Individual molecule description of kappa-type organic charge transfer salts

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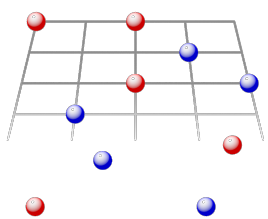
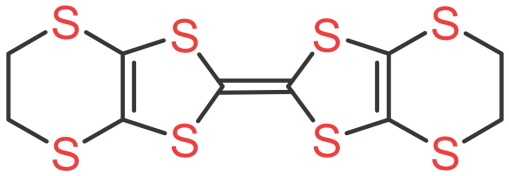


DFG Deutsche Forschungsgemeinschaft
SFB/TR 49

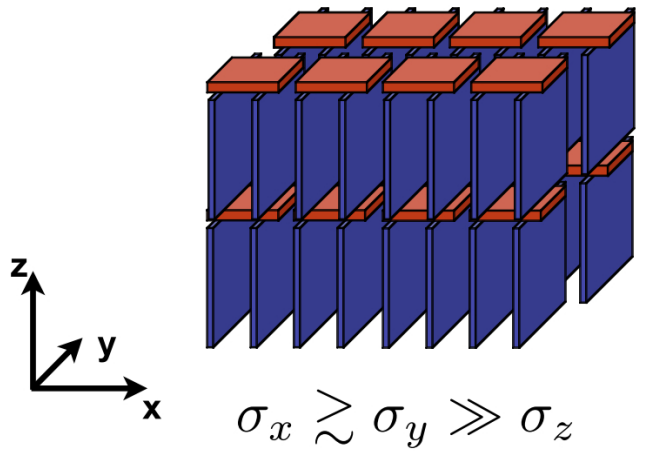
Outline

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 patterns
- κ-phase often superconducting
- features $(ET)_2$ dimers that donate one electron to acceptor layer
- here we concentrate on κ-$(ET)_2X$



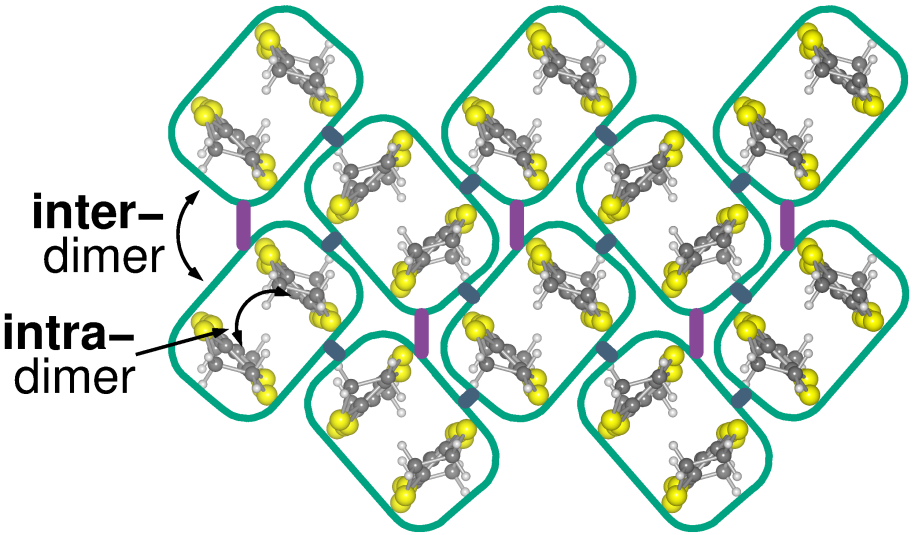
ET (BEDT-TTF)



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

Electronic structure of κ-$(ET)_2X$

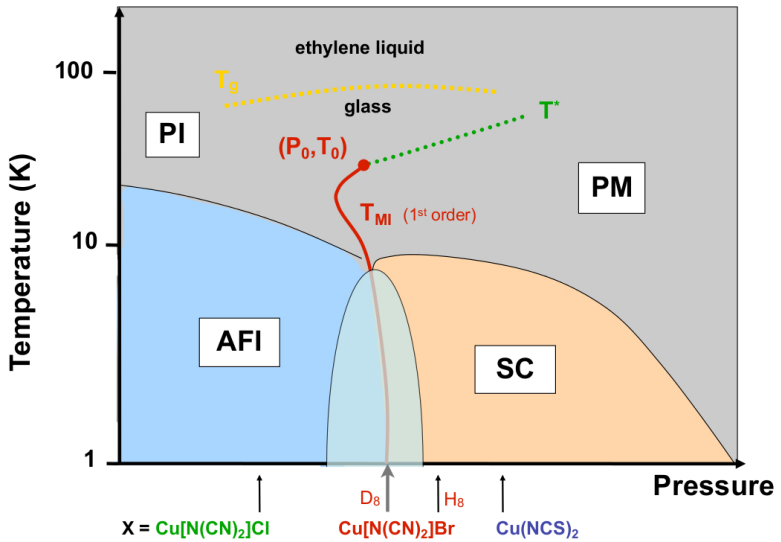
- two-dimensional electronic structure in the ET-plane
- anion layer has filled shells (e.g. Cu d^{10})
- bands at Fermi level only from organic molecules
- often modelled by 1/2-filled anisotropic triangular lattice of dimers
- alternative is 3/4-filled individual molecule model on complicated lattice
- Fermi surface is an ellipse larger than the first BZ

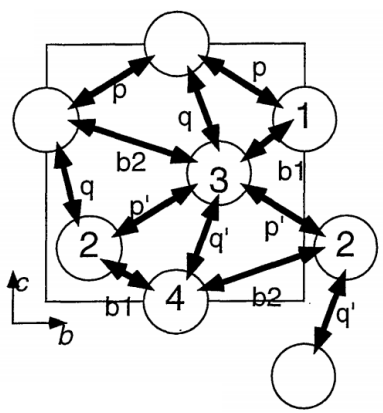


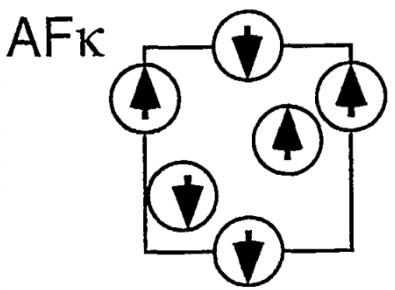
Ferber, Foyevtsova, Jeschke, Valentí, PRB **89**, 205106 (2014)

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 in AFI state
- 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



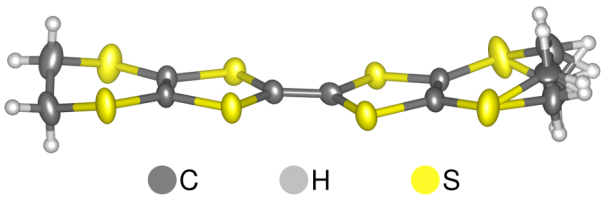


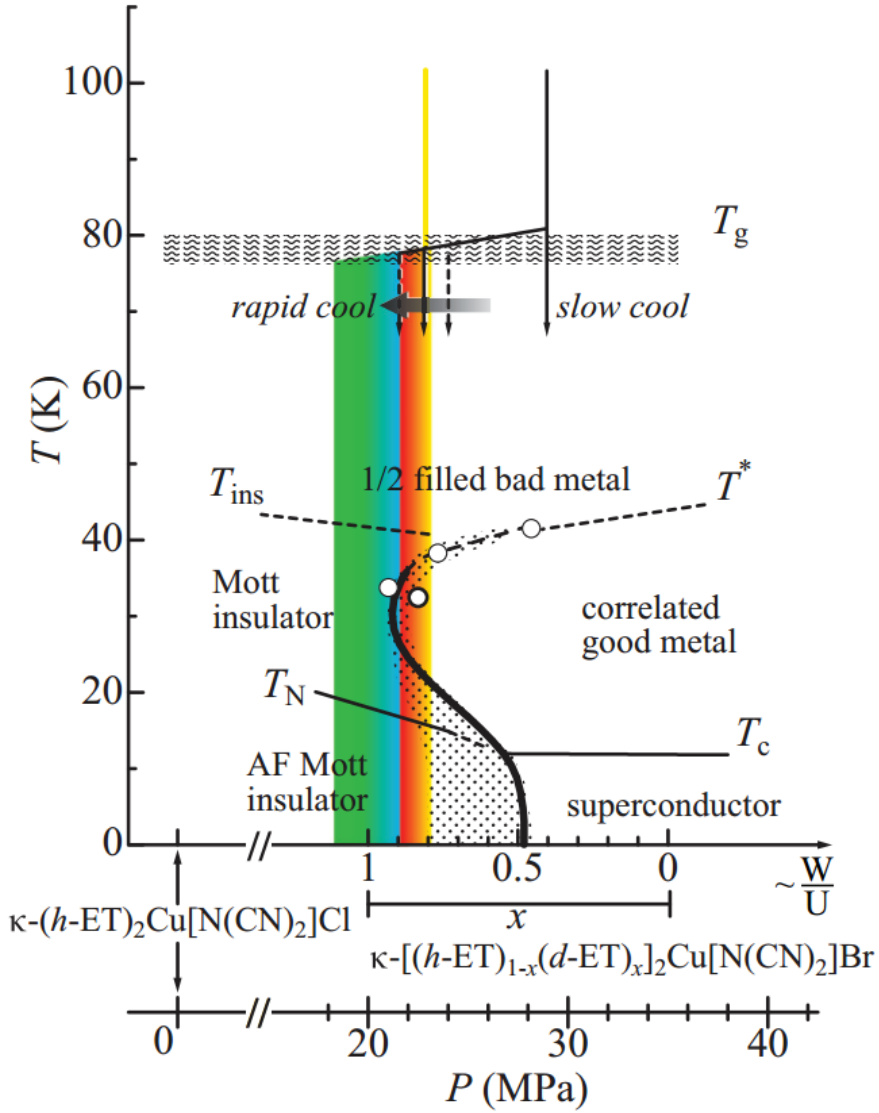


Müller, ChemPhysChem **12**, 1222 (2011); Kino, Fukuyama, JPSJ **65**, 2158 (1996)

Cooling-rate dependent Metal-Insulator transition

- ground state can be tuned by deuteration
- ethylene end group orientations metastable: parallel (eclipsed) and canted (staggered)
- glass transition for ethylene endgroups
- metal-insulator transition can be studied in one sample without application of pressure

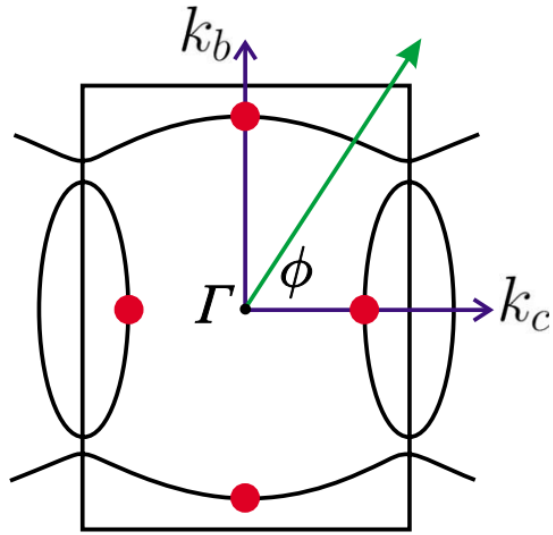


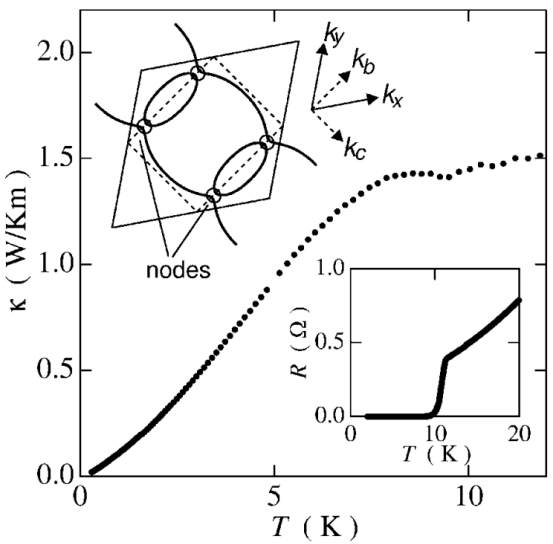


Hartmann, Müller, Sasaki, PRB **90**, 195150 (2014)

Experimental results for the SC order parameter

- experimentalists assume fourfold rotationally invariant order parameter
- all experiments subtract twofold rotationally invariant 'background'
- 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
- multitude of disagreeing experiments
- top panel result from magnetocalorimetry, bottom panel results from thermal conductivity

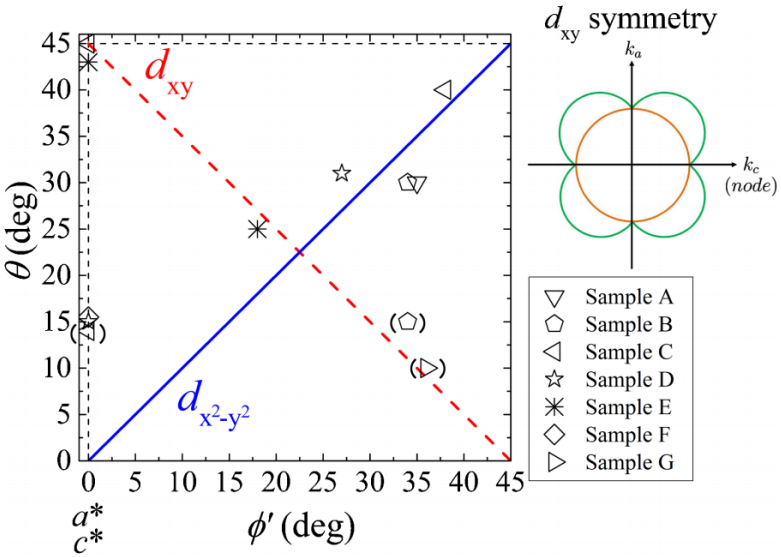


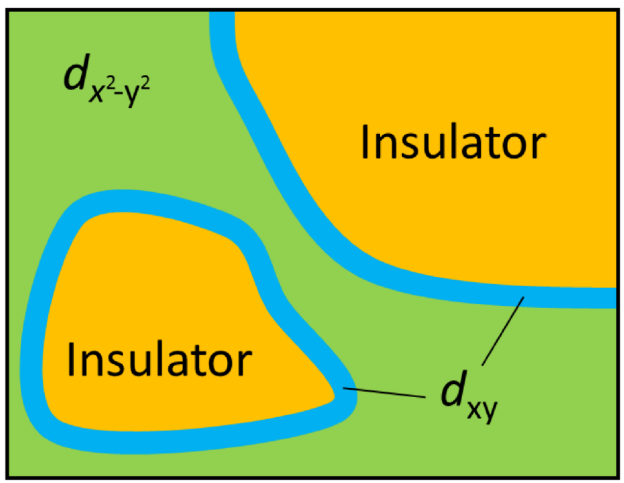


Malone, Taylor, Schlueter, Carrington, PRB **82**, 014522 (2010); Izawa, Yamaguchi, Sasaki, Matsuda, PRL **88**, 027002 (2002)

New results from scanning tunneling spectroscopy

- first time that clean surface was used
- more than one set of nodes in one sample
- consistent with both d_{xy} and $d_{x^2-y^2}$
- phase separation?
- insulating patches in SC matrix known for κ-$(ET)_2X$
- proximity of d_{xy} to AFI makes sense, square lattice physics
- how to explain $d_{x^2-y^2}$ phase?

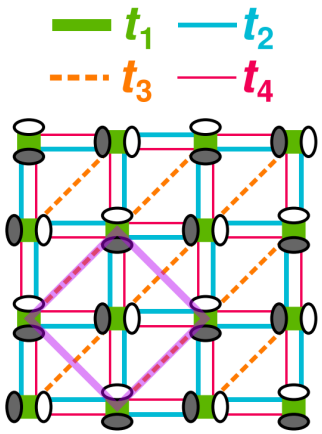


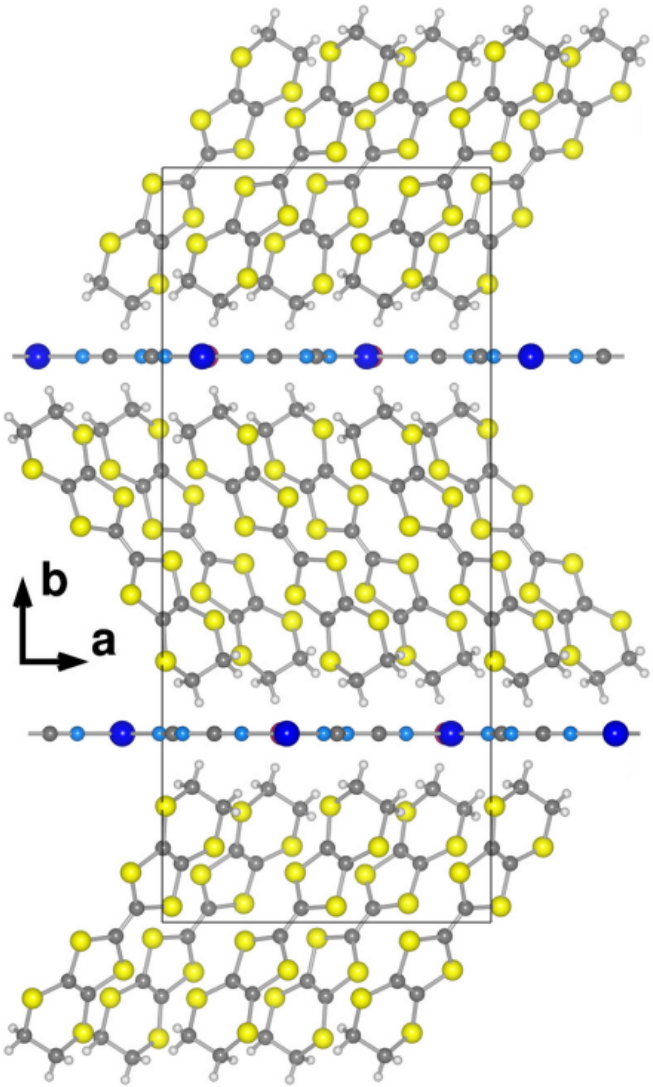


Oka et al., JPSJ **84**, 064713 (2015)

Ab-initio calculations for organic charge transfer salts

- all-electron full-potential DFT calculations (FPLO)
- more than 100 atoms per unit cell
- molecular orbital TB Hamiltonians from projective Wannier functions
- four hopping parameters sufficient
- $t_2/t_1 \in [0.538, 0.661]$, $t_3/t_1 \in [0.289, 0.404]$, $t_4/t_1 \in [0.099, 0.220]$

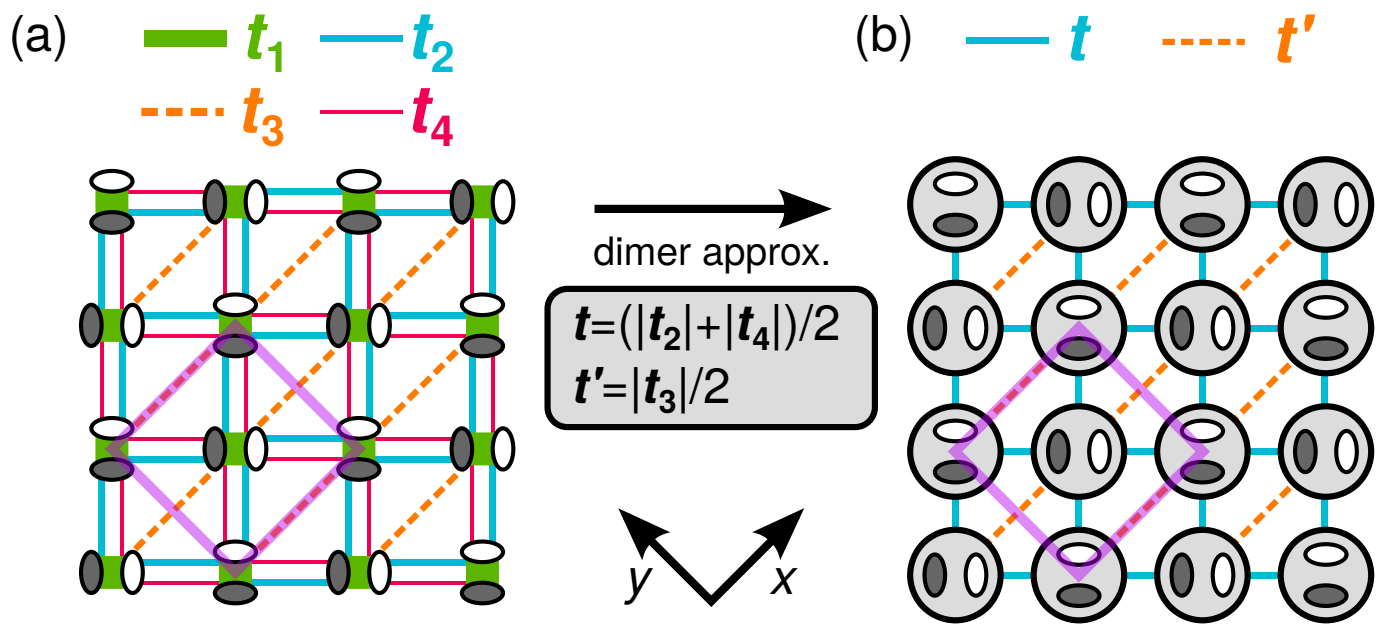




Guterding, Altmeyer, Jeschke, Valentí, arXiv:1605.07017; Ferber, Foyevtsova, Jeschke, Valentí, PRB **89**, 205106 (2014)

Relation between Dimer and Molecule model

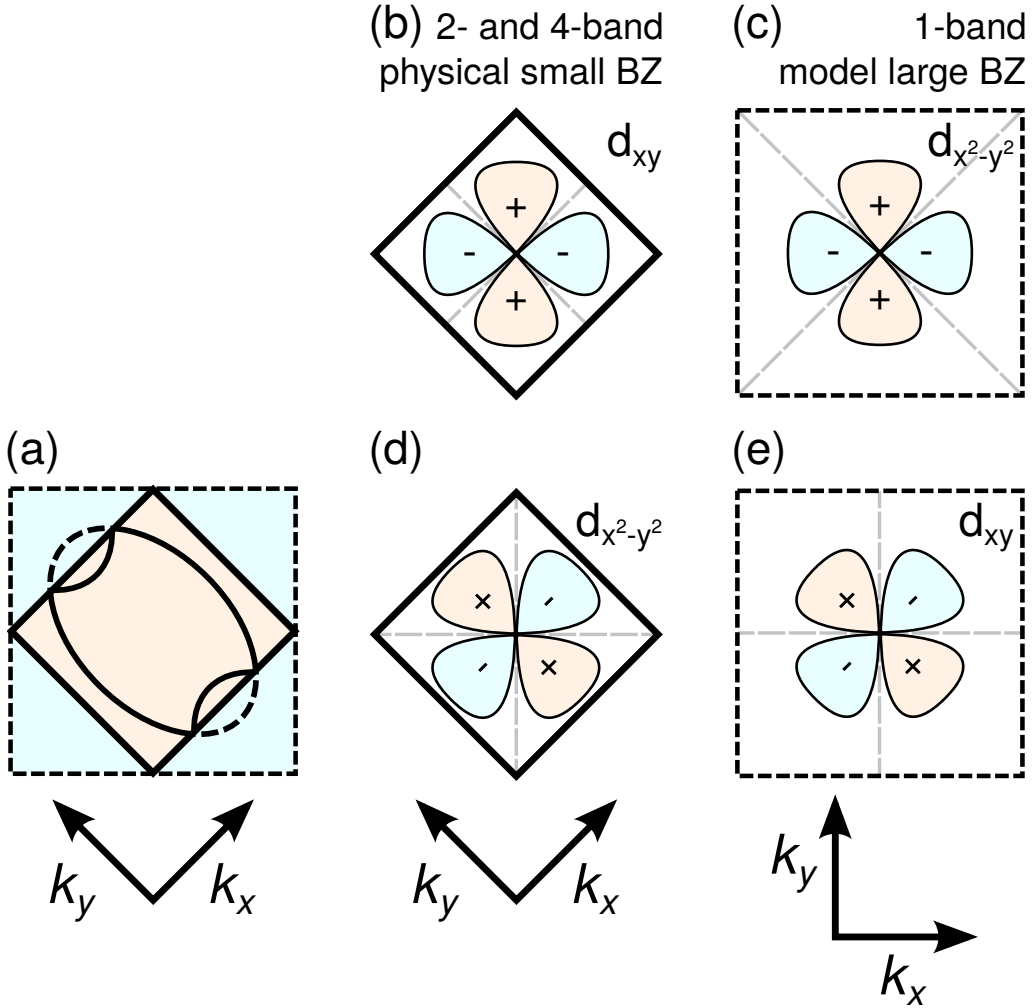
- original lattice structure encoded in molecule model
- traditionally dimer-approximated anisotropic triangular lattice is used
- one-band instead of four-band model
- averaging of t_2 and t_4 introduces C_4-symmetric hopping
- BZ can be unfolded from two- to one-band model



Guterding, Altmeyer, Jeschke, Valentí, arXiv:1605.07017

Brillouin zones and superconducting order parameters

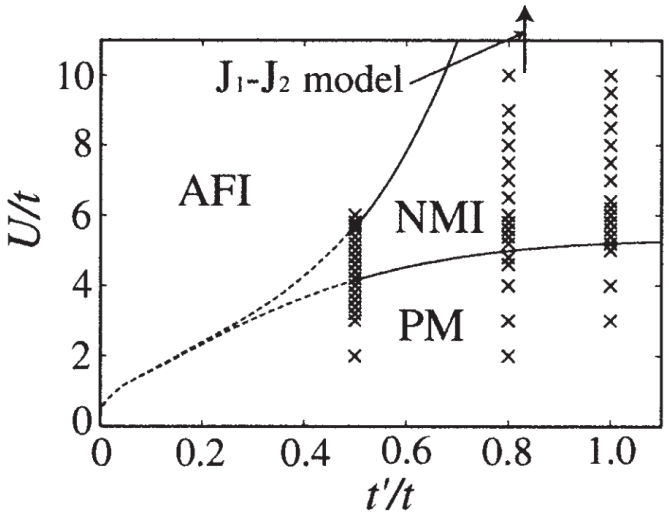
- physical BZ is that of four- or two-band model
- larger unfolded BZ and 45 deg. rotation in one-band model
- natural SC order parameter of square lattice is $d_{x^2-y^2}$
- becomes d_{xy} in physical BZ
- we label SC states in physical BZ

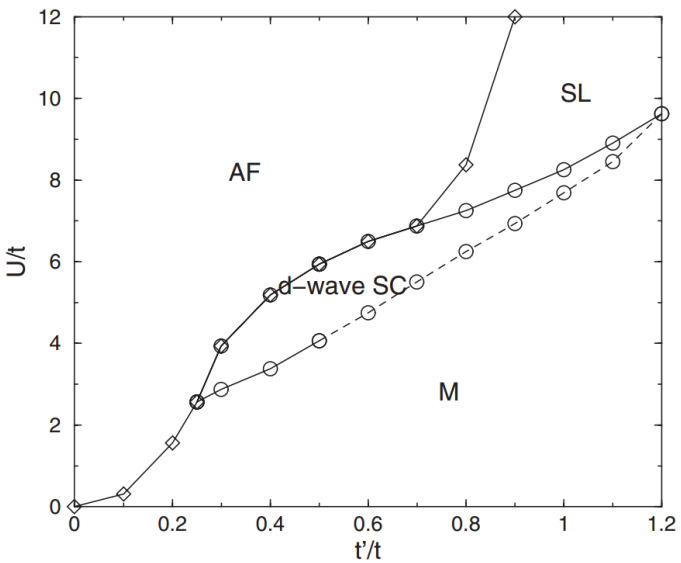


Guterding, Altmeyer, Jeschke, Valentí, arXiv:1605.07017

Phase diagram of the anisotropic triangular lattice model

- t'/t controls frustration
- on-site interaction term $H_{int} = U \sum_i n_{i\uparrow} n_{i\downarrow}$
- AFI, M, QSL and SC phases reproduced
- not all methods agree on phase boundaries and existence of SC
- top plot is PIRG, bottom plot is CDMFT (most extreme examples for disagreement)
- many studies find same SC order parameter as in cuprates (d_{xy})
- are $d_{x^2-y^2}$ experiments wrong?
- side note: intra-dimer charge ordering observed

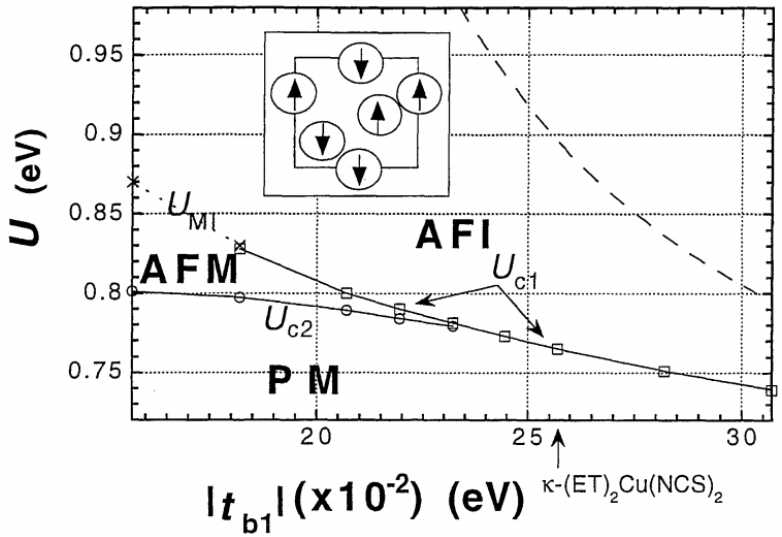


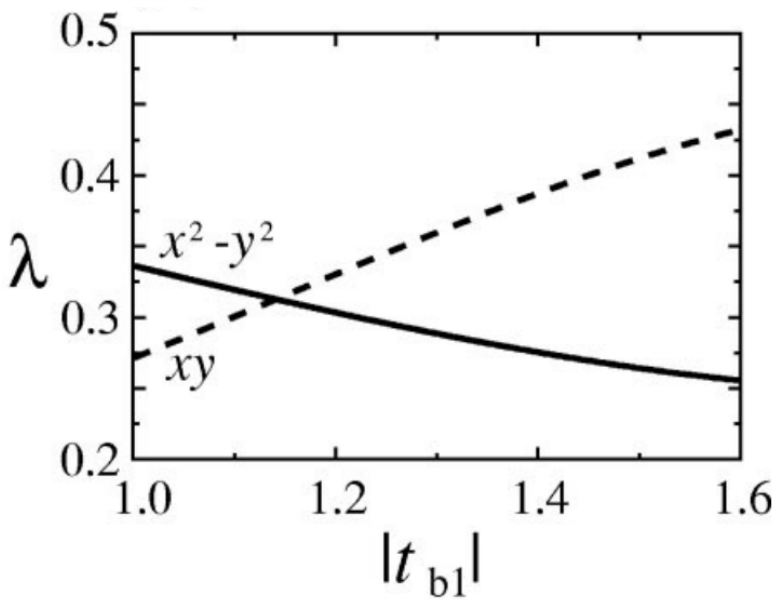


Morita, Watanabe, Imada, JPSJ **71**, 2109 (2002); Kyung, Tremblay, PRL **97**, 046402 (2006)

Phase diagram of the molecule model

- top panel HF, bottom panel FLEX
- HF reproduces important phases
- antiferromagnetic metal disappears for large dimerization
- SC order parameter changes as function of dimerization strength
- very few studies, no complete phase diagram
- influence of parameters aside from dimerization not studied

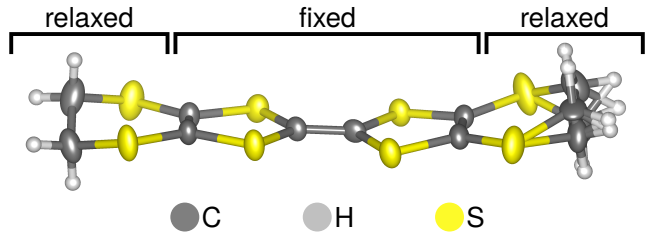


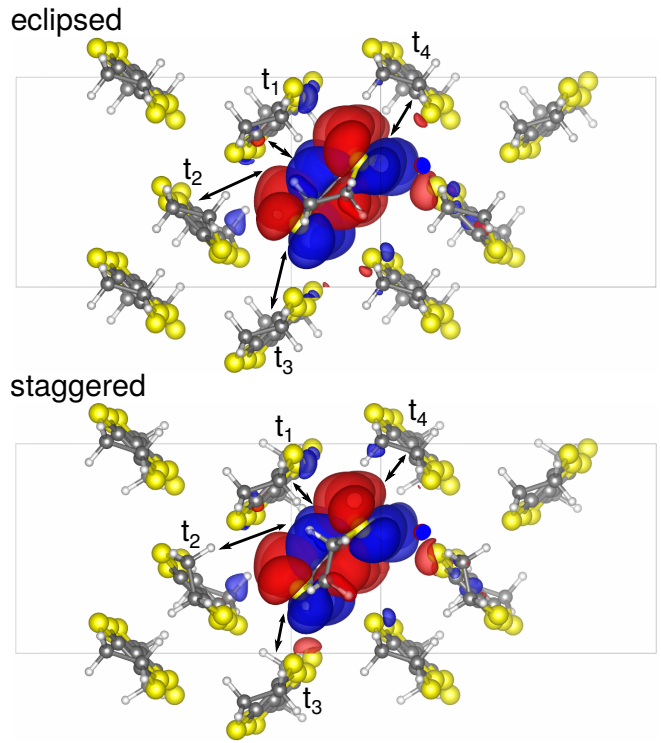


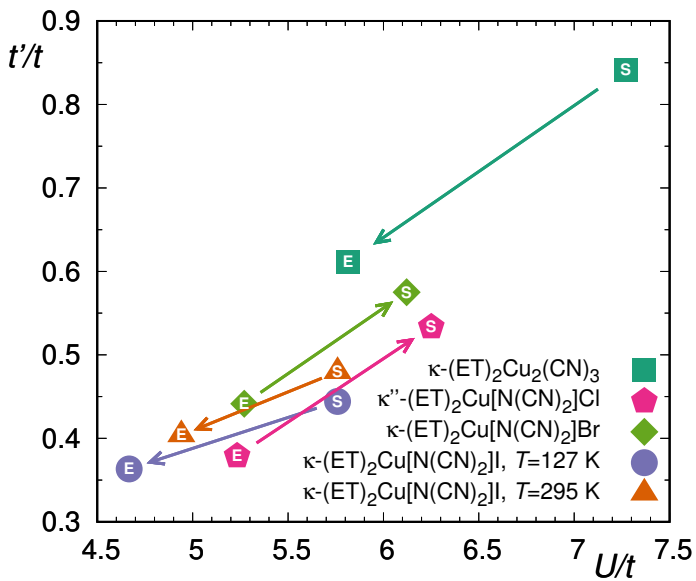
Kino, Fukuyama, JPSJ **65**, 2158 (1996); Kuroki, Kimura, Arita, Tanaka, Matsuda, PRB **65**, 100516(R) (2002)

Influence of molecular conformations on the electronic structure

- relax ethylene endgroups and adjacent sulfur atoms in DFT
- endgroups influence hopping amplitudes and Hubbard repulsion
- analyze within dimer model
- staggered endgroups have larger t'/t, U/t







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

Tight binding+RPA formalism in a nutshell

$$H = H_0 + H_{\text{int}} = \sum_{ij\sigma} t_{ij}(c^{\dagger}_{i\sigma}c_{j\sigma} + \text{h.c.}) + \frac{U}{2}\sum_{i\sigma} n_{i\sigma}n_{i\bar{\sigma}}$$

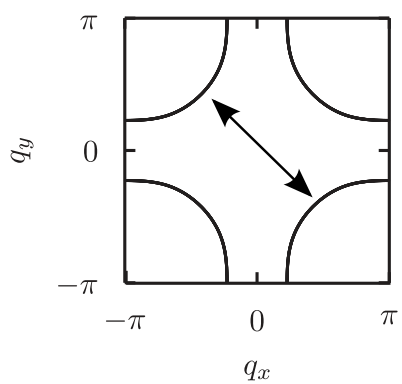
$$\chi^{pq}_{st}(\vec{q}) = -\frac{1}{N}\sum_{\vec{k},\mu,\nu} a^{s}_{\mu}(\vec{k})a^{p*}_{\mu}(\vec{k})a^{q}_{\nu}(\vec{k}+\vec{q})a^{t*}_{\nu}(\vec{k}+\vec{q})\frac{f(E_{\nu}(\vec{k}+\vec{q})) - f(E_{\mu}(\vec{k}))}{E_{\nu}(\vec{k}+\vec{q}) - E_{\mu}(\vec{k})}$$

$$\left[(\chi^{\text{RPA}}_{\text{spin}})^{pq}_{st}\right]^{-1} = [\chi^{pq}_{st}]^{-1} - (U_{\text{spin}})^{pq}_{st}$$

$$\Gamma^{pq}_{st}(\vec{k},\vec{k}') = \left[\frac{3}{2}U_s\,\chi^{\text{RPA}}_{s}(\vec{k}-\vec{k}')\,U_s + \frac{1}{2}U_s - \frac{1}{2}U_c\,\chi^{\text{RPA}}_{c}(\vec{k}-\vec{k}')U_c + \frac{1}{2}U_c\right]^{tq}_{ps}$$

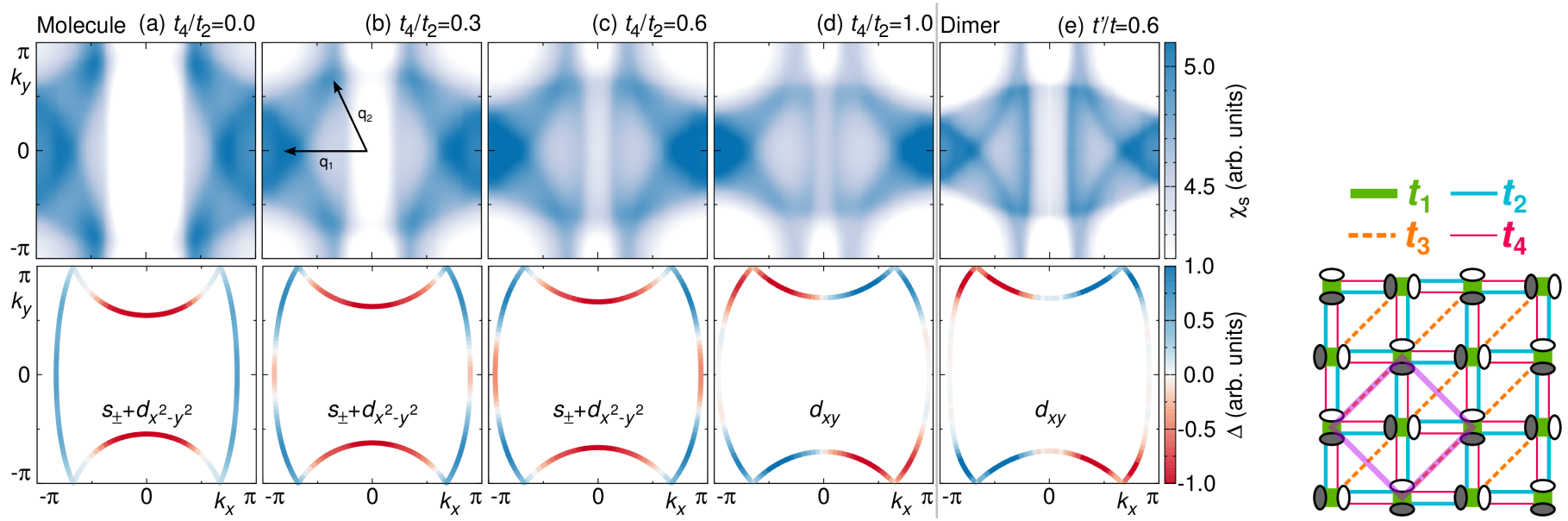
$$\Gamma_{ij}(\vec{k},\vec{k}') = \sum_{stpq} a^{t*}_{i}(-\vec{k})a^{s*}_{i}(\vec{k})\,\text{Re}\left[\Gamma^{pq}_{st}(\vec{k},\vec{k}')\right]\,a^{p}_{j}(\vec{k}')a^{q}_{j}(-\vec{k}')$$

$$-\sum_{j}\oint_{C_j}\frac{dk'_{\parallel}}{2\pi}\frac{1}{4\pi v_F(\vec{k}')}\left[\Gamma_{ij}(\vec{k},\vec{k}') + \Gamma_{ij}(\vec{k},-\vec{k}')\right]g_j(\vec{k}') = \lambda_i g_i(\vec{k})$$



Graser, Maier, Hirschfeld, Scalapino, NJP **11**, 025016 (2009)

Susceptibility and order parameter: connecting the molecule and dimer models at finite dimerization

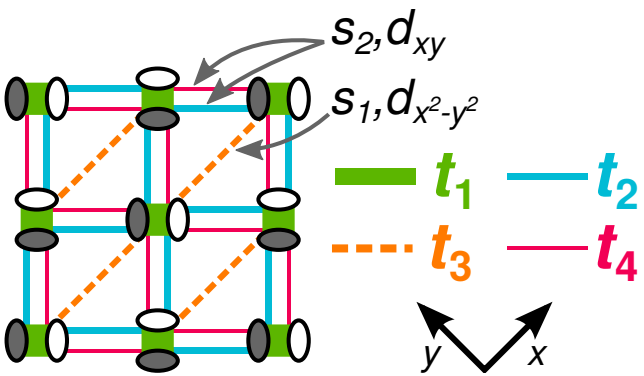


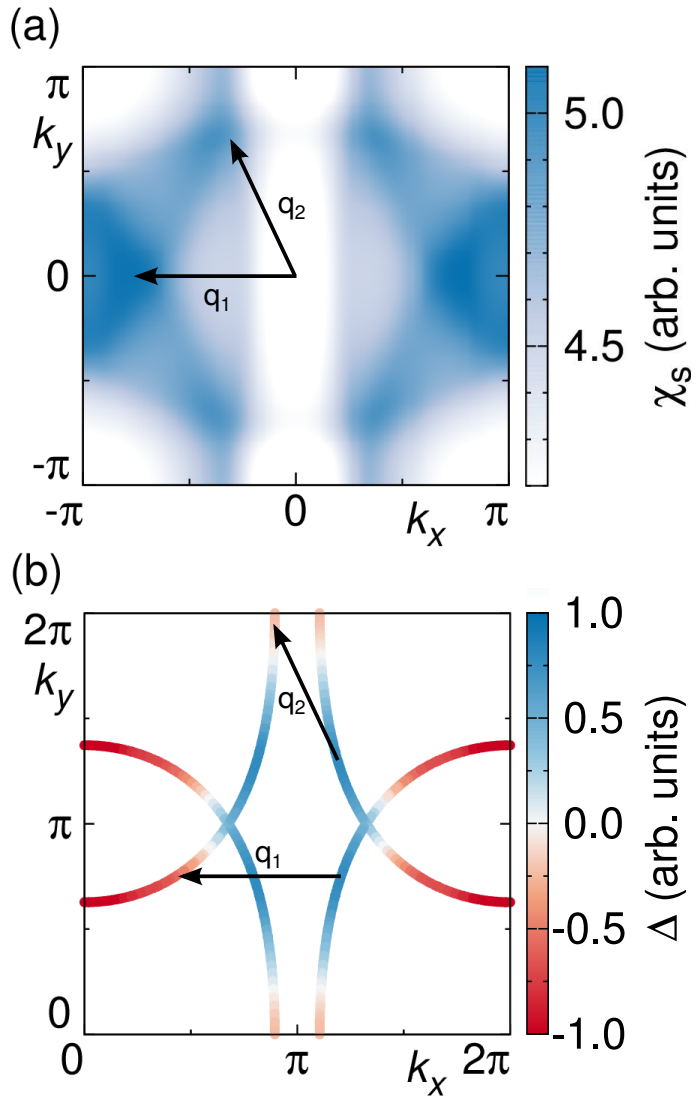
- dimer model physics is reproduced in molecule model for $t_4/t_2 \to 1$
- averaging of transfer integrals is crucial, not only dimerization strength
- additional set of nodes close to $k_y = 0$
- solution identified as $s_\pm + d_{x^2-y^2}$
- main features are q_1 and q_2

Guterding, Altmeyer, Jeschke, Valentí, arXiv:1605.07017

Connection between susceptibility features and hopping parameters

- s_1: $\cos k_x + \cos k_y$
- s_2: $\cos k_x \cdot \cos k_y$
- $d_{x^2-y^2}$: $\cos k_x - \cos k_y$
- d_{xy}: $\sin k_x \cdot \sin k_y$
- feature q_1 controlled by t_3
- feature q_2 controlled by t_2 and t_4
- increase of t_4/t_2 makes q_2 more square-like, drives d_{xy}

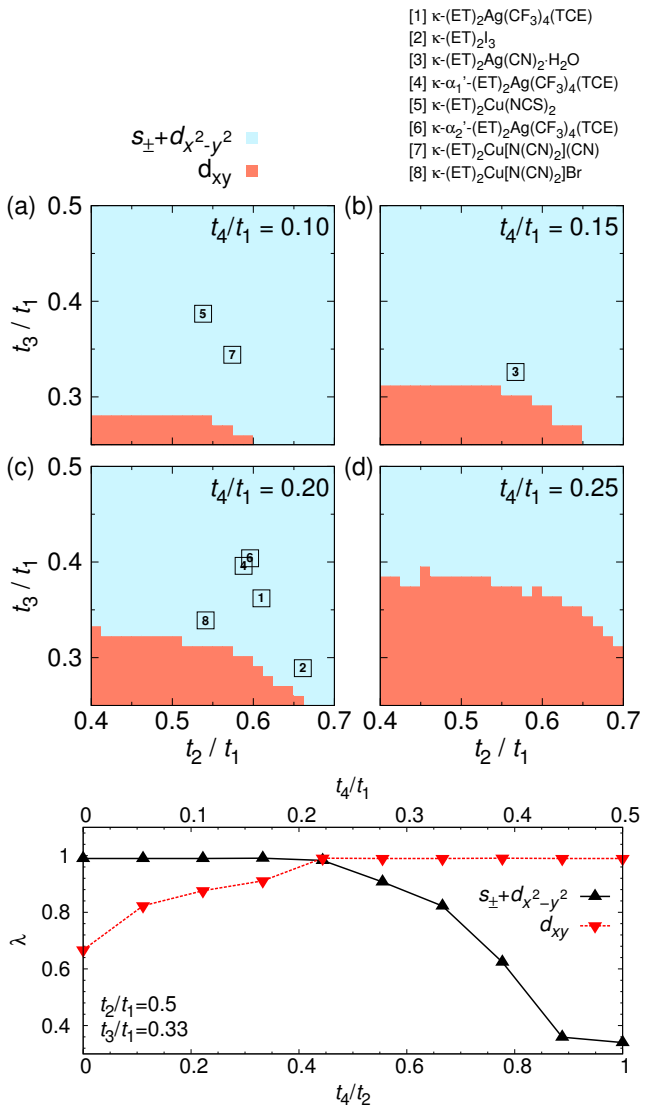




Guterding, Altmeyer, Jeschke, Valentí, arXiv:1605.07017

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 there
- 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



Guterding, Altmeyer, Jeschke, Valentí, arXiv:1605.07017

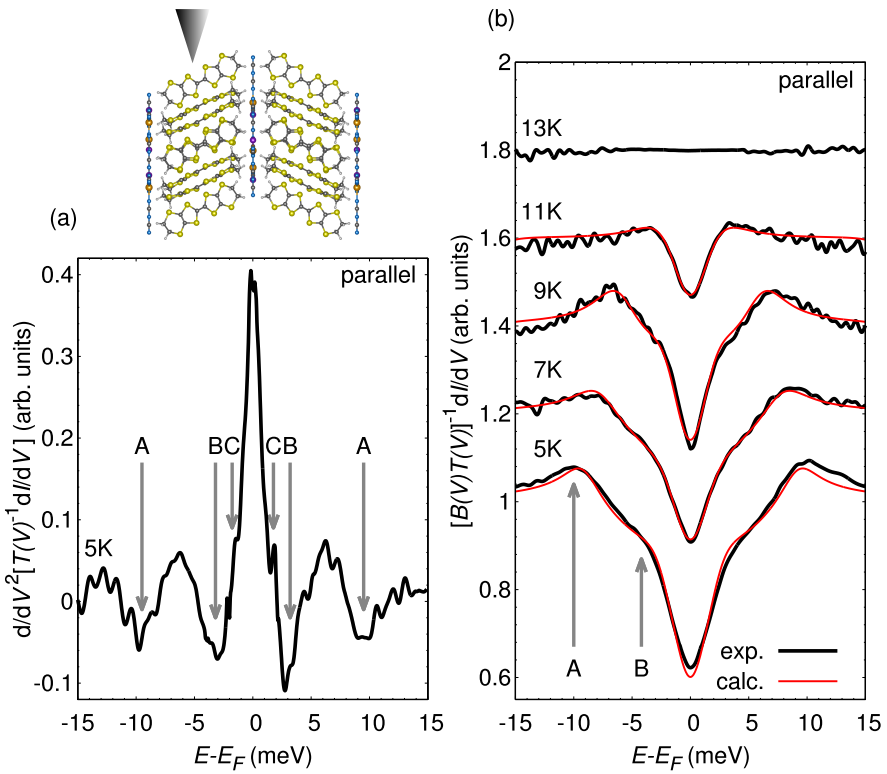
Connection to experiment: scanning tunneling spectroscopy

$$\Delta(\vec{k}) = \Delta_0[c_{s_1}(\cos k_x + \cos k_y) + c_{d_1}(\cos k_x - \cos k_y) + c_{s_2}(\cos k_x \cdot \cos k_y)]$$

$$\rho_{qp}(E,\Gamma) \propto \sum_{\vec{k}} \mathrm{Re}\frac{|E+i\Gamma|}{\sqrt{(E+i\Gamma)^2-\Delta(\vec{k})^2}}$$

$$S(V) = \frac{1}{B(V)T(V)}\frac{dI(V)}{dV} \propto \int_{-\infty}^{\infty} dE\ [\rho_{qp}(E)(1-x)+x]\frac{-df(E+eV)}{dV}$$

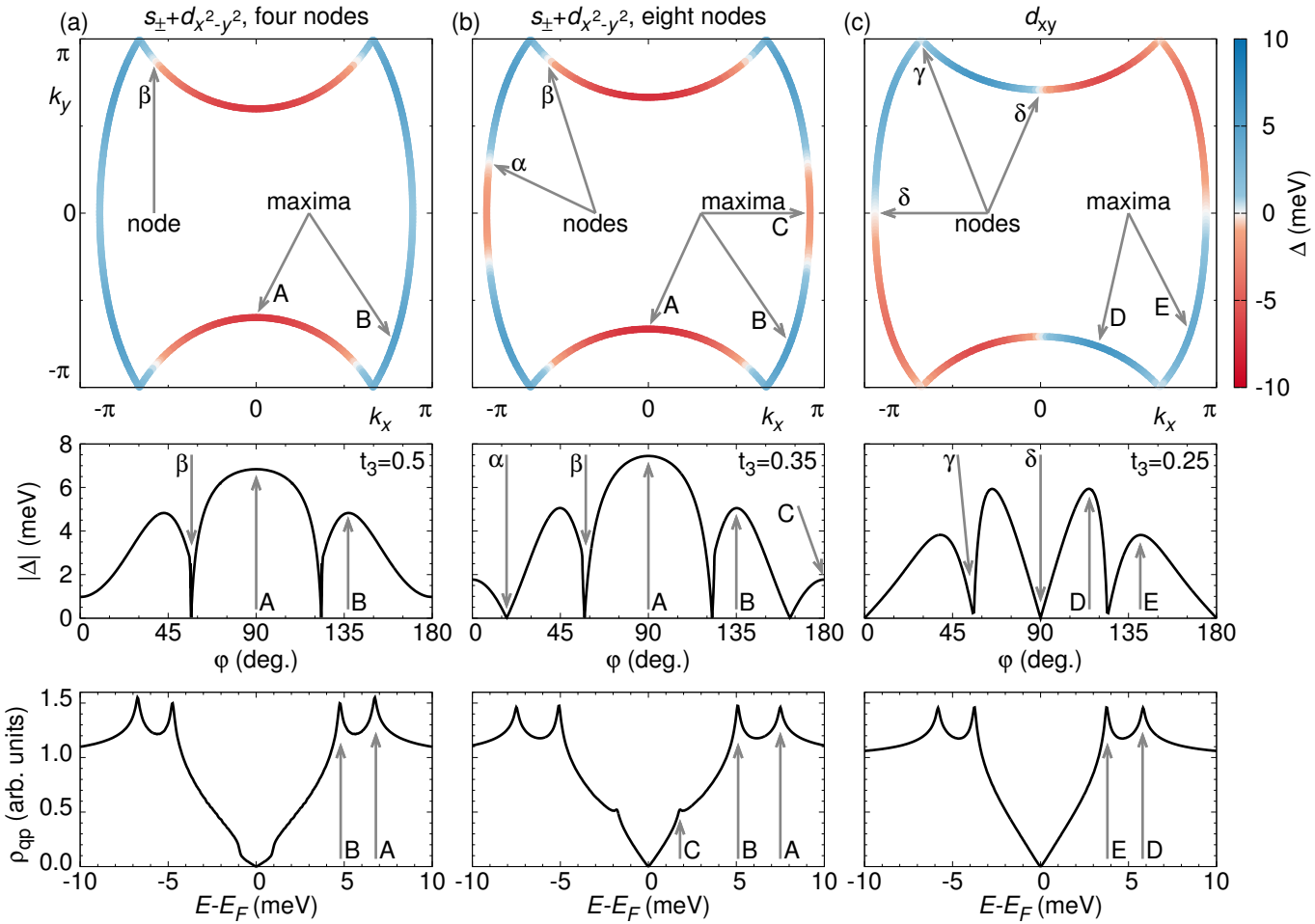
- simulate tunneling conductivity from quasiparticle DOS
- calculate QP DOS from Fermi surface approximation, FS not concentric circle
- introduce small broadening
- discriminates $d_{x^2-y^2}$ and d_{xy}



Guterding et al., PRL **116**, 237001 (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



Guterding, Altmeyer, Jeschke, Valentí, arXiv:1605.07017

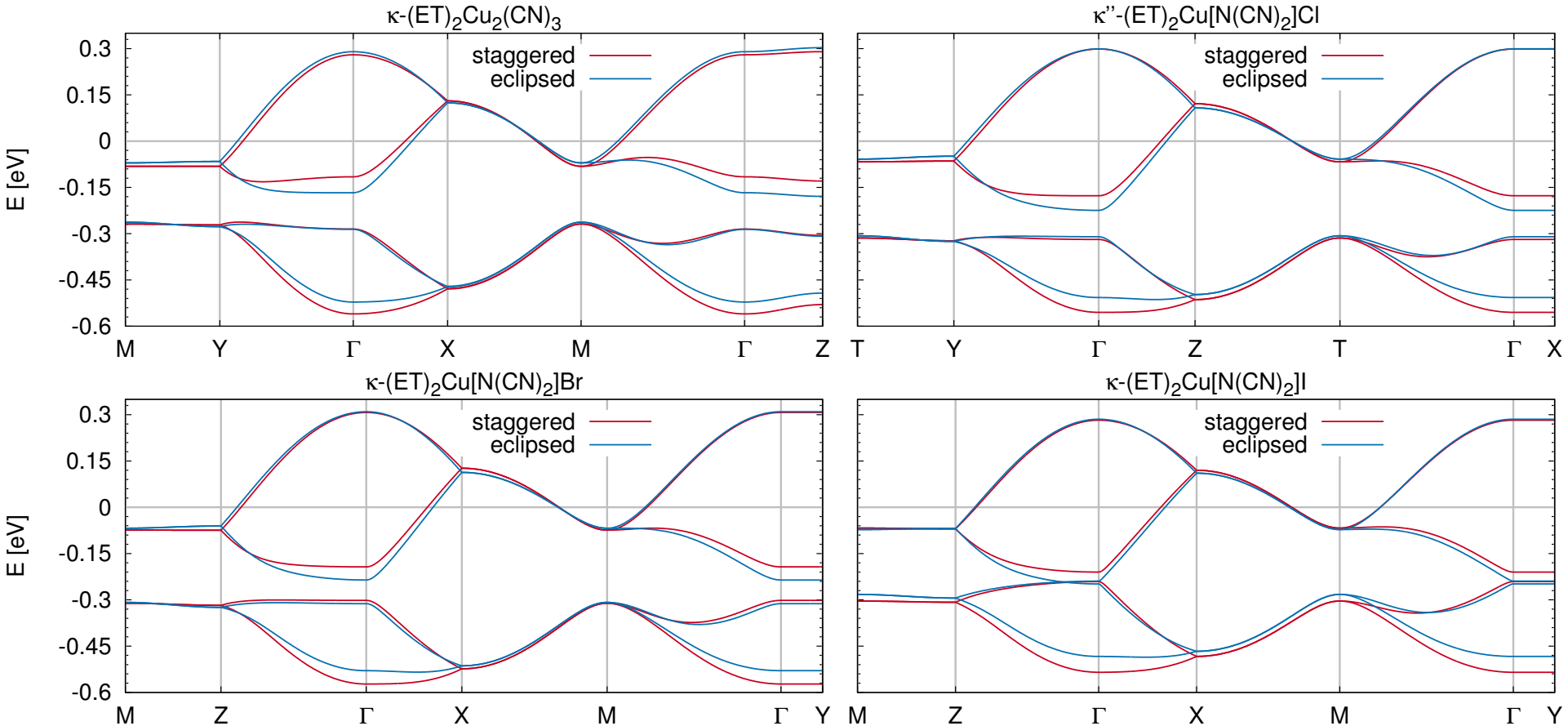
Summary

- κ-$(ET)_2X$ materials offer extraordinary tunability
- we calculated kinetic part of models for many κ-type materials
- dimer model describes phase diagram to first approximation
- blocked further progress regarding SC state
- molecule model mostly unexplored
  (spin-liquid, influence of V on phase boundaries)

References

- Guterding, Valentí, Jeschke, PRB **92**, 081109(R) (2015)
- Guterding et al., PRL **116**, 237001 (2016)
- Guterding, Altmeyer, Jeschke, Valentí, arXiv:1605.07017

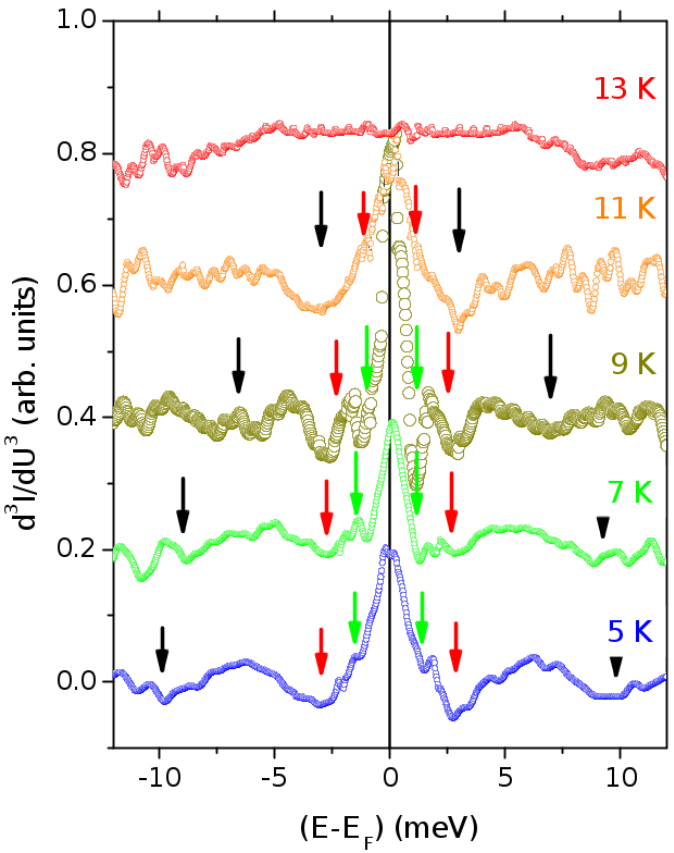
Electronic bandstructure for different ethylene endgroup configurations

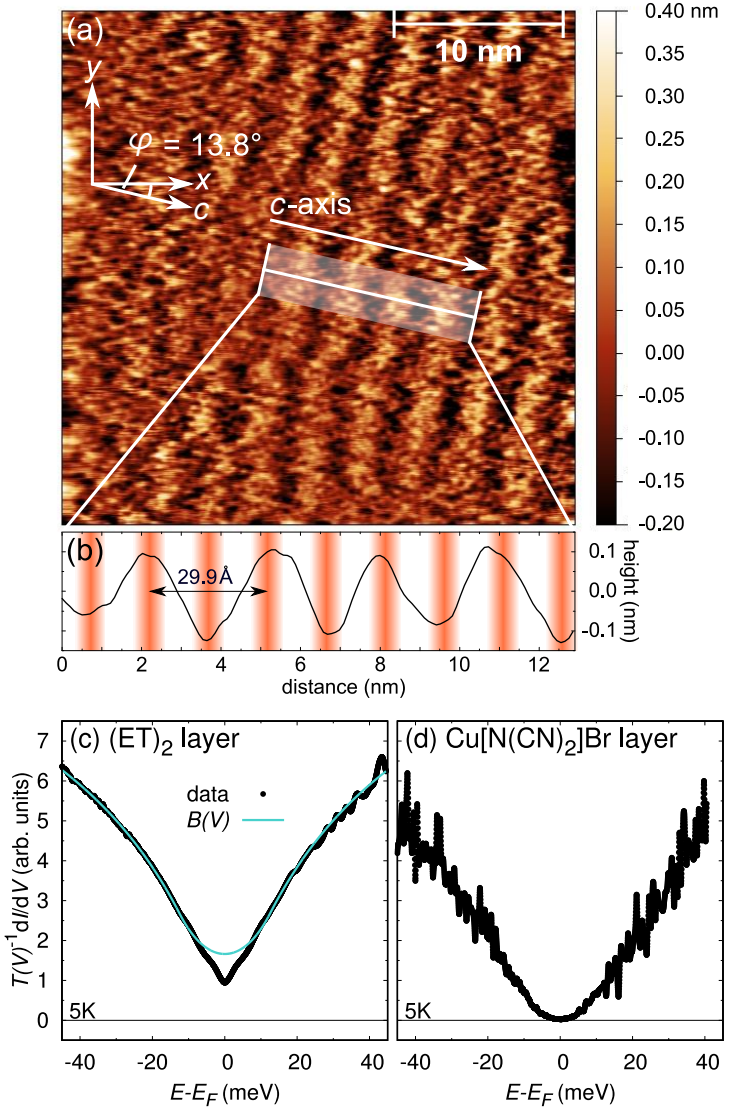


Guterding, Valentí, Jeschke, PRB **92**, 081109(R) (2015)

STS data for κ-$(ET)_2[N(CN)_2]Br$

- tunneling parallel to conducting layers
- background DOS is modelled by Anderson-Hubbard model

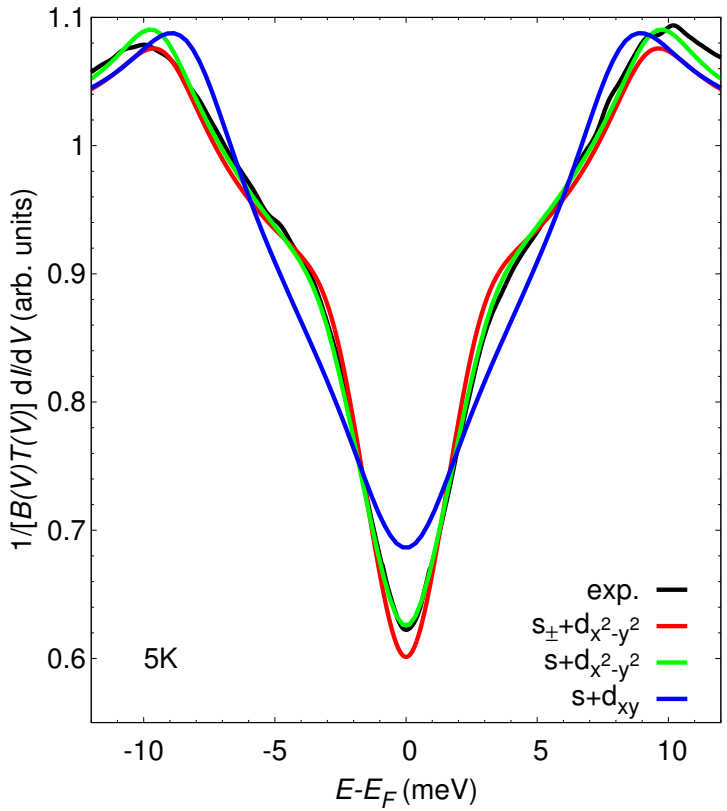




Guterding et al., PRL **116**, 237001 (2016)

Alternative fits for STS data

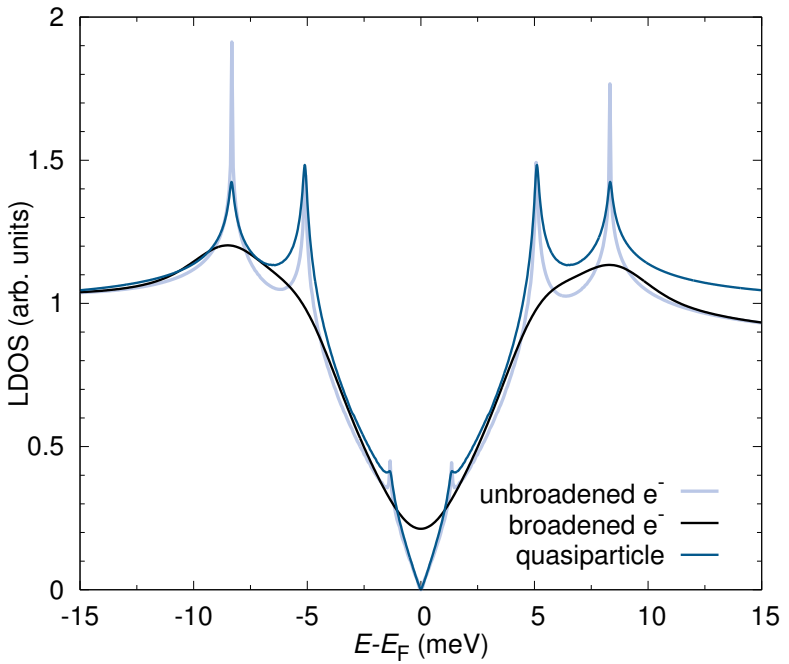
- $s + d_{x^2-y^2}$ and $s_\pm + d_{x^2-y^2}$ equally good
- meaning of plain s-wave component?



Guterding et al., PRL **116**, 237001 (2016)

Calculating the quasiparticle DOS

- use gap calculated from RPA and TB bands or Fermi surface
- full calculation uses bandstructure and tetrahedron method
- quasiparticle calculation uses Fermi surface only
- excellent agreement in relevant energy window



Guterding et al., PRL **116**, 237001 (2016)