Computational strongly correlated materials

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Physics & Astronomy

Current/recent students

- Saurabh Dayal (current PhD student)
- Wasanthi De Silva (new grad student 2012)
- Jeong-Pil Song (finished PhD Dec 2011)

recent Grant support

- 09/2006–08/2009 "Theory of coexisting density waves in low dimensional quarter-filled band molecular solids," Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division, Theoretical Condensed Matter Physics, $255,170, two PI's

- 09/2009–08/2012 "Charge frustration, spin singlets, and superconductivity in the 1/4-filled band paired electron crystal," Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division, Theoretical Condensed Matter Physics, Condensed Matter Theory. $420,000, two PI's

Materials Sciences and Engineering (MSE) Division

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Theoretical Condensed Matter Physics

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BES Budget

This research area supports theoretical condensed matter physics with emphasis on the theory, modeling, and simulation of electronic correlations. A major thrust is nanoscale science, where links between the electronic, optical, mechanical, and magnetic properties of nanostructures and their size, shape, topology, and composition are poorly understood. Other major research areas include strongly correlated electron systems, quantum transport, superconductivity, magnetism, and optics. Development of theory targeted at aiding experimental technique design and interpretation of experimental results is also emphasized. This research area supports the Computational Materials Science Network, which forms collaborating teams from diverse disciplines to address the increasing complexity of many current research issues. The research area also supports large-scale computation to perform complex calculations dictated by fundamental theory or to perform complex system simulations with joint funding from the Advanced Scientific Computing Research program. Capital equipment funding will be provided for items such as computer workstations and clusters.

This research area provides the fundamental knowledge for predicting the reliability and lifetime of energy use and conversion approaches and develops opportunities for next generation energy technology. Specific examples include inverse design of compound semiconductors for unprecedented solar photovoltaic conversion efficiency, solid-state approaches to improving capacity and kinetics of hydrogen storage, and ion transport mechanisms for fuel cell applications.

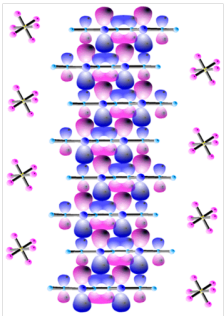
What are strongly correlated materials?

Conventional band picture of electrons in solid:

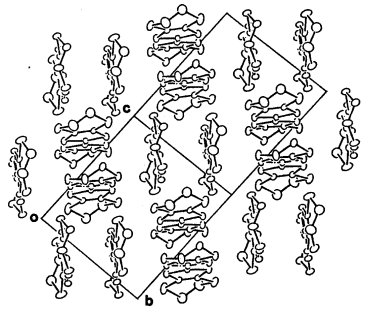
- screening reduces/removes effect of electron-electron repulsion
- Assume no e-e interaction, fill up single-particle bands

Strongly correlated materials: e-e interaction strongly affects properties, resulting in very interesting electronic properties

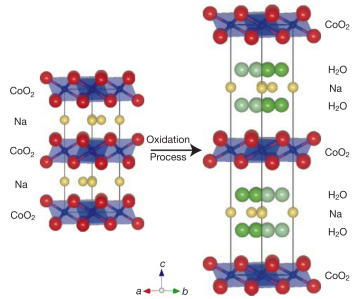
- No universal theory available
- Reduced dimensionality: quasi-2D or -1D. Reduces screening
- Unusual magnetic, charge, orbital orderings:
  antiferromagnetism $\uparrow\downarrow\uparrow\downarrow$ often due to strong e-e interaction
- Unconventional superconductivity (SC)



$(TMTSF)_2X$
T_c=1K SC



κ-$(BEDT\text{-}TTF)_2X$
T_c=13K SC



Na_xCoO_2
SC, thermoelectric

How to approach electron correlation problem

1. **More accurate *ab initio* methods:**
   - Hamiltonian describing electrons complex but completely specified
   - One method: Diffusion Quantum Monte Carlo
   - $\Longrightarrow$ not large enough systems for many properties

2. **Model Systems**
   - use simplified model Hamiltonian: Hubbard, Heisenberg, t-J, etc
   - we still can't solve these exactly!
   - try to give simple explanation of mechanisms

Many-body models

Ab-initio methods (DFT/etc): not presently accurate enough
$\rightarrow$ use *model* Hamiltonians. Example: Hubbard model

$$H = -t \sum_{\langle ij \rangle, \sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + H.c.) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

$\Longrightarrow$ Simple model with four possible states per orbital.
$\Longrightarrow$ Energy cost U for two electrons ($\uparrow$,$\downarrow$) in an orbital
$\Longrightarrow$ t term is "tight-binding" fit to bandstructure

- Computational challenge: # states grows exponentially
- also: longer-range Coulomb interactions $\sum_{\langle i,j \rangle} V(|r_i - r_j|) n_i n_j$
- also: electron-phonon interactions
- also: complex crystal structures (triangular lattice)
- also: multi-band systems

Numerical methods we use

Basic problem, quantum many-body models: exponential scaling

$$N_{states} \propto (states\ per\ orbital)^n$$

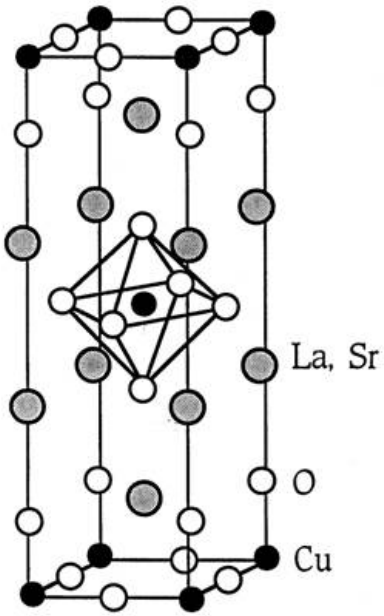
There is no *one* method that is universally applicable.

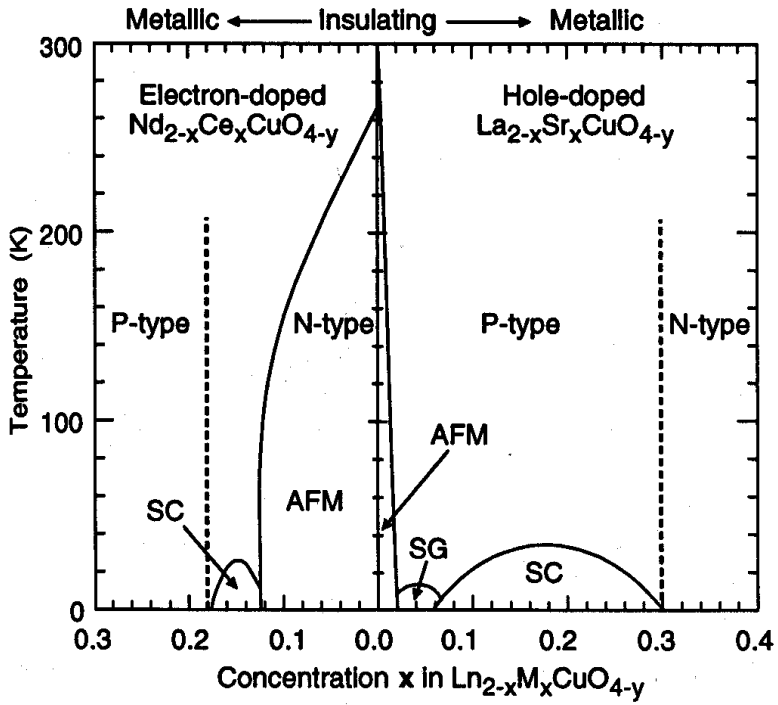
- Exactly diagonalize Hamiltonian matrix: memory limited
- Lanczos diagonalization:
  Don't store the H matrix, lowest eigenvalue only. $N_{states} \sim 10^6$, $n \sim 20$
- Variational methods:
  best parameters within assumed wavefunction form
- Quantum Monte Carlo:
  scales well, but has serious limitations (Fermion sign problem)

Must spend time developing new methods. No commercial codes available.

Project 1: spin-fluctuation mediated Superconductivity

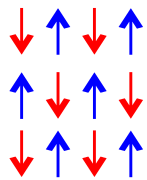
High-T_c cuprate superconductors: T_c up to 130 K
What is a minimal model?





$\Longrightarrow$ Undoped (insulating) material is an Antiferromagnet (AFM):

spin on Cu atoms:



Minimal model for AFM: 2D Hubbard model

- The Hubbard model: simplified electron-electron interaction. No exact solution except in one dimension

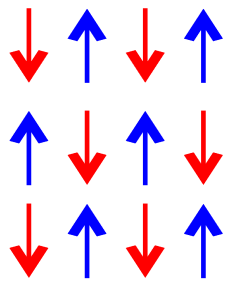
$$H = -t \sum_{\langle ij \rangle, \sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + H.c.) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

- Large U limit, 1 electron/orbital: antiferromagnetic Heisenberg model

$$H = J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j$$

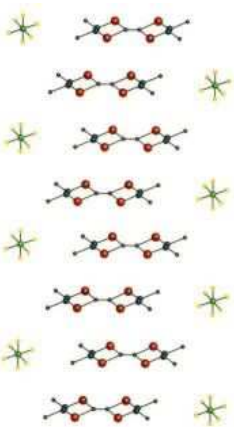
- Ground state, square lattice: AFM order
  Suggested by P.W. Anderson (and others): *doped* 2D AFM $\equiv$ superconductor!

  No exact solution or consensus yet...

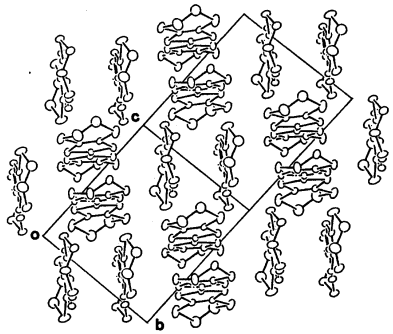


Organic superconductors

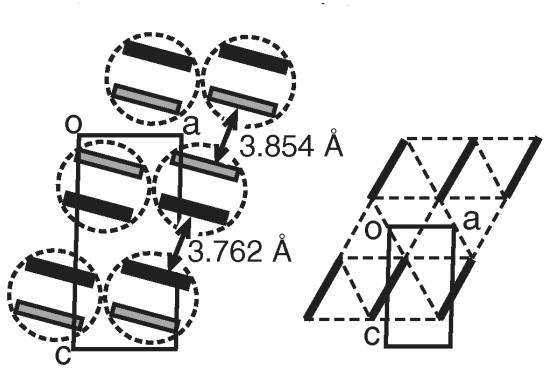
- 1950's-1960's: *charge transfer* complexes. Goal: create organic conductors
- 1973: TTF-TCNQ: almost metallic conductivity, quasi-one dimensional
- 1979: $(TMTSF)_2PF_6$ (TMTSF=tetramethyl tetraselena fulvalene) first organic superconductor. Can substitute many X for PF_6. $T_c \approx 1$ K
- Many more : BEDT-TTF, related molecules. different structures. T_c up to 13 K.



$(TMTSF)_2X$



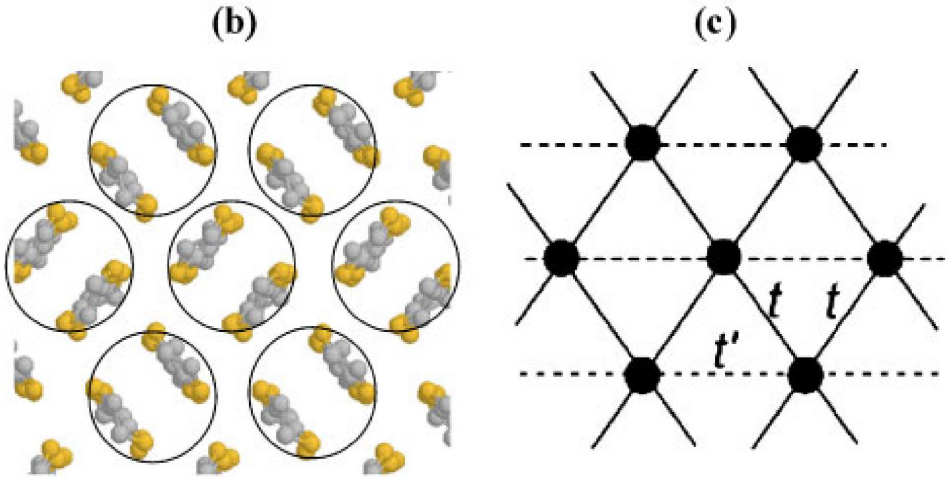
κ-$(ET)_2X$



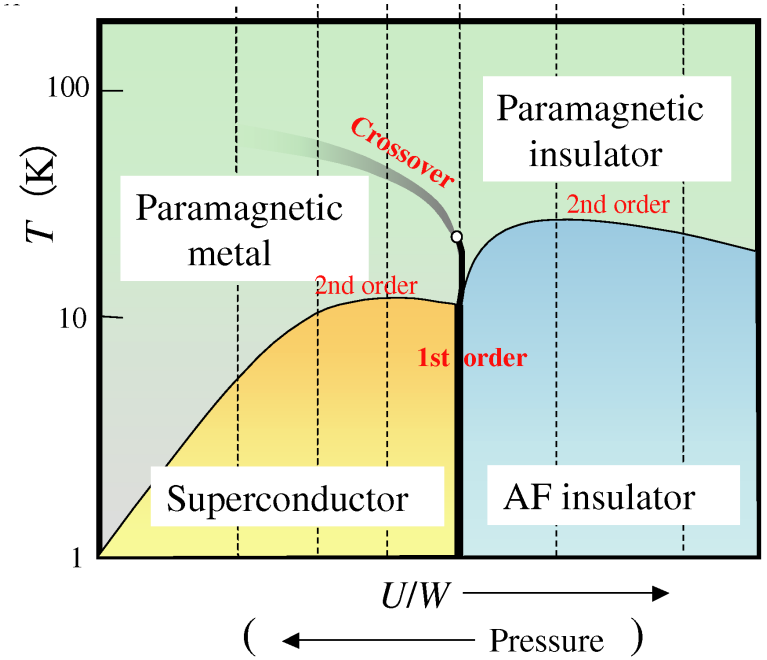
$Pd(dmit)_2$

Organic Superconductors

Some organic SC's seem to behave like cuprates!



κ-(BEDT-TTF)$_2$X structure



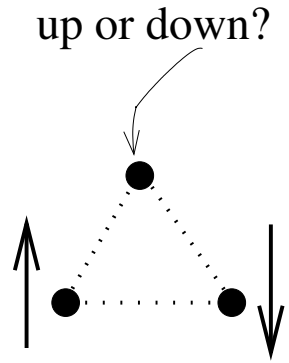
Phase diagram

κ-(BEDT-TTF)$_2$X : X is monovalent anion $\Longrightarrow$ 1 hole/two molecules

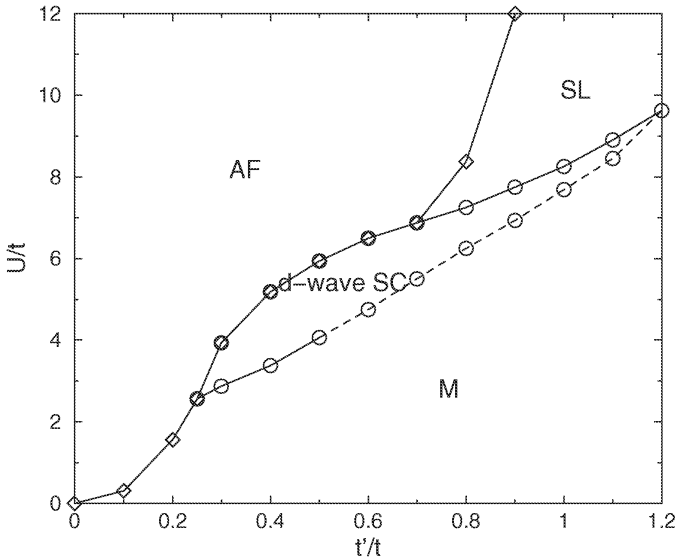
$\Longrightarrow$ Back to 2D Hubbard model...

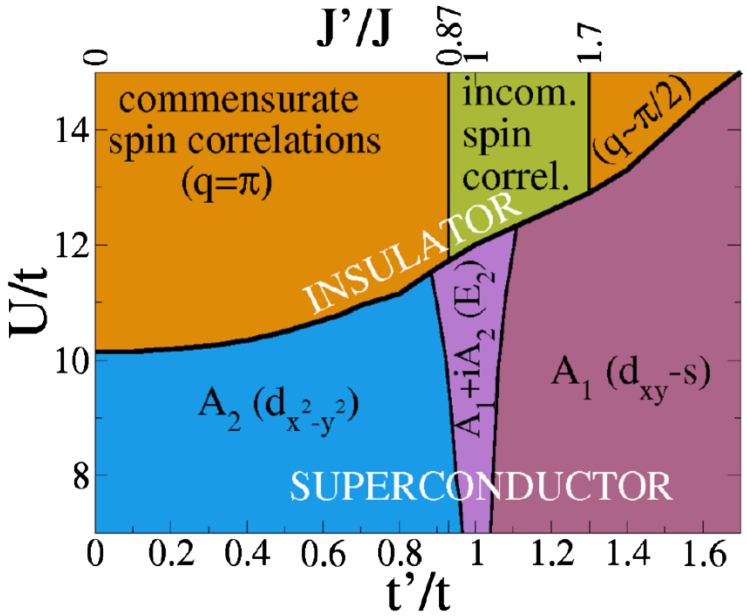
t smaller by 10, max T_c $\sim$13K rather than 130K

Back to spin-fluctuation Superconductivity...



No doping but *frustration* destroys AFM. Can this give SC?





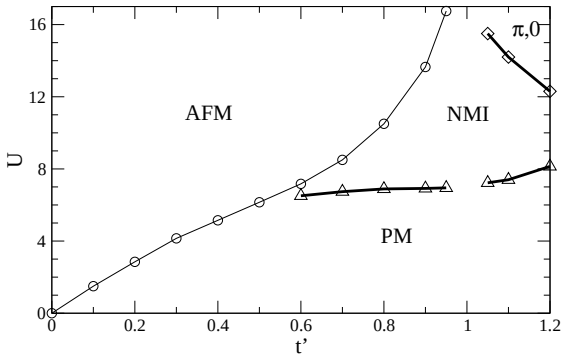
Kyung, Tremblay, PRL **97**, 046402 (2006), cluster DMFT, 4-site cluster
Powell, McKenzie, PRL **98**, 027005 (2007), RVB variational ansatz

Our results: no superconductivity in this model

Necessary conditions for SC:

- U enhances SC correlations
- must have at least short-range order

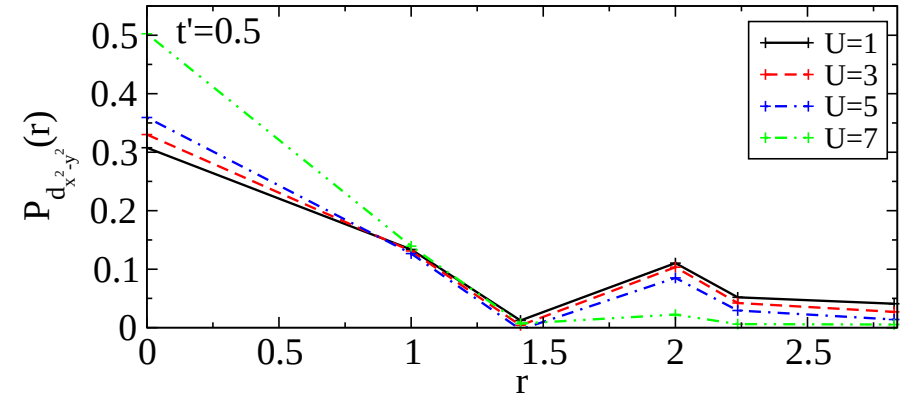
Our work: exact diagonalization (165 million states)

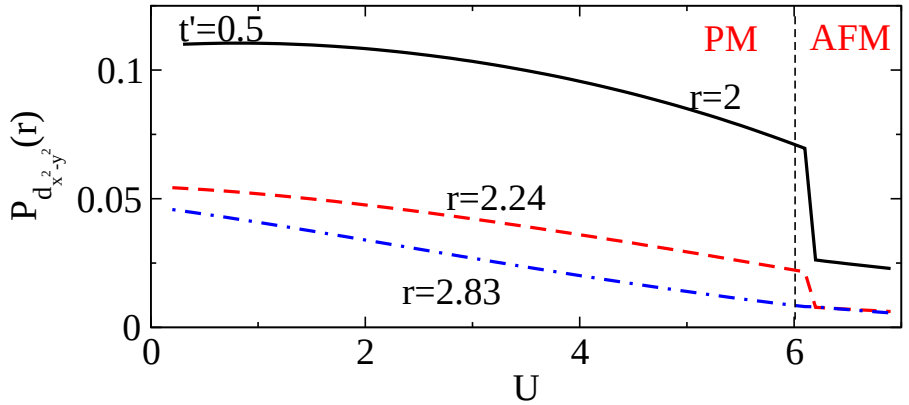


4×4 Phase diagram

Clay et al, *Phys. Rev. Lett.* 101, 166403(2008)

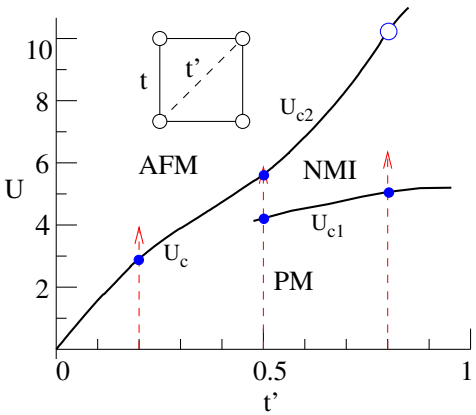
- Pair-pair correlations decrease *monotonically* from $U = 0$
- No long range order

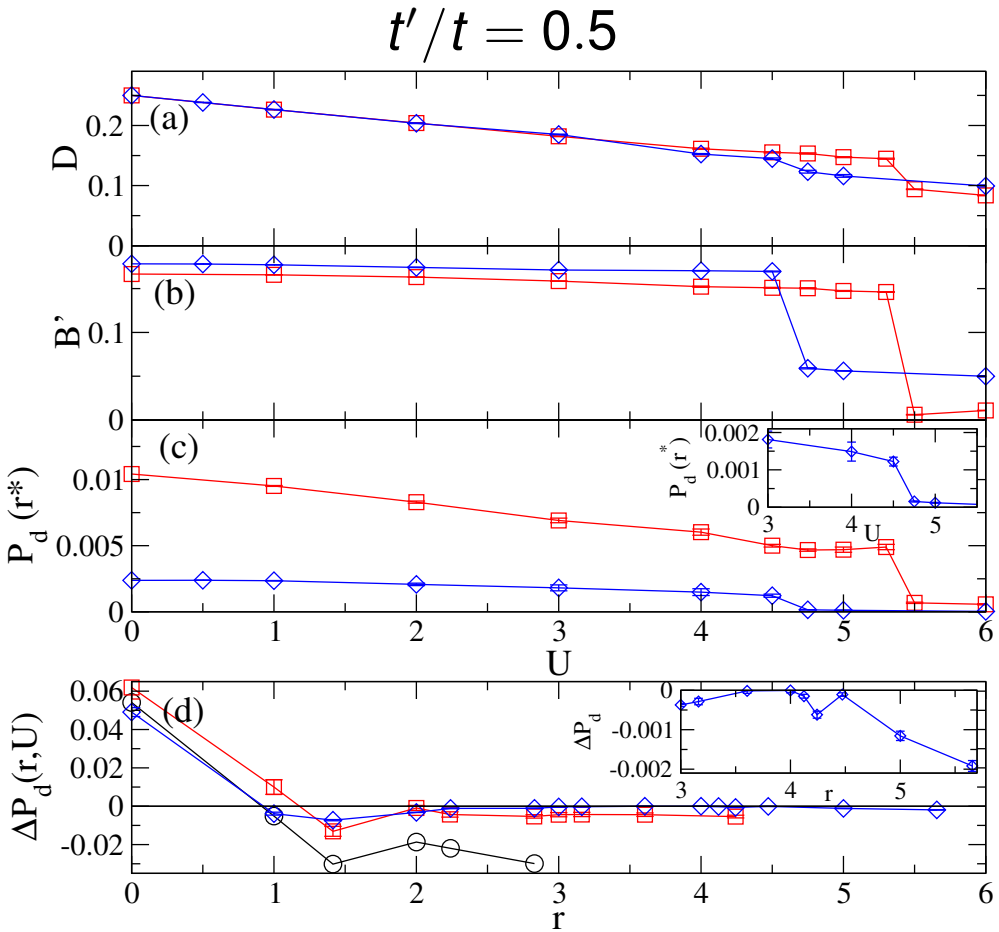




Followup: larger lattice (2011-2012)

Path Integral Renormalization Group (PIRG), up to 8×8 lattices

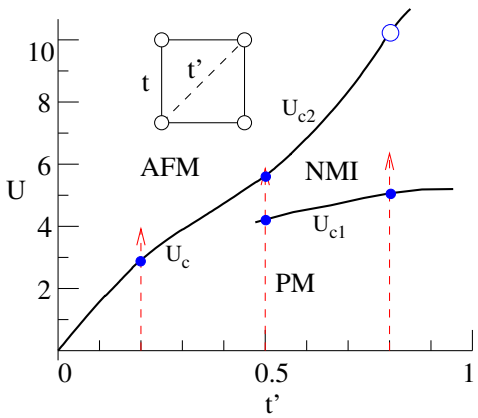


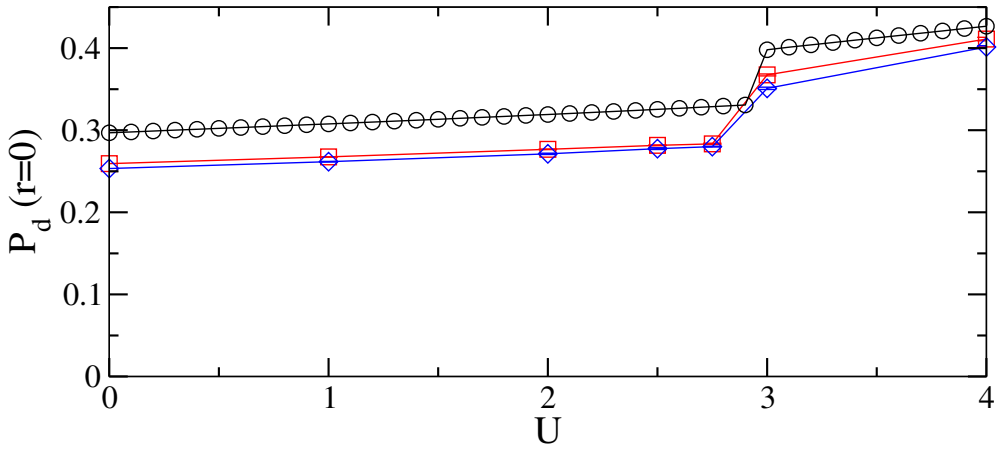


S. Dayal et al, to appear in *Phys. Rev. B* (PhD defense May 2)

Why mean-field fails here:

AFM/metal transition: trivial increase in *short-range* pairing correlations





We showed: at same time, *long range* correlations *decrease*

Publications 2011-2012

Conclusion: spin-fluctuation mediated SC is a dead end...

We have suggested an alternate mechanism for SC:

1. RTC, J.P. Song, S. Dayal, S. Mazumdar, "Ground state and finite temperature behavior of 1/4-filled zigzag ladders," http://arxiv.org/abs/1108.4169, submitted to Journal of the Physical Society of Japan (2011).
2. S. Mazumdar, RTC, H. Li, "Similarities in electronic properties of organic charge-transfer solids and layered cobaltates," Physica B 407, 1722 (2012).
3. S. Dayal, RTC, S. Mazumdar, "Absence of long-range superconducting correlations in the frustrated 1/2-filled band Hubbard model", http://arxiv.org/abs/1201.5139, to appear in Physical Review B (2012).
4. S. Mazumdar, RTC, "**Is there a common theme behind the correlated-electron superconductivity in organic charge-transfer solids, cobaltates, spinels, and fullerides?**", Physica Status Solidi B 249, 995 (2012).
5. RTC, S. Dayal, H. Li, S. Mazumdar, "**Beyond the quantum spin liquid concept in frustrated two dimensional organic superconductors**," Physica Status Solidi B, 249, 991 (2012).
6. H. Li, RTC, S. Mazumdar, "Theory of carrier concentration-dependent electronic behavior in layered cobaltates," Physical Review Letters 106, 216401 (2011).
7. S. Dayal, RTC, H. Li, S. Mazumdar, "**Paired electron crystal: Order from frustration in the quarter-filled band**," Physical Review B 83, 245106 (2011) (Selected as an "Editors' suggestions" paper).

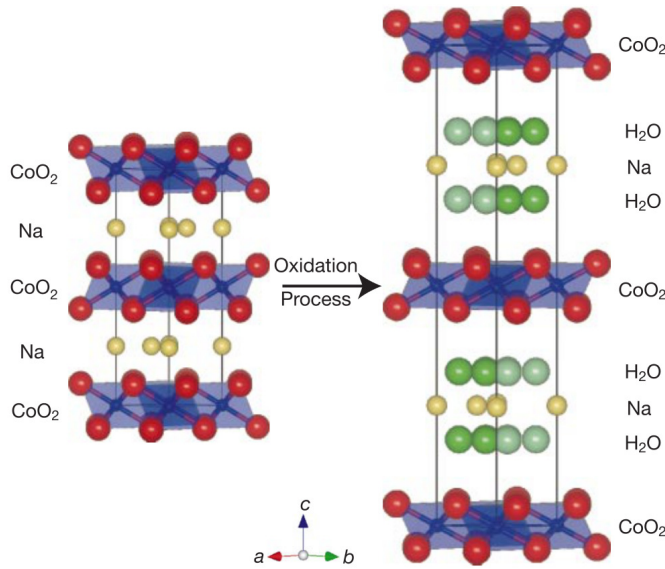
Example Project 2: Layered Cobaltates

Na_xCoO_2, Li_xCoO_2, $[Bi_2A_2O_4][CoO_2]_m$

- 2D CoO_2 layers separated by Na, Li, etc
- potentially useful: unusually large thermoelectric coefficient
- unconventional superconductivity
- Co ion triangular lattice: “frustration” for quantum spin models
- strongly correlated: DFT bands inconsistent with experiments

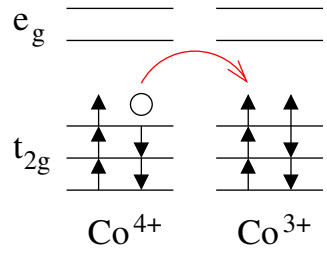
Important papers:

- I. Terasaki, Y. Sasago, K. Uchinokura, “Large thermoelectric power in $NaCo_2O_4$ single crystals,” Phys. Rev. B 56, R12685 (1997) ($>$1300 citations)
- K. Takada et al, “Superconductivity in two-dimensional CoO_2 layers,” Nature 422, 53 (2003) ($>$800 citations)



structure (K. Takada et al)

Na_xCoO_2: carrier concentration controlled by Na doping



- $x = 0$: Co valence = Co^{4+}
- $x = 1$: Co valence = Co^{3+}

  $\Longrightarrow$ Simplest model: Hubbard model on triangular lattice

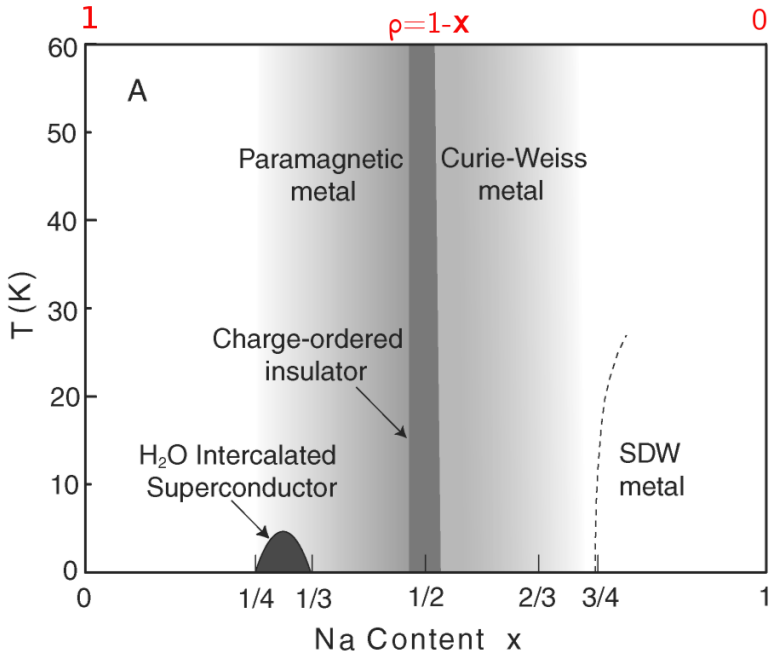
Experiments:

- Magnetic susceptibility behaves fundamentally differently for different x. No structural changes.

Our theory:

- simple Hubbard model insufficient
- requires *nearest-neighbor* interactions:

  $H = H_{\text{Hubbard}} + V \sum_{\langle i,j \rangle} n_i n_j$
- many-body effect. DFT, DFT+U, DMFT, $U \to \infty$ incorrect



M. L. Foo et al, PRL **92**, 247001 (2004)
more recent boundary x≈0.63-0.65

- $\rho < 0.35$: "strongly correlated"
- $\rho > 0.35$: "weakly correlated"

Magnetic susceptibility

1. Pauli paramagnetism: non-interacting electron gas
2. Curie-Weiss susceptibility: associated with strong correlations, electrons avoid each other

$\Longrightarrow$ Simple measure of "correlations": normalized *double occupancy*

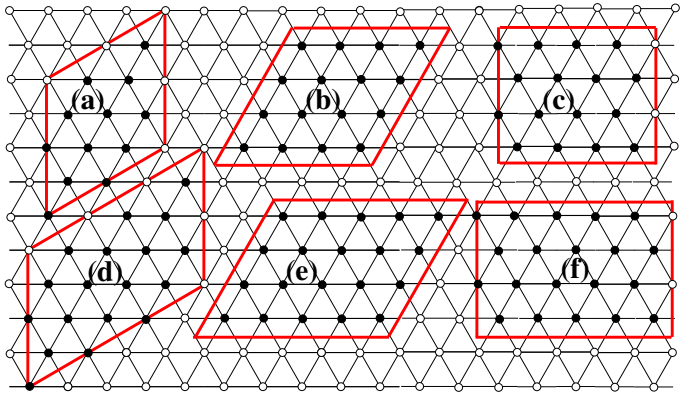
$$g(\rho) = \frac{\langle n_{i,\uparrow} n_{i,\downarrow} \rangle}{\langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle}$$

Key Point: $g(\rho)$ becomes strongly ρ-dependent when V included

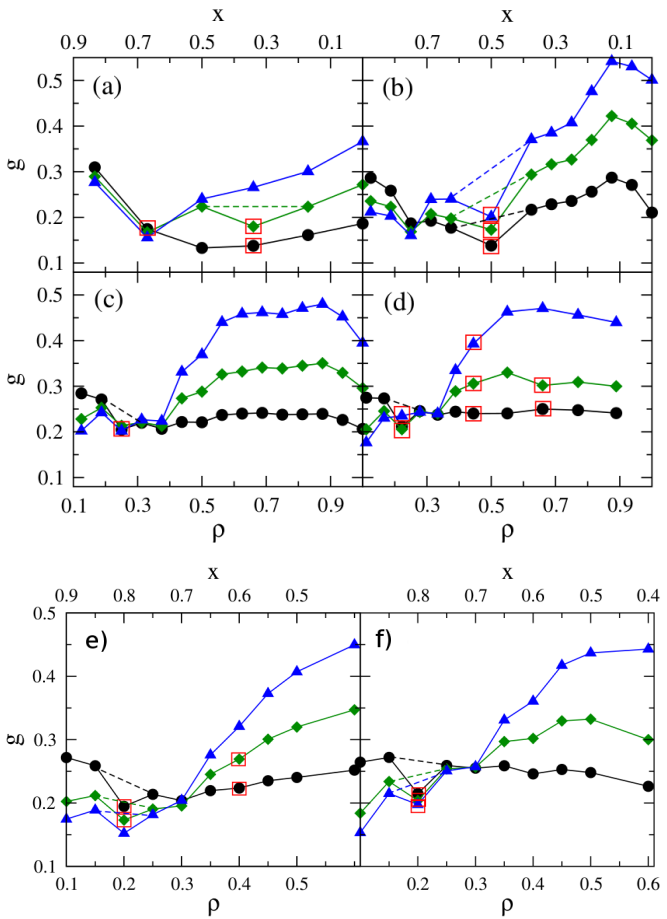
H. Li, R. T. Clay, S. Mazumdar, PRL **104**, 216401 (2011)

$$H = -t \sum_{\langle ij \rangle, \sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + H.c.) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow} + V \sum_{\langle ij \rangle} n_i n_j$$

Realistic parameter regime:
$6 < U/t < 14$, $1 < V/t < 4$



Calculate g for lattices $N \leq 20$
(lanczos, ∼20 GB largest)
Result: with $V > 0$, behavior changes at $\rho \sim \frac{1}{3}$ exactly as in experiments



$U = 10$; black squares $V = 0$; green diamonds $V = 2$; blue triangles $V = 3$

Our theory

- Simple and natural description of x dependence observed in cobaltates
  - does not require ρ-dependent U or V; solution of simple Hamiltonian
  - requires many-body treatment. $U \to \infty$ limit does not give correct behavior
- Works in both 1- and 3-band models (see PRL paper)

Similarities with other strongly-correlated SC's

- Many have suggested that cobaltates are similar to cuprates (layered, strong correlations, SC in doped Mott-Hubbard, ...)
- We have pointed out even stronger similarities between the cobaltates and the organic SC's:

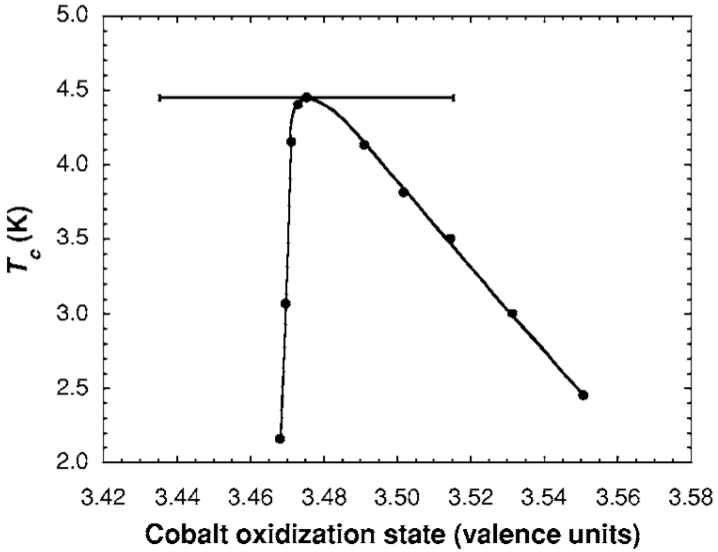
  Phys. Status Solidi B **249**, 995 (2012)

  - Both have frustrated lattices (e.g. κ-(BEDT-TTF)$_2$X)
  - Both are superconducting at only $\rho = 0.5$

Superconducting $Na_{0.35}CO_2 \cdot yH_2O$ is actually $\rho = 0.5$!

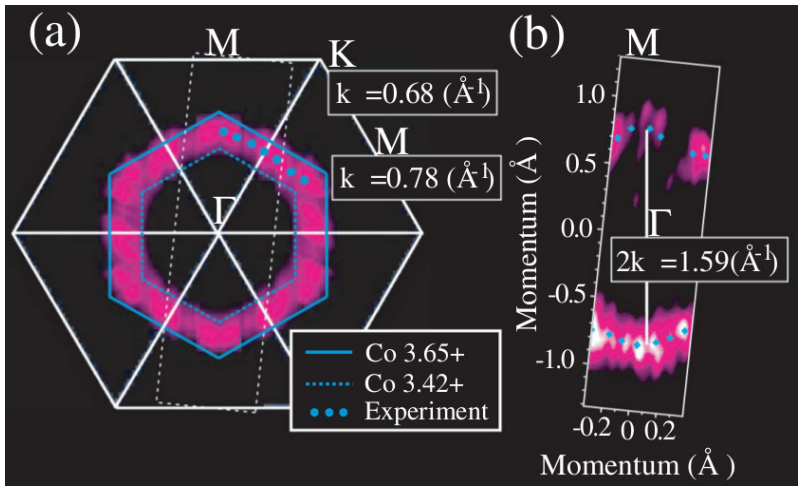
Water changes the doping:

some water enters as H_3O^+, *actual* ρ very close to 0.5



Max T_c when Co valence $\approx 3.5+$

Barnes et al, PRB 72, 134515 (2005)

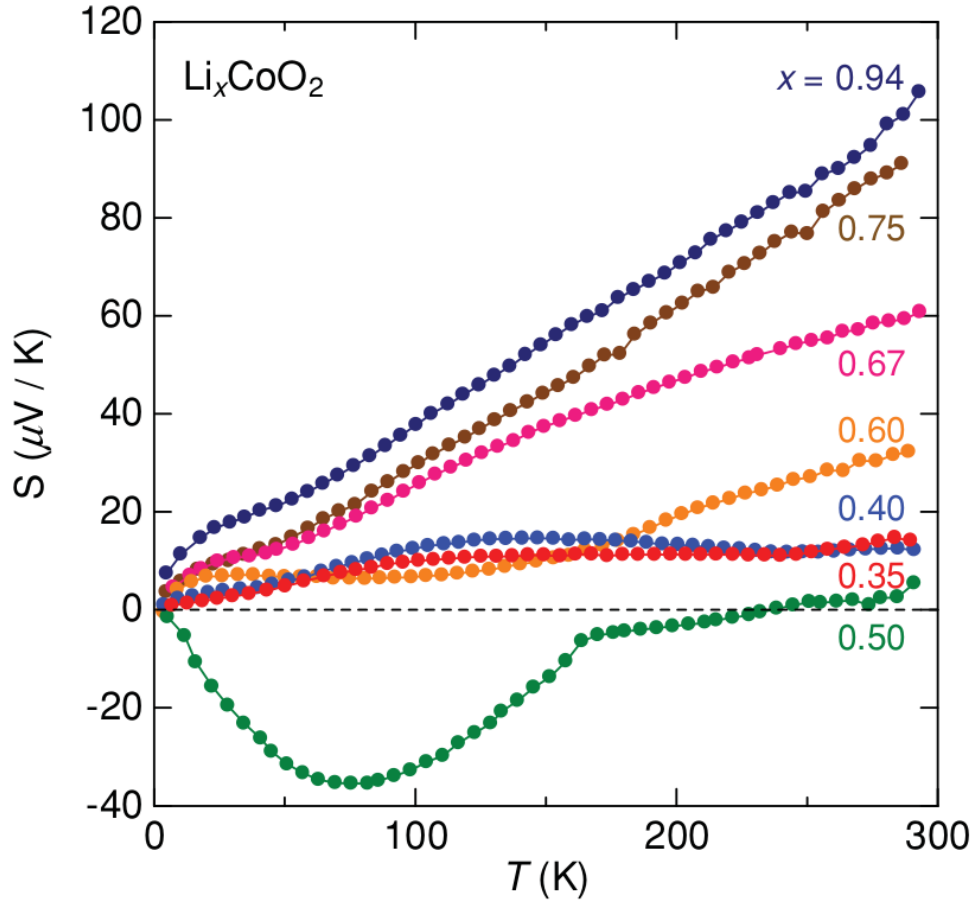


Photoemission on SC cobaltate

Shimojima et al, PRL 97, 267003 (2006)

Co valence=3.56$\pm$0.05

Normal state $\rho = 0.5$ has unique electronic properties:



T. Motohashi et al, PRB **83**, 195128 (2011)

- Na_xCoO_2: CoO_2 layers strongly influenced by Na ordering
- Li_xCoO_2: no Li ordering