Time-Reversal-Invariant Topological Superconductivity in n-type Doped BiH

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Intrinsic and symmetry protected topological states have attracted lots of interest in condensed matter physics recently. In particular, time reversal symmetry protected fermion topological insulators have been theoretically predicted and experimentally verified. However despite considerable experimental and theoretical works, definitive evidence for time reversal invariant (TRI) topological superconductivity is still lacking. Here we propose that upon electron doping the hydrogenated single bilayer Bi, namely BiH, will exhibit time reversal invariant topological superconductivity. If confirmed experimentally this material will constitute the first example of TRI topological superconductor.

A schematic representation of the optimized crystal structure for the bilayer BiH is shown in Figure 1(a). The bilayer of Bi atoms form a buckled honeycomb lattice, with sublattice A and B hydrogenated from above and below, respectively. The point group is $D_{3d}$ which possesses the inversion symmetry. The band structure is shown in Figure 1(b), from which one finds that the main component near the Fermi energy consists of the $p_x$ and $p_y$ orbitals of Bi, as its $p_z$ orbital bounds with hydrogen and thus only contributes to bands far away from the Fermi energy. On the experimental side the Bi(111) bilayer has been synthesized recently. It can be used as a starting template to fabricate the BiH studied here.

Based on the above crystal structures, we construct the following $p_x,y$-orbital tight-binding model to describe the low energy band structure of the Bi bilayer. The hopping integral $t_{\mu j, j^\prime}$ can be obtained from the Slater-Koster formula

$$H_0 = \sum_{\langle i,j \rangle, \sigma} t_{\mu j, j^\prime} c_{\mu i \sigma} d_{\mu j^\prime \sigma} - \lambda \sum_i c_{\mu, \sigma}^\dagger c_{\mu, -\sigma},$$

(1)

Here $i,j$ label the sites of the honeycomb lattice and $\mu/\nu = x,y$ designate the $p_x$ and $p_y$ orbitals. The hopping integral $t_{\mu j, j^\prime}$ denotes the angle from the $\mu$ direction to $j-j'$.

In Figure 1(d) we plot the band structure of Eq. 1. A direct band gap $\sim 1.2$ eV opens at the $K$-points due to the large on-site SOC. This gap pushes the conduction band minimum at $K$ above that at $\Gamma$ resulting in an indirect band gap. The above bandstructure captures all main features of the first principle results and is characteristic of all Bi-Hydride/Halide compounds. It turns out that the above bandstructure describes a quantum spin Hall (QSH) insulator. In Figure 1(e) we show the in-gap helical edge modes along the “zigzag” edges of the buckled honeycomb lattice.

Upon p-type doping, hole-pockets appear around the $K$-points, as shown in Figure 1(f) (for 5% doping). Upon n-type doping, an electron-pocket first appears around $\Gamma$ as shown in Figure 1(g) (for 4% doping). For larger n-type doping additional electron pockets appear around the $K$-points as shown in Fig. 1(h) (for 10%-doping).

To describe doped BiH it is important to take the electron correlation into account. We model the electron correlation by the intra and inter-orbital Coulomb repulsion $U,V$ and the Hund’s coupling $J_H$. These parameters are obtained from constrained density functional theory calculations (see Supplementary Information 2). The total Hamiltonian reads

$$H = H_0 + H_1,$$

(3)

$$H_1 = \sum_i \left\{ U \sum_{\sigma\sigma'} c_{i\sigma}^\dagger c_{i\sigma'}^\dagger c_{i\sigma} c_{i\sigma'} + V \sum_{\sigma} c_{i\sigma}^\dagger c_{i\sigma} + J_H \sum_{\sigma\sigma'} c_{i\sigma}^\dagger c_{i\sigma}^\dagger + h.c. \right\},$$

(4)

where the usual symmetry argument requires $U = V + 2J_H$. For BiH, our first principle calculation (Supplementary Information 2) yields the following estimates of the interaction parameters: $U = 1.16eV, V = 0.24eV, J_H = 0.46eV$. Upon doping, Eq. 4 is the starting point of our mean-field Cooper pairing analysis.

Due to the absence of Fermi surface (FS) nesting and the relatively weak electron correlation we expect superconducting pairing to be the primary electronic instability. We classify the pairing symmetry according to the transformation property of the gap function under the

$$t_{\mu j, j^\prime} = t_{\sigma} \cos \theta_{\mu, ij} \cos \theta_{\nu, ij^\prime} + t_{\Delta} \sin \theta_{\mu, ij} \sin \theta_{\nu, ij^\prime}.$$

(2)

where $\theta_{\mu, ij}$ denotes the angle from the $\mu$ direction to $j-j'$. The last term in Eq. 1 is the only symmetry allowed on-site spin-orbit coupling (SOC), where $\tau$ and $s$ are the orbital and spin Pauli matrices, respectively. In the following, we shall use $t_{NN} = -0.45t_{NN}$ (see Figure 1(c)) and $t_{NN}^{\dagger} = 0, t_{NN}^{\dagger} = -0.15t_{NN}^{\dagger}, \lambda = 0.35t_{NN}^{\dagger}$ (for more details see Supplementary Information 1). Here (NN) and (NNN) denote the nearest-neighbor and next-nearest-neighbor respectively.
TABLE I. The Cooper pair operators associated with seven different pairing symmetries. Here \( \epsilon_{\alpha \mu} \) annihilates an electron with sublattice index \( \alpha = (A,B) \), orbital index \( \mu = (x,y) \) and spin index \( \sigma = (\uparrow, \downarrow) \). The sign \( \epsilon_{\alpha} \) is equal to 1(-1) for sublattice-\( A(B) \), respectively.

| symmetry | pairing operator |
|----------|-----------------|
| \( s \) | \[ \sum_{\alpha} \left[ c_{\alpha x \uparrow} c_{\alpha y \downarrow} + c_{\alpha x \downarrow} c_{\alpha y \uparrow} + \beta \sum_{\mu} c_{\alpha \mu \uparrow} c_{\alpha \mu \downarrow} \right] \] |
| \( d_{xy} \) | \[ \sum_{\alpha} \left[ c_{\alpha x \uparrow} c_{\alpha y \downarrow} - c_{\alpha x \downarrow} c_{\alpha y \uparrow} \right] \] |
| \( f \) | \[ \sum_{\alpha} \epsilon_{\alpha} \left[ c_{\alpha x \uparrow} c_{\alpha y \downarrow} + c_{\alpha x \downarrow} c_{\alpha y \uparrow} + \beta \sum_{\mu} c_{\alpha \mu \uparrow} c_{\alpha \mu \downarrow} \right] \] |
| \( p_{x} \) | \[ \sum_{\alpha} \epsilon_{\alpha} \left[ c_{\alpha x \uparrow} c_{\alpha y \downarrow} - c_{\alpha x \downarrow} c_{\alpha y \uparrow} \right] \] |
| \( p_{y} \) | \[ \sum_{\alpha} \epsilon_{\alpha} \left[ c_{\alpha x \uparrow} c_{\alpha y \downarrow} + c_{\alpha x \downarrow} c_{\alpha y \uparrow} \right] \] |
| \( (p \pm ip')_{\uparrow\uparrow\downarrow\downarrow} \) | \[ \sum_{\alpha} \epsilon_{\alpha} c_{\alpha x \uparrow} c_{\alpha y \downarrow} \] |

The result of our mean-field analysis (see Supplementary Information 4) shows that for \( J_H > \frac{U}{\delta} \) (which is equivalent to \( J_H > V \) upon using the relation \( V = U - 2J_H \)) and for doping concentration < 10%, the leading pairing instability is the interorbital equal spin, \((p \pm ip')_{\uparrow\uparrow}\) and \((p \pm ip')_{\downarrow\downarrow}\) pairing (henceforth abbreviated as \((p \pm ip')_{\uparrow\uparrow\downarrow\downarrow}\)). This is listed in the 7th row of Table 1.

The real space gap function for the \((\uparrow\uparrow)\) pairing is shown in Figure 2(a). The real and imaginary part of the same gap function plotted around the FS (for \( \delta = 0.04 \)) are shown in Figure 2(b) and Figure 2(c), respectively. From Figure 2(b,c) it is apparent that the real (imaginary) part of the gap function has the \( p_{x} (p_{y}) \) symmetry. The momentum space \( \downarrow\downarrow\) gap function is the complex conjugate of that for \((\uparrow\uparrow)\) so that TR symmetry is respected.

The doping-dependence of the eigenvalue \((r)\) of the linearized gap equation \((r)\) is related to \( T_{c} \) via \( T_{c} \sim \text{cutoff energy} e^{-1/r} \) (see Supplementary Information 4) for various pairing symmetries is shown in Figure 3(a). The interaction parameter used to construct this figure is \( J_H = 0.4U \) (\( V = U - 2J_H \)) appropriate for BiH. From this figure it is apparent that \((p \pm ip')_{\uparrow\uparrow\downarrow\downarrow}\) is the leading pairing symmetry for doping < 10%. In the phase-diagram shown in Figure 3(c), we determine the leading pairing symmetry as a function of \( J_H/U \) and doping level \( \delta \). The result shows \((p \pm ip')_{\uparrow\uparrow\downarrow\downarrow}\) pairing is realized for low doping and \( U > J_H > U/3\). We emphasize that SOC plays a crucial role in stabilizing the \((p \pm ip')_{\uparrow\uparrow\downarrow\downarrow}\) pairing. When the SOC parameter \( \lambda \) is set to zero, the leading pairing symmetry becomes \( f\)-wave (shown in Figure 2(d)).

In the \((p \pm ip')_{\uparrow\uparrow\downarrow\downarrow}\) superconducting state there are gapless helical Majorana edge modes (marked by “A” in Figure 4(a) for the “zigzag” edge of the 4% n-type doped system). The gapless modes centered at large momenta, marked by “B”, are the remnant of the complex fermion helical edge modes of the QSH insulator. Such edge modes can not participate in the \((p \pm ip')_{\uparrow\uparrow\downarrow\downarrow}\) pairing because the partners of a Cooper pair are localized on opposite edges. Since the pairing interactions in Eq. (5) and Eq. (6) are completely local, such distant pairing can not occur. Thus we have an interesting situation where the edge modes of the \((p \pm ip')_{\uparrow\uparrow\downarrow\downarrow}\) superconductor are composed of the complex fermion edge modes of the parent QSH insulator and the superconducting helical Majorana edge modes. By degree of freedom counting these amount to five Majorana fermion modes per edge which can not be gapped out by TRI perturbations.

**Discussion:** In addition to the electron-electron interaction, phonon can play a substantial role in Cooper pairing, especially for weakly correlated materials. In general phonon mediates additional attractive interaction which can reduce the value of \( U \) and \( V \) in the preceding discussions. When such extra attraction is weak so that \( U \) is still positive \((V \) can have either sign), the main effect is to increase the \( J_H/U \) ratio. In Figure 3(b), the dop-
ing dependence of the pairing eigenvalue $r$ for the three leading pairing symmetries is shown for, e.g., $J_R = 0.7U$ and $V = -0.4U$. The result shows $(p \pm ip')^{\uparrow\downarrow,\downarrow\downarrow}$ remains the leading pairing symmetry. The only difference is the $T_c$ enhancement. Thus $(p \pm ip')^{\uparrow\downarrow,\downarrow\downarrow}$ can survive weak phonon-mediated attractive interaction. Finally, we discuss the effect of the inevitable inversion symmetry breaking caused by doping. Such breaking of symmetry will induce the Rashba SOC in the Hamiltonian. In Figure 4(b) we show the weak phonon-mediated attractive interaction. Finally, we predict the edge modes of such superconductors.

We believe the physics discussed here can also occur in other bilayer Bi-Hydride/Halide compounds.

In conclusion by combining first principle and mean-field calculations, we predict a single bilayer of hydrogenated Bismuth, BiH, to be a TRI topological superconductor. Moreover we predict the edge modes of such superconductor consist of a pair of helical Majorana fermion and two pairs of helical complex fermion edge modes. We believe the physics discussed here can also occur in other bilayer Bi-Hydride/Halide compounds.

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Authors Contribution: Fan Yang and Yugui Yao independently proposed to determine the pairing symmetry in BiH, they contribute to this paper equally. Dung-Hai Lee advised the research and wrote most of the paper. Other authors have significantly contributed to the calculations and data analysis that went into the paper.

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FIG. 1. (color online). (a) The structure of hydrogenated single bilayer Bismuth, BiH. Upper panel: top view and lower panel: side view. The Bi atoms in each layer form a sublattice of the buckled honeycomb lattice. The Bi-atoms in the upper/lower layer are bonded by hydrogens from above/below. This structure is also applicable for the Bismuth Halide compounds. (b) The band structure of the BiH single bilayer. The size of the symbols is proportional to the weight of the band eigenfunctions on different atomic orbitals (color coded). For undoped compound the Fermi level is set to zero. (c) The arrangement of the $p_x$ and $p_y$ orbitals in a hexagonal plaquette, and the $\sigma$ and $\pi$ bonds between them. (d) A comparison of the band structures in the presence of SOC for BiH calculated using the first principle (black dotted curve) and the tight binding methods (red solid curve). The tight binding parameters are given in Supplementary Information 1. (e) The edge spectrum (for the "zigzag" edges) computed using the tight-binding model. (f)-(h) The Fermi pockets for 5% hole doping (f) and 4%, 10% ((g) and (h)) electron doping respectively.

FIG. 2. (color online). (a) The $(p + ip')_{\uparrow\uparrow}$ gap function in real-space. The real (b) and imaginary (c) parts of the $(p + ip')_{\uparrow\uparrow}$ gap function and the $f$-wave gap function (d), for 4% electron doping, plotted around the FS.
FIG. 3. (color online). Doping-dependence of the pairing eigenvalue $r$ over $U/t_{NN}^\sigma$ for several leading pairing symmetries. (a) $J_H = 0.4U > 0$, (b) $J_H = 0.7U > 0$. (c). The phase-diagram for positive $U$.

FIG. 4. (color online). (a) The edge spectrum (for the "zigzag" edges) for the $(p\pm ip')_{\uparrow\uparrow,\downarrow\downarrow}$ superconducting state at 4%-doping. The in-gap states marked by “A” are helical Majorana modes. The in-gap states marked by “B” are helical complex fermion modes. They are the remnant of the edge modes of the parent QSH insulator. (b) The leading gap function on the Rashba-split Fermi surfaces for 4% electron doping. (The Rashba interaction used to construct this figure is $\lambda_R = 0.08t_{NN}^\sigma$).
Supplementary Information

The tight-binding parameters

A low energy four band tight binding Hamiltonian with the on-site SOC interaction is given by Eq.(1) of the main text. The Slater-Koster tight-binding (TB) parameters \[1\] are obtained by least square fitting the tight binding bandstructure to that obtained from the first principle calculation\[2\]. By including up to the next-nearest-neighbor (NNN) hoppings, our tight-binding model reproduces the first principle energy bands fairly well. This is shown in Figure 1(d) of the main text. Similarly, we obtain the Slater-Koster parameters for the Bi-Halide bilayer. The tight-binding parameters in units of \(t_{\text{NN}}^\sigma\) for the bilayer BiH and other Bi Halide are listed in Table I.

The estimates of the Interaction parameters

The interaction parameter \(J_H\)

Because the solid state screening of the Slater integrals \(F^2\) and \(F^4\) is usually small, we estimate the Hund’s coupling \(J_H\) by taking the atomic limit. For this purpose, we construct four simple cubic lattices composed purely of the Bi atoms with large lattice constants of 10, 20, 40, and 80. The full potential nonorthogonal local orbital (FPLO) code \[3,4\] within both local density approximation (LDA) and generalized gradient approximation(GGA) are employed to calculate the difference of the total energies between two magnetic states with different total Bi moment (1\(\mu_B\) and 3\(\mu_B\)) for each artificial crystal discussed above. When the total moment is 3\(\mu_B\), the spins of the three electrons in the 6p orbitals of each Bi atom are aligned. In contrast, when the total moment is 1\(\mu_B\), one of the three electrons has spin opposite to the other two. Assuming the above energy difference is due to the Hund’s rule interaction, namely, \(J_H = (E(m = 1) − E(m = 3))/2\), we obtain the results shown in Table II. From Table II it is clear that the obtained \(J_H\) has little dependence on the lattice parameters of the artificial crystal.

The interaction parameter \(U\)

Constrained LDA and GGA calculations \[5, 6\] implemented in the Wien2k code are carried out to estimate the screened Coulomb integral \(F_{\text{eff}}^0 = U − J_H\) \[5, 6\], which corresponds to the difference between the electron affinity and the ionization energy upon adding and removing an electron in the valence shell of a given atom. Such constrained LDA and GGA approaches are based on the observation that the energy of a system with increased or reduced particle number is in principle computable within density functional theory. \(F_{\text{eff}}^0\) is then defined as the derivative of the total energy with respect to the constrained occupation number on a given shell. Moreover, in order to avoid double counting of the hopping matrix elements in the calculation of \(F_{\text{eff}}^0\), one has to construct a supercell and set one of the atom as an impurity where hopping to the rest of the system is suppressed.

In our calculations, we constructed a superlattice which consists of \(2 \times 2 \times 1\) supercell where 8 Bi ions and 8 H ion are included. One of the Bi ion is set as the impurity where two 6p electrons are constrained to the core state to avoid the hopping to the rest of the system.

The results are shown in Table III.

Pairing symmetry

The point-group symmetry of the system includes the following operations: the inversion \(\hat{I}\), the reflection \(\hat{R}_{x,y}\) about the \(x\)- or \(y\)-axes (here the \(x, y\)-axes are shown in Figure 1(c) of the main text), and the rotation \(\hat{R}(\theta)\) about the \(z\)-axis with the angle \(\theta = \pm \frac{\pi}{3}, \pm \frac{2\pi}{3}\). Note that in the real material, the point-group is \(D_{3d}\) instead of \(D_{6h}\), because the material is buckled and the A and B sublattices locate in different planes. In this point-group, an extra \(xy\) plane mirror reflection should be added to the \(\hat{R}_y\) reflection and the \(\pm \frac{\pi}{3}\) rotations since these operations change the sublattice index of a lattice site. Thus in the definition of the point-group operations below, we have added the extra \(xy\) plane mirror reflection where it is needed. Under these operations, an electron operator \(c_{a\mu\sigma}\) (with \(a, \mu, \sigma\) labeling
TABLE I. The parameters $t_{\sigma}^{NN}$ (in unit of eV) as well as the ratios $t_{\sigma}^{NN}/t_{\sigma}^{NN}$, $t_{\sigma}^{NN}/t_{\sigma}^{NN}$, $t_{\sigma}^{NN}/t_{\sigma}^{NN}$, and $\lambda/t_{\sigma}^{NN}$ for the 2D Bi-Hydride/Halide bilayer family, which are obtained by fitting with the FP calculations. Note that $\lambda = E_g/2$, with $E_g$ to be the gap opened by SOC at the Dirac points.

| System | $t_{\sigma}^{NN}$ (eV) | $t_{\sigma}^{NN}/t_{\sigma}^{NN}$ | $t_{\sigma}^{NN}/t_{\sigma}^{NN}$ | $t_{\sigma}^{NN}/t_{\sigma}^{NN}$ | $\lambda/t_{\sigma}^{NN}$ |
|--------|----------------------|--------------------------|--------------------------|--------------------------|----------------------|
| BiH    | 1.79                 | -0.45                    | 0.04                     | -0.15                    | 0.35                 |
| BiF    | 1.51                 | -0.36                    | 0.15                     | -0.13                    | 0.36                 |
| BiCl   | 1.43                 | -0.39                    | 0.10                     | -0.13                    | 0.39                 |
| BiBr   | 1.39                 | -0.40                    | 0.09                     | -0.11                    | 0.48                 |
| BiI    | 1.31                 | -0.44                    | 0.08                     | -0.10                    | 0.50                 |

TABLE II. The Hund’s coupling $J_H$ of 6p orbital of Bi atom in a simple cubic lattice with large lattice constant. $J_H$ is estimated from the energy difference between two magnetic states with magnetic moments of $m = 1$ and $m = 3$. The groundstate energies of the magnetically ordered states are obtained from first principles calculations by FPLO code. Both LDA and GGA are used for comparison.

| $a()$ | $J_{H}^{LDA}$ (eV) | $J_{H}^{GGA}$ (eV) |
|-------|------------------|------------------|
| 80    | 0.455            | 0.563            |
| 40    | 0.455            | 0.562            |
| 20    | 0.455            | 0.562            |

the sublattice, orbital and spin degrees of freedom ) transforms as,

\[
\hat{\mathbf{I}} : c_{a\mu\sigma} \rightarrow -c_{a\mu\sigma}, \\
\hat{\mathbf{R}}_x : c_{a\mu\sigma} \rightarrow (-1)^\mu \sigma c_{a\mu\bar{\sigma}}, \\
\hat{\mathbf{R}}_y : c_{a\mu\sigma} \rightarrow (-1)^{\mu + 1} \sigma c_{a\mu\sigma}, \\
\hat{\mathbf{R}}(\theta) : c_{ax\sigma} \rightarrow e^{-i\sigma\theta} (c_{a',x\sigma} \cos \theta + c_{a'y\sigma} \sin \theta) \\
\hat{\mathbf{R}}(\theta) : c_{ay\sigma} \rightarrow e^{-i\sigma\theta} (-c_{a',x\sigma} \sin \theta + c_{a'y\sigma} \cos \theta),
\]

where

\[
(-1)^\mu = \begin{cases} 
1, & \mu = x \\
-1, & \mu = y 
\end{cases}, \\
\sigma = \begin{cases} 
1, & \sigma = \uparrow \\
-1, & \sigma = \downarrow 
\end{cases}, \\
a' = \begin{cases} 
\bar{a}, & \theta = \pm \pi/3 \\
a, & \theta = \pm 2\pi/3 
\end{cases},
\]

Here, $\bar{a}$ designates the opposite sublattice of $a$. Before going through the detailed transformation property of each pair operator, we note the following two points

(1). To determine the inversion parity, one can simply examine whether the pair operator on the two sublattices take the same form or differ by a sign. Therefore we shall focus on the other symmetry operations in the following.

(2). The factor $e^{-i\sigma\theta}$ is equal to unity for the total $S_z = 0$ Cooper pairs.

Now we check all seven pairing symmetries one by one.

s-wave

There can be two types of s-wave: one is inter-orbital and the other is intra-orbital, we analyze them separately.
TABLE III. The results of $U$ from constraint LDA and GGA calculations.

|       | LDA  | GGA  |
|-------|------|------|
| $U = E_{ij}^0 + J_{ij}(eV)$ | 1.16 | 1.49 |

inter-orbital s-wave

The pair operator associated with the inter-orbital s-wave is given by

$$\hat{\Delta}_{s}^{\text{inter}} = \sum_a c_{ax\uparrow} c_{ay\downarrow} + c_{ax\downarrow} c_{ay\uparrow}. \quad (3)$$

Acted by $\hat{R}_{x,y}$ and $\hat{R}(\theta)$, it transforms as

$$\begin{align*}
\hat{R}_x : \hat{\Delta}_{s}^{\text{inter}} &\rightarrow (-1)^{0+1}(-1)^{0+1} \left( \sum_a c_{ax\downarrow} c_{ay\uparrow} + c_{ax\uparrow} c_{ay\downarrow} \right) = \hat{\Delta}_{s}^{\text{inter}} \\
\hat{R}_y : \hat{\Delta}_{s}^{\text{inter}} &\rightarrow (-1)^{1+0}(-1)^{0+1} \left( \sum_a c_{ax\downarrow} c_{ay\uparrow} + c_{ax\uparrow} c_{ay\downarrow} \right) = \hat{\Delta}_{s}^{\text{inter}} \\
\hat{R}(\theta) : \hat{\Delta}_{s}^{\text{inter}} &\rightarrow \sum_a (\cos \theta c_{a'x\uparrow} + \sin \theta c_{a'y\uparrow}) (-\sin \theta c_{a'x\downarrow} + \cos \theta c_{a'y\downarrow}) \\
&\quad + (\cos \theta c_{a'x\downarrow} + \sin \theta c_{a'y\downarrow}) (-\sin \theta c_{a'x\uparrow} + \cos \theta c_{a'y\uparrow}) \\
&\quad = \sum_a c_{a'x\uparrow} c_{a'y\downarrow} + c_{a'x\downarrow} c_{a'y\uparrow} = \hat{\Delta}_{s}^{\text{inter}} \quad (4)
\end{align*}$$

In addition, this pair operator is obviously inversion even since on the A and B sublattices it has the same form. Thus it has s-wave symmetry.

intra-orbital s-wave

The pair operator associated with the intra-orbital s-wave is given by,

$$\hat{\Delta}_{s}^{\text{intra}} = \sum_{a\mu} c_{a\mu\uparrow} c_{a\mu\downarrow}. \quad (5)$$

When acted by $\hat{R}_{x,y}$ and $\hat{R}(\theta)$, it transforms as

$$\begin{align*}
\hat{R}_x : \hat{\Delta}_{s}^{\text{intra}} &\rightarrow \sum_{a\mu} (-1)^{n+\mu}(-1)^{0+1} c_{a\mu\downarrow} c_{a\mu\uparrow} = \sum_{a\mu} c_{a\mu\uparrow} c_{a\mu\downarrow} = \hat{\Delta}_{s}^{\text{intra}} \\
\hat{R}_y : \hat{\Delta}_{s}^{\text{intra}} &\rightarrow \sum_{a\mu} (-1)^{n+\mu+2}(-1)^{0+1} c_{a\mu\downarrow} c_{a\mu\uparrow} = \sum_{a\mu} c_{a\mu\uparrow} c_{a\mu\downarrow} = \hat{\Delta}_{s}^{\text{intra}} \\
\hat{R}(\theta) : \hat{\Delta}_{s}^{\text{intra}} &\rightarrow \sum_a (\cos \theta c_{a'x\uparrow} + \sin \theta c_{a'y\uparrow}) (\cos \theta c_{a'x\downarrow} + \sin \theta c_{a'y\downarrow}) \\
&\quad + (-\sin \theta c_{a'x\uparrow} + \cos \theta c_{a'y\uparrow}) (-\sin \theta c_{a'x\downarrow} + \cos \theta c_{a'y\downarrow}) \\
&\quad = \sum_a c_{a'x\uparrow} c_{a'x\downarrow} + c_{a'y\uparrow} c_{a'y\downarrow} = \hat{\Delta}_{s}^{\text{intra}} \quad (6)
\end{align*}$$

In addition, this pair operator is obviously inversion even. Thus this pair operator has s-wave symmetry.

Since the inter-orbital and intra-orbital s-wave pair operators transform identically, they are allowed to mix as

$$\hat{\Delta}_{s} = \sum_a (c_{ax\uparrow} c_{ay\downarrow} + c_{ax\downarrow} c_{ay\uparrow}) + \beta \sum_{a\mu} c_{a\mu\uparrow} c_{a\mu\downarrow} \quad (7)$$
d-wave

There are two types of d-wave pairings, i.e. $\Delta_{d_{x^2-y^2}}$ and $\Delta_{d_{xy}}$, which form a 2D representation of the point-group. In the following, we check the transformation properties of them separately.

$d_{xy}$-wave

The pair operator is given by

$$\hat{\Delta}_{d_{xy}} \equiv \sum_a c_{ax\uparrow}c_{ay\downarrow} - c_{ax\downarrow}c_{ay\uparrow}. \quad (8)$$

When acted upon by $\hat{R}_{x,y}$ and $\hat{R}(\theta)$, it transforms as

$$\hat{R}_x : \hat{\Delta}_{d_{xy}} \rightarrow (-1)^{0+1}(-1)^{0+1} \left( \sum_a c_{ax\uparrow}c_{ay\downarrow} - c_{ax\downarrow}c_{ay\uparrow} \right) = -\hat{\Delta}_{d_{xy}}$$

$$\hat{R}_y : \hat{\Delta}_{d_{xy}} \rightarrow (-1)^{1+0}(-1)^{0+1} \left( \sum_a c_{ax\uparrow}c_{ay\downarrow} - c_{ax\downarrow}c_{ay\uparrow} \right) = -\hat{\Delta}_{d_{xy}}$$

$$\hat{R}(\theta) : \hat{\Delta}_{d_{xy}} \rightarrow \sum_a (\cos \theta c_{a'x\uparrow} + \sin \theta c_{a'y\downarrow}) (-\sin \theta c_{a'x\downarrow} + \cos \theta c_{a'y\uparrow})$$

$$= \sum_a \cos 2\theta (c_{a'x\uparrow}c_{a'y\downarrow} - c_{a'x\downarrow}c_{a'y\uparrow}) - \sin 2\theta (c_{a'x\uparrow}c_{a'y\downarrow} - c_{a'x\downarrow}c_{a'y\uparrow})$$

$$= \cos 2\theta \hat{\Delta}_{d_{xy}} - \sin 2\theta \hat{\Delta}_{d_{x^2-y^2}} \quad (9)$$

In addition, it is obviously inversion even. Thus this pair operator has the $d_{xy}$ symmetry.

$d_{x^2-y^2}$-wave

The $d_{x^2-y^2}$ pair operator is given by

$$\hat{\Delta}_{d_{x^2-y^2}} \equiv \sum_{a\mu} c_{a\mu\uparrow}c_{a\mu\downarrow}(-1)^\mu = \sum_a (c_{ax\uparrow}c_{ay\downarrow} - c_{ax\downarrow}c_{ay\uparrow}). \quad (10)$$

When acted upon by $\hat{R}_{x,y}$ and $\hat{R}(\theta)$, it transforms as

$$\hat{R}_x : \hat{\Delta}_{d_{x^2-y^2}} \rightarrow \sum_{a\mu} (-1)^{\mu+\mu}(-1)^{0+1}c_{a\mu\uparrow}c_{a\mu\downarrow}(-1)^\mu = \sum_{a\mu} c_{a\mu\uparrow}c_{a\mu\downarrow}(-1)^\mu = \hat{\Delta}_{d_{x^2-y^2}}$$

$$\hat{R}_y : \hat{\Delta}_{d_{x^2-y^2}} \rightarrow \sum_{a\mu} (-1)^{\mu+\mu+2}(-1)^{0+1}c_{a\mu\uparrow}c_{a\mu\downarrow}(-1)^\mu = \sum_{a\mu} c_{a\mu\uparrow}c_{a\mu\downarrow}(-1)^\mu = \hat{\Delta}_{d_{x^2-y^2}}$$

$$\hat{R}(\theta) : \hat{\Delta}_{d_{x^2-y^2}} \rightarrow \sum_a (\cos \theta c_{a'x\uparrow} + \sin \theta c_{a'y\downarrow}) (\cos \theta c_{a'x\downarrow} + \sin \theta c_{a'y\uparrow})$$

$$= \sum_a \cos 2\theta (c_{a'x\uparrow}c_{a'y\downarrow} - c_{a'x\downarrow}c_{a'y\uparrow}) + \sin 2\theta (c_{a'x\uparrow}c_{a'y\downarrow} - c_{a'x\downarrow}c_{a'y\uparrow})$$

$$= \sin 2\theta \hat{\Delta}_{d_{xy}} + \cos 2\theta \hat{\Delta}_{d_{x^2-y^2}} \quad (11)$$

In addition, it is obviously inversion even. Thus this pair operator has the $d_{xy}$ symmetry. From the above transformation properties, it is apparent that the $d_{xy}$ and $d_{x^2-y^2}$ pair operators form a 2D representation of the point-group.

f-wave

There can be two types of f-wave (with total $S_z = 0$): one is inter-orbital and the other is intra-orbital, let’s analyze them separately.
inter-orbital f-wave

The pair operator of the inter-orbital f-wave is given by
\[
\hat{\Delta}_f^{\text{inter}} = \sum_a (c_{ax\uparrow}c_{ay\downarrow} + c_{ax\downarrow}c_{ay\uparrow}) \epsilon_a,
\]
where the sign \(\epsilon_a\) is equal to 1(-1) for sublattice-A(B), respectively. When acted upon by \(\hat{R}_{x,y}\) and \(\hat{R}(\theta)\), it transforms as
\[
\begin{align*}
\hat{R}_x : \hat{\Delta}_f^{\text{inter}} &\to (-1)^{0+1}(-1)^{0+1} \sum_a (c_{ax\downarrow}c_{ay\uparrow} + c_{ax\uparrow}c_{ay\downarrow}) \epsilon_a = \hat{\Delta}_f^{\text{inter}} \\
\hat{R}_y : \hat{\Delta}_f^{\text{inter}} &\to (-1)^{1+0}(-1)^{0+1} \sum_a (c_{ax\downarrow}c_{ay\uparrow} + c_{ax\uparrow}c_{ay\downarrow}) \epsilon_a = -\hat{\Delta}_f^{\text{inter}} \\
\hat{R}(\theta) : \hat{\Delta}_f^{\text{inter}} &\to \sum_a \epsilon_a [(\cos \theta c_{a'x\uparrow} + \sin \theta c_{a'y\uparrow}) (-\sin \theta c_{a'x\downarrow} + \cos \theta c_{a'y\downarrow}) \\
&\quad + (\cos \theta c_{a'x\downarrow} + \sin \theta c_{a'y\downarrow}) (-\sin \theta c_{a'x\uparrow} + \cos \theta c_{a'y\uparrow})] \\
&\quad = \sum_a \epsilon_a (c_{a'x\uparrow}c_{a'y\downarrow} + c_{a'x\downarrow}c_{a'y\uparrow}) \\
&\quad = \begin{cases} 
-\hat{\Delta}_f^{\text{inter}}, & \theta = \pm \pi/3 \\
\hat{\Delta}_f^{\text{inter}}, & \theta = \pm 2\pi/3
\end{cases}
\end{align*}
\]
This pair operator is obviously inversion odd since it changes sign on the two sublattices. Thus, this pairing operator has f-wave symmetry.

intra-orbital f-wave

The intra-orbital f-wave pair operator is given by
\[
\hat{\Delta}_f^{\text{intra}} = \sum_{a\mu} c_{a\mu\uparrow}c_{a\mu\downarrow} \epsilon_a.
\]
When acted upon by \(\hat{R}_{x,y}\) and \(\hat{R}(\theta)\), it transforms as
\[
\begin{align*}
\hat{R}_x : \hat{\Delta}_f^{\text{intra}} &\to \sum_{a\mu} (-1)^{\mu+\mu}(-1)^{0+1} c_{a\mu\uparrow}c_{a\mu\downarrow} \epsilon_a = \sum_{a\mu} c_{a\mu\uparrow}c_{a\mu\downarrow} \epsilon_a = \hat{\Delta}_f^{\text{intra}} \\
\hat{R}_y : \hat{\Delta}_f^{\text{intra}} &\to \sum_{a\mu} (-1)^{\mu+\mu+2}(-1)^{0+1} c_{a\mu\uparrow}c_{a\mu\downarrow} \epsilon_a = \sum_{a\mu} c_{a\mu\uparrow}c_{a\mu\downarrow} \epsilon_a = -\hat{\Delta}_f^{\text{intra}} \\
\hat{R}(\theta) : \hat{\Delta}_f^{\text{intra}} &\to \sum_a \epsilon_a [(\cos \theta c_{a'x\uparrow} + \sin \theta c_{a'y\uparrow}) (\cos \theta c_{a'x\downarrow} + \sin \theta c_{a'y\downarrow}) \\
&\quad + (-\sin \theta c_{a'x\uparrow} + \cos \theta c_{a'y\uparrow}) (-\sin \theta c_{a'x\downarrow} + \cos \theta c_{a'y\downarrow})] \\
&\quad = \sum_a \epsilon_a (c_{a'x\uparrow}c_{a'y\downarrow} + c_{a'x\downarrow}c_{a'y\uparrow}) \\
&\quad = \begin{cases} 
-\hat{\Delta}_f^{\text{intra}}, & \theta = \pm \pi/3 \\
\hat{\Delta}_f^{\text{intra}}, & \theta = \pm 2\pi/3
\end{cases}
\end{align*}
\]
In addition, this pair operator is obviously inversion odd. Thus, it has the f-wave symmetry.

Since the inter and intra-orbital f-wave pair operators transform identically under all point operations, they are allowed to mix as
\[
\hat{\Delta}_f = \sum_a \epsilon_a (c_{ax\uparrow}c_{ay\downarrow} + c_{ax\downarrow}c_{ay\uparrow}) + \beta \sum_{a\mu} \epsilon_a c_{a\mu\uparrow}c_{a\mu\downarrow}.
\]
There are two types of $p$-wave pair operators with the total $S_z = 0$, i.e., $p_x$ and $p_y$, which form a 2D representation of the point-group.

The pair operators for $p_x$ and $p_y$ can be obtained from those of $d_{x^2-y^2}$ and $d_{xy}$ by adding the extra sign factor $\epsilon_a$, which are given by

$$
\hat{\Delta}_{p_x} \equiv \sum_{\alpha} c_{\alpha\mu} c_{\alpha\mu} (-1)^\mu = \sum_a \epsilon_a (c_{a\uparrow} c_{a\downarrow} - c_{a\downarrow} c_{a\uparrow})
$$

$$
\hat{\Delta}_{p_y} \equiv \sum_a \epsilon_a (c_{a\uparrow} c_{a\downarrow} - c_{a\downarrow} c_{a\uparrow}).
$$

When acted upon by the elements of the point-group, they transform as

$$
\hat{R}_x : \hat{\Delta}_{p_x} \to \hat{\Delta}_{p_x}
$$

$$
\hat{R}_y : \hat{\Delta}_{p_x} \to -\hat{\Delta}_{p_x}
$$

$$
\hat{R}_x : \hat{\Delta}_{p_y} \to -\hat{\Delta}_{p_y}
$$

$$
\hat{R}_y : \hat{\Delta}_{p_y} \to \hat{\Delta}_{p_y}
$$

$$
\hat{R}(\theta) : \hat{\Delta}_{p_x} \to e^{3i\theta} (\cos 2\theta \hat{\Delta}_{p_x} + \sin 2\theta \hat{\Delta}_{p_y})
$$

$$
\hat{R}(\theta) : \hat{\Delta}_{p_y} \to e^{3i\theta} (-\sin 2\theta \hat{\Delta}_{p_x} + \cos 2\theta \hat{\Delta}_{p_y}).
$$

In addition, these pair operators are obviously inversion odd. Thus they have the $p_x$ and $p_y$ symmetries.

$p + ip'$

Although having the same symmetry, the $(p \pm ip')_{\uparrow\uparrow,\downarrow\downarrow}$ pair operator discussed here is not the supposition of the $p_x$ and $p_y$ operators discussed in the previous section (the latter turns out not to be the leading unstable pair operator). Rather it is given by

$$
\hat{\Delta}_{p+ip',\sigma} \equiv \sum_a \epsilon_a c_{a\sigma\uparrow} c_{a\sigma\downarrow}
$$

Due to the $\epsilon_a$ factor, this pair operator is inversion odd. Under $\hat{R}_{x,y}$ reflections, the $\hat{\Delta}_{p+ip',\sigma}$ for opposite spins transform into each other (since reflection change the sign of the spin).

In Supplementary Information 4, we show in equation (30) that the Cooper scattering amplitude for $\uparrow\uparrow$ is the complex conjugate of that for $\downarrow\downarrow$. Therefore, we can choose a gauge under which the expectation value of $\hat{\Delta}_{p+ip',\uparrow}$ is the complex conjugate of that of $\hat{\Delta}_{p+ip',\downarrow}$. Under this gauge, we define

$$
\hat{\Delta}_{p+ip'}^R \equiv \hat{\Delta}_{p+ip',\uparrow} + \hat{\Delta}_{p+ip',\downarrow}
$$

$$
\hat{\Delta}_{p+ip'}^I \equiv i \left( \hat{\Delta}_{p+ip',\uparrow} - \hat{\Delta}_{p+ip',\downarrow} \right).
$$

which are the real (imaginary) part of the $p + ip' \downarrow\downarrow$ pair operator. It is straightforward to show that

$$
\hat{R}_x : \hat{\Delta}_{p+ip'}^I \to \hat{\Delta}_{p+ip'}^I
$$

$$
\hat{R}_y : \hat{\Delta}_{p+ip'}^I \to -\hat{\Delta}_{p+ip'}^I
$$

$$
\hat{R}_x : \hat{\Delta}_{p+ip'}^R \to -\hat{\Delta}_{p+ip'}^R
$$

$$
\hat{R}_y : \hat{\Delta}_{p+ip'}^R \to \hat{\Delta}_{p+ip'}^R
$$

$$
\hat{R} : \hat{\Delta}_{p+ip'}^I \to e^{3i\theta} (\cos 2\theta \hat{\Delta}_{p+ip'}^I + \sin 2\theta \hat{\Delta}_{p+ip'}^R)
$$

$$
\hat{R} : \hat{\Delta}_{p+ip'}^R \to e^{3i\theta} (-\sin 2\theta \hat{\Delta}_{p+ip'}^I + \cos 2\theta \hat{\Delta}_{p+ip'}^R).
$$

Comparing Eq. (21) and Eq. (18), we find that $\hat{\Delta}^I$ and $\hat{\Delta}^R$ transform identically as $\Delta_{p_x}$ and $\Delta_{p_y}$. Therefore, we have obtained the $p_y + ip_x \uparrow\uparrow; p_y - ip_x \downarrow\downarrow$ pair operators, i.e $(p \pm ip')_{\uparrow\uparrow,\downarrow\downarrow}$.
Explicit Mean-field Analysis

We have performed two different mean-field calculations on equation (3) in the main text, with consistent results. In the first approach, real space mean-field decoupling of the interaction terms in equation (4) is made (see equation (5) and equation (6) of the main text). Solving the ground state of the mean-field Hamiltonian self-consistently, we derive the gap equation for each pairing channel. Solving the gap equations and compare the associated mean-field ground state energies, we determine the leading pairing symmetry.

In the second approach, the mean-field decoupling is performed in the momentum space. Upon Fourier transform, the Hamiltonian reads

$$H = \sum_{k, \sigma} h_{k\sigma} (k) c_{k\sigma}^\dagger c_{k\sigma} + \sum_{\sigma_1,\sigma_2,\mu,\nu} \epsilon_{k\sigma_1}^\dagger \epsilon_{k\sigma_2} c_{\mu\sigma_1}^\dagger c_{\nu\sigma_2} c_{\mu\sigma_2} c_{\nu\sigma_1}$$

$$\rightarrow \sum_{k, \sigma} \epsilon_{k\sigma}^\dagger \epsilon_{k\sigma} c_{k\sigma} + \sum_{k, \sigma_1, \sigma_2, \mu, \nu} \epsilon_{k\sigma_1}^\dagger \epsilon_{k\sigma_2} c_{\mu\sigma_1}^\dagger c_{\nu\sigma_2} c_{\mu\sigma_2} c_{\nu\sigma_1}. \quad (22)$$

Here $\mu/\nu = 1, \ldots, 4$ represent for orbital-sublattice indices (with 1(2) and 3(4) representing for the $p_x(p_y)$ orbitals on sublattice-A and B respectively), and $\alpha = 1, \ldots, 4$ are the band indices. The transformation between the orbital basis $c_{k\mu\sigma}$ and the band eigen basis $c_{k\alpha\sigma}$ is given by,

$$c_{k\mu\sigma} = \sum_{\alpha} \epsilon_{\mu\alpha}^\sigma (k) c_{k\alpha\sigma}. \quad (23)$$

Note that due to the time-reversal symmetry, we have the following relations,

$$\epsilon_{k\dagger} = \epsilon_{-k\dagger} \xi^\alpha (k \dagger) = \xi^\alpha (-k \dagger), \quad (24)$$

The interacting parameter $U_{\theta,\xi_{\sigma_2}}^{\mu\nu\sigma}$ is defined as

$$U_{l_1\ldots l_4}^{\mu\nu\sigma} = \begin{cases} \frac{\nu - \mu}{4}, & l_1 = l_2 \neq l_3 = l_4 \in \{1, 2\} \text{or} \{3, 4\} \\ \frac{\mu - \nu}{4}, & l_1 = l_3 \neq l_2 = l_4 \in \{1, 2\} \text{or} \{3, 4\} \end{cases} \quad (25)$$

Due to the local nature of the Hubbard interaction, in order to get a non-zero interaction parameter, the indices $l_i (i = 1, \ldots, 4)$ have to either all belong to the set $\{1, 2\}$ or all belong to the set $\{3, 4\}$. Moreover the fermion anticommutation relation implies,

$$U_{\theta,\xi_{\sigma_2}}^{\mu\nu\sigma} = U_{\theta,\xi_{\sigma_2}}^{\mu\sigma} = -U_{\theta,\xi_{\sigma_2}}^{\nu\sigma}, \quad U_{\theta,\xi_{\sigma_2}}^{\mu\nu\sigma} = U_{\theta,\xi_{\sigma_2}}^{\mu\sigma}. \quad (26)$$

Note that in the above we have restricted ourselves to the Cooper scattering channel.

In the weak pairing limit, only intra-band pairing needs to be considered. In that case

$$H_1 = \sum_{k, \theta, \xi_{\sigma_2}} U_{\theta,\xi_{\sigma_2}}^{\mu\nu\sigma} \epsilon_{\mu\sigma_1}^\dagger \epsilon_{\nu\sigma_2} c_{\mu\sigma_1}^\dagger c_{\nu\sigma_2} c_{-\mu\sigma_2} c_{-\nu\sigma_1}$$

$$= \sum_{k, \theta, \xi_{\sigma_2}} \sum_{\mu, \nu} \left[ U_{\theta,\xi_{\sigma_2}}^{\mu\nu\sigma} \epsilon_{k\sigma_1}^\dagger \epsilon_{k\sigma_2} c_{\mu\sigma_1}^\dagger c_{-\mu\sigma_2} c_{-\nu\sigma_1} \right] \left( k \xi^\alpha (q) \xi_{\theta\alpha} (q) \xi_{\theta\alpha} (q) \right)$$

$$= \sum_{k, \theta, \xi_{\sigma_2}} V_{\alpha\beta}^{\sigma_2} (k, q) c_{\alpha\sigma_1}^\dagger c_{\beta\sigma_1}^\dagger c_{-\beta\sigma_2} c_{-\alpha\sigma_2}, \quad (27)$$

where parameter

$$V_{\alpha\beta}^{\sigma_2} (k, q) = \sum_{\mu, \nu, \theta, \xi_{\sigma_2}} U_{\theta,\xi_{\sigma_2}}^{\mu\nu\sigma} \epsilon^\sigma \xi_{\mu\alpha} (q) \xi_{\nu\beta} (q) \xi_{\theta\alpha} (q) \xi_{\theta\beta} (q). \quad (28)$$
Due to the $S_z$-conservation and the inversion symmetry, the pairing potential $V^{(1)}_{\alpha\beta}(\mathbf{k},\mathbf{q})$ can take the following four possible forms,

\[
\begin{align*}
V^{(1,1)}_{\alpha\beta}(\mathbf{k},\mathbf{q}) & \equiv V^{\uparrow\uparrow}_{\alpha\beta}(\mathbf{k},\mathbf{q}) \\
V^{(1,-1)}_{\alpha\beta}(\mathbf{k},\mathbf{q}) & \equiv V^{\downarrow\downarrow}_{\alpha\beta}(\mathbf{k},\mathbf{q}) \\
V^{(1,0)}_{\alpha\beta}(\mathbf{k},\mathbf{q}) & \equiv \frac{1}{2} \left[ V^{\uparrow\downarrow}_{\alpha\beta}(\mathbf{k},\mathbf{q}) - V^{\uparrow\downarrow}_{\alpha\beta}(\mathbf{k},-\mathbf{q}) \right] \\
V^{(0,0)}_{\alpha\beta}(\mathbf{k},\mathbf{q}) & \equiv \frac{1}{2} \left[ V^{\uparrow\downarrow}_{\alpha\beta}(\mathbf{k},\mathbf{q}) + V^{\uparrow\downarrow}_{\alpha\beta}(\mathbf{k},-\mathbf{q}) \right]
\end{align*}
\]  

The first three channels are for odd-parity pairings with $S_z = 1, -1, 0$ respectively. The last channel is for even-parity. Particularly, from equation (24) and (28), we found

\[
V^{\uparrow\uparrow}_{\alpha\beta}(\mathbf{k},\mathbf{q}) = V^{\downarrow\downarrow}_{\alpha\beta}(-\mathbf{k},-\mathbf{q}).
\]  

To determine $T_c$, we use the following linearized gap equation for each pairing channel,

\[
- \frac{1}{(2\pi)^2} \sum_{\beta} \oint_{FS} d\mathbf{k}_\parallel \frac{V^{(i)}_{\alpha\beta}(\mathbf{k},\mathbf{k}')}{\nu_{F\beta}(\mathbf{k}')} \Delta_{\beta}(\mathbf{k}') = r \Delta_{\alpha}(\mathbf{k}).
\]  

Here, $\beta$ labels the Fermi surface (FS) and the integral is performed around each connected FS. Moreover, $\nu_{F\beta}(\mathbf{k}')$ is the Fermi velocity at $\mathbf{k}'$ on the $\beta$–th FS, and $\mathbf{k}_\parallel$ represents the tangential component of $\mathbf{k}'$. Solving Eq.(31) as an eigenvalue problem, we obtain the pairing eigenvalue $r$ and gap function $\Delta_{\alpha}(\mathbf{k})$. The leading gap function is the one corresponds to the largest eigenvalue $r$. 

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