Superconducting states of reduced symmetry: General order parameters and physical implications

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It is shown that the order parameter in reduced-symmetry superconductors can be represented in terms of a complete set of basis-function multiplets, which is analogous to a complete set of crystal harmonics. These complete sets are found for several symmetries that are germane to the study of heavy-fermion superconductors. The implications of a general order parameter are discussed for several physical properties: line nodes in the energy gap, the Knight shift, surface pair-breaking, and time-reversal symmetry.

I. INTRODUCTION

The purpose of this paper is to repair a small but important omission in the discussion to date[1–5] of the possible gap functions for superconductors in which the point-group symmetry of the normal state is broken in the superconducting state.[6–8] We shall show that although the basis functions of the irreducible representations in terms of which the gap is written are not unique, a group-theoretic theorem due to Hopfield[9] allows this nonuniqueness to be parametrized in terms of a certain finite set of basis-function multiplets, which we shall tabulate. Symmetry arguments alone cannot provide any information on how to reduce the nonuniqueness, so that in systems in which the pairing interaction is poorly known, the use of only some members of the set of basis functions can lead to special and perhaps unphysical features in the order parameter. One is guaranteed not to make such errors if one uses our basis function sets, although it may not be necessary to use *all* of them for a particular problem.

We have in mind chiefly the heavy-fermion superconductors, in which both the crystalline anisotropy and spin-orbit interactions are important.[10] We shall focus in particular on the point groups D_{4h}, D_{6h}, and O_h, which are relevant to $CeCu_2Si_2$ and URu_2Si_2, UPt_3, and UBe_{13}, respectively. We discuss the physical implications of our mathematical results for these systems, and clarify several points which a casual reading of Refs. 1–5 might not reveal, as the tables of basis functions presented therein often list only one multiplet, which is special in the sense discussed above. The greatest significance of our results is for odd-parity (pseudospin triplet) pairing. It becomes easier to understand Blount's result[4] that the energy gap (or gaps if the state is nonunitary) in this case has no line nodes. It also follows that one should not expect equal spin pairing in general, nor should one expect unitary pairing if time reversal is broken.[11] The lack of equal spin pairing means that one should expect a Pauli paramagnetic suppression of the upper critical field $H_{c2}(T)$ for all orientations of $\mathbf{H}$ in general. This last point is of particular relevance to UPt_3.[12,13]

We suspect that our mathematical results are known to some readers and the authors of Ref. 1–5, especially Blount,[4] as he lists more than one possible order parameter for some of the two-dimensional representations, separated by commas. It still seems worthwhile to present this paper as Blount does not explicitly state, and it may not to be clear to all readers (as it was not to us), that one is supposed to take linear combinations of these order parameters, and that when this is done, the special features of the gap mentioned above disappear.[14] We apologize in advance to those in the know, and hope that our discussion will clarify these matters for other readers.

Our tables of basis functions may also have practical use in the future, if knowledge about the normal state matures. One might attempt microscopic calculations of the superconducting properties, using our complete basis set, multiplied only by group-invariant functions [the F^{ja}'s in Eq. (2) below], which could be treated as variational *Ansatze*, for example.

The paper is organized as follows. We state a modest generalization of Hopfield's theorem in Sec. II, and give tables of sets of basis functions for D_{4h}, D_{6h}, and O_h. Tables for even-parity pairing can be found in Lax,[8] but those for odd parity are new. To provide a compilation in a uniform notation, we nevertheless give even-parity tables as well. A generalization of Lax's proof of this theorem is given in the Appendix. The physical implications of these results are discussed in Sec. III.

II. INDEPENDENT SETS OF BASIS FUNCTIONS

Let us denote the point group of the normal state by G, and assume that this contains the inversion element. The parity of the gap function is then definite, and it is a pure pseudospin singlet for even parity, and triplet for odd parity. If the highest transition temperature is attained for the irreducible representation Γ^j, then the gap function is given (in the Balian-Werthamer notation[15]) by a linear combination of the basis functions ψ^j_μ of Γ^j,

$$\Delta_0(\hat{\mathbf{k}}) = \sum_{\mu=1}^{l_j} \eta_\mu \psi^j_\mu(\hat{\mathbf{k}}), \quad \text{even parity},$$
$$d_n(\hat{\mathbf{k}}) = \sum_{\mu=1}^{l_j} \eta_\mu \psi^j_\mu(\hat{\mathbf{k}}, n), \quad \text{odd parity}, \tag{1}$$

TABLE I. Even-parity basis functions for D_{4h}. Linearly independent basis-function multiplets are separated by semicolons. Note that more than one basis function is given for the identity representation.

Γ_j	Basis functions
A_{1g}	$1,(k_x^2+k_y^2),k_z^2,\ldots$
A_{2g}	$k_xk_y(k_x^2-k_y^2)$
B_{1g}	$k_x^2-k_y^2$
B_{2g}	k_xk_y
E_g	$k_z(k_x,k_y)$; $k_z(k_x^3,k_y^3)$

where η_μ are arbitrary complex numbers and l_j is the dimensionality of Γ^j. Note that in the odd case, the basis functions must depend on the pseudospin index $n(=1,2,3)$ in addition to $\hat{\mathbf{k}}$.

The basis functions ψ_μ^j are clearly not unique. To write them in their most general form, we invoke (and slightly generalize) Hopfield's theorem on the number of independent crystal harmonics. This theorem states that the most general basis-function multiplet can be written as a linear combination over group-invariant functions of N independent basis-function multiplets, ψ_μ^{ja}, $a=1,2,\ldots,N$, where $N=l_j$ and $N=3l_j$ for the pseudospin singlet and triplet cases respectively. In other words, we can write

$$\psi_\mu^j(\hat{\mathbf{k}})=\sum_{a=1}^{l_j}F^{ja}(\hat{\mathbf{k}})\psi_\mu^{ja}(\hat{\mathbf{k}}),\quad \text{singlet}\ ,$$
$$\psi_\mu^j(\hat{\mathbf{k}},n)=\sum_{a=1}^{3l_j}F^{ja}(\hat{\mathbf{k}})\psi_\mu^{ja}(\hat{\mathbf{k}},n),\quad \text{triplet}\ , \tag{2}$$

where the functions $F^{ja}(\hat{\mathbf{k}})$ are arbitrary but invariant under all operations R in G.

We shall refer to the functions within one multiplet as *partners,* to μ as the partner index, and to the collection ψ_μ^{ja}, with $a=1,2,\ldots,N$ as a *set* of multiplets.[16] Since $\Delta_0(\hat{\mathbf{k}})$ and $d(\hat{\mathbf{k}})$ entail double expansions in the indices μ and a, it is important to distinguish between the roles of the F^{ja} and η_μ to avoid confusion. It is perhaps best to think of the F^{ja}'s as determined by interactions at energy scales large compared to T_c, so that in a weakly inhomogeneous situation such as the Abrikosov vortex state, the η_μ's will vary with position, but the F^{ja}'s will not.

We present a proof of the theorem in the Appendix, and complete sets of even- and odd-parity basis-function multiplets in Tables I–VI. The linear independence of the multiplets for the representations of the cubic group has been checked using MATHEMATICA. These functions

TABLE II. Odd-parity basis functions for D_{4h}.

Γ_j	Basis functions
A_{1u}	$k_z\hat{\mathbf{z}}$; $k_x^n\hat{\mathbf{x}}+k_y^n\hat{\mathbf{y}}$, $n=1;3$.
A_{2u}	$k_x\hat{\mathbf{y}}-k_y\hat{\mathbf{x}}$; $k_xk_y(k_x\hat{\mathbf{x}}-k_y\hat{\mathbf{y}})$; $k_xk_yk_z(k_x^2-k_y^2)\hat{\mathbf{z}}$
B_{1u}	$(k_x^2-k_y^2)k_z\hat{\mathbf{z}}$; $k_x^n\hat{\mathbf{x}}-k_y^n\hat{\mathbf{y}}$, $n=1;3$.
B_{2u}	$k_x\hat{\mathbf{y}}+k_y\hat{\mathbf{x}}$; $k_xk_y(k_x\hat{\mathbf{x}}+k_y\hat{\mathbf{y}})$; $k_xk_yk_z\hat{\mathbf{z}}$
E_u	$(k_x^{1+n},k_y^{1+n})\hat{\mathbf{z}}$; $k_z(k_x^n\hat{\mathbf{x}},k_y^n\hat{\mathbf{y}})$; $k_xk_yk_z(k_x^n\hat{\mathbf{y}},k_y^n\hat{\mathbf{x}})$, $n=0;2$.

TABLE III. Even-parity basis functions for D_{6h}. We have defined $k_\pm=k_x\pm ik_y$. It is easier to write the basis functions as the real or imaginary parts of complex functions than giving real functions. For the two-dimensional representations, E_{1g} and E_{2g}, the partners in any multiplet (i.e., functions corresponding to different values of the index μ with the same index a) are given by the real and imaginary parts of the complex valued functions listed. Note that more than one basis function is given for the identity representation.

Γ_j	Basis functions
A_{1g}	$1,(k_x^2+k_y^2),k_z^2,\ldots$
A_{2g}	$\mathrm{Im}k_+^6$
B_{1g}	$k_z\mathrm{Im}k_+^3$
B_{2g}	$k_z\mathrm{Re}k_+^3$
E_{1g}	$\begin{bmatrix}\mathrm{Re}\\ \mathrm{Im}\end{bmatrix}$: k_zk_+; $k_zk_-^5$
E_{2g}	$\begin{bmatrix}\mathrm{Re}\\ \mathrm{Im}\end{bmatrix}$: k_+^2; k_-^4

were obtained by noting that in each representation, one of the partners can be chosen to have a definite sign under the smallest rotation about the z axis, which allows it to be written as a linear combination of k_+^m (for even parity) or of $k_+^m\hat{\mathbf{z}}$, $k_-^{m\mp1}\mathbf{r}_\pm$, $k_+^{m\pm1}\mathbf{r}_\mp$ (for odd parity) with certain definite values of m. Here, $k_\pm=(k_x\pm ik_y)$, and $\mathbf{r}_\pm=\hat{\mathbf{x}}\pm i\hat{\mathbf{y}}$.

III. PHYSICAL IMPLICATIONS FOR PAIRING

In this section, we discuss the physical implications of the results of the last section. We focus on odd-parity pairing, except for Sec. D below, which applies to even parity also.

A. Line nodes of the gap

Blount's theorem[4] that line nodes do not in general exist is apparently contradicted if we do not allow for more than one multiplet of basis functions. Consider the E_{1u} representation of D_{6h}, for example. Volovik and Gorkov[2] choose only the first multiplet listed in Table IV, and write

$$\mathbf{d}\sim(\eta_xk_x+\eta_yk_y)\hat{\mathbf{z}}\ . \tag{3}$$

The fourth-order Ginzburg-Landau free energy has minima at (η_x,η_y) equal to (1,0) and $(1,i)$. For the first choice, the gap vanishes on the $k_x=0$ line on the Fermi surface. If we add in the next multiplet from Table IV, however, the gap function becomes

$$\mathbf{d}\sim(\eta_xk_x+\eta_yk_y)\hat{\mathbf{z}}+u(\hat{\mathbf{k}})k_z(\eta_x\hat{\mathbf{x}}+\eta_y\hat{\mathbf{y}})\ , \tag{4}$$

where $u(\hat{\mathbf{k}})$ is any invariant function of $\hat{\mathbf{k}}$. Now the gap does not vanish for $k_x=0$.

Note, however, that point nodes, when required by symmetry, are robust. For example, the A_{2u} order parameter for D_{4h} must be even under reflection in both the

TABLE IV. Odd-parity basis functions for D_{6h}. The notation is as in Table III. In addition, $\mathbf{r}_{\pm}=\hat{\mathbf{x}}\pm i\hat{\mathbf{y}}$.

Γ_j	Basis functions
A_{1u}	$k_z\hat{\mathbf{z}}$; $k_x\hat{\mathbf{x}}+k_y\hat{\mathbf{y}}$; $\mathrm{Re}k_+^5\mathbf{r}_+$
A_{2u}	Im: $k_-\mathbf{r}_+$; $k_+^5\mathbf{r}_+$; $k_+^6k_z\hat{\mathbf{z}}$
B_{1u}	Im: $k_+^3\hat{\mathbf{z}}$; $k_+^2k_z\mathbf{r}_+$; $k_+^4k_z\mathbf{r}_-$
B_{2u}	Re: $k_+^3\hat{\mathbf{z}}$; $k_+^2k_z\mathbf{r}_+$; $k_+^4k_z\mathbf{r}_-$
E_{1u}	$\begin{bmatrix}\mathrm{Re}\\ \mathrm{Im}\end{bmatrix}$: $k_+\hat{\mathbf{z}}$; $k_z\mathbf{r}_+$; $k_+^2k_z\mathbf{r}_-$; $k_-^5\hat{\mathbf{z}}$; $k_-^4k_z\mathbf{r}_-$; $k_-^6k_z\mathbf{r}_+$
E_{2u}	$\begin{bmatrix}\mathrm{Re}\\ \mathrm{Im}\end{bmatrix}$: $k_+\mathbf{r}_+$; $k_+^2k_z\hat{\mathbf{z}}$; $k_+^3\mathbf{r}_-$; $k_-^3\mathbf{r}_-$; $k_-^5\mathbf{r}_+$; $k_-^4k_z\hat{\mathbf{z}}$

x-z and y-z planes. This requires the coefficient of $\hat{\mathbf{x}}$ to be odd in k_y, that of $\hat{\mathbf{y}}$ to be odd in k_x, and that of $\hat{\mathbf{z}}$ to be odd in both k_x and k_y. These properties are obeyed by all three basis functions listed in Table II, and any linear combination vanishes at the north and south poles as required.

Finally, we note that for nonunitary order parameters, a restricted set of basis functions can lead to line nodes in the energy gap for one branch. For example, for the E_{2u} representation of D_{6h}, with $(\eta_x,\eta_y)=(1,i)$, Blount lists the order parameter as $k_+\mathbf{r}_+$, which resembles that of the A_1 phase for ^{3}He. The gap is nonvanishing only for the $S_z=1$ pseudospin state, in violation of the theorem. Even if the second basis function contribution $k_+^2k_z\hat{\mathbf{z}}$ is added, the $S_z=-1$ gap vanishes everywhere on the $k_z=0$ line, on the Fermi surface, in continued violation of the theorem. In fact, this nodal line persists for all combinations of only $\mathbf{r}_+$ and $\hat{\mathbf{z}}$ basis functions. One needs to add the $\mathbf{r}_-$ components in order to remove it.

B. Equal spin pairing and Knight shift

The pseudospin structure of the order parameter for the odd-parity states is very different from that of superfluid ^{3}He. As is obvious from the tables, in general an odd-parity state consists of pairs in all three $(S_z=-1,0,1)$ pseudospin states. It is thus not an equal spin pairing state for any direction in spin space, and the Knight shift (effectively the magnetic susceptibility) can be expected to decrease for *all* orientations of the magnetic field.[17] Thus, the observation of either a decreasing Knight shift below T_c, or of Pauli suppression in the upper critical field (even for all field directions), is *not* an indication of pseudospin singlet pairing.

However, the *absence* of a change in the Knight shift below T_c, or of Pauli suppression of H_{c2}, is then a very special case and thus can have strong implications. (We assume that the obvious possibilities like a small and unobservable contribution to the Pauli paramagnetism, small effective moments, or the presence of large numbers of spin-orbit scattering impurities, can be ruled out.) The H_{c2} data for UPt_3 (Ref. 12) have been interpreted as showing a Pauli suppression for fields along the c axis, but not for basal plane fields.[13] Such an interpretation implies (i) that the superconducting state involves almost entirely components with $\mathbf{d}\|\hat{\mathbf{c}}$,[18] and (ii) that the pseudospin coupling to the magnetic field involves predominantly $\mu_\perp(\hat{\mathbf{k}})\sigma_\perp H_\perp$ and $\mu_\parallel(\hat{\mathbf{k}})\sigma_\parallel H_\parallel$ terms [but not terms involving the *direction* of the momentum $\hat{\mathbf{k}}$ (Ref. 17)].

TABLE V. Even-parity basis functions for O_h. c.p. stands for "cyclic permutations" of the indices x,y,z.

Γ_j	Basis functions
A_{1g}	$1, k_x^4+k_y^4+k_z^4, \ldots$
A_{2g}	$(k_x^2-k_y^2)k_z^4+$c.p.
E_g	$[\sqrt{3}(k_x^n-k_y^n), 2k_z^n-(k_x^n+k_y^n)]$, $n=2;4$.
T_{1g}	$[k_xk_y(k_x^n-k_y^n)$, c.p.'s], $n=2;4;6$.
T_{2g}	$[k_xk_yk_z^n$, c.p's], $n=0;2;4$.

C. Surface pair-breaking

It is known that a *rough* surface is detrimental to reduced symmetry superconductivity in general. This need not be so, however, for a *smooth* surface for certain order parameters under some special circumstances. For example, the A phase of ^{3}He is not affected when the $\hat{\mathbf{l}}$ vector is normal to the surface,[19] because (i) all spin components of the order parameter are then even in $\hat{\mathbf{k}}\cdot\hat{\mathbf{n}}$, where $\hat{\mathbf{n}}$ is the surface normal, and (ii) the amplitude for spin-flip scattering is negligible as spin-orbit coupling is very weak for ^{3}He.

For reduced symmetry superconductors, neither of these two conditions holds in the general case. For example, the first basis functions listed for the E_u and E_{1u} representations of D_{4h} and D_{6h}, respectively, yield order parameters similar to that of ^{3}He-A. (The first listed B_{1u} and B_{2u} basis functions for D_{6h} are also similar.) However, when the other basis functions are added in, the order parameter is seen to always involve odd powers of all three components of $\hat{\mathbf{k}}$. (Compare this with the discussion of the Knight shift, above.) Thus, for any surface orientation, $\hat{\mathbf{n}}$, there is a part of $\mathbf{d}$ which is odd in $\hat{\mathbf{k}}\cdot\hat{\mathbf{n}}$. Second, one must now parametrize the surface scattering by both pseudospin-flip and non-pseudospin-flip scattering amplitudes, which will in general be completely independent except for the unitarity constraint. Let us first

TABLE VI. Odd-parity basis functions for O_h. The notation is as in Table V. In addition, $\mathbf{d}_0=(k_x\hat{\mathbf{x}}+k_y\hat{\mathbf{y}}+k_z\hat{\mathbf{z}})$.

Γ_j	Basis functions
A_{1u}	$k_x^n\hat{\mathbf{x}}+k_y^n\hat{\mathbf{y}}+k_z^n\hat{\mathbf{z}}$, $n=1;3;5$.
A_{2u}	$k_x^n(k_y^2-k_z^2)\hat{\mathbf{x}}+$c.p., $n=1;3;5$.
E_u	$[\sqrt{3}(k_x^n\hat{\mathbf{x}}-k_y^n\hat{\mathbf{y}}),2k_z^n\hat{\mathbf{z}}-(k_x^n\hat{\mathbf{x}}+k_y^n\hat{\mathbf{y}})]$, $n=1;3;5$. $[\sqrt{3}(k_x^m-k_y^m),2k_z^m-(k_x^m+k_y^m)]\mathbf{d}_0$, $m=2;4$. $[\sqrt{3}\{(k_x^5k_z^2\hat{\mathbf{x}}+k_x^2k_z^5\hat{\mathbf{z}})-(x\leftrightarrow y)\},\{(k_x^5(k_z^2-2k_y^2)\hat{\mathbf{x}}+k_x^2k_z^5\hat{\mathbf{z}})+(x\leftrightarrow y)\}]$
T_{1u}	$[k_z^m(k_y^n\hat{\mathbf{x}}-k_x^n\hat{\mathbf{y}})$,c.p.'s]; $m=0,2$; $n=1;3;5$ $[k_xk_y(k_x^2-k_y^2)k_z^n\hat{\mathbf{z}}$,c.p.'s]; $n=1;3;5$
T_{2u}	$[k_z^m(k_y^n\hat{\mathbf{x}}+k_x^n\hat{\mathbf{y}})$,c.p.'s]; $m=0;2$; $n=1;3;5$ $[k_xk_yk_z^n\hat{\mathbf{z}}$,c.p.'s]; $n=1;3;5$

imagine that pseudospin is conserved. In that case, the argument of Ref. 19 applies, and since $\mathbf{d}$ is not even in $\hat{\mathbf{k}}\cdot\hat{\mathbf{n}}$, the surface will break pairs. Even if pseudospin-flip scattering is included, the arbitrariness in its relation to non-pseudospin-flip scattering implies that the amplitudes and/or phases for the pseudospin pairs ($S_z=-1,0,1$) near the surface will differ from those in the bulk. Thus pseudospin-flip scattering (which is a necessary consequence of spin-orbit coupling) can be another pair-breaking mechanism in addition to pure momentum scattering.[20]

We thus conclude that for odd-parity pairing, surface scattering generally breaks pairs. The degree of depairing by a smooth surface depends not only on the representation but also on the actual linear combination of the different multiplets involved.

D. Ginzburg-Landau theory and time reversal

A question naturally arises about the form of the Ginzburg-Landau theory when we have more than one basis-function multiplet. From a microscopic viewpoint we expect that the highest T_c will be obtained for one particular linear combination, i.e., one particular choice of the functions $F_a(\hat{\mathbf{k}})$ in Eq. (2). (We suppress the representation index j, and lower the index a to a subscript.) One may now wonder if these functions can be relatively *complex*. If so, that would imply that one needed an order parameter of *twice* the dimension of the representation, since the choice $F_a^*(\hat{\mathbf{k}})$ would lead to the same free energy by time-reversal symmetry. This would contradict our earlier group theoretic argument[7] that time reversal causes no additional degeneracies.

One may convince oneself that this is not possible by examining a simplified Ginzburg-Landau theory in which the invariant functions are written as $h_aF_a(\hat{\mathbf{k}})$, with the $\hat{\mathbf{k}}$ dependent part $F_a(\hat{\mathbf{k}})$ taken to be real and fixed, and the scale factor h_a allowed to vary and be complex.[21] The order parameter [see Eq. (1)] is then written as

$$\mathbf{d}=\sum_{\mu,a}\eta_\mu h_a F_a(\hat{\mathbf{k}})\psi_\mu^a(\hat{\mathbf{k}}) , \tag{5}$$

and the quadratic part of the Ginzburg-Landau free energy is

$$f_{\mathrm{GL}}^{(2)}(h,\eta)=\sum_{a,b}C_{ab}(T)h_a^*h_b\sum_\mu\eta_\mu^*\eta_\mu . \tag{6}$$

The temperature dependent matrix $C_{ab}(T)$ can clearly be taken to be Hermitian. Because all our basis functions are real, the requirement of time-reversal invariance reduces to $f_{\mathrm{GL}}(h,\eta)=f_{\mathrm{GL}}(h^*,\eta^*)$. This leads to the condition $C_{ab}=C_{ba}$, which combined with Hermiticity, means that C_{ab} is a real symmetric matrix. All the eigenvectors of such a matrix, and in particular the one that corresponds to the highest T_c, can always be taken to be real. This completes the argument.[22]

It follows that the functions ψ_μ^j in Eq. (1) can always be chosen to be real. Therefore, time-reversal symmetry can be broken only when the state is a linear combination involving relatively complex coefficients η_μ, which is possible only when the representation is multidimensional.

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APPENDIX: PROOF OF THE GENERALIZED HOPFIELD THEOREM

We present a proof for the odd-parity case only, as that for even parity can be easily constructed from it.

Our proof follows Lax quite closely in its basic idea.[23] We deviate, however, by first constructing $3l_j$ multiplets $\psi_\mu^{ja}(\hat{\mathbf{k}},n)$. Let us take three arbitrary functions of $\hat{\mathbf{k}}$, which we write as $\chi(\hat{\mathbf{k}},n)$, $n=1,2,3$. These functions should be thought of as the components of a vector in pseudospin space. Writing the elements in G as $R_1,R_2,\ldots,R_g$, where g is the order of G, we construct $3g$ new "rotated" functions

$$\Psi_i(\hat{\mathbf{k}},n)=R_i\chi(\hat{\mathbf{k}},n) . \tag{A1}$$

The "rotations" are defined by

$$R_i\chi(\hat{\mathbf{k}},n)\equiv\sum_{m=1}^{3}\chi(\hat{\mathbf{k}}R_i,m)D_{mn}^{(1)}(R_i) , \tag{A2}$$

where $\hat{\mathbf{k}}R_i$ is the transformed direction, and $D^{(1)}$ is the three-dimensional representation of $O(3)$.

The definition (A2) is designed to ensure that for each n, the g functions $\Psi_i(\hat{\mathbf{k}},n)$ form a basis for a regular representation of G, in which Γ^j appears l_j times.[24] By choosing sufficiently arbitrary $\chi(\hat{\mathbf{k}},n)$ (strongly peaked functions in three nonspecial symmetry-unrelated directions, e.g.), we can ensure that the $\Psi_i(\hat{\mathbf{k}},n)$ are linearly independent. The desired $\psi_\mu^{ja}(\hat{\mathbf{k}},n)$ are now obtained by decomposing the regular representations into their irreducible parts. Since these $\psi_\mu^{ja}(\hat{\mathbf{k}},n)$ are obtained by a unitary transformation on the $\Psi_i(\hat{\mathbf{k}},n)$, they are linearly independent also.

The rest of the proof is as in Lax. For almost all $\hat{\mathbf{k}}$, and fixed $\hat{\mathbf{k}}$, j, and a, we can regard $\psi_\mu^{ja}(\hat{\mathbf{k}},n)$ as a vector of length $3l_j$ on the indices μ and n. The $3l_j$ vectors with $a=1,2,\ldots,3l_j$ are complete, and any other multiplet $\phi_\mu^j(\hat{\mathbf{k}},n)$ can be expanded for this fixed value of $\hat{\mathbf{k}}$ in terms of $\psi_\mu^{ja}(\hat{\mathbf{k}},n)$ as follows:

$$\phi_\mu^j(\hat{\mathbf{k}},n)=\sum_{a=1}^{3l_j} F^{ja}(\hat{\mathbf{k}})\psi_\mu^{ja}(\hat{\mathbf{k}},n)\ . \tag{A3}$$

The coefficients $F^{ja}(\hat{\mathbf{k}})$ are now $\hat{\mathbf{k}}$ dependent, but if ϕ_μ^j is to be a basis for Γ^j, then F^{ja} must be invariant under all group operations.

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

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

[6]Such superconductors have been referred to as "unconventional" in the literature. An alternative term such as "reduced symmetry superconductor" would be more informative.

[7]For the examples we consider, although time-reversal symmetry can also be broken, the time-reversed state can be made nonorthogonal to the original state by a point group operation. In other words, time reversal causes no additional degeneracies. This is because (i) the gap behaves as a two-particle wave function and (ii) the relevant point groups have only real representations. See Sec. 10.7 of Ref. 8.

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[10]For a review, see G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[11]See A. J. Leggett, Rev. Mod. Phys. **47**, 331 (1975), Sec. VII, for a discussion of equal spin pairing and unitary pairing.

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[13]C. H. Choi and J. A. Sauls, Phys. Rev. Lett. **66**, 484 (1991).

[14]Except for line nodes in the gap for certain nonunitary states. See the last paragraph of Sec. III A below.

[15]R. Balian and N. Werthamer, Phys. Rev. **131**, 1553 (1963).

[16]The term "multiplet" is used in the same sense that one intends in talking of an "angular momentum multiplet." Thus, a collection of spherical harmonics $\{Y_{lm}\}$ of the same degree l is a $2l+1$-dimensional multiplet, and the Y_{lm}'s with different m's are *partners*. Lax's term (Ref. 8) for our multiplet is "set" of basis functions; we avoid this usage to prevent confusion with the *set* of multiplets. Note also that a multiplet may sometimes have only one member.

[17]It should also be kept in mind that even in the case with equal spin pairing alone, a field parallel to the equal spin pairing axis can still cause pair breaking, because in a spin-orbit coupled system, the magnetic moment (or pseudospin) at a given point $\hat{\mathbf{k}}$ on the Fermi surface is not necessarily parallel to the external magnetic field. [In an isotropic system, for example, there may be couplings of the form $g_1(\boldsymbol{\sigma}\cdot\hat{\mathbf{k}})(\hat{\mathbf{k}}\cdot\mathbf{H})$; see F. Quader and S. K. Yip, Ann. Phys. (N.Y.) **195**, 1 (1989)].

[18]In Ref. 13, Choi and Sauls, relying on the tables of Ref. 2, inferred that if the order parameter was two dimensional, then the pairing must be of type E_{1u} with $\mathbf{d}\propto k_\pm\hat{\mathbf{z}}$. M. R. Norman, Physica C **194**, 203 (1992), has recently pointed out that an E_{2u} order parameter $k_\pm^2 k_z\hat{\mathbf{z}}$ also meets this requirement.

[19]V. Ambegaokar, P. G. de Gennes, and D. Rainer, Phys. Rev. A **9**, 2676 (1974).

[20]It is of course possible for these two scattering mechanisms to conspire to produce a nonpairbreaking surface in some artificial examples. This is so, for instance, if (i) the surface acts as an exact mirror, changing the signs of the components of $\mathbf{S}\perp\hat{\mathbf{n}}$ and of $\hat{\mathbf{k}}\parallel\hat{\mathbf{n}}$, and maintaining the components $\mathbf{S}\parallel\hat{\mathbf{n}}$ and $\hat{\mathbf{k}}\perp\hat{\mathbf{n}}$, and (ii) the order parameter is even under these operations. For such highly special scattering, a surface with $\hat{\mathbf{n}}\parallel\hat{\mathbf{z}}$ is nonpairbreaking for the examples listed in the text i.e., *any* E_u order parameter for D_{4h}, and *any* B_{1u}, B_{2u}, or E_{1u} order parameter for D_{6h}, since the x-y mirror plane has the same character as the identity for these representations.

[21]The generalization to a theory in which the $F_a(\hat{\mathbf{k}})$ are also allowed to vary is straightforward, and does not change the conclusions.

[22]Note that h_a [and more generally $F_a(\hat{\mathbf{k}})$] may be temperature dependent below T_c. This can come about because of quartic terms such as $h_b^* h_a|h_a|^2$ in the free energy.

[23]See Ref. 8, Sec. 3.8. We believe that Lax's proof is a little circular. He states that "by using spherical harmonics of all orders, we can certainly construct an infinite number of sets [*multiplets* in our terminology] of a given representation that are independent in the sense of not being linearly related." This begs the question since one is trying to prove that there exist l_j (or $3l_j$) linearly independent multiplets. By constructing a regular representation, we avoid this difficulty, and we can retain the simplicity of the rest of Lax's argument.

[24]The proof of this statement is assigned as problem 3.1.1 in Ref. 8.