MONTAN UNIVERSITÄT
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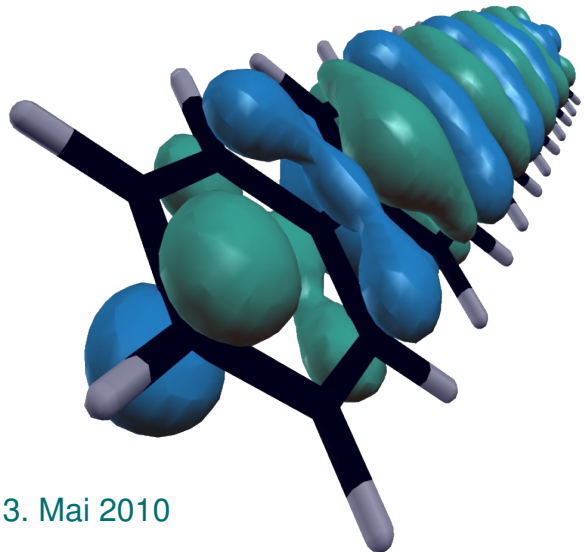
Atomistic Modelling of Organic Semiconductors



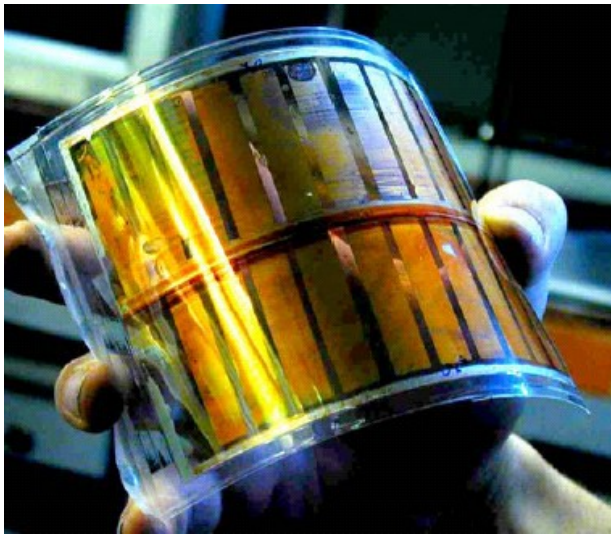
Organic Semiconductor Devices

White OLED

Area = 10x10 cm2 (from HC Starck CleviosTM PH510 PEDOT layer)

OLED display

(from Samsung, ultra-thin 0.05mm, 4-inch 480×272 resolution, 100,000:1 contrast , 200cd/m^2)



Organic Solar Cell

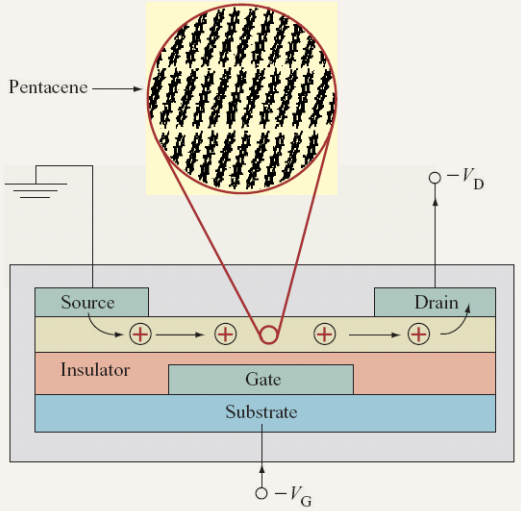
(Linz Institute for Solar Cells)

Advantages: large areas, mechanically flexible, low cost

π-Conjugated Molecules

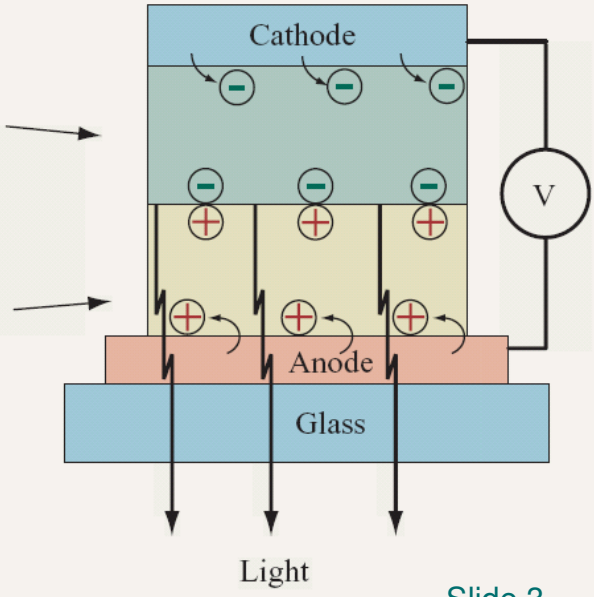
Pentacene ($C_{22}H_{14}$)

OFET
Organic
Field **E**ffect
Transistor



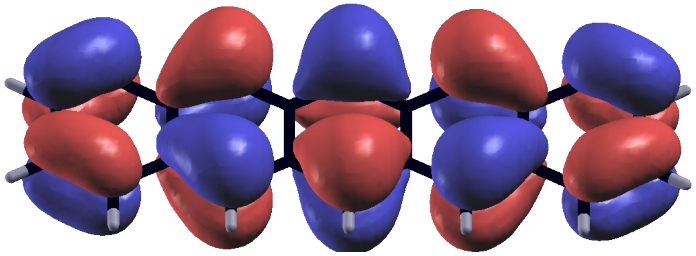
Para-Sexiphenyl ($C_{36}H_{26}$)

OLED
Organic
Light **E**mitting **D**iode

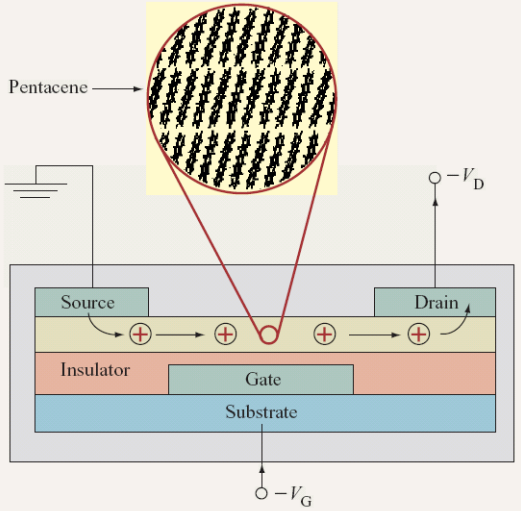


π-Conjugated Molecules

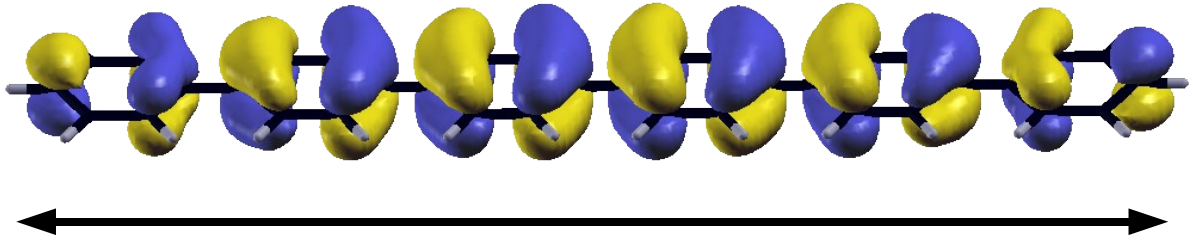
Pentacene ($C_{22}H_{14}$)



OFET
Organic
Field **E**ffect
Transistor

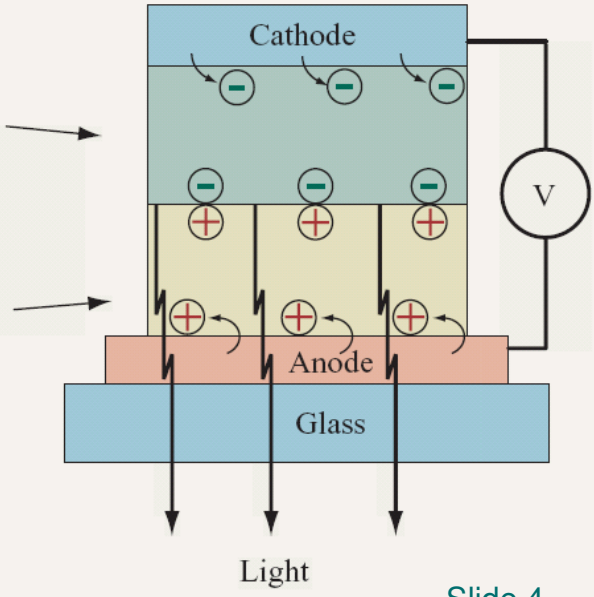


Para-Sexiphenyl ($C_{36}H_{26}$)

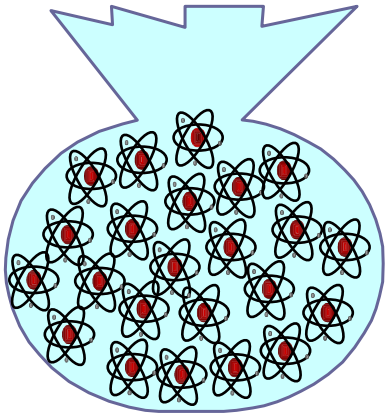


2.6 nm

OLED
Organic
Light **E**mitting **D**iode



From First-Principles



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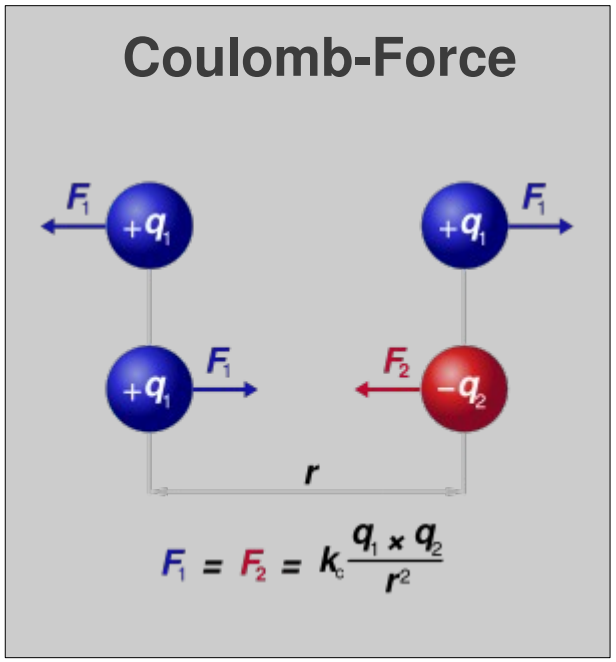

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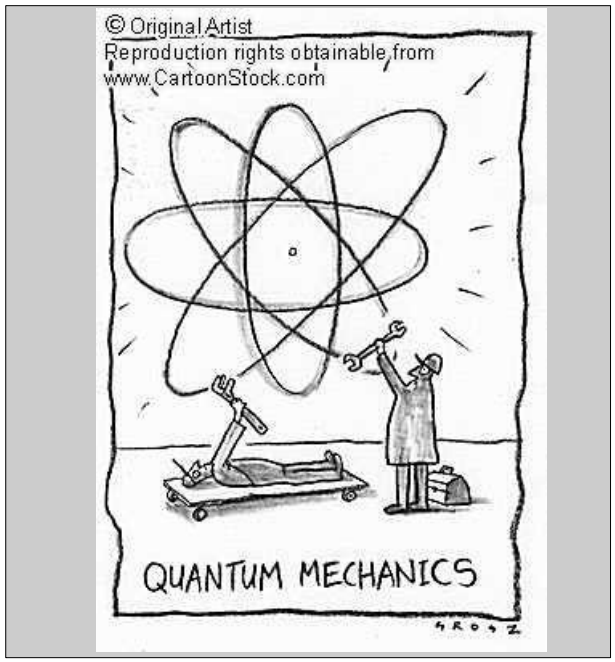
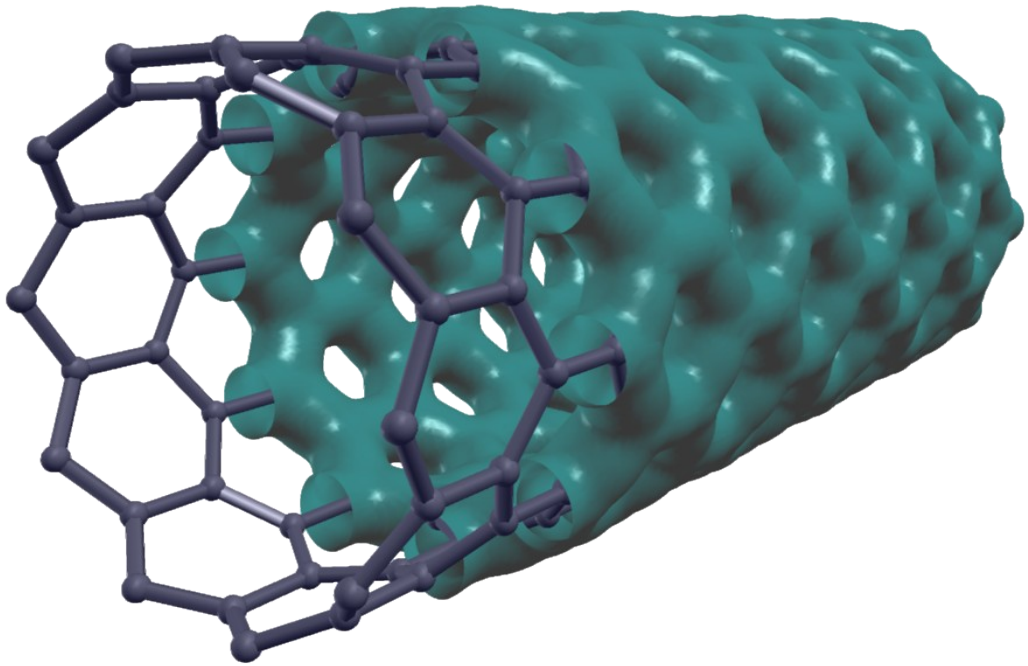


- type of bonding
- crystal structure
- elastic constants
- lattice vibrations
- band structure

Electron Density Distribution

- Electron density $n(\mathbf{r})$ is the basic variable
- Density Functional Theory (DFT) provides rigorous framework
- Microscopic and macroscopic properties depend on $n(\mathbf{r})$



Electron Density in a (10,0) single-walled Carbon Nano-Tube

Kohn-Sham Equations

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$-\frac{Z}{r}$ — Atomic nuclei

$\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r'$ — Hartree potential

$\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$ — „Exchange-correlation-potential“

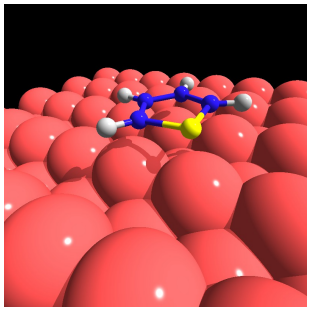
classical electro-static interactions

Quantum-mechanical effects

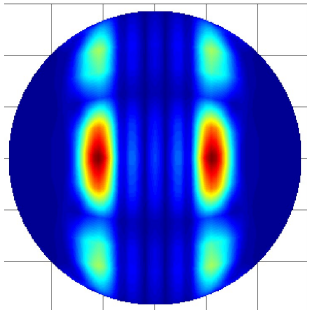
Overview

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

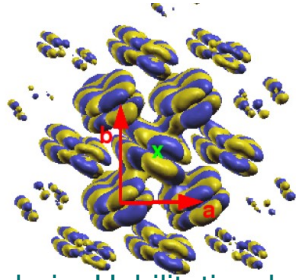
Density Functional Theory



Structural Properties



Electronic Structure



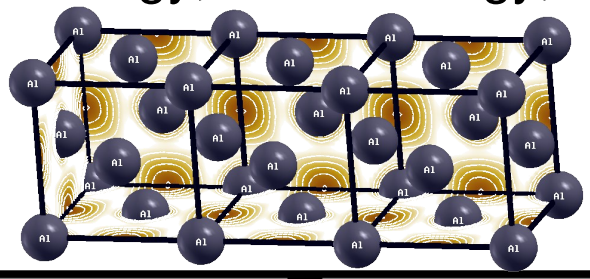
Optical Properties

Electronic Band Structure

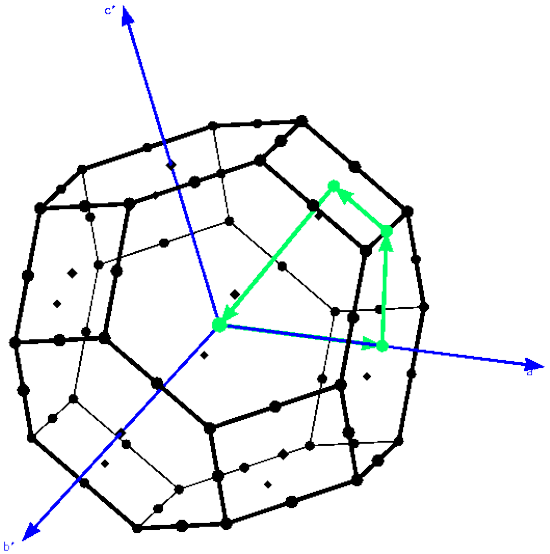
Self-consistent solution of the Kohn-Sham equations

$$\hat{H}\psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r})$$

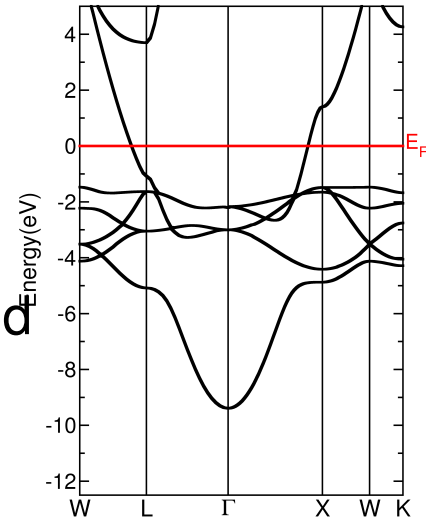
Self-consistent electron density, total energy, Fermi energy, ...



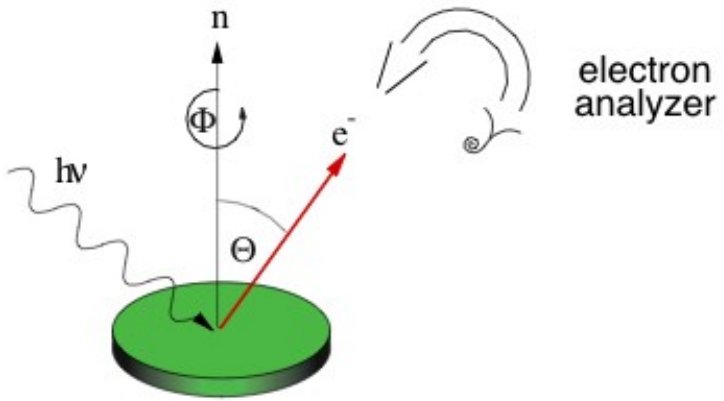
Choose k-path within Brillouin zone

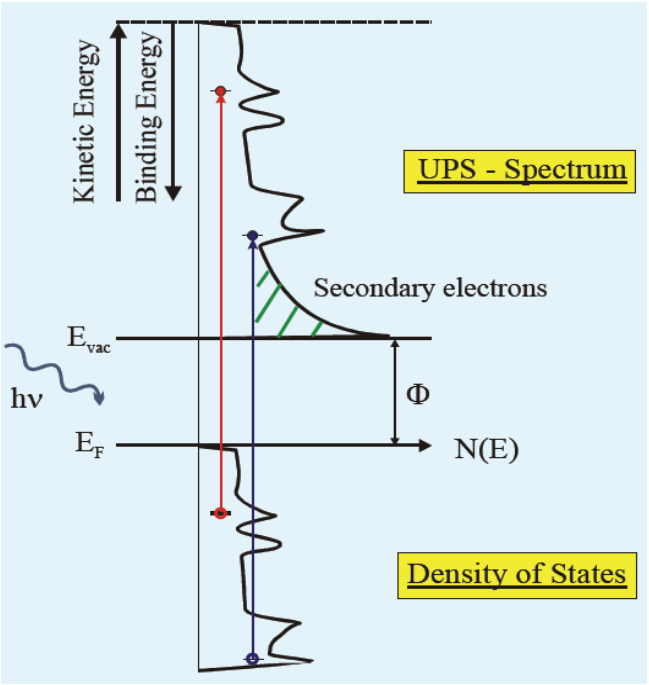


Solve KS-equations for k-points along selected k-path

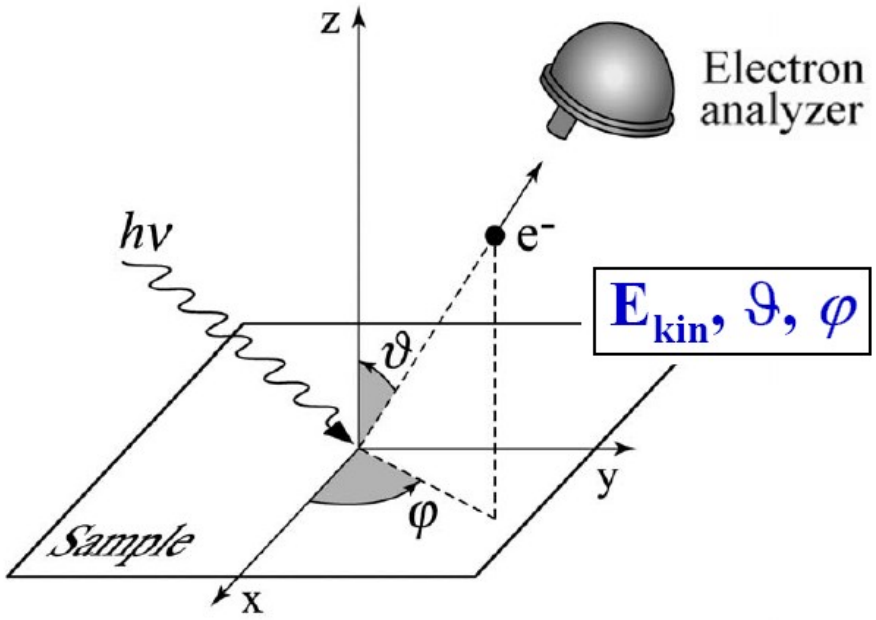


Photoelectric Effect





Angle-Resolved 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

E_{kin}

$\mathbf{K}$

Conservation laws

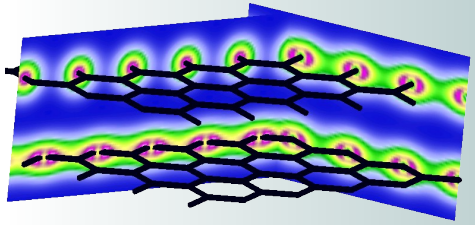
$$E_f - E_i = h\nu$$

$$\mathbf{k}_f - \mathbf{k}_i = \cancel{\mathbf{k}_{h\nu}}$$

Solid

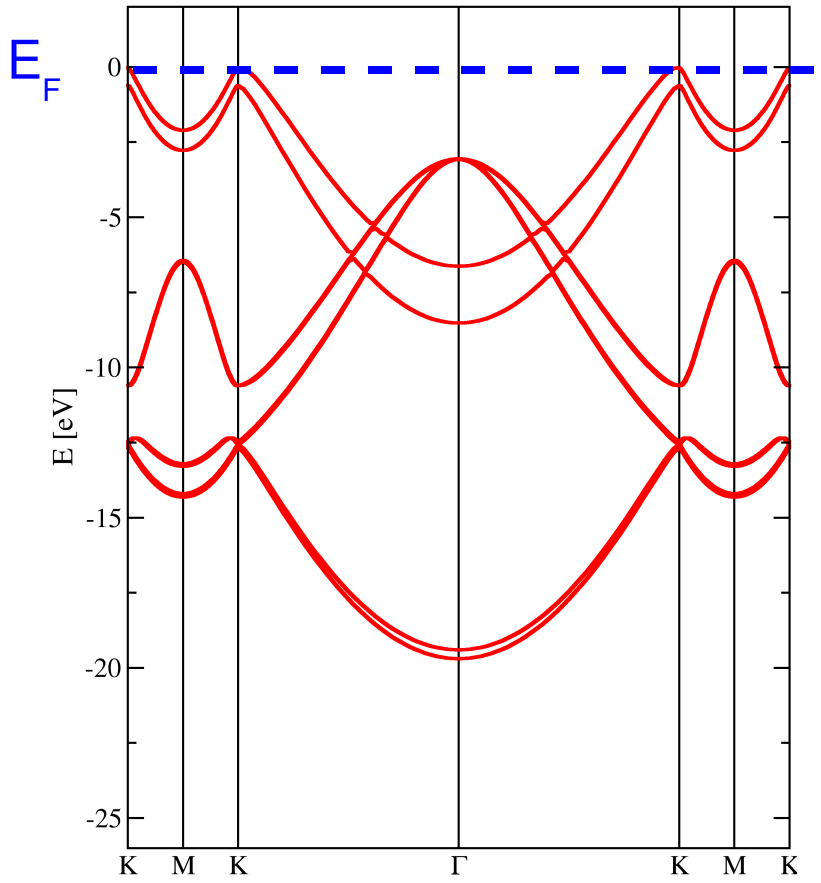
E_B

$\mathbf{k}$

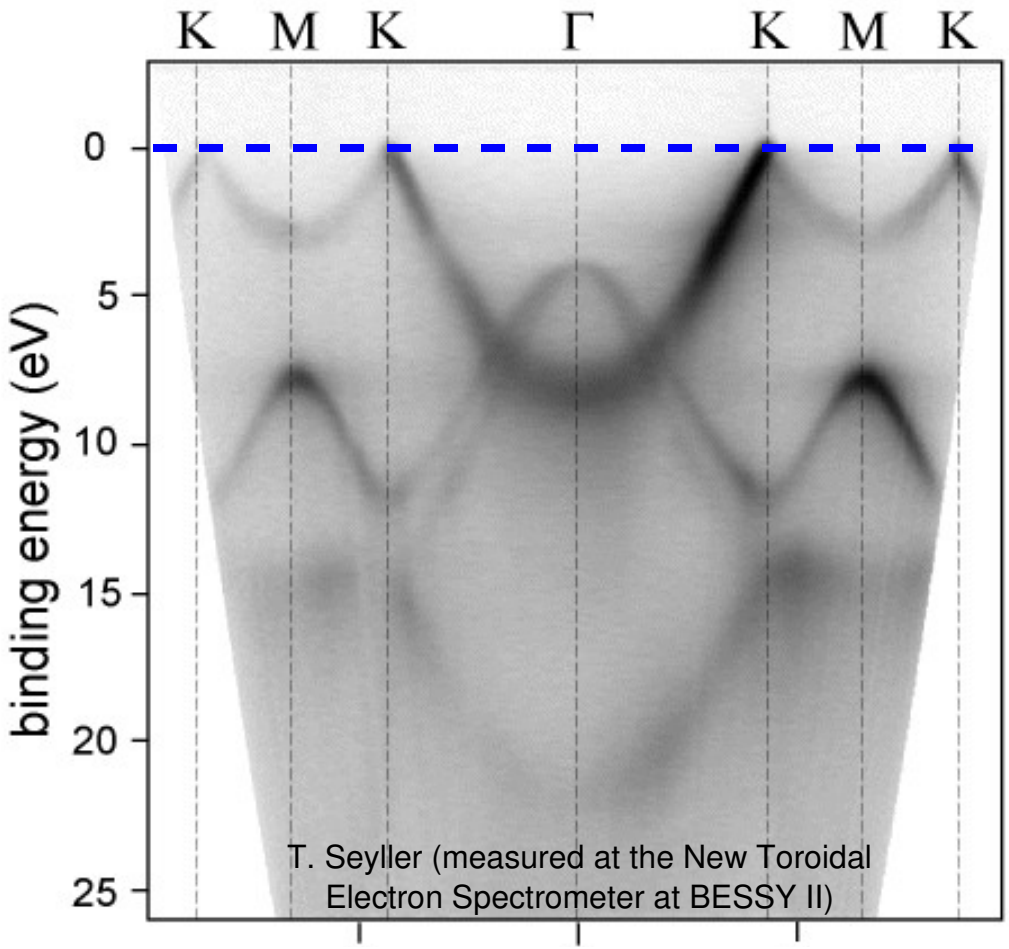


Band Structure of Graphite

DFT

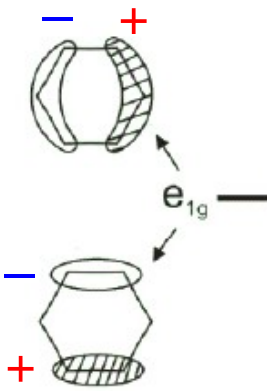


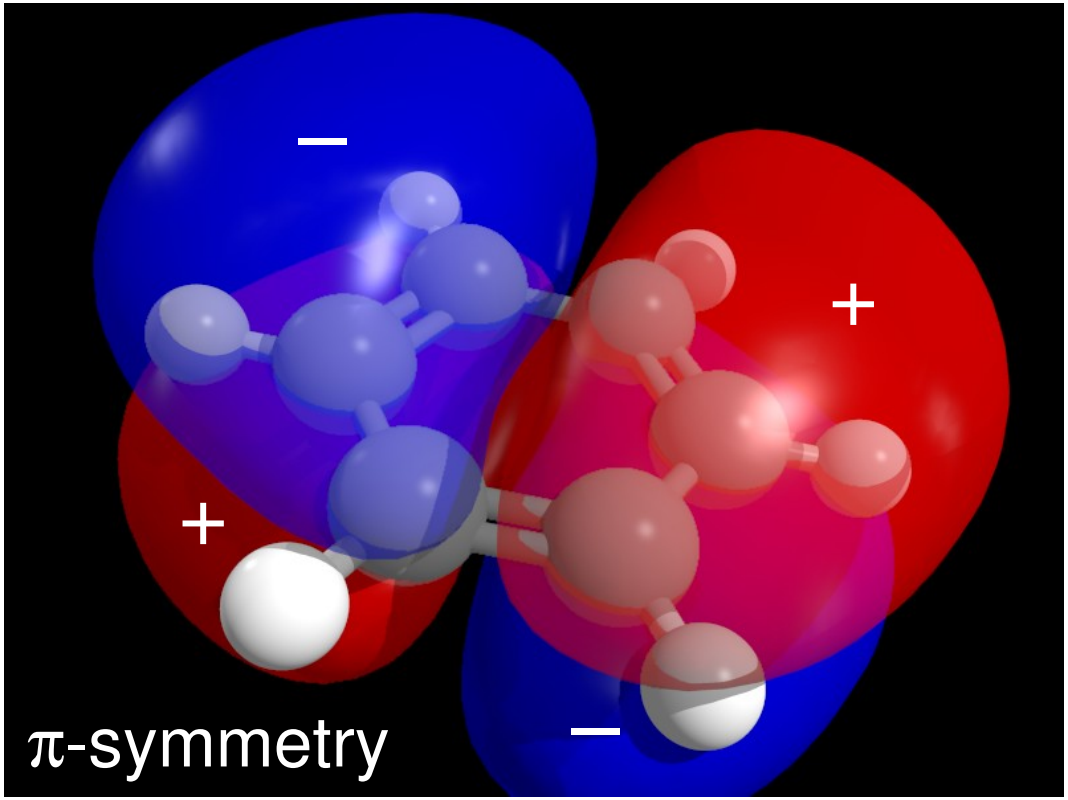
ARPES



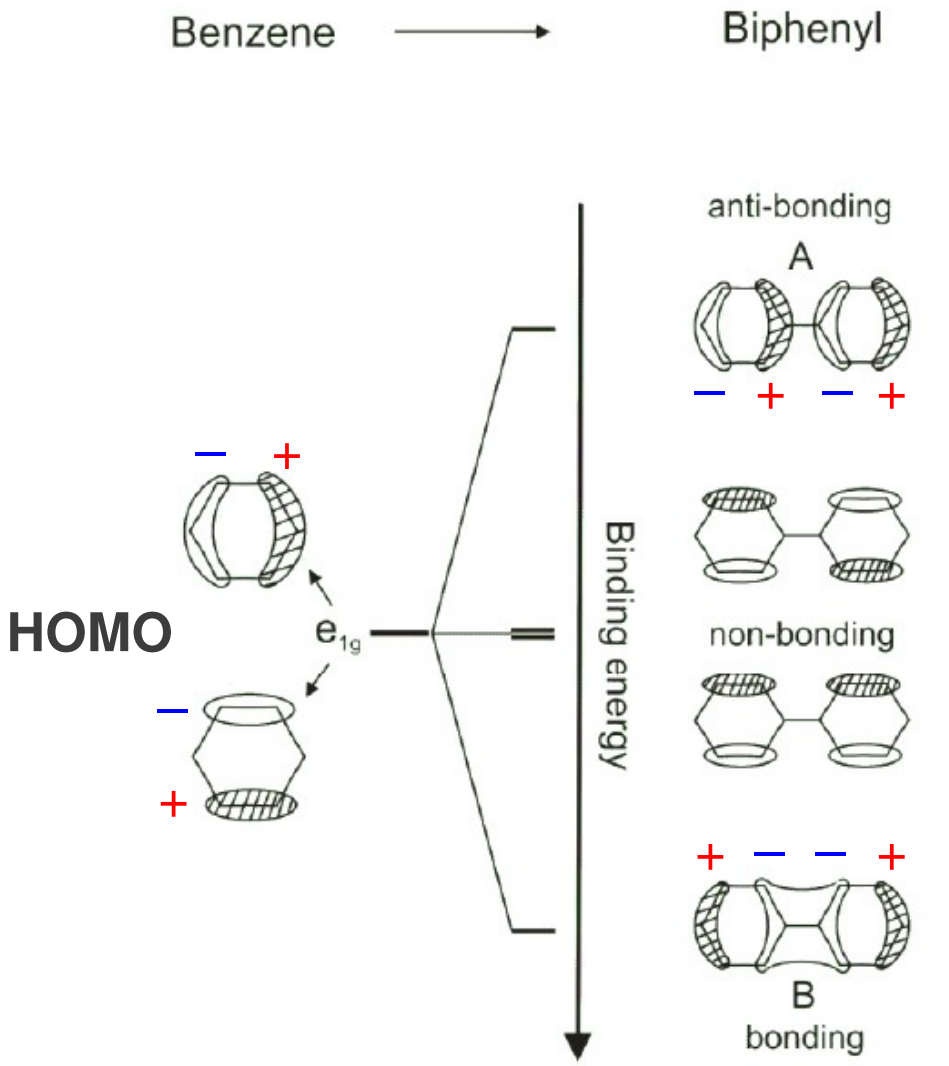
From Benzene to Sexiphenyl

Highest **O**ccupied **M**olecular **O**rbital (HOMO) of a benzene ring (C_6H_6)

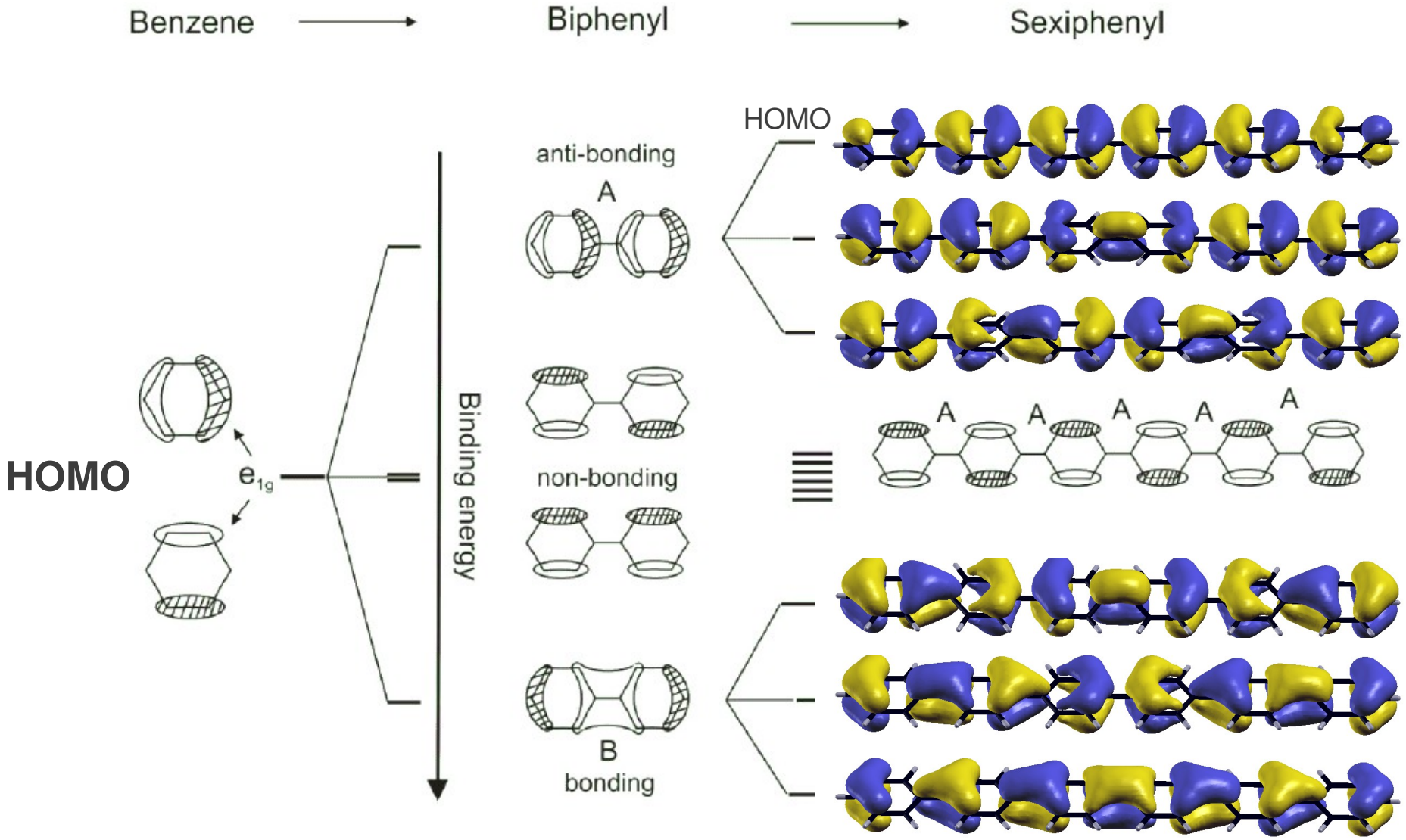




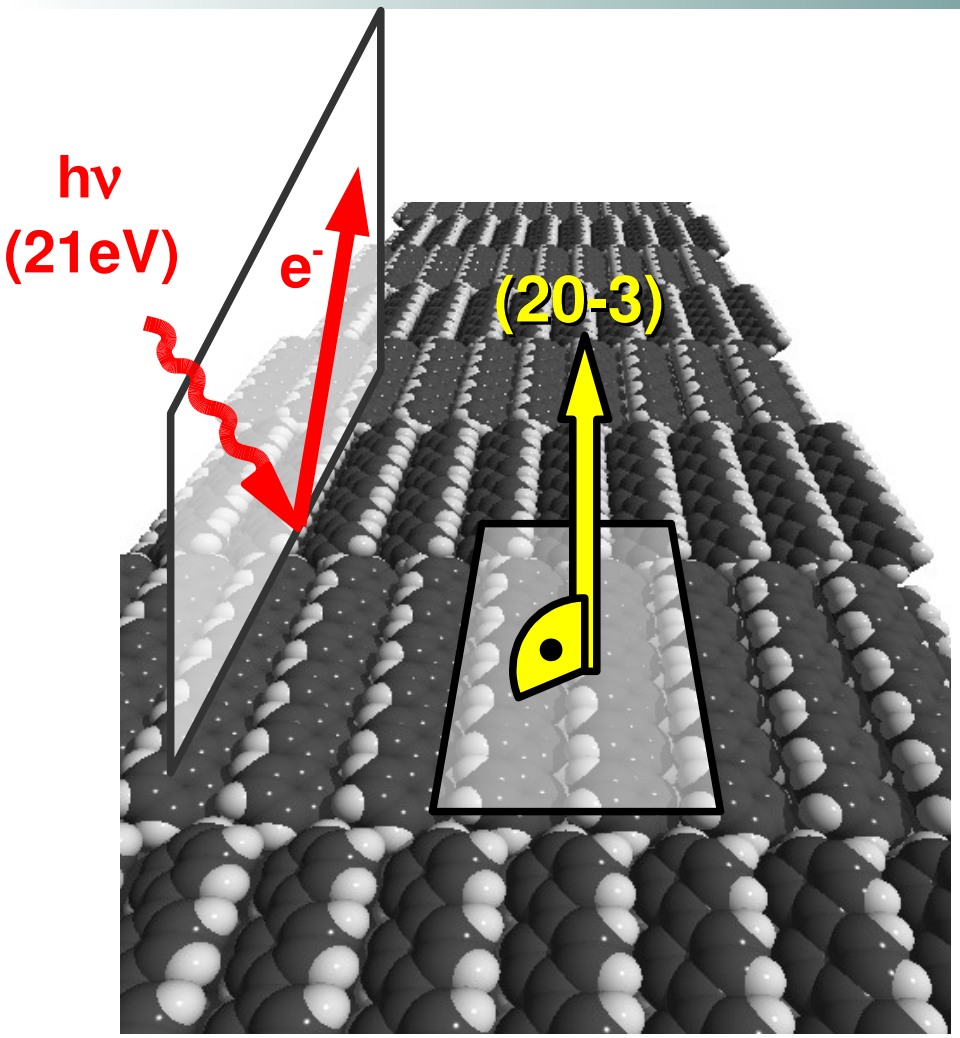
From Benzene to Sexiphenyl



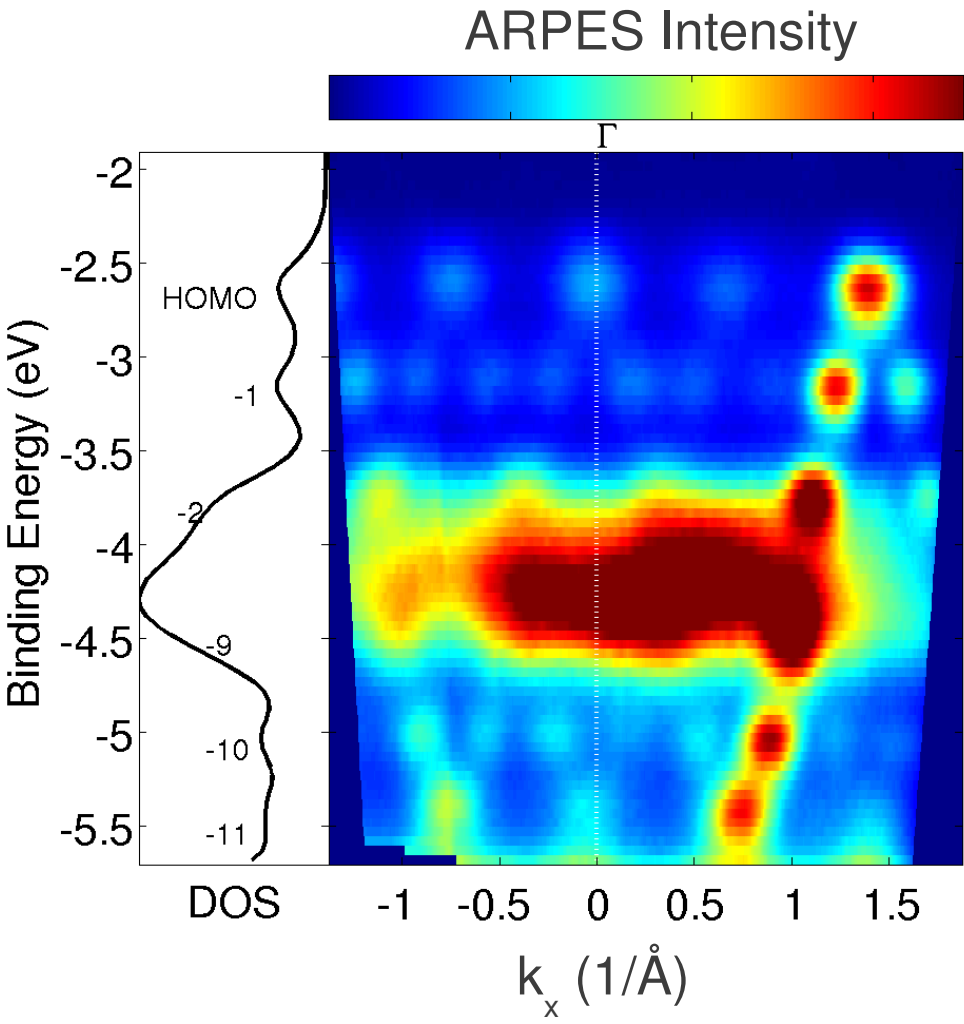
From Benzene to Sexiphenyl



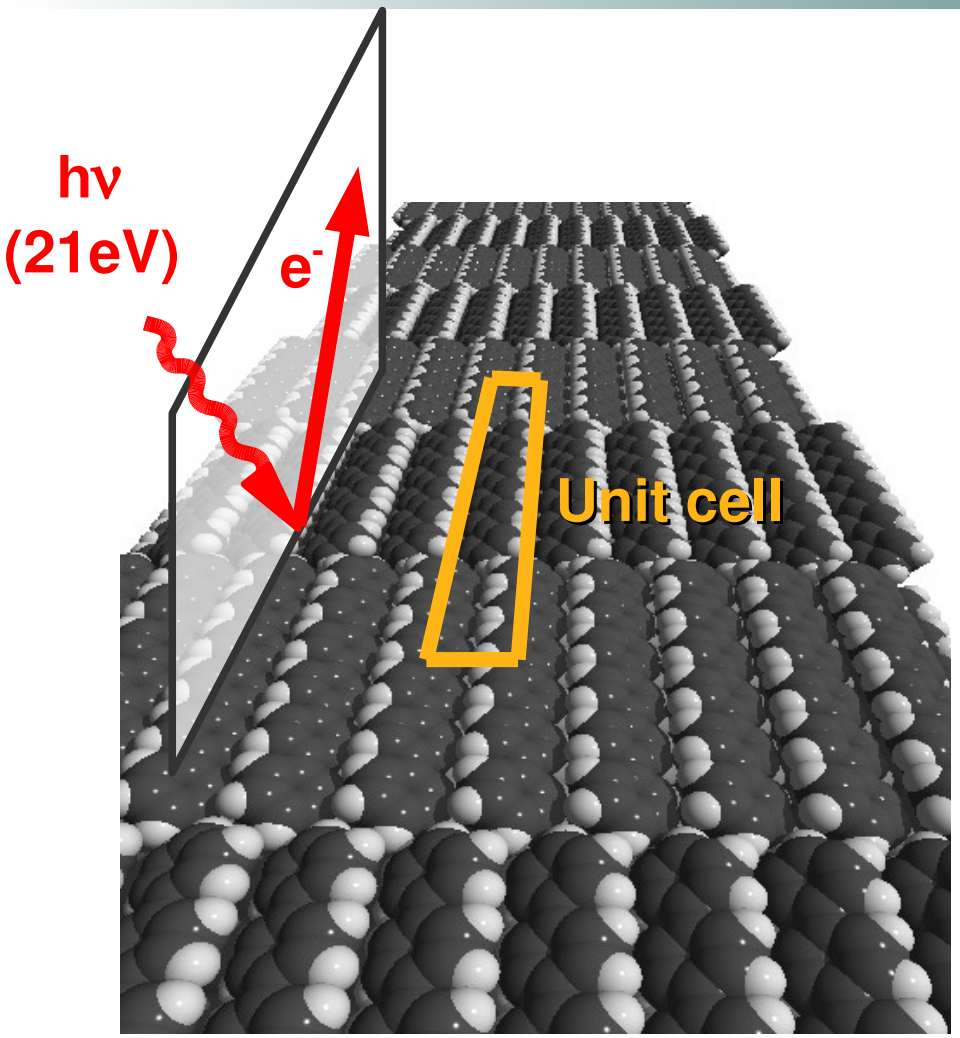
Uniaxially Aligned Sexiphenyl



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



Uniaxially Aligned Sexiphenyl



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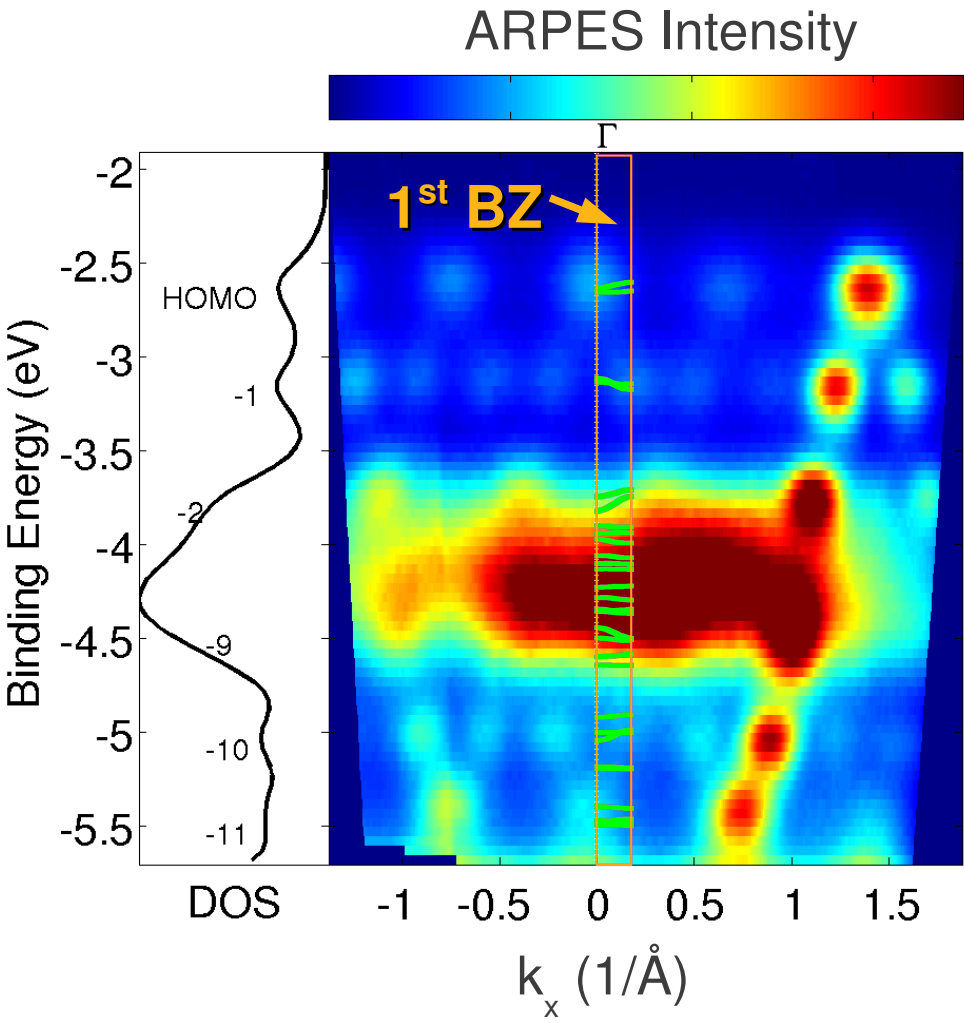
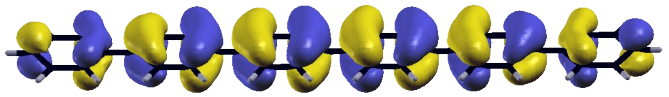


Photoemission Intensity

Fermi's Golden Rule (one-step model)

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



molecular orbital

Photoemission Intensity

Fermi's Golden Rule (one-step model)

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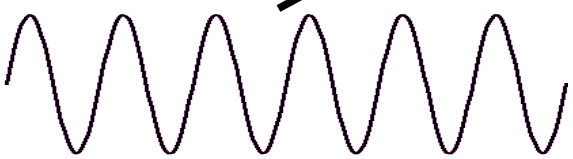
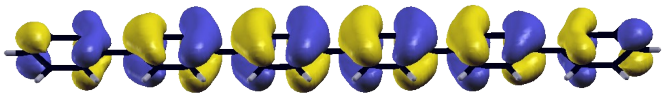


plane wave



molecular orbital

Approximation: final state = plane wave

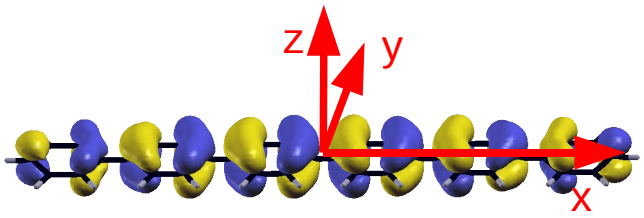
$$I_i(\theta,\phi) \propto \left|(\mathbf{A}\cdot\mathbf{k})\right|^2 \times \left|\tilde{\psi}_i(\mathbf{k})\right|^2$$

Fourier Transform of Initial State Orbital

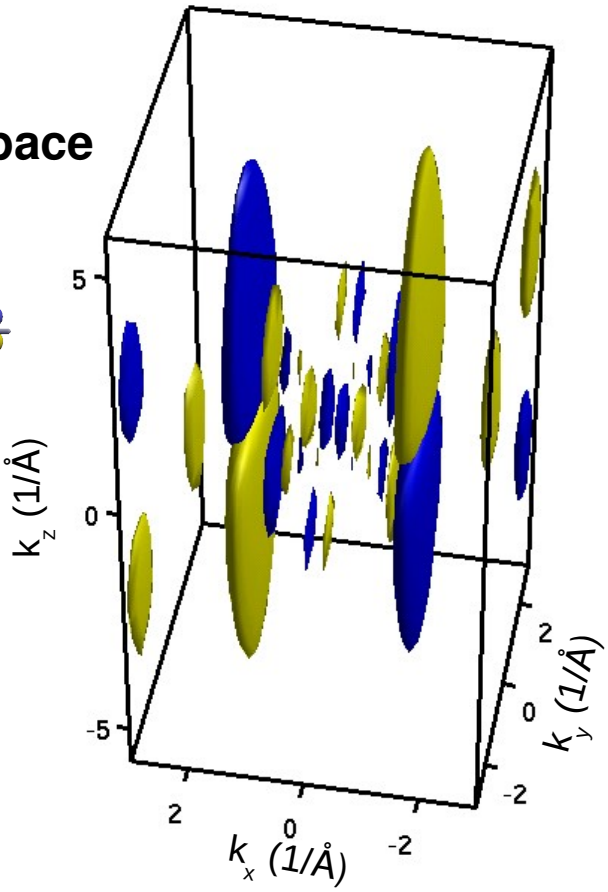
[Feibelman and Eastman, *Phys. Rev. B* **10**, 4932 (1974).]

Comparison with DFT

Molecular Orbital in Real Space

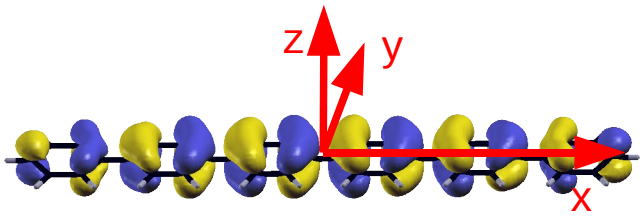


Calculation of the Fourier Transform

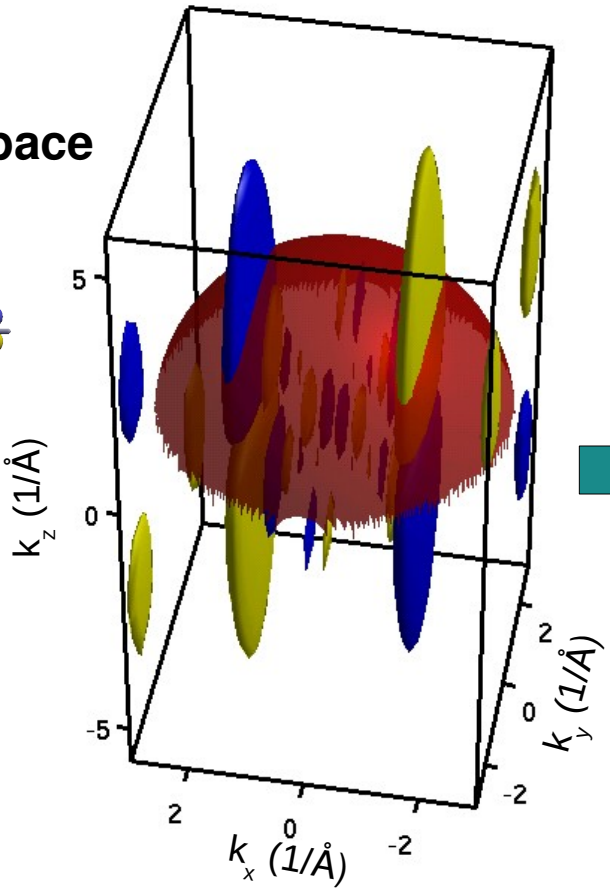


Comparison with DFT

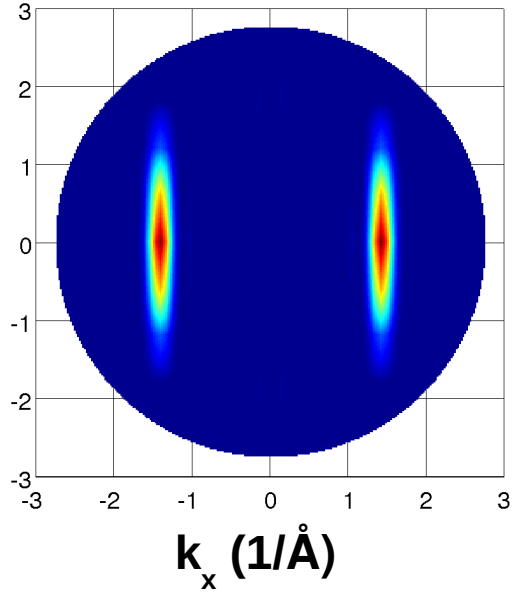
Molecular Orbital in Real Space



Calculation of the Fourier Transform

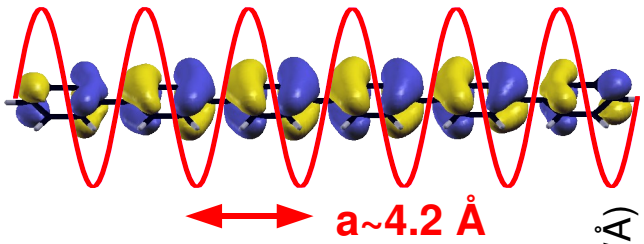


Hemispherical Cut Through 3D Fourier Transform

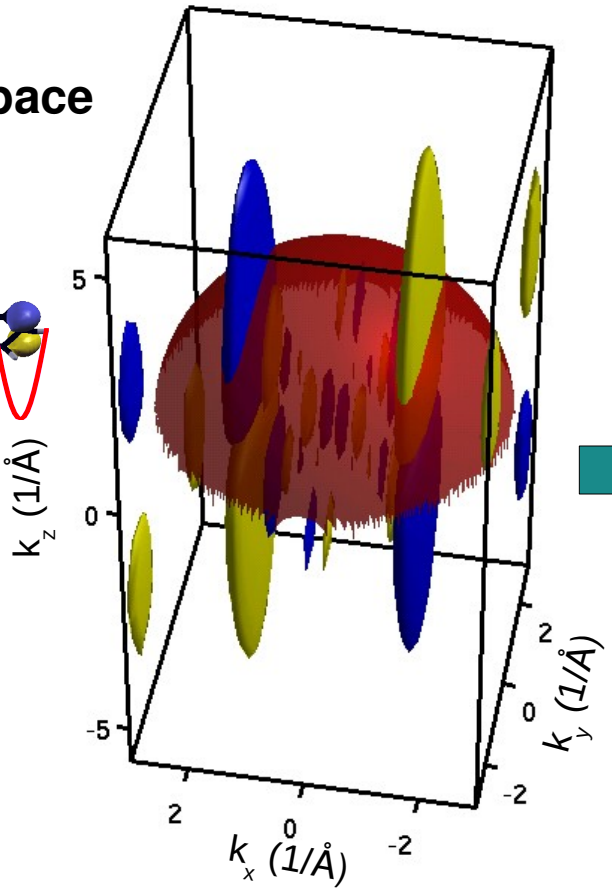


Comparison with DFT

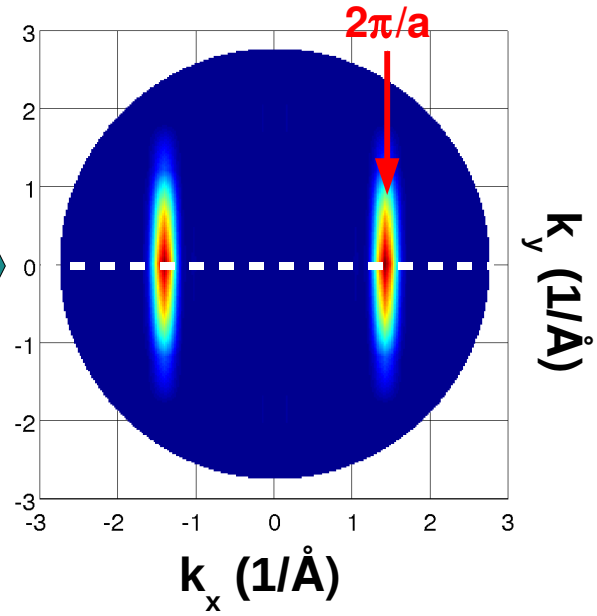
Molecular Orbital in Real Space



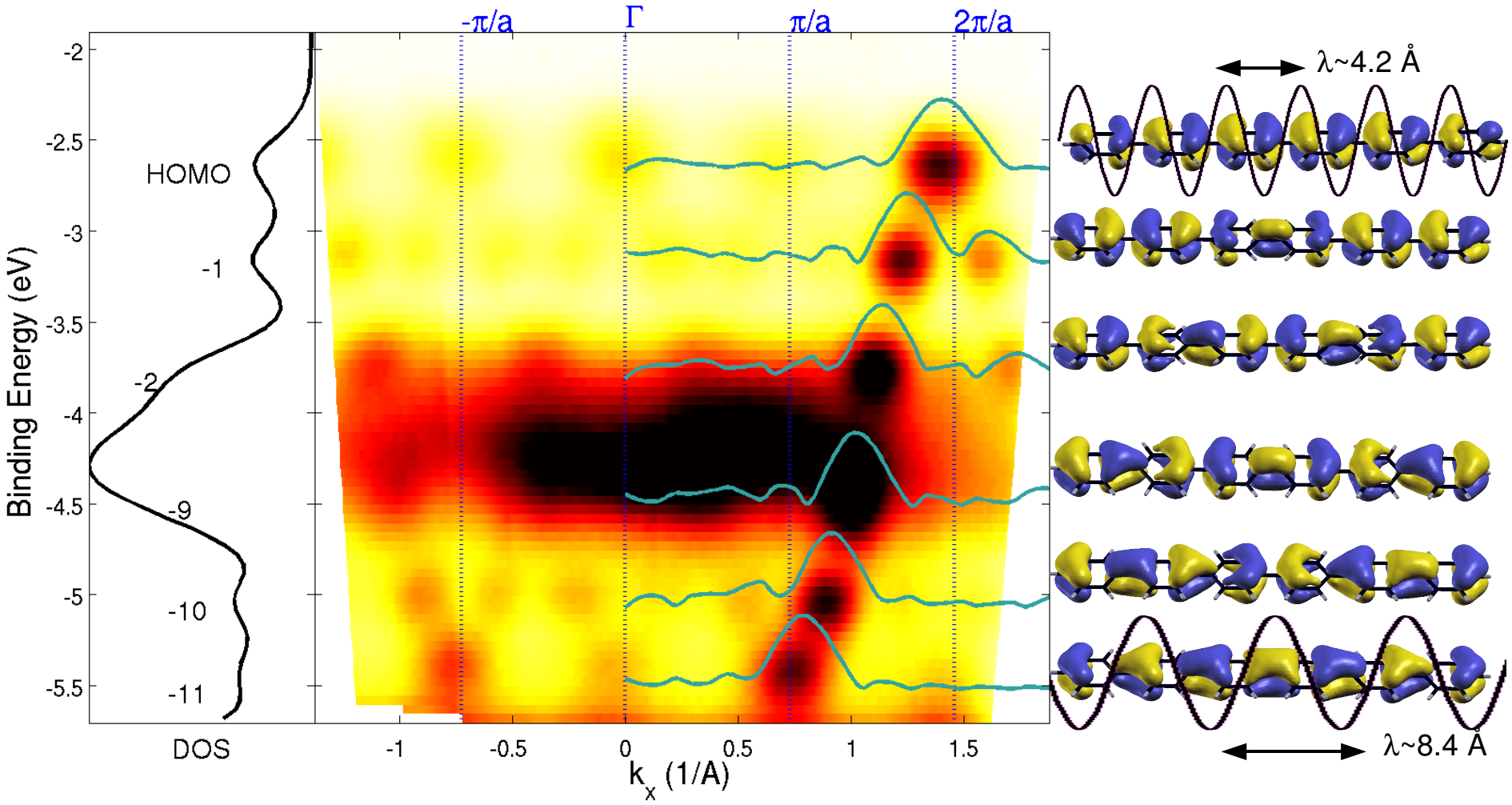
Calculation of the Fourier Transform



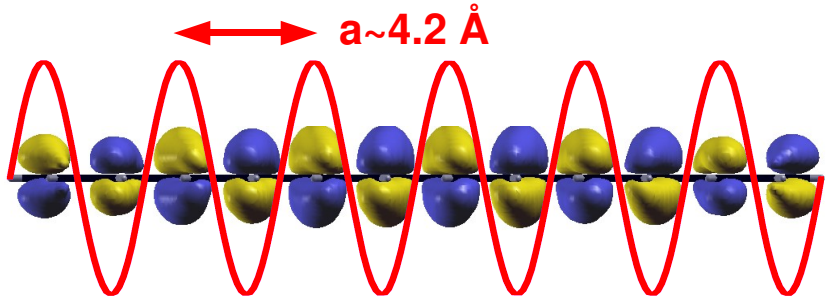
Hemispherical Cut Through 3D Fourier Transform

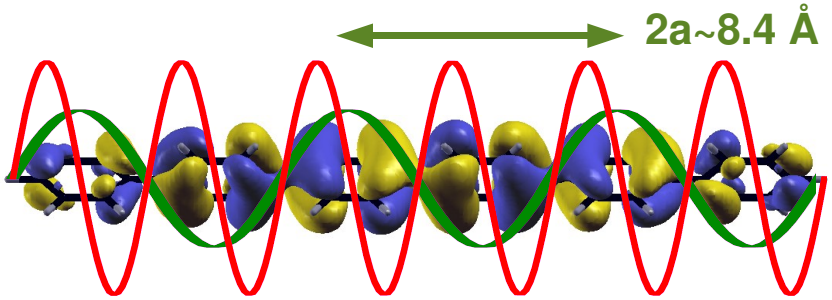


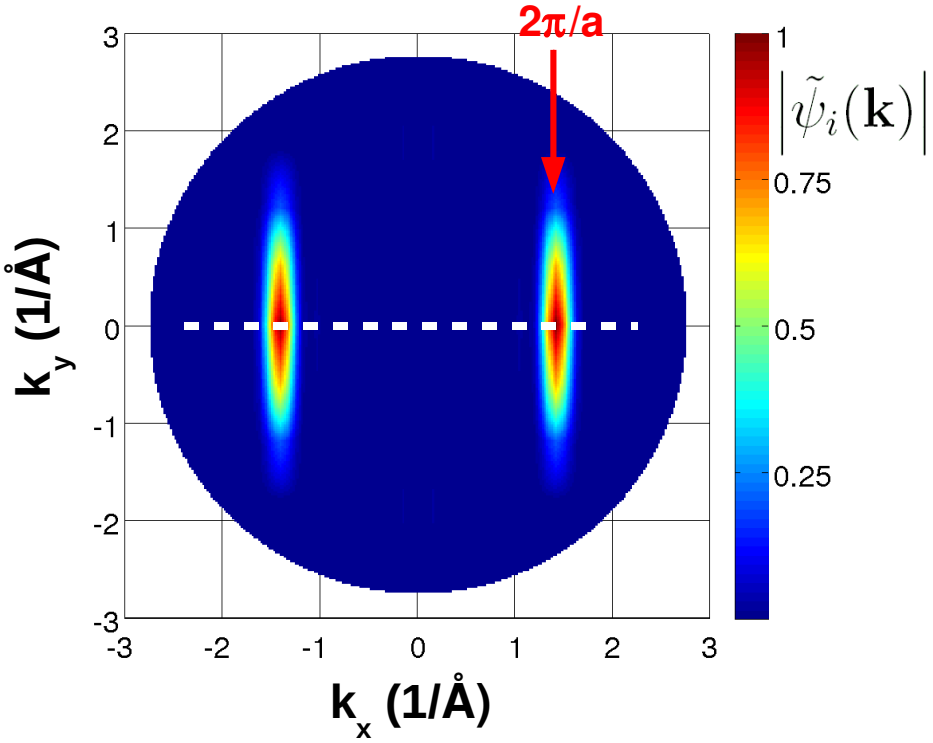
*Intra*molecular Band Structure

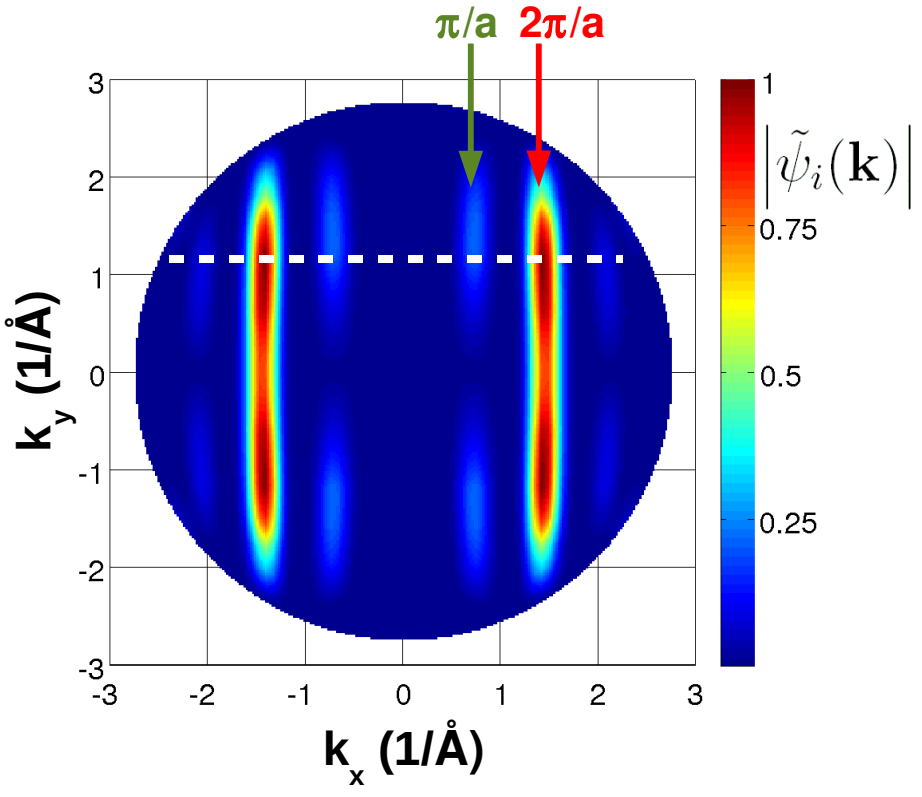


Planar vs. Twisted

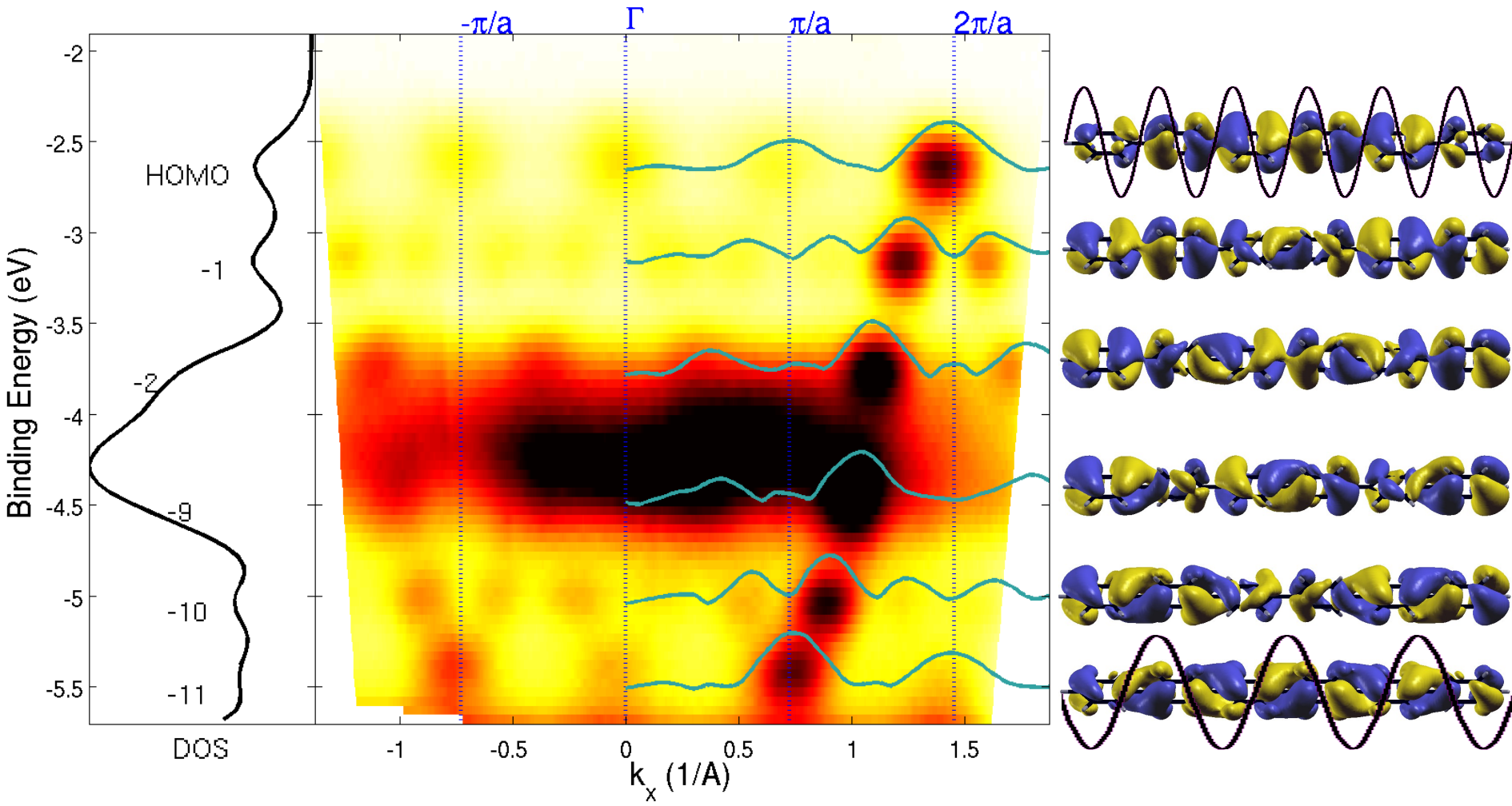






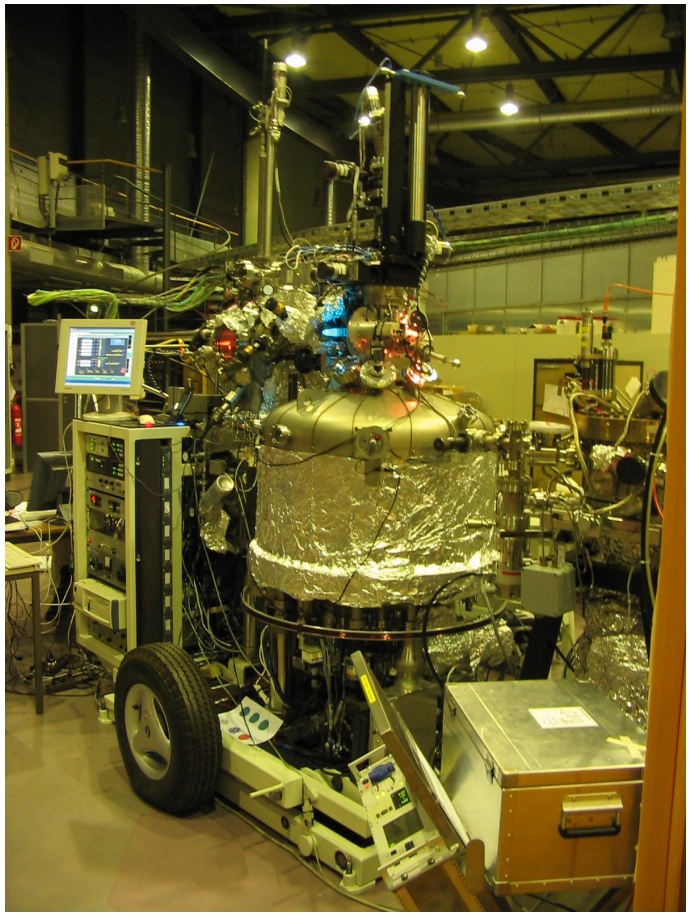


Twisted Sexiphenyl

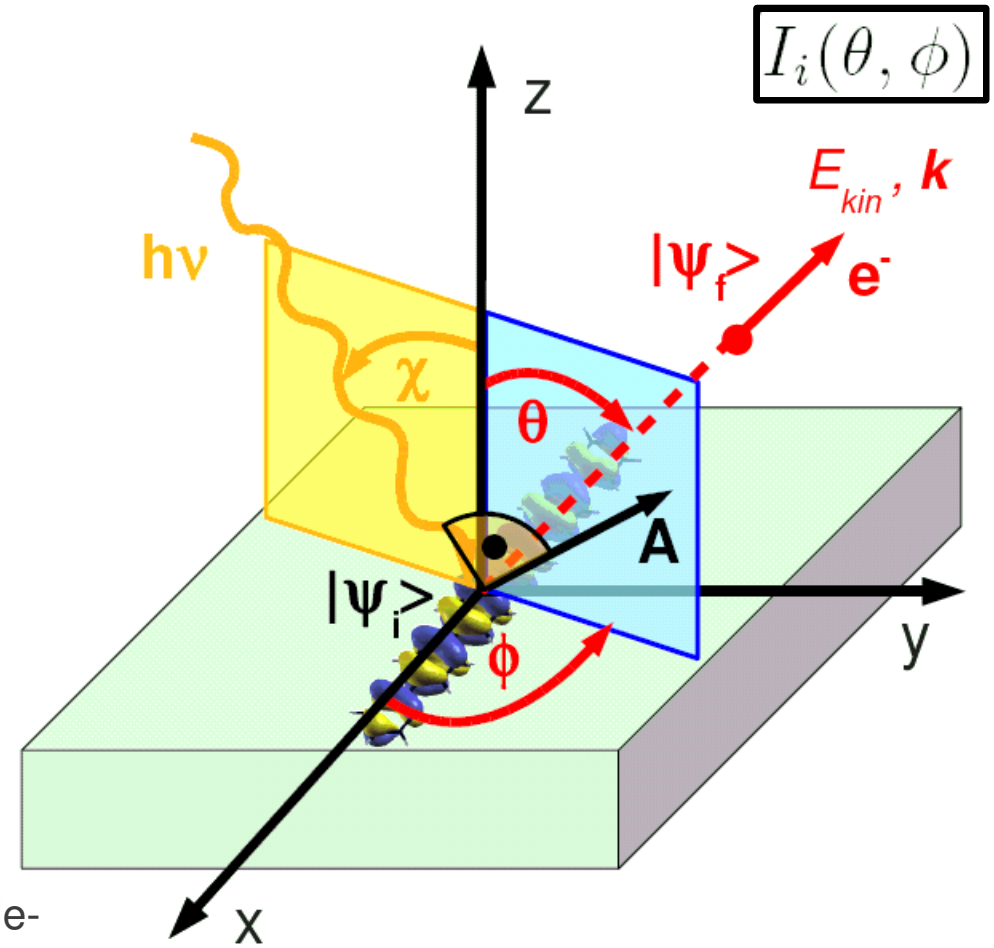


G. Koller et al., *Science* ***317****, 351 (2007).*

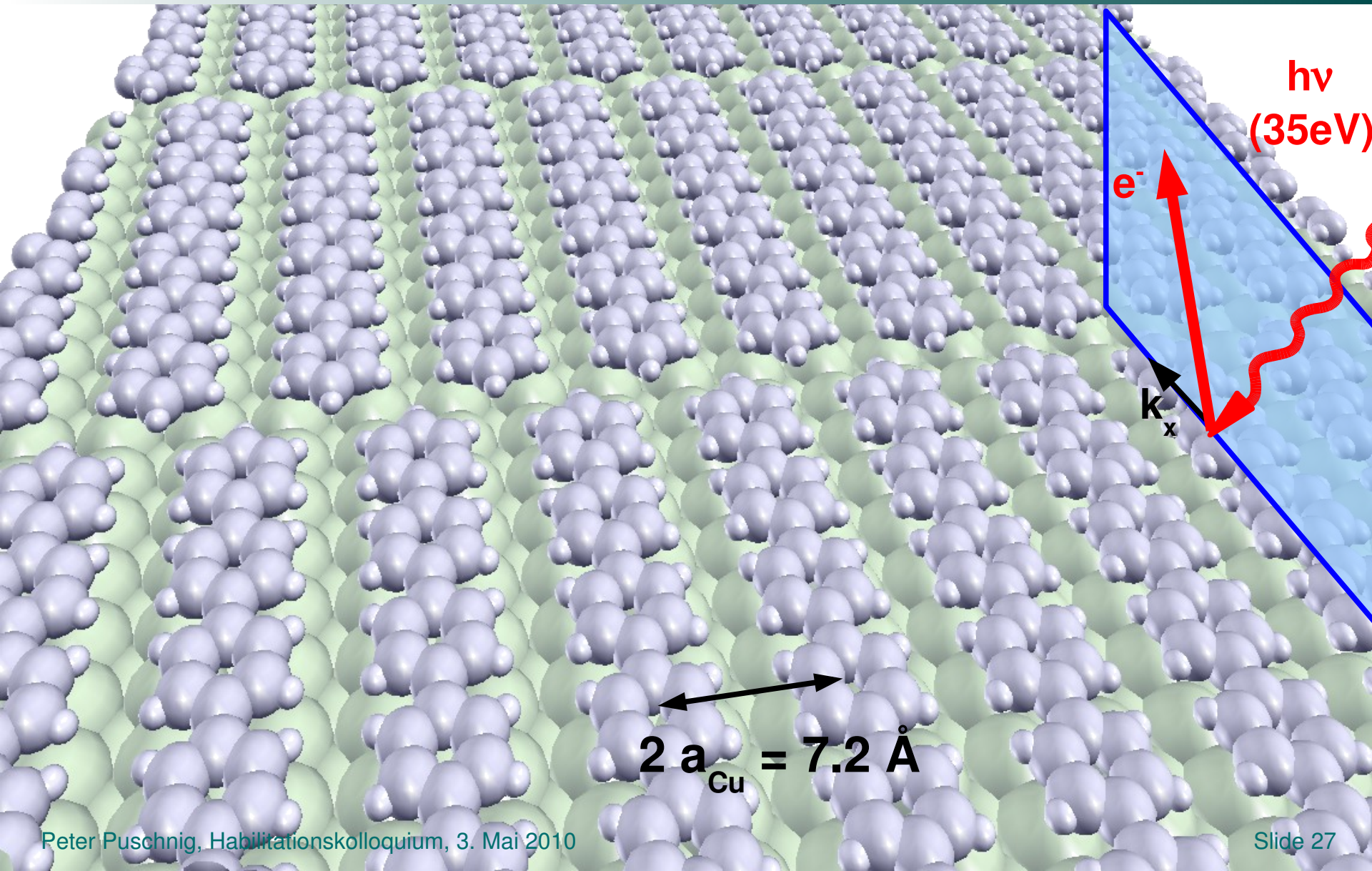
Orbital Tomography



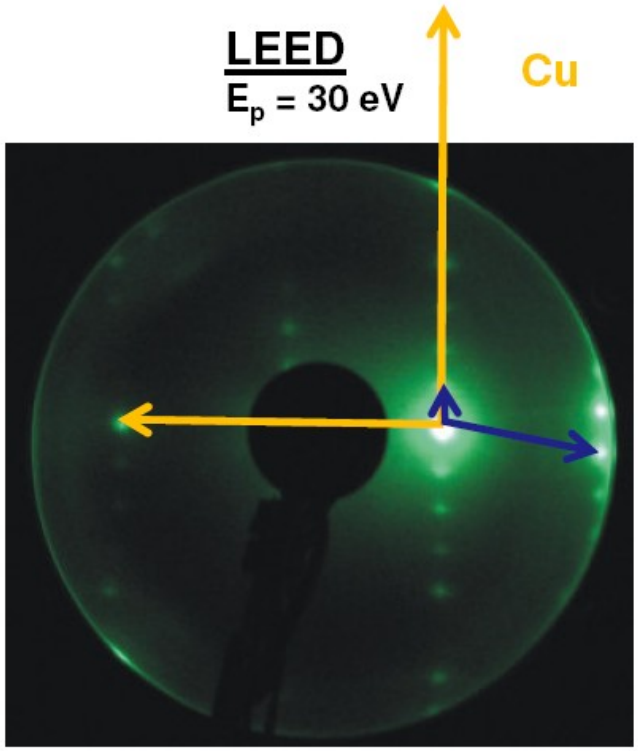
The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II

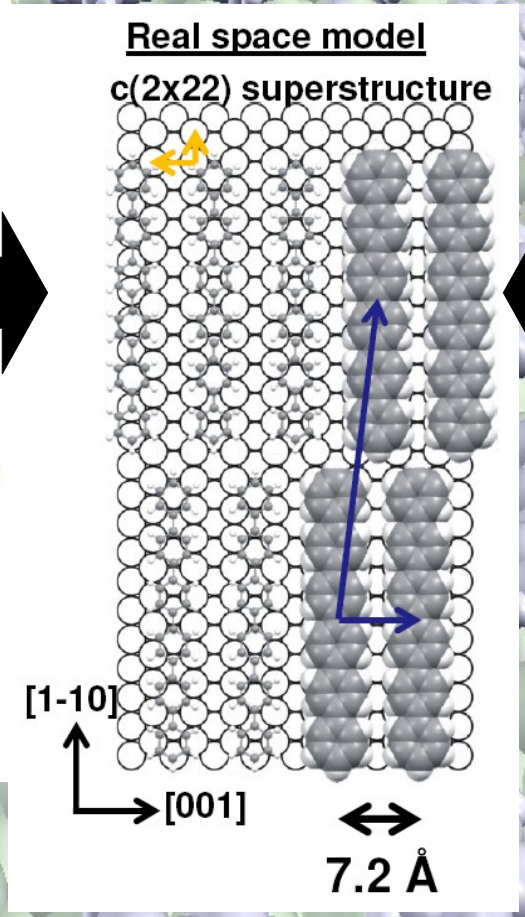


Sexiphenyl Monolayer on Cu(110)



Sexiphenyl Monolayer on Cu(110)





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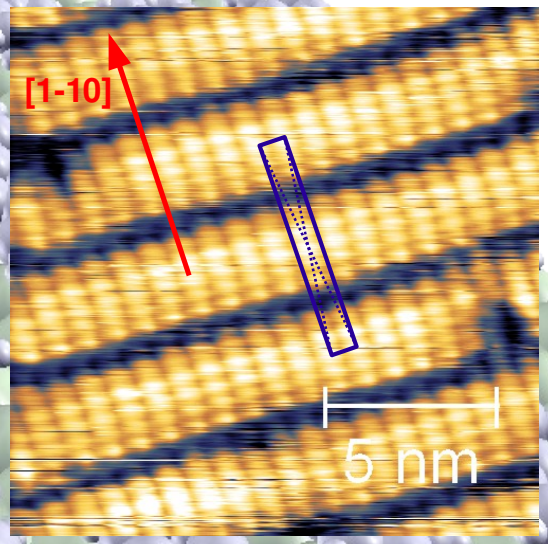

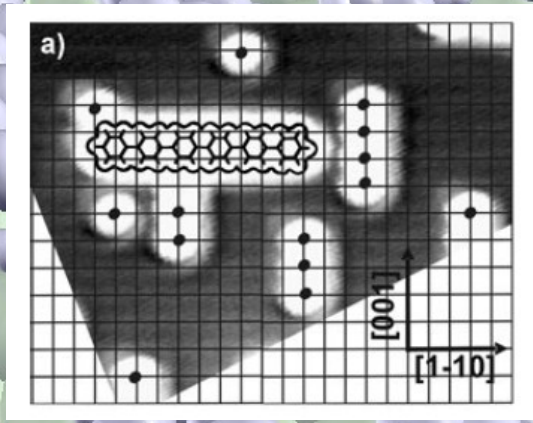

M. Oehzelt et al., ChemPhysChem 8, 1707 – 1712 (2007).

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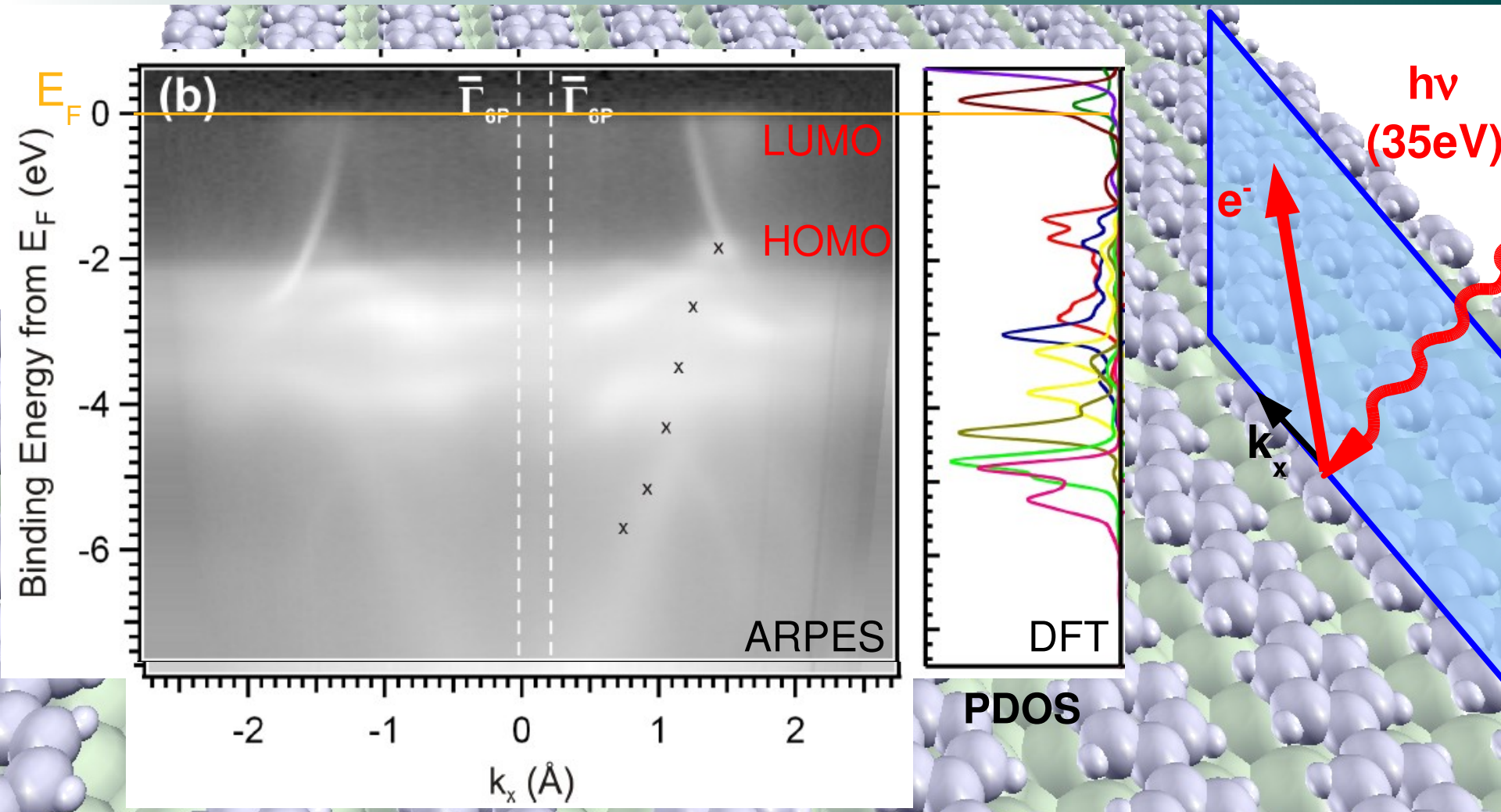
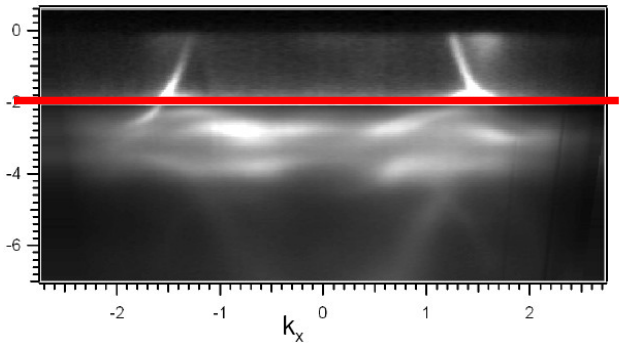
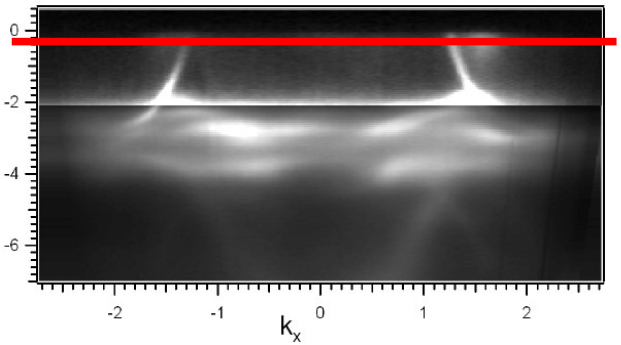


Berkebile et al. (submitted to PNAS)

2D-Momentum Maps

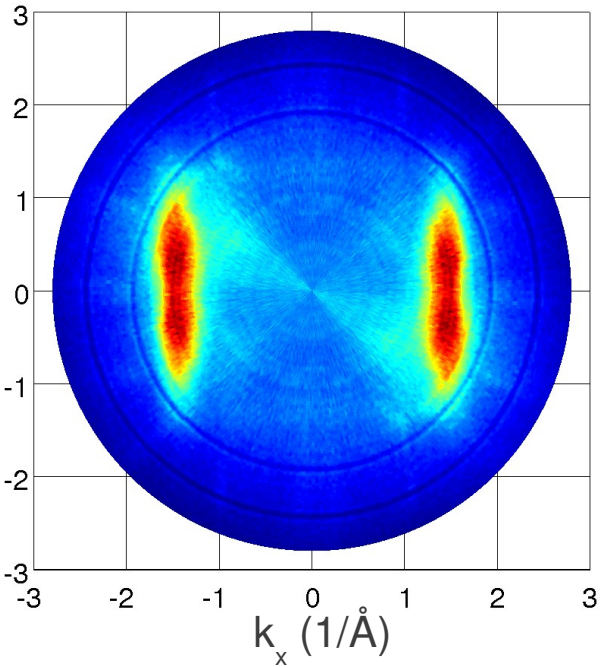


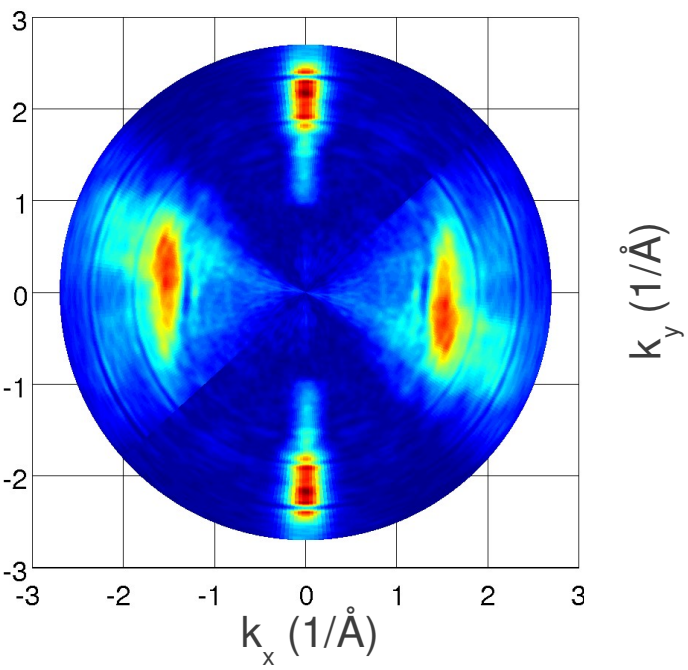
HOMO



filled LUMO

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





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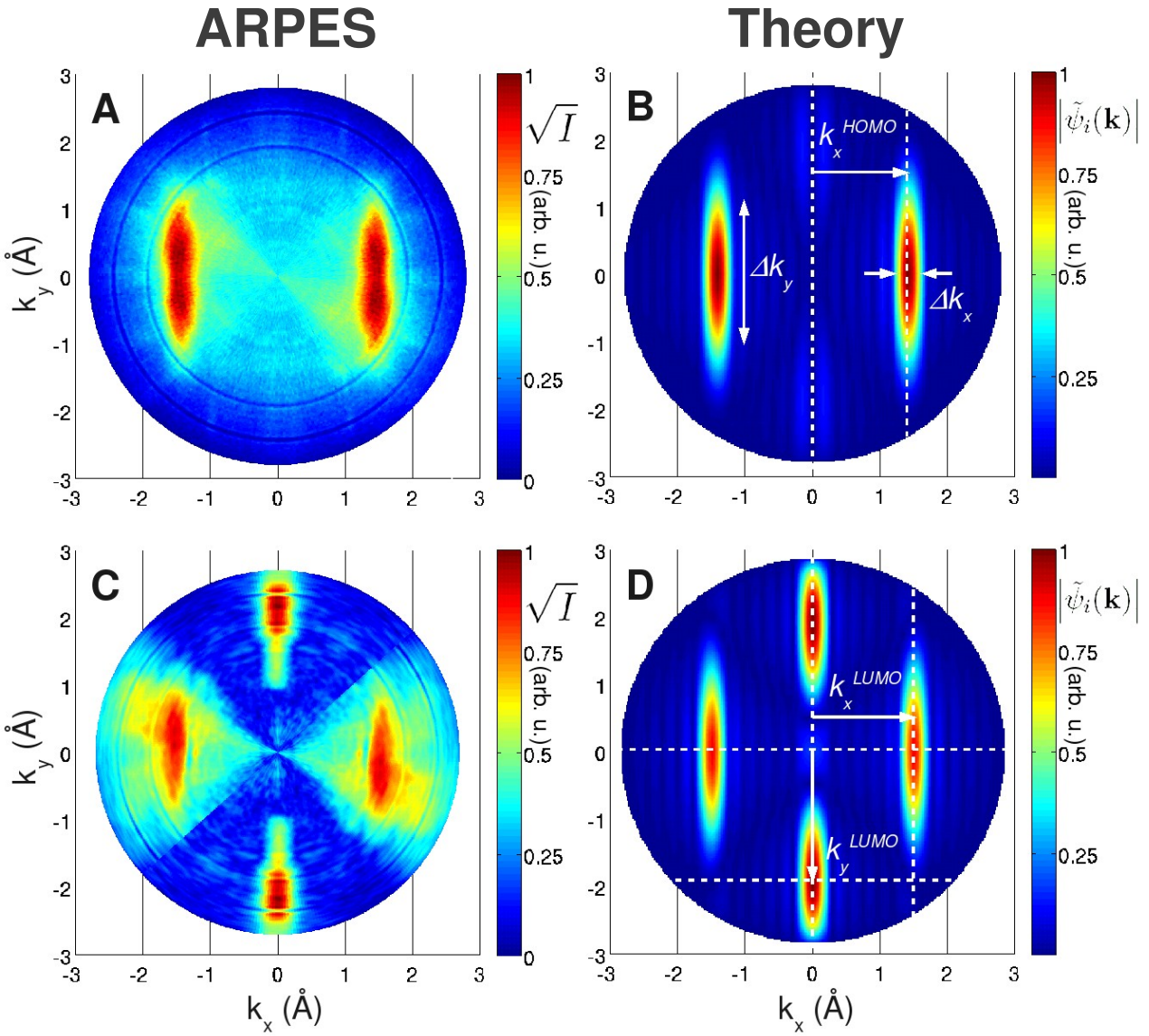
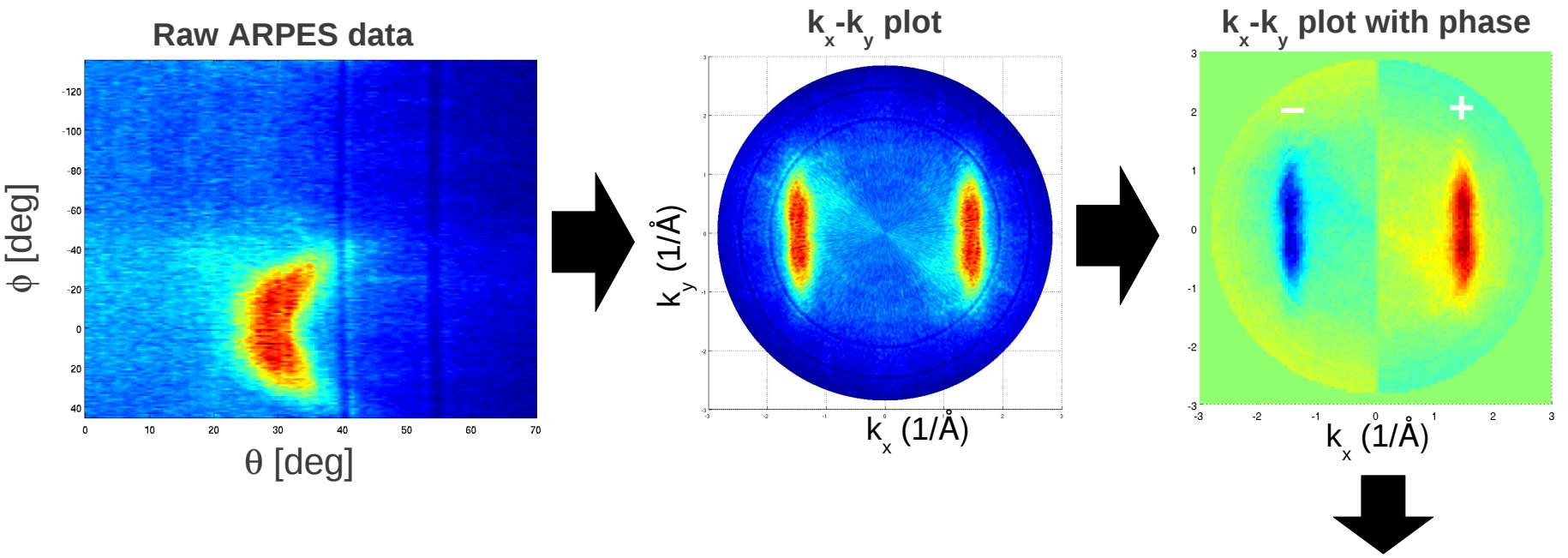
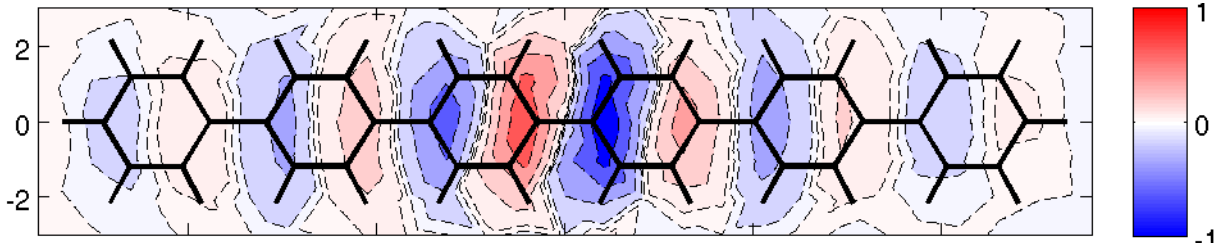


Reconstruction of Orbitals



6P HOMO from ARPES

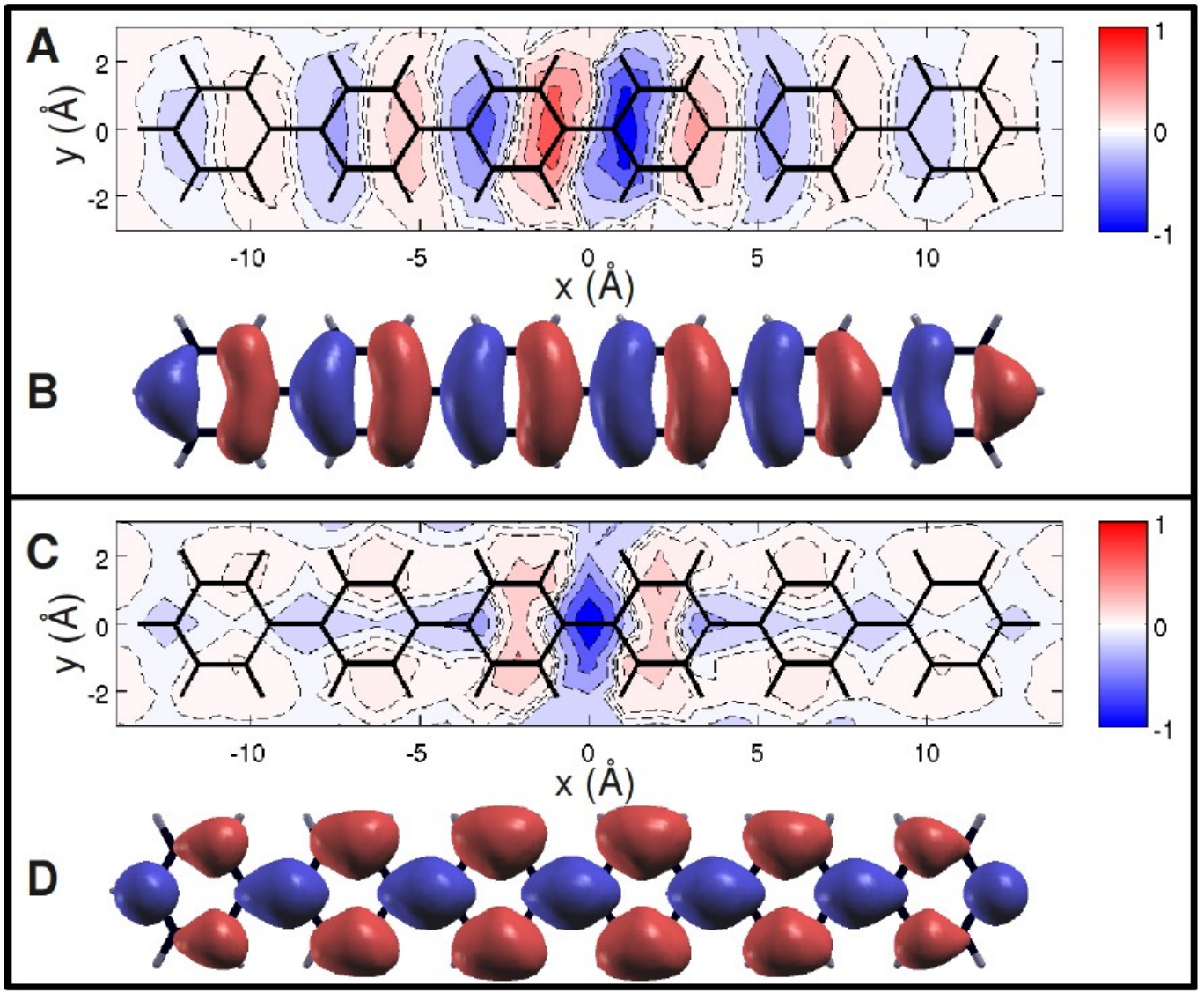


Puschnig et al., *Science* **326**, 702 (2009).

Reconstruction of Orbitals

HOMO

Filled LUMO



Conclusion and Outlook

Angle-resolved photoemission: From reciprocal space to real space

F.J. Himpsel, J. Electron Spectrosc. Relat. Phenom. (2010), doi:10.1016/j.elspec.2010.03.007

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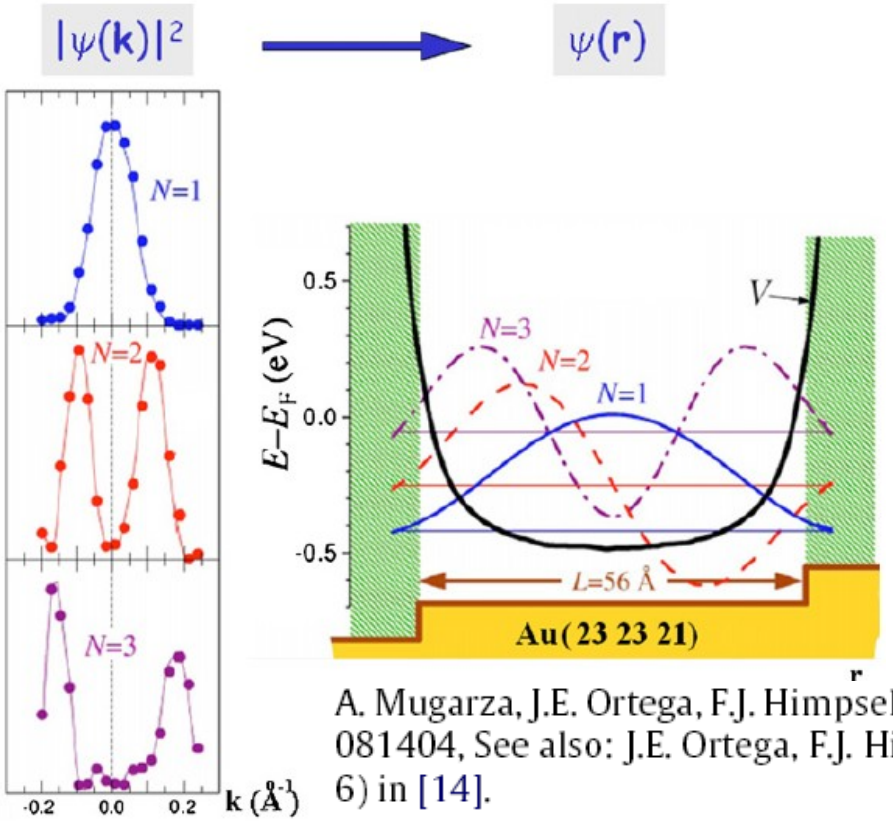

A. Mugarza, J.E. Ortega, F.J. Himpsel, F.J. García de Abajo, Phys. Rev. B 67 (2003) 081404, See also: J.E. Ortega, F.J. Himpsel, Atomic chains at surfaces, (Chapter 6) in [14].

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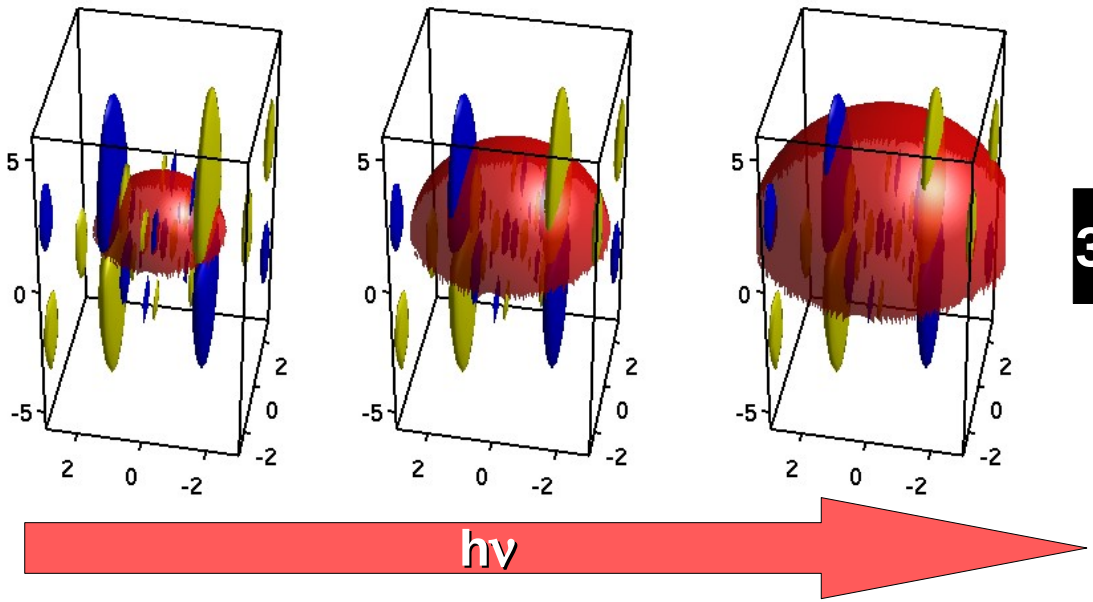

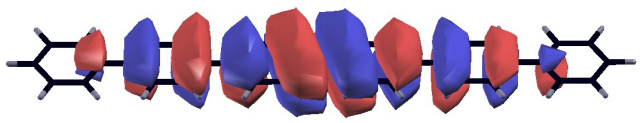

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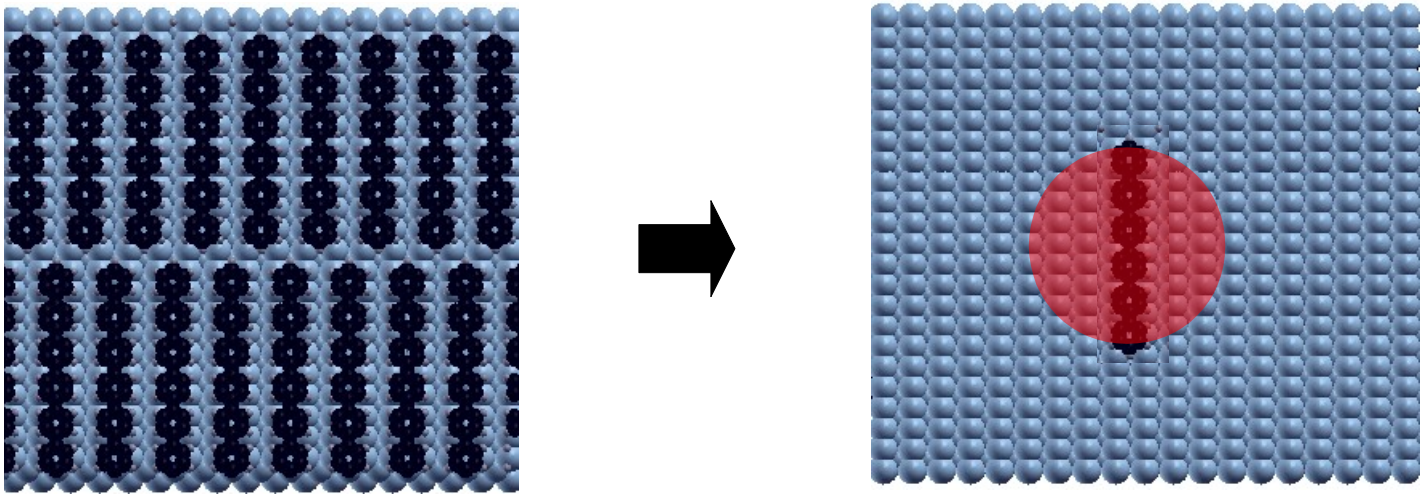
  (goal is to reach the focussing limit of soft x-rays 25 nm)



Conclusion and Outlook

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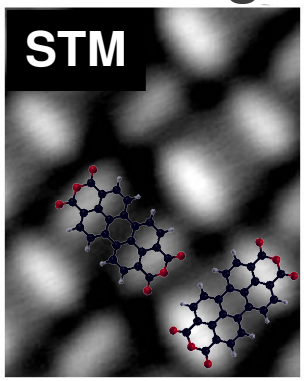
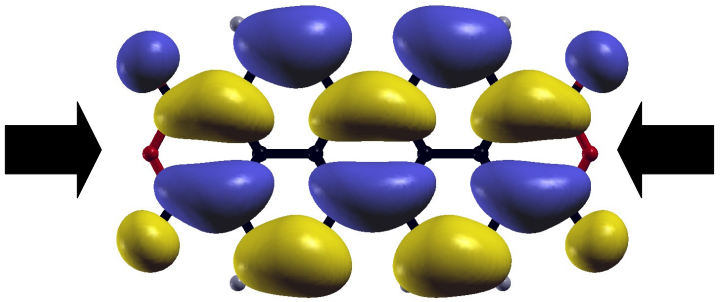
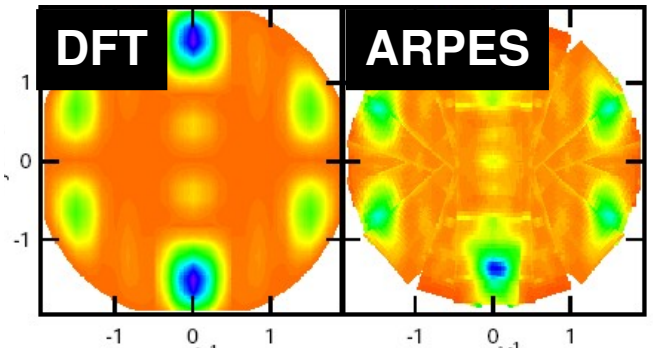
- Prospect of 3D imaging through scans of the photon energy
- Desireable to do PE experiments on individual nano-objects (goal is to reach the focussing limit of soft x-rays 25 nm)
- **Scanning tunneling microscopy and PE complement each other**







Rohlfing et al. PRB 76 (2007)

Ziroff et al. PRL (2010)

Where to Go in Theory?

- **Structural properties**
  - Van der Waals interactions: improvements in xc-functional
  - Thin film growth: multiscale modelling
- **Electronic structure**
  - Band structure: go beyond DFT
  - Photoemission experiments: more accurate description of final state
  - Electronic transport: electron-phonon coupling
- **Optical properties**
  - Excitons: Assess validity of usual approximations in BSE

Collaborations and Funding

Lehrstuhl für Atomistic Modelling and Design of Materials, MU Leoben
Dmitrii Nabok
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Christian Teichert

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Alexander Fleming
Georg Koller
Mike Ramsey

Institut für Festkörperphysik, TU Graz
Paul Frank
Adolf Winkler
Roland Resel

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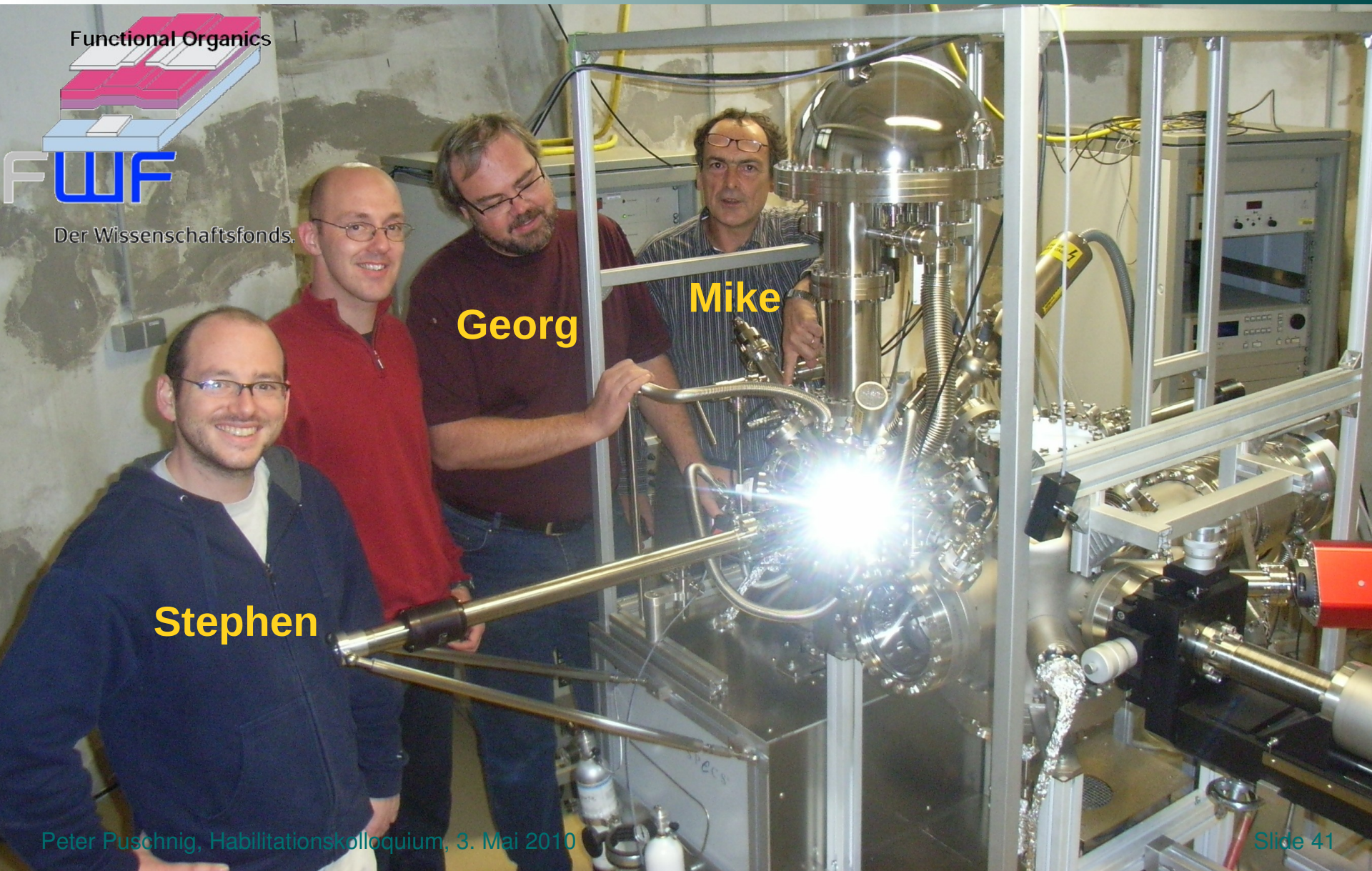
„Interface controlled and functionalized organic films“

Thank You!


Functional Organics
FWF
Der Wissenschaftsfonds.
Georg
Mike
Stephen