Individual molecule model of kappa-type organic charge transfer salts

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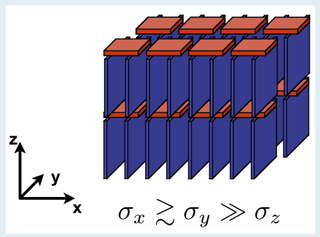
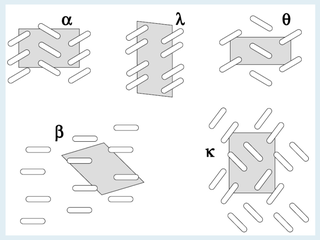
Crystal structure of organic charge transfer salts

- ET = BEDT-TTF = bis(ethylene-dithio)-tetrathiafulvalene is the electron donor
- X is the electron acceptor [e.g. $Cu(NCS)_2$]
- ET molecules can be packed in different motifs
- κ-phase often superconducting
- features $(ET)_2$ dimers that donate one electron to acceptor layer
- we concentrate on κ-$(ET)_2X$

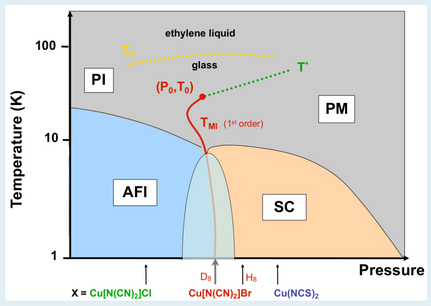


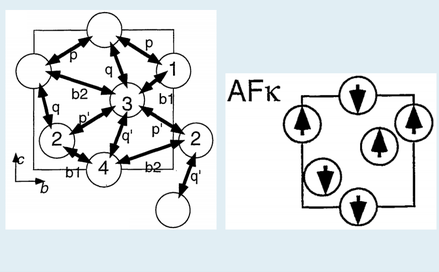


Figures: Müller, ChemPhysChem **12**, 1222 (2011)

Properties of κ-$(ET)_2X$

- AFI to SC transition with pressure or variation of X ('chemical pressure')
- spin-$1/2$ smeared out over $(ET)_2$ dimer (AFI)
- almost perfect triangular lattice in κ-$(ET)_2Cu_2(CN)_3$, quantum spin-liquid
- nature of the superconducting state?
- no phase sensitive probes as in cuprates, problems with sample preparation
- critical endpoint of the MIT line
- freezing of intramolecular degrees of freedom around ~ 100 K

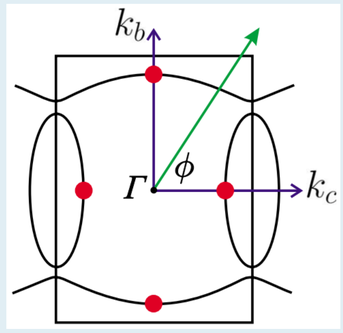


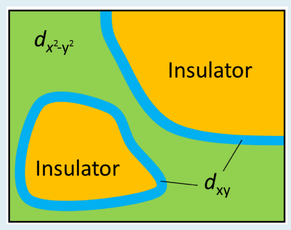


Figures: Müller, ChemPhysChem **12**, 1222 (2011); Kino, Fukuyama, JPSJ **65**, 2158 (1996)

Experimental results for the SC order parameter

- almost all experiments agree on presence of nodes
- try to determine locations
- both d_{xy} and $d_{x^2-y^2}$ have been concluded to exist in experiment, previously interpreted as contradiction
- scanning tunneling spectroscopy is consistent with both d_{xy} and $d_{x^2-y^2}$
- insulating patches in SC matrix known for κ-$(ET)_2X$
- proximity of d_{xy} to AFI makes sense, square lattice
- how to explain $d_{x^2-y^2}$ phase?

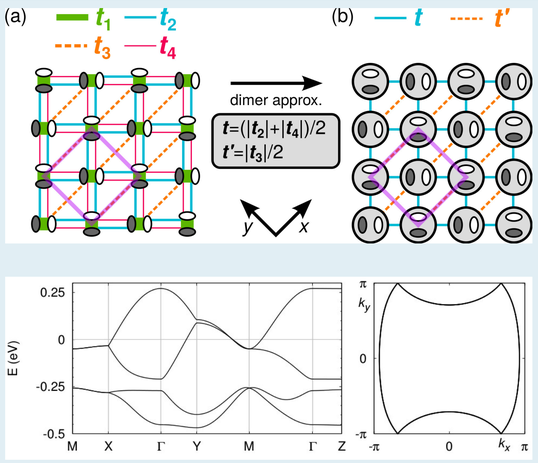




Figures: Malone, *et al.*, PRB **82**, 014522 (2010); Oka *et al.*, JPSJ **84**, 064713 (2015)

Ab-initio calculations for organic charge transfer salts

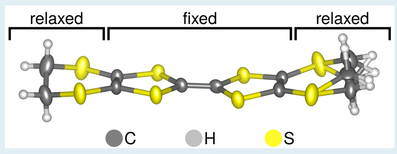
- all-electron full-potential DFT calculations (FPLO)
- molecular orbital TB Hamiltonians from projective Wannier functions
- four hopping parameters sufficient
- 3/4-filled individual molecule model
- 1/2-filled anisotropic triangular lattice of dimers

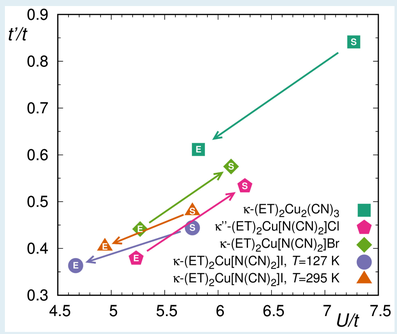


Figures: Guterding, Altmeyer, Jeschke, Valentí, PRB **94**, 024515 (2016)

Influence of molecular conformations on the electronic structure

- relaxed ethylene endgroups and adjacent sulfur atoms in DFT
- endgroups influence hopping amplitudes and Hubbard repulsion
- analyzed within dimer model
- staggered endgroups have larger t'/t, U/t
- explanation for reversible MIT





Figures: Guterding, Valentí, Jeschke, PRB **92**, 081109(R) (2015)

Brillouin zones and superconducting order parameters

- physical BZ is that of four- or two-band model
- larger unfolded BZ and 45 deg. rotation in one-band model
- natural SC order parameter of square lattice is $d_{x^2-y^2}$
- becomes d_{xy} in physical BZ
- we label SC states in physical BZ

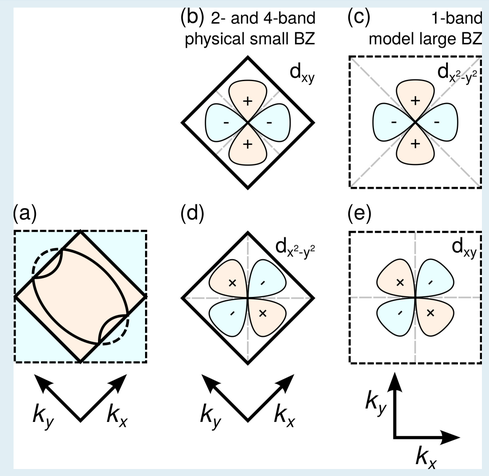
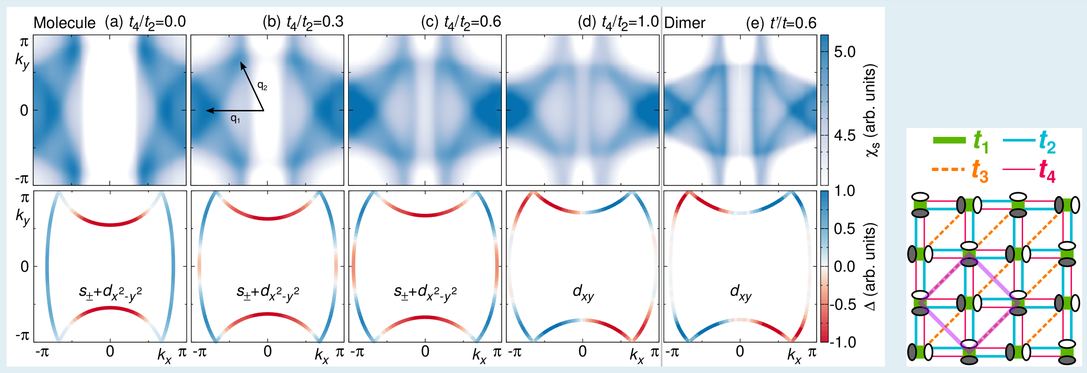


Figure: Guterding, Altmeyer, Jeschke, Valentí, PRB **94**, 024515 (2016)

Connecting the molecule and dimer models at finite dimerization



- dimer model physics is reproduced in molecule model for $t_4/t_2 \to 1$
- averaging of transfer integrals is crucial, not only dimerization strength
- additional set of nodes close to $k_y = 0$
- solution identified as $s_\pm + d_{x^2-y^2}$
- consistent with new STS experiment: PRL **116**, 237001 (2016)

Figures: Guterding, Altmeyer, Jeschke, Valentí, PRB **94**, 024515 (2016)

Pairing phase diagram of κ-$(ET)_2X$

- phase transition from d_{xy} to $s_\pm + d_{x^2-y^2}$
- dimerization plays only minor role
- competition between t_2, t_4 and t_3 controls phases
- many materials close to phase transition
- additional set of nodes appears
- some experimental reports of d_{xy} might have picked up those
- near-degeneracy of d_{xy} and $s_\pm + d_{x^2-y^2}$ in most materials

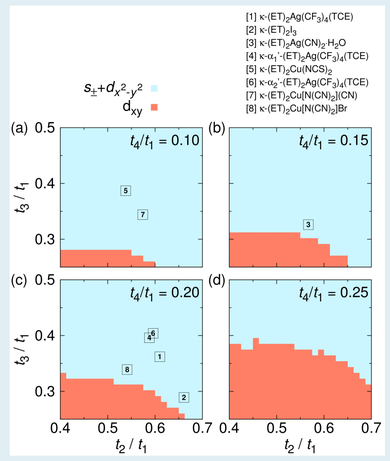


Figure: Guterding, Altmeyer, Jeschke, Valentí, PRB **94**, 024515 (2016)

Simulation of STS for the different SC states

- three different nodal states
- $s_\pm + d_{x^2-y^2}$ with four nodes
- $s_\pm + d_{x^2-y^2}$ with eight nodes close to phase transition
- d_{xy} state in square-like regime
- QP DOS somewhat similar, but different slopes

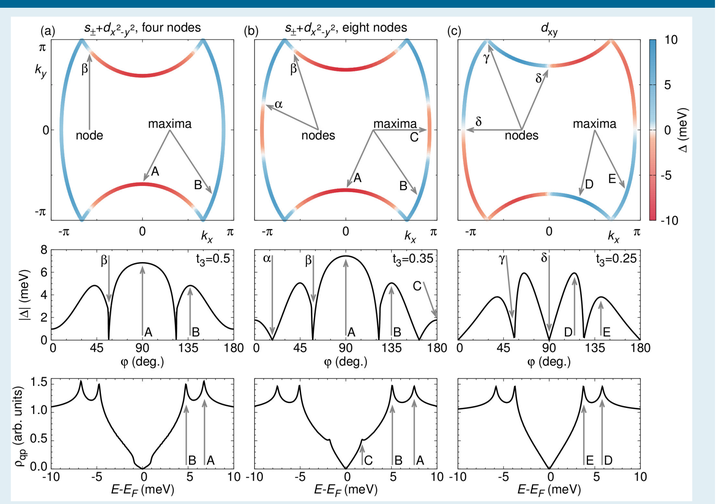


Figure: Guterding, Altmeyer, Jeschke, Valentí, PRB **94**, 024515 (2016)

Summary

- κ-$(ET)_2X$ materials offer extraordinary tunability
- we calculated kinetic part of models for many κ-type materials
- dimer model describes phase diagram only to first approximation
- mixed-symmetry SC state may resolve experimental controversy

References

- Guterding, Valentí, Jeschke, PRB **92**, 081109(R) (2015)
- Guterding *et al.*, PRL **116**, 237001 (2016)
- Guterding, Altmeyer, Jeschke, Valentí, PRB **94**, 024515 (2016)

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