MONTAN UNIVERSITÄT
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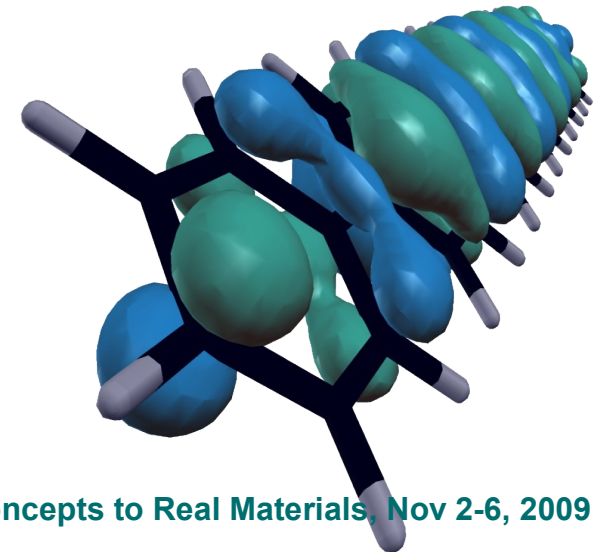
# Reconstruction of Molecular Orbitals from Angle-Resolved Photoemission



# Collaborations and Funding

Atomistic Modelling Group – University Leoben, Austria

- Peter Puschnig
- Claudia Ambrosch-Draxl

Experimental Surface Science Group – University Graz, Austria

- Stephen Berkebile
- Alexander Fleming
- Georg Koller
- Mike Ramsey

Lehrstuhl für Technische Physik – University Erlangen-Nürnberg, Germany

- Thomas Seyller
- Konstantin Emtsev

The work is part of the National Research Network
**„Interface controlled and functionalized organic films“**

# Outline

Motivation: Organic Semiconductors

Angle-Resolved Photoemission Spectroscopy

ARPES from Molecular Layers

- Multilayers and Monolayers of p-Sexiphenyl and Pentacene

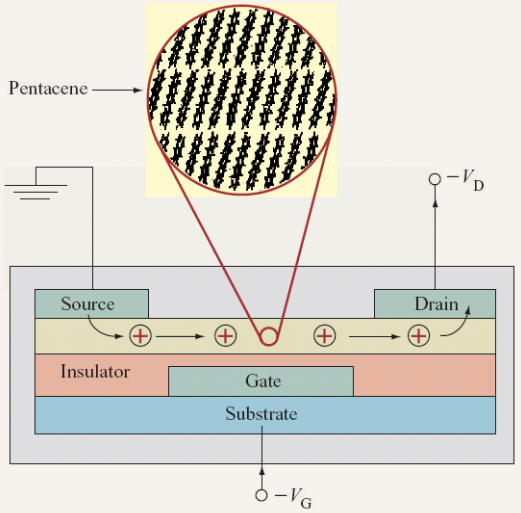
Reconstruction of Orbital Densities

Conclusion

# Organic π-Conjugated Molecules

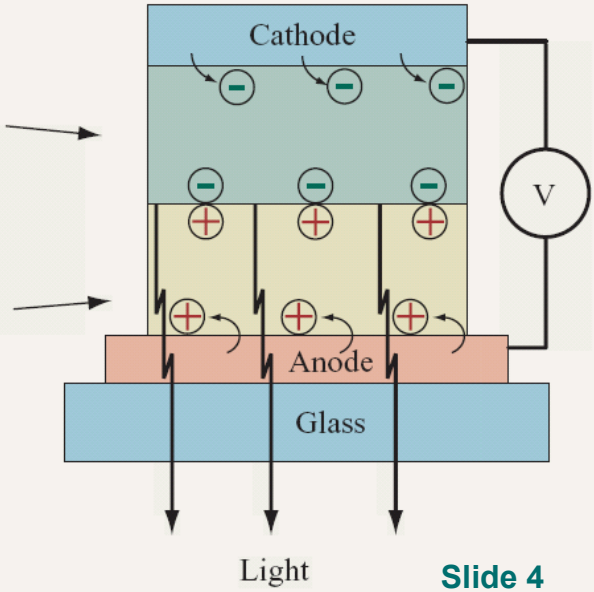
**Pentacene ($C_{22}H_{14}$)**

**OFET**
**O**rganic
**F**ield **E**ffect
**T**ransistor



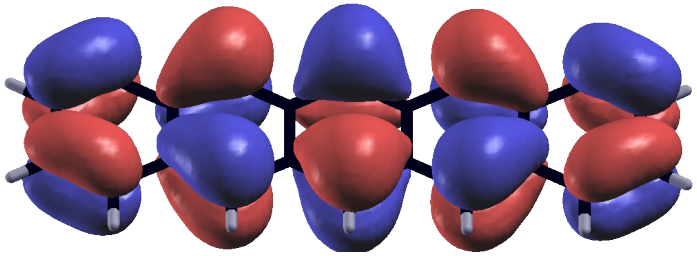

**Para-Sexiphenyl ($C_{36}H_{26}$)**

**OLED**
**O**rganic
**L**ight **E**mitting **D**iode

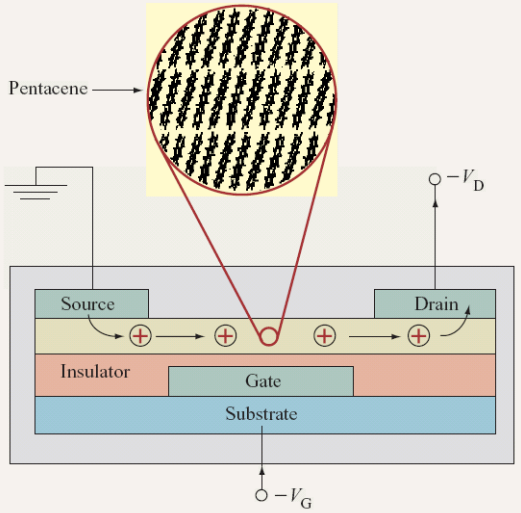


# Organic π-Conjugated Molecules

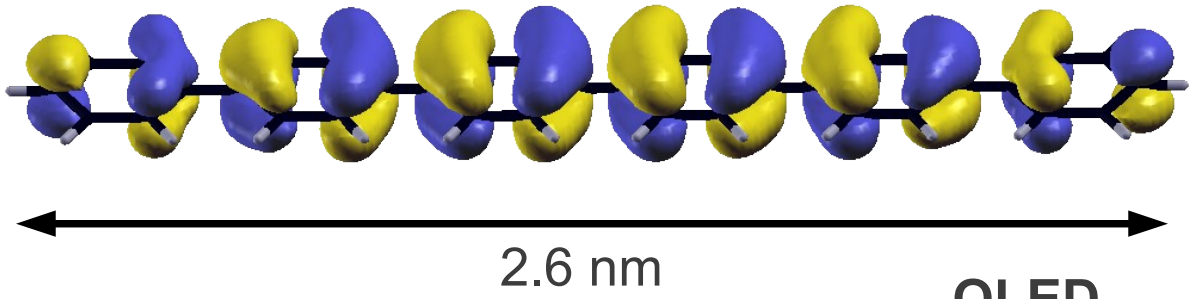
**Pentacene ($C_{22}H_{14}$)**



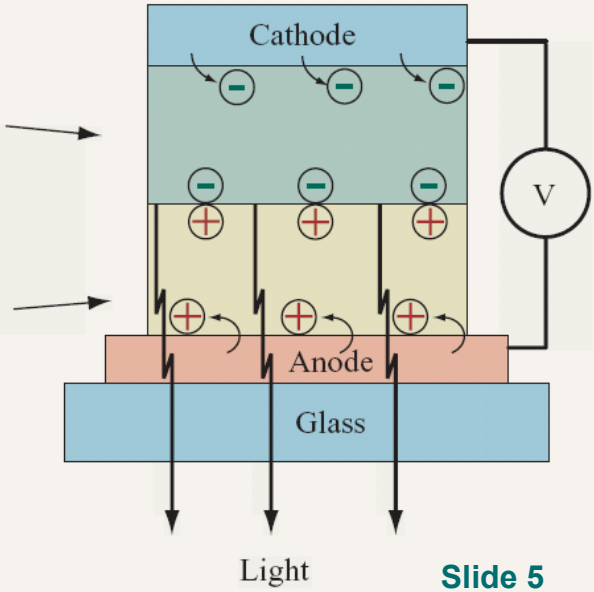
**OFET**
**O**rganic
**F**ield **E**ffect
**T**ransistor



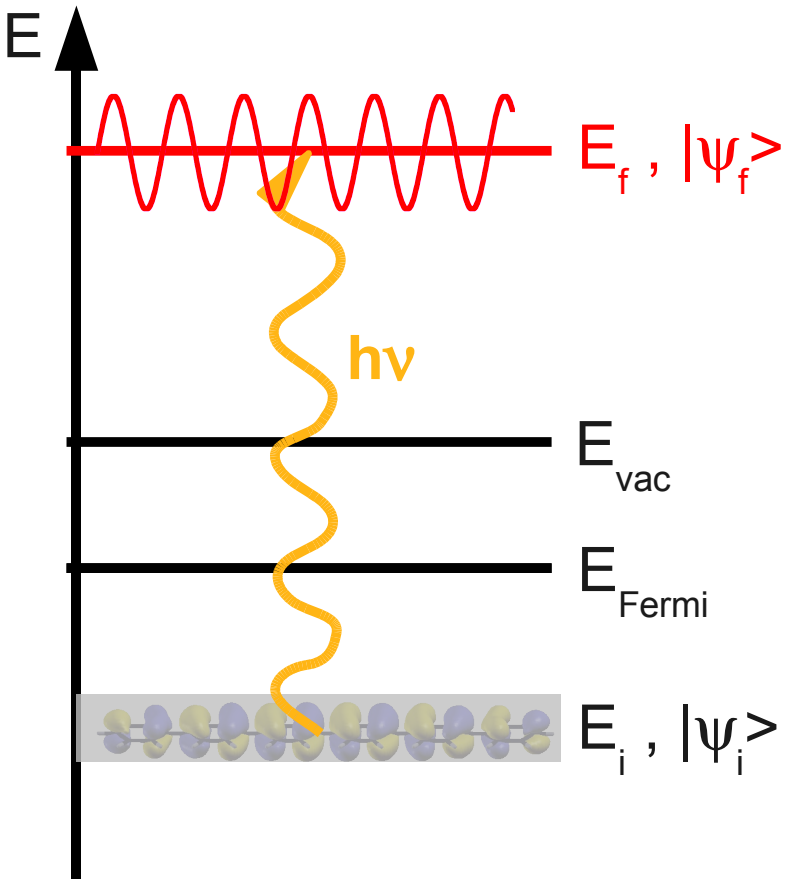

**Para-Sexiphenyl ($C_{36}H_{26}$)**

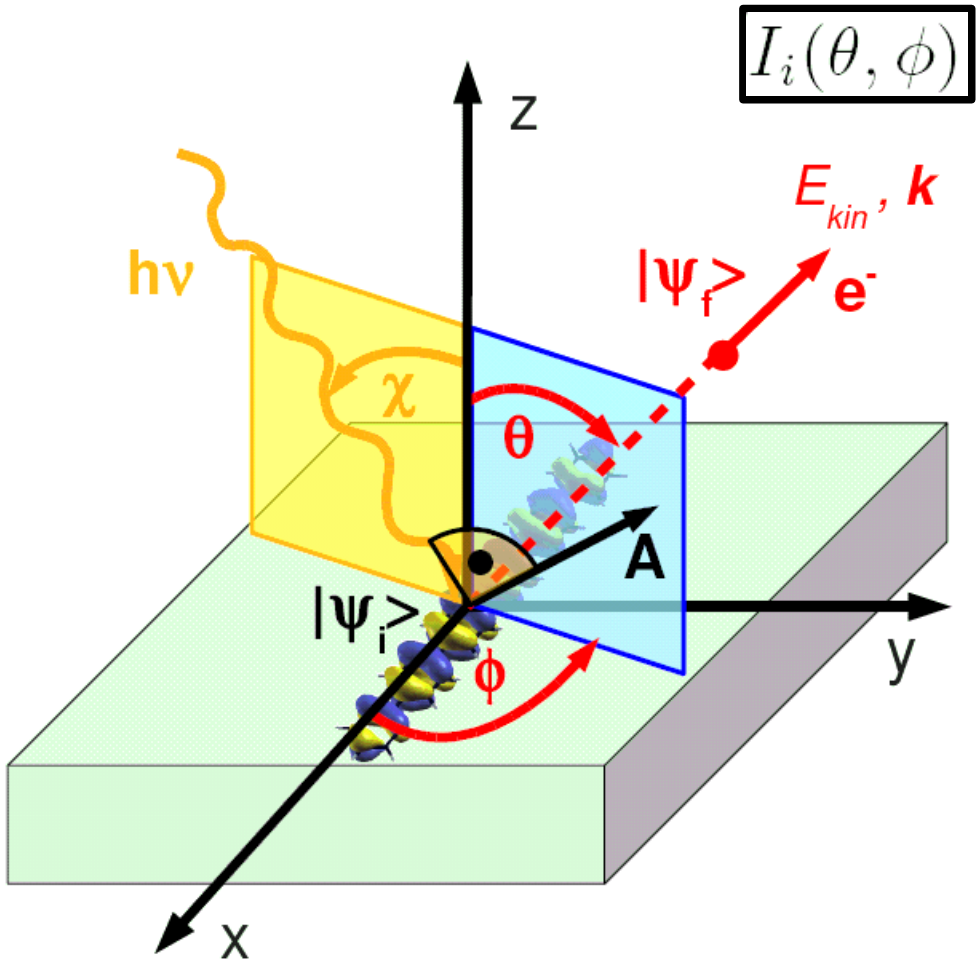



**OLED**
**O**rganic
**L**ight **E**mitting **D**iode



# Angle-Resolved Photoemission



# The Photoemission Intensity

## One-Step-Model

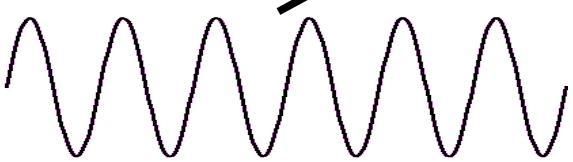
$$I(\theta, \phi; E_{\mathrm{kin}}) \propto \sum_i \left| \langle \psi_f^*(\theta, \phi; E_{\mathrm{kin}}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \right|^2 \times \delta \left( E_i + \Phi + E_{\mathrm{kin}} - \hbar\omega \right)$$

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

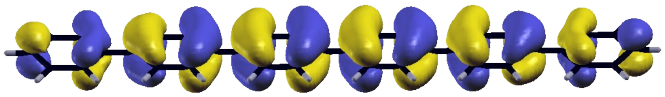
# The Photoemission Intensity

**A simple theory** (one-step model + final state = plane wave)

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



*plane wave*



*molecular orbital*

**... leads to a simple result**

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

Fourier Transform of Initial State Orbital

[Feibelman and Eastman, *Phys. Rev. B* **10**, 4932 (1974), E. Shirley *et al.*, *Phys. Rev. B* **51**, 13614 (1995).]

# Limitations of Plane Wave Approach

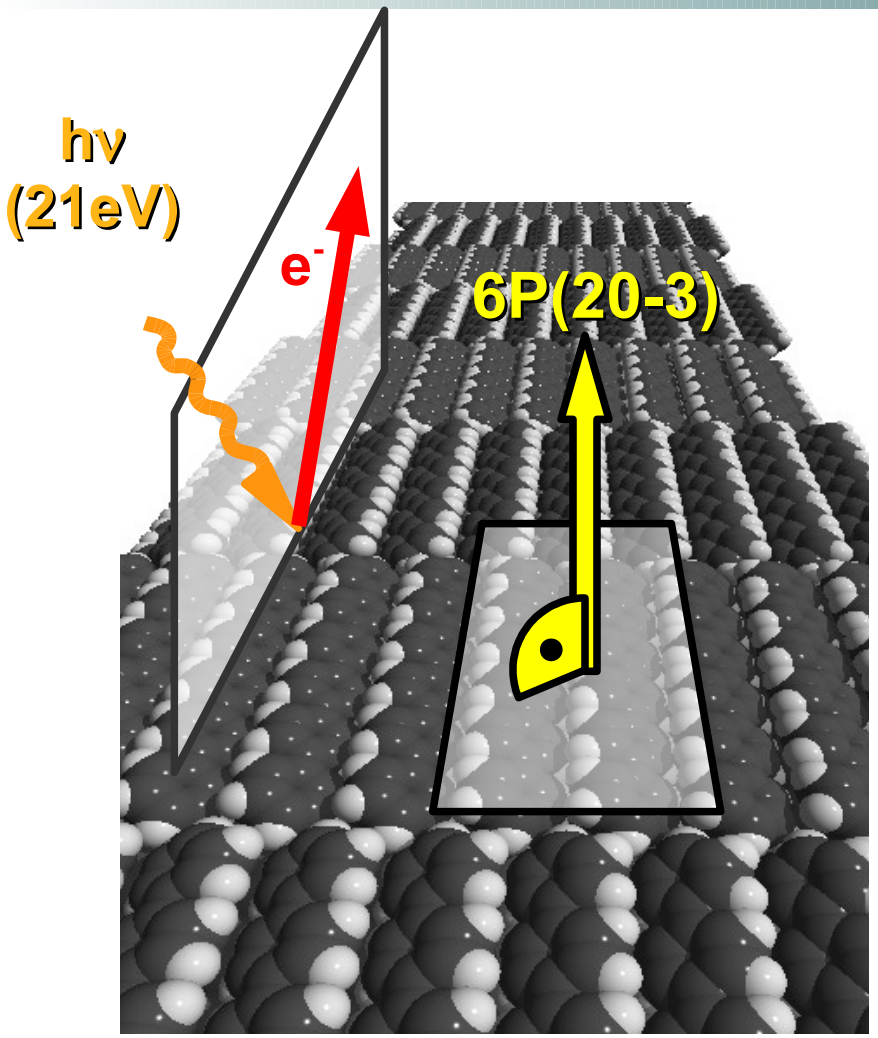
The **I**ndependent **A**tomic **C**entre approximation (IAC)
[W. D. Grobman, Phys. Rev. B **17**, 4573 (1978).]

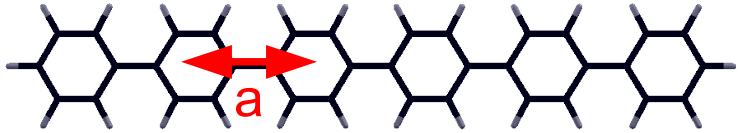
$$A(\mathbf{R}, E_{\mathrm{kin}}) = \sum_{\alpha} \sum_{nlm} C_{\alpha,nlm} e^{i\mathbf{k}\mathbf{R}_{\alpha}} \sum_{LM} M^{LM}_{\alpha,nlm}(E_{\mathrm{kin}}) Y_{LM}(\hat{R})$$

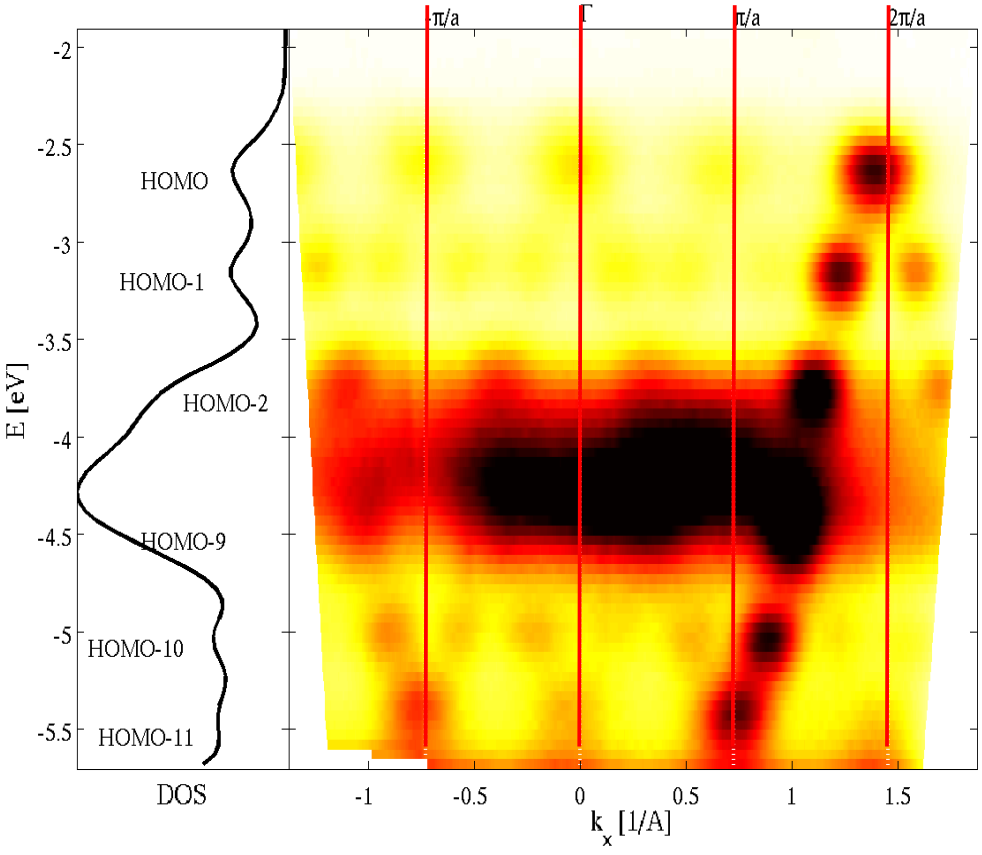
can be shown to reduce to the PW final state result, if
[Goldberg et al, Solid State Commun. **28**, 459-463 (1978),
Puschnig et al., supporting online material to Science **326**, 702 (2009)]

- **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**

# Uniaxially Aligned Sexiphenyl



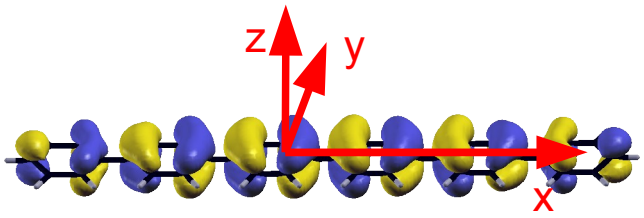



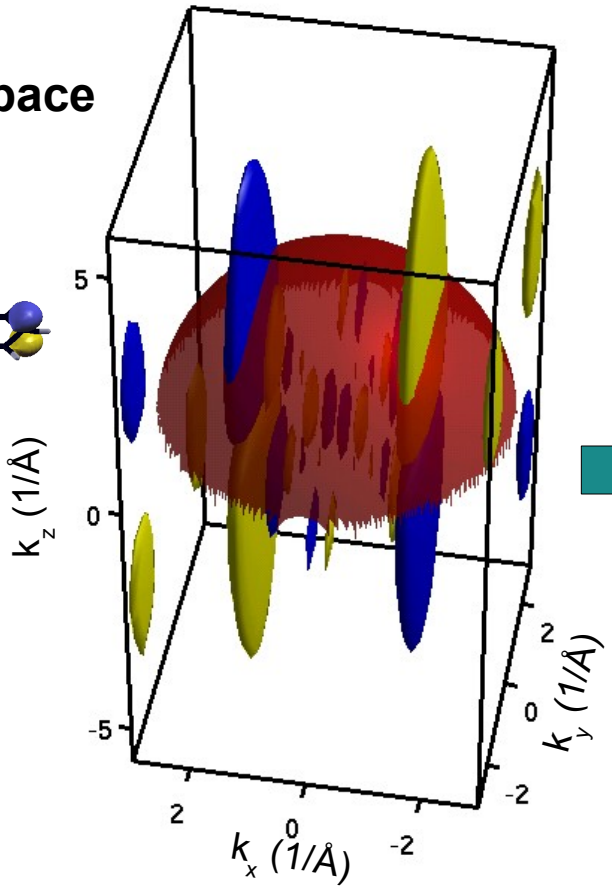

Uniaxially ordered para-sexiphenyl film on Cu(110)_(2x1)O

# Comparison with DFT

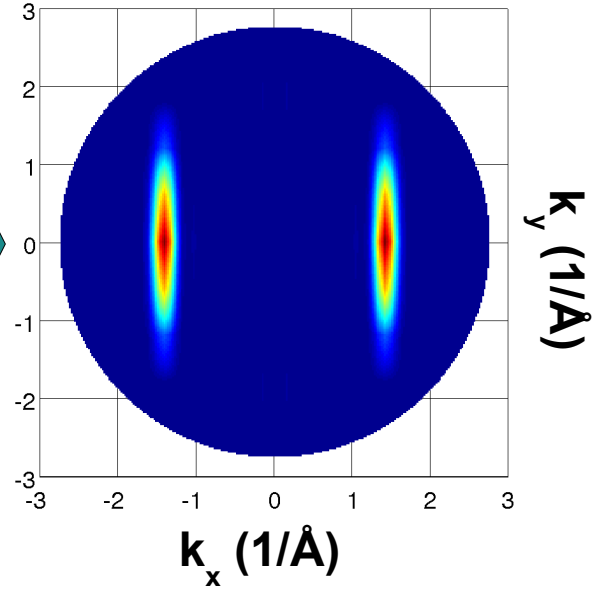
**Molecular Orbital in Real Space**




**Calculation of the Fourier Transform**

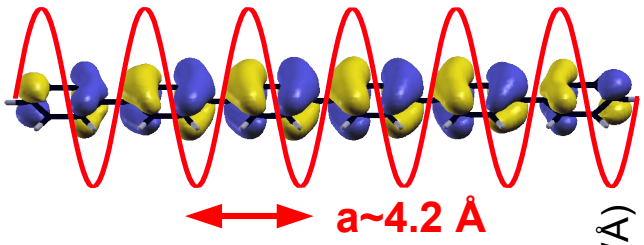



**Hemispherical Cut Through 3D Fourier Transform**

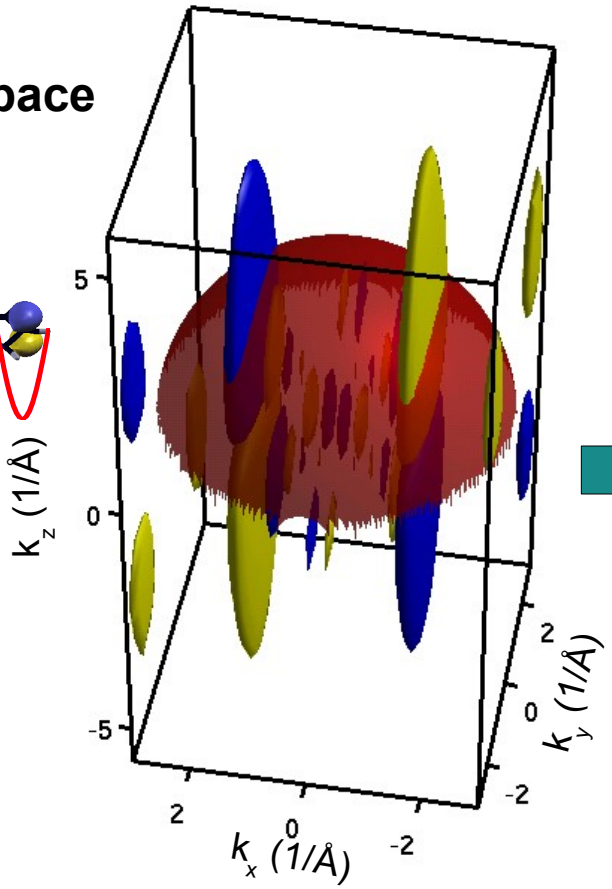


# Comparison with DFT

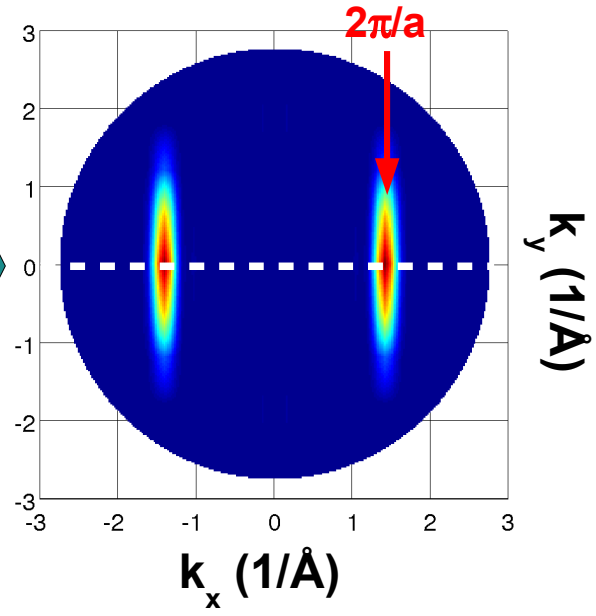
**Molecular Orbital in Real Space**



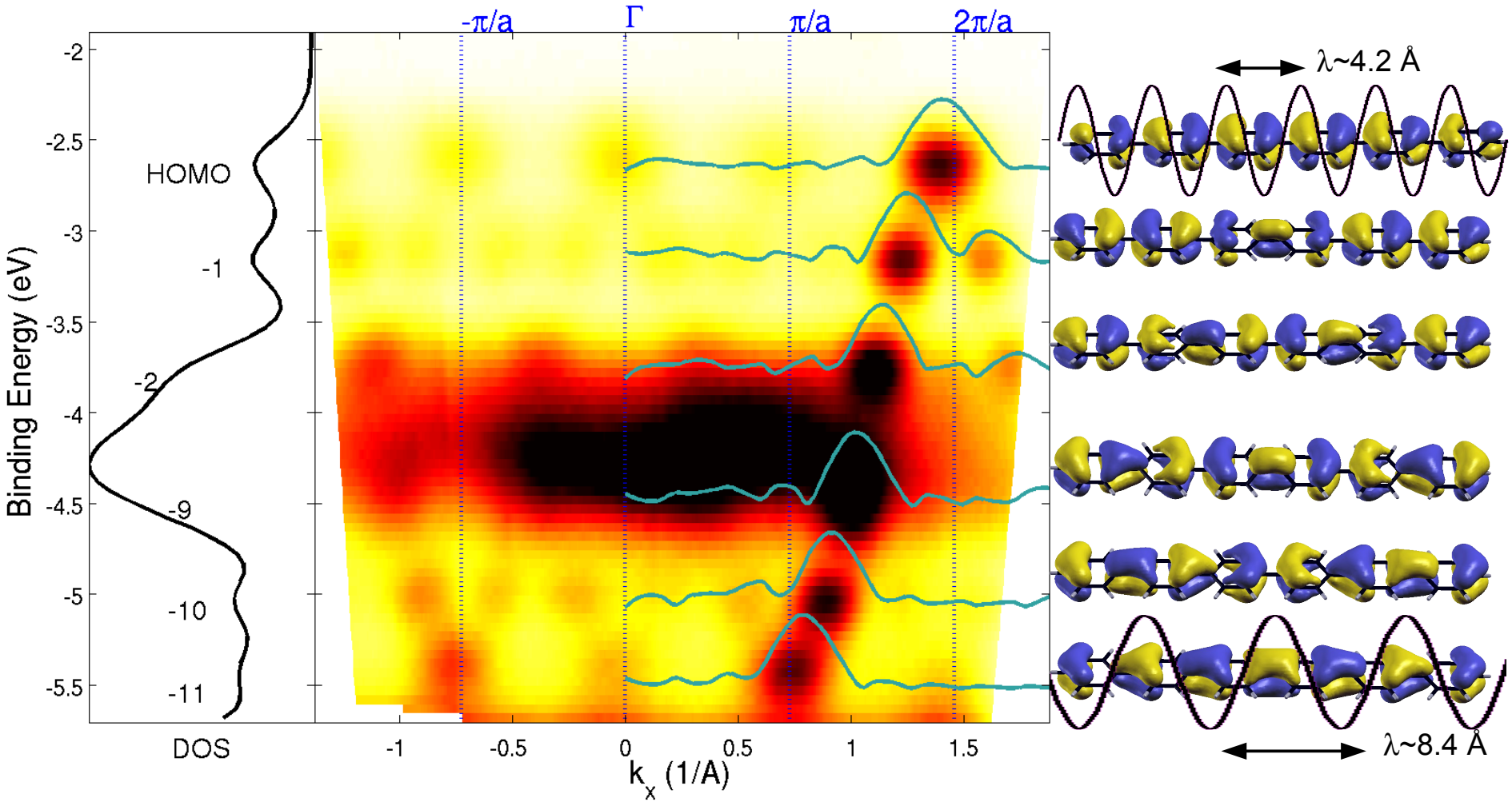

**Calculation of the Fourier Transform**



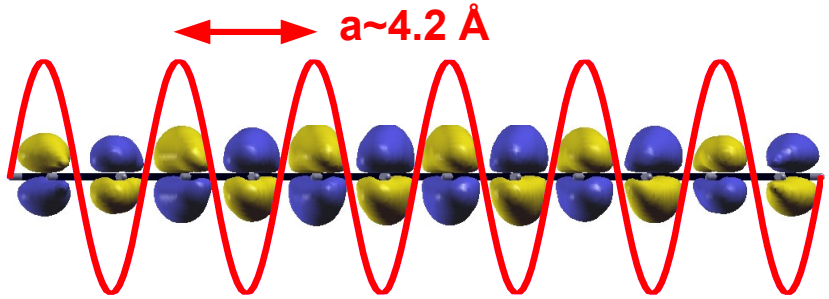

**Hemispherical Cut Through 3D Fourier Transform**

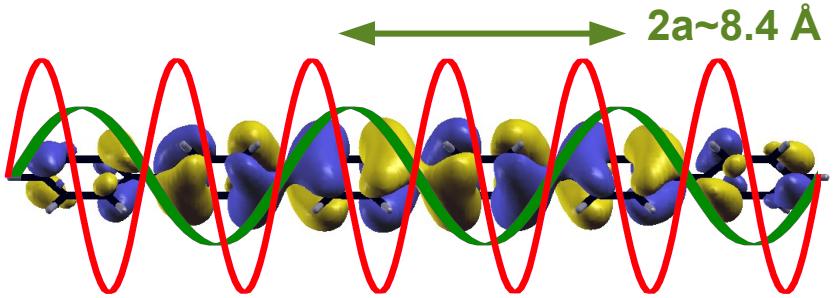


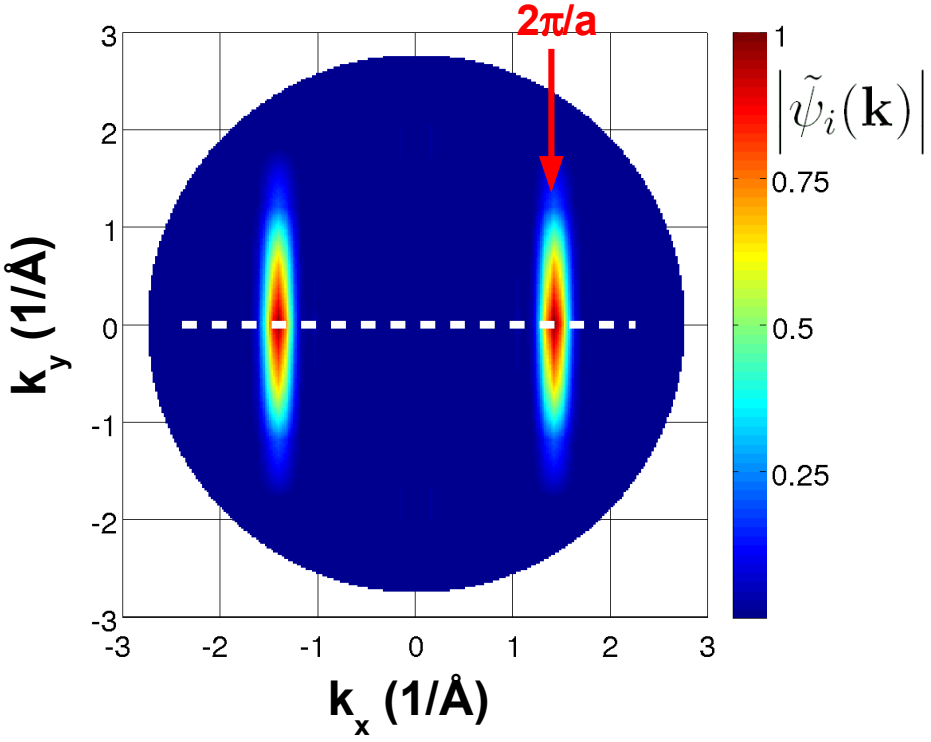
# 1D-Fourier Transform

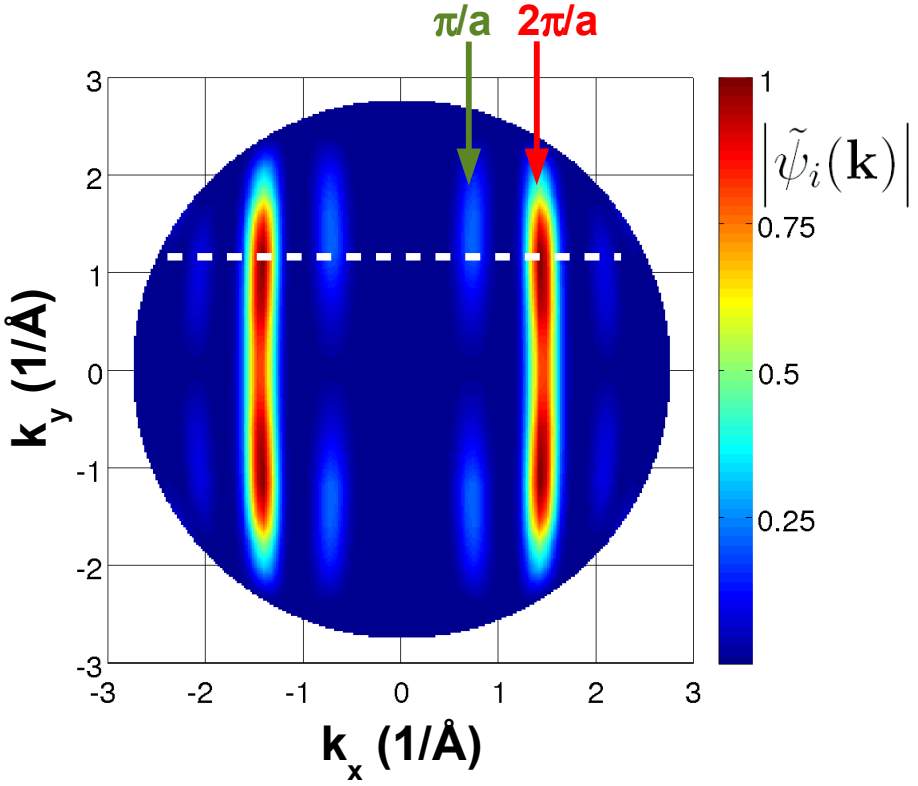


# Planar vs. Twisted

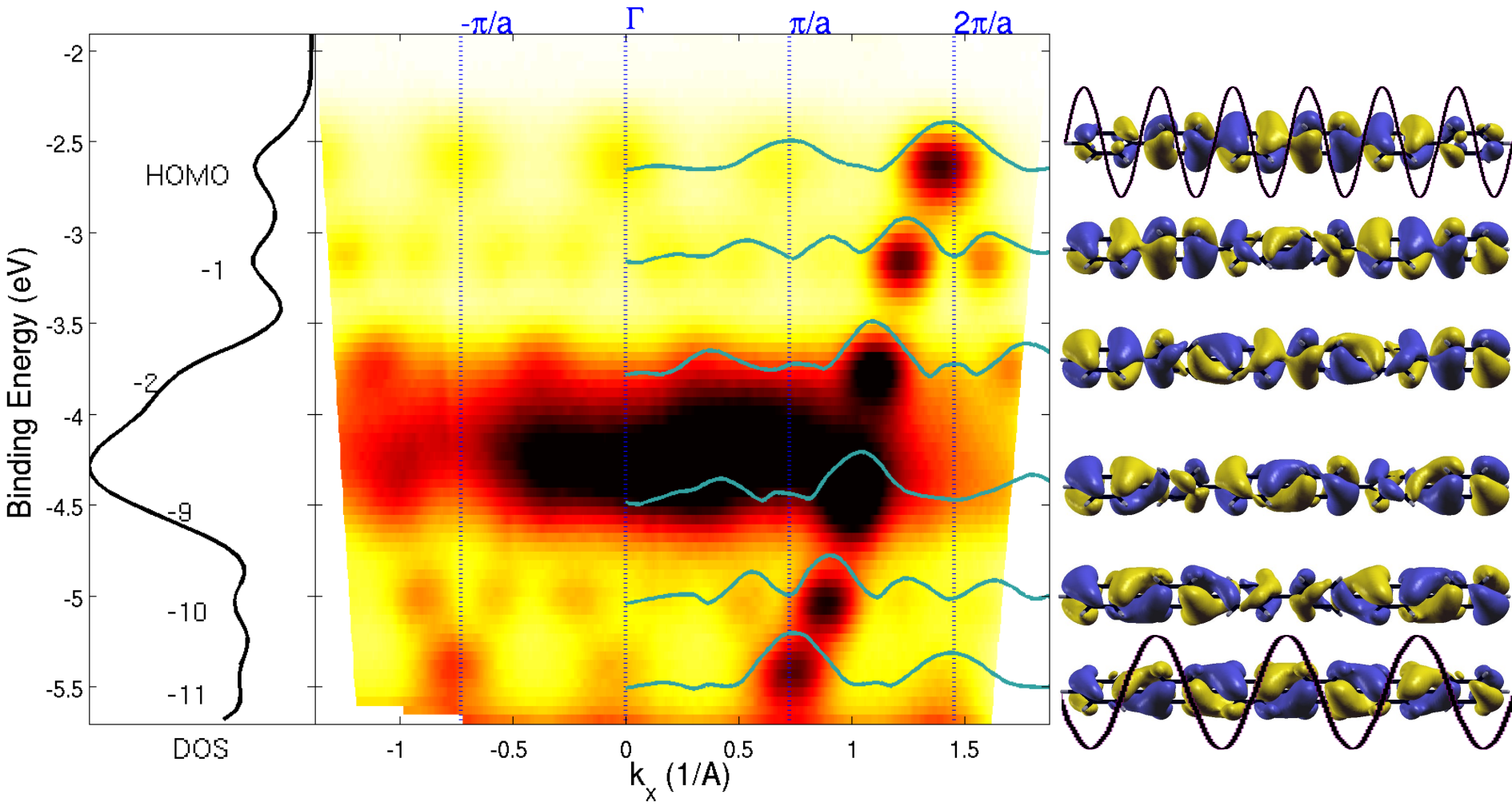


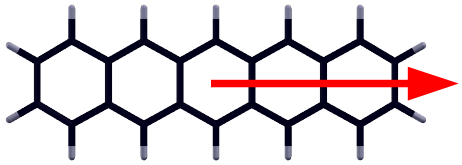



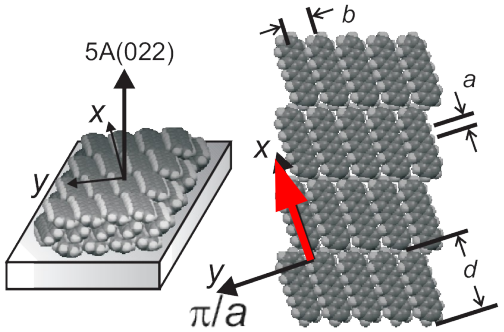
# ~~Planar or~~ Twisted by ~ 30 deg



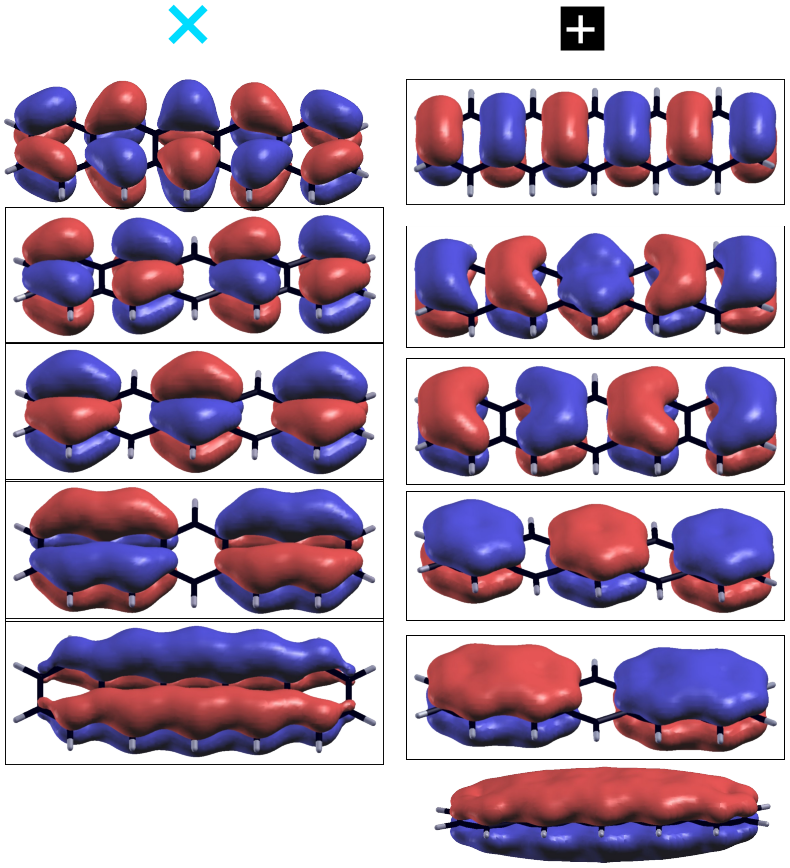

G. Koller et al., *Science* ***317****, 351 (2007).*

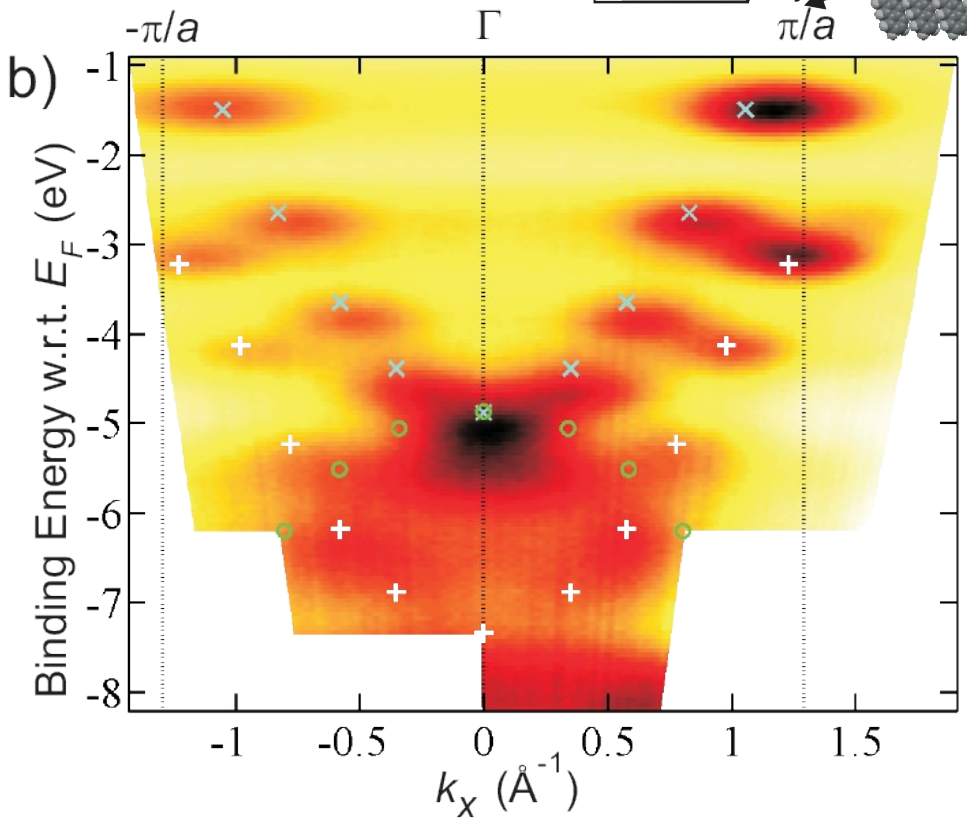
# ARPES of Pentacene






22 Carbons lead to
11 occupied π orbitals

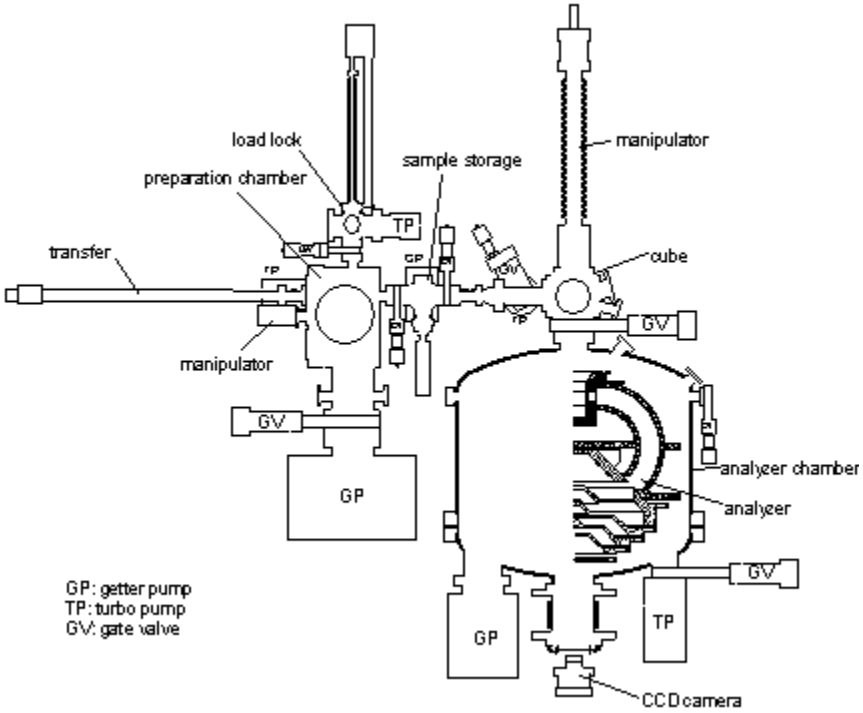


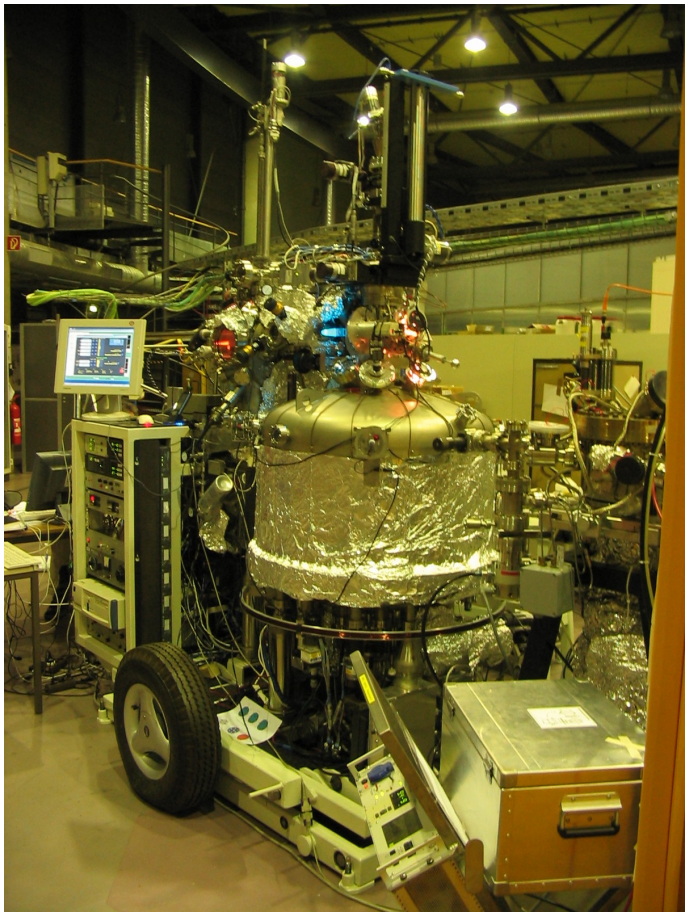



S. Berkebile, P. Puschnig, G. Koller, M. Oehzelt, F. P. Netzer, C. Ambrosch-Draxl, M. G. Ramsey, Phys. Rev. B 77, 115312 (2008)

# Toroidal Electron Spectrometer

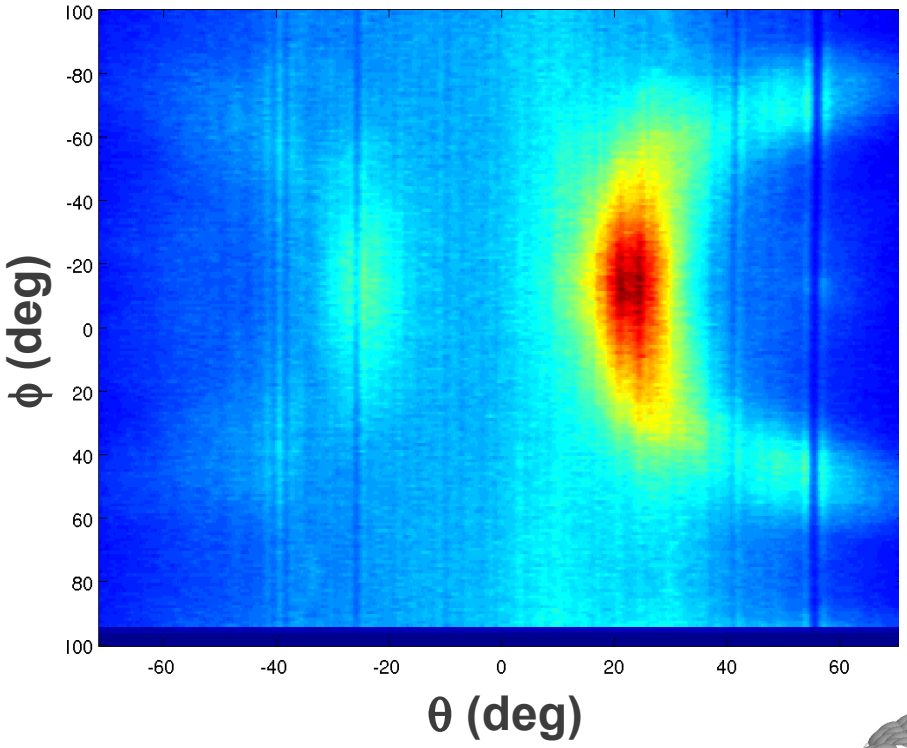
The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II

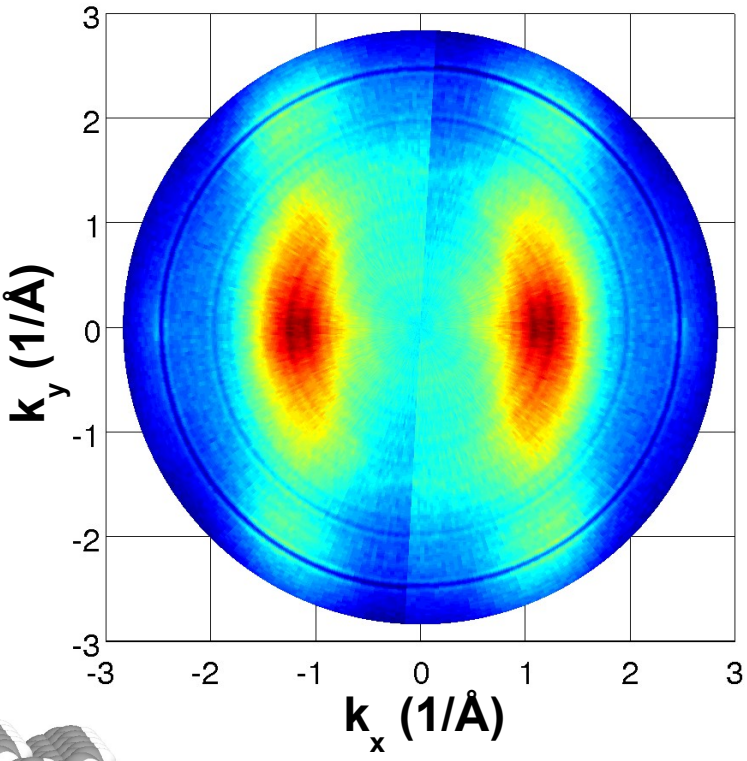


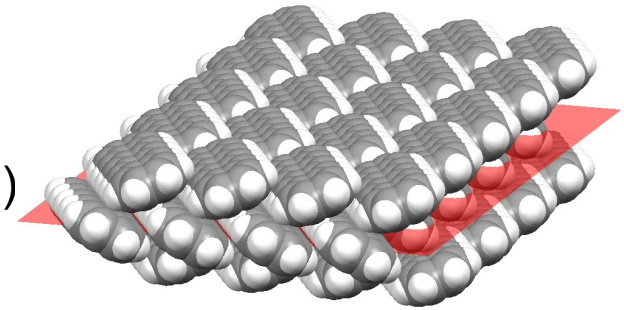
# Pentacene HOMO

**Azimuthal Scans at constant photon energy and constant kinetic energy**



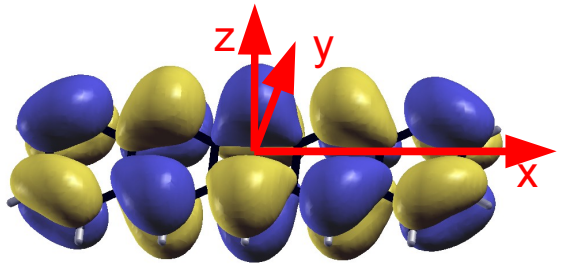

Azimuthal scan from a multilayer of **Pentacene**/Cu(110)_(2x1) at the **HOMO** energy



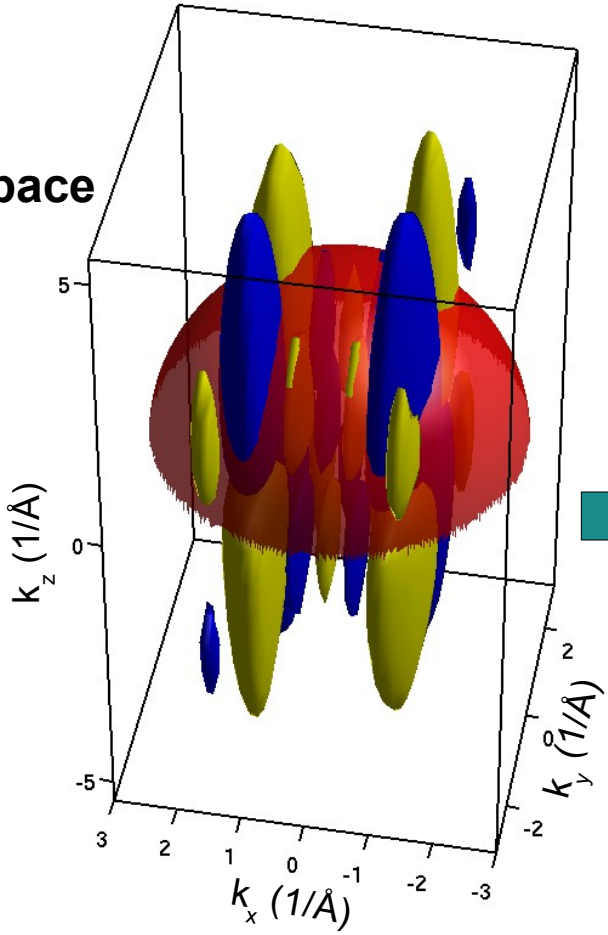
$$k_{\parallel} = \sqrt{\frac{2m}{\hbar^2} E_{\mathrm{kin}}} \sin\theta$$

# Pentacene HOMO from DFT

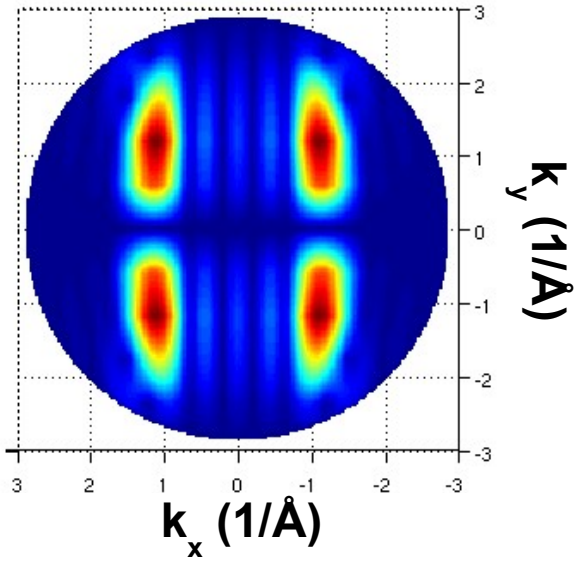
**Molecular Orbital in Real Space**




**Calculation of the Fourier Transform**

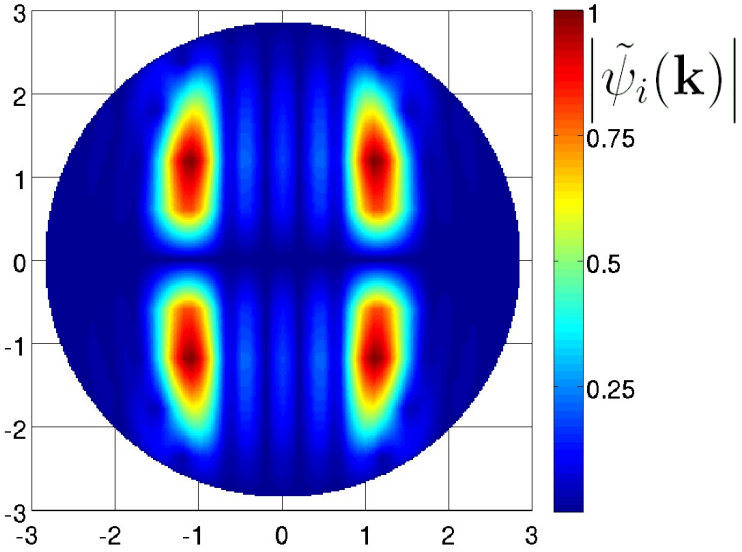


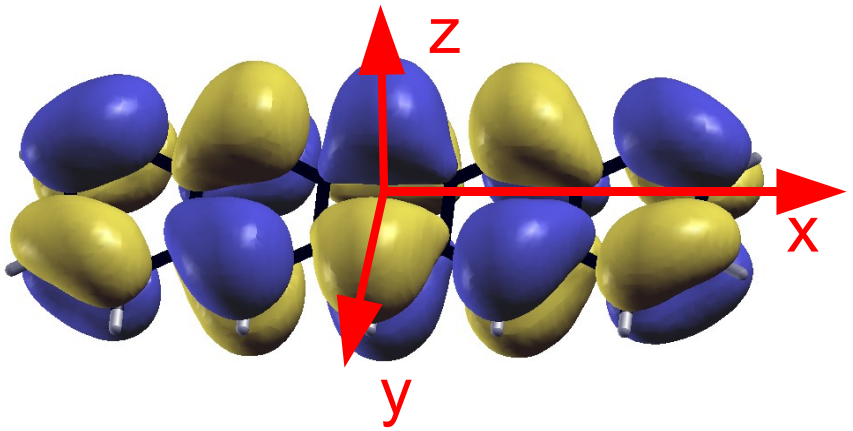

**Hemispherical Cut Through 3D Fourier Transform**



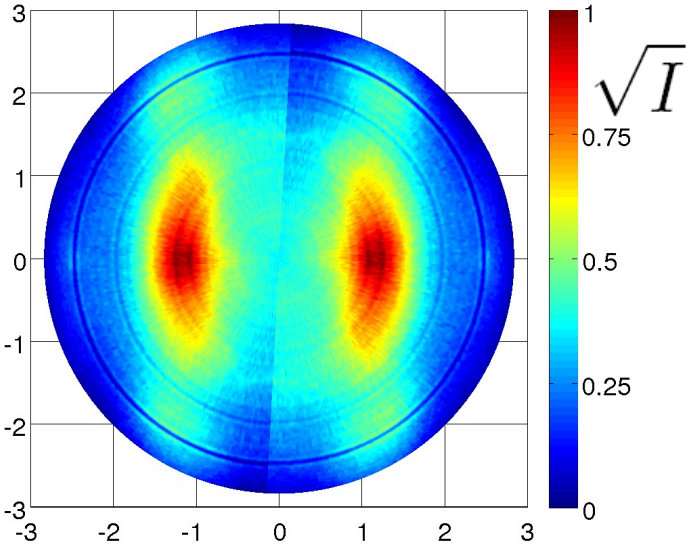
# Theory vs. Experiment

DFT




ARPES

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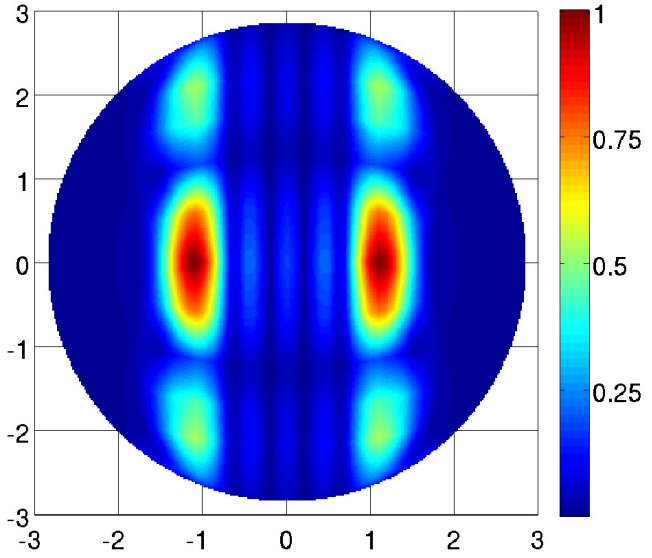
# Theory vs. Experiment

DFT



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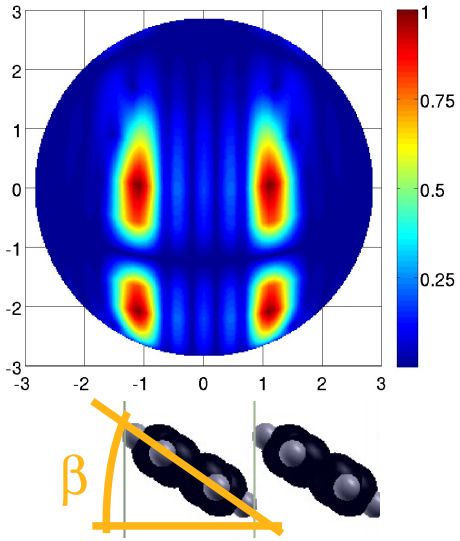
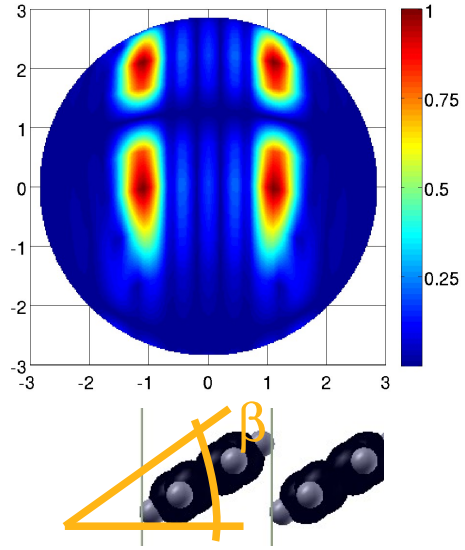


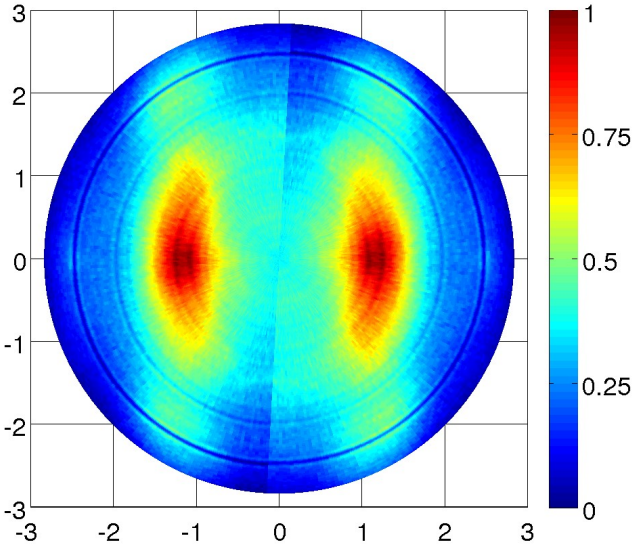

+26 deg tilt

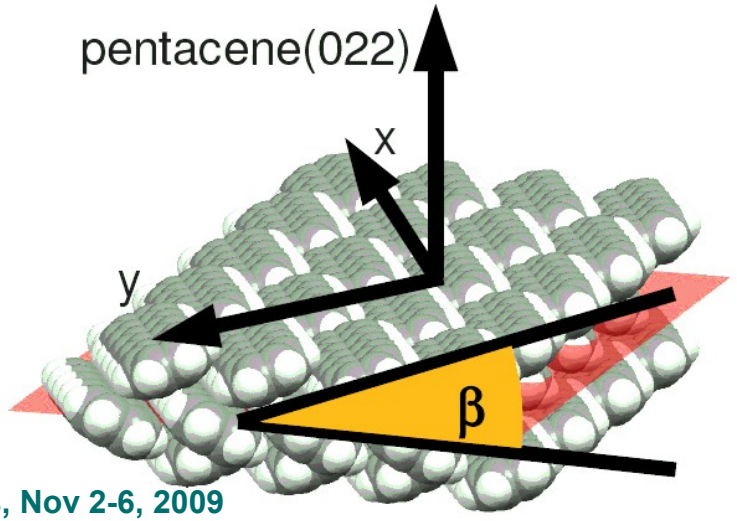
+




–26 deg tilt

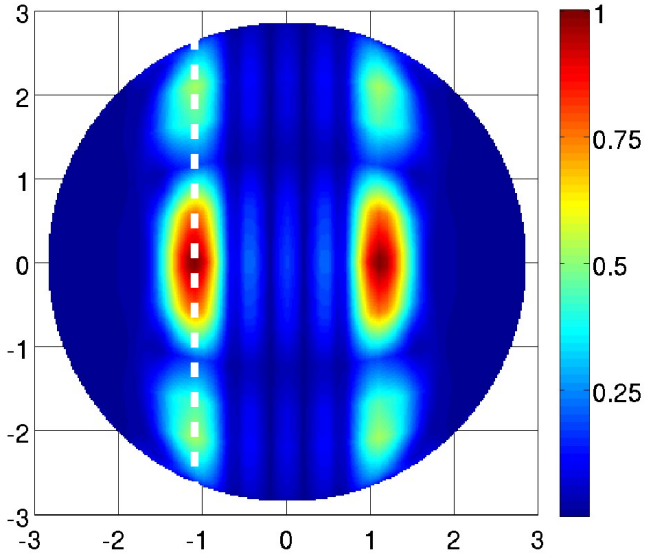
ARPES

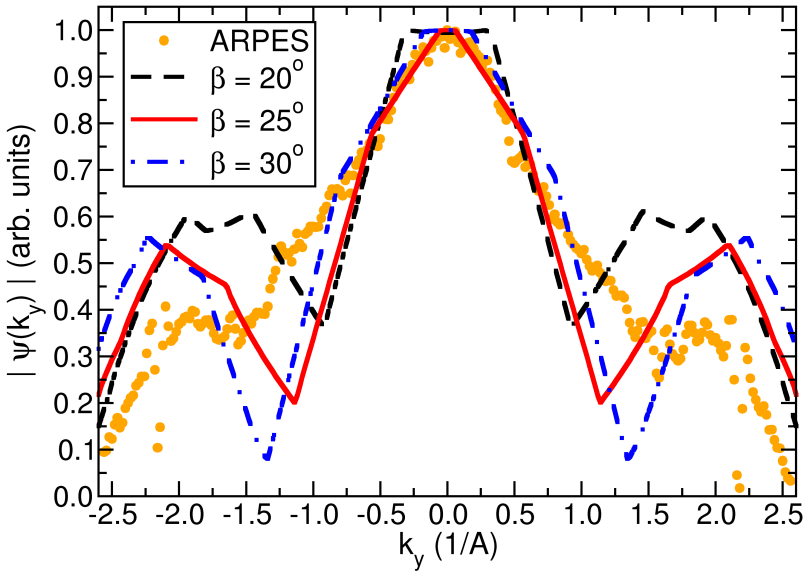




# Theory vs. Experiment

DFT

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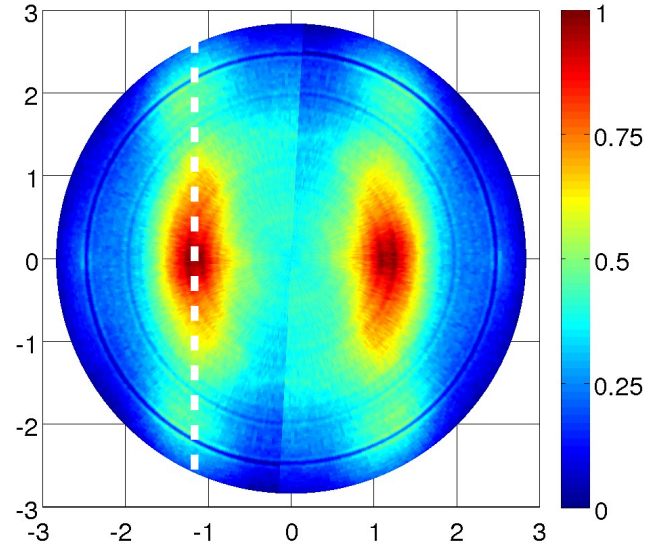
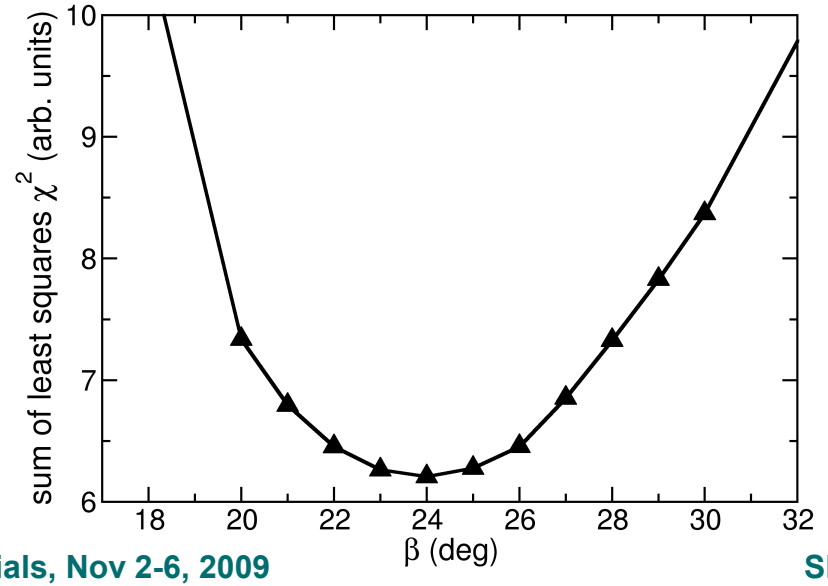
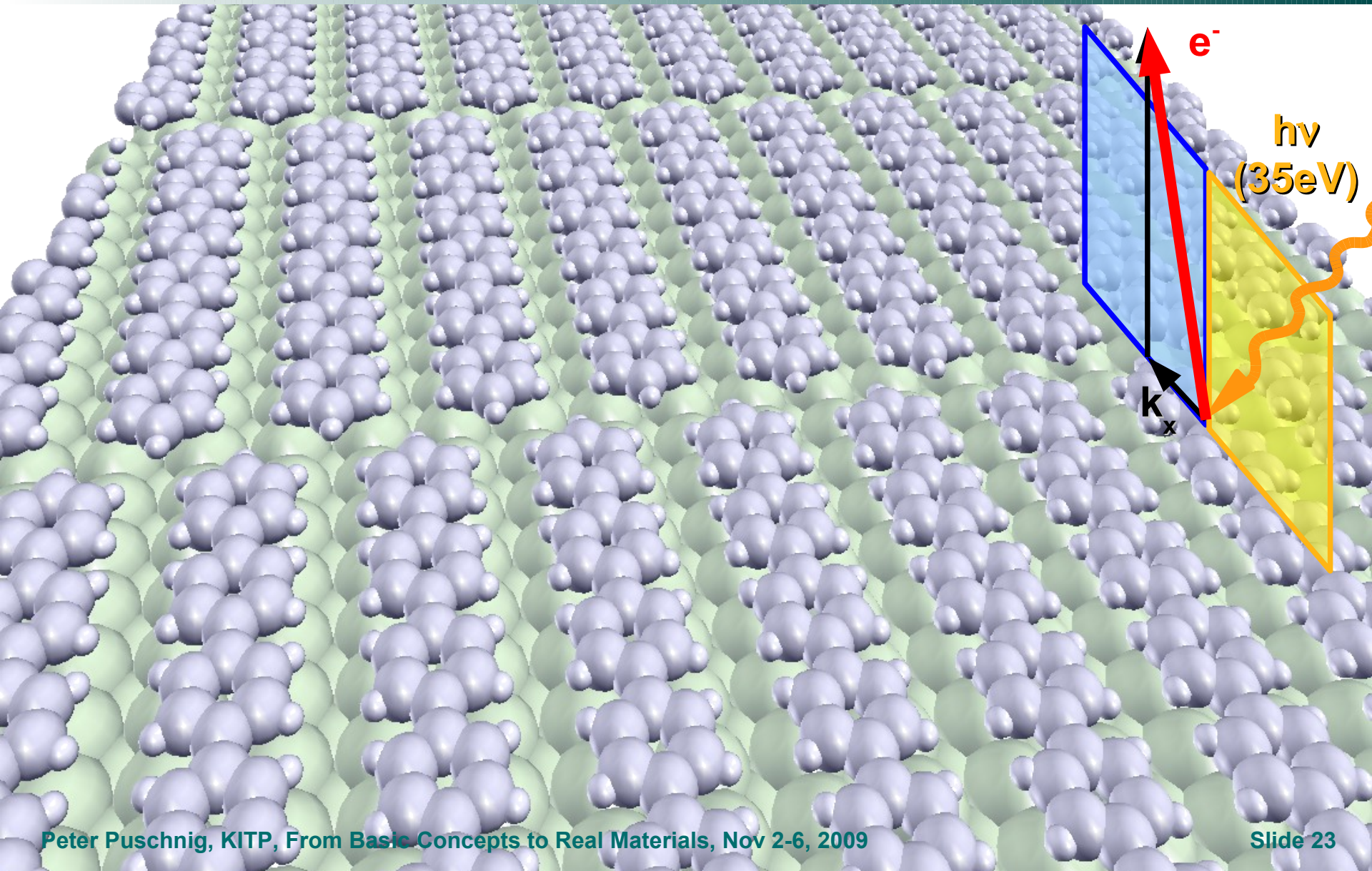
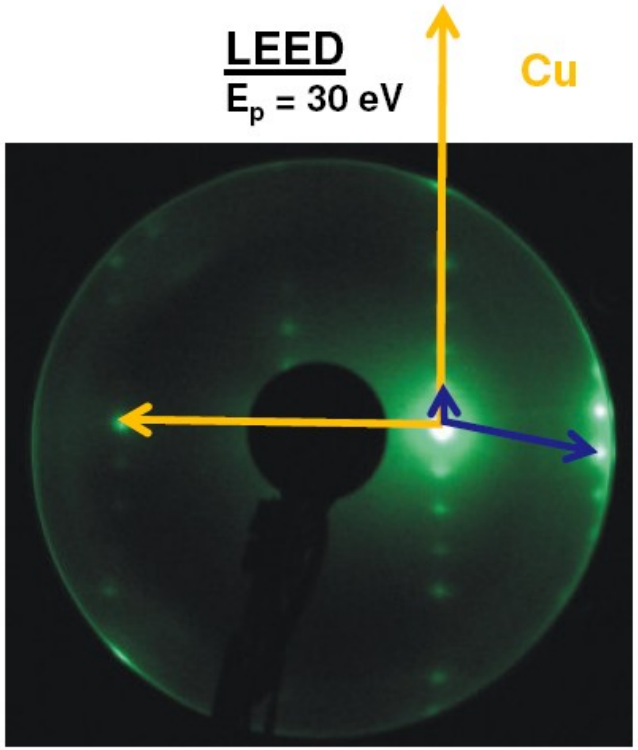


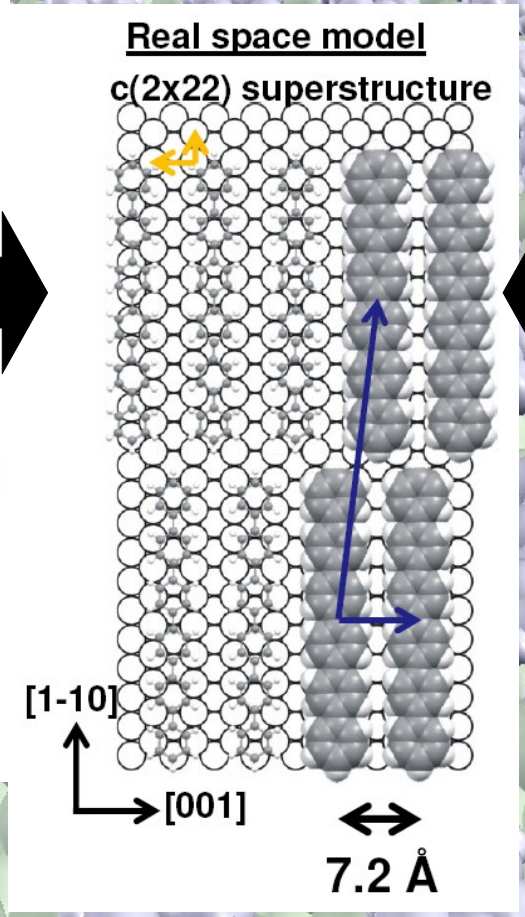



# Sexiphenyl Monolayer on Cu(110)

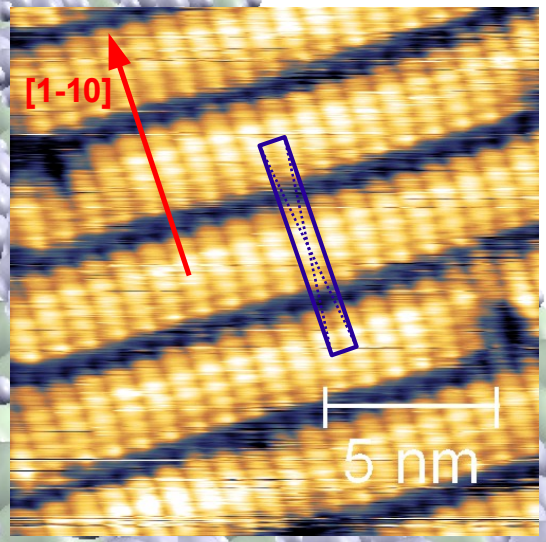


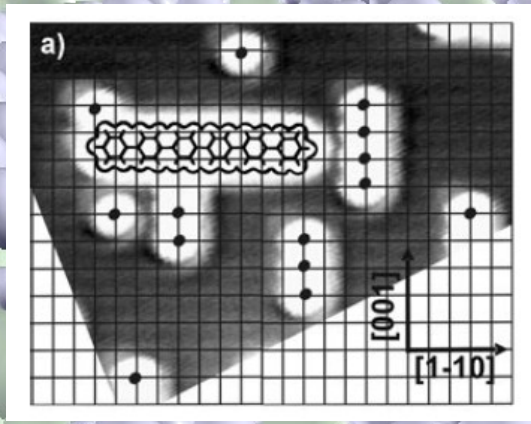
# Sexiphenyl Monolayer on Cu(110)



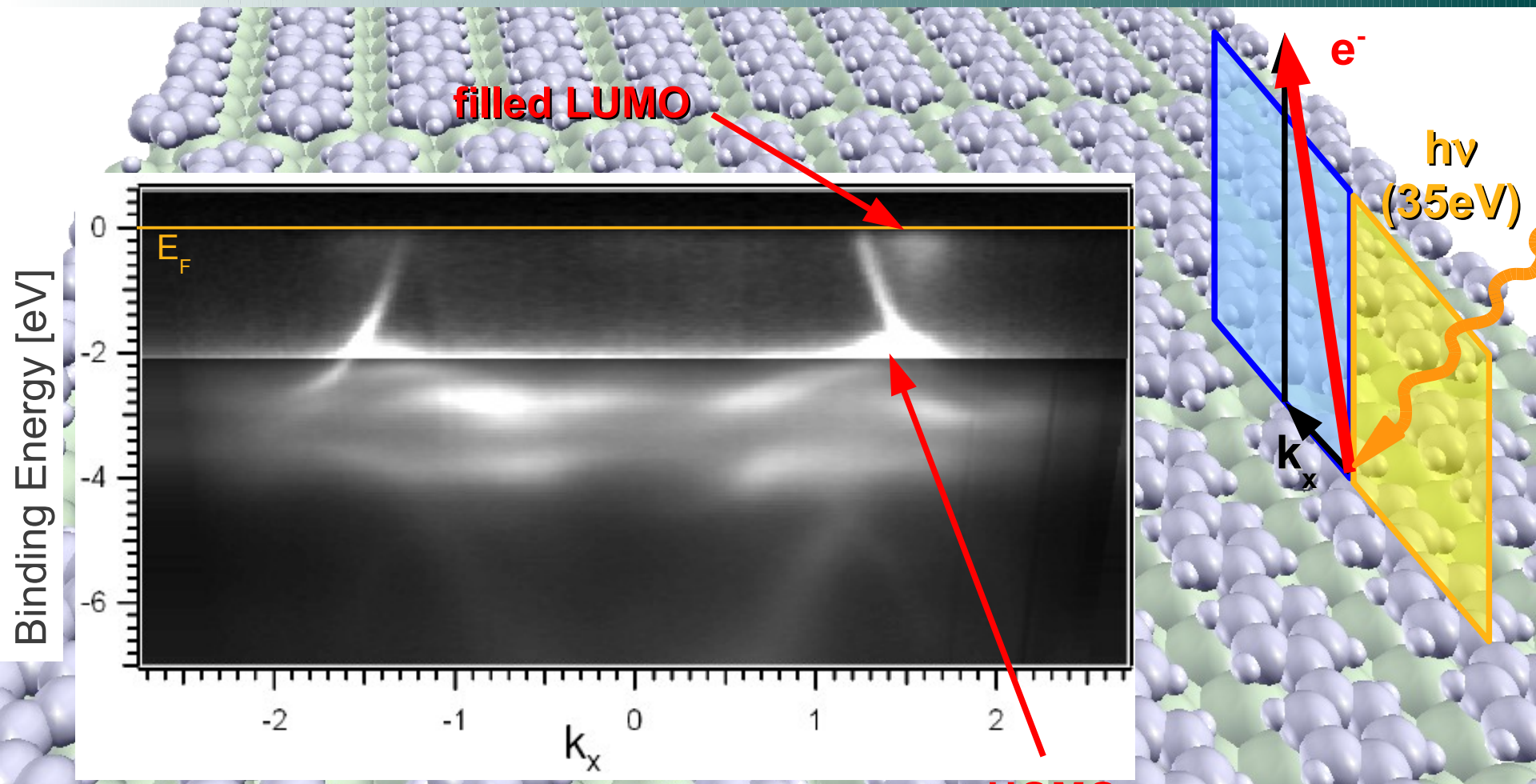

STM



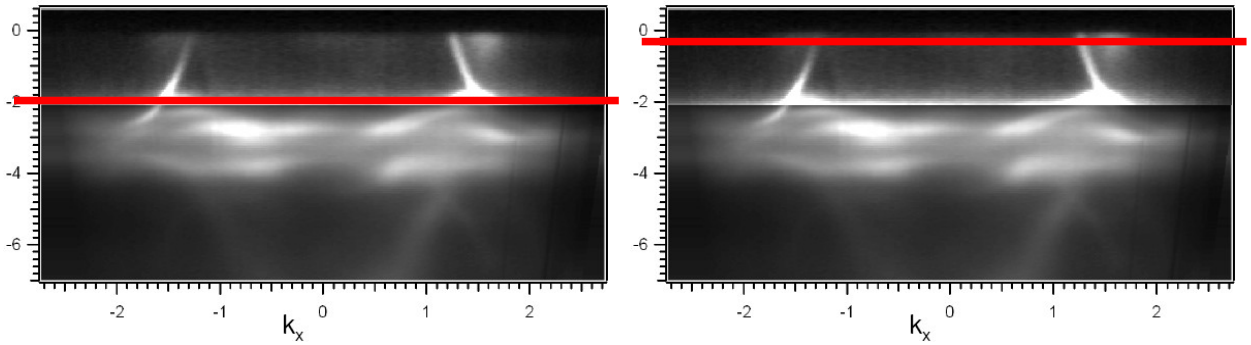




*M. Oehzelt et al., ChemPhysChem 8, 1707 – 1712 (2007).*

# Sexiphenyl Monolayer on Cu(110)

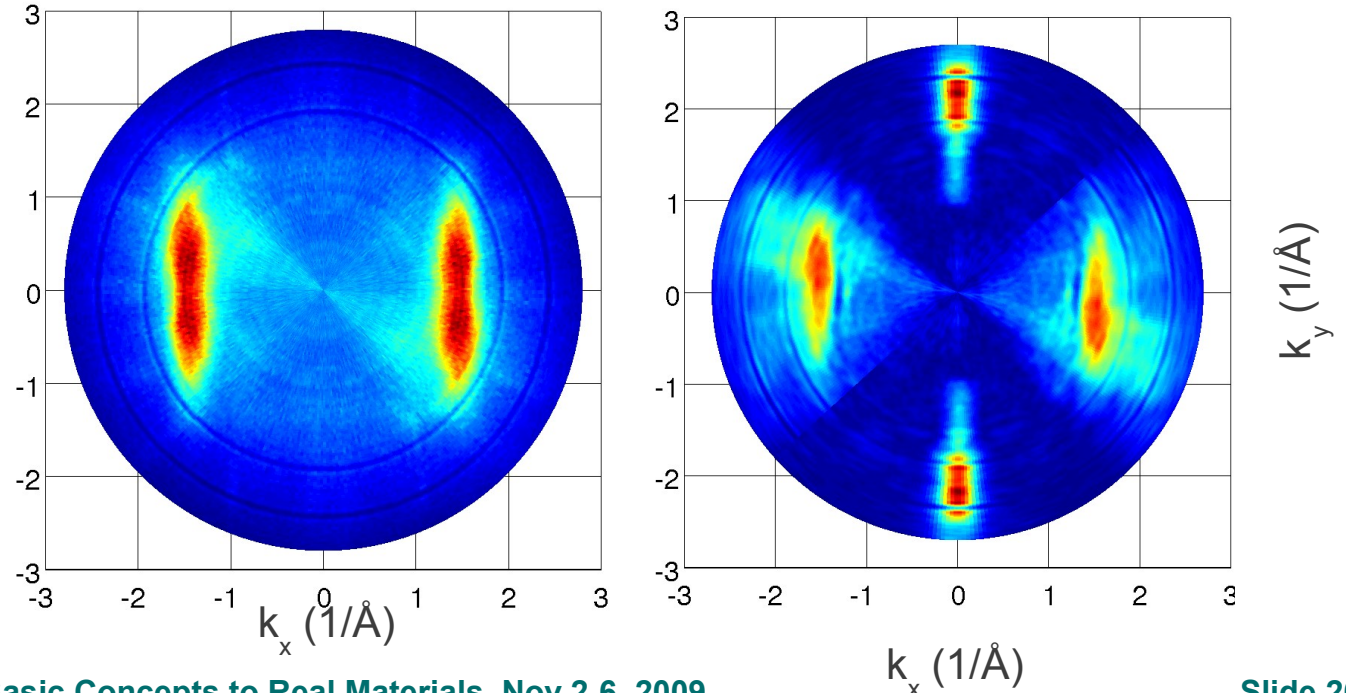


# 2D Momentum Maps: 6P/Cu(110)

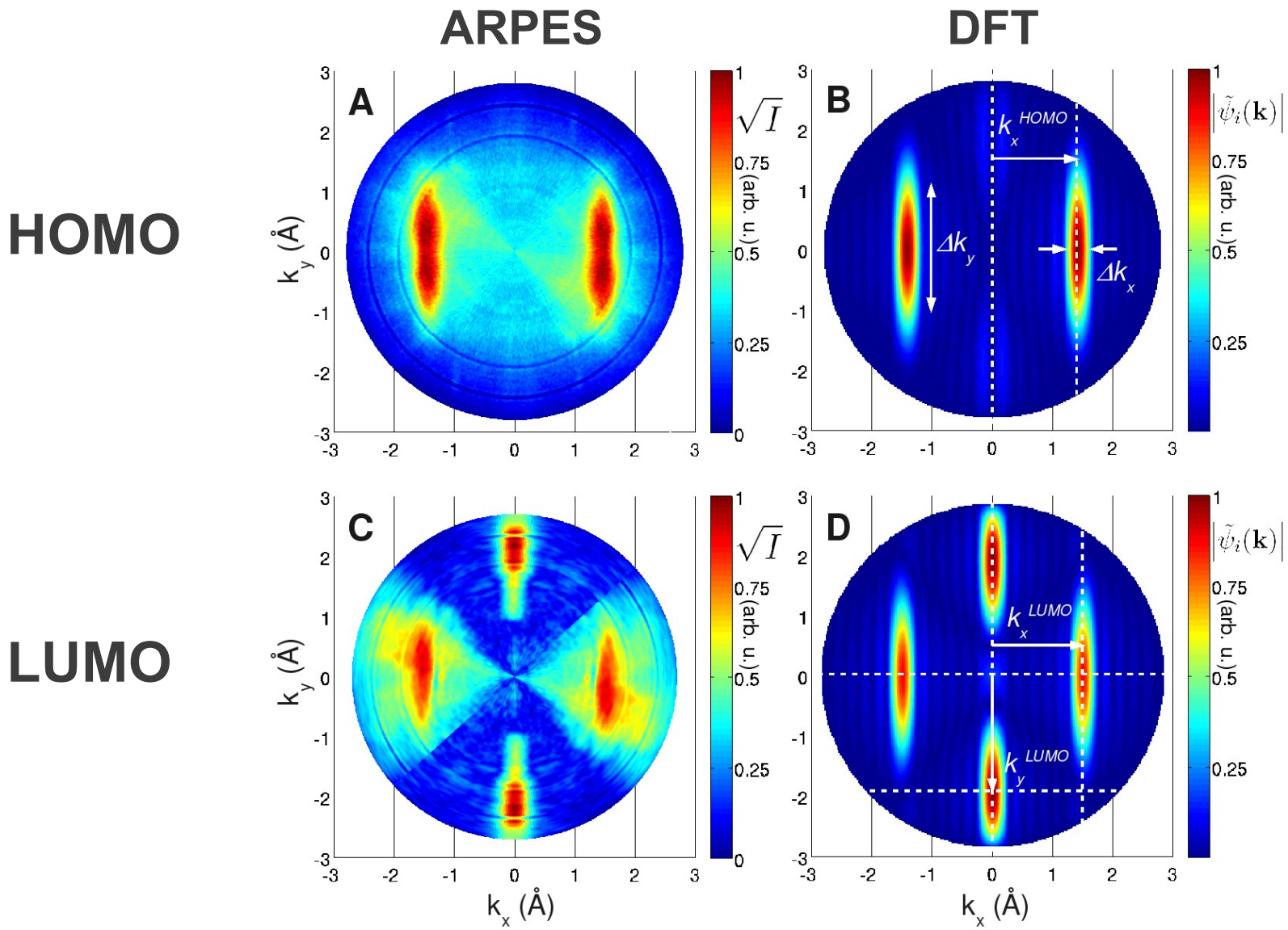



**HOMO** **filled LUMO**

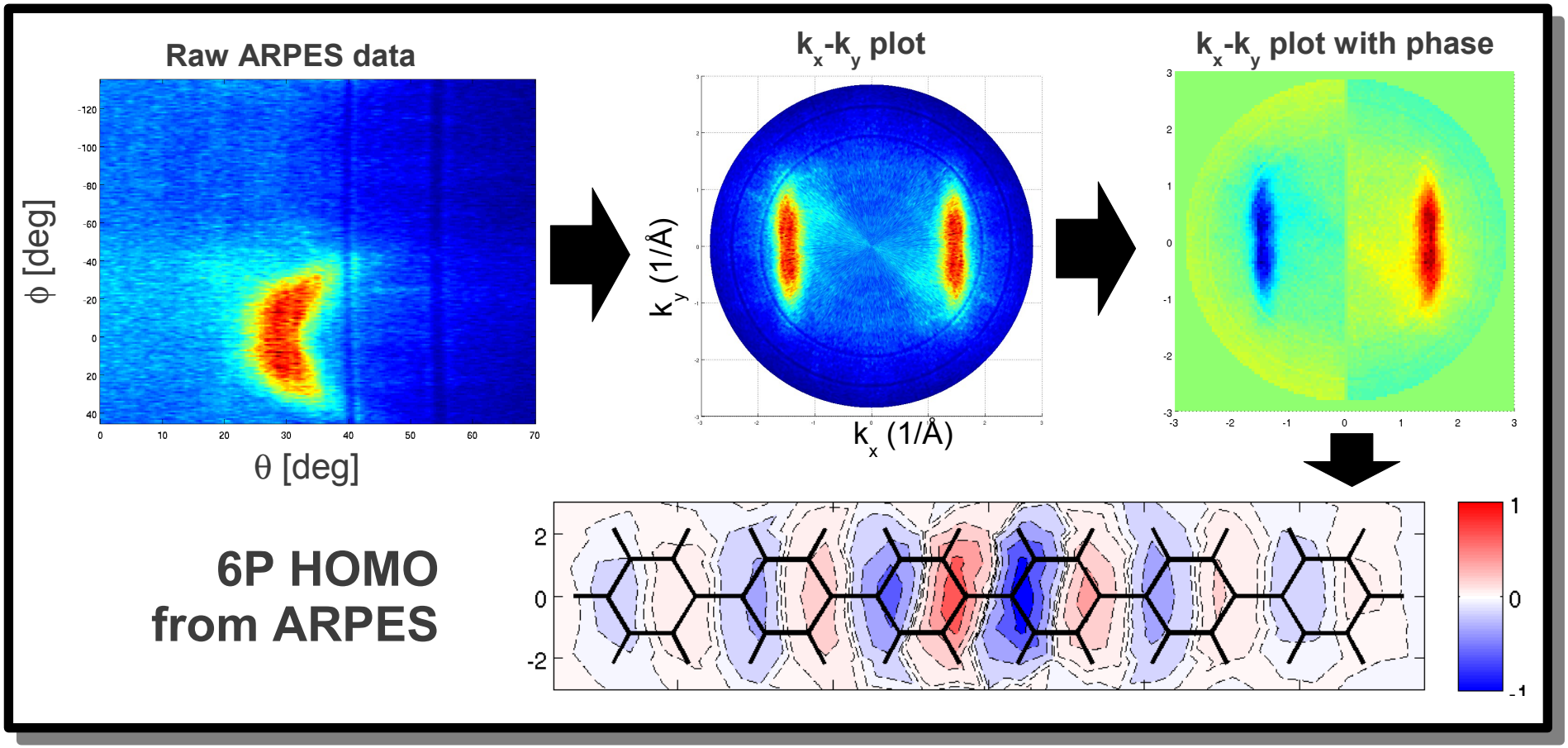
**ARPES** data for a monolayer of 6P / Cu(110)



# 2D Momentum Maps: 6P/Cu(110)



# Reconstruction of Orbitals

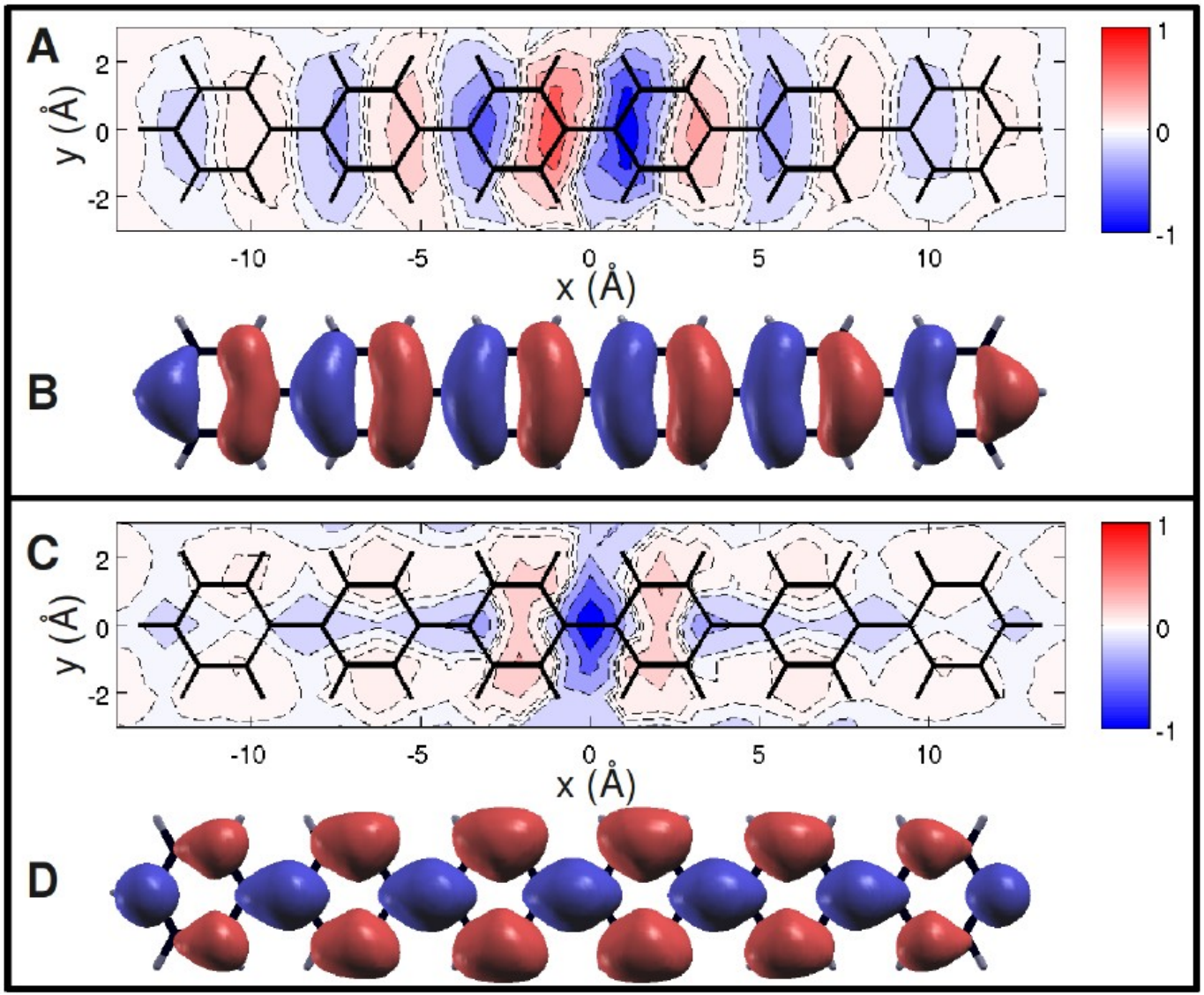



Puschnig et al., *Science* **326**, 702 (2009). (published online Sept. 10, 2009)

# Reconstructed Sexiphenyl Orbitals

HOMO

Filled LUMO



# Conclusions and Outlook

- Simple theory for PE intensity: works for ...
  - $\pi$-orbitals of large molecules
  - Emission direction close to polarization vector
  - Light atoms (C, N, O) with small scattering cross section
- 2D momentum maps provide fingerprints of molecular orbitals
- ARPES data can be used to identify and quantify molecular orientations and conformations
- Molecular orbitals can be reconstructed in cases where unique molecular orientations are present

# Thank You!

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„Interface controlled and functionalized organic films“