

# Group-theoretical analysis and synthesis of Hamiltonians

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## 1 Introduction

The purpose of this lecture is to show how group theory can be used to analyze model Hamiltonians and also to construct such Hamiltonians based on symmetries. It should help to answer questions such as: Why did the authors of paper X write down this weird Hamiltonian? Is the model used in paper Y generic for systems of the relevant symmetry or does it contain hidden assumptions? How can I construct a model Hamiltonian for some complicated lattice? Which symmetries of superconducting states are possible for a certain system?

While the method is very general, we will restrict ourselves to

- electronic systems, both in the normal and the superconducting states, which are nonmagnetic at least in the normal state, and
- point-group symmetries.

We will focus on practical procedures. Rigorous mathematical treatments can be found in many good textbooks on group theory.

## 2 Mathematical basics

### 2.1 Groups

A group is a set  $\mathcal{G}$  endowed with an operation, called *group multiplication*,

$$\begin{cases} \mathcal{G} \times \mathcal{G} \rightarrow \mathcal{G} \\ a, b \mapsto ab \end{cases} \quad (1)$$

with

- $ab \in \mathcal{G} \forall a, b \in \mathcal{G}$  (closure),
- $(ab)c = a(bc) \forall a, b, c \in \mathcal{G}$  (associativity),
- there exists an *identity element* or *unit element*  $e \in \mathcal{G}$  such that  $ea = ae = a \forall a \in \mathcal{G}$ ,
- for every  $a \in \mathcal{G}$ , there exists an *inverse element*  $a^{-1} \in \mathcal{G}$  such that  $aa^{-1} = a^{-1}a = e$ .

It is common to denote both the group and the corresponding set by the same symbol.

A group is called *Abelian* if, in addition,  $ab = ba \forall a, b \in \mathcal{G}$  (commutativity). The number of elements (more correctly, the cardinality) of a group  $\mathcal{G}$  is called its *order*  $|\mathcal{G}|$ . The order can be finite, countably infinite, or uncountably infinite. In this lecture, we are only dealing with finite groups.

### 2.2 Space groups and point groups

In physics, symmetries are mostly expressed in terms of the operations that leave an object invariant. Such symmetry operations naturally form groups with the composition as the group multiplication. We are here dealing with symmetries of electronic states in crystals. Spatial symmetry operations ( $R, T$ ) for lattices consist of a proper or improper rotation  $R$  and a translation  $T$ . A proper rotation takes a right-handed trihedron<sup>1</sup> (dreibein) into a right-handed trihedron, while an improper rotation takes a right-handed trihedron into a left-handed trihedron. The simplest improper rotation is the spatial inversion. Both the rotation part  $R$  and the translation part  $T$  can be trivial, i.e., the identity.

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<sup>1</sup>We only consider three-dimensional lattices but the procedure easily carries over to other cases.

The *space group* of a crystal is the group of all operations  $(R, T)$  that leave the crystal invariant.

The *point group* of a crystal is the group of all proper or improper rotations  $R$  that appear in the space group. Note that the point group need not be a subgroup<sup>2</sup> of the space group. It is a subgroup only if one can choose the origin of the coordinate system in such a way that for any  $R$  in the point group,  $(R, 0)$  is an element of the space group, where  $T = 0$  denotes the translation by the null vector.<sup>3</sup>

There are symmetry operations that are not spatial, in particular the *time reversal*  $\mathcal{T}$ . If we also consider time reversal and its combination with spatial transformations for a space group, we obtain a *magnetic space group*.<sup>4</sup> Similarly, if we do the same for a point group, we obtain a *magnetic point group*.

If time reversal is itself (not just in combination with rotations) an element of a magnetic point group, the group is called a *gray group*.<sup>5</sup> In this case, the magnetic point group  $\mathcal{G}_{\text{mag}}$  and the original point group  $\mathcal{G}$  are related by

$$\mathcal{G}_{\text{mag}} = \mathcal{G} \otimes \{e, \mathcal{T}\}, \quad (2)$$

which just means that any element of  $\mathcal{G}$  is contained in  $\mathcal{G}_{\text{mag}}$  both by itself and combined with time reversal. Hence, the orders of the groups satisfy  $|\mathcal{G}_{\text{mag}}| = 2|\mathcal{G}|$ .

## 2.3 Representations

A *representation* (“rep”) of a group  $\mathcal{G}$  is usually defined as a mapping from  $\mathcal{G}$  to a group of linear transformations on a vector space. Since we are here only concerned with finite groups, such linear transformations can be represented by matrices. We speak of a *real* (*complex*) rep if the vector space is over the field  $\mathbb{R}$  ( $\mathbb{C}$ ), i.e., the matrices are all real (can be complex). The following general statements hold for complex reps, unless stated otherwise.

We define a  $d$ -dimensional rep of a group  $\mathcal{G}$  as a mapping

$$\Gamma : \begin{cases} \mathcal{G} \rightarrow \text{GL}(d, \mathbb{C}) \\ a \mapsto \Gamma(a) \end{cases}, \quad (3)$$

where, for  $a, b, c \in \mathcal{G}$ ,

$$ab = c \quad \Rightarrow \quad \Gamma(a)\Gamma(b) = \Gamma(c). \quad (4)$$

More concisely, this can be written as

$$\Gamma(ab) = \Gamma(a)\Gamma(b) \quad \forall a, b \in \mathcal{G}, \quad (5)$$

i.e., the matrix multiplication in the representation is consistent with the group multiplication.

Note that the inference in Eq. (4) only goes in one direction. If it works in both ways,

$$ab = c \quad \Leftrightarrow \quad \Gamma(a)\Gamma(b) = \Gamma(c), \quad (6)$$

the rep is called *faithful*. In other words, a faithful rep is a *one-to-one* mapping between the original group and a group of matrices.

As the opposite extreme, a mapping that maps every group element to unity,

$$\Gamma(a) = 1 \quad \forall a \in \mathcal{G}, \quad (7)$$

is a one-dimensional rep, which obviously exists for any group. It is called the *trivial* representation.

The condition (4) or (5) remains invariant if we transform *all* matrices  $\Gamma(a)$  by

$$\Gamma(a) \mapsto U\Gamma(a)U^\dagger, \quad (8)$$

where  $U$  is an arbitrary but fixed unitary matrix. Hence, reps that only differ in such a transformation are called *equivalent*.

<sup>2</sup>A subgroup is a subset that is also a group.

<sup>3</sup>If this holds, the space group is called *symmorphic*, otherwise *nonsymmorphic*.

<sup>4</sup>Magnetically ordered systems are the ones that can behave nontrivially under time reversal.

<sup>5</sup>This is the case for nonmagnetic systems but also for antiferromagnetic systems that are invariant under the combination of time reversal and a pure translation.

A *unitary rep* is a rep made up of unitary matrices  $\Gamma(a)$ . For any finite group, all reps are equivalent to unitary reps. We can thus always assume the reps of crystallographic point groups to be unitary.

Magnetic groups contain the time reversal  $\mathcal{T}$ , at least in combinations with other elements. We know that time reversal is an *antilinear* operation on the Hilbert space since it involves a complex conjugation. However, time reversal is not special as far as the group properties are concerned and thus does not invalidate the general statements. In particular, the reps of the magnetic point group are unitary.

## 2.4 Irreducible representations

One can often simplify reps by a unitary transformation. For example, if all  $\Gamma(a)$  are unitary and commute with each other they can be diagonalized simultaneously. More generally, it may be possible to *block diagonalize* all  $\Gamma(a)$  simultaneously. If so, the transformed rep can be written as

$$a \mapsto \Gamma(a) = \begin{pmatrix} \Gamma_1(a) & 0 & & \\ 0 & \Gamma_2(a) & & \\ & & \ddots & \\ & & & \ddots \end{pmatrix}, \quad (9)$$

where  $\Gamma_1(a), \Gamma_2(a), \dots$  are unitary. The blocks  $\Gamma_1(a)$  etc. do not mix under matrix multiplication. This implies that  $\Gamma_1(a), \Gamma_2(a), \dots$  each are reps by themselves.

A rep is called *reducible* if all matrices can be block-diagonalized simultaneously by a unitary transformation. Otherwise it is called *irreducible*. Irreducible representations are called “irreps.”

The irreps of a group are unique up to unitary transformations. There are many theorems concerning irreps. For example, all one-dimensional reps are irreducible. A more interesting theorem states the following: let  $\Gamma_n$  be the irreps of a finite group  $\mathcal{G}$  and let their dimensions be  $d_n$ . Then

$$\sum_n d_n^2 = |\mathcal{G}|. \quad (10)$$

In practice, one rarely has to find the irreps of a group from scratch. In particular, the irreps of point groups are all tabulated. It would of course be possible to give representative matrices  $\Gamma(a)$  for all  $a \in \mathcal{G}$  for all irreps. Such tables would contain irrelevant information, though, since the irreps are only unique up to unitary transformations. It turns out to be sufficient for the unique characterization of irreps to list the traces  $\text{Tr} \Gamma(a)$  of matrices  $\Gamma(a)$  and not the full matrices, and to do so only for specific  $a$  that represent whole classes. Loosely speaking, classes contain point-group operations that are related by symmetries, such as all threefold rotations of a cubic point group.<sup>6</sup> The traces

$$\chi(a) = \text{Tr} \Gamma(a) \quad (11)$$

are called *characters* of the matrices  $\Gamma(a)$ . Many character tables and additional information for all crystallographic point groups can be found online. A comprehensive set of pages is [1], another useful set is [2]. A lot of material on magnetic and nonmagnetic space and point groups can be found in [3].

It is easy to see that the group identity must be represented by a unit matrix,  $\Gamma(e) = \mathbb{1}$ . This implies that its character  $\chi(e) = d$  is the dimension of the rep.

For some groups, it makes a difference whether we consider complex (as implied so far) or real irreps. Since reality is an additional condition, a rep can be irreducible as a real rep but reducible as a complex rep. For certain crystallographic point groups, a two-dimensional real irrep can be reduced into two one-dimensional complex irreps. For crystallographic point groups, all characters for real irreps must be integers. For point groups with two-dimensional real irreps that decompose into one-dimensional complex irreps, the resulting characters are generally complex numbers with unit modulus. Whether real or complex irreps should be considered depends on the physical question. For our purposes, real irreps are likely more useful but we will not discuss examples for which this makes a difference.

<sup>6</sup>See books on group theory for rigorous discussions of the concept of classes.

## 2.5 Basis functions

Let  $\mathcal{G}$  be a group of coordinate transformations in  $D$ -dimensional Euclidean space,<sup>7</sup> for example a point group. We are concerned with the case of  $D = 3$ . The coordinate transformations act analogously in real and momentum space; we will write them for momentum space since this will be needed later.  $d$  linearly independent functions  $c_n(\mathbf{k})$ ,  $n = 1, \dots, d$ , are called *basis functions* of a  $d$ -dimensional irrep  $\Gamma$  of  $\mathcal{G}$  if all  $a \in \mathcal{G}$  act as

$$c_n(\mathbf{k}) \xrightarrow{a} \sum_{m=1}^d \Gamma(a)_{mn} c_m(\mathbf{k}). \quad (12)$$

Note the order of indices of  $\Gamma(a)$ . One says that  $c_n(\mathbf{k})$  transforms as the  $n$ -th row of the irrep  $\Gamma$ .

To make Eq. (12) more explicit: a coordinate transformation  $a$  in  $D$  dimensions is expressed by multiplying the momentum  $\mathbf{k}$  by a proper or improper rotation matrix, which is an orthogonal matrix  $R_a^{-1} \in O(D)$ . The definition with the *inverse* matrix is a convention. For example, for the identity operation,  $R_a^{-1} = \mathbb{1}$ , while for spatial inversion,  $R_a^{-1} = -\mathbb{1}$ .<sup>8</sup> This means that the  $c_n(\mathbf{k})$  must satisfy

$$c_n(\mathbf{k}) \xrightarrow{a} c_n(R_a^{-1}\mathbf{k}) = \sum_{m=1}^d \Gamma(a)_{mn} c_m(\mathbf{k}). \quad (13)$$

Basis functions of irreps are tabulated. It is important to realize that the basis functions are not at all unique. The tables typically show the lowest-order polynomial (the “simplest”) functions that form a basis. Basis functions are extremely useful to get intuition for how the matrices  $\Gamma(a)$  act.

Example: we will only consider the point group  $O_h$ . The following table shows the lowest-order polynomial basis functions of the irreps of the nonmagnetic point group  $O_h$ . The first column contains the *Mulliken notation* for the irrep and the second the minimum order of polynomial basis functions.<sup>9</sup>

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<sup>7</sup>Do not mix up the dimension  $D$  of coordinate space with the dimension  $d$  of some rep.

<sup>8</sup>The matrices  $R_a^{-1}$  form a  $D$ -dimensional rep of the group  $\mathcal{G}$ , which is generally reducible.

<sup>9</sup>For the specialists: since we are dealing with fermionic systems, we should, in principle, consider *double groups*. The point is that a  $(2s + 1)$ -component spinor  $\psi(\mathbf{k})$  changes sign under rotation by  $360^\circ$  if  $s$  is half integer. For spin  $1/2$  this is easily seen for the example of a rotation about the  $z$ -axis: the rotation matrix for a rotation angle of  $\phi$  reads

$$U_z(\phi) = e^{-i\frac{\sigma_3}{2}\phi}.$$

This gives

$$U_z(2\pi) = e^{-i\pi\sigma_3} = \begin{pmatrix} e^{-i\pi} & 0 \\ 0 & e^{+i\pi} \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} = -\mathbb{1}.$$

Since rotation by  $360^\circ$  is certainly a symmetry (and for  $O_h$  is the square of the two-fold rotations about the principal axes, which are symmetries) it must be an element of the point group. However, it is not the identity element but rather its *square* is the identity element. This effectively doubles the order of the group, hence the term *double groups*. It also leads to the appearance of additional, so-called *extra* irreps. However, for our purposes of the classification of Hamiltonians, the extra irreps are not relevant, essentially because the second-quantized Hamiltonian consists of even-order products of fermionic creation and annihilation operators and is in this sense bosonic.

irrep	order	basis functions
$A_{1g}$	0	1
$A_{2g}$	6	$k_x^4(k_y^2 - k_z^2) + k_y^4(k_z^2 - k_x^2) + k_z^4(k_x^2 - k_y^2)$
$E_g$	2	$k_x^2 - k_y^2$ $\frac{1}{\sqrt{3}}(2k_z^2 - k_x^2 - k_y^2)$
$T_{1g}$	4	$k_y k_z (k_y^2 - k_z^2)$ $k_z k_x (k_z^2 - k_x^2)$ $k_x k_y (k_x^2 - k_y^2)$
$T_{2g}$	2	$k_y k_z$ $k_z k_x$ $k_x k_y$
$A_{1u}$	9	$k_x k_y k_z [k_x^4(k_y^2 - k_z^2) + k_y^4(k_z^2 - k_x^2) + k_z^4(k_x^2 - k_y^2)]$
$A_{2u}$	3	$k_x k_y k_z$
$E_u$	5	$\frac{1}{\sqrt{3}} k_x k_y k_z (2k_z^2 - k_x^2 - k_y^2)$ $-k_x k_y k_z (k_x^2 - k_y^2)$
$T_{1u}$	1	$k_x$ $k_y$ $k_z$
$T_{2u}$	3	$k_x (k_y^2 - k_z^2)$ $k_y (k_z^2 - k_x^2)$ $k_z (k_x^2 - k_y^2)$

We see that in the Mulliken notation the letter used for the irrep shows its dimension.  $A$  and  $B$  (which does not occur for  $O_h$ ) stand for one dimension,  $E$  for two, and  $T$  for three. Moreover, the subscript  $g$  or  $u$  indicates whether the irrep maps the inversion operation onto  $\mathbb{1}$  (even irreps,  $g$  for “gerade”) or  $-\mathbb{1}$  (odd irreps,  $u$  for “ungerade”). The basis functions are then also even or odd under inversion, respectively. This distinction of course only exists if the point group contains the inversion.

A few additional remarks on tabulated basis functions are in order:

- Often the basis function for the trivial irrep  $A_{1g}$  is given as  $k_x^2 + k_y^2 + k_z^2$ . This is certainly a correct basis function but not the lowest-order one.
- Often, only basis functions of first and second order are included, giving the incorrect impression that no basis functions exist for some of the irreps.
- For higher-dimensional (i.e., not one-dimensional) irreps, nonsingular transformations of the set of basis functions lead to other permissible sets of basis functions. While the basis shown in tables is typically of a certain form (for example, we choose  $k_x^2 - k_y^2$  as a basis function for  $E_g$ , and not  $k_y^2 - k_z^2$ ), there is no universally accepted order of the basis functions.
- Normalization factors (including minus signs) are often not included or random.

To continue with the example, we see that for all four three-dimensional irreps, the three basis functions are related in a simple way: they are mapped onto each other cyclically under the threefold rotation  $C_{3xyz}$  about the (111) direction. For the two-dimensional irreps, this is evidently not the case. For  $E_g$ , the mapping reads

$$k_x^2 - k_y^2 \xrightarrow{C_{3xyz}} k_y^2 - k_z^2 = -\frac{1}{2}(k_x^2 - k_y^2) - \frac{\sqrt{3}}{2} \frac{1}{\sqrt{3}}(2k_z^2 - k_x^2 - k_y^2), \quad (14)$$

$$\frac{1}{\sqrt{3}}(2k_z^2 - k_x^2 - k_y^2) \xrightarrow{C_{3xyz}} \frac{1}{\sqrt{3}}(2k_x^2 - k_y^2 - k_z^2) = \frac{\sqrt{3}}{2}(k_x^2 - k_y^2) - \frac{1}{2} \frac{1}{\sqrt{3}}(2k_z^2 - k_x^2 - k_y^2). \quad (15)$$

From Eq. (12), we see that the representation matrix of  $C_{3xyz}$  must be

$$\Gamma_{E_g}(C_{3xyz}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}. \quad (16)$$

As an example showing how to find reasonable basis functions for new irreps, we consider the irrep  $E_u$ . It makes sense to use the same representation matrices for *proper* rotations for  $E_u$  as for  $E_g$  since the only essential difference is that the inversion is represented by  $-\mathbb{1}$  instead of  $\mathbb{1}$ , which can be incorporated by multiplying all representation matrices for improper rotations by  $-1$ . Thus we take, in particular,  $\Gamma_{E_u}(C_{3xyz}) = \Gamma_{E_g}(C_{3xyz})$ . Possible basis functions for  $E_u$  can be inferred from the product relation  $E_g \otimes A_{2u} = E_u$ . It implies that basis functions for  $E_u$  can be constructed by multiplying basis functions for  $E_g$  by the basis function  $k_x k_y k_z$  of  $A_{2u}$ . However, the two functions naively obtained by this procedure do not transform correctly under point-group operations if we want to keep the same matrices for proper rotations. For example, the function  $k_x k_y k_z (k_x^2 - k_y^2)$  is even under the fourfold rotation  $C_{4z}$  about the  $z$ -axis, not odd like  $k_x^2 - k_y^2$ . Hence, we take the first basis function of  $E_u$  to be  $(1/\sqrt{3}) k_x k_y k_z (2k_z^2 - k_x^2 - k_y^2)$  since it is odd under  $C_{4z}$ . Applying  $C_{3xyz}$  to it, we get

$$\frac{1}{\sqrt{3}} k_x k_y k_z (2k_z^2 - k_x^2 - k_y^2) \xrightarrow{C_{3xyz}} \frac{1}{\sqrt{3}} k_y k_z k_x (2k_x^2 - k_y^2 - k_z^2) = -\frac{1}{2} \frac{1}{\sqrt{3}} k_x k_y k_z (2k_z^2 - k_x^2 - k_y^2) - \frac{\sqrt{3}}{2} c_{E_u}^{(2)}(\mathbf{k}), \quad (17)$$

where  $c_{E_u}^{(2)}(\mathbf{k})$  is the as yet unknown second basis function. This is trivially solved to give

$$c_{E_u}^{(2)}(\mathbf{k}) = -k_x k_y k_z (k_x^2 - k_y^2). \quad (18)$$

These basis functions have been included in the above table.

For gray magnetic point groups  $\mathcal{G}_{\text{mag}} = \mathcal{G} \otimes \{e, \mathcal{T}\}$ , time-reversal symmetry behaves similarly to inversion symmetry as far as the irreps are concerned. The number of irreps is twice that for the structural group  $\mathcal{G}$ : for any irrep  $\Gamma$  of  $\mathcal{G}$ , there are two irreps  $\Gamma_+$  and  $\Gamma_-$  of  $\mathcal{G}_{\text{mag}}$ , where the subscript  $\pm$  indicates whether the irrep and thus its basis functions are even (+) or odd (-) under time reversal. Hence, the irreps of the magnetic point group  $O_h$  are  $A_{1g+}$ ,  $A_{1g-}$ ,  $A_{2g+}$ ,  $A_{2g-}$ ,  $\dots$

Since momenta  $\mathbf{k}$  are odd under *both* inversion and time reversal any basis functions constructed out of their components can only be either even or odd under *both* these operations. This means that  $g+$  and  $u-$  irreps have momentum-space basis functions, whereas  $g-$  and  $u+$  irreps do not.<sup>10</sup>

## 2.6 Irreducible tensor operators

There is an extensive theory for irreducible tensor operators but we only need a small part of it. The main idea is to construct operators on the Hilbert space (or matrices that represent them in a specific basis) that transform like basis functions. Let  $\mathcal{G}$  be a point group in  $D$ -dimensional space. A symmetry operation  $a \in \mathcal{G}$  is associated, on the one hand, with a rotation matrix  $R_a^{-1}$  and, on the other, with a unitary operator  $U_a$  on the Hilbert space.  $U_a$  encodes, for example, the rotation of spins.

A set of  $d$  linearly independent operators  $Q_n(\mathbf{k})$ ,  $n = 1, \dots, d$ , are called *irreducible tensor operators* of a  $d$ -dimensional irrep  $\Gamma$  of  $\mathcal{G}$  if all  $a \in \mathcal{G}$  act as

$$Q_n(\mathbf{k}) \xrightarrow{a} U_a Q_n(R_a^{-1}\mathbf{k}) U_a^\dagger = \sum_{m=1}^d \Gamma(a)_{mn} Q_m(\mathbf{k}). \quad (19)$$

Note the similarity to Eq. (12). One says that  $Q_n(\mathbf{k})$  transforms as the  $n$ -th row of the irrep  $\Gamma$ .

The concept can be extended to antiunitary transformations, such as time reversal. Time reversal inverts momenta (but not positions) and on the Hilbert space acts as an antiunitary operator

$$\mathcal{T} = U_T \mathcal{K}, \quad (20)$$

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<sup>10</sup>This is different for real-space basis functions since position vectors  $\mathbf{r}$  are odd under inversion but even under time reversal. Hence, only the  $g+$  and  $u+$  irreps have real-space basis functions.

where  $U_T$  is a unitary operator and  $\mathcal{K}$  is complex conjugation.<sup>11</sup> Under time reversal, irreducible tensor operators must transform according to

$$Q_n(\mathbf{k}) \xrightarrow{\mathcal{T}} U_T Q_n^*(-\mathbf{k}) U_T^\dagger = \sum_{m=1}^d \Gamma(\mathcal{T})_{mn} Q_m(\mathbf{k}). \quad (21)$$

In the irreps of gray magnetic point groups,  $\mathcal{T}$  is represented by either  $\mathbb{1}$  (for “+” irreps) or  $-\mathbb{1}$  (for “-” irreps) so that we simply get

$$U_T Q_n^*(-\mathbf{k}) U_T^\dagger = \pm Q_n(\mathbf{k}). \quad (22)$$

The most important point to remember is that the concept of irreducible tensor operators is essentially a generalization of the one of basis functions to operator- (or matrix-) valued functions. The simplest application is to angular-momentum operators (or matrices). Let  $\mathbf{J} = (J_x, J_y, J_z)$  be a spin operator of length  $j$ . Its components  $J_i$  can be written as  $(2j + 1) \times (2j + 1)$  matrices. Then the proper rotation about an axis along the unit vector  $\hat{\mathbf{n}}$  by an angle  $\phi$  is expressed by the unitary  $SU(2j + 1)$  matrix

$$U_{\hat{\mathbf{n}}, \phi} = e^{-i \hat{\mathbf{n}} \cdot \mathbf{J} \phi}. \quad (23)$$

Improper rotations can be written as the product of the inversion and a proper rotation. Inversion leaves spins invariant so that the unitary matrices describing improper rotations are identical to those for the corresponding proper ones. This takes care of all operations in the structural point group.

Furthermore, the spin should change sign under time reversal, i.e.,

$$J_i \xrightarrow{\mathcal{T}} U_T J_i^* U_T^\dagger = -J_i, \quad (24)$$

where  $i = x, y, z$ . How should  $U_T$  be chosen? One can show that it is always possible to choose two of the spin components as real matrices. The third then must be imaginary since the spin commutation relation contains a factor  $i$ . By convention,  $J_y$  is imaginary. Then a suitable choice for  $U_T$  is

$$U_T = e^{i J_y \pi}. \quad (25)$$

$U_T$  itself obviously describes a rotation about the  $y$ -axis by  $180^\circ$ . Hence, we obtain

$$J_x \xrightarrow{\mathcal{T}} e^{i J_y \pi} J_x^* e^{-i J_y \pi} = e^{i J_y \pi} J_x e^{-i J_y \pi} = -J_x \quad (26)$$

and analogously for  $J_z$ , while

$$J_y \xrightarrow{\mathcal{T}} e^{i J_y \pi} J_y^* e^{-i J_y \pi} = e^{i J_y \pi} (-J_y) e^{-i J_y \pi} = -J_y e^{i J_y \pi} e^{-i J_y \pi} = -J_y. \quad (27)$$

We see that all three components are inverted.<sup>12</sup> For spins of length  $1/2$ , we thus find the simple form

$$U_T = e^{i \frac{\sigma_2}{2} \pi} = \sigma_0 \cos \frac{\pi}{2} + i \sigma_2 \sin \frac{\pi}{2} = i \sigma_2, \quad (28)$$

where  $\sigma_0 = \mathbb{1}_2$  is the  $2 \times 2$  unit matrix and we have used that  $\sigma_i^2 = \sigma_0$  and Taylor expansion of the matrix exponential.

We can now try to find irreducible tensor operators expressed in terms of angular-momentum operators for the various irreps and list them together with the basis functions. This is often done in tables of basis functions (the spin operators are usually called “rotations” and denoted by  $R_i$ ), but only to linear order. However, more complicated, in particular polynomial, functions of spin operators are possible. Such irreducible tensor operators can be called *spin basis functions*.

<sup>11</sup>Any antiunitary operator can be written like this. Complex conjugation is a basis-dependent operation. It is defined as leaving all basis vectors invariant and complex conjugating all coefficients.

<sup>12</sup>This shows that although  $U_T$  seems to break rotation symmetry by treating  $J_y$  differently from the other components, it actually does not.

It makes sense to consider only hermitian spin basis functions because we eventually want to expand Hamiltonians. Hermitian operators can sometimes but not always be constructed by symmetrization. For example,  $J_x J_y$  is generally not hermitian but  $(J_x J_y + J_y J_x)/2$  is. However, for spins of length  $1/2$ , this is zero since the Pauli matrices anticommute. Thus, symmetrization does not produce a spin basis function of order two and indeed such functions do not exist for spin  $1/2$ . To understand this more generally, recall that spins of length  $j$  are represented by  $(2j + 1) \times (2j + 1)$  matrices. The vector space over  $\mathbb{R}$  of hermitian  $(2j + 1) \times (2j + 1)$  matrices has dimension  $(2j + 1)^2$ . The number of linearly independent hermitian functions of spin operators of order  $n$  is  $2n + 1$ .<sup>13</sup> Since

$$\sum_{n=0}^{2j} (2n + 1) = (2j + 1)^2 \quad (29)$$

it is plausible and indeed true that one can form a basis of the vector space from polynomial functions of order up to  $2j$ . This means that higher powers can be expressed as linear combinations of lower ones. Hence, independent spin basis functions only exist up to the order  $2j$ . If we try to construct basis functions of higher order we either get zero or we can express them as linear combinations of basis functions of lower order, which may belong to different irreps.

Since spins are always even under inversion (pseudovectors!) and odd under time reversal spin basis functions for  $g+$  irreps must be even in spin and for  $g-$  irreps must be odd in spin. For  $u+$  and  $u-$  irreps, spin basis functions do not exist.

In practice, spin basis functions can be constructed from momentum basis functions by the following steps:

- Replace  $k_i$  by  $J_i$ .
- Disregard functions of order higher than  $2j$ .
- Symmetrize if required to make the matrix functions hermitian. Remove them if they become zero or if they are already accounted for, possibly by spin basis functions of different irreps.
- Shift spin basis functions of odd order from the  $u-$  to the corresponding  $g-$  irrep.

For illustration, the following table shows the momentum and spin basis functions for the four  $T_1$  irreps of the magnetic point group  $O_h$ , where “–” means that no basis functions exist.

irrep	momentum basis functions	spin basis functions
$T_{1g+}$	$k_y k_z (k_y^2 - k_z^2)$ $k_z k_x (k_z^2 - k_x^2)$ $k_x k_y (k_x^2 - k_y^2)$	$\frac{J_y J_z (J_y^2 - J_z^2) + (J_y^2 - J_z^2) J_z J_y}{2}$ $\frac{J_z J_x (J_z^2 - J_x^2) + (J_z^2 - J_x^2) J_x J_z}{2}$ $\frac{J_x J_y (J_x^2 - J_y^2) + (J_x^2 - J_y^2) J_y J_x}{2}$
$T_{1g-}$	– – –	$J_x$ $J_y$ $J_z$
$T_{1u+}$	– – –	– – –
$T_{1u-}$	$k_x$ $k_y$ $k_z$	– – –

The  $T_{1g+}$  spin basis functions are of order four and are thus appropriate for spins of length 2 or larger. What happens if we try to construct these for shorter spins?

<sup>13</sup>There is a single order-zero function,  $\mathbb{1}$ , three first-order functions,  $J_x, J_y, J_z$ , etc.

- For  $j = 1/2$ , the entries all vanish since  $\sigma_i^2 = \mathbb{1}$  and thus do not produce any basis functions.
- For  $j = 1$ , we find by explicit evaluation that, for example,

$$\frac{J_x J_y (J_x^2 - J_y^2) + (J_x^2 - J_y^2) J_y J_x}{2} = -\frac{J_x J_y + J_y J_x}{2}, \quad (30)$$

which is a spin basis function belonging to  $T_{2g}$ .

- For  $j = 3/2$ , the result is the same as for  $j = 1$ .

We also note that combinations of momentum and spin can generate additional basis functions also for irreps that do not have pure momentum or spin basis functions. For example, by replacing a single  $k_i$  by a  $J_i$  in the  $T_{1g+}$  basis functions, we obtain, after symmetrization,

$$\frac{k_y J_z + J_y k_z}{2} (k_y^2 - k_z^2) \quad (31)$$

etc. Since the transformation under all improper rotations changes sign compared to the momentum basis functions these combined basis functions belong to  $T_{1u+}$ .

### 3 Application to the normal-state Hamiltonian

In this section, we first outline the procedure for constructing a general Hamiltonian for the (nonmagnetic) normal state and then illustrate it for two examples. Since we are interested in a periodic lattice we treat the Hamiltonian in momentum space. The second-quantized Hamiltonian reads

$$\hat{H}_N = \sum_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} H_N(\mathbf{k}) c_{\mathbf{k}}, \quad (32)$$

where

$$c_{\mathbf{k}} = \begin{pmatrix} c_{\mathbf{k},1} \\ \vdots \\ c_{\mathbf{k},n} \end{pmatrix} \quad (33)$$

is an  $n$ -component spinor operator.  $i = 1, \dots, n$  counts the possible states of *internal* degrees of freedom such as spin, orbital, and basis site. The first-quantized Hamiltonian  $H_N(\mathbf{k})$  is an  $n \times n$  matrix.

The procedure is as follows:

- Find point group  $\mathcal{G}$  of the crystal. It will turn out to be useful to work with the magnetic point group  $\mathcal{G}_{\text{mag}} = \mathcal{G} \otimes \{e, \mathcal{T}\}$ . Obtain a list of the irreps of  $\mathcal{G}_{\text{mag}}$ .
- Construct a basis  $\{h_{\nu}\}$  of hermitian  $n \times n$  matrices in the space of the internal degrees of freedom so that the  $h_{\nu}$  transform as irreducible tensor operators of the magnetic point group  $\mathcal{G}_{\text{mag}}$ . We will call the  $h_{\nu}$  *basis matrices*. Often, not all irreps occur.
- Obtain a list of the irreps that possess momentum basis functions. It is also useful to obtain lowest-order polynomial basis functions for those irreps but these must be understood as placeholders for arbitrary basis functions with the same symmetry properties under point-group operations.
- Expand the Hamiltonian into the previously constructed basis,

$$H_N(\mathbf{k}) = \sum_{\nu} c_{\nu}(\mathbf{k}) h_{\nu}. \quad (34)$$

The Hamiltonian and thus every term in the expansion must be invariant under  $\mathcal{G}_{\text{mag}}$ , i.e., it must transform as an irreducible tensor operator belonging to the trivial irrep  $A_{\text{triv}}$ . This requires the *form factors*  $c_{\nu}(\mathbf{k})$  to transform as basis functions of the same irrep to which  $h_{\nu}$  belongs. Moreover,

for multidimensional irreps, the  $c_\nu(\mathbf{k})$  must transform as the basis functions that correspond to the irreducible tensor operators  $h_\nu$  (same component of the multiplet) and all of them must have the same amplitude if the basis functions and tensor operators are properly normalized.<sup>14</sup> This relies on the fact that the reduction of the product of any irrep with itself contains the trivial irrep. If there is no basis function  $c_\nu(\mathbf{k})$  for the irrep of some  $h_\nu$ , this term does not occur in Eq. (34).

### 3.1 Example: two $s$ -orbitals

As an example, we consider a material with the cubic point group  $O_h$  and two unrelated fully symmetric ( $s$ -like) orbitals, with spin, per lattice site. This is arguably the simplest example beyond a single orbital per site. While it is not very realistic for real materials—we would essentially need atoms with two different  $s$ -orbitals dominating the band structure close to the Fermi energy—it shows that even such a simple model is not trivial.

The Hilbert space of the internal degrees of freedom is four-dimensional (orbital times spin) and it is useful to write all  $4 \times 4$  matrices as Kronecker products  $A \otimes B$ , where  $A$  and  $B$  are  $2 \times 2$  matrices acting on the orbital and the spin degree of freedom, respectively.<sup>15</sup> Full symmetry of the orbitals means that they transform according to the trivial irrep  $A_{1g}$ . In particular, spatial inversion is described by the unitary matrix

$$P = \mathbb{1}_4 = \sigma_0 \otimes \sigma_0, \quad (35)$$

where  $\sigma_0 = \mathbb{1}_2$ , since inversion affects neither the fully symmetric orbitals nor the spin.

The unitary part of the time-reversal operator is

$$U_T = \sigma_0 \otimes i\sigma_2 \quad (36)$$

since the orbitals are invariant under time reversal and the spin is inverted, see Sec. 2.6.

For this case, one can easily see that the 16 hermitian matrices obtained as Kronecker products  $\sigma_i \otimes \sigma_j$ ,  $i, j = 0, 1, 2, 3$ , are irreducible tensor operators of irreps.<sup>16</sup> The resulting basis matrices are listed in the following table, together with their corresponding irreps.

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<sup>14</sup>For example, the irrep  $E_{g+}$  of the point group  $O_h$  for a model with total angular momentum of length  $j \geq 1$  involves the basis matrices  $h_4 = (J_x^2 - J_y^2)/\sqrt{3}$  and  $h_5 = (2J_z^2 - J_x^2 - J_y^2)/3$ . The corresponding form factors are, to leading order is powers of momentum,  $c_4(\mathbf{k}) = c_{E_g} (k_x^2 - k_y^2)/\sqrt{3}$  and  $c_5(\mathbf{k}) = c_{E_g} (2k_z^2 - k_x^2 - k_y^2)/3$ . Their linear combination reads

$$\begin{aligned} c_4(\mathbf{k}) h_4 + c_5(\mathbf{k}) h_5 &= \frac{1}{9} (4k_x^2 J_x^2 + 4k_y^2 J_y^2 + 4k_z^2 J_z^2 - 2k_x^2 J_y^2 - 2k_x^2 J_z^2 - 2k_y^2 J_x^2 - 2k_y^2 J_z^2 - 2k_z^2 J_x^2 - 2k_z^2 J_y^2) \\ &= \frac{2}{3} (k_x^2 J_x^2 + k_y^2 J_y^2 + k_z^2 J_z^2) - \frac{2}{9} (k_x^2 + k_y^2 + k_z^2) j(j+1) \mathbb{1}, \end{aligned}$$

which has the full  $A_{1g+}$  symmetry.

<sup>15</sup>The Kronecker product is, in block form,

$$A \otimes B = \begin{pmatrix} A_{11}B & A_{12}B \\ A_{21}B & A_{22}B \end{pmatrix},$$

where

$$A = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}.$$

One can say that the first factor describes the outer structure, while the second factor describes the inner structure.

<sup>16</sup>For more complicated cases, such Kronecker products are not necessarily basis matrices of irreps. However, since the Kronecker products form a basis it is always possible to construct the basis matrices of irreps as their linear combinations.

$h_\nu$	irrep
$\sigma_0 \otimes \sigma_0$	$A_{1g+}$
$\sigma_0 \otimes \sigma_1$	$T_{1g-}$
$\sigma_0 \otimes \sigma_2$	
$\sigma_0 \otimes \sigma_3$	
$\sigma_1 \otimes \sigma_0$	$A_{1g+}$
$\sigma_1 \otimes \sigma_1$	$T_{1g-}$
$\sigma_1 \otimes \sigma_2$	
$\sigma_1 \otimes \sigma_3$	
$\sigma_2 \otimes \sigma_0$	$A_{1g-}$
$\sigma_2 \otimes \sigma_1$	$T_{1g+}$
$\sigma_2 \otimes \sigma_2$	
$\sigma_2 \otimes \sigma_3$	
$\sigma_3 \otimes \sigma_0$	$A_{1g+}$
$\sigma_3 \otimes \sigma_1$	$T_{1g-}$
$\sigma_3 \otimes \sigma_2$	
$\sigma_3 \otimes \sigma_3$	

To understand the table, first consider the structural point group. Since the orbitals transform trivially under all point-group elements, the corresponding unitary matrices are all of the form  $\sigma_0 \otimes u$ , where  $u$  is a  $2 \times 2$  unitary matrix. In other words, the spin alone determines the irrep of the structural point group. But then  $\sigma_0$  obviously transforms trivially, i.e., according to  $A_{1g}$ , whereas the spin  $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$  is a pseudovector, which transforms according to  $T_{1g}$ . Regarding time reversal,  $\sigma_0$  in the spin sector is even, whereas  $\boldsymbol{\sigma}$  is odd. However, the time-reversal operator  $\mathcal{T}$  is antilinear so that the imaginary Pauli matrix  $\sigma_2$  in the orbital sector gives another sign change.

The point to note here is that although the orbital degree of freedom appears to be a trivial spectator, it does lead to the appearance of additional irreps. Without it, i.e., for a single-orbital model, we could only have  $A_{1g+}$  (with basis matrix  $\sigma_0$ ) and  $T_{1g-}$  (with basis matrices  $\sigma_1, \sigma_2, \sigma_3$ ).

Next, we need momentum basis functions. The lowest-order basis functions can be found in the table in Sec. 2.5. In the normal-state Hamiltonian  $H_N(\mathbf{k}) = \sum_\nu c_\nu(\mathbf{k}) h_\nu$ , all terms must transform according to  $A_{1g+}$ , thus  $c_\nu(\mathbf{k})$  and  $h_\nu$  must transform in the same way. Since  $c_\nu(\mathbf{k})$  only exist for  $g+$  and  $u-$  irreps,  $H_N(\mathbf{k})$  can only contain  $h_\nu$  belonging to  $g+$  or  $u-$  irreps. A look at the table above shows that these are the six matrices (with their irreps)

$$h_0 \equiv \sigma_0 \otimes \sigma_0 \quad A_{1g+}, \quad (37)$$

$$h_1 \equiv \sigma_1 \otimes \sigma_0 \quad A_{1g+}, \quad (38)$$

$$h_2 \equiv \sigma_3 \otimes \sigma_0 \quad A_{1g+}, \quad (39)$$

$$h_3 \equiv \sigma_2 \otimes \sigma_1 \quad T_{1g+}, \quad (40)$$

$$h_4 \equiv \sigma_2 \otimes \sigma_2 \quad T_{1g+}, \quad (41)$$

$$h_5 \equiv \sigma_2 \otimes \sigma_3 \quad T_{1g+}. \quad (42)$$

We note in passing that these matrices have interesting commutation relations, namely  $h_\mu h_\nu = \pm h_\nu h_\mu$  with the sign given in the following table. These relations lead to a very simple analytical form of the eigenvalues:  $\epsilon_{\mathbf{k}} = c_0(\mathbf{k}) \pm [\sum_{\nu=1}^5 c_\nu^2(\mathbf{k})]^{1/2}$ .

	$h_0$	$h_1$	$h_2$	$h_3$	$h_4$	$h_5$
$h_0$	+	+	+	+	+	+
$h_1$	+	+	-	-	-	-
$h_2$	+	-	+	-	-	-
$h_3$	+	-	-	+	-	-
$h_4$	+	-	-	-	+	-
$h_5$	+	-	-	-	-	+

Equations (37)–(42) show that  $H_N(\mathbf{k})$  contains two types of terms, generated by  $A_{1g+} \otimes A_{1g+}$  and by  $T_{1g+} \otimes T_{1g+}$ , respectively. The first part reads

$$H_N^{A_{1g}}(\mathbf{k}) = c_{00}(\mathbf{k}) \sigma_0 \otimes \sigma_0 + c_{10}(\mathbf{k}) \sigma_1 \otimes \sigma_0 + c_{30}(\mathbf{k}) \sigma_3 \otimes \sigma_0, \quad (43)$$

where  $c_{00}$ ,  $c_{10}$ , and  $c_{30}$  are basis functions of  $A_{1g+}$ . While the simplest allowed basis functions would simply be  $c_{\mu 0}(\mathbf{k}) = 1$ ,  $\mu = 0, 1, 3$ , for a real material they will be more complicated and distinct—the point group does not imply any relation between them. However, they must all transform according to  $A_{1g+}$ , i.e., be invariant under all elements of the magnetic point group. They are further constrained by being periodic under translations by reciprocal-lattice vectors. However, if the low-energy states are restricted to the vicinity of the  $\Gamma$  point  $\mathbf{k} = 0$  the functions can be expanded in  $\mathbf{k}$ .<sup>17</sup> The leading terms read (see [1] to understand the origin of these terms)

$$c_{\mu 0}(\mathbf{k}) = c_{\mu 0}^{(0)} + c_{\mu 0}^{(2)} (k_x^2 + k_y^2 + k_z^2) + c_{\mu 0}^{(4)} (k_x^4 + k_y^4 + k_z^4) + c_{\mu 0}^{(6)} k_x^2 k_y^2 k_z^2 + \dots \quad (44)$$

for  $\mu = 0, 1, 3$ .<sup>18</sup> We can interpret the three terms physically. To that end, note that

$$\sigma_0 + \sigma_3 = 2 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \sigma_0 - \sigma_3 = 2 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \quad (45)$$

i.e., the sum of the first and third terms refers only to the first orbital, whereas their difference refers only to the second orbital. Hence,  $c_{00}^{(0)} \pm c_{30}^{(0)}$  is twice the onsite energy of orbital one (two) and the corresponding sums (differences) of higher order terms describe hopping between like orbitals. The chemical potential is the same for all orbitals and spin directions and thus must be included in  $c_{00}^{(0)}$ . The second term, with  $\sigma_1 \otimes \sigma_0$ , is off-diagonal in orbital space. It describes hopping between unlike orbitals. For a reasonable definition of local orbitals, the onsite energy should be diagonal, i.e.,  $c_{10}^{(0)} = 0$ .

For the second type, from  $T_{1g+} \otimes T_{1g+}$ , we observe that there is a single triplet of matrices belonging to  $T_{1g+}$ , namely  $\sigma_2 \otimes \sigma_1$ ,  $\sigma_2 \otimes \sigma_2$ , and  $\sigma_2 \otimes \sigma_3$ . To obtain an invariant Hamiltonian, they must each be multiplied by the corresponding momentum basis function and have the same coefficient, which gives

$$H_N^{T_{1g}}(\mathbf{k}) = c_{T_{1g}1}(\mathbf{k}) \sigma_2 \otimes \sigma_1 + c_{T_{1g}2}(\mathbf{k}) \sigma_2 \otimes \sigma_2 + c_{T_{1g}3}(\mathbf{k}) \sigma_2 \otimes \sigma_3 \equiv \mathbf{c}_{T_{1g}}(\mathbf{k}) \cdot \sigma_2 \otimes \boldsymbol{\sigma}, \quad (46)$$

with the expansion

$$c_{T_{1g}1}(\mathbf{k}) = c_{T_{1g}}^{(4)} k_y k_z (k_y^2 - k_z^2) + c_{T_{1g}}^{(6)} k_y k_z (k_y^4 - k_z^4) + \dots, \quad (47)$$

$$c_{T_{1g}2}(\mathbf{k}) = c_{T_{1g}}^{(4)} k_z k_x (k_z^2 - k_x^2) + c_{T_{1g}}^{(6)} k_z k_x (k_z^4 - k_x^4) + \dots, \quad (48)$$

$$c_{T_{1g}3}(\mathbf{k}) = c_{T_{1g}}^{(4)} k_x k_y (k_x^2 - k_y^2) + c_{T_{1g}}^{(6)} k_x k_y (k_x^4 - k_y^4) + \dots, \quad (49)$$

see [1].<sup>19</sup> Physically, since these terms are nontrivial in spin space and necessarily depend on momentum they describe *spin-orbit coupling*. More specifically, the spin-orbit coupling here is linear in spin (and thus potentially strong). It is also nontrivial in orbital space ( $\sigma_2$ ). This is necessary—for a single-orbital model, the only allowed basis matrix in  $H_N(\mathbf{k})$  is  $\sigma_0$  since  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$  belong to  $T_{1g-}$ , which does not have momentum basis functions.

The full normal-state Hamiltonian is  $H_N(\mathbf{k}) = H_N^{A_{1g}}(\mathbf{k}) + H_N^{T_{1g}}(\mathbf{k})$ . The advantage of the group-theoretical approach is that one can be certain that no terms have been missed.

<sup>17</sup>This works analogously if the relevant states are close to other high-symmetry points in the Brillouin zone. In that case, one has to use the *little group* of this point instead of the full point group.

<sup>18</sup>If we need to respect translation symmetry, the simplest form depends on the Bravais lattice. For the simple cubic lattice with lattice constant set to 1, we have

$$c_{\mu 0}(\mathbf{k}) = \epsilon_{\mu 0} + \epsilon'_{\mu 0} (\cos k_x + \cos k_y + \cos k_z) + \dots$$

<sup>19</sup>On the simple cubic lattice, we have

$$c_{T_{1g}1}(\mathbf{k}) = \epsilon_{T_{1g}} \sin k_y \sin k_z (\cos k_y - \cos k_z) + \dots,$$

$$c_{T_{1g}2}(\mathbf{k}) = \epsilon_{T_{1g}} \sin k_z \sin k_x (\cos k_z - \cos k_x) + \dots,$$

$$c_{T_{1g}3}(\mathbf{k}) = \epsilon_{T_{1g}} \sin k_x \sin k_y (\cos k_x - \cos k_y) + \dots$$

### 3.2 Example: two orbitals of opposite parity

As a second example, we consider the point group  $O_h$  but now with two orbitals of opposite parity at each lattice site. The even and the odd orbital both must map onto itself multiplied by a phase factor under any element of the point group. The even orbital thus must transform as a basis function of a one-dimensional  $g$  irrep.  $O_h$  has two such irreps,  $A_{1g}$  and  $A_{2g}$ . The trivial case is  $A_{1g}$ , i.e., the orbital has the full symmetry of an  $s$ -orbital.<sup>20</sup> The odd orbital must transform as a basis function of a one-dimensional  $u$  irrep, i.e., of  $A_{1u}$  or  $A_{2u}$ .  $A_{2u}$  is the simpler case since it has the lowest-order real-space basis function  $xyz$  of order 3. Hence, a single odd-parity orbital can be realized by an  $f_{xyz}$  orbital.<sup>21</sup>

We consider the case that the even orbital transforms according to  $A_{1g}$  ( $s$ -orbital) and the odd according to  $A_{2u}$  ( $f_{xyz}$ -orbital). Now the inversion or parity operator is nontrivial:

$$P = \sigma_3 \otimes \sigma_0 \quad (50)$$

since the  $f_{xyz}$ -orbital is odd under inversion. Moreover, it is odd under all fourfold rotations (irrep  $A_{2u}$ !) but even under threefold rotations. The unitary part of the time-reversal operator is

$$U_T = \sigma_0 \otimes i\sigma_2 \quad (51)$$

like in the first example. The basis matrices can be written as Kronecker products, which transform according to the irreps as follows. To obtain this table, the nontrivial transformation properties of the  $f_{xyz}$ -orbital under rotations has been taken into account.

$h_\nu$	irrep
$\sigma_0 \otimes \sigma_0$	$A_{1g+}$
$\sigma_0 \otimes \sigma_1$	$T_{1g-}$
$\sigma_0 \otimes \sigma_2$	
$\sigma_0 \otimes \sigma_3$	
$\sigma_1 \otimes \sigma_0$	$A_{2u+}$
$\sigma_1 \otimes \sigma_1$	$T_{2u-}$
$\sigma_1 \otimes \sigma_2$	
$\sigma_1 \otimes \sigma_3$	
$\sigma_2 \otimes \sigma_0$	$A_{2u-}$
$\sigma_2 \otimes \sigma_1$	$T_{2u+}$
$\sigma_2 \otimes \sigma_2$	
$\sigma_2 \otimes \sigma_3$	
$\sigma_3 \otimes \sigma_0$	$A_{1g+}$
$\sigma_3 \otimes \sigma_1$	$T_{1g-}$
$\sigma_3 \otimes \sigma_2$	
$\sigma_3 \otimes \sigma_3$	

Compared to the example of two  $s$ -orbitals, the Pauli matrices  $\sigma_1$  and  $\sigma_2$  for the orbital degree of freedom are now odd under inversion so that  $u$  irreps occur.

The momentum basis functions  $c_\nu(\mathbf{k})$  in  $H_N(\mathbf{k}) = \sum_\nu c_\nu(\mathbf{k}) h_\nu$  must transform in the same way as the matrices  $h_\nu$ . However, momentum basis functions only exist for  $g+$  and  $u-$  irreps and thus only the  $h_\nu$  belonging to these irreps can occur. These are

$$h_0 \equiv \sigma_0 \otimes \sigma_0 \quad A_{1g+}, \quad (52)$$

$$h_1 \equiv \sigma_3 \otimes \sigma_0 \quad A_{1g+}, \quad (53)$$

$$h_2 \equiv \sigma_2 \otimes \sigma_0 \quad A_{2u-}, \quad (54)$$

$$h_3 \equiv \sigma_1 \otimes \sigma_1 \quad T_{2u-}, \quad (55)$$

<sup>20</sup>For  $A_{2g}$ , the lowest order of polynomial basis functions is 6, see the table in Sec. 2.5. This would be an  $i$ -orbital, which is irrelevant for atoms in the ground state.

<sup>21</sup>For  $A_{1u}$ , the lowest order of polynomial basis functions is 9, obviously irrelevant.

$$h_4 \equiv \sigma_1 \otimes \sigma_2 \quad T_{2u-}, \quad (56)$$

$$h_5 \equiv \sigma_1 \otimes \sigma_3 \quad T_{2u-}. \quad (57)$$

The normal-state Hamiltonian reads

$$H_N(\mathbf{k}) = c_{00}(\mathbf{k}) \sigma_0 \otimes \sigma_0 + c_{30}(\mathbf{k}) \sigma_3 \otimes \sigma_0 + c_{20}(\mathbf{k}) \sigma_2 \otimes \sigma_0 + \mathbf{c}_{T_2}(\mathbf{k}) \cdot \sigma_1 \otimes \boldsymbol{\sigma}, \quad (58)$$

where the leading terms are

$$c_{00}(\mathbf{k}) = c_{00}^{(0)} + c_{00}^{(2)} (k_x^2 + k_y^2 + k_z^2) + \dots, \quad (59)$$

$$c_{30}(\mathbf{k}) = c_{30}^{(0)} + c_{30}^{(2)} (k_x^2 + k_y^2 + k_z^2) + \dots, \quad (60)$$

$$c_{20}(\mathbf{k}) = c_{20}^{(3)} k_x k_y k_z + \dots, \quad (61)$$

$$c_{T_2 1}(\mathbf{k}) = c_{T_2}^{(3)} k_x (k_y^2 - k_z^2) + \dots, \quad (62)$$

$$c_{T_2 2}(\mathbf{k}) = c_{T_2}^{(3)} k_y (k_z^2 - k_x^2) + \dots, \quad (63)$$

$$c_{T_2 3}(\mathbf{k}) = c_{T_2}^{(3)} k_z (k_x^2 - k_y^2) + \dots \quad (64)$$

Terms appear that are odd in momentum although the system is inversion symmetric. These terms are allowed and thus generically present since they multiply orbital matrices that are also odd under parity.

## 4 Application to the superconducting-state Hamiltonian

In this section, we discuss the construction of Hamiltonians for superconducting states, based on point-group symmetries. We are here dealing with effectively noninteracting Hamiltonians, i.e., any interactions are incorporated at the mean-field level. In the case of superconductivity, this is conveniently expressed in the Bogoliubov-de Gennes-Nambu formalism. We will restrict ourselves to crystals with inversion symmetry so that superconducting states can be classified according to their parity.

### 4.1 Bogoliubov-de Gennes Hamiltonian

The second-quantized Hamiltonian reads

$$\hat{H} = \frac{1}{2} \sum_{\mathbf{k}} \Psi_{\mathbf{k}}^\dagger \mathcal{H}(\mathbf{k}) \Psi_{\mathbf{k}}, \quad (65)$$

with the Nambu spinor

$$\Psi_{\mathbf{k}} = \begin{pmatrix} c_{\mathbf{k},1} \\ \vdots \\ c_{\mathbf{k},n} \\ c_{-\mathbf{k},1}^\dagger \\ \vdots \\ c_{-\mathbf{k},n}^\dagger \end{pmatrix}, \quad (66)$$

which now has  $2n$  components. The first-quantized *Bogoliubov-de Gennes Hamiltonian* reads

$$\mathcal{H}(\mathbf{k}) = \begin{pmatrix} H_N(\mathbf{k}) & \Delta(\mathbf{k}) \\ \Delta^\dagger(\mathbf{k}) & -H_N^T(-\mathbf{k}) \end{pmatrix}. \quad (67)$$

For  $\Delta(\mathbf{k}) = 0$ , the remaining upper left and lower right blocks give identical contributions up to a constant. This leads to double counting, which is corrected for by the factor of 1/2 in Eq. (65). The off-diagonal blocks evidently couple two creation or two annihilation operators and are thus characteristic for superconductivity. The quasiparticle dispersion is obtained by diagonalizing  $\mathcal{H}(\mathbf{k})$ . This also double

counts degrees of freedom—for each eigenenergy at momentum  $\mathbf{k}$  there is another one with opposite sign at momentum  $-\mathbf{k}$ , which does not refer to a distinct state. One can view only half of the eigenenergies, larger or equal to zero, as physical since the quasiparticles are excitations above the BCS ground state and thus should have non-negative energies.

The off-diagonal blocks are restricted by fermionic antisymmetry.<sup>22</sup> The contribution of the upper right block to the second-quantized Hamiltonian reads, in components,

$$\frac{1}{2} \sum_{\mathbf{k}, ij} c_{\mathbf{k}, i}^\dagger \Delta(\mathbf{k})_{ij} c_{-\mathbf{k}, j}^\dagger = \frac{1}{2} \sum_{\mathbf{k}, ij} c_{-\mathbf{k}, i}^\dagger \Delta(-\mathbf{k})_{ij} c_{\mathbf{k}, j}^\dagger = -\frac{1}{2} \sum_{\mathbf{k}, ij} c_{\mathbf{k}, j}^\dagger \Delta(-\mathbf{k})_{ij} c_{-\mathbf{k}, i}^\dagger. \quad (68)$$

This can be summarized as

$$\frac{1}{2} c_{\mathbf{k}}^\dagger \Delta(\mathbf{k}) c_{-\mathbf{k}}^\dagger = -\frac{1}{2} c_{\mathbf{k}}^\dagger \Delta^T(-\mathbf{k}) c_{-\mathbf{k}}^\dagger. \quad (69)$$

Hence, the anticommutation of fermionic operators requires that  $\Delta(\mathbf{k}) = -\Delta^T(-\mathbf{k})$  or

$$\Delta^T(\mathbf{k}) = -\Delta(-\mathbf{k}). \quad (70)$$

We now turn to the transformation properties of  $\Delta(\mathbf{k})$  under point-group operations. Consider an arbitrary structural point-group operation  $a$  described by the three-dimensional proper or improper rotation matrix  $R_a^{-1}$  and the unitary  $n \times n$  matrix  $U_a$ . Any momentum-dependent  $n \times n$  matrix transforms as  $M(\mathbf{k}) \xrightarrow{a} U_a M(R_a^{-1}\mathbf{k}) U_a^\dagger$ . Of course,  $H_N(\mathbf{k})$  is such a matrix:

$$H_N(\mathbf{k}) \xrightarrow{a} U_a H_N(R_a^{-1}\mathbf{k}) U_a^\dagger. \quad (71)$$

Thus implies that the lower right block of Bogoliubov-de Gennes Hamiltonian  $\mathcal{H}(\mathbf{k})$  must transform as

$$-H_N^T(-\mathbf{k}) \xrightarrow{a} -[U_a H_N(-R_a^{-1}\mathbf{k}) U_a^\dagger]^T = -U_a^* H_N^T(-R_a^{-1}\mathbf{k}) U_a^T. \quad (72)$$

But this requires  $\mathcal{H}(\mathbf{k})$  to transform as

$$\mathcal{H}(\mathbf{k}) \xrightarrow{a} \begin{pmatrix} U_a & 0 \\ 0 & U_a^* \end{pmatrix} \mathcal{H}(R_a^{-1}\mathbf{k}) \begin{pmatrix} U_a^\dagger & 0 \\ 0 & U_a^T \end{pmatrix} \equiv U_a \mathcal{H}(R_a^{-1}\mathbf{k}) U_a^\dagger. \quad (73)$$

This relation shows how unitary  $n \times n$  matrices have to be lifted to  $2n$ -dimensional Nambu space.

The result has interesting consequences for  $\Delta(\mathbf{k})$ : making the upper right block of Eq. (73) explicit, we find

$$\Delta(\mathbf{k}) \xrightarrow{a} U_a \Delta(R_a^{-1}\mathbf{k}) U_a^T. \quad (74)$$

Hence,  $\Delta(\mathbf{k})$  does *not* transform like a matrix under point-group operations. Consequently, a-priori we do not know how to apply representation theory to  $\Delta(\mathbf{k})$ .

To make progress, we derive an auxiliary result. Any magnetic point group is a subgroup of  $O(3) \otimes \{\mathbb{1}, \mathcal{T}\}$ . Time reversal  $\mathcal{T}$  commutes with all elements of  $O(3)$  and thus with all elements of the structural point group. Now consider an arbitrary structural point-group operation  $a$  described by the unitary  $n \times n$  matrix  $U_a$ . Then the inverse operation  $a^{-1}$  is represented by  $U_a^{-1} = U_a^\dagger$ . The commutation relation

$$\mathcal{T} U_a^\dagger - U_a^\dagger \mathcal{T} = U_T \mathcal{K} U_a^\dagger - U_a^\dagger U_T \mathcal{K} = 0 \quad (75)$$

implies

$$U_T \mathcal{K} U_a^\dagger = U_a^\dagger U_T \mathcal{K} \quad (76)$$

and thus

$$U_a^\dagger U_T = U_T \mathcal{K} U_a^\dagger \mathcal{K} = U_T U_a^T. \quad (77)$$

We apply this relation to the transformation properties of  $\Delta(\mathbf{k})$ . Let us write the pairing matrix as

$$\Delta(\mathbf{k}) = D(\mathbf{k}) U_T, \quad (78)$$

---

<sup>22</sup>One can also argue starting from charge-conjugation symmetry.

which defines  $D(\mathbf{k})$ . We then find the transformation

$$D(\mathbf{k}) U_T \xrightarrow{a} U_a D(R_a^{-1} \mathbf{k}) U_T U_a^T \stackrel{\text{Eq. (77)}}{=} U_a D(R_a^{-1} \mathbf{k}) U_a^\dagger U_T \quad (79)$$

so that

$$D(\mathbf{k}) \xrightarrow{a} U_a D(R_a^{-1} \mathbf{k}) U_a^\dagger. \quad (80)$$

Hence,  $D(\mathbf{k})$  does transform like a matrix under structural point-group operations, unlike  $\Delta(\mathbf{k})$ .

Analogously, one finds that under time reversal,  $D(\mathbf{k})$  transforms like

$$D(\mathbf{k}) \xrightarrow{T} U_T D^*(-\mathbf{k}) U_T^\dagger, \quad (81)$$

i.e., also like a matrix, whereas  $\Delta(\mathbf{k})$  transforms as  $\Delta(\mathbf{k}) \mapsto U_T \Delta^*(-\mathbf{k}) U_T^\dagger$ . It is therefore reasonable to expand  $D(\mathbf{k})$  in the basis of matrices (irreducible tensor operators)  $h_\nu$ .<sup>23</sup>

Above, we have seen that fermionic antisymmetry implies  $\Delta^T(\mathbf{k}) = -\Delta(-\mathbf{k})$ . This is equivalent to  $U_T^T D^T(\mathbf{k}) = -D(-\mathbf{k}) U_T$  and thus

$$U_T^T D^T(\mathbf{k}) U_T^\dagger = -D(-\mathbf{k}). \quad (82)$$

We have noted above that for fermionic systems  $\mathcal{T}^2 = -\mathbb{1}$ . This relation can be rewritten as

$$U_T \mathcal{K} U_T \mathcal{K} = U_T U_T^* = -\mathbb{1}. \quad (83)$$

Since  $U_T^*$  is unitary, we conclude that

$$U_T = -(U_T^*)^{-1} = -(U_T^*)^\dagger = -U_T^T. \quad (84)$$

Hence,  $U_T$  is antisymmetric. Equation (82) then yields  $-U_T D^T(\mathbf{k}) U_T^\dagger = -D(-\mathbf{k})$  and thus<sup>24</sup>

$$U_T D^T(-\mathbf{k}) U_T^\dagger = D(\mathbf{k}). \quad (85)$$

We can now expand the matrix  $D(\mathbf{k})$  into all  $n^2$  hermitian basis matrices,

$$D(\mathbf{k}) = \sum_{\nu=1}^{n^2} d_\nu(\mathbf{k}) h_\nu. \quad (86)$$

The coefficients  $d_\nu(\mathbf{k})$  are generally complex since  $D(\mathbf{k})$  is not hermitian. Condition (85) must be satisfied for each term separately because of the linear independence of the  $h_\nu$ :

$$d_\nu(-\mathbf{k}) U_T h_\nu^T U_T^\dagger = d_\nu(\mathbf{k}) h_\nu. \quad (87)$$

Since the  $h_\nu$  are hermitian, this is equivalent to

$$U_T d_\nu(-\mathbf{k}) h_\nu^* U_T^\dagger = d_\nu(\mathbf{k}) h_\nu. \quad (88)$$

This is similar to time-reversal symmetry but not quite the same—time reversal would also replace  $d_\nu(-\mathbf{k})$  by  $d_\nu^*(-\mathbf{k})$  on the left-hand side. However, Eq. (88) stipulates that each contribution to  $D(\mathbf{k})$  must be time-reversal symmetric if its amplitude is real. In other words, time-reversal symmetry can only be broken by having amplitudes that have a nontrivial phase in the complex plane. Hence, only time-reversal-even (+) irreps occur in the expansion.

We transform both sides of Eq. (88) with the unitary matrix  $P$  for spatial inversion:

$$d_\nu(-\mathbf{k}) P U_T h_\nu^* U_T^\dagger P^\dagger = d_\nu(\mathbf{k}) P h_\nu P^\dagger. \quad (89)$$

<sup>23</sup>Since  $\Delta(\mathbf{k}) = D(\mathbf{k}) U_T$ ,  $\Delta(\mathbf{k})$  itself is expanded into the basis matrices  $\gamma_\nu = h_\nu U_T$ .

<sup>24</sup>Note that  $D^T$  is not generally equal to  $D^*$  since  $D$  need not be hermitian.

We have seen that generally some of the basis matrices are even under the combined  $PT$  transformation ( $g+$  or  $u-$  irreps) and some are odd ( $g-$  or  $u+$  irreps). Hence, we obtain  $\pm d_\nu(-\mathbf{k}) h_\nu = d_\nu(\mathbf{k}) P h_\nu P^\dagger$  and thus

$$P d_\nu(-\mathbf{k}) h_\nu P^\dagger = \pm d_\nu(\mathbf{k}) h_\nu. \quad (90)$$

The sign denotes the transformation property under  $PT$ . The left-hand side of the equation contains the full inversion transformation, including the inversion of the momentum. We have thus found that the  $PT$ -even ( $PT$ -odd) basis matrices  $h_\nu$  describe even-parity (odd-parity) superconductivity. The  $PT$ -even basis matrices are exactly the same ones that also appear in the expansion of  $H_N(\mathbf{k})$ . Thus the same  $h_\nu$  appear in  $H_N(\mathbf{k})$  and  $D(\mathbf{k})$  for even-parity superconductivity.

## 4.2 Construction procedure

Next, we extend the procedure to the construction of superconducting states. Here, we have much greater freedom than in constructing  $H_N(\mathbf{k})$  since the superconducting state may break symmetries contained in  $\mathcal{G}_{\text{mag}}$ . After the construction of  $H_N(\mathbf{k})$  as discussed above, the procedure continues as follows:

- Write the pairing matrix as  $\Delta(\mathbf{k}) = D(\mathbf{k}) U_T$  and expand  $D(\mathbf{k})$  in the basis of matrices  $h_\nu$ . For even-parity superconductivity, only the  $h_\nu$  belonging to  $g+$  or  $u-$  irreps need to be included (the same as for the normal-state Hamiltonian). Conversely, for odd-parity superconductivity, only the  $h_\nu$  belonging to  $g-$  or  $u+$  irreps need to be included. Write the expansion as

$$D(\mathbf{k}) = \sum_\nu \Delta_\nu d_\nu(\mathbf{k}) h_\nu \equiv \sum_\nu [\Delta_\nu^1 + i\Delta_\nu^2] d_\nu(\mathbf{k}) h_\nu, \quad (91)$$

where the complex pairing amplitudes  $\Delta_\nu$  have been separated from the real and suitably normalized structure factors  $d_\nu(\mathbf{k})$ .

- Consider all products of momentum basis functions  $f_\mu(\mathbf{k})$  and basis matrices  $h_\nu$ . Any product transforms according to the—generally reducible—product representation of the irreps of  $f_\mu(\mathbf{k})$  and  $h_\nu$ . Reduce them into irreps by standard methods and obtain momentum-dependent matrix basis functions of these irreps as linear combinations of products  $f_\mu(\mathbf{k}) h_\nu$ .
- Exclude all “-” irreps since they violate fermionic antisymmetry.
- Group together all pairing states transforming according to the same component of the same irrep since they will generically coexist.

## 4.3 Example: two $s$ -orbitals

We return to the system with the point group  $O_h$  and two unrelated  $s$ -orbitals per lattice site. The possible irreps of pairing states are obtained by reducing all products of the irreps of momentum basis functions  $f_\mu(\mathbf{k})$  and of basis matrices  $h_\nu$ . The former are  $A_{1g+}$ ,  $A_{2g+}$ ,  $E_{g+}$ ,  $T_{1g+}$ ,  $T_{2g+}$ ,  $A_{1u-}$ ,  $A_{2u-}$ ,  $E_{u-}$ ,  $T_{1u-}$ ,  $T_{2u-}$ , while the latter are  $A_{1g+}$ ,  $T_{1g+}$ ,  $A_{1g-}$ ,  $T_{1g-}$ , see the table of all 16 basis matrices in Sec. 3.1. The reduction of the products is shown in the following table.

form factor: irrep	pairing matrix: irrep			
	$A_{1g+}$	$T_{1g+}$	$A_{1g-}$	$T_{1g-}$
$A_{1g+}$	$\mathbf{A}_{1g+}$	$T_{1g+}$	$\circ$	$\circ$
$A_{2g+}$	$A_{2g+}$	$T_{2g+}$	$\circ$	$\circ$
$E_{g+}$	$E_{g+}$	$T_{1g+} \oplus T_{2g+}$	$\circ$	$\circ$
$T_{1g+}$	$T_{1g+}$	$\mathbf{A}_{1g+} \oplus E_{g+} \oplus T_{1g+} \oplus T_{2g+}$	$\circ$	$\circ$
$T_{2g+}$	$T_{2g+}$	$A_{2g+} \oplus E_{g+} \oplus T_{1g+} \oplus T_{2g+}$	$\circ$	$\circ$
$A_{1u-}$	$\circ$	$\circ$	$A_{1u+}$	$T_{1u+}$
$A_{2u-}$	$\circ$	$\circ$	$A_{2u+}$	$T_{2u+}$
$E_{u-}$	$\circ$	$\circ$	$E_{u+}$	$T_{1u+} \oplus T_{2u+}$
$T_{1u-}$	$\circ$	$\circ$	$T_{1u+}$	$A_{1u+} \oplus E_{u+} \oplus T_{1u+} \oplus T_{2u+}$
$T_{2u-}$	$\circ$	$\circ$	$T_{2u+}$	$A_{2u+} \oplus E_{u+} \oplus T_{1u+} \oplus T_{2u+}$

A few remarks are in order:

- Irreps that are odd under time reversal cannot occur since they violate fermionic antisymmetry. The reduction of product reps that are odd under time reversal is therefore not interesting here and is replaced by “o” in the table.
- The normal-state Hamiltonian  $H_N(\mathbf{k})$  can, and generically does, contain all combinations that transform according to  $A_{1g+}$ , as discussed in Sec. 3.1. These combinations are set in bold face.
- The first row of the table refers to a momentum-space form factor belonging to  $A_{1g+}$ . Only this irrep is compatible with the form factor being constant in momentum, which means purely local in real space. Hence, purely local pairing can only lead to the symmetries appearing in the first row of the table, here  $A_{1g+}$  and  $T_{1g+}$ . Note that  $T_{1g+}$  is only possible because the model contains two orbitals; in a single-orbital model, we would only find local  $A_{1g+}$  pairing.
- The  $g$  irreps (upper left block of the table) describe even-parity superconductivity. As noted above, the same basis matrices appear as in the normal-state Hamiltonian, here the ones transforming according to  $A_{1g+}$  and  $T_{1g+}$ . The  $u$  irreps (lower right block) describe odd-parity superconductivity.
- Time-reversal-symmetric pairing states generically have line nodes, the number of which is given by the minimum order of basis functions of the irrep, see the table in Sec. 2.5.

Which pairing state is actually realized is a question of energetics and thus cannot be answered by our symmetry analysis alone. Instead, one should solve the BCS gap equation, at least as the first approximation. However, a few general statements can be made. If the attractive pairing interaction is dominantly local the superconducting state will have  $A_{1g+}$  or  $T_{1g+}$  symmetry. However, if the local interaction is dominated by the *repulsive* Coulomb interaction pairing can only be driven by a nonlocal attraction. Then the symmetries in the rows below the first are possible, which are all “+” irreps.

Generically, pairing states belonging to different irreps will have distinct critical temperatures  $T_c$  and, upon lowering the temperature starting from the normal state, the pairing symmetry with the highest  $T_c$  will be realized. Typically, all contributions with the same symmetry will appear simultaneously.<sup>25</sup> It is possible to have pairing states that contain more than one irrep, then  $D(\mathbf{k})$  is a linear combination of contributions from the different irreps. However, this generically requires multiple phases transitions.

For multidimensional irreps, it is possible that only a single component or that several components appear. In the latter case, there may be a phase difference between them, i.e.,  $E_{g+}$  pairing could have the amplitudes  $(\Delta, i\Delta)$  for the two components. We have noted above that the only way to break time-reversal symmetry is to have complex amplitudes. Hence, this is most naturally realized for pairing symmetries with multidimensional irreps and several amplitudes with nontrivial relative phases.

We here only discuss one possible pairing state, namely  $E_{g+}$ . The previous table shows that this pairing is impossible for purely local pairing. Conversely, it is unaffected by an arbitrarily strong local repulsion.  $E_{g+}$  occurs in three places in the table: (a)  $E_{g+} \otimes A_{1g+}$ , (b)  $T_{1g+} \otimes T_{1g+}$ , and (c)  $T_{2g+} \otimes T_{1g+}$ . Since  $E_{g+}$  is a two-dimensional irrep, the pairing matrix

$$D(\mathbf{k}) = D^1(\mathbf{k}) + D^2(\mathbf{k}) \quad (92)$$

is the sum of two terms that belong to the two components of the  $E_{g+}$  doublet.

(a)  $E_{g+} \otimes A_{1g+}$  is trivial in orbital and spin space. The three  $A_{1g+}$  matrices are each combined with a doublet of  $E_{g+}$  form factors, giving

$$D_{E_g A_{1g}}^1(\mathbf{k}) = \Delta_{00}^1 f_{00}^1(\mathbf{k}) \sigma_0 \otimes \sigma_0 + \Delta_{10}^1 f_{10}^1(\mathbf{k}) \sigma_1 \otimes \sigma_0 + \Delta_{30}^1 f_{30}^1(\mathbf{k}) \sigma_3 \otimes \sigma_0, \quad (93)$$

$$D_{E_g A_{1g}}^2(\mathbf{k}) = \Delta_{00}^2 f_{00}^2(\mathbf{k}) \sigma_0 \otimes \sigma_0 + \Delta_{10}^2 f_{10}^2(\mathbf{k}) \sigma_1 \otimes \sigma_0 + \Delta_{30}^2 f_{30}^2(\mathbf{k}) \sigma_3 \otimes \sigma_0. \quad (94)$$

The leading terms of the form factors are

$$f_{m0}^1(\mathbf{k}) = (k_x^2 - k_y^2) + f_{m0}^{(4)}(k_x^4 - k_y^4) + \dots, \quad (95)$$

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<sup>25</sup>In a Ginzburg-Landau description, they are coupled by bilinear terms.

$$f_{m0}^2(\mathbf{k}) = \frac{1}{\sqrt{3}} (2k_z^2 - k_x^2 - k_y^2) + \frac{f_{m0}^{(4)}}{\sqrt{3}} (2k_z^4 - k_x^4 - k_y^4) + \dots, \quad (96)$$

where the coefficients of the second-order terms have been set to unity as a choice of normalization. The higher-order coefficients are then generally different from each other. These contributions can be described as  $d$ -wave (second order in momentum) spin-singlet pairing.

(b) The reducible representation  $T_{1g+} \otimes T_{1g+}$  has nine matrix basis functions  $f_\mu(\mathbf{k}) \sigma_2 \otimes \sigma_\nu$ ,  $\mu, \nu = 1, 2, 3$ , where  $f_\mu(\mathbf{k})$  are momentum basis functions of  $T_{1g+}$ . Without loss in generality, we take  $f_1(\mathbf{k})$ ,  $f_2(\mathbf{k})$ ,  $f_3(\mathbf{k})$  to transform like  $\sigma_2 \otimes \sigma_1$ ,  $\sigma_2 \otimes \sigma_2$ ,  $\sigma_2 \otimes \sigma_3$ , respectively (corresponding basis functions). The leading terms read

$$f_{T_{1g}}^1(\mathbf{k}) = k_y k_z (k_y^2 - k_z^2) + \dots, \quad (97)$$

$$f_{T_{1g}}^2(\mathbf{k}) = k_z k_x (k_z^2 - k_x^2) + \dots, \quad (98)$$

$$f_{T_{1g}}^3(\mathbf{k}) = k_x k_y (k_x^2 - k_y^2) + \dots, \quad (99)$$

where the common coefficient has been set to unity as normalization. The reduction  $T_{1g+} \otimes T_{1g+} = A_{1g+} \oplus E_{g+} \oplus T_{1g+} \oplus T_{2g+}$  is telling us that a doublet of matrix-valued basis functions of  $E_{g+}$  can be constructed as linear combinations of the  $f_\mu(\mathbf{k}) \sigma_2 \otimes \sigma_\nu$ . To find the correct linear combinations, we have to analyze how they transform under point-group operations.<sup>26</sup> The solution is

$$F_{T_{1g}T_{1g}}^1(\mathbf{k}) = f_{T_{1g}}^1(\mathbf{k}) \sigma_2 \otimes \sigma_1 - f_{T_{1g}}^2(\mathbf{k}) \sigma_2 \otimes \sigma_2, \quad (100)$$

$$F_{T_{1g}T_{1g}}^2(\mathbf{k}) = \frac{1}{\sqrt{3}} \left[ 2f_{T_{1g}}^3(\mathbf{k}) \sigma_2 \otimes \sigma_3 - f_{T_{1g}}^1(\mathbf{k}) \sigma_2 \otimes \sigma_1 - f_{T_{1g}}^2(\mathbf{k}) \sigma_2 \otimes \sigma_2 \right]. \quad (101)$$

These matrix basis functions are no longer simply the product of a scalar momentum-dependent form factor and a momentum-independent matrix. Their contributions to the pairing matrix are

$$D_{T_{1g}T_{1g}}^1(\mathbf{k}) = \Delta_{T_{1g}T_{1g}}^1 F_{T_{1g}T_{1g}}^1(\mathbf{k}), \quad (102)$$

$$D_{T_{1g}T_{1g}}^2(\mathbf{k}) = \Delta_{T_{1g}T_{1g}}^2 F_{T_{1g}T_{1g}}^2(\mathbf{k}). \quad (103)$$

two The leading terms are

$$D_{T_{1g}T_{1g}}^1(\mathbf{k}) = \Delta_{T_{1g}T_{1g}}^1 \left[ k_y k_z (k_y^2 - k_z^2) \sigma_2 \otimes \sigma_1 - k_z k_x (k_z^2 - k_x^2) \sigma_2 \otimes \sigma_2 \right] + \dots, \quad (104)$$

$$D_{T_{1g}T_{1g}}^2(\mathbf{k}) = \frac{\Delta_{T_{1g}T_{1g}}^2}{\sqrt{3}} \left[ 2k_x k_y (k_x^2 - k_y^2) \sigma_2 \otimes \sigma_3 - k_y k_z (k_y^2 - k_z^2) \sigma_2 \otimes \sigma_1 - k_z k_x (k_z^2 - k_x^2) \sigma_2 \otimes \sigma_2 \right] + \dots \quad (105)$$

This describes  $g$ -wave (order 4) spin-triplet pairing, made possible by nontrivial orbital content.

(c) The analysis for  $T_{2g+} \otimes T_{1g+} = A_{2g+} \oplus E_{g+} \oplus T_{1g+} \oplus T_{2g+}$  is analogous, except that the momentum basis functions belonging to  $T_{2g+}$  are simpler:

$$f_{T_{2g}}^1(\mathbf{k}) = k_y k_z + \dots, \quad (106)$$

$$f_{T_{2g}}^2(\mathbf{k}) = k_z k_x + \dots, \quad (107)$$

$$f_{T_{2g}}^3(\mathbf{k}) = k_x k_y + \dots, \quad (108)$$

where the common coefficient has been set to unity. We have the matrix basis functions

$$F_{T_{2g}T_{1g}}^1(\mathbf{k}) = \frac{1}{\sqrt{3}} \left[ 2f_{T_{2g}}^3(\mathbf{k}) \sigma_2 \otimes \sigma_3 - f_{T_{2g}}^1(\mathbf{k}) \sigma_2 \otimes \sigma_1 - f_{T_{2g}}^2(\mathbf{k}) \sigma_2 \otimes \sigma_2 \right], \quad (109)$$

$$F_{T_{2g}T_{1g}}^2(\mathbf{k}) = -f_{T_{2g}}^1(\mathbf{k}) \sigma_2 \otimes \sigma_1 + f_{T_{2g}}^2(\mathbf{k}) \sigma_2 \otimes \sigma_2. \quad (110)$$

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<sup>26</sup>It is sufficient to consider the transformation under a small subset of the point group, namely under its generators, which generate all group elements by multiplication.

Note that the forms of the expressions for the two components are interchanged compared to case (b) and there is an additional minus sign.<sup>27</sup> The contribution to the pairing matrix is

$$D_{T_{2g}T_{1g}}^1(\mathbf{k}) = \Delta_{T_{2g}T_{1g}}^1 F_{T_{2g}T_{1g}}^1(\mathbf{k}), \quad (111)$$

$$D_{T_{2g}T_{1g}}^2(\mathbf{k}) = \Delta_{T_{2g}T_{1g}}^2 F_{T_{2g}T_{1g}}^2(\mathbf{k}), \quad (112)$$

or explicitly to leading order:

$$D_{T_{2g}T_{1g}}^1(\mathbf{k}) = \frac{\Delta_{T_{2g}T_{1g}}^1}{\sqrt{3}} [2k_x k_y \sigma_2 \otimes \sigma_3 - k_y k_z \sigma_2 \otimes \sigma_1 - k_z k_x \sigma_2 \otimes \sigma_2] + \dots, \quad (113)$$

$$D_{T_{2g}T_{1g}}^2(\mathbf{k}) = \Delta_{T_{2g}T_{1g}}^2 [-k_y k_z \sigma_2 \otimes \sigma_1 + k_z k_x \sigma_2 \otimes \sigma_2] + \dots \quad (114)$$

This is  $d$ -wave spin-triplet pairing, again made possible by nontrivial orbital content.

As an application, we consider the nodal structure of a time-reversal-symmetric  $E_{g+}$  pairing state that only involves the first component of the doublet. This will be called a  $(1,0)$  state. One can show that in the limit of small pairing amplitudes (weak coupling), nodes appear on the normal-state Fermi surface wherever

$$c_0(\mathbf{k})\Delta_0 d_0(\mathbf{k}) - \sum_{\nu=1}^5 c_\nu(\mathbf{k})\Delta_\nu d_\nu(\mathbf{k}) = 0 \quad (115)$$

holds, where  $H_N(\mathbf{k}) = \sum_{\nu=0}^5 c_\nu(\mathbf{k})h_\nu$  and  $D(\mathbf{k}) = \sum_{\nu=0}^5 \Delta_\nu d_\nu(\mathbf{k})h_\nu$ . This simple condition follows from the simple commutation relations of the six matrices  $h_\nu$ , see Sec. 3.1, and does not persist for more complicated models. For illustration, we only write down the leading-order contribution to each term,

$$\begin{aligned} 0 &= c_{00}^{(0)}\Delta_{00}^1(k_x^2 - k_y^2) - c_{10}^{(0)}\Delta_{10}^1(k_x^2 - k_y^2) - c_{30}^{(0)}\Delta_{30}^1(k_x^2 - k_y^2) \\ &\quad - c_{T_{1g}}^{(4)} \left( \Delta_{T_{1g}T_{1g}}^1 [k_y^2 k_z^2 (k_y^2 - k_z^2)^2 - k_z^2 k_x^2 (k_z^2 - k_x^2)^2] \right. \\ &\quad \left. + \frac{\Delta_{T_{2g}T_{1g}}^1}{\sqrt{3}} [2k_x^2 k_y^2 (k_x^2 - k_y^2) - k_y^2 k_z^2 (k_y^2 - k_z^2) - k_z^2 k_x^2 (k_z^2 - k_x^2)] \right) \\ &= \left[ \left( c_{00}^{(0)}\Delta_{00}^1 - c_{10}^{(0)}\Delta_{10}^1 - c_{30}^{(0)}\Delta_{30}^1 \right) + c_{T_{1g}}^{(4)}\Delta_{T_{1g}T_{1g}}^1 k_z^2 (k_x^4 + k_y^4 + k_z^4 + k_x^2 k_y^2 - 2k_x^2 k_z^2 - 2k_y^2 k_z^2) \right. \\ &\quad \left. + \frac{c_{T_{1g}}^{(4)}\Delta_{T_{2g}T_{1g}}^1}{\sqrt{3}} (k_z^4 - 2k_x^2 k_y^2 - k_x^2 k_z^2 - k_y^2 k_z^2) \right] (k_x^2 - k_y^2). \end{aligned} \quad (116)$$

We see that the general  $E_{g+}$  pairing state has two line nodes at  $k_y = \pm k_x$ . These nodes are fixed to the diagonal mirror planes and therefore cannot be shifted by the various contributions. In addition, if the amplitudes  $\Delta_{T_{1g}T_{1g}}^1$  or  $\Delta_{T_{2g}T_{1g}}^1$  are sufficiently large the expression in square brackets can develop zeros in momentum space. This can lead to additional ‘‘accidental’’ nodes. These nodes are not pinned to high-symmetry planes.

Continuing this analysis, we find the following results, which we just state here:

- The  $(1, i)$  state, which breaks time-reversal symmetry, generically has point nodes in the (111) and equivalent directions, in the weak-coupling limit.<sup>28</sup>
- Beyond the weak-coupling limit, the point nodes ‘‘inflate’’ into Bogoliubov Fermi surfaces. These remain attached to the normal-state surface at the location of the weak-coupling point nodes.

<sup>27</sup>To determine which matrix basis functions is which, their behavior under twofold rotation about (110) has been examined. Furthermore, to find the relative factor, the behavior under threefold rotation about (111) has been considered.

<sup>28</sup>Condition (115) has to hold for both the real and the imaginary part of the pairing amplitudes. The point nodes then appear at the intersection of line nodes from the real and imaginary parts [the hermitian and antihermitian parts of  $D(\mathbf{k})$ ].

#### 4.4 Example: two orbitals of opposite parity

As a second example, we briefly consider the previously studied model with one  $A_{1g}$  ( $s$ ) orbital and one  $A_{2u}$  ( $f_{xyz}$ ) orbital per lattice site. Again, the possible irreps of pairing states are obtained by reducing all products of the irreps of momentum basis functions  $f_\mu(\mathbf{k})$  and of basis matrices  $h_\nu$ . The former are  $A_{1g+}$ ,  $A_{2g+}$ ,  $E_{g+}$ ,  $T_{1g+}$ ,  $T_{2g+}$ ,  $A_{1u-}$ ,  $A_{2u-}$ ,  $E_{u-}$ ,  $T_{1u-}$ ,  $T_{2u-}$ , while the latter are  $A_{1g+}$ ,  $A_{2u+}$ ,  $T_{1g+}$ ,  $T_{2u+}$ ,  $A_{1g-}$ ,  $A_{2u-}$ ,  $T_{1g-}$ ,  $T_{2u-}$  see the table of all 16 basis matrices in Sec. 3.2. The reduction of the products is shown in the following two tables showing  $g+$  form factors and  $u-$  form factors, respectively. All products not given in the tables are excluded since they violate fermionic antisymmetry.

form factor: irrep	pairing matrix: irrep			
	$A_{1g+}$	$A_{2u+}$	$T_{1g+}$	$T_{2u+}$
$A_{1g+}$	$\mathbf{A}_{1g+}$	$A_{2u+}$	$T_{1g+}$	$T_{2u+}$
$A_{2g+}$	$A_{2g+}$	$A_{1u+}$	$T_{2g+}$	$T_{1u+}$
$E_{g+}$	$E_{g+}$	$E_{u+}$	$T_{1g+} \oplus T_{2g+}$	$T_{1u+} \oplus T_{2u+}$
$T_{1g+}$	$T_{1g+}$	$T_{2u+}$	$\mathbf{A}_{1g+} \oplus E_{g+} \oplus T_{1g+} \oplus T_{2g+}$	$A_{2u+} \oplus E_{u+} \oplus T_{1u+} \oplus T_{2u+}$
$T_{2g+}$	$T_{2g+}$	$T_{1u+}$	$A_{2g+} \oplus E_{g+} \oplus T_{1g+} \oplus T_{2g+}$	$A_{1u+} \oplus E_{u+} \oplus T_{1u+} \oplus T_{2u+}$

form factor: irrep	pairing matrix: irrep			
	$A_{1g-}$	$A_{2u-}$	$T_{1g-}$	$T_{2u-}$
$A_{1u-}$	$A_{1u+}$	$A_{2g+}$	$T_{1u+}$	$T_{2g+}$
$A_{2u-}$	$A_{2u+}$	$A_{1g+}$	$T_{2u+}$	$T_{1g+}$
$E_{u-}$	$E_{u+}$	$E_{g+}$	$T_{1u+} \oplus T_{2u+}$	$T_{1g+} \oplus T_{2g+}$
$T_{1u-}$	$T_{1u+}$	$T_{2g+}$	$A_{1u+} \oplus E_{u+} \oplus T_{1u+} \oplus T_{2u+}$	$A_{2g+} \oplus E_{g+} \oplus T_{1g+} \oplus T_{2g+}$
$T_{2u-}$	$T_{2u+}$	$T_{1g+}$	$A_{2u+} \oplus E_{u+} \oplus T_{1u+} \oplus T_{2u+}$	$\mathbf{A}_{1g+} \oplus E_{g+} \oplus T_{1g+} \oplus T_{2g+}$

Two nontrivial results can be read off from the tables: First, two odd-parity pairing states ( $A_{2u}$  and  $T_{2u}$ , both corresponding to  $f$ -wave symmetry) now appear even for purely local pairing. This is possible since the odd parity is carried by the orbital makeup of the condensate. Second, pairing with full  $A_{1g}$  symmetry now generically has a contribution from  $T_{2u-} \otimes T_{2u-}$ . This pairing is odd in orbital, even in spin (triplet), and odd in momentum.

## References

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- [2] Character tables for chemically important point groups, <http://symmetry.jacobs-university.de/>.
- [3] D. B. Litvin, Magnetic Group Tables, <https://www.iucr.org/publ/978-0-9553602-2-0>.