

Renormalization group approach to a quasi-one-dimensional conductor with a triclinic band structure

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Abstract

This part of the thesis project is concerned with the theoretical understanding of the phase diagram of the Bechgaard salts series by the renormalization group method. The full triclinic electron spectrum, as it can be obtained from density functional theory, will be implemented in the one-loop renormalization group calculations in order to describe the spin-density-wave to superconducting sequence of instabilities of the interacting electron gas as a function of applied pressure. The Lindhard or density-wave response function, which is an essential part of the renormalization group flow equations, has to be first evaluated and studied near the best nesting vector for both orthorhombic and triclinic band structure models.

1 Introduction

1.1 The Bechgaard salts as organic molecular crystals

The $(\text{TMTSF})_2X$ ($X = \text{PF}_6, \text{AsF}_6, \text{ClO}_4, \dots$) series of organic molecular crystals, also known as the Bechgaard salts series [1, 2], are nearly or quasi one-dimensional systems. They consist of chains of organic flat TMTSF [tetramethyltetraselenofulvalene] molecules [see Fig. 1 (a)] aligned along the parallel a direction and separated by anion sheets X ¹. The molecules essentially retain their flat shape in the solid state, so that the π type molecular orbitals, also called the highest occupied molecular orbitals (HOMO) of the TMTSF molecule, have their highest overlap preferentially along the a direction. The corresponding π -molecular overlap along the two *transverse* \vec{OB} and \vec{OC} directions shown in Fig. 1 are smaller by order of magnitudes. This is the main reason why these are close realizations of one-dimensional systems.

From X-ray crystallographic studies, the chains are not uniform and are slightly *dimerized* with a shorter and a longer distances between molecules. The result of this dimerization is to ‘double’ the unit cell of the crystal, which effectively consists of two TMTSF molecules and one anion X [see Fig. 1]. The crystal structure is *triclinic* with angles that differ from 90° .

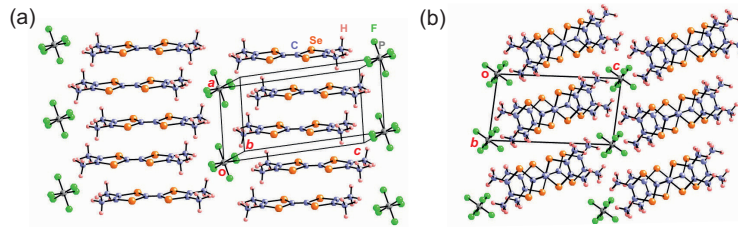


Figure 1: The crystal structure of the Bechgaard salts $(\text{TMTSF})_2X$. Side (left) and top (right) views. From Guster *et al.* [3].

1.2 Electronic structure

The molecular TMTSF unit contains many carbon, selenium and hydrogen atoms, each of them consisting of many electrons. Correspondingly, the number of electron bands is expected to be very large. However, it turns out that the HOMO is essentially the only relevant orbital at low energy that crosses the Fermi level. Different approaches to band calculations (Extended Huckel[4, 5], density functional theory (DFT)[3] ...) confirms this. In Figure 2 (a), for instance, we reproduce the band structure of a compound like $(\text{TMTSF})_2\text{PF}_6$. From the Figure we verify that within a width in energy of about 1 eV, only one

¹The role of anions X is to assure a so-called charge transfer in the solid state: the anion X captures one electron coming from two TMTSF molecules. The partially emptied HOMO π orbitals make then possible the existence of a metal for these systems.

band is present and crosses the Fermi level at energy zero. Note that here the presence of a small dimerization opens a gap in the middle of the band at points X and M in Fig. 2 (a). This dimerization gap makes the band effectively half-filled.²

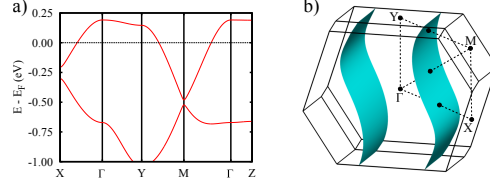


Figure 2: DFT band structure calculations (a) and the corresponding open Fermi surface (b) for the triclinic (TMTSF)₂X. From [3]

1.3 The phase diagram

Resistivity measurements confirm the existence of a metallic state in normal (ambient) pressure and temperature conditions for the Bechgaard salts. However, when cooled down, phase transitions take place indicating a collective behavior for the whole electron system. For instance, at low pressure, the system undergoes a sharp metal-insulator transition near $T_{SDW} \sim 10$ K with a gap that opens at the Fermi level. According to several other experiments (susceptibility, NMR, EPR, etc.), it is firmly established that the nature of the transition is magnetic in character and consists with a spin-density-wave ordered state of modulation wave vector q_0 [1, 2].

When pressure is applied, T_{SDW} undergoes a gradual decrease that becomes critical at the approach of a critical pressure. Instead of touching zero, the system becomes a superconductor at $T_c \sim 1$ K [6], which in its turn undergoes a gradual decrease [see Fig. 3] [7]. It follows that a ‘superconducting dome’ is formed, which is typically found in many unconventional superconductors (cuprates, pnictides, heavy fermions, etc. See Ref.[8])³. The characteristic sequence SDW \rightarrow SC under pressure also stands out as a clear example of quantum criticality emerging for the interplay from two ordered states.

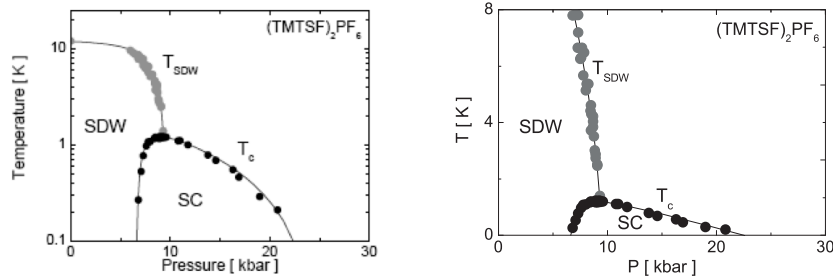


Figure 3: Phase diagram (TMTSF)₂PF₆ under pressure on a semi-logarithmic scale (a) and linear scale near the quantum critical point (b). SDW stands for spin-density-wave state and SC for superconductivity. From [7].

1.4 Triclinic and approximate orthorhombic electron spectrum

Triclinic tight-binding electron spectrum In the triclinic structure, the angles between the crystallographic axis differ from 90°; furthermore, possibilities of overlap along the transverse b direction are multiple, as can be seen in Figure 4. According to the work of Yamaji [9] and also Hasegawa and Kishigi[10], the tight-binding quasi-1D spectrum of (TMTSF)₂X, which is compatible with the triclinic structure, can be put in the following form:

$$\epsilon_k^p = v_F(pk - k_F) + \epsilon^p(k_\perp) \quad (1)$$

where $p = \pm$ is the branch index for right (+) and left (−) moving carrier, v_F their longitudinal velocity, and k_F is the 1D Fermi wave vector in the absence of ϵ_\perp^p . As for the transverse part of the spectrum, it can be written in series form

²From a purely stoichiometric viewpoint, that is, by neglecting dimerization, the (TMTSF)₂X compound should have 1/2 hole per TMTSF molecule and the band would be 3/4 filled. In presence of dimerization, a gap opens not at the Fermi level, but in the middle of the 3/4 filled band, which splits into one filled and one half-filled band (see Fig. 2 (a)).

³The superconducting dome following an antiferromagnetic ordered state in the Bechgaard salts is apparently the first to have been discovered in unconventional superconductors.

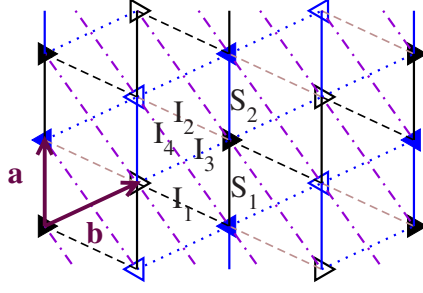


Figure 4: Possibilities of orbital overlaps in the ab plane of $(\text{TMTSF})_2\text{X}$ in their triclinic structure. From [10].

$$\begin{aligned} \epsilon^p(k_\perp) = & -2t_b \cos(k_\perp - p\phi) \\ & -2t'_\perp \cos[2(k_\perp - p\phi)b] - p2\tau'_\perp \sin[2(k_\perp - p\phi)] \\ & + \dots \end{aligned} \quad (2)$$

where t_\perp is the first nearest-neighbor interchain hopping; t'_\perp and τ'_\perp , etc., are next-nearest neighbor interchain hopping terms compatible with the triclinic structure. The angle $\phi (\leq \pi/2)$ can be connected to overlap integrals of the triclinic structure; its value varies for compound to compound, namely for different anion X . Here

$$k \equiv \mathbf{k} \cdot \mathbf{a}, \quad k_\perp \equiv \mathbf{k} \cdot \mathbf{b}.$$

where \mathbf{a} and \mathbf{b} are the lattice vectors of the ab plane in the triclinic cell. The expression for $\epsilon^p_{\mathbf{k}}$ in (1-2) gives an excellent fit of the DFT spectrum of Fig. 2 (a).

The triclinic spectrum has well defined nesting properties at some *nesting vector* that will be called \mathbf{q}'_0 . For instance, when next to nearest neighbor hopping terms t'_\perp and τ'_\perp are zero, one has the electron-hole symmetry relation:

$$\epsilon^+_{\mathbf{k}+\mathbf{q}'_0} = -\epsilon^-_{\mathbf{k}} \quad (3)$$

where according to (1-2), is satisfied for the nesting vector

$$\mathbf{q}'_0 = (2k_F, \pi + 2\phi) \quad (4)$$

at $t'_\perp = \tau'_\perp = 0$. Now when both $t'_\perp \neq 0$ and $\tau'_\perp \neq 0$, deviations are found and $\epsilon^+_{\mathbf{k}+\mathbf{q}'_0} \neq -\epsilon^-_{\mathbf{k}}$.

Orthorhombic approximation If we now focus on the simpler orthorhombic approximation for the spectrum for which a *square lattice* is considered in the ab plane, where $\mathbf{a} \perp \mathbf{b}$ are at right angles. This is the most common approximation of the spectrum used. In this case, the tight-binding spectrum (with respect the Fermi energy ϵ_F) reads

$$\epsilon_{\mathbf{k}} = -t_a \cos ka - 2t_\perp \cos k_\perp - \epsilon_F \quad (5)$$

where t_a and t_\perp are the intrachain and interchain hopping integrals. If we look at the equation for the Fermi surface $\mathbf{k}_F = (k_F(k_\perp), k_\perp)$, we use the condition $\epsilon_{\mathbf{k}_F} = 0$ for (5), which gives two ($p = \pm$) warped Fermi sheets

$$\begin{aligned} k_F^p(k_\perp) &= p \arccos \left(\frac{-\epsilon_F}{2t_a} - \frac{t_\perp}{t_a} \cos k_\perp \right) \Bigg|_{t_\perp/t_a \ll 1} \\ &\simeq p \left[k_F - \frac{1}{v_F} \epsilon_\perp^0(k_\perp) \right] \end{aligned} \quad (6)$$

where

$$\epsilon_\perp^0(k_\perp) = -2t_\perp \cos k_\perp - 2t'_\perp \cos 2k'_\perp + \dots \quad (7)$$

Here $v_F = 2t_a \sin k_F + \dots$ is the longitudinal velocity and t'_\perp, \dots are different harmonics of interchain hopping generated by the expansion of (6) at small t_\perp/t_a . These effective interchain hopping between second, ... neighbors chains introduce frustration in the nesting properties of the spectrum.

The Fermi sheets in this approximation are plotted in Figure 5 (compare with those of Fig. 2 (b) for the triclinic case). The

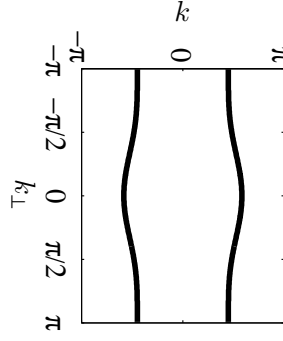


Figure 5: Quasi-one-dimensional open Fermi surface for a square lattice in the ab plane.

linearized spectrum around the Fermi sheets then takes the form:

$$\begin{aligned}\epsilon_k^p &\simeq v_F[pk - k_F^p(k_\perp)] \\ &= v_F(pk - k_F) + \epsilon_\perp^0(k_\perp)\end{aligned}\tag{8}$$

In the absence of t'_\perp , $\epsilon_\perp^0(k_\perp) \rightarrow -2t_\perp \cos k_\perp b$ and there is perfect nesting properties at

$$\mathbf{q}_0 = (2k_F, \pi)$$

which corresponds to an electron-hole symmetry in the spectrum at $t'_\perp = 0$. The latter takes the form

$$\epsilon_{\mathbf{k}+\mathbf{q}_0}^+ = -\epsilon_{\mathbf{k}}^-\tag{9}$$

When $t'_\perp \neq 0$, there are deviations which read

$$\epsilon_{\mathbf{k}+\mathbf{q}_0}^+ = -\epsilon_{\mathbf{k}}^- + 4t'_\perp \cos 2k_\perp\tag{10}$$

We note that only few points of perfect nesting remain and these occur at $k_\perp = \pm\pi/4, \pm3\pi/4$.

1.5 The Lindhard function

Part of the thesis project will be to first study the behavior of the so-called Lindhard function in the above two schemes of the electron spectrum. This function coincides with the response function of the electron system for density-wave formation at wave vector \mathbf{q} and will actually enter in the subsequent renormalization group flow equations.

The Lindhard function can be put in the form:

$$\chi^0(\mathbf{q}) = -\frac{2}{LN_\perp} \sum_{k, k_\perp} \frac{n[\epsilon_k^+] - n[\epsilon_{\mathbf{k}-\mathbf{q}}^-]}{\epsilon_k^+ - \epsilon_{\mathbf{k}-\mathbf{q}}^-}\tag{11}$$

where $n[x] = (e^{\beta x} + 1)^{-1}$ is the Fermi distribution factor.

This part of the project will consist of calculating $\chi^0(\mathbf{q})$ and study his behavior as a function of \mathbf{q} in i) the orthorhombic limit using (8) and retrieve known results, and in ii), the triclinic case using the spectrum (1) using (2) in its different limits and compare with the recent results of Guster *et al.*[3].

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