Symmetry analysis of odd- and even-frequency superconducting gap symmetries for time-reversal symmetric interactions

R. Matthias Geilhufe[1,*] and Alexander V. Balatsky[1,2,3]

[1]*Nordita, KTH Royal Institute of Technology and Stockholm University, Roslagstullsbacken 23, SE-106 91 Stockholm, Sweden*
[2]*Institute for Materials Science, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[3]*Department of Physics, University of Connecticut, Storrs, Connecticut 06269, USA*

Odd-frequency superconductivity describes a class of superconducting states where the superconducting gap is an odd function in relative time and Matsubara frequency. We present a group theoretical analysis based on the linearized gap equation in terms of Shubnikov groups of the second kind. By discussing systems with spin-orbit coupling and an interaction kernel which is symmetric under the reversal of relative time, we show that both even- and odd-frequency gaps are allowed to occur. Specific examples are discussed for the square lattice, the octahedral lattice, and the tetragonal lattice. For irreducible representations that are even under the reversal of relative time the common combinations of s- and d-wave spin singlet and p-wave spin triplet gaps are revealed, irreducible representations that are odd under reversal of relative time give rise to s- and d-wave spin triplet and p-wave spin singlet gaps. Furthermore, we discuss the construction of a generalized Ginzburg-Landau theory in terms of the associated irreducible representations. The result complements the established classification of superconducting states of matter.

I. INTRODUCTION

Unconventional superconductors such as the heavy fermion systems, e.g., $CeCu_2Si_2$ [1,2], Sr_2RuO_4 [3], and UPt_3 [4,5]; the cuprates, e.g., $YBa_2Cu_3O_7$ [6] and $HgBa_2CuO_{4+\delta}$ [7]; and the organic superconductors like the Bis(ethylenedithio)tetrathiafulvalene-based charge-transfer salts [8–12] exhibit symmetries of the superconducting gap beyond the conventional BCS s wave [13]. In this connection, a group theory analysis based on the underlying symmetry of the pairing potential is crucial in establishing a unified classification of the arising superconducting states of matter [14–19]. In general, the pairing wave function of two electrons has to be antisymmetric under particle interchange leading to the Pauli principle. At equal times, and by neglecting orbital degrees of freedom, two cases can occur: first, a gap odd in spin and even in parity, such as spin singlet s- and d-wave gaps, and, second, a gap even in spin and odd in parity, such as spin triplet p- and f-wave gaps.

However, as pointed out by Berezinskii [20] and Balatsky and Abrahams [21], a pairing of particles beyond the conventional ones is possible, if the particle-particle correlator is zero at equal times but nonzero otherwise. This is achieved when the superconducting gap is an odd function in relative time, leading to the notion of odd-time or odd-frequency superconductivity, respectively (odd-frequency also refers to gap functions odd in Matsubara frequency). Among others, odd-frequency contributions were reported to occur in connection to diffusive ferromagnet/superconductor junctions [22,23], normal-metal/superconductor junctions [24], topological insulators [25], heterostructures of transition-metal dichalcogenides and

s-wave superconductors [26], multiband superconductors [27], and driven systems [28,29]. Also, odd-frequency states were discussed in connection to time-reversal topological superconductivity in double Rashba wires, where it was found that odd-frequency pairing is strongly enhanced in the topological state [30]. For some of the above-mentioned systems, the respective signatures of odd-frequency correlations could also be verified experimentally [31–34]. An extensive discussion of edge states and topology in superconductors including odd-frequency gap functions was communicated by Tanaka, Sato, and Nagaosa [35]. A comprehensive review on odd-frequency superconductivity with the overview of possible realizations is given in Ref. [36].

In general, odd-frequency superconductivity can only occur when retardation is explicitly taken into account. Close to the superconducting transition temperature, the underlying gap equations can be linearized, leading to the so-called linearized gap equation or Bethe-Salpeter equation [37]. By solving for the eigenvalues of the Bethe-Salpeter equation, odd-frequency solutions were found numerically, for example, in the repulsive Hubbard model [38,39] and also in organic charge-transfer salts [40]. In such models with strong on-site repulsion, pairs can avoid the repulsion either by exhibiting a pair wave function with zero on-site amplitude, i.e., with nonzero angular momentum, or by establishing an odd-ω dependence which implies a vanishing equal-time pair amplitude.

Here, we extend the formalism of Refs. [14–19] and show how a symmetry analysis of the Bethe-Salpeter equation can be performed by explicitly incorporating reversal of relative time similarly to the construction of Shubnikov groups of the second kind. Since a solution of the Bethe-Salpeter equation, i.e., a superconducting gap function, transforms as one of the irreducible representations of the underlying symmetry group,

———————
*Geilhufe@kth.se

it generally breaks certain symmetries of the pairing potential. Therefore, gap functions that are odd under time-reversal symmetry can naturally occur even if the pairing potential itself is time-reversal symmetric.

The paper is structured as follows. First, we introduce the formalism by introducing the Bethe-Salpeter equation and the transformation behavior of the superconducting gap. Then, we summarize the construction of Shubnikov groups, together with the construction of faithful representations needed for the calculation of their character tables. Afterwards, we show possible superconducting gap symmetries for the examples of the square lattice, the cubic lattice, as well as the noncentrosymmetric tetragonal lattice. In the last part, we discuss the generalized Ginzburg-Landau theory for even- and odd-frequency superconductors.

II. LINEARIZED GAP EQUATION AND TRANSFORMATION BEHAVIOR OF THE SUPERCONDUCTING GAP

For a standard BCS approach, the superconducting gap is taken as frequency independent. Since the anomalous Green's function vanishes at zero time for odd-frequency superconductivity [41,42] we have to choose a formalism incorporating a summation over time or frequency, respectively. Therefore, we stick to the Eliashberg formalism which is valid in the the strong-coupling regime [43]. In general, the underlying Eliashberg equations which need to be solved self-consistently are nonlinear. However, in the region close to the superconducting transition temperature $T \approx T_c$, a corresponding linear equation can be formulated, which is called the linearized Eliashberg or Bethe-Salpeter equation. In the most general form it can be written as follows [37,39,40]:

$$v \Delta_{\alpha\beta}(\vec{k}, i\omega_n)$$
$$= -\frac{T}{N} \sum_{\gamma,\delta} \sum_{\vec{k}'} \sum_{m} \Gamma_{\alpha\beta\gamma\delta}(\vec{k}, \vec{k}', i\omega_m, i\omega_n)$$
$$\times G_\gamma(\vec{k}', i\omega_m) G_\delta(-\vec{k}', -i\omega_m) \Delta_{\gamma\delta}(\vec{k}', i\omega_m). \quad (1)$$

Here, $\Gamma_{\alpha\beta\gamma\delta}$ denotes the interaction kernel, the specific form of which depends on the system under consideration, e.g., electron-phonon interaction or a Berk-Schriefer-like interaction mediated by spin fluctuations [44,45], to name but a few. Furthermore, Greek indices denote the spin components, G_α is the Green's function for a particle with spin α, $\Delta_{\alpha,\beta}$ is the superconducting gap, and N denotes the total number of momenta in the Brillouin zone. The eigenvalue v corresponds to a generalization of the linearized Eliashberg formalism allowing for multiple solutions of Eq. (1), where a physical interpretation is only valid when the largest eigenvalue equals $v = 1$, indicating a superconducting transition exhibiting the respective superconducting gap corresponding to v. Yet, the knowledge of the competing eigenvalues even if not physically realized in the system of interest gives an important insight into the allowed superconducting instabilities. Additionally, even in the nonlinear regime the symmetry of the solutions of the linearized equation can be used to study admixed phases as described in Refs. [18,46,47]. As Eq. (1) is a linear eigenvalue equation, it can be written as $v\Delta = \hat{V}\Delta$, where $\hat{V}$ denotes the

kernel:

$$V_{\alpha\beta\gamma\delta}(\vec{k}, \vec{k}', i\omega_m, i\omega_n) = \Gamma_{\alpha\beta\gamma\delta}(\vec{k}, \vec{k}', i\omega_m, i\omega_n)$$
$$\times G_\gamma(\vec{k}', i\omega_m) G_\delta(-\vec{k}', -i\omega_m). \quad (2)$$

It is assumed that the symmetry of the crystal is reflected in the kernel V and described by the symmetry group $\mathcal{G}$. Each eigenvector of Eq. (1) transforms as a basis function of an irreducible representation Γ^p of $\mathcal{G}$ and the degeneracy of the corresponding eigenvalue is determined by the dimension of Γ^p, which will be denoted by d_p. Hence, the linearized gap equation can be reformulated as

$$v^{p,v} \tilde{\Delta}_m^{p,v} = \hat{V} \tilde{\Delta}_m^{p,v}, \quad (3)$$

where $m = 1, \ldots, d_p$ and $v = 1, 2, \ldots$ counts over the multiple nonequivalent subspaces transforming as the same irreducible representation. A superconducting instability with a gap transforming as an irreducible representation Γ^p occurs, if the corresponding eigenvalue $v^{p,v}$ reaches 1. Even though the pairing potential is invariant under every symmetry transformation of the group $\mathcal{G}$, the dominating gap function itself is only invariant under a subgroup, represented by one of the irreducible representations of $\mathcal{G}$.

It is assumed that the gap function transforms similarly to a pairing wave function. Considering spin-orbit coupling, each rotation in space (proper or improper) is connected to a specific rotation in spin space. Due to spin-orbit coupling, the single-particle states cannot be eigenstates of the spin operator in general, but can be labeled as pseudo-spin-states in a similar manner [18]. The pseudo-spin-state is generated from a spin eigenstate by turning on the spin-orbit interaction adiabatically, leading to a one-to-one correspondence between the original spin state and the pseudo-spin-state. Here we discuss the situation of having two states ($\uparrow, \downarrow$) similarly to the ordinary spin, where the transformations in the pseudo-spin space (or just spin space in the following) are generated by the Pauli matrices.

Applying the transformation operator $\hat{g}$ associated to a specific symmetry transformation $g \in \mathcal{G}$ gives

$$\hat{g} \tilde{\Delta}(\vec{k}) = \tilde{u}^T(g) \tilde{\Delta}[\tilde{R}^{-1}(g)\vec{k}] \tilde{u}(g). \quad (4)$$

Here, $\tilde{R}(g) \in O(3)$ denotes a three-dimensional rotation matrix and $\tilde{u}(g) \in SU(2)$ denotes the corresponding rotation matrix in spin space. The concept of odd- and even-frequency gaps relates to the gap function being an odd or even function of relative time or Matsubara frequency. For a given gap function $\tilde{\Delta}(\vec{k}, t_1, t_2)$, the relative time-reversal operator $\hat{T}$ acts by permuting the times t_1 and t_2. As shown in Appendix B, a similar representation of $\hat{T}$ is found by applying a combination of matrix transpose, and $\vec{k} \rightarrow -\vec{k}$,

$$\hat{T} \tilde{\Delta}(\vec{k}) = -\tilde{\Delta}^T(-\vec{k}). \quad (5)$$

Doing so, the action of $\hat{T}$ can be discussed without explicitly taking into account t_1 and t_2.

With respect to the interchange of the spin indices within the gap function, mediated by the operator $\hat{S}$, the gap function can be considered to be odd (singlet) or even (triplet). The resulting form of the gap in these cases is given by the antisymmetric matrix

$$\tilde{\Delta}(\vec{k}) = i \Psi(\vec{k}) \tilde{\sigma}^y \quad (6)$$

for the spin singlet and by the symmetric matrix

$$\tilde{\Delta}(\vec{k}) = i[\vec{d}(\vec{k}) \cdot \vec{\sigma}]\tilde{\sigma}^y \qquad (7)$$

for the spin triplet. Following Eqs. (4) and (5), the transformation under group elements $\hat{g}$ and under relative time reversal $\hat{T}$ can be expressed in terms of transformations of Ψ and $\vec{d}$ via

$$\hat{g}\Psi(\vec{k}) = \Psi[\tilde{R}^{-1}(g)\vec{k}], \qquad (8)$$

$$\hat{T}\Psi(\vec{k}) = \Psi(-\vec{k}) \qquad (9)$$

and

$$\hat{g}\vec{d}(\vec{k}) = \det[\tilde{R}(g)]\tilde{R}(g)\vec{d}[\tilde{R}^{-1}(g)\vec{k}], \qquad (10)$$

$$\hat{T}\vec{d}(\vec{k}) = -\vec{d}(-\vec{k}). \qquad (11)$$

The gap function has to be odd under the application of a combination of the parity operator ($\hat{P}$), spin interchange ($\hat{S}$), and relative time reversal ($\hat{T}$) [28]:

$$\hat{P}\hat{S}\hat{T} = -1. \qquad (12)$$

Therefore, by considering an even behavior under time reversal $\hat{T}\tilde{\Delta} = \tilde{\Delta}$, a spin singlet gap (odd under spin interchange) restricts the gap function to be even under parity, whereas a spin triplet gap (even under spin interchange) has to come with an odd parity. We now know, by allowing for an odd-time (or odd-frequency) dependence of the gap function, $\hat{T}\tilde{\Delta} = -\tilde{\Delta}$, that options for constructing an odd-parity spin singlet and an even-parity spin triplet gap arise. We proceed to show how the linearized gap equation allows for odd-frequency solutions.

III. SHUBNIKOV POINT GROUPS

Superconductivity is mediated by a pairing of electrons in $\vec{k}$ space. In three dimensions it is possible to define seven crystal systems and 32 crystal classes. The latter are connected to the 32 point groups. Whereas point groups only describe the spatial symmetries of the system they can be extended to incorporate time-reversal symmetry.

According to Eq. (5), relative time reversal is a symmetry element of order 2, i.e., $\hat{T}^2 = \hat{1}$. To include $\hat{T}$ as a symmetry element, we follow the Shubnikov construction for colored groups. However, note that the relative time-reversal considered here is a unitary symmetry element. Denoting the point group of the system by $\mathcal{G}$, three kinds of Shubnikov groups can be defined (Fig. 1). The Shubnikov group of the first kind is
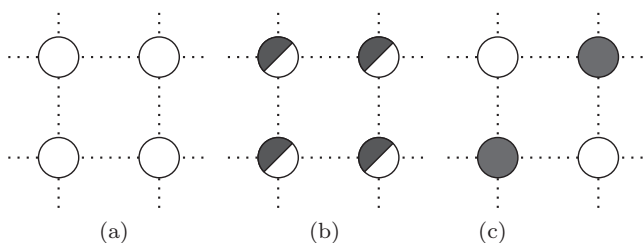
given by the point group itself:

$$\mathcal{G}^{\mathrm{I}} = \mathcal{G}. \qquad (13)$$

Shubnikov groups of the second kind are introduced by combining each element of $\mathcal{G}$ with $\hat{T}$:

$$\mathcal{G}^{\mathrm{II}} = \mathcal{G} + \hat{T}\mathcal{G}. \qquad (14)$$

Since each symmetry element occurs twice, once in connection to time reversal and once without, these groups are also referred to as gray groups. Shubnikov groups of the third kind describe systems without a global time-reversal symmetry, e.g., magnetic structures. Here, time-reversal symmetry is only connected to a few elements. Starting from an invariant subgroup $\mathcal{N} \subset \mathcal{G}$ of index 2 (ord $\mathcal{G}/\mathcal{N} = 2$), Shubnikov groups of the third kind are constructed via

$$\mathcal{G}^{\mathrm{III}} = \mathcal{N} + \hat{T}(\mathcal{G} - \mathcal{N}). \qquad (15)$$

If the pairing potential in Eq. (1) is time-reversal symmetric, it is invariant under a group $\mathcal{G}^{\mathrm{II}}$. Hence, to discuss odd- and even-frequency gaps for time-reversal symmetric pairing potentials, Shubnikov groups of the second kind are considered. In comparison to Shubnikov groups of the first kind and Shubnikov groups of the third kind, this approach allows for an explicit distinction between representations odd and even under relative time reversal, as will be explained within the next section.

For Shubnikov groups of the second kind it follows from Eq. (14) that ord $\mathcal{G}^{\mathrm{II}} = 2$ ord $\mathcal{G}$. Furthermore, $\hat{T}$ commutes with every element of $\mathcal{G}^{\mathrm{II}}$. Thus, $\{E, \hat{T}\}$ is an Abelian invariant subgroup. It follows that $\mathcal{G}^{\mathrm{II}}$ can be written as a semidirect product of $\mathcal{G}$ and $\{E, \hat{T}\}$ and, by induction [48], that twice as many irreducible representations occur for $\mathcal{G}^{\mathrm{II}}$ in comparison to $\mathcal{G}$. If Γ_i is an irreducible representation of $\mathcal{G}$, then Γ_i^+ and Γ_i^- are irreducible representations of $\mathcal{G}^{\mathrm{II}}$, where the characters are given by

$$\chi_i^+(\hat{T}g) = \chi_i(g), \qquad (16)$$

$$\chi_i^-(\hat{T}g) = -\chi_i(g), \qquad (17)$$

for all $g \in \mathcal{G}^{\mathrm{II}}$.

Since the linearized gap equation (3) is an eigenvalue equation, where the operator $\hat{V}$ is invariant under all transformations of a symmetry group $\mathcal{G}^{\mathrm{II}}$, each eigenfunction transforms as one of the irreducible representations. Hence, each eigenfunction or gap function is an eigenfunction of the character projection operator $\hat{\mathcal{P}}^p$, given by

$$\hat{\mathcal{P}}^p = \sum_{g \in \mathcal{G}} [\chi^p(g)]^* \hat{g}. \qquad (18)$$

Here, $\chi^p(g)$ denotes the character (the trace of the representation matrix) of the element g within the irreducible representation Γ^p of $\mathcal{G}$. Due to the orthogonality of irreducible representations $\hat{\mathcal{P}}^p$ has the property

$$\hat{\mathcal{P}}^q \tilde{\Delta}_m^{p,\nu} = \delta_{pq} \tilde{\Delta}_m^{p,\nu}. \qquad (19)$$

Applied to an arbitrary gap function $\tilde{\Delta}$, the character projection operator $\hat{\mathcal{P}}^p$ projects out the part of $\tilde{\Delta}$ transforming as the

FIG. 1. Illustration of the Shubnikov point-group construction. (a) first kind, (b) second kind, and (c) third kind.

TABLE I. Character table of the Shubnikov group D_{4h}^{II}.

	E	$2C_2'$	$2\sigma_v$	$2C_2''$	$2\sigma_d$	$2S_4$	$2C_4$	I	C_2	σ_h	$\hat{T}$	$2\hat{T}C_2'$	$2\hat{T}\sigma_v$	$2\hat{T}C_2''$	$2\hat{T}\sigma_d$	$2\hat{T}S_4$	$2\hat{T}C_4$	$\hat{T}I$	$\hat{T}C_2$	$\hat{T}\sigma_h$	
A_{1g}^+	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
A_{2g}^+	1	−1	−1	−1	−1	1	1	1	1	1	1	−1	−1	−1	−1	1	1	1	1	1	
B_{1g}^+	1	1	1	−1	−1	−1	−1	1	1	1	1	1	1	−1	−1	−1	−1	1	1	1	
B_{2g}^+	1	−1	−1	1	1	−1	−1	1	1	1	1	−1	−1	1	1	−1	−1	1	1	1	
E_g^+	2	0	0	0	0	0	0	2	−2	−2	2	0	0	0	0	0	0	2	−2	−2	$\hat{T}$ even
A_{1u}^+	1	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1	1	−1	−1	1	−1	1	−1	
A_{2u}^+	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	
B_{1u}^+	1	1	−1	−1	1	1	−1	−1	1	−1	1	1	−1	−1	1	1	−1	−1	1	−1	
B_{2u}^+	1	−1	1	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1	1	−1	−1	1	−1	
E_u^+	2	0	0	0	0	0	0	−2	−2	2	2	0	0	0	0	0	0	−2	−2	2	
A_{1g}^-	1	1	1	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	−1	−1	
A_{2g}^-	1	−1	−1	−1	−1	1	1	1	1	1	−1	1	1	1	1	−1	−1	−1	−1	−1	
B_{1g}^-	1	1	1	−1	−1	−1	−1	1	1	1	−1	−1	−1	1	1	1	1	−1	−1	−1	
B_{2g}^-	1	−1	−1	1	1	−1	−1	1	1	1	−1	1	1	−1	−1	1	1	−1	−1	−1	$\hat{T}$ odd
E_g^-	2	0	0	0	0	0	0	2	−2	−2	−2	0	0	0	0	0	0	−2	2	2	
A_{1u}^-	1	1	−1	1	−1	−1	1	−1	1	−1	−1	−1	1	−1	1	1	−1	1	−1	1	
A_{2u}^-	1	−1	1	−1	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1	−1	1	−1	1	
B_{1u}^-	1	1	−1	−1	1	1	−1	−1	1	−1	−1	−1	1	1	−1	−1	1	1	−1	1	
B_{2u}^-	1	−1	1	1	−1	1	−1	−1	1	−1	−1	1	−1	−1	1	−1	1	1	−1	1	
E_u^-	2	0	0	0	0	0	0	−2	−2	2	−2	0	0	0	0	0	0	2	2	−2	

irreducible representation Γ^p, denoted by $\tilde{\Delta}^p$:

$$\hat{\mathcal{P}}^p \tilde{\Delta} = \sum_\nu \sum_{m=1}^{d_p} \tilde{\Delta}_m^{p,\nu} = \tilde{\Delta}^p. \qquad (20)$$

Taking into account all N inequivalent irreducible representations Γ^p of a symmetry group $\mathcal{G}$ and summing over all Δ^p obtained by mutual application of $\hat{\mathcal{P}}^p$ to Δ, the original gap function has to be revealed:

$$\tilde{\Delta} = \sum_{p=1}^N \tilde{\Delta}^p. \qquad (21)$$

With these remarks we are now ready to analyze the self-consistent solution for gap functions.

IV. COMPUTATIONAL DETAILS

The group theoretical analysis was performed by applying the MATHEMATICA group theory package GTPack [48,49]. As a faithful representation of the point-group elements, rotation matrices of the group $O(3)$ are used. Since $\mathcal{G}^{\mathrm{II}}$ from Eq. (14) is isomorphic to the direct product group $\mathcal{G} \otimes \{1,-1\}$, a faithful representation for the Shubnikov point group is found by the 4×4 matrices

$$\tilde{D}(g) = \begin{pmatrix} \tilde{R}(g) & \tilde{0} \\ \tilde{0} & 1 \end{pmatrix}, \quad \text{and} \quad \tilde{D}(\hat{T}g) = \begin{pmatrix} \tilde{R}(g) & \tilde{0} \\ \tilde{0} & -1 \end{pmatrix}. \qquad (22)$$

Character tables were calculated by applying the Burnside algorithm [50], which is a reasonable choice due to the small order of the crystallographic point groups. For the general-

ized Ginzburg-Landau theory, representation matrices of the irreducible representations and the corresponding Clebsch-Gordan coefficients were calculated by applying the algorithms of Flodmark and Blokker [51] and van Den Broek and Cornwell [52], respectively. The superconducting gap can be expanded in terms of tesseral harmonics S_m^l (real spherical harmonics) as

$$\Psi(\vec{k}) = \sum_l \sum_{m=-l}^l c_m^l S_m^l(x,y,z) \qquad (23)$$

and

$$\vec{d}(\vec{k}) = \sum_l \sum_{m=-l}^l \vec{d}_m^l S_m^l(x,y,z). \qquad (24)$$

Throughout the paper the S_m^l are discussed in Cartesian form.

V. SQUARE LATTICE (D_{4h}^{II})

To give a specific example of the emergence of even- and odd-frequency superconducting states we choose a specific group. In the following, a square lattice having the point group D_{4h} is discussed. The group is generated by the elements $\{C_{4z}, C_{2y}, I\}$, where C_{4z} denotes a fourfold rotation about the z axis, C_{2y} denotes a twofold rotation about the y axis, and I denotes the inversion. In total, D_{4h} has 16 elements. Consequently, the corresponding Shubnikov group of the second kind D_{4h}^{II} has 32 elements and is constructed according to Eq. (14). The character table of D_{4h}^{II} is shown in Table I. For the irreducible representations the Mulliken notation is used [53,54]. Additionally, they are labeled with a superscript indicating an even $(+)$ or odd $(-)$ behavior with respect to time-reversal according to Eqs. (16) and (17).

TABLE II. Even- and odd-frequency gap symmetries for the square lattice (D_{4h}^{II}), considering s-, p-, and d-wave superconductivity.

Even frequency		
s wave:	A_{1g}^{+}	$\Psi \simeq \text{const}, k_x^2 + k_y^2 + k_z^2$
p wave:	A_{1u}^{+}	$\vec{d} \simeq k_x \vec{e}_x + k_y \vec{e}_y + k_z \vec{e}_z$
	A_{1u}^{+}	$\vec{d} \simeq 2k_z \vec{e}_z - k_x \vec{e}_x - k_y \vec{e}_y$
	A_{2u}^{+}	$\vec{d} \simeq k_y \vec{e}_x - k_x \vec{e}_y$
	B_{1u}^{+}	$\vec{d} \simeq k_x \vec{e}_x - k_y \vec{e}_y$
	B_{2u}^{+}	$\vec{d} \simeq k_y \vec{e}_x + k_x \vec{e}_y$
	E_u^{+}	$\vec{d} \simeq k_x \vec{e}_z$
		$\vec{d} \simeq k_y \vec{e}_z$
	E_u^{+}	$\vec{d} \simeq k_z \vec{e}_x$
		$\vec{d} \simeq k_z \vec{e}_y$
d wave:	A_{1g}^{+}	$\Psi \simeq 2k_z^2 - k_x^2 - k_y^2$
	B_{1g}^{+}	$\Psi \simeq (k_x^2 - k_y^2)$
	B_{2g}^{+}	$\Psi \simeq k_x k_y$
	E_g^{+}	$\Psi \simeq k_x k_z$
		$\Psi \simeq k_y k_z$
Odd frequency		
s wave:	A_{2g}^{-}	$\vec{d} \simeq (k_x^2 + k_y^2 + k_z^2)\vec{e}_z$
	E_g^{-}	$\vec{d} \simeq (k_x^2 + k_y^2 + k_z^2)\vec{e}_x$
		$\vec{d} \simeq (k_x^2 + k_y^2 + k_z^2)\vec{e}_y$
p wave:	A_{2u}^{-}	$\Psi \simeq k_z$
	E_u^{-}	$\Psi \simeq k_x$
		$\Psi \simeq k_y$
d wave:	A_{1g}^{-}	$\vec{d} \simeq k_y k_z \vec{e}_x - k_x k_z \vec{e}_y$
	A_{2g}^{-}	$\vec{d} \simeq k_x k_z \vec{e}_x + k_y k_z \vec{e}_y$
	A_{2g}^{-}	$\vec{d} \simeq (2k_z^2 - k_x^2 - k_y^2)\vec{e}_z$
	B_{1g}^{-}	$\vec{d} \simeq k_y k_z \vec{e}_x + k_x k_z \vec{e}_y$
	B_{1g}^{-}	$\vec{d} \simeq k_x k_y \vec{e}_z$
	B_{2g}^{-}	$\vec{d} \simeq k_x k_z \vec{e}_x - k_y k_z \vec{e}_y$
	B_{2g}^{-}	$\vec{d} \simeq (k_x^2 - k_y^2)\vec{e}_z$
	E_g^{-}	$\vec{d} \simeq k_x k_y \vec{e}_x$
		$\vec{d} \simeq k_x k_y \vec{e}_y$
	E_g^{-}	$\vec{d} \simeq k_z k_y \vec{e}_z$
		$\vec{d} \simeq k_z k_x \vec{e}_z$
	E_g^{-}	$\vec{d} \simeq (2k_z^2 - k_x^2 - k_y^2)\vec{e}_x$
		$\vec{d} \simeq (k_x^2 - k_y^2)\vec{e}_x$
	E_g^{-}	$\vec{d} \simeq (2k_z^2 - k_x^2 - k_y^2)\vec{e}_y$
		$\vec{d} \simeq (k_x^2 - k_y^2)\vec{e}_y$

For the spin singlet gaps, the allowed irreducible representations occurring for a certain angular momentum l can be determined by decomposing the representations of the orbital part only (see Appendix A). These are given by

$$s \text{ wave}: D_{g,+}^0 \simeq A_{1g}^{+}, \tag{25}$$

$$p \text{ wave}: D_{u,-}^1 \simeq A_{2u}^{-} \oplus E_u^{-}, \tag{26}$$

$$d \text{ wave}: D_{g,+}^2 \simeq A_{1g}^{+} \oplus B_{1g}^{+} \oplus B_{2g}^{+} \oplus E_g^{+}. \tag{27}$$

$$\mathbf{O(3)} \times \left\{ \mathbf{E}, \hat{\mathbf{T}} \right\} \quad \mathbf{D}_{4h}^{II} \qquad\qquad \mathbf{O(3)} \times \left\{ \mathbf{E}, \hat{\mathbf{T}} \right\} \quad \mathbf{D}_{4h}^{II}$$
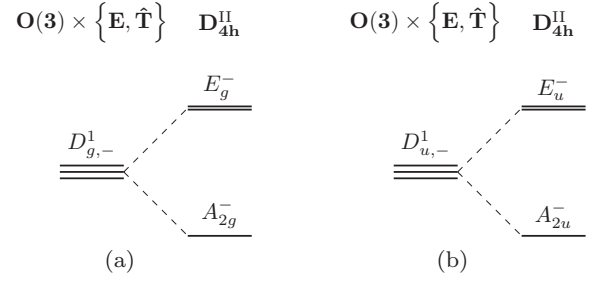
FIG. 2. Splitting of pairing states for a pairing potential with D_{4h}^{II} symmetry. (a) spin triplet, s-wave and (b) spin singlet, p-wave.

Analogously, for the spin triplet gaps the allowed irreducible representations are found by decomposing the direct product belonging to the orbital part with $D_{g,-}^1$, representing the transformation properties of the spin triplet state:

$$s \text{ wave}: D_{g,+}^0 \otimes D_{g,-}^1 \simeq A_{2g}^{-} \oplus E_g^{-}, \tag{28}$$

$$p \text{ wave}: D_{u,-}^1 \otimes D_{g,-}^1 \simeq A_{2u}^{+} \oplus B_{2u}^{+} \oplus B_{1u}^{+} \oplus 2A_{1u}^{+} \oplus 2E_u^{+}, \tag{29}$$

$$d \text{ wave}: D_{g,+}^2 \otimes D_{g,-}^1 \simeq A_{1g}^{-} \oplus 2A_{2g}^{-} \oplus 2B_{1g}^{-} \oplus 2B_{2g}^{-} \oplus 4E_g^{-}. \tag{30}$$

The obtained terms in Eqs. (25)–(30) are in agreement with Eq. (12). They reflect the following options: (1) spin singlet, even parity, even time [Eqs. (25) and (27)]; (2) spin singlet, odd parity, odd time [Eq. (26)]; (3) spin triplet, odd parity, even time [Eq. (29)]; and (4) spin triplet, even parity, odd time [Eqs. (28) and (30)]. Specific terms for gap symmetries are obtained by applying the character projection operator to Eqs. (23) and (24). The results are illustrated in Table II and discussed subsequently for two examples.

A. s-wave spin triplet

As a first example, we consider a s-wave superconductor. Whereas the conventional BCS theory [13] describes a s-wave spin singlet pairing which is even under time reversal, it is possible to construct a s-wave spin triplet that is odd under time reversal [Eq. (28)]. Under full rotational symmetry, a spin triplet transforms as the three-dimensional representation $D_{g,-}^1$ as discussed in Appendix A. However, for the square lattice, the triplet state splits into A_{2g}^{-} and E_g^{-} as illustrated in Fig. 2(a). Since the z axis is chosen as the principal axis, two linearly independent solutions belonging to E_g^{-} transform as $\vec{k}^2 \vec{e}_x$ and $\vec{k}^2 \vec{e}_y$. Solutions belonging to A_{2g}^{-} transform as $\vec{k}^2 \vec{e}_z$. The resulting gap functions are given by

$$\tilde{\Delta}_1^{E_g^{-}}(\vec{k}) = -\vec{k}^2 \tilde{\sigma}_z, \tag{31}$$

$$\tilde{\Delta}_2^{E_g^{-}}(\vec{k}) = i\vec{k}^2 \tilde{\sigma}_0, \tag{32}$$

and

$$\tilde{\Delta}_1^{A_{2g}^{-}}(\vec{k}) = \vec{k}^2 \tilde{\sigma}_x. \tag{33}$$

As expected, all three matrices are symmetric and thus even under spin interchange. They are even under parity since they

contain $\vec{k}^2$. But, they are odd with respect to the relative time reversal introduced in Eq. (5).

B. *p*-wave spin singlet

Another unconventional odd-frequency pairing is given by the *p*-wave spin singlet. Here, the three-dimensional odd-parity representation $D^1_{u,-}$ splits into the irreducible representations A^-_{2u} and E^-_u. The gap transforms as k_x and k_y for E^-_u and as k_z for A^-_{2u}. The resulting superconducting gaps behave as

$$\tilde{\Delta}^{E^-_u}_1(\vec{k}) = ik_x\tilde{\sigma}_y, \tag{34}$$

$$\tilde{\Delta}^{E^-_u}_2(\vec{k}) = ik_y\tilde{\sigma}_y, \tag{35}$$

and

$$\tilde{\Delta}^{A^-_{2u}}_1(\vec{k}) = ik_z\tilde{\sigma}_y. \tag{36}$$

Clearly, the three matrices are antisymmetric and odd under spin, odd under parity, and also odd under relative time reversal according to Eq. (5).

VI. OCTAHEDRAL SYMMETRY (O^{II}_h)

Similarly to D^{II}_{4h}, the gap symmetry is analyzed for O^{II}_h. As mentioned before, due to the semidirect product structure of Shubnikov groups of the second kind each irreducible representation of a point group occurs twice (see Table I for D^{II}_{4h}). Therefore, we stick to the standard nomenclature of the irreducible representations of O_h as can be found, e.g., in Refs. [48,55,56]. As in the example of D^{II}_{4h}, superscripts $+$ and $-$ distinguish between the even and odd symmetric representations with respect to relative time reversal. For O^{II}_h, the occurring irreducible representations for spin singlet and triplet gaps are given by

$$s \text{ wave}: \ D^0_{g,+} \simeq A^+_{1g}, \tag{37}$$

$$p \text{ wave}: \ D^1_{u,-} \simeq T^-_{1u}, \tag{38}$$

$$d \text{ wave}: \ D^2_{g,+} \simeq E^+_g \oplus T^+_{2g} \tag{39}$$

and

$$s \text{ wave}: \ D^0_{g,+} \otimes D^1_{g,-} \simeq T^-_{1g}, \tag{40}$$

$$p \text{ wave}: \ D^1_{u,-} \otimes D^1_{g,-} \simeq A^+_{1u} \oplus E^+_u \oplus T^+_{1u} \oplus T^+_{2u}, \tag{41}$$

$$d \text{ wave}: \ D^2_{g,+} \otimes D^1_{g,-} \simeq A^-_{2g} \oplus E^-_g \oplus 2T^-_{1g} \oplus 2T^-_{2g}, \tag{42}$$

respectively. The specific forms of the even- and odd-frequency gap symmetries are shown in Table III.

A. *s*-wave spin triplet

For octahedral symmetry the three-dimensional representation $D^1_{g,-}$ does not split and thus a threefold degenerate eigenvalue occurs, transforming as the irreducible representation T^-_{1g}. Similarly to Eqs. (31)–(33), the resulting gaps transform as

$$\tilde{\Delta}^{T^-_{1g}}_1(\vec{k}) = -\vec{k}^2\tilde{\sigma}_z, \tag{43}$$

TABLE III. Even- and odd-frequency gap symmetries for cubic lattices with octahedral symmetry (O_h), considering *s*-, *p*-, and *d*-wave superconductivity.

Even frequency		
s wave:	A^+_{1g}	$\Psi \simeq \text{const}, k_x^2 + k_y^2 + k_z^2$
p wave:	A^+_{1u}	$\vec{d} \simeq k_x\vec{e}_x + k_y\vec{e}_y + k_z\vec{e}_z$
	E^+_u	$\vec{d} \simeq k_x\vec{e}_x - k_y\vec{e}_y$
		$\vec{d} \simeq 2k_z\vec{e}_z - k_x\vec{e}_x - k_y\vec{e}_y$
	T^+_{1u}	$\vec{d} \simeq k_y\vec{e}_x - k_x\vec{e}_y$
		$\vec{d} \simeq k_z\vec{e}_y - k_y\vec{e}_z$
		$\vec{d} \simeq k_x\vec{e}_z - k_z\vec{e}_x$
	T^+_{2u}	$\vec{d} \simeq k_y\vec{e}_x + k_x\vec{e}_y$
		$\vec{d} \simeq k_z\vec{e}_y + k_y\vec{e}_z$
		$\vec{d} \simeq k_x\vec{e}_z + k_z\vec{e}_x$
d wave:	E^+_g	$\Psi \simeq (k_x^2 - k_y^2)$
		$\Psi \simeq (2k_z^2 - k_x^2 - k_y^2)$
	T^+_{2g}	$\Psi \simeq k_xk_y$
		$\Psi \simeq k_yk_z$
		$\Psi \simeq k_xk_z$
Odd frequency		
s wave:	T^-_{1g}	$\vec{d} \simeq (k_x^2 + k_y^2 + k_z^2)\vec{e}_x$
		$\vec{d} \simeq (k_x^2 + k_y^2 + k_z^2)\vec{e}_y$
		$\vec{d} \simeq (k_x^2 + k_y^2 + k_z^2)\vec{e}_z$
p wave:	T^-_{1u}	$\Psi \simeq k_x$
		$\Psi \simeq k_y$
		$\Psi \simeq k_z$
d wave:	A^-_{2g}	$\vec{d} \simeq k_yk_z\vec{e}_x + k_xk_z\vec{e}_y + k_xk_y\vec{e}_z$
	E^-_g	$\vec{d} \simeq k_yk_z\vec{e}_x - k_xk_z\vec{e}_y$
		$\vec{d} \simeq 2k_xk_y\vec{e}_z - k_yk_z\vec{e}_x - k_xk_z\vec{e}_y$
	T^-_{1g}	$\vec{d} \simeq k_xk_y\vec{e}_x + k_yk_z\vec{e}_z$
		$\vec{d} \simeq k_xk_z\vec{e}_x + k_yk_z\vec{e}_y$
		$\vec{d} \simeq k_xk_y\vec{e}_y + k_xk_z\vec{e}_z$
	T^-_{1g}	$\vec{d} \simeq (2k_x^2 - k_y^2 - k_z^2)\vec{e}_x$
		$\vec{d} \simeq (2k_y^2 - k_z^2 - k_x^2)\vec{e}_y$
		$\vec{d} \simeq (2k_z^2 - k_x^2 - k_y^2)\vec{e}_z$
	T^-_{2g}	$\vec{d} \simeq k_xk_y\vec{e}_x - k_yk_z\vec{e}_z$
		$\vec{d} \simeq k_xk_z\vec{e}_x - k_yk_z\vec{e}_y$
		$\vec{d} \simeq k_xk_y\vec{e}_y - k_xk_z\vec{e}_z$
	T^-_{2g}	$\vec{d} \simeq (k_y^2 - k_z^2)\vec{e}_x$
		$\vec{d} \simeq (k_z^2 - k_x^2)\vec{e}_y$
		$\vec{d} \simeq (k_x^2 - k_y^2)\vec{e}_z$

$$\tilde{\Delta}^{T^-_{1g}}_2(\vec{k}) = i\vec{k}^2\tilde{\sigma}_0, \tag{44}$$

$$\tilde{\Delta}^{T^-_{1g}}_3(\vec{k}) = \vec{k}^2\tilde{\sigma}_x. \tag{45}$$

The three matrices are even under spin interchange, even under parity, and odd under relative time reversal. The relationship between the *s*-wave spin triplets for O^{II}_h and D^{II}_{4h} symmetry is shown in Fig. 3.

B. *d*-wave spin triplet

Another option of having a spin triplet and even parity, but odd time pairing, is given by the *d*-wave spin triplet. According to Eq. (42) and Table III, the *d*-wave spin triplet pairing is
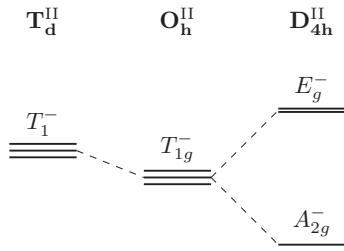
FIG. 3. s-wave spin triplet pairing for a pairing potential with T_d^{II}, O_h^{II}, and D_{4h}^{II} symmetry.

mediated by 15 eigenvectors belonging to six subspaces. As an example we consider the two subspaces belonging to T_{2g}^-. The corresponding gaps transform as

$$\tilde{\Delta}_1^{T_{2g}^-}(\vec{k}) = -k_x k_y \tilde{\sigma}_z - k_y k_z \tilde{\sigma}_x, \tag{46}$$

$$\tilde{\Delta}_2^{T_{2g}^-}(\vec{k}) = -k_x k_z \tilde{\sigma}_z - i k_y k_z \tilde{\sigma}_0, \tag{47}$$

$$\tilde{\Delta}_1^{T_{2g}^-}(\vec{k}) = i k_x k_y \tilde{\sigma}_0 - k_x k_z \tilde{\sigma}_x \tag{48}$$

and

$$\tilde{\Delta}_1^{T_{2g}^-}(\vec{k}) = -\left(k_y^2 - k_z^2\right)\tilde{\sigma}_z, \tag{49}$$

$$\tilde{\Delta}_2^{T_{2g}^-}(\vec{k}) = i\left(k_z^2 - k_x^2\right)\tilde{\sigma}_0, \tag{50}$$

$$\tilde{\Delta}_3^{T_{2g}^-}(\vec{k}) = \left(k_x^2 - k_y^2\right)\tilde{\sigma}_x. \tag{51}$$

Both sets of matrices belong to two different eigenvalues within the linearized gap equation (3). Due to the absence of $\tilde{\sigma}_y$, all matrices are symmetric and thus represent a gap even under spin interchange. Second-order terms in $\vec{k}$ guarantee even behavior under parity. Nevertheless, following Eq. (5) they are odd under relative time reversal.

VII. NONCENTROSYMMETRIC TETRAGONAL LATTICE (T_d^{II})

Even for noncentrosymmetric groups, i.e., groups that do not contain the inversion, it is possible to keep the notion of parity within the gap function. The point group T_d describes the point group of a tetragonal lattice having no inversion symmetry. However, as a subgroup of O_h, the irreducible representations of both groups can be related to each other. In the context of the Shubnikov group of the second kind $T_d^{\mathrm{II}} \subset O_h^{\mathrm{II}}$, the following correspondences can be found:

$$A_{1g}^{\pm}, A_{2u}^{\pm} \rightarrow A_1^{\pm}, \tag{52}$$

$$A_{2g}^{\pm}, A_{1u}^{\pm} \rightarrow A_2^{\pm}, \tag{53}$$

$$E_u^{\pm}, E_g^{\pm} \rightarrow E^{\pm}, \tag{54}$$

$$T_{1g}^{\pm}, T_{2u}^{\pm} \rightarrow T_1^{\pm}, \tag{55}$$

$$T_{2g}^{\pm}, T_{1u}^{\pm} \rightarrow T_2^{\pm}. \tag{56}$$

Hence, the specific gap symmetries for T_d^{II} can be taken from Table III. The occurring irreducible representations are given by

$$s \text{ wave}: D_{g,+}^0 \simeq A_1^+, \tag{57}$$

$$p \text{ wave}: D_{u,-}^1 \simeq T_2^-, \tag{58}$$

$$d \text{ wave}: D_{g,+}^2 \simeq E^+ \oplus T_2^+ \tag{59}$$

and

$$s \text{ wave}: D_{g,+}^0 \otimes D_{g,-}^1 \simeq T_1^-, \tag{60}$$

$$p \text{ wave}: D_{u,-}^1 \otimes D_{g,-}^1 \simeq A_2^+ \oplus E^+ \oplus T_2^+ \oplus T_1^+, \tag{61}$$

$$d \text{ wave}: D_{g,+}^2 \otimes D_{g,-}^1 \simeq A_2^- \oplus E^- \oplus 2T_2^- \oplus 2T_1^-. \tag{62}$$

The discussion of examples follows the line of O_h^{II} in the previous section. The relationship between T_d^{II}, O_h^{II}, and D_{4h}^{II} for s-wave spin triplet pairing is shown in Fig. 3.

VIII. GINZBURG-LANDAU THEORY

The transition to a superconducting state occurs when the largest eigenvalue of the Bethe-Salpeter equation (1) is equal to $\nu = 1$. This relation also uniquely defines the superconducting transition temperature T_c. The gap related to the first superconducting state arising immediately below T_c can be constructed as a linear combination of the eigenfunctions of the Bethe-Salpeter equation $\tilde{\Delta}_m^i$, $m = 1, \ldots, d_i$:

$$\tilde{\Delta}^i = \sum_{m=1}^{d_i} \eta_m \tilde{\Delta}_m^i. \tag{63}$$

The generalized Ginzburg-Landau free energy [18] can be entirely expressed in terms of η_m:

$$F(T, \vec{\eta}) = F_{\mathrm{Landau}}(T, \vec{\eta}) + F_{\mathrm{Gradient}}(\vec{\eta}) + \int dx^3 \frac{\vec{B}^2}{8\pi}. \tag{64}$$

We start the discussion with the Landau term, given by

$$F_{\mathrm{Landau}}(T, \vec{\eta}) = F_0(T) + V\left[A_i(T)\sum_{m=1}^{d_i}|\eta_m|^2 + f(\vec{\eta}^4)\right]. \tag{65}$$

Here, $f(\vec{\eta}^4)$ denotes all fourth-order terms in η_m and its complex conjugate η_m^*. Since $F(T, \vec{\eta})$ has to be real, only products containing the same number of η_m and η_m^* are allowed. Furthermore, $F(T, \vec{\eta})$ has the same symmetry as the system itself and thus transforms as the identity representation.

Since the gap and the anomalous Green's function vanish at equal times (effectively $t = 0$) the order parameter for odd-frequency superconductivity is widely discussed, e.g., by considering a composite order of a Cooper pair and a charge or spin fluctuation [36,41,42,57]. Since the minimum of Eq. (65) is achieved for a particular value of the time-independent vector $\vec{\eta}$, it can be regarded as a generalized order parameter covering both odd- and even-frequency superconductivity.

The fourth-order terms in Eq. (65) only depend on the dimension of the irreducible representation but not on the

specific characteristics. The number of different invariant terms can be determined by decomposing the direct product $[\Gamma]^4 = \Gamma^* \otimes \Gamma \otimes \Gamma^* \otimes \Gamma$. Here, we introduce the shorthand notation $[\Gamma]^4$ for convenience, e.g., $[A_{1g}^+]^4 = (A_{1g}^+)^* \otimes A_{1g}^+ \otimes (A_{1g}^+)^* \otimes A_{1g}^+$. For the groups D_{4h}^{II} and O_h^{II} it follows that

$$[A_{ix}^{\pm}]^4 \simeq [B_{ix}^{\pm}]^4 \simeq A_{1g}^+, \tag{66}$$

$$[E_x^{\pm}]^4 \simeq 4A_{1g}^+ \oplus 4A_{2g}^+ \oplus 4B_{1g}^+ \oplus 4B_{2g}^+ \tag{67}$$

and

$$[A_{ix}^{\pm}]^4 \simeq A_{1g}^+, \tag{68}$$

$$[E_x^{\pm}]^4 \simeq 3A_{1g}^+ \oplus 3A_{2g}^+ \oplus 5E_g^+, \tag{69}$$

$$[T_{ix}^{\pm}]^4 \simeq 4A_{1g}^+ \oplus 3A_{2g}^+ \oplus 7E_g^+ \oplus 10T_{1g}^+ \oplus 10T_{2g}^+, \tag{70}$$

respectively. The abbreviations $i = 1,2$ and $x = g,u$ were used. The analogous terms for T_d^{II} can be derived using Eqs. (52)–(56).

The gradient term F_{Gradient} of the free energy incorporates a gauge-invariant coupling of the order parameter to a magnetic field via the gradient vector $\vec{D} = \nabla - 2i\frac{e}{c}\vec{A}$. As $\vec{D}$ transforms as the vector representation Γ_V of the underlying point group, the contributions of F_{Gradient} are obtained from decomposing the direct product:

$$\Gamma_V^* \otimes \Gamma^* \otimes \Gamma_V \otimes \Gamma = [\Gamma]_V. \tag{71}$$

Similarly to $[\Gamma]^4$, $[\Gamma]_V$ is an abbreviation for the direct product in Eq. (71), e.g., $[A_{1g}^+]_V = (\Gamma_V)^* \otimes (A_{1g}^+)^* \otimes \Gamma_V \otimes A_{1g}^+$. The vector representation of D_{4h}^{II} is given by $\Gamma_V = A_{1u}^+ \oplus E_u^+$ and the vector representation of O_h^{II} is $\Gamma_V = T_{1u}^+$. The corresponding Clebsch-Gordan sums for the decomposition of the gradient terms are

$$[A_{ix}^{\pm}]_V \simeq [B_{ix}^{\pm}]_V \simeq 2A_{1g}^+ \oplus A_{2g}^+ \oplus B_{1g}^+ \oplus B_{2g}^+ \oplus 2E_g^+, \tag{72}$$

$$[E_x^{\pm}]_V \simeq 5A_{1g}^+ \oplus 5A_{2g}^+ \oplus 5B_{1g}^+ \oplus 5B_{2g}^+ \oplus 8E_g^+ \tag{73}$$

for D_{4h}^{II} and

$$[A_{ix}^{\pm}]_V \simeq A_{1g}^+ \oplus E_g^+ \oplus T_{1g}^+ \oplus T_{2g}^+, \tag{74}$$

$$[E_x^{\pm}]_V \simeq 2A_{1g}^+ \oplus 2A_{2g}^+ \oplus 4E_g^+ \oplus 4T_{1g}^+ \oplus 4T_{2g}^+, \tag{75}$$

$$[T_{ix}^{\pm}]_V \simeq 4A_{1g}^+ \oplus 3A_{2g}^+ \oplus 7E_g^+ \oplus 10T_{1g}^+ \oplus 10T_{2g}^+ \tag{76}$$

for O_h^{II}.

With respect to the second-order, fourth-order, and gradient terms within the Ginzburg-Landau free-energy functional (65) it turns out that the explicit forms of the invariant polynomials only depend on the dimension of the irreducible representation involved. This statement follows from Eqs. (72)–(76). However, we want to exemplify the derivation of the invariant terms for the example of a tetragonal symmetry (D_{4h}^{II}) and an odd-frequency p-wave gap transforming as the irreducible representation E_{2u}^-. Hence, the superconducting gap is expressed as

$$\tilde{\Delta}(\vec{k}) = \eta_1 \tilde{\Delta}_1(\vec{k}) + \eta_2 \tilde{\Delta}_2(\vec{k}), \tag{77}$$

where $\tilde{\Delta}_1$ and $\tilde{\Delta}_2$ transform as basis functions of E_{2u}^-. As $[E_{2u}^-]^4 \simeq (A_{1g}^+ \oplus A_{2g}^+ \oplus B_{1g}^+ \oplus B_{2g}^+) \otimes (A_{1g}^+ \oplus A_{2g}^+ \oplus B_{1g}^+ \oplus B_{2g}^+)$, we start with forming a direct product basis in η_i and η_i^*, $i = 1,2$, for the direct product representations $E_{2u}^{-*} \otimes E_{2u}^- \simeq A_{1g}^+ \oplus A_{2g}^+ \oplus B_{1g}^+ \oplus B_{2g}^+$. This can be done straightforwardly from the Clebsch-Gordan coefficients which were calculated using GTPack. Products of these basis functions span the invariant basis of the fourth-order terms. It turns out that only three independent fourth-order polynomial terms remain in total, which are given by

$$f(\vec{\eta}^4) = \beta_1[|\eta_1|^4 + |\eta_2|^4] + \beta_2[\eta_1^{2*}\eta_2^2 + \text{h.c.}] + \beta_3[|\eta_1|^2|\eta_2|^2]. \tag{78}$$

These expressions are similar to the ones reported by Sigrist and Ueda [18], by setting $\beta_1 = \beta_1'$, $\beta_2 = 4\beta_1' - 4\beta_2' + \beta_3'$, and $\beta_3 = \beta_3'$, where β_i' denote the coefficients chosen in Ref. [18]. For the gradient terms we follow a similar procedure as for the fourth-order terms. The basis of the vector representation is chosen to be D_x and D_y for E_u^+ and D_z for A_{2u}^+. The resulting terms are

$$\begin{aligned} F_{\text{Gradient}} = &\gamma_1[|D_x\eta_1|^2 + |D_y\eta_2|^2] + \gamma_2[|D_y\eta_1|^2 + |D_x\eta_2|^2] \\ &+ \gamma_3[D_x\eta_1 D_y^*\eta_2^* + \text{c.c.}] + \gamma_4[D_x\eta_2 D_y^*\eta_1^* + \text{c.c.}]. \end{aligned} \tag{79}$$

Explicit expressions of fourth-order invariant terms for D_{4h} and O_h were reported before and discussed in great detail [14–19].

Additional terms resulting from external fields can be included into the Ginzburg-Landau theory, leading to further contributions to the free-energy functional. With respect to odd-frequency superconductivity, fields which transform as an irreducible representation odd in time-reversal or Matsubara frequency, respectively, might be of special interest.

IX. CONCLUSION

We presented a general formalism for the classification of superconducting states of matter incorporating time-reversal symmetry. We find it necessary to extend the standard symmetry analysis to keep track of the time-reversal properties by analyzing colored, i.e., Shubnikov, groups. The specific approach that is conducive to analyze the pairing instabilities is the Shubnikov group of the second kind that keeps the relative time reversal as an explicit symmetry element. We thus develop an approach in terms of Shubnikov groups of the second kind that allows us to identify odd- and even-frequency solutions within the Bethe-Salpeter equation. In doing so we extend the previous ground-laying work by Volovik and Gor'kov [14,15], Sigrist and coworkers [17,18], and Blount [16]. Since the combination of spin interchange, parity, and relative time reversal has to be odd for a pair of electrons, the found odd-frequency gap symmetries are either both even under spin and even under parity or odd under spin and odd under parity. Consequently, for an experimental identification of the symmetry of a bulk superconducting gap in simple single-band systems, it is required to measure at least two of the three above-mentioned information, e.g., as performed in Ref. [34]. Even though signals for the experimental verification of odd-frequency states are often discussed in connection to systems which explicitly break

time-reversal symmetry [31–33], our paper reveals that odd-frequency solutions do not require a time-reversal breaking potential. Odd-frequency solutions can arise naturally for a time-reversal symmetric interaction as a symmetry-breaking ground state of a many-particle system with time-reversal invariant interactions. Although exhibiting a dynamical order, the phenomenon of odd-frequency superconductivity as such is similar to other symmetry-breaking transitions.

APPENDIX A: IRREDUCIBLE REPRESENTATIONS OF SO(3), $O(3)$, AND $O(3) \times \{xE, \hat{T}\}$

The group SO(3) contains all proper three-dimensional representation matrices, i.e., orthogonal matrices with determinant $+1$. The spherical harmonics Y_m^l represent a set of basis functions for all irreducible representations of SO(3). To each angular momentum quantum number l belongs a $d_l = 2l + 1$-dimensional irreducible representation D^l. Representation matrices $\tilde{D}^l(g)$ for an element $g \in$ SO(3) can be found from the transformation behavior of the spherical harmonics via

$$\hat{g} Y_m^l = \sum_{m'=-l}^{l} D_{m'm}^l(g) Y_{m'}^l. \tag{A1}$$

The $D_{m'm}^l(g)$ are also denoted as Wigner D functions. The group $O(3)$ contains all orthogonal matrices with determinant ± 1. Hence, it incorporates all proper and improper rotations, i.e., rotations, reflections, and the inversion I. The inversion acts on the spherical harmonics as

$$\hat{P}(I) Y_m^l = (-1)^l Y_{m'}^l. \tag{A2}$$

However, since $O(3)$ can be written as the semidirect product $O(3) = $ SO(3) $\times \{E, I\}$, we can construct odd (u) and even (g) representations with respect to inversion via

$$D_g^l(g) = D_u^l(g) = D^l(g), \tag{A3}$$

$$D_u^l(Ig) = -D^l(Ig), \tag{A4}$$

$$D_g^l(Ig) = D^l(Ig), \tag{A5}$$

where g denotes a proper rotation, i.e., $g \in$ SO(3) $\subset O(3)$. The spherical harmonics are basis functions of D_g^l for even values of l and basis functions of D_u^l for odd values of l. Incorporating the relative time reversal, a similar strategy can be applied to construct representations of $O(3) \times \{E, \hat{T}\}$. It follows for an

element $h \in O(3) \subset O(3) \times \{E, \hat{T}\}$ that

$$D_{x,+}^l(h) = D_{x,-}^l(h) = D_x^l(h), \tag{A6}$$

$$D_{x,-}^l(Tg) = -D_x^l(Tg), \tag{A7}$$

$$D_{x,+}^l(Tg) = D_x^l(Tg), \tag{A8}$$

where $x = u, g$.

APPENDIX B: TRANSFORMATION BEHAVIOR UNDER RELATIVE TIME-REVERSAL

We discuss the transformation behavior under relative time-reversal for the anomalous Green function F, given by

$$F_{\sigma\sigma'}(\vec{k}, t_1, t_2) = \langle \mathcal{T} c_\sigma(\vec{k}, t_1) c_{\sigma'}(-\vec{k}, t_2) \rangle. \tag{B1}$$

Here, the operator $\mathcal{T}$ denotes the time-ordering operator, i.e.,

$$F_{\sigma\sigma'}(\vec{k}, t_1, t_2) = \langle \theta(t_1 - t_2) c_\sigma(\vec{k}, t_1) c_{\sigma'}(-\vec{k}, t_2) \\ - \theta(t_2 - t_1) c_{\sigma'}(-\vec{k}, t_2) c_\sigma(\vec{k}, t_1) \rangle \tag{B2}$$

Reversing t_1 and t_2 leads to

$$F_{\sigma\sigma'}(\vec{k}, t_2, t_1) = \langle \theta(t_2 - t_1) c_\sigma(\vec{k}, t_2) c_{\sigma'}(-\vec{k}, t_1) \\ - \theta(t_1 - t_2) c_{\sigma'}(-\vec{k}, t_1) c_\sigma(\vec{k}, t_2) \rangle. \tag{B3}$$

Hence, by comparing (B2) and (B3), one obtains

$$F_{\sigma\sigma'}(\vec{k}, t_2, t_1) = -F_{\sigma'\sigma}(-\vec{k}, t_1, t_2). \tag{B4}$$

Since the gap $\tilde{\Delta}$ is related to $\tilde{F}$, a similar transformation behavior is present,

$$\Delta_{\sigma\sigma'}(\vec{k}, t_2, t_1) = -\Delta_{\sigma'\sigma}(-\vec{k}, t_1, t_2). \tag{B5}$$

For a spin singlet, the gap can be written as $\tilde{\Delta}^s(\vec{k}) = i\Psi(\vec{k})\tilde{\sigma}_y$,

$$\tilde{\Delta}^s(\vec{k}) = \begin{pmatrix} 0 & \Psi(\vec{k}) \\ -\Psi(\vec{k}) & 0 \end{pmatrix}. \tag{B6}$$

Hence, from (B5) it follows

$$\hat{T} \tilde{\Delta}^s(\vec{k}) = i\Psi(-\vec{k})\tilde{\sigma}_y \tag{B7}$$

$$\hat{T} : \Psi(\vec{k}) \to \Psi(-\vec{k}). \tag{B8}$$

As a result, the action of $\hat{T}$ is similar to the action of the parity operator $\hat{P}$ for a spin singlet gap. The product of both is equal to the identity,

$$\text{singlet:} \quad \hat{T}\hat{P} = \hat{1}. \tag{B9}$$

For a spin triplet, the gap is given by $\tilde{\Delta}^t(\vec{k}) = i(\vec{d}(\vec{k}) \cdot \vec{\tilde{\sigma}}) \cdot \tilde{\sigma}_y$,

$$\tilde{\Delta}^t(\vec{k}) = \begin{pmatrix} -d_1(\vec{k}) + i d_2(\vec{k}) & d_3(\vec{k}), \\ d_3(\vec{k}) & d_1(\vec{k}) + i d_2(\vec{k}) \end{pmatrix}. \tag{B10}$$

Applying equation (B5) leads to

$$\hat{T} \tilde{\Delta}^t(\vec{k}) = -i(\vec{d}(-\vec{k}) \cdot \vec{\tilde{\sigma}}) \cdot \tilde{\sigma}_y, \tag{B11}$$

$$\hat{T} : \vec{d}(\vec{k}) \to -\vec{d}(-\vec{k}). \tag{B12}$$

Hence, for the spin triplet, the action of $\hat{T}$ differs from the action of $\hat{P}$ by a minus sign, and the product of both operators

is equal to minus the identity,

$$\text{triplet:} \quad \hat{T}\hat{P} = -\hat{1}. \tag{B13}$$

As the action of $\hat{T}$ can be mediated entirely in spin and $\vec{k}$-space, a similar transformation behavior is revealed for reversing ω after a Fourier transform of the relative time.

---

[1] C. Pfleiderer, Rev. Mod. Phys. **81**, 1551 (2009).

[2] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).

[3] K. Nelson, Z. Mao, Y. Maeno, and Y. Liu, Science **306**, 1151 (2004).

[4] J. Strand, D. Bahr, D. Van Harlingen, J. Davis, W. Gannon, and W. Halperin, Science **328**, 1368 (2010).

[5] R. Joynt and L. Taillefer, Rev. Mod. Phys. **74**, 235 (2002).

[6] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[7] A. Schilling, M. Cantoni, J. Guo, and H. Ott, Nature (London) **363**, 56 (1993).

[8] B. Commeau, R. M. Geilhufe, G. W. Fernando, and A. V. Balatsky, Phys. Rev. B **96**, 125135 (2017).

[9] N. Tajima, A. Ebina-Tajima, M. Tamura, Y. Nishio, and K. Kajita, J. Phys. Soc. Jpn. **71**, 1832 (2002).

[10] G. Kamarchuk, A. Khotkevich, I. Ianson, and K. Pokhodnia, Fiz. Nizk. Temp. **16**, 711 (1990).

[11] A. Kobayashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, Chem. Lett. **16**, 459 (1987).

[12] H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett. **17**, 55 (1988).

[13] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[14] G. Volovik and L. Gor'kov, JETP Lett. **39**, 550 (1984).

[15] G. Volovik and L. Gor'kov, in *Ten Years of Superconductivity: 1980–1990* (Springer, New York, 1985), pp. 144–155.

[16] E. I. Blount, Phys. Rev. B **32**, 2935 (1985).

[17] K. Ueda and T. M. Rice, Phys. Rev. B **31**, 7114 (1985).

[18] M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991).

[19] M. Sigrist and T. Rice, Z. Phys. B **68**, 9 (1987).

[20] V. Berezinskii, JETP Lett. **20**, 287 (1974).

[21] A. Balatsky and E. Abrahams, Phys. Rev. B **45**, 13125 (1992).

[22] T. Yokoyama, Y. Tanaka, and A. A. Golubov, Phys. Rev. B **75**, 134510 (2007).

[23] A. F. Volkov, F. S. Bergeret, and K. B. Efetov, Phys. Rev. Lett. **90**, 117006 (2003).

[24] Y. Tanaka, Y. Tanuma, and A. A. Golubov, Phys. Rev. B **76**, 054522 (2007).

[25] A. M. Black-Schaffer and A. V. Balatsky, Phys. Rev. B **86**, 144506 (2012).

[26] C. Triola, D. M. Badiane, A. V. Balatsky, and E. Rossi, Phys. Rev. Lett. **116**, 257001 (2016).

[27] A. M. Black-Schaffer and A. V. Balatsky, Phys. Rev. B **88**, 104514 (2013).

[28] C. Triola and A. V. Balatsky, Phys. Rev. B **94**, 094518 (2016).

[29] C. Triola and A. V. Balatsky, Phys. Rev. B **95**, 224518 (2017).

[30] H. Ebisu, B. Lu, J. Klinovaja, and Y. Tanaka, Prog. Theor. Exp. Phys. **2016**, 083I01 (2016).

[31] A. Di Bernardo, S. Diesch, Y. Gu, J. Linder, G. Divitini, C. Ducati, E. Scheer, M. G. Blamire, and J. W. Robinson, Nat. Commun. **6**, 8053 (2015).

[32] A. Di Bernardo, Z. Salman, X. L. Wang, M. Amado, M. Egilmez, M. G. Flokstra, A. Suter, S. L. Lee, J. H. Zhao, T. Prokscha, E. Morenzoni, M. G. Blamire, J. Linder, and J. W. A. Robinson, Phys. Rev. X **5**, 041021 (2015).

[33] A. Pal, J. A. Ouassou, M. Eschrig, J. Linder, and M. G. Blamire, Scientific Reports **7**, 40604 (2017).

[34] F. L. Pratt, T. Lancaster, S. J. Blundell, and C. Baines, Phys. Rev. Lett. **110**, 107005 (2013).

[35] Y. Tanaka, M. Sato, and N. Nagaosa, J. Phys. Soc. Jpn. **81**, 011013 (2012).

[36] J. Linder and A. V. Balatsky, arXiv:1709.03986.

[37] P. S. Riseborough, G. M. Schmiedeshoff, and J. L. Smith, in *The Physics of Superconductors* (Springer, New York, 2004), pp. 889–1086.

[38] N. Bulut, D. J. Scalapino, and S. R. White, Phys. Rev. B **47**, 14599 (1993).

[39] K. Shigeta, S. Onari, K. Yada, and Y. Tanaka, Phys. Rev. B **79**, 174507 (2009).

[40] M. Vojta and E. Dagotto, Phys. Rev. B **59**, R713 (1999).

[41] A. Balatsky, E. Abrahams, D. Scalapino, and J. Schrieffer, Physica B **199-200**, 363 (1994).

[42] E. Abrahams, A. Balatsky, D. J. Scalapino, and J. R. Schrieffer, Phys. Rev. B **52**, 1271 (1995).

[43] D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev. **148**, 263 (1966).

[44] P. Monthoux and D. J. Scalapino, Phys. Rev. Lett. **72**, 1874 (1994).

[45] N. F. Berk and J. R. Schrieffer, Phys. Rev. Lett. **17**, 433 (1966).

[46] W. Wojtanowski and P. Wölfle, Phys. Lett. A **115**, 49 (1986).

[47] A. J. Leggett, Rev. Mod. Phys. **47**, 331 (1975).

[48] W. Hergert and R. M. Geilhufe, *Group Theory in Solid State Physics and Photonics: Problem Solving with Mathematica* (Wiley, New York, 2018).

[49] W. Hergert and M. Geilhufe, MATHEMATICA group theory package GTPack, Ver. 1.0, 2017.

[50] D. F. Holt, B. Eick, and E. A. O'Brien, *Handbook of Computational Group Theory* (CRC, Boca Raton, 2005).

[51] S. Flodmark and E. Blokker, Int. J. Quantum Chem. **1**, 703 (1967).

[52] P. van Den Broek and J. Cornwell, Phys. Status Solidi B **90**, 211 (1978).

[53] R. S. Mulliken, J. Chem. Phys. **23**, 1997 (1955).

[54] R. S. Mulliken, J. Chem. Phys. **24**, 1118 (1956).

[55] S. Altmann and P. Herzig, *Point-Group Theory Tables* (Oxford University, New York, 1994).

[56] J. Cornwell, *Group Theory in Physics* (Academic, New York, 1984), Vol. 1.

[57] H. P. Dahal, E. Abrahams, D. Mozyrsky, Y. Tanaka, and A. V. Balatsky, New J. Phys. **11**, 065005 (2009).