^{N/2} \epsilon_b(k(l)) \langle \Phi_p, \Phi_p \rangle, \]  

(6.4)

where \( \epsilon_b(k(1)) \leq \epsilon_b(k(2)) \ldots \leq \epsilon_b(k(|D|)) \) 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 \( \Phi_p \), it suffices to consider the case of \( \sigma = \uparrow \). By the translation symmetry, we can also assume \( x \in D_e \) without loss of generality. We first show that the left-hand side of (6.1) with \( \sigma = \uparrow \) is rewritten as

\[ \begin{align*}
\frac{\sum_{S \subset D_e : x \notin S} W_x(S)}{2 \sum_{S \subset D_e : x \notin S} W_x(S)} &= \frac{\sum_{S \subset D_e : x \notin S} W_x(S)}{2 \sum_{S \subset D_e : x \notin S} W_x(S) + \sum_{S \subset D_e : x \in S} W_x(S)} \tag{6.5}
\end{align*} \]

with the nonnegative weights

\[ \begin{align*}
W_x(S) &= \left( \prod_{z \in S} \tilde{\phi}_z \right) \Psi_0, b_{x,\downarrow}^\dagger b_{x,\downarrow} \left( \prod_{z \in S} \tilde{\phi}_z \right) \Psi_0 \tag{6.6}
\end{align*} \]

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

\[ \xi = \sum z \in D_e b_{z,\downarrow} a_{z,\uparrow} + \sum z \in D_e b_{z,\downarrow} a_{z,\uparrow} = \sum z \in D_e (b_{z,\downarrow} a_{z,\uparrow} + a_{z,\uparrow} b_{z,\uparrow}) = \sum \tilde{\phi}_z. \]  

(6.7)

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

\[ \begin{align*}
\Phi_p &= N_p! \sum_{S \subset D_e : |S| = N_p} \left( \prod_{z \in S} \tilde{\phi}_z \right) \Psi_0. \tag{6.8}
\end{align*} \]

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

\[ \left( \prod_{z \in S} \tilde{\phi}_z \right) \Psi_0, a_{x,\downarrow}^\dagger a_{x,\uparrow} b_{x,\downarrow}^\dagger b_{x,\downarrow} \left( \prod_{z \in S} \tilde{\phi}_z \right) \Psi_0 \right) = 0 \quad \text{for} \quad S' \neq S, \tag{6.9} \]

we have that

\[ \begin{align*}
\left\langle \Phi_p, a_{x,\downarrow}^\dagger a_{x,\uparrow} b_{x,\downarrow}^\dagger b_{x,\downarrow} \Psi_0 \rightangle &= \left( N_p! \right)^2 \sum_{S \subset D_e : x \notin S} \left( \prod_{z \in S} \tilde{\phi}_z \right) \Psi_0, a_{x,\downarrow}^\dagger a_{x,\uparrow} b_{x,\downarrow}^\dagger b_{x,\downarrow} \left( \prod_{z \in S} \tilde{\phi}_z \right) \Psi_0 \right) \tag{6.10}
\end{align*} \]

To get the second line we used

\[ \begin{align*}
\left\langle \psi_x^\dagger \Phi_0, a_{x,\downarrow}^\dagger a_{x,\uparrow} \psi_x^\dagger \Phi_0 \right\rangle = 1 = \left\langle \psi_x^\dagger \Phi_0, \psi_x^\dagger \Phi_0 \right\rangle \tag{6.11}
\end{align*} \]

Likewise, we have that

\[ \begin{align*}
\left\langle \Phi_p, b_{x,\downarrow}^\dagger b_{x,\downarrow} \Psi_0 \right\rangle &= \left( N_p! \right)^2 \sum_{S \subset D_e : x \notin S} W_x(S), \tag{6.12}
\end{align*} \]

which together with (6.10) leads to (6.5). Before proceeding, we need to introduce some notation. For each \( z \in D_e \), define

\[ D_{a,z} = \{ y ||y - z| = 1, y \in D_b \}, \]  

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
\[
W_x(S' \cup \{y\}) = \frac{1}{2} W_x(S),
\]
(6.13) since $a^i_{x,\sigma}$ with $|y' - y| \leq 1$ commutes with $b^i_{x,\downarrow} b_{x,\downarrow} \prod_{z \in S} \phi_z$ and thus
\[
\langle \Psi_0, \phi^i_{x,\uparrow} \phi_y \Psi_0 \rangle = \frac{1}{4} \sum_{y' \in D_x} \sum_{\sigma = \uparrow, \downarrow} \langle \Psi_0, a^i_{x,\sigma} a^j_{y',\sigma} a^j_{y,\sigma} a^j_{y,\sigma} \Psi_0 \rangle = \frac{1}{4} \langle \Psi_0, \Psi_0 \rangle.
\]
(6.14)
(Recall (6.11).) We denote by $D_x(N_p, l)$ the collection of subsets of $S$ 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
\[
\sum_{S \subset D_e} W_x(S) = \sum_{l=0}^{N_p} \sum_{S \in D_x(N_p, l)} W_x(S) \geq \sum_{l=1}^{N_p} \sum_{S \in D_x(N_p, l)} W_x(S).
\]
(6.15)
Now fix $l \geq 1$. Noting that there are $l$ isolated sites in $S \in D_x(N_p, l)$, we find
\[
\sum_{S \in D_x(N_p, l)} W_x(S) = \frac{1}{l} \sum_{S \in D_x(N_p, l)} \sum_{y \in D_x} W_x(S) \chi[y \in D_x(S)]
\]
\[
= \frac{1}{l} \sum_{S \in D_x(N_p, l)} \sum_{y \in D_x} W_x(S) \chi[y \in D_x(S)] \chi[S' = S \setminus \{y\}]
\]
\[
= \frac{1}{2l} \sum_{S' \in D_x(N_p-1, l-1)} \sum_{S \in D_x(N_p, l)} W_x(S') \sum_{y \in D_x} \chi[y \in D_x(S)] \chi[S = S' \cup \{y\}]
\]
\[
\geq \frac{1}{2N_p} \left( \frac{|D|}{2} - 9N_p \right) \sum_{S' \in D_x(N_p-1, l-1)} W_x(S').
\]
(6.16)
To get the second line, note that removing an isolated point in $S \in D_x(N_p, l)$ yields an element in $D_x(N_p - 1, l - 1)$. 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 $S' \in D_x(N_p - 1, l - 1)$, there exist at least $|D_x| - 9N_p$ sites, $y$, such that $y$ is an isolated point in $S' \cup \{y\}$, and $S' \cup \{y\}$ becomes an element in $D_x(N_p, l)$. Note that $|D_x| - 9N_p$ is a positive number by the assumption. Then, by using $l \leq N_p$, we get the last inequality.

From (6.15) and (6.16) we get
\[
\sum_{S \subset D_e} W_x(S) \geq \frac{1}{2N_p} \left( \frac{|D|}{2} - 9N_p \right) \sum_{l=0}^{N_p-1} \sum_{S \in D_x(N_p-1, l)} W_x(S).
\]
(6.17)
Here, for $x \notin S$, we have
\[
W_x(S \cup \{x\}) = \left( \prod_{z \in S} \phi_z \right) \Psi_0, a^i_{x,\downarrow} \phi_z b^j_{x,\uparrow} b_{x,\downarrow} \left( \prod_{z \in S} \phi_z \right) \Psi_0
\]
\[
= \frac{1}{2} \left( \prod_{z \in S} \phi_z \right) \Psi_0, \left( 1 - b_{x,\downarrow} b_{x,\uparrow} \right) b^j_{x,\uparrow} b_{x,\downarrow} \left( \prod_{z \in S} \phi_z \right) \Psi_0
\]
\[
\leq \frac{1}{2} W_x(S).
\]
(6.18)
A d-wave pairing state in terms of the Zhang–Rice singlets

It follows from this inequality and (6.17) that

\[
\sum_{S \subset D, x \in S, |S| = N_p} W_x(S) \geq \frac{1}{N_p} \left( \frac{|D|}{2} - 9N_p \right) \sum_{l=0}^{N_p-1} \sum_{S \in D_l(N_p-1,l)} W_l(S \cup \{x\}) = \left( \frac{|D|}{2N_p} - 9 \right) \sum_{S \subset D, x \in S, |S| = N_p} W_x(S). \tag{6.19}
\]

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 \(|D| < N_h \leq 2|D|\), we have constructed a pairing state \(\Phi_p\) 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 \(\Phi_p\) 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 \(\Phi_p\) 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 \(\Phi_p\) 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

\[
H_2 = J_2 \sum_{x,y \in D, |x-y|=1} S^d_{x \uparrow} \cdot S^d_{y \uparrow}, \tag{7.1}
\]

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 ODLRO 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 $\Phi_p$ is non-vanishing when the number of holes, $N_h = |D| + N$, satisfies $N = |D| - 2L_1L_2$ with some integer $0 \leq l_2 \leq (L_2 - 2)/2$. A similar argument will show that $\Phi_p$ is non-vanishing for $2L_1 \leq N \leq |D|$. It is easy to see that the collection of the states on the right-hand side of (6.8) is orthogonal. So $\Phi_p$ is non-vanishing if one of those terms is non-vanishing. We shall show that this is the case. Let

$$A_1 = \{ x = (x_1, x_2) \mid 1 \leq x_1 \leq L_1, 1 \leq x_2 \leq 2L_2, \text{ x_2 is odd} \}$$  \hspace{1cm} (A.1)

and

$$A_2 = \{ x = (x_1, x_2) \mid 1 \leq x_1 \leq L_1, 1 \leq x_2 \leq 2L_2, \text{ x_2 is even} \}. \hspace{1cm} (A.2)$$

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

$$\prod_{z \in S_0} (a_{z,\downarrow}b_{z,\uparrow} + b_{z,\downarrow}a_{z,\uparrow}) \Psi_0 = \sum_T \left( \prod_{z \in T} a_{z,\downarrow}b_{z,\uparrow} \right) \left( \prod_{z \in S_0 \setminus T} b_{z,\downarrow}a_{z,\uparrow} \right) \Psi_0. \hspace{1cm} (A.3)$$

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

$$\left( \prod_{z \in A_1} a_{z,\downarrow} \right) \left( \prod_{z \in A_2} a_{z,\uparrow} \right) \Psi_0, \left( \prod_{z \in S_1} a_{z,\downarrow}b_{z,\uparrow} \right) \left( \prod_{z \in S_0 \setminus S_1} b_{z,\downarrow}a_{z,\uparrow} \right) \Psi_0$$

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 $\Phi_p$ is non-vanishing.

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