Pairing Symmetry in a Two-Orbital Exchange Coupling Model of Oxynitrides

Kangjun Seo,1 B. Andrei Bernevig,2,3 and Jianping Hu1

1Department of Physics, Purdue University, West Lafayette, Indiana 47907, USA
2Department of Physics, University of California, Irvine, CA 92697
3Princeton Center for Theoretical Science, Princeton University, Princeton, NJ 08544

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We study the pairing symmetry of a two orbital $J_1-J_2$ model for FeAs layers in oxynitrides. We vary the doping and the value of $J_1$ and $J_2$ to compare all possible pairing symmetries in a mean-field calculation. We show that the mixture of an intra-orbital unconventional $s_{\pm}$ pairing and $d_{x^2-y^2}$ pairing is favored in a large part of $J_1-J_2$ phase diagram. A pure $s_{\pm}$ pairing state is favored for $J_2 \gg J_1$. The signs of the $d_{z^2-y^2}$ order parameters in two different orbitals are opposite. While a small $d_{xy}$ pairing occurs in the above phases, the intra-orbital $d_{xy}$ pairing symmetry is not favored even for large values of $J_2$.

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High temperature superconductivity (at 56K) has been recently reported in the rare-earth electron and hole-doped oxynitride compounds.2,3,4,5,6 Preliminary evidence2,5,6 suggests that the superconducting state in the electron-doped oxynitrides, like that in the Cuprates, has gapless nodal quasiparticle excitations and hence an unconventional pairing symmetry. A number of theoretical studies have predicted or conjectured different possible pairing symmetries, anywhere from $p$-wave to a $s$-wave.7

A natural approach to the physics of oxynitrides is by drawing comparisons with that of the Cuprates. In the case of Cuprates, superconductivity is produced by doping a half-filled antiferromagnetic insulator. The antiferromagnetic exchange naturally provides for a singlet pairing amplitude7,8 with equal mean-field critical temperatures for both $d$-wave and extended $s$-wave1,12,13 in the ultra-Mott limit. Upon doping, due to the Fermi surface shape, the $d$-wave condensate has higher mean-field transition temperature than the extended $s$-wave one12. The nearest neighbor hoping in the square lattice of Cu atoms is dominant and provides for a large Fermi surface with large effective mass in the Mott limit.

The electronic properties of oxynitrides differ from those in Cuprates in several important ways. Most importantly, the undoped oxynitrides are metallic but their resistivity is strikingly high. They can hence be interpreted both as a bad metal or as a poor insulator, leaving open the question of whether a weak or strong coupling fixed point governs their physics. From the band structure point of view, barring the existence of un-physically strong crystal fields, it seems likely that all $3d$ orbitals of the Fe atoms are involved in the low energy electronic properties. Numerical results based on first principle calculations show the presence of small Fermi surfaces.14 In the unfolded Brillouin zone consisting of one Fe per unit cell, electron and hole pockets exist around the $M$ and $\Gamma$, $(\pi, \pi)$ points respectively. The magnetic properties of the oxynitrides are also different from those of the Cuprates. Neutron experiments have shown that the magnetic structure in undoped oxynitrides is not a simple antiferromagnetic order14 but rather a stripe spin-density wave with onset temperature of about 150K.

The metallic behavior and the existence of Fermi pockets have led to proposals about the superconducting pairing symmetry and mechanism which originate in the weak coupling, itinerant limit15,16. In this limit, triplet pairing is possible and has been predicted17. Numerical and analytic research suggests that the antiferromagnetic exchange coupling between Fe sites is strong and due to As-mediated hopping, an antiferromagnetic exchange coupling exists only between the nearest neighbor (NN) Fe atom sites but also between next nearest neighbor (NNN) sites. The NNN coupling strength $J_2$ is comparable to the NN coupling strength $J_1$. The $J_1-J_2$ model provides for half-filled magnetic physics consistent with experimental neutron data.14 A nematic magnetic phase transition has been predicted in this model15,17,22, consistent with the experimental observation of a structural transition preceding the spin density wave formation. Therefore, the magnetic structure of the undoped oxynitrides suggests that the material is not far from the strongly coupling, Mott limit.

In the present paper we obtain the superconducting mean-field phase diagram of a $t-J_1-J_2$ model with the correct Fermi surface for the oxynitride compounds. We predict that two kinds of intra-orbital pairing order parameters, an extended $s$-wave of the unconventional form $s_{\pm} \sim \cos(k_x) \cos(k_y)$ or a $d_{x^2-y^2} \sim \cos k_x - \cos k_y$ wave order parameter are the only possibilities in the Mott limit. A mixture of the intra-orbital unconventional $s_{\pm}$ pairing symmetry and the $d_{z^2-y^2}$ pairing symmetry is favored in a large part of $J_1-J_2$ phase diagram. While a small $d_{xy} \sim \sin k_x \sin k_y$ inter-orbital pairing order coexists in the above phase, the intra-orbital $d_{xy}$ pairing symmetry is not favored even for large value of $J_2$ in contradiction with the predictions of several papers14,20,21 that rest on an analogy with the physics in cuprates. While $d_{xy}$ pairing would indeed be favored for $J_2 \gg J_1$ in the case of a large, single band, Fermi surface...
The hoppings have roughly the same magnitude with
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almost favorably. If the Fermi surface picture emerging
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equation 2
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the case of unphysically large crystal field splitting,
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\[ J \]
\[ H \]
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\[ n_{i, \alpha} \]
\[ \delta_{i} \]
\[ \beta \]
\[ \alpha \]
\[ \alpha \]
\[ \beta \]

\[ H_{1} = \sum_{\alpha, \beta} J_{\alpha, \beta}(\bar{S}(r, \alpha) \cdot \bar{S}(r + \delta_{1}, \beta) - n(r, \alpha)n(r + \delta_{1}, \beta)) \]

\[ H_{3} = - \sum_{\alpha} J_{\mu} \bar{S}(r, \alpha) \bar{S}(r, \alpha) \]

where \( \alpha \) is the orbital complementary to \( \alpha \). This Hamiltonian can be justified through different means. Hund’s rule is known to play an important effect in Fe, but is usually neglected in the recent calculations on superconductivity in oxypnictides. The antiferromagnetic \( J_{1} \) and \( J_{2} \) (both positive) are usually obtained from numerical calculations, although, in the Mott limit, they can be justified through a Hubbard-\( U \) Gutzwiller method. In the present case, numerical calculations predict a Hubbard \( U \) for electrons on the same site and same orbital a factor of 2 larger than the Hubbard \( U \) repulsion of electrons on the same site but different orbitals. In this case, the double occupancy constraint can be imposed by a product of the Gutzwiller projectors for the two orbitals \( P_{G} = \prod_{i}(1 - n_{i, \alpha}n_{i, \beta})(1 - n_{i, \alpha}n_{i, \alpha}) \). Simple perturbation theory leads us to Anderson exchange \( \sum_{i,j} J_{ij}(\delta_{ij} - n_{i, \alpha}n_{j, \alpha}) \) where \( \alpha, \beta \) are the two \( d_{xz} \) and \( d_{yz} \) orbitals. The hoppings in Eq. 2, give rise to NN exchange only between spins on the same orbitals, and NNN exchange between spins on both the same and opposite orbitals. However, other models for the spin-spin interactions, such as the one in Ref. 21, which implicitly take into account Hund’s rule by formulating the exchange in terms of spin-2 or spin-1 variables at each site, will also contain NN exchange between spins of opposite orbitals. Our mean-field solutions should be interpreted in the same spirit as the superconducting solutions of the original \( t - J \) model: at some value of the doping, the true undoped spin density wave groundstate disappears and gives way to a superconducting state.  

**Mean-field solution in the absence of orbital crossing exchange:** Keeping all of the above terms becomes analytically intractable. We proceed with a two-step process: we first mean-field decouple the interaction Hamiltonian assuming that exchange takes place only between spins on the same orbitals. While physically incomplete, this model has the advantage of being analytically tractable, and exposes the un-competitiveness of the \( d_{xy} \) order. We then numerically solve the full model in a superconducting mean-field decoupling. The interaction term reads
\[ \sum_{k,k'} V_{k,k'} c_{\alpha,k}^\dagger c_{\alpha,-k',\downarrow}^\dagger \text{ with} \\
V_{k,k'} = -\frac{J}{N} \sum_{\pm}(\cos k_x \pm \cos k_y)(\cos k_x' \pm \cos k_y') \\
-\frac{8J}{N} (\cos k_x \cos k_y \cos k_x' \cos k_y' + \sin k_x \sin k_y \sin k_x' \sin k_y') \] (5)

with obvious pairing amplitudes in four channels \( x^2 \pm y^2, xy \) and \( x'y', \Delta_\alpha(k) = \Delta_{x^2+y^2,\alpha}(k) + \Delta_{x'y',\alpha}(k) + \Delta_{xy,\alpha}(k), \) and

\[ \frac{\Delta_{x^2+y^2,\alpha}(k)}{\cos k_x \pm \cos k_y} = -\frac{2J_1}{N} \sum_{k'} (\cos k_x' \pm \cos k_y') d(k') \]
\[ \frac{\Delta_{xy,\alpha}(k)}{\cos k_x \cos k_y} = -\frac{8J_2}{N} \sum_{k'} (\cos k_x' \cos k_y') d(k') \]
\[ \frac{\Delta_{x'y',\alpha}(k)}{\sin k_x \sin k_y} = -\frac{8J_2}{N} \sum_{k'} (\sin k_x' \sin k_y') d(k') \] (6)

where \( d(k') = \langle c_{\alpha,-k',\downarrow} c_{\alpha,k',\downarrow} \rangle. \) We use \( \alpha = \{1, 2\} \) to represent the orbital index \((xz, yz)\).

We decouple the interaction Hamiltonian with exchange terms only between spins on the same orbitals in mean-field: \( H_m = \sum_k \Psi(k) A(k) \Psi(k) \) with

\[ A(k) = \begin{pmatrix} \epsilon_x(k) - \mu & \Delta_1(k) & \epsilon_{xy}(k) & 0 \\ \Delta_1^*(k) & -\epsilon_x(k) + \mu & 0 & \Delta_2(k) \\ 0 & 0 & -\epsilon_{xy}(k) & 0 \\ \epsilon_{xy}(k) & \Delta_2^*(k) & 0 & -\epsilon_x(k) \end{pmatrix} \] (7)

with \( \Psi(k) = (c_{1,k,\downarrow}, c_{1,-k,\downarrow}, c_{2,k,\downarrow}, c_{2,-k,\downarrow}) \). The particularization to oxygenides is present in the hopping terms, which couple different orbitals as in Eq[2]. \( A(k) \) can be diagonalized by an unitary transformation, \( U(k) A(k) U^\dagger(k) \), and the Bogoliubov quasiparticle eigenvalues \( E_1 = -E_2 \) and \( E_3 = -E_4 \) are given by

\[ E_{m=1,3}(k) = \frac{1}{\sqrt{2}} \sqrt{\left( 2\epsilon_x + 2\epsilon_y + 2\Delta_1 + \Delta_2 \right)^2 + \left( \epsilon_x^2 - \epsilon_y^2 - \Delta_1^2 - \Delta_2^2 \right)^2 + 4\epsilon_{xy}^2 (\epsilon_x^2 + \epsilon_y^2 + (\Delta_1 - \Delta_2)^2)} \] (8)

where \( \epsilon_{x,y} = \epsilon_{x,y} - \mu \). The self-consistent gap and density equations are

\[ \Delta_1(k) = \sum_{k',m} V_{k,k'} U^*_{m,k'} U_{1m}(k') F(E_m(k')) \] (9)
\[ \Delta_2(k) = \sum_{k',m} V_{k,k'} U^*_{m,k'} U_{3m}(k') F(E_m(k')) \] (10)
\[ n_{1,2} = 2 \sum_{k',m} U^*_{m,1,3} U_{m,1,3} F(E_m(k')) \] (11)

where \( F(E) \) is the Fermi-Dirac distribution function, \( F(E) = \frac{1}{1 + e^{(E-E_F)/T}} \). To obtain the transition temperature, we linearize the self-consistent equation for small \( \Delta_1, \Delta_2. \) After tedious algebra, we find the self-consistent equations around \( T_c \)

\[ \Delta_2(k) = \sum_{k'} V_{k,k'} (W_3(k') - W_1(k')) \] (12)

where

\[ W_i = \frac{((\epsilon_x - \mu)^2 - \tilde{E}_i^2) \Delta_2 + c_{xy}^2 \Delta_1}{2|\epsilon_x + \epsilon_y - 2\mu|} \tan(\beta \tilde{E}_i/2) \]
\[ \tilde{E}_i = E_i(\Delta_1 = \Delta_2 = 0). \] (13)

FIG. 2: A three dimensional plot of the pairing weight \( W_3 - W_1 \) as a function of \((k_x, k_y)\) (electron doped) by setting \( \Delta_1 = \Delta_2 = 1 \) in Eq[13].

\( J_2 > J_{2c} \sim 1.2 \) has pure extended \( s\)-wave pairing symmetry \( s_{x^2+y^2} \) phase. The phase on the right side, where \( J_1 > J_{1c} \sim 1.05 \), is a mixture of \( d_{x^2-y^2} \) and \( s_{x^2+y^2} \). The remaining large part of phase diagram is described by a phase with mixed \( s_{x^2+y^2} \) and \( d_{x^2-y^2} \) pairing order parameters. This part of phase diagram is believed to describe the real material since the estimated values of \( J_2 \sim 0.5 \) and \( J_1 \sim \frac{1}{2} J_{1,2} \) are smaller than \( J_{1,2} \). In this mixed state, the signs of the \( d_{x^2-y^2} \) order parameters in the two orbitals are opposite. Namely, if \( \Delta_1 = a \cos(k_x) \cos(k_y) + b(\cos(k_x) - \cos(k_y)), \Delta_2 = a \cos(k_x) \cos(k_y) - b(\cos(k_x) - \cos(k_y)) \). Moreover, we do not find a \( d_{xy} \) solution in the entire parameter re-
The above results can be understood analytically. First, we can plot a pairing weight $W_3-W_1$ as a function of the Brillouin zone momentum $(k_x, k_y)$ (Fig.2) by taking $\Delta_2 = \Delta_1 = 1$ in Eq.13. The values of order parameters are determined by the pairing symmetry factor function times this quantity. The dominant contribution is clearly around $\Gamma$, $M$ and $(\pi, \pi)$. The $d_{xy}$ order, in which the pairing symmetry factor, $\sin k_x \sin k_y$, is peaked around $(\pm \pi/2, \pm \pi/2)$ has small overlap with the pairing weight and is not favored. Second, the mixing strength of two order parameters is determined by multiplying the two symmetry factors $(f_1, f_2)$ of two order parameters and the pairing weight: $\sum_k f_1(k)f_2(k)(W_3(k) - W_1(k))$. It is easy to check, for a mixture of $s_{x^2-y^2}$ and $d_{x^2-y^2}$, i.e. $f_1 = \cos k_x \cos k_y$, $f_2 = (\cos k_x - \cos k_y)$ that the summation has a large contribution from the Brillouin zone momentum around the electron pocket. The mixture strength of the other two order parameters $(s_{xy}$ and $s_{x^2+y^2})$ is very small. This explains why the phase diagram is dominated by the mixture of $s_{x^2-y^2}$ and $d_{x^2-y^2}$. Finally, the difference of the relative sign between the $s_{x^2-y^2}$ and $d_{x^2-y^2}$ order parameters in the two different orbitals is a result of the fact that exchanging $k_x$ to $k_y$ maps the $xz$ to the $yz$ orbital. The part of the phase diagram in Fig.3 with mixed $s_{x^2-y^2}$ and $d_{x^2-y^2}$ pairing becomes larger as the electron doping concentration is reduced: the mixing strength of $s_{x^2-y^2}$ and $d_{x^2-y^2}$ order parameters is (very slightly) increased due to the enhanced contribution around the M points. In Fig.3, we plot the transition temperature as a function of electron doping level at the fixed values of $J_1 = 0.25$ and $J_2 = 0.5$. On the electron-doped side, $T_c$ is reduced by increasing the doping concentration. This is similar to Ref.22 and it is, of course, around half filling, an artifact of the mean-field solution. The true ground state at half-filling is a spin-density wave which gives way to a superconductor as the filling is increased.

**Solutions including orbital crossing exchange coupling and Hunds coupling:** We now consider the orbital crossing exchange antiferromagnetic coupling, $J_{1:12}$, $J_{2:12}$ and Hunds coupling $J_H$. In mean field, we can decouple this interaction in the particle-particle channel. The orbital crossing exchange coupling can be decoupled in four spin-singlet orbital crossing pairing order parameters, $\Delta'(k) = \Delta_{s_{x^2-y^2}}(k) + \Delta_{d_{x^2-y^2}}(k) + \Delta_{x^2+y^2}(k) + \Delta_{y^2}(k)$. Hunds coupling can be decoupled to an on-site spin-triplet, orbital-singlet, order parameter, $\Delta_H = \sum_{i,j}\Psi_i(k)^\dagger B(k)\Psi_j(k)$, where $H'_m = \sum_k\Psi(k)^\dagger B(k)\Psi(k)$ with $B(k) = A(k) + \delta A(k)$.

$$\delta A(k) = \begin{pmatrix}
0 & 0 & 0 & \Delta' + \Delta_H \\
0 & 0 & \Delta' - \Delta_H & 0 \\
0 & \Delta' - \Delta_H & 0 & 0 \\
\Delta' + \Delta_H & 0 & 0 & 0
\end{pmatrix}$$

**Discussion and Summary** Preliminary experimental evidence suggests the presence of gapless nodal quasiparticle excitations in oxypnictides. Our model predicts a mixed intra-orbital order parameter $\Delta_{1,2} = \delta_1(\cos k_x \cos k_y) + \delta_2(\cos k_x - \cos k_y)$. In general, the mixed state is gapped, but with a very small gap. For a typical value of $\delta_1 = 0.2$ and $\delta_2 = 0.1$, the mixed state will have a gap of 0.025, which is around one fifth of the averaged superconducting gap in momentum space. The sign change of the $d$-wave order parameters between the two orbitals and the sign change of the $s$-wave order parameter between the hole pockets and the electron pockets are interesting features of this state. The sign change

\[ \text{FIG. 3: The pairing transition temperature as a function of the electron doping concentration at } J_1 = 0.25 \text{ and } J_2 = 0.5. \text{ The dashed line indicates the region where the SDW competing phase takes over from the superconducting phase.} \]
can generate new physics, such as new bound states\textsuperscript{27} formed by impurity scattering.

Although our prediction is based on a two-orbital model, we believe that the pairing symmetry predicted should be robust even if other orbitals are added. The pairing symmetry induced by the antiferromagnetic exchange coupling is mainly determined by the structure of Fermi surfaces. As the Fermi surfaces in oxypnictides are located at $\Gamma$ and $M$ points, the $d_{xy}$ pairing symmetry never wins over $s_{x^2-y^2}$. Moreover, we find that the inter-orbital pairing is small even if the orbital crossing exchange is strong.

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