

Theory of layered organic and inorganic materials with charge-spin frustration

PI: Prof. R. Torsten Clay
Department of Physics & Astronomy
Mississippi State University
Mississippi State, MS 39762-5167
r.t.clay@msstate.edu

Co-PI: Prof. Sumit Mazumdar
Department of Physics
University of Arizona
Tucson, AZ 85721
sumit@physics.arizona.edu

Project Scope

This project focuses on understanding the properties of correlated electrons in two dimensional (2D) frustrated systems. We propose a bottom-up approach to the theory of superconductivity (SC) in organic charge-transfer solids (CTS) and related materials. We note that the antiferromagnetic-to-superconductor transition found within resonating valence-bond (RVB) theories of the $\frac{1}{2}$ -filled band Hubbard model on a triangular lattice is an artifact of approximations [2]. Since transitions to SC in the CTS occur from antiferromagnets as well as from correlated charge-ordered semiconductors, these different types of semiconductors must be linked. We discuss a pressure-induced lattice frustration-driven transition from antiferromagnetism (AFM) to a paired-electron crystal (PEC), within the dimerized $\frac{1}{4}$ -filled band with strongly interacting electrons [6,9]. We propose that further frustration drives a PEC-to-SC transition. The electron-pairs within our model are the mobile pseudo-molecules in Schafroth's theory of SC. We further propose that this theory can be applied to the layered cobaltates, spinels, as well as the hydrocarbon superconductors K₃phenanthrene, K₃picene, and K₃dibenzopentacene, which we argue have effectively $\frac{1}{4}$ -filled bands.

Recent Progress

Absence of superconductivity in the frustrated $\frac{1}{2}$ -filled band Hubbard model [2]

Many authors have proposed RVB and spin-fluctuation mediated theories of pairing within the $\rho = 1$ triangular lattice Hubbard model (ρ is the carrier density per site). In particular, because of their dimerized structure with one electron or hole per dimer, the $\rho = 1$ anisotropic model has long been proposed to describe the electronic properties of the κ -(BEDT-TTF)₂X family of superconductors. We have calculated superconducting correlations for large triangular lattices using the *Path Integral Renormalization Group* (PIRG) technique [2]. The large lattice calculations demonstrate unambiguously that (i) superconducting pair-pair correlations decrease monotonically with increasing Hubbard repulsion U for inter-pair distances greater than nearest neighbor, and (ii) the distance dependence of the correlations is the same as that within the noninteracting electrons model. We conclude that SC is not obtained within the $\rho = 1$ frustrated Hubbard model, and this model cannot describe SC in the CTS superconductors.

Layered cobaltates [3,5,7]

The organic CTS superconductors have often been compared to the cuprates because of their two dimensionality and the existence of AFM adjacent to SC. We have recently pointed out that in fact the organics are even more similar to another class of strongly-correlated superconductor, the layered cobaltates. Both the organics and the cobaltates are 2D and have frustrated lattices. We have recently shown that the same mechanism can explain the systematic variation of electronic properties with carrier density in both the cobaltates *and* quasi-one dimensional CTS [7].

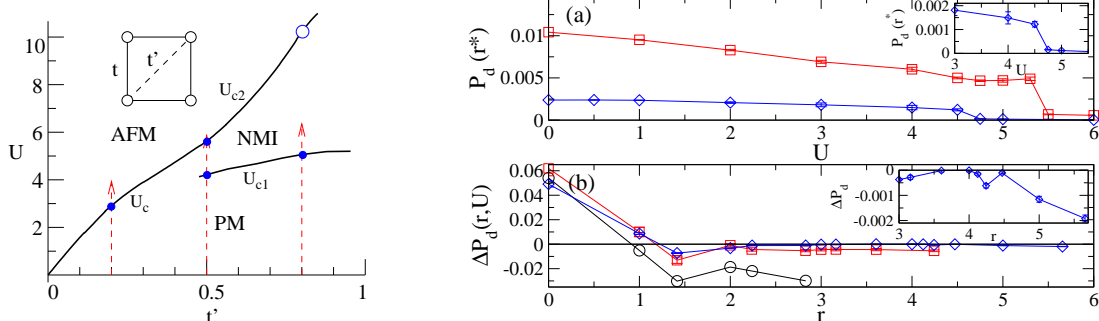


Figure 1: *Left: phase diagram of the $\frac{1}{2}$ -filled Hubbard model on the anisotropic triangular lattice. Right: (a) Long-range $d_{x^2-y^2}$ pair-pair correlation at zero temperature as a function of Hubbard U for $t'/t = 0.5$ (b) ΔP , the enhancement of the pairing over the noninteracting model, as a function of distance for $U/t = 4.5$. In (a) and (b), circles, squares, and diamonds are for 4×4 , 6×6 , and 8×8 lattices, respectively. In all cases we find that $P(r)$ decreases monotonically with increasing U .*

The unusual doping dependence of the electronic properties of the layered cobaltates Na_xCoO_2 , Li_xCoO_2 , and the “misfit” $[\text{Bi}_2\text{A}_2\text{O}_4][\text{CoO}_2]_m$, has attracted wide attention and was considered a theoretical challenge. These materials have a susceptibility that is characterized as Pauli paramagnetic for small x but Curie-Weiss for large x . We have given a natural explanation of this carrier concentration dependence within an extended Hubbard Hamiltonian with significant V/U (V is the nearest-neighbor Coulomb interaction). As a measure of correlations, we calculate the normalized probability of double occupancy, $g(\rho)$ in the ground state, $g(\rho) = \langle n_{i,\uparrow}n_{i,\downarrow} \rangle / \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle$. The holes are assumed to occupy nondegenerate a_{1g} orbitals on the Co-ions, based on photoemission spectroscopy. Smaller (larger) g corresponds to stronger (weaker) e-e correlations and enhanced (unenhanced) magnetic susceptibility. We performed exact calculations for six different finite clusters with realistic $U/t = 10$ and $0 \leq V/t \leq 3$. In all cases g is nearly x -dependent for $V/t = 0$; for $V/t \neq 0$ the ρ -dependence is exactly as expected from experiments. The calculated crossover between small g (strong correlations) and large g (weak correlations) is near $\rho \approx 0.30 - 0.35$ and not 0.5, which is precisely the density range where recent experiments find a crossover in magnetic properties.

Na_xCoO_2 is superconducting when hydrated, $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$, for $x \sim 0.35$. The original assumption that the Na-concentration determines the hole density also in the hydrated material has been found to be not true; some water molecules enter as H_3O^+ , and the actual ρ in the superconductor is much smaller than the 0.65 that would be guessed from the Na-concentration. There have been several reports that SC occurs over a very narrow range of hole density, and that maximum T_c occurs at or very close to Co-ion valency 3.5^+ , corresponding to $\rho = 0.5$, the density where SC is found in the organic CTS.

Future Plans

Search for the paired-electron liquid

We have shown that in the 2D correlated band with $\rho = 0.5$, a correlated insulating state, the Paired Electron Crystal (PEC) can occur [4,6,9]. The PEC gains stability in the presence of electron-electron interactions and lattice frustration, and can be viewed as the $\rho = 0.5$ equivalent

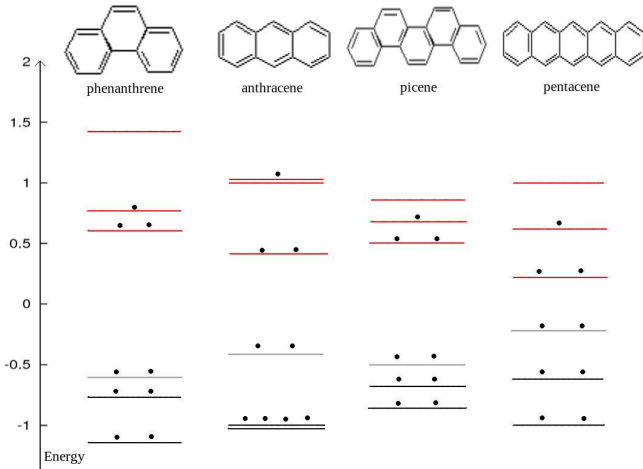


Figure 2: Bonding (black) and antibonding (red) molecular orbitals of the neutral molecules, and electron occupancies of the trinegative molecular ions, within nearest neighbor tight-binding theory. Energies are in units of the hopping integral $|t|$. The LUMO and LUMO+1 orbitals are unusually close in phenanthrene and picene, compared to anthracene and pentacene. In coronene (not shown) the LUMOs are doubly degenerate.

of the $\rho = 1$ valence bond solid (VBS). In the PEC, pairs of electrons are separated by “vacant” sites, so the PEC state necessarily contains coexisting charge, bond, and spin order. We further propose that localized PEC pairs can gain mobility, resulting in a “paired electron liquid” which is a realization of Schafroth’s theory of SC, which described a condensate of real-space pairs [3,6].

Except for our emphasis on $\rho = \frac{1}{2}$, our proposed model has strong parallels with other proposals for theories of correlated-electron SC. Within most, if not all, these theories, the evolution to the superconducting state occurs via a spin-singlet insulator at the boundary of a metal-insulator transition. This is for example true for all RVB theories of SC, irrespective of whether the singlet state appears as a function of doping of the $\rho = 1$ square lattice, or due to increased bandwidth and frustration within the $\rho = 1$ triangular lattice. The key differences between our theory and many of the existing proposals are that, (a) the occurrence of the spin-singlet insulating PEC state in our case is not a conjecture, it has been already proved [6,9]; (b) these singlets have the same character as that of the charged Bosons within Schafroth’s theory of SC; and (c) there appear to be several classes of materials in which SC appears to occur at strictly $\rho = \frac{1}{2}$, without doping [3]. At the very least, our proposed research in this subsection will give a definitive answer to the question whether or not the similarities between the different classes of materials we have indicated are merely coincidental or whether they are connected by a deep fundamental relationship.

Metal-intercalated hydrocarbon superconductors

A_3 phenanthrene, A_3 picene, A_3 coronene, and A_3 dibenzopentacene ($A = K, Rb$) are attracting attention as unconventional superconductors. In addition to the high T_c in A_3 dibenzopentacene (33 K), these systems exhibit other perplexing features: (i) while the doping concentration can vary over a wide range, SC is limited to anionic compounds with charge -3 on the hydrocarbons, and (ii) SC is absent in the charged acenes (anthracene and pentacene), which are obtained through “linear” fusions of the benzene rings. A_x pentacene is metallic but not superconducting. It is very likely that the limitation of SC to a specific stoichiometry (reminiscent of superconducting A_3C_{60}) and a specific molecular structure are both hints to a correct theoretical mechanism of the phenomenon.

Although electron-molecular vibration (e-mv) couplings in the doped acenes and phenacenes are strong, multiple observations suggest that the mechanism of SC is primarily electronic, with e-mv interactions playing however a significant role, as in the CTS. Early calculations giving strong e-mv

coupling suggested that monoanions should be superconducting. The calculated couplings decrease with increasing size of the hydrocarbon molecule, predicting a higher T_c in A₃phenanthrene than in A₃picene, contradicting experiments. Secondly, pressure *increases* T_c in both A₃phenanthrene and A₃picene. This is opposite to what is seen in BCS superconductors where pressure decreases T_c due to decreasing density of states. Finally, any electron-phonon mediated mechanism will fail to explain the absence of SC in acenes. Our goal is to derive a microscopic molecular site-based description of the A₃phenazine and A₃coronene focusing on the charged anions only. We believe that with exactly 3 extra electrons per phenacene (but not acene) molecule, the solid can be described as a doubly-degenerate $\rho = \frac{1}{2}$ system. If true, this will indicate a common theme between intercalated hydrocarbons and CTS.

Publications 2009-2012

1. R. T. Clay, J. P. Song, S. Dayal, S. Mazumdar, "Ground State and Finite Temperature Behavior of 1/4-Filled Band Zigzag Ladders," *J. Phys. Soc. Jpn.* **81**, 074707 (2012).
2. S. Dayal, R. T. Clay, S. Mazumdar, "Absence of long-range superconducting correlations in the frustrated half-filled-band Hubbard model", *Phys. Rev. B* **85**, 165141 (2012).
3. S. Mazumdar, R. T. Clay, "Is there a common theme behind the correlated-electron superconductivity in organic charge-transfer solids, cobaltates, spinels, and fullerenes?", *Phys. Status. Solidi B* **249**, 995 (2012).
4. R. T. Clay, S. Dayal, H. Li, S. Mazumdar, "Beyond the quantum spin liquid concept in frustrated two dimensional organic superconductors", *Phys. Status. Solidi B* **249**, 991 (2012).
5. S. Mazumdar, R. T. Clay, H. Li, "Similarities in electronic properties of organic charge-transfer solids and layered cobaltates," *Physica B* **407**, 1722 (2012).
6. S. Dayal, R. T. Clay, H. Li, S. Mazumdar, "Paired Electron Crystal: Order from Frustration in the Quarter-Filled Band," *Phys. Rev. B* **83**, 245106 (2011).
7. H. Li, R. T. Clay, S. Mazumdar, "Theory of Carrier Concentration-Dependent Electronic Behavior in Layered Cobaltates," *Phys. Rev. Lett.* **106**, 216401 (2011).
8. R. T. Clay, H. Li, S. Sarkar, S. Mazumdar, T. Saha-Dasgupta, "Cooperative orbital ordering and Peierls instability in the checkerboard lattice with doubly degenerate orbitals," *Phys. Rev. B* **82**, 035108 (2010).
9. H. Li, R. T. Clay, S. Mazumdar, "The Paired-Electron Crystal in the Two-Dimensional Frustrated Quarter-Filled Band," *J. Phys. Cond. Matt.* **22** 272201 (2010).
10. R. T. Clay, H. Li, S. Mazumdar, "Bipolaron density-wave driven by antiferromagnetic correlations and frustration in organic superconductors," *Physica B* **405** 253 (2010).
11. R. T. Clay, S. Mazumdar, H. Li, "Local singlets, frustration, and unconventional superconductivity in the organic charge-transfer solids," *Physica B*, **404**, 487 (2009).
12. S. Mazumdar, R. T. Clay, H. Li, "From valence bond solid to unconventional superconductivity in the organic charge-transfer solids," *Synth. Metals*, **159**, 2419 (2009).