Realistic many-body calculations with spatial correlations and for systems with molecular orbitals

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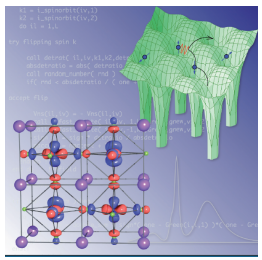
GOETHE UNIVERSITÄT FRANKFURT AM MAIN



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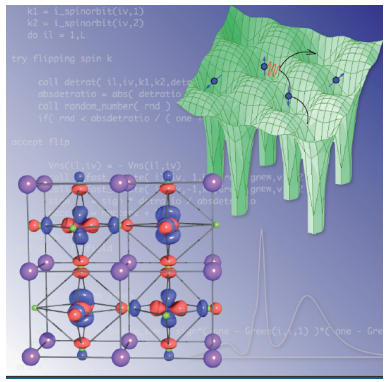
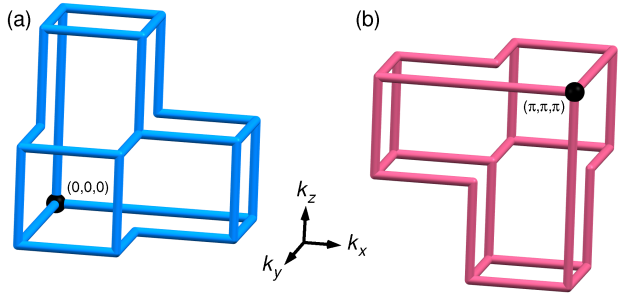
- DFG TR 49 "Condensed Matter Systems with Variable Many-Body Interactions"

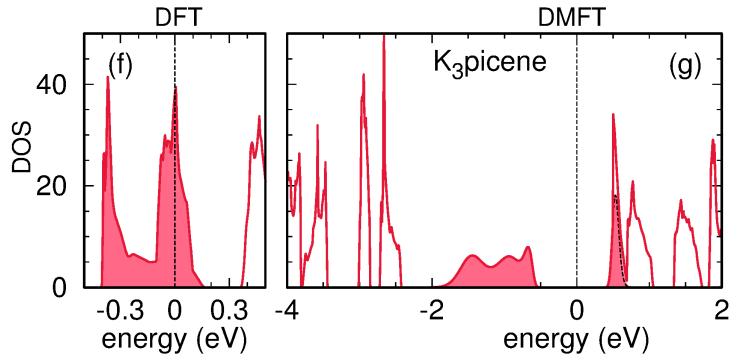


Topics

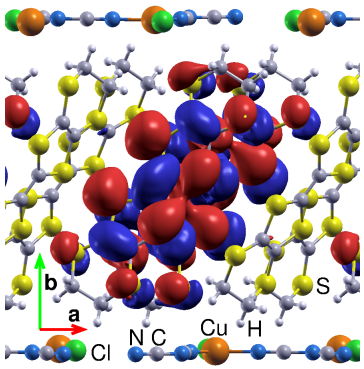
Introducing spatial correlations into realistic DMFT studies



Potassium doped picene: metallic or not?



Projectors for molecular orbitals: LDA+DMFT description of charge transfer salts



Introducing spatial correlations into realistic DMFT studies

Wanted: Momentum dependent selfenergy in realistic manybody calculations

- LDA+single site DMFT derives k dependence only from DFT; $\Sigma(\mathbf{k}, \omega) \equiv \Sigma(\omega)$
- Many systems with dimension < 3 show phenomena that are not captured by single site DMFT (cuprates, organic charge transfer salts)

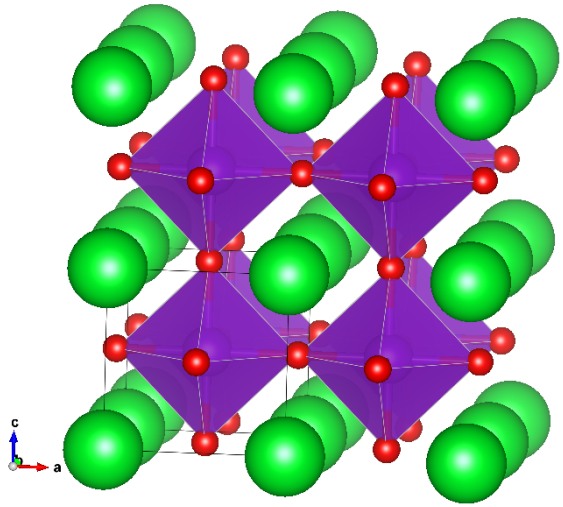
Hope comes from various recent developments:

1. dual fermions (DFT+DF) (Lichtenstein, Katsnelson, Hafermann, ...)
2. variational cluster approach (DFT+VCA) (Aichhorn, ...)
3. DFT+DVA (Held, ...)
4. GW+DMFT (Biermann, Georges, Held, ...)

Here, we try to combine DFT with DCA.

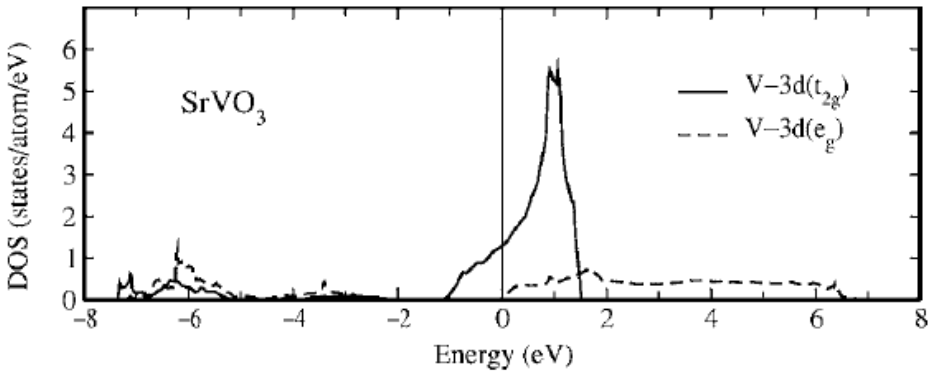
$SrVO_3$ as a test system

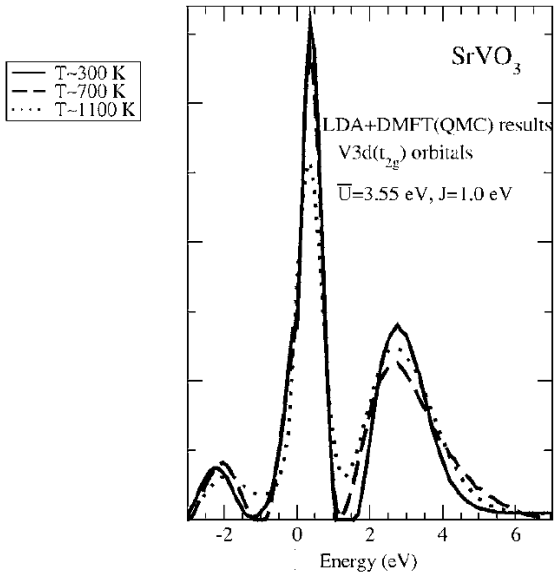
- $SrVO_3$ is a cubic perovskite



- V t_{2g} with $1/6$ filling
- correlated metal studied many times with LDA+DMFT
- intensively investigated experimentally; latest addition Aizaki *et al.*, PRL **109**, 056401 (2012).

Typical DFT, LDA+DMFT results:





Nekrasov *et al.*, Phys. Rev. B **72**, 155106 (2005).

LDA+DCA Method

Projective Wannier functions within FLAPW (Aichhorn *et al.*, PRB **80**, 085101 (2009)):

$$|\chi^{\alpha,\sigma}_{\mathbf{k},m}\rangle = \sum_{\nu\in W} \langle\psi^{\sigma}_{\mathbf{k},\nu}|\chi^{\alpha,\sigma}_{m}\rangle|\psi^{\sigma}_{\mathbf{k},\nu}\rangle,$$

with atom α, band ν, spin σ, orbital m, Bloch eigenfunction $|\psi^{\sigma}_{\mathbf{k},\nu}\rangle$, correlated orbital $|\chi^{\alpha,\sigma}_{m}\rangle = |u^{\alpha,\sigma}_{l}(E_l)Y^{l}_{m}\rangle$, linearization energies E_l, radial wave function $u^{\alpha,\sigma}_{l}$, and spherical harmonic function Y^{l}_{m}. Orthonormalized projectors:

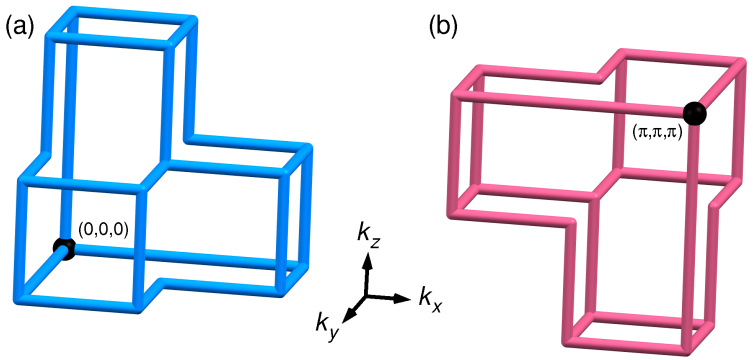
$$P^{\alpha,\sigma}_{m,\nu}(\mathbf{k}) = \sum_{\alpha',m'} \langle u^{\alpha',\sigma}_{l}(E_l)Y^{l}_{m'}|\psi^{\sigma}_{\mathbf{k},\nu}\rangle [O(\mathbf{k},\sigma)^{-1/2}]^{\alpha,\alpha'}_{m,m'}$$

LDA+DCA lattice Greens function (cluster momenta $\mathbf{K}$)

$$G^{\sigma}_{\nu,\nu'}(\mathbf{K}+\tilde{\mathbf{k}}, i\omega_n) = \left[i\omega_n+\mu-\epsilon^{\sigma}_{\mathbf{K}+\tilde{\mathbf{k}},\nu}-\Sigma^{\sigma}_{\nu,\nu'}(\mathbf{K}+\tilde{\mathbf{k}}, i\omega_n)\right]^{-1}$$

Lattice self-energy

$$\Sigma^{\sigma}_{\nu,\nu'}(\mathbf{K}+\tilde{\mathbf{k}}, i\omega_n) = \sum_{\alpha,m,m'} P^{\alpha,\sigma^*}_{\nu,m}(\mathbf{K}+\tilde{\mathbf{k}})\Delta\Sigma^{\sigma,\mathrm{imp}}_{m,m'}(\mathbf{K}, i\omega_n)P^{\alpha,\sigma}_{m',\nu'}(\mathbf{K}+\tilde{\mathbf{k}}).$$



Brillouin zone sectors

Double counting correction

$$\Delta\Sigma^{\sigma,\mathrm{imp}}_{m,m'}(\mathbf{K}, i\omega_n) = \Sigma^{\sigma,\mathrm{imp}}_{m,m'}(\mathbf{K}, i\omega_n) - \Sigma^{\mathrm{dc}}_{m,m'}$$

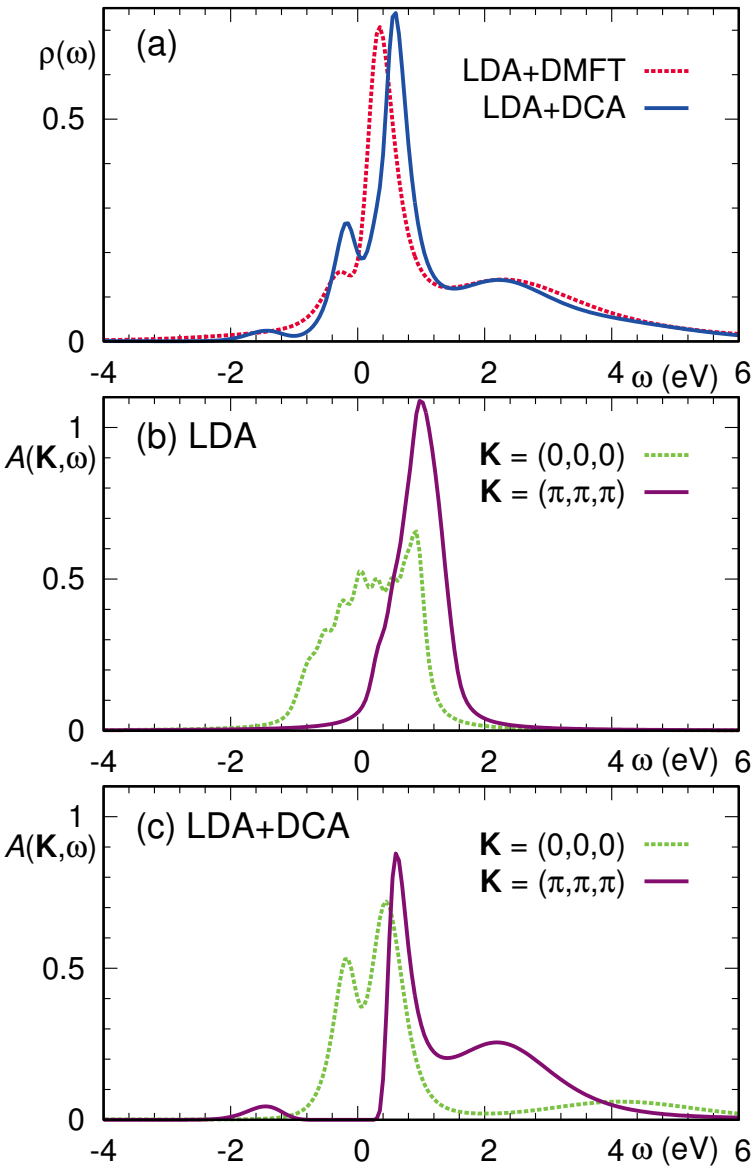
Local cluster Greens function

$$G^{\sigma,\mathrm{loc}}_{m,m'}(\mathbf{K}, i\omega_n) = \sum_{\tilde{\mathbf{k}},\nu,\nu'} P^{\alpha,\sigma}_{m,\nu}(\mathbf{K}+\tilde{\mathbf{k}}) \times G^{\sigma}_{\nu,\nu'}(\mathbf{K}+\tilde{\mathbf{k}}, i\omega_n)P^{\alpha,\sigma^{*\prime}}_{\nu',m'}(\mathbf{K}+\tilde{\mathbf{k}}),$$

Weiss field update

$$\left[G^{\sigma,0}_{m,m'}(\mathbf{K}, i\omega_n)\right]^{-1} = \Sigma^{\sigma,\mathrm{imp}}_{m,m'}(\mathbf{K}, i\omega_n) + \left[G^{\sigma,\mathrm{loc}}_{m,m'}(\mathbf{K}, i\omega_n)\right]^{-1}$$

Comparison between LDA+DMFT and LDA+DCA



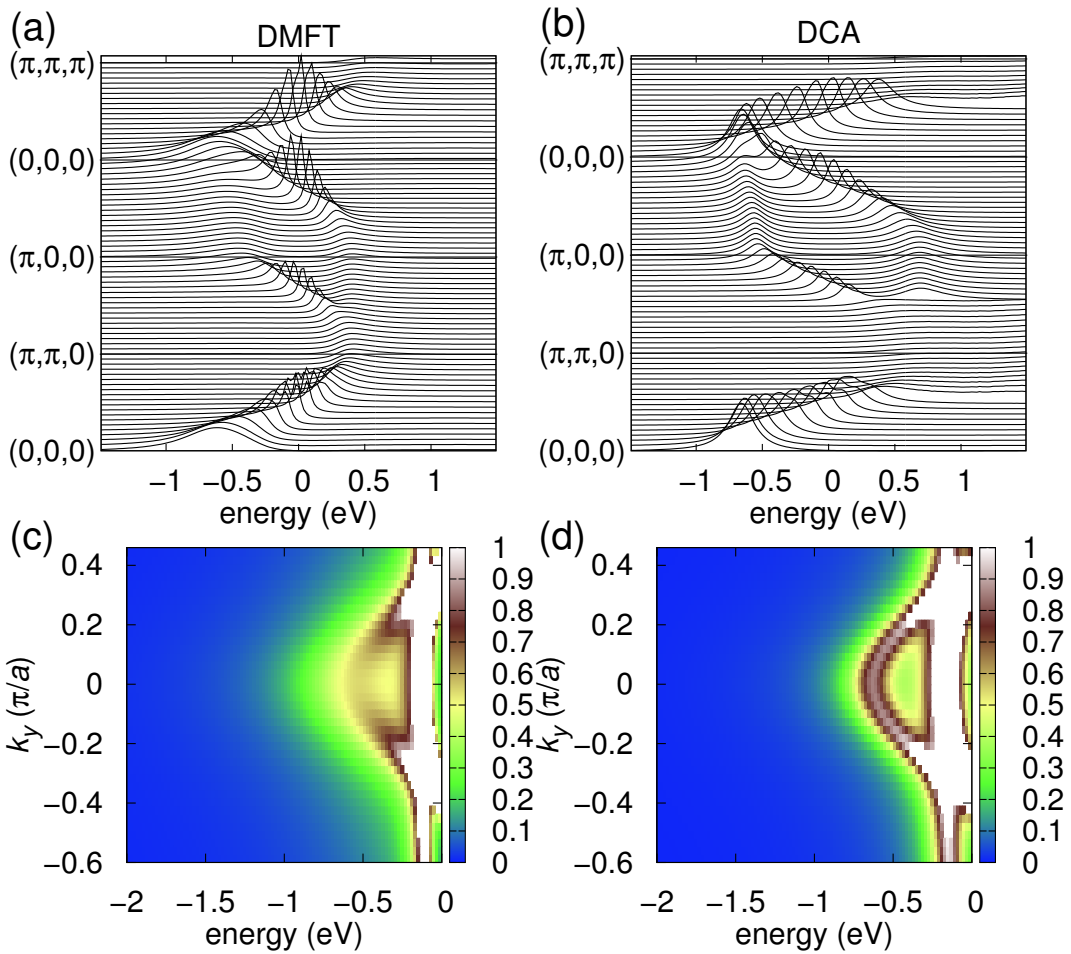
Interaction Hamiltonian to be solved:

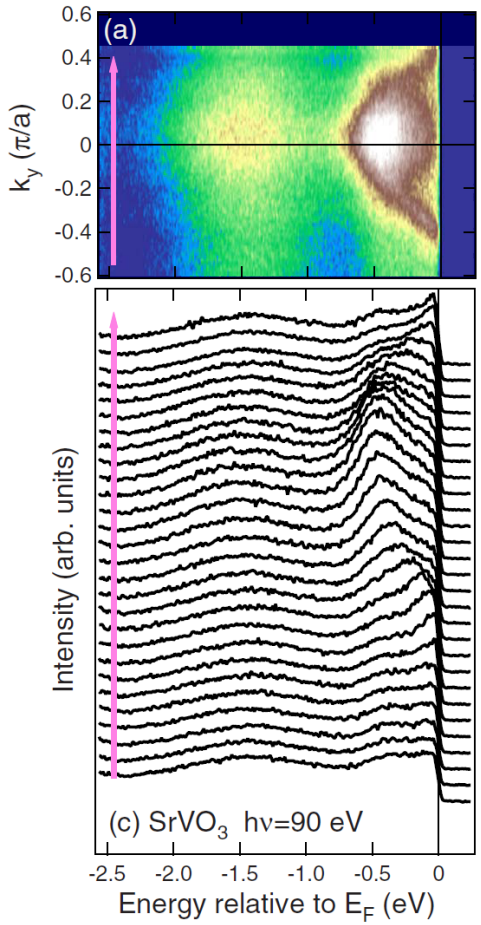
$$H_I = U \sum_m n_{m\uparrow} n_{m\downarrow} + \sum_{m<n,\sigma} \Big[U' n_{m\sigma} n_{n\bar{\sigma}} + (U' - J) n_{m\sigma} n_{n\sigma} \Big],$$

- LDA+DMFT, calculated with hybridzation expansion CT-QMC (from ALPS), agrees well with result of Aichhorn *et al.*, PRB **80**, 085101 (2009).
- LDA+DCA, calculated with interaction expansion CT-QMC, shows some extra structure.
- Understandable from **K** sector resolved spectral functions.
- $\Sigma^{\sigma,\mathrm{imp}}_{m,m'}(\mathbf{K}, i\omega_n)$ different for the two sectors

Compare also Zhang, Imada, PRB **76**, 045108 (2007); Lin, Millis, PRB **79**, 205109 (2009).

Comparison to experiment





LDA+DMFT (left) and LDA+DCA (right) comparison; (c), (d) at $k_z = 0.32\pi/a$

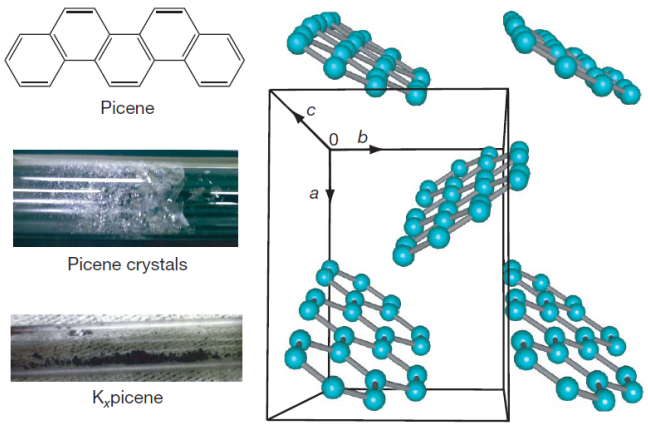
Yoshida *et al.*, Phys. Rev. B **82**, 085119 (2010).

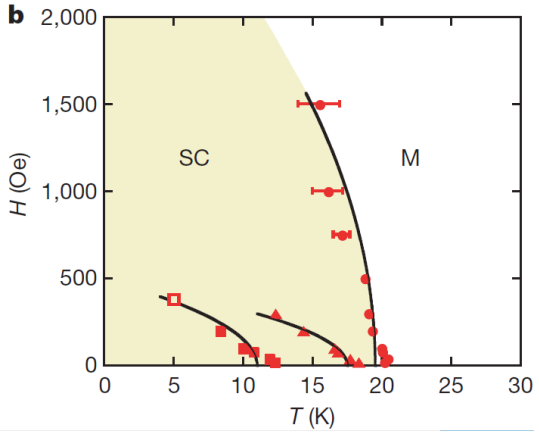
Lee, Foyevtsova, Ferber, Aichhorn, Jeschke, Valentí, Phys. Rev. B **85**, 165103 (2012).

Potassium doped picene: metallic or not?

Doping of organic molecular crystals

Superconductivity in K_3picene with $T_c = 18$ K:



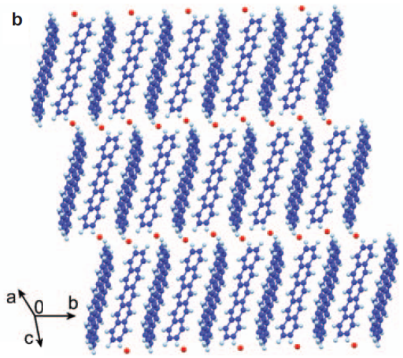


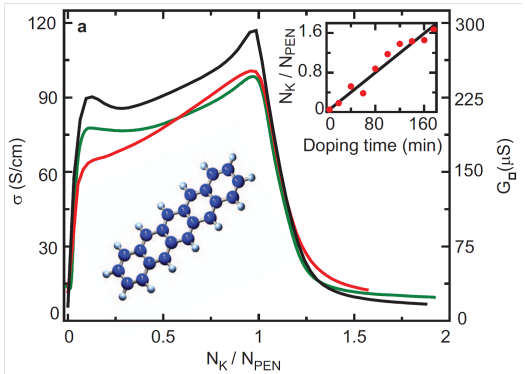
- unexpected
- observed through Meissner effect
- recently: zero conductivity at 7 K (PRB 2013)

Mitsuhashi *et al.*, Nature **464**, 76 (2010)

- SC subsequently found in phenantrene (5 K) and dibenzopentacene (33 K)
- Indication for Mott physics in doped organics: compare case of pentacene

K intercalated pentacene:

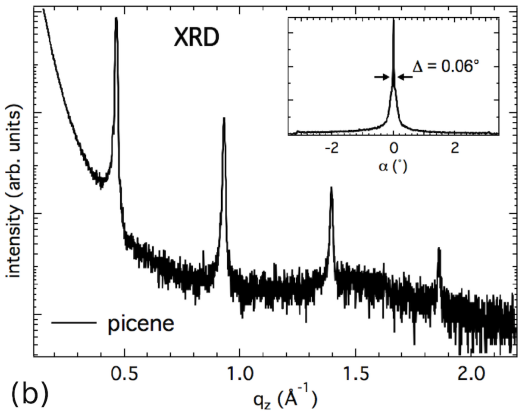


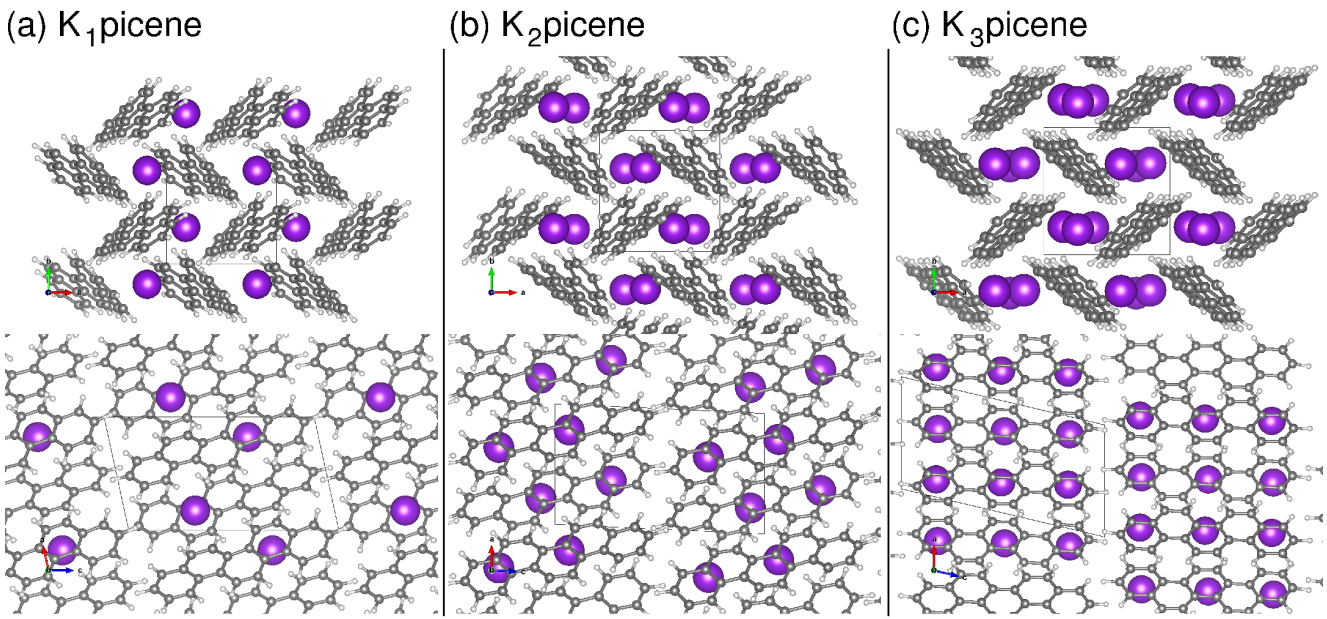


Craciun *et al.*, Phys. Rev. B **79**, 125116 (2009).

Problem for theory: Explain metallic state

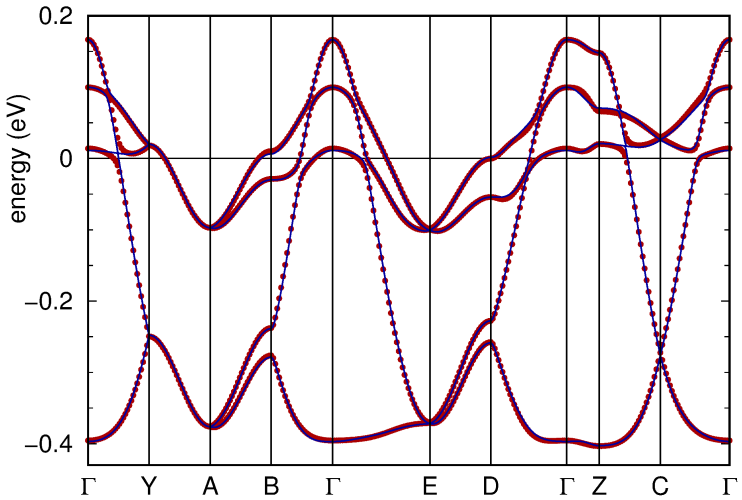
$K_x$picene structure and electronic structure





Structure not known experimentally

➜ need to simulate

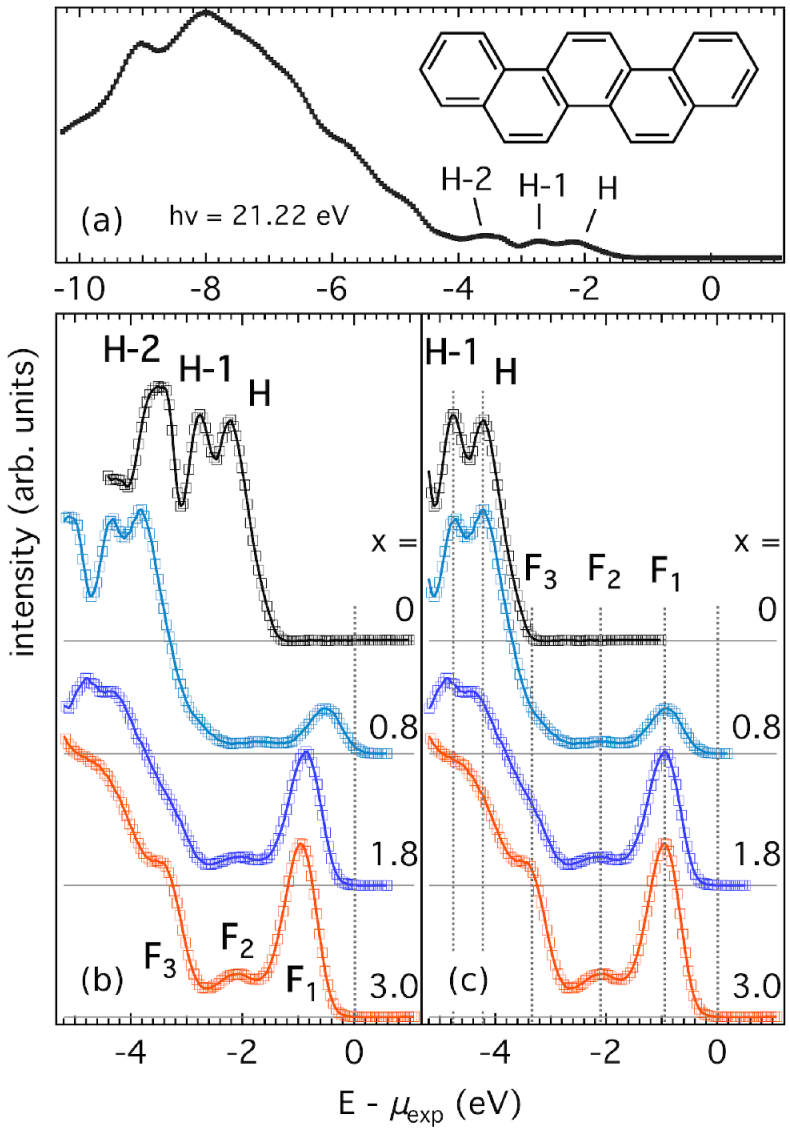


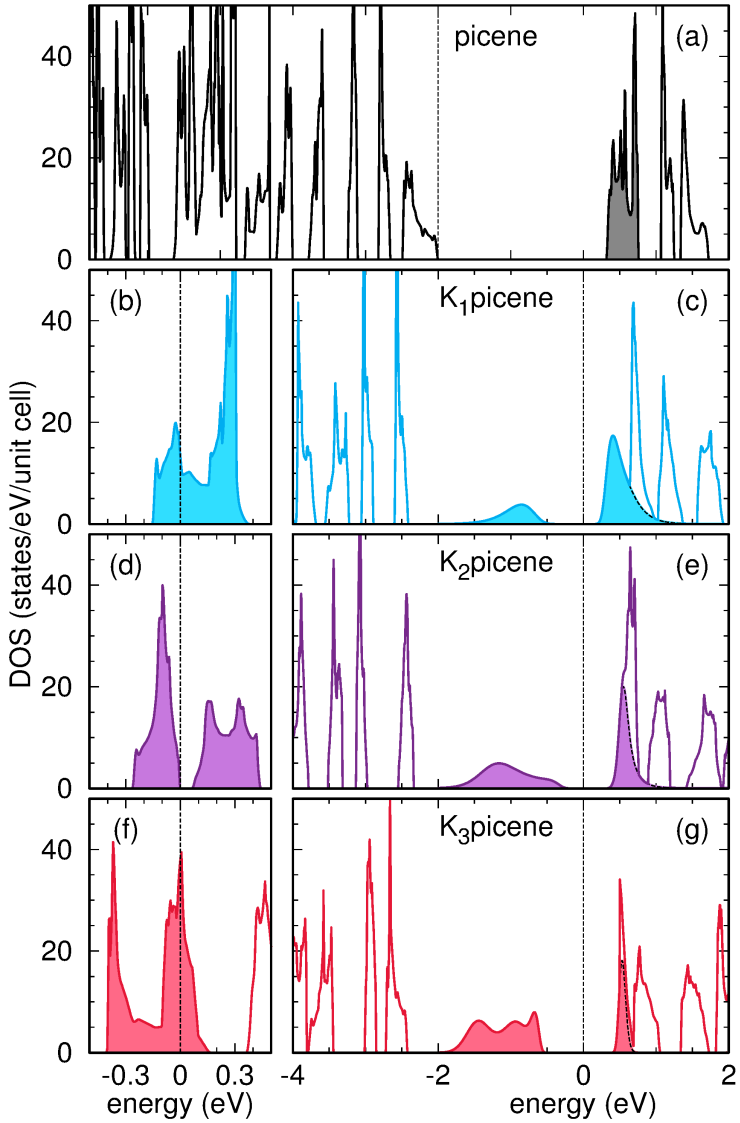
Hamiltonian we solve is

$$H_K = -\sum_{ijm\sigma} t_m c^\dagger_{mj\sigma} c_{mi\sigma} - t_\perp \sum_{i\sigma} c^\dagger_{1i\sigma} c_{2i\sigma}$$

$$H_I = U \sum_{mi} n_{mi\uparrow} n_{mi\downarrow} + \sum_{\sigma} \Big[(U - 2J_z) n_{1i\sigma} n_{2i\bar{\sigma}} + (U - 3J_z) n_{1i\sigma} n_{2i\sigma} \Big].$$

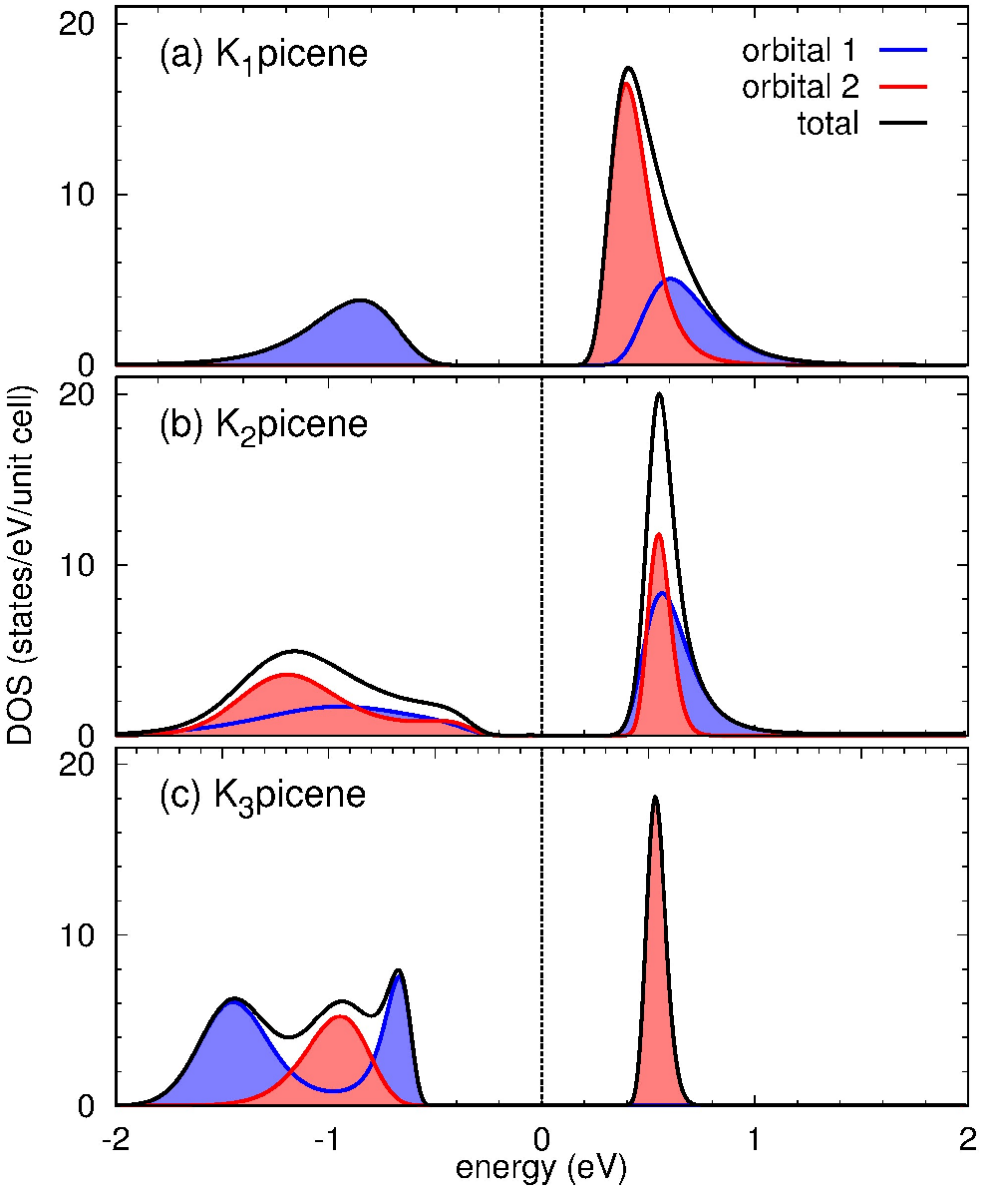
$K_x$picene: Photoemission and DFT/TB+DMFT





Ruff, Sing, Claessen, Lee, Tomić, Jeschke, Valentí, PRL **110**, 216403 (2013).

$K_x$picene: DMFT for two orbital model



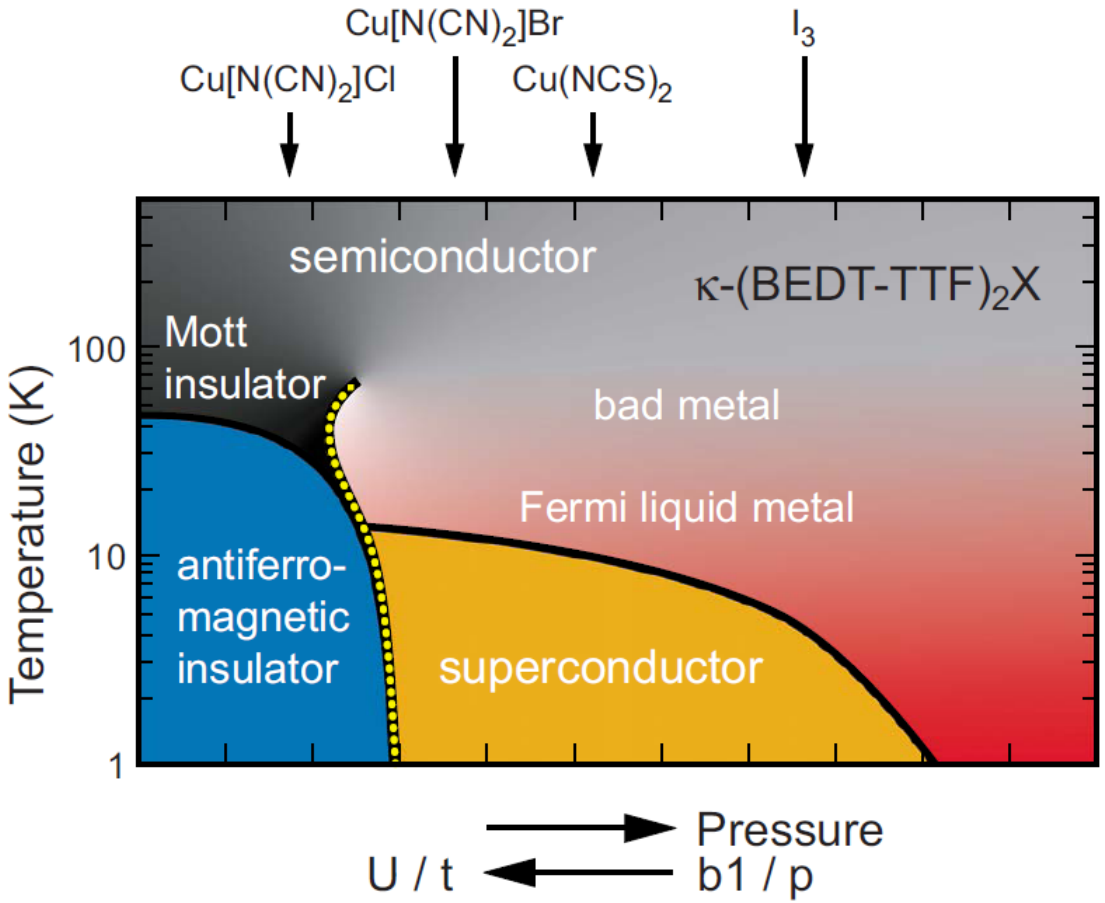
- essential ingredient: two orbital model with hybridization between orbitals
- off-diagonal Greens functions ➜ use of interaction expansion CT-QMC
- both bands gapped in K_2picene
- no metallic state for commensurate doping

➜ source of superconductivity unclear

Ruff, Sing, Claessen, Lee, Tomić, Jeschke, Valentí, PRL **110**, 216403 (2013).

Projectors for molecular orbitals: LDA+DMFT description of charge transfer salts

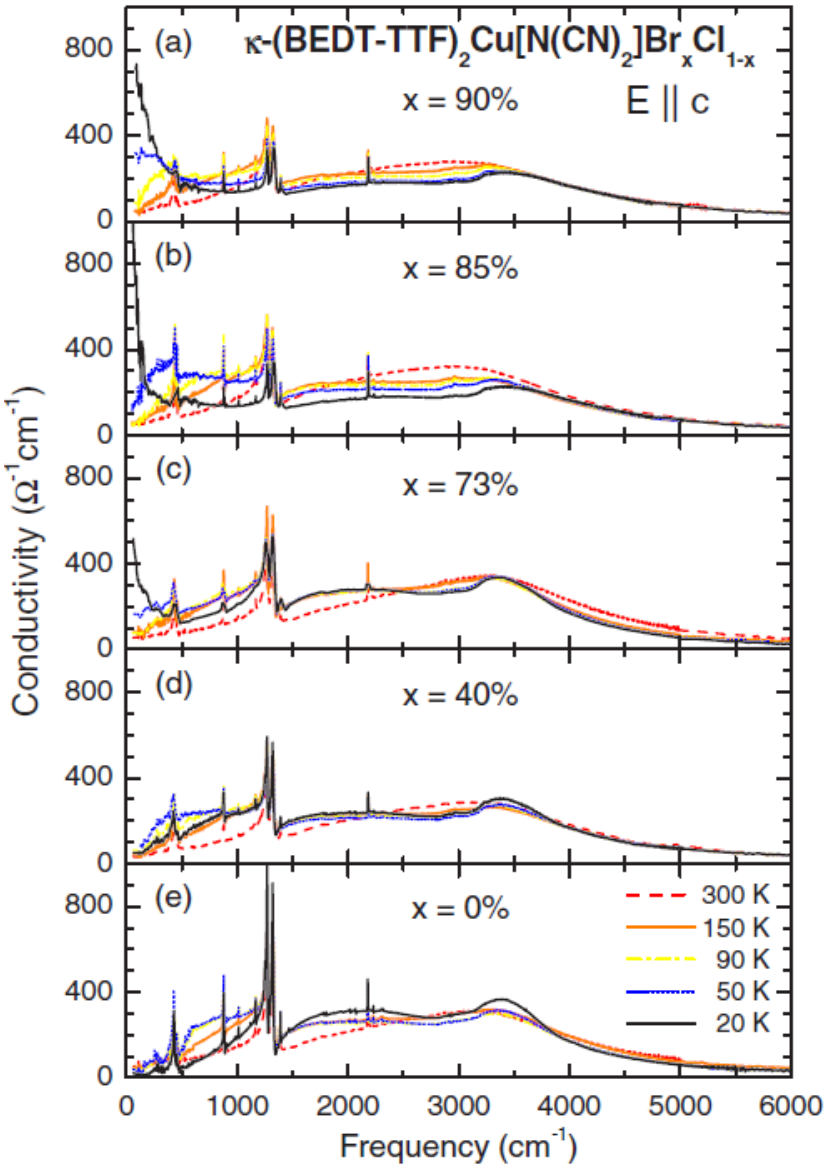
κ-phase BEDT-TTF based charge transfer salts

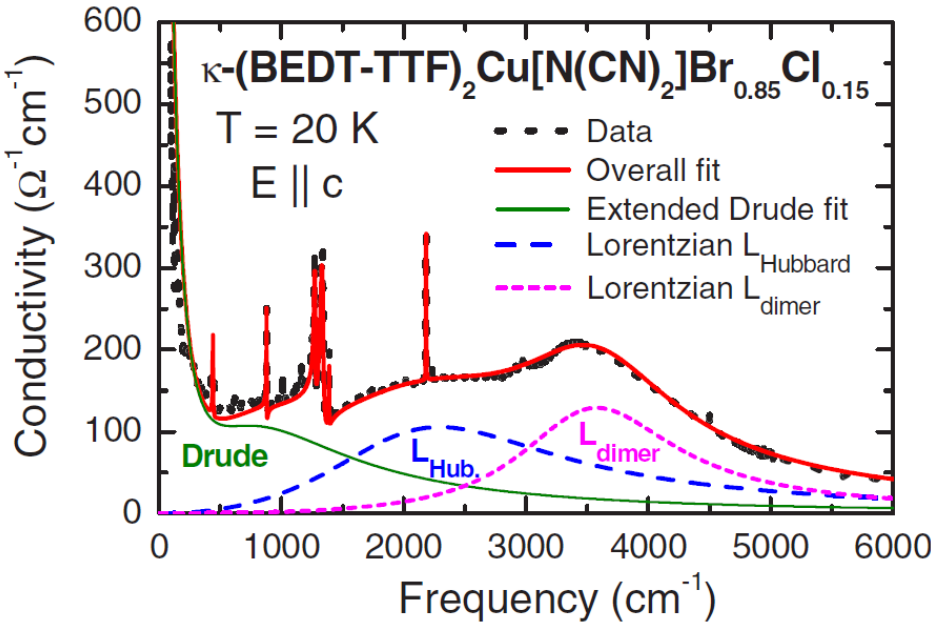


Dumm *et al.*, Phys. Rev. B **79**, 195106 (2009).

- Rich phase diagram accessible by chemical or physical pressure
- Extensively studied by theory
- So far: Model calculations, generic or based on Hückel/DFT extracted parameters, solved with myriad manybody methods.
- **Plan: apply full LDA+DMFT method.**

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





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

- Drude peak in κ-Br at low T, disappears at high T
- absence of Drude peak in κ-Cl
- conjecture about composition of midinfrared spectrum based on ED model calc. (Merino, McKenzie)

LDA+DMFT for molecular orbitals

Idea for projection on molecular orbital: Diagonalize occupation matrix in the basis of atomic orbitals within the correlated subspace.

Starting point: FLAPW projectors $\tilde{P}^{\alpha,\sigma}_{m\nu}(\mathbf{k})$

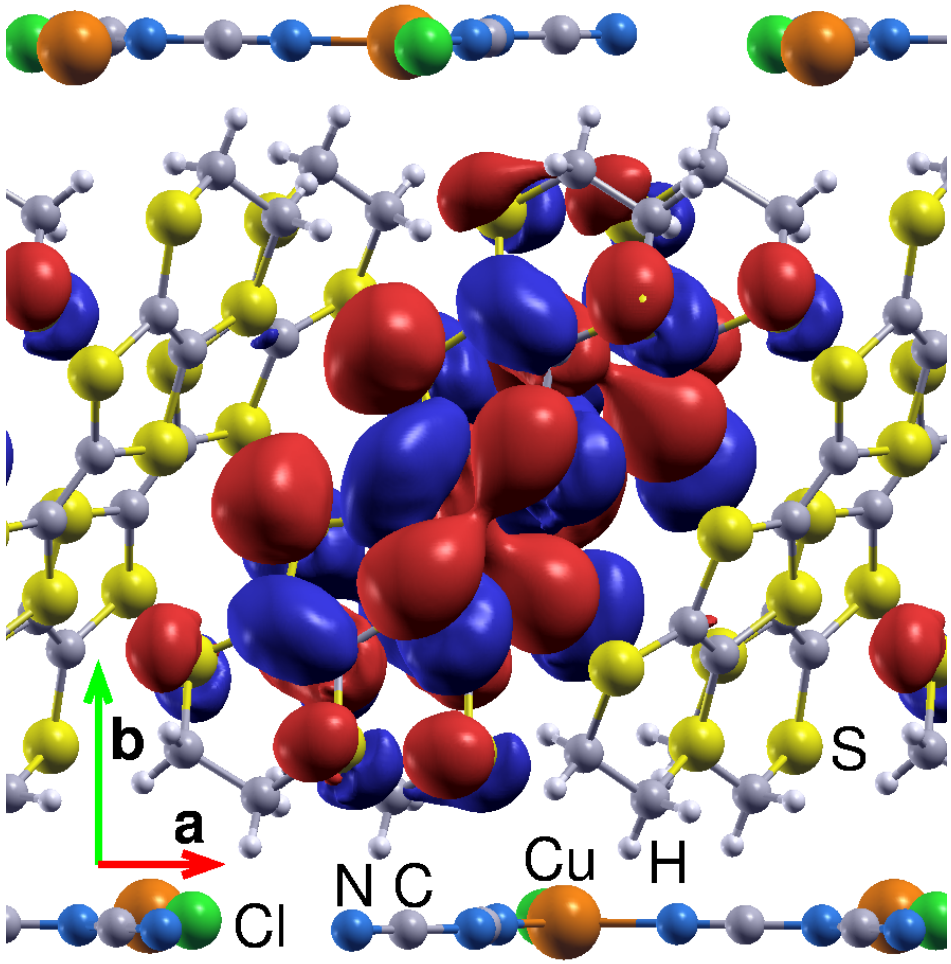
$$\mathcal{O}^{\alpha,\alpha'}_{m,m'}(\sigma) = \sum_{\nu \in W'} \tilde{P}^{\alpha,\sigma}_{m\nu}(0)\tilde{P}^{\alpha',\sigma *}_{m'\nu}(0).$$

Narrow energy window W', $\mathbf{k} = 0$, atomic orbitals $\{\alpha, m\}$.

Eigenvectors of $\mathcal{O}^{\alpha,\alpha'}_{m,m'}(\sigma)$ corresponding to largest eigenvalues now indicate composition of molecular orbitals in terms of $\{\alpha, m\}$.
If $U^{\alpha}_{m}(\sigma)$ is such an eigenvalue,

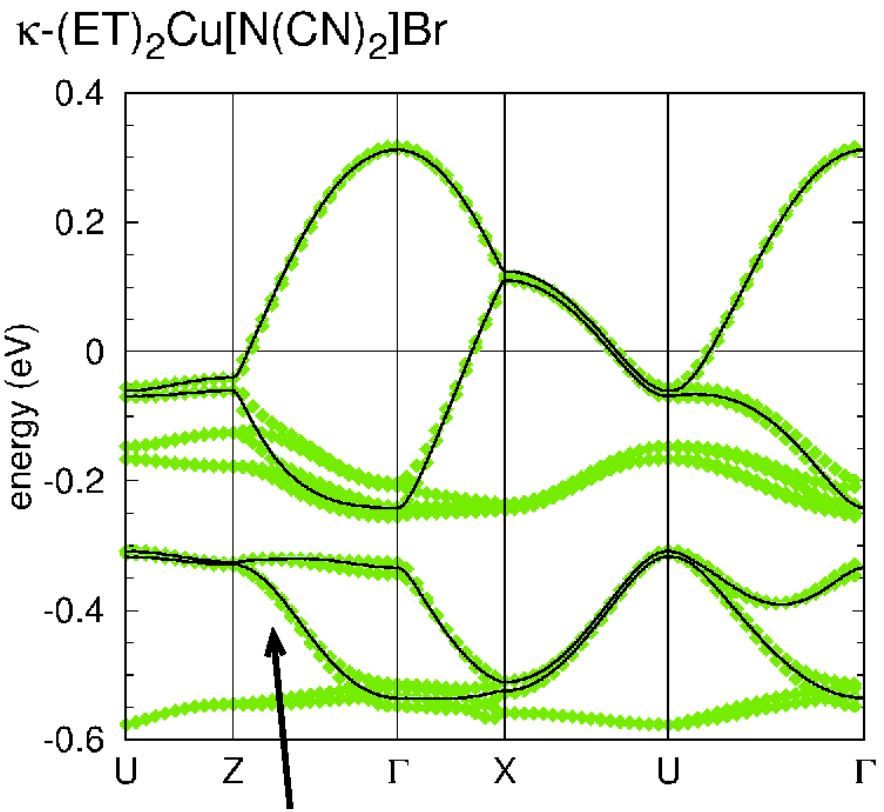
$$\tilde{\mathcal{P}}^{\sigma}_{M\nu}(\mathbf{k}) = \sum_{\alpha,m} U^{\alpha}_{m}(\sigma)\tilde{P}^{\alpha,\sigma}_{m\nu}(\mathbf{k})$$

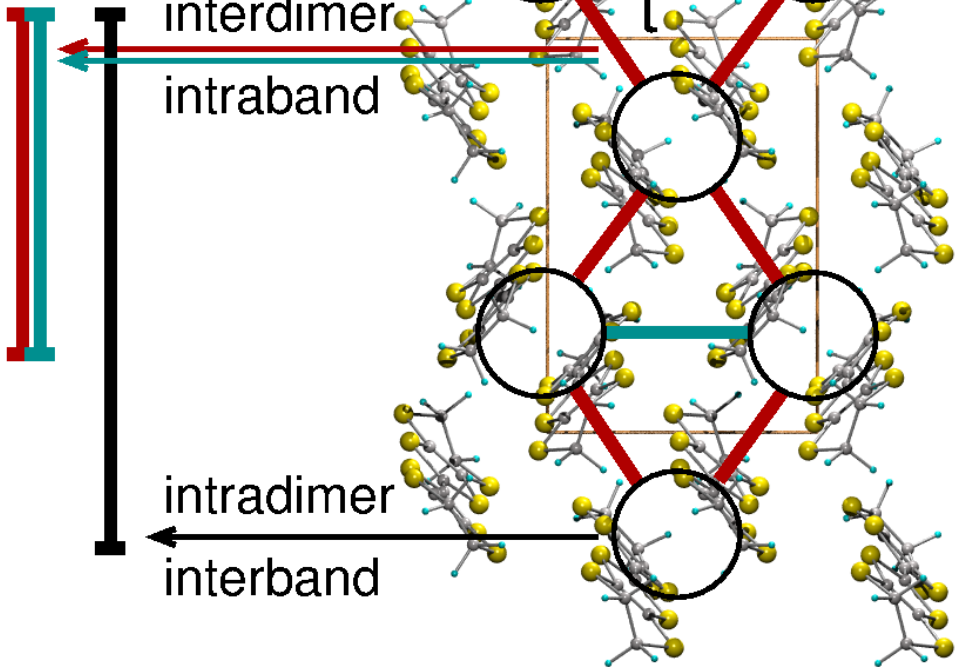
is a molecular projector for molecular orbital M.



κ-(BEDT-TTF)$_2$-Cu[N(CN)$_2$]Cl, BEDT-TTF dimer Wannier function

κ-(BEDT-TTF)$_2X$ structure and bands

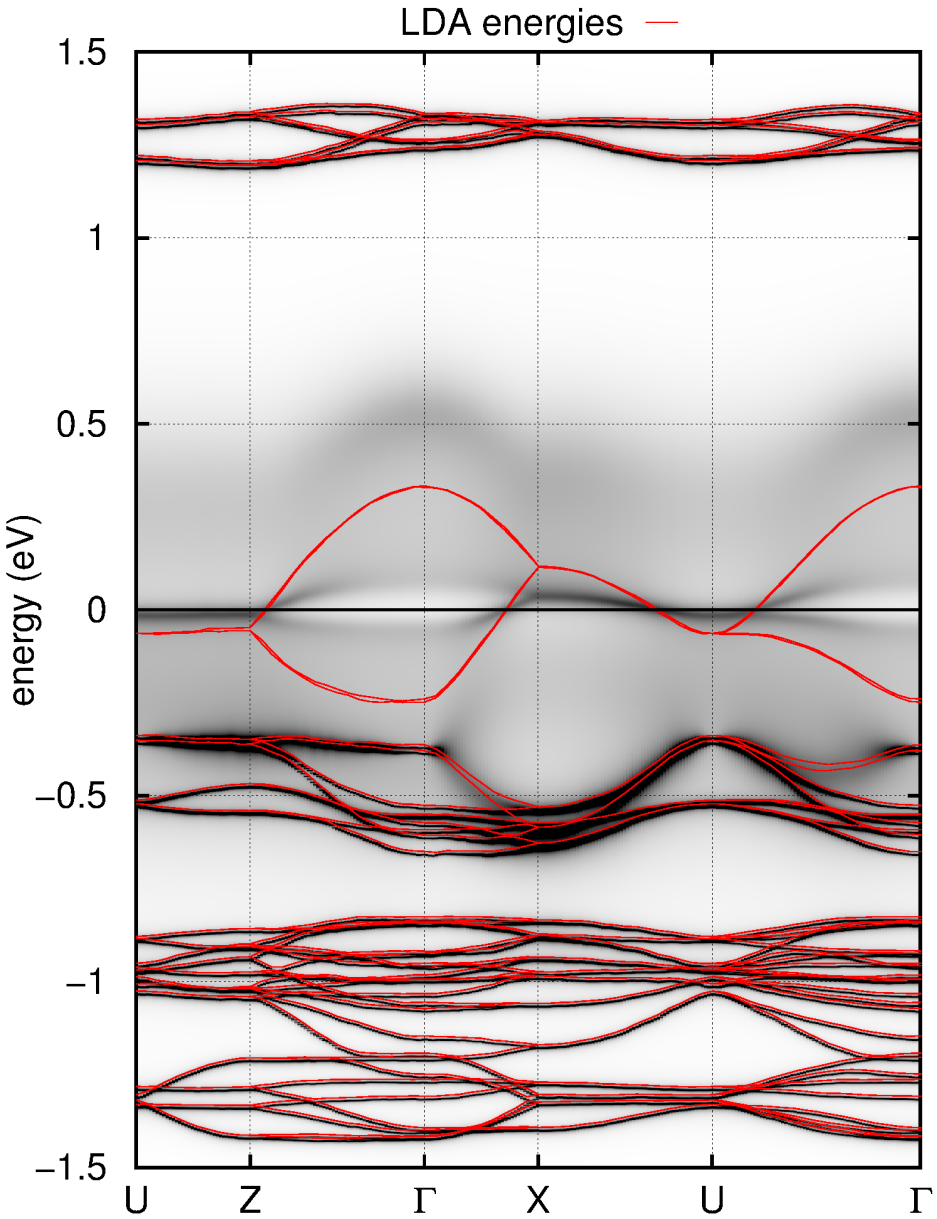




black band count: 8 from ET HOMO
or 4 from $(ET)_2$ HOMO–1, 4 from $(ET)_2$ HOMO

Kandpal, Opahle, Zhang, Jeschke, Valentí, PRL **103**, 067007 (2009).

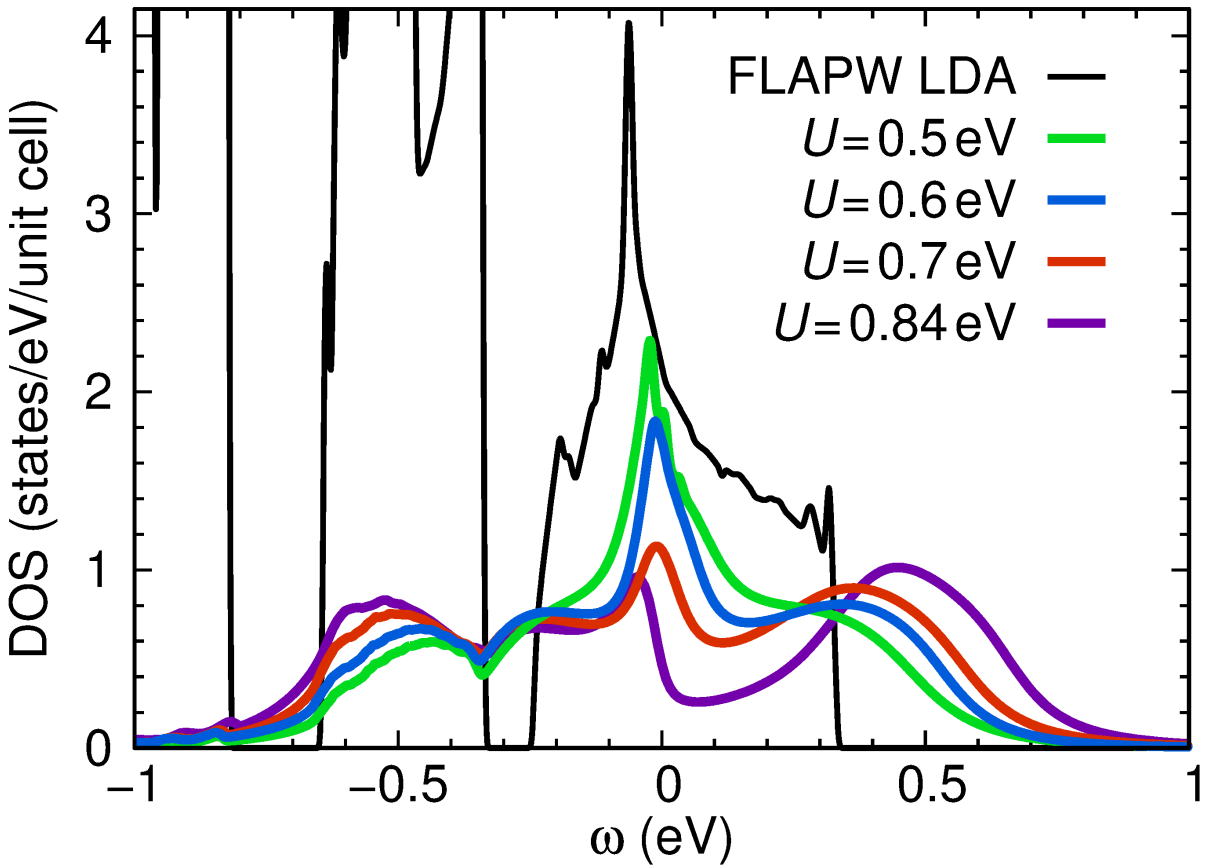
κ-$(ET)_2$-$Cu[N(CN)_2]Cl$ spectral function $A(\mathbf{k}, \omega)$



- Hybridization expansion CT-QMC impurity solver from ALPS project
- Temperature $T = 300$ K, $U = 0.6$ eV$\approx 10t$ (compare Nakamura *et al.*, J. Phys. Soc. Jpn. **78**, 083710 (2009)).
- Renormalized quasiparticle band and spectral weight transfer to lower and upper Hubbard bands

Ferber, Foyevtsova, Jeschke, Valentí, arXiv:1209.4466.

κ-(ET)$_2$-Cu[N(CN)$_2$]Cl DOS and $A(\omega)$



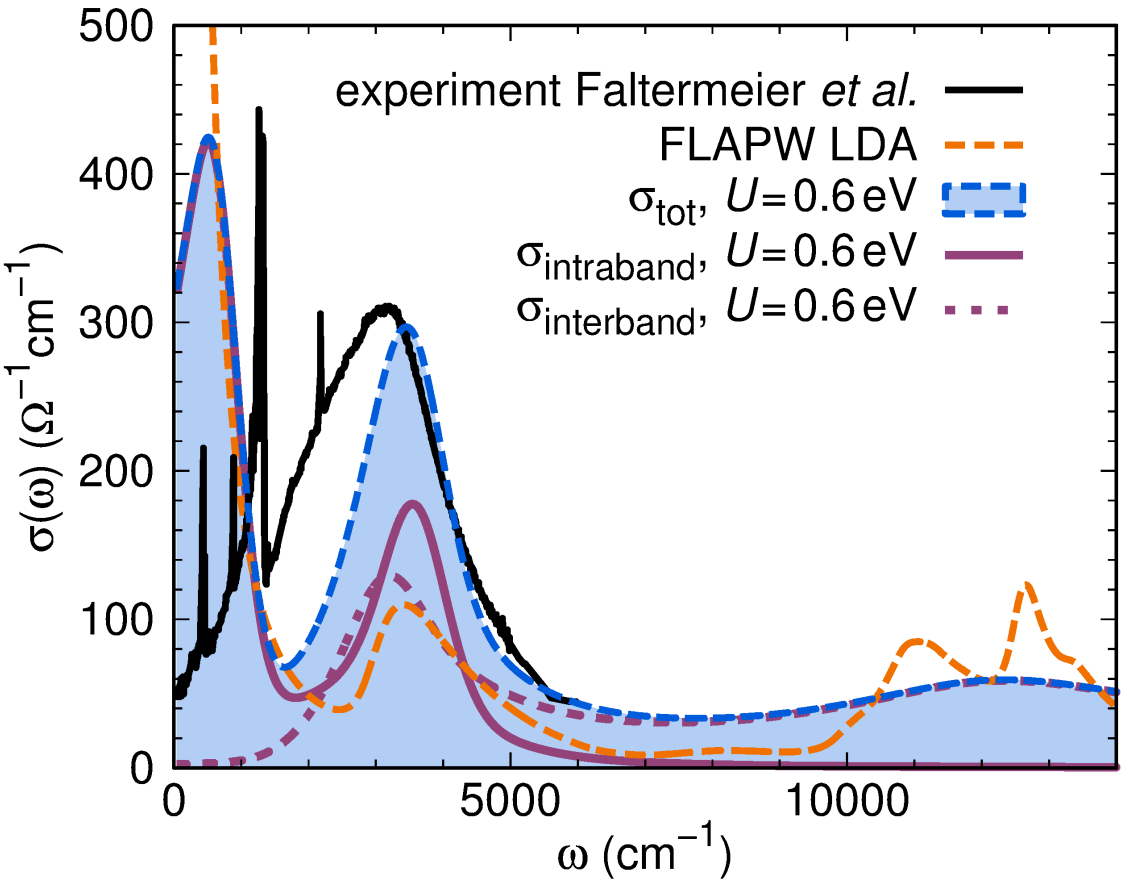
- evolution of quasiparticle peakd and Hubbard bands with interaction strength U
- $U = 0.84$ eV close to insulating state
- some underestimation of critical U due to use of single site DMFT

Ferber, Foyevtsova, Jeschke, Valentí, arXiv:1209.4466.

Optical conductivity

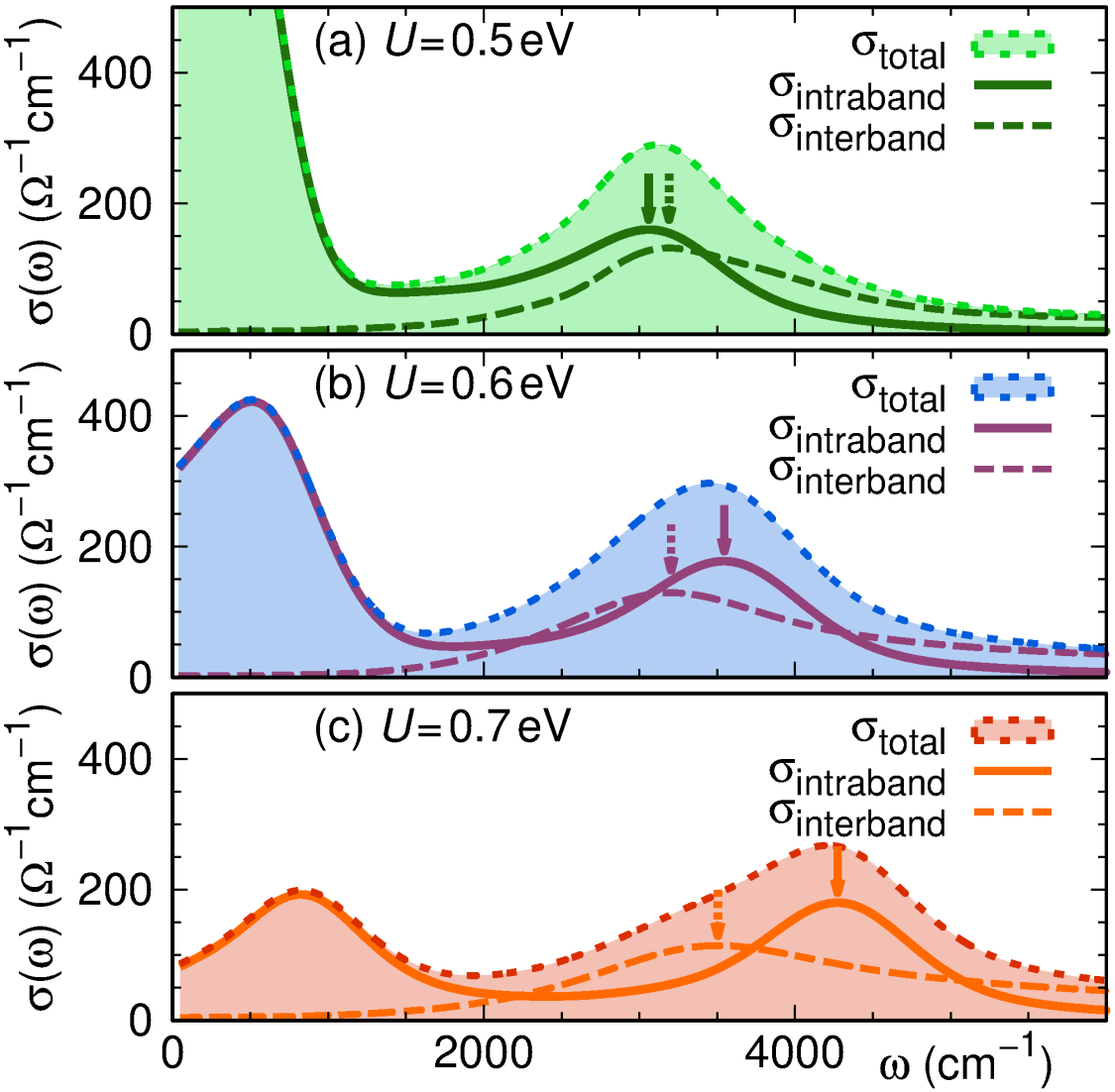
$$\sigma_{zz}(\tilde{\nu}_n) = \frac{e^2}{4\pi\epsilon_0 V \tilde{\nu}_n \beta} \sum_{\nu\nu'\nu''\nu''',\mathbf{k},\sigma} v_{z,\mathbf{k}}^{\nu\nu'} \; v_{z,\mathbf{k}}^{\nu''\nu'''} \sum_{\omega_n} G_{\mathbf{k}}^{\nu'\nu''}(i\omega_n + i\tilde{\nu}_n) \; G_{\mathbf{k}}^{\nu'''\nu}(i\omega_n)$$

(lattice Greens function $G_{\mathbf{k}}(i\omega_n)$, bosonic (fermionic) Matsubara freq. $\tilde{\nu}_n$ (ω_n), Fermi velocity $v_{\alpha,\mathbf{k}}^{\nu\nu'}$).



- comparison to $T = 300$ K measured optical conductivity (Faltermeier *et al.*, Phys. Rev. B **76**, 165113 (2007)).
- interband (intradimer) contribution nearly similar to DMFT result
- DMFT shifts spectral weight from Drude peak into intraband ("Hubbard") peak

Influence of the interaction strength



- Drude peak suppressed as interaction strength increases
- position of intraband (interdimer) peak shifts like Hubbard bands, proportional to $0.75U$ due to contributions from U and $U/2$
- position of interband (intradimer) peak nearly constant
- conjecture of Faltermeier *et al.* confirmed from first principles

Conclusions

LDA+DCA summary (Lee *et al.*, Phys. Rev. B **85**, 165103 (2012).)

- LDA+DCA introduces some momentum dependence into realistic calculations for strongly correlated materials.
- Low energy features seem to be described better in $SrVO_3$.

Theory&PES for $K_x$picene summary (Ruff *et al.*, PRL **110**, 216403 (2013)).

- Insulating state found in photoemission and DFT/TB+DMFT theory
- Importance of multiorbital nature

LDA+DMFT for CT salts summary (Ferber *et al.*, arXiv:1209.4466).

- Projector scheme for molecular orbitals within FLAPW allows LDA+DMFT calculation for Mott insulator κ-$(ET)_2$-$Cu[N(CN)_2]Cl$.
- Interband and intraband contributions to optical conductivity described at the same level.