Organic Superconductors: Reduced Dimensionality and Correlation Effects

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Abstract

In this tutorial we will tackle the problem of electronic correlations in quasi-one-dimensional organic superconductors. We will go through different pieces of experimental evidence showing the range of applicability of the Fermi and Luttinger liquid descriptions of the normal phase of the Bechgaard salts series and their sulfur analogs.

Keywords: organic superconductors, many-body theories, magnetic measurements, magnetic phase transitions.

1. Introduction

In solid-state physics the traditional approach to understand ordinary metals relies on the Landau theory of Fermi liquid. The concept of quasi-particles put forth by Landau proved to be quite successful in describing low-energy excitations, which effectively behave like non-interacting electrons. Besides the possibility of long range order which limits its range of applicability, the Fermi liquid theory turns out to be highly sensitive to the spatial dimensionality of the electron system. This is especially true for purely one-dimensional systems where the Landau Fermi liquid theory breaks down. It is pretty well understood that in one dimension there are no single-particle states that adiabatically connect with the non-interacting electrons. Instead elementary excitations are made of collective modes of bosonic character.

The possibility that such non-Fermi liquid correlation effects may be relevant to the description of the normal phase of real materials like quasi-one-dimensional organic conductors has attracted lot of interest over the past two decades. However, since these systems are not strictly one-dimensional, this raises the delicate question of the extent to which Fermi and non-Fermi liquid concepts are relevant to the understanding of the normal phase of these molecular compounds. In this tutorial we will pursue this issue for the well known isostructural series of sulfur-based \((TMTTF)_2X\) and selenium-based \((TMTSF)_2X\) series of quasi-1D organic conductors. We will review recent progress made in the analysis of the NMR spin-lattice relaxation rate, magnetic susceptibility and transport measurements in connection with correlation effects and non-Fermi liquid features found in these strongly anisotropic materials.

2. The low-field phase diagram

Following the synthesis of the isostructural sulfur \((TMTTF)_2X\) and selenide \((TMTSF)_2X\) series of quasi-1D organic conductors, it was soon recognized that a remarkable continuity can be drawn whenever their phase diagrams are combined as a function of applied hydrostatic pressure or anion \((X= PF_6, AsF_6, Br... )\) substitution. Depending on the choice of the anion at ambient pressure, members of the sulfur series can develop either spin-Peierls or commensurate/localized antiferromagnetic long range order whereas either itinerant antiferromagnetism (SDW) or superconductivity can be found for the selenide series under similar pressure conditions. Under pressure, however, the spin-Peierls and localized antiferromagnetic orderings alternately become unstable to the benefit of phases found in selenides thereby ensuring the characteristic sequence \(SP\rightarrow AF\rightarrow S\) of transitions shown in Figure 1.

The survey of existing results at low magnetic fields reveals that the critical temperature bracket for AF ordering is \(T_N \approx 1...24K\) (the highest \(T_N\) being found in sulfur series) and \(T_{SP} \approx 8...19K\) for the spin-Peierls ordering, while for superconductivity, it is scarecly more than 1K.

The study of the normal phase has shed some special light on the central role played by antiferromagnetism in the phase diagram of these quasi-1D materials. This is particularly revealing for \((TMTTF)_2X\) compounds for which precursors to magnetic ordering become manifest at a characteristic temperature \(T_\rho\) that can be in magnitude far above \(T_N\) under low pressure conditions. The scale \(T_\rho\) signals the loss of metallic character and in most cases the thermal activation of carriers corresponding to a gap \(\Delta_\rho \approx 2...3T_\rho\) in the normal phase temperature dependent electrical resistivity (Figure 2).

This contrasts with the temperature variation of magnetic susceptibility shown in Figure 3, which indicates that long wavelength spin degrees of freedom remain unaffected...
at $T_F$. As first pointed out by Emery et al. [8], this is the signature of a “$4k_F$” Mott-Hubbard localization of the carriers whose origin would result from 1D many-body physics at half-filling whenever repulsive interactions among carriers are combined with a slight dimerization of the organic stacks and the $4k_F$ anion potential. Here the possibility of sizeable short range repulsive Coulomb interaction in these kinds of molecular complexes is confirmed by detailed quantum chemistry calculations which tell us that the bare one-site repulsion parameter $U$ is of the order of one ev [8].

### 2.1. The Luttinger liquid concept and the description of the normal phase

The Mott-Hubbard instability is symptomatic of the breakdown of the Fermi liquid picture of the normal phase whose description would rather correspond to a limiting form of a **Luttinger liquid**. The concept of a Luttinger liquid was coined by Haldane fifteen years ago in order to characterize the peculiar features displayed by a many-electron quantum system in 1D [3]. It has been known for almost three decades that unlike a Fermi liquid, a Luttinger liquid at zero temperature has neither quasi-particle states nor a Fermi distribution step at the Fermi level [3]. The instability of single particle states occurs at the expense of collective modes related to spin and charge acoustic branches of excitations. These modes of different velocities $v_s$ and $v_\rho$ are decoupled at large distance and lead to the so-called spin-charge separation. At half-filling, the Mott-Hubbard localization magnifies the spin-charge separation in such a way that the gap $\Delta_F$ imposes a finite coherence length $\xi_\rho \sim v_\rho / T_F$ for spatial correlations of charge degrees of freedom, while the coherence length $\xi_s \sim v_s / T$ for spins is unaltered and reaches infinite range in the low temperature limit.

These features, however consistent with what is commonly observed in sulfur series at low pressure, are not the only signs in favor of a Luttinger liquid picture in these systems. Elaborate calculations using the abelian bosonization technique, predict that the single particle spectral weight

\[ A(k, \omega) \] (which gives the probability of having a single particle state at the wavevector $k$ with an energy $\omega$ measured from the Fermi level ($h = 1$)) has no single particle peaks but rather shows branch-cut singularities with non-universal exponents [3]. Albeit photoemission experiments have been carried out recently on a member of the selenide series [9], direct measurements of one-particle spectral properties of sulfur compounds are missing so far. Hallmarks of the Luttinger liquid can also be found in two-particle response functions, which turn out to be more accessible experimentally. This is especially true for the temperature dependent antiferromagnetic $(2k_F)$ susceptibilty $\chi(2k_F, T)$, which can be extracted from NMR spin-Lattice relaxation experiments. For repulsive interactions, $\chi(2k_F, T) \sim T^{-\gamma}$ develops a power law singularity with an exponent $\gamma = 1 - K_\rho$ that is expressed in terms of the non-universal charge degrees of freedom index $K_\rho$ whenever magnetic anisotropy is irrelevant. The Mott-Hubbard localization of charge degrees of freedom at $T < T_F$ imposes the exact constraint $K_\rho = 0$, which leads to $\chi(2k_F, T) \sim T^{-1}$ and which actually conveys the same type of singularity found in the exactly solved isotropic Heisenberg model [3].

### 2.2. Nuclear relaxation as a probe for Luttinger liquid

In the past fifteen years or so, a great deal of interest has been devoted to the study of electronic correlations using NMR spin-lattice relaxation rate ($T_1^{-1}$) measurements. The familiar Moriya formula

\[ T_1^{-1} \propto T \int d^Dq \frac{\Im \chi(q, \omega)}{\omega}, \]

that connects relaxation to the imaginary part of the dynamic spin susceptibility actually tells us how a local probe like NMR makes $T_1^{-1}$ sensitive to static, dynamic and dimensionality $D$ of spin fluctuations for all wavevectors $q$ [3]. From the results of Ref. [3, 11], the exact $D = 1$
Luttinger liquid prediction for $T_{1}^{-1}$ takes the form:

$$T_{1}^{-1} = C_{0} T \chi_{s}^{2}(T) + C_{1} T^{1-\gamma},$$

which consists of contributions coming from uniform ($q = 0$) and antiferromagnetic ($q \approx 2k_{F}$) spin fluctuations. Both generate deviations with respect to the Korringa law $(T_{1}T)^{-1} = constant$, found in ordinary metals with weak interactions. The uniform contribution, albeit related to the non-singular temperature dependent magnetic spin susceptibility, dominates at high temperature while the antiferromagnetic power law enhancement $(T_{1} T)^{-1} \sim C_{1} T^{-\gamma}$ in principle allows to extract the Luttinger liquid exponent $\gamma$. The combination of $\chi_{s}(T)$ and $T_{1}^{-1}$ measurements then proves to be a powerful tool in the analysis of correlation effects in the normal state of low-dimensional organic conductors [9, 10, 11].

This ability has been remarkably illustrated in the case of (TMTTF)$_{2}$X compounds as typified by the selected results shown in Figure 5. Let us consider for example the normal state of the spin-Peierls system (TMTTF)$_{2}$PF$_{6}$ at ambient pressure. This compound presents a well defined resistivity minimum at $T_{\rho} \approx 220K$ [2], whereas the spin susceptibility $\chi_{s}(T)$ shown in Figure 3, produces a regular downward slope as the temperature is lowered. As for the $T_{1}^{-1}$ temperature profile given in Figure 5, it also presents a monotonic decrease with an upward curvature down to the low temperature region where $T_{1}^{-1}$ shows signs of saturation. This persists down to 40K or so, below which the system is dominated by strong spin-Peierls lattice correlations, as borne out by x-ray experiments [3]. Plotting $T_{1}^{-1}$ vs $T \chi_{s}^{2}(T)$ in the temperature domain above 40K (where lattice fluctuations are weak), one finds that the Luttinger liquid prediction [2] with $\gamma = 1$ is again fully obeyed (inset of Figure 5). Therefore the existence of a constant term in $T_{1}^{-1}$ over all the temperature domain considered soundly supports the existence of a Mott-Hubbard localization which essentially coincides to a Luttinger liquid with a charge gap and gapless spin excitations. Similar features have been tracked down in other members of the same series. In this connection we have reproduced in Figure 5, the $T_{1}^{-1}$ temperature profile obtained for (TMTTF)$_{2}$Br where $T_{\rho} \approx 100K$ and $T_{N} \approx 15K$ [1]. Using the susceptibility data of Figure 3, the corresponding $T_{1}^{-1}$ vs $T \chi_{s}^{2}(T)$ plot in the inset shows that in the normal phase (above the critical domain taking place below 30K), the expression [2] with $\gamma = 1$ is again fully obeyed but with $C_{1}$ being smaller [1].

2.3. Interchain coupling and the one- and two-particle instability of the Luttinger liquid

Given the quasi-1D character of materials like (TMTTF)$_{2}$X, the presence of long range ordering invariably indicates that the Luttinger liquid becomes unstable at low temperature.
It can be shown, however, that it can still influence the formation of critical ordering in this case antiferromagnetic. The microscopic source of instability of the Luttinger liquid comes from the interchain coupling and in particular the interchain single particle hopping \( t_{\perp} \). This coupling is essential to the propagation of antiferromagnetic correlations perpendicular to the chains. According to band calculations \( [17] \), however, \( t_{\perp} \ll 100K \) in sulfur compounds, which means that a coherent interchain single particle hopping (band motion) is made irrelevant owing to the presence of a large charge gap \( \Delta_{\rho} > t_{\perp} \) in the normal phase \( [18] \). Nevertheless, bound electron-hole pairs can tunnel to neighboring chains via the virtual hops of single carriers leading to a perpendicular antiferromagnetic state.

The critical temperature \( T_N \) is obtained by considering the effect of \( J_{\perp} \) in molecular field approximation whereas intrachain correlations are treated exactly. One then gets the Stoner criteria \( 1 - J_{\perp}(2k_F,T_N) = 0 \) for \( T_N \). Now using the exact power law expression \( \chi(2k_F,T) \sim T^{-\lambda} \) at \( T \ll T_p \), one readily finds

\[
T_N \approx t_{\perp}^* / \Delta_{\rho}, \tag{3}
\]

which increases as \( \Delta_{\rho} \) or \( T_p \) decreases under pressure. \( T_p \) will merge in the critical domain of the transition and becomes irrelevant. In this range of intermediate pressure, the normal phase is metallic corresponding to a Luttinger liquid with gapless spin and charge excitations (Figure 1).

As for the interchain exchange interaction, it takes the form \( J_{\perp} \approx 2\pi v_F t_{\perp}^* / \Delta_{\rho} \), where \( \tilde{g} \) is a normalized effective electron-electron coupling constant divided by \( \pi v_F \). Therefore whenever \( T > T_{\perp} \approx t_{\perp}^* / 2 \) (that is above the single-particle dimensionality crossover temperature that marks the thermal deconfinement of along the stacks), \( J_{\perp} \) turns out to be still active in the development of long range order. The Stoner criteria in this case leads to

\[
T_N \approx 2\tilde{g}^* T_{\perp}, \tag{4}
\]

which decreases through \( \tilde{g}^* \) under pressure \( [15,16] \). Ultimately, the \( T_N \) pressure profile will show a maximum at a critical pressure \( P_m \) where \( T_p \) merges into the critical domain. A maximum of this kind has been found in all sulfur compounds that were the subject of pressure studies. The results of Klemme et al. \( [15] \) for the (TMTTF)$_2$Br, which are reproduced in Figure 6, indeed illustrate how the interchain exchange coupled to the Luttinger liquids of isolated chains give a controlled description of the antiferromagnetic transition in sulfur compounds up to intermediate pressure.

The interchain kinetic exchange will keep its key role for long range ordering as long as the carriers stay thermally confined in the transverse direction. In fact, as one moves away from the maximum of \( T_N \) by increasing pressure, the downward renormalization of \( t_{\perp}^* \) gets weaker due to a reduction of intrachain many-body effects. This progressively raises the single-particle dimensionality crossover temperature \( T_{\perp} \) up to a point where the exchange-induced temperature scale for critical fluctuations \( T_{\perp} \approx 2T_N \), as obtained from (4), becomes smaller than \( T_{\perp} \). This range of pressure then shows electronic deconfinement which is a one-particle type of instability of the Luttinger liquid that announces the formation of a Fermi liquid component.
spin-density-wave phase found in selenides (sulfur) series at low (high) pressure \([2, 3]\). It should be stressed, however, that the presence of nesting frustration indicates that a Fermi liquid component is present in the normal phase thus confirming that the characteristic scale \(T_{x1}\) for deconfinement really emerges in a pressure range that can safely be located somewhere between \(P_m\) and \(P_c\) (Figure 1). Since transients are likely to be associated with such a crossover, the deconfinement is not sharply defined so that at a given pressure it should be considered as somewhat spreaded in temperature. For systems like \((\text{TMTSF})_2X\) at ambient pressure or \((\text{TMTTF})_2X\) at relatively high pressure, the accepted range of values for \(T_{x1}\) may differ a lot from author to author. Following the example of what has been done for sulfur compounds at low pressure it is thus preferable to look at experiments in order to detect deviations to the Fermi liquid picture in the normal phase. If one looks for example at the existing results for the temperature dependent \(T^{-1}\) and \(\chi_s\) in the ambient pressure metallic phase of \((\text{TMTSF})_2\text{PF}_6\) \((T_\text{n} \approx 12\text{K})\), one observes from Figure 5 that deviations with respect to the \(T\chi_s^2\) law become perceptible below \(T\chi_s^2 \approx 1\), which corresponds to the actual temperature scale \(T < 200\text{K}\). According to [4], one can then extract the antiferromagnetic part of the enhancement in \((T_1T)^{-1}\) which is found to have increased by a factor 5 at \(T \approx 50\text{K}\), namely well outside the critical domain of the transition. This non-critical enhancement is thus too large to result from Fermi liquid conditions in which case \((T_1T)^{-1}[\Omega_0] \sim \text{constant}\) and should follow a Korringa law. This brings us to infer that a Luttinger liquid picture of the normal phase would still persist at 50K in \((\text{TMTSF})_2\text{PF}_6\) at ambient pressure suggesting an upper bound value \(T_{x1} < 50\text{K}\) for deconfinement. It is worth noting here that a similar enhancement has been detected in \((\text{TMTTF})_2\text{Br}\) at 13 kbar [5].

A connection has been made between these correlation effects and the anomalous photoemission data of Dardel et al. [6], which reveal a strong depression of the quasi-particle weight at the Fermi level for \((\text{TMTSF})_2\text{PF}_6\) at 50K. Deviations from the Drude response in optical conductivity of the normal phase of these materials have also been related to the presence of antiferromagnetic correlations, though their influence on transport properties is in general poorly understood [7].

### 3. Confinement under magnetic field

When a transverse magnetic field is applied in the pressure domain \(P \gtrsim P_c\) for compounds like \((\text{TMTSF})_2\text{PF}_6\) and \((\text{TMTSF})_2\text{ClO}_4\), another sector of the phase diagram opens up for which the concept of the Luttinger liquid may be relevant to the description of the normal phase. When the magnetic field is increased along the \(c^*\) direction, this prompts an anomalously large longitudinal resistance and a upturn in resistivity at a temperature \(T_p(H)\). As shown in Figure 7 for the \((\text{TMTSF})_2\text{PF}_6\) under 8.5 kbar and field up to 12T [7], the resistivity minimum moves away from the critical line of the cascade of field-induced-spin-density-wave phases. This giant magnetoresistance was soon recognized as one of the anomalous feature of the normal phase of these materials under field that does not entirely conform to classical magnetotransport [8].

![Figure 7: Longitudinal resistance of \((\text{TMTSF})_2\text{PF}_6\) at \(P = 8.5\) kbar as a function of temperature and magnetic field \(H = 0, 2, 3, 6, 8, 11, 12.5\)T. After Ref. [27].](image)

It was recently proposed that the unidimensionalization of electron motion under field not only bypasses the effect of \(t_{x1,2}\) (in inducing perfect but quantized nesting conditions that are responsible for the cascade of FISDW phases [28]), but improves longitudinal nesting conditions at \((2k_F, 0)\) as well. This gradually reacts again the singular nature of one-dimensional many-body effects below \(T_{x1}\) [4]. Since the dimerization of the organic stacks, though weak, causes longitudinal electron-electron umklapp scattering relevant (the \(g_3\) coupling in the “\(g\)-ology” notation), it may lead to a singular growth of the electron-electron scattering rate which takes the form \(\tau_{x1}^{-1} \sim T[g_3(T)]^2\). This may cause an upturn in resistivity which clearly is reminescent of the one found in sulfur series at low pressure (Figure 2) [3]. At variance with the more one-dimensional sulfur compounds, however, the restoration of longitudinal nesting is only gradual under a magnetic field, precluding the formation of a sharp charge gap that would entirely destroy the Fermi liquid component of the normal phase. The restoration of the Luttinger liquid under a field, though gradual, should have important consequences on spin correlations, especially those at \(2k_F\). Figure 8 shows \(^{77}\text{Se}\) \(T_{\chi_x}(H)\) and the Knight shift \(K_x(T)(T^2 \chi_x^2)\) data of \((\text{TMTSF})_2\text{ClO}_4\) at ambient pressure and for two different fields \((H = 6\text{T}, T_p \approx 5\text{K})\) and \(H = 15\text{T}\), with \(T_p \approx 15\text{K}\) [28, 30].

As one can see from the Figure 8, \(T_{\chi_x}^{-1}\) is dominated by the uniform \(TK^2_x\) component at sufficiently high temperature but deviations connected to the antiferromagnetic part of the relaxation emerge at low temperature. This enhancement appears to be quite distinct from the critical \(T_{\chi_x}^{-1}\) growth near the FISDW transitions taking place at \(T_x \approx 2.8\text{K}\) (6T) and 4.4 K (15T). Following the analysis made in Ref. [27], the relaxation rate in the normal phase can be very well described by an expression of the form

\[
T_{\chi_x}^{-1} \approx C_0T\chi_x^2(T) + C_1(H),
\]

where \(C_1(H)\) is a temperature independent contribution that increases as \(T_p(H)\) under a magnetic field. This is quite similar to what is found in the sulfur compounds at higher
temperature (see Figure 5). These results suggest that the progressive unidimensionalization of low-energy states under a field may gradually reactivate Luttinger liquid features in the normal phase precursor to the cascade of FISDW.

Ultimately, this emphasizes once again that the selenium series and their sulfur analogs are closely related to one another.

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