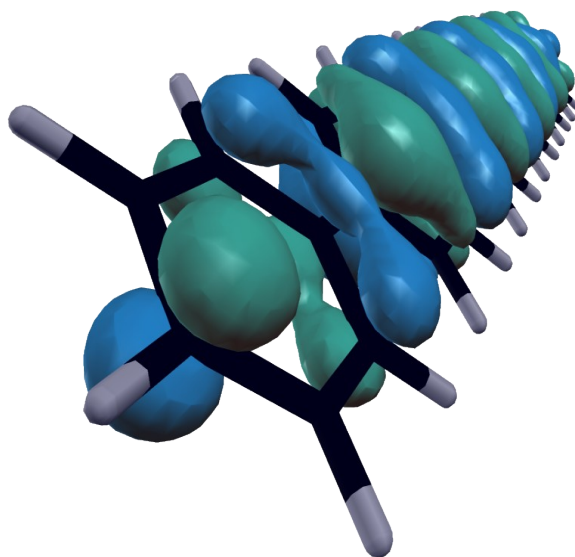


Orbital Tomography: Deconvoluting Photoemission Spectra of Organic Molecules



Collaborations and Funding

Lehrstuhl für Atomistic Modelling and Design of Materials – MU Leoben

Daniel Lüftner, Matus Milko
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Georg Koller, Mike Ramsey



Lehrstuhl für Technische Physik – University Erlangen-Nürnberg

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Experimentelle Physik VII – Universität Würzburg, Germany

Sophia Huppmann, Johannes Ziroff, Michael Wießner, Frank Forster,
Achim Schöll, Friedrich Reinert



Peter Grünberg Institut (PGI-3), JARA, Forschungszentrum Jülich,

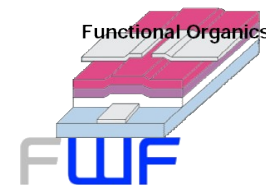
Sergey Soubatch
Stefan Tautz

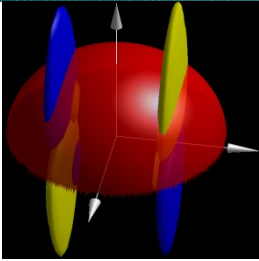


The work is part of the National Research Network

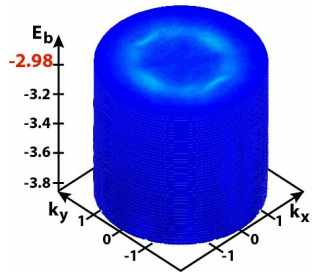
„**Interface controlled and functionalized organic films**“

and the single project P 23190-N16 „Understanding photoemission of organic thin films“

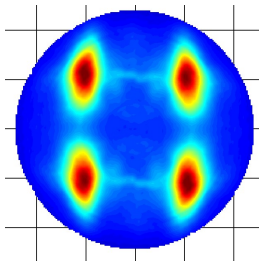




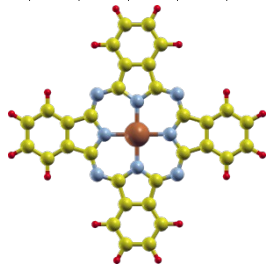
Angle-Resolved Photoemission



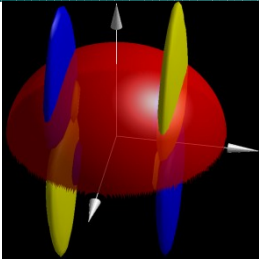
PTCDA / Ag(110)



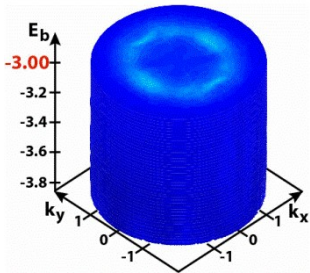
Pentacene / Ag(110)



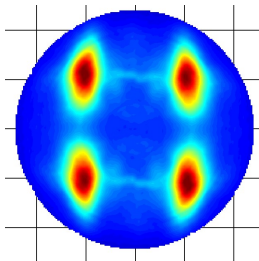
H2Pc and CuPc / Au(110)



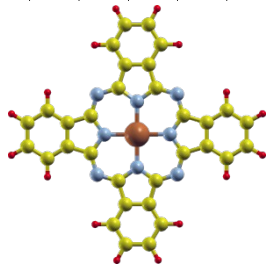
Angle-Resolved Photoemission



PTCDA / Ag(110)

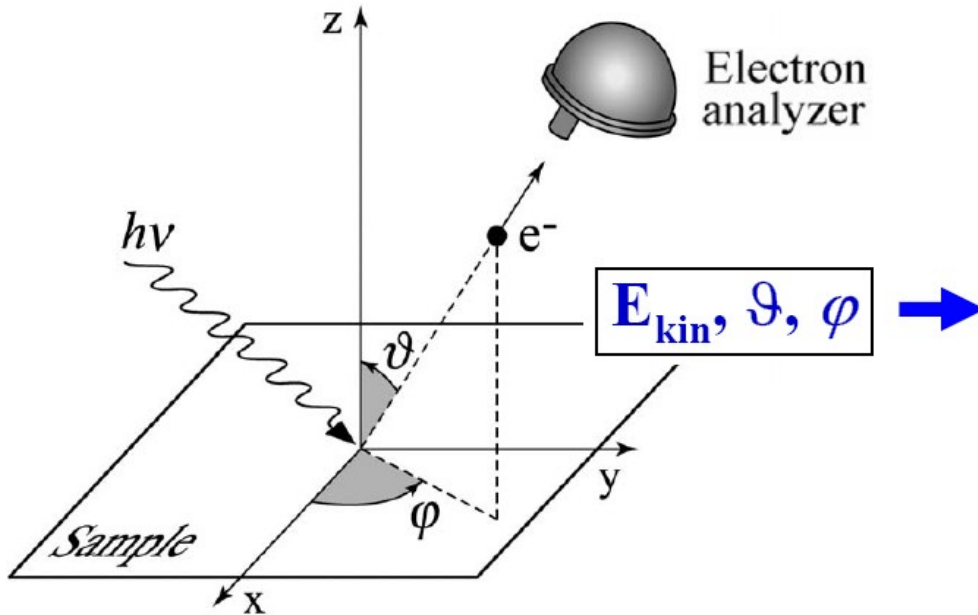


Pentacene / Ag(110)



H2Pc and CuPc / Au(110)

Photoemission Spectroscopy



$$\mathbf{K} = \mathbf{p} / \hbar = \sqrt{2mE_{kin}} / \hbar$$

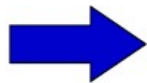
$$K_x = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \vartheta \cos \varphi$$

$$K_y = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \vartheta \sin \varphi$$

$$K_z = \frac{1}{\hbar} \sqrt{2mE_{kin}} \cos \vartheta$$

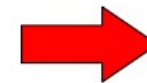
Vacuum

$$\begin{matrix} E_{kin} \\ \mathbf{K} \end{matrix}$$



Conservation laws

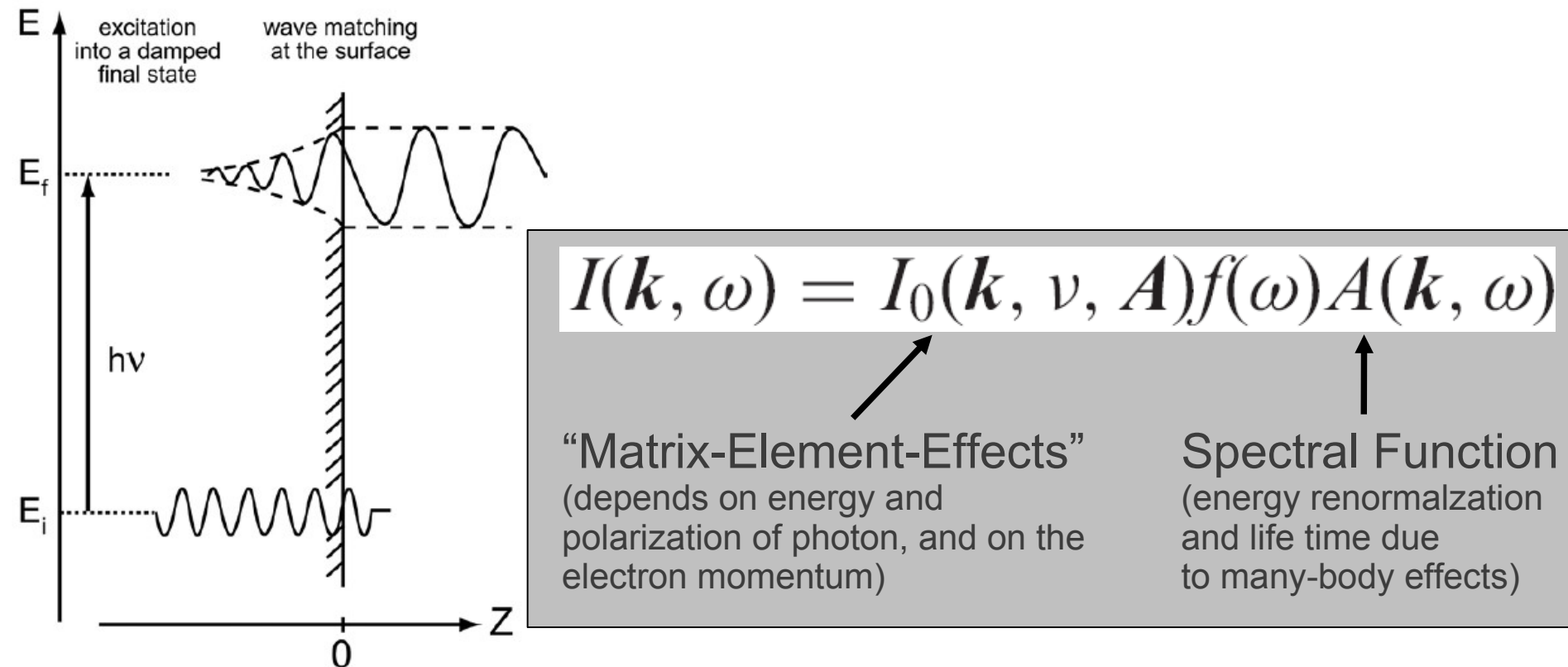
$$\begin{matrix} E_f - E_i = h\nu \\ \mathbf{k}_f - \mathbf{k}_i = \cancel{\mathbf{k}_{h\nu}} \end{matrix}$$



Solid

$$\begin{matrix} E_B \\ \mathbf{k} \end{matrix}$$

Photoemission Intensity

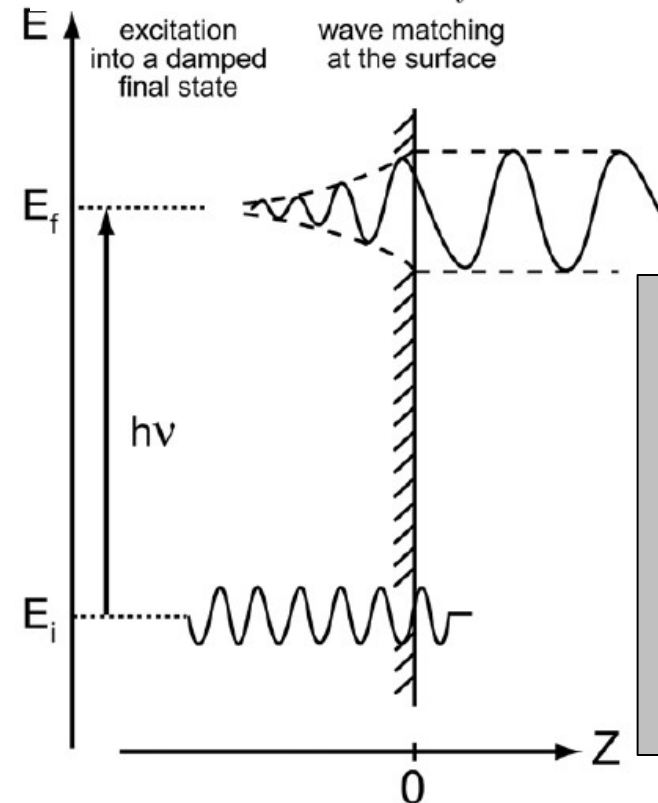


[Hüfner, “Photoelectron Spectroscopy,” (Springer, 1995), Damascelli, Phys. Scr., **T109**, 61-74 (2004).

Photoemission Intensity

One Step Model

$$I(\theta, \phi; E_{\text{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\text{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta(E_i + \Phi + E_{\text{kin}} - \hbar\omega)$$



- Independent-Particle Picture
- Sudden Approximation

$$I(\mathbf{k}, \omega) = I_0(\mathbf{k}, \nu, A) f(\omega) A(\mathbf{k}, \omega)$$

“Matrix-Element-Effects”
(depends on energy and polarization of photon, and on the electron momentum)

Spectral Function
(energy renormalization and life time due to many-body effects)

[Hüfner, “Photoelectron Spectroscopy,” (Springer, 1995). Damascelli, Phys. Scr., **T109**, 61-74 (2004).

Photoemission Intensity

One Step Model

$$I(\theta, \phi; E_{\text{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\text{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta(E_i + \Phi + E_{\text{kin}} - \hbar\omega)$$

Photoemission Intensity

One Step Model

$$I(\theta, \phi; E_{\text{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\text{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta(E_i + \Phi + E_{\text{kin}} - \hbar\omega)$$

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

$$[\mathbf{p}, \mathbf{A}] = -i\hbar \nabla \cdot \mathbf{A} = 0$$

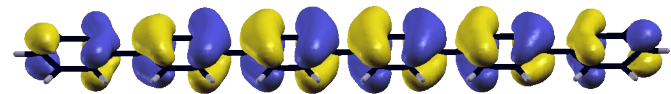
Interaction with the photon field treated as perturbation

Electric dipole approximation (electric field is constant over atomic dimensions, which holds for the ultra-violet regime)

Photoemission Intensity

One Step Model

$$I(\theta, \phi; E_{\text{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\text{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta(E_i + \Phi + E_{\text{kin}} - \hbar\omega)$$

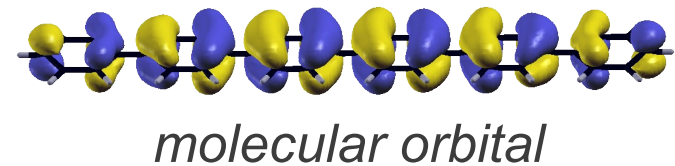
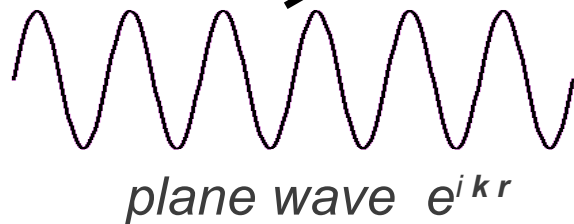


molecular orbital

Photoemission Intensity

One Step Model

$$I(\theta, \phi; E_{\text{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\text{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta(E_i + \Phi + E_{\text{kin}} - \hbar\omega)$$



Approximation: final state = plane wave

$$I_i(\theta, \phi) \propto |(\mathbf{A} \cdot \mathbf{k})|^2 \times \left| \tilde{\psi}_i(\mathbf{k}) \right|^2$$

Fourier Transform of Initial State Orbital

An arrow points from the $\tilde{\psi}_i(\mathbf{k})$ term in the equation above to this text.

[Feibelman and Eastman, *Phys. Rev. B* **10**, 4932 (1974).]

Plane Wave Final State

The Independent Atomic Centre approximation (IAC)

[W. D. Grobman, Phys. Rev. B **17**, 4573 (1978).]

$$A(\mathbf{R}, E_{\text{kin}}) = \sum_{\alpha} \sum_{nlm} C_{\alpha,nlm} e^{i\mathbf{k}\mathbf{R}_{\alpha}} \sum_{LM} M_{\alpha,nlm}^{LM}(E_{\text{kin}}) Y_{LM}(\hat{R})$$

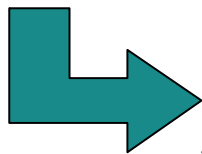
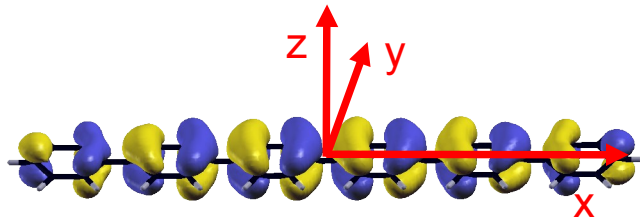
Reduces to the PW final state result, if

- All contributing atomic orbitals are of the same type (e.g. π -orbitals)
- The emission direction is close to the polarization vector of the incoming photon
- The molecule consists of only light atoms (C, N, O) with small scattering cross sections

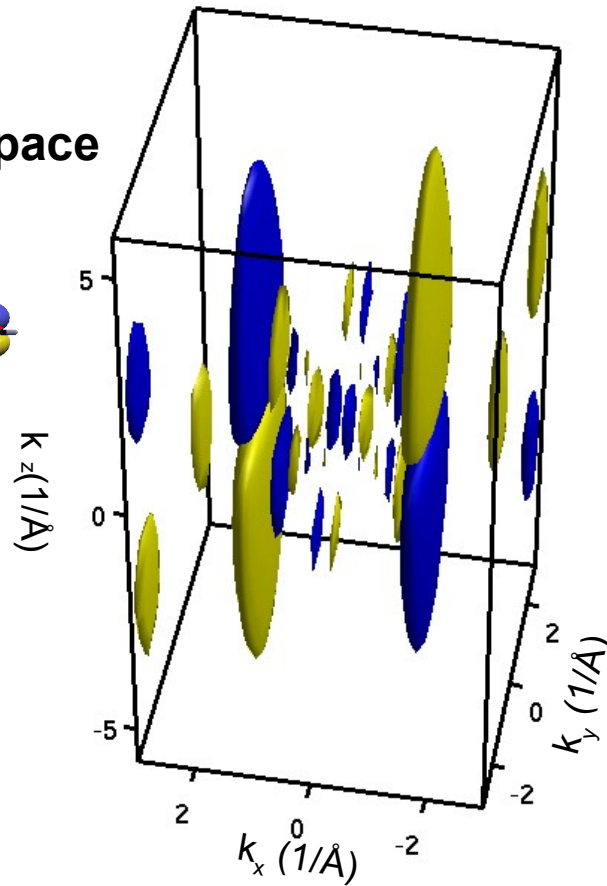
[Goldberg et al, Solid State Commun. **28**, 459-463 (1978),
Puschnig et al., supporting online material to Science **326**, 702 (2009)]

Comparison with DFT

Molecular Orbital in Real Space

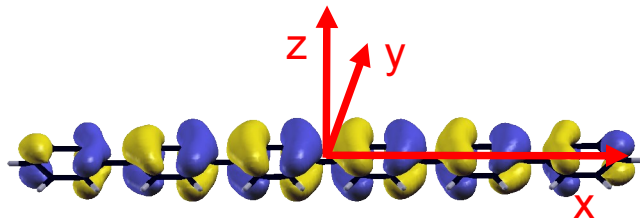


Calculation of
the Fourier Transform

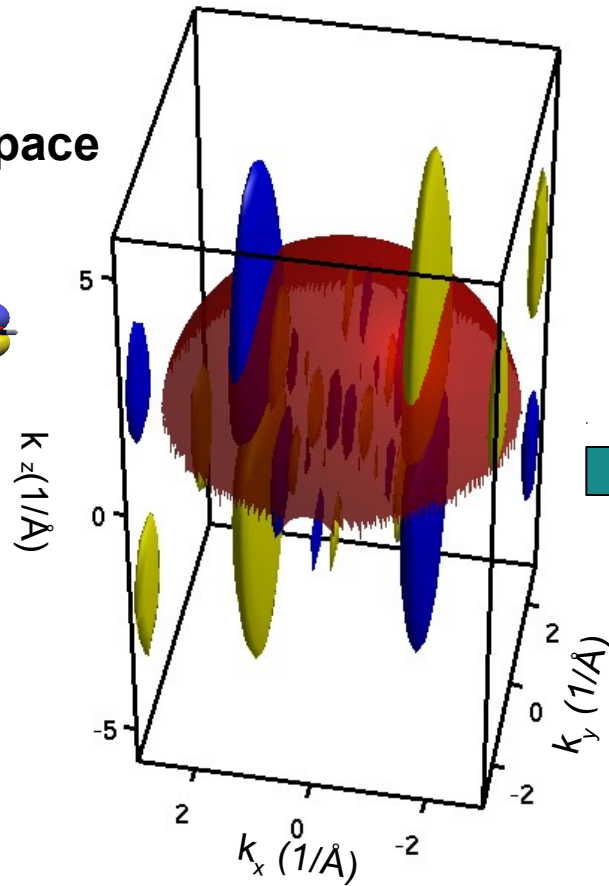
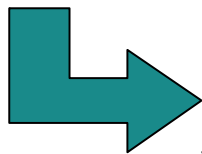


Comparison with DFT

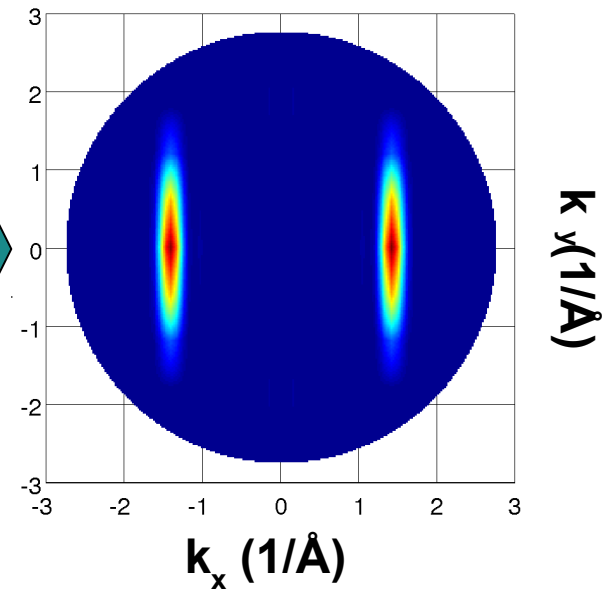
Molecular Orbital in Real Space



Calculation of the Fourier Transform

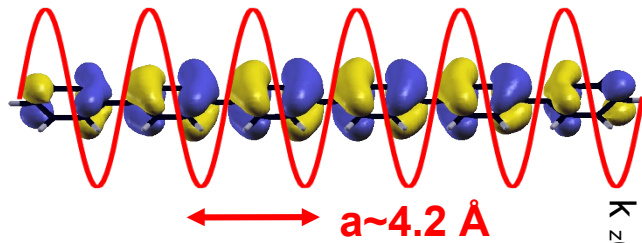


Hemispherical Cut Through 3D Fourier Transform

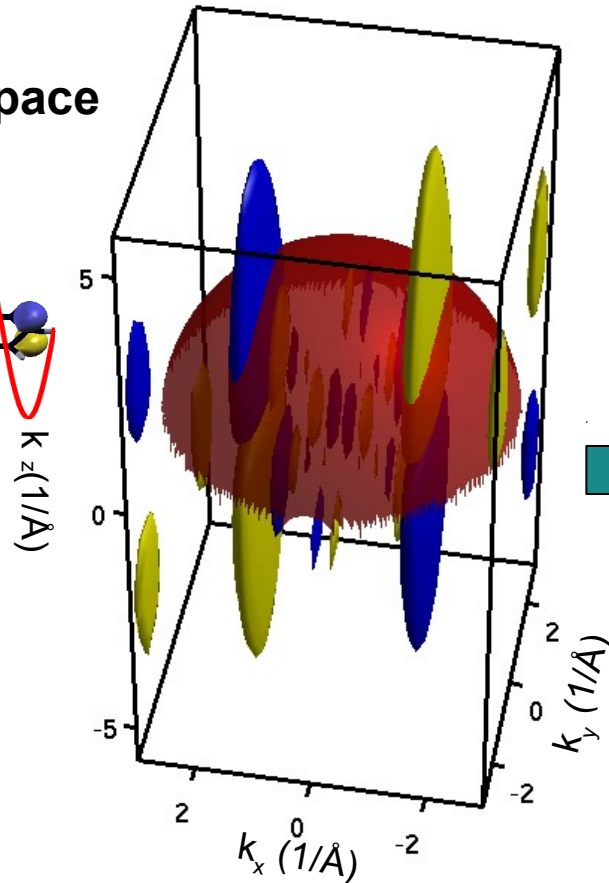


Comparison with DFT

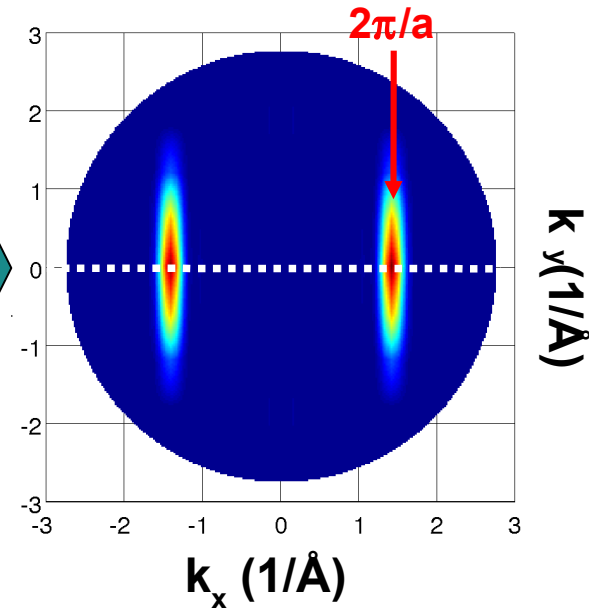
Molecular Orbital in Real Space



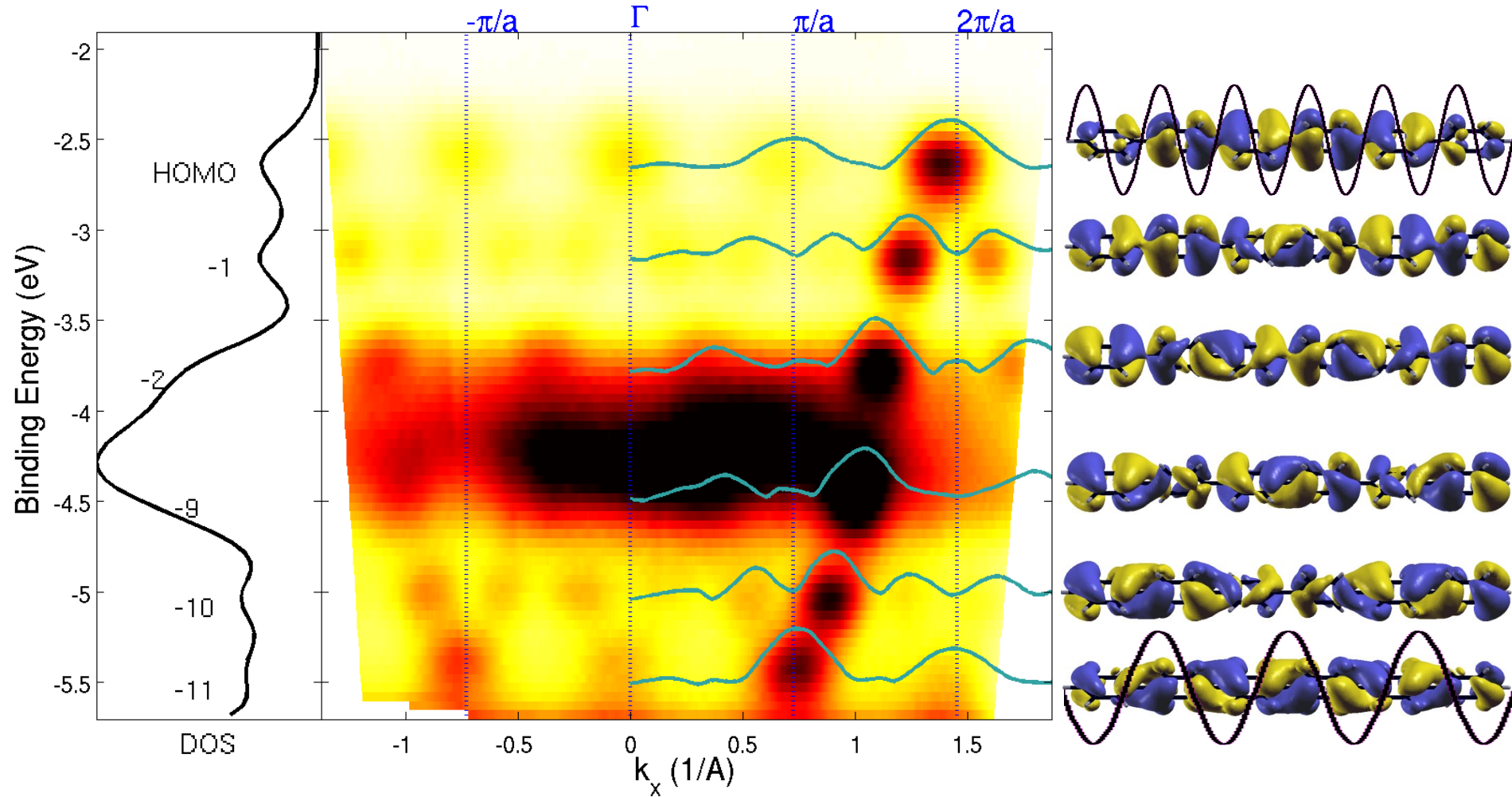
Calculation of
the Fourier Transform



Hemispherical Cut Through
3D Fourier Transform

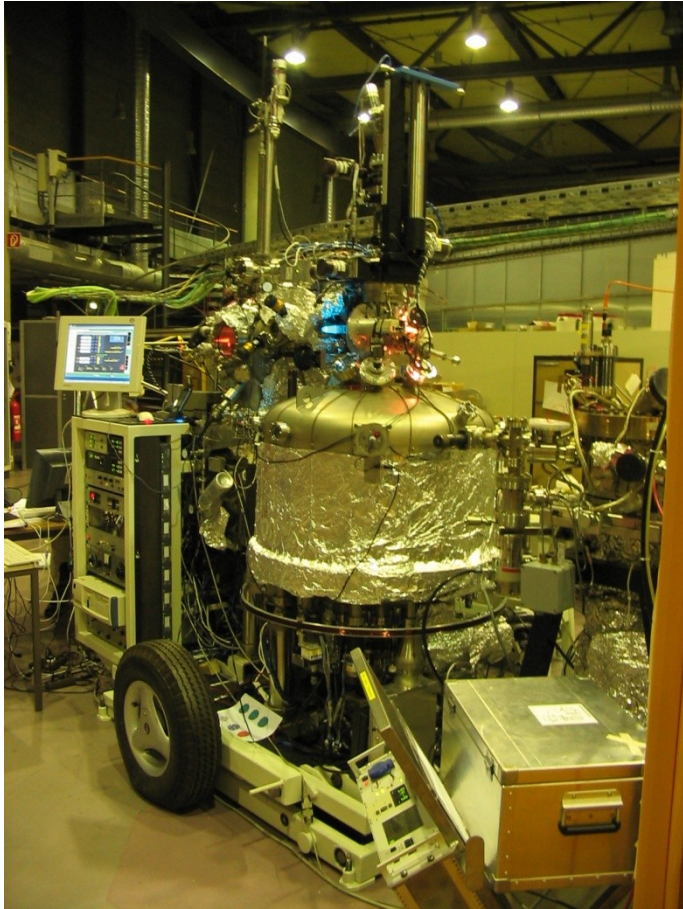


ARPES of *p*-Sexiphenyl

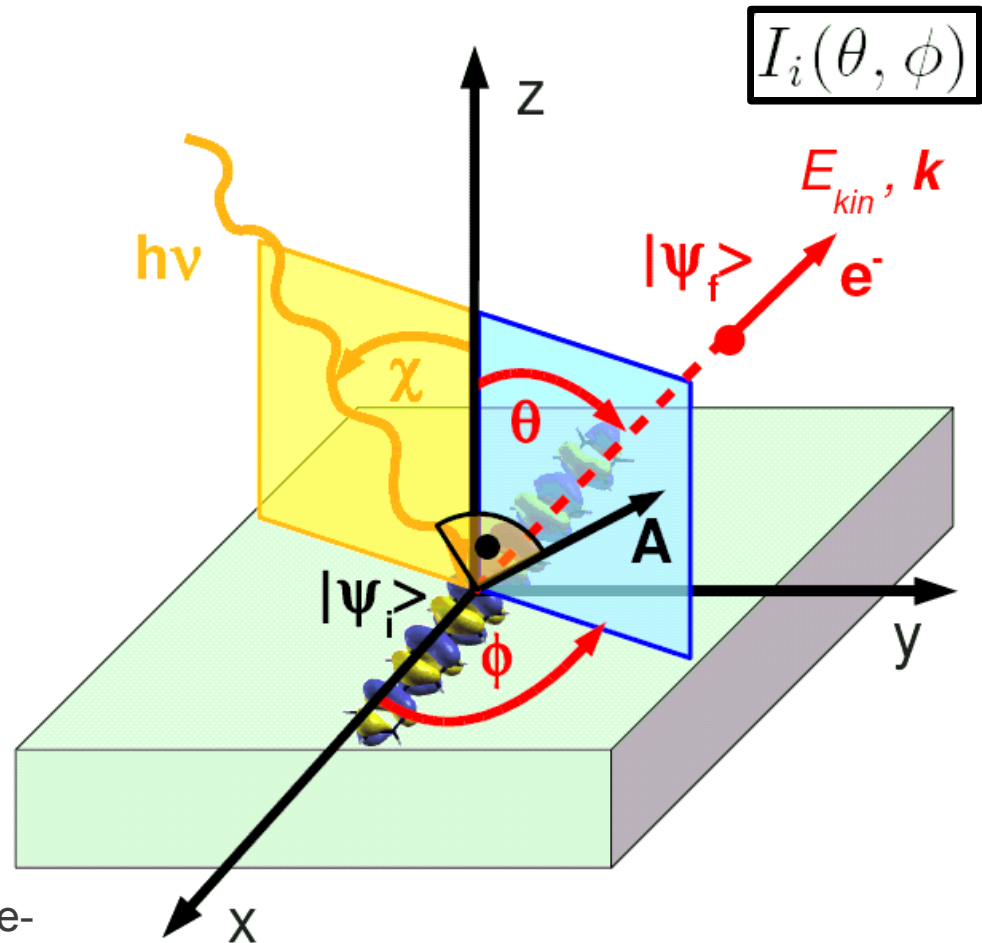


G. Koller et al., *Science* **317**, 351 (2007).

Toroidal Electron Energy Analyzer



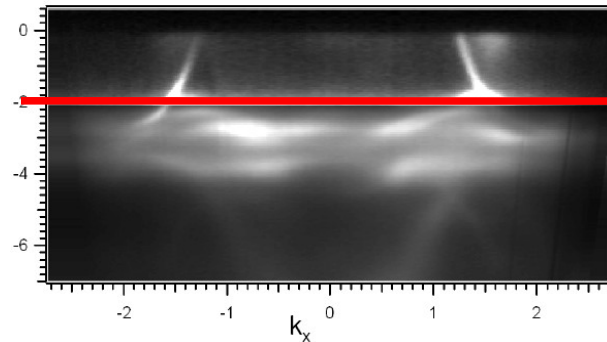
The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II



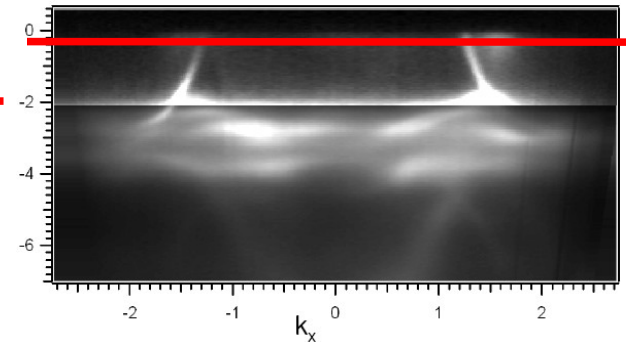
Sexiphenyl Monolayer on Cu(110)



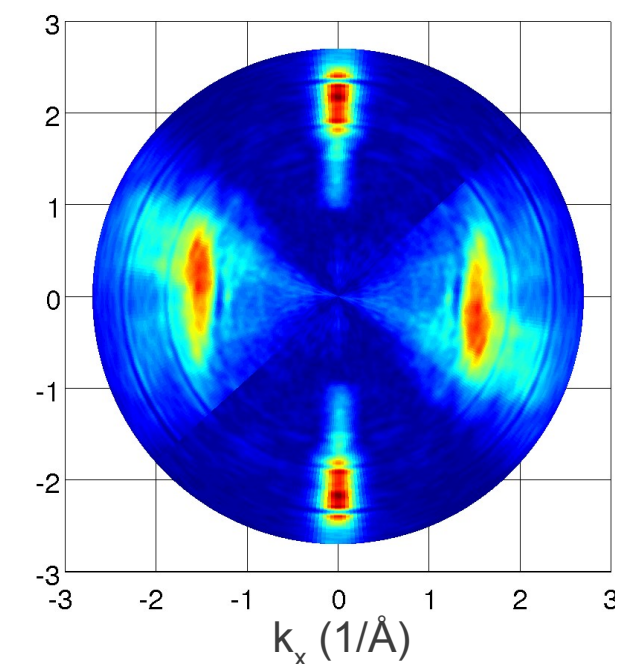
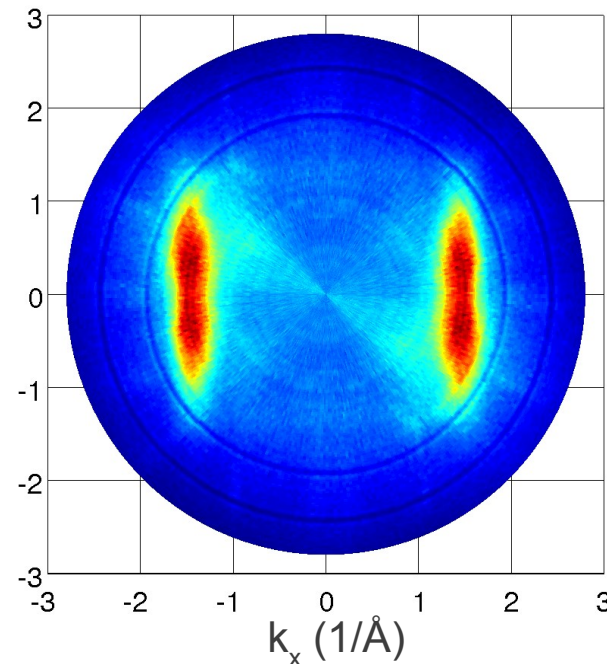
2D-Momentum Maps



HOMO



filled LUMO

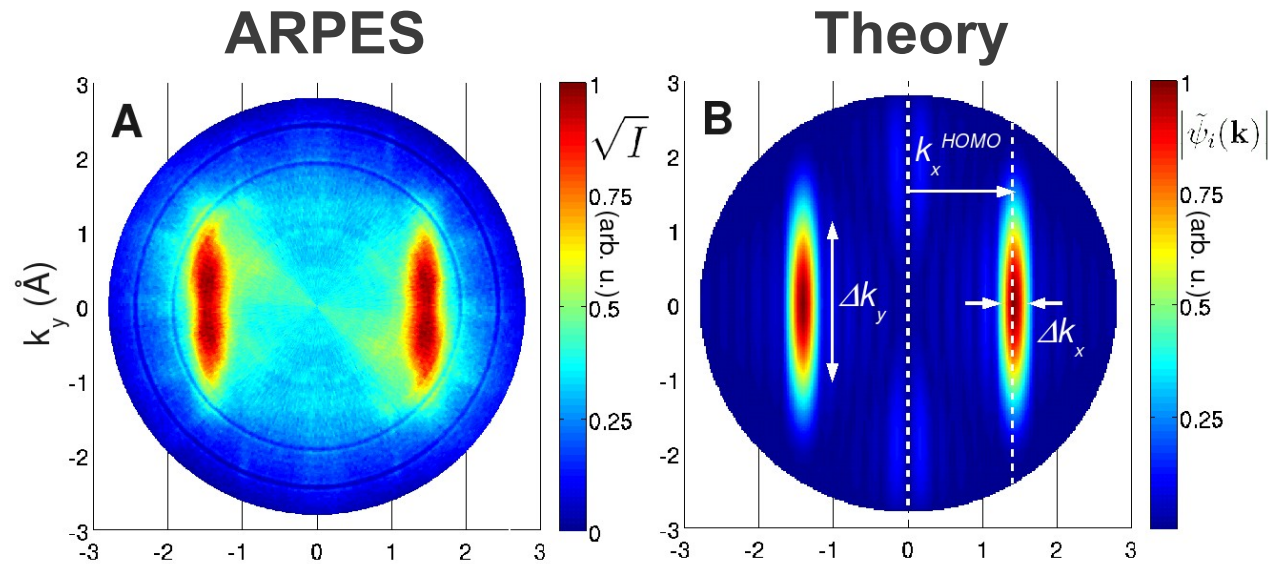


k_y (1/Å)

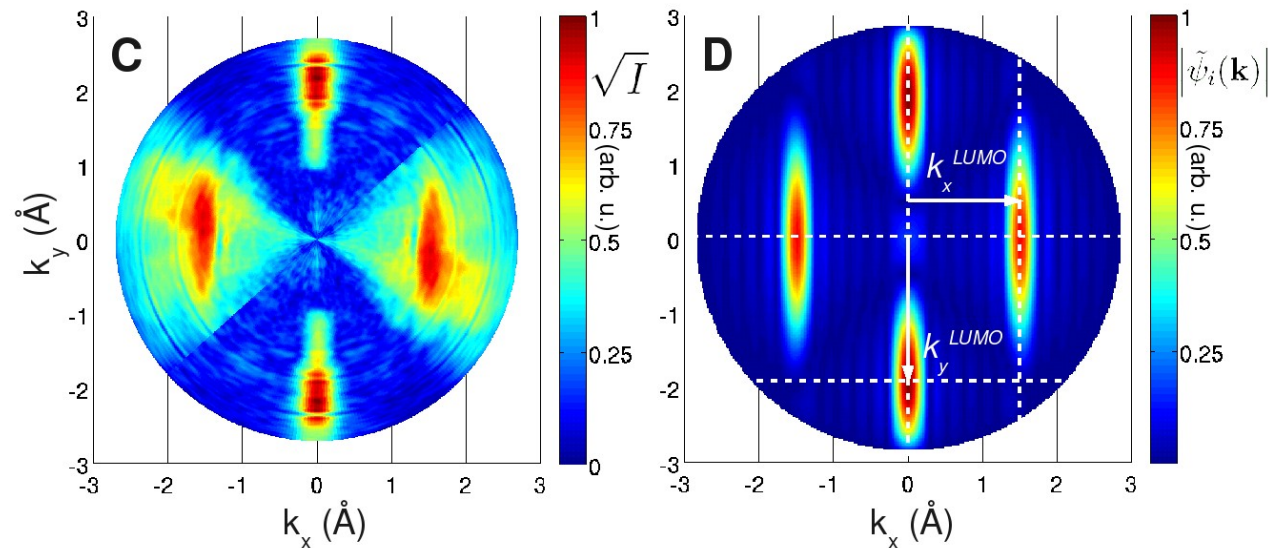
ARPES
data for a
monolayer of
6P / Cu(110)

2D-Momentum Maps

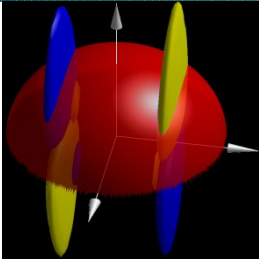
HOMO



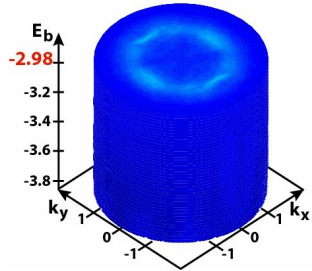
Filled
LUMO



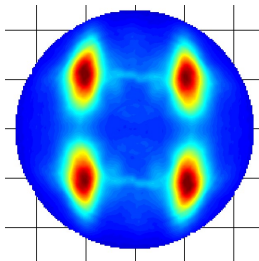
Puschnig et al.,
Science **326**, 702 (2009).



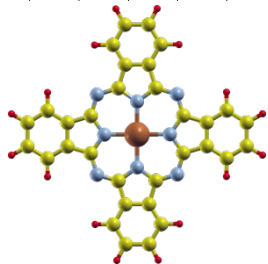
Angle-Resolved Photoemission



PTCDA / Ag(110)

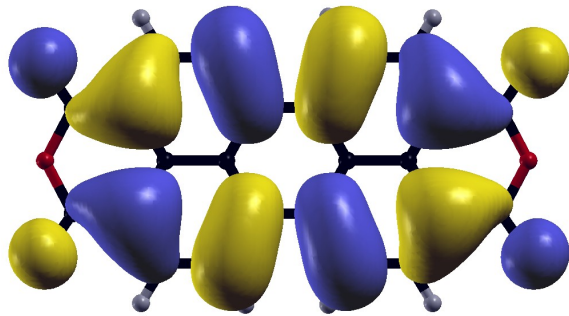


Pentacene / Ag(110)

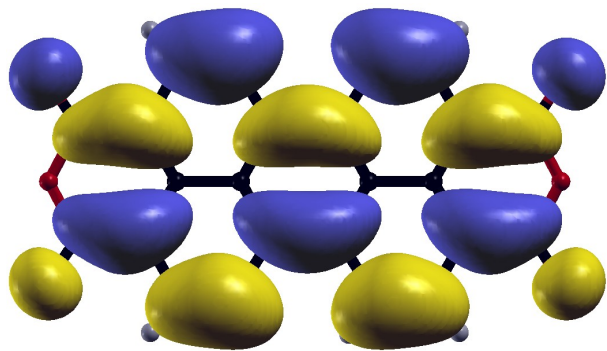


H2Pc and CuPc / Au(110)

Monolayer PTCDA / Ag(110)

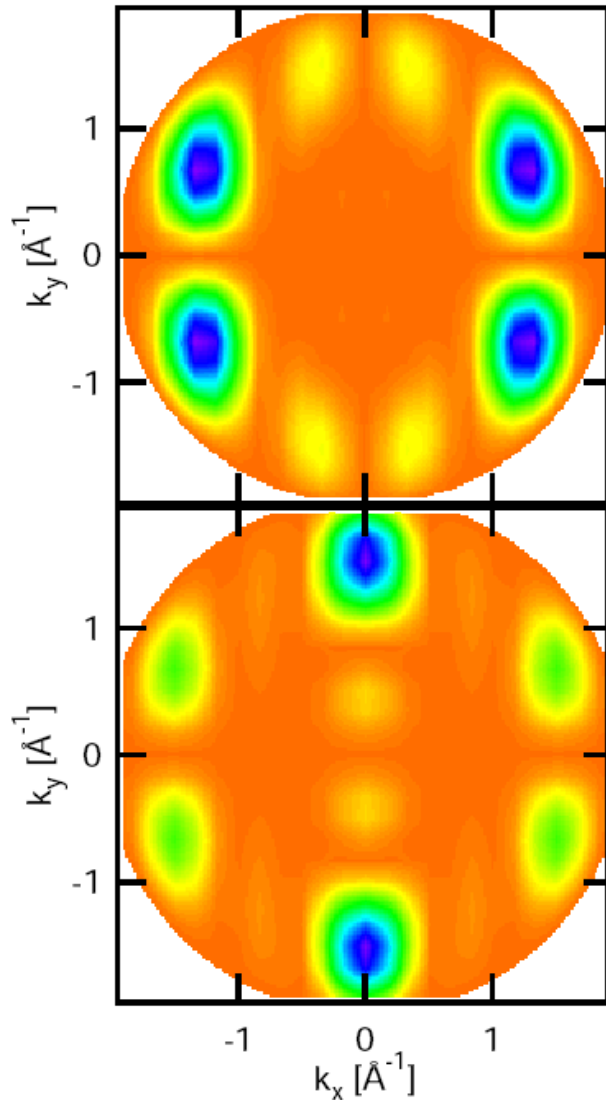


HOMO
 k_y [\AA^{-1}]



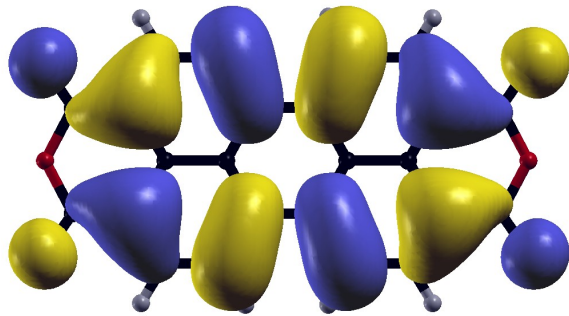
LUMO
 k_y [\AA^{-1}]

DFT



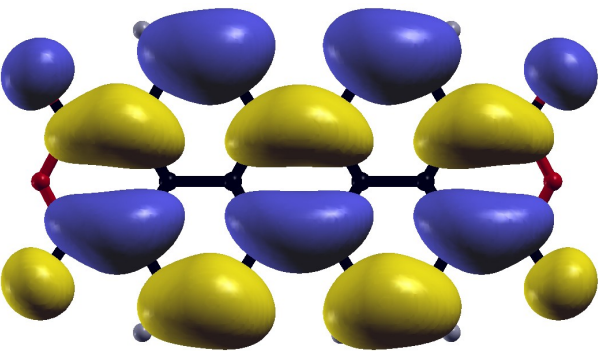
Zirotto et al., PRL **104**, 233004 (2010).

Monolayer PTCDA / Ag(110)



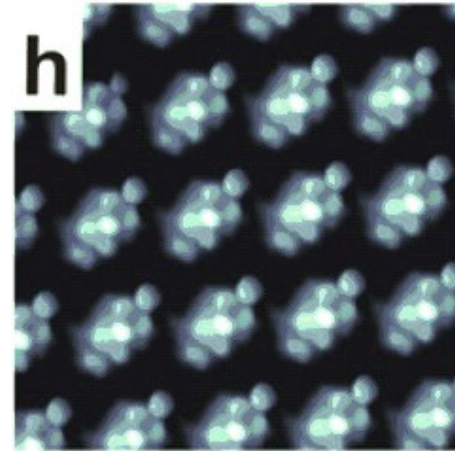
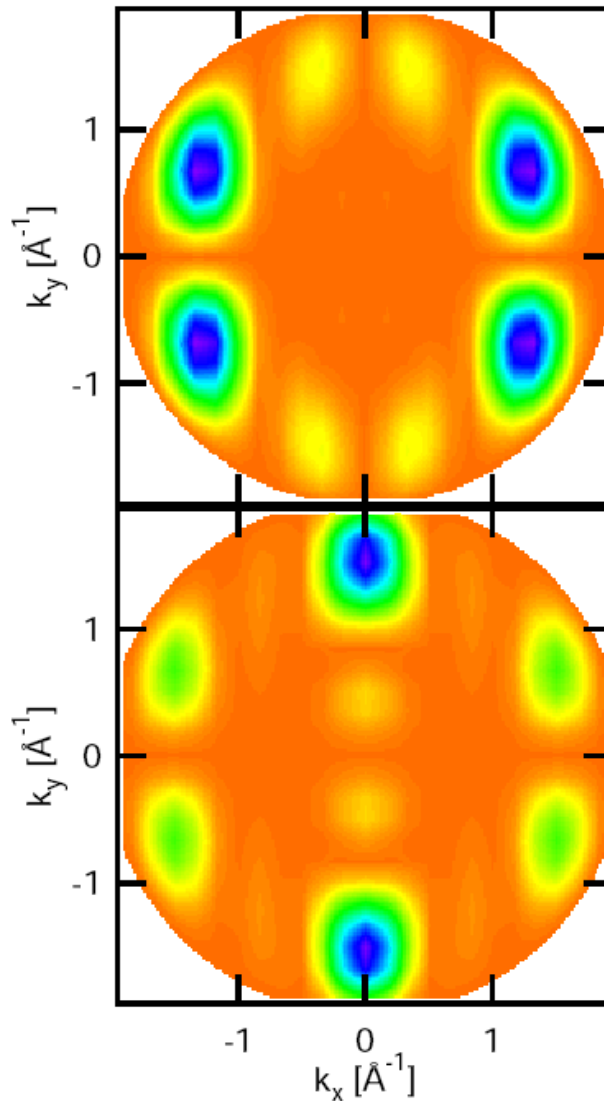
HOMO
 $k_y [\text{\AA}^{-1}]$

LUMO
 $k_y [\text{\AA}^{-1}]$



Ziroff et al., PRL **104**, 233004 (2010).

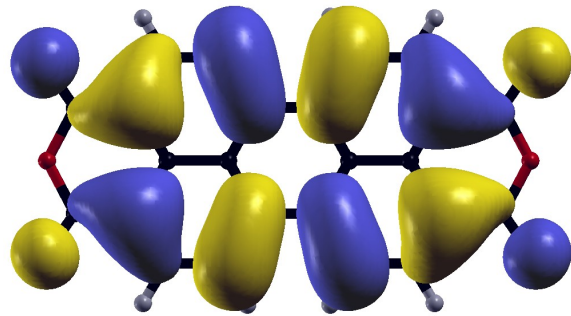
DFT



h
STM of
Uniaxially aligned
PTCDA/Ag(110)

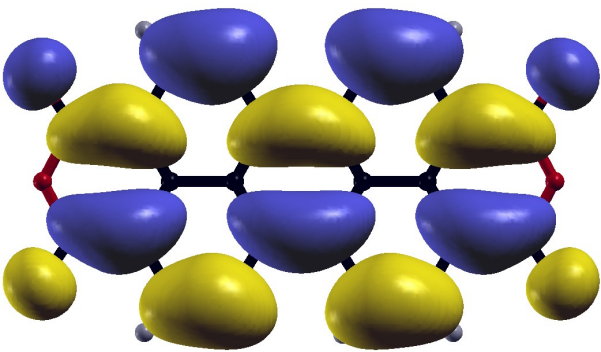
*Temirov et al.,
New J. Phys.
10, 053012 (2008)*

Monolayer PTCDA / Ag(110)



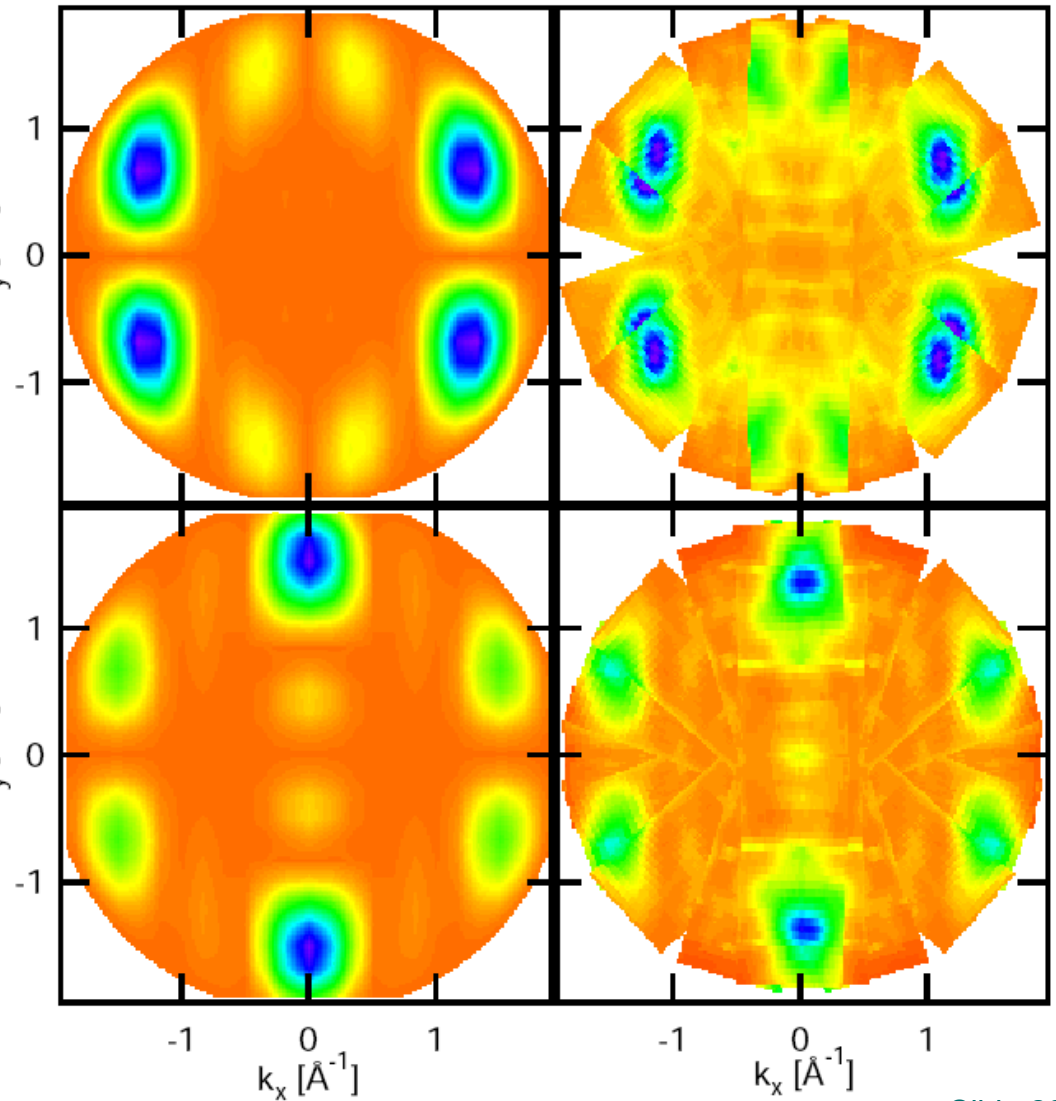
HOMO
 k_y [\AA^{-1}]

LUMO
 k_y [\AA^{-1}]



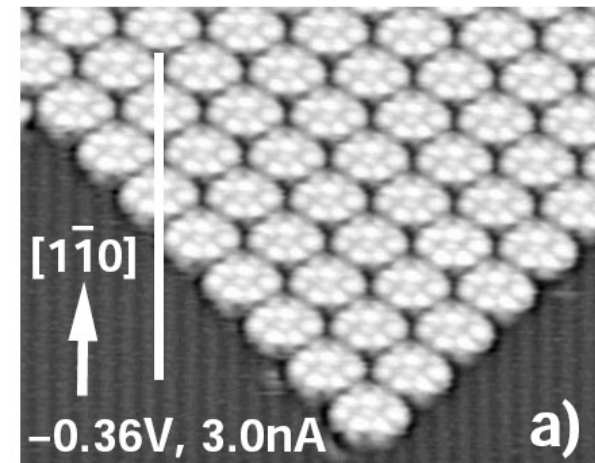
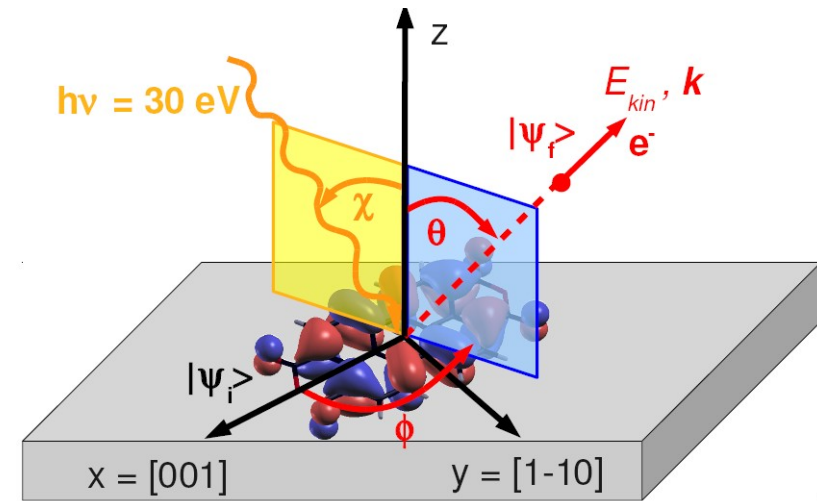
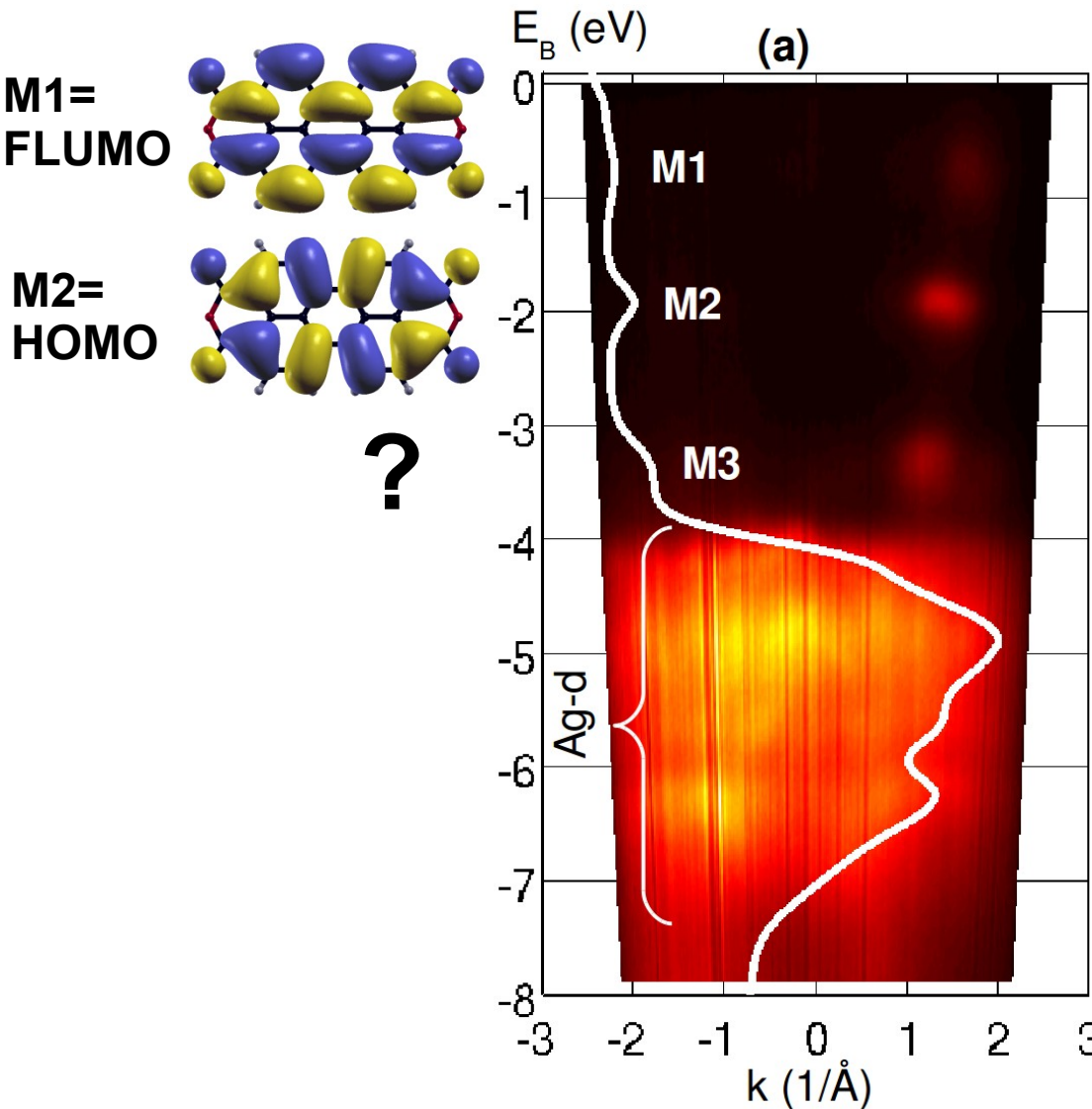
DFT

ARPES



Zirotto et al., PRL **104**, 233004 (2010).

Identifying Orbitals



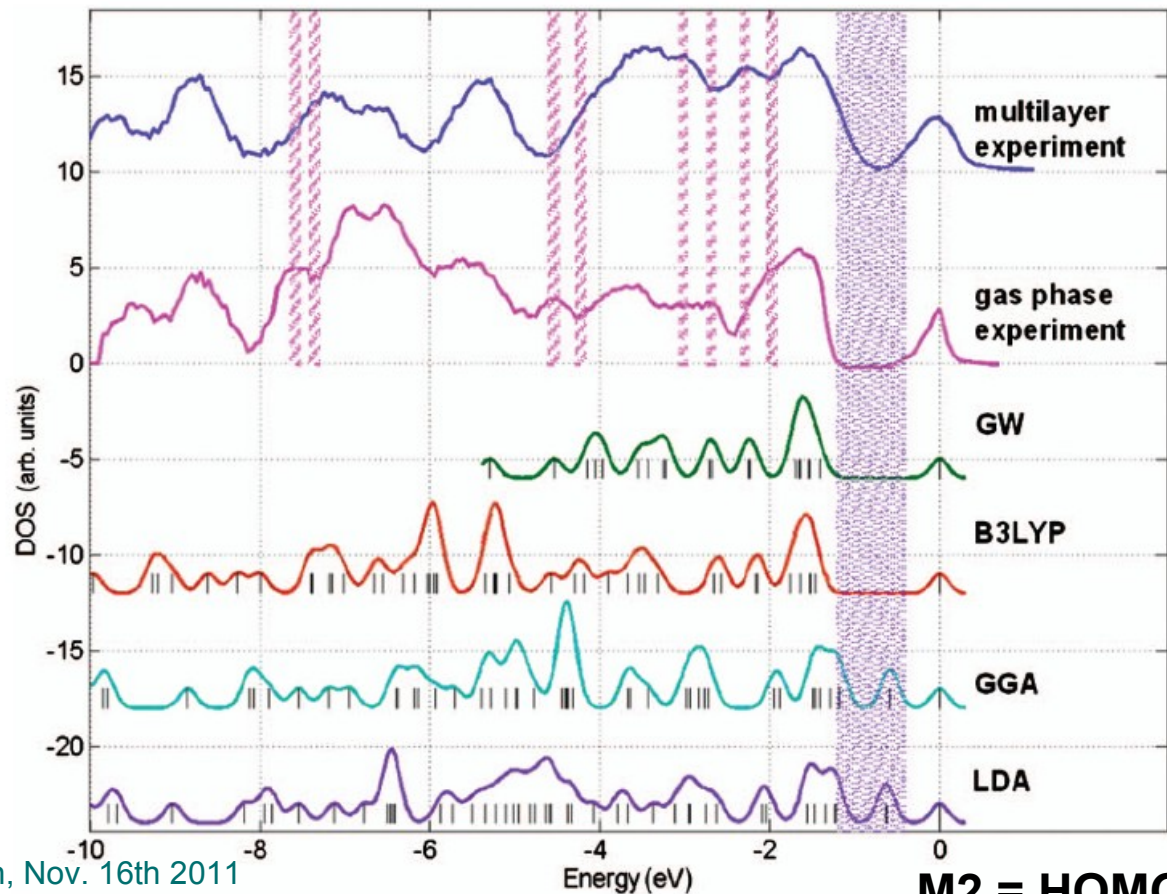
Böhringer et al., *Surf. Sci.* **419**, L95 (1998).

Identifying Orbitals

PHYSICAL REVIEW B 73, 195208 (2006)

Valence electronic structure of gas-phase 3,4,9,10-perylene tetracarboxylic acid dianhydride: Experiment and theory

Navit Dori,^{1,*} Mahesh Menon,^{1,*} Lennart Kilian,² Moritz Sokolowski,^{2,3} Leeor Kronik,^{1,†} and Eberhard Umbach²

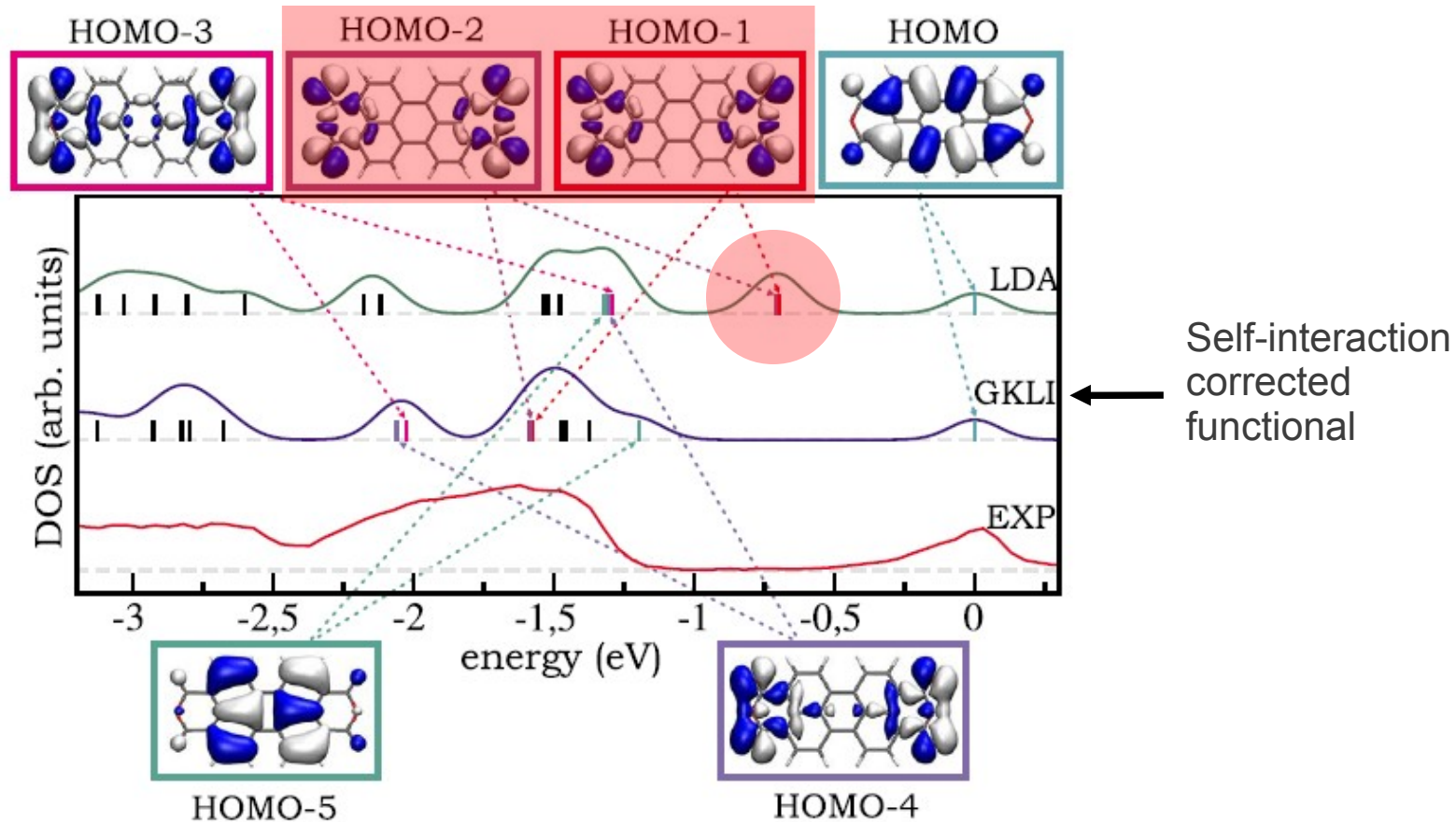


Identifying Orbitals

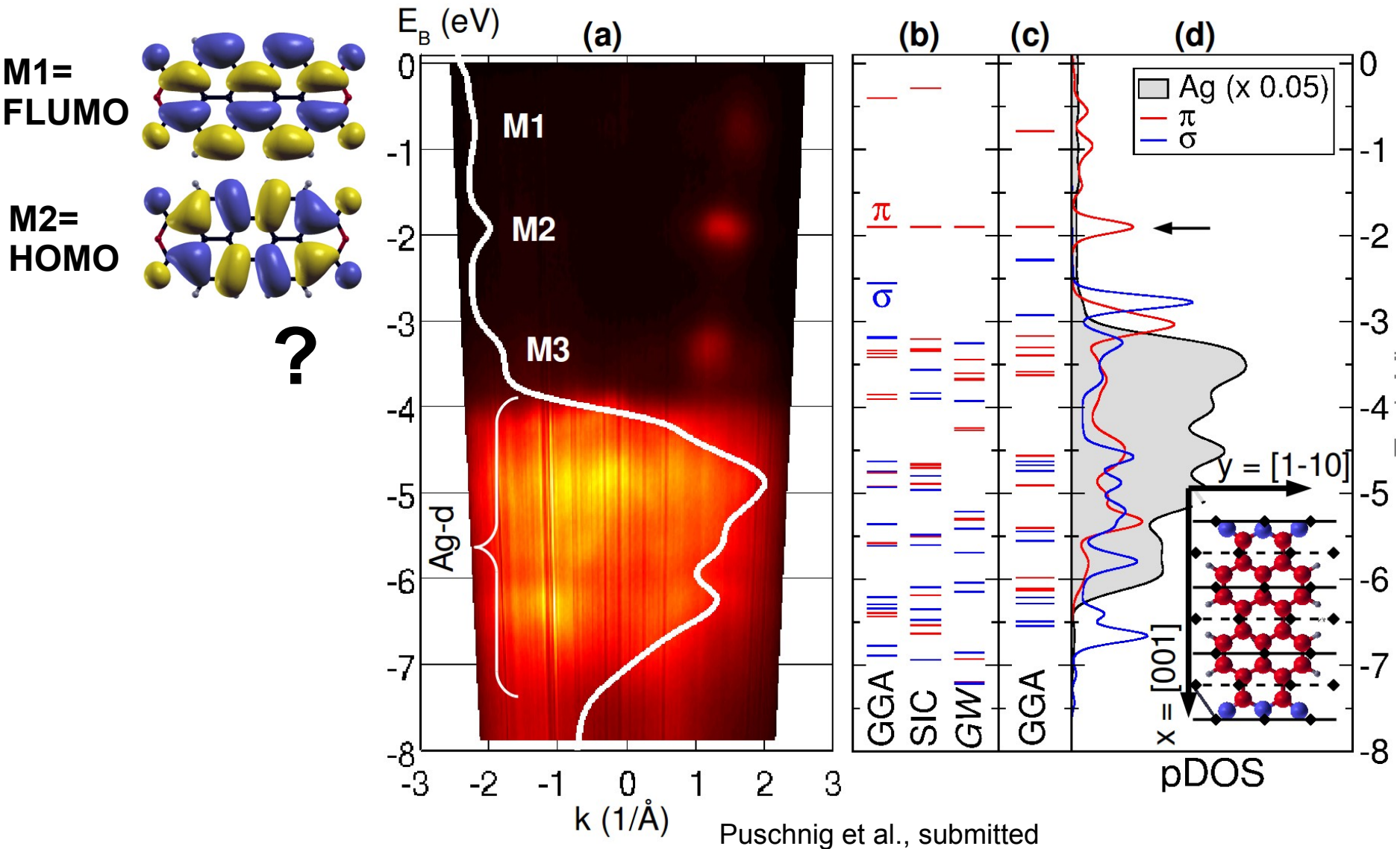
PHYSICAL REVIEW B 79, 201205(R) (2009)

When to trust photoelectron spectra from Kohn-Sham eigenvalues: The case of organic semiconductors

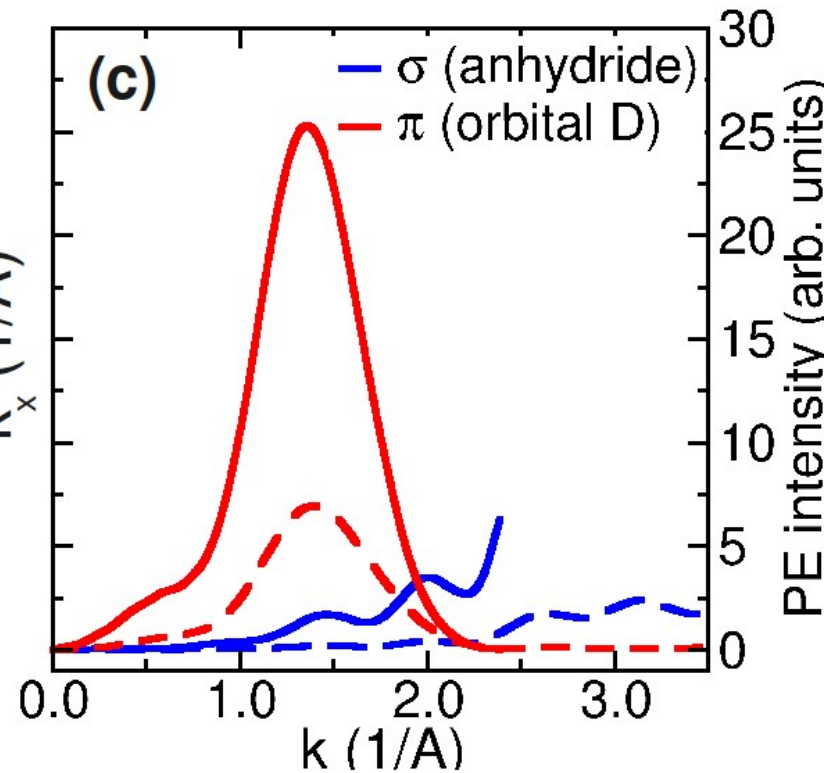
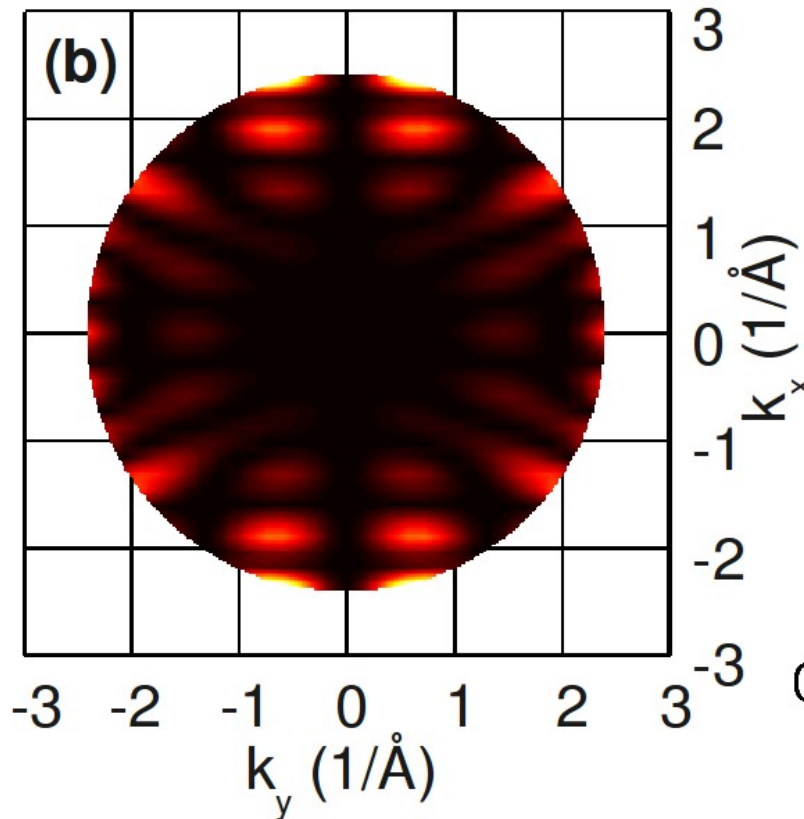
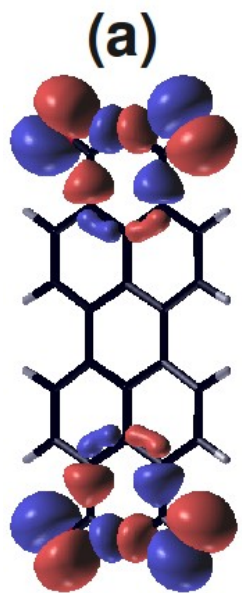
T. Körzdörfer and S. Kümmel N. Marom and L. Kronik



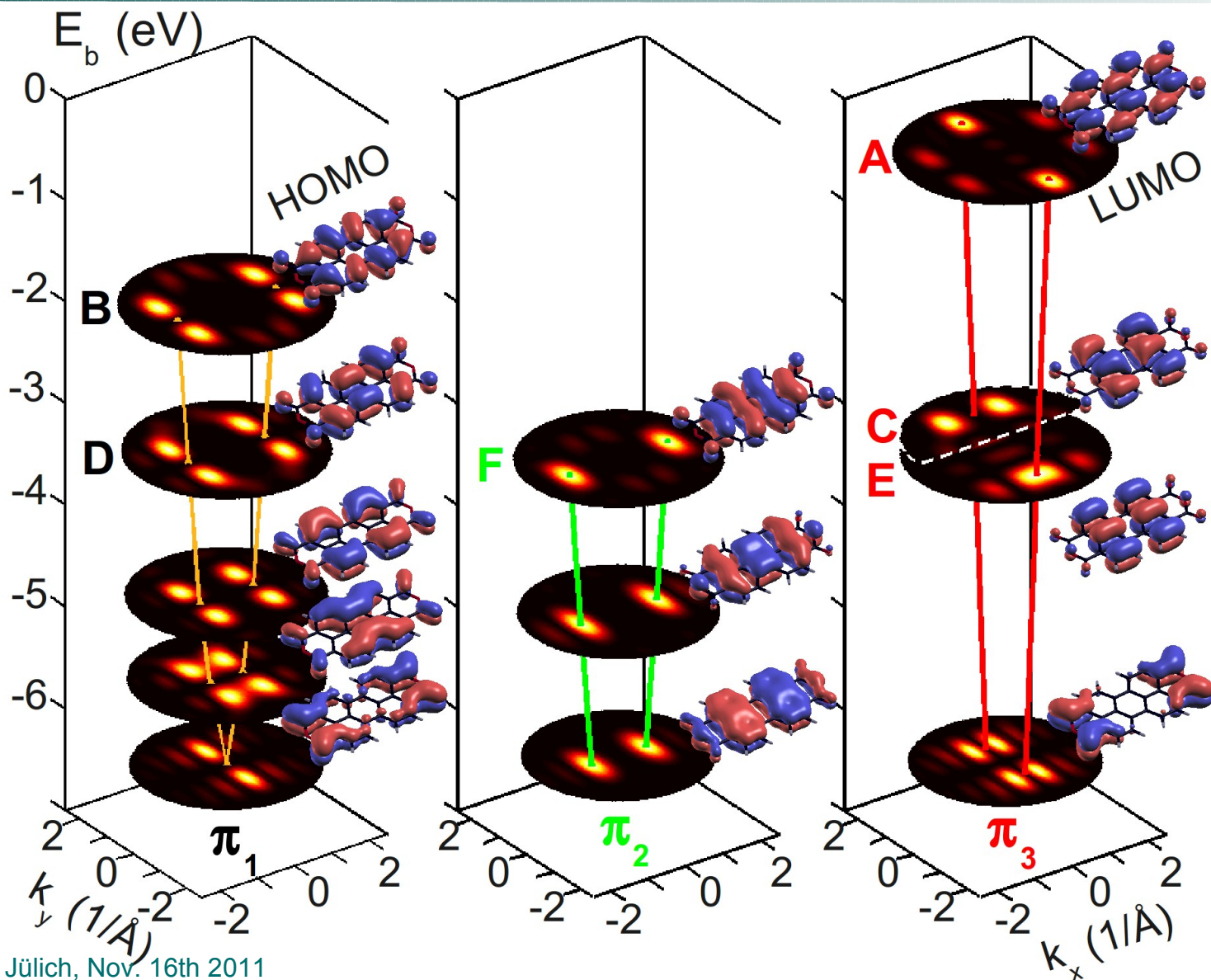
Identifying Orbitals



PE-Intensity: π vs. σ



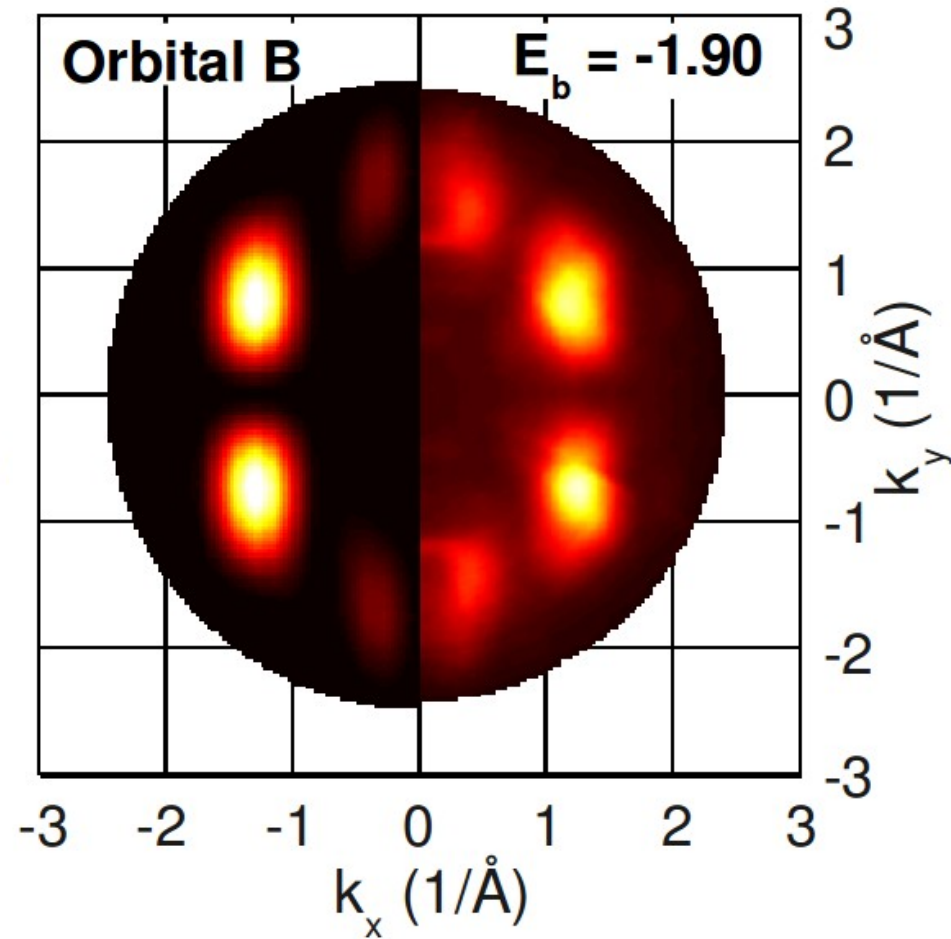
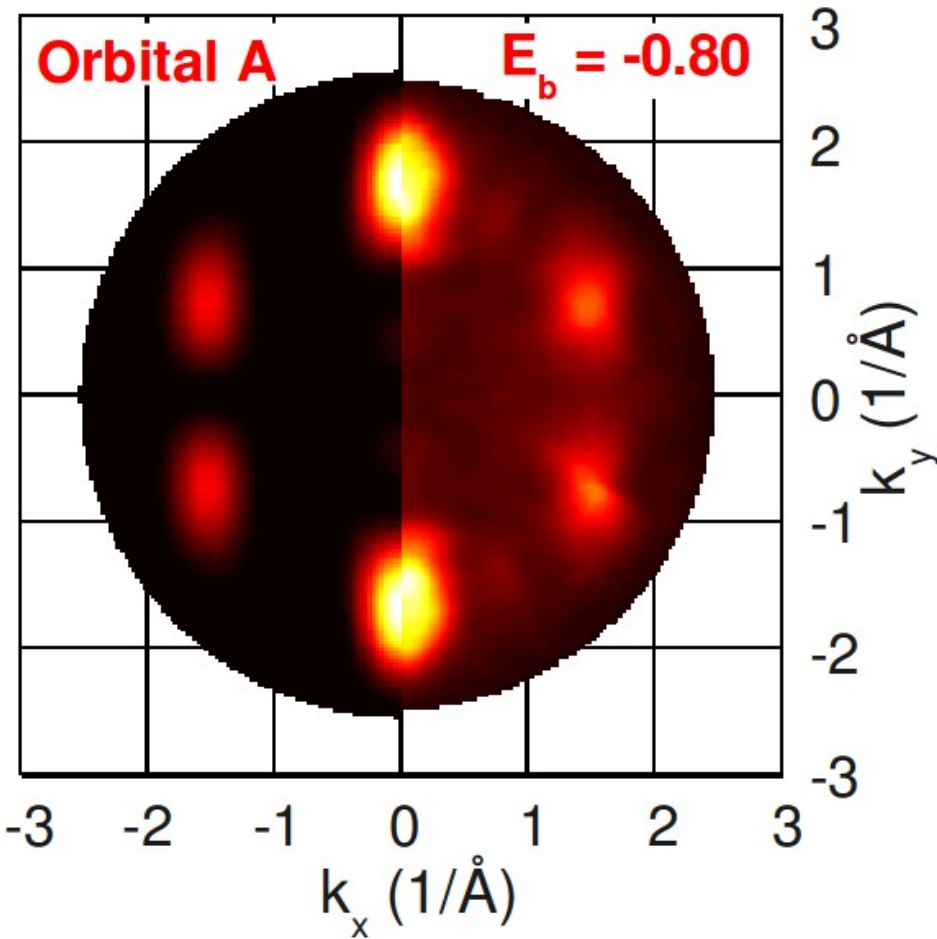
π -bands of PTCDA



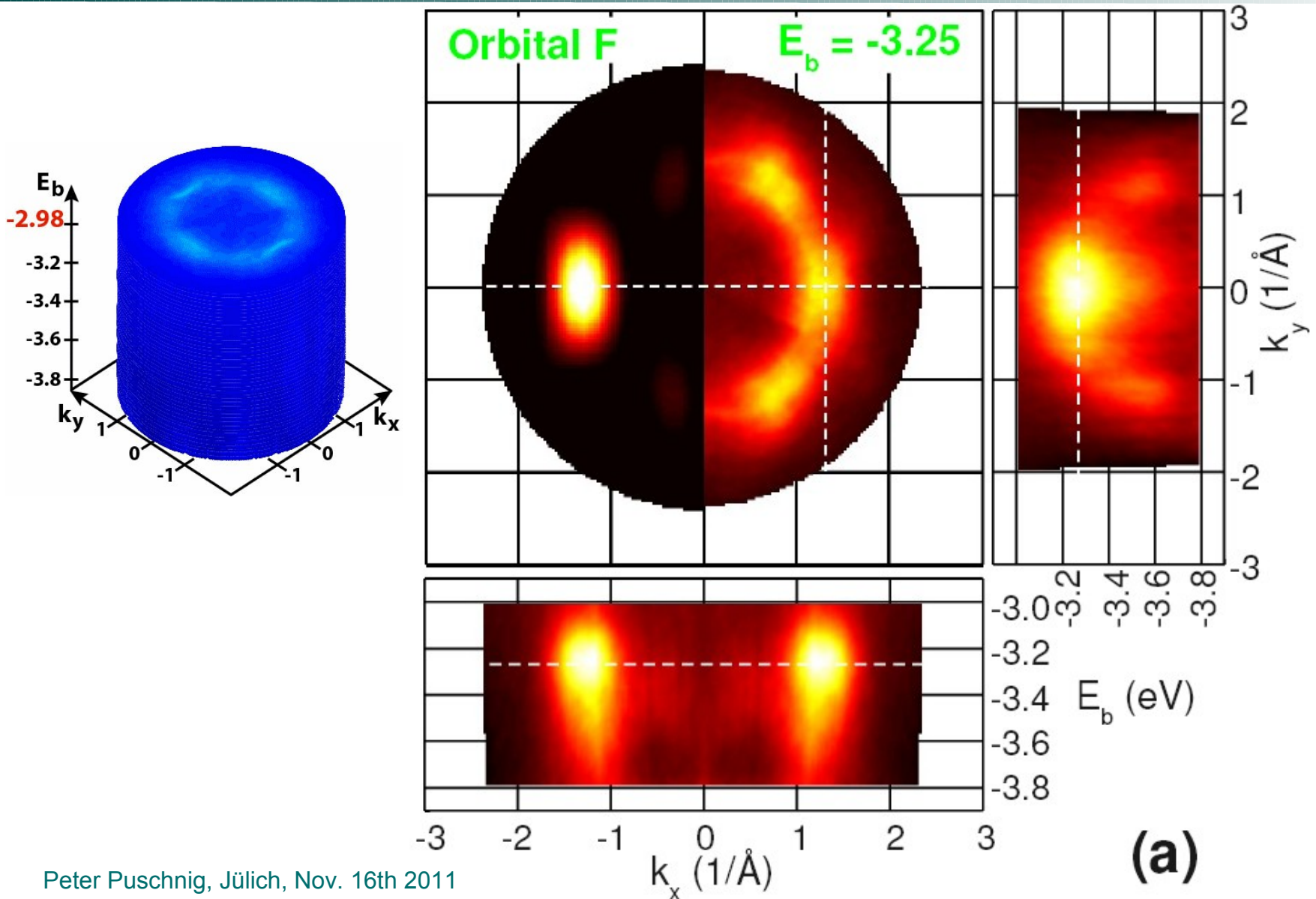
PTCDA / Ag(110)



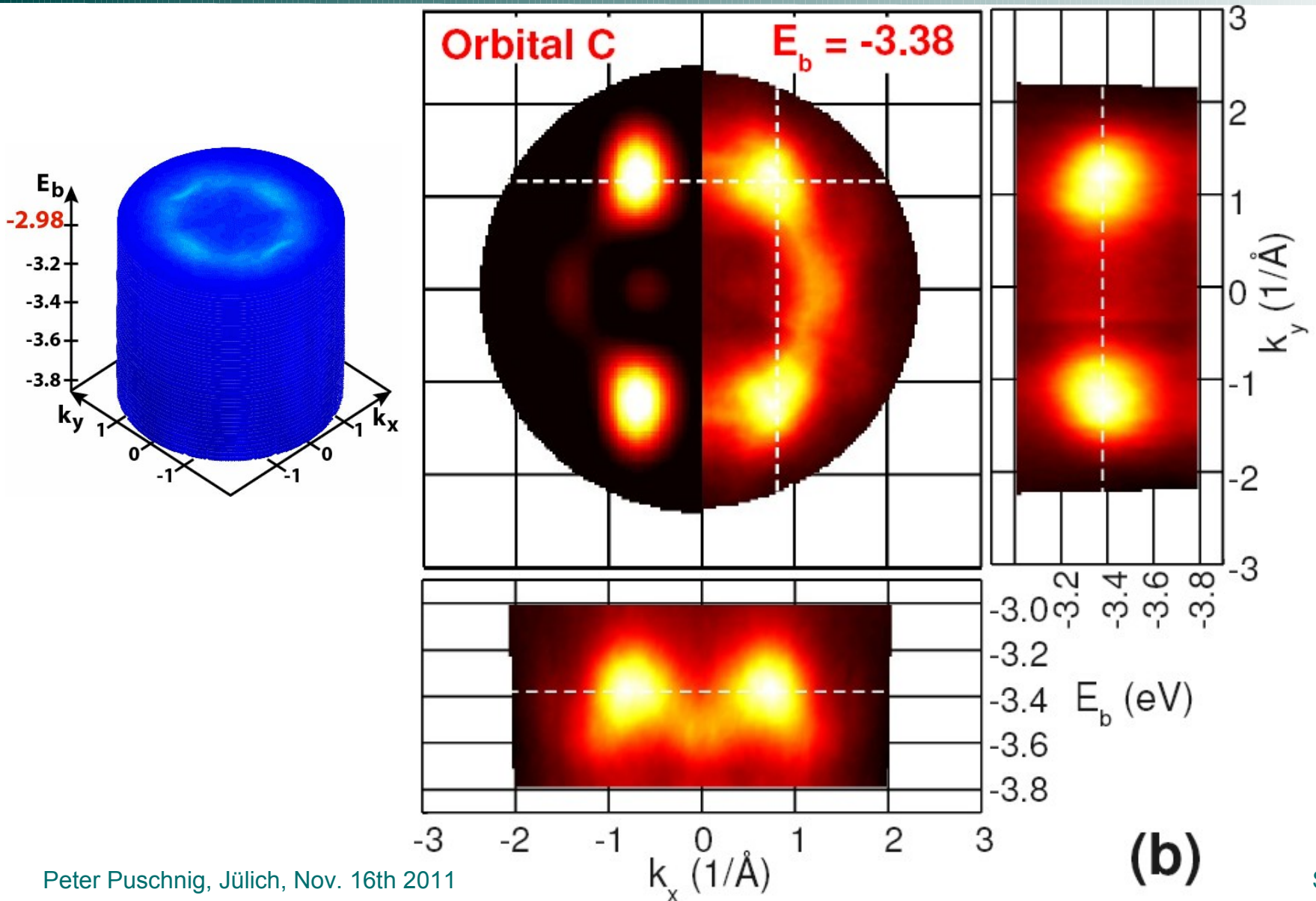
FLUMO (=M1) and HOMO (=M2)



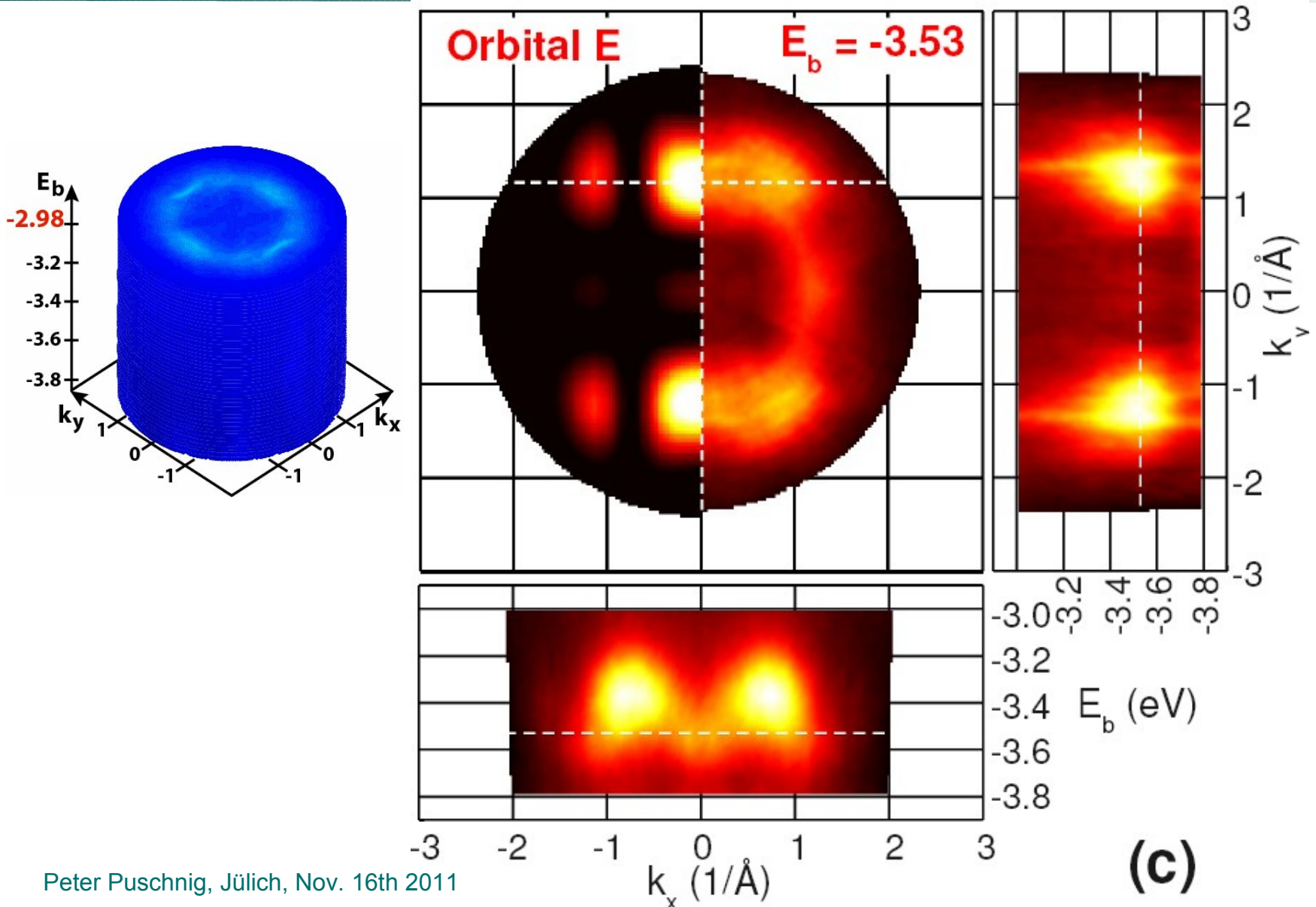
What is the Origin of M3?



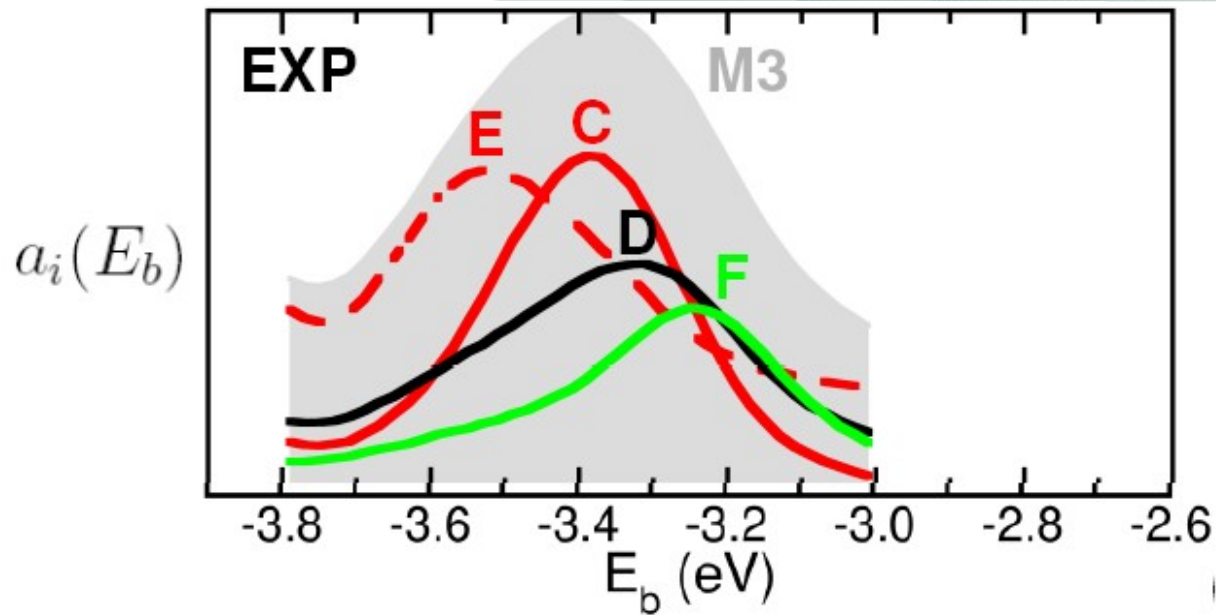
What is the Origin of M3?



What is the Origin of M3?



Projected DOS from ARPES!



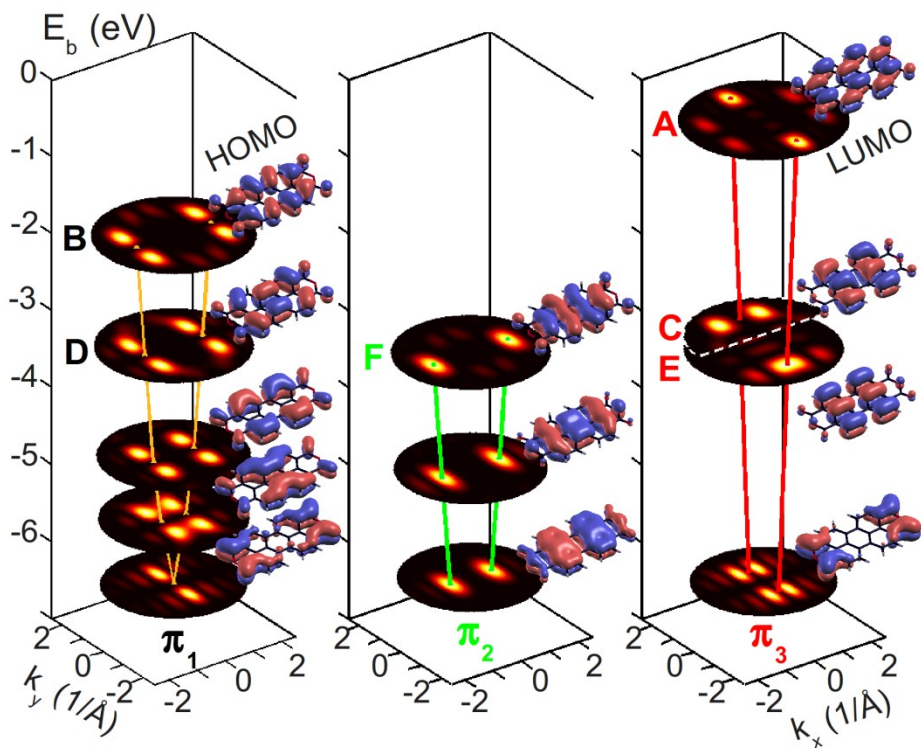
Fit parameters

$$\chi^2 = \int dk_x dk_y \left[I(E_b, k_x, k_y) - \sum_i a_i(E_b) \psi_i(k_x, k_y) \right]^2$$

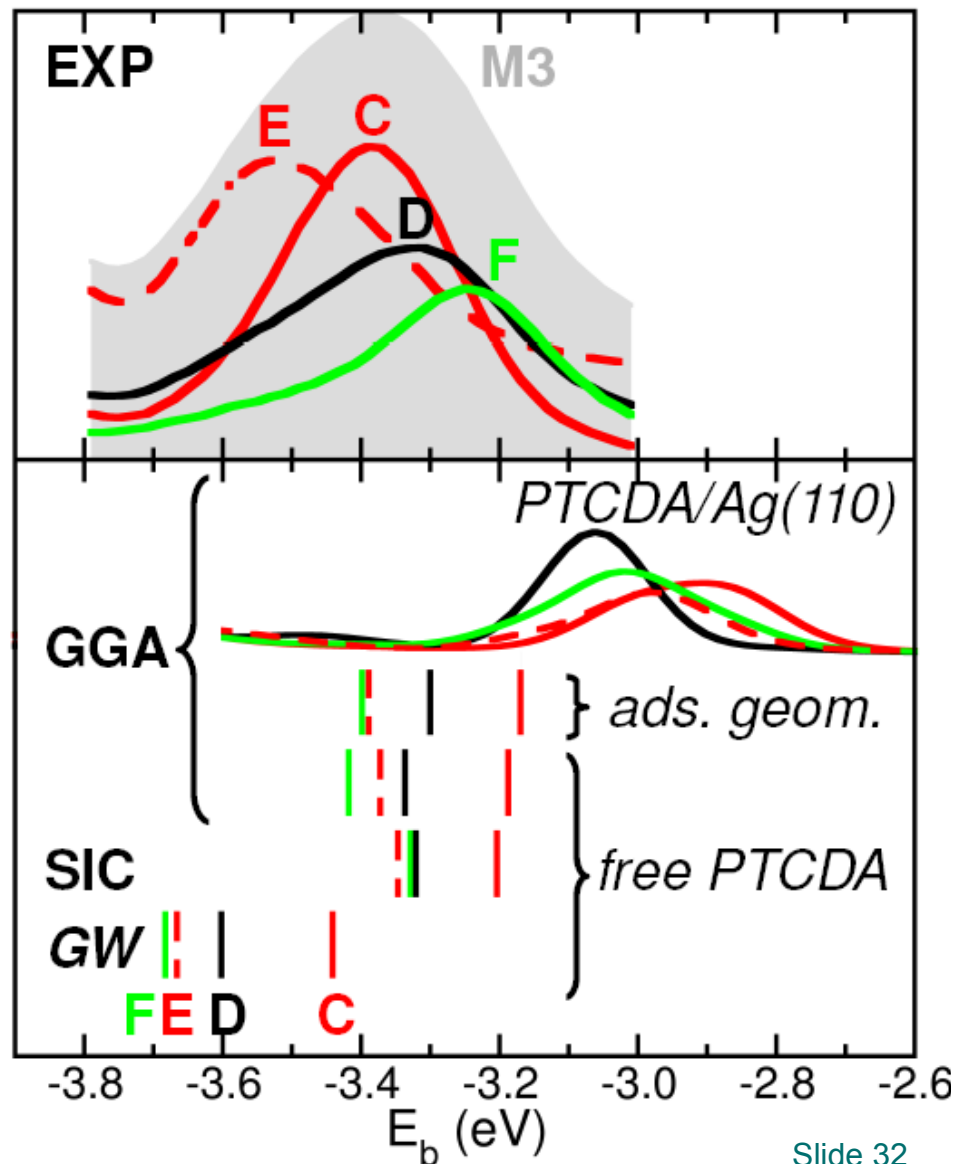
ARPES intensity

Theoretical
momentum maps

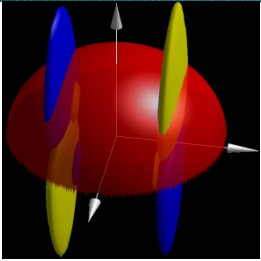
Benchmark for Theory



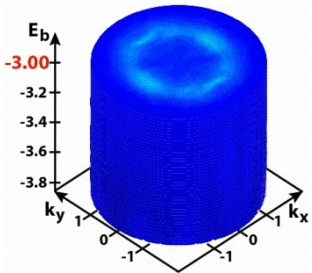
Peter Puschnig, Jülich, Nov. 16th 2011



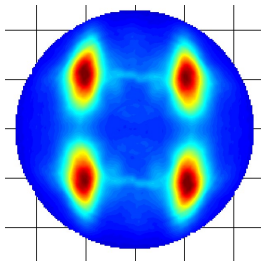
Slide 32



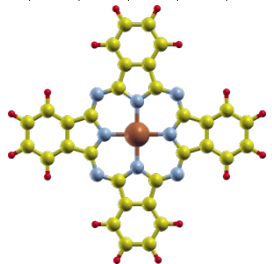
Angle-Resolved Photoemission



PTCDA / Ag(110)

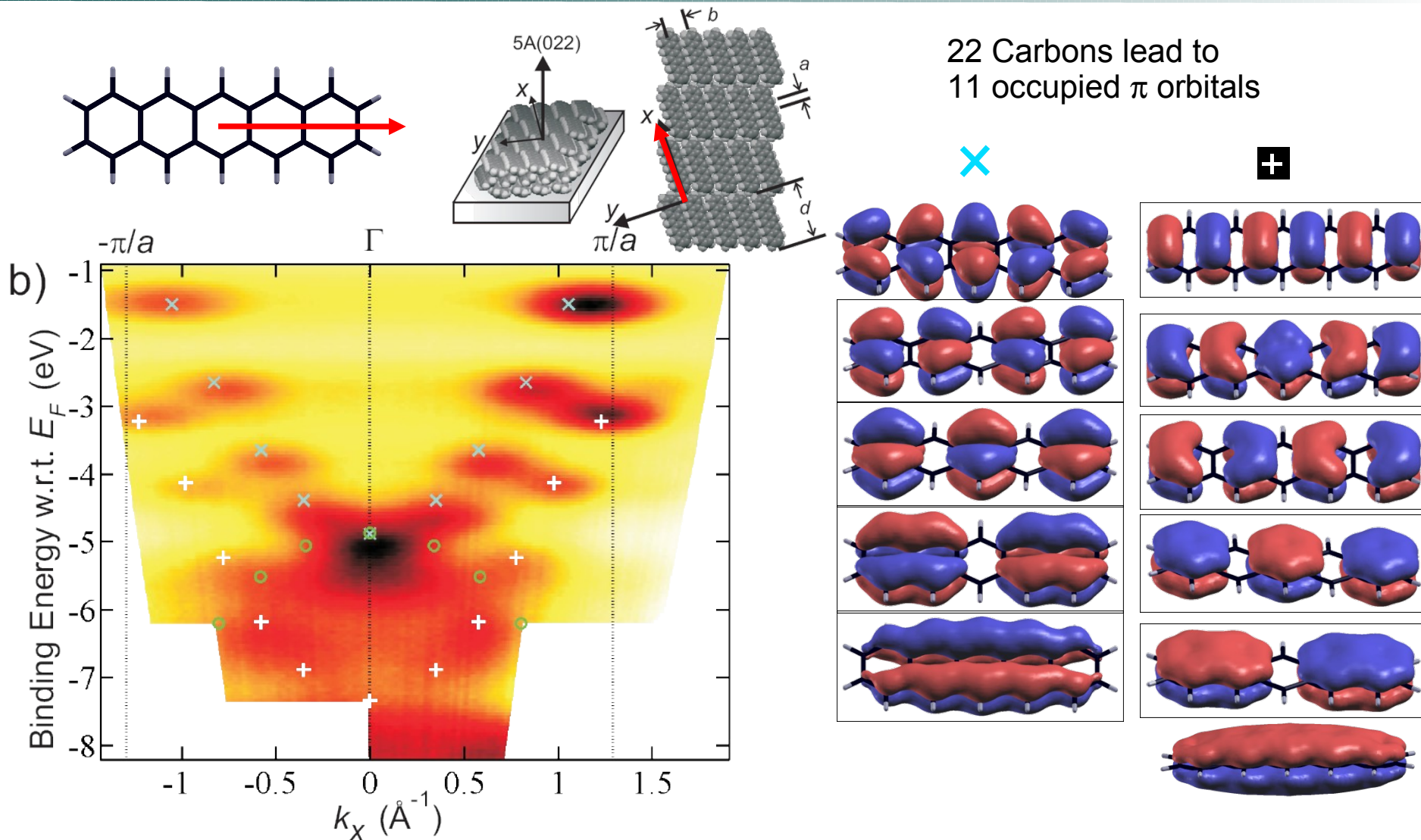


Pentacene / Ag(110)

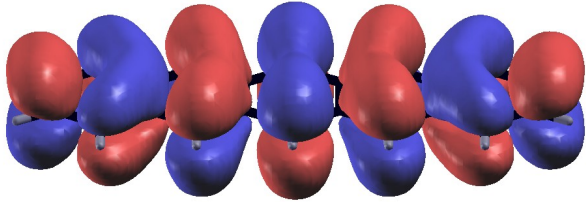


H2Pc and CuPc / Au(110)

Pentacene Multilayer



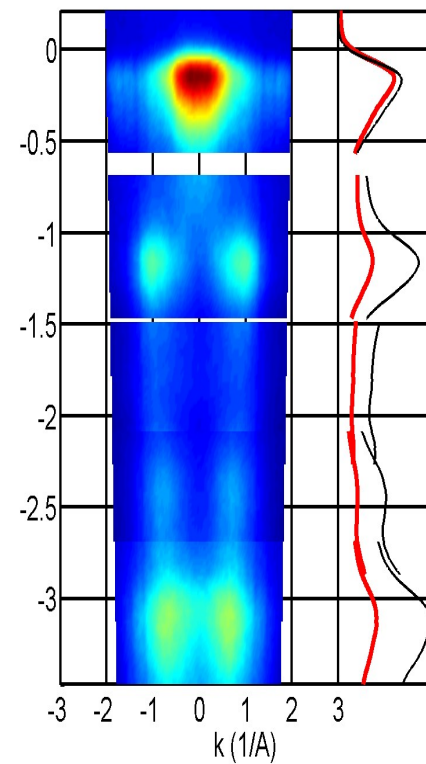
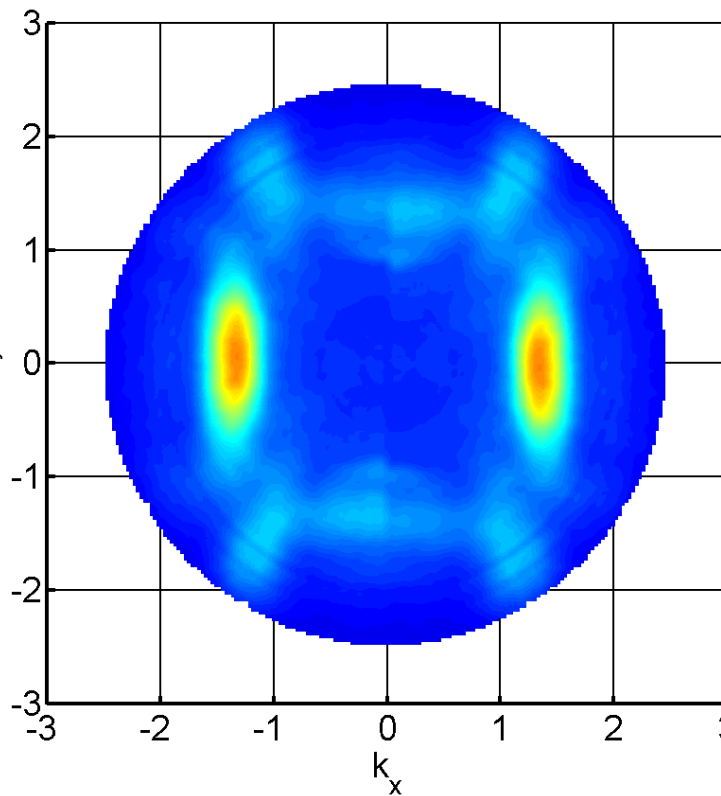
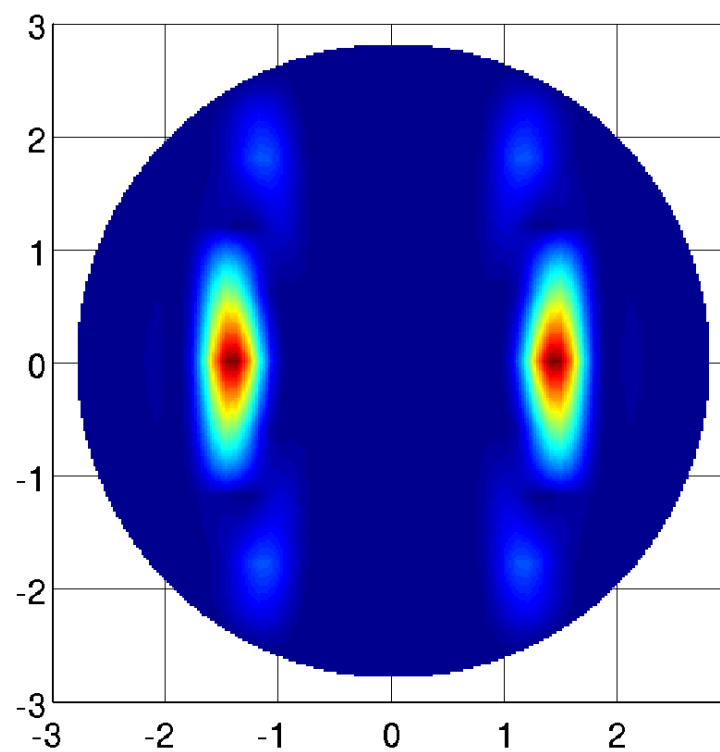
Pentacene / Ag(110): FLUMO



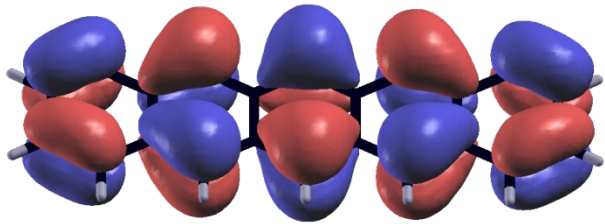
ARPES

$E_b = -0.1 \text{ eV}$

EDC-kx=1.44



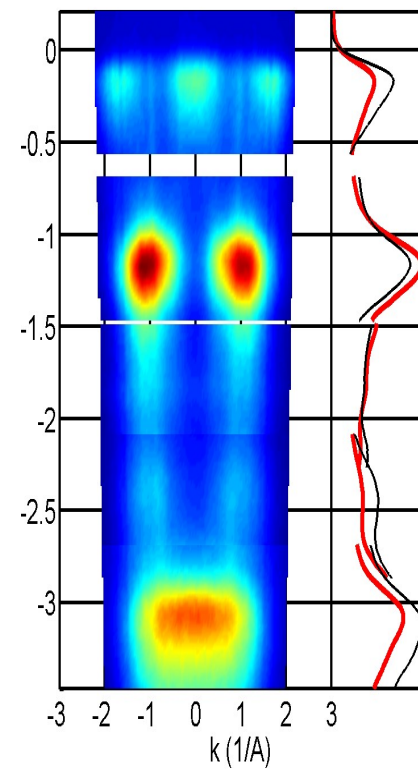
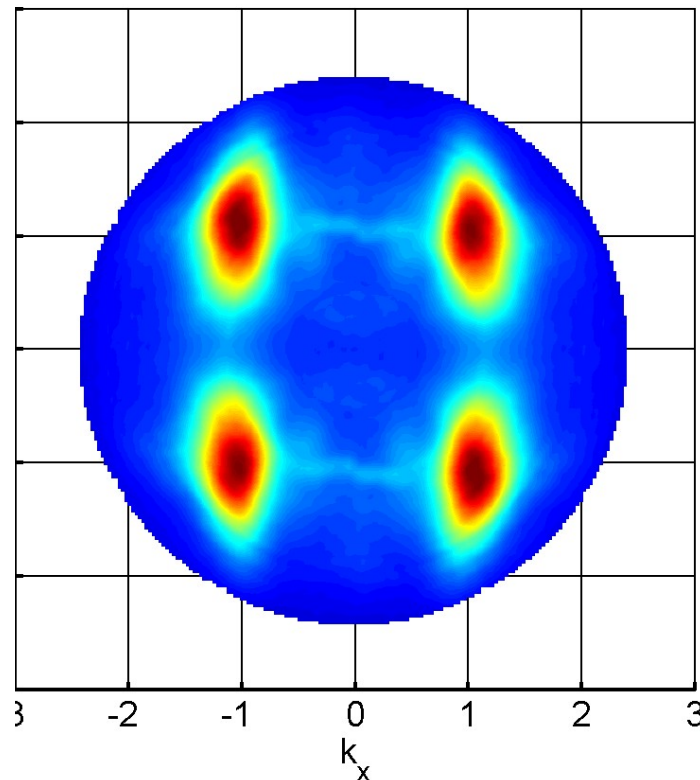
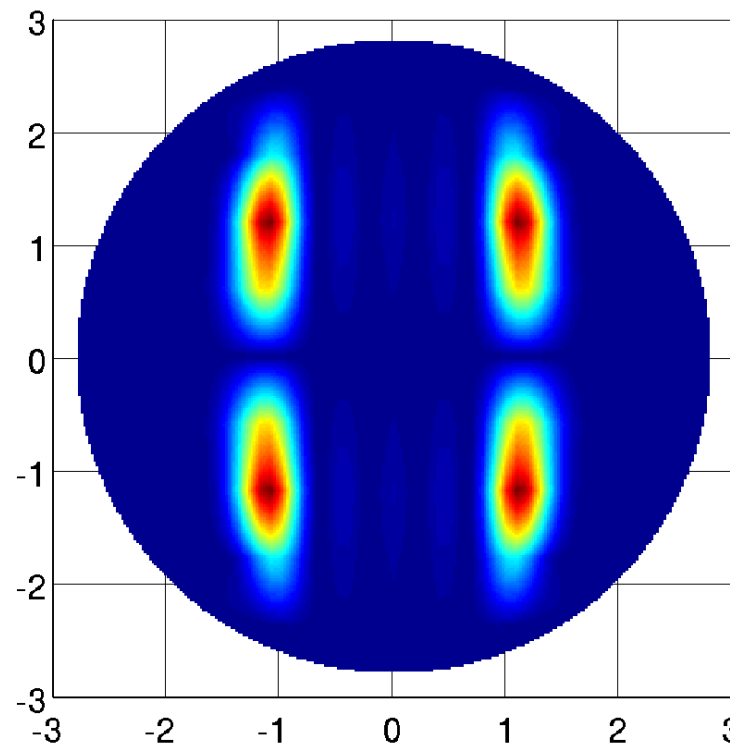
Pentacene / Ag(110): HOMO



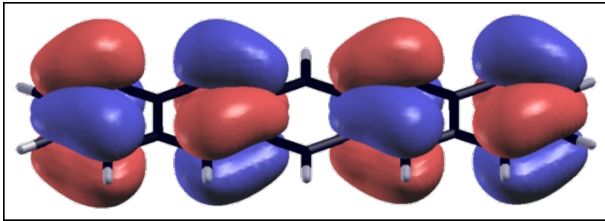
ARPES

$E_b = -1.2\text{eV}$

EDC-kx=1.11



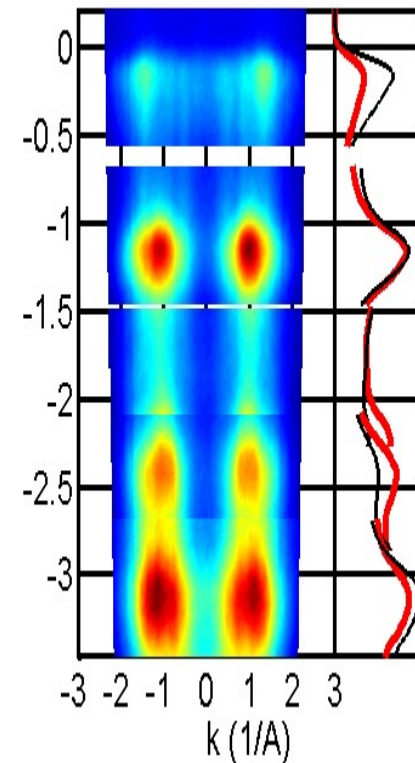
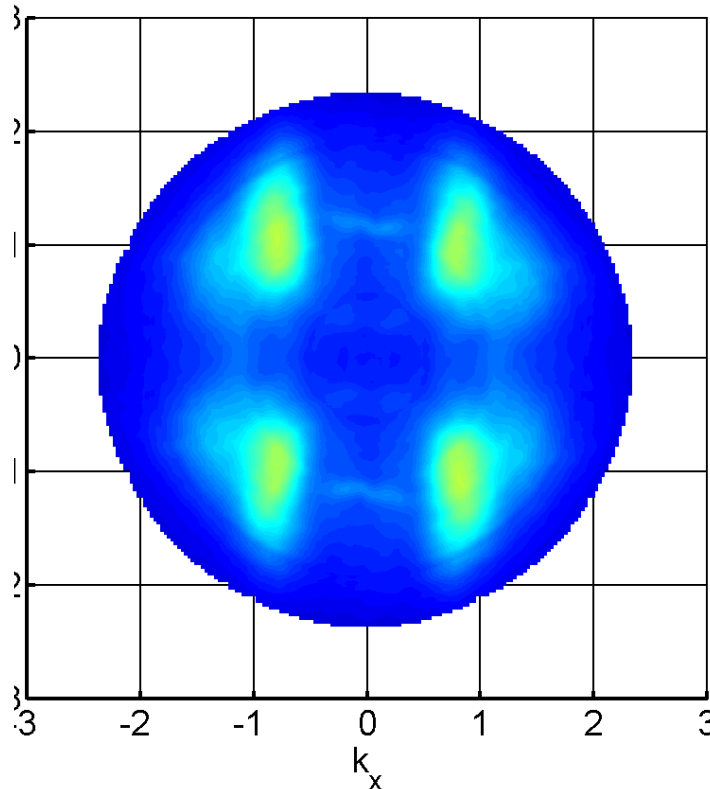
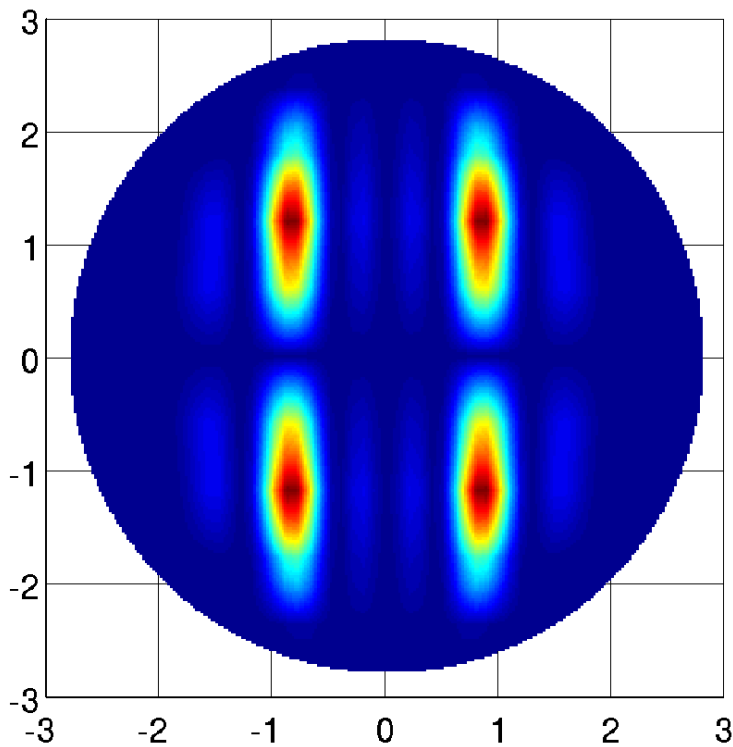
Pentacene / Ag(110): HOMO-1



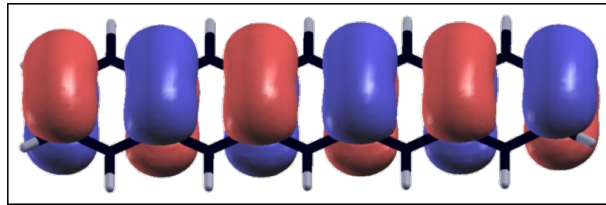
ARPES

$E_b = -2.4\text{eV}$

EDC-kx=0.8



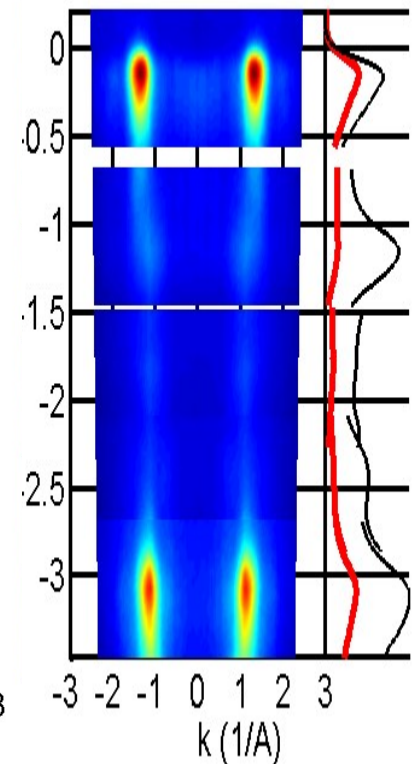
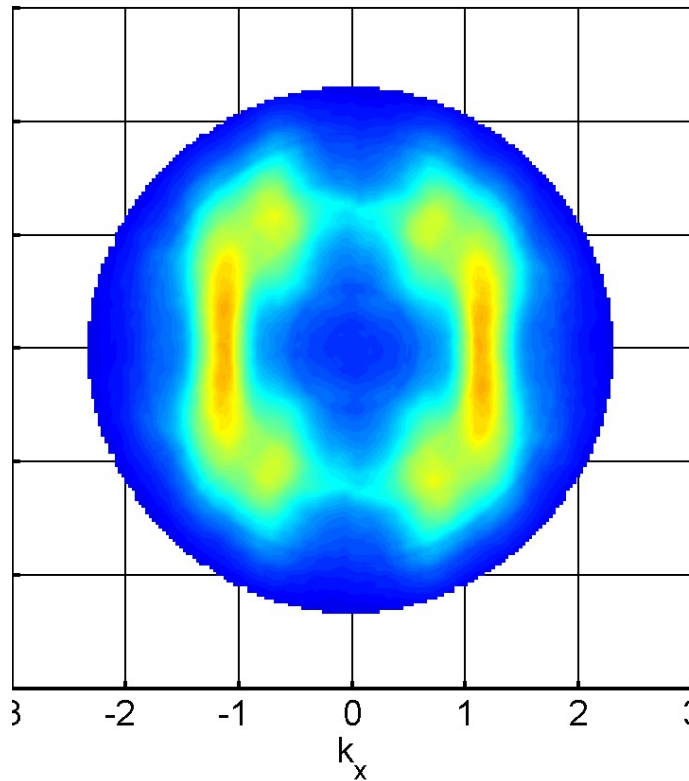
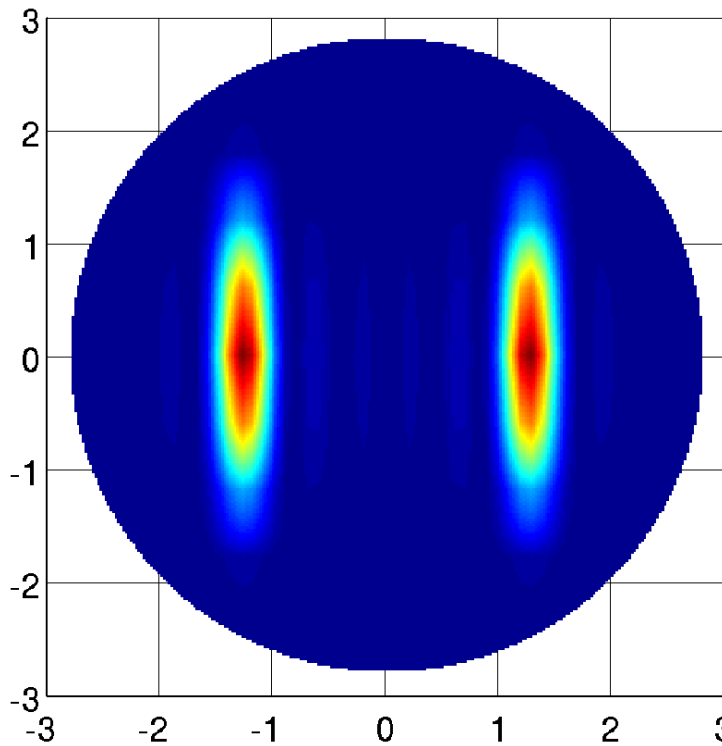
Pentacene / Ag(110): HOMO-2



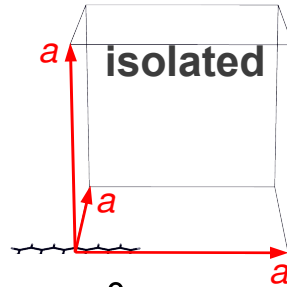
ARPES

$E_b = -3.1\text{eV}$

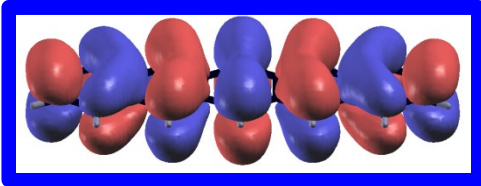
EDC- $k_y=0$



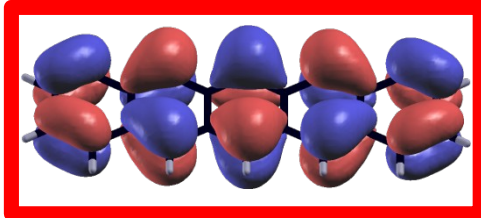
Pentacene: GW-Calculations



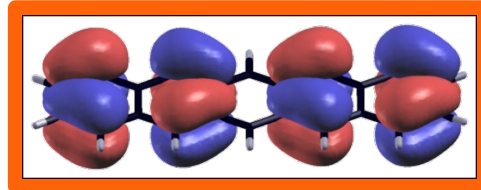
LUMO



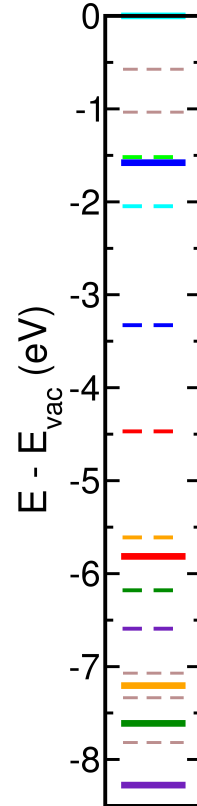
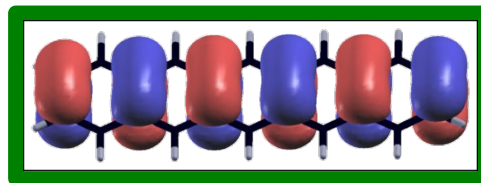
HOMO



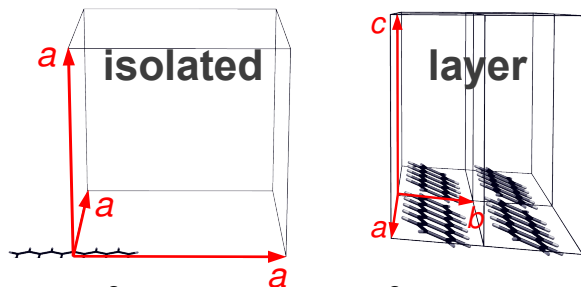
HOMO-1



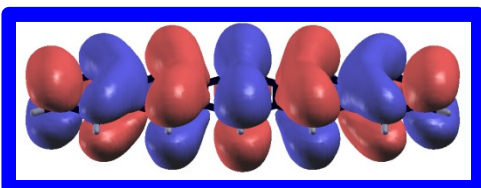
HOMO-2



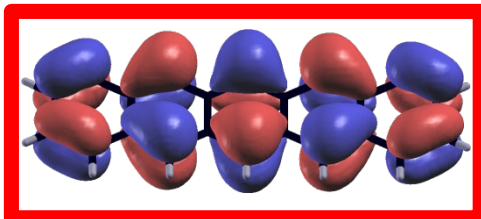
Pentacene: GW-Calculations



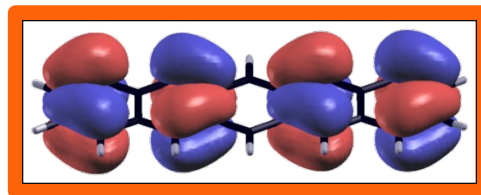
LUMO



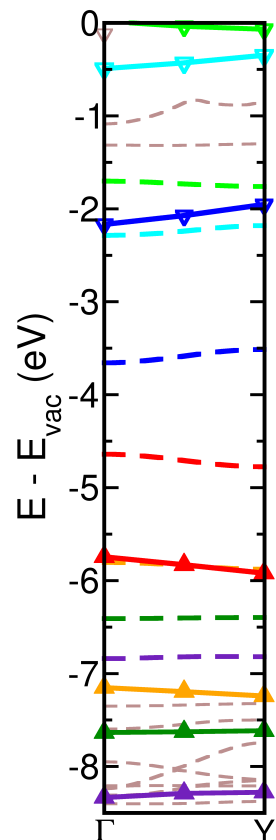
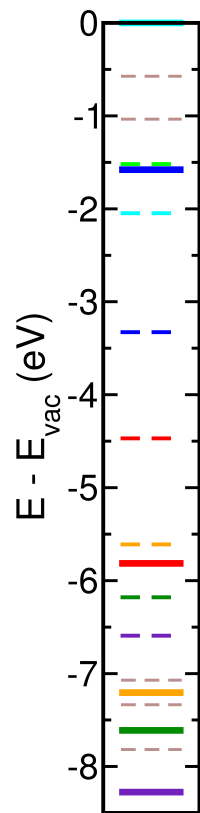
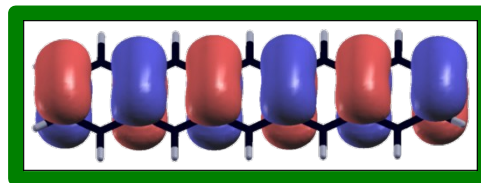
HOMO



HOMO-1

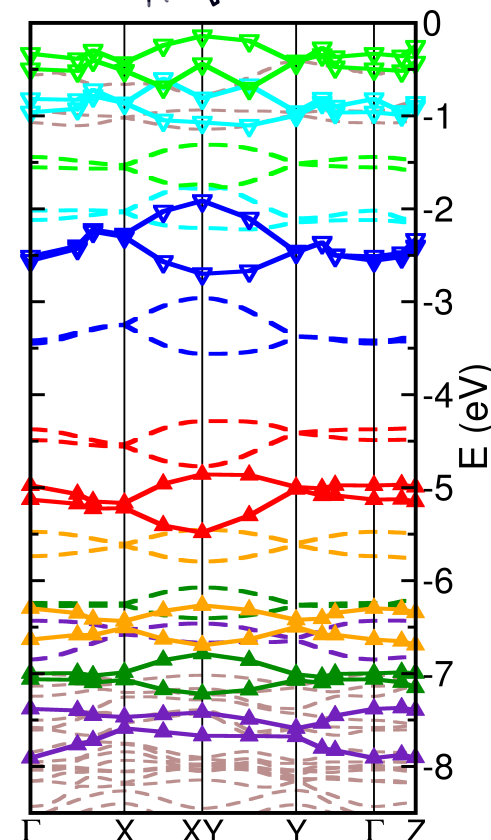
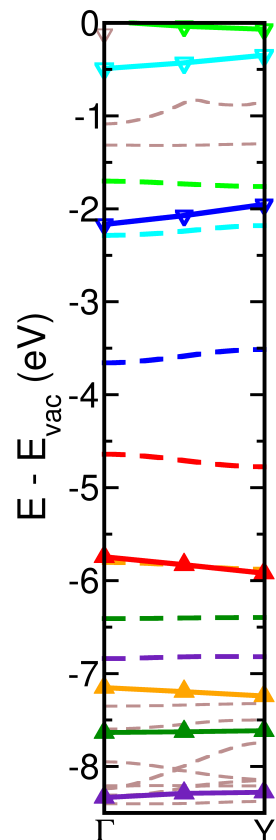
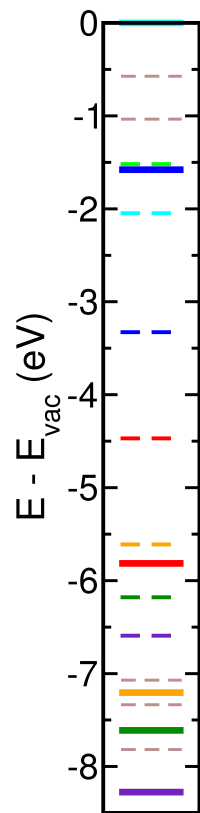
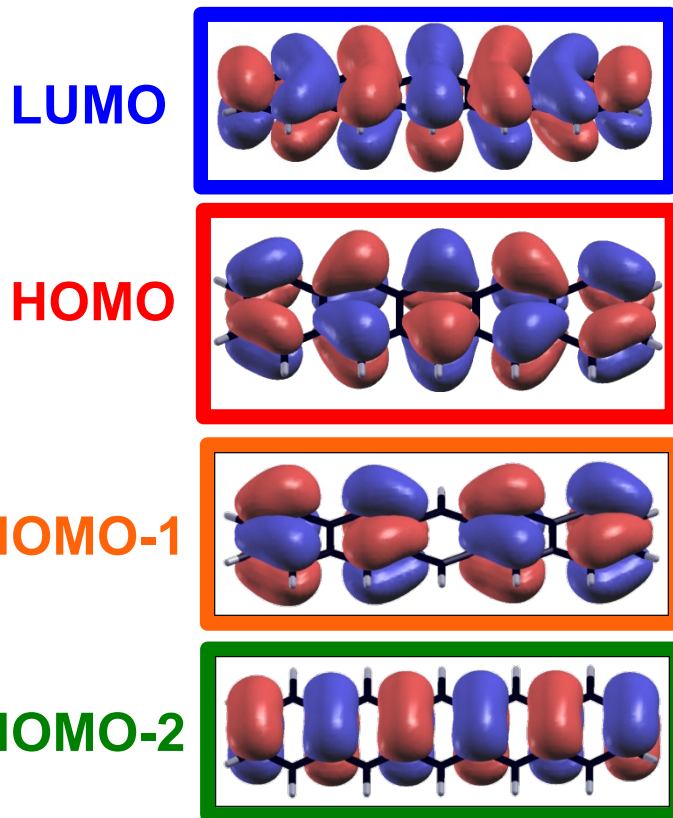
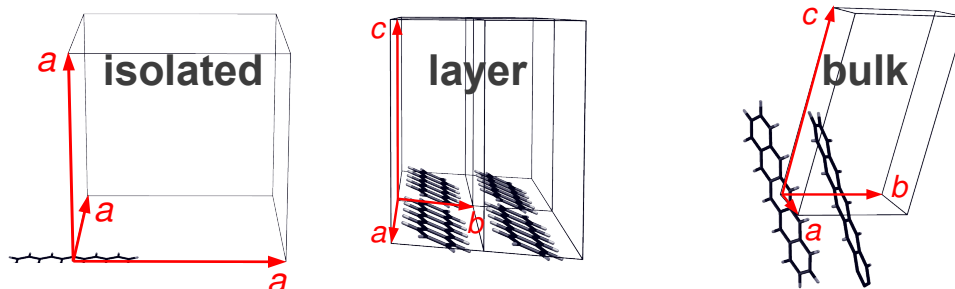


HOMO-2



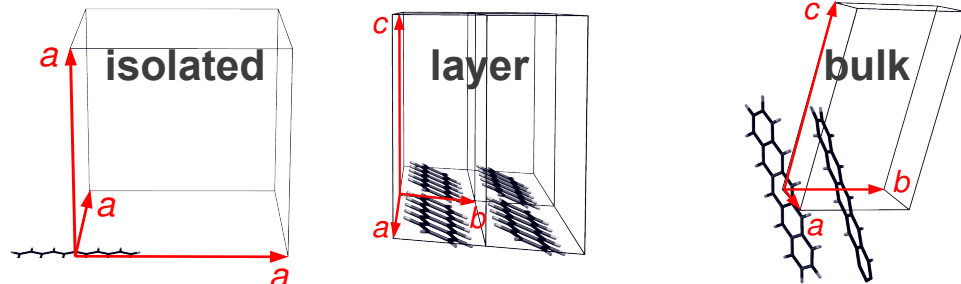
GGA (dashed) vs. G_0W_0 (full lines)

Pentacene: GW-Calculations



Pentacene: GW-Calculations

- [1] IPES: Amy, Org. Electr. 6,85 (2005).
- [2] Berkebile, PRB 77, 115312 (2008).
- [3] Ules et al., unpublished.



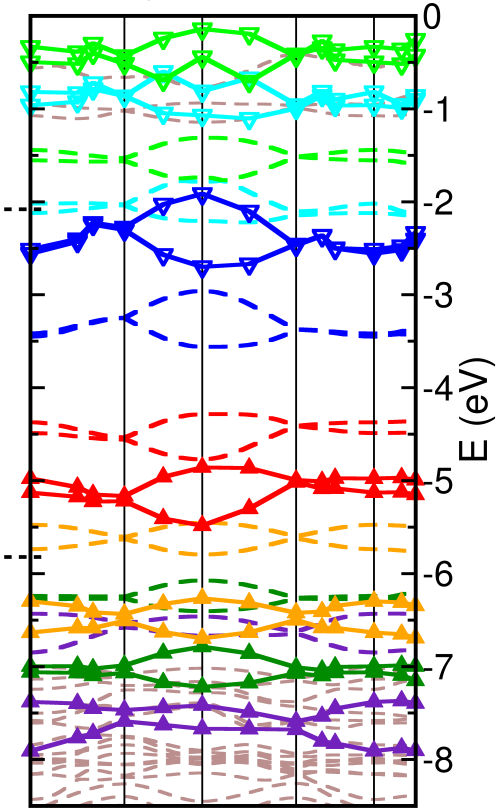
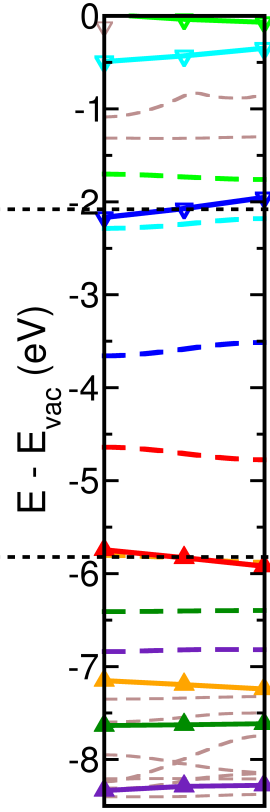
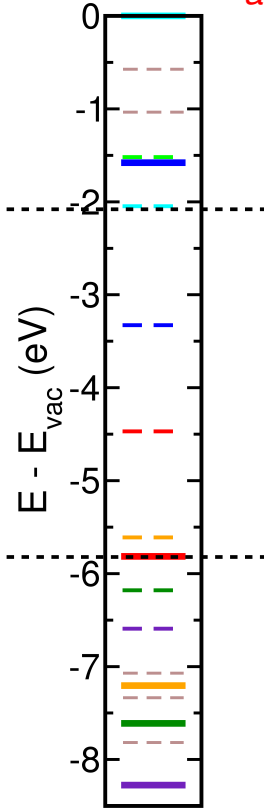
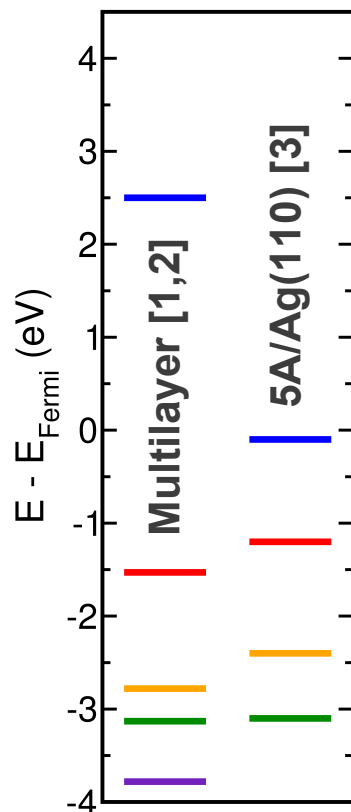
EXP

(F)LUMO

HOMO

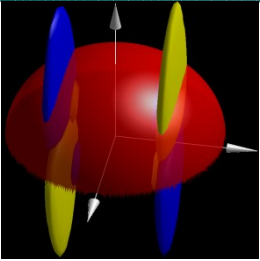
HOMO-1

HOMO-2

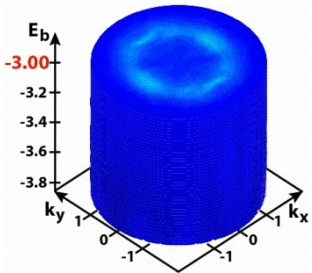


GGA (dashed) vs. G_0W_0 (full lines)

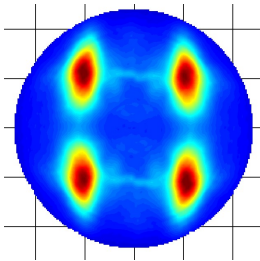
Overview



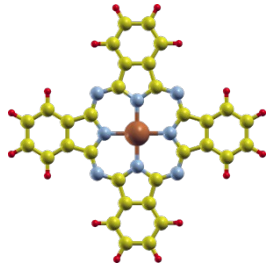
Angle-Resolved Photoemission



PTCDA / Ag(110)

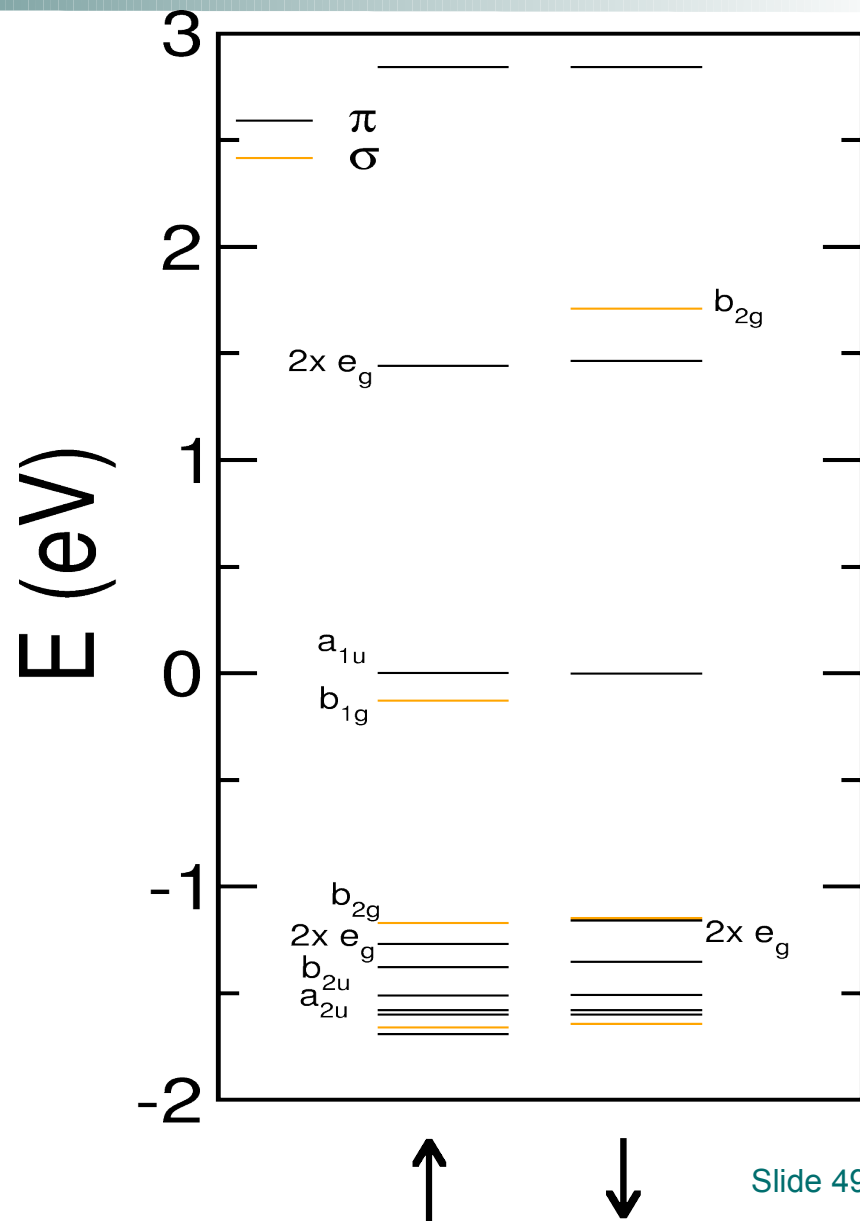
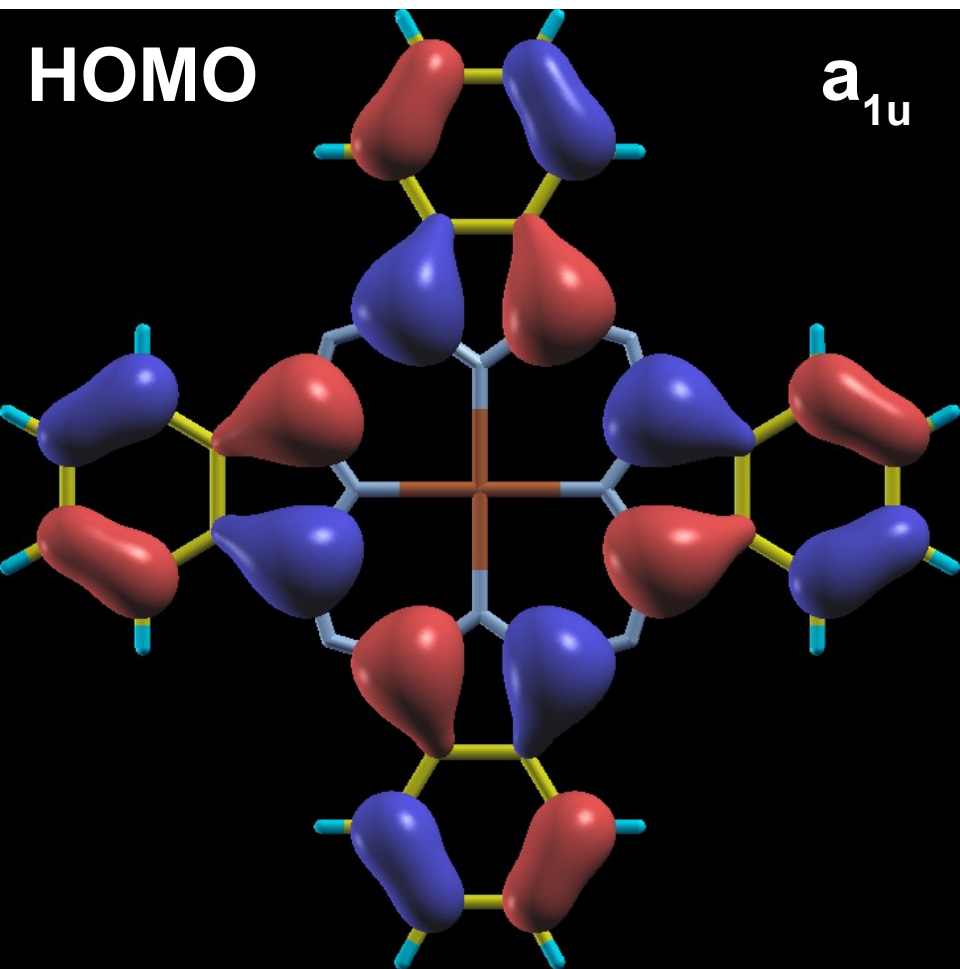


Pentacene / Ag(110)



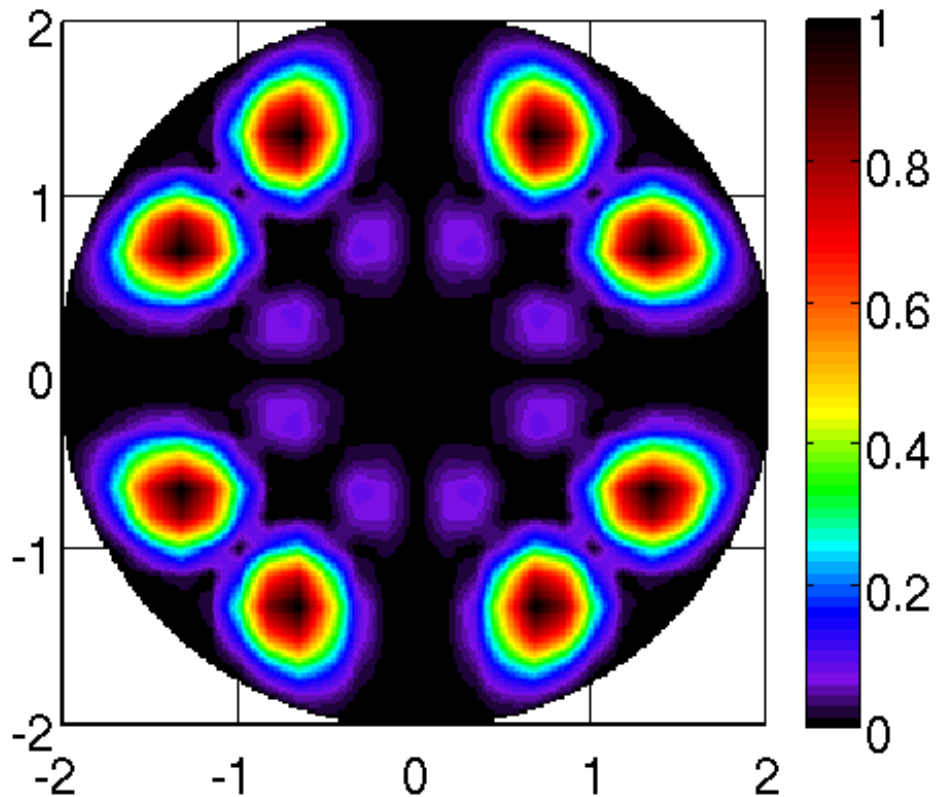
H₂Pc and CuPc / Au(110)

CuPc – Isolated Molecule

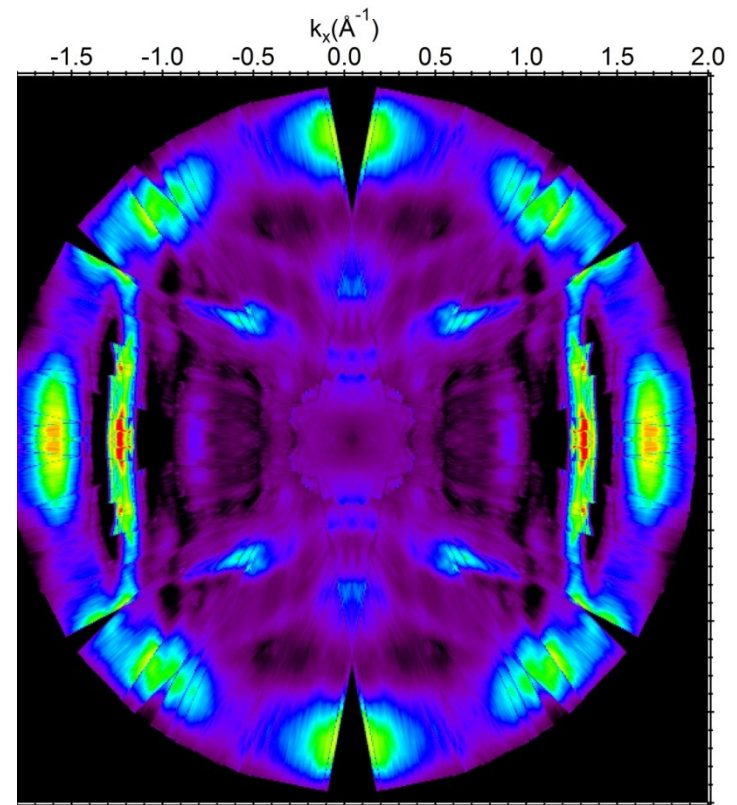


CuPc/Au(110) – HOMO

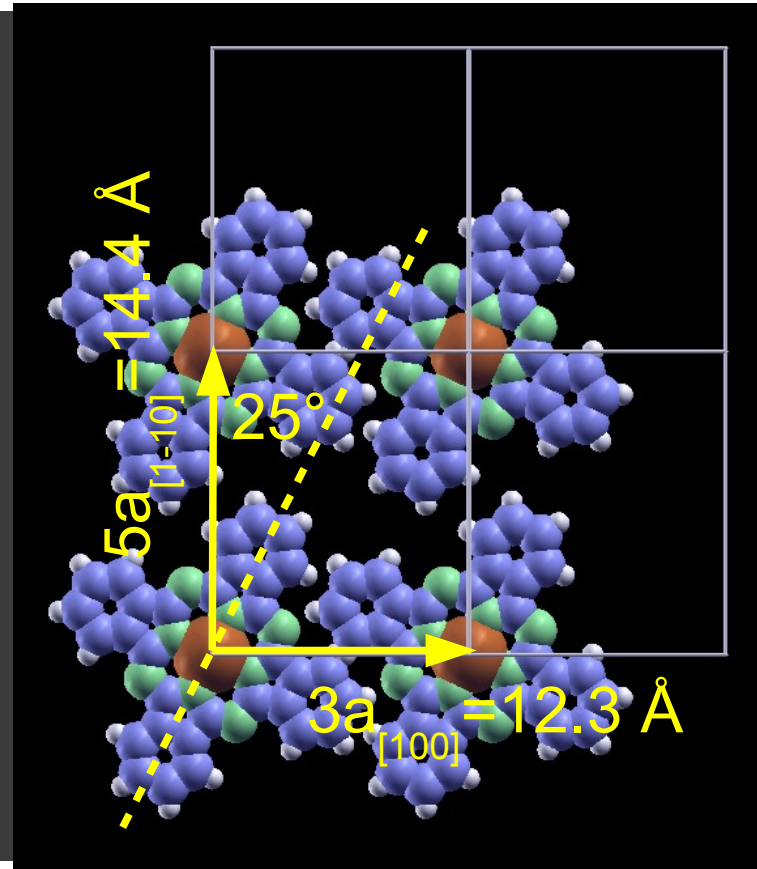
DFT



ARPES



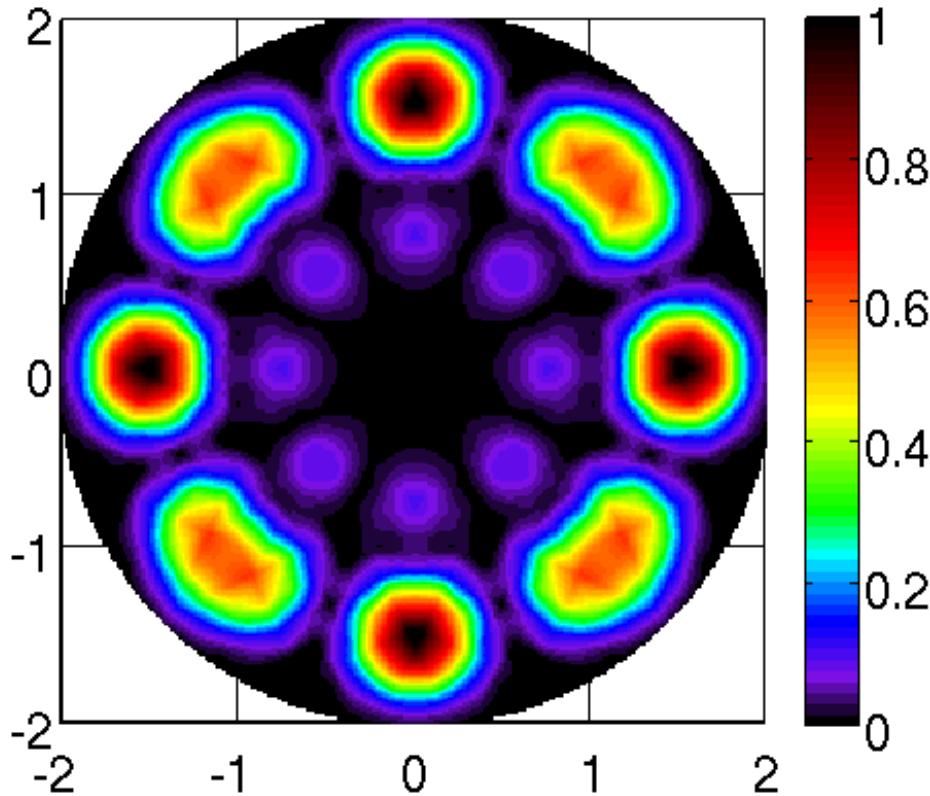
CuPc/Au(110)_(5x3)



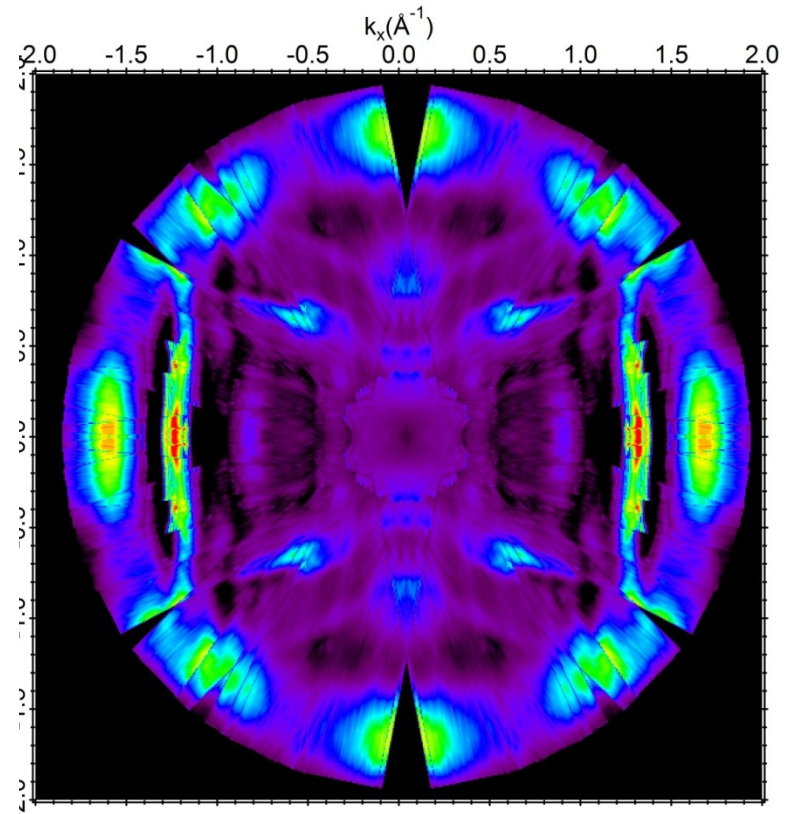
CuPc/Au(110): Two Domains

DFT

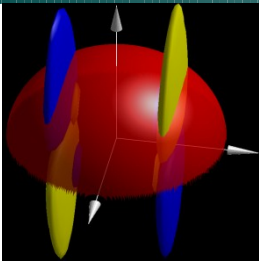
+25 deg and -25 deg



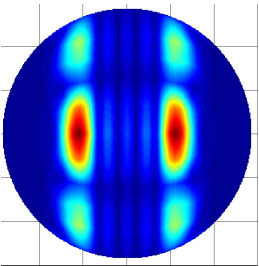
ARPES



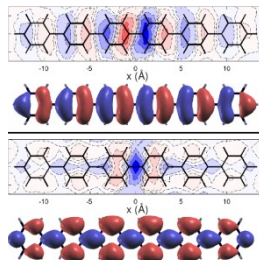
Summary



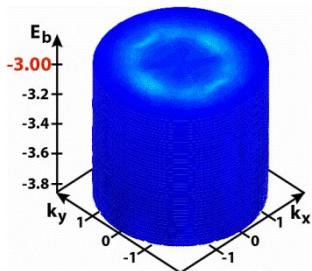
- **ARPES intensity proportional to FT of molecular orbital**
- Plane wave final state approximation works for ...
 - pi-orbitals of organic molecules
 - No heavy atoms
 - Electron emission direction close to electric field vector of incoming photon



- **Accurate determination of molecular tilt angles**
 - Pentacene thick film: *Science* **326**, 702 (2009).
 - Azimuthal orientation of tetraphenyl-porphyrine / Cu(110): *in preparation*
 - Azimuthal orientation of CuPc / Au(110): *in preparation*
 - Tilt angle of Cs-doped sexiphenyl / Cu(110) : *in preparation*



- **Orbital Reconstruction / Orbital Hybridization**
 - Real space images of p-6P HOMO and LUMO: *Science* **326**, 702 (2009).
 - Analysis of 6P / Cu(110) hybridization: *PCCP* **13**, 3604 (2011)
 - PTCDA / Ag(110): *PRL* **104**, 233004 (2010).
 - Coronene / Hexa-benzo-coronene („graphene quantum well states“), *submitted*



- **Orbital Tomography**
 - Identification of molecular orbitals
 - Experimentally determined DOS projected onto MOs
 - Comprehensive experimental data to benchmark ab-initio calculations
 - PTCDA / Ag(110) *submitted*
 - pentacene / Ag(110), pentacene / Cu(110) *in preparation*

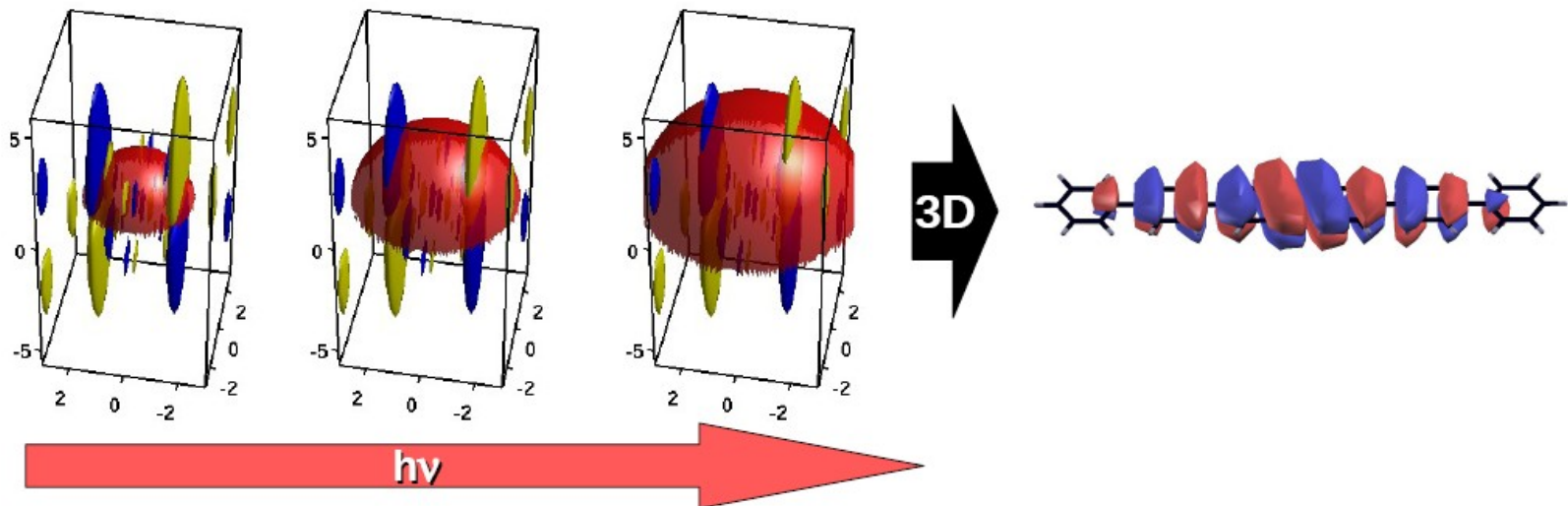
● Electronic Structure Calculations

- Band structure: go beyond DFT
- Accurate band energies and band alignments from GW
- Van der Waals Interactions

● Description of the Photoemission Intensity

- Take into account Molecule / Substrate Interactions
- More accurate description of final state

● Experiment: Constant Initial State Scans



Thank You for Your Attention!

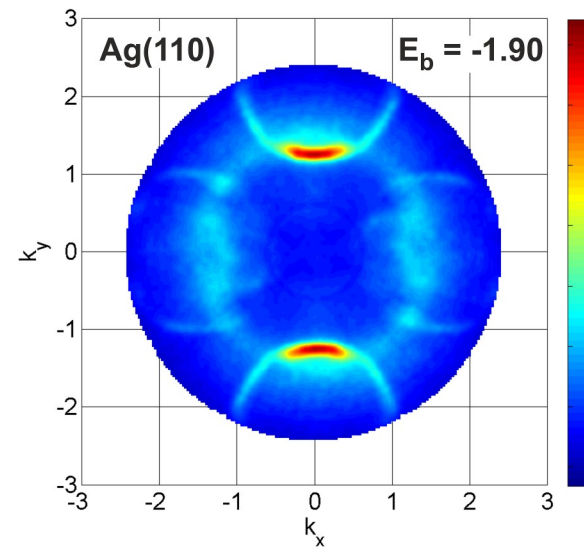
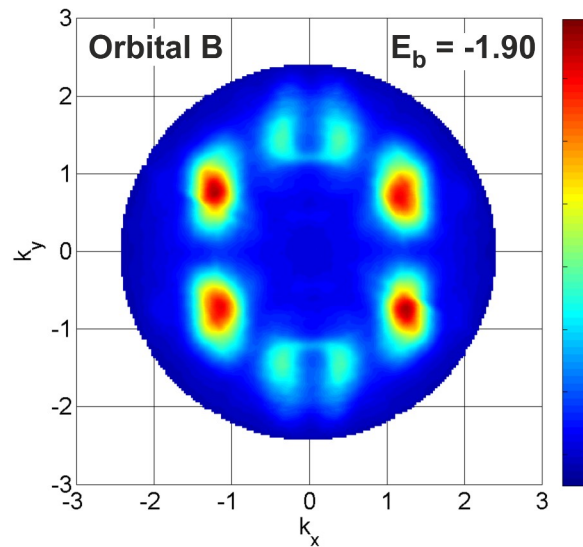
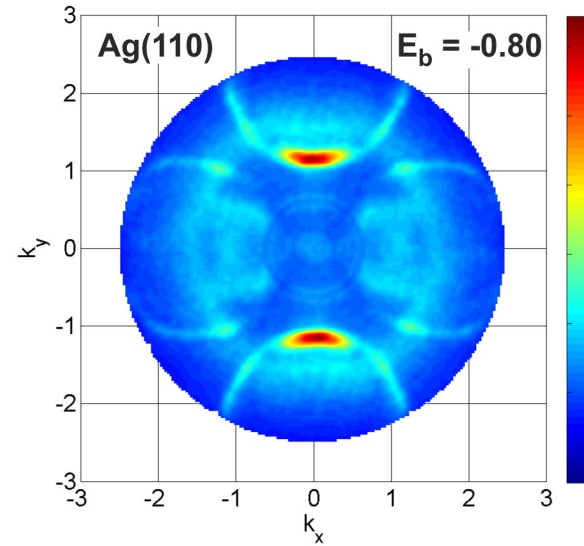
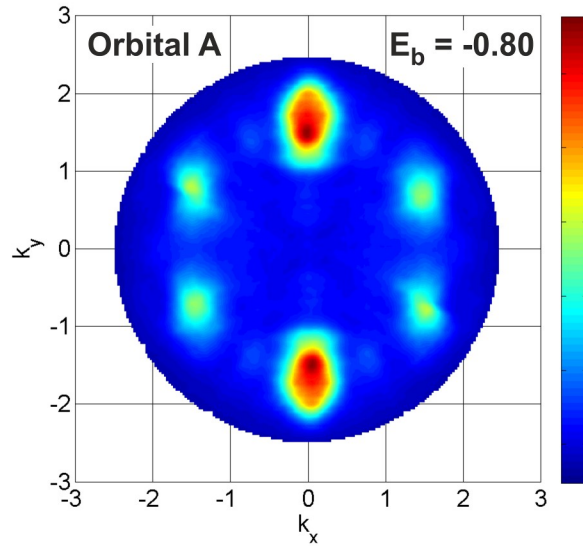


**Stephen
Berkebile**

**Georg
Koller**

**Mike
Ramsey**

Monolayer vs. Clean Ag(110)



Monolayer vs. Clean Ag(110)

