



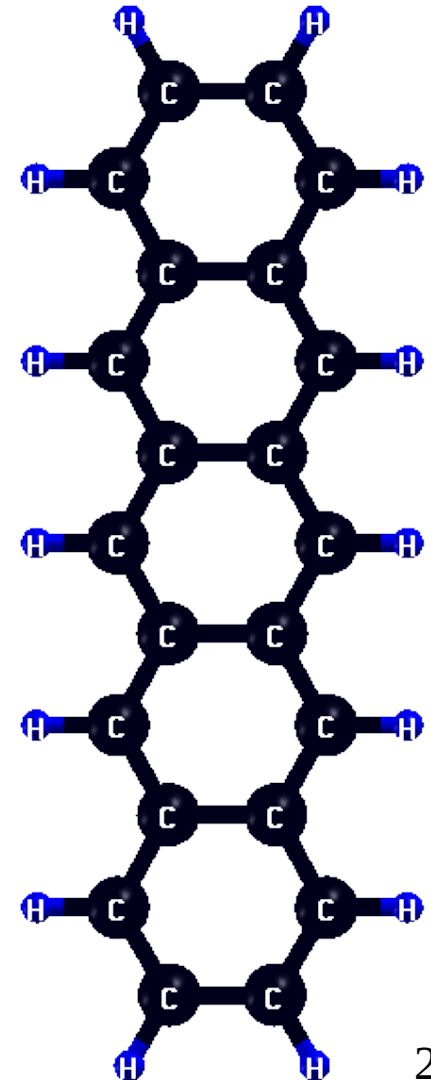
# The electronic structure of pentacene monolayers on Cu(110) and Ag(110) surfaces: DFT and $G_0W_0$ results vs. angle-resolved photoemission data

D. Lüftner<sup>1</sup>, T. Ules<sup>1</sup>, G. Koller<sup>1</sup>, M. Ramsey<sup>1</sup>, P. Puschnig<sup>1</sup>

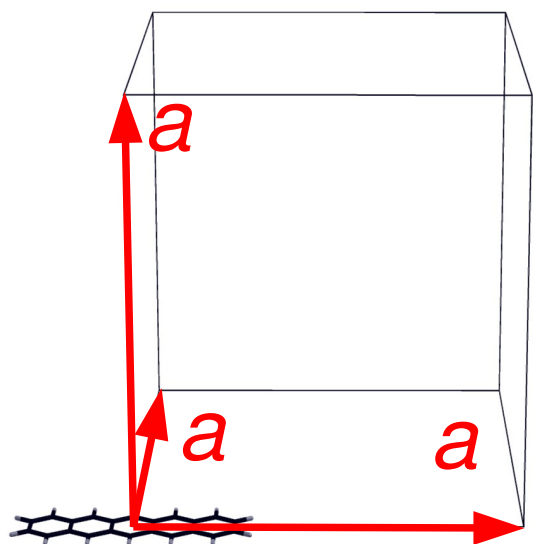
<sup>1</sup> University of Graz, Universitätsplatz 5, 8010 Graz, Austria

# Overview

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



# Isolated molecule

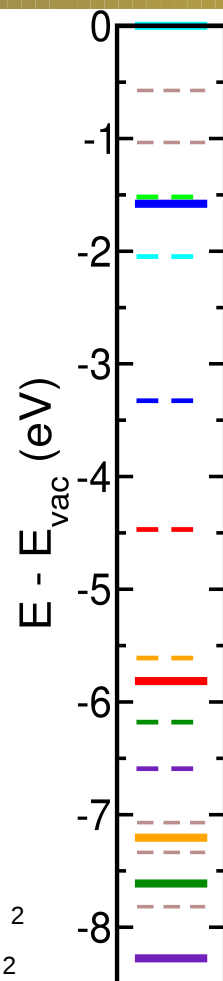


----- GGA  
—————  $G_0W_0$

experimental  $E_g = 5.2$  [eV]<sup>1</sup>

GGA  $E_g = 1.15$  [eV] comp.  $E_g = 1.1$  [eV]<sup>2</sup>

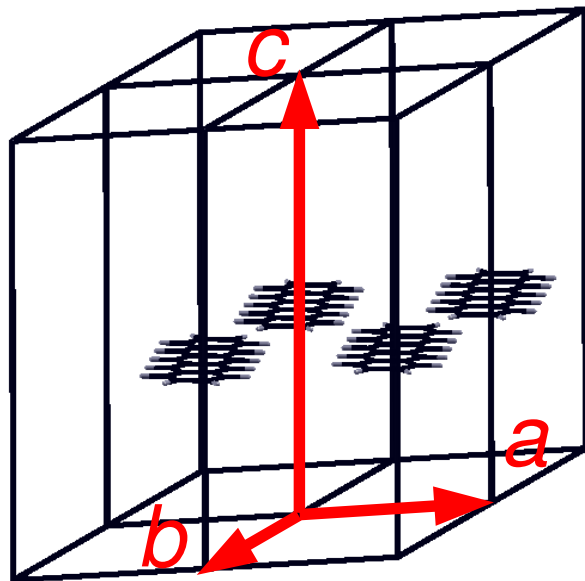
$G_0W_0$   $E_g = 4.2$  [eV] comp.  $E_g = 4.5$  [eV]<sup>2</sup>



<sup>1</sup> Organic Molecular Solids, Wiley-VCH Verlag GmbH, 2008, 217-305

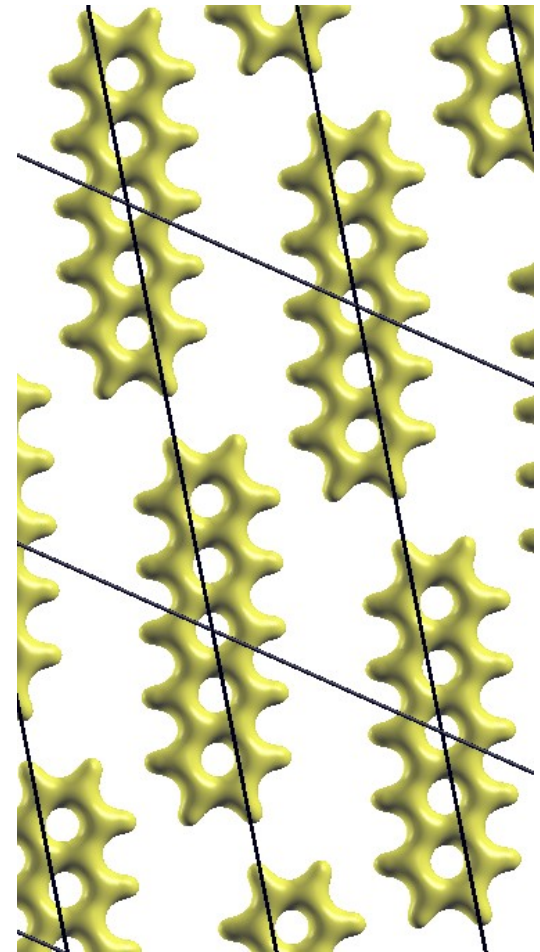
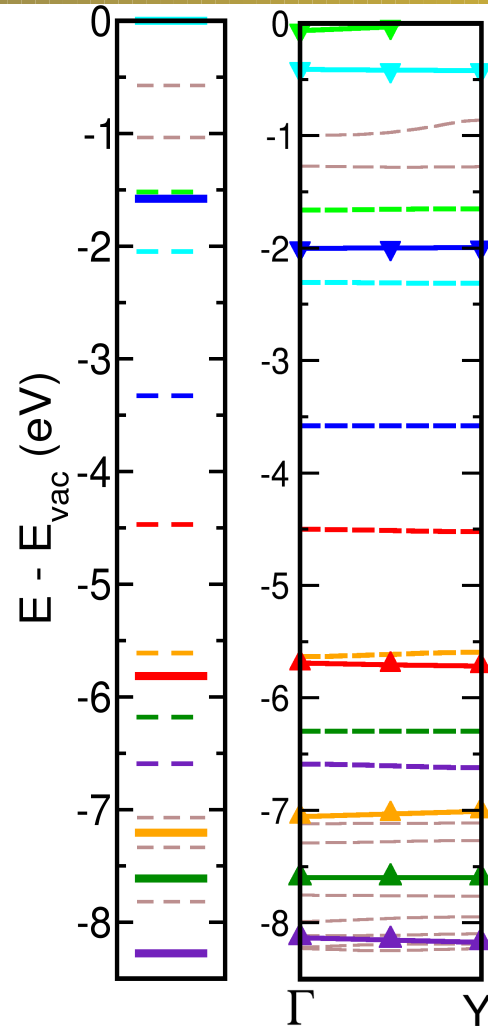
<sup>2</sup> Scharifzadeh et al PRB 85, 125307 (2012)

# Freestanding Monolayer

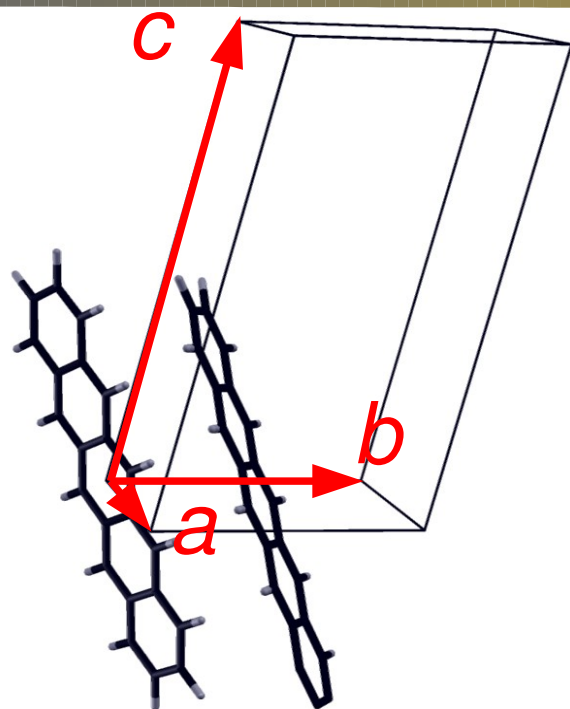


----- GGA  
—————  $G_0W_0$

GGA  $E_g = 0.9$  [eV]  
 $G_0W_0$   $E_g = 3.7$  [eV]



# Crystal bulk structure

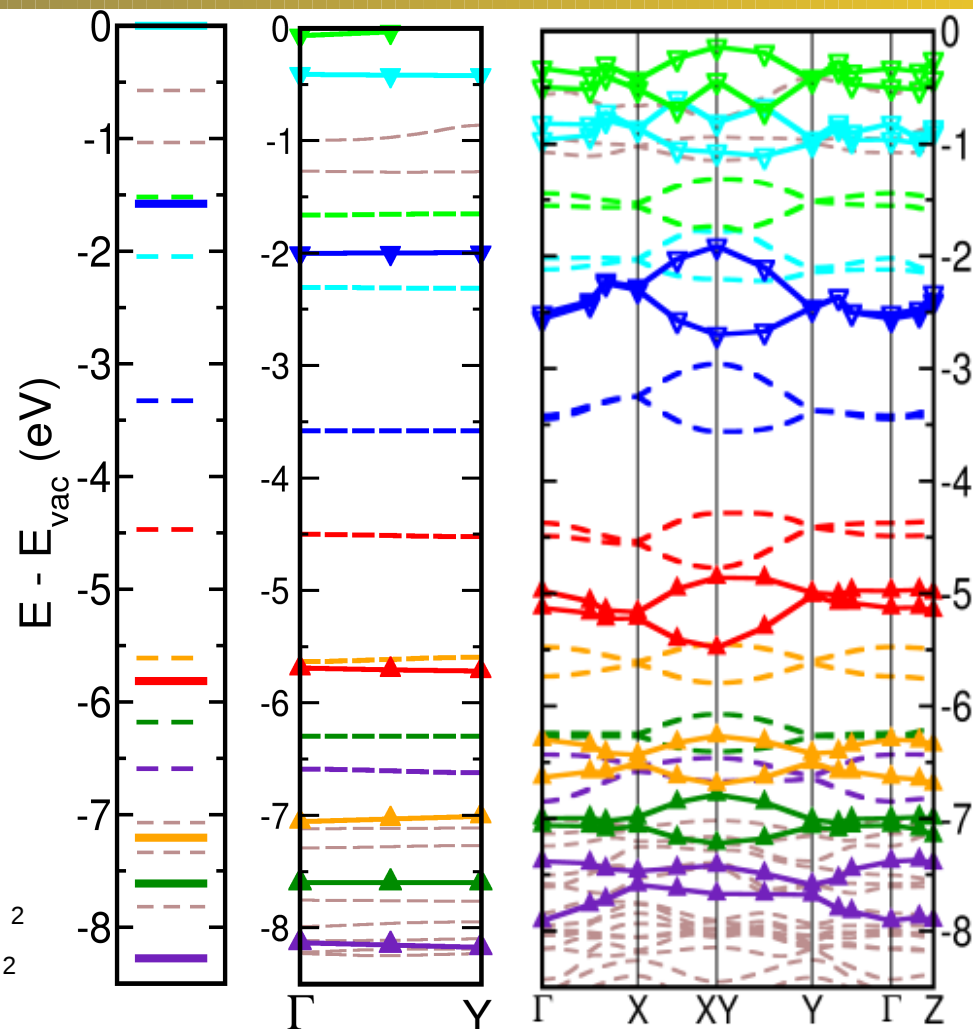


----- GGA  
 \_\_\_\_\_  $G_0W_0$

experimental  $E_g = 2.2$  [eV]<sup>1</sup>

GGA  $E_g = 0.8$  [eV] comp.  $E_g = 0.75$  [eV]<sup>2</sup>

$G_0W_0$   $E_g = 2.2$  [eV] comp.  $E_g = 2.2$  [eV]<sup>2</sup>



<sup>1</sup> Organic Molecular Solids, Wiley-VCH Verlag GmbH, 2008, 217-305

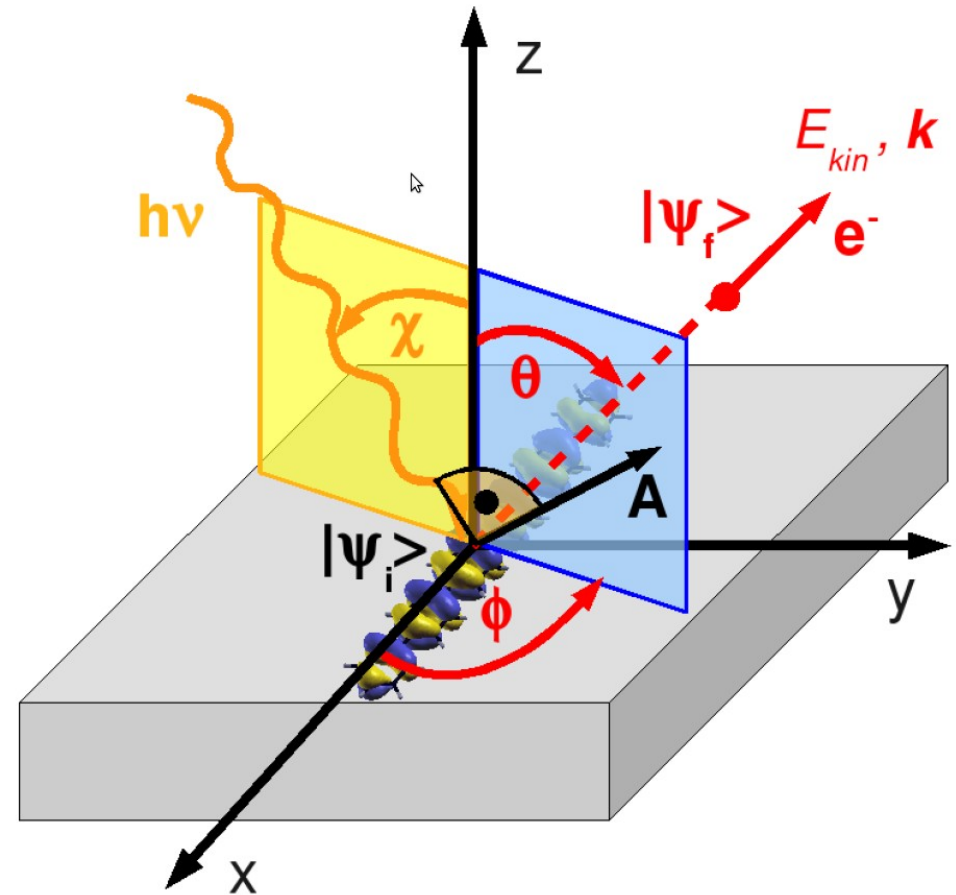
<sup>2</sup> PRB 85, 125307 (2012)

# 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:

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

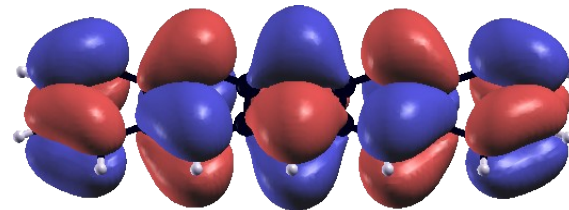
$$[p \cdot A] = -i \nabla \cdot A = 0$$

# 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

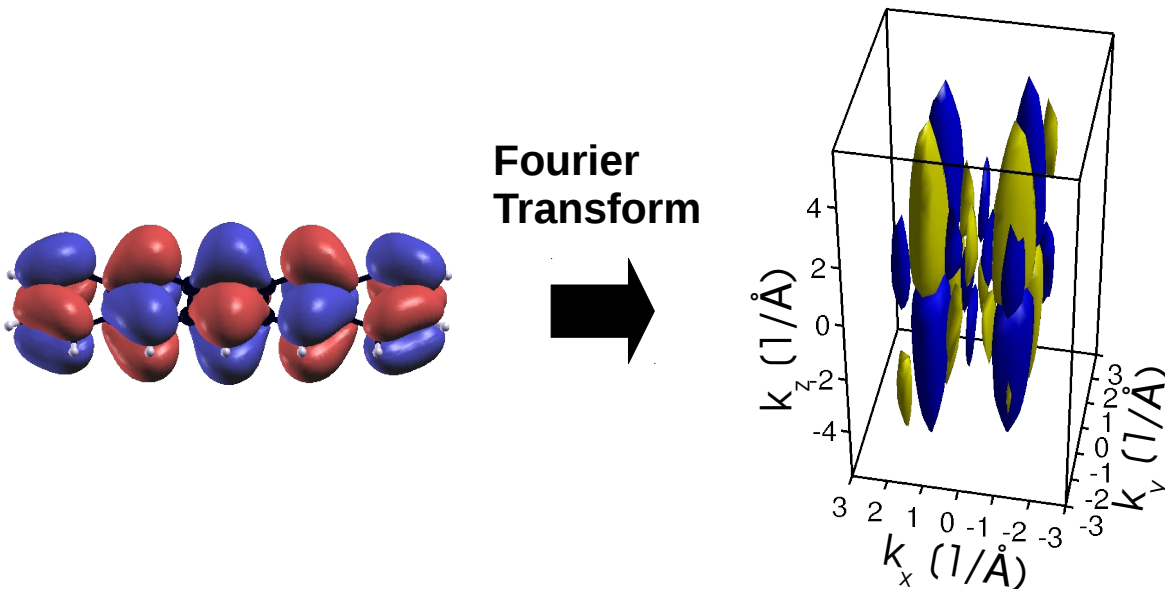


molecular orbital



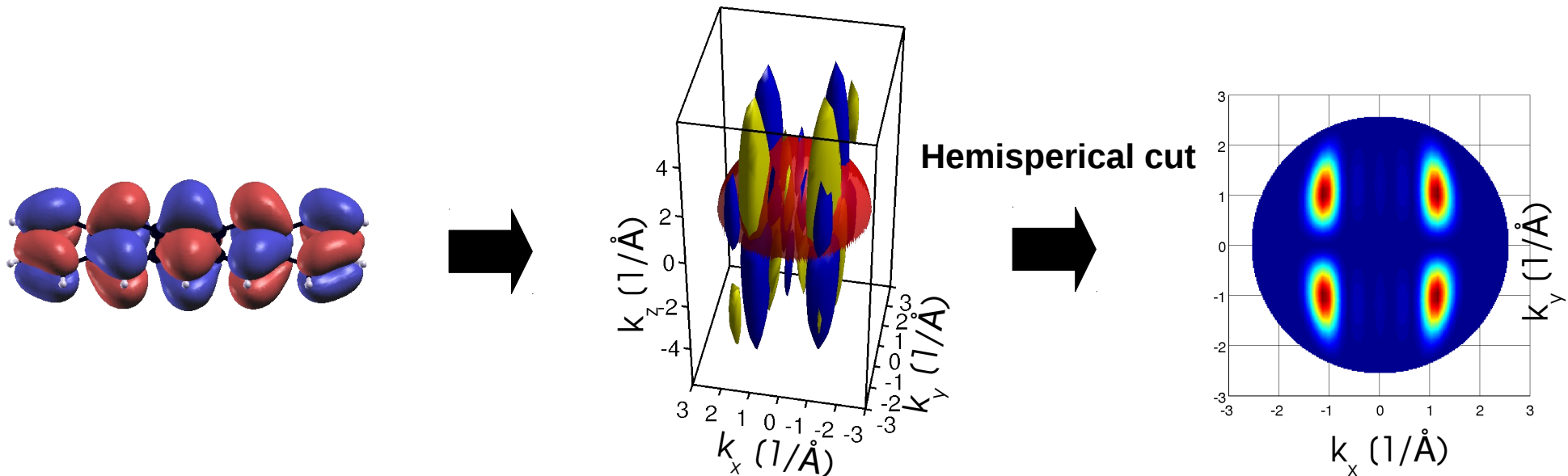
# Computation of Photoemission Intensity

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



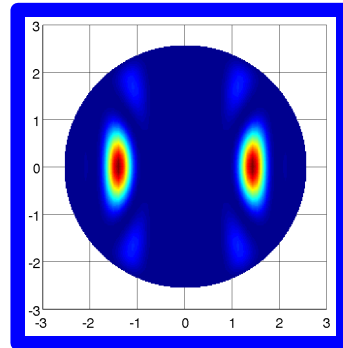
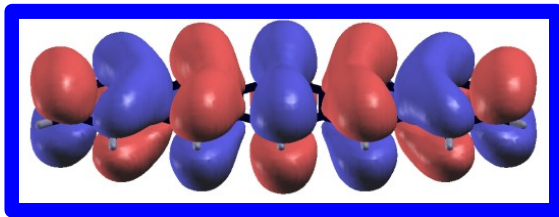
# Computation of Photoemission Intensity

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

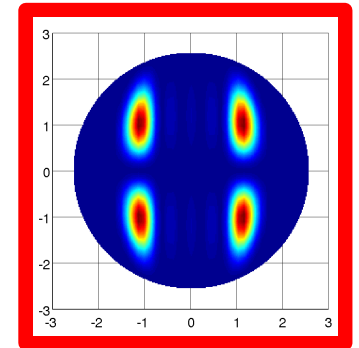
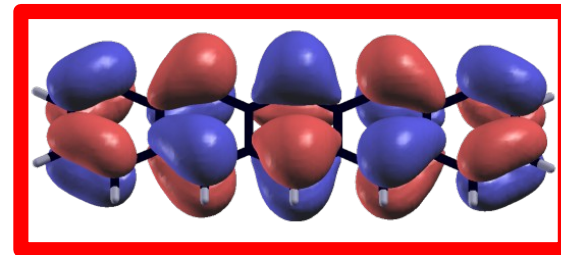


# Momentum maps for isolated molecule

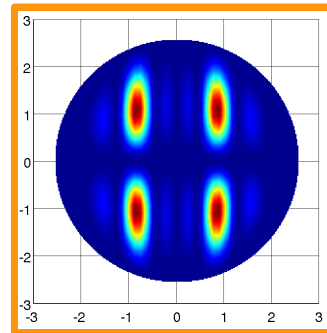
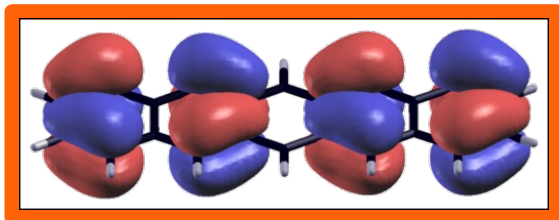
LUMO



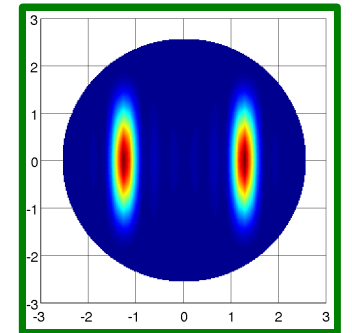
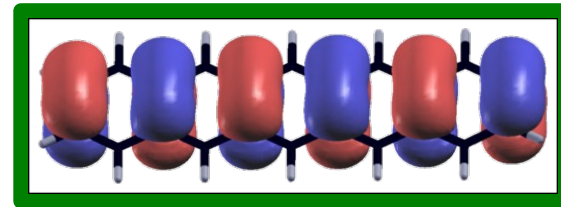
HOMO



HOMO-1



HOMO-2



# Pentacene on Ag(110)

- Epitaxial matrix

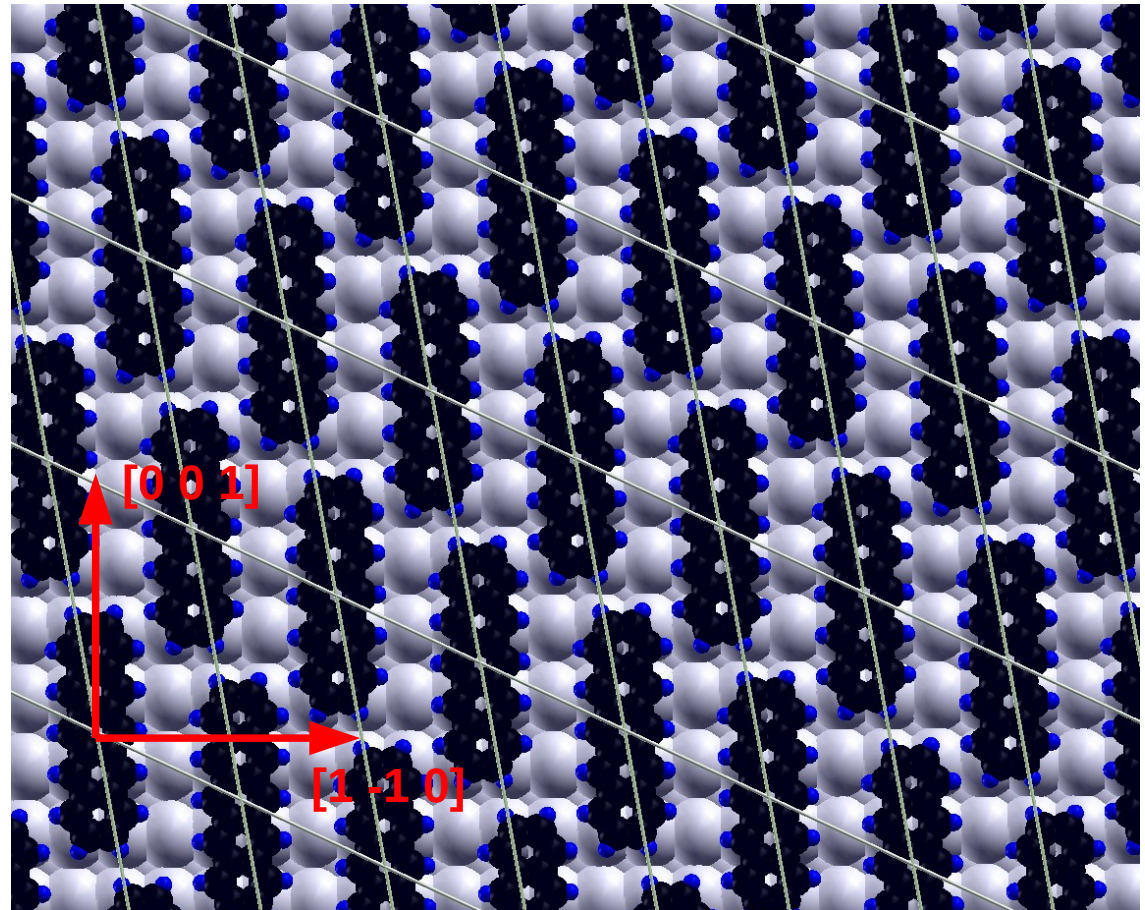
$$M = \begin{pmatrix} 3 & -1 \\ -1 & 4 \end{pmatrix}$$

from LEED measurements

- 5Å molecules orientated along

[0 0 1] direction of Ag substrate

- $d_{\text{Ag-5A}} = 2.6 \text{ [Å]}$



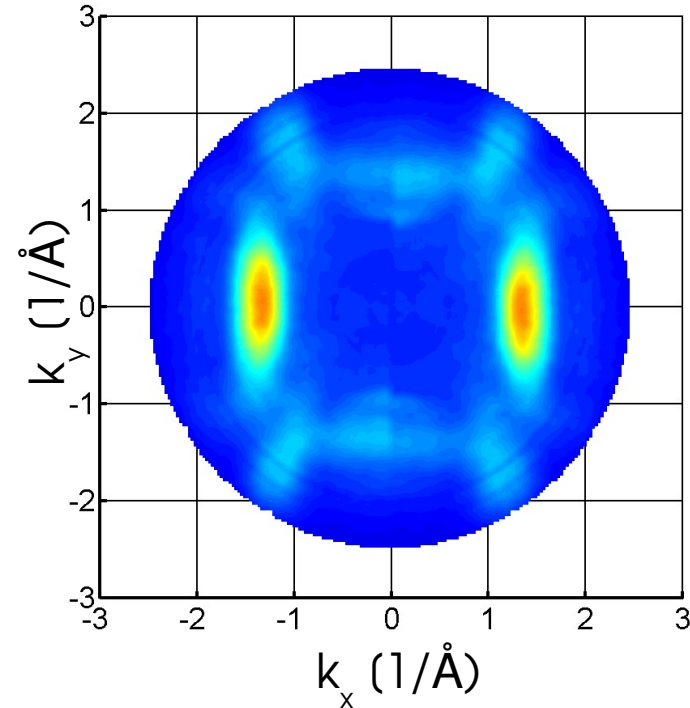
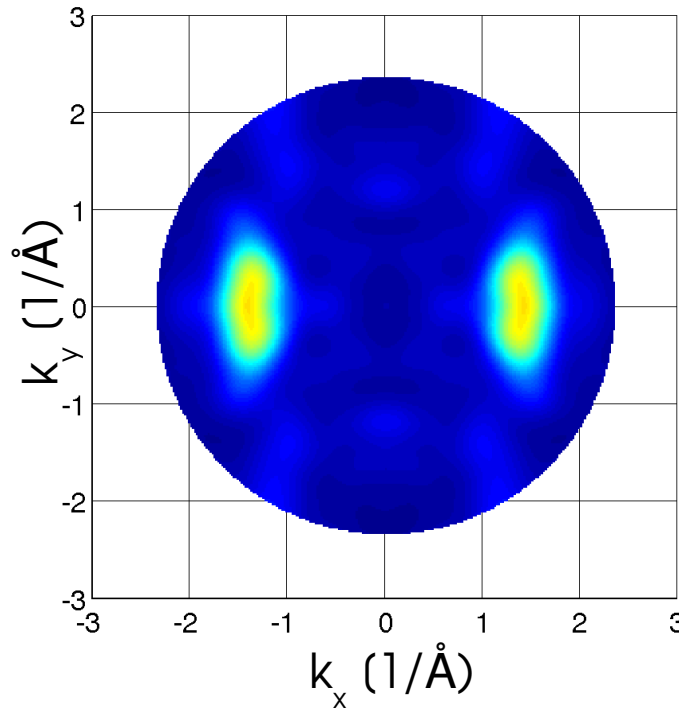
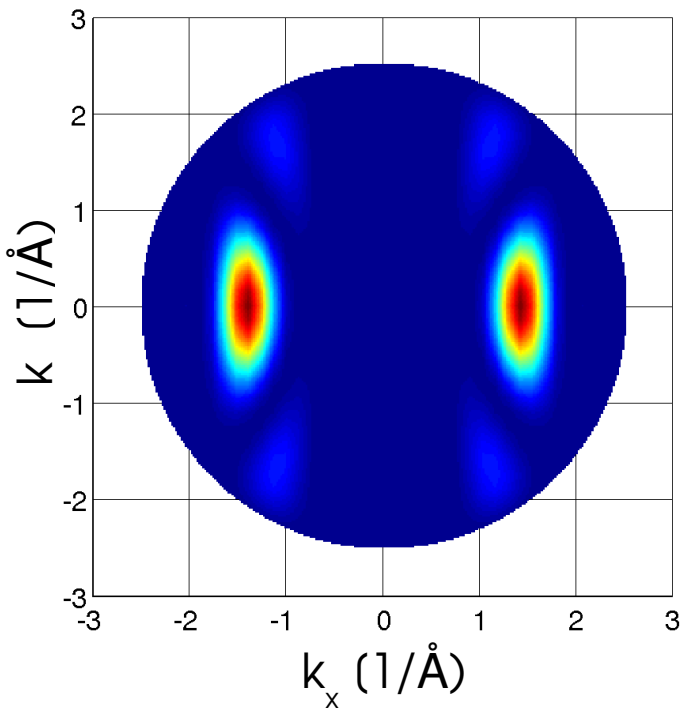
# 5A / Ag(110): LUMO

theory

experiment

Isolated molecule

5A/Ag(110)



LUMO

$E_b = -0.1$  [eV]

$E_b = -0.1$  [eV]

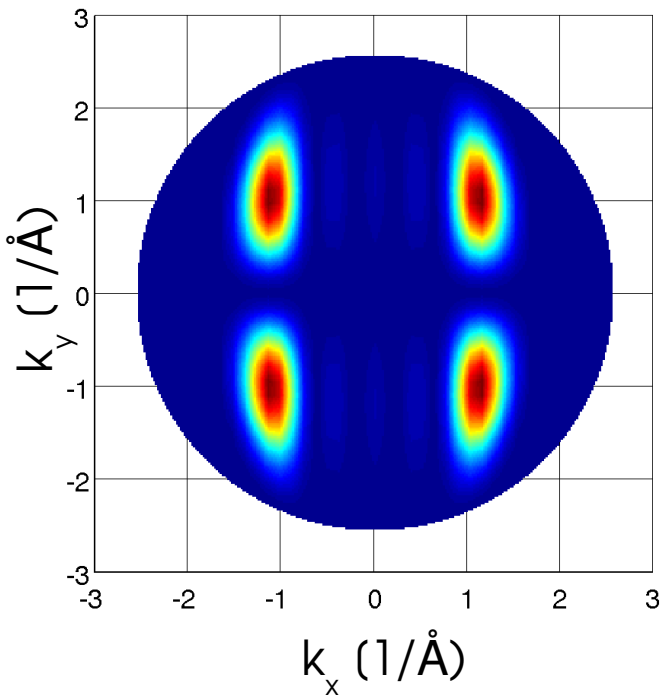
# 5A / Ag(110): HOMO

theory

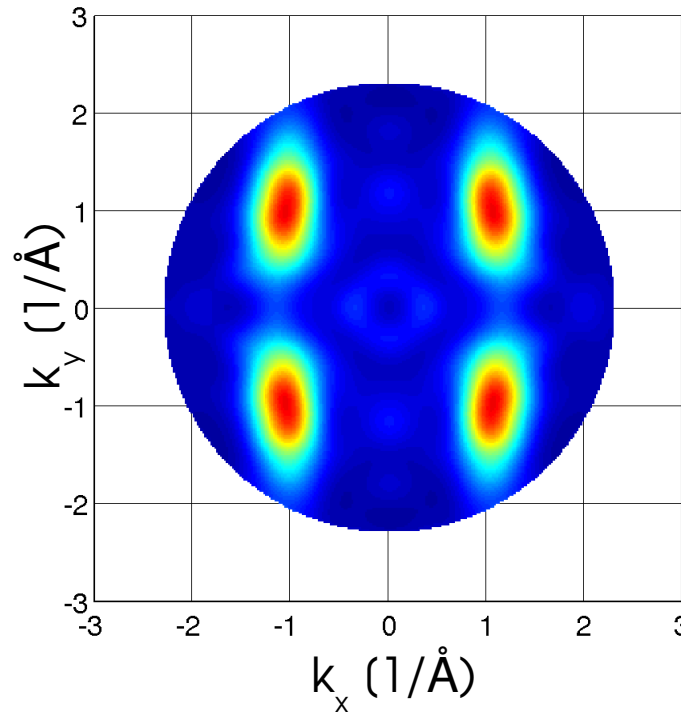
experiment

Isolated molecule

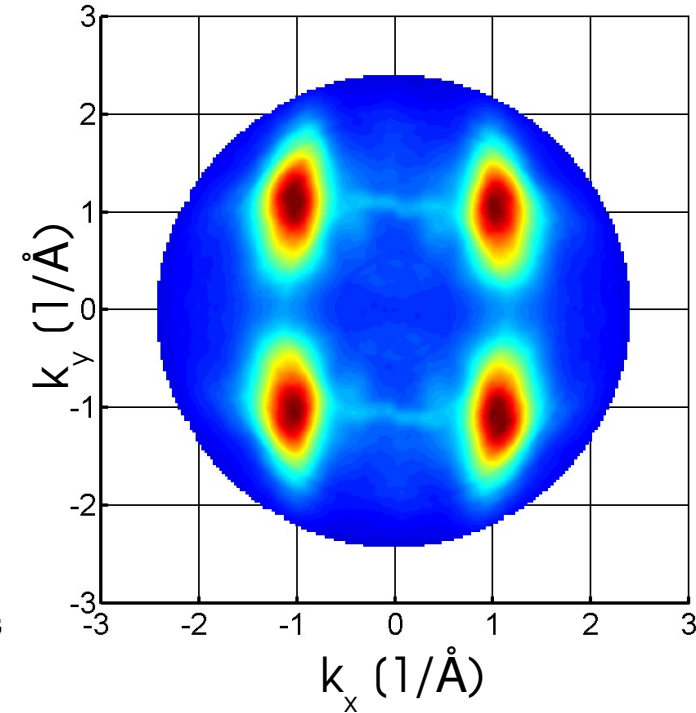
5A/Ag(110)



HOMO



$E_b = -1.1$  [eV]



$E_b = -1.2$  [eV]

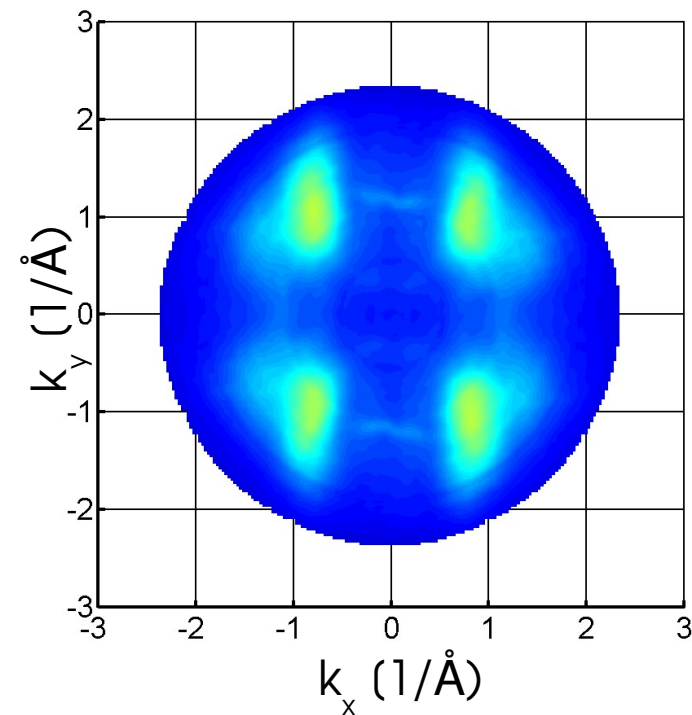
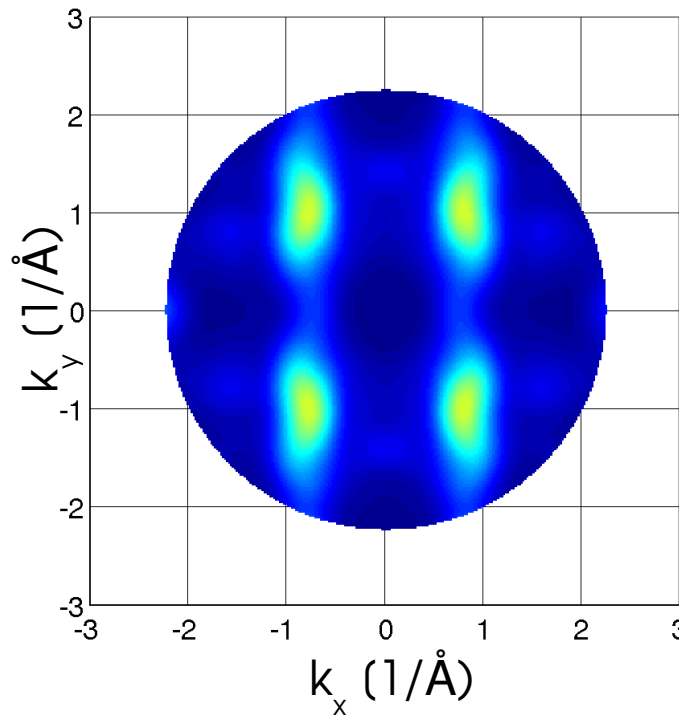
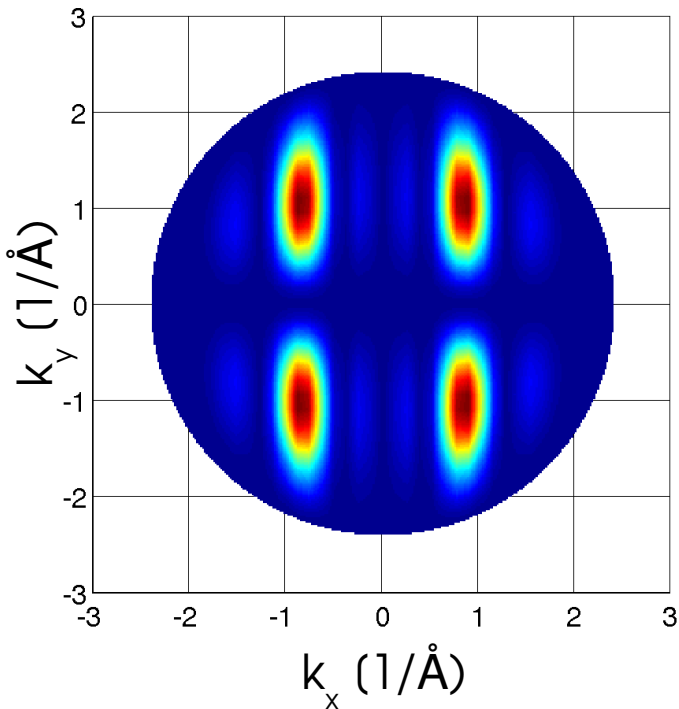
# 5A / Ag(110): HOMO-1

theory

experiment

Isolated molecule

5A/Ag(110)



HOMO-1

$E_b = -2.1$  [eV]

$E_b = -2.4$  [eV]

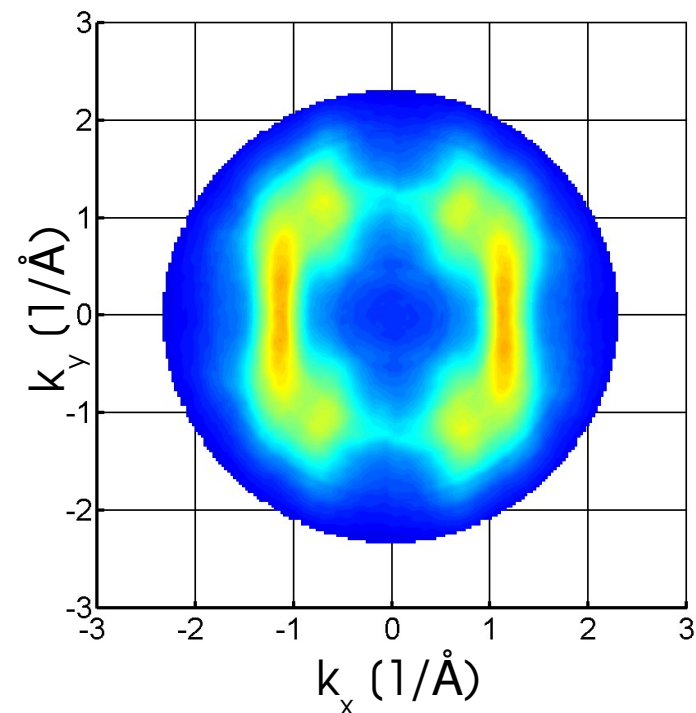
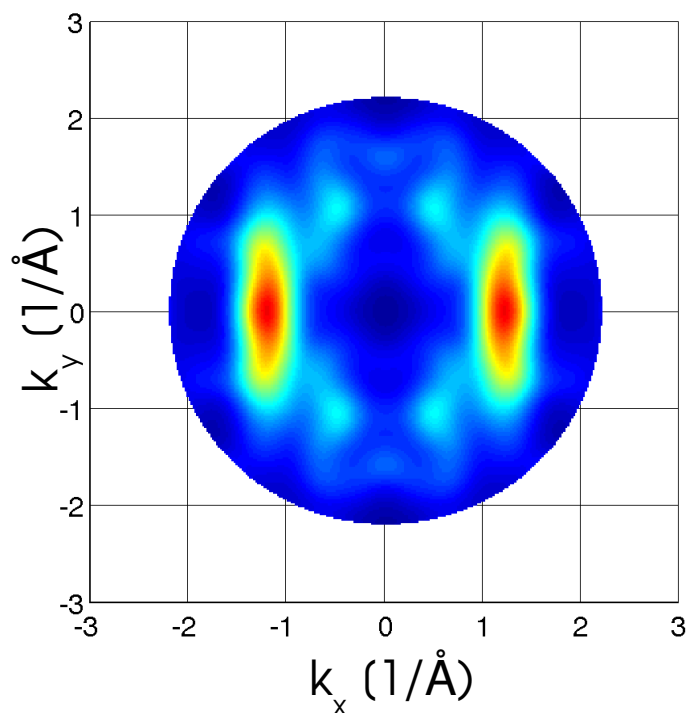
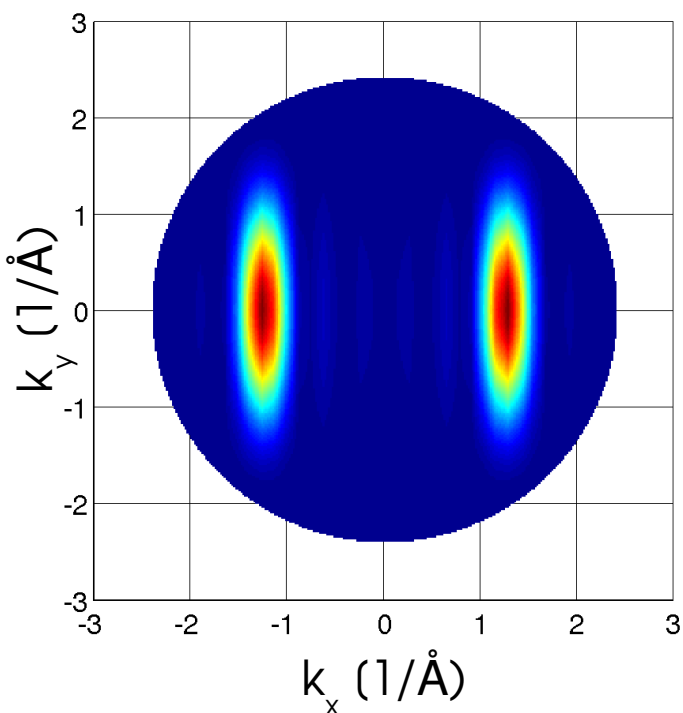
# 5A / Ag(110): HOMO-2

theory

experiment

Isolated molecule

5A/Ag(110)



HOMO-2

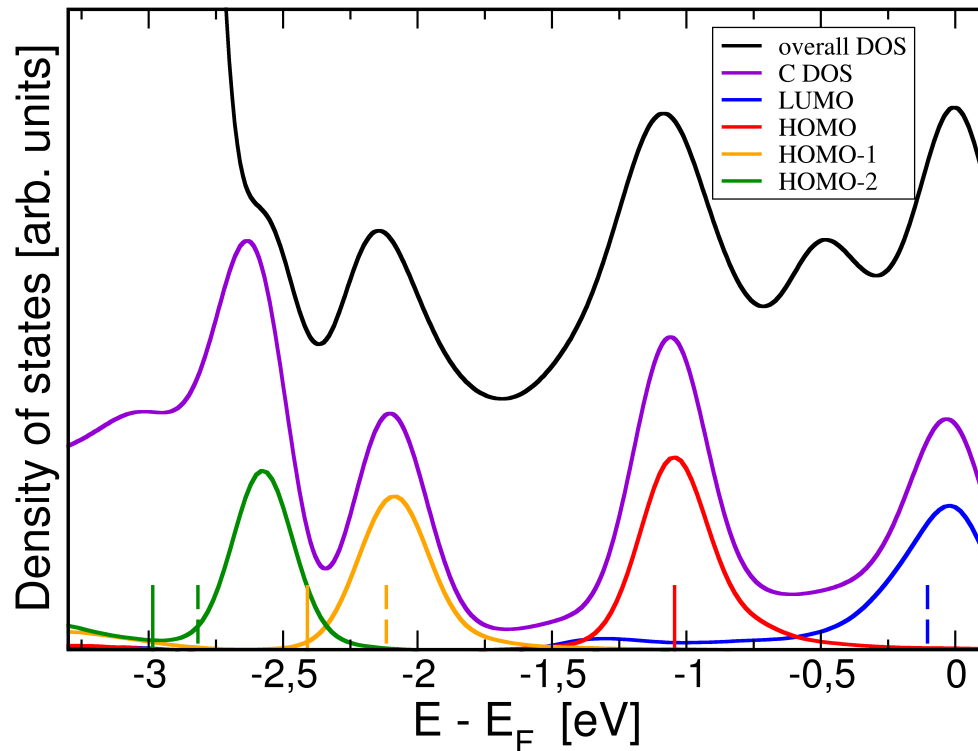
$E_b = -2.6$  [eV]

$E_b = -3.1$  [eV]

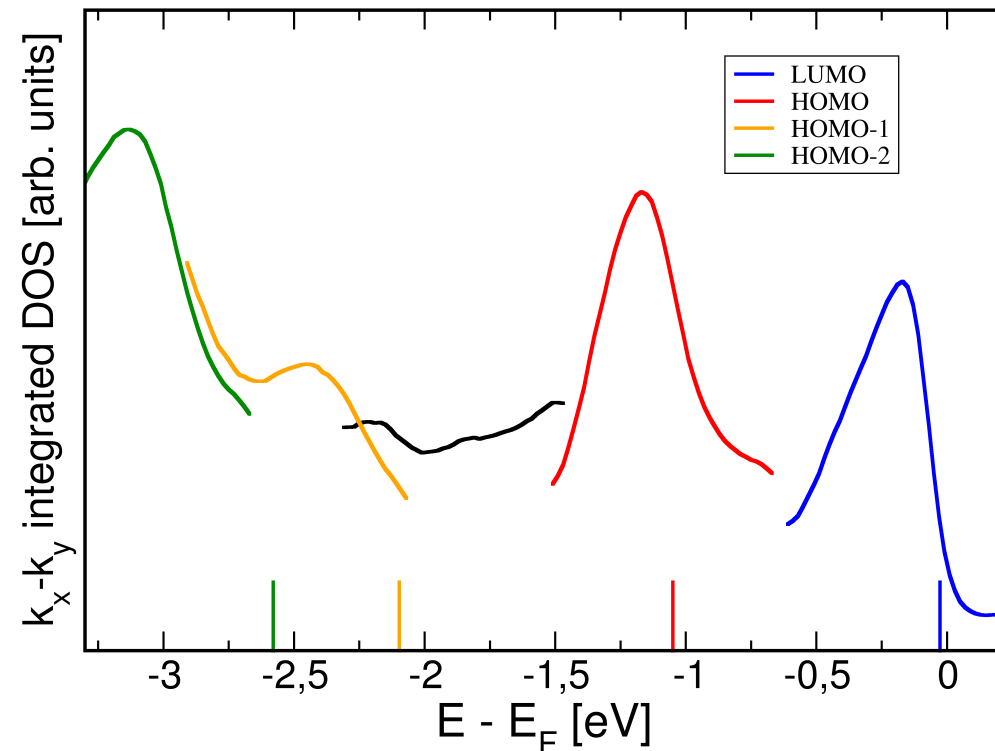


# 5A / Ag(110): DOS

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

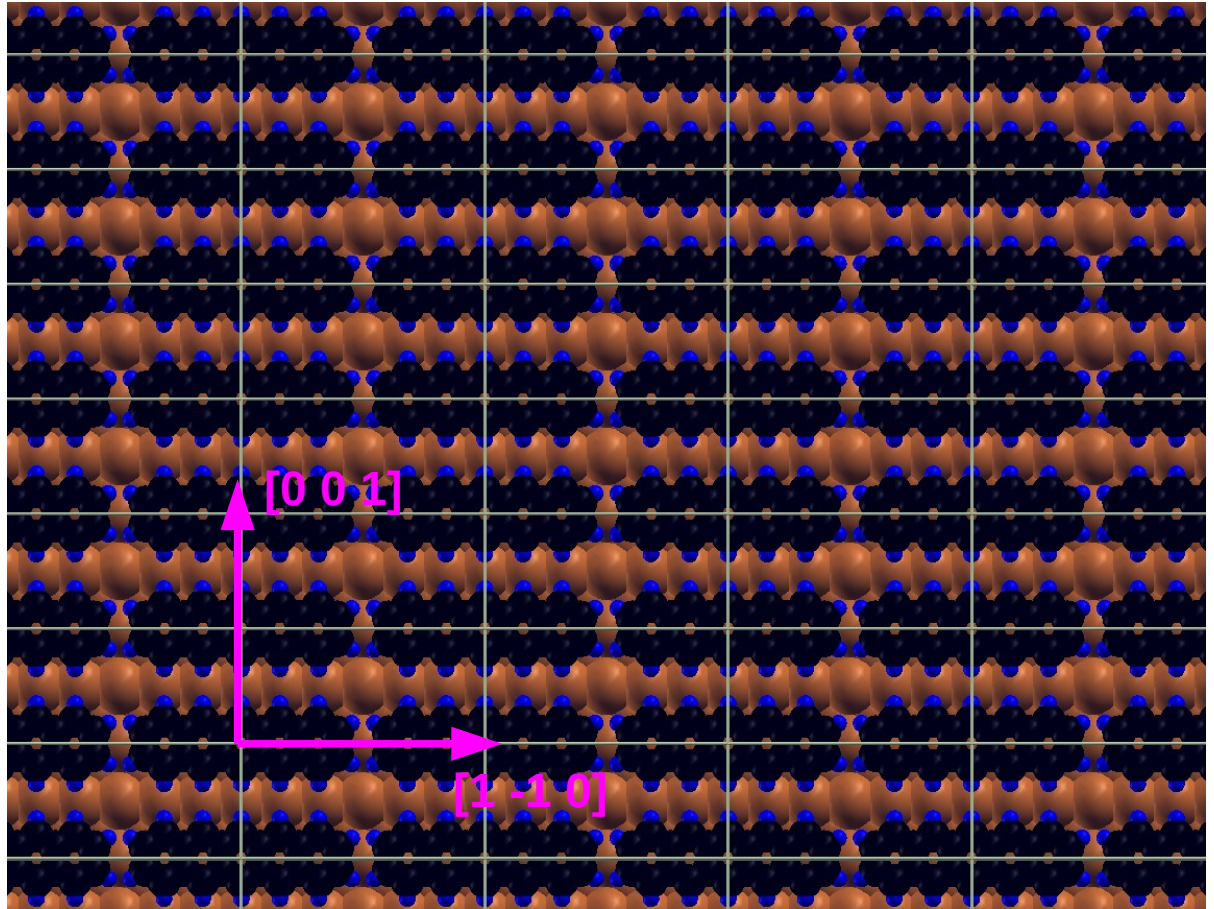
$$M = \begin{pmatrix} 6.5 & -1 \\ -0.5 & 2 \end{pmatrix}$$

from LEED measurement

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

from Ref <sup>1</sup>

- 5A molecules orientated along  
[1 -1 0] direction of Ag  
substrate
- $d_{\text{Cu-5A}} = 2.25 \text{ [\AA]}$



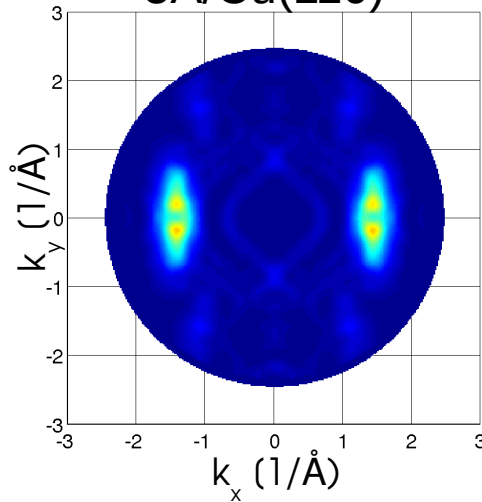
<sup>1</sup> Crystal Growth & Design 2011 11 (4), 1015-1020

# 5A / Cu(110): LUMO

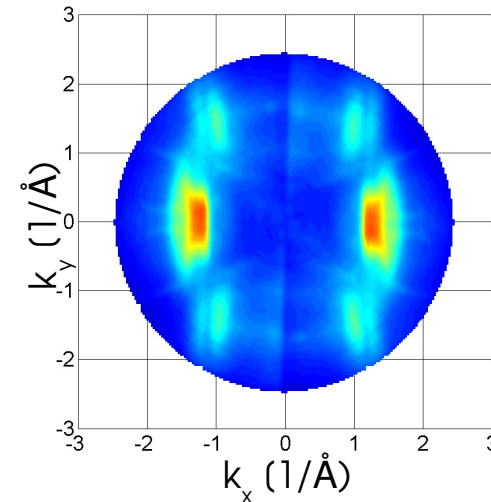
theory

experiment

5A/Cu(110)

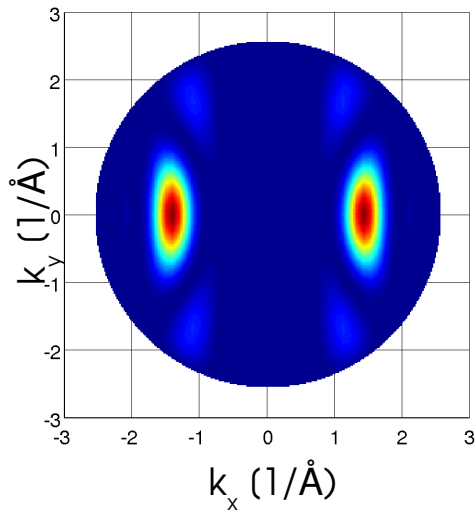


$E_b = -0.05$  [eV]

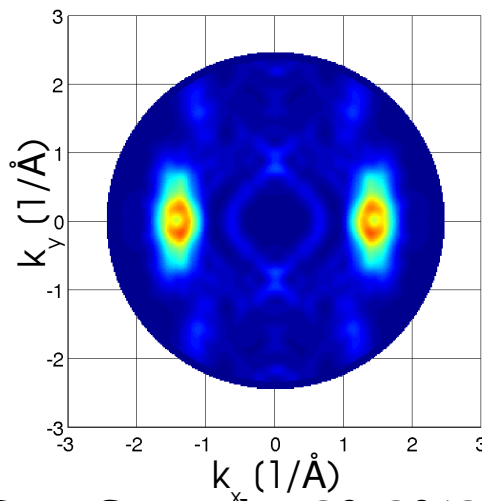


$E_b = -0.6$  [eV]

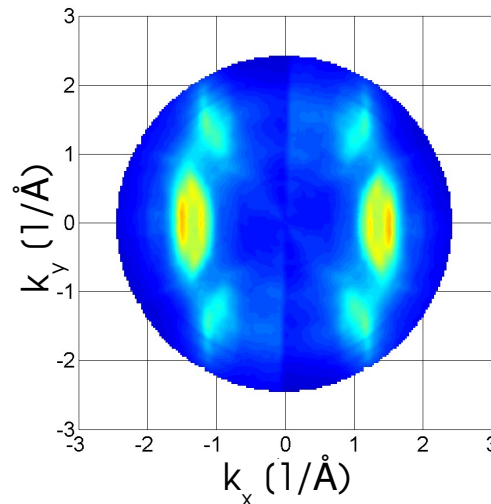
Isolated molecule



LUMO



$E_b = -0.15$  [eV]



$E_b = -0.9$  [eV]

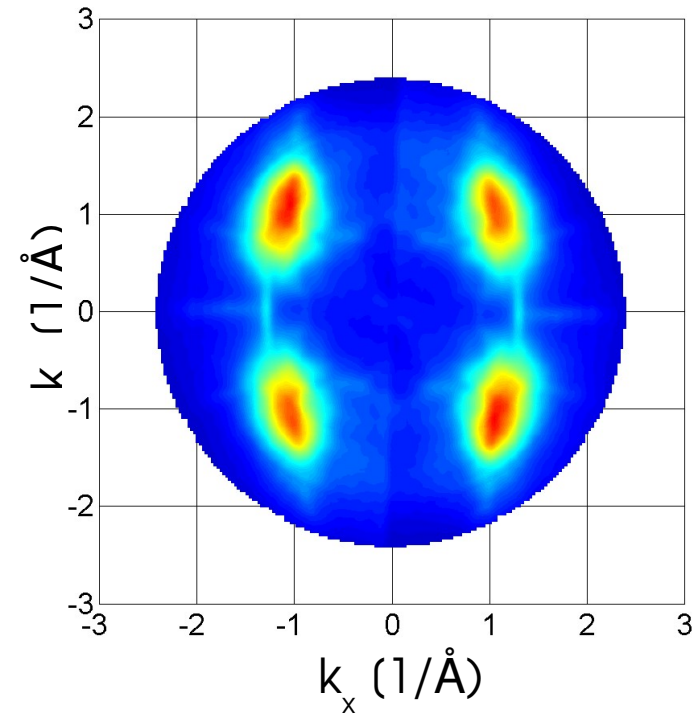
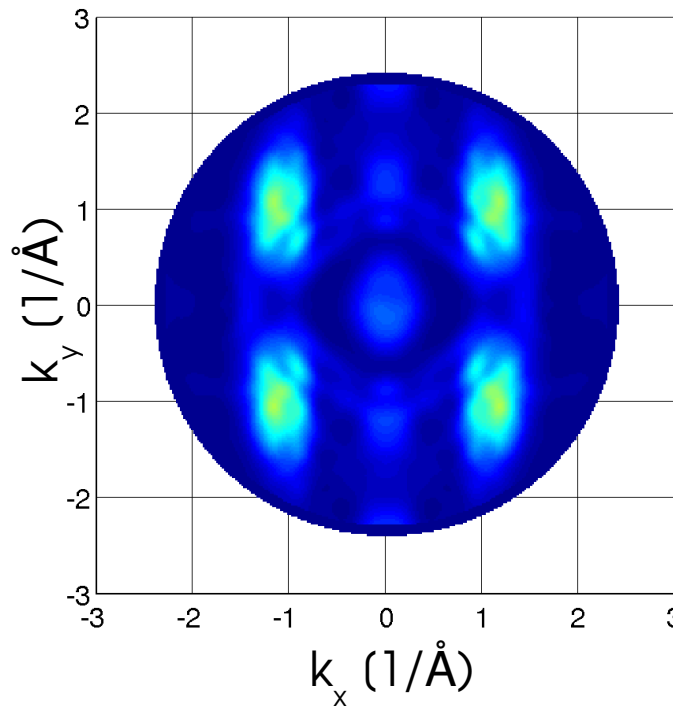
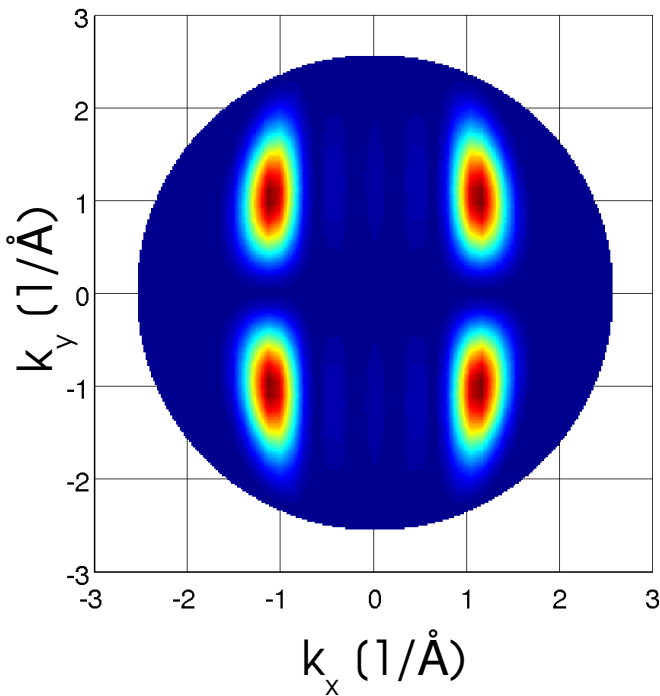
# 5A / Cu(110): HOMO

theory

experiment

Isolated molecule

5A/Cu(110)



HOMO

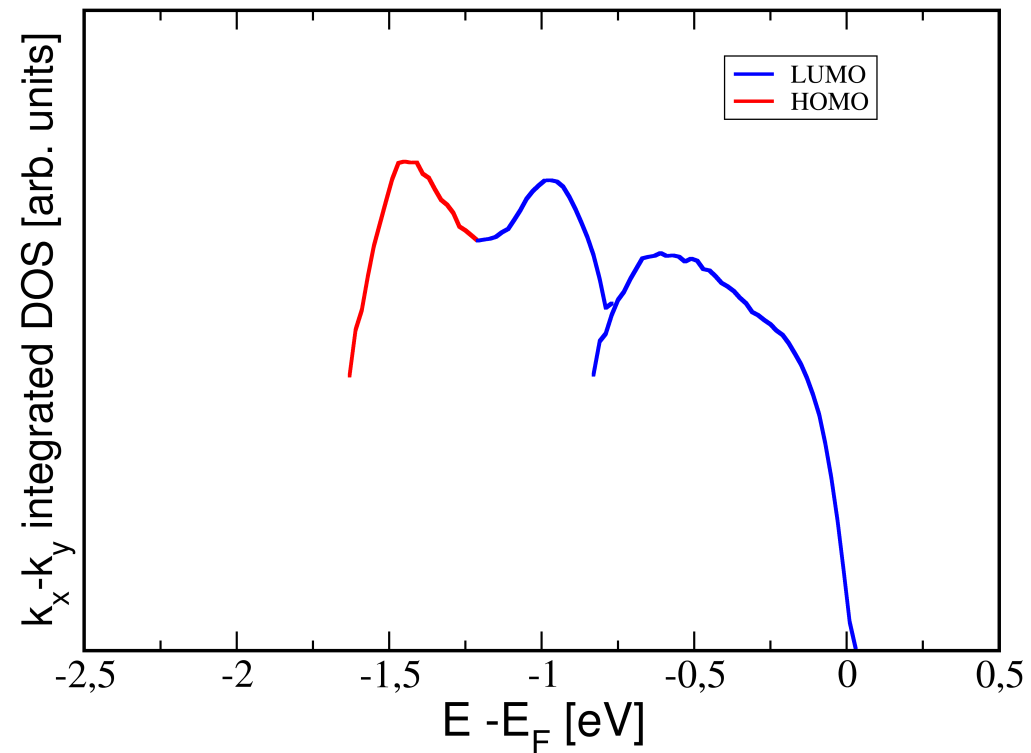
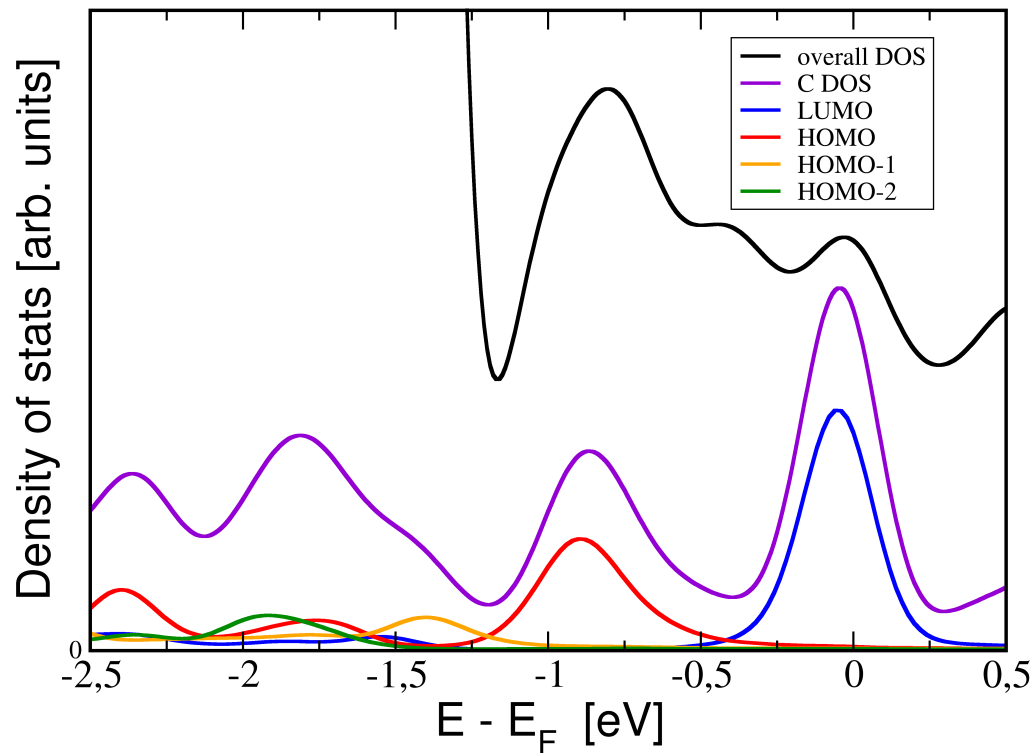
$E_b = -0.9$  [eV]

$E_b = -1.5$  [eV]

# 5A / Cu(110): DOS

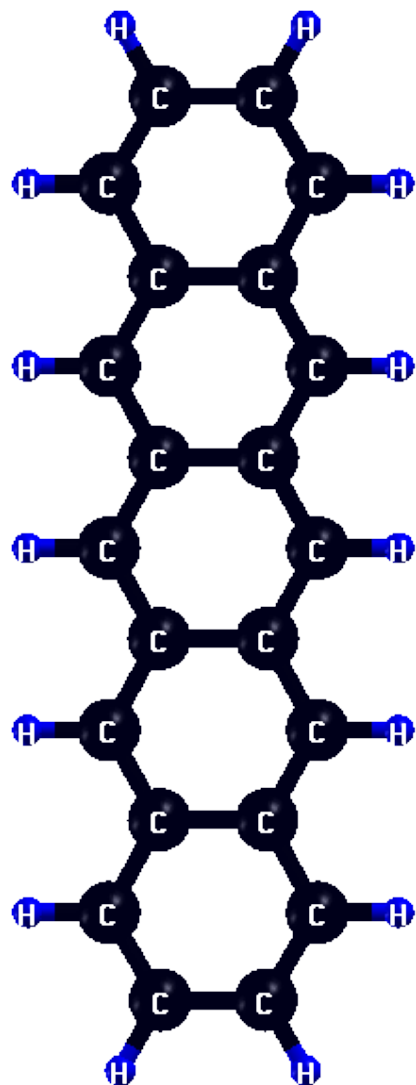
theory

experiment

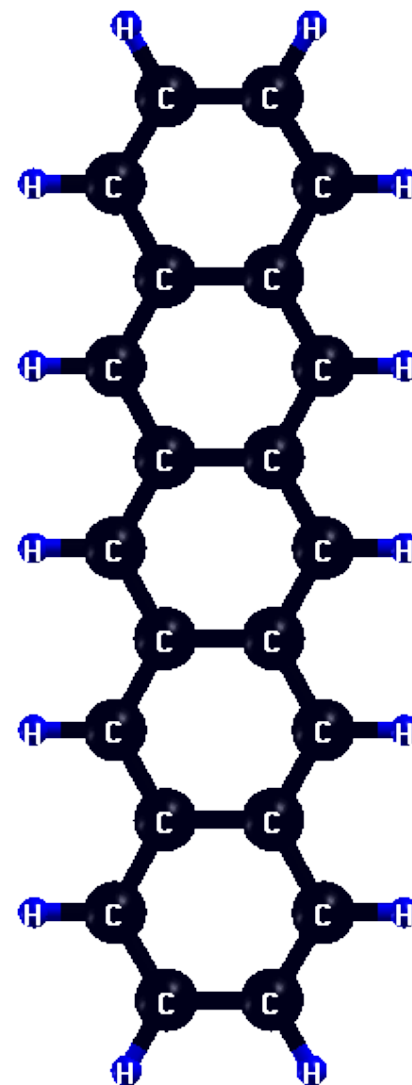


# Conclusion

- $G_0W_0$  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



# Computational approach

Kohn-Sham equation:

$$H_0(\mathbf{r})\psi_{KS}(\mathbf{r}) + V_{XC}(\mathbf{r})\psi_{KS}(\mathbf{r}) = \epsilon_{KS}\psi_{KS}(\mathbf{r})$$

$\nearrow$   
 $\frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$

GGA:

$$E_{XC}^{GGA} = \int d^3r n(\mathbf{r}) f(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

Quasiparticle equation:

$$H_0\phi_{QP}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \omega = E_{QP})\phi_{QP}(\mathbf{r}') = E_{QP}\phi_{QP}(\mathbf{r})$$

GW approximation:

$$\Sigma = iGW \qquad W = \epsilon^{-1}v$$

G<sub>0</sub>W<sub>0</sub> band structure:

$$E_{QP} - \epsilon_{KS} = \langle \psi_{KS} | \Sigma_{XC} - V_{XC} | \psi_{KS} \rangle$$