The dimer model for \(\kappa\)-phase organic superconductors

G. Visentini\(^1\), A. Painelli\(^1\), A. Girlando\(^1\) and A. Fortunelli\(^2\)

\(^1\) Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica e Chimica Fisica Università di Parma - I-43100 Parma, Italy
\(^2\) Istituto di Chimica Quantistica ed Energetica Molecolare Consiglio Nazionale delle Ricerche - I-56126 Pisa, Italy

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Abstract. – We prove that the upper electronic bands of \(\kappa\)-phase BEDT-TTF salts are adequately modeled by a tight-binding lattice with one site per cell. The band parameters are derived from recent \textit{ab initio} calculations, getting a very simple but extremely accurate one-electron picture. This picture allows us to solve the BCS gap equation adopting a real-space pairing potential. Comparison of the resulting superconducting properties with experiments points to isotropic \(s_0\)-pairing. Residual many-body or phonon-mediated interactions offer a plausible explanation of the large variety of physical properties observed in \(\kappa\)-phase BEDT-TTF salts.

Superconductivity (SC) in organic charge transfer (CT) salts has been discovered more than 15 years ago. At present, \(\kappa\)-phase BEDT-TTF (ET) salts are the most promising organic superconductors (OSC) [1]. OSC have similar features to cuprate superconductors [2]: they exhibit highly bidimensional structures, narrow electronic bands, low carrier densities and possibly strong electronic correlations and electron-phonon coupling. Superconducting properties are also similar in organics and cuprates, exhibiting singlet pairing [3], very low coherence lengths, high magnetic penetration depths and critical fields [1]. Perhaps the most characteristic feature of cuprate superconductors is the competition between SC and antiferromagnetism (AFM). This competition shows up also in OSC, as demonstrated by the presence of antiferromagnetic fluctuations in the metallic state of several compounds [3]. In this respect the family of \(\kappa\)-ET\(_2\)Cu[N(CN)\(_2\)]X (ET-X) salts where \(X = \text{Cl, Br}\) is particularly interesting: at ambient pressure ET-Br is a superconductor with \(T_c = 11.6\) K, deuterated ET-Br lies at the SC-AFM interface [4], and the Cl compound is a Mott insulator with commensurate antiferromagnetic ordering [3], but a small external pressure (270 bar) turns it to the superconducting ground state \((T_c = 12.8\) K) [1].

As in cuprates, the SC mechanism in OSC is not understood, but the amount of theoretical work on OSC is scarce if compared with that developed for cuprates, possibly due to the apparent complexity of OSC structures. In this paper we focus our attention on the \(\kappa\)-phase ET salts, and prove that their electronic band structure is \textit{accurately} described in terms of a rectangular lattice with nearest- and next-nearest-neighbor interactions. This simple,
analytical band structure allows one to attack the problem of SC: we present here the first explicit solution of the BCS gap equation for OSC. Moreover we discuss the role of residual many-body interactions in driving \( \kappa \)-phase salts towards AFM. In spite of its simplicity, the adopted model is very accurate as to allow for quantitative comparison with experiment. In this view OSC offer a more favourable opportunity to test SC theories than cuprates. One-band models similar to the one we derive for OSC have often been adopted for cuprates [5], but they lead to an oversimplified view of the complex cuprate band structures.

We solve the gap equation for a general real-space pairing potential in a BCS-like approach. The choice of a real-space pairing is basically due to numerical convenience. However, whereas other choices are possible and are worth being tested, the real-space potential is consistent with the short coherence length characteristic of OSC (\( \xi = 37 \) Å for ET-Br [6]). Due to the short coherence length it is not obvious if BCS applies to OSC [7]. It is difficult to work in the intermediate regime, so one must argue if OSC are better described in the BCS or in the Bose-condensation limit. Experiments do not settle the question: a few experiments have recently been interpreted in terms of the presence of a pseudogap [2], then favouring the Bose condensation limit, but other experiments [8] do not support this interpretation. Moreover, the extreme sensitivity of OSC to impurities and/or disorder [1] points to a BCS picture [7]. Furthermore, according to recent Ginzburg-Landau calculations [9], the ET-Br value \( k_F \xi \sim 11 \) locate OSC in the weak-coupling side of the crossover from BCS to Bose condensation, suggesting the BCS as the relevant limit for OSC.

The basic structural unit of \( \kappa \)-phases is a pair of ET molecules. These pairs (dimers) arrange themselves nearly perpendicularly in a check-board pattern to construct two-dimensional cation layers intercalated by anion sheets. As usual for organic CT salts, the relevant physics of ET compounds is described in terms of electrons hopping among the frontier molecular orbitals. Due to their special structural motif, in \( \kappa \)-phases the intradimer interactions are larger than all interdimer interactions. Therefore, as already suggested by other authors [10], [11], the bonding and antibonding dimer orbitals are a convenient basis for tight-binding calculations.

The electronic parameters have recently been estimated for ET-Br from \textit{ab initio} calculations [12]. Non-site diagonal electron-electron interactions are negligible, so that standard (repulsive) extended Hubbard model applies. The intradimer hopping \( b_1 = 0.272 \) eV is more than twice the interdimer integrals, \( p = 0.13 \) eV and \( q = 0.04 \) eV along \( c+a \), and \( b_2 = 0.085 \) eV along the \( c \)-direction. The dimer bonding and antibonding orbitals have energies differing by \( 2b_1 \), whereas interdimer hoppings are defined by \( (p \pm q)/4 \) and \( b_2/2 \). By neglecting the mixing between bonding and antibonding orbitals, the original four-site problem reduces to two independent two-site problems. Focusing on antibonding orbitals, each dimeric site has 2 nearest neighbors along the \( c \)-direction (interaction \( b_2/2 \)), and 4 next-nearest neighbors along the \( c \pm a \) directions (interaction \( (p + q)/2 \)). The resulting unit cell can be reduced to contain a single site. The analytical expression for the conduction band in the doubled Brillouin zone is

\[
\epsilon(k) = b_2 \cos k_z c + 2(p + q) \cos \frac{k_z c}{2} \cos \frac{k_x a}{2}.
\]

In fig. 1 we report the energy dispersion curves for the conduction and valence bands, the density of states (DOS) for the conduction band, and the Fermi surface (FS), calculated by solving the tight-binding problem with four interacting site orbitals as compared with results obtained in the dimer limit with fixed Fermi energy. The main features of the complete four-orbital model are well reproduced in the dimer approximation, namely, the bandwidth, FS topology and DOS. We stress that the hopping integrals and the calculated band structures are rather insensitive to structural details, so that, at this level of approximation, all \( \kappa \)-phase ET salts are described by similar band structures. The bands in fig. 1 compare well with EHT bands [13]. LDA bands for \( \kappa \)-ET\(_2\)Cu(NCS)\(_2\) and ET-Br [14] are also similar, apart
from an overall bandwidth narrowing. Moreover the FS topology agrees with the available experimental Shubnikov-de Haas (SdH) data on κ-ET$_2$Cu(NCS)$_2$ [10] and on κ-ET$_2$I$_3$ [15]. Therefore the dimer model offers a manifestly good description of the κ-phase band structure.

As a first application of the dimer model, we investigate SC in κ-phases. We choose the following non-retarded real-space pairing potential [16]:

$$V = -\sum_{i,j} g_{ij} a_i^\dagger a_j^\dagger a_j a_i.$$

The sum extends to nearest and next-nearest neighbors (with coefficients $g_{NN}$ and $g_{NNN}$, respectively), and also includes $i = j$ (on-site) $g_0$ interaction, with either positive (pairing) or negative (repulsion) coefficients. SC requires at least one attractive channel in the effective interaction, hence the bare electron-electron parameters [12] cannot account for the chosen pairing interaction. The adopted pairing potential is general: with the three parameters $g_{ij}$, one can explore all the possible symmetries of the gap function $\Delta(k)$ in the bidimensional space group pgg of the organic layers of the κ-phase crystals. The (singlet pairing) BCS gap function can be written as a linear combination of functions with different symmetries [16]:

$$\Delta(k) = \sum_{i=1}^{4} \Delta_i \eta_i(k),$$

where $\eta_1(k) = \sin \frac{k_x}{2} \sin \frac{k_y}{2}$ transforms as the $B_g$ irreducible representation, and $\eta_2(k) = \cos \frac{k_x}{2} \cos \frac{k_y}{2}$, $\eta_3(k) = 1$, $\eta_4(k) = \cos k_z c$ as $A_g$. Adopting the standard notation for cuprates [5], $\eta_1$ corresponds to $d_{xy}$ pairing and $\eta_3$ to $s_0$ isotropic pairing, while $\eta_2$ and $\eta_4$ correspond to the extended or generalized $s^*$ pairing.

By measuring $T$ in $T_c$ units, only two free pairing parameters survive in the gap equation, that we choose as the ratios of $g_0$ and $g_{NN}$ over $g_{NNN}$. We solve the BCS gap equation on a 1888×1248 lattice in the $g_0$-$g_{NN}$ parameter space to obtain the phase diagram in fig. 2, left panel. For several points in the phase diagram the calculated gap has been checked to correspond to the absolute minimum of the BCS free energy. At $T = T_c$ the phase diagram is very simple: the gap equation is linear and the mixing of pair functions with different symmetry is strictly forbidden. By lowering $T$ below $T_c$, the BCS equation becomes non-linear and the region of mixed $s$ and $d$ pairing widens with decreasing $T$. However, due to the low critical temperatures of OSC, the gap equation stays quasi-linear, and the actual amount of mixing remains small ($< 10^{-3}$).
We use the solution of the BCS equation to calculate the macroscopic properties of the superconducting state \[17\]. Low-energy macroscopic properties are strongly affected by the presence of nodes in the gap at the FS. A sharp crossover separates \(d\)- and \(s\)-wave regions. In the \(d\)-wave region nodes are found in the superconducting gap at the FS. In the \(s\)-region, at large \(|g_{NN}|\), pseudonodes (not necessarily implying a change of sign of the gap at the FS) are observed, pointing to \(s^*\), whereas at small \(|g_{NN}|\) the gap becomes quasi-isotropic \((s_0)\) with the BCS value \(\Delta_0 = 1.767T_c\). For the three representative points marked in the phase diagram in fig. 2, left panel, lying in the \(s_0\), \(s^*\), and \(d\) regions, we calculate the superconducting electronic specific heat, magnetic penetration depth, and tunneling bulk conductance. The low-energy behavior of these quantities is exponential-like in the isotropic case, whereas it is power law in the anisotropic case, in agreement with standard results for conventional BCS \[17\] and \(d\)-wave \[18\] SC. Experimental estimates of the specific heat \[19\] and tunneling \[20\] in OSC are affected by large uncertainties, and the comparison with the calculated quantities is not conclusive. Experimental studies of the temperature dependence of the magnetic penetration depth led to conflicting conclusions \[6\].

Frequency-dependent susceptibilities are largely dominated by the maximum of the gap at the FS, where a divergence in the superconducting DOS is located. In fig. 2, right panel, we report the maximum of \(|\Delta(k)|\) calculated at \(T = 0\). In the \(d\)-wave region the maximum gap is fixed to 2.09 \(T_c\). In the \(s\)-region, due to the competition between \(s_0\) and \(s^*\) components, the maximum gap at the FS shows a complex structure. For small \(|g_{NN}|\), where the gap is dominated by \(s_0\), we regain the BCS value \(\Delta_0\). For the three points marked in fig. 2, left panel, we explicitly calculate the superconducting-phonon self-energy. The self-energy presents a singularity at a frequency corresponding to twice the maximum of the gap at the FS \[21\]. By lowering \(T\) below \(T_c\), phonons lying below (above) this frequency soften (harden). The crossover frequency strongly depends on the topology of the FS, so that the choice of the model for the electronic structure is crucial. As shown in fig. 2, right panel, max \(|\Delta(k)|\) reaches its minimum value for isotropic \(s_0\) pairing, corresponding to the BCS value \(2\Delta_0 = 3.53T_c\). The salient feature of a recent low-energy Raman scattering study on ET-Br \[8\] is that below \(T_c\) all
relevant Raman peaks harden with the greatest relative shift exhibited by the lowest observed phonon at 27.4 cm\(^{-1}\) \(\approx 3.5 T_c\). This value fixes an upper limit for the maximum of the gap at the FS. On the basis of the chosen pairing potential, this result can only be interpreted assuming isotropic \(s_0\) pairing. A similar conclusion can also be reached for \(\kappa\)-(ET)\(_2\)Cu(NCS)\(_2\), as inferred from neutron scattering experiment [22].

The proposed picture for OSC is based on a single-particle description of the electronic structure, associated with a simple pairing potential. The single-particle parameters are taken from HF-SCF calculations [12]. Our results compare well with EHT and LDA calculations. The topology of the calculated FS agrees with available SdH data on \(\kappa\)-phase ET salts [10], [15], [23]. We observe that these experiments strongly support a Fermi-liquid picture for OSC. On the other hand, residual many-body effects are important in determining the electronic properties of OSC. The effective masses inferred from SdH data via the Lifshits-Kosevich formula for other hand, residual many-body effects are important in determining the electronic properties of OSC. The effective masses inferred from SdH data via the Lifshits-Kosevich formula for \(\kappa\)-ET\(_2\)Cu(NCS)\(_2\) [10], \(\kappa\)-ET\(_2\)I\(_3\) [15], and ET-Br [23] are about two times larger than our calculated effective masses. Moreover, the calculated normal-state electronic specific heat is quasi-linear with \(T\), but its slope, \(\gamma \approx 7.5\) mJ/mole \(\cdot\) K\(^2\), is 2–3 times larger than the experimental values for ET-Br, \(\kappa\)-(ET)\(_2\)Cu(NCS)\(_2\), and \(\kappa\)-ET\(_2\)I\(_3\) [19]. However, it is important to recognize that our picture for SC robustly survives the inclusion of residual many-body interactions, at least in the hypothesis that these interactions do not modify the topology of the FS, but only lead to an overall renormalization of single-particle parameters. As we have explicitly verified, in fact, this would only imply an overall rescaling of pairing parameters. Therefore, at least for \(\kappa\)-ET\(_2\)Cu(NCS)\(_2\) and \(\kappa\)-ET\(_2\)I\(_3\), whose experimental FS are well reproduced by the dimer model, the calculated SC properties are accurate enough, as to allow a sound test of SC theories against experiment.

On the other hand, \(\kappa\)-phases, in spite of having similar structures and therefore similar calculated dispersion curves, show a wide variety of physical properties, suggesting a possibly important role of residual interactions in modifying the FS topology. This is especially true for the ET-X family. In this connection, the proposed dimer model is simple enough to offer clues about the fine tuning of the physical properties of \(\kappa\)-phases as induced by variations of the FS topology. As a second powerful application of the dimer model we discuss how residual interactions can drive \(\kappa\)-phase salts towards AFM.

The band structure in fig. 1 shows an extended van Hove singularity (vHs) along the MZ direction, at energy \(-b_2\) with respect to the Fermi level. Even a small reduction of \(b_2\) would imply a large increase of the effective mass. In the extreme limit of vanishing \(b_2\) the vHs would lie at the FS, and the FS itself would be rectangular with perfect commensurate nesting. Thus the electronic structure of \(\kappa\)-phases presents an intrinsic instability, that manifests itself through the competition between SC and AFM, as seen in ET-Cl, ET-Br and deuterated ET-Br. This picture is also attractive to rationalize the magnetic ordered state in ET-X, recently investigated by Hall effect experiments [24]. High-pressure SdH experiments on ET-Br [25] nicely confirm this picture: in fact, the measured area of the \(\alpha\)-orbit is much smaller than the calculated value, supporting a reduction of the \(b_2\) integral.

In ET-Cl and ET-Br the Cl and Br atoms are near to the \(b_2\) dimer [13], possibly affecting the corresponding transfer integral. \(Ab\) initio calculations are in progress to test the effect of counterions and of residual electron-electron interactions on the \(b_2\) hopping. A different source of renormalization of the hopping parameters involves electron-phonon interactions. The vHs observed in the MZ direction implies very large effective electronic masses, even larger than the phonon masses, so that, along this direction, \(b_2\) can be reduced by a polaron narrowing mechanism [7]. Furthermore, the frequency corresponding to \(b_2\) \((\approx 685\) cm\(^{-1}\)) is smaller than the frequencies of most of intramolecular phonons (conversely, the other electronic frequency \(2(p+q) \sim 2700\) cm\(^{-1}\) is higher than all relevant phonon frequencies). From the known coupling
constants \((g_i)\) and phonon frequencies \((\omega_i)\) of the ET molecule \([26]\) we estimate the polaron reduction of \(b_2\) as \(\exp\left(-\sum g_i^2/\omega_i^2\right) \sim 1/2\). This equation, strictly valid in the inverse adiabatic limit \([7]\), is summed over all phonons with \(\omega_i > b_2\).

In summary, we have shown that in spite of the apparent complexity of \(\kappa\)-phase salts, their electronic properties can be accurately described in terms of a simple, analytical band structure. At variance with cuprates, our one-band model is derived from first-principle calculations, so that significant comparisons with experiment are possible. Introducing an effective real-space pairing potential, we are able to present the first solution of the BCS gap equation for OSC. The results support isotropic SC. Different choices of the pairing potential are also feasible, as demonstrated by preliminary calculations. We discuss the proximity of \(\kappa\)-phases to AFM, as due to an extended vHs near the FS, and to the sensitivity of the FS topology to small variations of hopping integrals. Polaron narrowing and the screening due to counterions are suggested as possible sources of renormalization of the relevant hopping terms.

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