Strong correlations in organic charge transfer salts: superconductors, Mott insulators, bad metals and spin liquids

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Some reasons to study organic molecular materials

- Fascinating range of strongly correlated q2d systems - I will limit myself to half filled systems, but quarter filled and non-stoichiometric salts also exist
  - Mott transition driven by bandwidth control & wide range of associated phenomena
- Clean systems
  - Typically stoichiometric
  - Quantum oscillations are readily seen (simple, well understood Fermi surfaces)
- Low energy scales
  - $T_c$ may only be $\sim 10$ K [bad for applications]
  - But this also means “large” fields only means $\sim 10$ T [good for experimentalists]
- Chemical control
  - Organic chemists have can make subtle changes to the molecular structure, which allow them to tune the emergent physics
Overview

\[ \kappa-(\text{BEDT-TTF})_2X \]
\[ \beta'-Z[\text{Pd(dmit)}_2] \]

- Structure and phase diagram
- Model Hamiltonian
- Metal-insulator transition
- Spin liquid
- Strongly correlated metal
- Nernst effect
- Superconductivity
- Parameters for the model Hamiltonian
Structure of $\kappa$-ET$_2$X (ET=BEDT-TTF)

For a review see BJP and McKenzie, JPCM 18, R827 (2006)

Charge transfer

$\kappa$-(ET)$_2^+X^-$

$X$ is a monovalent anion, e.g., I$_3$, so the charge is localised in the anion layer, but the holes in the ET layer are not localised at a non-interacting level.
Molecular orbitals

Highest occupied molecular orbital (HOMO) of a neutral monomer from DFT [Scriven and BJP, J. Chem. Phys. ’09]
Molecular orbitals

Highest occupied molecular orbital (HOMO) of a neutral monomer from DFT [Scriven and BJP, J. Chem. Phys. '09]

HOMO of ET$_2^+$ [Scriven and BJP, Phys. Rev. B '09]
Structure of $\kappa$-$\text{ET}_2X$ (ET=BEDT-TTF)
For a review see BJP and McKenzie, JPCM 18, R827 (2006)

\[ \hat{H} = -t \sum_{\langle ij \rangle \sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} + U \sum_i \hat{n}_{i\sigma} \hat{n}_{i\sigma} \]

half filled
Experimental phase diagram
For a review see BJP and McKenzie, JPCM 18, R827 (2006)
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Experimental phase diagram
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Metal insulator transition driven by deuteration!
Taniguchi et al. PRB ’03

This shows that molecular crystals can be controlled by subtle changes in the molecular chemistry

This gives experimentalists an extra “dial”
The observed critical exponents are not Ising like as in V$_2$O$_3$ and DMFT [cf. Limelette et al. Science ’03]

Various theoretical proposals [e.g., Misawa et al. JPSJ ’06 - proximity to QCP; Papanikolaou et al. PRL ’08 - not deep enough into critical region]

Same $\delta$ exponent seen in NMR experiments [Kagawa et al. Nature Phys. ‘09]
Spin liquid

\( \kappa-(ET)_2Cu[N(CN)_2]Cl \) (henceforth \( \kappa-\text{Cl} \)) has an antiferromagnetic ground state — there is a slight canting of the moments leading to a large effect in the static susceptibility.

\( \kappa-(ET)_2Cu(CN)_3 \) (henceforth \( \kappa-\text{CN}_3 \)) has a spin-liquid ground state [Shimizu et al. PRL ’03] — no long range order in magnetic ground state.

A splitting is observed in the NMR below \( T_N \) in \( \kappa-\text{Cl} \) — no such splitting is seen in \( \kappa-\text{CN}_3 \).

[The line in the figure is a fit to high-T series expansions for the isotropic \( J=J' \) triangular lattice Heisenberg model, which give \( J \sim 250 \text{ K} \)].
Gapped or gapless spin liquid?

[Graph and equations]

\[ C_0 T^{-1} = \gamma T + \beta T^3 \]

\[ \beta T^3 \]

\[ \kappa-CN_3 \]

\[ \kappa-(d_8\text{-BEDT-TTF})_2\text{Cu[N(CN)]}_2\text{Br} \]

\[ \kappa-(\text{BEDT-TTF})_2\text{Cu[N(CN)]}_2\text{Cl} \]

\[ \beta-(\text{BEDT-TTF})_2\text{Cl}_2 \]
Gapped or gapless spin liquid?

\[ C_p(T) = \gamma T + \beta T^3 \]

\( \gamma = 12 \text{ mJ K}^{-2} \text{ mol}^{-1} \)

fermions (gapless spinons?)

\[ \kappa-\text{CN}_3 \]
Gapped or gapless spin liquid?

Why the difference?

M. Yamashita et al. argue it is because of the Schottky anomaly (from the Cu spins in the anion) in the anion affecting $C_p$

Also see discussion (particularly the comments) at

http://condensedconcepts.blogspot.com/2009/08/can-we-see-visons.html
6 K anomaly

A “bump” is seen below ~6 K in the heat capacity, thermal conductivity, and spin-lattice relaxation rate.

Many possible explanations have been proposed including: visons (vortices in a $Z_2$ spin liquid) [Qi et al. PRL ‘09], crossover to spin liquid [Yamashita et al. NP ‘08], “Amperean pairing of spinons [Lee et al. PRL ‘07], spin-chirality ordering [Baskaran PRL ‘89], excitation condensation [Qi & Sachdev PRB ‘08],...
Bad metal
Merino & McKenzie, PRB 00, Limelette et al. PRL 03, Merino et al. PRL 08

Many of the experiments on the normal state are quantitatively consistent with the “bad metal” phase predicted by DMFT

Non-monotonic temperature dependence of thermopower, resistivity [top fig.: Limelette et al. PRL 03] and Hall coefficient

Resistivity values above the Mott-Ioffe-Regel limit

Absence of Drude peak in the high-T optical conductivity [lower figs.: Merino et al. PRL 08]
Kadowaki-Woods ratio ($A/\gamma^2$)

$$\rho(T) = \rho(0) + AT^2$$
$$C_v = \gamma T + \beta T^3$$

Dressel, Wosnitza and others have noted that $A/\gamma^2$ is very large in the organics.

Miyake et al. [SSC 71, 1149 ('89)] argued that the heavy fermion materials have a large KWR because $\partial \Sigma/\partial \omega$ is large (strongly correlated) and that the KWR is much smaller in the transition metals because $\partial \Sigma/\partial \omega$ is much smaller.

Hussey [JPSJ 74, 1107 ('05)] proposed plotting $\gamma$ in volumetric units for oxides etc.

Does the same physics give rise to the mass enhancement ($\gamma$) and $A$?
Following Miyake, Matsuura, and Varma, [Solid State Commun. 71, 1149 (‘89)], we study a phenomenological local Fermi liquid theory where the imaginary part of the self energy is given by

\[ \Sigma''(\omega, T) = -\frac{\hbar}{2\tau_0} - \frac{2n}{3\pi D_0} \frac{\omega^2 + (\pi k_B T)^2}{\omega^*} \quad \text{for } |\omega^2 + (\pi T)^2| < \omega^* \]

\[ = -\left( \frac{\hbar}{2\tau_0} + \frac{2n}{3\pi D_0} \right) F \left( \sqrt{\frac{\omega^2 + (\pi k_B T)^2}{\omega^*}} \right) \quad \text{for } |\omega^2 + (\pi T)^2| > \omega^* \]

\[ F(1) = 1, \ F(\infty) = 0, \ F(y) \text{ is an unspecified monotonic function.} \]

\[ A \text{ to } \gamma \text{ via the Kramers-Kronig transform for the self energy} \]

\[ A = \frac{16nk_B^2}{\pi \hbar e^2 \langle v_{0x}^2 \rangle D_0^2 \omega^*}; \quad \gamma = \gamma_0 \left( 1 - \frac{\partial \Sigma'}{\partial \omega} \right) \approx \frac{8nk_B^2 \xi}{9\omega^*} \]

where \[ f_{dx}(n) \equiv nD_0^2\langle v_{0x}^2 \rangle \xi^2 \]
This suggests that a more natural ratio is
\[
\frac{A f_{dx}(n)}{\gamma^2} = \frac{81}{4\pi \hbar k_B^2 e^2}
\]
Assume simple model band structures to calculate \( f_{dx} \equiv n D_0^2 \langle v_{0x}^2 \rangle \xi^2 \)
Spherical Fermi surfaces for 3D materials
Cylindrical Fermi surfaces for quasi-2D materials
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Spherical Fermi surfaces for 3D materials

Cylindrical Fermi surfaces for quasi-2D materials

We find excellent agreement with data from a broad range of strongly correlated materials.

This shows that the main difference between the heavy fermions and the transition metals are due to band structure \([f_{dx}(n)]\), rather than correlations.

The same correlations cause \( A \) and \( \gamma \) in the organics
Disorder and transport
Analytis, BJP et al., PRL 96, 177002 (2006)

- Defects induced into samples by x-ray and proton irradiation
- Matthiessen’s rule obey at low T, but strongly violated at high T
- Resistivity independent of disorder at T=T_{\text{cross}}\approx 46 \text{ K}
- Can be explained if we assume that the impurities have two effects
  1. Scattering in the usual way
  2. Act to assist interlayer tunnelling [Graf et al., PRB 93; Rojo et al., PRB 93, etc.]

\[ \sigma(x, T) = \frac{1}{\rho_{\text{clean}} + x \rho_{\text{imp}}} + x \sigma_{\perp} \]

- This leads to the prediction that the residual resistivity is proportional to the peak conductivity, which is observed
Disorder and transport
Analytis, BJP et al., PRL 96, 177002 (2006)

- Defects induced into samples by x-ray and protons
- Matrosov and Balents find violations of Matthiessen’s rule
- Reduced resistivity is observed at different T
- Calculated ratio leads to defect-assisted transport

Disordered Hubbard model (DMFT)
Radonjić et al. arXiv:0910.5100

This leads to the prediction that the residual resistivity is proportional to the peak conductivity, which is observed

![Graph showing resistivity curves on Fig. 3(a)]
Pseudogap?
BJP, Yusuf & McKenzie, PRB 80, 054505 (2009)

Pseudogap + coherent transport
$\rho(T) \sim T^2$
SdH and dHvA oscillations
Spin gap observed in NMR

Fermi Liquid
$\rho(T) \sim T^2$
SdH and dHvA oscillations
No gap observed in NMR

Nernst effect near the Mott insulator
[Nam et al. Nature 07]

In κ-NCS one sees a small Nernst effect in the normal state, and a large vortex Nernst below $T_c$

In κ-Br Nernst signal is large in a significant region about $T_c$

κ-Br is very close to being a Mott insulator, whereas κ-NCS is at a higher “chemical pressure”

This is reminiscent of what is seen in the underdoped cuprates
d-wave superconductivity in $\kappa$-Br and $\kappa$-NCS
For a review see BJP and McKenzie, JPCM 18, R827 (2006)

There has been a long debate about the pairing symmetry
My view is that the most likely answer is d-wave but others would still argue for s-wave (everyone agrees it is singlet)
Disorder suppresses $T_c$ [BJP & McKenzie, PRB 04] - but story is more complicated than it appeared at first sight [Analytis, BJP et al. PRL 06]
Power laws in low temperature heat capacity [left: Taylor et al. PRL 07] and NMR [Kanoda et al. PRB 96]
Absence of Hebel-Slichter peak in NMR
Small superfluid stiffness
BJP & McKenzie, JPCM 16, 367 (‘04)

Data from Pratt et al., Polyhedron (‘03), Lang et al. PRB (‘92) and Larkin et al. PRB (‘01) for a variety of organic superconductors (different shapes denote different anions). Also see Pratt & Blundell PRL (‘05).

Note that the superfluid stiffness is smallest far from the Mott transition
Gossamer-RVB and organics
BJP & McKenzie; Gan et al.; Liu et al. [all PRL ‘05]

First theory of organics to be able to study the competition between the superconducting and insulating phases.

We take a partially Gutzwiller projected BCS wavefunction – solve for the fraction of doubly occupied sites as a variational parameter simultaneously with the BCS variational problem.

\[ |\text{Gossamer-RVB}\rangle = \prod_i (1 - \alpha \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}) |\text{BCS}\rangle \]

cf. the “plain vanilla” RVB theory where

\[ |\text{RVB}\rangle = \prod_i (1 - \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}) |\text{BCS}\rangle \]

In qualitative agreement with many experiments [BJP & McKenzie, PRL ‘05] and CDMFT [Kyung & Tremblay, PRL ‘06], variational cluster perturbation theory calculations [Sahebsara & D. Sénéchal, PRL ‘06] and VMC [Watanabe et al. JPSJ ‘06]

But does not explain the vanishing superfluid stiffness at high pressures (yet)
On the isotropic triangular lattice a group theoretical analysis suggests that it is natural for $d_{x^2-r^2} + id_{xy}$ superconductivity to be realised. This occurs because they transform according to the different bases of a 2d irrep.

But as we break the symmetry we regain either $d_{x^2-r^2}$ or $d_{xy}$ superconductivity.

$\epsilon$ is a symmetry breaking parameter (e.g. $\epsilon \sim 1-t'/t$) because of the low crystal symmetry we always have $\epsilon \neq 0$. $\beta' PnMe_{4-n}Et_n [Pd(dmit)_{2}]_2$ seem a particularly promising class of systems to look for this double transition in.
As the spin correlations change this drives changes in the superconducting state. The $d+id$ state breaks time reversal symmetry. This could be directly detected in, for example, muon spin relaxation experiments.
What is the structure of the order parameter?

The d+id state breaks time reversal symmetry.
This could be directly detected in, for example, muon spin relaxation experiments.
Most band structure calculations for BEDT-TTF and Pd(dmit)$_2$ salts have historically been based on the Huckel approximation (a parameterised tight-binding method).

More recent DFT calculations seem to confirm one’s fears that these are not accurate.

For example for $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$ Huckel gives $t'/t \sim 1$, i.e. an (nearly) isotropic triangular lattice - but the triangular lattice Heisenberg model has 120° order (ring exchange [Motrunich PRB ‘05, ‘06]?)

But two recent tight-binding parameterisations of DFT band-structures [Nakamura et al., JPSJ ‘09; Kandpal et al., PRL ‘09] find that $t'/t = 0.8$ for $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$.

Does this resolve the conflict with the 120°-state?

But, high-T series expansions for the isotropic triangular lattice Heisenberg model seem to fit well with the magnetic susceptibility data [Zheng et al. PRB ‘05].
Parameterisation of Hubbard models: Hubbard $U$
Scriven & BJP, JCP 130, 105408 (‘09); PRB 80, 205107 (2009).

$$U_d = E_d(0) + E_d(+2) - 2E_d(+1)$$
where $E_d(q)$ is the energy of a (BEDT-TTF)$_2$ dimer of charge $q$

Previous approach has been to treat that dimer as a two site Hubbard model, where each site is a monomer

$$\mathcal{H} = t_m \sum_\sigma \hat{c}_1^{\dagger} \hat{c}_2^\sigma + \text{h.c.} + U_m \sum_i \hat{n}_i^{\uparrow} \hat{n}_i^{\downarrow} + V_m \hat{n}_1 \hat{n}_2$$

For $V_m=0$ and $U_m>>t_m$ one finds that $U_d=|2t_m|$ - therefore $U_d=0.2-2\text{ eV}$ (variation both between groups and between materials) estimated from Huckel calculations

DFT calculations of $E_d(q)$ give $U_d=3.2\text{ eV}$ - for a wide range of $\kappa$ and $\beta$ phase BEDT-TTF salts

Further we find that $U_m\sim V_m>>t_m$, which leads to $U_d=\frac{1}{2}(U_m+V_m)>>|2t_m|$

Thus we expect a $U_d$ to be reduced by the polarisability of the crystalline environment, hence

$$U_{d\text{eff}} = U_d - \delta U_d$$

$\delta U$ calculated in other molecular crystals (A$_3$C$_{60}$, TTF-TCNQ, oligoacene, thiopenes, etc.), but it is complicated in the BEDT-TTF salts by the polymeric anions, geometry, etc. [Merino et al.]

However, $\delta U_d$ may well be quite sensitive to hydrostatic and chemical pressure, and may, therefore, be important for properly explaining the pressure dependence of these materials

$U_{d\text{eff}} = 0.8\text{ eV}$ from DFT + constrained-RPA [Nakamura et al., JPSJ '09]

$U_{d\text{eff}} = 0.3\text{ eV}$ from comparison of DFMT to optical conductivity [Merino et al., PRL '08]
\[ \beta'Z[Pd(dmit)_2] \]


\[ dmit = 1,3\text{-dithiol-2-thione-4,5-dithiolate} \]

\[ Pd(dmit)_{2} \] is a member of a larger class of molecules \( M(dmit)_{2} \), where \( M \) is a transition metal.

Another interesting molecule is \( Ni(dmit)_{2} \), which forms a similar set of charge transfer salts.

The \( Ni \) salts seem to be quite one-dimensional, but I will not discuss them much today.
Structure of $\beta'$-Et$_2$Me$_2$As[Pd(dmit)$_2$]$_2$

In alternating layers the dimers stack along different directions (a+b and a-b) this is known as the "solid crossing" structure.
Cations

We will focus on cations of the form $\text{Et}_n\text{Me}_{(4-n)}V$, where $V$ is a pnictogen (group V element) and $n$ is an integer.

We will introduce a shorthand notation to $V-n$ to represent $\beta'$-$\text{Et}_n\text{Me}_{(4-n)}V[\text{Pd(dmit)}_2]_2$.

E.g., $\text{As}-3 = \text{Et}_3\text{MeAs}[\text{Pd(dmit)}_2]_2$

The pnictogen has to give up one electron in order to form the four bonds - this bond is donated to $\text{Et}_2\text{Me}_2\text{As}$ - the cation in As-2
(Non-interacting) electronic structure of the [Pd(dmit)$_2$]$_2^-$ dimer

Picture from Huckel (confirmed by DFT [Miyazaki & Ohno, PRB ‘99])

The HOMO-LUMO splitting, $\Delta < 2t$ (or, more accurately, $t_H + t_L$)
Band structure (extended Huckel-tight binding)
Miyazaki & Ohno, PRB 59, R5269 (1999)
Metal-insulator transition

Note that both of the DFT and the Huckel calculations predict that the $Z^+[\text{Pd(dmit)}_2]_2^-$ salts are metals - as they have half filled bands

Experimentally they are insulators

This suggests that they are Mott insulators

A Mott metal insulator transition can be driven in some materials by hydrostatic pressure [Shimizu et al. PRL 07; P-1, upper Fig.] or uniaxial stress [e.g. Kato et al. PRB ‘02; As-0; lower Fig.] (but not by chemical pressure)
Spin liquid in Sb-1
Itou et al., PRB 77, 104413 (2008)

- No magnetic phase transition observed down to the lowest temperature studied
- \( J \sim 240 \) K from fits to high temperature series expansions
- Very reminiscent of \( \kappa\text{-CN}_3 \)

\[ \text{Triangular Lattice, } J = 250 \text{ K} \]

\[ J = 220 \text{ K} \]

\[ \text{Temperature (K)} \quad \text{Spin Susceptibility (}10^{-4}\text{ emu/mol)} \]

\[ \text{Frequency (MHz)} \quad \text{Intensity} \]

(a) EtMe\(_3\)Sb[Pd(dmit)\(_2\)]\(_2\)

- 1.37 K
- 2.53 K
- 4.23 K
- 6.67 K
- 10.35 K
- 15.3 K
- 19.3 K
- 27.7 K
- 51.9 K
- 75.3 K
- 149 K
- 272 K
Valence bond solid in P-1?
Tamura et al. JPSJ 75, 093701 (2006)

- Sudden drop in the magnetic susceptibility, $\chi$, at 25 K.
- The transition is hysteric (first order)
- Below the transition there susceptibility displays an Arrhenius behaviour (i.e., a gap opens between the ground state and the lowest lying triplet excitation - there is no such gap in the high temperature phase)
- The VBS phase has a gap between the ground state and the lowest lying triplet excitation
Satellite reflections are also seen in the x-ray diffraction pattern below 25 K. These correspond to a loss of periodicity in the crystal. In the low temperature phase the distances between (the planes of S atoms neighbouring the Pd atom in) neighbouring dimers is either 3.85 or 3.76 Å, whereas in the high temperature phase the all dimers are separated by 3.82 Å. This is what one would expect in the VBS phase as the spin-phonon coupling would favour exactly this type of disorder in the VBS phase.
What is special about P-1?

None of the other V-n salts show a VBS phase so we would like to understand what is special about P-1.

P-1 has a P2₁/m crystal whereas most of the others have a C2/c crystals.

The loss of the glide plane (.../m instead of .../c) in P-1 corresponds to absence of the “solid crossing” crystal packing (shown, right).

In P-1 all the organic layers are equivalent.

Tamura et al. argued that in the C2/c crystals the lattice distortion in different layers would be in different directions, and so would cause a large strain making the VBS phase unfavourable.
Charge ordered insulator in Sb-2 and Cs-00?

Tamura et al. CPL 411, 133 (2005)

- P-2 and Cs-00 show very similar phase transitions are 70 & 65 K respectively
- The susceptibility vanishes rapidly in both materials, suggest all the spins pair up
- Cs-00 undergoes a metal-insulator transition at the same temperature (I am not aware of equivalent data for Sb-2)
Nakao et al. [JPSJ 74, 2754 (2005)] found that this phase transition is associated with a crystallographic phase transition C2/c → P2₁/m. This basically corresponds to a doubling of the unit cell. The phase transition appears to be first order.
Shimizu et al. [JPCM ‘07] have argued that controlling the frustration drives the system into the spin liquid state.

However their phase diagram does not match what is known theoretically about the model.

Their $t$ values come from Huckel - is this the problem?

It is known the Huckel overestimates $t'/t$ in the BEDT-TTF salts.

Another trend in the data is that systems near the Mott transition have lower $T_{NS}$ (i.e., become antiferromagnetic at lower temperatures).

A simple trend is that salts with larger cations have lower $T_{NS}$.

Weihong et al., PRB 59, 14367 (1999).
Superconductivity

Very little is known about the superconducting state.

Zero resistance has been observed under pressure or uniaxial stress in several Pd(dmit)$_2$ salts - this tells us that they superconduct, but not much more ($T_c$ is typically a few K)

The Meisner state has been observed in P-1 [Ishii et al., JPSJ ‘07], which confirms that it’s bulk superconductivity

As far as I’m aware we don’t know any more about the superconducting state
Overview
For a review see BJP and McKenzie, JPCM 18, R827 (2006)

\[ \kappa - \text{(BEDT-TTF)}_2 X \]

\[ \beta' - \text{Z[Pd(dmit)}_2 \]

Structure and phase diagram
Model Hamiltonian
Metal-insulator transition
Spin liquid
Strongly correlated metal
Nernst effect
Superconductivity
Parameters for the model Hamiltonian

Structure and phase diagram
Model Hamiltonian
Metal-insulator transition
Spin liquid
Valence bond solid
Charge ordered insulator
Superconductivity
White space for theorists!