Nonunitary superconductivity in complex quantum materials

Aline Ramires

Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

E-mail: aline.ramires@psi.ch

Received 24 February 2022, revised 20 April 2022
Accepted for publication 5 May 2022
Published 1 June 2022

Abstract
We revisit the concept of nonunitary superconductivity and generalize it to address complex quantum materials. Starting with a brief review of the notion of nonunitary superconductivity, we discuss its spectral signatures in simple models with only the spin as an internal degree of freedom. In complex materials with multiple internal degrees of freedom, there are many more possibilities for the development of nonunitary order parameters. We provide examples focusing on d-electron systems with two orbitals, applicable to a variety of materials. We discuss the consequences for the superconducting spectra, highlighting that gap openings of band crossings at finite energies can be attributed to a nonunitary order parameter if this is associated with a finite superconducting fitness matrix. We speculate that nonunitary superconductivity in complex quantum materials is in fact very common and can be associated with multiple cases of recently reported time-reversal symmetry breaking superconductors.

Keywords: unconventional superconductivity, nonunitary superconductivity, complex quantum materials

(Some figures may appear in colour only in the online journal)

1. Introduction

Superconducting complex quantum materials have recently attracted a lot of attention given their unusual phenomenology. Heavy fermion materials such as CeRh$_2$As$_2$ [1] and UTe$_2$ [2] host multiple superconducting phases, Sr$_2$RuO$_4$ has been puzzling the condensed matter community with experimental results that are hard to reconcile [3], doped topological insulators in the family of Bi$_2$Se$_3$ display unusual robustness in presence of impurities despite the unconventional nature of the order parameter [4], and transition metal dichalcogenides have upper critical fields much larger than the one set by the Pauli limit [5]. From a theoretical perspective, what is common among these families of materials is the presence of multiple internal degrees of freedom (DOFs), such as orbitals [6–8], layers [9], sublattices [10], and valleys [11], or multiple bands [12, 13] in the respective effective models for the normal state electronic structure.

The presence of internal DOFs in the effective description of these materials opens new possibilities for the internal structures of the superconducting order parameter. For simple superconductors, with only the spin as an internal DOF, pairing can be even-parity spin-singlet, or odd-parity spin-triplet. In presence of one extra internal DOF, one can then have pairs that are symmetric or anti-symmetric with respect to this new DOF. For example, even-parity spin-triplet orbital-antisymmetric states are possible, among others. With a single extra internal DOF which can acquire two values (such as an internal DOF that can be associated with $d_{xz}$ or $d_{yz}$ orbitals), the number of distinct internal structures for the order parameters jumps to sixteen, in contrast to four in case the spin is the only internal DOF (one singlet and three triplet states). With an enlarged order parameter space, we commonly find multiple order parameters with distinct internal structures falling within the same irreducible representation of the relevant symmetry.
group. As a consequence, order parameters are generally a linear superposition of components with different internal structures. As we discuss in detail below, this linear superposition generally leads to non-unitary order parameters.

Given a superconducting state characterized by the order parameter matrix $\Delta(k)$, if the gauge invariant combination $\Delta(k)\Delta^\dagger(k)$ is proportional to the identity matrix, the superconducting state is called unitary, otherwise it is called nonunitary. Most superconducting states discussed in the literature are unitary. Nonunitary states were first discussed in the context of the $A_1$ phase in superfluid He-3 in the presence of an applied magnetic field [14, 15]. The first mention of nonunitary superconducting states was made in the context of UPt$_3$ [16–18]. These ideas have been recently revisited considering the nonsymmetric structure of this material [19]. Recently, nonunitary superconductivity has also been proposed for the time-reversal symmetry breaking superconductors LaNiC$_2$ [20–23] and LaNiGa$_3$ [24–26], the former noncentrosymmetric, and the later centrosymmetric and recently discovered to be non-symmetric [27, 28]. The newly reported multiple superconducting phases in UTe$_2$ [29] could also be associated with nonunitary order parameters based on the magnetic space group classification [30], or on triplet pairing on the border of magnetism [31]. Furthermore, recent reports on the superconducting state of Weyl nodal-line semimetals such as LaNiSi, LaPtSi and LaPtGe [32], and on silicide superconductors (Ta, Nb)O$_5$Si [33], suggest that nonunitary superconducting states are the best candidates to reconcile the observation of time-reversal symmetry breaking with the presence of nodeless superconducting gap structures.

Recently, nonunitary superconductors started to attract special attention given its association with Bogoliubov Fermi surfaces [34, 35], anapole superconductivity with asymmetric Bogoliubov spectra [36], topological classification in terms of $q$-helicity [37], and multiple Majorana fermion phases [38]. Theoretical works in the context of nonunitary superconductivity have explored general aspects of impurity induced density of states and residual electric and thermal transport [39], disorder-induced mixed-parity superconductivity in noncentrosymmetric monolayer transition-metal dichalcogenides [40], and field-induced mixed-parity in locally noncentrosymmetric materials [41]. Experimental observables such as the magnetoelectric Andreev effect [42] and signatures in the conductance spectra in ferromagnetic metal/nonunitary superconductor junctions [43] were proposed. More recently, the opening of gaps away from the Fermi surface in Dirac materials was suggested as a signature of multi-orbital nonunitary superconductivity [44]. The stability of nonunitary superconducting states is not yet completely understood. The presence of ferromagnetism [45], or other auxiliary order parameters was recently suggested as a mechanism for stabilizing non-unitary multiorbital superconductivity [46–48].

In this paper, we propose a comprehensive discussion on nonunitary superconductivity in complex quantum materials. We start introducing the concept of superconducting fitness, which is going to be key in the later discussion of spectral signatures for both simple and complex scenarios. We review the notion of nonunitary order parameters in simple superconductors, emphasizing that the development of nonunitary superconductivity is directly associated with symmetry-breaking order parameters (beyond the standard $U(1)$ gauge symmetry). Without delving into the details of the pairing mechanism, we discuss the spectral signatures of these order parameters. We highlight that in the context of simple superconductors, gap openings away from the Fermi level at particle–hole band crossings are primarily associated with a non-zero superconducting fitness matrix, not with the nonunitary character of the order parameter. In the context of complex materials, with multiple internal DOFs, nonunitary order parameters can develop without extra symmetry breaking (beyond the standard $U(1)$ gauge symmetry). We highlight some examples of nonunitary pairing in complex materials focusing on d-electron systems with two orbitals. We discuss the consequences for the superconducting spectrum in these more complex scenarios based on our refined understanding of nonunitary superconductivity in simple systems. In particular, we highlight that nonunitary superconducting states are associated with gap openings of particle–particle band crossings away from the Fermi level in case the order parameter is associated with a finite superconducting fitness matrix. We conclude providing a discussion that connects with recent work, and we speculate on the connections between nonunitary and time-reversal symmetry breaking superconductivity in complex materials.

2. The concept of superconducting fitness

Before starting the discussion on nonunitary superconductivity, it is useful to introduce the concept of superconducting fitness [49, 50], as this is going to be a key ingredient in the analysis that follows. The superconducting fitness framework has been a useful theoretical tool allowing for the understanding of the stability and nodal structure of unexpected superconducting states [8, 51–53], the robustness of unconventional superconducting states in the presence of impurities [4, 54], and the unusual behavior of complex superconductors under external symmetry breaking fields, such as strain [55]. This seems to be one of the most appropriate frameworks for the description of superconductivity in complex quantum materials, allowing for the understanding of apparently contradicting responses of complex superconductors.

We start introducing the effective Bogoliubov–de Gennes (BdG) Hamiltonian:

$$H_{\text{BdG}} = \sum_{k} \frac{1}{2} \Psi_k^\dagger \hat{H}_{\text{BdG}}(k) \Psi_k,$$

where

$$\hat{H}_{\text{BdG}}(k) = \begin{pmatrix} H_0(k) & \Delta(k) \\ \Delta^\dagger(k) & -H_0^\dagger(-k) \end{pmatrix},$$

and $\Psi_k = (\Phi_k^\uparrow, \Phi_k^\downarrow)$ is a Nambu spinor, where $\Phi_k^\uparrow = (c_{k1\uparrow}, c_{k2\uparrow}, c_{k3\uparrow}, \ldots, c_{km\uparrow}, c_{kn\uparrow})$, and $c_{k\alpha\sigma}^\dagger$ (c$_{k\alpha\sigma}$) creates (annihilates) an electron with momentum $k$ and spin $\sigma$ in the internal DOF $\alpha$, which can be associated with orbitals, sublattice, or valley structures. $H_0(k)$ corresponds to the normal
state Hamiltonian, and $\Delta(k)$ encodes the order parameter, both are $2n \times 2n$ matrices in case the parameter $\alpha$ can acquire $n$ different values.

### 2.1. Superconducting fitness and inter-band pairing

Superconductivity is usually discussed as an electronic instability out of a metallic state characterized by one or more bands. Even in the case of a single internal DOF, we can find multiple bands in presence of external symmetry breaking fields, such as Zeeman fields or Rashba spin–orbit coupling (SOC). In case of multiple internal DOFs, we naturally find multiple electronic bands, which can be doubly degenerate in presence of time-reversal and inversion symmetries. If pairing happens between electrons in the same band (intra-band pairing), superconductivity is established for an arbitrarily small attractive interaction through the Cooper instability with the formation of superconducting pairs of electrons with total zero momentum. If pairing happens between electrons in different bands (inter-band pairing), the superconducting state is not as stable as a finite attractive interaction is necessary. Based on these ideas, below we present an heuristic discussion and introduction of the concept of superconducting fitness [49].

In presence of external symmetry breaking fields or multiple orbitals or sublattices, the normal state Hamiltonian $\hat{H}_0(k)$ is generally not diagonal in the microscopic basis. As the Hamiltonian is an Hermitian matrix, there is always a unitary transformation $U(k)$ which diagonalizes it, or rotates it to the band basis: $\hat{H}_B^0(k) = U(k)\hat{H}_0(k)U(k)$ (the superscript $B$ stands for the band basis). The gap matrix, by connecting particle and hole spaces, transforms in a slightly different manner: $\Delta^B(k) = U(k)\Delta(k)U^T(-k)$. In case of pure intra-band pairing $\Delta^B(k)$ is block diagonal. A non block-diagonal gap matrix is an indication of inter-band pairing.

To get some intuition on the origin of the concept of superconducting fitness, we consider the minimal multi-orbital problem consisting of two orbitals. In presence of time reversal and inversion symmetries, $\hat{H}_B^0(k)$ has doubly degenerate states with energy $\epsilon_\alpha$, where $a$ is the band label, and therefore has a structure with $2 \times 2$ blocks proportional to the identity $\delta_0$. Concerning the gap matrix, an arbitrary gap structure has both intra- $\Delta_a$ and inter- $\Delta_{ab}$ components. Under these conditions, we can write, omitting the momentum dependence:

$$\hat{H}_0(k) = \begin{pmatrix} \epsilon_1 \delta_{a} & 0 \\ 0 & \epsilon_2 \delta_{a} \end{pmatrix}, \quad \Delta^B = \begin{pmatrix} \Delta_{11} & \Delta_{12} \\ \Delta_{21} & \Delta_{22} \end{pmatrix}. \tag{3}$$

Note that these matrices do not commute for finite inter-band pairing, unless the artificial condition $\epsilon_1 = \epsilon_2$ is satisfied. On the other hand, in case $\Delta_{12} = \Delta_{21} = 0$, $\Delta^B(k)$ is block diagonal and commutes with the bare Hamiltonian $\hat{H}_B^0(k)$ in the band basis.

We can then look at the condition for absence of inter-band pairing from the microscopic basis perspective. Using the unitary transformation introduced above and the fact that $\hat{H}_B^0(k)$ and $\Delta^B(k)$ commute in case of pure intra-band pairing, we can write:

$$\hat{H}_0(k)\Delta(k) = U^T(k)\hat{H}_B^0(k)U(k)\Delta^B(k)U^T(-k),$$

$$= U^T(k)\hat{H}_B^0(k)\Delta^B(k)U^T(-k),$$

$$= U^T(k)\Delta^B(k)\hat{H}_B^0(k)U^T(-k),$$

$$= U^T(k)\Delta^B(k)U^T(-k)\hat{H}_B^0(k)U^T(-k). \tag{4}$$

We can identify the first three factors in the last line with $\Delta(k)$. For the last three factors, we use inversion symmetry (already assumed above to guarantee the double degeneracy of the bands) and the fact that the eigenvalues of $\hat{H}_B^0(k)$ are real to write $\hat{H}_B^0(-k) = U^T(-k)\hat{H}_B^0(k)U^T(-k)$, so we have:

$$\hat{H}_0(k)\Delta(k) - \Delta(k)\hat{H}_B^0(-k) = 0. \tag{5}$$

If $\hat{H}_0(k)$ and $\Delta(k)$ satisfy this condition, the system develops only intra-band pairing and consequently has a robust superconducting instability. In case the identity above is not satisfied, we have a measure of the incompatibility between the superconducting state and the normal state, associated with the presence of inter-band pairing, which we label as the superconducting fitness matrix $\hat{F}_C(k)$:

$$\hat{F}_C(k) = \hat{H}_0(k)\Delta(k) - \Delta(k)\hat{H}_B^0(-k). \tag{6}$$

### 2.2. Superconducting fitness and the critical temperature

A finite superconducting fitness matrix $\hat{F}_C(k)$ has been shown to be directly associated with the suppression of the superconducting critical temperature from its maximum possible value in single band superconductors [49]. For models with up to two orbitals or sublattices, the superconducting critical temperature can be explicitly written as [50]:

$$k_B T_C = \frac{4\pi}{\gamma} \frac{\omega_C}{2} e^{-1/2|\gamma|} e^{-\beta/\alpha}, \tag{7}$$

where $\gamma$ is the Euler constant, $\omega_C$ is an energy cutoff (associated with the energy scale within which the effective interaction between electrons is attractive, the Debye frequency for conventional superconductors), $|\gamma|$ is the magnitude of the effective attractive interaction in the superconducting channel of interest. In addition,

$$\delta = \frac{\omega_C^2}{32} \sum_a N_a(0) \left( \frac{||\hat{F}_C(k)||^2}{q(F^a)} \right)_{FSa}, \tag{8}$$

and

$$\alpha = \frac{1}{16} \sum_a N_a(0) (||\hat{F}_A(k)||^2)_{FSa}, \tag{9}$$

where the sum over the index $a$ runs over the bands with density of states at the Fermi surface $N_a(0)$, and $\{\ldots\}_{FSa}$ denotes the average over the respective Fermi surface. Here $q(k) = \epsilon_a(k) - \epsilon_f(k)$ is the energy difference between the two bands, which we assume are well separated, $q(k) \gg \omega_C$. $||M||^2 = Tr[M^\dagger M]$ is the Frobenius norm of the matrix $M$. The matrix inside the trace for the parameter $\alpha$ is the anti-commutator.
counterpart of the first superconducting fitness matrix defined above:
\[ \tilde{F}_\alpha(k) = \tilde{H}_0(k)\tilde{\Delta}(k) + \tilde{\Delta}(k)\tilde{H}_0(-k). \] (10)

From the closed form equation for the critical temperature, equation (7), it is clear that the larger the parameter \( \alpha \) (so the larger \( F_\alpha(k) \)), the larger the critical temperature, while a finite \( \delta \) (or a finite \( F_C(k) \)) suppresses the critical temperature from its potentially maximum value.

2.3. Superconducting fitness and odd frequency correlations

Recently, the superconducting fitness measure \( F_C(k) \) was also associated with the presence of odd-frequency superconducting correlations [56]. This can be shown by manipulating the BdG Green’s function, defined as:
\[ \tilde{G}_{BdG}(k, i\omega_n) = [i\omega_n\tilde{I}_{4n} - \tilde{H}_{BdG}(k)]^{-1}, \] (11)
where \( \tilde{I}_{4n} \) is the \( 4 \times 4n \) identity matrix, and \( i\omega_n \) is a Matsubara frequency. This Green’s function can be broken down in particle and hole spaces, such that we can write:
\[ \begin{pmatrix} \tilde{G}_e(k, i\omega_n) & \tilde{F}(k, i\omega_n) \\ \tilde{F}^\dagger(k, i\omega_n) & \tilde{G}_h(k, i\omega_n) \end{pmatrix} \cdot \begin{pmatrix} I_{2n}i\omega_n - \tilde{H}_0(k) & -\tilde{\Delta}(k) \\ -\tilde{\Delta}^\dagger(k) & I_{2n}i\omega_n + \tilde{H}_0^*(-k) \end{pmatrix} = \tilde{I}_{4n}. \] (12)

From the equation above we can extract two identities:
\[ \tilde{G}_e(k, i\omega_n)[I_{2n}i\omega_n - \tilde{H}_0(k)] - \tilde{F}(k, i\omega_n)\tilde{\Delta}^\dagger(k) = I_{2n}, \] (13)
\[ -\tilde{F}^\dagger(k, i\omega_n)\tilde{\Delta}(k) + \tilde{G}_h(k, i\omega_n)(I_{2n}i\omega_n + \tilde{H}_0^*(-k)) = 0. \] (14)

Isolating \( \tilde{G}_e(k, i\omega_n) \) from the first equation, substituting it in the second and identifying \( \tilde{G}_e^0(k, i\omega_n) = [I_{2n}i\omega_n - \tilde{H}_0(k)]^{-1} \) and \( \tilde{G}_h^0(k, i\omega_n) = [I_{2n}i\omega_n + \tilde{H}_0^*(-k)]^{-1} \) as the normal state particle and hole Green’s functions, we can write:
\[ \tilde{F}(k, i\omega_n) = \tilde{F}_0^0(k, i\omega_n)I_{2n} - \tilde{\Delta}^\dagger(k)\tilde{F}(k, i\omega_n), \] (15)
where we identified \( \tilde{F}_0^0(k, i\omega_n) = \tilde{G}_h^0(k, i\omega_n)\tilde{\Delta}(k)\tilde{G}_h^0(k, i\omega_n) \) as the first order contribution in \( \tilde{\Delta}(k) \) to the anomalous correlation function \( \tilde{F}(k, i\omega_n) \).

Note that all the frequency dependence in \( \tilde{F}(k, i\omega_n) \) appears through \( \tilde{F}_0^0(k, i\omega_n) \), such that if the last is even in frequency, the first should also be. This simplifies the discussion, as we can consider the simpler form of \( \tilde{F}_0^0(k, i\omega_n) \) to extract the condition for the presence of odd frequency anomalous correlations. Writing \( \tilde{F}_0^0(k, i\omega_n) \) explicitly:
\[ \tilde{F}_0^0(k, i\omega_n) = [\tilde{I}_{2n}i\omega_n - \tilde{H}_0(k)]^{-1}\tilde{\Delta}(k)[\tilde{I}_{2n}i\omega_n + \tilde{H}_0^*(-k)]^{-1}, \] (16)
we can make the first and last factors even in frequency by multiplying them by a convenient identity factor. After some manipulation we find:
\[ \tilde{F}_0^0(k, i\omega_n) = [\tilde{I}_{2n}i\omega_n^2 - \tilde{H}_0(k)^2]^{-1} \times \left[ (i\omega_n^2)\tilde{\Delta}(k) - \tilde{H}_0(k)\tilde{\Delta}(k)\tilde{H}_0^*(-k) + i\omega_n\tilde{F}_C(k) \right] \times [\tilde{I}_{2n}i\omega_n^2 - \tilde{H}_0^*(-k)]^{-1}. \] (17)
Writing explicitly the odd-frequency component of the anomalous correlation function:
\[ \tilde{F}_0^0(k, i\omega_n) = [\tilde{F}_0^0(k, i\omega_n) - \tilde{F}_0^0(k, -i\omega_n)]/2 \\
= i\omega_n[\tilde{I}_{2n}i\omega_n^2 - \tilde{H}_0(k)^2]^{-1}\tilde{F}_C(k) \times [\tilde{I}_{2n}i\omega_n^2 - \tilde{H}_0^*(-k)]^{-1}, \] (18)
it is evident that the presence of odd frequency correlations is directly associated with a nonzero superconducting fitness matrix \( \tilde{F}_C(k) \).

3. Superconductivity in simple metals

The normal state Hamiltonian, \( \tilde{H}_0(k) \), has the general form for a system with only the spin as an internal DOF:
\[ \tilde{H}_0(k) = \epsilon(k)s\tilde{\sigma}_0 + s(k) \cdot \tilde{\sigma}, \] (19)
where \( \epsilon(k) \) describes a doubly degenerate electronic dispersion in presence of time-reversal symmetry (TRS) and inversion symmetry (IS). The three-dimensional vector \( s(k) \) introduces time-reversal symmetry breaking (TRS) as an external magnetic field, if \( s(k) = -B \), or inversion symmetry breaking (ISB) in the form of odd-momentum spin–orbit coupling (SOC), if \( s(k) = g(k) = -g(-k). \) Here \( \tilde{\sigma}_0 \) is the two-dimensional identity matrix and \( \tilde{\sigma} = \{ \tilde{\sigma}_x, \tilde{\sigma}_y, \tilde{\sigma}_z \} \) is a three-dimensional vector of Pauli matrices.

In this context, the most general superconducting order parameter, \( \tilde{\Delta}(k) \), can be written as
\[ \tilde{\Delta}(k) = [d_0^\dagger(k) + d(k) \cdot \tilde{\sigma}](i\tilde{\tau}_2). \] (20)
Following fermionic antisymmetry, the order parameter matrix should satisfy \( \tilde{\Delta}(k) = -\tilde{\Delta}^\dagger(-k) \). As a consequence, \( d_0 \) is even and \( d(k) \) is odd in momentum. TRS is implemented as \( \tilde{\Theta} = (i\tilde{\tau}_2)\mathcal{K} \), where \( \mathcal{K} \) stands for complex conjugation, and should be accompanied by the change in momenta \( k \to -k \). This definition, when applied to the superconducting gap gives \( \tilde{\Delta}_T(k) = \tilde{\Theta}\tilde{\Delta}(k)(\tilde{\Theta})^{-1} = d_0^\dagger(k)(i\tilde{\tau}_2) + d(k) \cdot \tilde{\sigma}(i\tilde{\tau}_2), \) such that if we choose the function \( d_0(k) \) and all components of \( d(k) \) to have the same phase, the order parameter is time-reversal invariant (up to an overall \( U(1) \) gauge transformation).
A gauge-invariant composition of the order parameter with itself is
\[ \tilde{\Delta}(k)\tilde{\Delta}^\dagger(k) = \Delta^2(k)\sigma_0 + q_{\text{NU}}(k) \cdot \sigma, \]
where
\[ \Delta(k) = |d_0(k)|^2 + |d(k)|^2 \]
is the magnitude of the unitary part of the gap, and
\[ q_{\text{NU}}(k) = d_0(k)d^\ast(k) + d_0^\ast(k)d(k) + id(k) \times d^\ast(k), \]
is the vector that characterizes the nonunitary part of the gap. As a definition, the order parameter is unitary if \( q_{\text{NU}}(k) = 0 \), and is nonunitary otherwise. From the explicit form of \( q_{\text{NU}}(k) \), we can conclude that the order parameter is nonunitary if at least one of the following conditions are met: (i) ISB in the normal state, allowing parity mixing in the superconducting state; (ii) TRSB order parameter with \( d^\ast(k) \) not parallel to \( d(k) \).

Note that in the latter case the order parameter can spontaneously break the mentioned symmetry (assuming a TRS normal state). In the case of a parity mixed order parameter, IS is generally already broken in the normal state, so it is not spontaneously broken in the superconducting state. One exception is the fine-tuned case with an accidental degeneracy between an even and an odd parity superconducting state [57].

A nonunitary order parameter leads to a finite expectation value of \( \langle \tilde{\Delta}(k)\sigma\tilde{\Delta}(k) \rangle \), which is associated with a finite spin polarization of the pair at a given \( k \). Note that the average over the Fermi surface can lead to a zero net spin polarization (as in the case of ISB in the normal state, since \( d_0(k) \) is even and \( d(k) \) is odd in momenta). This tells us that only a TRSB superconductor could sustain a finite average spin polarization of the pair.

In this context, it is useful to refine the notion of nonunitary order parameters introducing the time-reversal-odd gauge-invariant product [34]:
\[ \tilde{\Delta}(k)\tilde{\Delta}^\dagger(k) - \Delta^2(k)\tilde{\Delta}^\dagger(k) = q_{\text{TRO}}(k) \cdot \sigma \]
where \( \tilde{\Delta}(k) \) is the time-reversed order parameter defined above, and
\[ q_{\text{TRO}}(k) = 2id(k) \times d^\ast(k). \]
If \( q_{\text{TRO}}(k) \neq 0 \) the TRSB order parameter develops a spin polarization. It has recently been proposed that a finite \( q_{\text{TRO}}(k) \), and not a finite \( q_{\text{NU}}(k) \), should be taken as the definition of nonunitary pairing [34].

4. Signatures of nonunitary order parameters in the single orbital scenario

The energy spectrum in the superconducting state can be evaluated by diagonalizing the BdG Hamiltonian in equation (2). To understand some of the features of the spectrum, it is convenient to take the square of the BdG Hamiltonian, which gives us as eigenvalues the squares of the eigenenergies. The explicit form of the square of the BdG Hamiltonian is very suggestive:

\[ H_{\text{BCG}}(k) = \left( \begin{array}{cc} H_0(k)^2 + \Delta(k)\tilde{\Delta}(k) & \tilde{F}_C(k) \\ \tilde{F}_C(k) & H_0^\ast(-k)^2 + \Delta^\dagger(k)\Delta(k) \end{array} \right) \]

where \( \tilde{F}_C(k) \) is the superconducting fitness matrix, defined in equation (6). A summary of the superconducting fitness matrices for a single internal DOF (spin) is given in Table 1.

| \( q_{\text{TRO}}(k) \neq 0 \) | Always finite | Always zero |
|-----------------|--------------|--------------|

4.1. Case I: unitary order parameter

Let us start with the simpler case with \( \tilde{F}_C(k) = 0 \), so the square of the BdG Hamiltonian matrix, equation (26), is block diagonal. The upper left block reads:

\[ \left[ H_0(k)^2 + \Delta(k)\tilde{\Delta}(k) = \{ |\epsilon(k)|^2 + |s(k)|^2 + |\Delta_U(k)|^2 \} \sigma_0 + 2\epsilon(k)s(k)\sigma \right. \]

The eigenvalues of the upper left block of the square of the BdG Hamiltonian are then

\[ \mathcal{E}_\pm = \pm \sqrt{[\epsilon(k)]^2 + |s(k)|^2} \pm [\epsilon(k)s(k)] \]

and the eigenvalues of the original BdG Hamiltonian are:

\[ E_{\pm} = \pm \sqrt{[\epsilon(k) \pm |s(k)|]^2} \pm |\Delta_U(k)|^2}. \]

This result corresponds to two bands in the normal state, \( \xi_{\pm}(k) = \epsilon(k) \pm |s(k)| \), developing the same gap with magnitude \( |\Delta_U(k)| \). From this quadrant we already recover the four eigenenergies that are expected for the four-dimensional BdG Hamiltonian (the lower right quadrant gives the same result, assuming \( g(k) \cdot B = 0 \)). In the simplest case of a normal state with both TRS and IS, we find a doubly-degenerate superconducting spectrum, as depicted in the top left corner of figure 1.

If the normal state breaks IS, TRS, or both, the normal state spectrum is non-degenerate and the particle and hole bands cross away from the Fermi energy. This crossing is inherited by the superconducting spectrum and is protected in case \( \tilde{F}_C(k) = 0 \), as depicted on the three last lines of the left column of figure 1.

To understand the effects of \( \tilde{F}_C(k) \neq 0 \), let us focus on the scenario with a spin singlet superconductor developing out of a normal state subject to an external magnetic field.
Figure 1. Energy versus momentum plots of the normal and superconducting state spectra for unitary order parameters. The momentum is taken along the $k_\parallel$ direction. The blue lines correspond to the superconducting spectrum, while the gray dashed lines correspond to the normal state bands (both particle and hole sectors). The horizontal gray lines marks the Fermi level. Each row encodes different symmetries in the normal state Hamiltonian specified on the left. The left (right) column corresponds to cases of unitary superconductivity, depending on the symmetry breaking fields we take $F_C(k) = 0$ [$F_C(k) \neq 0$]. The gray box indicates that there is no example for the respective conditions. In brackets we highlight the finite parameters: $\{d_0, d_1, d_2, d_3\}$ correspond to the d-vector parametrization of the superconducting order parameter, as given by equation (20), $B = (B_x, B_y, B_z)$ correspond to magnetic field components, and $g(k) = (-A_1 k_x, A_1 k_y, -A_2 k_z)$ correspond to Rashba ($A_1$) or Ising ($A_2$) SOC. For the plots we consider a simple parabolic dispersion $\epsilon(k) = \hbar^2 k^2/(2m) - \mu$. Here we set $\hbar^2/(2m) = 1$ (with units of energy times length squared), and $\mu = 2$ (in units of energy). For the superconducting order parameters we take $d_0 = d_1 = d_2 = d_3 = 1$ (in units of energy), and for the symmetry breaking fields we take $B_x = B_y = 0.25$ (in units of energy), and $A_1 = A_2 = 0.25$ (in units of energy times length). The parameters for the plots were chosen such that the energy associated with symmetry breaking fields are smaller than the magnitude of the energy gap. This is a general requirement for the superconducting state not to be completely suppressed by the symmetry breaking fields. On the left block in the third row we highlight the different bands crossing discussed in the text: particle–hole (PH), particle–particle (PP) and hole–hole (HH).

along the $z$-direction. In this case $[\hat{H}_0(k)]^2$ is diagonal and $\hat{F}_C(k) = f_s(k)\hat{\sigma}_z$, omitting the momentum dependence in the matrix for conciseness:

$$\hat{H}_{\text{BdG}}^z(k) = \begin{pmatrix} h_0 + h_z & 0 & f_s \\ 0 & h_0 - h_z & f_s \\ f_s^\ast & f_s & h_0 + h_z & 0 \\ 0 & 0 & 0 & h_0 - h_z \end{pmatrix}. \quad (30)$$

Figure 2. Superconducting spectra for nonunitary order parameters preserving TRS. The red lines correspond to the superconducting spectrum, while the gray dashed lines correspond to the normal state bands (both particle and hole sectors). Same description as for figure 1. The parameters used for the plots are the following: $d_0 = 0.5, d_1 = d_2 = 0.25$ and $B_x = 0.25$ (in units of energy), and $A_1 = A_2 = 0.25$ (in units of energy times length).

where $h_0(k) = \epsilon^2(k) + B_z^2 + d_0^2(k)$, $h_z(k) = 2\epsilon(k)B_z$, and $f_s(k) = 2d_0(k)B_z$. Note that $f_s(k)$ connects different eigenvalues $E_s(k)$ (for the case of $\hat{F}_C(k) = 0$). The ultimate effect on the spectrum can be then understood by splitting the matrix above in two $2 \times 2$ matrices:

$$\hat{H}_{\text{BdG}}^z(k) = \begin{pmatrix} h_0(k) & f_s(k) \\ f_s^\ast(k) & h_0(k) - h_z(k) \end{pmatrix}. \quad (31)$$

with eigenvalues $h_0(k) \pm \sqrt{h_z^2(k) + |f_s(k)|^2}$. This means that the original eigenvalues $E_s(k) = h_0(k) \pm h_z(k)$ (for $\hat{F}_C(k) = 0$) are split. At the crossing of the particle and hole bands away from the Fermi level there is a gap opening in the superconducting state, creating a ‘mirage gap’ at finite energy. This aspect can also be understood by the fact that the fitness measure is written in terms of products of the normal state Hamiltonian $H_0(k)$, which connects particle and particle spaces, and the superconducting gap matrix $\Delta(k)$, which connects particle and hole spaces. The fitness matrices therefore connects particle and hole spaces, and can be thought of as an hybridization between these sectors, allowing for gap openings when bands associated with these different sectors cross at finite energy.

Figure 1 displays the superconducting spectra for selected cases of unitary superconductivity, depending on the symmetries in the normal state and a zero or finite fitness matrix. The first row corresponds to the normal state with both TRS
In this case the normal state bands are doubly degenerate (dashed lines for both particle and hole sectors) and $F_C(k) = 0$, as the normal state Hamiltonian is simply proportional to the identity matrix. A unitary order parameter opens the same gap in both bands and the superconducting spectrum is doubly degenerate (blue lines). The second row corresponds to TRSB in the normal state, introduced by an external magnetic field. The bands in the normal state are Zeeman split, and once we consider both particle and hole sectors, we note crossings at finite energy (PH crossings). According to table 1, for the example with $F_C(k) = 0$ we choose a singlet order parameter and observe that the superconducting spectrum in this case inherits both PH and PP crossings. For the example with $F_C(k) \neq 0$ we choose a triplet order parameter with a $d$-vector perpendicular to the Rashba SOC vector and observe that the PH crossings away from the Fermi level are lifted. A similar discussion holds for the fourth row, with normal state Hamiltonian breaking both IS and TRS.

**4.2. Case II: nonunitary order parameter preserving TRS**

The upper left block of the BdG Hamiltonian, equation (26), reads:

$$[\hat{H}_0(k)]^2 + \hat{\Delta}(k)\hat{\Delta}^\dagger(k) = \{[\epsilon(k)]^2 + |s(k)|^2 + |\Delta_U(k)|^2\} \sigma_0 + [2\epsilon(k)s(k) + q_{\text{NU}}(k)] \cdot \hat{\sigma}. \quad (32)$$

The eigenvalues of the square of the BdG Hamiltonian for $F_C(k) = 0$ are then

$$E_\pm = [\epsilon(k)]^2 + |s(k)|^2 + |\Delta_U(k)|^2 \pm 2\epsilon(k)s(k) + q_{\text{NU}}(k)$$

$$\pm 4|\epsilon(k)s(k)||q_{\text{NU}}(k)| \cos \theta, \quad (33)$$

where $\theta$ is the angle between $q_{\text{NU}}(k)$ and $s(k)$.

The eigenvalues of the BdG Hamiltonian for $F_C(k) = 0$ are:

$$E_{\pm \pm} = \pm \left[[\epsilon(k) \pm |s(k)|]^2 + |\Delta_U(k)|^2 \pm |q_{\text{NU}}(k)|^2\right]^{1/2} + 4|\epsilon(k)s(k)||q_{\text{NU}}(k)| \cos \theta. \quad (34)$$

Under the simplifying assumption that $q_{\text{NU}}(k)$ and $s(k)$ are perpendicular, the dispersion corresponds to two bands, $\xi_{\pm}(k) = \epsilon(k) \pm |s(k)|$, developing gaps with different magnitude $\Delta_{\pm}(k) = \sqrt{|\Delta_U(k)|^2 \pm |q_{\text{NU}}(k)|^2}$. Again, from this quadrant we already recover the four eigenenergies that are expected for the superconducting dispersion of a two band superconductor (the lower right quadrant gives the same result, assuming $g(k) \cdot B = 0$).

Figure 2 displays the superconducting spectra for selected cases of TRS nonunitary superconductivity. As the nonunitary order parameter is not associated with TRS, it must be associated with ISB, therefore we chose a mix of spin singlet and spin triplet states. This would be a natural possibility for noncentrosymmetric materials, but a fine-tuned scenario for centrosymmetric systems. The first row corresponds to the normal state with both TRS and IS. In this case the normal state bands are doubly degenerate (dashed lines for both particle–particle or hole–hole band crossings (PP or HH crossings) away from the Fermi energy. According to table 1, for the example with $F_C(k) = 0$ we choose a singlet order parameter and observe that the superconducting spectrum in this case inherits both PH and PP crossings. For the example with $F_C(k) \neq 0$ we choose a triplet order parameter with a $d$-vector perpendicular to the Rashba SOC vector and observe that the PH crossings away from the Fermi level are lifted. A similar discussion holds for the fourth row, with normal state Hamiltonian breaking both IS and TRS.
4.3. Case III: nonunitary order parameter breaking TRS

The discussion concerning the superconducting spectrum for $F_C(k) = 0$ as the normal state Hamiltonian is simply proportional to the identity matrix. A nonunitary order parameter opens two different gaps and the superconducting spectrum is not degenerate (red lines). The second row corresponds to TRSB in the normal state introduced by an external magnetic field. As the superconducting state contains a spin singlet component, we necessarily have a finite superconducting fitness matrix $F_C(k)$ (see Table 1). Note that in this case the bands in the normal state are Zeeman split and there are PH crossings away from the Fermi level which are lifted in the superconducting state. The third row corresponds to ISB in the normal state, introduced by Rashba or Ising SOC. The bands in the normal state are split and there are both PH and PP/HH band crossings at finite energy. According to Table 1, for the example with $F_C(k) = 0$ we choose the SOC vector to be parallel to the $d$-vector and we find that the superconducting spectrum displays both PH and PP/HH band crossings. For the case with $F_C(k) \neq 0$ we choose a SOC with a component perpendicular to the $d$-vector. Note that in this case both PH and PP/HH crossings at finite energies are lifted (in contrast to the unitary case discussed above, for which only the PH crossings were lifted for a finite fitness matrix). A similar discussion holds for the fourth row, with normal state Hamiltonian breaking both IS and TRS.

Table 2. Symmetry allowed $(a, b)$ terms in the normal state Hamiltonian under TRS and IS for different scenarios: equal parity orbitals (EP), opposite parity orbitals (OP), and sublattice structure (SL). The second column indicates if the respective $h_{ab}(k)$ is an even or an odd function of momenta.

| $(a, b)$ | $k$ | EP | OP | SL |
|---------|-----|----|----|----|
| (0, 0)  | Even | ✓  | ✓  | ✓  |
| (0, 1)  | Odd  | ✓  | ✓  | ✓  |
| (0, 2)  | Odd  | ✓  | ✓  | ✓  |
| (0, 3)  | Odd  | ✓  | ✓  | ✓  |
| (1, 0)  | Even | ✓  | ✓  | ✓  |
| (1, 1)  | Odd  | ✓  | ✓  | ✓  |
| (1, 2)  | Odd  | ✓  | ✓  | ✓  |
| (1, 3)  | Odd  | ✓  | ✓  | ✓  |
| (2, 0)  | Odd  | ✓  | ✓  | ✓  |
| (2, 1)  | Even | ✓  | ✓  | ✓  |
| (2, 2)  | Even | ✓  | ✓  | ✓  |
| (2, 3)  | Even | ✓  | ✓  | ✓  |
| (3, 0)  | Even | ✓  | ✓  | ✓  |
| (3, 1)  | Odd  | ✓  | ✓  | ✓  |
| (3, 2)  | Odd  | ✓  | ✓  | ✓  |
| (3, 3)  | Odd  | ✓  | ✓  | ✓  |

4.3. Case III: nonunitary order parameter breaking TRS

The discussion concerning the superconducting spectrum for $F_C(k) = 0$ is similar to the one provided for case II above.

Figure 3 displays the superconducting spectra for selected cases of TRSB nonunitary superconductivity. The first row corresponds to the normal state with both TRS and IS. As in the last case, a nonunitary order parameter opens two different gaps and the superconducting spectrum is not degenerate (green lines). The second row corresponds to TRSB in the normal state, introduced by an external magnetic field. The bands in the normal state are Zeeman split, and once we consider both particle and hole sectors, we note crossings at finite energy. According to Table 1, for the example with $F_C(k) = 0$ we choose a triplet order parameter with a complex multi-component $d$-vector perpendicular to the magnetic field. The superconducting spectrum in this case inherits the crossing of the particle and hole bands in the normal state. For the example with $F_C(k) \neq 0$ we choose a complex multi-component $d$-vector with a component parallel to the magnetic field. Note that in this case the crossings away from the Fermi level are lifted. The third row corresponds to ISB in the normal state introduced by Rashba SOC. There are both PH and PP/HH crossings away from the Fermi level in the normal state electronic spectrum. According to Table 1, the only possibility is to have a finite superconducting fitness matrix, and as a consequence both PH and PP/HH band crossings are lifted in the superconducting state. A similar discussion holds for the fourth row, with normal state Hamiltonian breaking both IS and TRS.

From the discussion above, we conclude that for simple superconductors with only the spin as an internal DOF: (i) crossings in the superconducting spectra are inherited from the normal state spectra, considering both particle and hole sectors; (ii) the crossings are protected in the presence of symmetry breaking fields with $F_C(k) = 0$; (iii) PH crossings are lifted if $F_C(k) \neq 0$ for both unitary and nonunitary order parameters; (iv) PP/HH crossings are lifted if $F_C(k) \neq 0$ only in case of a nonunitary order parameter. Therefore the opening of gaps away from the Fermi level is a feature primarily associated with a finite fitness measure, and the opening of PP/HH types of crossings are necessarily associated with the nonunitary aspect of the superconducting state.

5. Superconductivity in complex quantum materials

The discussion of nonunitary order parameters becomes much richer if we move to scenarios with more than one internal degree of freedom. The first non-trivial scenario appears considering models with one extra internal DOF, which can be associated with two orbitals, or a two sublattice structure. The BdG Hamiltonian for the two orbital scenario has the same form as the one displayed in equation (2), with $n = 2$.

The normal state Hamiltonian can be generally written as:

$$H_0(k) = \sum_{ab} h_{ab}(k) \hat{\tau}_a \otimes \hat{\sigma}_b, \quad (35)$$

where $h_{ab}(k)$ are real functions of momenta encoding all the information about hopping amplitudes and SOC. $\hat{\tau}_a$ and $\hat{\sigma}_a$ are Pauli matrices for $a = \{1, 2, 3\}$ or the $2 \times 2$ identity matrix for $a = 0$, encoding the orbital or sublattice and spin DOFs, respectively. TRS is implemented by $\hat{\Theta} = K \tau_0 \otimes (i \sigma_z)$, accompanied by the change in momenta $k \rightarrow -k$, leaving the orbital and sublattice DOFs invariant. IS can appear in different flavors, depending on the nature of the extra DOF. In
We can evaluate the gauge-invariant composition of the order parameter (omitting the momentum dependence for a more concise notation):

$$\tilde{\Delta}^1 = \Delta^1 \tau_0 \otimes \sigma_0 + q_{\text{SU}}^b \tau_a \otimes \sigma_b,$$

(37)

where we define, in analogy to the case of simple superconductors discussed above:

$$\Delta^2_U = \sum_{[a,b]} |d_{ab}|^2$$

(38)

as the magnitude of the unitary part of the gap, and

$$q_{\text{SU}}^b = \text{Tr}[\tilde{\Delta}^1 \tau_a \otimes \sigma_b] / 4 = \sum_{[a,b]} [d_{00}d_{0b}^* + d_{0b}d_{0a}^*] + 2 \sum_{[m,n],[p,q]} [d_{mn}d_{pq}^* \text{Tr}[\tilde{\Delta}^1 \tau_m \sigma_n \tau_a \sigma_b \tilde{\Delta}^1] / 4,$$

(39)

the nonunitary component of the order parameter. Note that non-unitarity can be associated with both spin and orbital polarization, with the finite expectation value $\langle \tilde{\Delta}^1 \rangle$ for a given momentum, which can have a finite average over the Fermi surface.

In analogy to the single band scenario, we can again define a TRS odd gauge-invariant product [34]:

$$\tilde{\Delta}(k)\tilde{\Delta}^1(k) - \tilde{\Delta}^1(k)\tilde{\Delta}(k) = \sum_{[a,b]} q_{\text{TRI}}^b[k] \tau_a \otimes \sigma_b.$$  

(40)

If there is at least one $q_{\text{TRI}}^b[k] \neq 0$, the TRSB order parameter develops a spin–orbital polarization.

Note that we can think about the set of sixteen matrices $\tau_a \otimes \sigma_b$ as basis matrices, since these allow us to write any normal state Hamiltonian or order parameter for systems with spin and an extra internal degree of freedom that can acquire two values. This is in analogy to the $n$ basis vectors that allow us to write any vector quantity in $n$-dimensional space. Compared to systems with only the spin as an internal degree of freedom (with only four basis matrices), a greater number of basis matrices in complex superconductors allows for many more possibilities to generate nonunitary superconductivity. As we are going to discuss next, in contrast to the scenario with only the spin as an internal degree of freedom, these are not necessarily associated with symmetry breaking.

5.1 Inversion symmetry

If IS is present, the order parameters are split in two sectors of distinct parity. Focusing on order parameters that are even in $k$ (see third column in table 3), we can gather the following possible superpositions for each scenario (EP, OP, SL), omitting the momentum dependence of the $d_{ab}(k)$ functions:

$$\Delta_{\text{EP}}^{\text{Even}} = [d_{00} \tau_0 \otimes \sigma_0 + d_{01} \hat{\tau}_1 \otimes \sigma_0 + d_{02} \hat{\tau}_2 \otimes \sigma_0 + d_{03} \hat{\tau}_3 \otimes \sigma_0] \hat{\sigma}_2$$

(41)
Note that, if IS is the only relevant spatial symmetry, there are even-parity non-unitary order parameters, in contrast to the scenario with only the spin as an internal degree of freedom. In particular, if the internal DOF is associated with two orbitals of equal parity, there are potentially five different basis matrices contributing to the superconducting order parameter, including inter-orbital spin-singlets and spin-triplets.

Below we refine the discussion considering point group symmetries, and show that in certain cases multiple realizations of order parameters can be found in the trivial irrep, such that no extra symmetry is broken (beyond the standard U(1) gauge symmetry).

6. Application to d-electron systems

Here we focus on d-electron systems, belonging to the EP scenario discussed above. The conclusions drawn here can be applied to multiple families of materials already associated with nonunitary superconductivity. Specifically, both LaNiC2 and LaNiG2 have been shown to carry significant contributions of Ni 5d electrons near the Fermi level [20, 58]. The noncentrosymmetric Weyl semimetals LaNiSi, LaPtSi, and LaPtGe are inherently multi-orbital systems, with La 5d electrons dominating the electronic contribution near the Fermi level [59]. (Ta, Nb)O3Si are also multi-orbital systems with Nb 4d (Ta 5d) and Os 5d electrons contributing the most to the density of states near the Fermi level [33]. Other materials in the family of transition metal oxides and rhenates [60], iron pnictides [61, 62], and transition metal dichalcogenides [63, 64] are also known to host electronic structures with strong d-electron character near the Fermi surface.

In order to give a concrete example, in appendix A we explicitly derive the symmetry classification of the order parameters for the D2h point group for different choices of pairs of d-electrons. The derivations for other point groups follow the very same lines. The results for point groups D2h, D4h, and D4d with IS and C2v, D2h and C2v, without IS are shown in tables 8–13 in appendix B. Interestingly, these groups are associated with several materials that develop TRSB SC, according to table 1 in reference [65]. In absence of IS, orbitals of different parity can mix, but here we assume that the mixing is small and explore the discussion only with d-electrons in the case of ISB in the normal state.

For the classification of the order parameters labeled as [a, b] according to the irreducible representations of the point group, we write the point group operations as unitary transformations acting as \( \Delta(k) \rightarrow \Delta'(k') = U \Delta(k) U^T \), where the superscript T indicates the transpose and \( k' = U k \) is the rotated k vector. Note that since the inversion operation acts trivially on the matrix structure of the order parameters in the EP scenario, their parity is directly determined by the parity of the accompanying momentum dependent function \( d_{ab}(k) \), which is pre-determined by fermionic antisymmetry (see third column of table 3).

We focus on even parity momentum independent order parameters to simplify the discussion. In this case, the symmetry properties of the order parameters are completely determined by their matrix structure. As a concrete example, we consider \( \{d_{ab}, d_{ac}\} \) orbitals in a lattice with D2h point group symmetry. Table 4 summarizes how each matrix \( \tilde{\gamma}_0 \otimes \tilde{\gamma}_3(i\tilde{\tau}_2) \), labeled as \([a, b]\), transforms under the point group operations (see appendix A), allowing for the identification of the irreducible representations in accordance with the character table (table 7 in the appendix), as summarized in the right column of table 4.

In appendix B we provide tables compiling the results for multiple point group symmetries and different choices of pairs of d-orbitals (tables 8–13). The bottom line is that there are always two or more basis matrices that transform according to the trivial representation (A1g or A1, for groups with and without IS, respectively): \([0, 0], [3, 0], [2, 0], [2, 3]\), or \([3, 0], [2, 0], [2, 3]\), for \( b = 1, 2, 3 \). For these scenarios, the gap can be a linear superposition of the basis matrices and follows (note that there is no sum over the index \( h \)):

\[
\Delta(k) = |d_{ab}(k)| \tilde{\gamma}_0 \otimes \tilde{\gamma}_0 + |d_{ab}(k)| \tilde{\gamma}_1 \otimes \tilde{\gamma}_0 + d_{ab}(k) \tilde{\gamma}_2 \otimes \tilde{\gamma}_0 + d_{ab}(k) \tilde{\gamma}_3 \otimes \tilde{\gamma}_0. \tag{46}
\]

such that, omitting the k dependence:

\[
\Delta \sim |d_{ab}(k)| \tilde{\gamma}_0 \otimes \tilde{\gamma}_0 + |d_{ab}(k)| \tilde{\gamma}_1 \otimes \tilde{\gamma}_0 + d_{ab}(k) \tilde{\gamma}_2 \otimes \tilde{\gamma}_0 + d_{ab}(k) \tilde{\gamma}_3 \otimes \tilde{\gamma}_0. \tag{47}
\]

Note that, in case all \( d_{ab} \) coefficients are real (the order parameter is TRS), the matrices which appear in \( \Delta \Delta^\dagger \) are necessarily in the trivial representation \( \tilde{\gamma}_0 \otimes \tilde{\gamma}_0, \tilde{\gamma}_1 \otimes \tilde{\gamma}_0, \tilde{\gamma}_2 \otimes \tilde{\gamma}_0, \tilde{\gamma}_3 \otimes \tilde{\gamma}_0 \). This reflects the fact that non-unitarity in multi-orbital superconductors (as defined by a finite \( g_{ab}(k) \)) is not necessarily associated with symmetry breaking, in contrast to the

| Table 4 | Identification of the irreps of the order parameters for \( \{d_{ac}, d_{ab}\} \) orbitals in the D2h point group. Highlighted in bold are the three realizations of order parameters with A1g symmetry. |
|---------|--------|--------|--------|--------|--------|
| [a, b]  | E      | C2v    | C2v    | C2v    | Irrep  |
| [0, 0]  | 1      | 1      | 1      | 1      | A1g    |
| [1, 0]  | 1      | 1      | –1     | –1     | B1g    |
| [3, 0]  | 1      | 1      | 1      | 1      | A1g    |
| [2, 1]  | 1      | –1     | –1     | 1      | B2g    |
| [2, 2]  | 1      | –1     | 1      | –1     | B3g    |
| [2, 3]  | 1      | 1      | 1      | 1      | A1g    |

\[ \hat{A}_{\text{even}} = \begin{bmatrix} d_{00} \tilde{\tau}_0 \otimes \tilde{\tau}_0 + d_{30} \tilde{\tau}_3 \otimes \tilde{\tau}_0 \end{bmatrix} i \tilde{\tau}_2 \tag{42} \]

\[ \hat{A}_{\text{odd}} = \begin{bmatrix} d_{10} \tilde{\tau}_1 \otimes \tilde{\tau}_0 + d_{21} \tilde{\tau}_2 \otimes \tilde{\tau}_1 \\
+ d_{22} \tilde{\tau}_2 \otimes \tilde{\tau}_2 + d_{23} \tilde{\tau}_2 \otimes \tilde{\tau}_3 \end{bmatrix} i \tilde{\tau}_2 \tag{43} \]

\[ \hat{A}_{\text{even}} = \begin{bmatrix} d_{00} \tilde{\tau}_0 \otimes \tilde{\tau}_0 + d_{10} \tilde{\tau}_1 \otimes \tilde{\tau}_0 \end{bmatrix} i \tilde{\tau}_2 \tag{44} \]

\[ \hat{A}_{\text{odd}} = \begin{bmatrix} d_{00} \tilde{\tau}_0 \otimes \tilde{\tau}_0 + d_{10} \tilde{\tau}_1 \otimes \tilde{\tau}_0 + d_{21} \tilde{\tau}_2 \otimes \tilde{\tau}_1 \\
+ d_{22} \tilde{\tau}_2 \otimes \tilde{\tau}_2 + d_{23} \tilde{\tau}_2 \otimes \tilde{\tau}_3 \end{bmatrix} i \tilde{\tau}_2. \tag{45} \]
discussion in the single orbital scenario. If the order parameter breaks TRS and develops a finite $g_{FAB}^0(k)$, there is a finite spin–orbital polarization of the pairs. In the next section we are going to discuss how these aspects are reflected in the superconducting energy spectra.

7. Signatures of nonunitary order parameters in the two orbital scenario

In this section we translate some of the conclusions we found for the case of simple superconductors, carrying only the spin as an internal DOF, to the more complex scenario of superconductors with an extra orbital DOF.

In the normal state, in presence of inversion and time-reversal symmetries, the normal state spectrum in presence of TRS and IS can be obtained by diagonalizing $H_0(k)$ given by equation (35) with coefficients $h_{ab}(k)$ given in table 2 for the EP scenario, leading to:

$$\xi_{\pm}(k) = h_{00}(k) \pm |h(k)|,$$  \hspace{1cm} (48)

where $h(k)$ is the vector formed by the five symmetry allowed $h_{ab}(k)$ for $(a, b) \neq (0, 0)$, in analogy to the $s(k)$ vector for the single DOF case discussed above. For concreteness, here we take the example of d-electrons $\{d_{xz}, d_{yz}\}$ and point group $D_{2h}$. We write the parameters $h_{ab}(k)$ as expansions around the $\Gamma$ point:

$$h_{00}(k) = |k|^2 / (2m_1) - \mu_1,$$
$$h_{10}(k) = \beta k_x k_y,$$
$$h_{23}(k) = \gamma_1 k_x k_y,$$
$$h_{21}(k) = \gamma_2 k_x k_y,$$
$$h_{30}(k) = |k|^2 / (2m_2) - \mu_2,$$  \hspace{1cm} (49)

here $h_{00}(k)$ and $h_{30}(k)$ correspond to intra-orbital hopping, $h_{10}(k)$ to inter-orbital hopping, $h_{23}(k)$ to atomic SOC, and $h_{21,22}(k)$ to $k$-dependent SOC. For the plots below we choose the parameters $(m_1, m_2, \mu_1, \mu_2, \alpha, \beta, \gamma_1, \gamma_2) = (0.5, -2.5, 1.2, -0.5, 0.1, 0.15, 0.12, 0.17)$. Here we take $\hbar = 1$ (in units of energy times second), $m_1$ and $m_2$ have units of mass, $\mu_1$, $\mu_2$ and $\alpha$ have units of energy, and $\gamma_1$ and $\gamma_2$ have units of energy times length squared. For the discussion in absence of SOC we take $\alpha = \gamma_1 = \gamma_2 = 0$. The parameters were chosen such that in absence of SOC the two bands in the normal state cross near the Fermi energy.

With the possible order parameters listed in table 4 and the normal state Hamiltonian detailed above, we can evaluate the superconducting fitness for a system with two orbitals with equal parity.

For the discussion of the spectrum in the superconducting state, it is again useful to consider the square of the BdG Hamiltonian which has the same structural form as equation (26). In case $F_C(k) = 0$, the square of the BdG Hamiltonian is block diagonal. The top left block reads:

$$[H_0(k)]^2 + \hat{\Delta}(k)\hat{\Delta}^\dagger(k)$$
$$= \{[h_{00}(k)]^2 + [h(k)]^2 + [\Delta_U(k)]^2\} \tau_0 \otimes \sigma_0$$
$$+ \sum_{a,b} [2h_{00}(k)h_{ab}(k) + q_{ab}^{00}(k)] \tau_a \otimes \sigma_b,$$  \hspace{1cm} (50)

where the primed sum in the last term excludes the case with both $a = 0$ and $b = 0$. Note that the square of the dispersion for the two-orbital model, given by equation (50), and for the single orbital scenario with external symmetry breaking fields, given by equation (32), have the same structure. This indicates that we can build up the discussion for the two-orbital scenario on similar lines.

Starting with unitary order parameters, the eigenenergies of the square of the BdG Hamiltonian simplify to:

$$E_{\pm} = [h_{00}(k) \pm h(k)]^2 + |\Delta_U(k)|^2,$$  \hspace{1cm} (51)

such that the eigenenergies of the BdG Hamiltonian are

$$E_{\pm} = \pm \sqrt{[h_{00}(k) \pm h(k)]^2 + |\Delta_U(k)|^2},$$  \hspace{1cm} (52)

which are doubly degenerate. As in the case of a single DOF, we find two bands, $\xi_{\pm}(k) = h_{00}(k) \pm |h(k)|$, that develop gaps of same magnitude.

For nonunitary order parameters, the eigenenergies of the square of the BdG Hamiltonian are:

$$E_{\pm} = [h_{00}(k) \pm h(k)]^2 + |\Delta_U(k)|^2$$
$$\pm \sum_{a,b} [2h_{00}(k)h_{ab}(k) + q_{ab}^{00}(k)],$$  \hspace{1cm} (53)

In case the vectors formed by the components $h_{ab}(k)$ and $q_{ab}^{00}(k)$ are orthogonal, the square of the dispersion simplifies to:

$$E_{\pm} = [h_{00}(k) \pm h(k)]^2 + |\Delta_U(k)|^2 \pm \sum_{a,b} |q_{ab}^{00}(k)|,$$  \hspace{1cm} (54)

and the eigenenergies of the BdG Hamiltonian are

$$E_{\pm} = \pm \sqrt{[h_{00}(k) \pm h(k)]^2 + |\Delta_U(k)|^2} \pm \sum_{a,b} |q_{ab}^{00}(k)|.$$  \hspace{1cm} (55)

Here the two doubly-degenerate bands, $\xi_{\pm}(k) = h_{00}(k) \pm |h(k)|$, develop distinct gaps $|\Delta_{\pm}(k)|^2 = |\Delta_U(k)|^2 \pm \sum_{a,b} |q_{ab}^{00}(k)|$.

Figure 4 illustrates selected scenarios for the superconducting spectrum for unitary and nonunitary order parameters, with zero or finite fitness matrix. On the left column we have the cases with SOC, in which there are PH crossings but no PP/HH crossings in the normal state. On the right column we have the scenario without SOC, in which case there are PP/HH crossings, in addition to the PH crossings. In the first row we have examples of spectra corresponding to unitary order parameters and $F_C(k) = 0$. According to table 5, the only possibility...
When finite, these parameters acquire the following values:

highlight the finite parameters among

that there is no example for these specific conditions. In brackets we

scenario without SOC (with SOC, and the right column corresponds to the fine-tuned

is zero or non-zero. The left columns corresponds to the scenario

away from the Fermi level. On the left of each row it is indicated if

lines correspond to the superconducting spectrum, while the gray
dashed lines correspond to the normal state bands (both particle and
hole sectors). The horizontal gray line corresponds to the Fermi
level. Note the presence of both PH crossings and PP/HH crossings

for each term \( h_{\alpha \beta}(k) \) in the normal-state Hamiltonian indicated in the

first row as \((c, d)\).

Table 5. Superconducting fitness analysis for effective models with
two orbitals of equal parity. This table is in direct parallel to table 1
and should be read as follows: the first column corresponds to the
function \( d_{\alpha \beta}(k) \) accompanied by the basis matrix \([a, b]\) contributing
to the order parameter in equation (36), while the first line specifies
the \( h_{\alpha \beta}(k) \) terms in the normal state Hamiltonian in equation (35),
accompanied by the corresponding basis matrix. The table entries

| Conditions | PH | PP |
|------------|----|----|
| Unitary    | \( F_c(k) = 0 \) | Cross | Cross |
| Unitary    | \( F_c(k) \neq 0 \) | Open | Cross |
| Nonunitary | \( F_c(k) = 0 \) | Cross | Cross |
| Nonunitary | \( F_c(k) \neq 0 \) | Open | Open |

Table 6. Summary of the band crossings in the superconducting
state for different conditions. PH corresponds to the superposition
of particle and hole bands and PP to the superposition of particle bands
in the two DOF scenario.

Figure 4. Superconducting spectra for order parameters in the
two-orbital models with TRS and IS along the \( k_z \) axis. The orange
lines correspond to the superconducting spectrum, while the gray
dashed lines correspond to the normal state bands (both particle and
hole sectors). The horizontal gray line corresponds to the Fermi
level. Note the presence of both PH crossings and PP/HH crossings
away from the Fermi level. On the left of each row it is indicated if
the order parameter is unitary or nonunitary, and if the fitness matrix
is zero or non-zero. The left columns corresponds to the scenario
with SOC, and the right column corresponds to the fine-tuned
scenario without SOC (\( \alpha = \gamma_1 = \gamma_2 = 0 \)). The gray box indicates
that there is no example for these specific conditions. In brackets we
highlight the finite parameters among \([d_{00}, d_{01}, d_{21}, d_{22}, d_{23}, d_{30}]\).
When finite, these parameters acquire the following values:
\( d_{00} = 0.5 \), \( d_{30} = 0.25 \), \( d_{21} = d_{23} = 0.25 \), and \( d_{22} = 0.25 \).

for \( \hat{F}_c(k) = 0 \) corresponds to a intra-orbital spin-singlet state
labeled as \([0, 0]\). Note that for this case both types of crossings
are preserved in the superconducting state. In the second row,
following table 5, we choose unitary order parameters
with \( F_c(k) \neq 0 \) and observe that the PH crossings are lifted.
In the third row we have an example of a TRS nonunitary
state with \( F_c(k) = 0 \). Note that this configuration is rather special
as depends on setting all SOC terms to zero and is valid
only for certain directions in momentum space (see table 5 and
equation (49)). What is important to note here is that both types
of crossings are preserved in case \( \hat{F}_c(k) = 0 \) even for a nonunitary
order parameter. In the fourth row we have examples of
spectra for TRS nonunitary states with finite fitness matrix.
For the scenario without SOC we see that the PP crossings
are lifted, in addition to the PH crossings. In the fifth row we
display spectra for TRSB nonunitary superconducting states.
The spectrum in presence of SOC is more complex due to
the degeneracy breaking associated with the TRSB nonunitary
order parameter. For the fine-tuned scenario without SOC we
do not see the splitting due to the choice of momentum along
the \( k_z \) direction. Any other direction away from the symmetry
axes would display the splitting, as expected. For both cases,
with and without SOC, the spectrum does not display crossings
of the PH or PP/HH types at finite energy.

These results confirm what we had already discussed within
the single DOF scenario: a finite fitness matrix is a necessary
condition for the opening of gaps associated with PH crossings.
For the PP/HH crossings intrinsic to the band structure,
the minimal requirement for their lifting is a nonunitary order
parameter and a finite fitness matrix. In conclusion, the opening
of gaps at energies away from the Fermi level is primarily
associated with a finite superconducting fitness. In case the
crossing was already present in the normal state electronic
structure (purely in the PP sector), it indicates a nonunitary
order parameter. These results are summarized in table 6.

8. Discussion and conclusion

In this work we have revisited the notion of nonunitary order
parameters. We have started with simple superconductors,
emerging from electronic states with only the spin as an internal
DOF. We highlight the fact that nonunitary superconducting
states are necessarily associated with either ISB or TRSB
of the superconducting order parameter and with the development
of a two-gap structure (most clearly observed for a
normal state with both IS and TRS). Furthermore, we discuss how external symmetry breaking fields in the normal state change the spectra in the superconducting state. In particular, we find that symmetry breaking terms in the normal state lead to crossings of the particle and hole bands at energies away from the Fermi energy, and that these crossings are inherited by the superconducting state in case the fitness matrix is zero, $\hat{F}_c(k) = 0$. Once the fitness matrix is nonzero, $\hat{F}_c(k) \neq 0$, these crossings are lifted. In this context, the lifting of the PH crossings does not give us any information about the unitary or nonunitary character of the superconducting order parameter.

With this more refined understanding of the superconducting spectra in simple superconductors, we moved to the minimal scenario to treat complex superconductors, considering an extra internal DOF which can acquire two flavors. We find that there are many more possibilities to construct a nonunitary order parameter. Focusing on d-electron systems, with even-parity momentum-independent order parameters, we find that multiple point group symmetries allow for nonunitary order parameters in the trivial irreducible representation. Concerning the spectra, we find that particle–hole and particle–particle band crossings are protected for unitary order parameters with $\hat{F}_c(k) = 0$, but that the particle–hole crossings are lifted as soon as $\hat{F}_c(k) \neq 0$, as discussed in the context of simple superconductors. In contrast, if we consider nonunitary order parameters, both crossings are again protected for $\hat{F}_c(k) = 0$, but both particle–particle and particle–hole crossings are lifted as soon as $\hat{F}_c(k) \neq 0$. In conclusion, the particle–hole crossings away from the Fermi energy are lifted as soon as $\hat{F}_c(k) \neq 0$, but the lifting of particle–particle crossings require both $\hat{F}_c(k) \neq 0$ and a nonunitary order parameter. The later type of gap opening can be used as a direct indicator of nonunitary superconductivity.

Nonunitary order parameters have been recently discussed in multiple contexts, motivated by materials characterization and theoretical investigations. It was recently proposed that one of the signatures of nonunitary order parameters is the opening of gaps away from the Fermi surface in Dirac materials [44]. Previous works have associated these gap openings to a measure of odd-frequency pairing correlations in Ising [66] and multi-band superconductors [67]. The discussion in this manuscript comes as a reference to clarify how these spectral signatures proposed for the identification of both nonunitary superconducting states and odd-frequency correlations are more general than the context in which they were originally proposed. This work also clearly ties these works together, highlighting that they are all connected to the underlying concept of superconducting fitness.

One last note on the experimental identification of nonunitary superconducting states. Within simple superconductors, the most clear evidence of nonunitary pairing is the observation of a two-gap structure in the superconducting spectrum. Indirect evidence of nonunitarity can come from experiments that can probe spontaneous TRSB in the superconducting state, such as muon spin resonance or polar Kerr effect (note that this is not a unique signature of nonunitary superconductors, as chiral unitary superconductors are also associated with spontaneous TRSB). Furthermore, the absence of ISB in the normal state would naturally lead to a superconducting order parameter with mixed parity, which is by definition nonunitary. In conclusion, in the context of simple superconductors, the investigation of the presence or absence of key symmetries can give us indications about the nonunitary character of the order parameter.

In complex superconductors, nonunitarity is not necessarily associated with any symmetry breaking and its experimental identification becomes elusive. As discussed here, investigating the superconducting spectra, in particular the appearance of gaps at particle–particle band crossings in the superconducting state seems to be a reliable indicator of nonunitarity. Note, though, that the presence of band crossings close to the Fermi level is not very common, what makes this specific indicator not widely useful. One recent potential example of this phenomenology was observed in the topological surface states of FeTe$_{1-x}$Se$_x$. Once this material goes to the superconducting state, the surface states develop a gap at the Fermi surface and a second gap at the nearby Dirac point [68]. FeSe thin films are also stablished to host band crossings in the form of Dirac points in the band structure near the Fermi surface, as reported by ARPES experiments [69]. This suggests that Fe-based superconductors are promising materials for nonunitary superconductors to be identified. Interestingly, nonunitary superconductors breaking both TRS and IS (not discussed here) but invariant under the product of these symmetries, are expected to be associated with exotic phenomena such as supercurrent-induced strain or photon-induced supercurrents [36]. This suggests that transport experiments could directly probe the nonunitary character of superconductors, at least within a subclass of nonunitary superconducting states.

An interesting perspective of this work is the general association of nonunitary order parameters with TRSB. In complex superconductors with multiple basis matrices for the order parameter within a single irreducible representation, a TRSB order parameter is possible within the trivial irreducible representation. The discussion of the stabilization this type of order parameter is left for future investigation.

Acknowledgments

The author thanks Daniel F Agterberg, Philip M R Brydon, and Carsten Timm for useful discussions. The author also acknowledges the financial support of the Swiss National Science Foundation through the Ambizione Grant No. 186043.

Data availability statement

No new data were created or analysed in this study.

Appendix A

The point group $D_{2h}$ consists of the following operations: $E$, the identity; $C_{2n}$, two-fold rotations along the axis $n = x, y, z$,
Table 8. $D_{2h}$ point group. The results for $\{d_{x^2}, d_{y^2}\}$ also apply to $\{d_{x^2}, d_{z^2}\}$, the results for $\{d_{z^2}, d_{y^2}\}$ also apply to $\{d_{z^2}, d_{x^2}\}$, and the results for $\{d_{y^2}, d_{z^2}\}$ also apply to $\{d_{y^2}, d_{x^2}\}$.

| $[a, b]$ | $\{d_{x^2}, d_{y^2}\}$ | $\{d_{y^2}, d_{z^2}\}$ | $\{d_{z^2}, d_{x^2}\}$ | $\{d_{3z^2}, d_{y^2}\}$ | $\{d_{3z^2}, d_{x^2}\}$ |
|----------|----------------|----------------|----------------|----------------|----------------|
| [0, 0]   | $A_g$          | $A_g$          | $A_g$          | $A_g$          | $A_g$          |
| [1, 0]   | $B_{3g}$       | $B_{3g}$       | $B_{3g}$       | $B_{3g}$       | $B_{3g}$       |
| [3, 0]   | $A_g$          | $A_g$          | $A_g$          | $A_g$          | $A_g$          |
| [2, 1]   | $B_{2g}$       | $A_g$          | $B_{2g}$       | $B_{2g}$       | $B_{2g}$       |
| [2, 2]   | $B_{2g}$       | $B_{2g}$       | $B_{2g}$       | $B_{2g}$       | $B_{2g}$       |
| [2, 3]   | $A_g$          | $B_{2g}$       | $B_{2g}$       | $B_{2g}$       | $B_{2g}$       |

If we choose $\{d_{x^2}, d_{y^2}\}$ as basis orbitals, these orbitals transform as:

$C_{2x} : \{x, y, z\} \rightarrow \{x, -y, -z\}$, \hspace{1cm} (56)

$C_{2y} : \{x, y, z\} \rightarrow \{-x, y, -z\}$, \hspace{1cm} (57)

$C_{2z} : \{x, y, z\} \rightarrow \{-x, -y, z\}$, \hspace{1cm} (58)

$i : \{x, y, z\} \rightarrow \{-x, -y, -z\}$. \hspace{1cm} (59)

If we choose $\{d_{x^2}, d_{y^2}\}$ as basis orbitals, these orbitals transform as:

$C_{2x} : \{d_{x^2}, d_{y^2}\} \rightarrow \{-d_{x^2}, d_{y^2}\} \Rightarrow -\hat{\tau}_3$, \hspace{1cm} (60)

$C_{2y} : \{d_{x^2}, d_{y^2}\} \rightarrow \{d_{x^2}, -d_{y^2}\} \Rightarrow \hat{\tau}_3$, \hspace{1cm} (61)

$C_{2z} : \{d_{x^2}, d_{y^2}\} \rightarrow \{-d_{x^2}, -d_{y^2}\} \Rightarrow -\hat{\tau}_0$, \hspace{1cm} (62)

$i : \{d_{x^2}, d_{y^2}\} \rightarrow \{d_{x^2}, d_{y^2}\} \Rightarrow \hat{\tau}_0$, \hspace{1cm} (63)

such that we can associate a given $\hat{\tau}_i$ matrix in orbital space to each transformation.

Concerning the spin DOF, these transformations act as follows:

$C_{2x} : e^{-i\varphi \sigma_z / 2} = -i\hat{\sigma}_x$, \hspace{1cm} (64)

$C_{2y} : e^{-i\varphi \sigma_y / 2} = -i\hat{\sigma}_y$, \hspace{1cm} (65)

$C_{2z} : e^{-i\varphi \sigma_z / 2} = -i\hat{\sigma}_z$, \hspace{1cm} (66)

$i : \hat{\sigma}_0$. \hspace{1cm} (67)

The complete matrix form of the point group operations above are then:

$C_{2x} : i\hat{\tau}_3 \otimes \hat{\sigma}_x$, \hspace{1cm} (68)

$C_{2y} : i\hat{\tau}_3 \otimes \hat{\sigma}_y$, \hspace{1cm} (69)

$C_{2z} : i\hat{\tau}_0 \otimes \hat{\sigma}_z$. \hspace{1cm} (70)
\[ i : \hat{\tau}_0 \otimes \hat{\sigma}_0. \] (71)

The order parameter transforms under any unitary operation as \[ \Delta(k) \rightarrow \hat{\Delta}^*(k') = U^T \Delta(k') U, \] where the superscript \( T \) indicates the transpose and \( k' = \hat{U} k \) is the rotated \( k \) vector. Note that since the inversion operation acts trivially on the matrix structure of the order parameters, their parity in the EP scenario is directly determined by the parity of the accompanying momentum dependent function \( \mu_\alpha(k) \), which is pre-determined by fermionic antisymmetry. Applying this prescription for the classification of order parameters, we find table 4 in the main text.

**Appendix B**

Below are tables proving the classification of s-wave \((k\text{-}\text{independent})\) order parameters for two-orbital models with distinct pairs of d-electrons considering different point groups.

**ORCID iDs**

Aline Ramires https://orcid.org/0000-0002-1949-363X

**References**

[1] Khim S et al 2021 Field-induced transition within the superconducting state of CeRh1-xAs2, Science 373 1012–6
[2] Ran et al 2019 Extreme magnetic field-boosted superconductivity Nat. Phys. 15 1250–4
[3] Mackenzie A P, Scaffidi T, Hicks C W and Maeno Y 2017 Even odder after twenty-three years: the superconducting order parameter of Sr2RuO4, npj Quantum Mater. 4 20
[4] Andersen L, Ramires A, Wang Z, Lorenz T and Ando Y 2020 Generalized Anderson’s theorem for superconductors Phys. Rev. B 102 114502
[5] Lu J M, Zheliuk O, Leermakers I, Yuan N F Q, Zeitler U, Law M H and Wu H Q 2013 Evidence for two-gap superconductivity in the non-centrosymmetric compound LaNi2Cu2, Phys. Rev. B 87 144511
[6] Chen J, Jiao L, Zhang J L, Chen Y, Yang L, Nicklas M, Steglich F and Yuan H Q 2013 Evidence for two-gap superconductivity in the non-centrosymmetric compound LaNi2Cu2, Phys. Rev. B 87 104501
[7] Quan Y, Taufour V and Pickett W E 2022 Nonsymmorphic band sticking in a topological superconductor Phys. Rev. B 105 084517
[8] Andrade J A M et al 2022 Dirac lines and loop at the Fermi level in the time-reversal symmetry breaking superconductor LaNi2Cu2, Commun. Phys. 5 22
[9] Yearzmysky G V and Teplyakov E A 2020 Time reversal symmetry and the structure of Cooper pair wavefunction in topological superconductor UT2, Phys. Rev. B 101 045124
[10] Nevidomskyy A H 2020 Stability of a nonunitary triplet pairing on the border of magnetism in UT2, arXiv:2001.02699
[11] Wang T et al 2022 Spin-triplet superconductivity in Weyl nodal-line semimetals, arXiv:2202.05561
[12] Ghosh S K, Biswas P K, Xu C, Li B, Zhao J Z, Hillier A D and Yuan H Q 2013 Evidence for two-gap superconductivity in the non-centrosymmetric compound LaNi2Cu2, Phys. Rev. B 87 144511
[13] Brydon P M R, Agterberg D F, Menke H and Timm C 2018 Bogoliubov Fermi surfaces: general theory, magnetic order, and topology Phys. Rev. B 98 224509
[14] Agterberg D F, Brydon P M R and Timm C 2017 Bogoliubov Fermi surfaces in superconductors with broken time-reversal symmetry Phys. Rev. Lett. 118 127001
[15] Kanasaigi S and Yanase Y 2021 Anapole superconductivity from †PT-symmetric mixed-parity interband pairing, arXiv:2107.07096
[16] Hatsuji Y, Ryu S and Kohmoto M 2004 Superconductivity and abelian chiral anomalies Phys. Rev. B 70 054502
[38] Takagi D, Mercaldo M T, Tanaka Y and Cuoco M 2021 Odd-frequency pairing in a nonunitary p-wave superconductor with multiple Majorana fermions (arXiv:2112.01009)

[39] Abu Alrub T R and Curnoe S H 2007 Impurity induced density of states and residual transport in nonunitary superconductors Phys. Rev. B 76 184511

[40] Möckli D and Khodas M 2018 Robust parity-mixed superconductivity in disordered monolayer transition metal dichalcogenides Phys. Rev. B 98 144518

[41] Yoshida T, Sigrist M and Yanase Y 2014 Parity-mixed superconductivity in locally non-centrosymmetric system J. Phys. Soc. Japan 83 013703

[42] Tkachov G 2017 Magnetoelectric Andreev effect due to proximity-induced nonunitary triplet superconductivity in helical metals Phys. Rev. Lett. 118 016802

[43] Linder J, Grønsleth M S and Sudbø A 2007 Conductance spectra of ferromagnetic superconductors; quantum transport in a ferromagnetic metal/non-unitary ferromagnetic superconductor junction Phys. Rev. B 75 054518

[44] Lado J L and Sigrist M 2019 Detecting nonunitary multiorbital superconductivity with Dirac points at finite energies Phys. Rev. Res. 1 033107

[45] Mineev V P 2002 Superconducting states in ferromagnetic metals Phys. Rev. B 66 134504

[46] Wolf T M R, Holst M F, Sigrist M and Lado J L 2021 Non-unitary multiorbital superconductivity from competing interactions in Dirac materials (arXiv:2108.01452)

[47] Zeng M, Xu D-H, Wang Z-M and Hu L-H and Zhang F-C 2022 Spin–orbit–vector in a two-band spin-singlet superconductor: application to nematic superconductivity (arXiv:2109.06039)

[48] Zeng M, Xu D-H, Wang Z-M and Hu L-H 2022 Spin–orbit–vector in a two-band spin-singlet superconductor: application to Sr2RuO4 Phys. Rev. B 94 104501

[49] Ramires A and Sigrist M 2016 Identifying detrimental effects for multiorbital superconductivity: application to Sr2RuO4 Phys. Rev. B 94 104501

[50] Ramires A, Agterberg D F and Sigrist M 2018 Tailoring $T_c$ by symmetry principles: the concept of superconducting fitness Phys. Rev. B 98 024501

[51] Suh H G, Menke H, Brydon P M R, Timm C, Ramires A and Agterberg D F 2020 Stabilizing even-parity chiral superconductivity in Sr2RuO4 Phys. Rev. Res. 2 032023

[52] Ramires A 2022 Nodal gaps from local interactions in Sr2RuO4 J. Phys.: Conf. Ser. 2164 012002

[53] Möckli D and Ramires A 2021 Two scenarios for superconductivity in CeRh2As2 Phys. Rev. Res. 3 023204

[54] Zinkl B and Ramires A 2022 Sensitivity of superconducting states to the impurity location in layered materials (arXiv:2201.05045)

[55] Beck S, Hampel A, Zingl M, Timm C and Ramires A 2021 The effects of strain in multi-orbital superconductors: the case of Sr2RuO4 (arXiv:2111.13506)

[56] Triola C, Cayao J and Black-Schaffer A M 2020 The role of odd-frequency pairing in multiband superconductors Ann. Phys., Lpc. 532 1900298

[57] Wang Y and Fu L 2017 Topological phase transitions in multi-component superconductors Phys. Rev. Lett. 119 187003

[58] Singh D J 2012 Electronic structure and ferromagnetism of superconducting LaNiGa2 Phys. Rev. B 86 174507

[59] Zhang P, Yuan H and Cao C 2020 Electron–phonon coupling and nontrivial band topology in noncentrosymmetric superconductors LaNiSi, LaPtSi, and LaPtGe Phys. Rev. B 101 245145

[60] Georges A, de’ Medici L and Mravlje J 2013 Strong correlations from Hund’s coupling Annu. Rev. Condens. Matter Phys. 4 137–78

[61] Stewart G R 2011 Superconductivity in iron compounds Rev. Mod. Phys. 83 1589–652

[62] Wen H-H and Li S 2011 Materials and novel superconductivity in iron pnictide superconductors Annu. Rev. Condens. Matter Phys. 2 121–40

[63] Silva-Guillén J Á, Ordejón P, Guinea F and Canadell E 2016 Electronic structure of 2H-NbSe2 single-layers in the CDW state 2D Mater. 3 035028

[64] Roldán R, López-Sancho M P, Guinea F, Cappelluti E, Silva-Guillén J A and Ordejón P 2014 Momentum dependence of spin–orbit interaction effects in single-layer and multi-layer transition metal dichalcogenides 2D Mater. 1 034003

[65] Ghosh S K, Smidman M, Shang T, Annett J F, Hillier A D, Quintanilla J and Yuan H 2020 Recent progress on superconductors with time-reversal symmetry breaking J. Phys.: Condens. Matter. 33 033001

[66] Tang G, Bruder C and Belzig W 2021 Magnetic field-induced ‘mirage’ gap in an Ising superconductor Phys. Rev. Lett. 126 237001

[67] Komendová L, Balatsky A V and Black-Schaffer A M 2015 Experimentally observable signatures of odd-frequency pairing in multiband superconductors Phys. Rev. B 92 094517

[68] Zaki N, Gu G, Tsvelik A, Wu C and Johnson P D 2021 Time-reversal symmetry breaking in the Fe-chalcogenide superconductors Proc. Natl Acad. Sci. 118 e2007241118

[69] Tan S Y et al 2016 Observation of Dirac cone band dispersions in FeSe thin films by photoemission spectroscopy Phys. Rev. B 93 104513