Iron-Based Superconductors As Odd Parity Superconductors

Jiangping Hu$^{1,2}$

$^1$Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China
$^2$Department of Physics, Purdue University, West Lafayette, Indiana 47907, USA

Parity is a fundamental quantum number to classify a state of matter. Materials rarely possess ground states with odd parity. We show that the superconducting state in iron-based superconductors is classified as an odd parity s-wave spin-singlet pairing state in a single trilayer FeAs/Se, the building block of the materials. In a low energy effective model constructed on the Fe square bipartite lattice, the superconducting order parameter in this state is a combination of a s-wave normal pairing between two sublattices and a s-wave $\eta$-pairing within the sublattices. Parity conservation was violated in proposed superconducting states in the past. The state has a fingerprint with a real space sign inversion between the top and bottom As/Se layers. The results demonstrate iron-based superconductors being a new quantum state of matter and suggest that the measurement of the odd parity can establish fundamental principles related to high temperature superconducting mechanism.

I. INTRODUCTION

Symmetry plays the central role in the search for beauty in physics. It controls the structure of matter and allows us to simplify a complicated problem. Gauge principle is a fundamental principle in physics. Models formulated in different gauge settings are equivalent. Symmetry and gauge principles together make the foundations of modern physics to solve complicated problems.

The recently discovered high temperature superconductors (high-$T_c$), iron-based superconductors$^{[1-3]}$, are layered materials with complicated electronic structures. The complexity causes a major difficulty in understanding pairing symmetry which arguably is the most important property and clue to determine pairing mechanism$^{[4,5]}$.

In a strongly correlated electron system, major physics is determined locally in real space. Important properties, such as pairing symmetry in a superconducting state, are expected to be robust against small variation of Fermi surfaces in reciprocal space. Although superconducting mechanism related to high temperature superconductors (high $T_c$) is still unsettled, the robust d-wave pairing symmetry in cuprates$^{[6]}$ can be understood under this principle.

Is this principle still held for iron-based superconductors? Namely, do all iron-based superconductors possess one universal pairing state? Unlike cuprates, the answer to this question is highly controversial because different theoretical approaches have provided different answers and no universal state has been identified$^{[5]}$. Nevertheless, as local electronic structures in all families of iron-based superconductors are almost identical and phase diagrams are smooth against doping$^{[3,5]}$, it is hard to argue that the materials can approach many different superconducting ground states.

In conventional wisdom, there are several obvious requirements regarding electron pairing in superconducting states. First, pairing symmetry is known to be classified according to lattice symmetry. Second, in a uniform superconducting state, the total momentum for the Cooper pairs (modulo a reciprocal lattice vector) must be vanished. Finally, for a central symmetric lattice with a space inversion center, the parity of superconducting order parameters normally is even for a spin-singlet pairing and odd for spin-triplet pairing$^{[7]}$. These requirements are easily fulfilled in a system with a simple electronic structure, such as cuprates. However, for iron-based superconductors, they are highly non-trivial.

The unit cell in iron-based superconductors is intrinsically a 2-Fe unit cell while for simplicity, most theoretical models are effectively constructed based on an 1-Fe unit cell$^{[8-13]}$. Obviously, these effective models have different lattice symmetry from the models defined on the original lattice. The difference may cause serious problems. For example, in the effective models, the pairings have been limited to two electrons with opposite momentum $(\vec{k}, -\vec{k})$, which we call it normal pairing in this paper, where $\vec{k}$ is momentum defined with respect to the 1-Fe unit cell in an iron square lattice. The momentum vector $Q = (\pi, \pi)$ is a reciprocal lattice vector in the original lattice with a 2-Fe unit cell. Thus, the pairings $(\vec{k}, -\vec{k}+Q)$, in principle, are also allowed according to the above second requirements. We will refer this pairing channel as an extended $\eta$-pairing$^{[14,15]}$ and simply call it $\eta$-pairing in this paper. The possible existence of $\eta$-pairing was discussed in simplified models$^{[16-18]}$. As order parameters are classified differently under different symmetry groups, we need to understand these orders under the original lattice symmetry. Otherwise, conservation laws could be violated.

In this paper, we show that the superconducting state in iron-based superconductors is a new state of matter which is classified as an odd parity s-wave spin-singlet pairing state in a single trilayer FeAs/Se, the building block of the materials. The superconducting states that were proposed in the past based on the effective d-orbital models of an iron square lattice are not parity eigenstates. Parity conservation was violated. We show that the su-
perconducting state which conserves parity includes both normal pairing between two sublattices of the iron square lattice and $\eta$-pairing within each sublattices. The states have a fingerprint with a real space sign inversion between the top and bottom As/Se layers. Our derivation is based on general symmetry and gauge requirements on the effective models for iron-based superconductors.

In the following, we first provide a complete symmetry analysis for pairing symmetries in iron-based superconductors. While the pairing symmetries can be classified according to $D_{2d}$ point group at iron sites or $C_{4v}$ point group at the center of an iron square, there are two types of pairing symmetries for a spin-singlet pairing state because of the intrinsic 2-Fe unit cell. They are distinguished from each other by opposite parity numbers. Second, we discuss the hidden symmetry properties of the effective models under the original lattice symmetry. We show that the effective hopping terms between two sublattices and within each sublattice have different symmetry characters. Third, we discuss a general gauge principle related to the definition of pairing symmetries and conclude that parity conservation was violated in the past. We provide the meanfield Hamiltonian in the new superconducting state and show that it can provide a unified description of all families of iron-based superconductors including both iron-pnictides and iron-chalcogenides. Fourth, we discuss the smoking-gun experiments that can reveal the parity of the superconducting state. Finally, we discuss the fundamental impact on high $T_c$ superconducting mechanism if it is confirmed.

Before we start the main content, we first make clear about a gauge setting for the effective models that were constructed based on all five iron $d$-orbitals. In those effective models with an 1-Fe unit cell, a new gauge setting is taken, which effectively changes the momentum $\vec{k}$ to $\vec{k} + Q$ for $d_{xz}$ and $d_{yz}$ orbitals. In the following, without further clarification, the momentum $\vec{k}$ used in the definition of our normal pairing ($\vec{k}, -\vec{k}$) and $\eta$-pairing ($\vec{k}, -\vec{k} + Q$) is the same momentum used in those papers rather than the momentum in a natural gauge setting.

II. SYMMETRY OF A SINGLE FE-AS(SE) TRILAYER

Iron-based superconductors are layered materials. The essential electronic physics is controlled by a single trilayer Fe-As(Se) structure, the building block of the superconductors. Although the coupling along $c$-axis between the building blocks has many interesting effects, the superconducting mechanism and the fundamental properties of the superconducting states, such as pairing symmetries, are expected to be solely determined within the single building block. The observation of superconductivity in a single FeSe layer grown by MBE has further justified this two-dimensional nature. Therefore, we first focus on the study of a single Fe-As(Se) trilayer structure.

We start our analysis by understanding the lattice symmetry. As shown in Fig. 1, the structure has an inversion center, the origin, located at the center of each Fe-Fe link. The unit cell with the origin at the center is marked by the shadowed area, which includes two irons and two As/Se atoms. We denote $T$ as the translation group with respect to the unit cell. The symmetry group, thus, is described by a non-symmorphic space group $G = P4/mmm$. The quotient group $G/T$ is specified by 16 symmetry operations that include a space inversion $I$. It is easy to check that these operations can be specified equivalently as $C_{4v} \oplus IC_{4v}$ or $D_{2d} \oplus ID_{2d}$, where $C_{4v}$ is the point group with respect to the point at the middle of an iron square and $D_{2d}$ is the point group defined at an iron site. It is important to note that both $C_{4v}$ and $D_{2d}$ are not defined with respect to the inversion center. Therefore, some symmetry operations in $C_{4v}$ or $D_{2d}$ are non-symmorphic. For example, the $C_4$ rotation operation in $C_{4v}$ is equivalent to $(C_4, i_2)$, which represents $C_4$, an rotation $\frac{\pi}{2}$ along z-axis at the inversion center, followed by a translation operation $t_2$ that translates $(\frac{1}{2}, \frac{1}{2}, 0)$ in the coordinate of an iron square lattice, a half of unit lattice cell along X direction labeled in Fig.1.

In summary, the full symmetry group can be written as

$$G/T = Z_2 \otimes D_{2d} = Z_2 \otimes C_{4v} \quad (1)$$

where $Z_2 = (E, I)$. The group is a direct product of two subgroups which are defined with respect to different operation centers. $I$ commutates with all symmetry operations in $D_{2d}$ or $C_{4v}$ in a sense that operations are considered to be identical if they only differ by a lattice transition with respect to the 2-Fe unit cell.

III. PARITY AND PAIRING SYMMETRY CLASSIFICATION

The pairing symmetry of a translation invariant superconducting state is classified by the IRs of $G/T$. If we ignore spin-orbital coupling, the ground state is expected to be a parity eigenstate. Since spin-singlet pairing is overwhelmingly supported experimentally in iron-based superconductors, we focus on spin-singlet pairing states.

Conventionally, for a spin-singlet pairing state, the parity is even. However, due to the unit cell doubling, the parity operation here essentially takes mapping between two sublattices, A and B, in the iron square lattice as shown in Fig.1. Therefore there is no parity constraint for the pairing within each sublattice governed by $D_{2d}$. Thus, for each irreducible representation of $D_{2d}$, there are two different pairing states with opposite parities. The IRs of $G/T$ are direct product of the IRs of two subgroups.
where \( \hat{C}_4 \) is the \( \pi/2 \) rotation operation in \( C_{4v} \). For one-dimensional IRs in \( D_{2d} \), the above equation reduces to \( \hat{S}_4 = i\hat{C}_4 \). Therefore, for parity even pairing, namely normal pairing, there is no difference whether states are classified according to \( D_{2d} \) or \( C_{4v} \) since \( S_4 = \hat{C}_4 \). Namely, a normal pairing state has the same IRs with respect to both \( C_{4v} \) and \( D_{2d} \). For parity odd \( \eta \)-pairing, \( \hat{S}_4 = -\hat{C}_4 \), which implies that an \( s \)-wave state classified by \( A \)-IRs in \( D_{2d} \) must become an \( d \)-wave state classified by \( B \)-IRs in \( C_{4v} \). For example, an \( \eta \)-pairing \( A_1 \) \( s \)-wave state classified in \( D_{2d} \) belongs to the \( B_2 \) \( d \)-wave in \( C_{4v} \). Therefore, for an \( \eta \)-pairing parity odd state, the name of the state depends on how it is classified. For above example, one can either name the \( \eta \)-pairing state as \( B_{2u} \) \( d \)-wave or \( A_{1u} \) \( s \)-wave, depending on the classification point groups \( C_{4v} \) or \( D_{2d} \) respectively.

An odd parity superconducting state must have a sign change between the top and bottom \( \text{As/Se} \) layers. However, this information is hidden in an effective model with only \( d \)-orbitals constructed on an iron square lattice. From above symmetry analysis, we can track the parity information simply using \( \hat{\sigma}_h \). Although \( \hat{\sigma}_h \) is not a symmetry operation for a single \( \text{Fe-As(Se)} \) trilayer, the \( \eta \)-pairing state can be viewed as a state with an internal negative iso-spin defined by \( \hat{\sigma}_h \). For any normal pairing, \( \hat{\Delta}^a \) and \( \eta \)-pairing \( \hat{\Delta}^\eta \) order parameters which belong to one-dimensional IRs of \( D_{2d} \), we have

\[
\hat{\sigma}_h \hat{\Delta}^a \hat{\sigma}_h = \Delta^a \quad (4) \\
\hat{\sigma}_h \hat{\Delta}^\eta \hat{\sigma}_h = -\Delta^\eta \quad (5)
\]

We can extend above discussion for order parameters in a bulk material. There are two different lattice structures along \( c \)-axis in iron-based superconductors, 11-type (which includes 111(\( NaFeAs \)) and 1111(\( LaOFsAs \)) structures) and 122-type where the 11-type is translation invariant along \( c \)-axis while the 122-type is not.

For the 11-type, we can simply extend above analysis to the nearest-neighbour (NN) inter-layer pairing. For an even parity order parameters, we can have two possible terms: \( (\vec{k}, -\vec{k}) \) pairing which is proportional to \( \cos(k_z) \) and the \( \eta \)-pairing \( (\vec{k}, -\vec{k} + Q) \) which is proportional to \( isin(k_z) \). For an odd parity order parameters, the two possible terms become \( (\vec{k}, -\vec{k}) \) pairing which is proportional to \( isin(k_z) \) and the \( \eta \)-pairing \( (\vec{k}, -\vec{k} + Q) \) which is proportional to \( \cos(k_z) \). Both terms can be in a same irreducible representations of \( D_{2d} \).

For the 122-type, the situation is rather different because the 122 structure has a symmmorphic space group \( I4/mmm \) with a point group \( D_{4h} \), centered in the middle of two NN \( \text{Fe-As(Se)} \) layers. The translation symmetry is specified by \( (1,1,0), (1,0,1), \) and \( (0,1,1) \). The
space inversion and $\bar{\sigma}_h$ have identical characters in any one-dimensional IRs. A state with odd parity which belongs to one-dimensional IRs must have node lines on Fermi surfaces when $k_z = 0$. Therefore, we are only allowed to construct even parity states. For the intra-layer pairing, there are two different even parity order parameters: one is constructed by $(\vec{k}, -\vec{k})$ pairing and the other is constructed by $(\vec{k}, -\vec{k} + Q_3)$ pairing where $Q_3 = (\pi, \pi, \pi)$, namely the $\eta$-pairing. The difference between these two order parameters is that the latter breaks $(1, 0, 1)$ and $(0, 1, 1)$ translation symmetry. Now if we consider the NN inter-layer pairing, we can have two terms which are parity even and keep the translation symmetry: the normal pairing $(\vec{k}, -\vec{k})$ which is proportional to $\cos(k_z)$ and $(\vec{k}, -\vec{k} + Q) \eta$-pairing which is proportional to $isin(k_z)$. Here we refer $Q = (\pi, \pi, 0)$. For the $(\vec{k}, -\vec{k} + Q_3)$ $\eta$-pairing, there are also two terms in the NN inter-layer pairing: the $\eta$-pairing $(\vec{k}, -\vec{k} + Q_3)$ proportional to $\cos(k_z)$ and $(\vec{k}, -\vec{k} + Q)$ pairing proportional to $\cos(k_z)$. Therefore, if the inter-layer pairing is included, the superconducting state generally breaks translation symmetry of the iron-square lattice.

IV. EFFECTIVE HAMILTONIAN AND HIDDEN SYMMETRY

The above symmetry analysis is based on the original lattice symmetry. As we mentioned above, an effective model based on $d$-orbitals appears to have a different symmetry. In the past studies, we treated the model in 1-Fe unit cell with a $D_{4h}$ point group at iron sites. The treatment, in general, violated the fundamental spirit of symmetry principle and might have resulted in fundamental errors. To pay a full respect to symmetry principle, we must understand the symmetry properties of the effective model under the original lattice symmetry.

We consider a general Hamiltonian in a single trilayer $Fe - As(Se)$ structure coordinated by Fe and As(Se) atoms,

$$H = \hat{H}_{dd} + \hat{H}_{dp} + \hat{H}_{pp} + H_I \tag{6}$$

where $\hat{H}_{dd}$, $\hat{H}_{dp}$ and $\hat{H}_{pp}$ describe the direct hopping between two $d$-orbitals, the $d-p$ hybridization between Fe and As(Se) and the direct hopping between two $p$-orbitals respectively. $H_I$ describes any standard interactions. Here we do not need to specify the detailed parameters. This Hamiltonian has a full symmetry defined by the non-symmorphic space group.

An effective Hamiltonian is obtained by integrating out $p$-orbitals, which can be written as

$$\hat{H}_{eff} = \hat{H}_{dd,eff} + \hat{H}_{I,eff} \tag{7}.$$ 

The effective band structure can be written as $\hat{H}_{dd,eff} = \hat{H}_{dd} + \hat{H}_{dpd}$, where $\hat{H}_{dpd}$ is the effective hopping induced through $d-p$ hybridization. $\hat{H}_{dd,eff}$ has been obtained by many groups[8, 10, 24, 25]. The major effective hopping terms in $\hat{H}_{dpd}$ can be divided into two parts $\hat{H}_{dpd,NN}$, which describes NN hopping and $\hat{H}_{dpd,NNN}$, which describes NNN hopping in the iron square lattice. If one carefully checks the effective hopping parameters for $t_{2g}$ orbitals in $\hat{H}_{dpd,NN}$, one finds that they have opposite sign to what we normally expect in a natural gauge setting as shown in fig. 2(a, b), where $d_{xy}$ orbital is illustrated as an example. We see that the hopping parameter $t_{dd}$ must be negative. However the effective hopping parameter $t_{dpd}$ is positive and even larger than $|t_{dd}|$ in [8, 10, 24, 25]. In a tetragonal lattice, $t_{dpd}$ can only be generated through $d_{xy} - p_z$ hybridization. A positive value of $t_{dpd}$ suggests that virtual hopping which generates $t_{dpd}$ must go through an unoccupied $p_z$ state. As shown in fig. 2(a, b), a $d_{xy}$ equally couples to $p_z$ orbitals of top and bottom As atoms. A high energy $p_z$ state must be an anti-bonding $p_z$ state between NN As atoms. This analysis is held for all $t_{2g}$ orbitals which play the dominating role in low energy physics. It is also easy to check that the effective NNN hoppings between $t_{2g}$ orbitals are dominated through an occupied $p$ states, which is primarily a bonding state of $p$-orbitals. Therefore, the NN effective hoppings are generated through $d-p_a$ hybridization, where $p_a$ represents an anti-bonding $p$-orbital states and the NNN effective hoppings are generated through $d-p_b$ hybridization where $p_b$ is the bonding $p$-state.

FIG. 2: (Color online) The nearest neighbor hopping parameters for intra-$d_{xy}$-orbital are shown in (a) and (b). $t_{dd}$ is the amplitude of the direct hopping of $d_{xy}$ orbital while $t_{dpd}$ is the amplitude of the indirect hopping through $p_z$ orbital of As/Se atom. The reason of sign change for $t_{dpd}$ between (a) and (b) is that the $p_z$ orbitals in top layer and bottom layer form occupied bonding states in (a) and empty anti-bonding states in (b). The difference is illustrated by filled and empty $p_z$ orbitals in (a) and (b). (c) and (d) shows the local $p - d$ s-wave pairing pattern and the gauge transformation between them.
The above microscopic understanding is not surprising. In fact, it is known in LDA calculations that p-orbitals in As/Se are not fully occupied and there are significant overlappings between p-orbitals on bottom and top As/Se layers. Moreover, since $H_{dpd,NN}$ and $H_{dpd,NNN}$ primarily affect hole pockets around $\Gamma$ and electron pockets at $M$ separately, we can check the distribution of anti-bonding p states and bonding p states in band structure to further confirm the analysis. In fig.3(a), we plot the band structure of FeSe and the distribution of p orbitals. The $p_z$ orbitals of Se are mainly at $+1.5$ eV at $\Gamma$ and $-3$ eV at $M$. By analyzing the bands at $\Gamma$ and $M$ as shown in Fig.3(b) and (c), we confirm that the $p_z$ orbitals of Se at $\Gamma$ and $M$ belong to anti-bonding and bonding states separately.

Knowing the above hidden microscopic origins in a derivation of an effective Hamiltonian allows us to understand the symmetry characters of the effective Hamiltonian in the original lattice symmetry.

The $d - p_a$ hybridization is odd under $\hat{\sigma}_h$ while the $d - p_b$ hybridization is even under $\hat{\sigma}_h$. Thus, the NN hopping $\hat{H}_{dpd,NN}$ and NNN hopping $\hat{H}_{dpd,NNN}$ should be classified as odd and even under $\hat{\sigma}_h$ respectively. Namely,

\[
\begin{align*}
\hat{\sigma}_h \hat{H}_{dpd,NN} \hat{\sigma}_h &= -\hat{H}_{dpd,NN} \\
\hat{\sigma}_h \hat{H}_{dpd,NNN} \hat{\sigma}_h &= \hat{H}_{dpd,NNN}
\end{align*}
\]

(8)

The above hidden symmetry property is against the main assumption taken in many weak coupling approaches, which assume that the essential physics is driven by the interplay between hole pockets at $\Gamma$ and electron pockets at $M$. As indicated in fig.3(a), the interplay between the hole and electron pockets must be minimal because of their distinct microscopic origins.

V. GAUGE PRINCIPLE AND PARITY CONSERVATION

The symmetry difference in eq\(^{8}\) has fundamental impact on how to consider the parity of a superconducting state if superconducting pairing is driven by local d-p hybridization.

It has been shown that in a system where short range pairings in real space dominate, superconducting order parameters are momentum dependent and a gauge principle must be satisfied because the phases of superconducting order parameters can be exchanged with those of the local hopping parameters\[^{16, 28}\] by gauge transformations. As an example, a d-wave superconducting state in cuprates can be mapped to a s-wave superconducting state by a gauge mapping which changes the hopping terms from s-type symmetry to d-type symmetry\[^{29}\]. Therefore, only the combined symmetry of hopping terms and pairing orders associated to them is a gauge-independent symmetry character to classify superconducting states. Namely, the symmetry of a superconducting state is characterized by

\[
\text{Symmetry}_{sc} = [\hat{\Delta}_{\text{hopping}}][\hat{\Delta}]
\]

(9)

where $[\hat{\Delta}]$ indicates the symmetry of $\hat{\Delta}$. This gauge principle does not exist in a conventional BCS-type superconductor in which the information of pairing in real space is irrelevant.

Now we apply the gauge principle and let $\hat{\Delta}_{NN}$ and $\hat{\Delta}_{NNN}$ be superconducting order operators associated with $\hat{H}_{dpd,NN}$ and $\hat{H}_{dpd,NNN}$ respectively. In a superconducting state which belongs to a pure IR of the original lattice symmetry, we must have

\[
[\hat{\Delta}_{NN}][\hat{H}_{dpd,NN}] = [\hat{\Delta}_{NNN}][\hat{H}_{dpd,NNN}]
\]

(10)

If we consider a superconducting state which conserves
parity, following eq. [8] we have

\[
[\Delta_{NNN}] = -[\Delta_{NNN}]
\]

(11)

under \(\delta_h\). Therefore, based on the classification of pairing symmetries in Eq. [5], a parity conserved superconducting state must be a combination of normal pairing and \(\eta\)-pairing. If \(\Delta_{NNN}\) is a normal pairing, we immediately conclude that the state is parity odd and the superconducting order \(< \Delta_{NNN} >\) must be an \(\eta\)-pairing.

The above analysis can be easily illustrated in real space. As shown in fig. [4] if superconducting pairing is driven by local d-p hybridization, the superconducting gap depends on all Fermi surfaces were observed [30–39]. These experimental facts place a constraint that the superconducting pairing, \(< \hat{\Delta}_{NNN} >\) in the effective model, must originate from \(< \hat{d}^+ \hat{\rho}_a^+ >\) and thus is also parity odd. The gauge principle can be understood as shown in fig. [2c,d]. If we can take a new gauge for Fermion operators of p-orbitals, \(\hat{\rho} \rightarrow -\hat{\rho}\), in one of the two A\(\alpha\)(Se) layers, the anti-bonding operator \(\hat{\rho}_a\) maps to the bonding operator \(\hat{\rho}_b\). This gauge mapping exactly transfers the parity between hopping terms and superconducting order parameters.

VI. MEANFIELD HAMILTONIAN FOR PARITY CONSERVED S-WAVE STATE

The above analysis can be generalized to all effective hoppings. The basic idea is to divide the iron square lattice into two sublattices. In an odd parity state, the pairing between two sublattices must be normal pairing while the pairing within sublattices must be \(\eta\)-pairing. In an even parity state, the pairing between two sublattices must be \(\eta\)-pairing while the pairing within sublattices must be normal pairing. This means that the pairing between two sublattices must be vanished in an even parity state.

In all of measured samples of iron-based superconductors, no universal node along \(\Gamma - M\) and \(\Gamma - X\) directions on all Fermi surfaces were observed [30] [39]. These experimental facts place a constraint that the superconducting state must be in the \(A_1\) IR of \(D_{2d}\), namely, an s-wave viewed at iron sites. Then, the remaining question is about the parity of the state.

An even parity s-wave state, the normal pairing between two sublattices must be vanished. Therefore, the meanfield Hamiltonian for an even parity s-wave state is

\[
H_{mf}^o = H_{dd,eff} + \sum_{\alpha,\beta,k} (\delta_{\alpha,\beta,n}^o \hat{\Delta}_{\alpha,\beta,n}(\hat{k}) + h.c.)
\]

(12)

where \(\hat{\Delta}_{\alpha,\beta,n} = \hat{d}_{\alpha\uparrow}(\hat{k})\hat{d}_{\beta\downarrow}(-\hat{k}) - \hat{d}_{\alpha\downarrow}(\hat{k})\hat{d}_{\beta\uparrow}(-\hat{k})\) and \(\alpha,\beta\) label orbital. In general, the normal pairing order parameters must satisfy

\[
\delta_{\alpha,\beta,n}^o(\hat{k}) = \delta_{\alpha,\beta,n}^o(\hat{k} + Q)
\]

(13)

All superconducting states derived before from weak coupling approaches were considered as even parity [5] [8] [9] [40] [41]. However, as a normal pairing between two sublattices is included, the parity is not conserved. In strong coupling models [44] [47], the superconducting order was derived from NNN antiferromagnetic exchange coupling \(J_2\), which is a normal pairing within sublattices, satisfies Eq. [15]. Therefore, if superconductivity is only originated from \(d_{2z}\), the proposed state is an even parity s-wave state, namely, the \(A_{1g}\) s-wave.

This state provides a good understanding of superconducting gaps in iron-based superconductors. However, it cannot explain dual symmetry characters with both s-wave and d-wave type observed in the superconducting state, for example, the spin relaxation [48] measured by nuclear magnetic resonance(NMR). A coherent peak around \(T_c\) is expected in a full gap s-wave state even if it is an s\(^+\) [49]. Experimentally, in an extremely clean sample where the exponential temperature dependence was measured, no coherent peak was observed yet at \(T_c\) [49]. For iron-chalcogenides [19] [22], this state is highly questionable because of the absence of sign change on Fermi surfaces so that it is hard to explain the possible sign change evidence from neutron scattering [50]. It is also worth mentioning that many weak coupling methods suggest that the superconducting state in iron-chalcogenides is a d-wave with normal pairing [18] [51] [52]. This state is not consistent with experimental results showing the absence of nodes on high symmetry lines [37] [39] and the presence of strong ferromagnetic NN exchange coupling [53] [54]. Nevertheless, this d-wave state should be considered as an odd parity state in the original lattice symmetry because it only includes normal pairing between two sublattices.

A meanfield Hamiltonian to describe the odd parity s-wave state in 1-Fe unit cell (\(A_{1u}\) s-wave) can be generally written as

\[
H_{mf}^o = H_{dd,eff} + \sum_{\alpha,\beta,k} (\delta_{\alpha,\beta,n}^o \hat{\Delta}_{\alpha,\beta,n}(\hat{k}) + \hat{\Delta}_{\alpha,\beta,\eta}(\hat{k} + \frac{Q}{2}) + h.c.)
\]

(14)

where \(\hat{\Delta}_{\alpha,\beta,\eta} = \hat{d}_{\alpha\uparrow}(\hat{k})\hat{d}_{\beta\downarrow}(-\hat{k} + Q) - \hat{d}_{\alpha\downarrow}(\hat{k})\hat{d}_{\beta\uparrow}(-\hat{k} + Q)\). In general, the normal and \(\eta\) pairing order parameters satisfy

\[
\delta_{\alpha,\beta,n}^o(\hat{k}) = -\delta_{\alpha,\beta,n}^o(\hat{k} + Q)
\]

(15)

\[
\delta_{\alpha,\beta,\eta}(\hat{k}) = \delta_{\alpha,\beta,\eta}(\hat{k} + Q)
\]

(16)

These equations capture the sign change of superconducting order parameters in momentum space. The sign change here is required by odd parity symmetry.

While detailed studies will be carried out in the future, the meanfield Hamiltonian captures superconducting gaps in both iron-pnictides and iron-chalcogenides. As the inter-orbital pairing can be ignored for s-wave pairing and the pairing is dominated by NN and NNN pairings, the important parameters are

\[
\begin{align*}
\delta_{\alpha,\alpha,\alpha,n}^o &\propto \cos k_x + \cos k_y \\
\delta_{\alpha,\alpha,\eta}^o &\propto \cos 2\cos k_y
\end{align*}
\]

(17)
Thus, the superconducting gaps on hole pockets are mainly determined by \( \delta_{\alpha \alpha, n} \) and those on electron pockets are mainly determined by \( \delta_{\alpha \alpha, \eta} \).

In the odd parity s-wave state, there is no symmetry protected node. However, accidental nodes can easily take place. In Fig.5 we plot numerical results for two cases. Parameters are specified in the caption of the figure. The superconducting gap in the first case is a full gap while it has gapless nodes on electron pockets in the second case. This may provide an explanation why gapless excitations were observed in some materials\(^5\). The detailed studies will be reported in future.

The odd parity s-wave state also explains the dual symmetry characters of both s-wave and d-wave type in iron-based superconductors. The \( \eta \)-pairing s-wave order in \( D_{2d} \) essentially is a d-wave type order according to \( C_{4v} \) as shown in Fig.4. For a d-wave pairing symmetry, the vanishing of the coherence factor is required by symmetry. Thus, current NMR results really support the odd parity state.

The Hamiltonian in Eq.14 can not be reduced to a translationally invariant Hamiltonian in 1-Fe unit cell. The 2-Fe unit cell becomes intrinsic. Unique features related to 2-Fe unit cell should be observed and studied\(^55\). A detailed study will be carried out in future.

In summary, we provide the meanfield Hamiltonian for parity conserved superconducting states. Parity conservation was seriously violated in the past studies. Comparing odd and even parity s-wave states, we show that the odd parity s-wave state can naturally explain many intriguing properties of iron-based superconductors.

VII. SIGNATURE OF ODD PARITY SUPERCONDUCTING STATE

The fingerprint of the odd parity state is the negative iso-spin of \( \hat{\sigma}_h \), which indicates the sign change of order parameters between top and bottom As(Se) layers. This property was first revealed in the recent constructed effective \( S_4 \) symmetry model based on the 2-Fe unit cell\(^11\)\(^29\)\(^58\). However, as the \( S_4 \) model is a simplified effective model based on two effective orbitals, the parity characters were not revealed.

The odd parity indicates that a superconducting single Fe-As(As) trilayer is a \( \pi \)-junction along c-axis, which can be measured in a single crystal material as shown in Fig.6 a uniform superconducting state is characterized by sign change between top and bottom surfaces along c-axis in 11-type structure while in the 122-type structure, the sign change only presents when the number of layers are odd.

VIII. DISCUSSION

In the history of condensed matter physics, a new quantum state of condensed matter is hardly obtained by solving a model. Here we use fundamental principles to show that an odd parity state can be naturally taken place in Iron-based superconductors and suggest smoking-gun experiments to detect or falsify it. With microscopic understanding proposed here, a detection of the odd parity state can have a tremendous impact on high \( T_c \) mechanism for iron-based superconductors and other high \( T_c \) superconductors.

In the past five years, many researches based on effective models suggest that pairing symmetries in iron-based superconductors are very fragile. Those studies essentially suggest that principles to understand the robustness of superconductivity and pairing symmetry are still missed in our standard approach. The results in this paper demonstrate that previous studies did not correctly take parity conservation and hidden symmetry in effective models into account and mishandled symmetry and gauge principles. In the past, the effective Hamiltonian was viewed in the symmetry group \( D_{4h} \) at iron sites rather than the original lattice symmetry \( G \). We can see that if \( \hat{\sigma}_h \) could be set to one, \( G \) is equivalent to \( D_{4h} \). However, due to the anti-bonding \( p \) orbital states, the effective Hamiltonian does not represent correct symmetry of the original lattice in a natural gauge setting. It will be interesting to see how the missing pieces can be properly implemented in our standard methods.
Our results suggest that gauge principle needs to be properly implemented when we derive effective Hamiltonian to simplify a complex system. The correct physics can only be understood after the hidden gauge is revealed. For an order parameter which is momentum dependent, this gauge information is critical. The gauge principle becomes very important for us to search new physics in other complex electron systems.

The odd parity state also suggests the importance of correlated electron physics. It is believed that sign change superconducting order is inevitable in a superconducting state of strongly correlated electron systems because of the existence of strong repulsive interaction. This principle is violated in a parity even s-wave state. A measurement of the party odd s-wave state can provide a strong support of this principle.

The microscopic mechanism revealed here fundamentally differs from those proposed in weak coupling approaches which only emphasize Fermi surfaces. Fermi surfaces are only determined by energy dispersion. It provides no information about underlying microscopic processes which are local and bound with high energy physics. In correlated electron systems, these processes essentially determine many important properties. This is also the reason why iron-pnictides and iron-chalcogenides can be unified even if their Fermi surfaces are drastically different.

If the odd parity state is confirmed, the fundamental objects in superconducting states of high $T_c$ materials must be the tightly binding Cooper pairs between d and p orbitals. In this view, the odd parity s-wave state closely resembles the d-wave state in a CuO plane of cuprates. We expect an identical mechanism to select sign changed superconducting orders in both materials. From Fig.1(b), one can see that the $\eta$-pairing part in the odd parity state can be viewed as two d-wave states formed in two sublattices, a direct analogy to the d-wave in cuprates.

This study opens a promising new direction for the research in iron-based superconductors and suggests that the physics in these materials is deeper and much more inspiring than what we realized before. It leaves many unanswered questions for us. A few questions are in order. First, what is relationship between magnetism and superconductivity? One can see that the collinear antiferromagnetic (C-AFM) state observed in iron-pnictides has odd parity. This may partially answer why superconductivity and C-AFM order can coexist in the phase diagram. Second, what are other unique properties in an odd parity s-wave state? It is known that an odd parity p-wave state displays many unique properties. Third, what is the relationship between nematism and superconductivity? Nematism breaks rotational symmetry and was observed at high temperature. Fourth, how robust is an odd parity state in response to impurity? Finally, this study points out that there are three possible scenarios related to parity in superconducting states, even, odd or broken. Experiments proposed here will finally nail down the truth. All the previous studies took even parity for granted without knowing that the parity was actually broken in the proposed states. However, a parity breaking superconducting state is also an interesting state to explore.

In summary, using symmetry and gauge principles, we show that iron-based superconductors are unified into an odd parity s-wave superconducting state. We demonstrate that in an effective model based on d-orbitals, superconducting states studied in the past violate parity conservation. The existence of the odd parity state can have tremendous impact on high $T_c$ superconducting mechanism.

Acknowledges: The author acknowledges NN Hao for useful discussion and providing the numerical results for superconducting gaps and XX Wu for providing the figure of the distribution of p-orbital in LDA calculations. The author wants to thank for H. Ding, P. Coleman, D. Scalapino, T. Xiang, X. Dai, and D.L. Feng for useful discussion. The work is supported by the Ministry of Science and Technology of China 973 program(2012CB821400) and NSFC-1190024.

![FIG. 6: Sketch of real space sign distribution along c-axis for an $\eta$-pairing state in (a) 11-type structure, (b) 122-type structure with odd number of layers and (c) 122-type structure with even number of layers.](image)

[1] Kamihara, Y., Watanabe, T., Hirano, M. & Hosono, H. Iron-based layered superconductor la[ox]Fe[fx] (x) 0.05-0.12) with tc 26 k. JACS 130, 3296 (2008).
[2] Chen, X. H. et al. Superconductivity at 43 k in samarium-arsenide oxides smf easo1fx. Nature 453, 761 (2008).
[3] Chen, G. F. et al. Superconductivity at 41 k and its competition with spin-density-wave instability in layered ces(1-x)(f)(x)feas. Phys. Rev. Lett. 100 (2008).
[4] Johnston, D. C. The puzzle of high temperature superconductivity in layered iron pnictides and chalcogenides. Adv. in Phys. 59, 803 (2010).
[5] Hirschfeld, P. J., Korshunov, M. M. & Mazin, I. I. Gap symmetry and structure of fe-based superconduc-
tors. Rep. Prog. Phys. 74, 124508 (2011).
[6] Tsuei, C. C. & Kirtley, J. R. Pairing symmetry in cuprate superconductors. Reviews of Modern Physics 72, 969–1016 (2000).
[7] Anderson, P. W. Structure of "triplet" superconducting energy gaps. Phys. Rev. B 30, 4000 (1984).
[8] Kuroki, K. et al. Unconventional pairing originating from the disconnected fermi surfaces of superconducting LaFeAsO1−xFs. Phys. Rev. Lett. 101, 087004 (2008).
[9] Graser, S. et al. Spin fluctuations and superconductivity in a three-dimensional tight-binding model for bafes2as2. Phys. Rev. B 81, 214503 (2010).
[10] Eschrig, H. & Koepernik, K. Tight-binding models for the iron-based superconductors. Phys. Rev. B 80, 104503 (2009).
[11] Lee, P. A. & Wen, X.-G. Spin-triplet p-wave pairing in a three-orbital model for iron pnictide superconductors. Phys. Rev. B 78, 144517 (2008).
[12] Daghofer, M., Nicholson, A., Moreo, A. & Dagotto, E. Three orbital model for the iron-based superconductors. Phys. Rev. B 81, 145110 (2010).
[13] Raghu, S., Qi, X. L., Liu, C. X., Scalapino, D. J. & Zhang, S. C. Minimal two-band model of the superconducting iron oxypnictides. Phys. Rev. B 77, 220503 (2008).
[14] Yang, C. Eta pairing and off diagonal long-range order in a hubbard model. Phys. Rev. Lett. 63, 2144 (1989).
[15] Yang, C. & Zhang, S. S04 symmetry in a hubbard model. Mod. Phys. Lett. B 4, 759 (1990).
[16] Hu, J. & Hao, N. S4 symmetric microscopic model for iron-based superconductors. Phys. Rev X 2, 021009 (2012).
[17] Gao, Y., Su, W.P & Zhu, J.X. Interorbital pairing and its physical consequences for iron pnictide superconductors. Phys. Rev B 81, 104504 (2010).
[18] Khodas, M. & Chubukov, A. V. Inter-pocket pairing and gap symmetry in fe-based superconductors with only electron pockets. Phys. Rev. Lett 108 (2012).
[19] Guo, J. et al. Superconductivity in the iron selenide KxeF2se2 (0×1×0). Phys. Rev. B 82, 180520(R) (2010).
[20] He, S. et al. Phase diagram and high temperature superconductivity at 65 k in tuning carrier concentration of single-layer fese films. arxiv:1207.6823 (2012).
[21] Liu, D. et al. Electronic origin of high-temperature superconductivity in single-layer fese superconductor. Nature Comm. 3, 931 (2012).
[22] Tan, S. Y. et al. Interface-induced superconductivity and strain-dependent spin density wave in fese/srtio3 thin films. Arxiv:1301.2748 (2012).
[23] Fischer, M. H., Loder, F. & Sigrist, M. Superconductivity and local noncentrosymmetry in crystal lattices. Phys. Rev. B 84, 184533 (2011).
[24] Miyake, T., Nakamura, K., Arita, R. & Imada, M. Comparison of ab initio low-energy models for lafeo, lafeaso, bafe2as2, lifees, fes, and fete: Electron correlation and covalency. J. Phys. Soc. Jpn. 79, 044705 (2009).
[25] Graser, S., Maier, T. A., Hirschfeld, P. J. & Scalapino, D. J. Near-degeneracy of several pairing channels in multiorbital models for the fes pnictides. New Journal of Physics 11, 5016 (2009).
[26] Ma, F. & LU, Z.-Y. Iron-based layered compound lafeaso is an antiferromagnetic semimetal. Phys. Rev. B 78, 033111 (2008).
[27] Singh, D. J. Electronic structure and doping in bafe2as2 and lifees: Density functional calculations. Phys. Rev. B 78, 094511 (2008).
[28] Berg, E., Kivelson, S. A. & Scalapino, D. J. A twisted ladder: relating the fe superconductors to the high-tc cuprates. New Journal of Physics 11, 085007 (2009).
[29] Hu, J. A short review of the s4 symmetric microscopic model for iron-based high temperature superconductors. arXiv:1208.6201 (2012).
[30] Zhao, L. et al. Multiple nodeless superconducting gaps in Ba(0.6)Fe(2)As2 superconductor from angle-resolved photoemission spectroscopy. Chin. Phys. Lett. 25, 4402–4405 (2008).
[31] Ding, H. & et al. Observation of fermi-surfacedependent nodeless superconducting gaps in ba 0.6 k 0.4 fe 2 as 2. EPL (Europhysics Lett.) 83, 47001 (2008).
[32] Wray, L. et al. Momentum dependence of superconducting gap, strong-coupling dispersion kink, and tightly bound cooper pairs in the high- tc (sr,ba)1x(k,na)xfe2as2 superconductors. Phys. Rev. B 78, 184508 (2008).
[33] Ding, H. et al. Electronic structure of optimally doped pnictide ba0.6k0.4Fe2As2: a comprehensive arpes investigation. J. Phys.: Condens. Matter 23 (2011).
[34] Ding, L. et al. Nodeless superconducting gap in electron-doped bafe1.9ni0.1as2 probed by quasiparticle heat transport. New Journal of Physics 11, 3018 (2009).
[35] Nakayama, K. et al. Universality of superconducting gaps in overdoped ba0.3k0.7fe2as2 observed by angle-resolved photoemission spectroscopy. Phys. Rev. B 83, 020501(R) (2011).
[36] Zhang, Y. et al. Nodeless superconducting gap in a(x)fe(2)se(2) (a = k, cs) revealed by angle-resolved photoemission spectroscopy. Nature Materials 10, 273–277 (2011).
[37] Zhang, Y. et al. Out-of-plane momentum and symmetry-dependent energy gap of the pnictide ba0.6k0.4fe2as2 superconductor revealed by angle-resolved photoemission spectroscopy. Phys. Rev. Lett. 105, – (2010).
[38] Wang, X.-P. et al. Observation of an isotropic superconducting gap at the brillouin zone center of t10.3k0.37se1.78as2. EPL (Europhysics Lett.) 99, 67001 (2012).
[39] Xu, M. et al. Angle-resolved photoemission evidence of s-wave superconducting gap in kxe2yes2 superconductor. Phys. Rev. B 85, 220504(R) (2012).
[40] Mazin, I. I., Singh, D. J., Johannes, M. D. & Du, M. H. Unconventional superconductivity with a sign reversal in the order parameter of lafeaso1-xfs. Phys. Rev. Lett. 101, 57003 (2008).
[41] Wang, F., Zhai, H., Ran, Y., Vishwanath, A. & Lee, D.-H. Functional renormalization-group study of the pairing symmetry and pairing mechanism of the feas-based high-temperature superconductor. Phys. Rev. Lett. 102, 47005 (2009).
[42] Chubukov, A. V. Renormalization group analysis of competing orders and the pairing symmetry in fe-based superconductors. Physica C Superconductivity 469, 640–650 (2009).
[43] Thomale, R., Platt, C., Hu, J. P., Honerkamp, C. & Bernevig, B. A. Functional renormalization-group study of the doping dependence of pairing symmetry in the iron pnictide superconductors. Phys. Rev. B 80, – (2009).
[44] Seo, K. J., Bernevig, B. A. & Hu, J. P. Pairing symmetry in a two-orbital exchange coupling model of oxypnictides. Phys. Rev. Lett. 101, 206404 (2008).
[45] Lu, X., Fang, C., Tsai, W.-F., Jiang, Y. & Hu, J. s-wave superconductivity with orbital-dependent sign change in checkerboard models of iron-based superconductors. Phys. Rev. B 85, 54505 (2012).

[46] Fang, C., Wu, Y.-L., Thomale, R., Bernevig, B. A. & Hu, J. Robustness of s-wave pairing in electron-overdoped $A_{1-y}Fe_{2-x}Se_2$. Phys. Rev X 1, 011009 (2011).

[47] Yu, R., Goswami, P., Si, Q., Nikolic, P. & Zhu, J.-X. Pairing strength and symmetries of (k,t)fxse2 in comparison with iron pnictides. arxiv: 1103.3259 (2011).

[48] Parish, M. M., Hu, J. P. & Bernevig, B. A. Experimental consequences of the s-wave cos(k(x))cos(k(y)) superconductivity in the iron pnictides. Phys. Rev. B 78, – (2008).

[49] Li, Z. et al. Nodeless energy gaps of single-crystalline ba0.68k0.32fe2as2 as seen via as75 nmr. Phys. Rev. B 83, 140506 (2011).

[50] Park, J. T. et al. Magnetic resonant mode in superconducting rb2fe4se5. Phys. Rev. Lett. 107, 177005 (2011).

[51] Maier, T., Graser, S., Hirschfeld, P. & Scalapino, D. d-wave pairing from spin fluctuations in the kxfe2-yses2 superconductors. Phys. Rev. B 83, 100515(R) (2011).

[52] Wang, F. et al. The electron pairing of kxfe2-yses2. EPL (Europhysics Lett.) 93, 57003 (2011).

[53] Wang, M. et al. Spin waves and magnetic exchange interactions in insulating rb0.89fe1.58ses2. Nature Comm., 2, 580 (2011).

[54] Hu, J., Xu, B., Liu, W., Hao, N.-N. & Wang, Y. Unified minimum effective model of magnetic properties of iron-based superconductors. Phys. Rev. B 85, 144403 (2012).

[55] Brouet, V. et al. Impact of the 2 fe unit cell on the electronic structure measured by arpes in iron pnictides. Phy. Rev. B 86, 075123 (2012).

[56] Ma, T., Lin, H.-Q. & Hu, J. Quantum monte carlo study of pairing symmetry and correlation in iron-based superconductors. Phys. Rev. Lett. 110, 107002 (2013).

[57] Dai, P., Hu, J. & Dagotto, E. Magnetism and its microscopic origin in iron-based high-temperature superconductors. Nature Physics 8, 709 (2012).

[58] Fisher, I. R., Degiorgi, L. & Shen, Z. X. In-plane electronic anisotropy of underdoped ”122” fe-arsenide superconductors revealed by measurements of detwinned single crystals. Reports on Progress in Physics 74, 124506 (2011).