Wigner-Mott transition, charge frustration and Hund’s coupling in layered triangular lattices

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Outlook

• Coulomb induced charge ordering: Wigner/Mott electron correlations away from integer fillings

• Frustration of CO on triangular lattices: pinball liquid non FL, bad metal, heavy fermion behavior…

• Experimental realizations? AgNiO₂, multiband system pinball order stabilized by Coulomb + Hund’s coupling
On the Interaction of Electrons in Metals

E. Wigner, Princeton University
(Received October 15, 1934)

If the electrons had no kinetic energy, they would settle in configurations which correspond to the absolute minima of the potential energy. These are closed-packed lattice configurations, with energies very near to that of the body-centered lattice.

\[ V(r) = \frac{e^2}{r} \]

\[ \frac{e^2}{R_s} \gg \frac{\hbar^2}{2mR_s^2} \]
Coulomb interactions: Wigner vs Mott insulator

\[ V(r) = \frac{e^2}{r} \]

\[ \frac{e^2}{R_s} \gg \frac{\hbar^2}{2mR_s^2} \]

**Wigner crystal**
- no underlying lattice
- long range interactions
- low electron density

**Mott insulator**
- commensurate underlying lattice
- on-site interactions, Hubbard model
- high electron density, \( n=1 \)

Electrons in a solid, periodic lattice, half filled bands, (d-, p-orbitals), 1 el per site. Cuprates, \( \kappa \)-organics, fullerenes.
Coulomb induced CO in solids: Wigner AND Mott physics

- intermediate electron density, \( n=1/2 \): quarter filling (common in 2D organics, some oxides)
- interplay of charge order and electronic correlations
- Extended Hubbard Model: on-site + long range interactions

\[
H = -t \sum_{\langle ij \rangle \sigma} (c_i^{\dagger} c_j^{\sigma} + \text{H.c.}) + U \sum_i n_i^{\uparrow} n_i^{\downarrow}
\]
Triangle = Frustration

Magnetic

\[ J \sum_{\langle ij \rangle} S_i S_j \]

- Charge (n=1/2)

\[ V \sum_{\langle ij \rangle} (n_i - 1/2)(n_j - 1/2) \]

- charge frustration is far less studied than its spin analogue
- contrary to spins, charges are itinerant
- to be explored!
Square vs. Triangular lattice

[Kaneko et al. PRB’06, Hotta et al. PRB’06, Cano-Cortés et al. PRL’10, PRB’11, Merino et al. PRL’13]

square lattice, one electron per two sites (n=1/2)

- nearest neighbor Coulomb repulsion
  \[ V n_i n_j \]
  Extended Hubbard Model

- all bonds are happy
  - “checkerboard” order
  - CO insulator (gapped)
  - 2x degenerate
Square vs. Triangular lattice

[Kaneko et al. PRB’06, Hotta et al. PRB’06, Cano-Cortés et al. PRL’10, PRB’11, Merino et al. PRL’13]

triangular lattice, one electron per two sites (n=1/2) \( \theta-(\text{BEDT-TTF})_2X \)

"stripes"

\[ E/N = V/2 \]

Classical ground state infinitely degenerate.

- Thermal fluctuations
- L. Rademaker tomorrow
- Quantum fluctuations lead to exotic phases

frustrated neighbors!
on the triangular lattice we can’t make $n=1/2$ electrons happy, but at least can we make them less unhappy?

- same electrostatic energy as stripes, but gains kinetic energy
- frustration is released via quantum fluctuations
- coexisting localized charges (pins) and itinerant carriers (balls) on the honeycomb lattice
- pinball liquid: CO metal, with quite interesting properties
2 routes to non Fermi liquid behavior

1) **quantum criticality**: approaching the CO transition, scattering by critical charge fluctuations up to T~t (bad metallic properties, large mass enhancement, destruction of qp...) consistent with exp. in $\theta$-(BEDT-TTF)$_2$I$_3$

2) **pinball liquid**: within the CO phase, spontaneous separation into localized and itinerant carriers

analogy with **heavy fermions**

- pins
- balls
- conduction electrons are scattered by the fluctuations of the **localized moments**
- f-electrons
- d-electrons

[Cano-Cortés et al. PRL’10, PRB’11] single band EHM on triangular lattice

[Merino et al. PRL’13]
Pinball liquid: exciting properties
[Merino et al. PRL’13]

Can be mapped to the Periodic Anderson Model

\[ H_{PAM} = \sum_{i\sigma} \epsilon_A a_{i\sigma}^{\dagger} a_{i\sigma} + \sum_{k\sigma\alpha} \epsilon_{k,\alpha} \gamma_{k\alpha\sigma}^{+} \gamma_{k\alpha\sigma}^{\dagger} + \sum_{ik,\alpha} (V_{k,\alpha} e^{ikR_i} a_{i\sigma}^{\dagger} \gamma_{k\alpha\sigma}^{\dagger} + \text{H.c.}) + U\sum_{i} a_{i\uparrow}^{\dagger} a_{i\uparrow} a_{i\downarrow}^{\dagger} a_{i\downarrow}, \]

<table>
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<tr>
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<th>heavy fermions</th>
<th>pinball liquid</th>
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<tr>
<td>localized moments</td>
<td>f-electrons</td>
<td>pins</td>
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<td>d-electrons</td>
<td>balls</td>
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Emergent heavy fermion behavior expected (Non FL, bad metal, quantum criticality etc.)
Experimental realizations?
Layered ET$_2$X organic conductors

- charge transfer: 1 hole/2 molecules -> quarter filled bands
- single band tight binding description, $W \sim 0.5 \text{eV}$
- narrow bands, effects of interactions should be strong
- $U, V > W$ lead to charge ordered phases
- BUT triangular lattice is anisotropic: striped phases commonly observed, but no PL
dichalcogenides, oxides

2D transition metal dichalcogenides
TaS$_2$, NbSe$_2$, ...


1T-TaS$_2$:
Mott physics driven by CO
David-star $\sqrt{13} \times \sqrt{13}$ unit cell

2D transition metal oxides
ex. cobaltates Na$_x$CoO$_2$

but also: dichalcogenide monolayers,
ionic liquid doped organic semiconductors,
adsorbate lattices, trapped cold ions,…
The case of AgNiO$_2$

- triangular lattice of Ni ions
- 1 electron per site per 2 orbitals -> quarter filling
- Pinball liquid physics expected!

E. Wawrzynska, et. al. PRB 77, 094439 (2008).
X-ray / neutron scattering

T < 365 K

Resistivity (1): CO transition

- CO is a metal-metal transition
- weak anomaly in resistivity

Resistivity (2): bad metal

- resistivity larger than Mott-Ioffe-Regel limit ($\sim m \Omega \text{cm}$) -> bad metal
- deviations from $T^2$ behavior above $T^* \sim 150$K

\[ \rho(T) \approx AT^\alpha, \; \alpha \leq 1 \]

Curie-Weiss susceptibility

- Large local moments $\mu_{\text{eff}} = 1.81-1.96$ (from DFT $\mu_{\text{eff}} = 1.3-1.5$)
- change of slope at $T^*$

\[
\frac{1}{\chi_{\text{mol}}} [\text{mol/cm}^3]
\]

\[
T \ [\text{K}]
\]

Thermopower


\[ S \approx T \]

Change of sign!

[Merino, Mc Kenzie PRB(00)]
Optical conductivity
Electronic properties of AgNiO$_2$

Unlike conventional metals:

- Charge ordered and metallic, CO is threefold
- Large local moments, order at $T_N << T_{CO}$
- Large resistivity, deviates from $T^2$
- Maximum in thermopower at $T^*$ signals crossover from coherent to incoherent excitations. Change of sign at 260 K.
- Large specific heat ($m^*/m \sim 2.6$)
- No Fermi surface at RT (but ARPES only on polycrystals).
- Electronic correlations, destruction of qp above $T^*$

PINBALL LIQUID?
2 orbitals: Extended Hubbard Model + Hund

\[ H = -t \sum_{\langle ij \rangle} \sum_{\tau, \sigma} (d_{i,\tau \sigma}^\dagger d_{j,\tau \sigma} + \text{H.c.}) + H_V + H_{\text{Hund}} \]

\[ H_{\text{Hund}} = U \sum_{i, \tau} n_{i \tau \uparrow} n_{i \tau \downarrow} + (U - 2J_H) \sum_{i, \tau \neq \tau'} n_{i \tau \uparrow} n_{i \tau' \downarrow} \]

\[ + (U - 3J_H) \sum_{i, \tau < \tau', \sigma} n_{i \tau \sigma} n_{i \tau' \sigma} \]

\[ - J_H \sum_{i, \tau \neq \tau'} (d_{i \tau \uparrow}^\dagger d_{i \tau \downarrow}^\dagger d_{i \tau' \downarrow} d_{i \tau' \uparrow} - d_{i \tau \downarrow}^\dagger d_{i \tau' \uparrow}^\dagger d_{i \tau \uparrow} d_{i \tau' \downarrow}) \]
2 orbitals: Extended Hubbard Model + Hund

\[
H = -t \sum_{\langle ij \rangle} \sum_{\tau, \sigma} (d_{i,\tau \sigma}^{\dagger} d_{j,\tau \sigma} + \text{H.c.}) + H_V + H_{\text{Hund}}
\]

- Hund exchange is maximum on doubly occupied sites with aligned spins
- adds to Coulomb V and favors pinball liquid with large (spin 1) moments

\[9V/4 + U/3 - J_H\]
Phase diagram (HF + DMFT)

- pinball liquid stabilized by Hund coupling
- realistic range of microscopic parameters
quasiparticle renormalization (DMFT)

- Hund exchange stabilizes the pinball liquid and induces “Mottness” on the charge rich sublattice
- pinball liquid is strongly correlated, consistent with experiments
magnetic moments and ordering (DMFT)

- Antiferromagnetic $J>0$ consistent with experimental magnetic order.

- Experimental local magnetic moments: $1.8-1.95\mu_B$, consistent with DMFT for $U/t>10$. 
Conclusions

- The interplay of **Coulomb induced charge ordering** and **geometric frustration** on the triangular lattice leads to many interesting phenomena.

- AgNiO$_2$ contains rich and poorly understood physics: charge ordering, large magnetic moments, renormalization effects, “bad” metallic behavior. It is an experimental realization of a multiband **pinball liquid**.

- Further confirmations? theory ($T^*$) / experiment (optical conductivity?)