Amplitude or Higgs modes in *d*-wave superconductors

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In Lorentz-invariant systems spontaneously broken gauge symmetry results in three types of fundamental excitations: density excitations, Higgs bosons (amplitude modes), and Goldstone bosons (phase modes). The density and phase modes are coupled by electromagnetic interactions while the amplitude modes are not. In s-wave superconductors, the Higgs mode, which can be observed only under special conditions, has been detected. We show that unconventional d-wave superconductors, such as the high-temperature cuprate superconductors, should have a rich assortment of Higgs bosons, each in a different irreducible representation of the point-group symmetry of the lattice. We also show that these modes have a characteristic singular spectral structure and discuss conditions for their observability.

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The concept of "broken symmetry,"[1] that the symmetry of the vacuum may be lower than the Hamiltonian of a quantum theory, plays an important role in modern physics. A manifestation of this phenomenon is the Higgs boson in particle physics,[2] whose long-awaited discovery appears to have been made. Spurred by some mysterious experimental results,[3] the theory of the oscillation of the amplitude modes of s-wave superconductivity was provided[4] in the 1980s. This is equivalent to the Higgs modes in s-wave superconductors.[5] It was also shown that a necessary condition for this to occur[6] is the emergent Lorentz invariance in the superconducting state while the metallic state and the region just below T_c are manifestly non-Lorentz-invariant.

The order parameter Ψ in s-wave superfluids and superconductors is a complex number. The oscillation of the phase of Ψ is massless at long wavelengths in a neutral superfluid. This phase mode may be understood as the azimuthal oscillation of a particle near the bottom of a Mexican hat potential, depicted in Fig. 1(a). In a charged superconductor, it moves to the frequency of the plasmon in a gauge-invariant theory coupling phase modes to electromagnetism.[7] While very interesting as the W boson in particle physics, it tells nothing new about excitations of the superconducting state. In contrast, the amplitude mode, which oscillates in the radial direction, does not couple to charge and has an excitation gap at long wavelengths equal to twice the superconducting gap 2Δ. This is just where the continuum of particle-hole excitations begins; hence it is heavily damped and usually unobservable. Special situations which lower its energy are therefore required to detect this mode in s-wave superconductors.[4] Interesting related modes have also been discussed in superfluid ^{3}He.[8]

Even before the discussion of amplitude fluctuations in superconductors, Bardasis and Schrieffer[9] showed that electron density fluctuations in angular momentum channels $\ell \neq 0$ may occur for s-wave superconductors as bound states with energy below 2Δ because such ℓ have only short-range interactions. There does not appear to have been any clear evidence in experiments of such collective exciton modes.[10] Many variants of these states have also been predicted to appear in different superconducting compounds.[11–13] We discuss them in Appendix A.

In this paper we show that superconductors with lower symmetries support additional amplitude or Higgs modes labeled by the point-group symmetry in which the deformation of the order parameter occurs.[14] As expected, one of these modes is the conventional s-wave Higgs mode which appears at 2Δ. The other amplitude modes, however, in general, have lower energies than 2Δ. As these additional modes correspond to deformation of the ordered state to different irreducible representations with variable relative phases θ_i, the Higgs modes acquire a characteristic singular two-peak line shape which is derived here.

A very important point about the amplitude modes is that, being chargeless and spinless, external probes do not directly couple to them, just as they do not to the Higgs modes in particle physics. (For discussion of this point, see Appendix A and Ref. 4.) They can only be excited by other excitations which shake the ground state. If such other excitations are coupled to external probes, the amplitude modes only appear by stealing weight from them. So to experimentally identify such modes, there must exist excitations in the normal state whose intensity decreases on transition to the superconducting state and is transferred to the amplitude mode with the sum preserved. Since what shakes the superconducting ground state are generally the normal state excitations which cause it, this also serves as an identification of the fluctuations which are responsible for pairing.[15] This conservation of weight can be used to distinguish the Higgs amplitude modes from the exciton or Bardasis-Schrieffer modes,[9] which can directly couple to external probes, in experiments.

Besides the $U(1)$ gauge symmetry, anisotropic superconductors are also invariant under a point-group symmetry determined by the crystal lattice structure.[16] For definiteness, we consider a two-dimensional unconventional d-wave superconductor with $d_{x^2-y^2}$ ordering on a square lattice, point-group symmetry D_4.[17] The high-temperature cuprate superconductors belong to this category. The nature of the additional amplitude modes is sketched in Fig. 2 and corresponds to excited states with admixtures of additional $d_{x^2-y^2}$, d_{xy}-wave, $g_{xy(x^2-y^2)}$-wave, and $s+g_{(x^2-y^2)^2}$-wave components to the ground state, respectively.

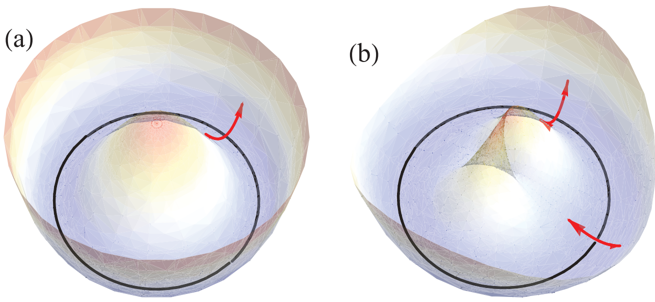

FIG. 1. (Color online) Pictorial representation of the effective potential corresponding to (a) s-wave Higgs mode and (b) additional non-s-wave Higgs modes. The phase mode (black circle) oscillates in the azimuthal direction, whereas the amplitude (Higgs) mode (red curve) oscillates in the radial direction. In (a) the constant curvature of the effective potential results in an angle-independent finite mass gap. In (b) the effective potential plotted for the nonconventional Higgs modes $V(\rho_i,\theta_i) = (a + b\sin^2\theta)(\rho_i^2 - \Delta_i^2)^2$ exhibits twofold symmetry leading to a periodic angular dependent curvature. The non-s-wave amplitude mode results in a more massive fluctuation at $\theta_i = \pi/2$ than $\theta_i = 0$, in contrast with the s-wave Higgs mode. This leads to an angular-dependent energy $\omega(\theta_i)$ with the minimum and maximum occurring at $\theta_i = 0,2\pi$ and $\theta_i = \pi/2,3\pi/2$ respectively.

We represent the ground state and the oscillations about it by the order parameter,

$$\Psi(\mathbf{Q},\mathbf{k}) = \Psi_0(\mathbf{k}) + \delta\Psi(\mathbf{Q},\mathbf{k},\omega)e^{i\theta(\mathbf{Q})}. \qquad (1)$$

$\Psi_0(\mathbf{k})$ is the uniform ground state which we assume to be in the B_{1g}, i.e $(k_x^2 - k_y^2)$, symmetry with phase $\theta = 0$. $\delta\Psi(\mathbf{Q},\mathbf{k},\omega)$ are the amplitude of the deviations representing the collective modes with total center-of-mass momentum $\mathbf{Q}$ and internal momentum $\mathbf{k}$ with phase $\theta(\mathbf{Q})$. At long wavelengths, $\delta\Psi$ may be written as a separable function of $\mathbf{Q}$ and $\mathbf{k}$. The $\mathbf{k}$ dependence is expressed in the four one-dimensional even-parity irreducible representations $(B_{1g},A_{1g},B_{2g},A_{2g})$ of the D_4 point-group symmetry. For notational simplicity, we will represent $\delta\Psi(0,\mathbf{k})$ as linear combinations of $\phi_i(\mathbf{k}) = |\phi_i(\mathbf{k})|\exp(i\theta_i), i = 0,1,2,3$, respectively.

In the limit $\mathbf{Q} = 0$, the field theory is given by the Lagrangian (see Appendix A)

$$\mathcal{L} = \sum_{i=0}^{3} |\partial_t\phi_i|^2 + a_i|\phi_i|^2 - b_i|\phi_i|^4 - \sum_{i<j}\left(c_{ij}|\phi_i|^2|\phi_j|^2 + \frac{d_{ij}}{2}(\phi_i^\star\phi_j - \phi_j^\star\phi_i)^2\right). \qquad (2)$$

We include only second-order time derivatives; this is only valid well below the Ginzburg-Landau regime near T_c, where a first derivative in time representing dissipation dominates and the Higgs mode cannot occur due to lack of Lorentz invariance.[6] We have introduced two distinct set of parameters c_{ij} and d_{ij} in (2) so that the energy of the collective modes depends on the relative phase θ_i between the assumed ground state representation and the others. This is required by symmetry and introduces distinctive features in the spectra of the collective modes as we see below.

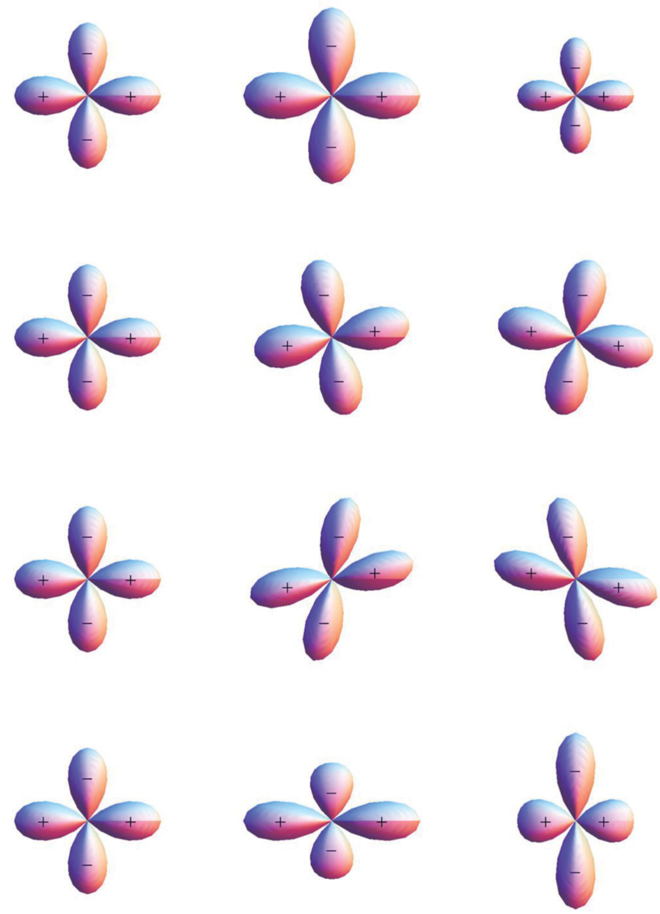

FIG. 2. (Color online) Pictorial representation of the additional Higgs or amplitude modes of the d-wave superconducting order parameter predicted in this paper. Each mode can be labeled by an irreducible representation of the point-group symmetry of the lattice in which the deformation of the order parameter occurs (see text for details). The horizontal direction represents the fluctuations of the order parameter due to the admixture of other symmetries. For the case of $d_{k_x^2-k_y^2}$ order parameter depicted above these amplitude fluctuations are different admixtures of $d_{x^2-y^2}$-wave ("breathing mode"), d_{xy}-wave ("rotating mode"), $g_{xy(x^2-y^2)}$-wave ("clapping mode"), and $s + g_{(x^2-y^2)^2}$-wave ("osculating mode") components to the ground state, labeled from top to bottom.

The equations of motion using (2) give the energy of the collective modes at $\mathbf{Q} = 0$ to be

$$\omega_i(\theta_i) = \pm\sqrt{[c_{i0} + d_{i0}\sin^2(\theta_i)]|\Psi_0|^2 + a_i}; \qquad (3)$$

here θ_i is the relative phase of the $i \neq 0$ order parameters with respect to the ground state order parameter $|\Psi_0|^2 = -a_0/2b_0$. The $(k_x^2 - k_y^2)$ order parameter assumed for Ψ_0 implies $a_0 < 0$ for $T < T_0^c = T^c$ (where T^c is the critical temperature). $a_i's$ $(i \neq 0)$ remain positive as T approaches T^c from below. $c_{ij} > d_{ij} > 0$'s are expected because of the competition between different order parameters. $\omega_0 = \sqrt{4b_0|\Psi_0|^2}$ corresponds to the simple s-wave Higgs mode of the d-wave superconductor and appears at 2Δ. The energies ω_i correspond to fluctuations of the $d_{k_x^2-k_y^2}$ order parameter in which it deforms to other point-group symmetries as depicted in Fig. 2.

The mass ω_i of the modes can be estimated from general considerations and by comparison with the s-wave Higgs mode. In order to compare the energies ω_i with ω_0 one can gain insight by using a two-parameter Landau-Ginzburg energy functional in the parameter subspace (ϕ_0,ϕ_i). The phase diagram in this subspace allows for three broken-symmetry phases (a) $|\phi_0|^2 = -a_0/(2b_0), |\phi_i|^2 = 0$, for $a_0 < 0, a_i > 0$; (b) $|\phi_0|^2 = 0, |\phi_i|^2 = -a_i/(2b_i)$ for $a_0 > 0, a_i < 0$; and a mixed phase (c) $|\phi_0|^2 \neq 0, |\phi_i|^2 \neq 0$ which only appears for $a_i < 0$ and $a_0 < 0$. Since we assume that the broken-symmetry superconducting state has $d_{k_x^2-k_y^2}$ order, we must require that $|a_0| > |a_i|$ for $a_i < 0$ and $a_0 < 0$. In order to avoid a second-order transition to the mixed phase we must satisfy

$$c_{i0} < 2\sqrt{b_0 b_i} \quad \text{and} \quad c_{i0} > 2b_0\frac{|a_i|}{|a_0|}, \tag{4}$$

which establishes an upper and a lower bound on the energies ω_i.

In order to estimate the values for b_i and a_i we assume an attractive potential is dominant for all the irreducible representations,

$$V(\vec{k}-\vec{k}') = V_1 + V_0\alpha_0(\hat{k})\alpha_0(\hat{k}') + V_3\alpha_2(\hat{k})\alpha_2(\hat{k}') + V_4\alpha_0(\hat{k})\alpha_2(\hat{k})\alpha_0(\hat{k}')\alpha_2(\hat{k}'), \tag{5}$$

where $\alpha_0(\hat{k}) = \hat{k}_x^2 - \hat{k}_y^2$ and $\alpha_2(\hat{k}) = \hat{k}_x\hat{k}_y$, with $V_i < 0$ for all values of i and $|V_0| \gg |V_i|$ $(i \neq 0)$. This is a natural assumption for the d_{xy} symmetry, since the difference from $d_{x^2-y^2}$ arises only due to the anisotropy in the density of states, and so also for the $d_{xy(x^2-y^2)}$ case. No such strong argument can be given for the s-wave case and so a repulsive potential is allowed for this case.[18] In the "weak coupling" limit $N_F V_0 \ll 1$, where N_F is the density of states evaluated at the Fermi energy, an estimate for the values of a_i and b_i gives

$$a_i = a_0\frac{V_i}{V_0}\frac{\ln(T/T_i^c)}{(T-T^c)}, \quad b_i = b_0\frac{V_i}{V_0}, \tag{6}$$

for $T \sim T^c$. Since $a_i > 0$ for $T \sim T^c$ the energies ω_i starting initially at a nonzero value decrease in magnitude for temperatures below the transition temperature T^c as $a_i \to 0$ for $T \to T_i^c$, whereas ω_0 increases in magnitude as the temperature is lowered from the transition temperature T^c. This can be seen from a combination of energy expression (3) and the upper bound on the values of $c_{i0} \sim d_{i0}$ which gives $c_{i0} < 2b_0(V_i/V_0)^{1/2} \ll 4b_0$. This indicates that there exist temperatures $T_i^\star < T^c$ where $\omega_i \ll \omega_0$, thus establishing an upper bound on the energies ω_i.

The lower bound in Eq. (4) follows from the condition that energies ω_i are always positive, so that no transition from the chosen ordered phase is allowed. The collective mode energies ω_i for the Higgs modes as a function of a combination of the phenomenological parameters and superfluid density are depicted schematically in Fig. 3(a). An examination of Eq. (3) and subsequent considerations reveals that ω_i at $T = 0$ for $(i \neq 0)$ is simply the difference of the ground-state energy of the ith symmetry from that of the realized $(i = 0)$ symmetry, as could have been guessed at the outset.

Since, at low energies, the quasiparticle density of states in a d-wave superconductor is proportional to the energy, the lower the energy of the modes in Fig. 3(a), the less they are damped. All the Higgs modes in d-wave superconductors, being oscillations of the amplitude of the superconducting condensate, are neutral spin 0 modes. As such they do not couple to the usual external probes. In the case of s-wave superconductors,[4] they could be discovered only through appearing in the self-energy of the superconducting state of phonons which promotes superconductivity, and steal intensity from them. Similarly, for cuprates, we expect that if the broad quantum-critical fluctuations, whose $q \to 0$ limit is visible in Raman scattering, promote superconductivity,[19] they will partially give their weight to the Higgs modes.

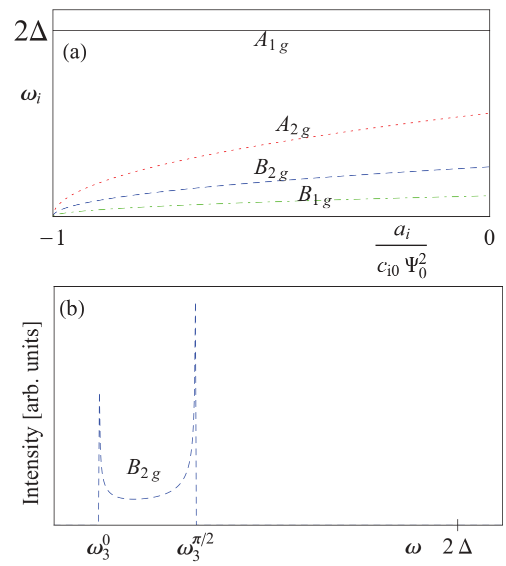

FIG. 3. (Color online) (a) Schematic behavior of the energies for the additional Higgs modes at $\theta_i = 0$ as a function of the coupling constants and superfluid density $a_i/c_{i0}|\Psi_0|^2$ at $T = 0$. The modes are labeled by their Raman scattering geometry, the black (solid) line corresponds to the rotationally symmetric A_{1g}-Higgs mode, whereas the red (dotted), blue (dashed), and green (dot-dashed) lines correspond to the additional A_{2g}-, B_{2g}-, B_{1g}-Higgs modes (see text for details). We have assumed an attractive potential in all the irreducible representations. (b) Schematic representation of the line shape associated with the "clapping" B_{2g}-Higgs mode (chosen arbitrarily) indicating the energy continuum and square-root singularities at the edges of the energy spectrum $\omega_3(0)$ and $\omega_3(\pi/2)$.

Elementary considerations indicate that ω_2 or the breathing mode occurs in the s-wave or A_{1g} symmetry because for it $\delta\Psi$ also has $(x^2 - y^2)$ symmetry, the rotating mode occurs in the A_{2g} symmetry because for it $\delta\Psi$ has xy symmetry, the clapping mode occurs in the B_{2g} symmetry because for it $\delta\Psi$ has $xy(x^2 - y^2)$ symmetry, and the osculating mode occurs in the B_{1g} symmetry because for it $\delta\Psi$ has s-wave symmetry. The line shapes, which can be calculated from Eq. (3), exhibit a two-peak structure with square-root singularities at the edges of the energy spectrum as shown in Fig. 3(b) (see Appendix C). This line shape is characteristic of the additional amplitude modes predicted in this paper which can further distinguish these modes from the exciton modes. The actual observation of the A_{1g} mode will likely occur as a sharp peak below 2Δ through coupling to the continuum. Indeed a mysterious intense mode in the A_{1g} channel has already been detected.[20]

In Appendix B we deduce the Lagrangian for the gradient terms to derive the leading $\mathbf{Q}$ dependence of the energies. We find that there are interesting couplings between phase and amplitude modes, which are not influenced by Coulomb interactions, because counterflow in the excited states of supercurrents in two different symmetries keeps the system charge neutral. However, to quadratic order in $\mathbf{Q}$, the energy spectrum $\omega_i(\theta_i)$ remains unchanged due to this coupling, only acquiring a quadratic dependence in the wave vector $\mathbf{Q}$ [see Eq. (10) in Appendix B]. Any effects of this coupling appear beyond quadratic order in $\mathbf{Q}$.

The low-energy physics of many condensed matter systems (lattice bosons near a Mott transition,[21] antiferromagnets,[22] incommensurate charge-density waves, and superconductors[23]), close to a quantum critical point, is captured by a Lorentz invariant critical theory. One consequence of spontaneous breaking of a continuous symmetry in a Lorentz-invariant local gauge theory is the appearance of bound states; one could call such bound states the "Higgs" modes. We show that when such symmetries are endowed with an additional discrete space symmetry, a rich assortment of Higgs modes should be present. The number of these Higgs modes should be equal to the number of irreducible representations of the discrete point-group symmetry consistent with any internal symmetries (such as spin or valley) of the system.

We wish to thank Yuan Li and Alan Sacuto for discussion of Raman scattering results.

APPENDIX A: COLLECTIVE MODES IN SINGLET SUPERCONDUCTORS

In describing superconducting order and its excitations, for the purposes of our discussion it is prudent to express the Hamiltonian in the form $\mathcal{H} = \mathcal{H}_{BCS} + \mathcal{H}_{\text{int}}$ with

$$\mathcal{H}_{BCS} = \sum_{\mathbf{k}} \psi_{\mathbf{k}}^{\dagger}(\epsilon_k - \Delta_k \hat{\tau}_1)\psi_{\mathbf{k}}, \tag{A1}$$

where we take Δ_k real, $\hat{\tau}_i$ are the Pauli matrices $i = 1,2,$ and 3, and $\psi_{\mathbf{k}}^{\dagger} = (c_{\mathbf{k}\uparrow}^{\dagger}, c_{-\mathbf{k}\downarrow})$ is the Nambu-Gorkov spinor. The Hamiltonian describing the residual interaction can be expressed as

$$\mathcal{H}_{\text{int}} = \frac{1}{2L^2}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} v_{\mathbf{q}}(\psi_{\mathbf{k}+\mathbf{q}}^{\dagger}\hat{\tau}_3\psi_{\mathbf{k}})(\psi_{\mathbf{k}'-\mathbf{q}}^{\dagger}\hat{\tau}_3\psi_{\mathbf{k}'}) + \sum_{\mathbf{k}} \Delta_{\mathbf{k}}\psi_{\mathbf{k}}^{\dagger}\hat{\tau}_1\psi_{\mathbf{k}}, \tag{A2}$$

where $v_{\mathbf{q}}$ is the renormalized density-density interaction that includes the effect of phonons. To further simplify our discussion we decompose the density-density interaction in angular momentum channels l,

$$v(\mathbf{q}) = \sum_{L} V_l \sum_{m=-l}^{m=l} Y_{lm}^{\dagger}(\theta,\phi)Y_{lm}(\theta,\phi), \tag{A3}$$

and assume that the superconducting state forms in the angular momentum channel of the ground state L (for example, in s-wave superconductors $L = 0$). Since we are working within a thin energy shell around the Fermi surface the renormalized interactions for a given channel V_l can be attractive or repulsive. Next, we describe all excitations that can exist in conventional superconductors.

TABLE I. Excitations.

Modes	Channel	Type
Density	$\hat{\tau}_3$	$e\sum_{\sigma} c_{k,\sigma}^{\dagger}c_{k,\sigma}$
Phase	$\hat{\tau}_2$	$c_{k,\sigma}^{\dagger}c_{-k,-\sigma}^{\dagger} - c_{k,\sigma}c_{-k,-\sigma}$
Amplitude	$\hat{\tau}_1$	$c_{k,\sigma}^{\dagger}c_{-k,-\sigma}^{\dagger} + c_{k,\sigma}c_{-k,-\sigma}$

In conventional s-wave superconductors there are three types of long-wavelength fluctuations: the electron-density fluctuations ρ, the fluctuation of the phase ϕ, and the fluctuation in the amplitude of the superconducting order parameter Δ. In the Nambu-Gorkov notation used above the electron density fluctuations are in the $\hat{\tau}_3$ channel, the phase fluctuations, which are coupled to the density fluctuations, appear in the $\hat{\tau}_2$ channel, whereas the amplitude fluctuations appear in the $\hat{\tau}_1$ channel. In the long-wavelength limit ($q \to 0$) the excitations are listed in Table I. From now on we use capital L for the ground-state angular momentum and lowercase l to denote the relative angular momentum associated with the excitation.

In the $L = 0$ channel the electronic density and the superconducting phase excitations are coupled to the long-range part of the Coulomb interaction and are therefore pushed up to the plasmon energy.[7,24] For s-wave superconductors Bardasis and Schriffer[9] showed that density excitations can occur in angular momentum channels $l \neq 0$ different from the ground-state pairing channel $L = 0$. Due to the residual density-density attractive (repulsive) interactions with a coupling strength proportional to V_l, the spectrum might contain the bound state with Cooper pairs or the excitonic mode below 2Δ. Since these excitation have an angular momentum quantum number $l \neq 0$, the role of Coulomb interactions is drastically reduced as the long-range Coulomb interaction is decoupled. These modes are discussed explicitly in Tutto and Zawadawski[12] for Nb_2Se, s-wave superconductors. They have also been discussed in the context of pnictides by Scalapino and Devereaux.[13] It should also be mentioned that this mode has not been observed in experiments, most likely as the binding energy of the bound pairs is small.

It is interesting to note that the different angular momenta excitations in the normal state correspond to the Landau-Pomeranchuk excitations. In the long-wavelength ($q \to 0$) limit, they correspond to distortion of the Fermi surface in different angular momentum channels. In the superconducting state due to the presence of a gap, they have bound-state parts. These excitations directly couple to light probes, and can exist as sharp excitations for s-wave superconductors. For non-s-wave superconductors $L \neq 0$ these modes will be overdamped. Klein and Dierker[25] considered the effect of the penetration depth of light which can lead to mixing of angular momentum channels. In a normal metal surface plasmon excitations result from this. In s-wave superconductors, these surface plasmons may appear as sharp peaks if their energy is below the energy gap 2Δ. However, in non-s-wave

TABLE II. Collective modes.

Modes	Pairing momentum	Relative momentum	Name	Energy	Damping
Phase, ϕ	$L = 0$		Goldstone	ω_p	
Density, ρ	$L = 0$	$l = 0$	Plasmon	ω_p	
	$L = 0$	$l \neq 0$	Bardasis-Schrieffer	$<2\Delta$	
	$L \neq 0$	$l = 0$	Plasmon	ω_p	
	$L \neq 0$	$l \neq 0$	Bardasis-Schrieffer	$<2\Delta$	Overdamped
Amplitude, Δ	$L = 0$	$l = 0$	Higgs	2Δ	
	$L = 0$	$l \neq 0$		$<2\Delta$	Overdamped
	$L \neq 0$	$l = 0$	Higgs	2Δ	
	$L \neq 0$	$l \neq 0$		$<2\Delta$	Depends on point group

superconductors they are unlikely to appear as sharp bound states because of the continuum of particle-hole excitations.

In the 1980s Littewood and Varma[4] realized that, other than the Nambu-Goldstone mode, a massive and completely orthogonal mode results from the excitations of the order parameter Δ_k. This is similar to the Higgs mode in particle physics. For s-wave superconductors this mode has the energy 2Δ. In our language it appears as a pole in the Bethe-Salpeter equation in the $\hat{\tau}_1$ or amplitude channel. As mentioned before, these modes modes do not couple to usual probes and are hard to detect. However, Littlewood and Varma[4] showed that this mode can be detected in Nb_2Se. In Nb_2Se the phase transition to superconductivity goes through an intermediate charge-density-wave (CDW) phase. In this system the CDW phonon modulates the CDW amplitude, which is coupled to the superconducting order parameter, by changing the number of electrons available for superconducting order. Furthermore, due to the close proximity of the phonon pole (which appears at $\approx 5\Delta$) this amplitude mode can be observed in the renormalized phonon propagator by Raman spectroscopy. Experimentally, the situation is very different from the excitonic mode as the Higgs mode has spin zero and is charge neutral so it does not directly couple to light. It does, however, couple indirectly to light and appears as a pole in the phonon propagator.

For s-wave superconductors $L = 0$, one can imagine amplitude excitation in relative angular momentum channels $l \neq 0$. This can be done by calculating the pole in the Bethe-Salpeter equation for interactions in the respective angular momentum channel. However, these amplitude modes will couple to the phase of the superconducting order parameter ϕ. Since the phase couples to the density the modes will couple to external probes and will be overdamped.

In our current work we have extended the concept of this amplitude mode to systems which are additionally invariant under some point-group symmetry, such as d-wave superconductors $L = 2$. We analyze the excitations of the order parameter in different irreducible representations of the point-group symmetry of the lattice by expressing

$$\Delta_{\mathbf{k}} = \sum_{\Gamma_i} \Delta_\Gamma(\Gamma_i), \tag{A4}$$

where Γ_i are the irreducible representations of the point-group symmetry which are consistent with the other additional spin and valley symmetries. Since we are constrained by the point-group symmetry we only have a finite number of these modes. Contrary to the Bardasis and Schrieffer mode or generalization thereof, these modes are in the $\hat{\tau}_1$ channel. These amplitude modes are orthogonal to those predicted earlier. Furthermore, unlike the case of s-wave superconductors, whether these modes couple to phase depends on the point group in question. For example, in the case of D_4 point-group symmetry considered, only the A_{1g}-Higgs couples to the phase.

In our current work we have explored consequences of these excitations and discussed their experimental detection based on symmetry grounds. In order to put our predictions in perspective we have summarized the known collective modes in superconductors in Table II.

APPENDIX B: CONSTRUCTION OF THE ENERGY FUNCTIONAL

Since the free energy originates from the Hamiltonian, it must be invariant under the symmetry group of the Hamiltonian. In the case of a d-wave superconductor the phenomenological Landau-Ginzburg action should satisfy the $U(1)$ gauge symmetry of the order parameter along with the point-group symmetry D_4 of the lattice.[16] In the following we construct the most general energy functional invariant under the $U(1) \otimes D_4$ symmetry.

In the presence of a crystal field the symmetry group of the Hamiltonian contains the lattice point-group symmetry. We use the fact that the eigenfunction space of every single eigenvalue of the microscopic BCS gap equation forms a basis of an irreducible representation of the symmetry group of the Hamiltonian. In the case of the D_4 point group, which consists of transformations of the square, there are five irreducible representations. The even parity irreducible representations contain the following basis functions:[17]

$$\begin{aligned}
&A_{1g} \quad 1, 2\left(k_x^2 - k_y^2\right)^2 - 1,\\
&A_{2g} \quad k_x k_y\left(k_x^2 - k_y^2\right),\\
&B_{1g} \quad k_x^2 - k_y^2,\\
&B_{2g} \quad k_x k_y,\\
&E_g \quad (k_x k_z, k_y k_z),
\end{aligned}$$

where E corresponds to a 2-dimensional representation which we state for completeness. Since we restrict our system to two dimensions, $k_z = 0$. The order parameter can be expressed in

TABLE III. Invariant terms.

$\|\phi_0\|^2$	$\|\phi_1\|^2$	$\|\phi_2\|^2$	$\|\phi_3\|^2$
$\|\phi_0\|^4$	$\|\phi_1\|^4$	$\|\phi_2\|^4$	$\|\phi_3\|^4$
$\|\phi_0\|^2\|\phi_1\|^2$	$\|\phi_0\|^2\|\phi_2\|^2$	$\|\phi_0\|^2\|\phi_3\|^2$	$\|\phi_1\|^2\|\phi_2\|^2$
$\|\phi_1\|^2\|\phi_3\|^2$	$\|\phi_2\|^2\|\phi_3\|^2$		
$\phi_0^2(\phi_1^\star)^2 + \text{c.c.}$	$\phi_0^2(\phi_2^\star)^2 + \text{c.c.}$	$\phi_0^2(\phi_3^\star)^2 + \text{c.c.}$	$\phi_1^2(\phi_2^\star)^2 + \text{c.c.}$
$\phi_1^2(\phi_3^\star)^2 + \text{c.c.}$	$\phi_2^2(\phi_3^\star)^2 + \text{c.c.}$		

term of the irreducible representations outlined above,

$$\Psi(\mathbf{Q},\mathbf{k}) = \phi_0(\mathbf{Q})\left(k_x^2 - k_y^2\right) + \phi_1(\mathbf{Q}) + \phi_2(\mathbf{Q})(2k_xk_y) + \phi_3(\mathbf{Q})\left[2k_xk_y\left(k_x^2 - k_y^2\right)\right], \tag{B1}$$

where $\mathbf{Q} = (Q_x, Q_y)$ denote the center of mass momentum of the Cooper pair. The set $\{\phi_i\}$ live in the different even-parity representations $(B_{1g}, A_{1g}, B_{2g}, A_{2g})$, labeled by $i = 0,1,2,3$, respectively.

Time-reversal symmetry and gauge invariance requires that the energy functional must be invariant under $\phi_i \to \phi_i^*$ and $\phi_i \to \phi_i e^{i\theta}$. Hence, only real even-ordered products of ϕ_i's can occur in the expansion of the free energy. The point-group symmetry imposes that the energy functional must only contain terms that belong to the trivial A_{1g} representation.[16] The invariant terms allowed by the $D_4 \otimes U(1)$ symmetry, up to fourth order, are given in Table III.

Terminating the expansion at fourth order we find that the free-energy functional has the form

$$\mathcal{L} = \sum_{i=0}^{3} |\partial_t\phi_i|^2 + a_i|\phi_i|^2 - b_i|\phi_i|^4 - \sum_{i<j}\left(c_{ij}|\phi_i|^2|\phi_j|^2 + \frac{d_{ij}}{2}(\phi_i^\star\phi_j - \phi_j^\star\phi_i)^2\right). \tag{B2}$$

Because the fields ϕ_i belong to different irreducible representations they do not couple at the quadratic level, but can certainly couple at the quartic level. Thermodynamic stability imposes restrictions on the coefficients which parametrize this energy functional; these constraints are used to determine the upper and lower bounds on the excitation energies. Since the orbital angular momentum is conserved modulo 4, the last term is required in the energy functional. The energy functional is written to highlight this feature; the importance of the last term becomes apparent in the next section.

Now let us write down the derivative terms. Landau-Ginzburg formalism also allows spatial variations of the order parameter; to satisfy the $U(1)$ gauge and lattice symmetries one must combine the gradient operator $\nabla = (\nabla_X, \nabla_Y)$ with the order parameters ϕ_i into invariant second-order terms that transform in the A_{1g} representation. Since the derivative operator belongs in the two-dimensional E representation, the A_{1g}-invariant derivative terms allowed for the D_4 point-group symmetry are

$$F_{\text{grad}} = \sum_i |\nabla\phi_i|^2 + \nabla_X\phi_1^\dagger\nabla_X\phi_0 - \nabla_Y\phi_1^\dagger\nabla_Y\phi_0 + \text{c.c.} + \nabla_X\phi_2^\dagger\nabla_X\phi_3 - \nabla_Y\phi_2^\dagger\nabla_Y\phi_3 + \text{c.c.} \tag{B3}$$

Derivative terms of the form $\nabla_X\phi_1^\dagger\nabla_Y\phi_2 + \nabla_Y\phi_1^\dagger\nabla_X\phi_2 + \text{c.c.}$, which also belong in the A_{1g} representation, are excluded as they violate inversion symmetry. These terms are important in the presence of an external magnetic field, which acts on the center of mass of the Cooper pair. Combining the gradient terms with the energy functional gives the field theory describing the $\mathbf{Q} \neq 0$ collective modes:

$$\mathcal{L}_{\text{grad}} = \sum_{i=1}^{4} |\nabla\phi_i|^2 + \nabla_x\phi_1^\dagger\nabla_x\phi_0 - \nabla_y\phi_1^\dagger\nabla_y\phi_0 + \text{c.c.} + \nabla_x\phi_2^\dagger\nabla_x\phi_3 - \nabla_y\phi_2^\dagger\nabla_y\phi_3 + \text{c.c.} + \mathcal{L}. \tag{B4}$$

The collective mode energies form a continuum, and in the presence of spatial variations of the order parameter allow coupling of phase and amplitude modes, which we work out in the following section. This coupling is due to the anomalous derivative terms whose presence is a direct consequence of the D_4 point-group symmetry of the lattice.

APPENDIX C: CALCULATION OF THE COLLECTIVE MODES

To calculate the energy dispersion of the normal mode fluctuations of the $d_{k_x^2-k_y^2}$ order parameter we write $\phi_0 = [|\Psi_0| + \rho_0(\mathbf{Q})]e^{i\theta(\mathbf{Q})}$ and $\phi_i = \rho_i(\mathbf{Q})e^{i\theta_i(\mathbf{Q})}$ for $(i \neq 0)$. Expanding Eq. (2) to quadratic order in the amplitude $\rho_i(\mathbf{Q})$ and phase $\theta_i(\mathbf{Q})$ fields gives

$$\delta\mathcal{L} = \sum_{i\neq 0}[\omega^2 - a_i - (c_{i0} + d_{i0}\sin^2\theta_i)|\Psi_0|^2]\rho_i^2 + (\omega^2 - 4b_0|\Psi_0|^2)\rho_0^2 + |\Psi_0|^2(\omega\theta)^2 + \cdots, \tag{C1}$$

where "$\cdots$" denotes quartic or higher order terms in the amplitude and phase fields. The phase mode θ is gapless; similarly to the case of s-wave superconductors it gets pushed to the plasmon energy due its to coupling with charge.[7] The collective mode energies for the non-s-wave amplitude modes $\omega_i(\theta_i)$ $(i \neq 0)$ acquire a dependence on the relative phase differences θ_i, resulting in a continuum,

$$\omega_i(\theta_i) = \pm\sqrt{[c_{i0} + d_{i0}\sin^2(\theta_i)]|\Psi_0|^2 + a_i}, \tag{C2}$$

corresponding to an admixture of the ordered state ϕ_0 with the field ϕ_i $(i \neq 0)$. The s-wave Higgs mode energy $\omega_0 = \pm\sqrt{4b_0|\Psi_0|^2}$ appears at 2Δ as expected. The dependence of $\omega_i(\theta_i)$ on the relative phase difference θ_i leads to singular features in the density of states, which can be easily calculated,

$$\rho_i(\omega) = \frac{2\omega\left[\Theta\left(\omega^2 - \omega_i^2(0)\right) + \Theta\left(\omega_i^2(\pi/2) - \omega^2\right)\right]}{\sqrt{\left[\omega^2 - \omega_i^2(0)\right]\left[\omega_i^2(\pi/2) - \omega^2\right]}}. \tag{C3}$$

The spectral line shape of the additional Higgs modes exhibit a two-peak structure with square-root singularities at the edges of the energy continuum $\omega_i(0)$ and $\omega_i(\pi/2)$. As we argue in the paper, these additional modes and their distinct spectral signatures can be identified through Raman spectroscopy.

Now we address the modification of the collective mode energies for $\mathbf{Q} \neq 0$, i.e., the result of spatial variation of the order parameters. As before expressing the fields in terms of amplitude and phase, expanding the action about the $d_{k_x^2-k_y^2}$ order parameter, and keeping only quadratic terms in the amplitude and phase modes gives

$$\begin{aligned}\delta\mathcal{L}_{\rm grad} = &\left[\omega^2 - \left(Q_x^2+Q_y^2+\omega_0^2\right)\right]\rho_0^2 + 2\cos(\theta_{01})\left(Q_x^2-Q_y^2\right)\rho_1\rho_0 + \left\{\omega^2 - \left[Q_x^2+Q_y^2+\omega_1^2(\theta_1)\right]\right\}\rho_1^2 + \cdots \\ &+\left\{\omega^2 - \left[Q_x^2+Q_y^2+\omega_2^2(\theta_2)\right]\right\}\rho_2^2 + 2\cos(\theta_{23})\left(Q_x^2-Q_y^2\right)\rho_2\rho_3 + \left\{\omega^2 - \left[Q_x^2+Q_y^2+\omega_3^2(\theta_3)\right]\right\}\rho_3^2 + \cdots \\ &+|\Psi_0|^2\left[\omega^2-\left(Q_x^2+Q_y^2\right)\right]\theta_0^2 + 2\sin(\theta_{01})|\Psi_0|\rho_1\left(Q_x^2-Q_y^2\right)(\theta_1+\theta_0)+\cdots,\end{aligned} \tag{C4}$$

where "$\cdots$" denotes higher order terms and the ω_i's are the collective mode frequencies defined in (C2). Due to the fact that the "breathing" and "osculating" modes leave the symmetries of the square undisturbed, whereas the "clapping" and "rotating" modes deform the square, the two pairs of modes are coupled. Assuming that $\theta_i = 0$ the collective mode energies of the "breathing" and "osculating" amplitude modes ρ_1 and ρ_0 can be analytically expressed as

$$\omega_\pm^2 = \mathbf{Q}^2 + \tfrac{1}{2}\left(\omega_1^2+\omega_2^2\right) \pm \sqrt{\left(Q_x^2-Q_y^2\right)^2 + \tfrac{1}{2}\left(\omega_1^2-\omega_2^2\right)^2}, \tag{C5}$$

where $\omega_i = \omega_i\ (\theta_i = 0)$. The collective mode energies for the rotating and clapping amplitude modes ρ_2 and ρ_3 can be recovered by substituting $\omega_1 \to \omega_2$ and $\omega_0 \to \omega_3$ in the above expression. In the long-wavelength limit, the behavior of these modes remains isotropic to quadratic order in $\mathbf{Q}$,

$$\omega_+ = \omega_1 + \frac{\mathbf{Q}^2}{2\omega_1} + \cdots, \quad \omega_- = \omega_2 + \frac{\mathbf{Q}^2}{2\omega_2} + \cdots, \tag{C6}$$

where "$\cdots$" denotes higher order anisotropic terms.

As before any relative phase differences θ_i modify collective mode energies at $\mathbf{Q} = 0$ which become θ_i dependent. Any modification due to spatial gradients is difficult to express in a simple analytic form; therefore we only address the long-wavelength behavior in the following. The collective mode energies for the rotating and clapping modes in the presence of the spatial variations, to quadratic order in $\mathbf{Q}$, can be recovered from (C6) by substituting $\omega_i \to \omega_i(\theta)$. Since the energy of the Goldstone mode which lives at the plasmon energy is large,[7] to quadratic order in $\mathbf{Q}$, the energy for the osculating mode can also be recovered from (C6) by the substitution $\omega_i \to \omega_i(\theta)$. Therefore, in the long-wavelength limit all energies, except for the s-wave Higgs mode, can be recovered from (C6) by the substitution $\omega_i \to \omega_i(\theta)$.

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