Local singlets, frustration, and unconventional superconductivity in the organic charge-transfer solids

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Abstract

We suggest that superconductivity (SC) in the organic charge transfer solids (CTS) is reached from a Bond-Charge Density Wave (BCDW). We discuss an effective model for the BCDW to SC transition, an attractive $U$ extended Hubbard Hamiltonian with repulsive nearest neighbor interaction $V$. We discuss experimental consequences of the theory for different classes of CTS superconductors as well as related inorganic materials.

1. Introduction

After thirty years of experimental and theoretical effort, the mechanism of superconductivity (SC) in the organic charge-transfer solids (CTS) is still elusive. Electron-electron (e-e) interactions, electron-phonon (e-p) interactions, and lattice frustration all play key roles in the unusual insulating phases found in the CTS, but it is not clear how these apparently very different effects come together in the SC state. In this paper we outline a unified theoretical approach to unconventional SC in the entire family of organic CTS, and argue that all three of the above interactions are essential for SC. Unlike existing theories of SC in the CTS, our work can potentially explain the pairing mechanism in all $\frac{1}{4}$-filled molecular superconductors, spanning from the quasi-one-dimensional (1D) (TMTTF)$_2$X to the nearly isotropic two-dimensional (2D) $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Z[Pd(dmit)$_2$]$_2$. The theory may additionally explain SC found in inorganic $\frac{1}{4}$-filled superconductors.

SC in many CTS, for example in $\kappa$-(ET)$_2$X is proximate to antiferromagnetism (AFM). Further, these 2D CTS are strongly dimerized suggesting the possibility of describing the material by an effective $\frac{1}{4}$-filled band (one carrier per dimer). It has consequently been proposed that the $\frac{1}{4}$-filled band repulsive Hubbard model on an anisotropic triangular lattice can explain the superconducting behavior of the 2D CTS [1, 2].

The $\frac{1}{4}$-filled band triangular lattice Hubbard model believed to show SC has two parameters, the onsite Coulomb interaction, $U$, and the lattice anisotropy, $t'/t$. The limit $t' = 0$ corresponds to the square-lattice Hubbard model, which is an AFM insulator for any $U > 0$. With increasing $t'$ the AFM state is destroyed giving a paramagnetic metal (PM). Mean field and variational calculations find a narrow $d$-wave SC region in between AFM and PM phases [1, 2].

A necessary condition for SC mediated by antiferromagnetic fluctuations is that $U$ must enhance the superconducting pair-pair correlations. We have calculated exact superconducting pair-pair correlation functions for the $\frac{1}{4}$-filled band triangular Hubbard model, and find instead that the strength of pairing correlations always decays monotonically with
charge-rich (charge-poor) molecules. Circled pairs of sites contains inter-site e-p coupling, intra-site e-p coupling, and Hubbard and extended Hubbard e-e interactions. In this notation, '1' indicates a charge density of 0.5+δ, and '0' a charge density of 0.5-δ. For realistic U/t ~ 6-8 and V/t ~ 1 - 3 the BCDW state tends to dominate [4-9]. Fig. 1(a)-(c) shows the BCDW state for 1D, a zig-zag ladder lattice, and 2D.

The BCDW in all cases consists of nearest-neighbor singlet bipolarons. It gains energy from the exchange interaction between electrons in the pairs and also from e-p interaction via the lattice distortion. Singlet formation within the BCDW pairs leads to a non-magnetic ground state in the 1D SP state [5], the zigzag ladder [8], as well as the 2D BCDW [9]. Such nonmagnetic insulating states coexisting with CO are found in many CTS.

We map the nearest-neighbor pairs of singly occupied (vacant) sites into double occupancies (vacancies) as shown in Fig. 1(d). The Hamiltonian describing this effective model now has a negative U and a positive V [10]:

\[ H_{\text{eff}} = -t \sum_{\langle ij \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + H.c.) + t' \sum_{\langle kl \rangle, \sigma} (c_{k,\sigma}^\dagger c_{l,\sigma} + H.c.) - |U| \sum_{i} n_{i,\uparrow} n_{i,\downarrow} + V \sum_{\langle ij \rangle} n_{i} n_{j} + V' \sum_{\langle kl \rangle} n_{k} n_{l} \]

Eq. 2 describes the effective lattice of Fig. 1(d), with hopping t along the x and y directions (nearest-neighbor bonds ⟨ij⟩) and t' along the x+y direction. Both V and V' nearest-neighbor Coulomb interactions are included.

Using exact diagonalizations we have shown that the ground state of Eq. 2 is charge ordered for t' = 0 with the checkerboard CO of Fig. 1(d). As t' increases there is a transition from CO to SC [10]. Fig. 2 shows the phase diagram as a function of t'.

**2. Effective model for BCDW/SC transition**

SC in CTS is proximate to not only AFM but to many other exotic insulating states such as charge ordering (CO) and spin-Peierls (SP) states. We argue that to understand the SC in the CTS, one must first understand these insulating states. This requires returning to the full Hamiltonian with the correct band filling (\( \frac{1}{2} \)-filled or a carrier density of \( n = \frac{1}{2} \)). For the 1D systems our Hamiltonian contains inter-site e-p coupling, intra-site e-p coupling, and Hubbard and extended Hubbard e-e interactions, \( H = H_{\text{inter}} + H_{\text{intra}} + H_{\text{ee}} \):

\[ H_{\text{inter}} = -t \sum_{\langle ij \rangle, \sigma} [1 + \alpha(x_j - x_i)](c_{j,\sigma}^\dagger c_{i,\sigma} + H.c.) \]

\[ H_{\text{intra}} = g \sum_i \nu_i n_i + \frac{1}{2}K_{\text{intra}} \sum_i \nu_i^2 \]

\[ H_{\text{ee}} = U \sum_i n_{i,\uparrow} n_{i,\downarrow} + V \sum_{\langle ij \rangle} n_{i} n_{j} \]

\( c_{i,\sigma}^\dagger \) creates an electron of spin \( \sigma \) on site \( i \), \( x_i \) is the position coordinate of molecule \( i \), and \( n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma} \), \( n_i = n_{i,\uparrow} + n_{i,\downarrow} \). \( \nu_i \) is the coordinate of the intra-molecular vibration on site \( i \), and \( K_{\text{inter}} \) and \( K_{\text{intra}} \) are the spring constant for inter-site and intra-site phonons. The density of carriers is \( n = \frac{1}{2} \).

In a series of works, we have investigated this Hamiltonian and its 2D counterparts [4–9]. In general two different kinds of charge ordered states are possible: (i) Wigner-crystal ..1010.. CO driven by the nearest-neighbor interaction \( V \), and (ii) bond-charge density-wave (BCDW) ordering with CO pattern ..1100.., driven by the cooperation of e-e and e-p interactions. In this notation, ‘1’ indicates a charge density of 0.5+δ, and ‘0’ a charge density of 0.5-δ. For realistic \( U/t \sim 6-8 \) and \( V/t \sim 1 - 3 \) the BCDW state tends to dominate [4-9]. Fig. 1(a)-(c) shows the BCDW state for 1D, a zig-zag ladder lattice, and 2D.

Fig. 1. (a) The ..1100.. 1D BCDW state. Double, double-dashed and single-dashed lines indicate strong, weak and weakest bonds, respectively. (b) The zigzag ladder BCDW state. Double, single and dashed lines again indicate strong, weak and weakest bonds. (c) 2D BCDW (Valence-Bond Solid (VBS)) state in the CTS. Filled (open) ellipses are solid (VBS) state in the CTS. Filled (open) ellipses are solid (VBS) state in the CTS.
U and \( t' - V \). The SC pairing in the effective model is of the onsite singlet form. We note however that in terms of the original lattice, pairing is primarily nearest-neighbor, and a full calculation of the original \( U > 0 \) Hamiltonian would likely lead to further pair structure such as nodes in the gap function. Furthermore, modifications of the simple square++ lattice structure shown in Fig. 1(d) are needed to describe the lattices of specific CTS, for example the more anisotropic Bechgaard salt superconductors. We believe however that this effective model can describe the BCDW/SC transition found across the various CTS families.

3. Discussion: CTS materials

**Quasi-1D CTS \((TMTSF)_2X\):** We believe that our theory gives the correct insight into understanding the SC state in all the \( \frac{1}{4} \)-filled CTS superconductors, including both quasi-1D and 2D CTS. Even for the quasi-1D materials triangular lattice structure is present in the interchain hopping integrals\[11\]. The addition of intrinsic dimerization to Eq. 1 acts to further stabilize the \( .1100... \) BCDW over the \( .1010... \) CO state\[12\]. The role of pressure is to increase interchain coupling and the effective frustration, giving mobility to the insulating pairs in the BCDW. In the quasi-1D \((TMTSF)_2X\) (C=Se,S), we have shown that while the high temperature CO found in this series can have the CO pattern \( .1010... \), the CO pattern found in the SP state and coexisting with the SDW adjacent to SC is the \( .1100... \) BCDW \[5, 6\].

Very large upper critical fields are found in \((TMTSF)_2X\) \[13\] and other CTS SC \[14\], along with an upward curvature of \( H_{c2} \) as a function of temperature. These features are a common characteristic of superconductivity with short-range local pairing and would be expected within our theory\[15\].

\( \kappa-(ET)_2X \): While many authors have suggested that the mechanism of SC in the 2D CTS is linked to the presence of the AFM state, AFM adjacent to SC is perhaps more unusual than common in the 2D CTS. For example, within the \( \kappa-(ET)_2X \) series, \( X=\text{Cu}_{2}(\text{CN})_{3} \) is a superconductor where the insulating state is a spin liquid with no apparent spin ordering to millikelvin temperatures \[16, 17\]. As discussed below, there are many examples of CO/SC transitions within the CTS; this suggests that the AFM and BCDW states are quite close in energy, and that under pressure the BCDW can replace AFM order.

Precision dilatometry measurements on \( \kappa-(ET)_2\text{Cu}[\text{N(CN)}_2]\text{Br} \) find strong lattice effects near the AFM/SC transition \[18\]. Magneto-optical measurements on \( \kappa-(ET)_2\text{Cu(SCN)}_2 \) find changes in the vibrational spectra between SC and normal states, suggesting that intramolecular vibrations are involved in the superconducting transition \[19\]. These experiments suggest strongly the importance of lattice degrees of freedom in the SC transition even when AFM is present, in agreement with our theory.

**Dmrt salts:** \( \text{EtMe}_3\text{Z}[\text{Pd(dmrt)}_2]^2 \) has a charge/bond ordered insulating state that has been described as valence-bond solid (VBS) ordering \[20, 21\]. We point out that the charge ordering found in the VBS is the same as in our \( .1100... \) BCDW, see Fig. 3 in reference \[20\]. Under pressure, the VBS state becomes superconducting.

\( \beta-(\text{meso-DMBEDT-TTF})_2\text{PF}_6 \): \( \beta-(\text{meso-DMBEDT-TTF})_2\text{PF}_6 \) is another 2D CTS that has CO and undergoes a CO/SC transition under pressure \[22\]. The CO state has been described as a “checkerboard” pattern, implying that the local CO is \( .1010... \) driven by the \( V \) interaction. We point out however, that the checkerboard here is in terms of dimers, and the CO pattern again corresponds to the BCDW shown in Fig. 1(c).
4. Relationship to other theories

Our theory has strong similarities with RVB and bipolaron models of SC simultaneously. As in the RVB model, pairing is (partly) driven by AFM correlations also in our model. The key difference in our model is the filling: at density \( n = \frac{1}{2} \) because of the fewer number of neighbors it is much favorable energetically to form a nearest-neighbor singlet state. Furthermore, at \( n = \frac{1}{2} \) e-e and e-p interactions tend to act cooperatively [4–9].

Traditional bipolaronic SC is based on overscreening of the e-e interaction by strong e-p interactions [15]. This leads to an unphysically large effective mass of the paired electrons. In contrast, because of the co-operation between the AFM and e-p interactions, no overscreening is required in our theory. Furthermore, it has recently been shown that bipolarons are especially mobile on triangular lattices [23]. Both \( n = \frac{1}{2} \) and frustration are hence essential ingredients of the insulator-to-superconductor transition in the CTS.

5. Application to other materials

We believe that our theory may be relevant to other \( \frac{1}{2} \)-filled superconductors. Several of these materials were known before superconducting CTS. LiTi\(_2\)O\(_4\) with \( \frac{1}{2} \)-filled Ti bands is one of the first oxide superconductors discovered with at \( T_c \) of 12 K [24]. Because of the presence of frustration in the spinel lattice structure, a resonating valence bond (RVB) ground state has been suggested [25]. However, e-p coupling also appears to be strong in this material, and it is still unclear of the relative importance of e-e and e-p interactions [26].

Very complicated CO ordering occurs in other \( \frac{1}{2} \)-filled spinels and is in fact a combination of orbital and charge ordering. In CuIr\(_2\)S\(_4\), CO and a nonmagnetic (spin singlet) ground state are found. This state has been explained as an orbitally driven Peierls state, with the pattern Ir\(^{3+}\).Ir\(^{3+}\).Ir\(^{4+}\).Ir\(^{4+}\) [27]. This is again the .1100. BCDW CO pattern.

A CO/SC transition was found under pressure in \( \beta\)-Na\(_{0.33}\)V\(_2\)O\(_5\) [28]. While the stoichiometry of \( \beta\)-Na\(_{0.33}\)V\(_2\)O\(_5\) gives \( \frac{1}{2} \) filling of vanadium sites on average, there occur here three inequivalent vanadium sites with unequal electron distribution. Experiment indicates \( \frac{1}{2} \)-filled zig-zag chains as in the quasi-1D CTS [29]. The SC state in this material is extremely sensitive to the concentration of Na, with the SC transition disappearing for a tiny change in Na concentration (\( x = 0.32 \) rather than \( x = 0.33 \)) [30]. This strongly suggests that the CO/SC transition here is a property of the exact band filling of the system, rather than being driven by doping where a broad peak around the optimal \( x \) would be expected.

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