Single Spin Superconductivity:
Formulation and Ginzburg-Landau Theory

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Abstract

We describe a novel superconducting phase that arises due to a pairing instability of the half-metallic antiferromagnetic (HM AFM) normal state. This single spin superconducting (SSS) phase contains broken time reversal symmetry in addition to broken gauge symmetry, the former due to the underlying magnetic order in the normal state. A classification of normal state symmetries leads to the conclusion that the HM AFM normal phase whose point group contains the inversion operator contains the least symmetry possible which still allows for a zero momentum pairing instability. The Ginzburg-Landau free energy for the superconducting order parameter is constructed consistent with the symmetry of the normal phase, electromagnetic gauge invariance and the crystallographic point group symmetry including inversion. For cubic, hexagonal and tetragonal point groups, the possible symmetries of the superconducting phase are classified, and the free energy is used to construct a generalized phase diagram. We identify the leading candidate out of the possible SSS phases for each point group. The symmetry of the superconducting phase is used to determine the cases where the gap function has generic zeros (point or line nodes) on the Fermi surface. Such nodes always occur, hence thermodynamic properties will have power-law behavior at low temperature.

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I. INTRODUCTION

The pairing theory [1,2] of superconductivity and superfluidity is based on a normal state with time reversal symmetry and inversion symmetry. The former symmetry requires that the two spin directions are related by symmetry, and spin-space rotations have played a central role in the classification of broken symmetry phases. The latter symmetry is sufficient to ensure that states with identical spin directions at $\vec{k}$ and $-\vec{k}$ are degenerate. Electrons at $\vec{k}$ and $-\vec{k}$ can then be paired to have zero total momentum and can be classified by spin state as singlet or triplet. The question of inversion symmetry and time-reversal-breaking is central in the specification of the pairing states, [2–10] and in this paper we present some new aspects of these relationships.

It has recently been pointed out [11] that there is a normal state with broken time reversal symmetry that has a pairing instability in direct analogy with that in BCS theory. [1] This magnetically ordered normal state, in which inequivalent up-spin and down-spin magnetizations cancel exactly, has been termed “half-metallic antiferromagnet” (HM AFM) by van Leuken and de Groot. [12] This normal state, which we describe in Sec. II, has considerable theoretical and probable technological interest in itself. Its lack of macroscopic magnetization means that considerations of pairing do not have to confront the question of competition between superconducting order and a pre-existing magnetic field.

In this paper we outline in more detail the characteristics of this “single spin superconductivity” (SSS) phase. In Sec. II we review the characteristics of the HM AFM state, which is the precursor normal state of the SSS. In Sec. II we show that the phenomenon maps onto the BCS model with minor but non-trivial changes. Comparison to liquid $^3$He, conventional BCS superconductors, and more exotic heavy fermion superconductors in Sec. IV demonstrates that the HM AFM state has the minimum symmetry required of the normal state to allow $\vec{q} = 0$ pairing instability, and that in SSS theory inversion symmetry plays a role analogous to that of time-reversal symmetry in BCS theory. In Sec. V we provide the classification of all possible order parameter symmetries for high symmetry crystal point groups, and present results of a symmetry analysis of the Ginzburg-Landau free energy that enumerates the possible SSS states for cubic, tetragonal, and hexagonal crystals.

II. THE NORMAL STATE

A. Half-metallic ferromagnetism

A half-metallic (HM) ferromagnetic (FM) electronic structure arises in a ferromagnetic material when the Fermi level ($E_F$) of one spin direction lies within a gap in the spectrum of the other spin direction. [13] The gap may occur in either the majority or the minority channel. In either case, we will take the up channel to be the metallic one. We also confine this discussion to stoichiometric compounds, which have an integer number of electrons per cell. The system of up spins then forms a metallic fermion liquid, while the down spins form an insulating system that may be thought of as an inert background for the purposes of studying low temperature, low energy processes. This specific occurrence, the placement of the Fermi level of the metallic channel in a gap of the other channel, defines half-metallic.
character: the up-spin “half” of the electrons is metallic, while the down-spin “half” is insulating. Fig. 1(a) shows a model spectrum of exchange split bands that leads to HM character.

Half-metallicity leads to several features of a crystalline solid that are qualitatively distinct from conventional metallic ferromagnets. Unlike in a conventional FM, electron transport is 100% polarized, and there are no allowed low energy spin flips. In a common FM, the spin moment is a continuous quantity whose value is determined by the balance of exchange energy and kinetic energy. In a HM FM, however, the spin moment is constrained to be precisely an integer $M$. This is so because the insulating channel contains an integer number of filled bands, and hence an integer spin $N_\downarrow$, the cell contains an integer number of electrons $N_{tot}$, so the metallic up channel contains an integer number of spins $N_\uparrow = N_{tot} - N_\downarrow$. Then $M \equiv N_\uparrow - N_\downarrow$ is an integer, and the moment is $M \mu_B$ per cell. This follows for any placement of $E_F$ within the gap in the down-spin density of states. The application of a magnetic field $H$ shifts up and down spin bands by $\pm g\mu_B H$ but does not change the occupation or the net spin moment. Hence the spin susceptibility is precisely zero, which is a direct consequence of the lack of low-energy spin flips. There is then no Stoner continuum to damp spins waves by single spin flips of carriers. In fact, the situation can be categorized as extreme spin-charge separation in the carrier system, in which the spin degree of freedom has been separated from the charge fluctuations and frozen out entirely. In this paper we do not address possible effects due to spin waves.

Perhaps the simplest example of a HM FM is CrO$_2$, in which the moment is 2$\mu_B$. de Groot and collaborators [13] have identified calculationally various Heusler alloys that are likely HM FMs, and experimental work on several members (especially UNiSn and NiMnSb) has been reported. [16,17] Pickett and Singh [18] presented theoretical evidence that the colossal magnetoresistance manganites, viz. La$_{2/3}$Ca$_{1/3}$MnO$_3$, are HM in their low temperature FM phase. Recently several candidates for HM behavior have been found with the double perovskite crystal structure. [19] These examples indicate that half-metallic character is not a rare phenomenon.

B. Half-metallic antiferromagnetism

It may occur that the integer spin moment $M$ in a half-metallic system is zero. This situation has been termed half-metallic antiferromagnetism (HM AFM). [12] Its properties are like that of the HM FM discussed above, with one essential difference: there is no macroscopic magnetic field. The HM AFM has 100% polarized charge transport without any net magnetization. It must be kept in mind that the HM AFM is not antiferromagnetic in the usual sense of the term, as there is no symmetry operation that connects spin up and spin down states or densities. In fact, it is essential that the two spins channels are electronically (and thus chemically) distinct, so a gap can occur in one channel only at the same band filling. A model illustrating this situation is shown in Fig. 1(b). This model uses the same two-band form of Fig. 1(a), but the bands for the two spin channels must be displaced in opposite directions, reflecting the necessary inequivalence of the channels.

In a HM AFM the spins are precisely balanced, so there is no majority or minority spin. In this paper we will call (when the need arises) the metallic channel the “up” spin and
the insulating channel the “down” spin. For low energy and low temperature processes the insulating channel becomes inert and drops out of consideration. van Leuken and de Groot [12] have suggested one quintinary compound, intermetallic V₇MnFe₈Sb₇In in a Heusler-like crystal structure, that should be a HM AFM. One of the present authors [11,19] has found candidates for HM AFM states within the class of magnetic double perovskites. An example of a HM AFM spectrum is shown in Fig. 1 for the double perovskite compound La₂VCuO₆, calculated using accurate spin density functional methods. [18] This is nominally a Cu²⁺, V⁴⁺ compound for which both ions have spin ½. When the spins are parallel (top panel) the spectrum is that of a conventional metallic FM. When the spins are antialigned, however, the Fermi level falls where the spin up density of states is large, but within a gap in the spin down channel. This compound, and other double perovskites, are discussed in more detail elsewhere [19].

We leave further discussion of proposed HM materials to future papers, and address below the pairing instability of the HM AFM normal state, and its consequences.

C. Experimental Consequences

An important practical consideration is how a HM magnetic material can be identified. The anticipated properties (questions of many-body corrections [20] aside) have not previously been enumerated. We include a partial list here to provide guidelines. The general feature of course that as the temperature is lowered through the magnetic ordering (Curie or Néel) temperature $T_M$, the material changes from a nonmagnetic (conducting or non-conducting) system to a metallic magnetically ordered system at low T where the spin excitations are frozen out. [21]

a. **Metal with fully polarized transport at low T.** Metallic resistivity, but vanishing magnetoresistance at low T. There is no clear signature in the Hall or Seebeck coefficients. At intermediate temperature there may be a negative magnetoresistance for a HM FM, reflecting the field induced increase in magnetic order and reduced spin scattering as the carriers in one channel become non-conducting. For HM AFM, this field induced effect will not apply.

b. **Magnetic order.** There is no obvious signature of the HM character in the spin wave spectrum or temperature dependence of the magnetic order parameter.

c. **Vanishing spin susceptibility.** However, core diamagnetism, van Vleck (orbital) paramagnetism of the metallic channel, Landau diamagnetism of the insulating channel, and temperature variation of the net order of the local moments will make the magnetic susceptibility difficult to analyze.

d. **Non-Korringa behavior in NMR.** This technique may provide the most direct indication of HM character. The longitudinal relaxation rate $T_1^{-1}$, which is a measure of the conduction electron spin flips, is proportional to the product of the densities of states of each spin channel $[N_↑(E_F)N_↓(E_F)]$, which vanishes for a HM phase. The Knight shift, normally dominated by the spin susceptibility in normal metals, should be small. An NMR study of the proposed HM magnet UNiSn has been reported. [22]
e. Spin-polarized electron spectroscopies. At first glance, these spectroscopies seem ideal, but both photoelectron emission and STM tunneling are sensitive to surface properties. In addition, the magnetic order may be different at the surface, mitigating against HM character in the surface region. Spin-polarized photoemission studies of CrO$_2$ were inconclusive. [23,15]

f. Spin-polarized positron annihilation. This technique, which takes advantage of the natural polarization of the positron beam, has been claimed to establish within narrow bounds that NiMnSb is a HM ferromagnet. [17] It is a bulk probe.

g. Thermodynamic properties. We will show that SSSs necessarily have point or line nodes of the gap (not always the case in previously studied cases of triplet pairing). The resulting gapless excitations lead to heat capacity, penetration depth, thermal conductivity, etc. that have power-law in T (or $\omega$) rather than exponential.

h. Tunnelling. Tunnelling between an SSS and a ferromagnet will show a strong dependence on the direction of magnetization of the ferromagnet. Josephson coupling between an SSS and a singlet pairing superconductor should not occur.

III. PAIRING INSTABILITY IN THE HM AFM

The HM AFM is a single component fermion liquid as a result of underlying magnetic order and electronic structure that renders one spin channel insulating. The lack of a microscopic magnetic field in a HM AFM suggests the possibility that a superconducting instability may occur in the metallic channel. The Cooper instability [1] is spin-blind: the two fermions that undergo the pairing instability can have antiparallel spins as in BCS theory, or they can have parallel spins as in $^3$He, and the instability is straightforwardly extended to a spinless fermion system. We now show that this instability maps directly onto the BCS model of superconductivity [1] in a simple but not quite trivial manner. This new superconducting state has been called single spin superconductivity [1].

A. Formal Relationship to BCS Theory

In BCS theory an electron in state $K$ is paired with its time-reversed partner $TK$. $K = (\vec{k}, \uparrow)$ is an index that together with its partner $TK = (-\vec{k}, \downarrow)$ exhausts all states on the ($\uparrow$ and $\downarrow$) Fermi surface(s). In a SSS, an electron in state $K = (\vec{k}, +)$ is paired with its inversion partner $IK = (-\vec{k}, -)$. To cover all states on the Fermi surface once only, $K$ must range over only half of the Fermi surface, say the ‘top’ half with $k_z > 0$ (hence the notation ‘$+$’), and states with $k_z = 0$ can be assigned to ‘$+$’ and ‘$-$’ components of the pairs also.

In terms of the general two-body interaction

$$\hat{V} = \sum_{k_1,k_2,k_3,k_4} V_{k_1,k_2,k_3,k_4} a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3} a_{k_4}, \quad (3.1)$$

all terms except $\vec{k}_1 = -\vec{k}_2 \equiv \vec{k}, \vec{k}_3 = -\vec{k}_4 \equiv \vec{k}'$ are irrelevant for pairing. To count the pair states properly, the full Brillouin sums in the above expression must be expressed in terms
of pair indices $K$. Using the anticommutation relations of the electron field operators $a_{\vec{k}}, a_{\vec{k}}^\dagger$, and defining the pair annihilation operator $b_{\vec{k}} = a_{\vec{k}}^\dagger a_{-\vec{k}}$, the resulting interaction is (making the notational simplification $V_{\vec{k},-\vec{k}} \rightarrow V_{\vec{k}}$),

$$\hat{V}_{\text{pair}} = \sum_{\vec{k}} b_{\vec{k}}^\dagger b_{\vec{k}} = \sum_{\vec{k}} \sum_{\vec{k}'} U_{\vec{k},\vec{k}'} b_{\vec{k}}^\dagger b_{\vec{k}'}.$$ (3.2)

The ‘+’ sign indicates that the summation extends only over the ‘top’ half $k_z > 0$ of the Brillouin zone. The symmetry of the matrix element noted by Sigrist and Ueda \[2\] results in all terms in the braces being identical, so $U_{\vec{k},\vec{k}'} = 4V_{\vec{k}}$. We return to the implications of the form of the matrix element in the next subsection. From $V_{\vec{k},\vec{k}'} = \langle \vec{k}', -\vec{k}' | V | \vec{k}, -\vec{k} \rangle = \langle K', IK'|V|K, IK \rangle = V_{K,K'}$, and similarly for $U_{K,K'}$, and the expression for the kinetic energy in terms of pair labels (running over half of the Fermi surface), the pairing Hamiltonian then is

$$H_{\text{pair}} = \sum_{\vec{k}} \epsilon_{\vec{k}} (a_{\vec{k}}^\dagger a_{\vec{k}} + a_{\vec{k}IK}^\dagger a_{\vec{k}IK}) + \sum_{\vec{k}} U_{\vec{k},\vec{k}'} b_{\vec{k}}^\dagger b_{\vec{k}'}.$$ (3.3)

where $b_{\vec{k}} = a_{\vec{k}}^\dagger a_{\vec{k}IK}$. Note that we do not use the BCS convention of separating out a negative sign from the interaction matrix elements.

The Bogoliubov-Valatin transformation \[24\] is analogous to its form in BCS theory,

$$a_{\vec{k}} = u_{\vec{k}} \alpha_{\vec{k}} + v_{\vec{k}} \alpha_{\vec{k}}^\dagger, \quad a_{\vec{k}IK}^\dagger = u_{\vec{k}}^\ast \alpha_{\vec{k}IK} + v_{\vec{k}}^\ast \alpha_{\vec{k}IK},$$ (3.4)

(3.5)

and the formalism of SSS pairing theory maps onto BCS theory. Specifically, the SSS ground state is

$$\Phi_0 = \prod (u_{\vec{k}} + v_{\vec{k}} b_{\vec{k}}) \Phi_{\text{vac}}.$$ (3.6)

and the gap function is given by

$$\Delta_{\vec{k}} = \sum_{\vec{k}'} U_{\vec{k},\vec{k}'} \langle b_{\vec{k}} \rangle.$$ (3.7)

The gap is a scalar, \textit{i.e.} it has no spinor indices, which distinguishes SSS from all superconducting systems discussed previously. The gap equation is formally identical to BCS:

$$\Delta_{\vec{k}} = -\sum_{\vec{k}'} \frac{U_{\vec{k},\vec{k}'}^2}{2E_{\vec{k}'}} \Delta_{\vec{k}'} \tanh \left( \frac{1}{2} \beta E_{\vec{k}'} \right)$$ (3.8)

where $\beta = 1/kT$ is the inverse temperature. With $\mu$ denoting the chemical potential,

$$E_{\vec{k}} \equiv E_{\vec{k}} = [(\epsilon_{\vec{k}} - \mu)^2 + |\Delta_{\vec{k}}|^2]^{\frac{1}{2}}$$ (3.9)

is the quasiparticle excitation energy, which is even in $\vec{k}$.

It is useful to express the gap equation as usual in terms of a full Brillouin zone summation. It is readily verified that extending the sum over the full zone introduces an expected factor of $\frac{1}{2}$, and the gap equation,

$$\Delta_{\vec{k}} = -\sum_{\vec{k}'} \frac{W_{\vec{k},\vec{k}'}^2}{2E_{\vec{k}'}} \Delta_{\vec{k}'} \tanh \left( \frac{1}{2} \beta E_{\vec{k}'} \right)$$ (3.10)

where $W_{\vec{k},\vec{k}'} = \frac{1}{2} U_{\vec{k},\vec{k}'}^2 = 2V_{\vec{k},\vec{k}'}$, indicates the final formal equivalence to the BCS equation.
B. Simple Consequences of Single Spin Pairing

The combination of matrix elements in Eq. (3.2), and the symmetry noted by Sigrist and Ueda, indicate explicitly the \( k \)-space structure that is necessary for SSS pairing. A \( \vec{k} \)-independent attractive potential \( V_{\vec{k},\vec{k}'} = -\bar{V} \), which leads to singlet pairing in the BCS model, contributes nothing toward SSS pairing; likewise, a \( \vec{k} \)-independent repulsion is harmless. The simplest form of such coupling, which is odd in both \( \vec{k} \) and \( \vec{k}' \), is of the form \( W\hat{\vec{k}} \cdot \hat{\vec{k}}' \). When this is substituted into the gap equation Eq. (3.10) (see below), a non-vanishing solution requires \( W < 0 \). Thus the pairing interaction must be attractive for small angle (“forward”) pair scattering and repulsive for large angle scattering of pairs. This behavior is reminiscent of the situation in high \( T_c \) theory, where the spin-fluctuation picture has an everywhere-positive interaction, which peaks at large \( q \) (more specifically, at \((\pi/a, \pi/a)\)).\[25\] That type of interaction favors a \( d_{x^2-y^2} \) symmetry of \( \Delta \) for singlet pairing.

Using the pairing interaction in normalized form

\[
W_{\vec{k},\vec{k}'} = -|W| \frac{\vec{k} \cdot \vec{k}'}{k_F^2/3},
\]

(3.12)

where \( k_F \) is the Fermi wave vector, the \( T=0 \) gap equation can be solved readily for several trial gap symmetries. Gap functions of the form \( \Delta_\vec{k} \propto \hat{d} \cdot \hat{\vec{k}} \), for some constant vector \( \hat{d} \), give the lowest order possibilities (in terms of polynomials of the components of \( \vec{k} \)). If \( \hat{d} \) is real, or purely imaginary, its direction can be taken as the \( \hat{z} \) axis (\( \hat{d}=(0,0,1) \)) so \( \Delta_\vec{k} \propto k_z \) with a line of nodes on the equator of the Fermi surface. Complex \( \hat{d} \) can be represented by \( \hat{d}=(1,i,0)/\sqrt{2} \), in which case \( \Delta_\vec{k} \propto k_x + ik_y \) with point nodes at the poles. We also consider the “highest symmetry” single dimensional function \( \Gamma_1^{(-)} \propto k_x k_y (k_x^2 - k_y^2)(k_y^2 - k_z^2)(k_z^2 - k_x^2) \) (see the following Section) as an exotic possibility – it has nine lines of nodes.

We treat the usual weak-coupling case, where

\[
\sum_\vec{k} \rightarrow \int_{-\omega_c}^{\omega_c} d\omega N(\omega) \int \frac{d\Omega(\hat{k})}{4\pi} \rightarrow N(0) \int_{-\omega_c}^{\omega_c} d\omega \int \frac{d\Omega(\hat{k})}{4\pi},
\]

(3.13)

where \( N(\omega) \) is the density of states per spin which is assumed to be constant over the energy scale \( \omega_c \) of the pairing interaction. We display in Fig. 3 the resulting \( T=0 \) gap value, relative to the energy cutoff \( \omega_c \), versus the coupling strength \( \lambda = N(0)|W| \) for these gap symmetries. The BCS result is given for comparison. Given the same coupling \( \lambda \), it is evident that the zero temperature gap magnitude is comparable to the BCS value, even for the \( \Gamma_1^{(-)} \) function.

It is straightforward to obtain the limiting behaviors of the zero temperature gap from Eq. (3.10). In the weak-coupling limit,

\[
\Delta_{rms} = 2\omega_c e^{-1/\lambda} C_1 (1 + C_2 e^{-2/\lambda}),
\]

(3.14)

while for large \( \lambda \) the asymptotic form is
\[ \Delta_{rms} = \omega_c \lambda \left( D_1 - \frac{D_2}{\lambda^2} \right). \]  

(3.15)

Here \( C_1, C_2, D_1, D_2 \) are symmetry dependent constants (cf. Appendix B). This latter relation explains the linear behavior at larger \( \lambda \) that is evident in Fig. 3. Note that strong coupling corrections will change this to a \( \sqrt{\lambda} \) behavior. [26]

At \( T = T_c \), \( E_{\vec{k}} \rightarrow \epsilon_{\vec{k}} \) (we take \( \mu = 0 \)). Taking \( \vec{k} \) along \( \hat{a} \) (or along one non-zero component if \( \hat{a} \) is complex), the only difference from the corresponding BCS equation is an angular integral. This integral is unity, however, due to the expansion of \( W_{\vec{k},\vec{k}'} \) in normalized functions. Thus the equation for \( T_c \) versus coupling constant \( \lambda = N(0)|W| \) is identical in form to that of BCS:

\[ \frac{1}{\lambda} = \int_0^{\omega_c} d\epsilon \frac{\tanh(\beta_c \epsilon/2)}{\epsilon}, \]  

(3.16)

where \( \beta_c = 1/k_B T_c \).

Although there is every reason to expect that SSS will arise in the appropriate transition metal (or \( f \) electron) compounds, there is not yet any expectation of high \( T_c \). For one thing, the necessary interaction \( W_{\vec{k},\vec{k}'} \) is of a particular kind (see above); however, this is also the case for the \( d \) wave scenario in high \( T_c \) cuprates. More to the point, however, is that at larger \( T \) transverse spin fluctuations increase strongly and tend to reduce the AFM order parameter, finally causing the system to revert to the paramagnetic state above the Néel temperature. The manner in which the HM AFM state will thereby be weakened has not yet been explored.

**IV. SYMMETRY: RELATIONS TO PREVIOUS THEORY**

It is instructive to clarify the relationship between the degree of symmetry of the normal state and the degree of richness of broken symmetry in the condensed phase. \(^3\)He has the highest symmetry possible in its (liquid) normal state. It has continuous real space \( L \) and spin rotation \( S \) symmetries, it has time reversal \( T \) and inversion \( I \), and of course gauge symmetry U(1). The group of its normal phase then is \( L \times S \times T \times I \times U(1) \). In the condensed superfluid phase, U(1) is a broken symmetry and one or more of the other symmetries can be broken concomitantly. Much work has been done to characterize the more likely cases among the infinite possibilities (infinite because the relative angular momentum \( L \) of the pair can be any non-negative integer). The observed phases correspond to particular states within the (pair spin and orbital angular momentum quantum numbers) \( S = 1, L = 1 \) complex that is described by an 18 component order parameter in general.

When considering pairing in a crystal, the continuous real space rotation symmetry is replaced by the finite crystalline point group \( G \) (see Table [I], where the classifications of this subsection are collected). The group of the normal state then is \( G \times S \times T \times I \times U(1) \). The number of broken states is finite because the space of basis functions of irreps is spanned by a few small-L sets. The necessary values of \( L \) for cubic crystals are presented under the BCS case in Table [I]. The allowed symmetries in cubic, tetragonal, and hexagonal crystals have been exhaustively categorized. [2,27]
In crystals with strong spin-orbit coupling, it may be appropriate to consider the spin as frozen into the crystalline lattice, in which case spin rotation is no longer a separate symmetry. (On this matter there are arguments both pro and con in the literature.) Then the normal state symmetry is lowered further, and the number of distinct broken symmetry states is further reduced. The next lowest symmetry situation, where inversion symmetry is absent from the point group, has been considered by Poluěktov [28] with the spins frozen to the lattice, distinction between singlet and triplet pairing vanishes and the order parameter becomes a low symmetry combination.

For the SSS discussed in this paper, the two spin systems are inequivalent, so time-reversal and spin rotation symmetries are strongly broken by the normal state. The symmetry of the normal state is described by $G \times I \times U(1)$. The number of distinct possibilities for broken symmetry states, which we enumerate below, is reduced still further. In fact, this state of affairs gives the lowest possible symmetry normal state that still allows pairing in the usual sense of zero net momentum $\vec{Q}$ of the pair. Inversion symmetry ensures that $\varepsilon_{\vec{k}} \equiv \varepsilon_K \equiv \varepsilon_{-\vec{k}}$, so that if $\vec{k}$ lies on the Fermi surface then so does $-\vec{k}$, and these two states can pair to total momentum $\vec{Q} = \vec{k} + (-\vec{k}) = 0$. Without inversion symmetry, i.e. for $G \times U(1)$ normal state symmetry, $\vec{Q} = 0$ pairing is not allowed. This result indicates that inversion, not time-reversal symmetry, is the minimal symmetry requirement for a pairing instability. For convenience, inversion $I$ will be considered part of the point group $G$ below.

Because for a SSS state time-reversal symmetry is already broken in the normal state, it is natural to expect (and indeed we find) that broken symmetry phases with unusual properties are likely to arise. Such considerations occupy the rest of the work reported here.

V. GINZBURG-LANDAU FREE ENERGY

A. Allowed Superconducting Phase Symmetries

The spontaneous symmetry breaking at the superconducting phase transition is governed by the free energy. Below $T_c$ the minimum is a superconducting phase whose order parameter breaks the $U(1)$ gauge invariance and possibly other symmetries as well. This physics may be described through a phenomenological Ginzburg-Landau free energy that describes the mean field theory of the superconductor in terms of a few parameters related to matrix elements of the effective potential. Despite its simplicity, the mean field free energy captures all of the generic information about the allowed symmetries of the superconducting phase.

The order parameter describing the Cooper pair condensate is taken to be the gap function,

$$\Delta_{\vec{k}} = \sum_{\vec{k}'} W_{\vec{k},\vec{k}'} \langle a_{\vec{k}'} a_{-\vec{k}'} \rangle,$$

which was introduced in Equation (3.7). Below $T_c$ the gap function is non-zero, and it transforms under the full symmetry group of the normal phase. In particular, it is not invariant under the $U(1)$ Abelian gauge symmetry (and the concomitant global $U(1)$ of electron number), since Cooper pairs have electric charge $-2$ (electron number 2). The $U(1)$
symmetry is broken to the cyclic group $\mathbb{Z}_2$. The gap function may break other symmetries as well, and this is the main focus of this Section.

The gap function must form an irreducible representation (irrep) of the symmetry group, $\mathcal{G} = G \times U(1)$, at least in the vicinity of the phase transition. This follows from the fact that near the transition, the gap function satisfies the linearized gap equation, which for a spherical Fermi surface is given by

$$\Delta_{\vec{k}} = -\gamma \left( \omega_c / kT_c \right) \int d\vec{k}' W_{\vec{k},\vec{k}'} \Delta_{\vec{k}'}$$

with \( \gamma(x) = N(0) \int_{-x}^{x} dy \tanh \left( \frac{1}{2} y \right) \) \( \tanh(y) \) (5.2)

where $\omega_c$ is the cutoff for the interaction. This is a $\mathcal{G}$-invariant eigenvalue equation where $\Delta$ is an eigenvector and therefore must transform as a member of an irrep of $G$. As usual, we start with the assumption that the transition temperature for the first irrep to condense is much higher than that of the others. This lets us focus on each irrep separately.

Under a $U(1)$ gauge transformation $a_{\vec{k}} \rightarrow e^{-i\varphi} a_{\vec{k}}$, $\Delta \rightarrow e^{-2i\varphi} \Delta$. $\Delta$ may transform under the point group, $G$, as well. Consider the case where there is an element of $G$ that sends $\Delta$ to another function which is not related to $\Delta$ by a gauge transformation; i.e. there is $g \in G$ such that $\hat{g}\Delta = \Delta'$ where $|\Delta| \neq |\Delta'|$. This breaks the point group symmetry to a subgroup $H$ of $G$ that does leave $\Delta$ invariant up to a gauge transformation. This non-trivial form of spontaneous symmetry breaking occurs exactly when $\Delta$ is in an irrep $\Gamma$ of $G$ whose dimension is greater than one \[29\].

The overall symmetry breaking scheme may be described as follows. When $\Delta$ is in the irrep $\Gamma$ of $G$, there is a maximal subgroup $H$ of $G$ under which $\Delta$ transforms as a one dimensional irrep $\Gamma'$. Then $\mathcal{G}$ is broken to the little group $H$, $\mathcal{G} \rightarrow H$. All such decompositions of irreps of the crystallographic points groups are tabulated in “compatibility tables” \[30\]. It is merely a matter of looking up the maximal subgroup $H$ in which each distinct one dimensional irrep appears. This classifies all of the possible superconducting phases according to symmetry.

There is one subtlety in this analysis. The gap function is not gauge invariant, so it is not a physical observable. The physical residual symmetry group $H_{\text{phys}}$ may be larger than $H$. For example, the spectrum of quasiparticle excitations \[31\] has the symmetry of the gauge invariant product $\Delta^* \Delta$. If $\Delta$ is in a complex irrep, there may exist an element $g$ of $G$ that switches $\Gamma'$ and its complex conjugate $\Gamma'$; that is, $\hat{g}\psi = \psi$ for $\psi \in \Gamma'$. Then $g$ leaves $|\Delta|^2$ invariant, but it is not an element of $H$. The residual symmetry of the physical observables below $T_c$ is the group $H_{\text{phys}}$ generated by $H$ and $g$ ($H_{\text{phys}} \cong H \times \mathbb{Z}_2$). On the other hand, if there is no such $g$ such as when the irrep is real, then $H_{\text{phys}} = H$.

It is convenient to expand the gap function in terms of explicit representatives of the irrep $\Gamma$. A general form of the mode expansion of $\Delta_{\vec{k}}$ is

$$\Delta_{\vec{k}} = \sum_{\Gamma,m} \sum_{n_i} \eta_m(\Gamma; n_i) \psi(\Gamma, m; n_i; \vec{k})$$

(5.3)

where $\eta_m(\Gamma; n_i)$ is a complex coefficient, $m = 1, \cdots, \dim \Gamma$ labels the components of $\Gamma$ and the indices $n_i$ distinguish polynomials of different degrees. (For multiple or aspherical Fermi
surfaces Allen’s Fermi surface harmonics \[31\] would be used.) A suitable choice of basis elements \( \psi(\Gamma, m; n_i = 0; \vec{k}) \) is given in Table II. A complete basis of higher modes of the linearized gap equation may be constructed using standard techniques.

B. Construction of the Free Energy

At this point we have identified the possible residual symmetries of the superconducting phase. It remains to show how each is realized as a minimum of the free energy. The Ginzburg-Landau free energy, \( F \), is a functional of the mean field \( \Delta_{\vec{k}} \) in which the fluctuations about the mean field have been integrated out \[32,33\]. It must be invariant under the full symmetry group \( \mathcal{G} \) which describes the physics of the normal state. This constrains the combinations of the modes of \( \Delta_{\vec{k}} \) that enter \( F \). Only invariant \((\Gamma_1^+)^n\) combinations contribute. In a perturbative expansion of \( F \) in terms of \( \Delta_{\vec{k}} \), the form of the low order terms is highly constrained by \( \mathcal{G} \)-invariance.

The group symmetry imposes a very restricted form. Many terms that could appear in the free energy vanish. This is usually computed with a Clebsch-Gordon decomposition \[2,30\], but we develop a more powerful technique in which the group symmetry is used directly. The result is an explicit computation of the allowed terms in the free energy to arbitrarily high order in perturbation theory.

The group symmetry imposes a number of constraints. Gauge invariance requires that the polynomial have equal numbers of \( \eta \)'s and \( \bar{\eta} \)'s. The restrictions due to the point group are implemented as follows. Each group operation may be considered to act on the \( \eta \)'s in a way that leaves the free energy invariant. If \( \Delta \) is transformed under an operation from \( \mathcal{G} \), it may be restored to its original form by a linear transformation of the constants \( \eta_m \); that is, they form the contragredient representation of \( \Gamma \) of \( G \) with charge 2 under global \( U(1) \). The free energy is invariant under \( \mathcal{G} \), so it must be an invariant polynomial in \( \eta_m \) under the action of \( \mathcal{G} \). In addition to the symmetry constraints, the free energy must be real and bounded below for stability.

Invariant polynomials have been studied extensively in the mathematics literature. In particular, invariant polynomials for the symmetric and alternating groups \[34\] and for Abelian and non-Abelian gauge groups \[35\] have been constructed explicitly. These polynomials play an important role in gauge theory \[36,37\]. Invariant polynomials for \( G \times U(1) \) require an extension of this theory, and since it has not been discussed in the condensed matter literature, we will give some details.

Since \( G \) is a finite group, its action on the coefficients \( \eta_j \) is isomorphic to a direct product of finite simple groups—in particular the symmetric groups, \( S_3 \) and \( S_2 \), the alternating groups \( A_3 \) and \( A_2 \) and the cyclic groups, \( \mathbb{Z}_3 \) and \( \mathbb{Z}_2 \). The form of invariant polynomials for each of these groups is well known, and our task is to form combinations of them that are invariant under \( \mathcal{G} \times U(1) \).

The free energy is almost trivially constructed for the one dimensional representations. Gauge invariance requires that the free energy be a function of \( |\eta_1|^2 \). This is also invariant under the point group operations. The perturbative expansion of the free energy takes the form

\[
F = \alpha |\eta_1|^2 + \beta |\eta_1|^4 + \gamma |\eta_1|^6 + \cdots \quad \text{for } \dim \Gamma = 1
\]
where α, β and γ are parameters describing the expansion of the effective potential for the order parameter in terms of the basis elements of the irreducible representation. Note that the \( \vec{k} \) integrals for matrix elements of the effective potential \( W_{\vec{k},\vec{k}'} \) have been included in these parameters, so they encode the physics. In general, there are exponentially small corrections to this perturbation series of the form \( P(|\eta_1|^{2}) e^{-1/(\alpha^2|\eta_1|^{2})} \) where \( P \) is a polynomial. These non-perturbative corrections can be important at very low temperatures or in strongly coupled systems, but they are beyond the scope of this paper.

The treatment of higher dimensional representations is more involved. The first step is to find a basis for the point group irrep that respects the simple group decomposition. Each simple group generator should correspond to a specific element of \( G \). This makes the symmetries of the invariant polynomials manifest, permitting a straightforward description. Using invariant polynomial techniques, we will construct the free energy for \( \Gamma_3^- \) and \( \Gamma_4^+ \) of \( O_h, \Gamma_5^- \) of \( D_{6h} \) and \( \Gamma_5^+ \) of \( D_{4h} \).

Consider the two dimensional representation \( \Gamma_3^- \) of \( O_h \). The standard real basis shown in Table II does not respect the simple group decomposition. The appropriate basis is composed of the complex functions

\[
\begin{align*}
\psi'_1 &= [\psi_1(\Gamma_3^-) + i \psi_2(\Gamma_3^-)]/\sqrt{2} = k_x k_y k_z (k_x^2 + \omega k_y^2 + \omega^2 k_z^2) \\
\psi'_2 &= [\psi_1(\Gamma_3^-) - i \psi_2(\Gamma_3^-)]/\sqrt{2} = k_x k_y k_z (k_z^2 + \omega^2 k_z^2 + \omega k_z^2).
\end{align*}
\]

The action of \( O_h \) on this basis is isomorphic to \( \mathbf{Z}_3 \times \mathbf{Z}_2 \times \mathcal{I} \), where \( \mathbf{Z}_3 = \{ E, C_{3a}, C_{3b} \} \), \( \mathbf{Z}_2 = \{ E, C_{2a} \} \) and \( \mathcal{I} \) is inversion (another \( \mathbf{Z}_2 \)). In addition to \( U(1) \), we only need to consider the following two point group operations:

\[
\begin{align*}
\hat{C}_{3a} &= \begin{pmatrix} \omega^2 & 0 & 0 \\ 0 & \omega & 0 \\ 0 & 0 & \omega \end{pmatrix}, \\
\hat{C}_{2a}' &= \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\end{align*}
\]

Consider a monomial \( (\eta_1')^{N_1} (\eta_2')^{N_2} (\overline{\eta_1})^{\overline{N_1}} (\overline{\eta_2})^{\overline{N_2}} \) in the perturbative expansion of the free energy. Invariance under \( O_h \times U(1) \) imposes the following constraints

a. \( U(1) \): \( N_1 + N_2 = \overline{N}_1 + \overline{N}_2 \).

b. \( C_{3a} \): \( N_1 - N_2 - \overline{N}_1 + \overline{N}_2 \equiv 0 \mod 3 \).

c. \( C_{2a}' \): invariance under \( \eta_1' \rightarrow -\eta_1', \eta_2' \rightarrow -\eta_2' \).

This leads to a basis of invariant polynomials of the form

\[
\begin{align*}
\left( |\eta_1'|^{2\beta} |\eta_2'|^{2\gamma} + |\eta_1'|^{2\gamma} |\eta_2'|^{2\beta} \right) \Re e \left( (\eta_1' \overline{\eta}_2')^{3a} \right) \\
\left( |\eta_1'|^{2\beta} |\eta_2'|^{2\gamma} - |\eta_1'|^{2\gamma} |\eta_2'|^{2\beta} \right) \Im m \left( (\eta_1' \overline{\eta}_2')^{3a} \right).
\end{align*}
\]

They can be reexpressed in terms of the polynomial generators for \( \Gamma_3^- \) of \( O_h \)

\[
\begin{align*}
P_1 &= |\eta_1'|^2 + |\eta_2'|^2 \\
P_2 &= 4|\eta_1' \eta_2'|^2 \\
P_3 &= 8\Re e \left( (\eta_1' \overline{\eta}_2')^{3a} \right) \\
P_4 &= 8 \left( |\eta_1'|^2 - |\eta_2'|^2 \right) \Im m \left( (\eta_1' \overline{\eta}_2')^{3a} \right).
\end{align*}
\]
where the complete set of invariant basis elements are powers of these four elements, in one of the two forms

\[
P_{(m,n,p)}^+ = P_1^n P_2^p P_3^m \quad P_{(m,n,p)}^- = P_1^n P_2^p P_3^m P_4.
\]  

These invariant polynomials have not been constructed previously.

Using the invariant basis the most general form of the perturbative expansion of the free energy may be written

\[
F(O_h(\Gamma_5^{-})) = \sum_{m,n,p} F_{(m,n,p)}^+(\eta'_1, \eta'_2) + F_{(m,n,p)}^-(\eta'_1, \eta'_2)
= \alpha (|\eta'_1|^2 + |\eta'_2|^2) + \beta'_1 (|\eta'_1|^2 + |\eta'_2|^2)^2 + 4\beta'_2 |\eta'_1\eta'_2|^2 + \cdots
\]

where \(\alpha = F_{(0,0,0)}^+, \beta'_1 = F_{(0,2,0)}^+, \beta'_2 = F_{(0,0,1)}^+, \) etc. For comparison, Sigrist and Ueda \[2\] use the coefficients \(\beta_1 = \beta'_1 + \beta'_2\) and \(\beta_2 = \beta'_2\). The minima of this free energy will be studied in the next Subsection.

The next case is the two dimensional representations \(\Gamma_5^-\) and \(\Gamma_6^-\) of \(D_{6h}\). The analysis is essentially identical to the case of \(\Gamma_3^-\) of \(O_h\). Again the action of \(D_{6h}\) on these two irreps is isomorphic to \(\mathbb{Z}_3 \times \mathbb{Z}_2 \times I\), where \(\mathbb{Z}_3 = \{E, C_{3z}, C_{3z}^{-1}\}\), and \(\mathbb{Z}_2 = \{E, C_{2x}\}\). The difference in the two cases comes from the way \(\mathbb{Z}_2 \times I\) is embedded in the group; e.g. \(\hat{C}_{2y}(\Gamma_5^-) = i\hat{C}_{2y}(\Gamma_6^-)\).

A complex basis is necessary to make the simple group decomposition manifest

\[
\psi'_1 = \begin{bmatrix} \psi_1 + i \psi_2 \end{bmatrix} / \sqrt{2}
= (k_x + i k_y) / \sqrt{2}
= k_y k_z (k_x + i k_y)(k_y^2 - 3 k_z^2) / \sqrt{2}
\text{ for } \Gamma_5^-\]

\[
\psi'_2 = \begin{bmatrix} \psi_1 - i \psi_2 \end{bmatrix} / \sqrt{2}
= (k_x - i k_y) / \sqrt{2}
= k_y k_z (k_x - i k_y)(k_y^2 - 3 k_z^2) / \sqrt{2}
\text{ for } \Gamma_6^-\]

The generators for the invariant polynomials of \(\Gamma_5^-\) of \(D_{6h}\) are the same as those for \(\Gamma_3^-\) of \(O_h\) \[5,8\], and the free energy may be expressed

\[
F(D_{6h}(\Gamma_5^-)) = \sum_{m,n,p} F_{(m,n,p)}^+(\eta'_1, \eta'_2) + F_{(m,n,p)}^-(\eta'_1, \eta'_2)
= \alpha (|\eta'_1|^2 + |\eta'_2|^2) + \beta'_1 (|\eta'_1|^2 + |\eta'_2|^2)^2 + 4\beta'_2 |\eta'_1\eta'_2|^2 + \cdots
\]

This is identical in form to \(F(O_h(\Gamma_5^-))\), so the phase transitions take place at the same values of \(\alpha, \beta_1, \gamma_1, \) etc. Of course, the symmetries of the phases are different in the two cases. Also, the dependence of the parameters \(\alpha, \beta_1, \ldots\) on physical quantities such as couplings, masses, the temperature and the pressure are different, so systems with different normal state symmetries do not sit at analogous locations in the superconducting phase diagram in general.

Next we consider the two dimensional representation \(\Gamma_5^-\) of \(D_{4h}\). The action of \(D_{4h}\) on this irrep is isomorphic to \(S_2 \times \mathbb{Z}_2^2\); that is, it permutes \(\eta_1\) and \(\eta_2\) and changes their signs. In particular, \(S_2 = \{E, C_{2x}\}\), and \(\mathbb{Z}_2 = \{E, C_{2y}\}, \{E, C_{2z}\}\). The generators for the invariant polynomials of \(\Gamma_5^-\) of \(D_{4h}\) are
\[ P_1 = |\eta_1|^2 + |\eta_2|^2 \]
\[ P_2 = \left[ |\eta_1|^2 + |\eta_2|^2 \right] - \left( |\eta_1|^2 + |\eta_2|^2 \right)^2 = -4 \left[ \Im (\eta_1 \overline{\eta}_2) \right]^2 \]
\[ P_3 = 4 |\eta_1 \eta_2|^2 \]
\[ P_4 = 4 \left( |\eta_1|^2 - |\eta_2|^2 \right) \Im \left[ (\eta_1 \overline{\eta}_2) \right] \]

The basis elements are generated exactly as in the case of \( \Gamma_3^- \) of \( O_h \) \((5.3)\), and the free energy is given by

\[ F(D_{4h}(\Gamma_5^-)) = \sum_{m,n,p} F_{(m,n,p)}^+ P_{(m,n,p)}^- (\eta_1, \eta_2) + F_{(m,n,p)}^- P_{(m,n,p)}^+ (\eta_1, \eta_2) = \alpha (|\eta_1|^2 + |\eta_2|^2) + \beta_1 (|\eta_1|^2 + |\eta_2|^2)^2 - 4\beta_2 \left[ \Im (\eta_1 \overline{\eta}_2) \right]^2 + 4\beta_3 |\eta_1 \eta_2|^2 + \cdots \]

\( (5.14) \)

The coefficients agree with those used by Sigrist and Ueda \([2]\) to fourth order, except for \( \beta_3 \) which differs by a factor of 4 with theirs larger.

The final irreps are the three dimensional representations \( \Gamma_4^- \) and \( \Gamma_5^- \) of \( O_h \). The action of \( O_h \) on each of these irreps is isomorphic to \( S_3 \times \mathbb{Z}_2^3 \), that is, it permutes \( \eta_1, \eta_2 \) and \( \eta_3 \) and changes any of the signs. Of course, the correspondence between specific group elements and these transformations differs in the two cases. In \( \Gamma_4^- \), \( S_3 \) is generated by \( C_{3d} \) and \( C_4 C_2 \) and the three copies of \( \mathbb{Z}_2 \) are generated by the reflections \( \sigma_x, \sigma_y \) and \( \sigma_z \). On the other hand, in \( \Gamma_5^- \), \( S_3 \) is generated by \( C_{3d} \) and \( C_{2h} \) and the \( \mathbb{Z}_2 \) actions are generated by the reflections \( \sigma_y, \sigma_z \) and \( \sigma_x \). The details of the construction of these invariant polynomials and those for the two dimensional irreps are presented elsewhere \([38]\). The generators for the invariant polynomials of \( \Gamma_{4,5} \) of \( O_h \) are

\[ P_1 = |\eta_1|^2 + |\eta_2|^2 + |\eta_3|^2 \] \( (SO(6)) \)
\[ P_2 = |\eta_1 \eta_2|^2 + |\eta_2 \eta_3|^2 + |\eta_1 \eta_3|^2 \] \( (U(1)^3 \times O_h) \)
\[ P_3 = |\eta_1 \eta_2 \eta_3|^2 \] \( (U(1)^3 \times O_h) \)
\[ P_4 = \eta_1^2 + \eta_2^2 + \eta_3^2 \] \( (U(1) \times SO(3)) \)
\[ P_5 = \eta_1^2 \eta_2^2 + \eta_2^2 \eta_3^2 + \eta_3^2 \eta_1^2 - P_2^2 \]
\[ P_6 = \Re \left[ |\eta_1|^2 \left( \eta_2^2 \eta_3^2 - |\eta_2|^2 \right) \right] + \text{cyc.} \]
\[ P_7 = \Im \left[ |\eta_1|^2 \left( |\eta_1|^2 - |\eta_2|^2 \right) \right] + \text{cyc.} \]
\[ P_8 = \Re \left[ |\eta_1|^2 |\eta_2|^2 \eta_3^2 \left( 2|\eta_1|^2 - |\eta_2|^2 - |\eta_3|^2 \right) \right] + \text{cyc.} \]
\[ P_9 = \Im \left[ |\eta_1|^4 \eta_2^2 \eta_3^2 + \eta_2^4 \eta_1^2 \eta_3^2 + \eta_3^4 \eta_1^2 \eta_2^2 \right] \]
\[ P_{10} = \Im \left[ |\eta_1 |^2 |\eta_2 |^2 |\eta_3 |^2 \left( |\eta_1|^2 - |\eta_2|^2 \right) \right] + \text{cyc.} \]
\[ P_{11} = \Re \left[ \left( |\eta_1 |^2 |\eta_2 |^2 |\eta_3 |^2 \right) \left( |\eta_2|^2 + |\eta_3|^2 \right) \right] + \text{cyc.} \]
\[ P_{12} = \Im \left[ |\eta_1 |^2 |\eta_2 |^2 |\eta_3 |^2 \left( |\eta_2|^2 + |\eta_3|^2 \right) \right] + \text{cyc.} \]
\[ P_{13} = \Im \left[ |\eta_1 |^2 |\eta_2 |^2 |\eta_3 |^4 \left( |\eta_1|^2 - |\eta_2|^2 \right) \right] + \text{cyc.} \]
where “cyc.” denotes additional terms with the indices cyclically permuted and we have noted that four of the generators have extra continuous symmetries. Also, $P_5, P_9, P_{11}$ and $P_{12}$ have a $\mathbb{Z}_6$ symmetry in addition to the requisite $U(1) \times O_h$ for fixed $r = P_1^{1/2}$. An arbitrary $O_h(\Gamma_{4,5})$ invariant polynomial may be expressed in terms of the generators (5.15)

$$P(\eta_1, \eta_2, \eta_3) = \sum_{n_1, \ldots, n_5, X} C_{n_1, \ldots, n_5}^{(X)} P_{n_1, \ldots, n_5}^{(X)}(\eta_1, \eta_2, \eta_3)$$

where the basis is given by

$$P_{n_1, \ldots, n_5}^{(X)} = P_{1}^{n_1} P_{2}^{n_2} P_{3}^{n_3} P_{4}^{n_4} P_{5}^{n_5} P_{X}$$

where $P_X = 1, P_6, P_9, P_{11}, P_{12}, P_{13}$. This basis has not been constructed previously.

The free energy for $O_h(\Gamma_{4,5})$ is expressed in terms of the invariant polynomials (5.15):

$$F = \sum_{n_1, \ldots, n_5} F_{n_1, \ldots, n_5}^{(X)} P_{n_1, \ldots, n_5}^{(X)}$$

$$= \alpha P_1 + \beta_1 P_2 + \beta_2 P_4 + \beta_3 P_2 + \gamma_1 P_1^3 + \gamma_2 P_1 P_4 + \gamma_3 P_1 P_2 + \gamma_4 P_3 + \gamma_5 P_6 + \gamma_6 P_7 + \cdots$$

where the sum runs over the indices described above. These coefficients agree with those used by Sigrist and Ueda [2] to fourth order, and they do not consider the free energy for $\Gamma_{4,5}$ of $O_h$ at higher order.

### C. Minimization of the Free Energy

The physical gap function minimizes the free energy. The minimum determines both the magnitude and the direction of $\Delta$ in representation space. The magnitude depends on the parameters $\alpha, \beta, \gamma, \ldots$ in a complicated fashion. Fortunately, its exact value is unimportant. It is zero above $T_c$, small just below the second order critical point and possibly large at low temperatures. The direction in $\eta$ space is more interesting, since it determines the symmetry of the superconducting phase.

Theorem 2 in Appendix A guarantees that regardless of the value of the parameters $\alpha, \beta, \gamma, \ldots$ at least one pair of critical points of the free energy lies on each rotational symmetry axis of the representation space ($\eta$ space). The theorem does not say which of these critical points if any is the absolute minimum, but sufficiently close to the critical point one of them is $\Gamma_{4,5}^-$. This is a consequence of the Morse Theory of critical points combined with an accounting of the critical points of a fourth order polynomial ($F$) in terms of point group orbits. Even as the magnitude of $\Delta$ grows, an intermediate symmetry phase is the ground state for most values of the parameters.

#### 1. 1D Irreps

Because of its simple form, the minimization of the free energy for one dimensional representations (5.4) is straightforward in principle. To fourth order, the free energy is given by
\[ F = \alpha |\eta_1|^2 + \beta |\eta_1|^4 + \cdots \]  

(5.19)

For \( \alpha \sim (T - T_c) < 0 \) and \( \beta > 0 \), the minimum is \( \eta_0^\beta = r_0 e^{2i\theta} \) with

\[ r_0 = \sqrt{\frac{|\alpha|}{2\beta}} + \cdots \]  

(5.20)

where \( \theta \) is an arbitrary phase angle which parameterizes the ground state degeneracy. This breaks the \( U(1) \) symmetry to \( \mathbb{Z}_2 \), but it does not break the point group symmetry.

Higher terms in the free energy may be considered as well. The Ginzburg-Landau formulation is best near the second order critical point where it is well-known that the fourth order free energy (perturbed by a few higher order terms to break the residual degeneracy) provides a good description of the system. At lower temperatures, the magnitude of the gap grows and higher order terms become important. Eventually the perturbative expansions in \( \Delta/\omega_c \) and \( V_{k,k'} \) may break down due to a finite radius of convergence and asymptoticity, respectively. Also, the exact form of the temperature dependence of the coefficients becomes important, so it no longer suffices to make the ansatz that the coefficients are independent of temperature except for \( \alpha \sim (T - T_c) \). Nevertheless, there does exist an effective free energy even at low temperatures which is related to the perturbative Ginzburg-Landau free energy through resummation, and information about the system at low temperatures (especially the symmetries) can be extracted from the higher order terms.

As these terms are considered, the magnitude of the gap function \( r_0(\alpha, \beta, \ldots) \) takes values on a branched cover of the parameter space. Consider the minimization of the sixth order free energy,

\[ F = \alpha |\eta_1|^2 + \beta |\eta_1|^4 + \gamma |\eta_1|^6 + \cdots, \]  

which is of interest in the case of higher dimensional irreps. The minimum becomes

\[ r_0 = \sqrt{-\sgn(\beta) + \sqrt{1 + 3|\alpha|\gamma/\beta^2}} \frac{|\beta|}{3\gamma} + \cdots \]  

(5.21)

The value of the free energy at the minimum is conveniently expressed in terms of the function

\[ \Phi(x, y) \equiv -\frac{1}{27x} \left\{ 2(1 + 3y)^{3/2} - \sgn(x)(2 + 9y) \right\} \]

\[ = -\frac{1}{4x} \left( 1 - \frac{1}{3} y + \frac{9}{16} y^2 - \cdots \right) \quad x > 0, |y| < \frac{1}{3} \]  

(5.22)

where the series is its critical (small \( \alpha \)) expansion. The free energy is given by

\[ F_{\min} = \alpha^2 \Phi(\beta, |\alpha|\gamma/\beta^2). \]  

(5.23)

The function \( \Phi(x, y) \) is convenient because it is a monotonically increasing function of both \( |x| \) and \( y \).

It is possible to have first order phase transitions in this parameter space at eighth order, where a small change in one parameter causes a large change in the gap function because the minimum hops from one sheet to another. The location of these critical points is non-universal. The symmetry of the superconducting state need not change at this type of phase transition, and we do not consider them further. Note that away from the transitions, the higher order terms simply renormalize the leading non-zero coupling \( \beta \) according to (5.22), and we define \( \beta_R \equiv -1/(4\Phi(\beta, |\alpha|\gamma/\beta^2)) \) so that \( F_{\min} = -\alpha^2/(4\beta_R) \).
2. 2D Irreps

The free energy for the two dimensional irreps has the same general features, but it also allows the point group symmetry to be broken. We express $F$ in terms of one real and one complex variable

$$r^2 = |\eta_1'|^2 + |\eta_2'|^2, \quad e^w = \frac{\eta_1'}{\eta_2'}$$

and conversely,

$$\eta_1' = re^{2i\theta+w/2}{\text{sech}}^{1/2}(\text{Re} \ w)/\sqrt{2}, \quad \eta_2' = re^{2i\theta-w/2}{\text{sech}}^{1/2}(\text{Re} \ w)/\sqrt{2}.$$  \hspace{1cm} (5.25)

The remaining degree of freedom in $\eta_1'$ and $\eta_2'$ is a phase, $\theta$. This is the zero mode of the Goldstone boson which is irrelevant by gauge invariance. These variables behave nicely under $O_h \times U(1)$. For example, in $\Gamma_3^-$ of $O_h$, $C_{3\alpha_1} : w \rightarrow w + 2\pi i/3$ and $C_{4z} : w \rightarrow -w$. Consider the two dimensional irreps $\Gamma_3^-$ of $O_h$ and $\Gamma_{5,6}$ of $D_{6h}$ first. The generators of the invariant polynomials for these irreps \text{(5.8)} become

$$P_1 = r^2, \quad \quad P_2 = r^4\text{sech}^2(\text{Re} \ w), \quad \quad P_3 = r^6 \cos(\text{Im} \ 3w) \text{sech}^3(\text{Re} \ w), \quad \quad P_4 = r^8 \sin(\text{Im} \ 3w) \text{sech}^3(\text{Re} \ w) \tanh(\text{Re} \ w)$$

which are manifestly invariant under the symmetry operations. In the $(r, w)$ variables, the free energy is

$$F = \alpha r^2 + \beta_1' r^4 + \beta_2' r^4\text{sech}^2(\text{Re} \ w) + \gamma_1 r^6 + \gamma_2 r^6\text{sech}^2(\text{Re} \ w) + \gamma_3 r^6 \cos(\text{Im} \ 3w) \text{sech}^3(\text{Re} \ w) + \cdots$$  \hspace{1cm} (5.27)

with the same coefficients defined in Eq. \text{(5.10)}.

The order parameter $\Delta(r, w)$ is non-zero below the critical point, breaking the $U(1)$ symmetry. The value of $w$ (the direction of $\Delta$ in $\eta$ space) below $T_c$ determines whether and how the point group is broken. A glance at the functions $P_1, \ldots P_4$ \text{(5.26)} which generate the invariant polynomials reveals that the generic extrema are $w = +\infty, -\infty, 0, i\pi/3, \ldots, 5\pi i/3$. These are the critical points identified by Theorem 2 in Appendix A, since the rotational symmetry axes in the two dimensional $\eta'$ representation space are $(1, 0), (0, 1), (1, \pm 1), (1, \pm \omega)$ and $(1, \pm \omega^2)$. They give a non-trivial residual symmetry.

The minimization of the free energy is straightforward. We consider $F$ to sixth order. The imaginary part of $w$ only enters through $\cos(\text{Im} \ 3w)$, so

$$\text{Im} \ w = \begin{cases} 0, \frac{2\pi}{3}, \frac{4\pi}{3} & \gamma_{3R} < 0 \\ \frac{\pi}{3}, \frac{5\pi}{3} & \gamma_{3R} > 0 \end{cases}$$  \hspace{1cm} (5.28)
where the renormalized coupling $\gamma_{3R} = \gamma_3$ at sixth order. At this order of perturbation theory, $\Im m w$ is unconstrained if $\gamma_3 = 0$. The free energy takes the form $F = \alpha r^2 + \beta'_1 r^4 + \beta'_2 r^4 x^2 + \gamma_1 r^6 + \gamma_2 r^6 x^2 - |\gamma_3| r^6 x^4$ to sixth order with $\Im m w$ given by (5.28) and $x = \text{sech}(\Re e w) \in [0, 1]$. The minima either have $x = 0$ or $x = 1$, since the coefficient of $x^3$ is negative and there is no term proportional to $x$. They correspond to phases in which the point group is only partially broken, and $\Delta$ points along a rotational symmetry axis in $\eta$ space. Specifically, these phases are

$$x = 0 :$$

$$\Delta = r_0 k_x k_y k_z (k_x^2 + \omega k_y^2 + \omega^2 k_z^2)$$
$$\Delta = r_0 k_x k_y k_z (k_x^2 + \omega^2 k_y^2 + \omega k_z^2)$$
$$\Delta = r_0 (k_x \pm i k_y)$$
$$\Delta = r_0 k_y k_z (k_x \pm i k_y) (k_y^2 - 3k_z^2)$$

for $\Gamma^-_3$ of $O_h$

$$x = 1 :$$

$$\Delta = r_0 k_x k_y k_z (2k_z^2 - k_x^2 - k_y^2), \text{cyc.}$$
$$\Delta = \sqrt{3} r_0 k_x k_y k_z (k_x^2 - k_y^2), \text{cyc.}$$
$$\Delta = r_0 k_x, r_0 (\frac{1}{2} k_x \pm \frac{\sqrt{3}}{2} k_y)$$
$$\Delta = r_0 k_y, r_0 (\frac{1}{2} k_y \pm \frac{\sqrt{3}}{2} k_x)$$
$$\Delta = r_0 k_z k_x (k_y^2 - 3k_z^2), \cdots$$
$$\Delta = r_0 k^2 k_z (k_y^2 - 3k_x^2), \cdots$$

for $\Gamma^-_5$ of $D_{6h}$

for $\Gamma^-_6$ of $D_{6h}$

where $r_0$ is the value of $r$ for the ground state, and “cyc.” means terms of the same form with the indices cyclically permuted.

The magnitude of the ground state gap function, $r_0$, is given by an expression of the same form as Eq. (5.21), with $\beta = \beta'_1$ and $\gamma = \gamma_1$ for $x = 0$ and $\beta = \beta'_1 + \beta'_2$ and $\gamma = \gamma_1 + \gamma_2 - |\gamma_3|$, for $x = 1$. It is natural to define the following renormalized couplings

$$\beta_{1R} = -\frac{1}{4\Phi(\beta'_1, |\alpha|\gamma_1/\beta'_1)}$$
$$\beta_{2R} = -\beta_{1R} + \frac{1}{4\Phi(\beta'_1 + \beta'_2, |\alpha|(|\gamma_1 + \gamma_2 - |\gamma_3|)/(\beta'_1 + \beta'_2))^2}$$

so that the free energy of the ground state is given by $F_{\min}(x = 0) = -\alpha^2/(4\beta'_1)$ and $F_{\min}(x = 1) = -\alpha^2/(4(\beta'_1 + \beta'_2))$. The ground state is $x = 0$ when $\beta_{2R} > 0$ and $x = 1$ when $\beta_{2R} < 0$. The ground state gap functions for the three distinct phases are shown in Table III. Typically, the value of $r_0$ changes discontinuously at the boundary between these phases, so the transition is first order, as expected when the symmetry does not break to a subgroup.

At eighth and higher orders, there are small regions of the parameter space in which the ground state has $0 < x < 1$ and the point group is broken completely: $\Gamma^-_3(O_h) \rightarrow \Gamma^-_1(D_{2h}), \Gamma^-_5(D_{6h}) \rightarrow \Gamma^-_1(C_i)$ and $\Gamma^-_6(D_{6h}) \rightarrow \Gamma^-_1(C_i)$, where $C_i$ is inversion. Second order transitions to these phases can result from frustration due to the competition between the terms minimized at $x = 0$ and those minimized at $x = 1$ (or from the contribution of the symmetry breaking generator $P_4$). Consider the eighth order free energy. It has the terms $\beta'_2 r^4 x^2$ and $\delta_4 r^8 x^4$ which compete when $\beta'_2 < 0$ and $\delta_4 > 0$. The free energy is a fourth degree polynomial in $x$, which decreases as $x$ increases from 0, then reaching a minimum, it increases. If the minimum occurs at $x > 1$, then the ground state is $x = 1$ since $x = \text{sech}\Re e w \leq 1$. 

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On the other hand, if the minimum occurs at $x < 1$, the ground state is the low symmetry phase. We can estimate the critical point taking $|\beta_{2R}| \ll \beta_{1R}$, for which the low symmetry phase exists when

$$|\alpha| \geq \left( \frac{4|\beta_{2R}|^{3/2}}{\delta_4} \right)^{1/2}$$  \hspace{1cm} (5.31)

with $\beta_{2R} < 0$ and $\delta_4 > 0$. Since $\alpha \sim (T - T_c)/T_c$ is small near the initial superconducting critical point, this secondary phase transition would occur at much lower temperatures.

The other two dimensional irrep is $\Gamma_5^-$ of $D_{4h}$. Again, the simple groups act nicely on the projective variables, $C_{2y}: w \to w + i\pi$ and $C_{2e}: w \to -w$. The rotational symmetry axes in the two dimensional representation space are $(1,0), (0,1), (1,\pm1)$ and $(1,\pm i)$, which correspond to $w = \infty, -\infty, 0, i\pi, i\pi/2$ and $-i\pi/2$. The generators of the invariant polynomials are

\begin{align*}
P_1 &= r^2 \\
P_2 &= -r^4 \sin^2(Im \ w) \text{sech}^2(Re \ w) \\
P_3 &= r^4 \text{sech}^2(Re \ w) \\
P_4 &= r^6 \sin(Im \ 2w) \text{sech}^2(Re \ w) \tanh(Re \ w)
\end{align*}

which are manifestly invariant. The free energy becomes

$$F = \alpha r^2 + \beta_1 r^4 + \beta_2 r^4 \sin^2(Im \ w) \text{sech}^2(Re \ w) + \beta_3 r^4 \text{sech}^2(Re \ w) + \gamma_1 r^6 - \gamma_2 r^6 \sin^2(Im \ w) \text{sech}^2(Re \ w) + \gamma_3 r^6 \text{sech}^2(Re \ w) + \gamma_4 r^6 \tanh(Re \ w) \text{sech}^2(Re \ w) \sin(Im \ 2w) + \cdots$$  \hspace{1cm} (5.33)

The structure of the solution is more complicated than in the case of the other two dimensional representations because the generator $P_4$ that explicitly breaks the intermediate symmetries occurs at sixth order rather than eighth order. This leads to low temperature phases in which the point group is broken to $I$.

We restrict our attention to the sixth order free energy with no symmetry breaking parameter: $\gamma_4 = 0$. The relative phase for the ground state is given by

$$Im \ w = \begin{cases} 
0, \pi, & \beta_{2R} < 0 \\
\frac{\pi}{2}, \frac{3\pi}{2}, & \beta_{2R} > 0
\end{cases}$$  \hspace{1cm} (5.34)

with $\beta_{2R} = \beta_2 + \cdots$ (See Eq. (5.33)). The free energy reduces to $F(Im \ w = \pi/2) = \alpha r^2 + \beta_1 r^4 - \beta_2 r^4 x^2 + \beta_3 r^4 x^2 + \gamma_1 r^6 - \gamma_2 r^6 x^2 - \gamma_3 r^6 x^2$, and $F(Im \ w = 0)$ given by the same expression with $\beta_2 = \gamma_2 = 0$. Note that the free energy is quadratic in $x$. The phase boundaries are again best expressed in terms of renormalized couplings,

\begin{align*}
\beta_{1R} &\equiv -\frac{1}{4\Phi(\beta_1, |\alpha|\gamma_1/\beta_1^2)} \\
\beta_{3R} &\equiv -\beta_{1R} + \frac{1}{4\Phi(\beta_1 + \beta_3, |\alpha|\gamma_1 + \gamma_3)/(\beta_1 + \beta_3)} \\
\beta_{2R} &\equiv \beta_{1R} + \beta_{3R} + \frac{1}{4\Phi(\beta_1 - \beta_2 + \beta_3, |\alpha|(\gamma_1 - \gamma_2 + \gamma_3)/(\beta_1 - \beta_2 + \beta_3)^2)}
\end{align*}  \hspace{1cm} (5.35)
to sixth order, so that $F_{\text{min}} = -\alpha^2/(4\beta)$ with $\beta = \beta_1 R$ for $w = \pm \infty$, $\beta = \beta_1 R + \beta_3 R$ for $w = 0, i\pi$, $\beta = \beta_1 R - \beta_2 R + \beta_3 R$ for $w = \pm i\pi/2$. The ground states are $w = 0, i\pi$ when $\beta_2 R, \beta_3 R < 0$, $w = \pm \infty$ when $\beta_3 R > \max(0, \beta_2 R)$, and $w = \pm i\pi/2$ when $\beta_2 R > \max(0, \beta_3 R)$. Expressions for the gap function in terms of the original variables for each of the three phases are given in Table I.

3. 3D Irreps

In analogy with the analysis of the two dimension irreps, the free energy for the three dimensional irreps $\Gamma^{-}_4$ and $\Gamma^{-}_5$ of $O_h$ should be expressed in terms of complex projective coordinates. There are two relative magnitudes and two relative phases, so $\eta_1, \eta_2$ and $\eta_3$ should be expressed in terms of a two dimensional vector in complex projective space $\vec{w} \in \mathbb{CP}^2$; however, there is no known vector that behaves simply under the $O_h$ operations. The best we can do is to use the homogeneous coordinates, $\eta_3/(\rho e^{2i\theta})$, and there is no apparent simplification of the free energy.

The ground state of the free energy to sixth order is given by a generic critical point provided the symmetry breaking parameter $\gamma_6$ is taken to be zero. The generic critical points are $(0, 0, 1), (1, 1, 0), (1, 1, 1), (1, i, 0), (1, \omega, \omega^2)$ and $(1, \omega, \omega^2)$ up to symmetry, according to Theorem 2 of Appendix A. At these points, the invariant polynomial generators (5.13) have the following values

\[
\begin{array}{cccccccc}
\hat{\eta} & P_1 & P_2 & P_3 & P_4 & P_5 & P_6 & P_7-13 \\
(0, 0, 1) & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\
(1, 1, 0) & 1 & \frac{1}{4} & 0 & 1 & 0 & 0 & 0 \\
(1, 1, 1) & 1 & \frac{1}{3} & \frac{1}{27} & 1 & 0 & 0 & 0 \\
(1, \omega, \omega^2) & 1 & \frac{1}{3} & \frac{1}{27} & 0 & 0 & -\frac{1}{6} & 0 \\
(1, i, 0) & 1 & \frac{1}{4} & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

at $r = 1$. Let $\beta_1 R \equiv -1[4\Phi(\beta_1, |\alpha|\gamma_1/\beta_2^3)]^{-1}$, and define the other renormalized couplings such that the free energy of each phase is given by

\[
\begin{align*}
F_{(0,0,1)} & = \frac{-\alpha^2}{4(\beta_1 R + \beta_2 R)} \\
F_{(1,i,0)} & = \frac{-\alpha^2}{4(\beta_1 R + \frac{1}{3}\beta_3 R)} \\
F_{(1,1,1)} & = \frac{-\alpha^2}{4(\beta_1 R + \beta_2 R + \frac{1}{3}\beta_3 R)} + \frac{\gamma_{4R}}{27} \left( \frac{|\alpha|}{2(\beta_1 R + \beta_2 R + \frac{1}{3}\beta_3 R)} \right)^3 \\
F_{(1,\omega,\omega^2)} & = \frac{-\alpha^2}{4(\beta_1 R + \frac{1}{3}\beta_3 R)} + \left( \frac{\gamma_{4R}}{27} - \frac{\gamma_{5R}}{6} \right) \left( \frac{|\alpha|}{2(\beta_1 R + \frac{1}{3}\beta_3 R)} \right)^3 \\
F_{(1,1,0)} & = \frac{-\alpha^2}{4(\beta_1 R + \beta_2 R + \frac{1}{3}\beta_3 R)} + \cdots
\end{align*}
\]

where the couplings are defined sequentially, $\beta_2 R$ by $F_{(0,0,1)}$, then $\beta_3 R$ by $F_{(1,i,0)}$, then $\gamma_{4R}$ by $F_{(1,1,1)}$ and finally $\gamma_{5R}$ by $F_{(1,\omega,\omega^2)}$. The free energies may be expressed in terms of the
original (bare) couplings through the $\Phi$ function as before, using the coefficients listed above. Note that $\beta_{jR} = \beta_j$ to fourth order, but the renormalized $\gamma$'s receive corrections even at sixth order, $\gamma_{4R} = \gamma_4 + \cdots$ and $\gamma_{5R} = \gamma_5 + \cdots$.

The ground state of the cubic system is shown in Table III, and the phase diagram is shown in Fig. 4 taking $\gamma_{4R} = \gamma_{5R} = \gamma_{6R} = 0$. When $\gamma_{4R}$ and $\gamma_{5R}$ are non-zero, the phase boundaries shift by a small amount. They also have a more interesting qualitative effect in that they allow the possibility of stabilizing $(1, 1, 0)$ as the ground state. At fourth order, even though $(1, 1, 0)$ is a rotational symmetry axis, the $(1, 1, 0)$ phase only exists on the negative $\beta_2$ axis (see Fig. 4) where it is degenerate with the $(0, 0, 1)$ and the $(1, 1, 1)$ phases. This degeneracy is the result of the enhanced $SO(3) \times U(1)$ symmetry (see Appendix C). The fact that the $\hat{\eta} = (1, 1, 0)/\sqrt{2}$ is only a saddle point at fourth order and not a minimum follows from Morse Theory constraints. This is no longer true in the larger parameter space of the sixth order free energy, and the ground state is allowed to be $(1, 1, 0)$. Taking $\beta_3 = 0$, we find this occurs for $\gamma_4 > -\frac{27}{12} \gamma_3 > 0$.

D. Weak Coupling

This completes the construction of the generalized phase diagrams for SSS with cubic, hexagonal and tetragonal symmetry in the normal phase. We are now in a position to reexamine the superconducting phase transition in the weakly coupled theory. Using standard techniques [40], we find that the weak coupling expansion of the free energy for $\Delta$ in an irrep of $G$ is given by

$$F = F_N + \frac{1}{2} N(0) \log \frac{T}{T_c} \langle |\Delta(\vec{v}_k)|^2 \rangle_k + \sum_{m=1}^{\infty} F_{2m+2} \langle |\Delta(\vec{v}_k)|^{2m+2} \rangle_k,$$

$$F_{2m+2} = -\frac{1}{2} \frac{(2m-1)!!}{(m+1)!} \left( 2^{2m+1} - 1 \right) \zeta(2m+1) \left( -\frac{\beta_c^2}{8\pi^2} \right)^m N(0)$$

(5.37)

where $F_N$ is the free energy of the normal phase and $\beta_c = 1/k_B T_c$. Note that weak coupling means that the parameter $\beta_c^2 |\Delta|_{RMS}^2$ is small. As in Sec. III.B, the simplest ansatz is to consider an interaction of the form (3.12)

$$W_{k,k'} = -|W| \frac{\vec{v}_k \cdot \vec{v}_{k'}}{v_F^2/3},$$

(5.38)

where we have rewritten it in terms of the Fermi velocity appropriate for non-spherical Fermi surfaces. The coefficients in the free energy (5.18) are then integrals over Fermi surface harmonics [31], which are found to equal $\alpha = \frac{1}{6} N(0) \log(T/T_c), \beta_1 = \frac{2}{15} F_4, \beta_2 = 15 F_4, \gamma_1 = \frac{2}{35} F_6, \gamma_2 = \frac{2}{35} F_6$ and $\beta_3 = \gamma_3 = \gamma_4 = \gamma_5 = 0$ assuming a spherical Fermi surface. In this case, the free energy reduces to the form invariant under $SO(3) \times U(1)$ which is studied in Appendix C and the weakly coupled system sits at the point on the positive $\beta_{2R}$ axis near the origin, denoted by an “×” on the phase diagram in Fig. 4. As the Fermi surface is deformed outward at the diagonals inducing a positive hexadecapole moment, $\beta_3$ becomes positive, and $(1, i, 0)$ becomes the ground state. On the other hand, if the Fermi surface is deformed inward, $\beta_3$ is negative, and $(1, \omega, \omega^2)$ is the ground state. Therefore, we identify
(1, i, 0) and (1, ω, ω^2) in Γ^-4 of O_h as the leading candidates for the SSS ground state in cubic systems. In hexagonal and tetragonal systems, the candidates are \Delta \propto (1, i, 0) \cdot \vec{v}_k in Γ^-5 of D_{6h} and D_{4h}.

VI. THERMODYNAMIC PROPERTIES

The gap function \Delta_k may be zero for certain values of \vec{k}. This can occur accidentally, but in some cases the gap function is required to vanish by symmetry. Such zeros are robust and have a marked impact on the low temperature behavior of thermodynamic quantities such as the heat capacity and acoustic attenuation. The characteristic e^{-2\Delta/kT} exponential behavior due to the finite gap, changes to a power law behavior when the gap function has zeros.

The gap function for SSS always has zeros. This is a consequence of its odd parity and the fact that it has a single spin component. The zeros are guaranteed by topological considerations very reminiscent of the so-called “Hairy Ball” Theorem (the Hopf or Poincaré-Hopf Theorem) which relates the total index of a vector field to the Euler characteristic of the underlying (closed, orientable) surface [41]. Consider the field e^{i\phi} = \Delta / |\Delta| where \phi is real, which is a well-defined field on the Fermi surface assuming that \Delta has no zeros. It takes values on the unit circle in the complex plane. Since \Delta changes sign under inversion, \phi(-\vec{k}) = \phi(\vec{k}) + (2k + 1)\pi. Following the value of \phi(\vec{k}) as \vec{k} is taken around any equatorial circle on the (closed) Fermi surface, we find that \phi comes back to itself up to an odd winding number, \delta\phi = 2\pi(2k + 1). The non-zero winding number prevents the equatorial circle from being contracted smoothly to a point on the Fermi surface. It must encounter a zero of \Delta. Although the gap function may have zeros in singlet and triplet superconductivity, only in SSS is it guaranteed to have them. The gapped states of triplet superconductivity (the Balian-Werthamer ground state [42]) do not occur because \Delta only has one spin component in SSS.

These generic zeros of the gap function may be found using Theorem 1 in Appendix A. They are given by fixed points of elements of the residual symmetry group H with a non-trivial character, and are tabulated in Table V. Isolated point nodes arise as fixed points of rotations, whereas lines of zeros are associated with reflections. The nodal structure of \Delta determines the density of states near the Fermi surface and consequently the scaling of thermodynamic quantities. With a few assumptions the scaling exponents may be computed. For example, the heat capacity, which for a constant gap vanishes exponentially, scales as T^3, T^2 and T with point nodes, line nodes and vanishing order parameter, respectively, in a defect-free superconductor [27]. Multiple line nodes lead to T log T [43]. This power law scaling is a hallmark of unconventional superconductivity [27]. It must occur in SSS. For example, the candidate ground states (1, i, 0) and (1, ω, ω^2) of Γ^-4 of O_h discussed above have point nodes, so their intrinsic heat capacities scale as T^3.

VII. SUMMARY

The occurrence of a HM AFM normal state, with one conducting and one insulating spin channel, has been shown to provide the possibility of a novel superconducting phase for
which the operation of time reversal has no part. The state is best considered as a condensed
phase of spinless fermions, with a gap function that is odd in $\vec{k}$ and a pair wave function
that is odd upon interchange of particles. The form of anisotropic interaction required to
form this state was obtained, and the resulting gap equation is found to be of the BCS form.
The allowed symmetries of the gap function have been enumerated for cubic, hexagonal and
tetragonal lattices, and the corresponding conditions on the parameters of the free energy
have been determined. The quasiparticle spectrum is necessarily gapless. For point nodes or
a line of nodes, this gaplessness gives rise to power-law behavior in $T$ or $\omega$. For intersecting
lines of nodes, there will be logarithmic terms such as $T \log T$ as enumerated by Nazarenko
[43].

It is anticipated that examples of such phases can be found in transition metal comp-
ounds. The recent suggestions that Sr$_2$RuO$_4$ may be displaying triplet superconductivity
[44], together with predictions of HM AFM states in transition metal oxides [19], both in-
dicate that transition metal oxide compounds present a favorable possibility of obtaining
single spin superconductors.

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APPENDIX A: TWO THEOREMS

The minimum of the free energy determines the order parameter of the superconducting
phase, and the zeros of the gap function in turn determine the scaling of thermodynamic
properties with temperature. The generic values of these minima and zeros are fixed by
the symmetries of the system, and they may be determined without resorting to explicit
representatives of the symmetry.

This Appendix presents two theorems which are useful in this regard. Theorem 1 may be
used to find the generic zeros of the gap function. The zeros arise as fixed points of elements
of the residual symmetry group $H$ that have non-trivial character. This is a refinement of
the procedure used by Volovik and Gor’kov [3], who identified the zeros with specific group
elements. The utility of our theorem is that the appropriate group elements may be read off
of standard character tables.

Theorem 2 may be used to find the direction of the generic critical points of the free energy
in representation space. Note that the magnitude of the solution (the magnitude of the gap
function) is not determined, but this does not affect the symmetry of the superconducting
phase. The theorem also applies to more traditional applications, such as to show that the
Fermi surface is orthogonal to the axes of rotation of the crystal where they intersect. This
theorem applies to the full non-perturbative free energy.

Theorem 1 Suppose $\Delta(\vec{k})$ is in the irrep $\Gamma'$ of the little group $H$, and suppose $g \in H$ has a
non-trivial character, $\chi_{\Gamma'}(g) \neq 1$. Then $\Delta(\vec{k}_0) = 0$ for any fixed point $\vec{k}_0$ of $g$ (i.e. for any
$\vec{k}_0$ such that $\hat{g}\vec{k}_0 = \vec{k}_0$).

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$\vec{k}_0$ such that $\hat{g}\vec{k}_0 = \vec{k}_0$).
Proof: Since $H$ is the little group, $\dim \Gamma’ = 1$ and

$$g : \Delta(\bar{k}_0) \rightarrow \Delta(\hat{g}\bar{k}_0) = \chi_{\Gamma’}(g) \Delta(\bar{k}_0) \quad (A.1)$$

But $\bar{k}_0$ is a fixed point, so

$$(1 - \chi_{\Gamma’}(g)) \Delta(\bar{k}_0) = 0. \quad (A.2)$$

And we arrive at the result, $\Delta(\bar{k}_0) = 0$ provided $\chi_{\Gamma’}(g) \neq 1$. □

This theorem provides a relatively easy means to identify the nodes of the gap function guaranteed by symmetry. As an example, consider the $(1, \theta, \omega^2)$ state of $\Gamma^-_4$ of $O_h$, which transforms as $\Gamma^-_2$ of the little group $C_{3i}$ (see Table III). The characters of the elements of $C_{3i}$ are listed in common character tables $[30]$. The characters of $C_3, C_3^{-1}, I, S_6$ and $S_6^{-1}$ have non-trivial characters and of those, $C_3$ and $C_3^{-1}$ have fixed points, the two points where the axis of rotation (1,1,1) intersects the Fermi surface.

This information is tabulated in Table V. Note that in some cases any function in the specified irrep must have a divisor whose little group is larger than the little group of the function itself. Theorem 1 applies to these factors as well, and any zero of the factor is also a zero of the function. An example is $k_y^2k_z^2 - 3k_y^2$ which transforms as $\Gamma^-_6$ of $D_{6h}$. Its little group is $D_{2h}$, but it has the factor $k_y^2k_z^2 - 3k_y^2$ that transforms as the one-dimensional irrep $\Gamma^+_4$ of $D_{6h}$. This accounts for two additional lines of nodes.

**Theorem 2** Suppose that $\eta$ transforms as the irrep $\Gamma$ of $G$, a subgroup of $O_h$ or $D_{6h}$, where $\eta$ is a $\dim \Gamma$ dimensional complex vector and suppose that the $U(1)$ invariant function $\mathbf{F}(\eta)$ is in the trivial irrep $\Gamma^+_1$ of $G$. Also suppose that there exists an element $g \in G$ with a fixed point $\eta_0$ up to a phase: $\hat{g}\eta_0 = e^{i\phi}\eta_0$. Then $e^{i\phi}g$ lies in the little group of the gradient $\frac{\partial \mathbf{F}(\eta_0)}{\partial \eta_j}$. Note that $\dim \Gamma’ \leq 3$. Also note that $\frac{\partial \mathbf{F}}{\partial \eta_j} \equiv \partial_j \mathbf{F}$ is the complex gradient, which could be expressed in terms of its $2 \dim \Gamma$ real components. The theorem states that all of these components are invariant under $e^{i\phi}g$ where the phase is equal to the one that appears in the $\eta_0$ transformation.

Proof:

$$g : \partial_j \mathbf{F}(\eta_0) \rightarrow \partial_j \mathbf{F}(\eta)\big|_{\hat{g}\eta_0} = \hat{g}_{ij}\partial_j \mathbf{F}(\eta_0) \quad (A.3)$$

Since $\hat{g}\eta_0 = e^{i\phi}\eta_0$, we have

$$e^{i\phi} \hat{g}_{jk}\partial_k \mathbf{F}(\eta_0) = \partial_j \mathbf{F}(\eta_0) \quad (A.4)$$

Thus, $\partial_j \mathbf{F}(\eta_0)$ is invariant under $e^{i\phi}g$; that is, $e^{i\phi}g$ is in the little group of $\partial_j \mathbf{F}(\eta_0)$. □

This theorem is particularly useful when $g$ is a non-trivial rotation (and $\phi \neq \pi$); i.e. when $\det \hat{g} = +1$ and $\hat{g}$ is not the identity matrix. Then the fixed points of $g$ are on the axis of rotation. In this case, the theorem states that on an axis of rotation, $\partial_j \mathbf{F}$ points along the axis: $\partial_j \mathbf{F}(\eta_0) \propto \eta_0$. If we restrict to a surface of constant $|\eta|^2 = r^2$, then we find

$$\left. \frac{\partial \mathbf{F}}{\partial \eta_j} \right|_{|\eta|=r} = 0 \quad (A.5)$$
on an axis of rotation. The axes of rotation are critical points of $F$ in the angular variables.

We again consider $(1, \omega, \omega^2)$ of $\Gamma^-_{4}$ of $O_h$ as an example. This is a fixed point of $C_3$ about the $(1,1,1)$ axis up to a phase which is a third root of unity: $\hat{C}_3(1, \omega, \omega^2) = \omega(1, \omega, \omega^2)$. According to the theorem, the gradient of the free energy at $(1, \omega, \omega^2)$ must be invariant under $\omega\hat{C}_3$; hence, it is proportional to the dual vector $(1, \omega^2, \omega)$. This radial vector projects to 0 when $r$ is held fixed, so $(1, \omega, \omega^2)$ is a critical point of the free energy.

Note that perturbation theory is not used directly in the proof of these theorems. To the extent that we can say that the functions of interest lie in a particular irrep, the theorems are non-perturbative.

Theorem 2 also has implications for solutions of the gap equation. Since it is an auxiliary equation of motion for the free energy, the theorem implies that the full gap equation is stable for $\Delta$ (or more precisely, $\eta_m(\Gamma)$) pointing along any of the rotational symmetry axes of the representation space. Stability means that the function

$$-\frac{1}{\Delta} \sum_{\bar{k'}} \frac{W_{\bar{k},\bar{k'}}}{2E_{\bar{k'}}} \Delta_{\bar{k'}} \tanh \left( \frac{1}{2} \beta E_{\bar{k'}} \right)$$

is invariant under $G$. This reduces the gap equation to a one dimensional problem, only slightly less tractable than the usual singlet BCS solution.

**APPENDIX B: SOME EXACT RESULTS**

In this Appendix we present an exact solution of the gap equation at zero temperature for two of the cases studied in Section III. These two gap functions, $\hat{d} = (0,0,1)$ and $\hat{d} = (1,i,0)$ of $\Gamma^-_{4}$ of $O_h$, are plotted in Figure 3 along with the $\Gamma^-_{1}$ gap function, which has not been calculated in closed form.

For $\hat{d} = (0,0,1)$,

$$\frac{1}{\lambda_{(0,0,1)}} = \arcsinh (\nu/\sqrt{3}) + \frac{1}{6} \nu \sqrt{3} + \nu^2 + \frac{\nu^3}{6 \sqrt{3}} \log \left( \frac{\nu}{\sqrt{3} + \sqrt{3} + \nu^2} \right)$$

where $\nu = \omega c/\Delta_{\text{rms}}$.

For $\hat{d} = (1,i,0)$,

$$\frac{1}{\lambda_{(1,i,0)}} = \frac{\nu^2}{6} + \frac{\nu(9 - 2 \nu^2)}{6 \sqrt{6}} \arctan \left( \frac{\sqrt{3}}{2} \nu^{-1} \right) + \frac{1}{2} \log \left( 1 + \frac{2 \nu^2}{3} \right)$$

It is evident from the plot that the magnitude of the gap function at low temperature decreases as the number of gap function nodes increases, but that the effect is not dramatic.

**APPENDIX C: THE ROTATIONALLY INVARIANT FREE ENERGY**

In the text we constructed and analyzed the free energy with the gap function in various irreducible representations of the cubic, hexagonal and tetragonal point groups. The resulting phase diagram is quite complicated because of the many couplings necessary to specify the pairing interaction. Only a small subset of these couplings corresponds to physical perturbations.
The free energy simplifies greatly if we make the natural ansatz that the dominant channel for pairing comes from the interaction (3.12)

\[ W_{\vec{k},\vec{k}'} = -|W|\frac{\vec{k} \cdot \vec{k}'}{k_F^2/3}, \]

and that the Fermi surface is spherical. This interaction has an \(O(3)\) symmetry, a higher symmetry than we have considered in Section V. Let the gap function be in \(\Gamma_{-4}\) of \(O_h\), the only cubic irreps that pairs under the interaction (C.1). It has two non-cyclic degrees of freedom, the magnitude, \(r\), and the angle, \(\varphi\), between its real and imaginary parts:

\[ \Delta = r (1 + i \cos \varphi, i \sin \varphi, 0) \cdot \vec{k}/\sqrt{2}. \]  

(C.2)

The overall phase and the three Euler angles do not affect the energy. The free energy is expressed in terms of the well-known \(O(3)\) invariant polynomials [13]

\[ P_1 = |\eta_1|^2 + |\eta_2|^2 + |\eta_3|^2 = r^2 \]

\[ P_2 = |\eta_1^2 + \eta_2^2 + \eta_3^2|^2 = r^4 \cos^2 \varphi \]

(C.3)

and it is given by

\[ F = \alpha r^2 + \beta_1 r^4 + \beta_2 r^4 \cos^2 \varphi + \gamma_1 r^6 + \gamma_2 r^6 \cos^2 \varphi + \cdots \]  

(C.4)

According to Theorem 2 (extended to \(O(3)\)), the generic critical points are \(r_0(0, 0, 1) \cdot \vec{k} \) and \(r_0(1, i, 0) \cdot \vec{k}/\sqrt{2} \) up to rotation. Note that these have a line of zeros and 2 point zeros, respectively. The free energy has non-generic critical points in small regions of parameter space at eighth order in \(\Delta\).

At sixth order, the ground state gap function is given by

\[ \Delta = r_0k_z, \quad \beta_{2R} \leq 0 \]

\[ \Delta = r_0(k_x + ik_y)/\sqrt{2}, \quad \beta_{2R} \geq 0 \]

(C.5)

where \(\beta_{2R} = -\left[4\Phi(\beta_1 + \beta_2, |\alpha|/(\gamma_1 + \gamma_2)/\beta_1^2)^{-1} \right]^{-1}\)

and note that \(\beta_{2R} = \beta_2\) at fourth order. The value of \(r_0\) is given by the expression in Eq. (5.21) with \(\beta = \beta_1\) and \(\gamma = \gamma_1\) in the first case, and \(\beta = \beta_1 + \beta_2\) and \(\gamma = \gamma_1 + \gamma_2\) in the second.
TABLE I. Categorization of normal state symmetries, number of allowed broken symmetry broken states, and allowed values of $S$ and $L$ for several fermion liquids ($S$, $L$ values for the BCS case refer to cubic crystal symmetry). “HFS” refers to the picture where the spin is frozen into the lattice and therefore is not a separate symmetry of the normal state; it is still unclear if this picture gives the best description of the heavy fermion superconductors. “No $\mathcal{I}$” indicates “HFS” without inversion (see text). Symmetry group notation is given in the text.

| System | Normal | Broken Symmetries | Pairing Type            |
|--------|--------|-------------------|-------------------------|
| $^3$He | $\mathcal{L} \times S \times \mathcal{T} \times \mathcal{I} \times U(1)$ | $\infty$ | $S=0$, $L=$even/odd |
|        |        |                   |                         | $S=1$, $L=$odd           |
| BCS    | $\mathcal{G} \times S \times \mathcal{T} \times \mathcal{I} \times U(1)$ | Finite | $S=0$, $L=0,2,4,6$   |
|        |        |                   |                         | $S=1$, $L=1,3,5,9$       |
| HFS    | $\mathcal{G} \times \mathcal{T} \times \mathcal{I} \times U(1)$ | Fewer | S,L Coupled           |
|        |        |                   |                         | Even or Odd Parity       |
| No $\mathcal{I}$ | $\mathcal{G} \times \mathcal{T} \times U(1)$ | Still Fewer | Impure States       |
| SSS    | $\mathcal{G} \times \mathcal{I} \times U(1)$ | Fewest | L=odd                   |

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| Irrep $\Gamma$ | Basis $\psi(\Gamma, m; \vec{k})$ |
|---------------|---------------------------------|
|               | Octagonal $- O_h$               |
| $\Gamma^-$    |                                 |
| $\Gamma_1^-$  | $\psi(\Gamma_1^-, 1; \vec{k}) = k_xk_yk_z(k_x^2 - k_y^2)(k_y^2 - k_z^2)$ |
| $\Gamma_2^-$  | $\psi(\Gamma_2^-, 1; \vec{k}) = k_xk_yk_z$ |
| $\Gamma_3^-$  | $\psi(\Gamma_3^-, 1; \vec{k}) = k_xk_yk_z(2k_x^2 - k_x^2 - k_y^2)$ |
|               | $\psi(\Gamma_3^-, 2; \vec{k}) = \sqrt{3}k_xk_yk_z(k_x^2 - k_y^2)$ |
|               | $\psi(\Gamma_3^-, 1'; \vec{k}) = k_xk_yk_z(k_x^2 + \omega k_x^2 + \omega^2 k_y^2)$ |
| $\Gamma_4^-$  | $\psi(\Gamma_4^-, 1; \vec{k}) = k_x$ |
|               | $\psi(\Gamma_4^-, 2; \vec{k}) = k_y$ |
|               | $\psi(\Gamma_4^-, 3; \vec{k}) = k_z$ |
| $\Gamma_5^-$  | $\psi(\Gamma_5^-, 1; \vec{k}) = k_x(k_y^2 - k_z^2)$ |
|               | $\psi(\Gamma_5^-, 2; \vec{k}) = k_y(k_z^2 - k_y^2)$ |
|               | $\psi(\Gamma_5^-, 3; \vec{k}) = k_z(k_x^2 - k_y^2)$ |
|               | Hexagonal $- D_{6h}$             |
| $\Gamma^-$    |                                 |
| $\Gamma_1^-$  | $\psi(\Gamma_1^-, 1; \vec{k}) = k_xk_yk_z(k_x^2 - 3k_y^2)(k_y^2 - 3k_z^2)$ |
| $\Gamma_2^-$  | $\psi(\Gamma_2^-, 1; \vec{k}) = k_z$ |
| $\Gamma_3^-$  | $\psi(\Gamma_3^-, 1; \vec{k}) = k_y^3 - 3k_x^2k_y$ |
| $\Gamma_4^-$  | $\psi(\Gamma_4^-, 1; \vec{k}) = k_x^3 - 3k_y^2k_x$ |
| $\Gamma_5^-$  | $\psi(\Gamma_5^-, 1; \vec{k}) = k_x$ |
|               | $\psi(\Gamma_5^-, 2; \vec{k}) = k_y$ |
| $\Gamma_6^-$  | $\psi(\Gamma_6^-, 1; \vec{k}) = k_xk_yk_z(k_y^2 - 3k_x^2)$ |
|               | $\psi(\Gamma_6^-, 2; \vec{k}) = k_y^2k_x(k_y^2 - 3k_x^2)$ |
|               | Tetragonal $- D_{4h}$            |
| $\Gamma^-$    |                                 |
| $\Gamma_1^-$  | $\psi(\Gamma_1^-, 1; \vec{k}) = k_xk_yk_z(k_x^2 - k_y^2)$ |
| $\Gamma_2^-$  | $\psi(\Gamma_2^-, 1; \vec{k}) = k_x$ |
| $\Gamma_3^-$  | $\psi(\Gamma_3^-, 1; \vec{k}) = k_xk_yk_z$ |
| $\Gamma_4^-$  | $\psi(\Gamma_4^-, 1; \vec{k}) = (k_x^2 - k_y^2)k_z$ |
| $\Gamma_5^-$  | $\psi(\Gamma_5^-, 1; \vec{k}) = k_x$ |
|               | $\psi(\Gamma_5^-, 2; \vec{k}) = k_y$ |
### TABLE III. SSS symmetry breaking phases.

| $\Gamma$ | $H(\Gamma')$ | $H_{\text{phys}}$ | $\beta_i$ | \# | $\Psi(\hat{k})$ |
|----------|---------------|------------------|-----------|----|----------------|
| $\Gamma^-_1$ | $O_h(\Gamma^-_1)$ | $O_h$ | — | 1 | $k_xk_yk_z(k^2_x - k^2_y)(k^2_y - k^2_z)(k^2_z - k^2_x)$ |
| $\Gamma^-_2$ | $O_h(\Gamma^-_2)$ | $O_h$ | — | 1 | $k_xk_yk_z$ |
| $\Gamma^-_3$ | $D_{4h}(\Gamma^-_1)$ | $D_{4h}$ | $\beta_{2R} < 0, \gamma_{3R} > 0$ | 3 | $\sqrt{3}k_xk_yk_z(k^2_x - k^2_y)$ |
|  | |  | $\beta_{2R} < 0, \gamma_{3R} < 0$ | 3 | $k_xk_yk_z(2k^2_x - k^2_z - k^2_y)$ |
| $T_h(\Gamma^-_2)$ | $O_h$ | $\beta_{2R} > 0$ | 1 | $k_xk_yk_z(k^2_z + \omega k^2_y + \omega^2 k^2_x)$ |
|  | |  | $\beta_{2R} > 0$ | 1 | $k_xk_yk_z(k^2_z + \omega k^2_y + \omega^2 k^2_x)$ |
| $\Gamma^-_4$ | $C_{3h}(\Gamma^-_1)$ | $D_{3d}$ | $\beta_{3R} < 0 < \beta_{2R}$ | 4 | $k_x + \omega k_y + \omega^2 k_y$ |
|  | |  | $\beta_{3R} < 0 < \beta_{2R}$ | 4 | $k_x + \omega^2 k_x + \omega k_y$ |
| $D_{3d}(\Gamma^-_3)$ | $D_{3d}$ | $\beta_{3R}, \beta_{3R} < 0$ | 4 | $k_x + k_y$ |
| $D_{4h}(\Gamma^-_2)$ | $D_{4h}$ | $4\beta_{2R} < \beta_{3R}, \beta_{3R} > 0$ | 3 | $k_z$ |
| $C_{4h}(\Gamma^-_3)$ | $D_{4h}$ | $0 < \beta_{3R} < 4\beta_{2R}$ | 3 | $k_x + ik_y$ |
| $C_{4h}(\Gamma^-_4)$ | $D_{4h}$ | $0 < \beta_{3R} < 4\beta_{2R}$ | 3 | $k_x - ik_y$ |
| $D_{2h}(\Gamma^-_2)$ | $D_{2h}$ | $\beta_{3R} = 0, \beta_{2R} < 0$ | 3 | $k_x + k_y$ |
|  | |  | $\beta_{3R} = 0, \beta_{2R} < 0$ | 3 | $k_x - k_y$ |
| $\Gamma^-_5$ | $C_{3h}(\Gamma^-_2)$ | $D_{3d}$ | $\beta_{3R} < 0 < \beta_{2R}$ | 4 | $k_x(k^2_x - k^2_y) + \omega k_x(k^2_y - k^2_z) + \omega^2 k_y(k^2_z - k^2_x)$ |
|  | |  | $\beta_{3R} < 0 < \beta_{2R}$ | 4 | $k_x(k^2_x - k^2_y) + \omega^2 k_x(k^2_y - k^2_z) + \omega k_y(k^2_z - k^2_x)$ |
| $D_{3d}(\Gamma^-_1)$ | $D_{3d}$ | $\beta_{2R}, \beta_{3R} < 0$ | 4 | $k_x(k^2_x - k^2_y) + k_x(k^2_y - k^2_z) + k_y(k^2_z - k^2_x)$ |
| $D_{4h}(\Gamma^-_1)$ | $D_{4h}$ | $4\beta_{2R} < \beta_{3R}, \beta_{3R} > 0$ | 3 | $k_x(k^2_x - k^2_y)$ |
| $C_{4h}(\Gamma^-_1)$ | $D_{4h}$ | $0 < \beta_{3R} < 4\beta_{2R}$ | 3 | $k_x(k^2_x - k^2_y) + ik_y(k^2_y - k^2_z)$ |
| $C_{4h}(\Gamma^-_3)$ | $D_{4h}$ | $0 < \beta_{3R} < 4\beta_{2R}$ | 3 | $k_x(k^2_x - k^2_y) - ik_y(k^2_y - k^2_z)$ |
| $D_{2h}(\Gamma^-_3)$ | $D_{2h}$ | $\beta_{3R} = 0, \beta_{2R} < 0$ | 3 | $k_x(k^2_x - k^2_y) + k_y(k^2_z - k^2_x)$ |
|  | |  | $\beta_{3R} = 0, \beta_{2R} < 0$ | 3 | $k_x(k^2_x - k^2_y) - k_y(k^2_z - k^2_x)$ |

$\omega = e^{2\pi i/3}$
**TABLE IV. SSS symmetry breaking phases (cont.).**

| Hexagonal — $D_{6h}$ |  |  |  |  |
|-----------------------|----------------|----------------|----------------|----------------|
| $\Gamma_1^-$         | $D_{6h}(\Gamma_1^-)$ | $D_{6h}$ | $-$ | 1 | $k_x k_y k_z (k_x^2 - 3k_y^2)(k_y^2 - 3k_x^2)$ |
| $\Gamma_2^-$         | $D_{6h}(\Gamma_2^-)$ | $D_{6h}$ | $-$ | 1 | $k_z$ |
| $\Gamma_3^-$         | $D_{6h}(\Gamma_3^-)$ | $D_{6h}$ | $-$ | 1 | $k_y^3 - 3k_x^2 k_y$ |
| $\Gamma_4^-$         | $D_{6h}(\Gamma_4^-)$ | $D_{6h}$ | $-$ | 1 | $k_x^3 - 3k_x^2 k_y$ |
| $\Gamma_5^- \quad D_{2h}(\Gamma_1^-)$ | $D_{2h}$ | $\beta_{2R} < 0$, $\gamma_{3R} < 0$ | 3 | $k_x$ |
| $\quad D_{2h}(\Gamma_2^-)$ | $D_{2h}$ | $\beta_{2R} < 0$, $\gamma_{3R} > 0$ | 3 | $k_y$ |
| $\quad C_{6h}(\Gamma_5^-)$ | $D_{6h}$ | $\beta_{2R} > 0$ | 1 | $k_x + ik_y$ |
| $\quad C_{6h}(\Gamma_6^-)$ | $D_{6h}$ | $\beta_{2R} > 0$ | 1 | $k_x - ik_y$ |
| $\Gamma_6^- \quad D_{2h}(\Gamma_1^-)$ | $D_{2h}$ | $\beta_{2R} < 0$, $\gamma_{3R} < 0$ | 3 | $k_x k_y k_z (k_y^2 - 3k_x^2)$ |
| $\quad D_{2h}(\Gamma_3^-)$ | $D_{2h}$ | $\beta_{2R} < 0$, $\gamma_{3R} > 0$ | 3 | $k_y^2 k_z (k_y^2 - 3k_x^2)$ |
| $\quad C_{6h}(\Gamma_2^-)$ | $D_{6h}$ | $\beta_{2R} > 0$ | 1 | $k_y k_z (k_x + ik_y) (k_y^2 - 3k_x^2)$ |
| $\quad C_{6h}(\Gamma_3^-)$ | $D_{6h}$ | $\beta_{2R} > 0$ | 1 | $k_y k_z (k_x - ik_y) (k_y^2 - 3k_x^2)$ |

| Tetragonal — $D_{4h}$ |  |  |  |  |
|-----------------------|----------------|----------------|----------------|----------------|
| $\Gamma_1^-$         | $D_{4h}(\Gamma_1^-)$ | $D_{4h}$ | $-$ | 1 | $k_x k_y k_z (k_x^2 - k_y^2)$ |
| $\Gamma_2^-$         | $D_{4h}(\Gamma_2^-)$ | $D_{4h}$ | $-$ | 1 | $k_z$ |
| $\Gamma_3^-$         | $D_{4h}(\Gamma_3^-)$ | $D_{4h}$ | $-$ | 1 | $k_x k_y k_z$ |
| $\Gamma_4^-$         | $D_{4h}(\Gamma_4^-)$ | $D_{4h}$ | $-$ | 1 | $(k_x^2 - k_y^2) k_z$ |
| $\Gamma_5^- \quad C_{4h}(\Gamma_3^-)$ | $D_{4h}$ | $\beta_{2R} > \beta_{3R}, \beta_{2R} > 0$ | 1 | $k_x + ik_y$ |
| $\quad C_{4h}(\Gamma_4^-)$ | $D_{4h}$ | $\beta_{2R} > \beta_{3R}, \beta_{2R} > 0$ | 1 | $k_x - ik_y$ |
| $\quad D_{2h}(\Gamma_2^-)$ | $D_{2h}$ | $\beta_{2R}, \beta_{3R} < 0$ | 1 | $k_x + k_y$ |
| $\quad D_{2h}(\Gamma_4^-)$ | $D_{2h}$ | $\beta_{2R}, \beta_{3R} < 0$ | 1 | $k_x - k_y$ |
| $\Gamma_6^- \quad D_{2h}(\Gamma_2^-)$ | $D_{2h}$ | $\beta_{3R} > \beta_{2R}, \beta_{3R} > 0$ | 1 | $k_y$ |
| $\quad D_{2h}(\Gamma_4^-)$ | $D_{2h}$ | $\beta_{3R} > \beta_{2R}, \beta_{3R} > 0$ | 1 | $k_x$ |
TABLE V. Zeros of the gap function guaranteed by symmetry.

| $\Gamma$ | $H(\Gamma')$ | Non-trivial Mappings | Generic Zeros |
|----------|--------------|----------------------|---------------|
| $\Gamma_1^-$ | $O_h(\Gamma_1^-)$ | $I, 8S_6, 3\sigma_h, S_4, 6\sigma_d$ | 9 circles: $\{k_i = 0\}_{i=1,2,3}, \{k_i = \pm k_j\}_{i \neq j}$ |
| $\Gamma_2^-$ | $O_h(\Gamma_2^-)$ | $6C_4, 6C_2', I, 8S_6, 3\sigma_h$ | 3 circles: $\{k_i = 0\}_{i=1,2,3}$ |
| $\Gamma_3^-$ | $D_{4h}(\Gamma_3^-)$ | $I, 2S_4, \sigma_h, 2\sigma_v, 2\sigma_d$ | 5 circles: $\{k_i = 0\}_{i=1,2,3}, \{k_1 = \pm k_2\}$ |
| $\Gamma_3^-$ | $D_{4h}(\Gamma_3^-)$ | $2C_4, 2C_2'', I, \sigma_h, 2\sigma_v$ | 3 circles and 8 points: $\{k_i = 0\}_{i=1,2,3}, \{(\pm 1, \pm 1, \pm 1)/\sqrt{3}\}$ |
| $\Gamma_3^-$ | $T_h(\Gamma_3^-)$ | $4C_3, 4C_3^{-1}, I, 3\sigma_h, 4S_6, 4S_6^{-1}$ | 3 circles and 8 points: $\{k_i = 0\}_{i=1,2,3}, \{(\pm 1, \pm 1, \pm 1)/\sqrt{3}\}$ |
| $\Gamma_4^-$ | $C_3(\Gamma_4^-)$ | $C_3, C_3^{-1}, I, S_6, S_6^{-1}$ | 2 points: $\{(\pm 1, 1, 1)/\sqrt{3}\}$ |
| $\Gamma_4^-$ | $C_3(\Gamma_4^-)$ | $C_3, C_3^{-1}, I, S_6, S_6^{-1}$ | 2 points: $\{(1, 1, 1)/\sqrt{3}\}$ |
| $\Gamma_4^-$ | $D_{3d}(\Gamma_4^-)$ | $3C_2', I, 2S_6(\sigma_h)$ of $D_{6d}$ | 1 circle: $\{k_x + k_y + k_z = 0\}$ |
| $\Gamma_4^-$ | $D_{4h}(\Gamma_4^-)$ | $2C_4', 2C_2', I, 2S_4, \sigma_h$ | 1 circle: $\{k_z = 0\}$ |
| $\Gamma_4^-$ | $C_4(\Gamma_4^-)$ | $C_4, C_2, C_4^{-1}, I, S_4, S_4^{-1}$ | 2 points: $\{(0, 0, 1)\}$ |
| $\Gamma_4^-$ | $C_4(\Gamma_4^-)$ | $C_4, C_2, C_4^{-1}, I, S_4, S_4^{-1}$ | 2 points: $\{(0, 0, 1)\}$ |
| $\Gamma_5^-$ | $C_3(\Gamma_5^-)$ | $C_3, C_3^{-1}, I, S_6, S_6^{-1}$ | 2+12 points: $\{(\pm 1, \pm 1, \pm 1)/\sqrt{3}\}$, $\{(0, 0, \pm 1)\} + cyc.$ |
| $\Gamma_5^-$ | $C_3(\Gamma_5^-)$ | $C_3, C_3^{-1}, I, S_6, S_6^{-1}$ | 2+12 points: $\{(\pm 1, \pm 1, \pm 1)/\sqrt{3}\}$, $\{(0, 0, \pm 1)\} + cyc.$ |
| $\Gamma_5^-$ | $D_{3d}(\Gamma_5^-)$ | $I, 2S_6, 3\sigma_d$ | 3 circles: $\{k_i = k_j\}_{i \neq j}$ |
| $\Gamma_5^-$ | $D_{4h}(\Gamma_5^-)$ | $2C_4, 2C_2', I, 2S_4, \sigma_h, 2\sigma_d$ | 3 circles: $\{k_z = 0\}, \{k_x = \pm k_y\}$ |
| $\Gamma_5^-$ | $C_4(\Gamma_5^-)$ | $C_4, C_2, C_4^{-1}, I, S_4, S_4^{-1}$ | 2+12 points: $\{(0, 0, \pm 1)\} + cyc., \{(\pm 1, \pm 1, \pm 1)/\sqrt{3}\}$ |
| $\Gamma_5^-$ | $C_4(\Gamma_5^-)$ | $C_4, C_2, C_4^{-1}, I, S_4, S_4^{-1}$ | 2+12 points: $\{(0, 0, \pm 1)\} + cyc., \{(\pm 1, \pm 1, \pm 1)/\sqrt{3}\}$ |
### TABLE VI. Zeros of the gap function guaranteed by symmetry (cont.)

#### Hexagonal — \( D_{6h} \)

| Group | \( \Gamma_1 \) | \( \Gamma_2 \) | \( \Gamma_3 \) | \( \Gamma_4 \) | \( \Gamma_5 \) |
|-------|----------------|----------------|----------------|----------------|----------------|
| \( D_{6h}(\Gamma_1^-) \) | \( D_{6h}(\Gamma_1^-) \) | \( D_{6h}(\Gamma_1^-) \) | \( D_{6h}(\Gamma_1^-) \) | \( D_{6h}(\Gamma_1^-) \) | \( D_{6h}(\Gamma_1^-) \) |
| \( I, \sigma_d, 2S_3, 2S_6, 3\sigma_d, 3\sigma_v \) | \( 3C_2', 3C_2'', 2C_2', 2C_2'', 3\sigma_d, 3\sigma_v \) | \( C_2, 2C_6, 3C_2', 2C_2'', 2S_6, 3\sigma_d \) | \( C_2, 2C_6, 3C_2', 2C_2'', 2S_6, 3\sigma_v \) | \( C_2, C_3, C_3', C_3'', 2C_6, C_6', 2I, 2S_3, 2S_6 \) | \( C_2, C_3, C_3', C_3'', 2C_6, C_6', 2I, 2S_3, 2S_6 \) |
| \( 7 \) circles: \( \{ k_i = 0 \}_{i=1,2,3}, \{ \sqrt{3} k_x = \pm k_y \}, \{ \sqrt{3} k_y = \pm k_x \} \) | \( 1 \) circle: \( \{ k_x = 0 \} \) | \( 3 \) circles: \( \{ k_y = 0 \}, \{ \sqrt{3} k_x = \pm k_y \} \) | \( 3 \) circles: \( \{ k_x = 0 \}, \{ \sqrt{3} k_y = \pm k_x \} \) | \( 1 \) circle: \( \{ k_y = 0 \} \) | \( 2 \) points: \( \pm (0.0,1) \) |

#### Tetragonal — \( D_{4h} \)

| Group | \( \Gamma_1 \) | \( \Gamma_2 \) | \( \Gamma_3 \) | \( \Gamma_4 \) | \( \Gamma_5 \) |
|-------|----------------|----------------|----------------|----------------|----------------|
| \( D_{4h}(\Gamma_1^-) \) | \( D_{4h}(\Gamma_1^-) \) | \( D_{4h}(\Gamma_1^-) \) | \( D_{4h}(\Gamma_1^-) \) | \( D_{4h}(\Gamma_1^-) \) |
| \( I, 2S_4, \sigma_h, 2\sigma_d, 2\sigma_v \) | \( 2C_2', 2C_2'', 2C_2', 2C_2'', 2\sigma_d, 2\sigma_v \) | \( 2C_2', 2C_2'', 2C_2', 2C_2'', \sigma_h, 2\sigma_v \) | \( 2C_4, 2C_2', 2C_2'', 2\sigma_d, 2\sigma_v, \sigma_h \) | \( C_4, C_2, C_4', C_4'', I, 2S_4, 2S_6, 2\sigma_d, 2\sigma_v \) |
| \( 5 \) circles: \( \{ k_i = 0 \}_{i=1,2,3}, \{ k_x = \pm k_y \} \) | \( 1 \) circle: \( \{ k_x = 0 \} \) | \( 3 \) circles: \( \{ k_i = 0 \}_{i=1,2,3} \) | \( 3 \) circles: \( \{ k_z = 0 \}, \{ k_x = \pm k_y \} \) | \( 2 \) points: \( \pm (0.0,1) \) |

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| Group | \( D_{2h}(\Gamma_2^-) \) | \( D_{2h}(\Gamma_3^-) \) | \( D_{2h}(\Gamma_4^-) \) | \( D_{2h}(\Gamma_5^-) \) |
|-------|----------------|----------------|----------------|----------------|
| \( C_2, \sigma_y, 2C_6, 2C_2', 2C_2'', 3\sigma_d, 3\sigma_v \) | \( C_2, C_3, C_3', C_3'', 2C_6, C_6', 2I, 2S_3, 2S_6 \) | \( C_2, C_3, C_3', C_3'', 2C_6, C_6', 2I, 2S_3, 2S_6 \) | \( C_2, C_3, C_3', C_3'', 2C_6, C_6', 2I, 2S_3, 2S_6 \) |
| \( 1 \) circle: \( \{ k_x = 0 \} \) | \( 1 \) circle: \( \{ k_x = 0 \} \) | \( 2 \) points: \( \pm (0.0,1) \) | \( 2 \) points: \( \pm (0.0,1) \) |
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FIG. 1. (a) Model spectrum with rigid exchange splitting that illustrates a HM FM system. (b) Model spectrum for a HM AFM illustrating that the channels must have different structure. The peak at the Fermi level is merely an artifact of the form and symmetry of the model.
FIG. 2. Total densities of states for each spin direction in the double perovskite compound La$_2$VCuO$_6$. Top panel: parallel alignment of the Cu$^{2+}$ and V$^{4+}$ spins, with exchange splitting of 0.25 eV for the lower lying (Cu) states and 0.5 eV for the higher lying (V) states. Bottom panel: antiparallel alignment of the spins, resulting in a HM AFM system with the Fermi level $E_F$ lying in the gap of the down spin channel.
FIG. 3. The RMS value of the gap function at $T = 0$ relative to the coupling boson frequency cutoff, $\omega_c$, for the singlet BCS case, and for three SSS cases. The coupling strength $\lambda$ is defined in the text. Note that the point nodes of the “1i0” gap, the line nodes of the “001” gap, and the set of nine line nodes for the $\Gamma_1^{(-)}$ case do not affect the RMS gap value drastically.
FIG. 4. The Ginzburg-Landau phase diagram for SSS with $\Gamma_{4,5}$ cubic symmetry has five phases near $T_c$. The cubic group is only partly broken in each of these phases. The notation is explained fully in the text, but for $\Gamma_4$ the gap function is proportional to $\hat{d} \cdot \vec{k}$, where $\hat{d}$ is the vector labelling each phase. The phases at the top of the diagram have point nodes and those at the bottom have line nodes. The phase with $\hat{d} = (1,1,0)$ is only stable on the negative $\beta_{2R}$ axis (see the text). The “×” on the positive $\beta_{2R}$ axis denotes the weak coupling point with a spherical Fermi surface and the interaction (5.38). When the Fermi surface is deformed outward or inward at the diagonals as pictured, the ground state is a phase on the right or left side of the diagram, respectively.