Amperean Pairing Instability in the U(1) Spin Liquid State with Fermi Surface and Application to κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

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Recent experiments on the organic compound κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ raise the possibility that the system may be described as a quantum spin liquid. Here we propose a pairing state caused by the "Amperean" attractive interaction between spinons on a Fermi surface mediated by the U(1) gauge field. We show that this state can explain many of the observed low temperature phenomena and discuss testable consequences.

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The organic compound κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ shows great promise as the first candidate [1,2] which realizes the spin liquid state in dimension greater than one [3]. It is a quasi-two-dimensional material where each plane forms a half filled triangular lattice. While it is a Mott insulator, there is no magnetic long range order. The uniform spin susceptibility and the spin lattice relaxation rate $1/T_1T$ are finite in the zero temperature limit [1,4]. Recently, a specific heat measurement was reported which extrapolates to a linear T coefficient γ [5]. The γ and spin susceptibility form a Wilson ratio close to unity. These are properties usually associated with metals rather than insulators. While an alternative interpretation in terms of Anderson localization has been proposed, we find that the variable range hopping fit to the resistivity [4], when combined with the density of states derived from γ, implies a localization length of 0.9 lattice spacing. Such a short localization requires very strong disorder, which make this interpretation implausible.

Theoretically, the existence of the spin liquid state has been suggested from the studies of the Heisenberg model extended to include ring exchange [6,7] and the Hubbard model [8–10] on the triangular lattice on the insulating side of the Mott transition. In the spin liquid state, the low energy effective theory becomes the U(1) gauge theory coupled with a spinon which forms a Fermi surface [9]. The spinon carries only spin but not charge, and it contributes to the specific heat and thermal conductivity even in the insulating state. The system of the gapless spinon and the gauge field is a non-Fermi liquid state [11,12] and exhibits singular temperature dependence of a specific heat coefficient $\gamma \sim T^{-1/3}$. However, recent specific heat measurement does not show this singular behavior [5]. Moreover, there exists a kink in the specific heat around 6 K, which suggests that there is a peak in the electronic specific heat if the phonon part is assumed to be smooth. Around the same temperature, the uniform susceptibility also shows a sharp drop before it saturates to a finite value in the zero temperature limit. These suggest that there is a phase transition or a crossover from the high temperature phase which is described by the non-Fermi liquid state to a low temperature Fermi liquid state. In the present Letter, we propose that the low temperature phase may be understood as a novel paired state of spinons that arises out of the U(1) spin liquid state with spinon Fermi surface.

Inspired by Ampere's discovery that two wires carrying parallel currents attract each other [13], we note that the interaction is attractive when the two spinons have parallel momenta. We therefore explore the possibility of pairing two spinons on the same side of the Fermi surface. The resulting state has a number of properties that are attractive for an explanation of the experiments in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. In particular, the pairing gaps out the gauge field so that the unpaired portion of the Fermi surface gives a linear specific heat at low temperature. We discuss various consequences of our proposal that may be tested in future experiments.

Consider the system of a spinon with the Fermi surface interacting with a (noncompact) U(1) gauge field in 2 + 1D:

$$\mathcal{L} = \psi_\sigma^*(\partial_0 - i\phi - \mu)\psi_\sigma + \frac{1}{2m}\psi_\sigma^*(-i\nabla - \mathbf{a})^2\psi_\sigma + \frac{1}{4g^2}f_{ij}f_{ij}. \quad (1)$$

Here x_0 is the imaginary time and $\mathbf{x} = (x_1, x_2)$ is the $2d$ spatial coordinate. ψ_σ is the spinon field with spin σ, and μ is the chemical potential. Repeated spin indices are summed. $a_i = (\phi, \mathbf{a})$ is the U(1) gauge field, with $i = 0, 1, 2$, f_{ij} is the field strength tensor, and g is the gauge coupling. We expect g^2 to be proportional to the charge gap and will ignore the last term in Eq. (1) in the following. We choose the Coulomb gauge where $\nabla \cdot \mathbf{a} = 0$. We are interested in the stability of a local Fermi surface in the momentum space, and we focus on a patch of Fermi surface which is centered at a momentum $\mathbf{Q}$, with $|\mathbf{Q}| = k_F$. Therefore, we integrate out the spinon fields except for those in the patch. The massless spinons screen the temporal gauge field ϕ. However, the transverse gauge field is not screened, and it can mediate a long range interaction between spinons. The dressed propagator of the transverse gauge field is given by

$$D(k) = \frac{1}{\gamma_o \frac{|k_0|}{\sqrt{|\mathbf{k}|^2 + (k_0/\bar{v}_F)^2} + |k_0|/\bar{v}_F} + \chi_d |\mathbf{k}|^2}, \qquad (2)$$

where $k = (k_0, \mathbf{k})$ is the energy-momentum vector, and $\gamma_o = \bar{v}_F \bar{m}/\pi$ and $\chi_d = 1/12\pi\bar{m}$ are the Landau damping and diamagnetic susceptibility, respectively. $\bar{v}_F$ is the Fermi velocity and $\bar{m}$ is the mass, which are averaged over the Fermi surface which has been integrated out. The transverse gauge field mediates an interaction between spinons

$$S_{\text{int}} = -\frac{1}{2V\beta} \sum_{p_1, p_2, k} D(k) \times \frac{(\mathbf{p}_1 \times \hat{\mathbf{k}}) \cdot (\mathbf{p}_2 \times \hat{\mathbf{k}})}{m^2} \psi^*_{\sigma p_1 + k} \psi_{\sigma p_1} \psi^*_{\sigma' p_2 - k} \psi_{\sigma' p_2}, \qquad (3)$$

where V is the volume of the system, $\beta = 1/(k_B T)$, and m is the mass of the spinon in the vicinity of $\mathbf{Q}$ on the Fermi surface. Motivated by the Amperean attraction, consider the pairing of two spinons with energy-momenta $p_1 = Q + p$, $p_2 = Q - p$, where $2Q$ is the net energy-momentum of the pair with $Q_0 = 0$, $|\mathbf{Q}| = k_F$, and p is the relative energy-momentum, with $|\mathbf{p}| \ll |\mathbf{Q}|$. Note that the pair is made of two spinons on the same side of the Fermi surface, and it carries a large net momentum of $2k_F$. We decompose the two body interaction into a pairing channel by introducing the Hubbard Stratonovich field $\Delta_p^{\sigma'\sigma}$:

$$S_{\text{int}} = \frac{1}{2V\beta} \sum_{p, p'} v(p' - p) \times [\Delta_{p'}^{\sigma'\sigma *} \Delta_p^{\sigma'\sigma} - \Delta_{p'}^{\sigma'\sigma *} \psi_{\sigma' Q + p} \psi_{\sigma Q - p} - \text{c.c.}], \qquad (4)$$

where $v(k) = (|\mathbf{Q} \times \hat{\mathbf{k}}|^2/m^2) D(k)$, and we used $(\mathbf{Q} + \mathbf{p}) \times \hat{\mathbf{k}} \approx \mathbf{Q} \times \hat{\mathbf{k}}$. Pairing may occur in the singlet channel, i.e., $\Delta_p^{\uparrow\downarrow} = \Delta_p$, $\Delta_p^{\downarrow\uparrow} = -\Delta_{-p}$, and $\Delta_p^{\uparrow\uparrow} = \Delta_p^{\downarrow\downarrow} = 0$, in which case Δ_p is an even function of $\mathbf{p}$, or the triplet channel, where Δ_p is odd in $\mathbf{p}$. Now we integrate out the rest of the spinon field to obtain the Landau-Ginzburg free energy density [14]:

$$f[\Delta] = \Delta^\dagger (v - v\Pi v)\Delta + O(\Delta^4). \qquad (5)$$

Here every product is a contraction of energy-momentum indices with a measure $\frac{1}{V\beta}$. Δ is a vector with component Δ_p, and v and Π are matrices with elements $v_{p',p} = v(p' - p)$ and $\Pi_{p',p} = V\beta g(Q + p) g(Q - p) \delta_{p',p}$, respectively. $g(p)$ is the spinon propagator given by $g(p) = 1/\{i[p_0 + \lambda |p_0|^{2/3} \text{sgn}(p_0)] + \epsilon_{\mathbf{p}}\}$, with $\lambda = v_F / 2\pi\sqrt{3}\chi_d^{2/3}\gamma_o^{1/3}$ and $\epsilon_{\mathbf{p}}$ is the spinon energy dispersion. Here v_F is the Fermi velocity at the patch, which generally differs from the averaged one ($\bar{v}_F$).

The system is unstable against developing pairing amplitude when an eigenvalue of the kernel $(v - v\Pi v)$ becomes zero or negative. Defining $\Phi = v\Delta$, we write the integral eigenvalue equation at zero temperature:

$$E\Phi(p) = \int \frac{dp'}{(2\pi)^3} v(p - p') g(Q + p') g(Q - p') \Phi(p'), \qquad (6)$$

where E is the eigenvalue and Φ is the eigenvector. Along the direction of the eigenvector, the free energy density becomes $f[\Delta] \approx \Delta^\dagger (1 - v\Pi)\Phi = (1 - E)\Delta^\dagger v \Delta$, and the system becomes unstable if $E > 1$. First, we approximately solve the equation analytically by guessing an ansatz for the eigenvector. Then we will check the validity of the analytic solution by solving the equation numerically without assuming a specific form of the eigenvector. We first consider singlet pairing.

In order to guess the form of the eigenvector, we determine the important region of integration for $\mathbf{p}'$ in Eq. (6). If the pairing interaction were instantaneous and the spinon did not have the frequency-dependent self-energy correction, the p_0' integration would impose the constraint that both of the constituent spinons of a pair should be on the outside of the Fermi surface, that is, $|v_F p'_\parallel| < p'^2_\perp/2m$, where $p'_\parallel$ ($p'_\perp$) is the momentum along (perpendicular to) the $\mathbf{Q}$ as is shown in the bottom inset in Fig. 1. In the presence of the frequency-dependent interaction and spinon self-energy, the sharp constraint is smeared out. However, the dominant contribution of the momentum integration still comes from the region $|v_F p'_\parallel| < p'^2_\perp/2m$, which is denoted as the shaded area in the bottom inset in Fig. 1. This has been checked by performing a numerical integration of p_0'. Knowing the important region for $\mathbf{p}'$, we consider an approximate ansatz $\Phi(p_0, p_\perp, p_\parallel) = \tilde{\Phi}(p_0, p_\perp)\Theta(p_\perp^2/m - |v_F p_\parallel|)$, where we take the range

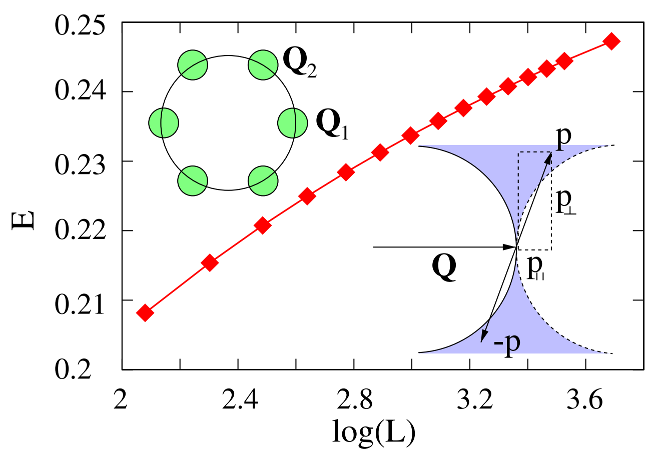

FIG. 1 (color online). The largest eigenvalue of $M(p, p')$ as a function of the system size L where the mesh of the discrete energy and momentum is given by $\Delta k = 2\pi/L$. Top inset: Schematic picture of partial gapping of the spinon Fermi surface. Bottom inset: Definition of $p_\parallel$ and $p_\perp$.

of $p_\parallel$ twice larger than $|v_F p_\parallel| < p_\perp^2/2m$ in order to take into account the smearing effect. This ansatz is singular at the curve $p_\parallel = p_\perp^2/m$, which includes the point $p_\parallel = p_\perp = 0$. A better treatment will smear out this singularity. For this ansatz, the typical momentum transfer $k = p' - p$ also satisfies the condition $|k_\parallel| < k_\perp^2/k_F \ll k_\perp$ and we can ignore the $k_\parallel$ dependence in the gauge propagator. We can also replace $|\mathbf{Q} \times \hat{\mathbf{k}}|^2/m^2$ by v_F^2 because $\mathbf{k}$ is almost perpendicular to $\mathbf{Q}$. We perform the $k_\parallel$ integration in the Eq. (6), and we obtain

$$E\tilde{\Phi}(p_0, p_\perp) = \frac{v_F}{(2\pi)^3} \int dk_0 \int dk_\perp \frac{|k_\perp|}{\gamma_o |k_0| + \chi_d |k_\perp|^3} \times \frac{m}{(k_\perp + p_\perp)^2} \times \ln\left(1 + \frac{8[\frac{(k_\perp + p_\perp)^2}{2m}]^2}{[\frac{(k_\perp + p_\perp)^2}{2m}]^2 + \lambda^2 |k_0 + p_0|^{4/3}}\right) \times \tilde{\Phi}(p_0 + k_0, p_\perp + k_\perp). \quad (7)$$

Here we use the simpler form of gauge propagator which is obtained from Eq. (2) in the limit $v_F|\mathbf{k}| \gg |k_0|$, and we keep only the leading frequency-dependent term in the spinon propagator. Therefore, the integration for the energy or momentum should be understood as having an ultraviolet cutoff of the order of the Fermi energy or momentum.

The right-hand side of Eq. (7) has a smooth and weak p_0 dependence. Therefore, we ignore the p_0 dependence in the kernel and consider a frequency-independent eigenvector. The gauge propagator $|k_\perp|/(\gamma_o|k_0| + \chi_d|k_\perp|^3)$ is sharply peaked at $k_\perp \sim (\gamma_o|k_0|/\chi_d)^{1/3}$ as a function of $k_\perp$ and can be approximated by a delta function $(\gamma_o \chi_d^2 |k_0|)^{-1/3} \sum_{s=\pm 1} \delta(k_\perp - s(\gamma_o|k_0|/\chi_d)^{1/3})$, and we can perform the $k_\perp$ integration. Changing the integration variable k_0 by $t = s|(\gamma_o/\chi_d)k_0|^{1/3}$, we obtain the eigenvalue equation

$$E\tilde{\Phi}(p_\perp) = 6\frac{m v_F}{(2\pi)^3 \gamma_o} \int dt \frac{|t|}{|t + p_\perp|^2} \times \ln\left(1 + \frac{8|t + p_\perp|^4}{|t + p_\perp|^4 + A|t|^4}\right) \tilde{\Phi}(t + p_\perp), \quad (8)$$

where $A = [2m\lambda(\chi_d/\gamma_o)^{2/3}]^2$ is a dimensionless constant. If we consider the spinon pair right on the Fermi surface ($p_\perp = 0$) and use the ansatz $\Phi(p_\perp) = \text{const}$, the right-hand side of Eq. (8) is logarithmically divergent. This signifies that we can find an eigenvector which has an arbitrarily large eigenvalue. However, the momentum-independent ansatz cannot satisfy the eigenvalue equation because the kernel strongly depends on $p_\perp$. In view of the singular dependence of the kernel on $p_\perp$, we consider an ansatz $\tilde{\Phi}(p_\perp) = \tilde{\Phi}_0(1/|p_\perp|^\alpha)$, where α should be smaller than $3/2$ in order for the eigenvector to be normalizable. This ansatz solves the eigenvalue equation with the eigenvalue $E \sim [6/(2\pi)^2 c] \ln[1 + 24c^2/(3c^2 + 1)]\frac{1}{\alpha}$, where $c = \bar{m}\bar{v}_F/m v_F$ measures the local curvature of the Fermi surface. For small enough α, the eigenvalue can be arbitrarily large. Thus, within the present mean field treatment there is a pairing instability.

Now we check the validity of the analytic solution by solving the eigenvalue equation numerically. We do not assume a specific form of $\Phi(p)$ in Eq. (6). Then the natural cutoff for the $k_\parallel = p_\parallel - p'_\parallel$ integration is $k_\perp$, not $k_\perp^2/m$, because the coupling $|\mathbf{Q} \times \hat{\mathbf{k}}|^2/m^2$ becomes small for $k_\parallel > k_\perp$. Ignoring the $k_\parallel$ dependence of the gauge propagator, we can cast the equation into a 2D integral equation by applying $\int_{-p_\perp}^{p_\perp} (dp_\parallel/2\pi) g(Q + p) g(Q - p)$ on both sides of Eq. (6). The resulting equation involves only two integrations, and one can easily diagonalize the kernel $M(p, p')$ numerically to find the eigenvalue and the eigenvector. The largest eigenvalue corresponds to singlet pairing (even Δ_p) and as shown in Fig. 1 increases logarithmically with increasing L, where L determines the mesh of the discrete energy and momentum as $\Delta k = 2\pi/L$. The eigenvalue will become larger than 1 for a large enough L, and there exists pairing instability in the thermodynamic limit. The infrared divergence of the eigenvalue in the thermodynamic limit is consistent with the analytic result that the eigenvalue diverges as $\alpha \to 0$. Although not shown here, the numerically calculated eigenvector is qualitatively consistent with the analytic ansatz with $\alpha < 1$. The second largest eigenvalue corresponds to triplet pairing and is also logarithmically divergent with a slope 10 times smaller than that shown in Fig. 1. In the rest of the Letter, we assume singlet pairing, even though we should be mindful that triplet pairing is also unstable and may be preferred by short range repulsion.

The origin of the mean field pairing instability should be contrasted with conventional superconductors where electrons with momenta $\mathbf{p}$ and $-\mathbf{p}$ form a pair, which uses the whole Fermi surface to lower its energy. In the present case, spinon pairs carry a momentum of the order of $2k_F$. While the Larkin-Ovchinnikov-Fulde-Ferrell (LOFF) state also carries finite momentum [15], our case is fundamentally different because pairing fermions on the same side of the Fermi surface severely restricts the available phase space. Consequently, the pairing instability found here can happen only if the pairing interaction is sufficiently singular. To see this, consider the scale transformation $p_0 \to s p_0$, $p_\parallel \to s^{2/3} p_\parallel$, and $p_\perp \to s^{1/3} p_\perp$, under which the measure of the energy-momentum integration goes as s^2, the two Green's functions $s^{-4/3}$, and the interaction $s^{-2/3}$ in Eq. (7). This results in the logarithmic divergence. If the interaction were less singular than $s^{-2/3}$, there would be no instability.

Now consider possible instabilities in the particle-hole channel [16]. A mean field treatment similar to that above reveals the existence of $2k_F$ density wave instabilities in both the singlet and triplet channels, albeit with nontrivial momentum dependence for the internal wave function for the particle-hole pair. We point out that the Amperean pairing is favored for large local curvature c, while the $2k_F$ instability prefers small c.

Theoretically, the mean field results above should be regarded as merely suggestive of possible low temperature instabilities of the spinon Fermi surface state. Lacking a better theoretical treatment, we will take experiments as a guide for further discussion.

The NMR measurement does not observe the line broadening expected for the incommensurate spin density wave [1,17]. Thus, we discard the triplet spinon density wave. Since the singlet spinon density wave state preserves the U(1) gauge structure, it will have a non-Fermi liquid specific heat unless a further Amperean pairing instability develops at low temperature to restore Fermi liquid behavior (see below). However, in the latter case two separate transitions would have been expected as a function of temperature (for instance, as visible signatures in the specific heat) which is not observed. Therefore, we focus on the scenario where only the spinon pairing occurs and explore some consequences.

In the paired state, gaps will open on the patches of the Fermi surface where the pairing occurs. The momentum point at which the pairing instability first occurs depends on the details of the Fermi surface. In general, there will be a number of preferred points related by hexagonal symmetry. Once the pairing occurs on parts of the Fermi surface, the U(1) gauge group is reduced to Z_2. Since the Z_2 gauge field is gapped, the low energy theory becomes the Fermi liquid theory, and the remaining Fermi surface can remain gapless without further instability. This is consistent with the observation that there exists a finite specific heat coefficient γ in the zero temperature limit rather than the singular $T^{-1/3}$ behavior. The proposed spinon pair state will generically break lattice translation, rotational, or even time reversal symmetries. As shown in the top inset in Fig. 1, suppose the pairing occurs at two distinct favored momenta $\mathbf{Q}_1$ and $\mathbf{Q}_2$, with Δ_1 and Δ_2 the corresponding pairing order parameters. These are, of course, not gauge-invariant, but the gauge-invariant combination $(\Delta_1)^*(\Delta_2)$ is at nonzero momentum $2(\mathbf{Q}_2 - \mathbf{Q}_1)$ and is also condensed as Δ_1 and Δ_2 are individually condensed. This represents a spontaneous breakdown of lattice symmetry. As we are discussing a spin system, this order corresponds to an incommensurate version of the valence bond solid (spin Peierls state). However, we emphasize that this broken lattice symmetry state coexists with fractionalized spinons. The broken lattice symmetry implies a finite temperature phase transition. However, due to the incommensurate ordering, the transition should be $2d$ X-Y-like and shows no observable singularity in the specific heat. The translational symmetry breaking should couple to lattice distortion and may be observable by x-ray scattering.

A key prediction is that the low temperature thermal conductivity $\kappa \sim T$ like in a metal, in contrast to the vanishing thermal conductivity expected in an Anderson insulator or the enhanced $\kappa \sim T^{1/3}$ for the spinon Fermi surface state with a gapless U(1) gauge field [9].

In contrast with BCS theory but in common with the LOFF state, the Amperean pairing is not destroyed by the Zeeman limiting field, because the spinon with up spin with momentum $|\mathbf{Q}_\uparrow| = |\mathbf{Q}| + \mu_B H/v_F$ and the spinon with down spin with momentum $|\mathbf{Q}_\downarrow| = |\mathbf{Q}| - \mu_B H/v_F$ can both be on the Fermi surface and paired without the energy cost of the Zeeman energy. This property is crucial in explaining the lack of field dependence up to $8T$ in the specific heat [5].

The spinon pairing state is not a superconductor, because the spinon does not carry charge. However, if the charge gap is suppressed by driving the system across the Mott transition point with pressure [2], Bose condensation of the charge degrees of freedom converts the Amperean pairing state to a real superconductor. One signature of this unconventional superconductor is that the Knight shift will hardly change across the transition temperature, which is highly unusual for singlet pairing. This signature is consistent with recent data [18].

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