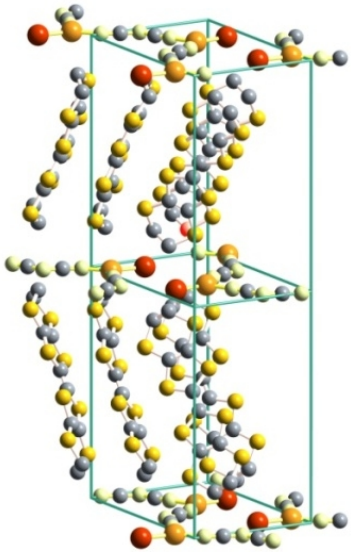
Correlation effects in organic charge-transfer salts: A combined *ab-initio* and many-body investigation



$(BEDT\text{-}TTF)_2X$

Roser Valentí
Institut für Theoretische Physik

GOETHE UNIVERSITÄT FRANKFURT AM MAIN

Exotic Phases in Frustrated Magnets, KITP October 8th 2012

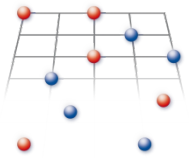
Collaborators

Theory: **Kateryna Foyevtsova, Johannes Ferber, Anthony Jacko and Harald Jeschke** Univ. Frankfurt

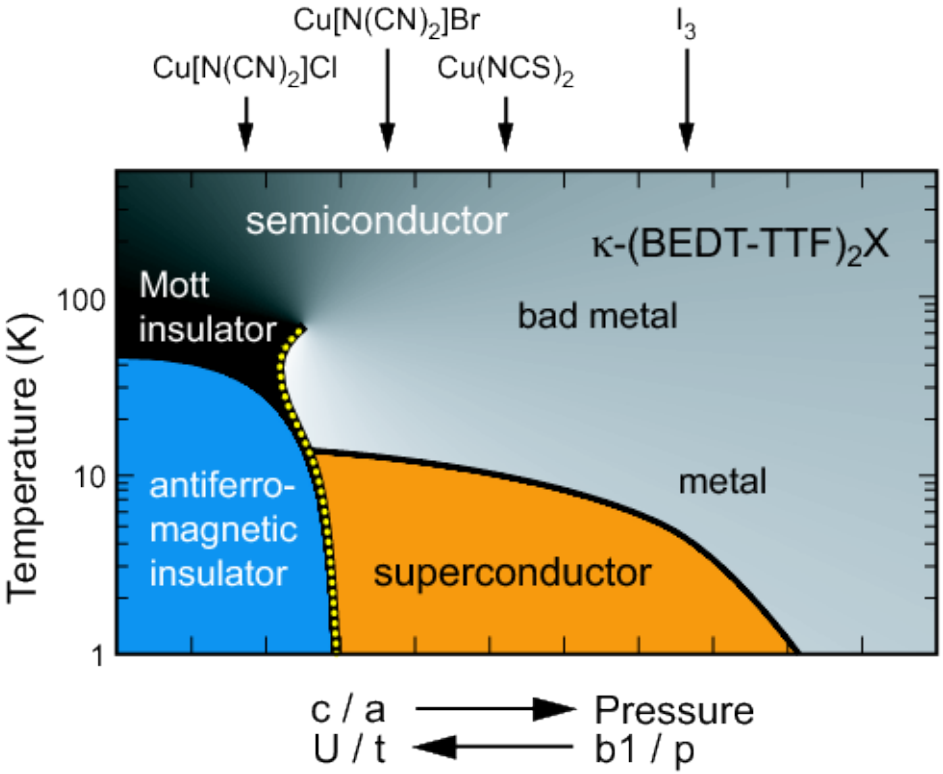
Experiment: **Rudra Manna**, **Mariano de Souza, Michael Lang** Univ. Frankfurt

John Schlueter Argonne Nat. Lab. IL, USA

Financial support: German Science Foundation DFG
SFB/TR 49, SPP1458

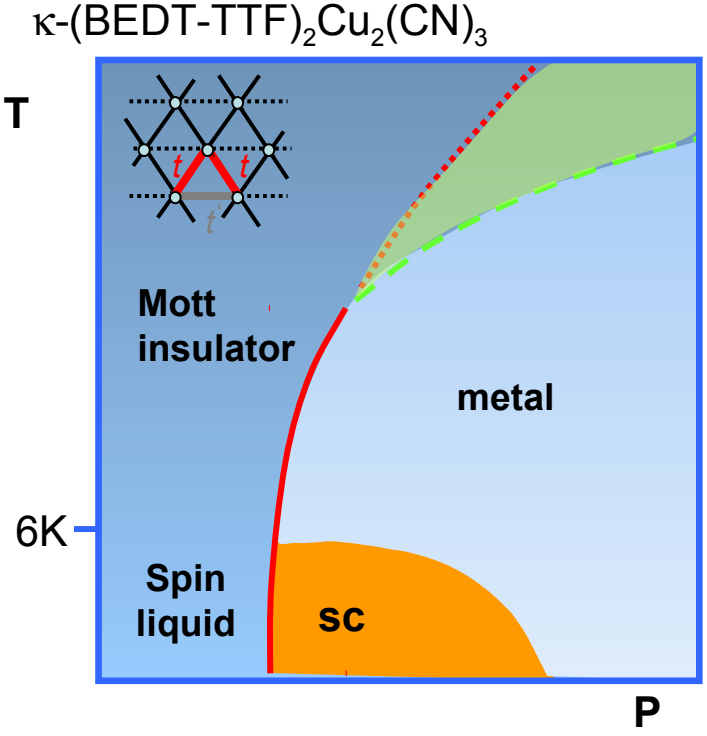


κ-(BEDT-TTF)$_2$X



Faltermeier *et al*. PRB **76**, 165113 (2007)

Dumm *et al*. PRB **79**, 195106 (2009)



Shimizu et al.PRL **91,** 107001 (2003)

S. Yamashita et al. Nat. Phys.**4,** 459 (2008)

M. Yamashita et al. Nat. Phys.**5,** 44 (2008)

Manna et al. PRL **104,** 016403 (2010)

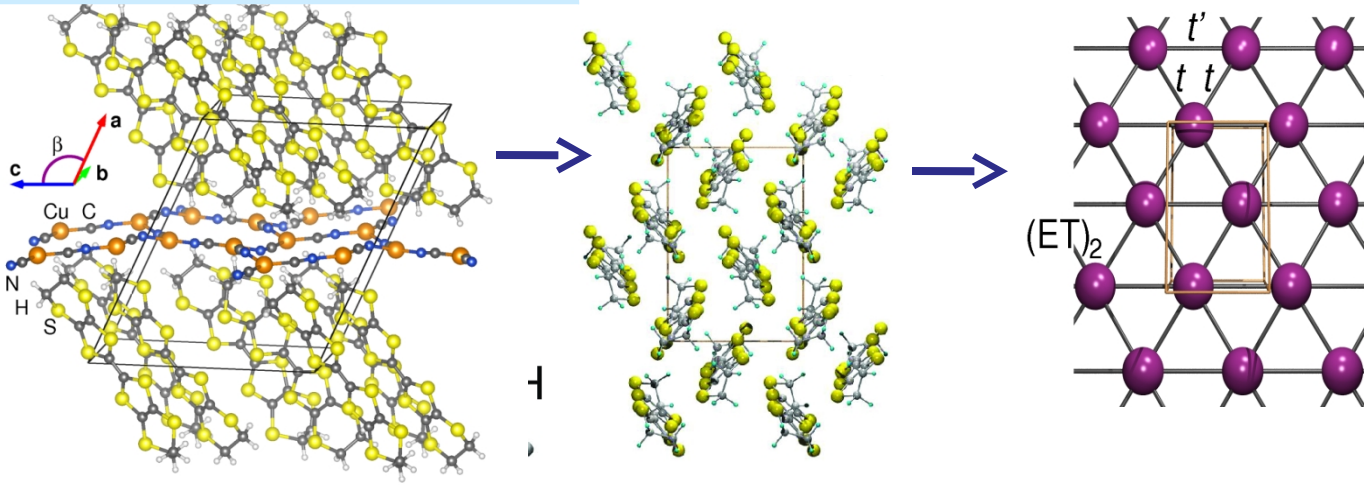
Pratt et al. Nature **472,** 612 (2011)

Spin liquid candidate I

Microscopic description of organic CT salts

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

S=1/2 triangular lattices



1 hole/dimer

$$H = \sum_{i,j\sigma} t_{ij} [c_i^{+} c_j + c_j^{+} c_i] + U \sum n_{i\uparrow} n_{i\downarrow}$$

Microscopic description of organic CT salts

κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

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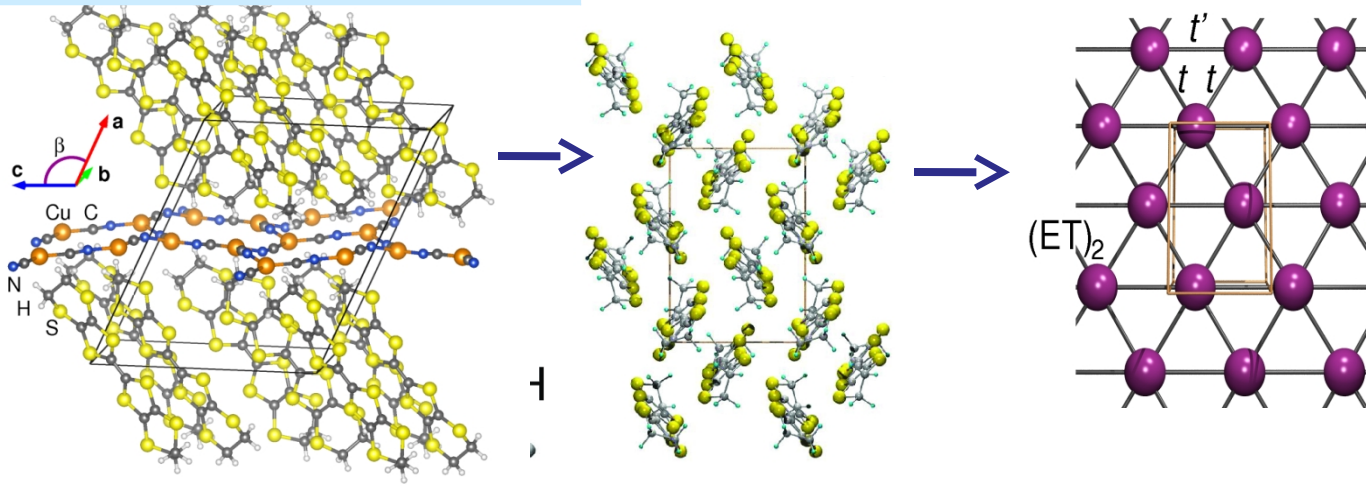


1 hole/dimer

$$H = \sum_{i,j\sigma} t_{ij} [c_i^+ c_j + c_j^+ c_i] + U \sum n_{i\uparrow} n_{i\downarrow}$$

- t_{ij}, U, V ?
- Effects of T and pressure?

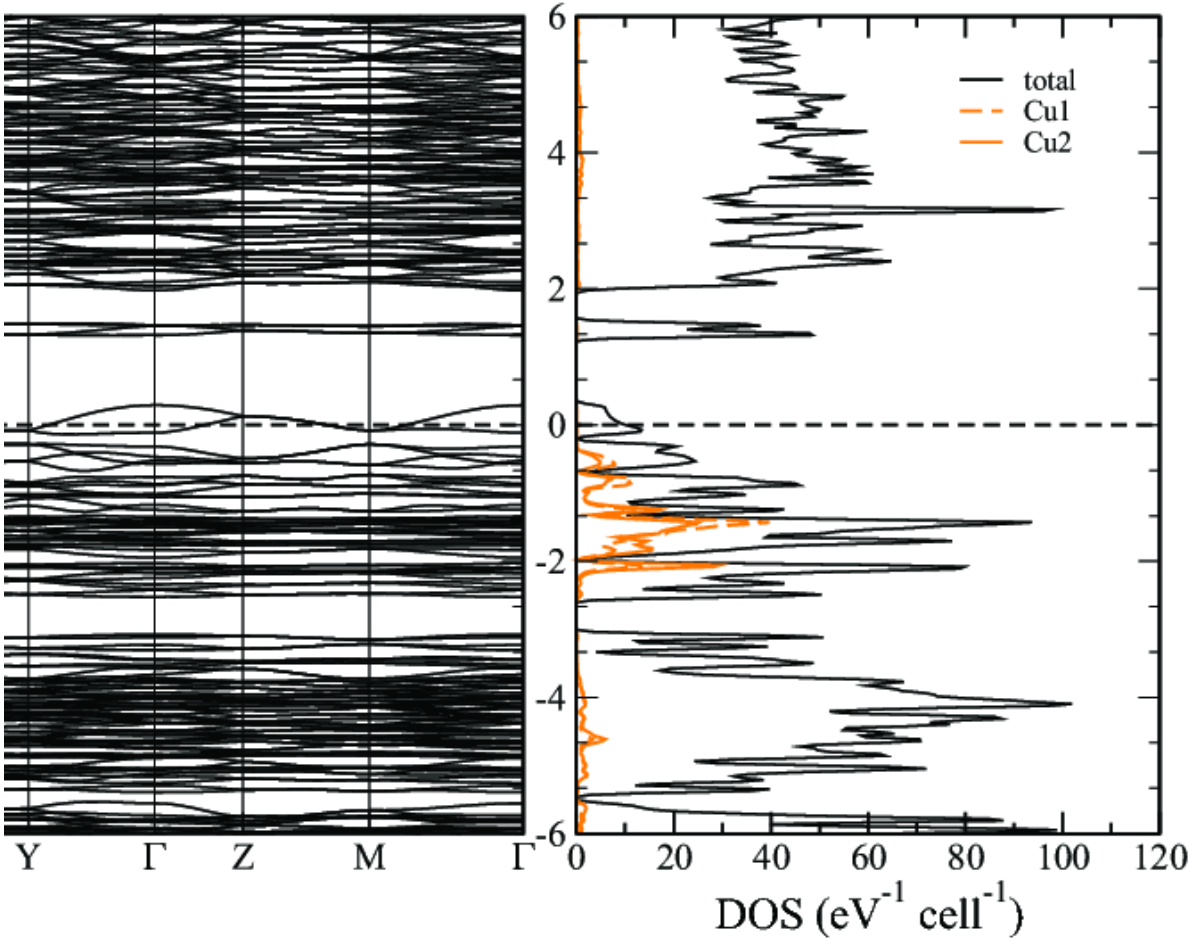
- **ab initio Density Functional Theory (DFT) + downfolding**
- **combine material specific input from DFT + nonperturbative many-body treatment of correlations DFT+DMFT**

spectral properties, optical conductivity

Ab initio DFT for κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

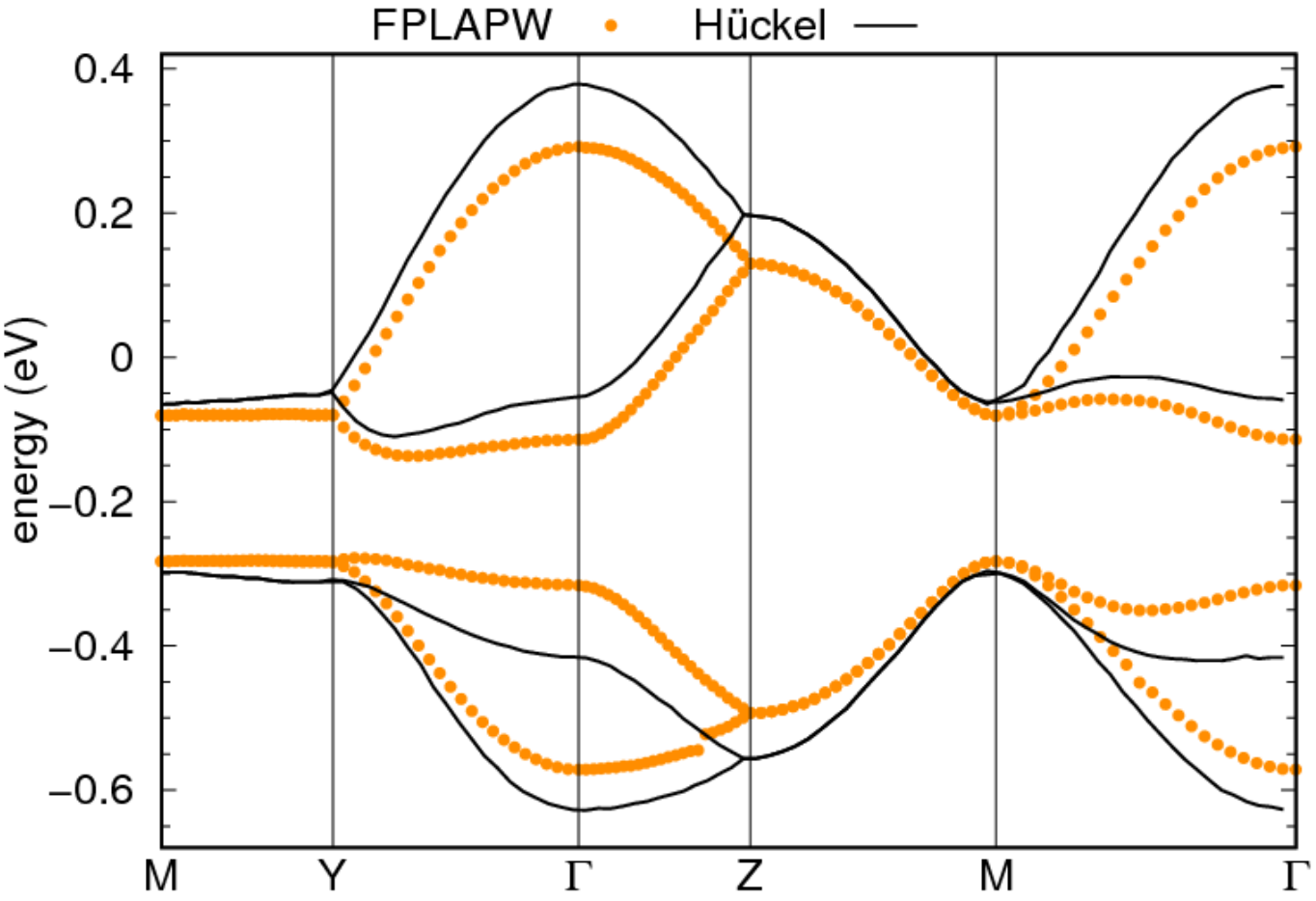
Kandpal, Opahle, Zhang, Jeschke, Valenti PRL 103, 067007 (2009)

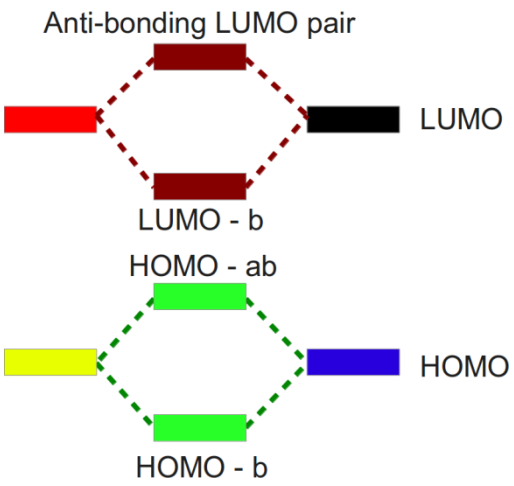
- relaxation atomic positions CP-PAW
- electronic structure basis: FPLO, FPLAPW (Wien2k) Exchange Functional: GGA, LDA



Comparison bandstructures for κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

Kandpal, Opahle, Zhang, Jeschke, Valenti PRL 103, 067007 (2009)

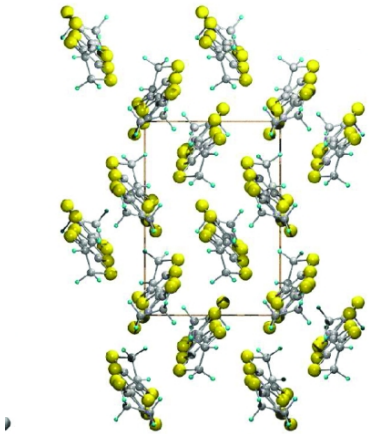




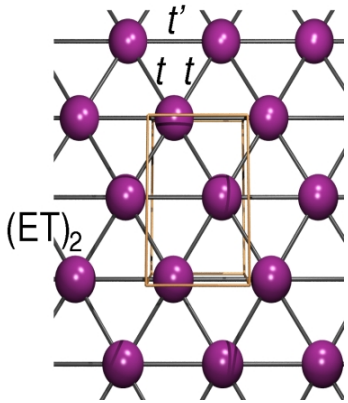
Effective hamiltonian for κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

$$H = \sum_{i,j\sigma} t_{ij} [c_i^{+} c_j + c_j^{+} c_i] + U \sum n_{i\uparrow} n_{i\downarrow}$$

Tight-binding- downfolding approach on the DFT bandstructure:



molecule picture



dimer picture

Hückel: t'/t = 1.06 DFT: t'/t = 0.83 +/- 0.08

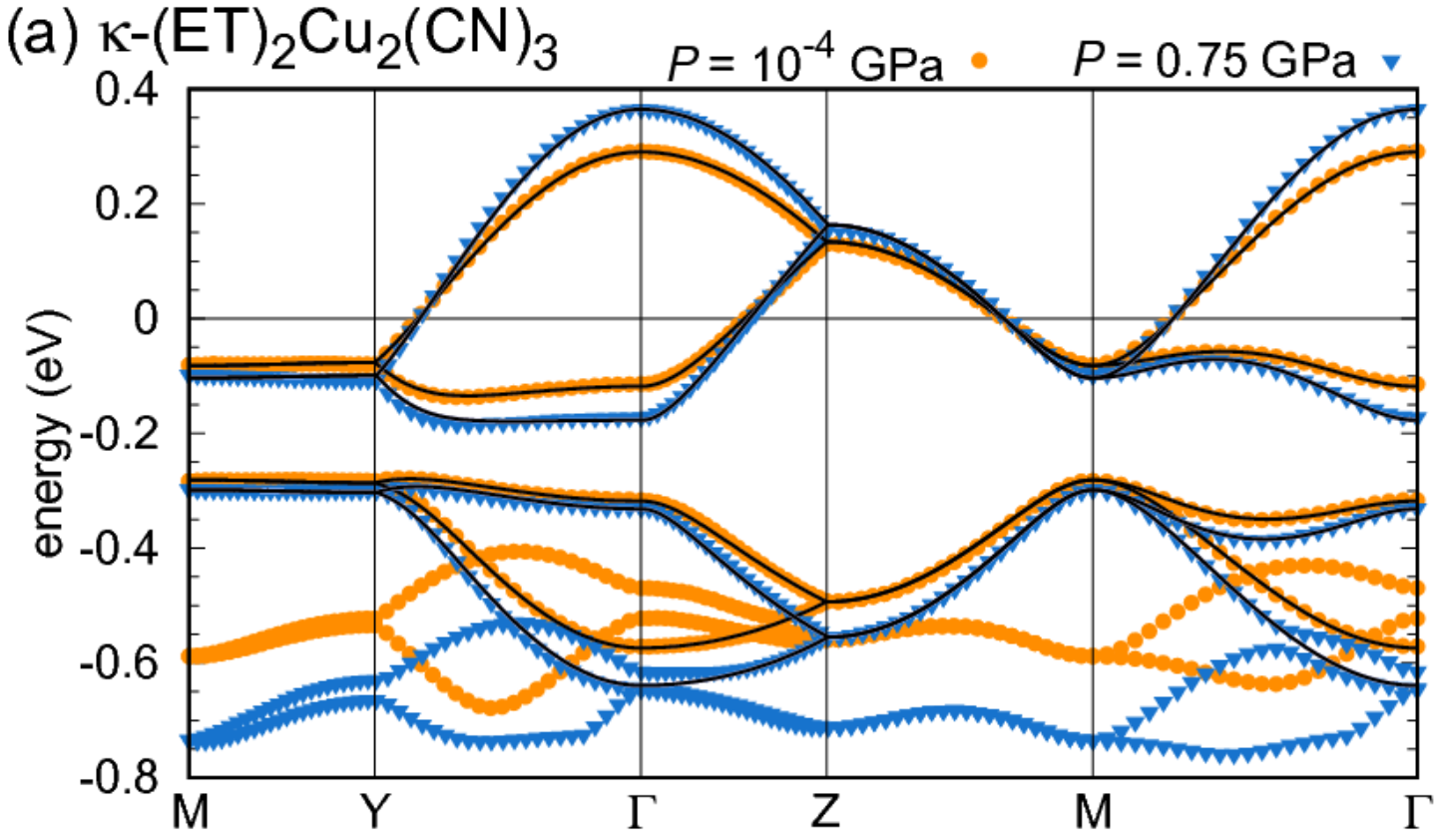
Kandpal et al. PRL (2009)

Nakamura et al. JPSJ (2009)

Revision of model parameters!

hydrostatic pressure on κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

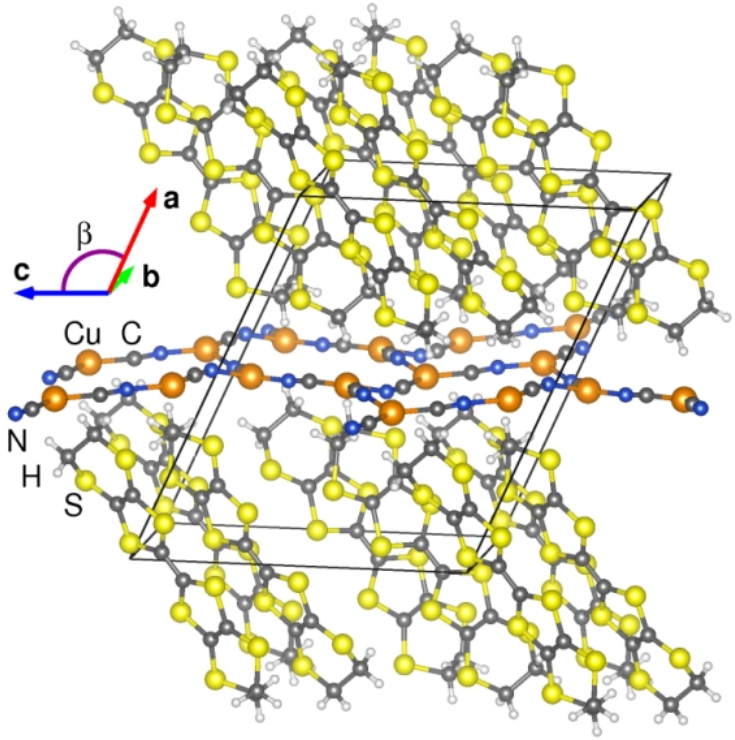
- high-pressure structure obtained with CP-PAW
- electronic structure FPLAPW (Wien2k) Exchange: GGA

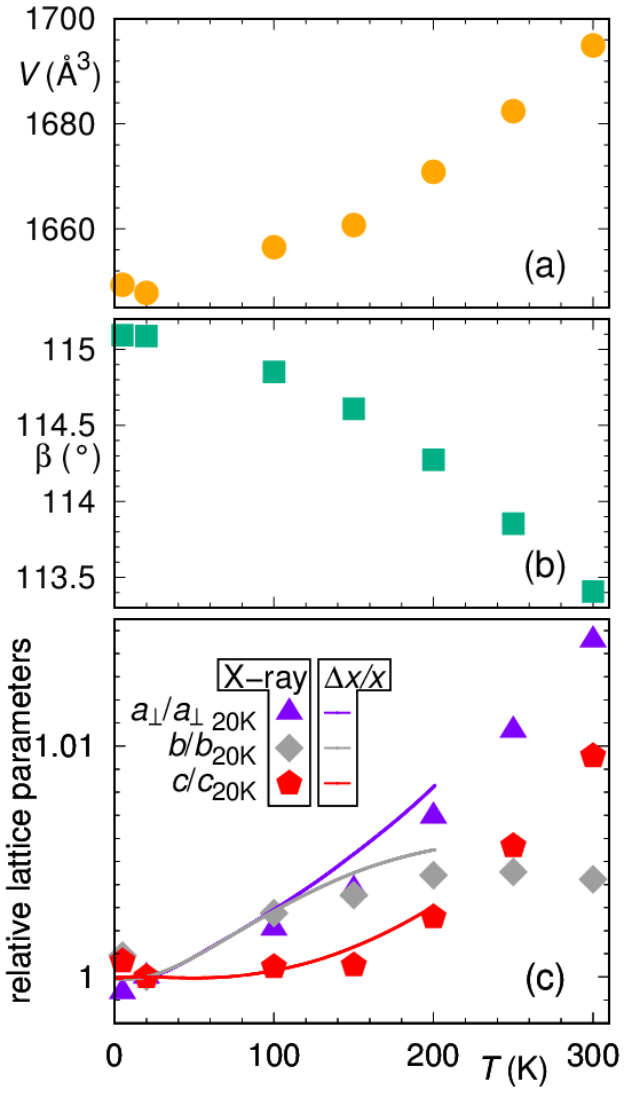


pressure decreases t‘/t ratio → less frustration!!

Temperature dependence of structural parameters in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

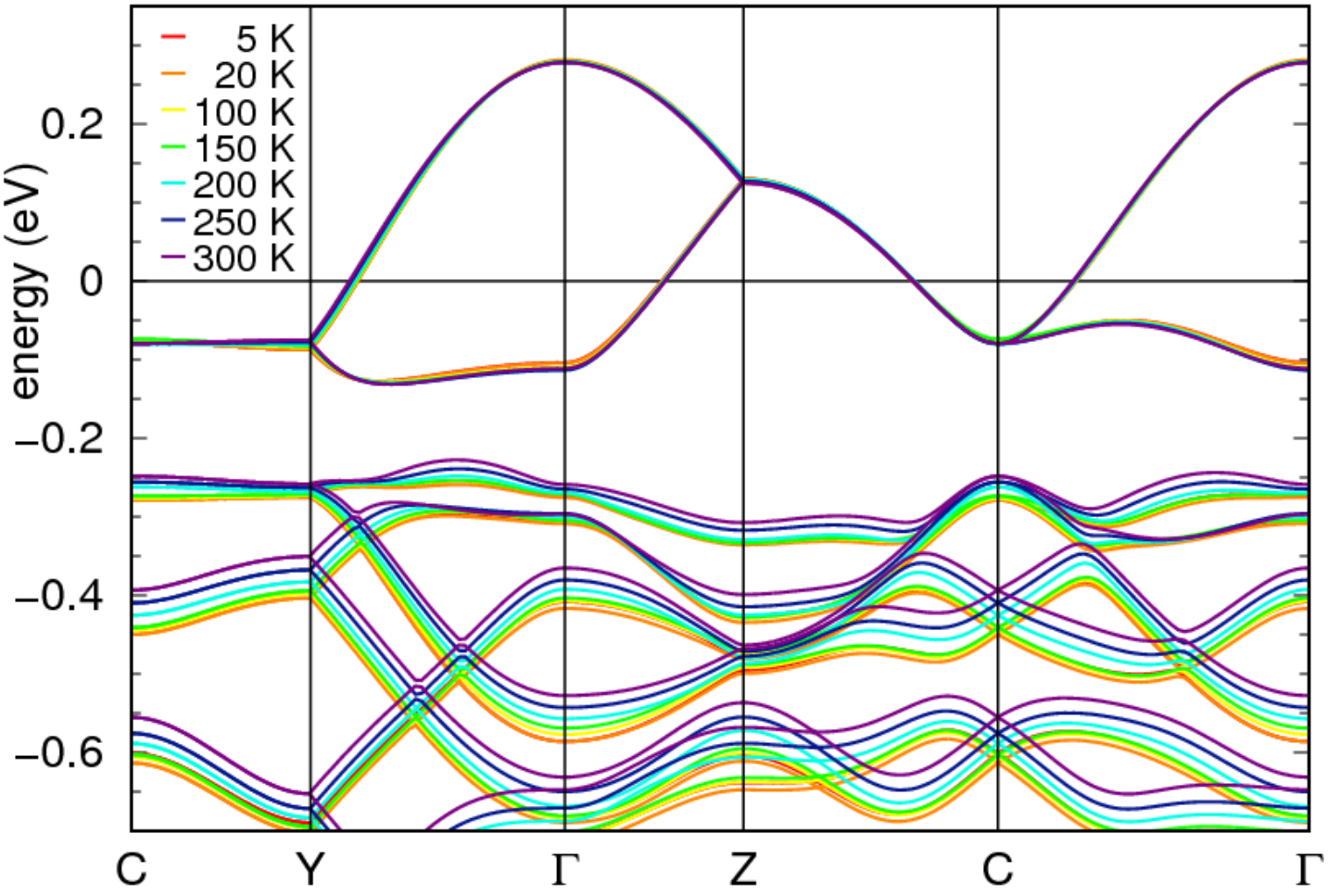
Jeschke, Souza, Valenti,
Manna, Lang, Schlueter PRB 85, 035125 (2012)



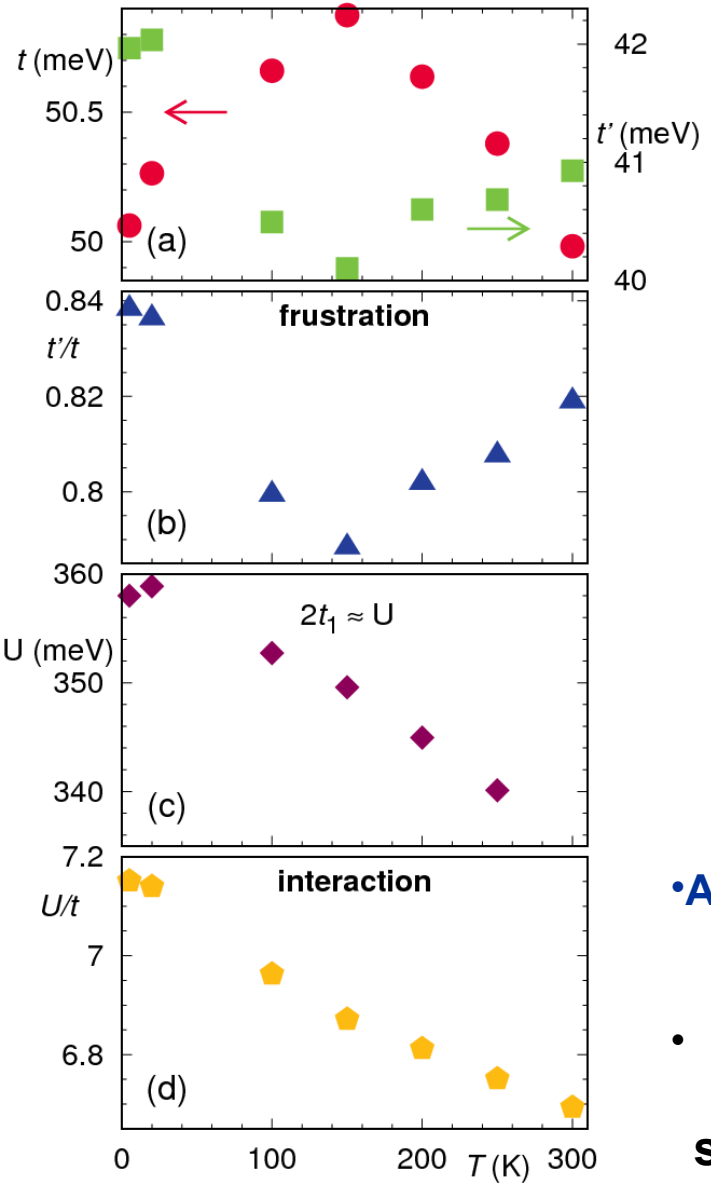


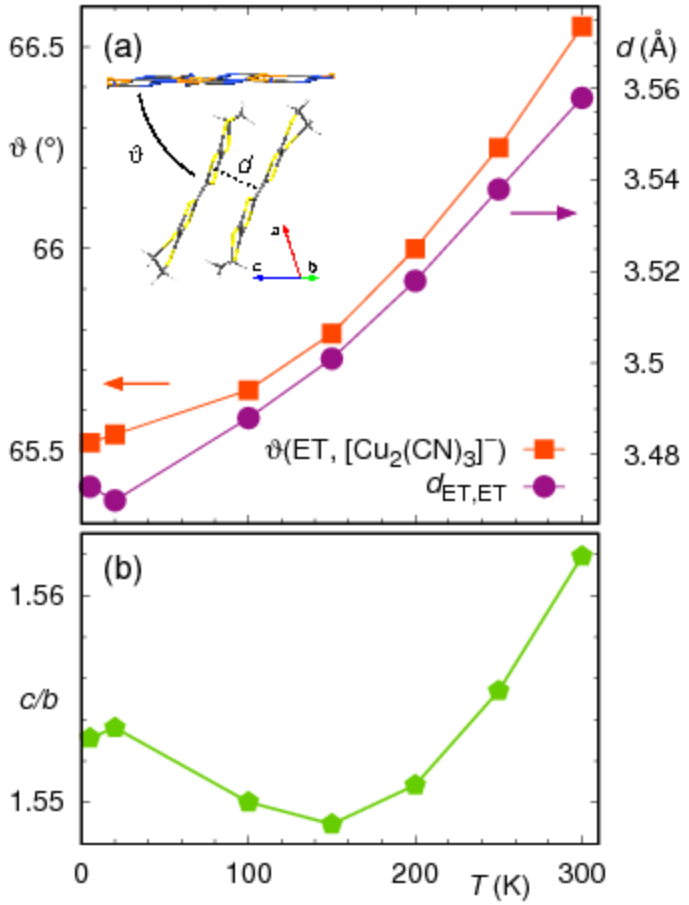
Temperature dependence of electronic properties in κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

Jeschke, Souza, Valenti,
Manna, Lang, Schlueter PRB 85, 035125 (2012)



Temperature dependence of electronic properties in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$





- **Anomaly at 150K**:
  Possibly related to the ordering of the ethylene groups

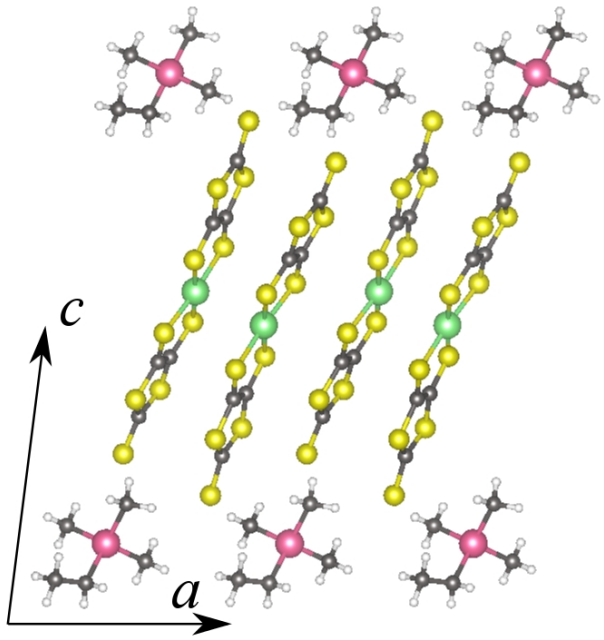
- **no** indication of **structural phase transition at 6K**

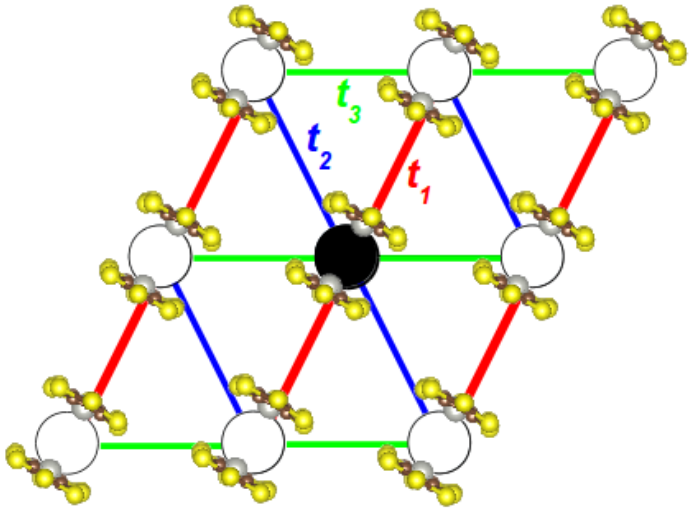
subtle dependence of model parameters on T

Ab initio DFT for $Me_3EtSb[Pd(dmit)_2]_2$

Spin liquid candidate II

Itou, Oyamada, Maegawa, Tamura, Kato
PRB 77, 104413 (2008)





1 electron/dimer

Ab initio DFT for $Me_3EtSb[Pd(dmit)_2]_2$

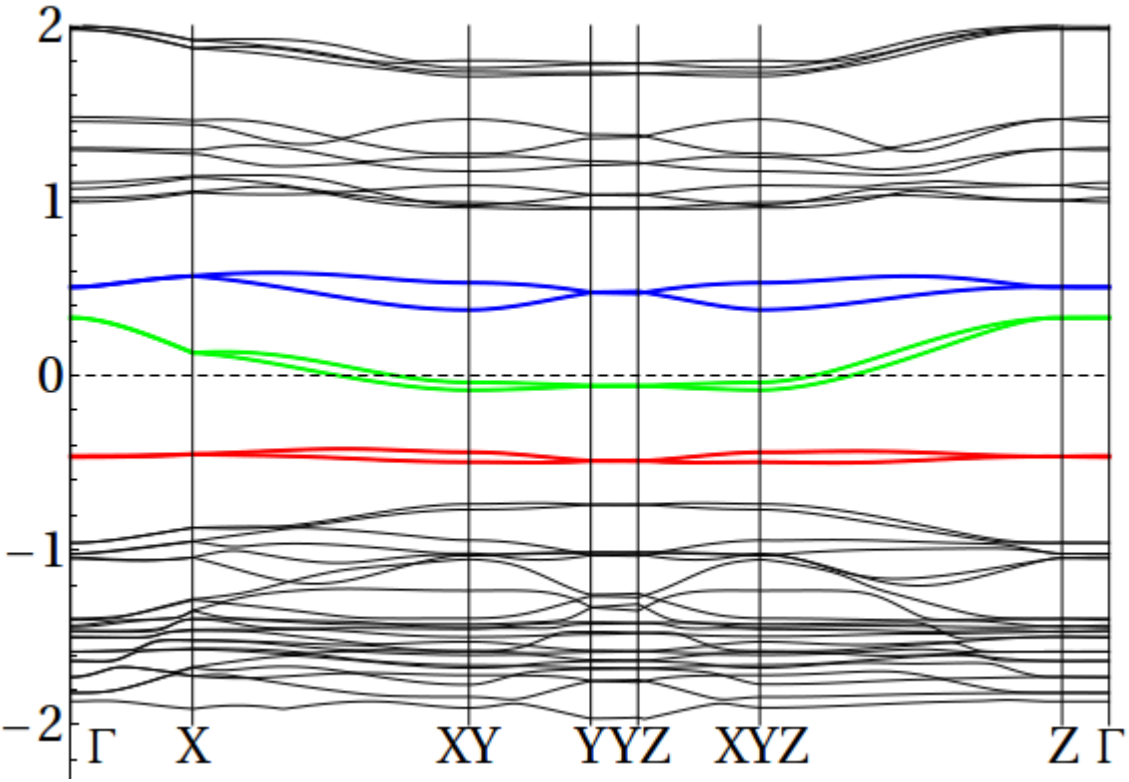
Spin liquid candidate II

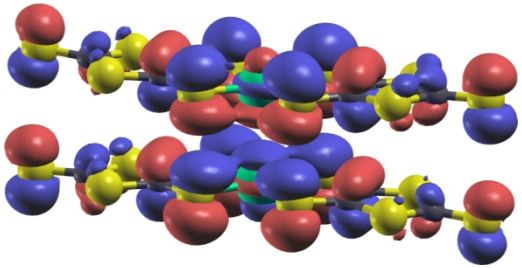
- electronic structure basis: FPLO
  Exchange Functional GGA

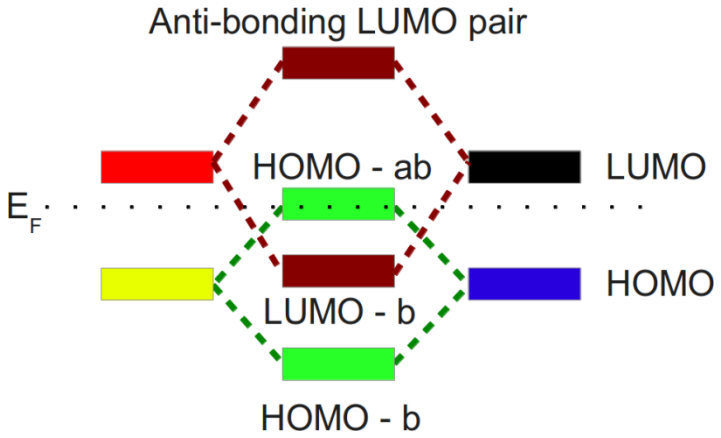
Scriven, Powell PRL 109, 097206 (2012)

Nakamura, Yoshimoto, Imada arXiv:1208.3954

Jacko, Jeschke, Valenti in preparation (2012)







Ab initio DFT for $Me_3EtSb[Pd(dmit)_2]_2$

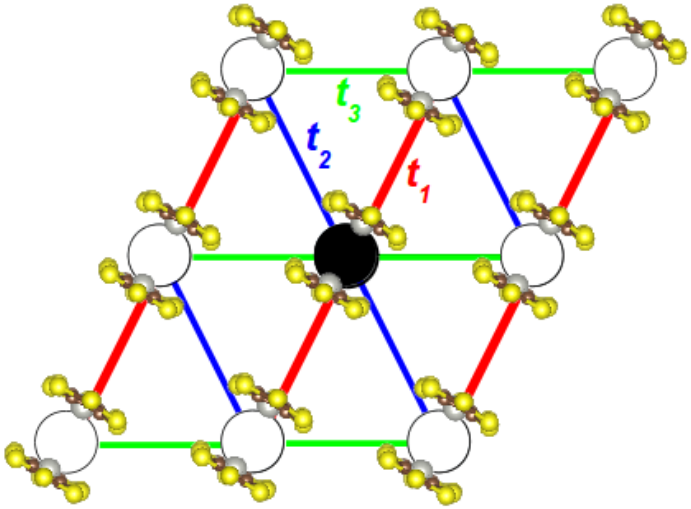
Spin liquid candidate II

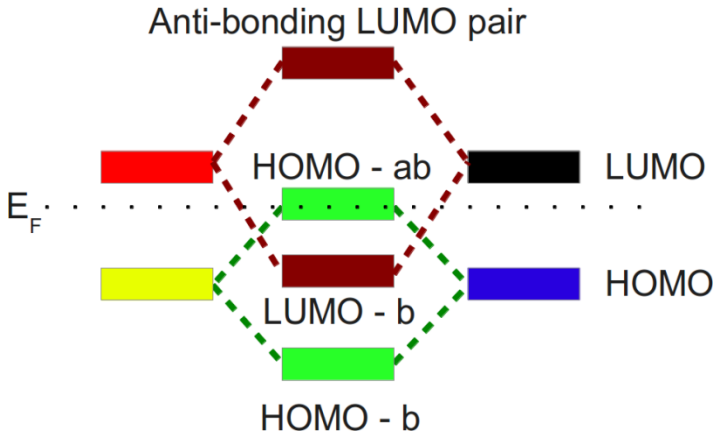
Scriven, Powell PRL 109, 097206 (2012)

Nakamura, Yoshimoto, Imada arXiv:1208.3954

Jacko, Jeschke, Valenti in preparation (2012)

Bandstructure downfolding





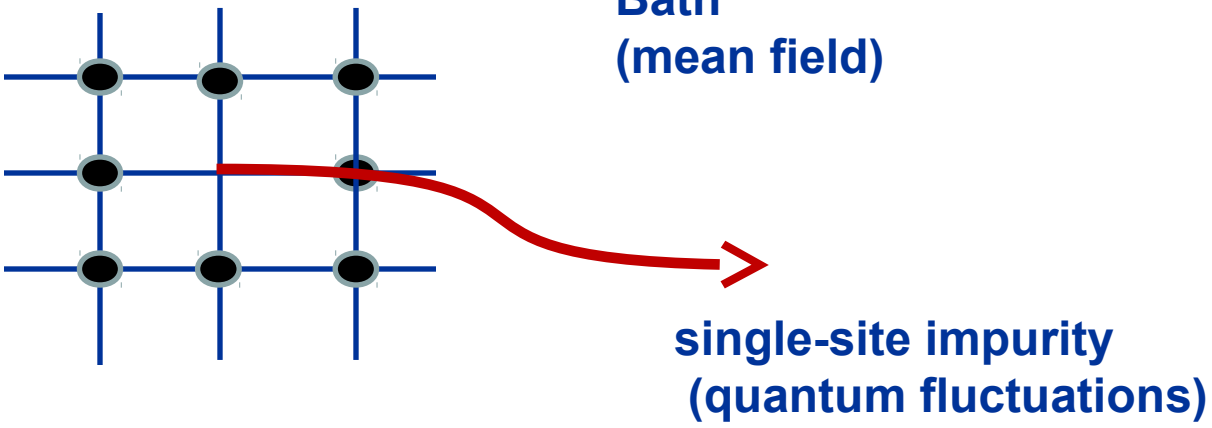
(meV)	μ	t_1	t_2	t_3
LUMO-b	−454	0.7	−14.6	8.5
HOMO-ab	32.3	56.5	39.8	46.9
LUMO-ab	515	−24.4	13.4	23

Anisotropic triangular lattice

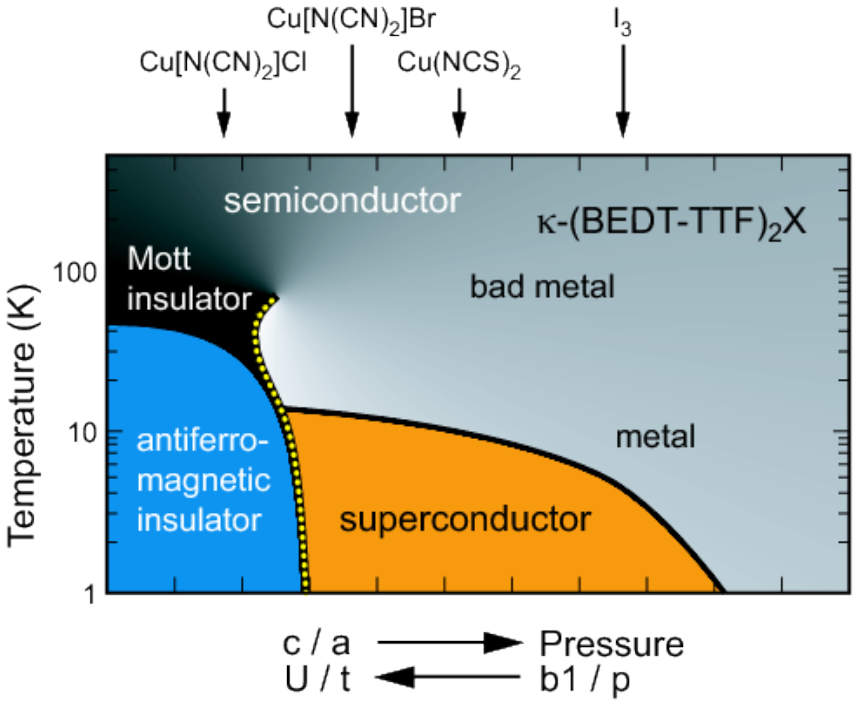
Realistic description of correlation effects

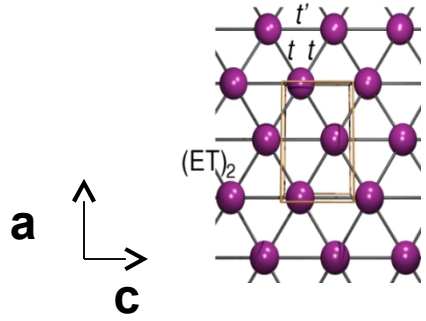
LDA + DMFT for organic molecular crystals

We combine the material specific input from **DFT** with a non-perturbative many-body treatment of correlations as implemented in the **dynamical mean field theory**

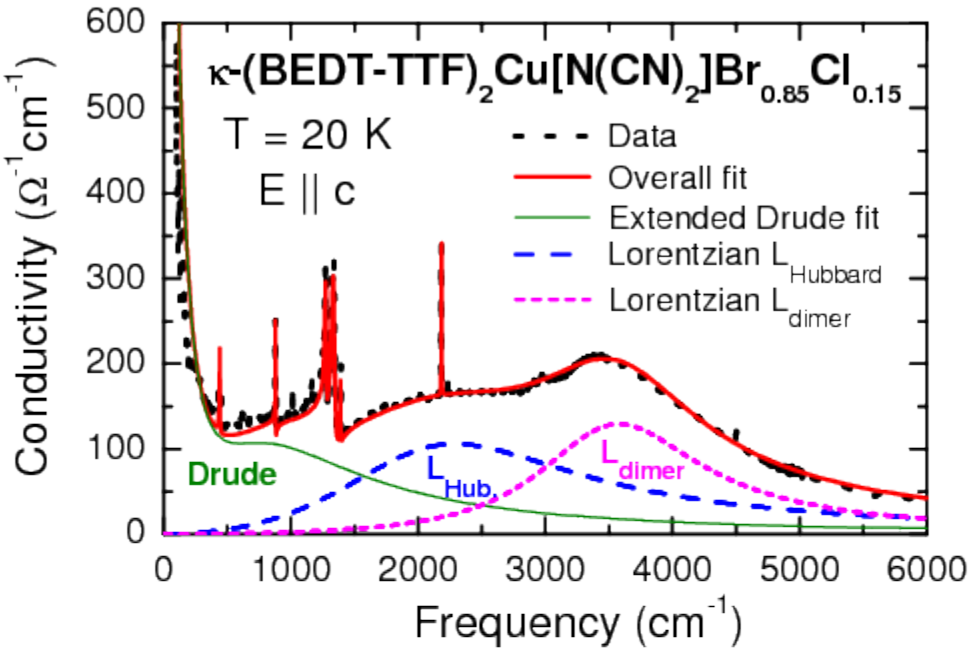


correlations in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$



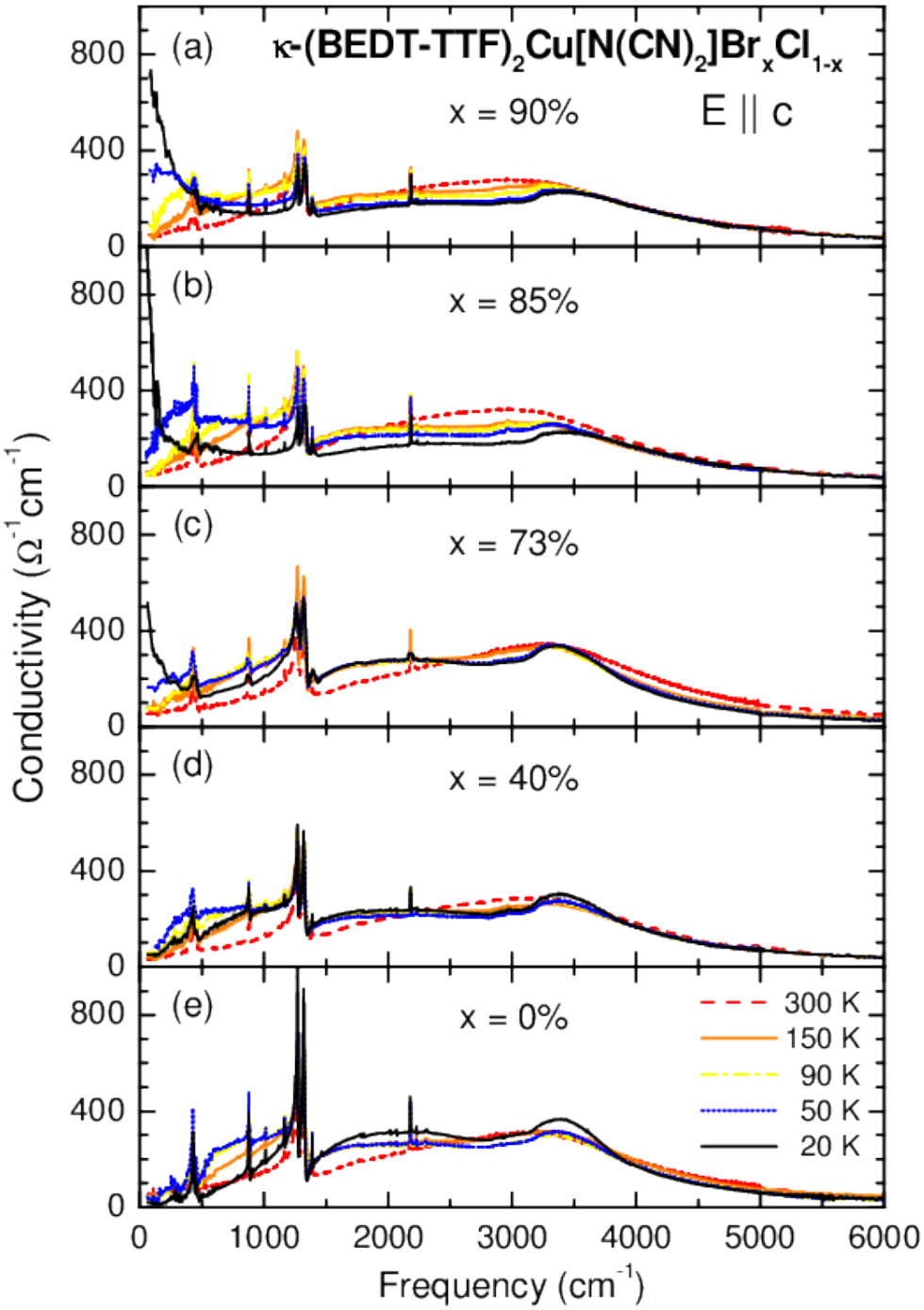


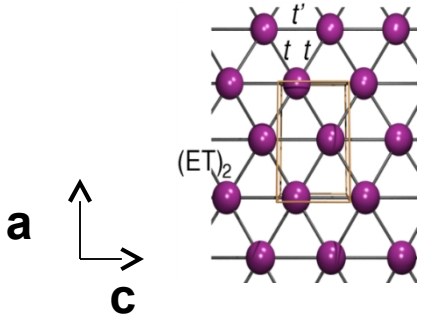
Optical conductivity



Faltermeier *et al*. PRB **76**, 165113 (2007)

Dumm *et al*. PRB **79**, 195106 (2009)





Optical conductivity

Faltermeier *et al*. PRB **76**, 165113 (2007)

Dumm *et al*. PRB **79**, 195106 (2009)

LDA+DMFT for κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br_xCl_{1-x}$ X=0

LDA+DMFT:

-electronic structure calculations within LDA, LAPW basis (Wien2K)

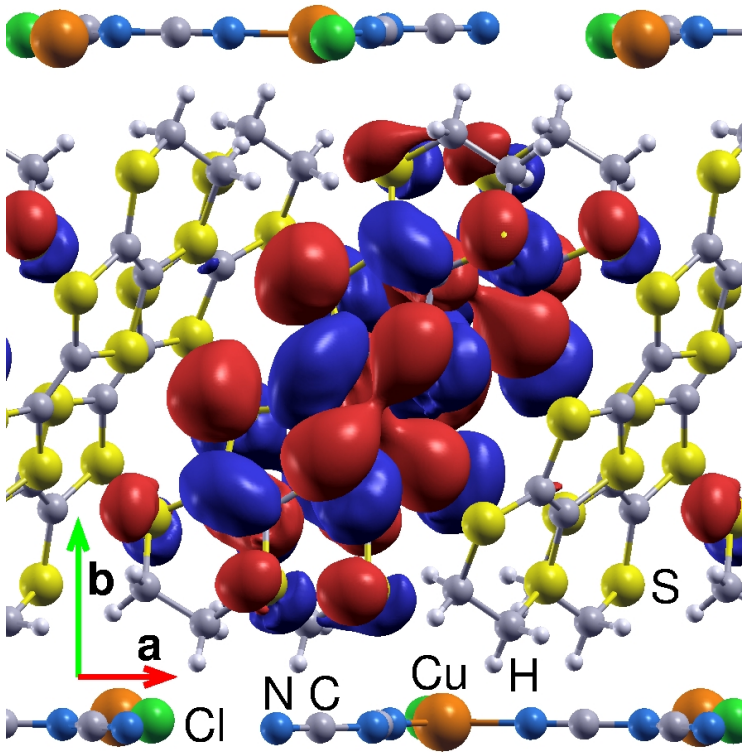
-construction of localized Wannier-like functions

→ **new scheme to construct molecular Wannier functions!**

- DMFT self-consistency / impurity solver: CT QMC

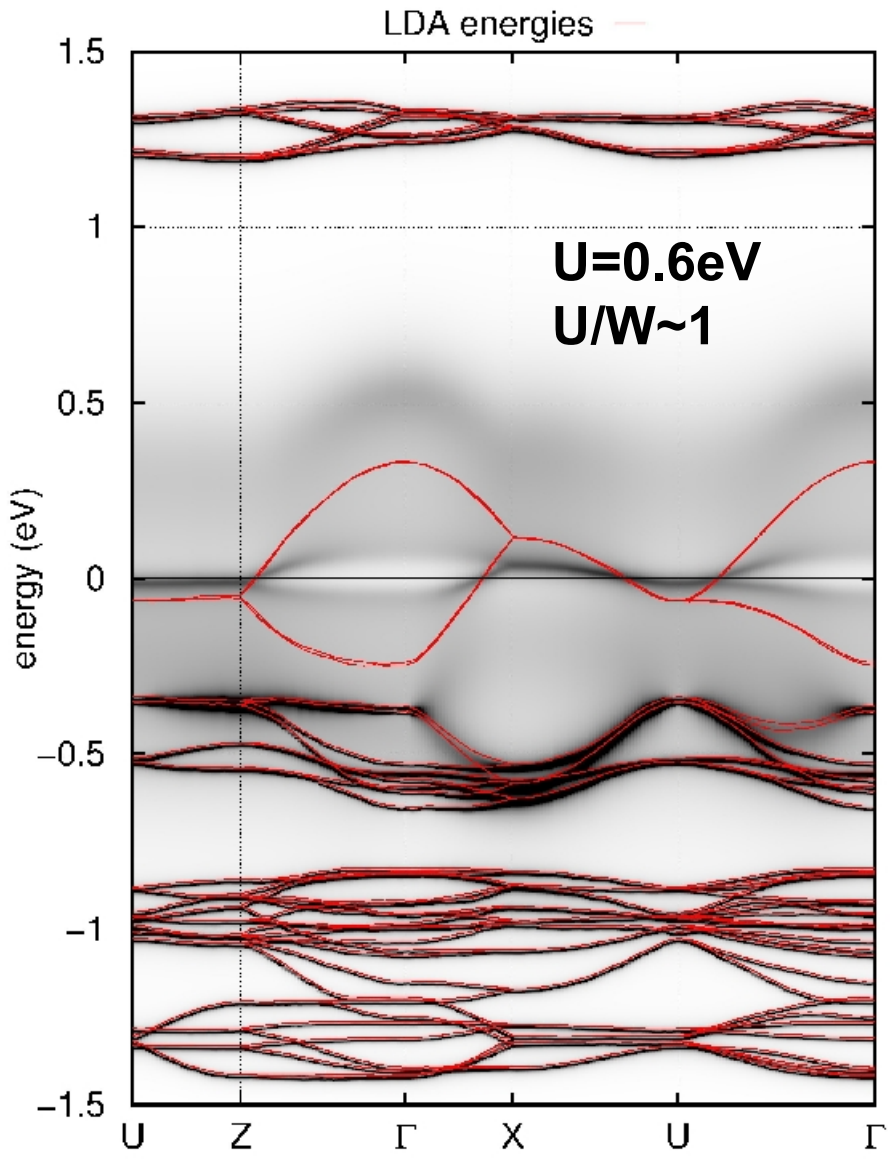
Hubbard parameters **U= 0.5-0.85 eV T=300K**

HOMO Wannier function For the $(ET)_2$ dimer

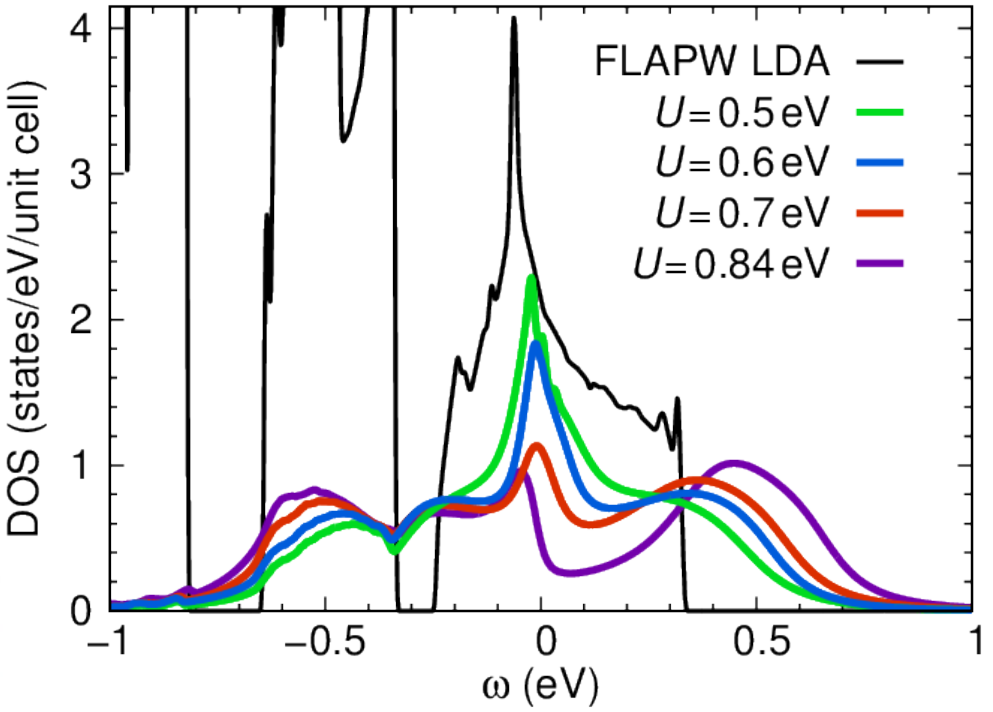


LDA+DMFT for κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br_xCl_{1-x}$ X=0

LDA vs. LDA+DMFT bandstructure



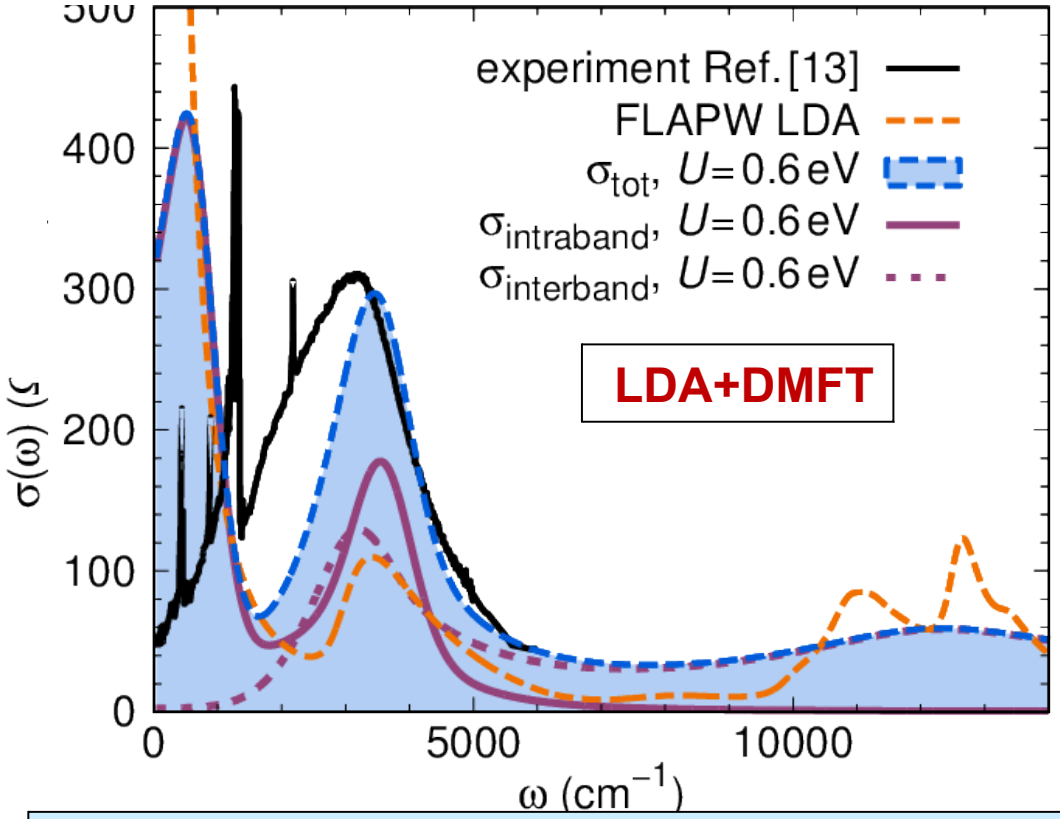
Density of states

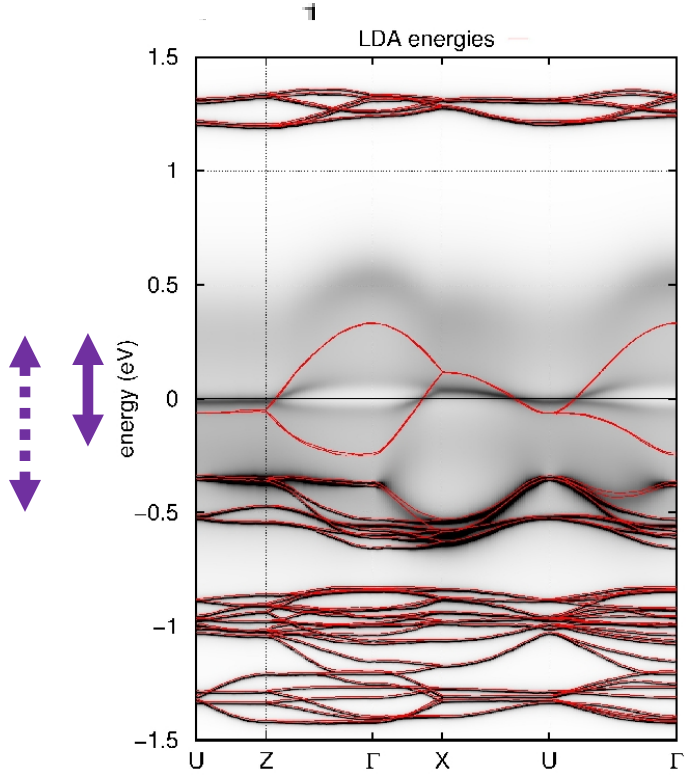


correlations are important!

Optical conductivity for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$ X=0

$$\sigma_{zz}(\tilde{\nu}_n) = \frac{\epsilon^2}{4\pi\epsilon_0 V \tilde{\nu}_n \beta} \sum_{\nu\nu'\nu''\nu''',\mathbf{k},\sigma} v_{z,\mathbf{k}}^{\nu\nu'} v_{z,\mathbf{k}}^{\nu''\nu'''} \sum_{\omega_n} G_{\mathbf{k}}^{\nu'\nu''}(i\omega_n + i\tilde{\nu}_n) G_{\mathbf{k}}^{\nu'''\nu}(i\omega_n)$$





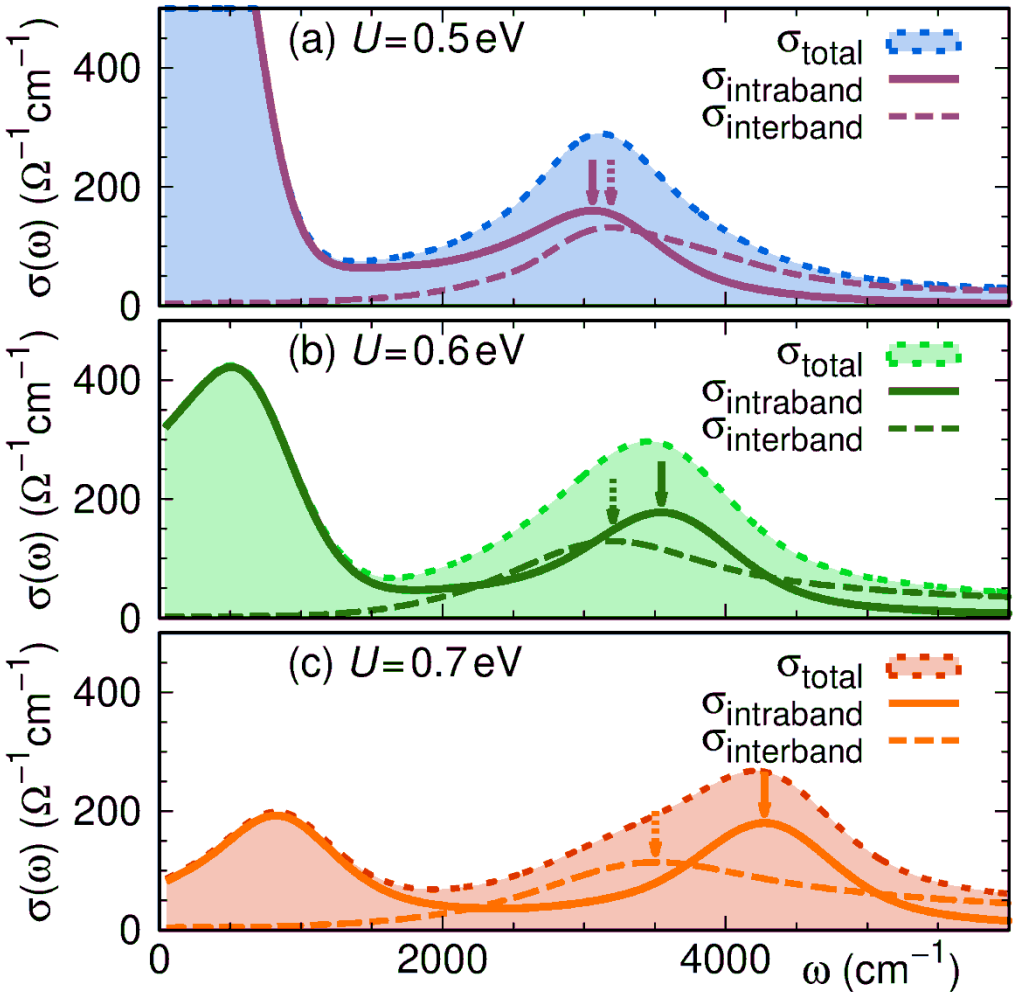
$\sigma_{intraband}$: *inter*dimer transitions **correlation induced**

$\sigma_{interband}$: *intra*dimer transitions + rest

agreement with experiment!

Ferber, Foyevtsova, Jeschke Valenti arXiv: 1209.4466

Optical conductivity for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$ X=0



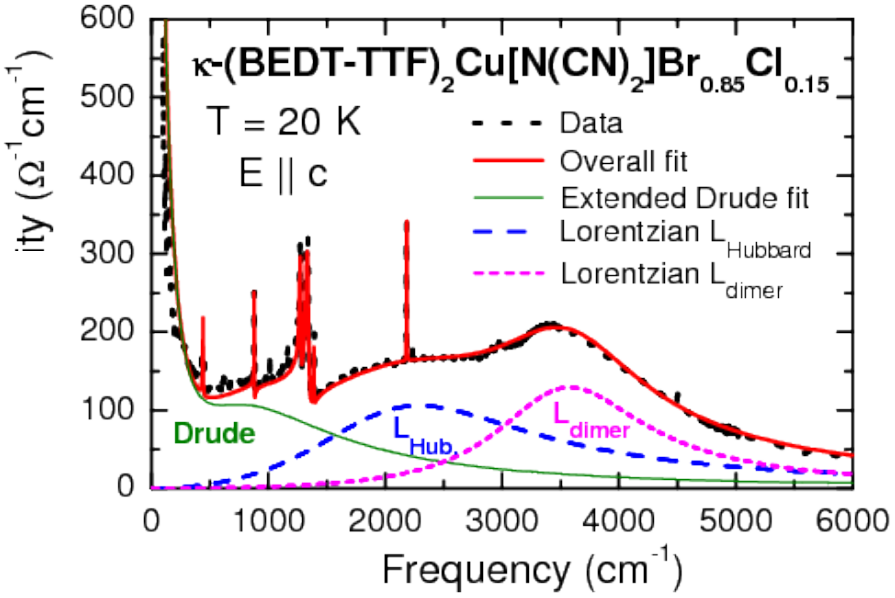
Ab initio-based evidence for the nature of the infrared peaks!!

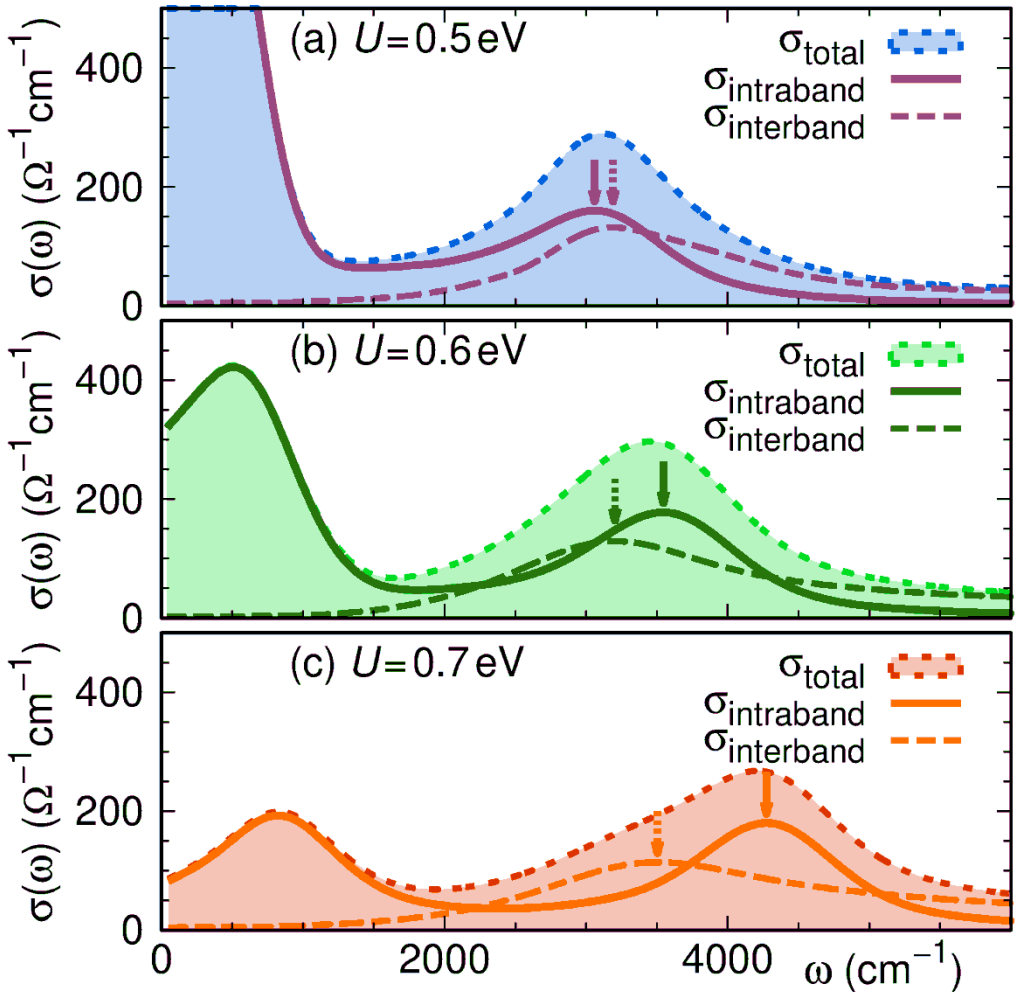
$\sigma_{intraband}$: *inter*dimer transitions **correlation-induced/ scale with U**

$\sigma_{interband}$: *intra*dimer transitions + rest **unaffected by correlations**

Ferber, Foyevtsova, Jeschke Valenti in preparation (2012)

Optical conductivity for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br$_x$Cl$_{1-x}$ X=0





Ab initio-based evidence for the nature of the infrared peaks!!

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Ferber, Foyevtsova, Jeschke Valenti arXiv: 1209:4466

DFT + many-body calculations

→ realistic description of correlated systems : organic triangular lattices

- **Microscopic model for** κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

Hubbard model

- t'/t = 0.83 (degree of frustration)
- t'/t decreases under **P**
- nonmonotonous t'/t under **T** → minimum at 150K

- **Microscopic model for** $Me_3EtSb[Pd(dmit)_2]_2$

- anisotropic triangular lattice

- **LDA+DMFT for** κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$

- **new scheme for constructing Wannier molecular functions**
- Hump **in optical conductivity** → correlation effects!
- extension to other molecular crystals

Car-Parrinello Method

DFT + Molecular Dynamics

Car, Parrinello PRL (1985)

$$L = \frac{1}{2}\sum_i M\dot{R}_i^2 + \sum_n f_n \left\langle \dot{\Psi}_n | M_\Psi | \dot{\Psi} \right\rangle - E(R,\Psi) + \sum_{n,m}(\langle \Psi_n | \Psi_n \rangle - \delta_{n,m})\lambda_{n,m}$$

- **Parrinello-Rahman Lagrangian:**

Parrinello , Rahman JAP (1981)

$$-p\Omega$$

- **basis: Projected Augmented Wave**

P. Blöchl

- functional: LDA, GGA, LDA+U, Hybrid

CP-PAW

Description of phase transitions