Mechanism for Odd Parity Superconductivity in Iron-Based Superconductors

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Under the assumption that superconducting pairing is driven by local d-p hybridization, 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 with only d-orbitals in an iron 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 results demonstrate iron-based superconductors being a new quantum state of matter and suggest that a measurement of odd parity can establish fundamental principles related to high temperature superconducting mechanism.

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 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. Nevertheless, as local electronic structures in all families of iron-based superconductors are almost identical and phase diagrams are smooth against doping, it is hard to argue that the materials can approach many different superconducting ground states.

In a recent paper, one of us provided a complete symmetry classification for pairing symmetries in iron-based superconductors and showed that spin-singlet pairing with odd parity can naturally take place because of the intrinsic 2-Fe unit cell, which was ignored in previous theoretical studies based on effective models with 1-Fe unit cell. It was further argued that the pairing between electron pockets is most likely $A_{1u}(D_{2d})$ s-wave or $B_{2u}(C_{4v})$ d-wave $\eta$-pairing. The pairing state has both s-wave characters, such as no symmetry-protected nodes or nodal lines on superconducting gap functions, and d-wave characters, such as a sign change between top and bottom As/Se layers in real space. However, no microscopic mechanism has been proposed for odd parity pairing.

In this Letter, we provide a microscopic understanding to show that the superconducting state in iron-based superconductors is classified as an odd parity s-wave spin-singlet pairing state (OPS) in a single trilayer FeAs/Se, the building block of the materials. This conclusion is only based on the consensus that As(Se) plays a critical role in driving superconductivity so that superconducting pairing is determined locally by d-p hybridization. Under this consensus, in a low energy effective model with only d-orbitals in an iron square lattice, we show that a normal pairing order defined between two iron sublattices is parity odd. Namely, it carries a sign change between top and bottom As/Se layers. This is because the effective nearest neighbor (NN) hopping of $t_{2g}$ d-orbitals induced by d-p hybridization is generated through the antibonding state of p-orbitals formed between top and bottom As/Se layers. As parity is a good quantum number, a superconducting order parameter between two next NN (NNN) sites must be an $\eta$-pairing. Thus, in the effective d-orbital models, a superconducting state that does not violate parity conservation must include both normal and $\eta$ pairing. An OPS, classified as a $A_{1u}(D_{2d})$ s-wave or $B_{2u}(C_{4v})$ d-wave in a full lattice symmetry, is a combination of a s-wave normal pairing between two sublattices and a s-wave $\eta$-pairing within the sublattices. We show that the meanfield Hamiltonian of this state explains the dual s-wave and d-wave type characters observed experimentally and unifies the description of iron-pnictides and iron-chalcogenides. The results conclude that parity conservation was violated in proposed superconducting states in the past. The confirmation of the odd parity state will have a tremendous impact on understanding high-$T_c$ mechanism.

Before we start our analysis, we repeat the definition of normal and $\eta$ pairing in $\hat{\eta}$. Let $\vec{k}$ be momentum with respect to the 1-Fe unit cell in an iron square lattice. The normal pairing refers to ($-\vec{k}, \vec{k}$) pairing and the $\eta$-pairing refers to ($-\vec{k}, \vec{k}+Q$) pairing where the momentum vector $Q = (\pi, \pi)$ is a reciprocal lattice vector in a 2-Fe unit cell.

**Effective Hamiltonian** We consider a general Hamiltonian in a single trilayer Fe–As(Se) structure coordinated by Fe and As(Se) atoms,

$$\hat{H} = \hat{H}_{dd} + \hat{H}_{dp} + \hat{H}_{pp} + \hat{H}_{I} \quad (1)$$
through d-p hybridization. \hat{N}NN hopping in the iron square lattice. If one carefully describes NN hopping and \hat{N}NN hopping between two \textit{d}-orbitals, which can be written as \( \hat{H}_{dd} \), \( \hat{H}_{dp} \) 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. \( \hat{H}_I \) describes any standard interactions. Here we do not need to specify the detailed parameters. This Hamiltonian has a full symmetry defined by a non-symmorphic group which can be specified equivalently as \( G = (\hat{E}, \hat{I}) \otimes C_{4v} \) or \( G = (\hat{E}, \hat{I}) \otimes D_{2d} \) as shown in [8], where \( \hat{I} \) is the space inversion operation defined at the center of a NN Fe link, \( D_{2d} \) is the point group at iron sites and \( C_{4v} \) is the point group at the center of an iron square.

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

\[
\hat{H}_{\text{eff}} = \hat{H}_{dd,\text{eff}} + \hat{H}_I,\text{eff}.
\]  

(2)

The effective band structure can be written as \( \hat{H}_{dd,\text{eff}} = \hat{H}_{dd} + \hat{H}_{dpd} \), where \( \hat{H}_{dpd} \) is the effective hopping induced through d-p hybridization. \( \hat{H}_{dd,\text{eff}} \) has been obtained by many groups [13][17]. 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 hoppings 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.1(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 [13][17]. 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.1(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 \( d-p_{z} \) hybridization, where \( p_{z} \) represents an anti-bonding \( p \)-orbital states and the NNN effective hoppings are generated through \( d-p_{z} \) hybridization where \( p_{z} \) is the bonding \( p \)-state.

The above microscopic understanding is not surprising. In fact, it is known in LDA calculations [11][18][19] that p-orbitals in As/Se are not fully occupied and there are significant overlaps between p-orbitals on bottom and top As/Se layers. Moreover, since \( \hat{H}_{dpd,NN} \) and \( \hat{H}_{dpd,NNN} \) primarily affect hole pockets around \( \Gamma \) and electron pockets at \( M \) and \( \Gamma \) electron pockets at \( M \) 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.2(b) and (c), we confirm that the \( p_{z} \) orbitals of Se at \( \Gamma \) and \( M \) belong to anti-bonding and bonding states separately.

Hidden \( Z_2 \) symmetry characters in effective Hamiltonian: Knowing the above hidden microscopic origins in a derivation of an effective Hamiltonian allows us to understand the symmetry characters of the effective Hamiltonian.
nian in the original lattice symmetry. As shown in Ref. 8, in the original lattice symmetry, $G$, we can introduce a $Z_2$ classification specified by $\hat{\sigma}_h$, where $\hat{\sigma}_h$ is the reflection along $z$-axis.

The original Hamiltonian is invariant under $(\hat{\sigma}_h, \hat{T})$, where $\hat{T}$ is an in-plane translation by one Fe-Fe lattice. 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 $\hat{H}_{d\sigma,p\sigma,NN}$ and NNN hopping $\hat{H}_{d\sigma,p\sigma,NNN}$ should be classified as odd and even under $\hat{\sigma}_h$ respectively. Namely,

$$\hat{\sigma}_h \hat{H}_{d\sigma,p\sigma,NN} \hat{\sigma}_h = -1$$
$$\hat{\sigma}_h \hat{H}_{d\sigma,p\sigma,NNN} \hat{\sigma}_h = 1$$

(3)

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 $\bar{M}$ $[6]$. As indicated in fig. 2(a), the interplay between the hole and electron pockets must be minimal because of their distinct microscopic origins.

**Gauge transformation and parity of pairing order parameter:** The symmetry difference in eq. 3 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 $[20, 21]$ 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 $[22]$. Therefore, only the combined symmetry of hopping terms and pairing orders associated to them is a gauge-independent symmetry character to classify states. 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 $\hat{H}_{d\sigma,p\sigma,NN}$ and $\hat{H}_{d\sigma,p\sigma,NNN}$ respectively. In a superconducting state, we must have

$$[\hat{\Delta}_{NN}] [\hat{H}_{d\sigma,p\sigma,NN}] = [\hat{\Delta}_{NNN}] [\hat{H}_{d\sigma,p\sigma,NNN}]$$

(4)

where $[\hat{A}]$ indicate the symmetry of $\hat{A}$. Following eq. 3, we have $[\hat{\Delta}_{NN}] = -[\hat{\Delta}_{NNN}]$ under $\hat{\sigma}_h$. Therefore, based on the classification of pairing symmetries in Ref. 8, we immediately conclude that the parity is odd and the superconducting order $<\hat{\Delta}_{NNN}>$ must be an $\eta$-pairing if $<\hat{\Delta}_{NN}>$ is a normal pairing.

The above analysis can be easily illustrated in real space. As shown in fig. 3, if superconducting pairing is driven by local $d-p$ hybridization, the superconducting order is a pairing between $d$ and $p$ orbitals $\Delta_{dp} = <\hat{d}^+ \hat{p}^+>$. A uniform $<\hat{d}^+ \hat{p}_a^+>$ is parity odd. The NN pairing, $<\hat{\Delta}_{NN}>$, in the effective model, must originate from $<\hat{d}^+ \hat{p}_a^+>$ and thus is also parity odd. The gauge principle can be understood as shown in fig. 3(c, d). If we can take a new gauge for Fermion operators of $p$-orbitals, $\hat{p} \rightarrow -\hat{p}$, in one of the two As(Se) layers, the anti-bonding operator $\hat{p}_a$ maps to the bonding operator $\hat{p}_b$. This gauge mapping exactly transfers the parity between hopping terms and superconducting order parameters.

**Meanfield Hamiltonian for odd-parity s-wave state:** The above analysis can be generalized to all effective hopping patterns with odd parity are shown in (a) and (b) in the natural gauge. Note that $p$ orbitals of As/Se in (a) form the anti-bonding states while that in (b) form the bonding states. We distinguish the two states with different filled green balls between (a) and (b). The $p-d$ pairings can be projected into effective $d-d$ pairings shown in the bottom row.

FIG. 3: (Color online) The NN and NNN $p-d$ local pairing patterns with odd parity are shown in (a) and (b) in the natural gauge. Note that $p$ orbitals of As/Se in (a) form the anti-bonding states while that in (b) form the bonding states. We distinguish the two states with different filled green balls between (a) and (b). The $p-d$ pairings can be projected into effective $d-d$ pairings shown in the bottom row.
only add a chemical potentials to tune the fermi level. We terms and hopping parameters can be found in [15]. Here, we model in [15] are shown in (a) and (b). The forms of hopping lines with arrows. The quasi-particle spectrum of the superconducting order parameters are denoted by the black points on the fermi surface are denoted by the black arrows. These equations capture the sign change of superconducting gaps obtained from eq. 5 can explain experimental results observed in both iron-nitrides and iron-chalcogenides [23]. There is no symmetry protected node in this superconducting state. However, accidental nodes can easily take place. In fig. 4 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.

Impact to High-\(T_c\) Mechanism In ref. [8], the odd parity s-wave state was conjectured based on intriguing experimental facts. With microscopic mechanism proposed here, we can address important impact on high \(T_c\) mechanism for iron-based superconductors and other high \(T_c\) superconductors if the state is confirmed.

First, 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 underlining microscopic processes which are local and bound with high energy physics. In correlated electron systems, these processes essentially determine many important properties.

Second, our study provides fundamental reasons why we failed to recognize the odd parity symmetry in the past. The symmetry principle and gauge principle were not properly handled. In the past, the effective Hamiltonian was viewed in the symmetry group \(C_{4v}\) at iron sites rather than the original lattice symmetry \(G\). We can see that if \(\hat{\sigma}_b\) could be set to one, \(G\) is reduced to \(C_{4v}\). 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. 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.

Finally, 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 Cu-O plane of cuprates. We expect an identical mechanism to select sign changed superconducting orders in both materials.

In summary, we provide a microscopic mechanism to support the formation of an odd parity s-wave superconducting state in iron-based superconductors. We demonstrate that in an effective model based on \(d\)-orbitals, both normal pairing and \(\eta\) pairing must be included if the superconducting state conserves parity. Superconducting states studied in the past violate parity conservation.

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