Coulomb enhancement of superconducting pair-pair correlations in a \( \frac{3}{4} \)-filled model for \( \kappa-(\text{BEDT-TTF})_2X \)

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We present the results of precise correlated-electron calculations on the monomer lattices of the organic charge-transfer solids \( \kappa-(\text{BEDT-TTF})_2X \) for 32 and 64 molecular sites. Our calculations are for band parameters corresponding to \( X = \text{Cu}_2[\text{N(CN)}_2]\text{Cl} \) and \( \text{Cu}_4(\text{CN})_3 \), which are semiconducting antiferromagnetic and quantum spin liquid, respectively, at ambient pressure. We have performed our calculations for variable electron densities \( \rho \) per \( \kappa-(\text{BEDT-TTF})_2 \) molecule, with \( \rho \) ranging from 1 to 2. We find that \( d \)-wave superconducting pair-pair correlations are enhanced by electron-electron interactions only for a narrow carrier concentration about \( \rho = 1.5 \), which is precisely the carrier concentration where superconductivity in the charge-transfer solids occurs. Our results indicate that the enhancement in pair-pair correlations is not related to antiferromagnetic order, but to a proximate hidden hidden spin-singlet state that manifests itself as a charge-ordered state in other charge-transfer solids. Long-range superconducting order does not appear to be present in the purely electronic model, suggesting that electron-phonon interactions also must play a role in a complete theory of superconductivity.

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I. INTRODUCTION

The family of layered organic superconductors \( \kappa-(\text{BEDT-TTF})_2X \) (hereafter \( \kappa-(\text{ET}) \)) has attracted strong interest because of its apparent similarity with the high \( T_c \) cuprates. As in the cuprates, superconductivity (SC) in \( \kappa-(\text{ET}) \) is proximate to semiconducting magnetic states, antiferromagnetic (AFM) or quantum spin liquid (QSL). SC in the \( \kappa-(\text{ET})_2X \) as well as organic charge-transfer solids (CTS) in general is however reached by application of pressure rather than doping with charge carriers. Thus SC is a consequence of change of one or more parameters in the Hamiltonian that describes both the semiconducting and superconducting states, at fixed carrier concentration. The \( \kappa-(\text{ET}) \) lattice is strongly dimerized, with strong intradimer electron hoppings between ET molecules belonging to the same dimer, and relatively weaker interdimer hoppings (see Fig. 1). Complete CT of one electron to the acceptor molecule \( X \) occurs from each dimer, which creates cations \( \text{ET}^{0.5+} \) with 0.5 holes (1.5 electrons) in the highest occupied molecular orbital (MO) of each ET molecule. The dimer lattice is anisotropic, and the magnetic behavior of the family can be understood within an effective \( \frac{1}{2} \)-filled band Hubbard model, wherein the dimers \( \text{ET}^{2+} \) of the ET molecules (rather than the molecules themselves) constitute the individual sites. AFM in the strongly anisotropic \( X = \text{Cu}_2[\text{N(CN)}_2]\text{Cl} \) (hereafter \( \kappa-\text{Cl} \)), and QSL behavior in the nearly isotropic \( X = \text{Cu}_2(\text{CN})_3 \) (hereafter \( \kappa-\text{CN} \)) are both expected within the effective model.

In the context of the cuprates, there exists a large body of theoretical literature claiming that SC occurs within the Hubbard model for bandfilling slightly away from \( \frac{1}{2} \) but no consensus has yet been reached on this matter. In analogy to these theories, mean-field and dynamic mean-field theories of \( \kappa-(\text{ET})_2X \) have proposed that SC also occurs within the exactly \( \frac{1}{2} \)-filled band Hubbard model on an anisotropic triangular lattice, for a range of Hubbard \( U \) and anisotropy \( \Delta \). A necessary condition for SC within any interacting electrons model however is that interactions must enhance superconducting pair-pair correlations relative to the noninteracting model. Precise numerical calculations within the \( \frac{1}{2} \)-filled band Hubbard model on triangular lattices have shown that pair-pair correlations decrease with Hubbard \( U \) for all anisotropies, thus indicating the need for going beyond the effective \( 1/2 \)-filled band model in our search for the mechanism of SC in \( \kappa-(\text{ET})_2X \).

Recently an ubiquitous charge-ordered (CO) phase of unknown origin has been discovered in the cuprates that competes with both AFM and SC\(^{29-32}\). The CO and SC orders have similar energy scales, and some investigators have suggested that “CO and SC appear as joint instabilities of the same normal state”\(^{28}\). Given that SC proximate to CO is also seen in (ET)\(_2\)X with crystal structures different from \( \kappa-(\text{ET})_2X \), it is natural to ask whether the mechanisms of SC in all (ET)\(_2\)X are actually related, and whether even in the \( \kappa-(\text{ET}) \) family there exists a hidden competing CO state. Uniquely for the case of carrier density precisely 0.5 or 1.5 per site, we have shown that there can indeed occur a spin-paired CO state, a paired-electron crystal (PEC), in frustrated lattices\(^{33,34}\). The PEC is a Wigner crystal of spin-bonded pairs, rather than of single electrons\(^{35}\). In the \( \kappa \) materials, the PEC would require unequal charge densities on the monomer molecules that constitute each ET dimer, with interdimer spin-pairing between monomers with large charge densities\(^{37,38}\). Other groups have also...
proposed related theories of fluctuating intradimer charge disproportionation\textsuperscript{36–38}, in order to explain the peculiar dielectric responses of $\kappa$-CN\textsuperscript{22} and $\kappa$-Cl\textsuperscript{42}. While recent experiments have shown the absence of static CO in both materials\textsuperscript{21}, and ascribe the electrodynamic response of $\kappa$-CN to coupling of ET cations to anions\textsuperscript{23}, dynamic fluctuating CO is not precluded\textsuperscript{41,43,44}. Such a fluctuating CO may perhaps explain the low temperature “6 K transition” in $\kappa$-CN that remains unexplained\textsuperscript{45–48}. Experimentally, static PEC has been observed in the $\kappa$ compound $X = \text{Hg(SCN)}_2\text{Cl}$\textsuperscript{35,36}, while pressure-induced transition from a dimer AFM to an intradimer charge segregated state has been observed in the compound $\beta'$-(BEDT-TTF)$_2\text{ICl}$\textsuperscript{40}, which like $\kappa$-(ET) has a dimerized lattice structure.

We have recently proposed that SC in the (ET)$_2X$ evolves from a paired-electron liquid (PEL), which can be thought of as a destabilized PEC\textsuperscript{31} (thus a static PEC is not a requirement for the PEL or SC.) Our conclusion is based on precise numerical calculations of pair-pair correlations within the Hubbard model on anisotropic triangular lattices, for variable carrier densities $\rho$ per site. We showed that in each case the pair-pair correlations are enhanced relative to the noninteracting limit uniquely for $\rho \approx 0.5$. At all other $\rho$ ($0 \leq \rho \leq 1$) pair-pair correlations are suppressed by the Hubbard $U$. Although the PEL does not have true long-range superconducting correlations, to the best of our knowledge this was the first demonstration of enhancement of pair-pair correlations within the Hubbard model. The fundamental theoretical picture that emerges is related to an earlier proposition that SC can evolve from the paired Wigner crystal in the electron gas at intermediate densities, upon weak doping\textsuperscript{15}. Our work has extended this idea of evolution from a paired crystal to a paired liquid to the case of a real lattice. Both paired states on the lattice are however unique to a particular carrier density.

The anisotropic triangular lattice lacks the strong dimerization of $\kappa$ lattice, and the possibility of mapping to the effective $\rho = 1$ model\textsuperscript{22} thus does not exist in this case. Whether or not Coulomb-induced enhancement of pair-pair correlations occurs in the realistic $\kappa$ lattice, also uniquely for the same carrier concentration $\rho$, as well as the symmetry of the superconducting order parameter, if any, are of strong interest. We report here the results of such calculations of spin-spin and pair-pair correlations on the actual $\kappa$ lattice, for realistic band parameters appropriate for $\kappa$-Cl and $\kappa$-CN. As before\textsuperscript{31}, we perform these calculations for variable $\rho$. We demonstrate PEL formation on the $\kappa$ lattices uniquely at or near $\frac{1}{2}$ filling with electrons, giving further credence to our proposal\textsuperscript{31} that there occurs an effective electron-electron (e-e) attraction selectively at this $\rho$.

The majority of computational studies of correlated models for $\kappa$-ET have focused on the effective $\frac{1}{2}$-filled band model. For the monomer lattice exact diagonalizations within 16-site clusters within the Hubbard and extended Hubbard models have been performed\textsuperscript{35–38,52–54}, as well as dynamical mean-field (DMFT) studies\textsuperscript{55} To our knowledge, the present results report the first direct calculations of pair-pair correlations on large lattices. System sizes available to exact diagonalization are able to demonstrate spin correlations consistent with AFM order between dimers, but are not large enough for measurement of pair-pair correlations between non-overlapping pairs.

The outline of the paper is as follows: in Section \textbf{II} we describe the theoretical model, the lattices and the computational methods we use; in Section \textbf{III} we present our computational results for the spin structure factor and pair-pair correlations in the ground state; and in Section \textbf{IV} we discuss our results in relationship to the current experimental data on $\kappa$-ET, as well as implications for theories of correlated-electron SC in general.

\section{Theoretical Model, Lattice, Parameters, and Methods}

As a minimal model for the electronic properties of the conducting layer of BEDT-TTF molecules in $\kappa$-ET, we consider the Hubbard Hamiltonian,

$$ H = \sum_{\langle ij \rangle, \sigma} t_{ij} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{H.c.)} + U \sum_i n_{i,\uparrow} n_{i,\downarrow}. \quad (1) $$

In Eq. \textbf{1} $c_{i,\sigma}^\dagger$ ($c_{i,\sigma}$) creates (annihilates) an electron of spin $\sigma$ on the highest MO of a monomer ET molecule $i$, $n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$, and $U$ is the onsite e-e interaction. The
lattice structure of the conducting layers in $\kappa$-ET is shown in Fig. 1. In order to differentiate our approach from theories emphasizing the effective $\frac{1}{2}$-filled band picture, in what follows instead of using the “bandfilling” we will present our computational results as a function of the average electron density per monomer molecule, $\rho$. As mentioned above, $\rho$ in the (ET)$_2$X family is 1.5. While our calculations of the spin-spin correlations are for this density only, we have performed the calculations of superconducting pair-pair correlations for a wide range of $\rho$, $1 \leq \rho \leq 2$. The motivation behind studying the density dependence of pair-pair correlations is two-fold. First, this allows us to investigate whether or not SC is unique to $\rho \approx 1.5$, which is a necessary condition if the SC is indeed evolving from a hidden PEC. Secondly, it also allows us to probe carrier density slightly away from the stoichiometric $\rho = 1.5$ in view of recent experiments that have suggested that SC can occur in the $\kappa$-ET system for weak doping away from $\rho = 1.5$.

Hopping integrals for $\kappa$-ET have been previously calculated using the extended Hückel and density-functional methods. Each molecule in the lattice has significant overlaps with six nearest neighbors (see Fig. 1) with hopping integrals $t_{b1}, t_{b2}, t_{p},$ and $t_q$ in order of decreasing magnitude. In the effective dimer model the two molecules connected by $t_{b1}$ are considered a single effective site, with the dimers forming an anisotropic triangular lattice. The effective hopping integrals along $x$ and $y$ are $t = (t_p + t_q)/2$ and the frustrating hopping integral $t' = t_{x+y} = t_{x-y} = t_{b2}/2$. The degree of frustration in the effective dimer model is then given by the ratio $t'/t = t_{b2}/(t_p + t_q)$. Frustration is weakest in $\kappa$-Cl and strongest in $\kappa$-CN; these are the systems we consider.

In our calculations we have used the following sets of hopping parameters, given in meV, from Reference 60 for $\kappa$-Cl (207, 67, -102, -43), and for $\kappa$-CN (199, 91, -85, -17). Both sets were determined from low-temperature crystal data, $T=5$ K in the case of $\kappa$-CN, and $T=15$ K in the case of $\kappa$-Cl. For these two sets of parameters, the ratio $t'/t$ is 0.46 (0.89) for $\kappa$-Cl ($\kappa$-CN). While different computational techniques report somewhat different $t'/t$, all have found that in terms of the effective dimer model $\kappa$-CN is significantly more frustrated and closer to an isotropic triangular dimer lattice than is $\kappa$-Cl. It is however not known how the effect of the larger frustration within the dimer model affects the electronic properties of the full monomer lattice.

We considered two different periodic lattices with 32 and 64 molecular sites. The 32 site lattice is four dimers each along the $c$ and $a$ directions in Fig. 1. The lattice is chosen such that the effective dimer lattice (along the $x$ and $y$ axes of Fig. 1) is a $4 \times 4$ square lattice. This is possible if the vectors defining the edges of the 32 site cluster are along the $a$ and $y$ directions in Fig. 1. The 64 site cluster was constructed in a similar way and corresponds to an $8 \times 4$ lattice in terms of dimers. The full lattices are shown in the Supplemental Material. On both lattices, the $t_{ij}$ parameters for $\kappa$-Cl and $\kappa$-CN gave different single-particle Fermi level degeneracies; the degeneracy for $\rho = 1.5$ is twofold in $\kappa$-Cl and fourfold in $\kappa$-CN, in agreement with the greater frustration in the latter.

Conventional quantum Monte Carlo methods cannot be used in the highly frustrated $\kappa$-ET lattice due to the fermion sign problem. The two methods we used are the Path Integral Renormalization Group (PIRG) and Constrained Path Monte Carlo (CPMC). Both PIRG and CPMC are ground state projector methods that project out the ground state from an arbitrary initial wavefunction. In PIRG the projection is done in a finite basis of Slater determinants, followed by an extrapolation in the energy variance. In CPMC the projection is done using random walkers constrained by a trial wavefunction. Here we have used the $U = 0$ wavefunction for the constraint. We have extensively benchmarked calculations of superconducting pair-pair between these two methods in previous work on the anisotropic triangular Hubbard model both at $\frac{1}{2}$-filling as well as the complete density range. While PIRG can be considered exact provided large enough basis sets are used and the projection is done with care, the constraining wavefunction in CPMC does introduce a systematic error. In our previous work, we found that CPMC results for pairing correlations agreed well with PIRG for small to intermediate $U$, provided use of CPMC was restricted to systems which in the noninteracting $U = 0$ limit have nondegenerate closed-shell Fermi level occupancies.

### III. RESULTS

We performed PIRG calculations for the 32-site lattice over the full density range $1 < \rho < 2$ and for $\rho = 1.5$ for the 64-site lattice. For the other densities of the 64 site lattice with nondegenerate Fermi level occupations we performed CPMC calculations. We used the full set of spatial symmetries within the symmetrized version of PIRG (QP-PIRG), which has been shown to significantly improve the results compared to earlier PIRG calculations. The symmetries we used for the 32 site lattice were translations, a $\pi$ rotation, and a glide-plane symmetry. We also projected out the even spin parity state. The PIRG basis size was up to $L=512$ Slater determinants for 32 sites and $L=768$ for 64 sites.

#### A. Spin structure factor

AFM is best explained within the effective dimer model, where the charge densities on the molecules of the dimer are equal. Accordingly we define the total $z$-component of spin on dimer $i$ as

$$S_z^i = \frac{1}{2} (n_{i,\uparrow} + n_{i,\downarrow} - n_{i,\downarrow} - n_{i,\uparrow}).$$

Eq. 2 $i_1$ and $i_2$ refer to the two different molecules within the dimer $i$ and $n_{ij,\sigma} = c_{i,j,\sigma}^\dagger c_{i,j,\sigma}$. We calculate the
dimer spin structure factor defined as

\[ S(q) = \frac{1}{N_d} \sum_{j,k} e^{iq \cdot (r_j - r_k)} \langle S_j^z S_k^z \rangle, \tag{3} \]

where \( N_d \) is the number of dimers and dimer position vectors \( r_j \) are defined on a conventional square lattice, whose \( x \) and \( y \) axes are indicated on Fig. 1. In Fig. 2 we show results for \( S(q) \) for both \( \kappa\text{-Cl} \) (Fig. 2(a)) and \( \kappa\text{-CN} \) (Fig. 2(b)). \( S(q) \) for \( \kappa\text{-Cl} \) has a peak at \( q_{\pi,\pi} \) consistent with Néel AFM correlations as expected in the \( \rho = 1 \) effective model for moderate frustration. As shown in Fig. 2(a), the \( (\pi, \pi) \) peak for \( \kappa\text{-Cl} \) grows with increasing \( U \). In contrast, we found no clear magnetic ordering peak in \( S(q) \) for \( \kappa\text{-CN} \), consistent with the greater frustration within the effective dimer model in this case.

For the 64 site \( \kappa\text{-Cl} \) lattice \( S(\pi, \pi) \) is smaller in magnitude than for 32 sites, and the peak appears somewhat broader in momentum space. At present we do not have access to large enough system sizes to perform a finite-size scaling for \( S(q) \), but the decrease of \( S(\pi, \pi) \) with increasing system size indicates that our \( \kappa\text{-Cl} \) results are consistent with a metallic state with AFM correlations rather than an AFM insulating state \( (S(\pi, \pi)/N_d \) should scale to a non-zero value in the presence of long-range AFM order at \( T = 0 \) in the thermodynamic limit). We discuss this issue further in Section IV. For the 64 site \( \kappa\text{-CN} \) lattice, we find that the variation \( S(q) \) with \( q \) is less than for 32 sites; this behavior is consistent with lack of magnetic order in the Mott insulating state of \( \kappa\text{-CN} \).

### B. Pair-pair correlations

We calculate equal-time superconducting pair-pair correlations \( P_{ij} = \langle \Delta_i^\dagger \Delta_j \rangle \), where \( \Delta_i^\dagger \) is creates a superconducting pair centered at dimer \( i \). There are two requirements for a complete theory of correlated-electron superconductivity: (i) e-e correlations should enhance the value of \( P_{ij} \) compared to its uncorrelated value, and (ii) \( P_{ij} \) has long-range order at \( T = 0 \). Here we focus on (i).

As mentioned above, previous works have shown (i) suppression of pair-pair correlations within the effective \( \rho = 1 \) model, and (ii) the possibility of a fluctuating CO within models focusing on the monomer molecules. We therefore construct pair creation operators that allow unequal charge densities on the monomer molecules that constitute a dimer to superimpose between sites 1 and 2 and the surrounding sites 3–8. In order to restrict the number of pair operators \( \Delta_i^\dagger \) and simplify the calculation, we restrict the singlets to only the stronger interdimer bonds of the lattice, i.e. the \( t_b \) and \( t_c \) bonds (we ignore the weak \( t_q \) bonds). As an example, \( d_{2x-\nu z} \) singlet pairs (labeled \( d_1 \) here, see below) similar to the conventional definition in the square effective lattice can be defined as follows for the dimer (1,2) in Fig. 4:

\[ \Delta_{d_1}^\dagger = \frac{1}{2} \left[ \frac{1}{\sqrt{2}} (c_{1,1}^\dagger c_{8,4}^\dagger - c_{1,4}^\dagger c_{8,1}^\dagger) - \frac{1}{\sqrt{2}} (c_{1,1}^\dagger c_{3,4}^\dagger - c_{1,4}^\dagger c_{3,1}^\dagger) + \frac{1}{\sqrt{2}} (c_{2,1}^\dagger c_{5,4}^\dagger - c_{2,4}^\dagger c_{5,1}^\dagger) - \frac{1}{\sqrt{2}} (c_{2,1}^\dagger c_{6,4}^\dagger - c_{2,4}^\dagger c_{6,1}^\dagger) \right]. \tag{4} \]

Given that the monomer lattice deviates strongly from...
FIG. 4. (color online) The enhancement factor $\Theta_P$ for the long-range component of the pair-pair correlation ($\Theta_P > 0$ implies pair-pair correlations enhanced over their $U = 0$ values, see text), as a function of $\rho$, for the $\kappa$-Cl system for $U=0.5$ eV. Pair symmetries are (a) $d_1$, (b) $d_2$, (c) $d_3$, and (d) $d_4$ as defined in Fig. 3. Shaded (striped) bars are for 32 (64) site lattices. The symbols '*' and '#' indicate densities not shown, for 32 and 64 sites, respectively; finite-size effects are particularly strong at these excluded $\rho$. Pair-pair correlations are suppressed by $U$ at these excluded $\rho$, precluding pairing; see Supplemental Material.

FIG. 5. (color online) Same as in Fig. 4 but for parameters for $\kappa$-CN. As in Fig. 4 behavior of all pair-pair correlations against $U$, including those for the excluded $\rho$ are shown in the Supplemental Material. See text regarding the peak in panel (b) at $\rho \approx 1.16$; we believe the apparent enhancement here is a finite-size effect.

the square lattice geometry several other pair symmetries are possible. Fig. 3 summarizes the pair symmetries we considered. These include four types of $d$-wave pairing (defined as symmetries with four nodes), with four as well as six neighbors. We do not show the results for $s$-wave pairing symmetries, as suppression of pair correlations were found with these, with four or six neighbors. The difference between the four $d$-wave pair symmetries we consider is in the locations of the nodes, which we discuss further in Section IV.

We calculate the average long-range value of the pair-pair correlations $\bar{\rho}_{ij}$ on each lattice, $\bar{\rho} = 1/N_P \sum_{|i-j|>2} \rho_{ij}$. Here $N_P$ is the number of terms in the sum, and distances are defined in units of the nearest neighbor lattice distance of the effective dimer lattice. The restricted sum in the definition of $\bar{\rho}$ is necessary to disentangle AFM and SC correlations. For the 32-site cluster for example, there are five $\rho_{ij}$ separated by two or more lattice spacings in the equivalent $4 \times 4$ effective model.

In order to compare the extents of enhancements of pair-pair correlations by the Hubbard $U$ at different densities we normalize $\bar{\rho}$ by its value for $U = 0$, and show results for the enhancement factor $\Theta_P = [\bar{\rho}(U)/\bar{\rho}(U = 0)] - 1$. In Figs. 4 and 5 we have shown $\Theta_P$ as a function of $\rho$ for $U = 0.5$ eV. The normalization of $\bar{\rho}$ fails for certain densities, where due to finite-size effects $\bar{\rho}(U = 0)$ is identically zero or very small in magnitude. For this reason, in Fig. 4 and Fig. 5 we have excluded densities for which pair-pair correlations are very small in magnitude at nonzero $U$, or (b) pair-pair correlations are negative. The complete data including the points excluded in Figs. 4 and 5 for both the $\kappa$-Cl and $\kappa$-CN lattices, for 32 as well as 64 sites are shown in the Supplemental Material. As seen there suppression of pair-pair correlations with $U$ occurs at any $\rho$ that has been excluded. Most of the data we excluded are also for densities significantly away from $\rho = 1.5$.

The results of Figs. 4 and 5 are remarkable, from multiple perspectives. First, in both cases suppression of $\bar{\rho}$ is observed at all $\rho$ except at or near $\rho = 1.5$, where...
there occur enhancements of $\bar{P}$. We are ignoring the enhancement seen in the Supplement Material, Fig. S28. At this density, a discontinuous transition occurs at small $U$, suggesting a bandstructure effect. Furthermore at this $\rho$, $\bar{P}$ for the $d_2$ symmetry is much smaller (but slightly above our cutoff) than for other symmetries. This and the fact that we do not see enhancement in any of our other results in the same density region suggests that it is a finite-size effect. Second, the strongest pairing enhancement occurs for the $d_2$ symmetry for both 32 and 64 sites. Finally, only for the $d_2$ pairing symmetry strong enhancement of $\bar{P}$ at $\rho \approx 1.5$ occurs for both the $\kappa$-Cl and $\kappa$-CN lattice parameters. This is a highly significant result, for as remarked above, the $\kappa$-Cl and $\kappa$-CN have different $U = 0$ single-particle level degeneracies at $\rho = 1.5$. It gives us confidence that the enhancement in pair correlations found here is not an artifact of the one-electron band structure.

In Fig. 6 we show the complete $U$-dependence of $\bar{P}$ at the densities where significant enhancements in pair-pair correlation occur, for both 32 and 64-site lattices, for both $\kappa$-Cl and $\kappa$-CN structures. Compared to the 32 site data, $\bar{P}$ as well as $\Theta_P$ are smaller in magnitude for 64 sites, although we do expect that in the 64 site lattice $\bar{P}$ will continue to increase at $\rho \approx 1.5$ for $U > 0.5$ eV. The $\Theta_P$ data however indicate the absence of true long-range superconducting order within our purely electronic model. If long-range superconducting order were present, $\bar{P}$ would have reached a constant value with increasing system size, while $\bar{P}(U = 0)$ decreased, in which case $\Theta_P$ would be expected to increase with lattice size. The enhancement of pair-pair correlations uniquely at $\rho \approx 1.5$ is nevertheless significant, because this is precisely the carrier concentration in the superconducting $\kappa$-(ET)$_2$X. We elaborate on this aspect of our result further in the following section.

IV. DISCUSSIONS

We summarize our most significant results in this section, and discuss the implications of our work for $\kappa$-(ET)$_2$X in particular, and for the family of 2D organic CTS in general.

A. AFM correlations versus long range AFM, and proximity to other broken symmetries

The calculated decrease of $S(\pi, \pi)$ with increasing lattice size for the $\kappa$-Cl lattice suggests that the ground state of the present model does not have long-range AFM order, but is rather metallic with short-range AFM correlations. We did not find any evidence for a quantum phase transition to an AFM state in the 32-site lattice up to $U \approx 1$ eV. While this conclusion appears counterintuitive, given the strong emphasis on AFM in theoretical works on these materials, it is in agreement with the experimental behavior of the $\kappa$-(ET) family as a whole. Experimentally, $\kappa$-Cl and deuterated $\kappa$-Br are the only compounds that exhibit AFM, and all other compounds are either ambient pressure superconductors ($\kappa$-Br$_2$ and $\kappa$-NCS$_2$), QSL ($\kappa$-CN$_2$) or PEC ($\kappa$-Hg(SCN)$_2$Cl)$_2$. Several of the more complicated $\kappa$ materials such as $\kappa$-(ET)$_4$[M(CN)$_6$][N(C$_2$H$_5$)$_4$]$[3\text{H}_2\text{O}]$[66,67] and $\kappa$-(ET)$_4$[M(CN)$_6$][N(C$_2$H$_5$)$_4$]$[2\text{H}_2\text{O}]$[68,69] (M = Co, Fe and Cr) are charge-ordered. Charge-ordering in the last group of materials is accompanied by spin-singlet formation and is apparently driven by strong interdimer coupling[67,68], which is also the condition for PEC formation[63,64]. Taken together, these results suggest that even as AFM spin-spin correlations in $\kappa$-ET are significant, these systems are at the threshold of transitions to proximate broken symmetries that include the PEC as well as SC. This observation is reminiscent of the occurrence of a CO phase competing with both AFM and SC in the cuprates[21,28], mentioned in Section I.

We speculate that the origin of long range AFM is due to either the nearest neighbor Coulomb interaction $V$, or the coupling between ET$_i^+$ cations and anions, both of which have been ignored in our calculations. Because of the triangular dimer lattice, interdimer Coulomb interactions are nearly the same in all directions and the consequence of interdimer $V$ is small; conversely, intradimer $V$ promotes single electron occupancy of dimers, and
enhances AFM. Similarly, it is conceivable that cation-anion coupling determines the extent of electron localization in the cation layer. The role of anions in the electrodynamics of $\kappa$-CN, for example, has been emphasized by Dressel et al.\textsuperscript{42}

B. Enhancement of pair-pair correlations and carrier density

Our most significant result is the calculated enhancement of pair-pair correlations by Hubbard $U$ within a narrow electron density range about $\rho = 1.5$. Enhanced pair-pair correlations is a necessary though not sufficient condition for SC. We previously used this criterion to evaluate the possibility of SC within the $\rho = 1$ Hubbard model on triangular lattices.\textsuperscript{17,19,20} Suppression of pair-pair correlations by the Hubbard $U$ was found for all the lattices we investigated. To the best of our knowledge, our results in Reference\textsuperscript{51} for the first time showed an enhancement of pair-pair correlations within the single-band Hubbard model in large 2D clusters (up to 100 sites). It is then remarkable that we find here enhanced superconducting pair-pair correlations for two different $\kappa$ lattices ($\kappa$-Cl and $\kappa$-CN), for two different lattice sizes in each case, for precisely the same narrow carrier concentration range that would be anticipated from Reference\textsuperscript{51}. This is particularly so considering the relevance of this carrier density to experimental (ET)$_2$X.

Within our theory, AFM is a signature of strong correlations, but is not the driver of electron pairing. Enhanced pair-pair correlations originate from the strong tendency to spin-singlet coupling at $\rho = 0.5$ and 1.5, both because of the existence of a commensurate PEC at these densities,\textsuperscript{33,34} and because the stabilization due to the kinetic energy gain from pair motion is highest at these carrier concentrations. Consideration of nearest neighbor spin-bonded sites as effective “negative U” centers has a long history, especially in the context of bipolaron theories of SC. Such a “mapping” for $\rho$ exactly 0.5 or 1.5 leads to an effective $\frac{1}{2}$-filled band of bosons, with nearly degenerate CO and SC. We emphasize that the effective “negative U” model is different from the existing effective $\frac{1}{2}$-filled band theories emphasizing AFM,\textsuperscript{7,15} within which no CO phase is anticipated. Thus within our theory, SC proximate to AFM (as occurs in the $\kappa$-(ET)$_2$X), as well as to CO (as occurs in other crystal structures or in the anionic superconductors),\textsuperscript{29,33} are manifestations of the same correlation effects and to be anticipated. Of course, the CO in these cases should have the characteristic pattern of the PEC (as opposed to the Wigner crystal) with ground state spin singlet character.

C. PEL versus SC

Our work indicates that while repulsive e-e interactions can drive the transition to a PEL with short range pair-pair correlations at $\rho \approx 1.5$, additional interactions missing in the purely electronic Hubbard model will be necessary to obtain long-range superconducting correlations. The most likely such interactions are that between the electrons and lattice vibrations involving intramolecular Holstein phonons\textsuperscript{72} and intermolecular Su-Schrieffer-Heeger (SSH) phonons.\textsuperscript{21} We emphasize that there are many counterexamples to the notions that e-e and electron-phonon (e-p) interactions invariably negate each others effects and that e-p coupling can only generate SC of $s$-wave symmetry. One widely known counterexample is the enhancement of the e-p interaction driven Peierls bond-alternation in the one-dimensional half-filled band by e-e interactions.\textsuperscript{74,75} With the Holstein-type e-p coupling, integrating out the phonon degrees of freedom leads to an effective negative $U$ interaction giving on-site CDW order or $s$-wave SC.\textsuperscript{22} However, for the 2D dispersionless SSH model, integrating out the phonons leads to an attractive term proportional to the square of the kinetic energy.\textsuperscript{76} This term mediates $d_{x^2-y^2}$ SC and competes with AFM mediated by $U$ at $\rho = 1.78$.\textsuperscript{80}

We have similarly found co-operative interactions between the effects of e-e and e-p interactions in the formation of the PEC in both 1D\textsuperscript{51} and 2D\textsuperscript{73,74} cases. In all these cases the retardation of phonon interactions can be thought as “following” the instantaneous correlations driven by the e-e interactions. Thus the interpretation of our result that the PEL is unique to $\rho \approx 1.5$ should be that in the presence of e-p interactions this is the carrier density in the $\kappa$ lattice where correlated-electron SC is most likely.

The idea that AFM coupling may be driving the formation of nearest neighbor Cooper pairs, whose mobility is then enhanced by e-p interactions has also been proposed within later versions of the bipolaron theory of SC.\textsuperscript{82,83} These calculations are for only two electrons on a lattice. The significant advancement reached in our work is that we have demonstrated here the formation of similar mobile bipolarons within the electron-only Hamiltonian for the full many-electron system as opposed to one with only two electrons.

D. Symmetry of superconducting order parameter

Experiments using a wide range of probes suggest that the SC pairing throughout the $\kappa$-(ET)$_2$X family is singlet with nodes in the order parameter. Site-selective $^{13}$C NMR experiments have been performed on the ambient-pressure superconductors $\kappa$-Bi,\textsuperscript{84,85} $\kappa$-NCS,\textsuperscript{86} and also for $\kappa$-CN under pressure in its superconducting state.\textsuperscript{87} Common features found from the NMR experiments include singlet pairing, no coherence peak in 1/T$_1$, and 1/T$_1 \propto T^3$ at low temperatures. These suggest a non-BCS mechanism and the presence of nodes. In contrast to early specific heat measurements that supported $s$-wave pairing,\textsuperscript{88,89} more recent measurements are consistent with a nodal order parameter.\textsuperscript{90} Microwave penetration depth measurements\textsuperscript{91,92} as well as STM tunneling
experiments are also consistent with nodes.

While experiments are generally in agreement that the SC is singlet and has a nodal order parameter, there is less agreement on the specific form of the order parameter and the location of nodes in the conducting plane. Candidate symmetries $d_{x^2−y^2}$ and $d_{xy}$ differ in the locations of their nodes; in the experimental literature $d_{x^2−y^2}$ symmetry is usually assumed to have nodes at 45° to the crystal axes, while $d_{xy}$ has nodes along the crystal axes. It is important to note that in theoretical work based on the effective half-filled model, these two symmetries are interchanged, as the effective $x$ and $y$ axes are rotated with respect to the crystal axes (see Fig. 1). Magneto-optical and specific heat measurements in a magnetic field find the nodes to coincide with the crystal axes. Thermal conductivity and STM measurements have found the nodes between the crystal axes, although STM measurements on a partially deuterated $κ$-Br suggest a mixture of two order parameters. Experiments sensitive to the position of the nodes have not been performed on $κ$-CN, which is superconducting only under pressure.

In our calculations (see Fig. 3), the $d_1$ symmetry has nodes along the crystal axes, while the $d_2$ symmetry instead has nodes at an angle between the crystal axes. The $d_3$ and $d_4$ have one node along a crystal axis and one off-axis. In our results we found the strongest enhancement for the symmetry $d_2$, which is also the only symmetry with enhanced pairing for both $κ$-Cl and $κ$-CN. However, Fig. 4 shows that several pairing symmetries are enhanced for $κ$-Cl, suggesting the possibility that the optimum pairing symmetry may vary for different $X$ in the $κ$-ET series.

V. CONCLUSIONS

To summarize, from numerical calculations on the Hubbard model on the monomer lattice of $κ$-(ET)$_2X$ solids we have found a PEL state with enhanced superconducting pair-pair correlations exactly for the cationic charge where SC is found experimentally. We have also demonstrated that the pair-pair correlations are suppressed by the Hubbard interaction at all other carrier densities. The superconducting order we find is short-range, and considerable work involving both e-e and e-p interactions will be necessary before a complete theory of SC in the CTS is reached. To the best of our knowledge, however, robust Coulomb enhancement of pair correlations has not been found before. Taken together with our previous work, this gives us confidence that the physical ideas behind this work, viz., (i) enhancement of superconducting pair correlations requires a proximate spin-singlet state in the phase diagram, and (ii) such a spin-singlet is strongly stabilized in 2D for $ρ = 0.5$ or 1.5, are fundamentally correct. The spin-singlet state in our case has a strong tendency to form a CO. As pointed out earlier, CO proximate to SC has been found within the pseudogap phase of the hole-doped cuprates. We are currently investigating the implication of our results for the cuprates.

VI. ACKNOWLEDGMENTS

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