Correlation-Enhanced Odd-Parity Interorbital Singlet Pairing in the Iron-Pnictide Superconductor LiFeAs

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(Received 22 June 2016; published 20 September 2016)

The rich variety of iron-based superconductors and their complex electronic structure lead to a wide range of possibilities for gap symmetry and pairing components. Here we solve in the two-Fe Brillouin zone the full frequency-dependent linearized Eliashberg equations to investigate spin-fluctuations mediated Cooper pairing for LiFeAs. The magnetic excitations are calculated with the random phase approximation on a correlated electronic structure obtained with density functional theory and dynamical mean field theory. The interaction between electrons through Hund’s coupling promotes both the intraorbital $d_{xz(yc)}$ and the interorbital magnetic susceptibility. As a consequence, the leading pairing channel, conventional $s^{++}$, acquires sizable interorbital $d_{xy} - d_{xz(yc)}$ singlet pairing with odd parity under glide-plane symmetry. The combination of intra- and interorbital components makes the results consistent with available experiments on the angular dependence of the gaps observed on the different Fermi surfaces.

Hence, here we revisit spin-fluctuation mediated pairing by considering both Fe-$3d$ and As-$4p$ orbitals in the two-Fe unit cell. We solve the linearized Eliashberg equations [27] in the two-Fe Brillouin Zone (BZ) to investigate SC pairing and gap symmetry. Since there is increasing evidence that superconductivity does not emerge as a FS instability [40], we work in the orbital representation instead of projecting the gap equation on the FSs. Our results show that in the leading channel, with the conventional $s^{++}$ symmetry, odd-parity interorbital pairing accompanies the usual intraorbital pairing and increases with interactions, in particular, with Hund’s coupling. In contrast to previous studies [8,11–13] we find that this state can reproduce the angular dependence of the gap on the electron pockets.

Electronic structure.—In LiFeAs, the bandwidth observed in ARPES is narrower than in LDA calculations and there are experimental evidences of long-lived magnetic moments [9]. This indicates the importance of correlations, so we employ the LDA + DMFT method to obtain the electronic structure [41–43]. Figure I illustrates the LDA + DMFT partial spectral weight, $A_{g}(k,0)$, of Fe $t_{2g}^{*}$ orbitals $d_{xy}$ and $d_{xz(yc)}$ on the FSs of LiFeAs [44]. The Fe $e_g$ orbitals $d_{z^2}$ and $d_{x^2-y^2}$ hybridize with As-$p$ orbitals and contribute to the spectral weight lying above and below the Fermi level. The FS consists of three holelike and two electronlike sheets around the center and corners of the BZ, respectively. The two inner hole pockets are predominantly composed of $d_{xz}$ and $d_{yz}$ orbitals. The smallest hole pocket crosses the Fermi level only in close vicinity to the $\Gamma$ point. It hybridizes with the $d_{z^2}$ orbital near the Z point and is closed there, while remaining two dimensions away from this point. The middle pocket has moderate $k_z$ dispersion.
The large holelike Fermi surface originates purely from in-plane $d_{xy}$ orbitals and therefore is two-dimensional without noticeable $k_z$ dispersion. The electron pockets are made from an admixture of $d_{xz}$, $d_{yz}$, and $d_{xy}$ orbitals. The electron pockets intersect at small $k_z$ and their order flips; i.e., the inner pocket at $k_z = 0$ is the outer pocket at $k_z = \pi/c$.

Comparison to LDA [27] shows that in LDA + DMFT (a) the two inner hole pockets shrink while the outer one expands. (b) The middle hole pocket also deforms and takes on a butterfly shape at small $k_z$ [45]. (c) At finite $k_z$, the outer hole pocket acquires some $d_{xz}$ and $d_{yz}$ orbital weight in the direction of the $A$ point. (d) The shrinkage of the two inner hole pockets leads to larger patches where $d_{xz}$ and $d_{yz}$ orbitals mix on these pockets. (e) The electron pockets are moderately expanded and they become closer to each other [27].

The $t_{2g}$ orbitals are the most strongly correlated [43,45] as is apparent from the mass enhancements $m^*/m_{\text{LDA}} = 2.0$, 1.85, 3.13, and 2.7 for $d_z^2$, $d_{z^2-x^2}$, $d_{xy}$, and $d_{x^2+y^2}$ orbitals, respectively. The $d_{xy}$ orbital has the strongest mass enhancement and shortest quasiparticle lifetime.

**Effective pairing interaction.**—A SC instability in the singlet channel occurs when the corresponding pairing susceptibility diverges as one lowers temperature. A divergent susceptibility signals the appearance of a pole in the corresponding reducible complex vertex function, which describes all scattering processes of two propagating particles. Using the Bethe-Salpeter equation, the condition for an instability is that an eigenvalue of the matrix $-\Gamma^{\text{irr},s} \chi^{\beta \beta}_{pp}$ becomes unity. Here $\Gamma^{\text{irr},s}$ is the irreducible vertex function (effective pairing interaction) in the singlet channel, and $\chi^{\beta \beta}_{pp}$ is the bare susceptibility in the particle-particle ($p-p$) channel [27,46,47].

The density and magnetic fluctuations contribute to the pairing interaction by entering the ladder vertex defined by $\Pi_{\text{ph}} \equiv -(1/2) \Gamma^{\text{irr},d} \chi^{\beta \beta}_{pp} \Gamma^{\text{irr},d} + (3/2) \Gamma^{\text{irr},m} \chi^{\beta \beta}_{pp} \Gamma^{\text{irr},m}$ where $\chi^{m(d)}$ and $\Gamma^{\text{irr},m(d)}$ denote respectively the dressed susceptibility and the irreducible vertex function in the magnetic (density) channel [27]. These vertices can be calculated in the DMFT approximation [48]. However, such a calculation is prohibitively difficult for multiorbital systems at the low temperatures necessary to study superconductivity [27]; hence, here we employ the random phase approximation (RPA) [49]. In the RPA, the irreducible vertex function is replaced by a static effective vertex that is parametrized by the screened intraorbital Hubbard interaction, $U_s$, and the Hund’s coupling $J_s$ [16,27,50,51]. The interorbital interaction and pair hopping are determined assuming spin-rotational symmetry. Note that even though the static effective vertices $U_s$ and $J_s$ capture Kanamori-Brückner screening effects, they do not fully capture the dynamics of screening. In particular, the RPA treatment misses the fact that at high fermionic frequencies one should recover the bare interactions.

Figure 2 shows the pairing interaction, $\Pi_{\text{ph}}$, at $k_B T = 0.01$ eV for two sets of screened interaction parameters that yield the same magnetic Stoner factor [52]. Here we only present the intrasublattice components because the inter-sublattice components are relatively small. In what follows, we focus on the Fe-1 and Fe-2 (on $A$ and $B$ sublattices, respectively) $t_{2g}$ orbitals: $d_{xy}$ is referred to as 2 (7) and $d_{xz}$ and $d_{yz}$ orbitals as 4 (9) and 5 (10). The dominant effective pairing interaction components are repulsive. As can be seen in Fig. 2(a), due to better nesting, the $d_{xy}$ intraorbital

![Figure 1](image1.png)

**FIG. 1.** Partial spectral weight, $A_H(k, \omega)$, of Fe $t_{2g}$- orbitals on the FS in the $k_x$-$k_y$ plane with $k_z = 0$ (left) and $k_z = \pi/c$ (right) obtained from the LDA + DMFT calculation. Here the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals are illustrated by green, blue, and red colors, respectively. The $\alpha_1$ pocket crosses the Fermi level only in close vicinity to the $\Gamma$ point (not visible on this scale).

![Figure 2](image2.png)

**FIG. 2.** Several components of the pairing interaction of LiFeAs at $k_B T = 0.01$ eV in the particle-hole channel. There are two sets of screened interaction parameters yielding the same magnetic Stoner factor, namely, $J_s = 0.1U_s$, $U_s = 2.4$ eV on the top and $J_s = 0.3U_s$, $U_s = 1.68$ eV on the bottom. The legend for the color coding is spread over both figures.
However, at larger $J_s/U_s$ the situation changes. For a fixed Stoner factor (proximity to magnetic transition) upon increasing the $J_s/U_s$ ratio from Fig. 2(a) to Fig. 2(b), the $d_{xy}$ intraorbital pairing component decreases while the $d_{xz}(yz)$ intraorbital components and the interorbital components increase slightly. This shows that a higher $J_s$ through coupling to the more correlated components. The $d_{xy}$ orbital ($44;44$) is subdominant, yet on average it is larger than interorbital vertices ($22;44$) and ($44;55$).

$\Delta_p$ pairing vertex is dominant and the $d_{xz}(yz)$ intraorbital ($44;44$) is subdominant, yet on average it is larger than interorbital vertices ($22;44$) and ($44;55$).

In the BCS approximation, only real parts survive for the components considered here, due to a summation over Matsubara frequencies. In this case, the interorbital pairing is suppressed. Including the imaginary part in the full gap equation changes this trend. The imaginary parts of the interorbital components change sign between the corner and center of the BZ. They have some symmetries that transfer to the gap function: (i) They are odd under exchange of orbital indices; i.e., there is also a $\pi$ phase difference between the two Fe ions (see Supplemental Material).

**SC pairing symmetry in LDA + DMFT + RPA.**—The leading pairing channel is a channel with dominant $d_{xy}$, $d_{xz}$, and $d_{yz}$ intraorbital pairing. In our gauge, the gap function components have both real and imaginary parts that satisfy

$$\text{Re} \Delta^{AA/BB}_{\nu} = -\text{Im} \Delta^{AA/BB}_{\nu}. $$

All intraorbital components change sign between the center and corner of the BZ (see Fig. 4), as expected in conventional $s^\pm$ pairing. The $d_{xy}$ intraorbital component dominates, but has a small value on the $\gamma$ pocket. The $d_{xz}$ and $d_{yz}$ intraorbital components are out of phase, i.e., $\Delta_{55}^{AA/BB} = -\Delta_{44}^{AA/BB}$ (not shown). They take large values on the $\alpha_{1,2}$ hole pockets. The intersublattice components are much smaller than intrasublattice ones, $\Delta^{AA/BB}_{aa} \gg \Delta^{AB/BA}_{aa}$. The largest intersublattice component is $\Delta_{BB}^{AA}$. In the orbital basis, the gap functions do not change much between $k_z = 0$ and $k_z = \pi/c$; hence, we present only $k_z = 0$ results. 

In agreement with the above pairing-interaction analysis, upon increasing $J_s/U_s$ the $d_{xz/yz}$ intraorbital pairing strengthens. Furthermore, the $d_{xy} - d_{xz}$ and $d_{xy} - d_{yz}$ interorbital pairings increase. Although they vary on a smaller interval, they are comparable with the $d_{xz/yz}$ intraorbital components on the electron FSs (compare Fig. 4's top and bottom panels).

We verify that the gap function components of the leading channel satisfy the relations $\Delta_{l_1l_2}^{AA/BB}(k, io_m) = \Delta_{l_1l_2}^{BB/AA}(-k, -io_m)$, and $\Delta_{l_1l_2}^{AA/BB}(k, io_m) = \Delta_{l_1l_2}^{BB/AA}(-k, -io_m)$ [55]. The first relation says that the superconducting state does not break parity: In LiFeAs the inversion center is located in the middle of Fe-Fe link. Under parity operation the sublattice $A$ maps to sublattice $B$ and vice versa and $k \rightarrow -k$. The components of the gap function also satisfy the relation $\Delta_{l_1l_2}^{AA/BB}(k_x, k_y, io_m) = p_{l_1} p_{l_2} \Delta_{l_1l_2}^{BB/AA}(k_x, k_y, io_m)$, where $p_{l_1}$ denotes the parity of orbital $l_1$ with respect to in-plane
mirror reflection symmetry [56]. This symmetry is defined by
in-plane mirror reflection followed by a half-translation,
expressed in units of the two-Fe unit cell, \( \{ \sigma^z | 1/2 \} \). Thus,
the intraorbital components on the two Fe are equal, while
the interorbital components between one even-parity (\( d_{xy} \)) and
one odd-parity (\( d_{xz} \)) orbital change sign between two Fe
ions. These components are the parity-odd under \( \{ \sigma^z | 1/2 \} \)
spin singlet pairings [26]. Furthermore, as can be seen from Fig. 4,
the in-plane intraorbital components satisfy
\( \Delta_{\alpha\beta}^{AA(BB)}(k_x, k_y) = \Delta_{\alpha\beta}^{AA(BB)}(-k_x, -k_y) \),
while the interorbital components between \( d_{xy} \) and \( d_{xz} \)
satisfy \( \Delta_{\alpha\beta}^{AA(BB)}(k_x, k_y) = -\Delta_{\alpha\beta}^{AA(BB)}(-k_x, -k_y) \)
and \( \Delta_{\alpha\beta}^{AA(BB)}(k_x, k_y) = -\Delta_{\alpha\beta}^{AA(BB)}(-k_x, -k_y) \).

Our calculations show that the gap symmetry of the
leading channel is conventional \( s^+ \). Indeed, although there
is a phase difference between the \( d_{xy} \) and \( d_{xz} \) components of
the gap function in the orbital basis, this phase difference is
removed by another phase difference that arises when
going to the Bloch basis corresponding to the \( \alpha_{1,2} \) pockets
[27]. In the subleading pairing channel, the \( d_{xy} \) intraorbital
component is in phase with \( d_{xz} \) and out of phase with \( d_{xz} \)
intraorbital components, which in the band representation
gives \( s^+ \) gap symmetry with a sign change between \( \alpha_{1,2} \)
and \( \gamma \) pockets and between electron pockets and accidental
nodes on the \( \beta_2 \) pocket [14].

Finally, we comment on the SC gap magnitude on
different FSs [57]. Diagonalizing the Bogoliubov quasiparticle
Hamiltonian leads to a gap magnitude that has
predominant \( \cos \theta \) angular dependence on all pockets, as
can be seen from Fig. 5. The angular dependence of the gap
on the \( \gamma \) and of the average gap on the \( \beta_{1,2} \) pockets is
consistent with ARPES data: The gap is maximum at
\( \theta = 0, \pi/2 \) and decreases when approaching \( \theta = \pi/4 \) (the
direction toward the \( M \) point) on the \( \gamma \) pocket, while the
average gap is maximum at \( \theta = \pi/4 \) (direction toward
the \( \Gamma \) point) on the \( \beta \) pockets and decreases when
approaching \( \theta = 0, \pi/2 \) where the two pockets cross.
The gap on the \( \beta_2 \) electron pocket is increased in the
direction of the \( \Gamma \) point due to a larger \( d_{xy} \) orbital content
with a large pairing amplitude (see Fig. 4, upper panels).
The gap on the \( \beta_1 \) electron pocket also shows a local
enhancement at \( \theta = \pi/4 \). Because of interchange of electron
pockets as a function of \( k_z \), the gap on the inner pocket
becomes larger than that on the outer pocket at a finite \( k_z \).
Hence, for these pockets, a direct comparison with ARPES
data has to take averaging over a range of \( k_z \) into account
[58]. The ratio between the average gap magnitude on the \( \beta \)
pockets and \( \gamma \) pocket is also consistent with ARPES results
[7,8]. However, the gap magnitude on the \( \alpha \) pockets is not
the largest. This discrepancy with ARPES results may
come from the fact that ARPES is performed at very low
temperature while the linearized Eliashberg gap equation is
valid at temperatures infinitesimally close to the transition
temperature. The tunneling spectroscopy study of LiFeAs
has shown a temperature evolution of superconductivity
[59]. A calculation at a lower temperature shows that the
sharp peaks in the 44 and 55 bare paring susceptibilities,
Fig. 3(a), grow faster than the wider peak for 22. This leads
to an increase of the gap on the \( \alpha \) pockets at lower
temperatures.

Conclusion.—Solving the full linearized Eliashberg gap
equation with both real and imaginary parts and including
correlations in the LDA + DMFT framework leads to a
detailed description of the leading pairing channel in
LiFeAs. Accounting for correlations in the spin-fluctuation
approach allows us to correctly capture not only nesting
effects but also Fe-\( d \) orbital fluctuating moments with
orbitally dependent dynamics. Although the intraorbital \( d_{xy} \)
spin susceptibility is dominant, Hund’s coupling between orbitals on individual Fe atoms promotes both the intraorbital $d_{x^2-y^2}$ component and the interorbital $d_{xy} - d_{x^2-y^2}$ components of the magnetic susceptibility. As a consequence, the leading pairing channel, conventional $s^+$, acquires an interorbital singlet pairing component with odd parity under glide-plane symmetry. This type of pairing may also be realized in other iron-based superconductors. Antiphase $s^+$ pairing [14] is subleading. The combination of interorbital odd-parity and intraorbital even-parity singlet pairing leads to a description of the angle dependence of the relative magnitudes of the gap on the $\beta$ and $\gamma$ Fermi surfaces that is consistent with state of the art experiments.

R. N. is deeply indebted to M. E. Pezzoli and F. Marsiglio for many insightful discussions. We thank K. Haule for his LDA + DMFT code and for discussions. R. N. and A.-M. S.T. are supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) under Grant No. RGPIN-2014-04584, by the Tier I Canada Research Chair Program, and by the Research Chair on the Theory of Quantum Materials (A.-M. S.T.). G.K. is supported by Grant No. NSF-DMR1308141. We acknowledge the hospitality of the CIFAR quantum materials program. Simulations were performed on computers provided by CFI, MELS, Calcul Québec, and Compute Canada.


[44] To keep a minimum variation of orbital content within a pocket, the electron pockets are chosen as inner and outer pockets $\beta_1$ and $\beta_2$ rather than as two crossed ellipselike pockets of equal size.


[52] The distance from magnetic and charge or orbital fluctuation criticality is determined by the corresponding (dimensionless) magnetic (density) Stoner factor $a_m^{\text{m(d)}}(i\nu_n)$, which is the largest eigenvalue of $\Gamma^{\text{m(r)},\text{ph}}(q, i\nu_n = 0) = -\Gamma^{\text{m(r)},\text{ph}}(q, i\nu_n = 0)]$.

[53] The 22;44 (44;55) components in the magnetic and charge susceptibilities in the $p$-$h$ channel are related to the 24;42 and 42;42 (45;54 and 54;54) components of the pairing interaction in the $p$-$p$ channel.


[55] The combination of these relations gives $\Delta_{\text{AA(BR)}}(k, i\nu_n) = \Delta_{\text{BB(AA)}}(k, -i\nu_n)$.

[56] The five Fe-3$d$ orbitals can be categorized into even orbital parity $(d_{3z^2}, d_{x^2−y^2}, d_{xz})$ with $p_l = +1$ and odd orbital parity $(dxz, d_{yz})$ with $p_l = −1$.

[57] The linearized Eliashberg gap equation only gives gap symmetry, not gap magnitude. But to make contact with experiment one can approximately extract the relative size of the gaps on the different FSs. This can be done by defining a Bogoliubov quasiparticle Hamiltonian including the real part of the self-energy at the Fermi level in the normal part, and employing the gap function obtained from the gap equation as an estimate of the anomalous self-energy [14]. After diagonalizing the Bogoliubov quasiparticle Hamiltonian, the gap magnitude at momentum $k$ is given by half of the difference between the smallest positive eigenvalue and the largest negative eigenvalue. This is the quasiparticle gap that reduces to the SC gap on the FSs. For this calculation, the gap function on a very dense $k$ mesh is required. Since the gap function is a smooth function, its magnitude on a denser mesh can be obtained by spline interpolation.
