g-wave pairing in BiS$_2$ superconductors

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Abstract – Recent angle-resolved photoemission spectroscopy (ARPES) experiments have suggested that BiS$_2$-based superconductors are at very low electron doping. Using random phase approximation (RPA) and functional renormalization group (FRG) methods, we find that g-wave pairing symmetry belonging to the $A_{2g}$ irreducible representation is dominant at electron doping $x < 0.25$. The pairing symmetry is determined by inter-pocket nesting and orbital characters on the Fermi surfaces and is robust in a two-orbital model including both Hund’s coupling $J$, and Hubbard-like Coulomb interactions $U$ and $U'$ with relatively small $J$ ($J \leq 0.2U$). With the increasing electron doping, the g-wave state competes with both the s-wave $A_{1g}$ and d-wave $B_{2g}$ states and no pairing symmetry emerges dominantly.

When electron-electron correlations are the driving force for pairing, unconventional pairing symmetries arise naturally. There have been quite a few theoretical studies about possible pairing symmetries in these new superconductors [19–22]. As the nominal compositions of the superconducting materials indicated high electron doping [3,11], all these previous studies concentrated on the high electron doping region where the electronic structure was featured with large Fermi surfaces (FS) at $\Gamma$ and $M$ points in the Broullioun zone (BZ) in close vicinity to Van Hove singularity. However, very recently, two ARPES groups have reported that there are only two small electron pockets around $X$ points [23,24] and the true electron fillings are much smaller than those expected from the nominal compositions.

In this paper, we investigate the pairing symmetry of BiS$_2$-based superconductors at low-doping level using random phase approximation (RPA) and functional renormalization group (FRG) methods. We find that the g-wave pairing state that belongs to the $A_{2g}$ irreducible representations of the lattice symmetry is dominant at electron doping $x < 0.25$ in a two-orbital model including both Hund’s coupling $J$, and Hubbard-like Coulomb interactions $U$ and $U'$ in the reasonable parameter region $J \leq 0.2U$. This robust pairing symmetry is determined by inter-pocket nesting and orbital characters on the FS. With the increase of $J$ or electron doping level, the g-wave

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loses its dominance and competes with other pairing symmetries. In both cases, there is no single dominant pairing wave. For example, with a large $J$, a $d$-wave ($B_{1g}$) is only slightly favored over a $s$-wave ($A_{1g}$) and the $g$-wave, and at high doping near the Lifshitz transition on which the previous studies concentrated, the $s$-wave and the other $d$-wave ($B_{2g}$) are almost equally favored. Due to the close competition between $s$-wave and $d$-wave, we speculate that superconductivity may not takes place at high electron doping. Our results, therefore, predict a new pairing symmetry for the BiS$_2$ superconductors. As the $g$-wave pairing state has a distinct nodal structure on FS, our prediction can be experimentally tested.

We adopt the two-band model, the tight binding Hamiltonian [12] is

\[ H_0 = \sum_{k\sigma} \Psi_{k\sigma}^\dagger T(k) \Psi_{k\sigma}, \]

![Image](39x388)  

where $\Psi_{k\sigma}^\dagger = (c_{Xk\sigma}^\dagger, c_{Yk\sigma}^\dagger)$ is the creation operator for spin $\sigma$ electrons in the two orbitals $p_X, p_Y$ and $c_{\alpha}(k)$, $\epsilon_X(k)$ and $\epsilon_Y(k)$ are the same as those defined in ref. [20]. As the observed electron doping is much less than those inferred from the nominal composition, we discuss the pairing properties based on FS before the Lifshitz transition. For the case after Lifshitz transition, RPA calculations have been done in ref. [21]. Figure 1(a) shows the FS electron pockets for four different electron fillings $x = 0.08, 0.14, 0.25$ and $0.45$. The corresponding bare spin susceptibilities are shown in fig. 1(b). There is a rectangle-shaped electron pocket centered at each X point for $x = 0.14$. Compared with experimental data [23,24], a smaller electron pocket at X point is absent because the real materials contain two BiS$_2$ layers but the model is based on a single BiS$_2$ layer and neglects the inter-layer coupling. The orbital characters on FS are shown in fig. 1(c), where the colors correspond to the dominant orbital weight (red for $p_X$ and green for $p_Y$). The two high peaks (in the blue dash-dotted line) at $q_1 = (0.62\pi, 0.62\pi)$ and $q_2 = (0.32\pi, 0.32\pi)$ correspond to inter- and intra-FS nesting, respectively. The broad peak at $(\pi, \pi)$, interpreted as inter-pocket nesting, resembles the FS nesting in iron-based superconductors [25]. The nesting wave vectors are shown in fig. 1(c). When interactions are introduced, the peaks at $q_1$ and $q_2$ in $\chi_0$ are the ones that diverge in the RPA spin susceptibility (fig. 1(d)). With the increasing of electron doping, $q_1$ moves to the right but $q_2$ moves to the left. Near the Lifshitz transition point ($x = 0.45$), the broad peak disappears and many peaks appear in $\chi_0$ due to the inter-pocket FS nesting. The RPA spin susceptibility diverges at certain $k$, indicating that the system is unstable to a long-range magnetic order. At low doping concentration ($x < 0.2$), the FS are rectangle-shaped. The orbital characters on FS and inter-pockets nesting clearly play a crucial role in determining the pairing symmetry.

![Image](39x388)  

The interaction part of Hamiltonian for this multi-orbital system is

\[ H_{\text{int}} = U \sum_{i\alpha} n_{i\alpha \uparrow} n_{i\alpha \downarrow} + U' \sum_{i\alpha < \beta} n_{i\alpha} n_{i\beta} \]

\[ + J \sum_{i, \alpha < \beta, \sigma \sigma'} c_{i\alpha \sigma}^\dagger c_{i\alpha \sigma'}^\dagger c_{i\beta \sigma'} c_{i\beta \sigma} \]

\[ + J' \sum_{i, \alpha \neq \beta} c_{i\alpha \uparrow}^\dagger c_{i\beta \downarrow} c_{i\beta \uparrow} c_{i\alpha \downarrow}, \]

where $n_{i\alpha} = n_{i\alpha \uparrow} + n_{i\alpha \downarrow}$. Here we adopt the parameter notations given in ref. [26]. The effective interaction obtained in the RPA approximation is

\[ V_{\text{eff}} = \sum_{ij, kk'} \Gamma_{ij}(k, k') c_{ik\sigma}^\dagger c_{jk\sigma}\mathcal{C}_{i-k-k'} \]

where the momenta $k$ and $k'$ are restricted to different FS $C_i$ with $k \in C_i$ and $k' \in C_j$ and $\Gamma_{ij}(k, k')$ is the pairing scattering vertex in the singlet channel [26]. The pairing vertex is

\[ \Gamma_{ij}(k, k') = R \epsilon \left[ \sum_{l \neq i, l \neq j} a_{li}^{(2)\ast}(k)a_{lj}^{\ast}(-k) \right. \]

\[ \times \Gamma_{li, li'}(k, k', \omega = 0) a_{li'}^{(1)}(k') a_{lj}^{\ast}(-k'), \]

where $a_{li}^{(l)}$ (orbital index $l$ and band index $v$) is the component of the eigenvectors from the diagonalization of the tight binding Hamiltonian. The orbital vertex function
\( \Gamma_{1s2l3l4} \) in the fluctuation exchange formulation [26–28] are given by
\[
\Gamma_{1s2l3l4}(k, k', \omega) = \left[ \frac{3}{2} \hat{U}^s \chi^{RPA}_{1s2l3l4}(k - k', \omega)\hat{U}^s + \frac{1}{2} \hat{U}^c \right]_{1s2l3l4}.
\]

The \( \hat{U}^s \) is the spin interaction matrix and the \( \hat{U}^c \) the charge spin interaction matrix, defined in ref. [26]. The \( \chi^{RPA}_{1s2l3l4} \) describes the charge fluctuation contribution and the \( \chi^{RPA}_{1s2l3l4} \) the spin fluctuation contribution. For a given gap function \( g(k) \), the pairing strength functional is
\[
\lambda(g(k)) = \frac{\sum_{ij} \int d\omega \frac{dC_{ij}}{v_F(k)} \chi_{ij}(k,k')g(k)g(k')}{4\pi^2 \sum_{ij} \int d\omega \frac{dC_{ij}}{v_F(k)}|g(k)|^2},
\]
where \( v_F(k) = |\nabla_k E_i(k)| \) is the Fermi velocity on a given Fermi surface sheet \( C_i \). \( g(k) \) is determined as the station solution of eq. (6). The obtained gap function should have the symmetry of one of the irreducible representations of the corresponding point group. Although the point group for the BiS\(_2\) layer is \( D_{4h} \), the point group symmetry in our effective model is \( C_{4v} \). We consider one-dimensional irreducible representations \( A_{1g}, A_{2g}, B_{1g} \) and \( B_{2g} \). We perform calculations in the spin-rotational invariance case, where \( U' = U - 2J \) and \( J = J' \). The typical temperature \( T = 0.02 \) is used and \( \eta = 0.005 \) is adopted to regularize the Green’s functions. All the summations over the Brillouin Zone are performed with uniform \( 200 \times 200 \) meshes.

First, we consider the case where Hund’s rule coupling is negligible compared with the intra-orbital Coulomb interaction. Figure 2(a) shows the pairing strength eigenvalues for the four leading eigenvalues as a function of \( U \) at the electron doping \( x = 0.14 \). We find that the dominant gap function has the symmetry \( A_{1g} \) and the order parameter of this state is shown in fig. 2(b) for \( U = 2.5 \). This pairing symmetry is \( g \)-wave, which changes sign 8 times in a \( 2\pi \) rotation. This state is odd over all the mirror reflections \((x, y) \) and diagonal reflections. Therefore, nodes appear in the \( k_x/k_y = 0, \pi \) lines. There is also a sign change within FS sheets. Figure 2(c) shows the subdominant gap function which has \( A_{1g} \) symmetry. This extended s-wave state features a sign change and an anisotropic gap distribution on the FS sheets. We can calculate the contributions of intra-sheet and inter-sheet scattering processes for the two leading pairing states separately. We find that the intra-sheet process contributes negatively to the \( g \)-wave state while inter-sheet process contributes positively. Both of them show rapid increase with the increasing of \( U \). As the inter-sheet scattering always overcomes the intra-sheet scattering, the \( A_{2g} \) is stable. The contribution of both intra-sheet and inter-sheet processes are positive for the \( A_{1g} \) s-wave. The strong inter-pocket nesting results in a sign change of the superconducting order between the green \( px \) (red \( py \)) regions on the two electron pockets shown in fig. 1(c). This is the essential reason why the \( g \)-wave symmetry is more stable than the \( s \)-wave with the increasing of \( U \).

Second, we consider the effect of Hund’s coupling on the pairing symmetry. Figure 2(d) shows the pairing strength \( \lambda \) for the four leading eigenvalues as a function of \( J \) with \( U = 2.5 \) and \( x = 0.14 \). The figure shows that \( J \) has a significant effect on the \( g \)-wave state but a negligible effect on the \( s \)-wave state. Around \( J \sim 0.55 \), the \( g \)-wave pairing and a \( B_{1g}(d_{x^2-y^2}) \) pairing become equally favored. The \( d \)-wave pairing state (not shown) is quite similar to that shown in fig. 3(b). There is no sign change on the same pocket but a sign change between the two pockets. Due to the enhancement of inter-orbital scattering with the increasing of \( J \), both intra- and inter-orbital scattering in the inter-pocket processes become important. Then, the system favors a gap with a sign change between the FS sheets. Consequently, the gap with symmetry \( d_{x^2-y^2} \) is favored. However, as shown in fig. 2(d), the pairing strength eigenvalues of the four leading state are very close to each other, indicating the intense competition between those states.
When the electron filling is less than 0.14, we find the g-wave state is always strongly favored if $J$ is relative small. With the increasing of electron doping, the pockets enlarge and the shapes deviate from rectangle. The inter-pocket nesting becomes weaker while the intra-pocket nesting becomes stronger, which greatly affects the pairing strength of the g-wave pairing. In fact, we find that the g-wave and the $d_{x^2-y^2}$-wave ($B_{1g}$) are almost equally favored at $x = 0.25$ when $U = 1.75$ and $J = 0.17$. The two leading gap functions are shown in fig. 3. Near the Lifshitz transition point ($x = 0.45$), the two leading states are the s-wave $A_{1g}$ and the d-wave $B_{2g}$, shown in fig. 4. The symmetries of the two leading gaps are the same as those at higher electron doping (after Lifshitz transition), studied in ref. [21]. Nevertheless, there are always strong competitions among multi-pairing channels at high electron doping. There is no obviously leading pairing symmetry.

We use FRG calculations to justify the above RPA results. The FRG approach is described in ref. [29,30]. Each electron pocket is discretized into 128 patches. With $U = 2.5$ and $J = 0.25$, we find a very weak pairing divergence for electron-doped system ($x = 0.14$), shown in fig. 5. Although there is no instability in FRG flow, the calculation can still tell us that g-wave $A_{2g}$ state is more likely to be developed than s-wave $A_{1g}$ state, which is consistent with the results of RPA. The pairing form factors of the two channels are shown in fig. 6(a) and (b), which are quite similar to the corresponding gaps obtained from RPA. The FRG result shows that the pairing strength of the g-wave state become weaker with the increasing of $J$ but it is always the leading one for $J < 0.5$. We also perform calculation with larger $U$ and find that the g-wave state is always the leading one if $J/U < 0.2$. When $J/U > 0.2$, the leading pairing symmetry becomes the $d_{x^2-y^2}$-wave ($B_{1g}$ state). The g-wave state is robust in a wide range of electron doping before the Lifshitz transition if $J$ is relative small. However, the leading pairing symmetry becomes the s-wave $A_{1g}$ close to the Lifshitz transition point. The subleading pairing symmetry is the $d_{x^2-y^2}$-wave, which slightly differs from the one obtained by RPA calculations.

As Hund’s coupling is relatively weak, the g-wave is robustly favored for BiS$_2$ superconductors at low doping. The superconducting gap is quite similar to that of g-wave state proposed for cuprate [31]. In fact, the low-doping region is the only region that a single g-wave pairing can stand out. If one checks the pairing symmetry near Lifshitz transitions, all results show that no pairing symmetry is clearly favored [21]. In the high-doping region, two degenerate $A_{1g}$ and $B_{2g}$ states compete with each other.
in the RPA calculation. A similar \( A_{1g} \) state is obtained but no competing \( B_{2g} \) state in ref. [20], where the strong-coupling \( t-J \) model is adopted. This indicates \( B_{2g} \) state is suppressed with the increasing of the interaction. As our calculations mainly focus on the experimental low doping levels, the pairing symmetry is different from the previous studies that focus on relative high doping levels [12,21,22]. Actually, near the Lifshitz transition point, the obtained pairing symmetry is consistent with that of ref. [21].

In the above calculation, we do not consider spin orbital coupling in Bi. Due to the absence of \( p_{z} \)-orbitals, the spin orbital coupling does not involve spin-flips and spin is still a good quantum number. The spin orbital coupling has little effect on the topology of FSs and the distribution of orbital characters on FSs. Therefore, we should expect that spin orbital coupling has little effect on the pairing symmetry in BiS\(_{2}\) superconductors.

Can we find other materials with \( g \)-wave pairing symmetry? Like the high-\( T_{c} \) materials, we consider materials containing \( d \)-orbitals. The correlation effect in \( d \)-orbitals is much stronger than that of \( p \)-orbital. We consider a material where the states near the Fermi level are mainly contributed by \( d_{x^{2}-y^{2}} \) and \( d_{xy} \)-orbitals due to the crystal field splitting. The Fermi surfaces and orbital characters (\( d_{x^{2}-y^{2}} \sim p_{x} \), \( d_{xy} \sim p_{y} \)) are similar to those in fig. 1(c), where electron or hole pockets are around the \( X \) point. If this system becomes superconducting, the pairing symmetry may be \( g \)-wave. This can help us to find \( g \)-wave superconducting materials.

The \( g \)-wave pairing state can be easily justified or falsified by experiments. The most distinct feature is the symmetry protected nodes on Fermi surfaces as shown fig. 2(b). There are 8 nodal points on Fermi surfaces. The high resolution ARPES can directly probe the nodal structure. Physical properties related to low energy excitations, such as thermal conductivity, spin relaxation and penetration depth, should be very similar to the \( d \)-wave state in cuprates.

In summary, we have studied the pairing properties of BiS\(_{2}\)-based superconductors at low electron doping level using RPA and FRG methods. Our calculations suggest that a \( g \)-wave (\( A_{2g} \)) state is dominant at electron doping \( x < 0.25 \) when Hund’s rule coupling is relatively small compared with intra-orbital Coulomb interactions (\( J \leq 0.2U \)). The \( g \)-wave state can be falsified by its distinctive nodal structures. A proof of the \( g \)-wave will not only crown BiS\(_{2}\) as the first superconductor with the \( g \)-wave pairing, but also shed light on the mechanism of unconventional superconductors.

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