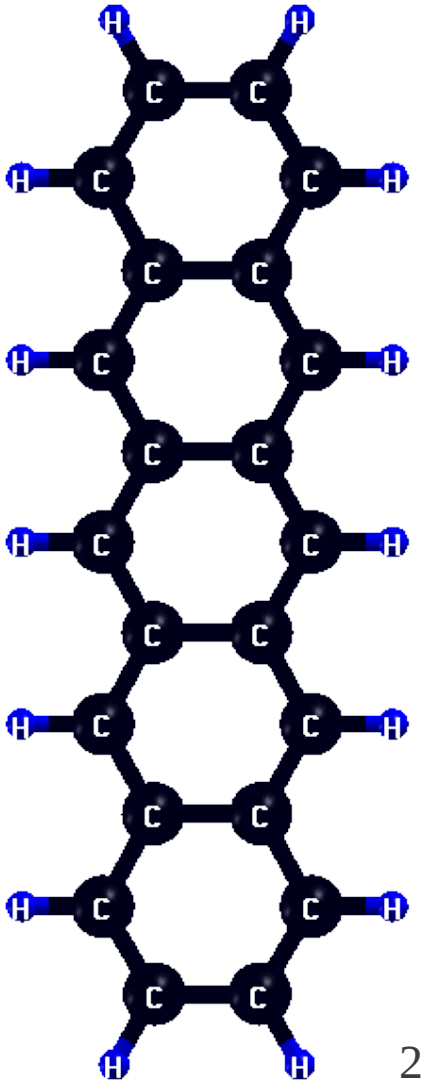
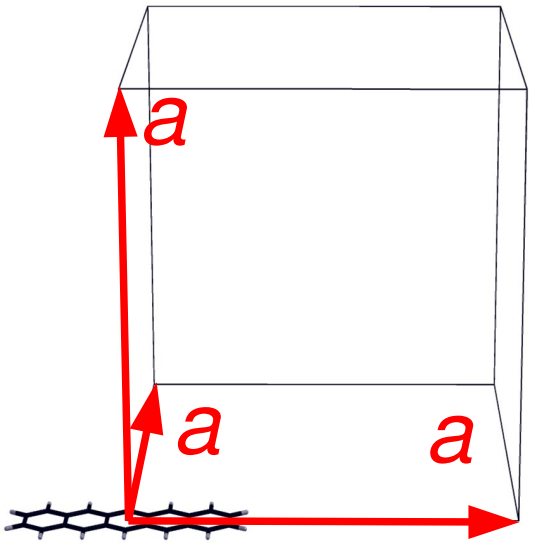
The electronic structure of pentacene monolayers on Cu(110) and Ag(110) surfaces: DFT and G_0W_0 results vs. angle-resolved photoemission data

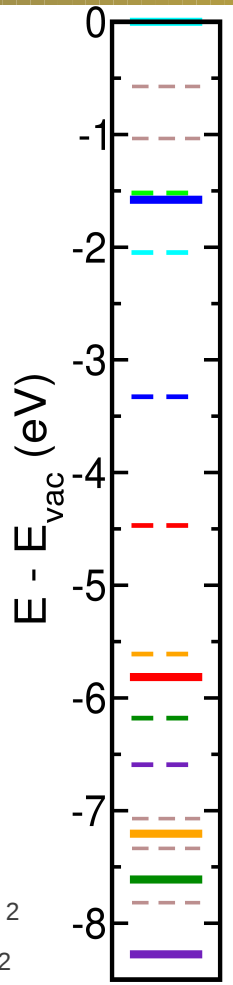
Overview

- DFT vs G_0W_0 of different geometrical arrangements of pentacene molecules
- ARPES experiment
- 5A on Ag(110)
- 5A on Cu(110)
- Conclusion



Isolated molecule





GGA

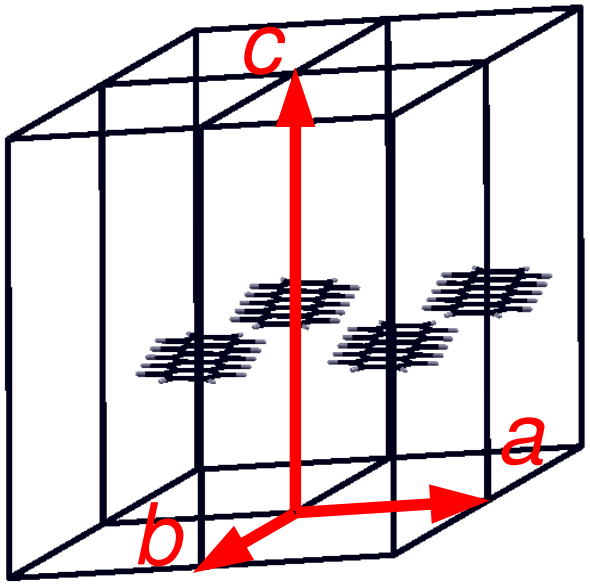
G_0W_0

experimental Eg = 5.2 [eV] [1]
GGA Eg = 1.15 [eV] comp. Eg = 1.1 [eV] [2]
G_0W_0 Eg = 4.2 [eV] comp. Eg = 4.5 [eV] [2]

[1] Organic Molecular Solids, Wiley-VCH Verlag GmbH, 2008, 217-305

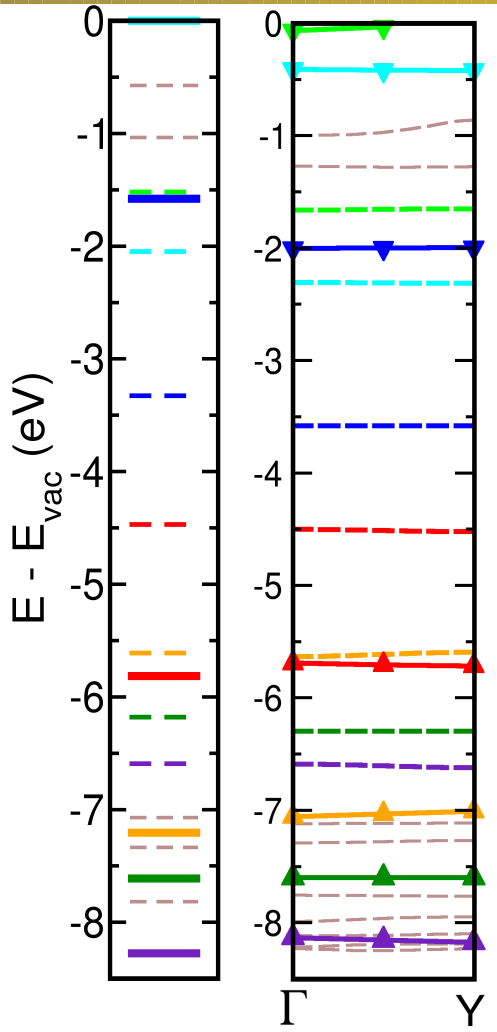
[2] Scharifzadeh et al PRB 85, 125307 (2012)

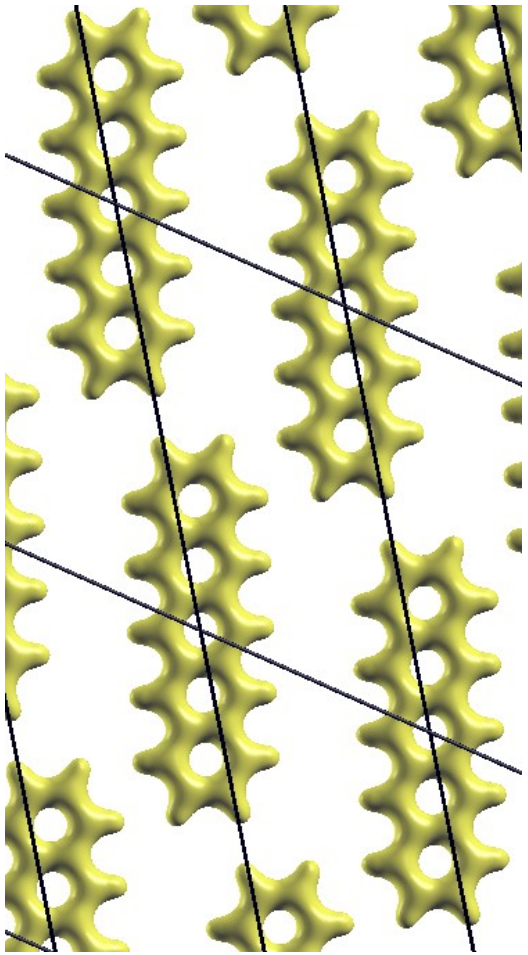
Freestanding Monolayer



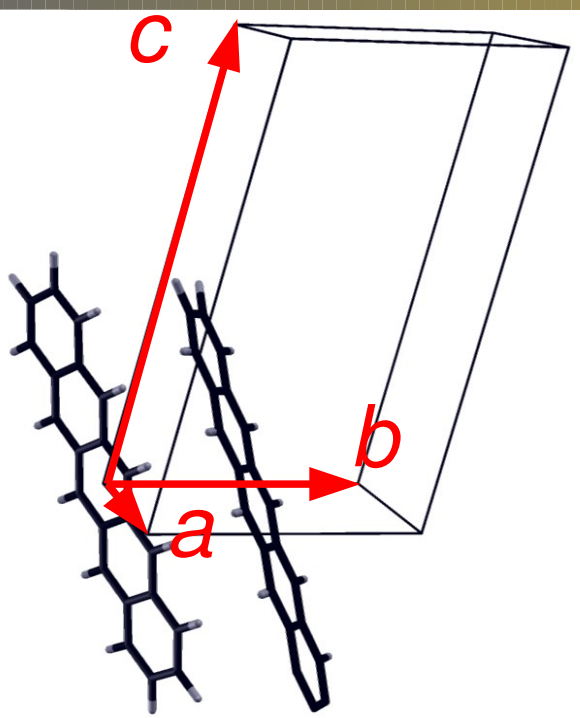
GGA
G_0W_0

GGA Eg = 0.9 [eV]
G_0W_0 Eg = 3.7 [eV]



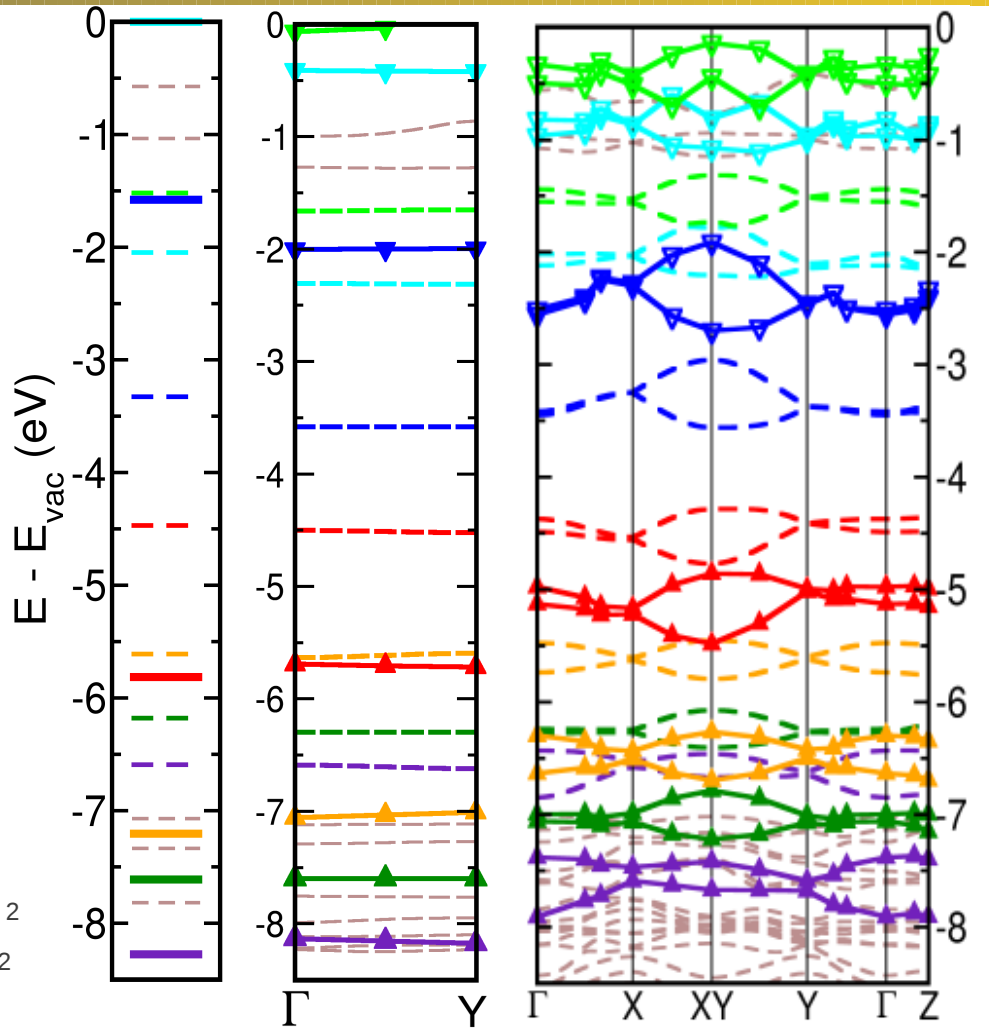


Crystal bulk structure



GGA

G_0W_0



experimental Eg = 2.2 [eV] [1]

GGA Eg = 0.8 [eV] comp. Eg = 0.75 [eV] [2]

G_0W_0 Eg = 2.2 [eV] comp. Eg = 2.2 [eV] [2]

[1] Organic Molecular Solids, Wiley-VCH Verlag GmbH, 2008, 217-305

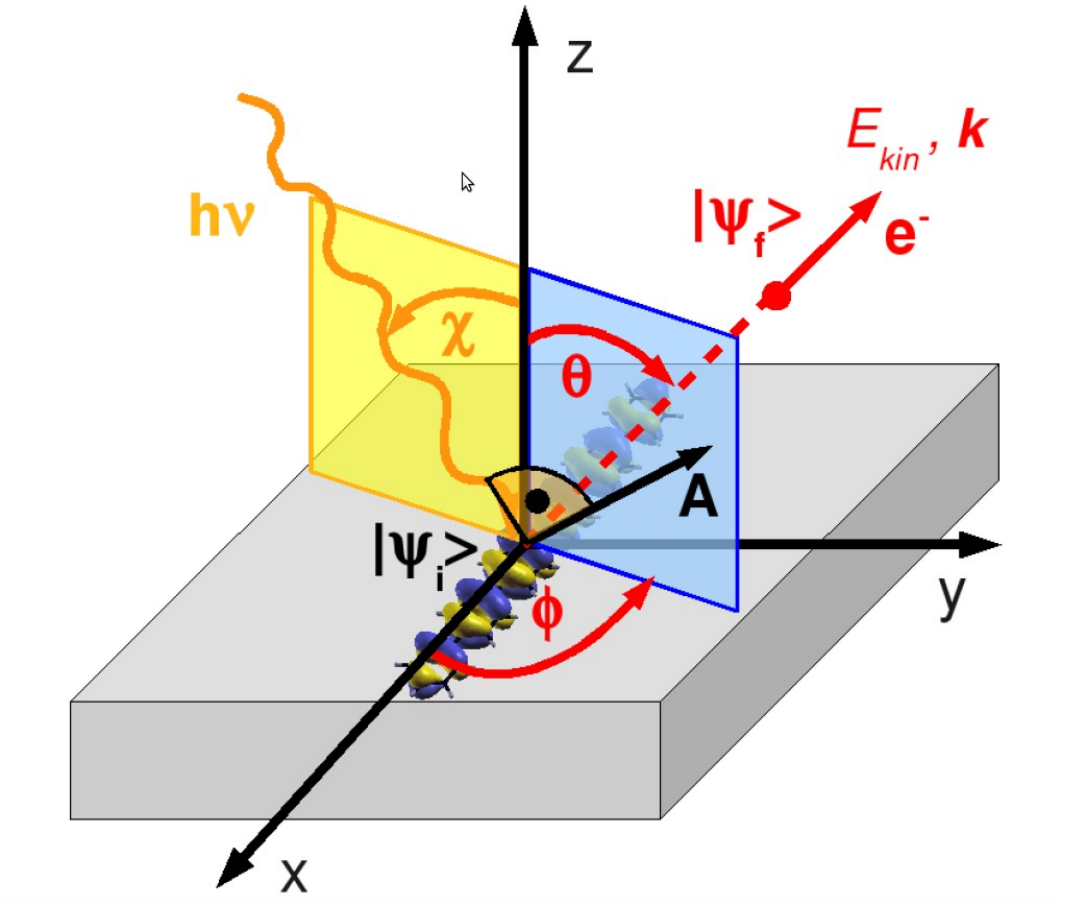
[2] PRB 85, 125307 (2012)

ARPES experiment

Conservation laws:

$$E_{kin} = h\nu - \phi - |E_i|$$

$$k_{i||} = k_{f||} = \sqrt{2mE_{kin}} \sin\Theta$$



Computation of Photoemission Intensity

$$I(\Theta,\Phi;E_{kin}) \propto \sum_i \left| \langle \psi_f^*(\Theta,\Phi;E) | p\cdot A | \psi_i \rangle \right|^2 \times \delta(E_i + \phi + E_{kin} - h\nu)$$

p electronic momentum operator

A electromagnetic vector potential

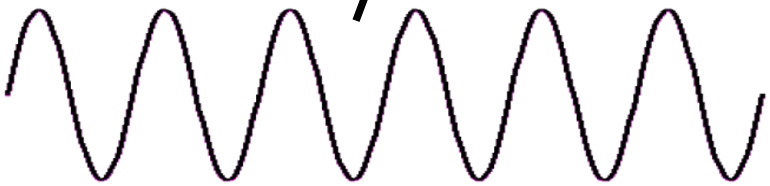
Interaction with photon treated as perturbation with Hamiltonian:

$$H_{\text{int}} = \frac{e}{2mc}(A\cdot p + p\cdot A) = \frac{e}{mc} A\cdot p$$

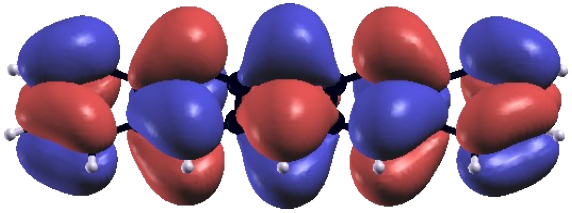
$$[p\cdot A] = -i\nabla\cdot A = 0$$

Computation of Photoemission Intensity

$$I(\Theta,\Phi;E_{kin}) \propto \sum_i \left| \langle \psi_f^*(\Theta,\Phi;E) | p \cdot A | \psi_i \rangle \right|^2 \times \delta(E_i + \phi + E_{kin} - h\nu)$$



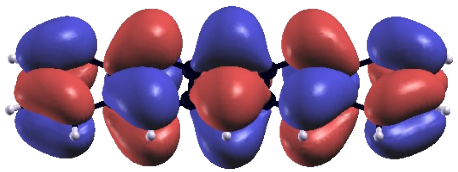
plane wave



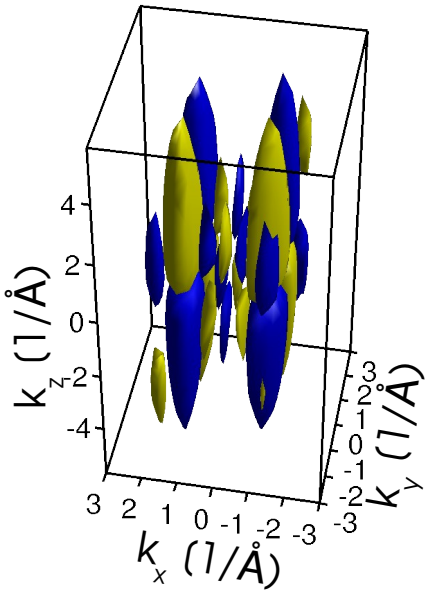
molecular orbital

Computation of Photoemission Intensity

$$I(\Theta,\Phi;E_{kin}) \propto \sum_i \left| \langle \psi_f^*(\Theta,\Phi;E) | p \cdot A | \psi_i \rangle \right|^2 \times \delta(E_i + \phi + E_{kin} - h\nu)$$

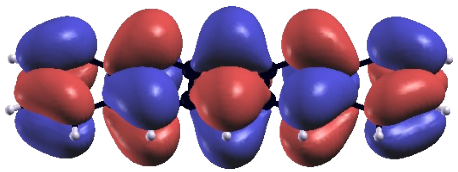


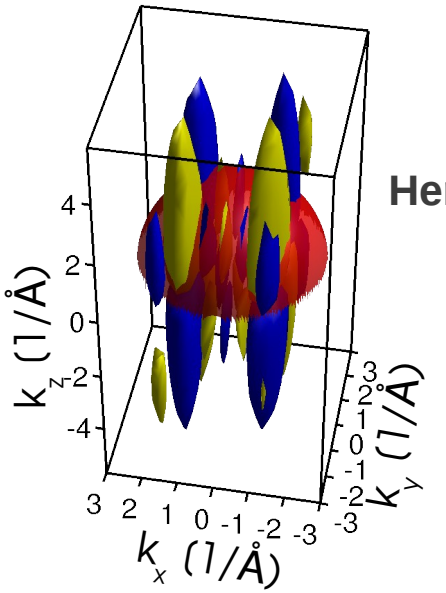
Fourier Transform



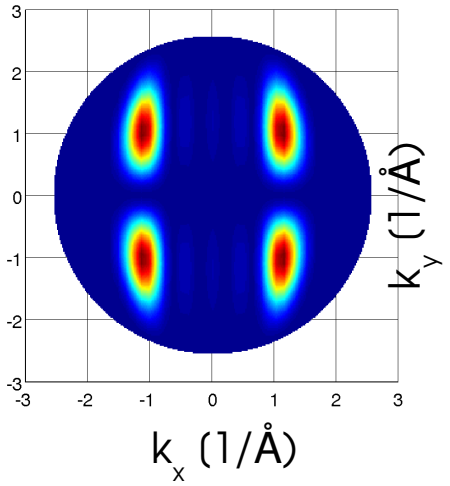
Computation of Photoemission Intensity

$$I(\Theta,\Phi;E_{kin}) \propto \sum_i \left| \langle \psi_f^*(\Theta,\Phi;E) | p \cdot A | \psi_i \rangle \right|^2 \times \delta(E_i + \phi + E_{kin} - h\nu)$$



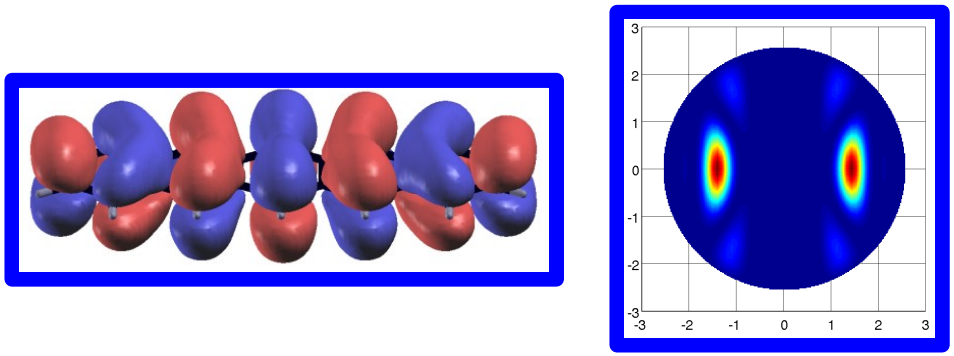


Hemisperical cut

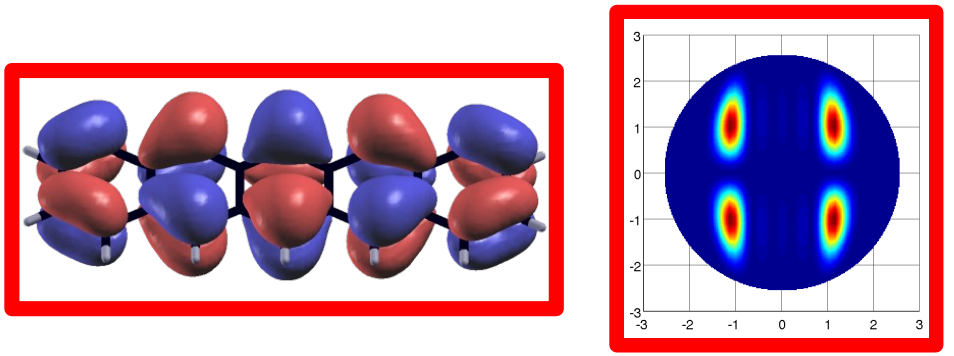


Momentum maps for isolated molecule

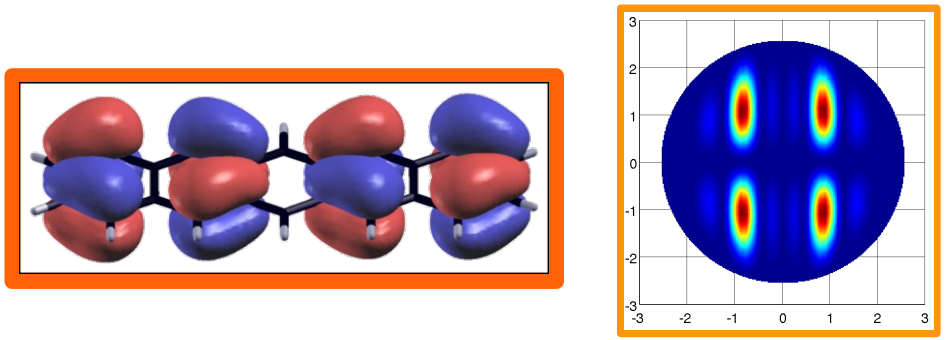
LUMO



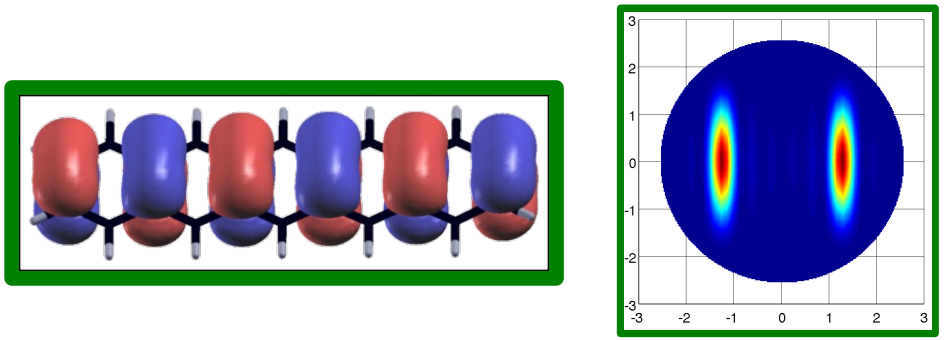
HOMO



HOMO-1



HOMO-2



Pentacene on Ag(110)

- Epitaxial matrix

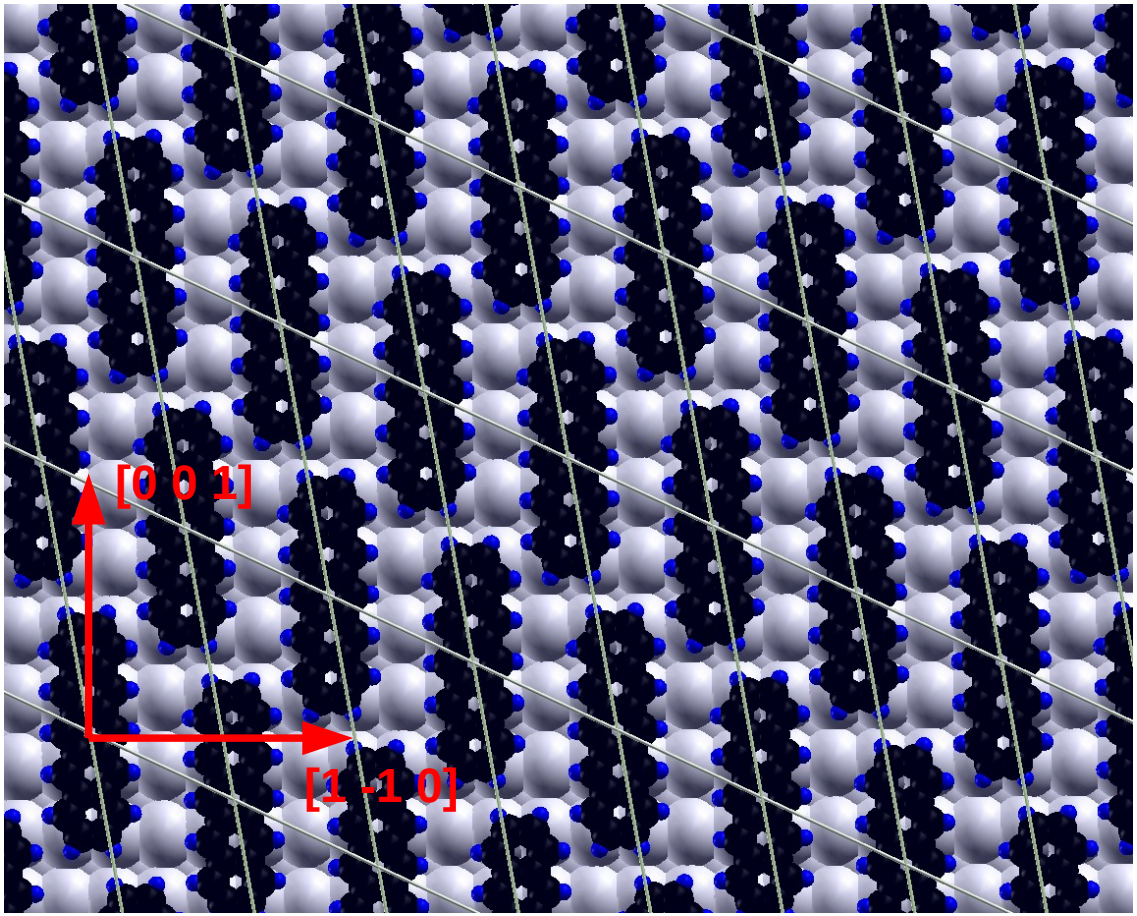
$$M = \begin{pmatrix} 3 & -1 \\ -1 & 4 \end{pmatrix}$$

  from LEED measurments

- 5A molecules orientated along

  [0 0 1] direction of Ag substrate

- $d_{Ag\text{-}5A}$ = 2.6 [Å]

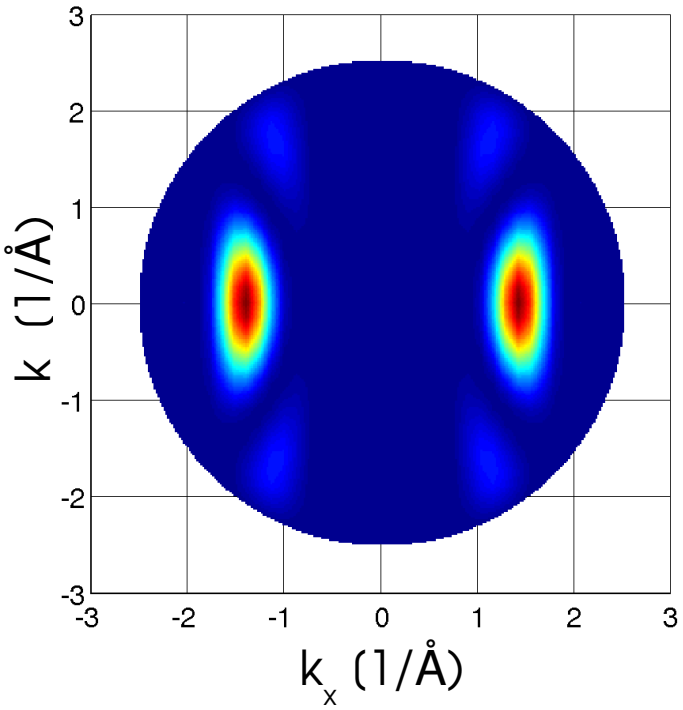


5A / Ag(110): LUMO

theory

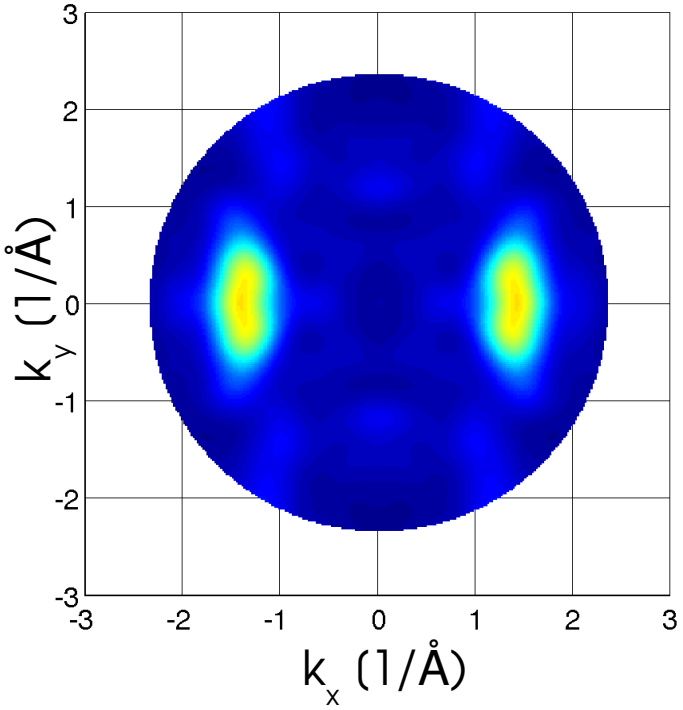
experiment

Isolated molecule

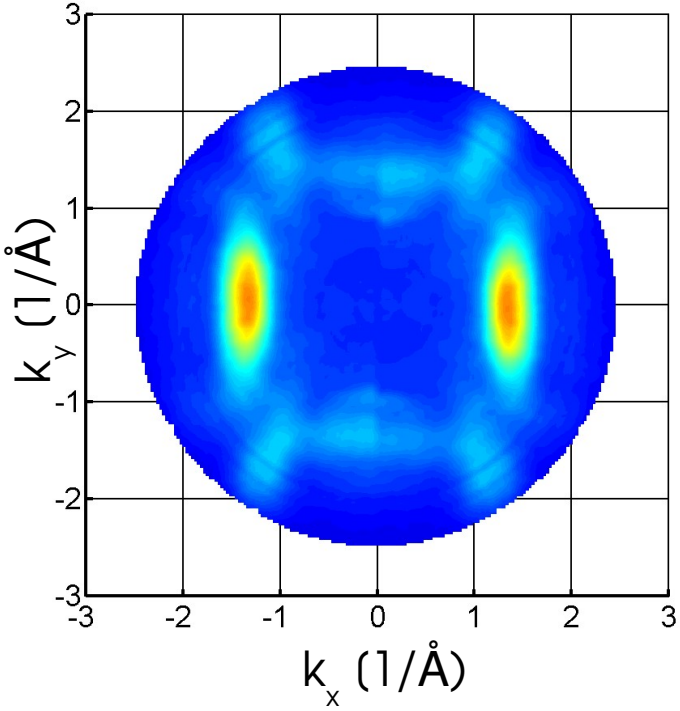


LUMO

5A/Ag(110)



E_b = -0.1 [eV]



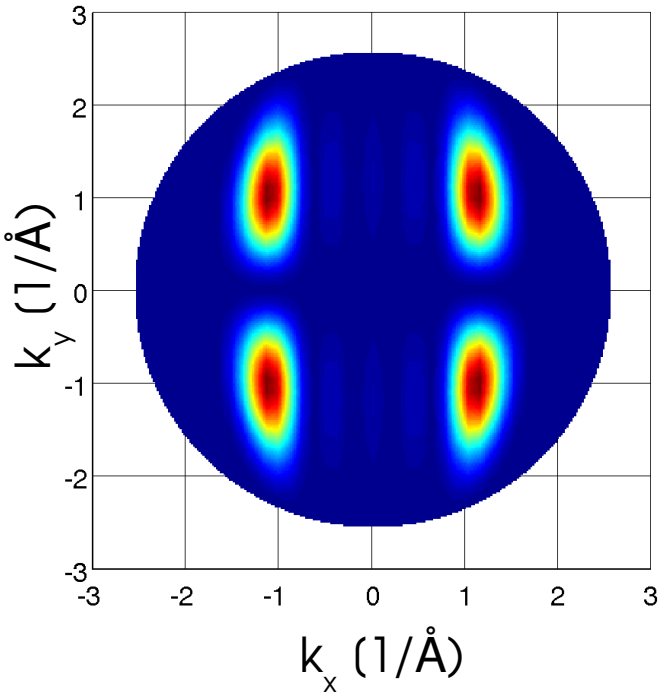
E_b = -0.1 [eV]

5A / Ag(110): HOMO

theory

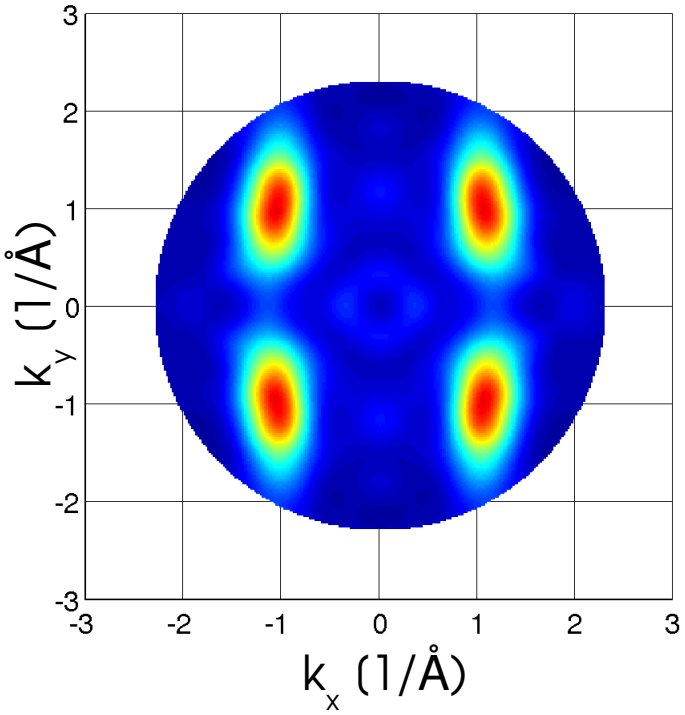
experiment

Isolated molecule

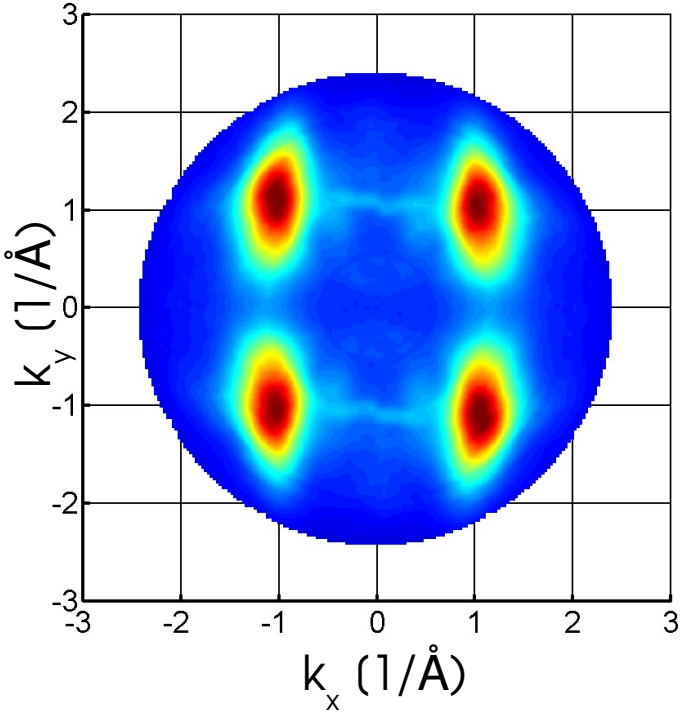


HOMO

5A/Ag(110)



E_b = -1.1 [eV]



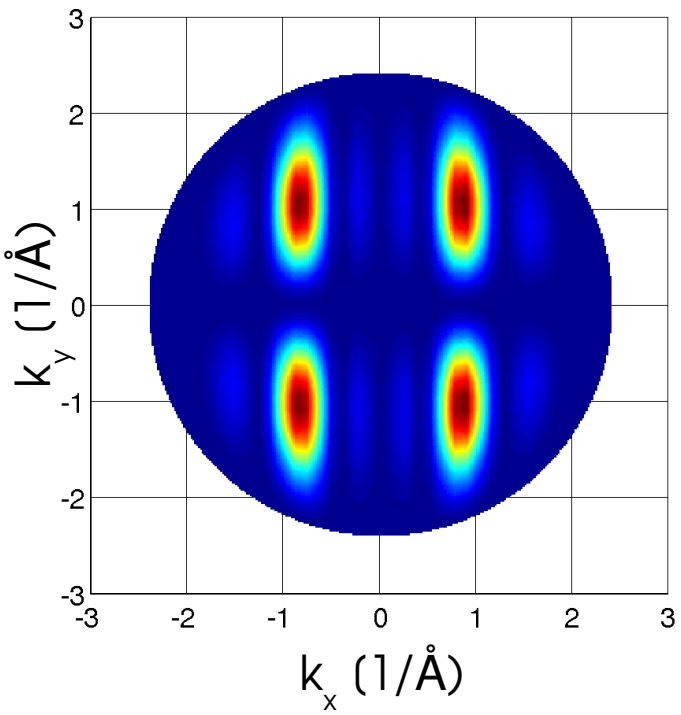
E_b = -1.2 [eV]

5A / Ag(110): HOMO-1

theory

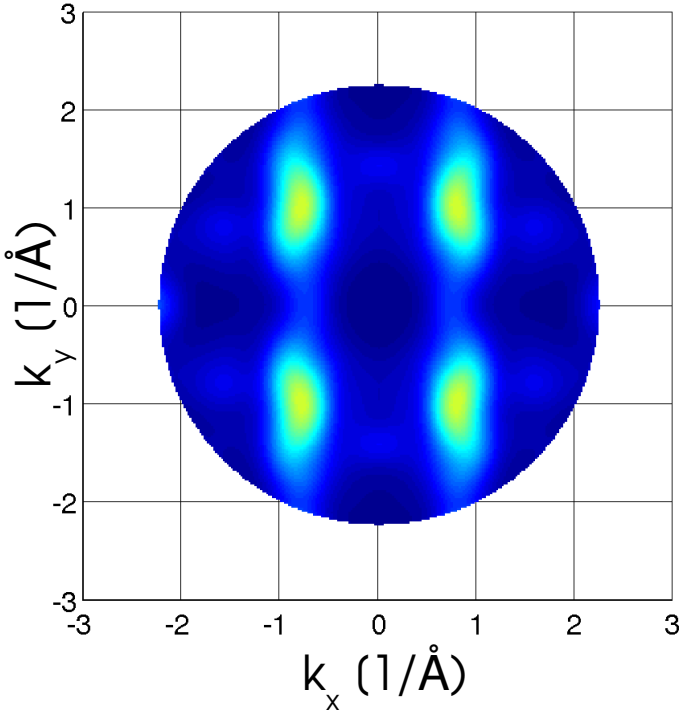
experiment

Isolated molecule

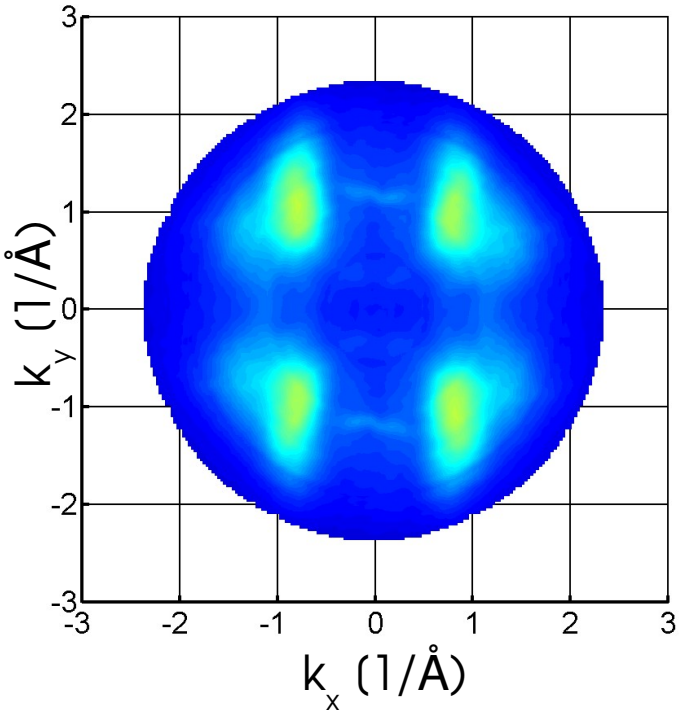


HOMO-1

5A/Ag(110)



E_b = -2.1 [eV]



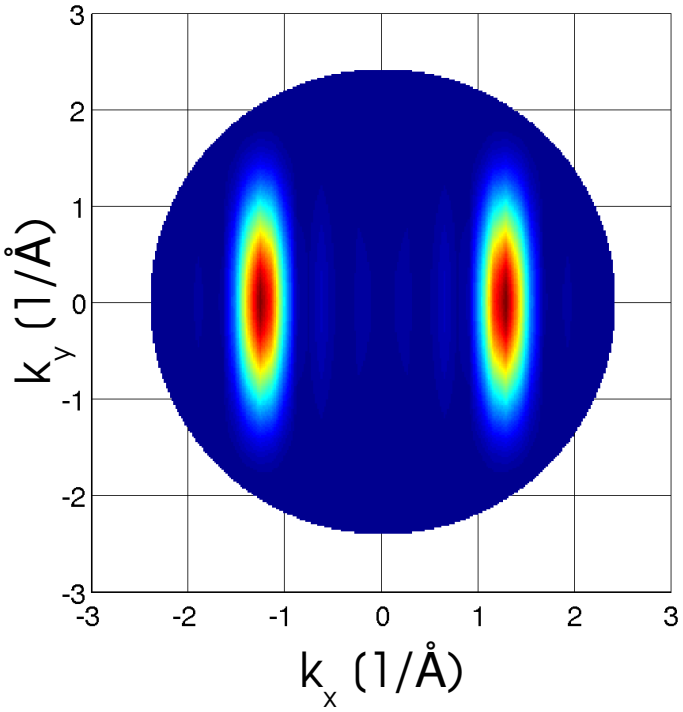
E_b = -2.4 [eV]

5A / Ag(110): HOMO-2

theory

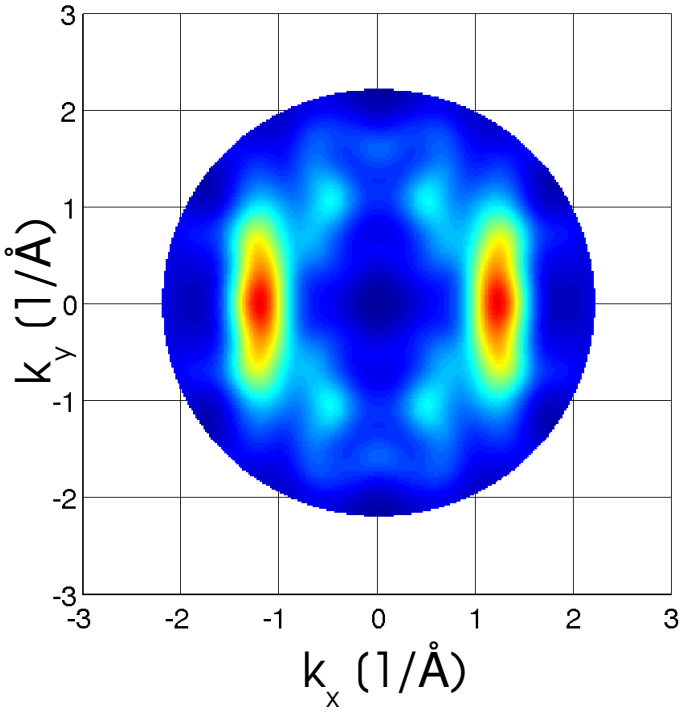
experiment

Isolated molecule

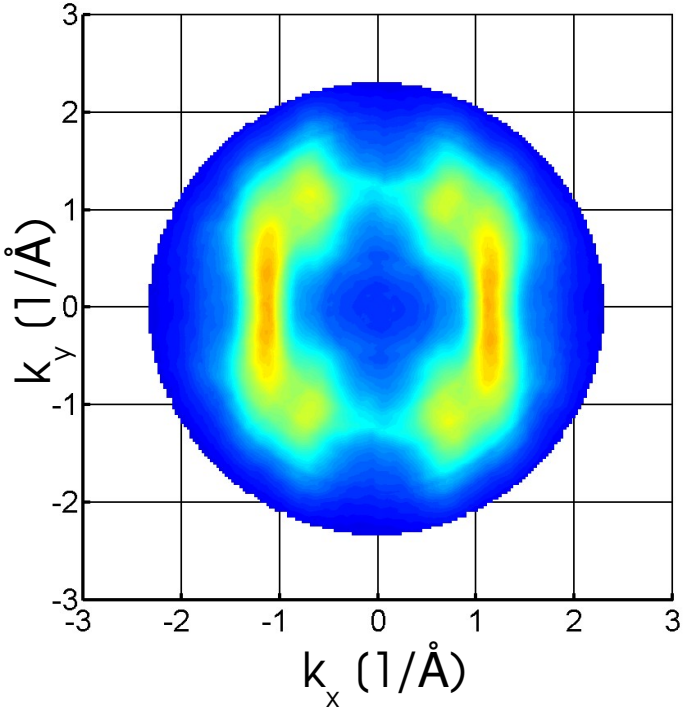


HOMO-2

5A/Ag(110)



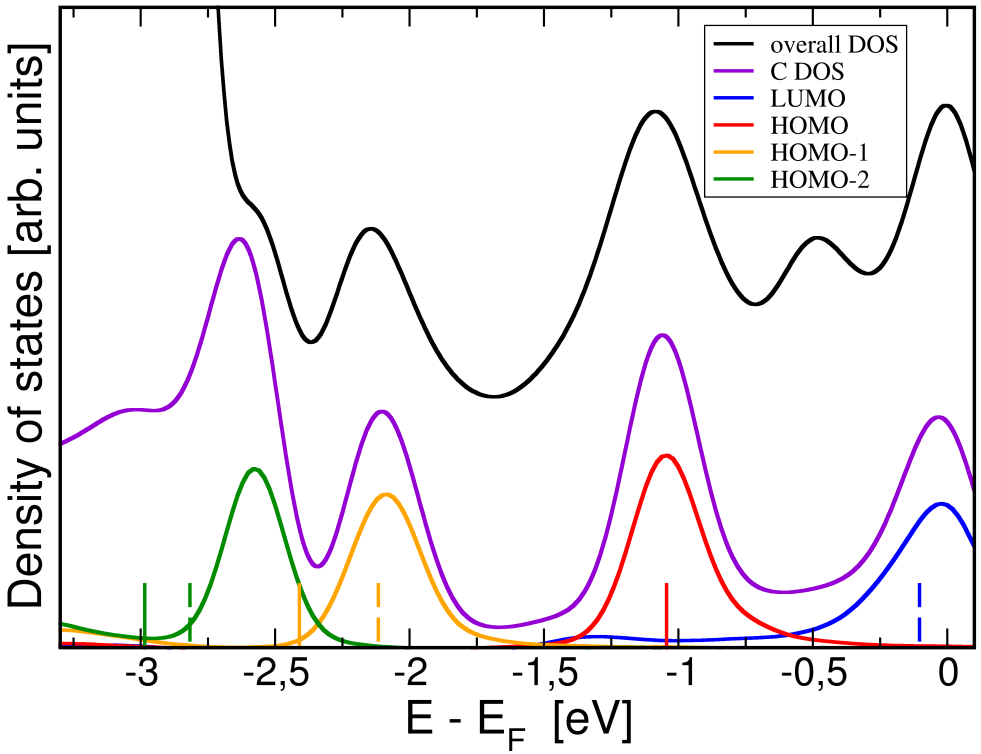
E_b = -2.6 [eV]



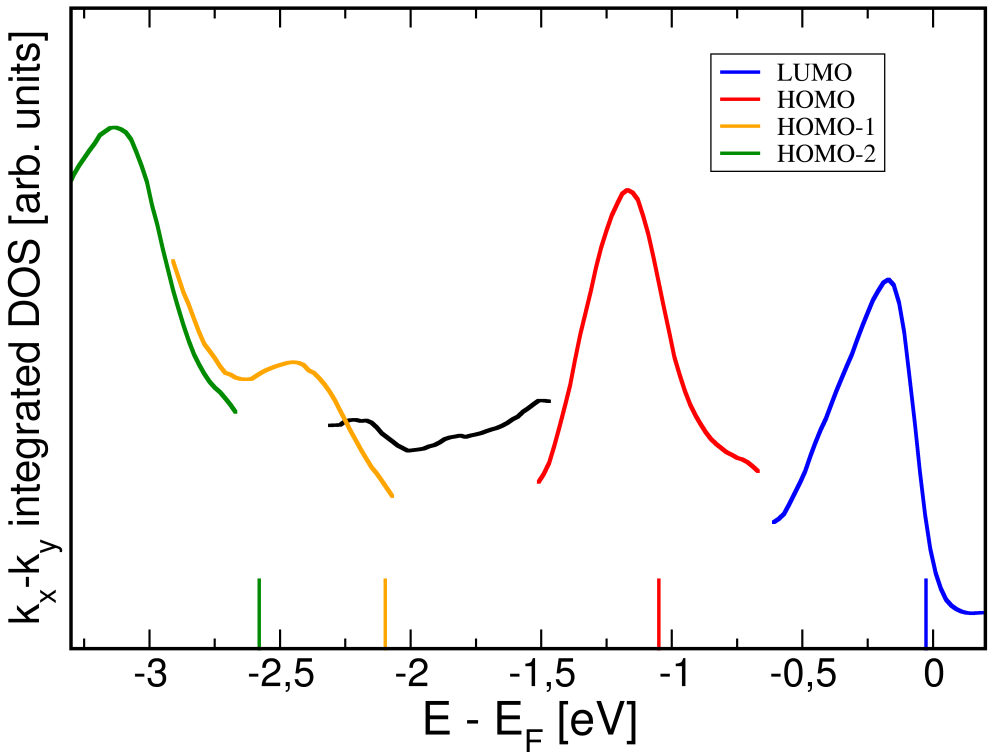
E_b = -3.1 [eV]

5A / Ag(110): DOS

theory



experiment



$$\rho_{\Phi_i}(E) = \sum_n |\langle \Phi_i | \psi_{n\vec{k}} \rangle|^2 \delta(E - \epsilon_n)$$

Pentacene on Cu(110)

- Epitaxial matrix

$$M = \begin{pmatrix} 6.5 & -1 \\ -0.5 & 2 \end{pmatrix}$$

from LEED measurement

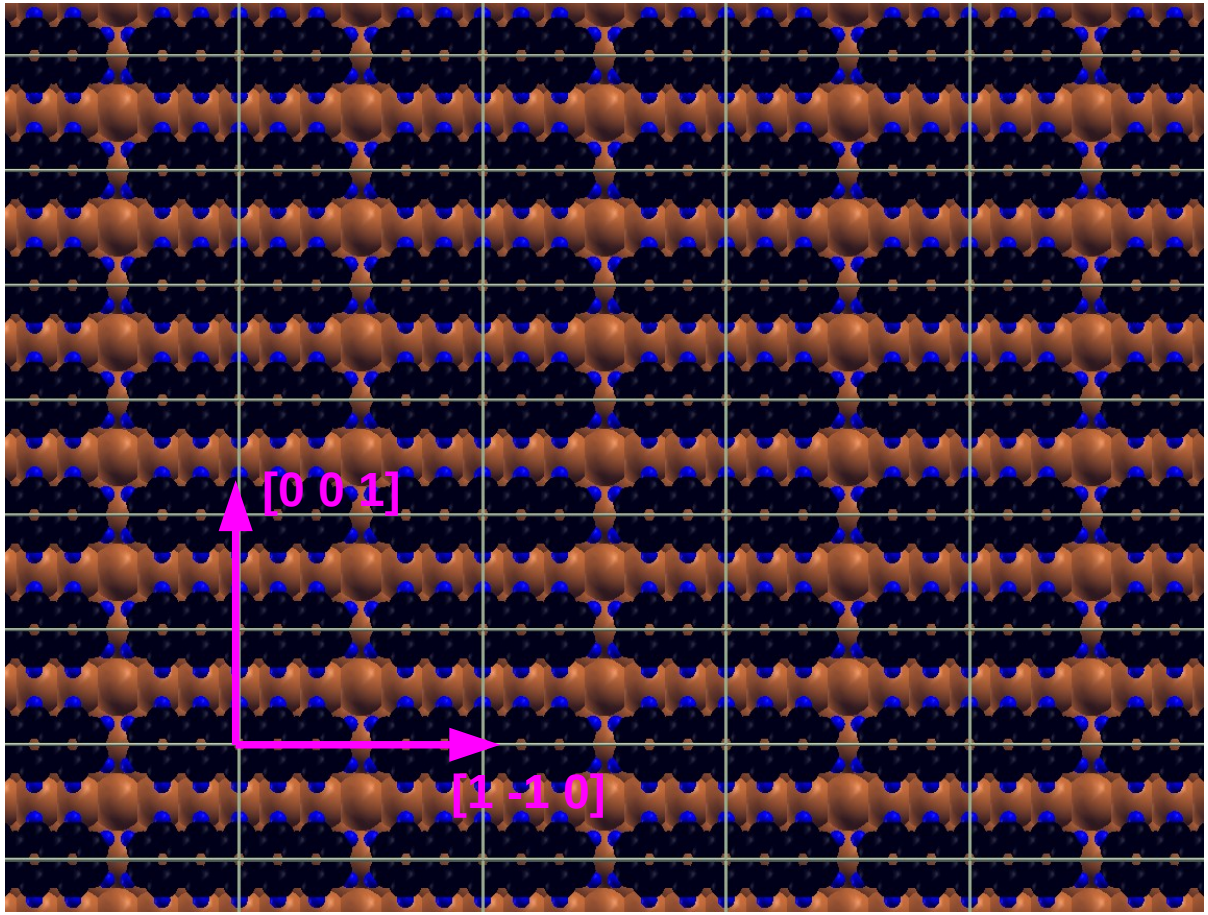
$$M = \begin{pmatrix} 6 & 0 \\ 0 & 2 \end{pmatrix}$$

from Ref [1]

- 5A molecules orientated along

  [1 -1 0] direction of Ag substrate

- $d_{CU\text{-}5A}$ = 2.25 [Å]



[1] Crystal Growth & Design 2011 11 (4), 1015-1020

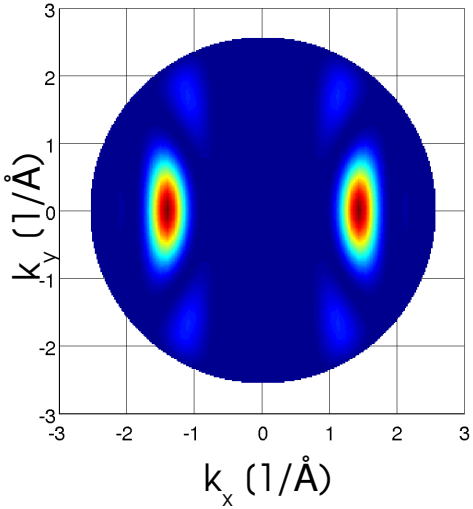
5A / Cu(110): LUMO

theory

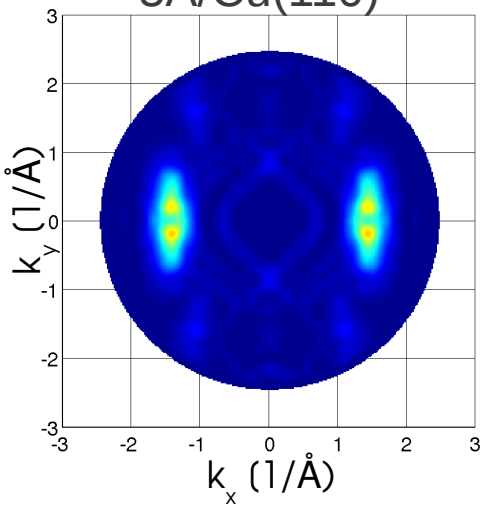
experiment

5A/Cu(110)

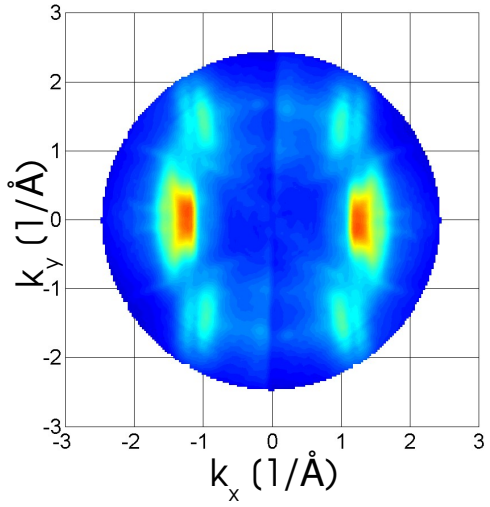
Isolated molecule



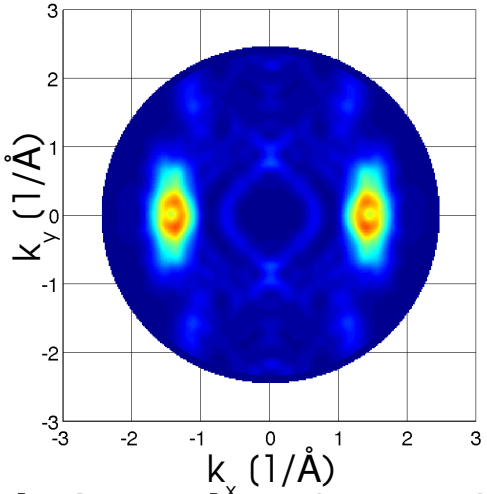
LUMO



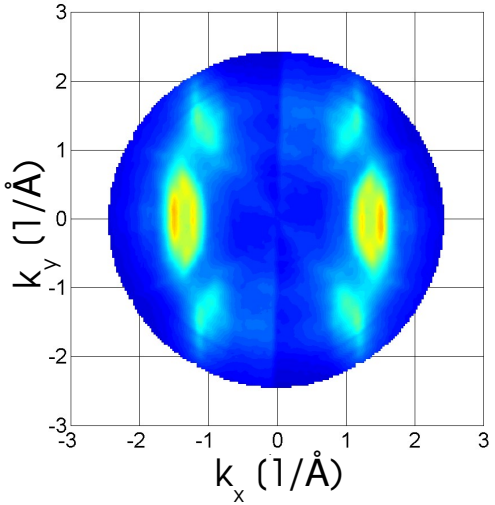
E_b = -0.05 [eV]



E_b = -0.6 [eV]



E_b = -0.15 [eV]



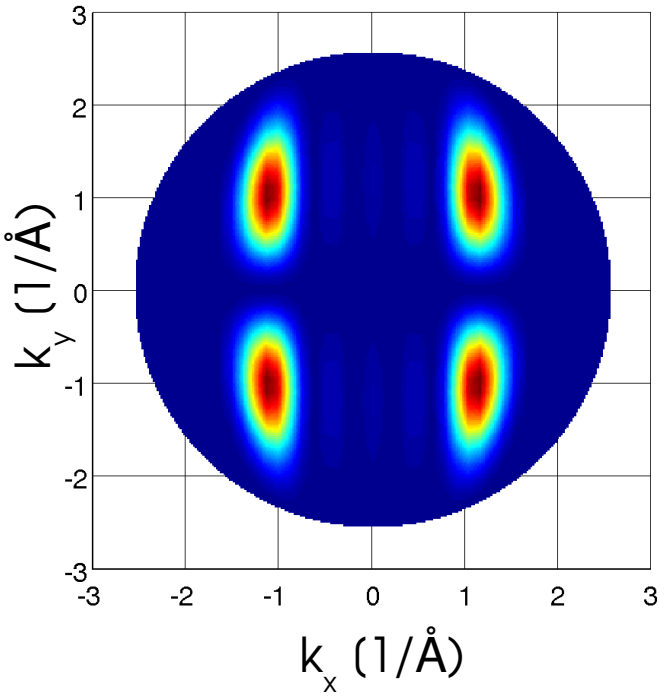
E_b = -0.9 [eV]

5A / Cu(110): HOMO

theory

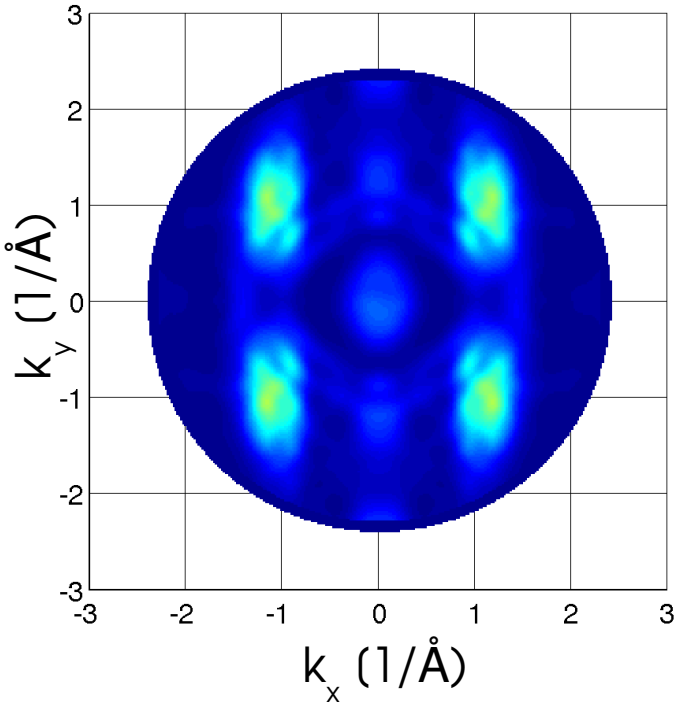
experiment

Isolated molecule

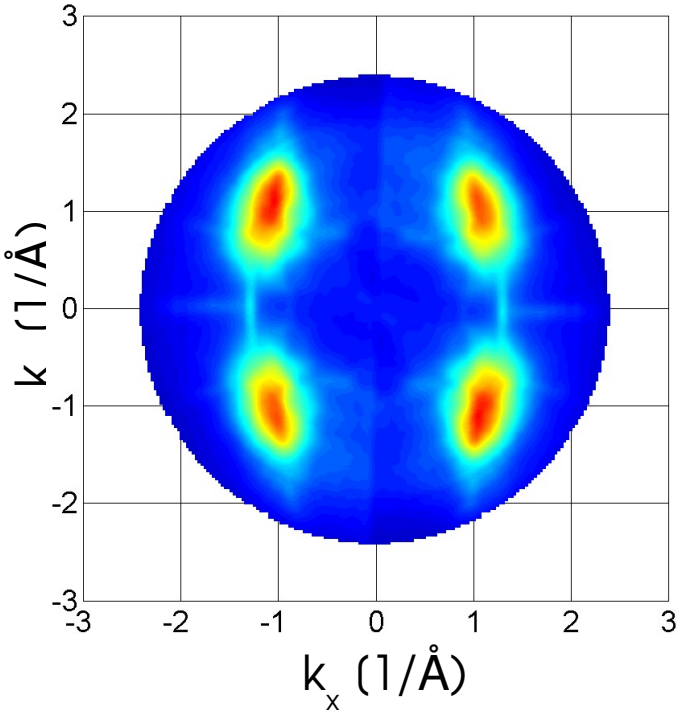


HOMO

5A/Cu(110)



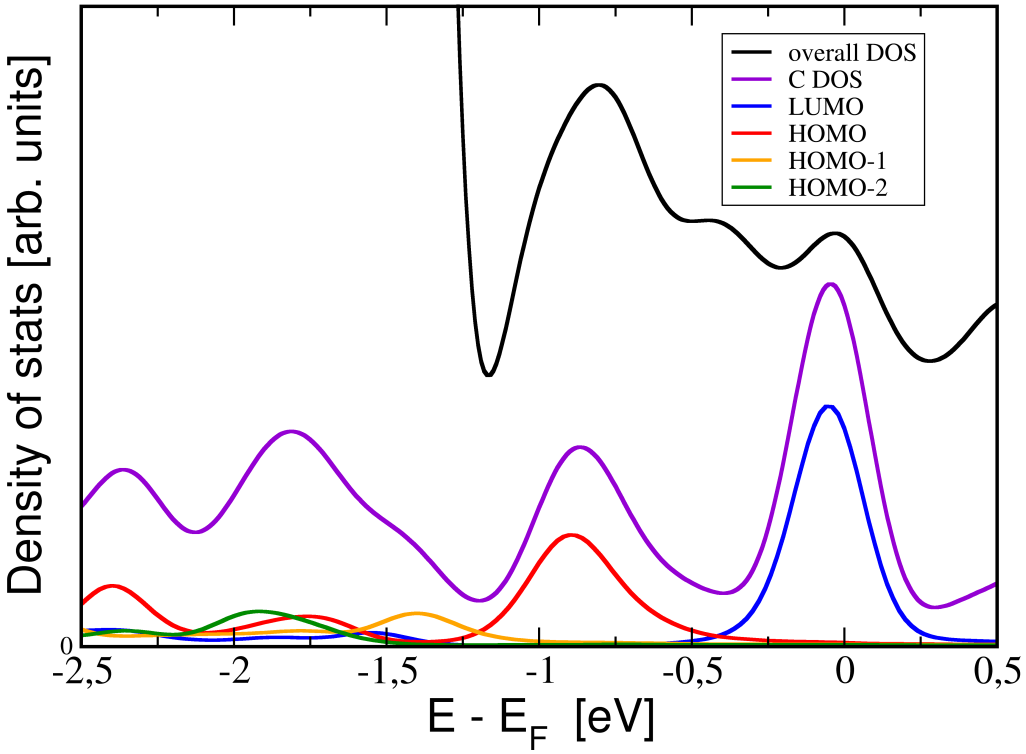
E_b = -0.9 [eV]



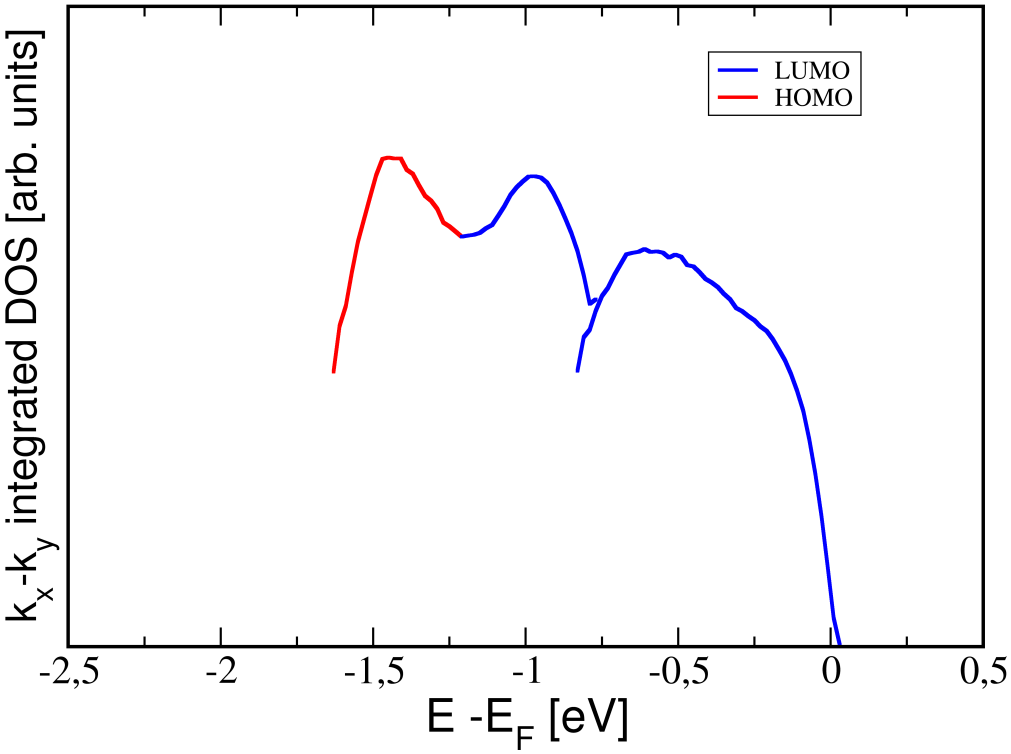
E_b = -1.5[eV]

5A / Cu(110): DOS

theory

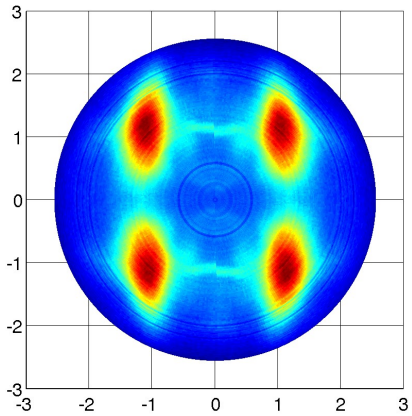


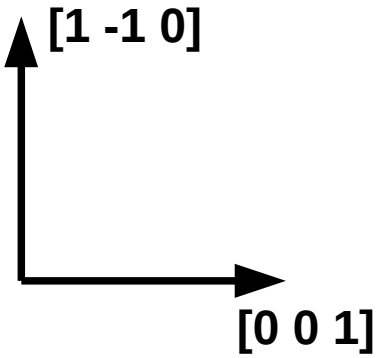
experiment



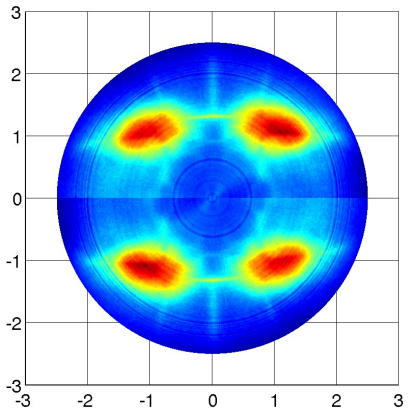
Reconstruction of wavefunction

Ag



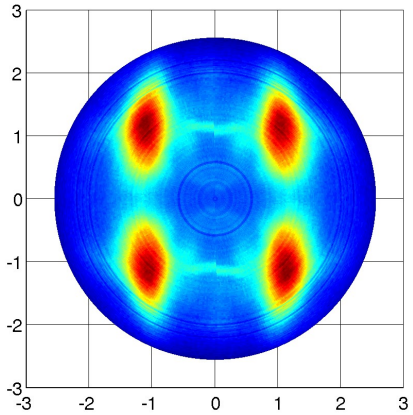


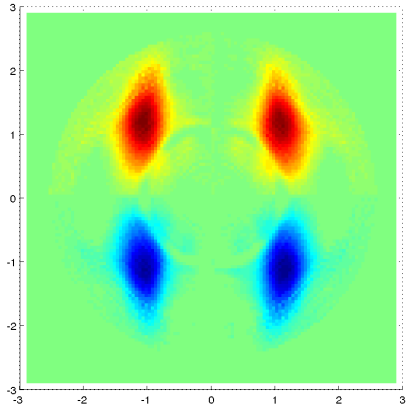
Cu



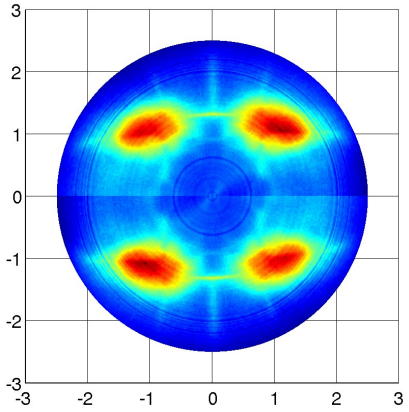
Reconstruction of wavefunction

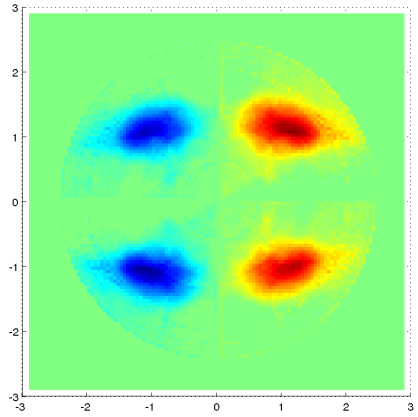
Ag





Cu



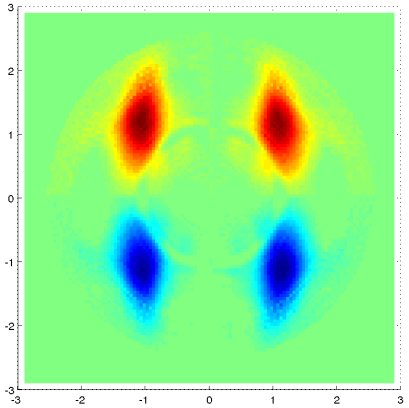


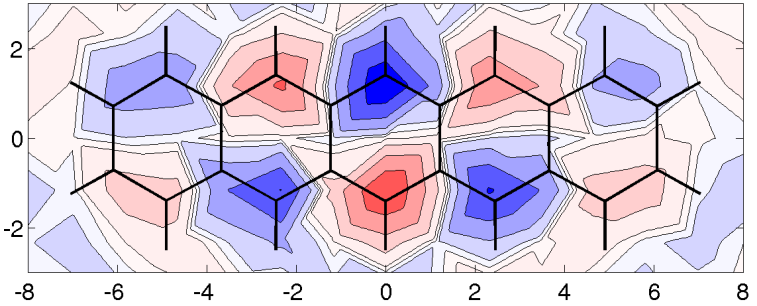
add phase information

subtract background

Reconstruction of wavefunction

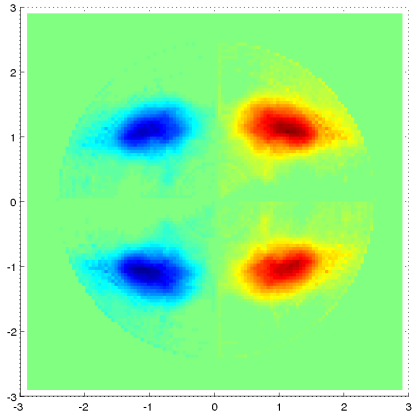
Ag

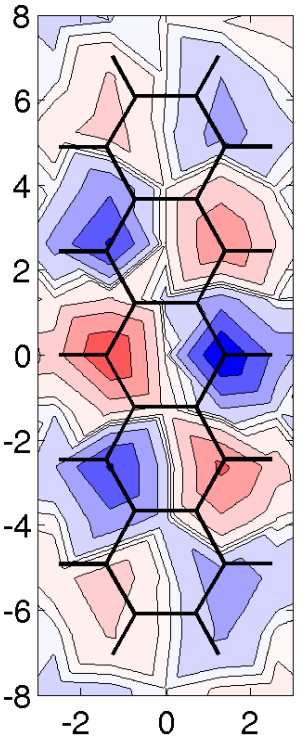




Inverse Fourier Transformation

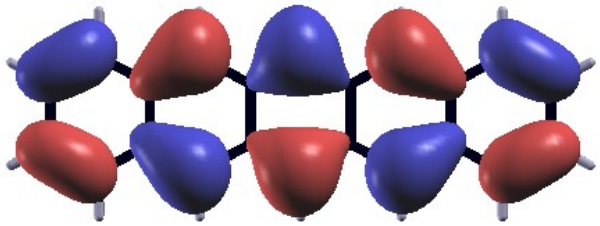
Cu

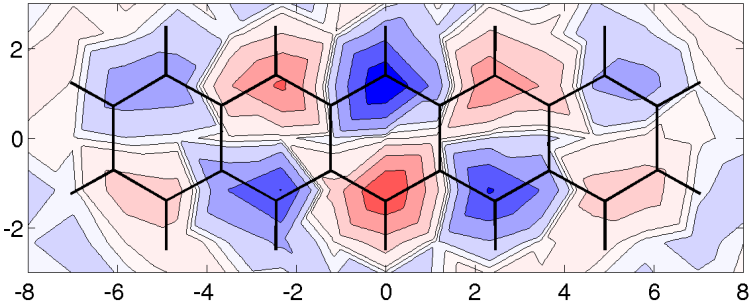




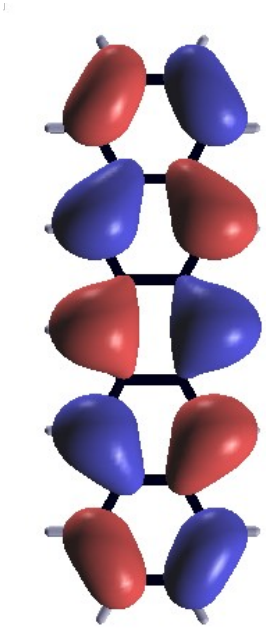
Reconstruction of wavefunction

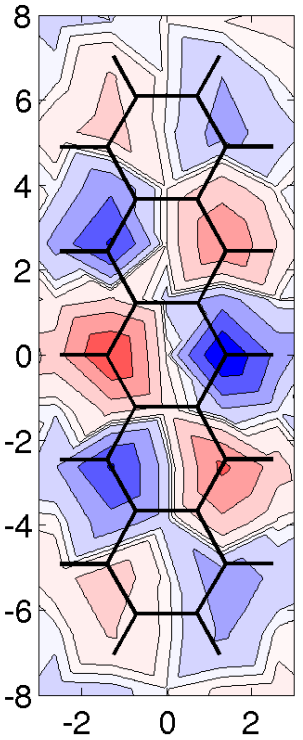
Ag





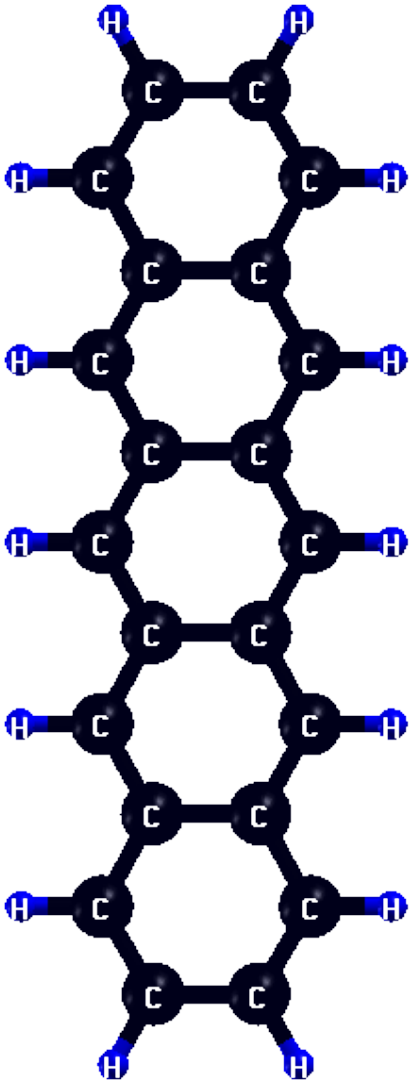
Cu





Conclusion

- G_0W_0 improves DFT results as expected
- Theoretical approach works good for the studied systems
- Interaction of 5A on copper stronger than on silver



Thank you for your attention