MONTAN UNIVERSITÄT
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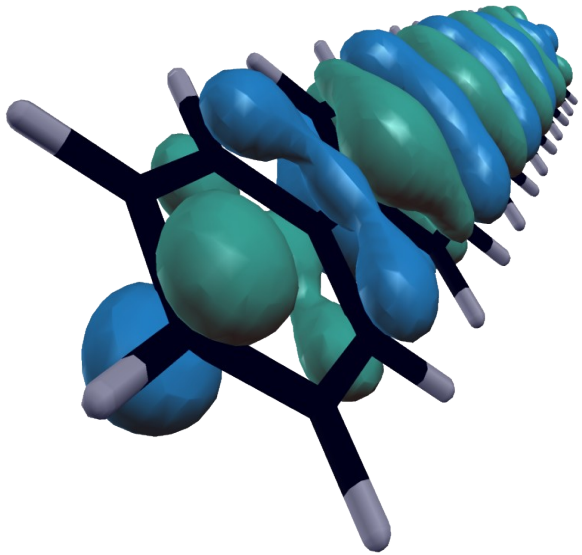
Imaging Molecular Orbitals Through Photoemission Spectroscopy



Collaborations and Funding

Lehrstuhl für Atomistic Modelling and Design of Materials – MU Leoben
- Peter Puschnig
- Claudia Ambrosch-Draxl

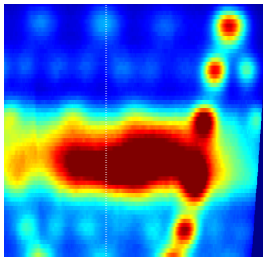
Experimental Surface Science Group – University Graz, Austria
- Stephen Berkebile
- Alexander Fleming
- Georg Koller
- Mike Ramsey
- Falko Netzer

Lehrstuhl für Technische Physik – University Erlangen-Nürnberg
- Thomas Seyller
- Konstantin Emtsev

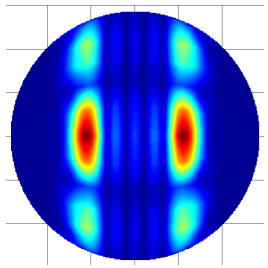
The work is part of the National Research Network
„Interface controlled and functionalized organic films“

Outline

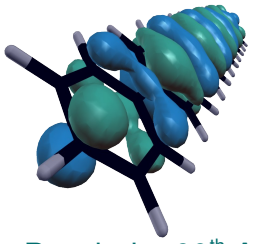
Motivation



Photoemission Spectroscopy



From Reciprocal to Real Space

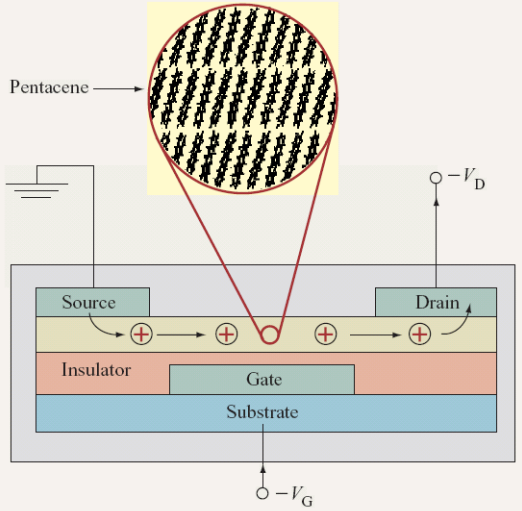


Conclusion and Outlook

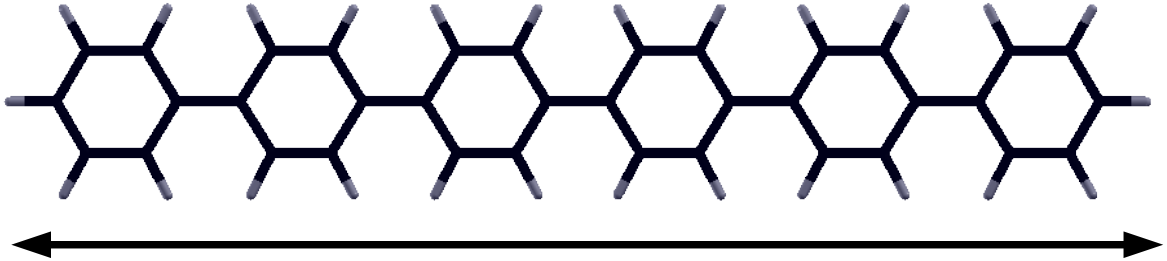
Organic Semiconductors

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

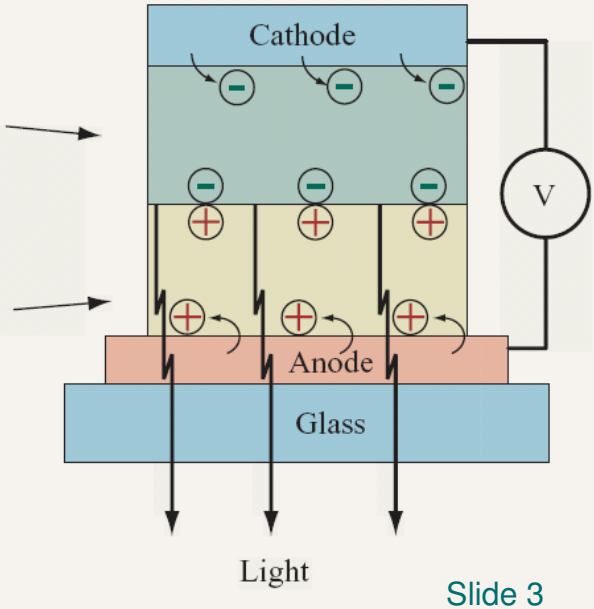
OFET
Organic
Field **E**ffect
Transistor



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

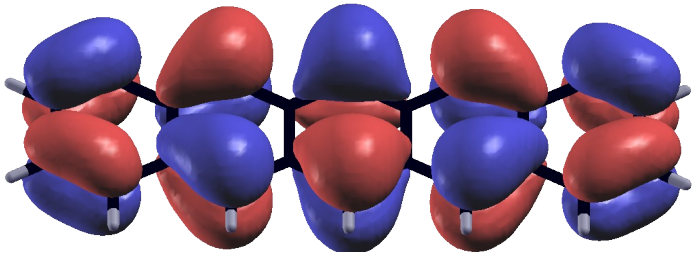


OLED
Organic
Light **E**mitting **D**iode

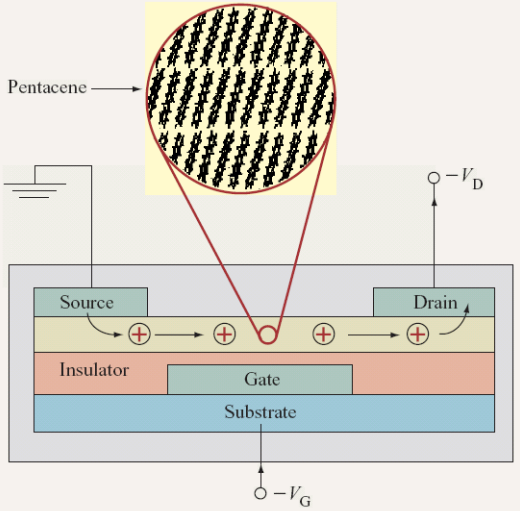


Organic Semiconductors

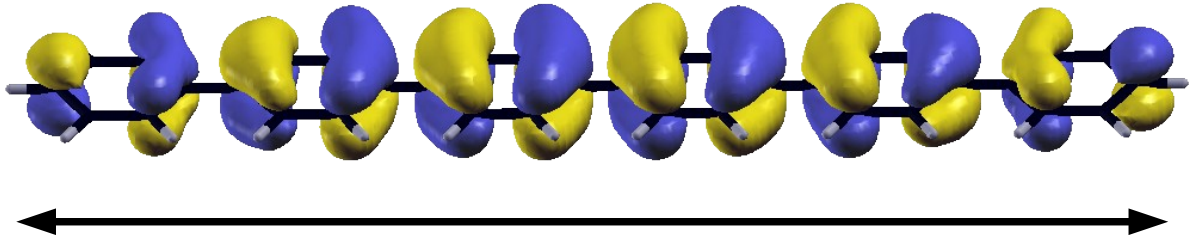
Pentacene ($C_{22}H_{14}$)



OFET
Organic
Field **E**ffect
Transistor

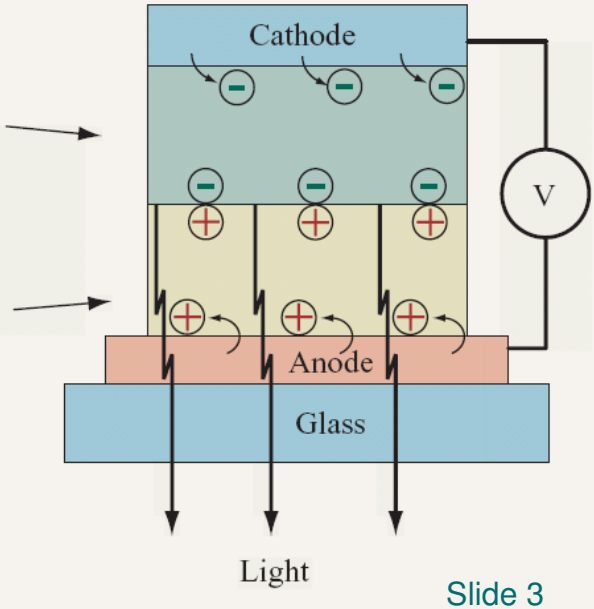


Para-Sexiphenyl ($C_{36}H_{26}$)

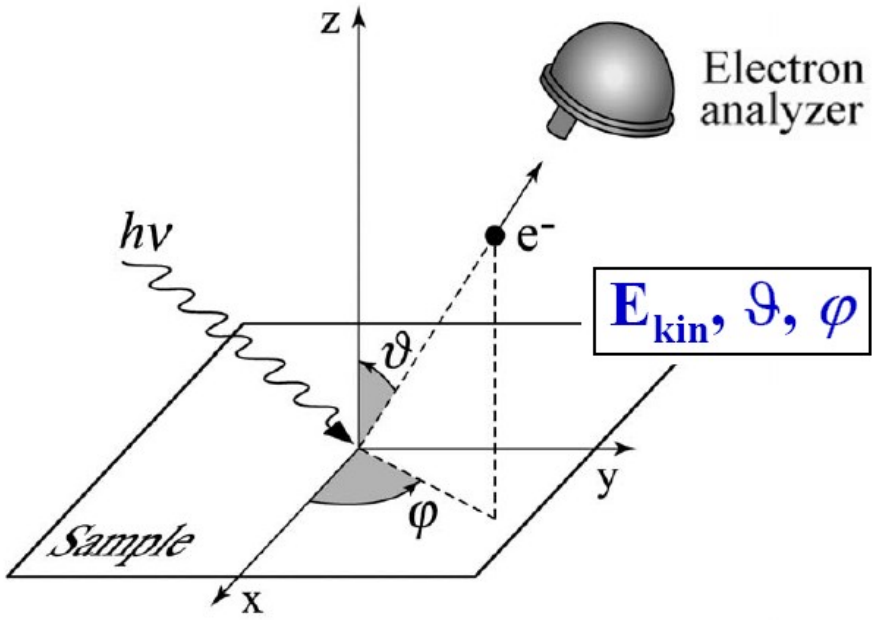


2.6 nm

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



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 → **Conservation laws** → **Solid**

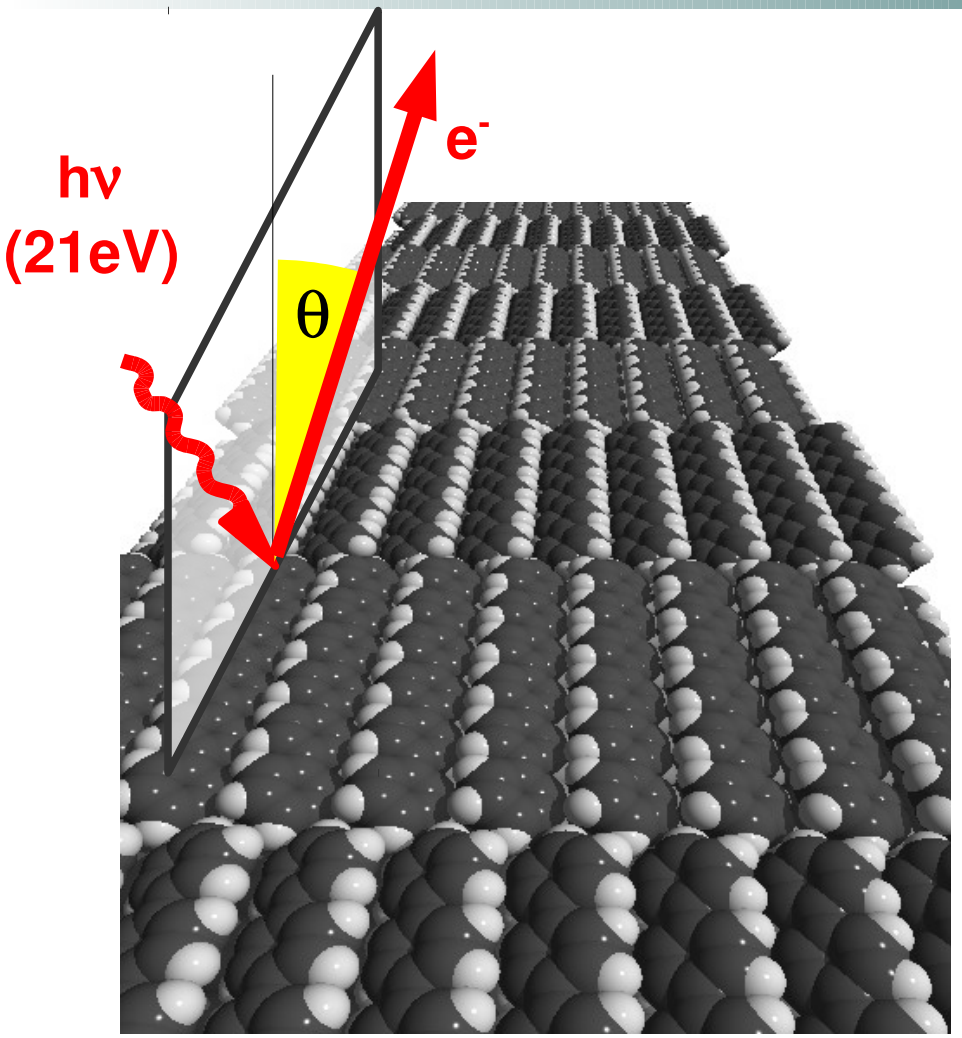
E_{kin}, $\mathbf{K}$

$$E_f - E_i = h\nu$$

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

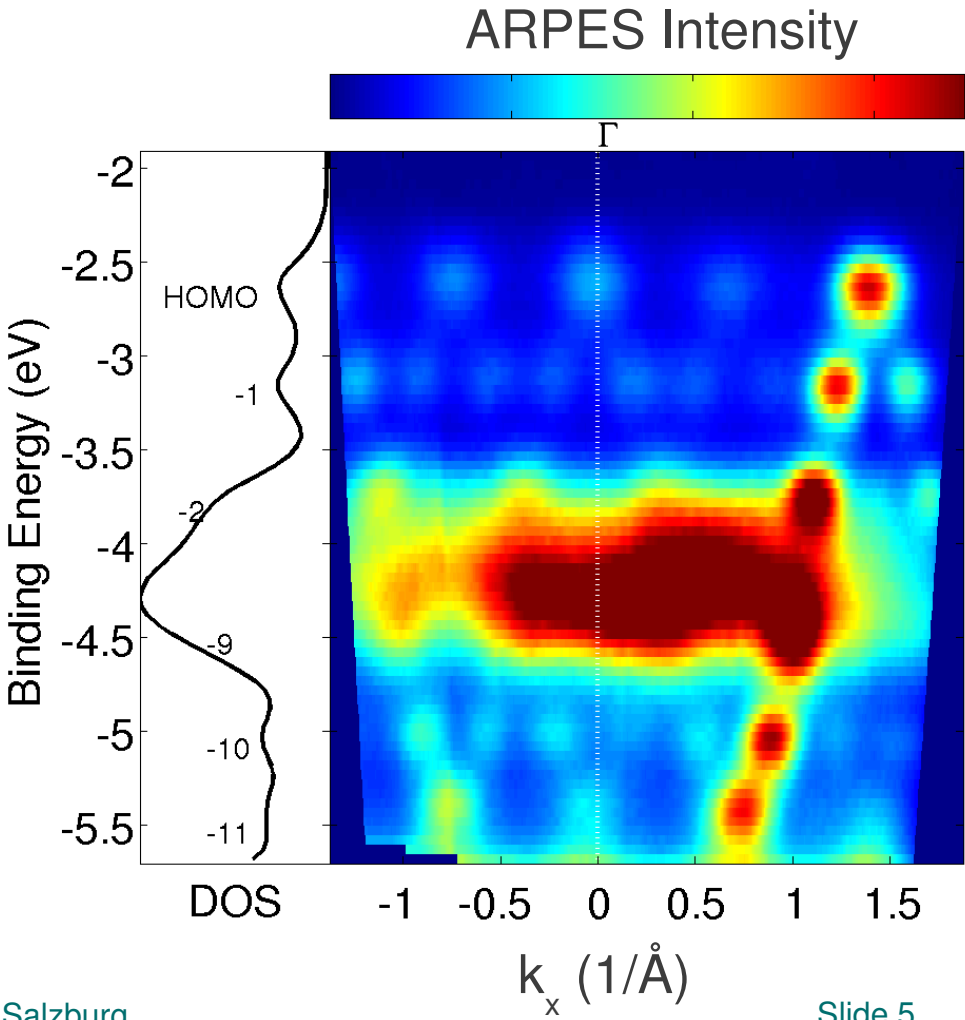
E_B, $\mathbf{k}$

Uniaxially Aligned Sexiphenyl

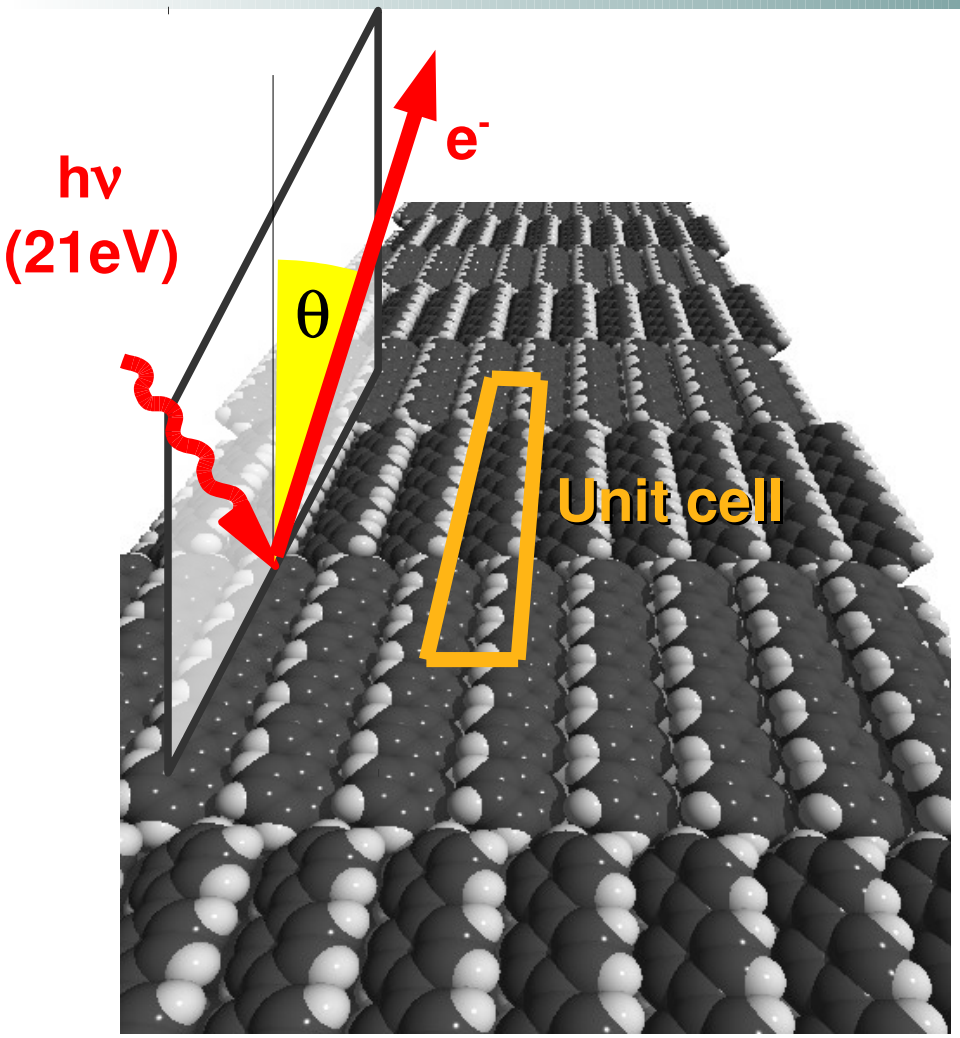


Uniaxially ordered para-sexiphenyl
Multi-layer film on Cu(110)_(2x1)O

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

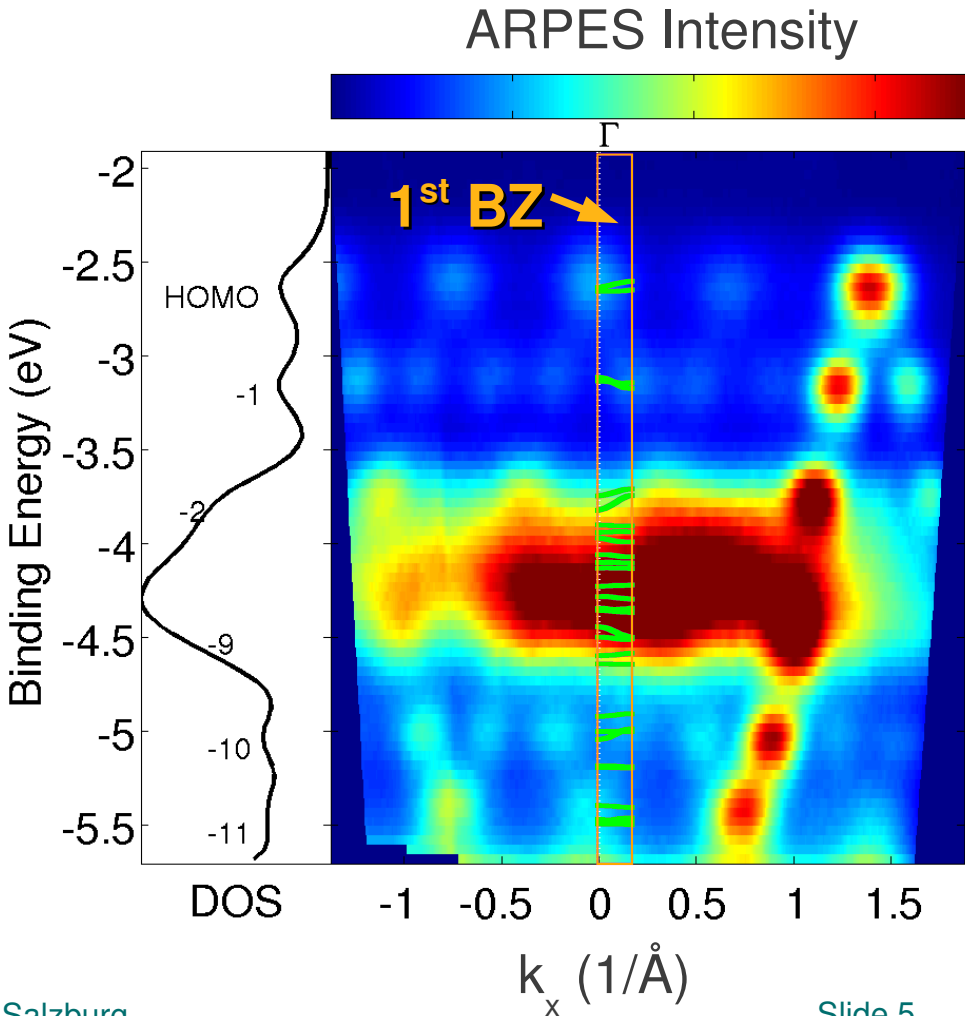


Uniaxially Aligned Sexiphenyl



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

Koller et al., Science **317**, 351 (2007)
Puschnig et al., *PRB* **60**, 7891 (1999)



Photoemission Intensity

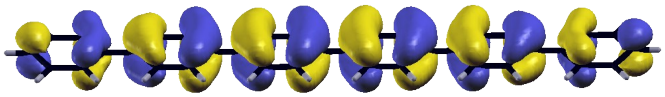
One Step Model

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

Photoemission Intensity

One Step Model

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

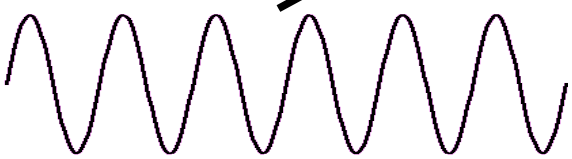


molecular orbital

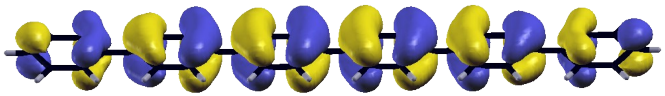
Photoemission Intensity

One Step Model

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



plane wave $e^{i\,\mathbf{k}\,\mathbf{r}}$



molecular orbital

Approximation: final state = plane wave

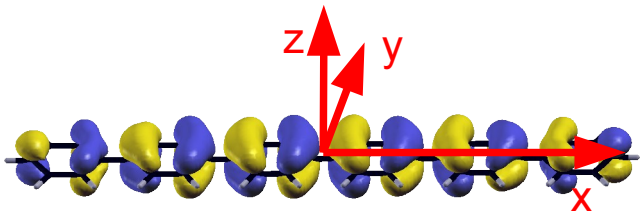
$$I_i(\theta, \phi) \propto \left|(\mathbf{A} \cdot \mathbf{k})\right|^2 \times \left|\tilde{\psi}_i(\mathbf{k})\right|^2$$

Fourier Transform of Initial State Orbital

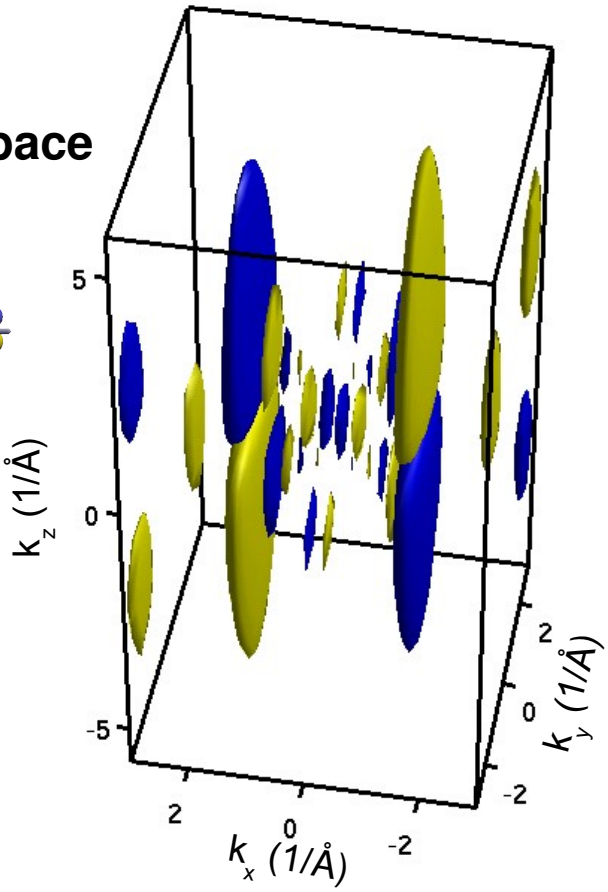
[Feibelman and Eastman, *Phys. Rev. B* **10**, 4932 (1974).]

Photoemission Intensity in Pictures

Molecular Orbital in Real Space

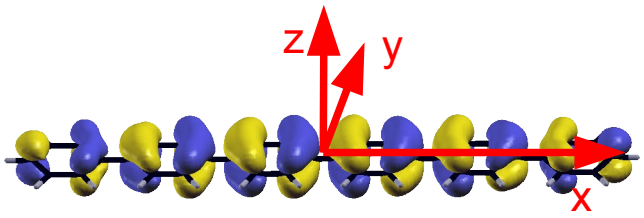


Fourier Transform

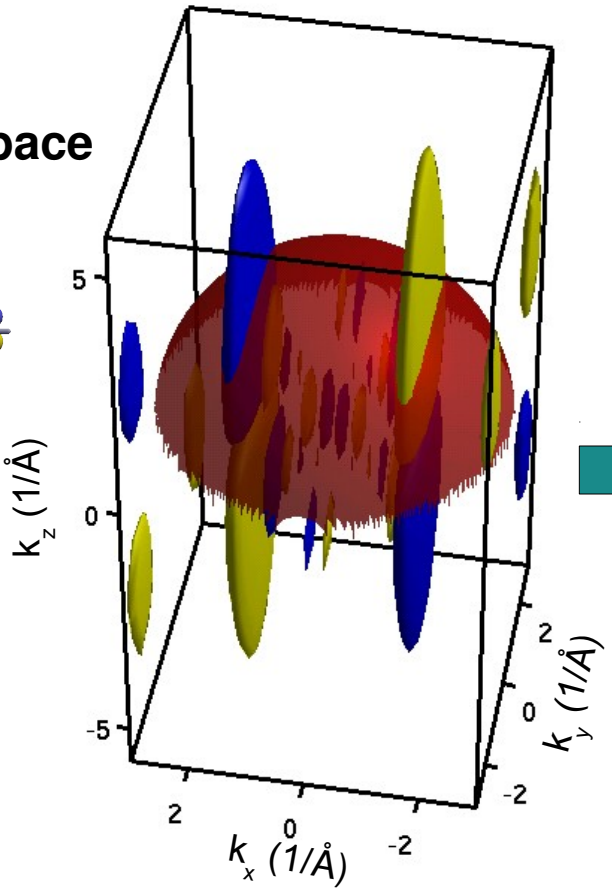


Photoemission Intensity in Pictures

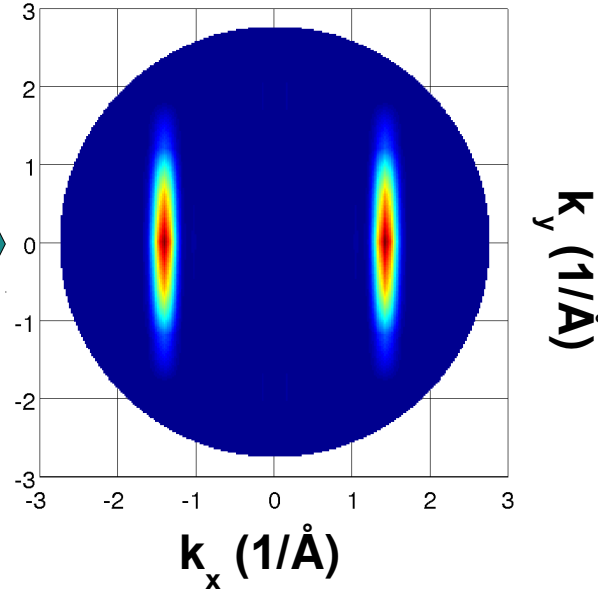
Molecular Orbital in Real Space



Fourier Transform

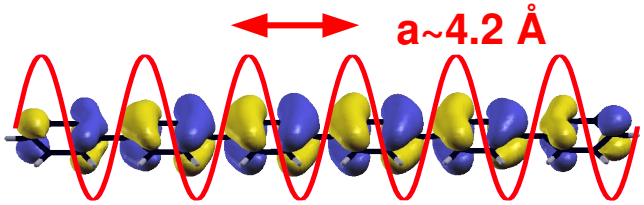


Hemispherical Cut Through 3D Fourier Transform

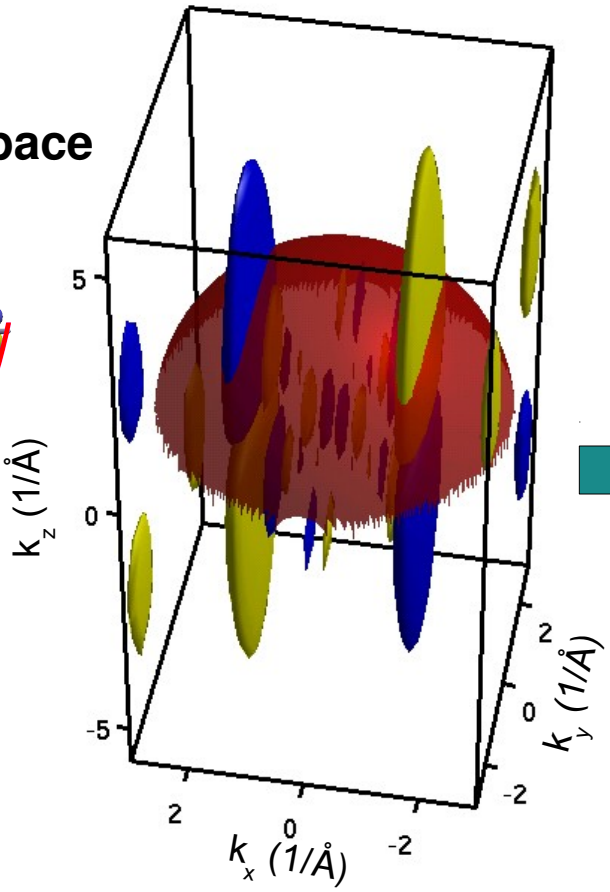


Photoemission Intensity in Pictures

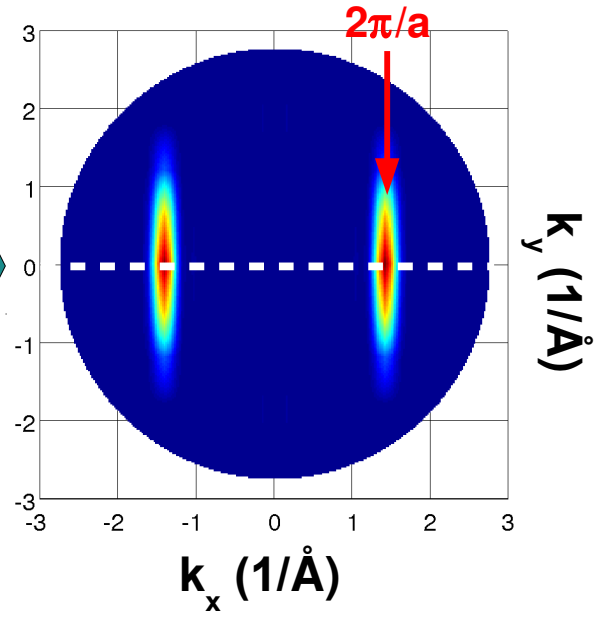
Molecular Orbital in Real Space



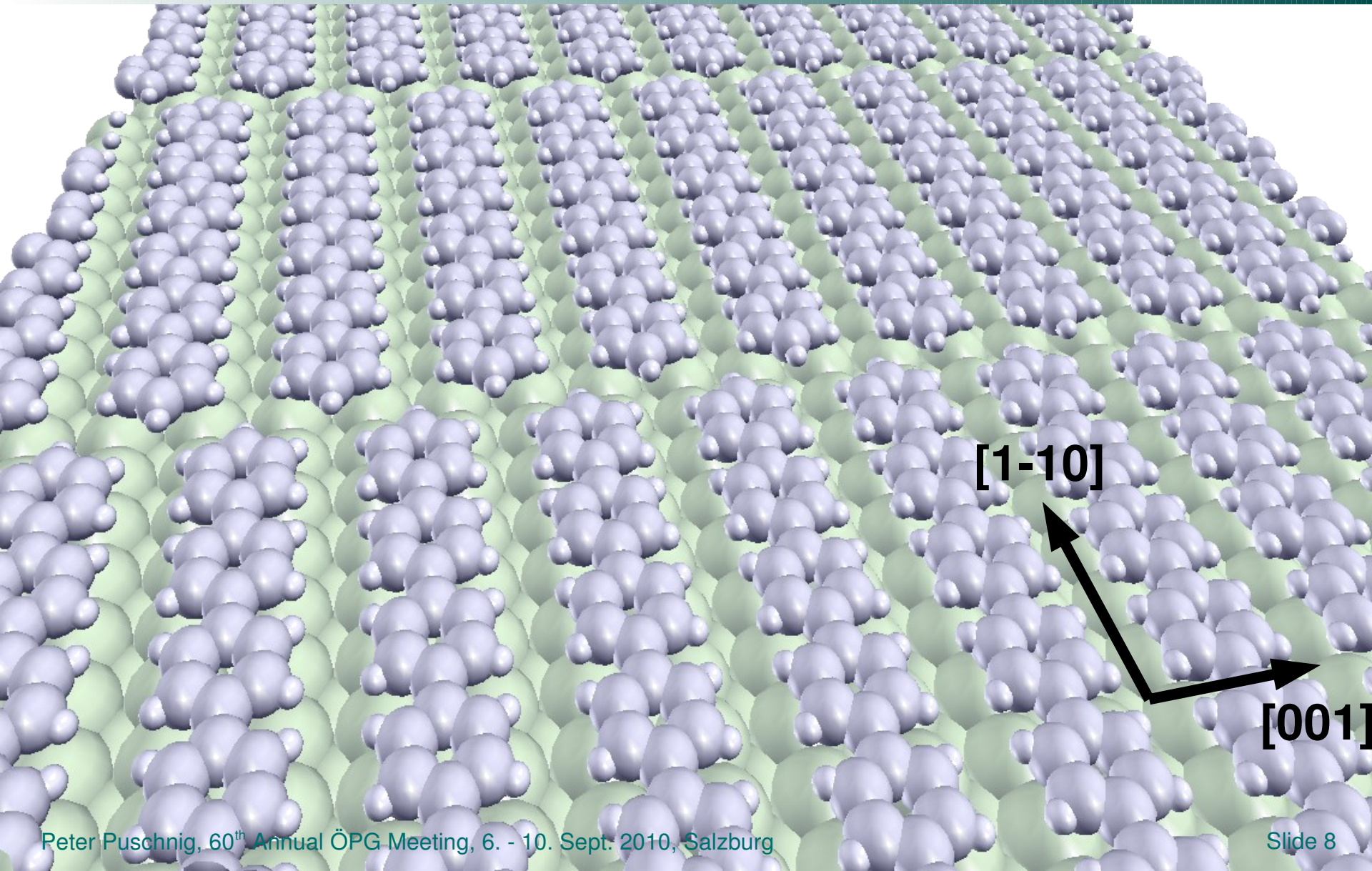
Fourier Transform



Hemispherical Cut Through 3D Fourier Transform



Sexiphenyl Monolayer on Cu(110)



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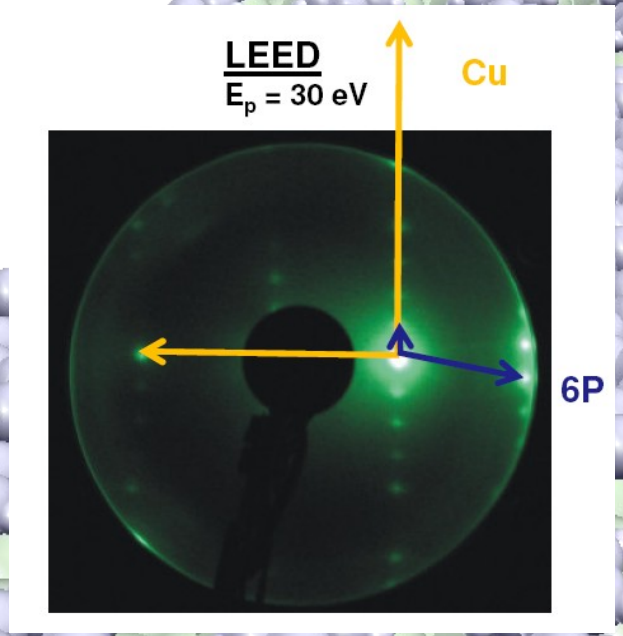
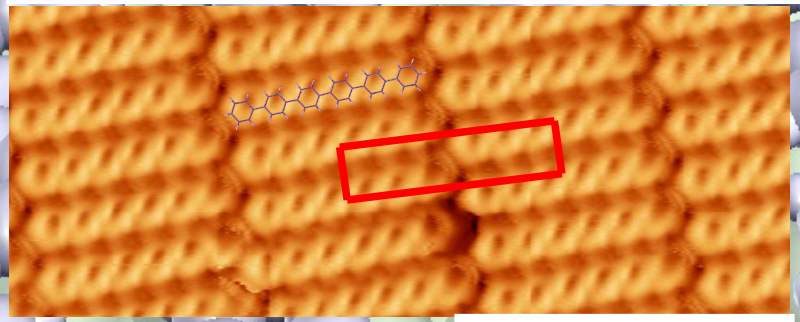


Low-T STM by courtesy of Stephen Berkebile



-130 mV / 0.38 nA

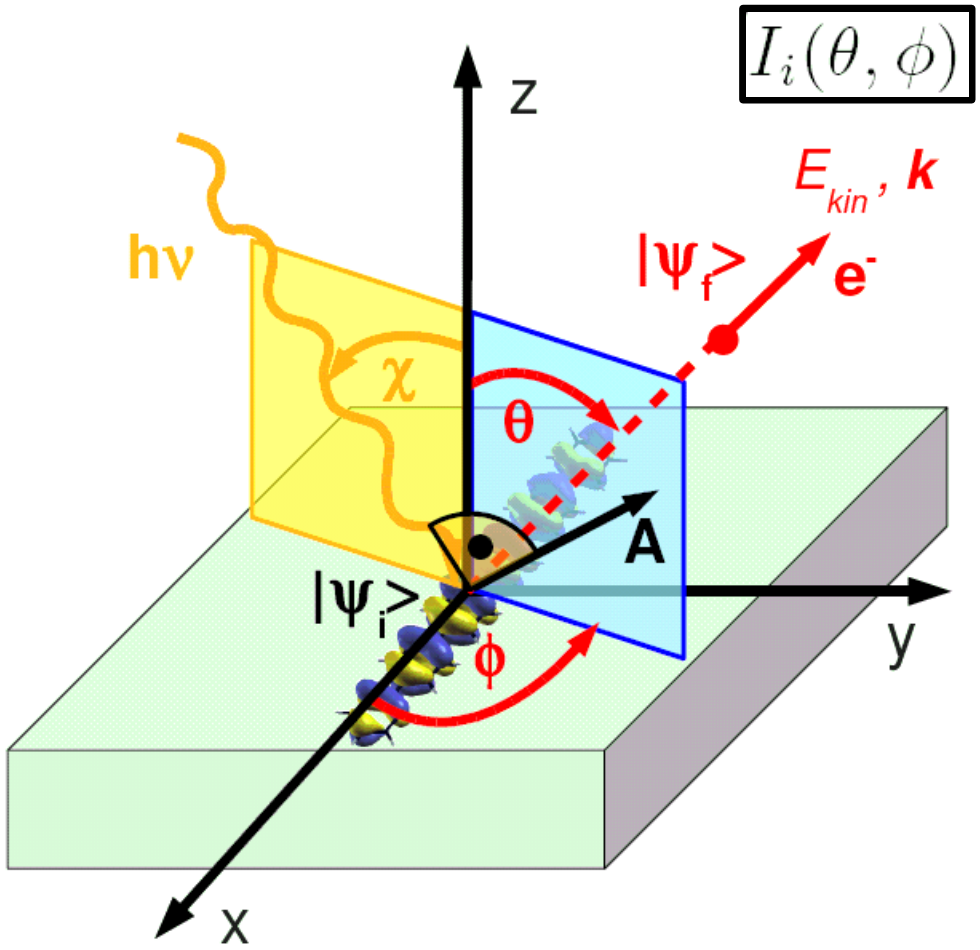
$11\ a_{Cu}$ / sqrt(2)

$2\ a_{Cu}$

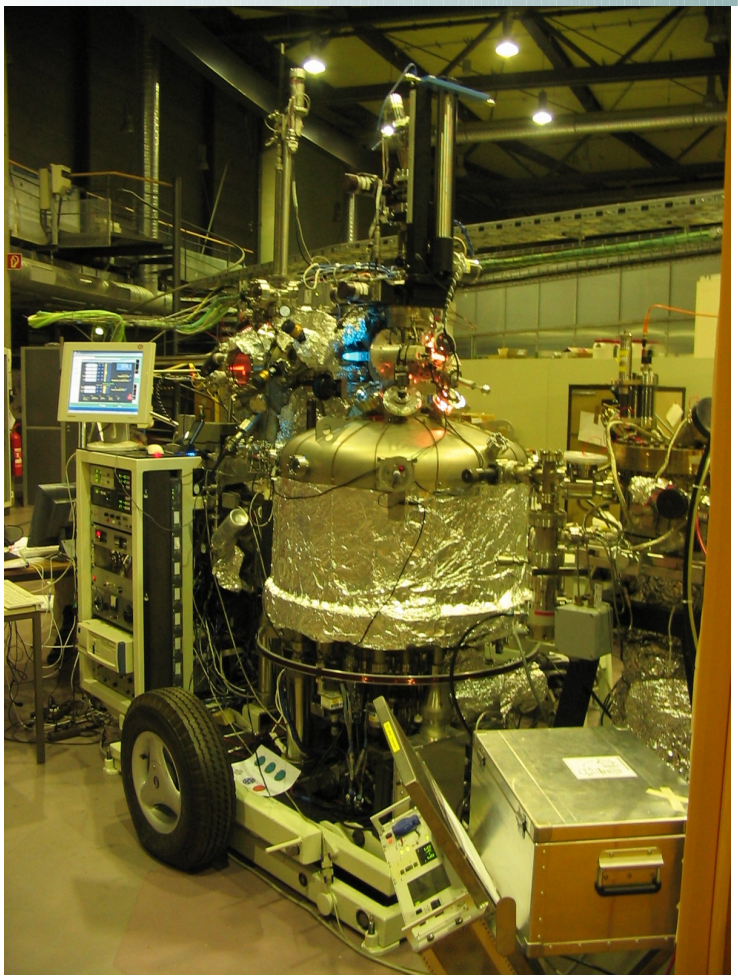
[1-10]

[001]

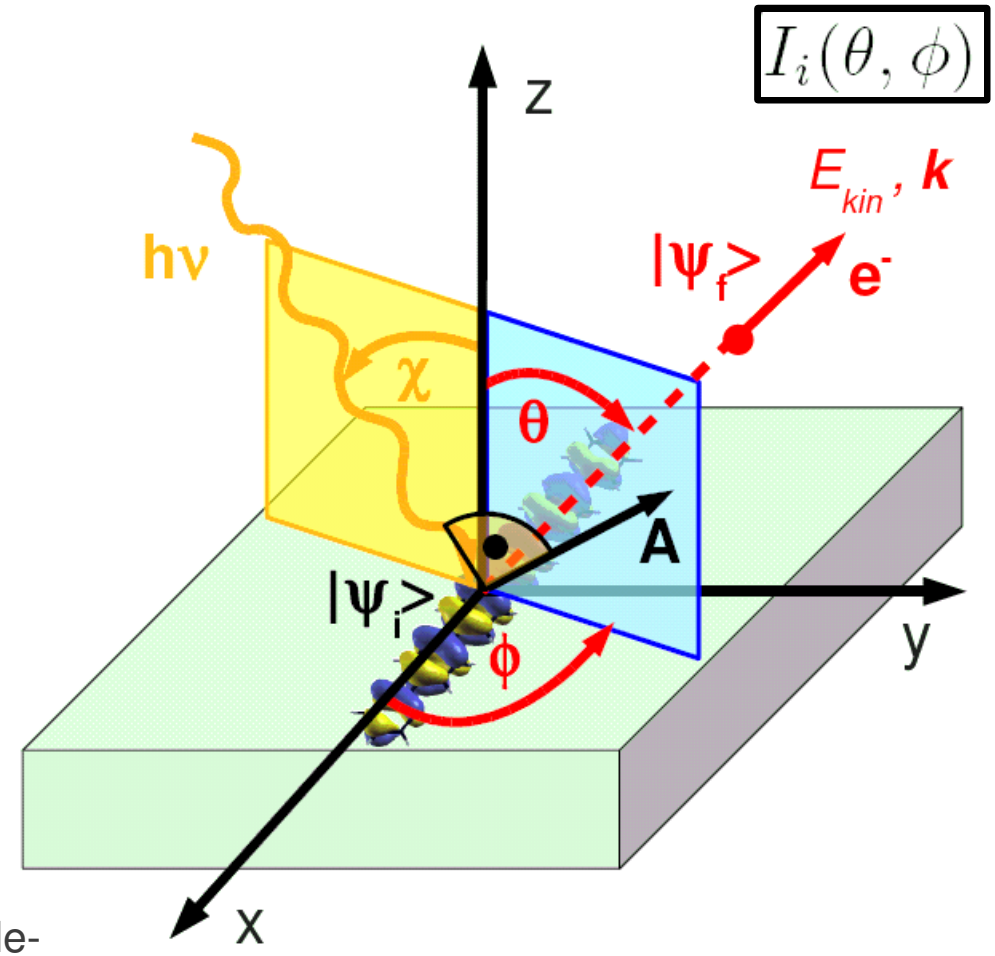
2D-Momentum Maps



2D-Momentum Maps

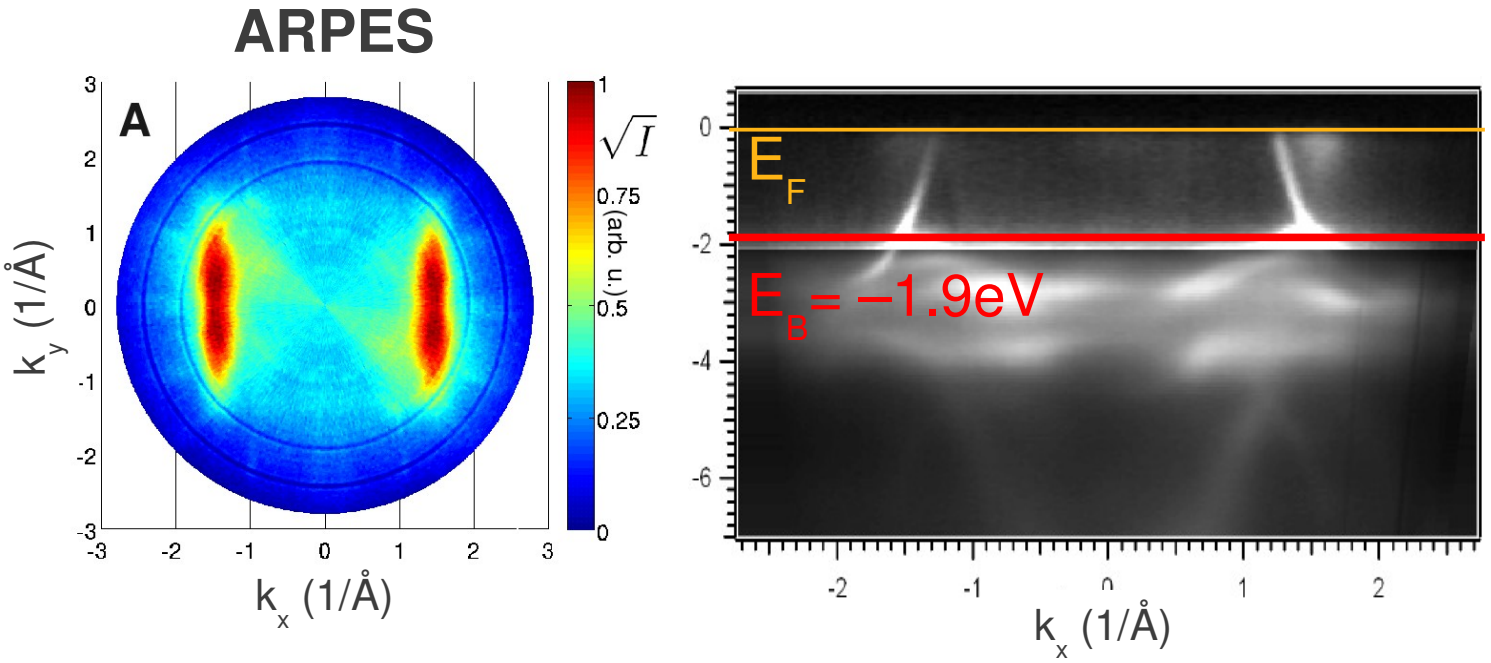


The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II



2D-Momentum Maps

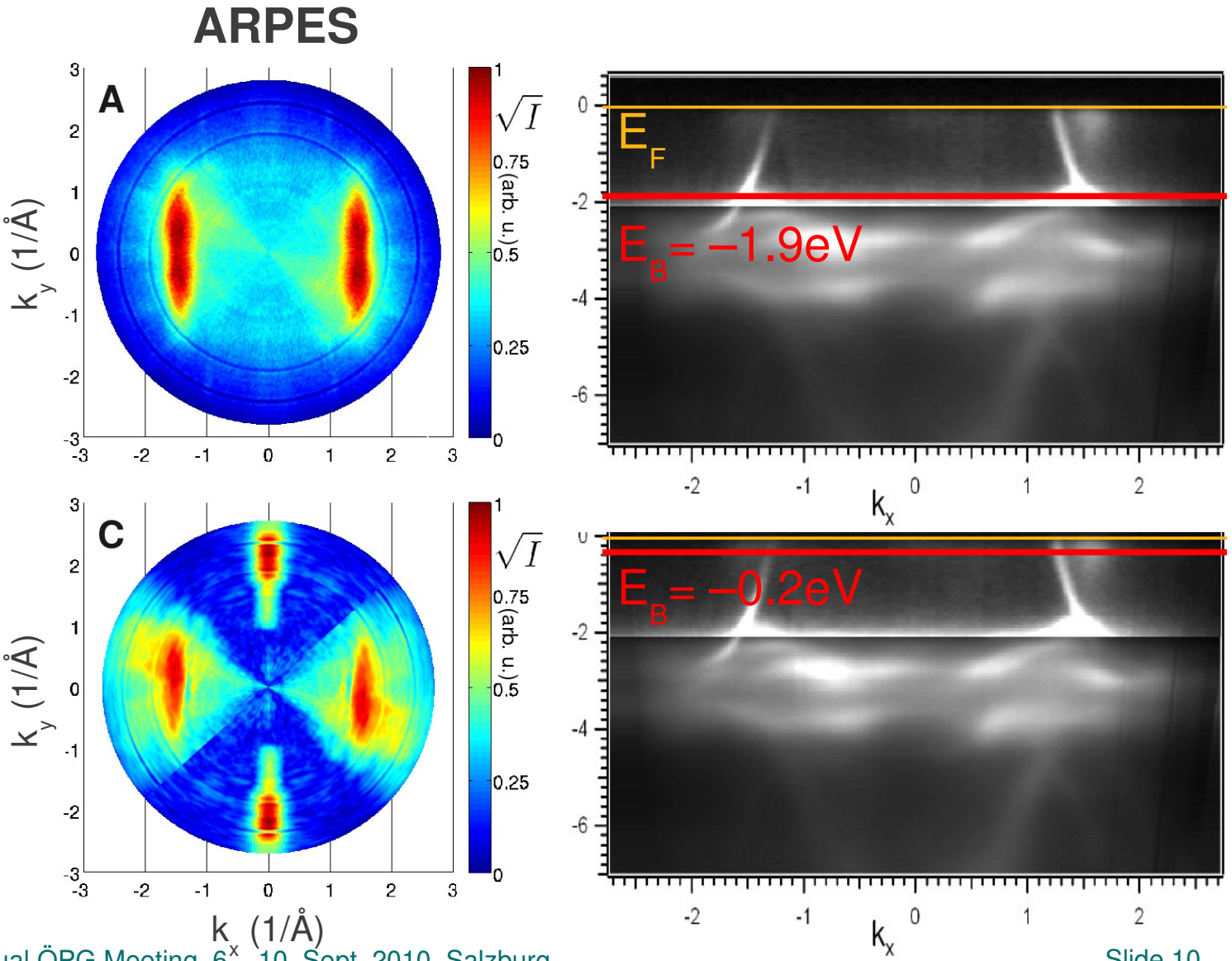
HOMO



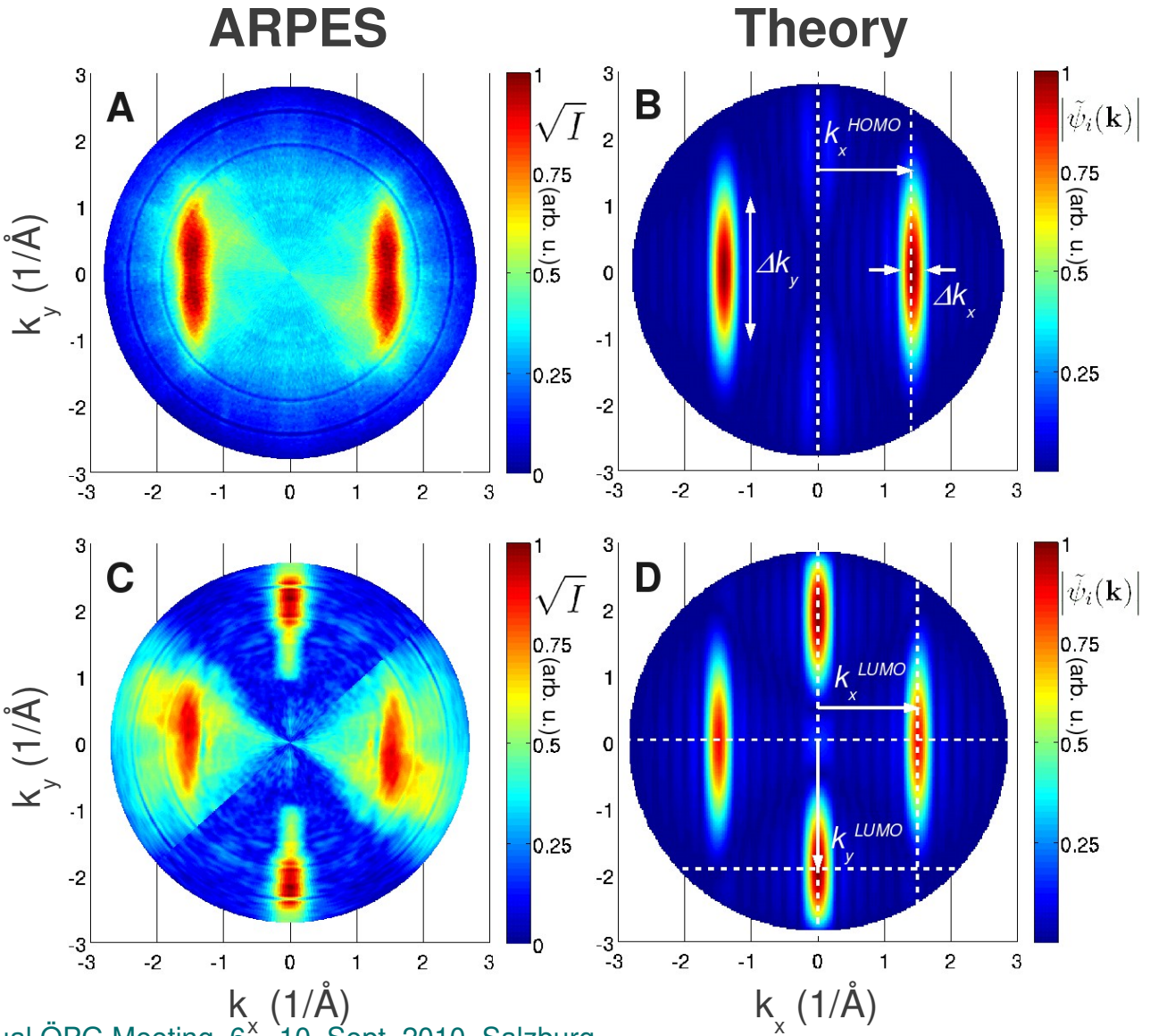
2D-Momentum Maps

HOMO

Filled LUMO



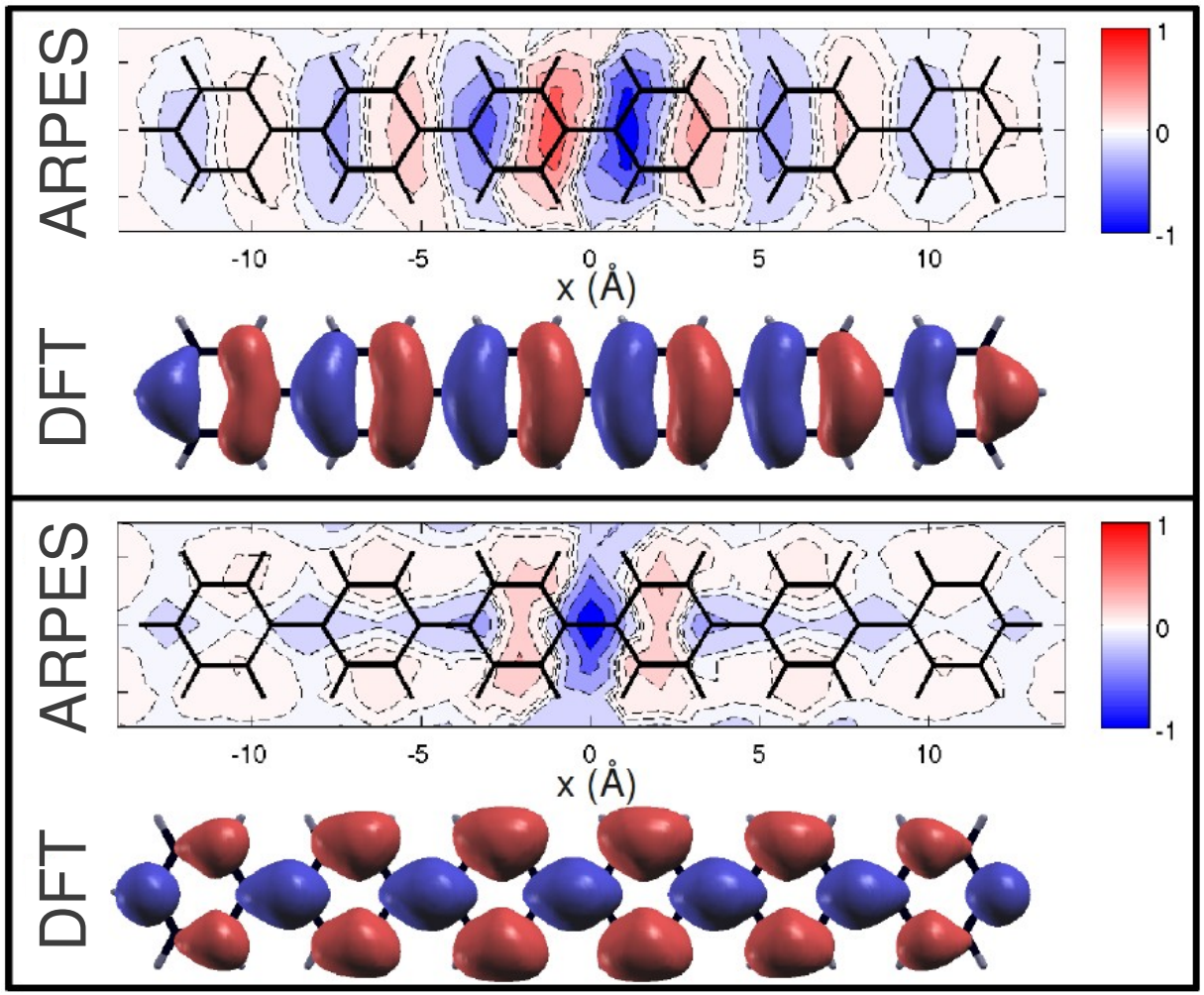
2D-Momentum Maps



Reconstruction of Orbitals

HOMO

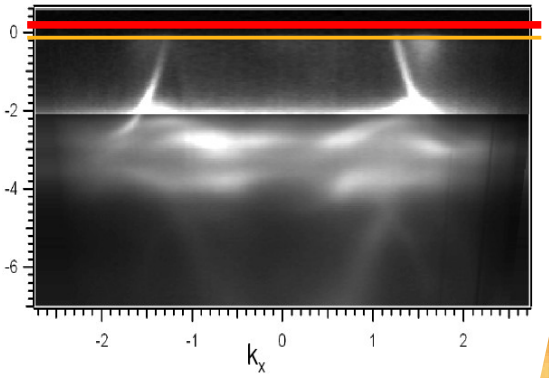
Filled LUMO



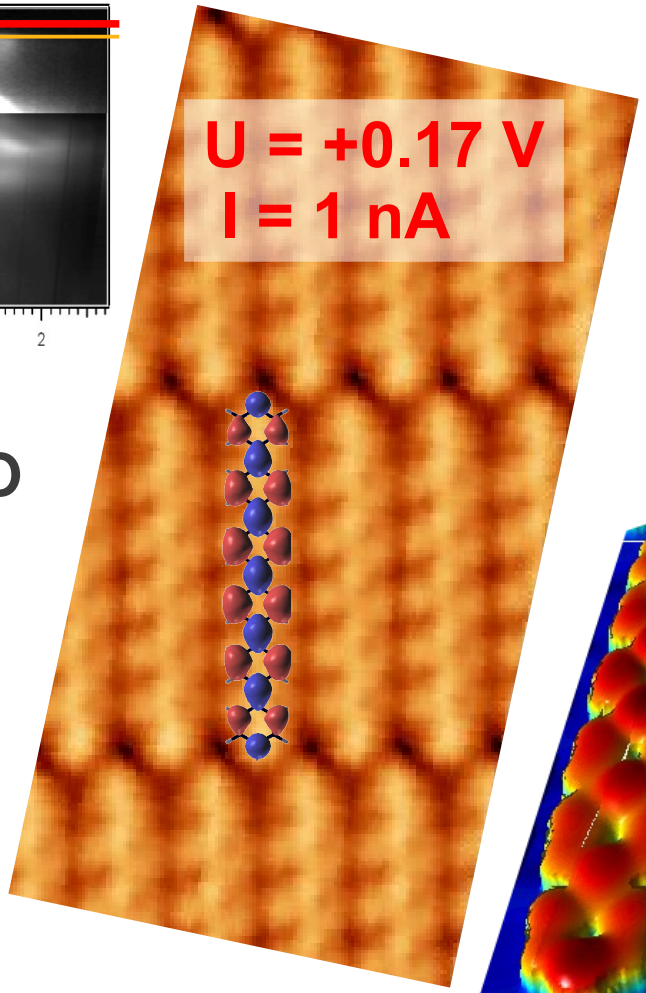
Puschnig et al., Science **326**, 702 (2009)

Scanning Tunneling Microscopy

ARPES

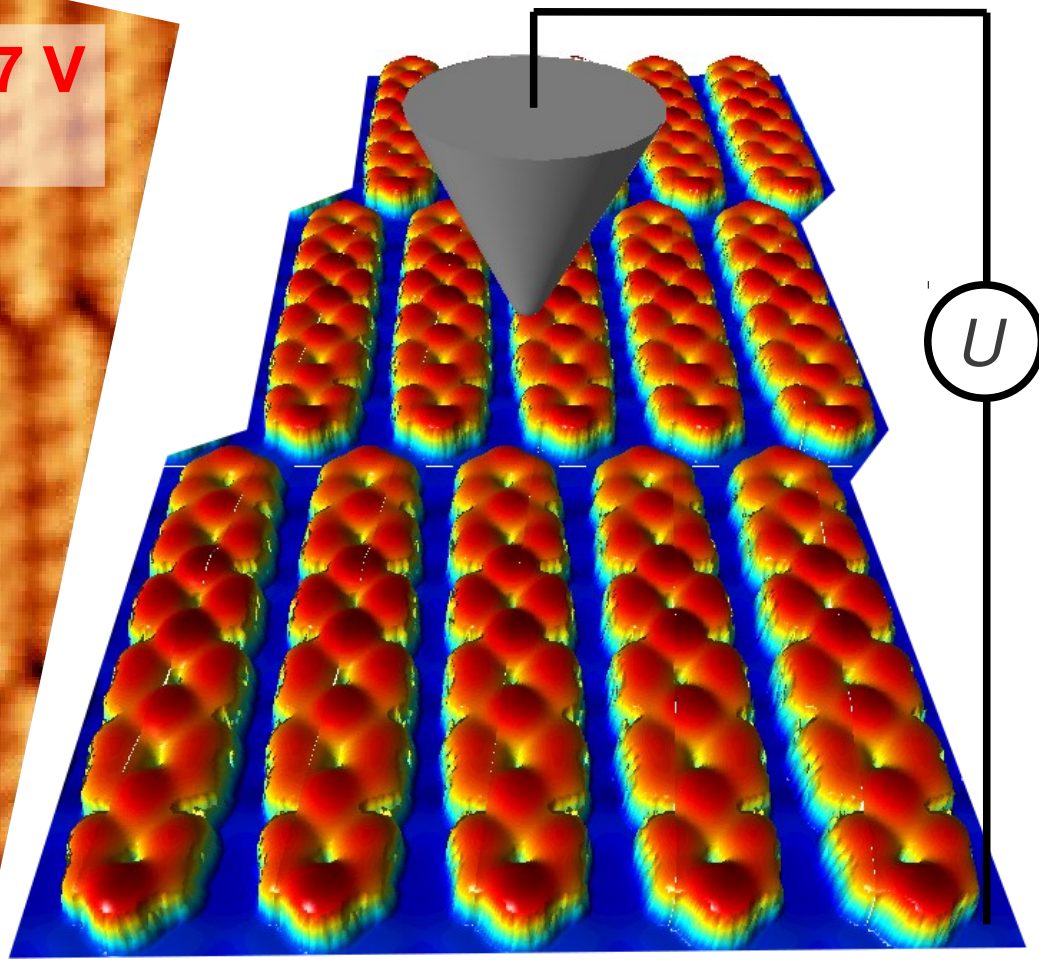


low-T-STM

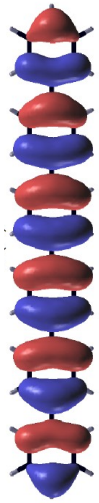


STM – Simulation

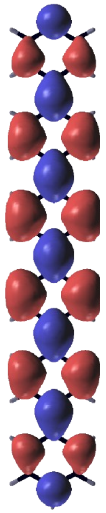
(Tersoff-Hamann approximation)



HOMO

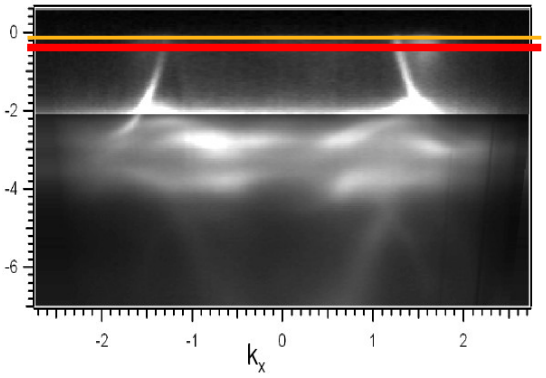


LUMO

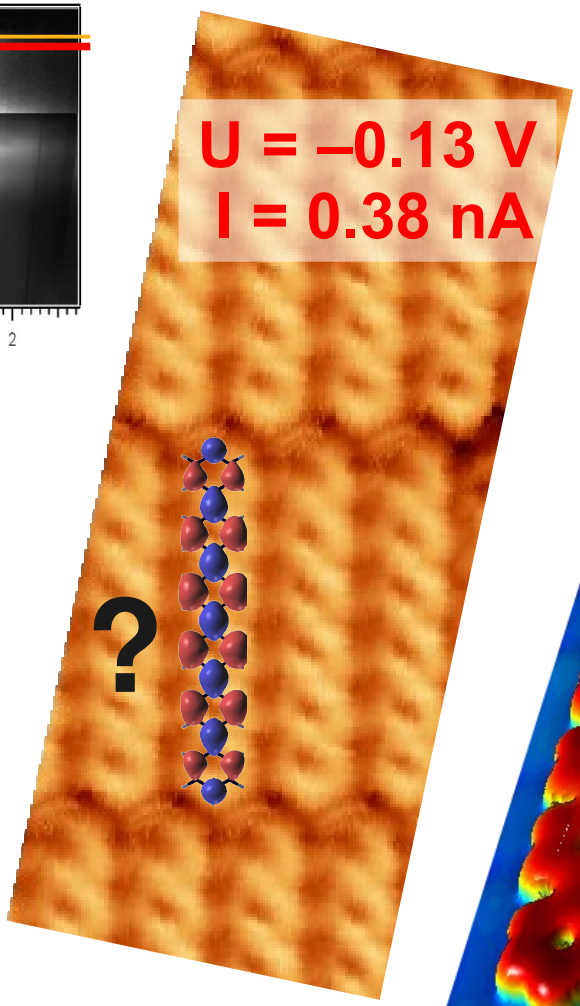


Scanning Tunneling Microscopy

ARPES

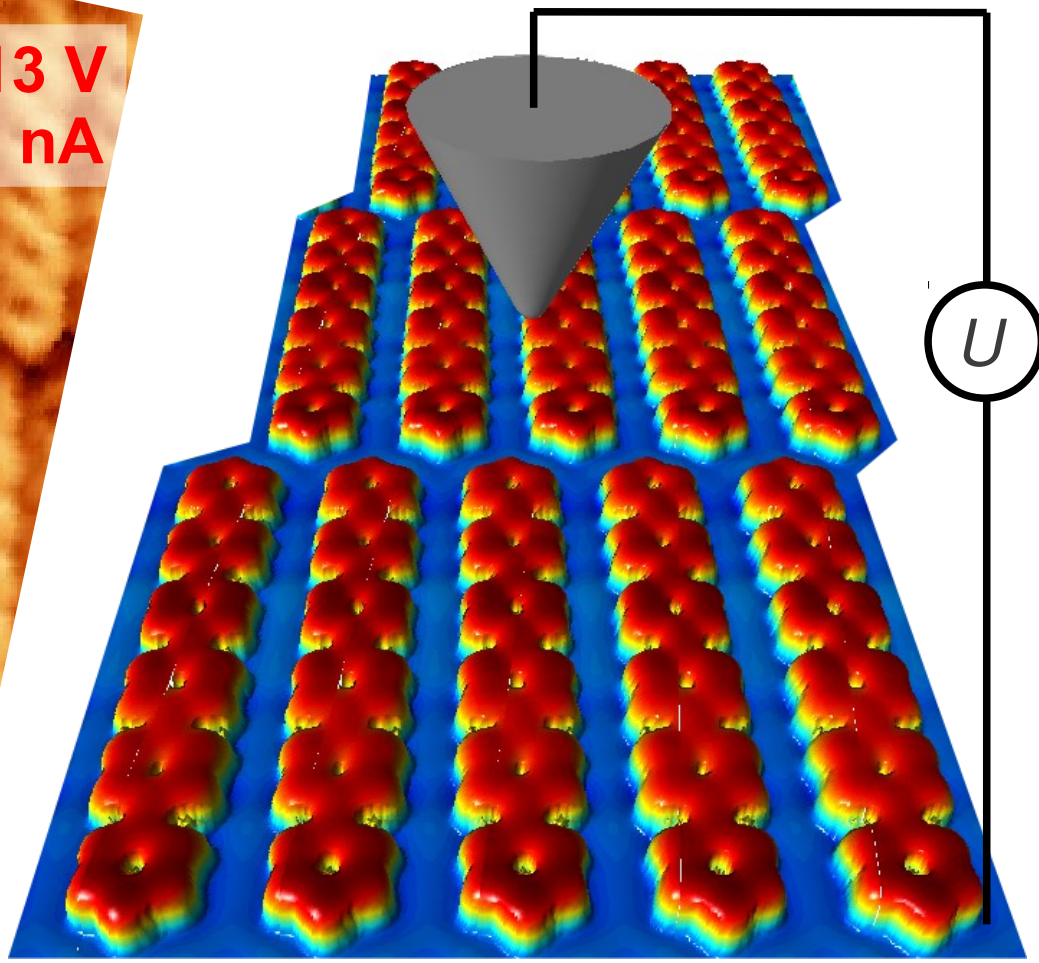


low-T-STM

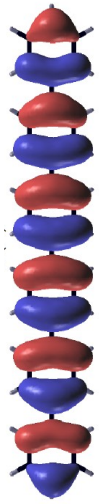


STM – Simulation

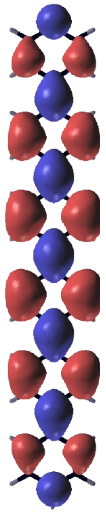
(Tersoff-Hamann approximation)



HOMO



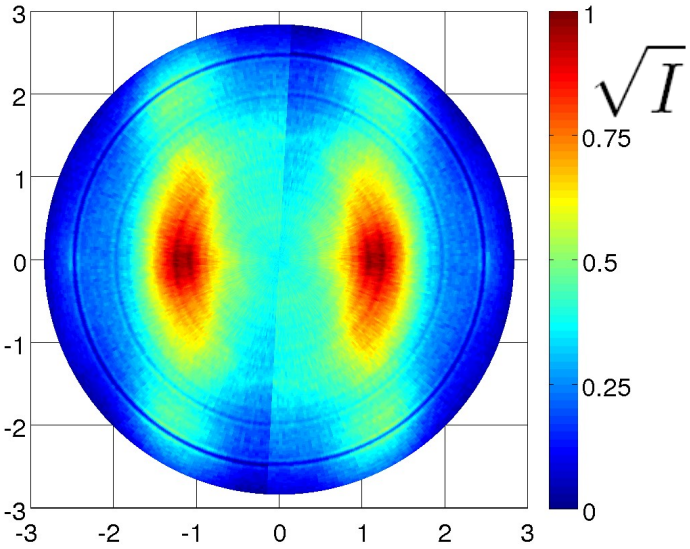
LUMO

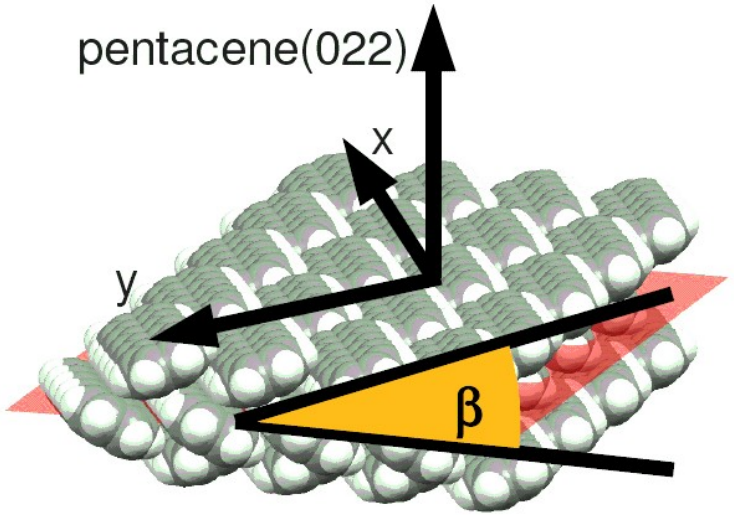


Pentacene HOMO from a Multilayer

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

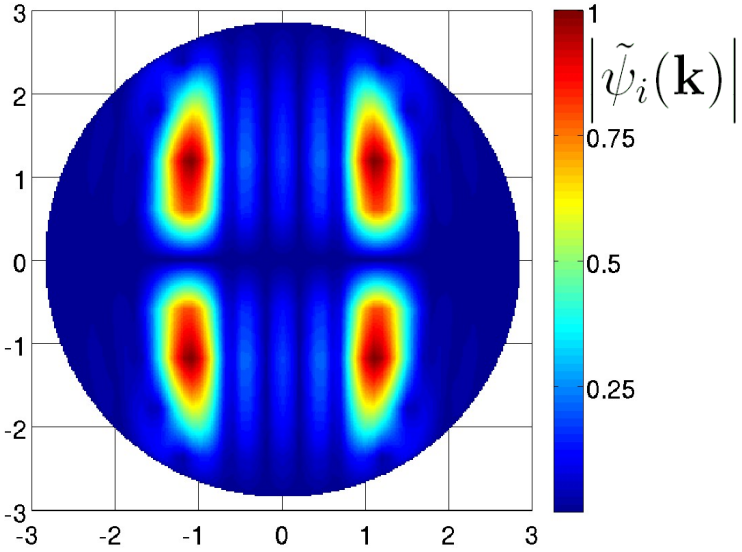
ARPES

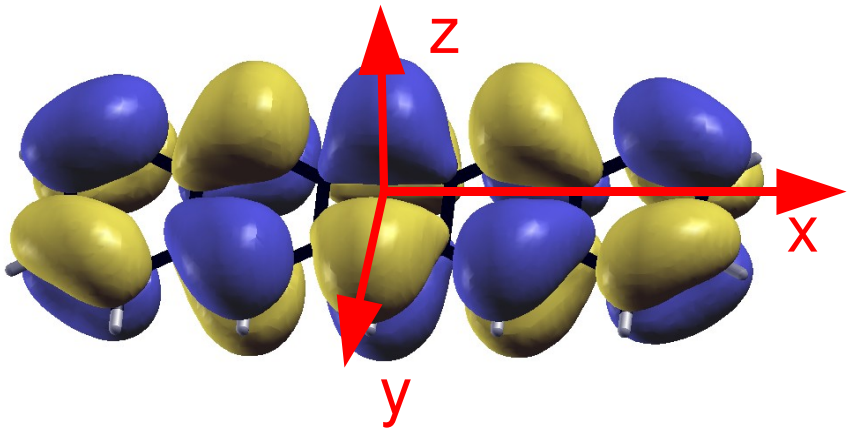




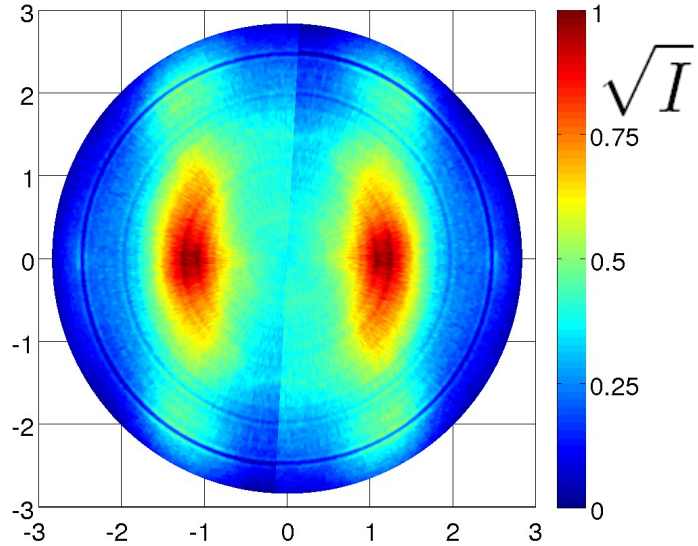
Pentacene HOMO from a Multilayer

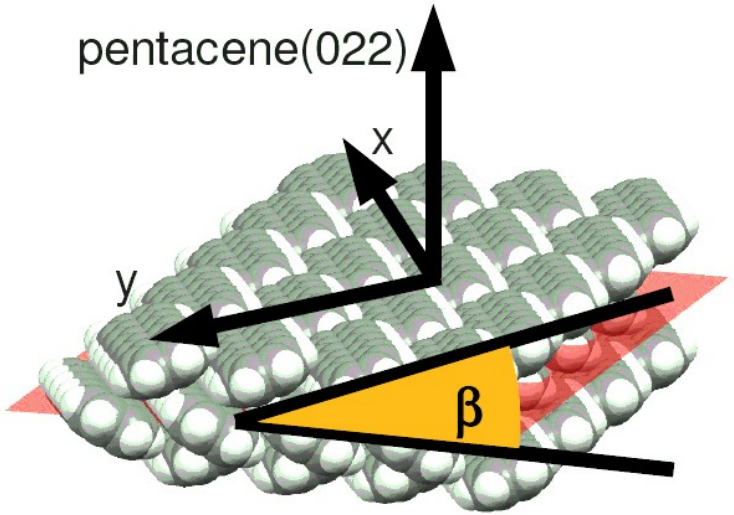
Theory



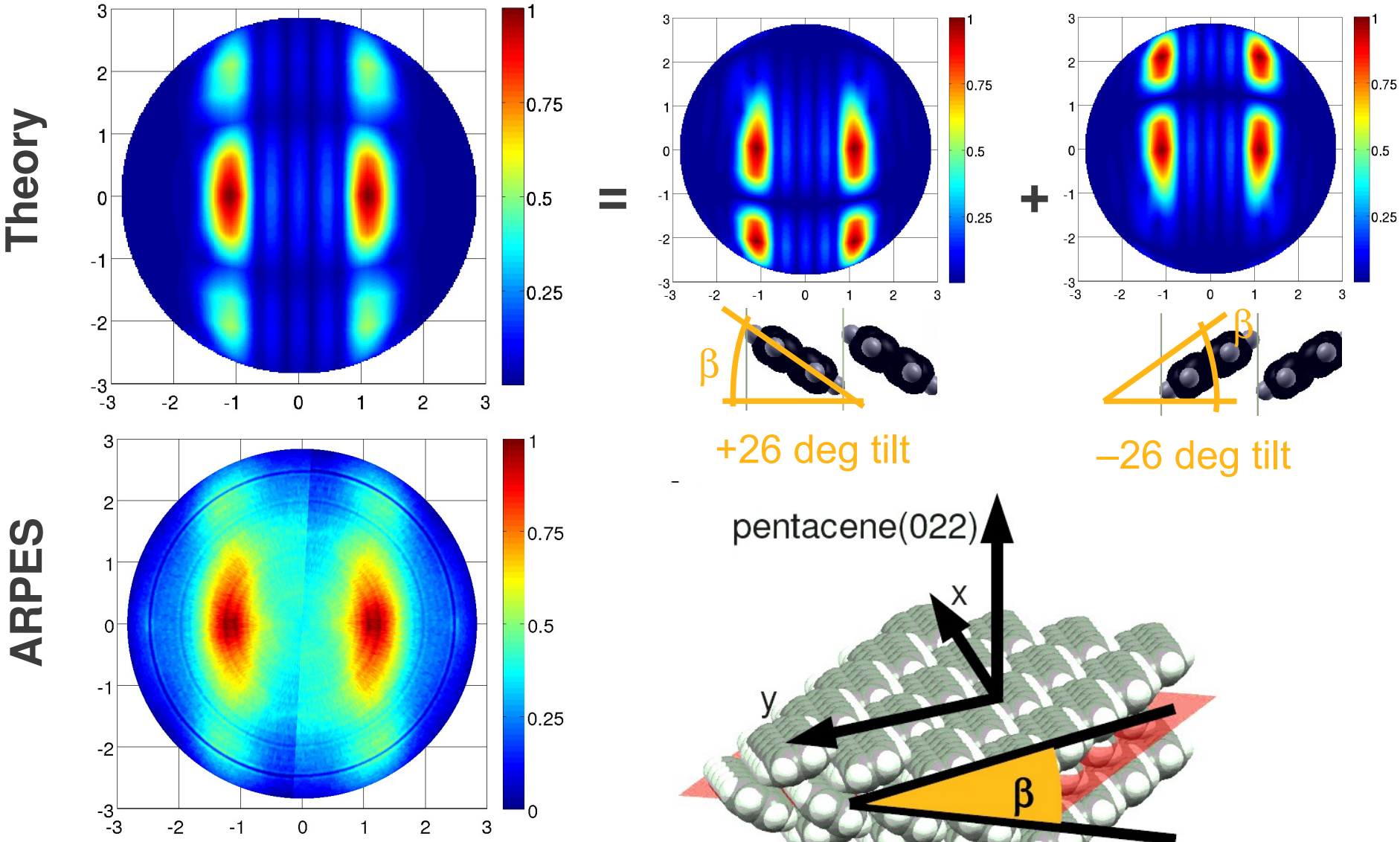


ARPES





Pentacene HOMO from a Multilayer

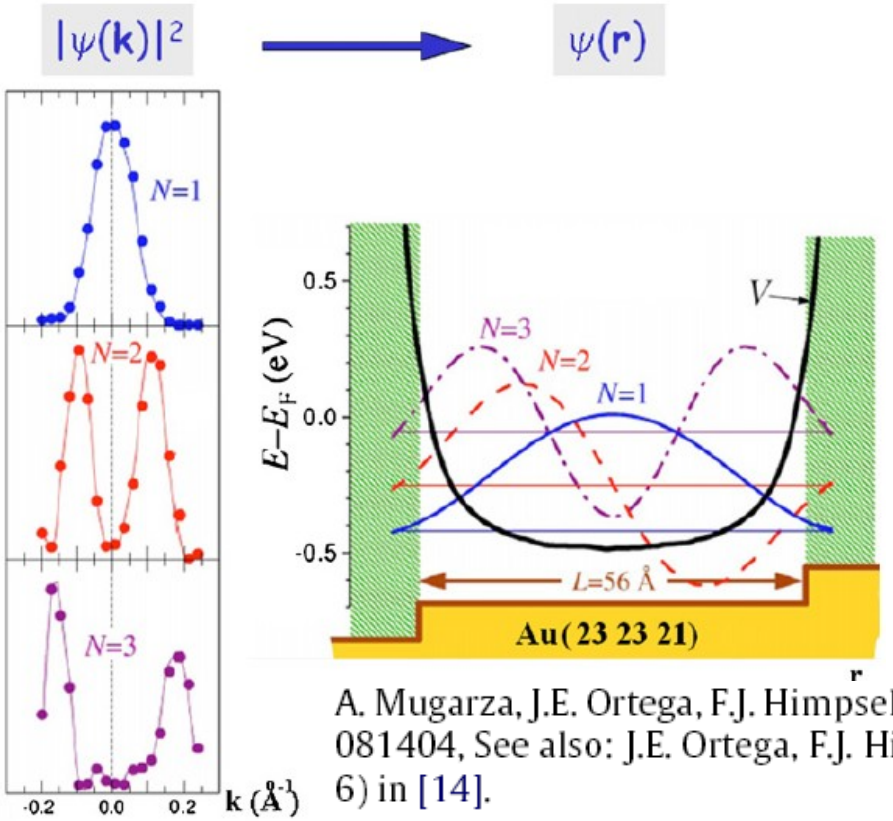


Conclusion and Outlook

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

- **1D and 2D wave function imaging demonstrated**



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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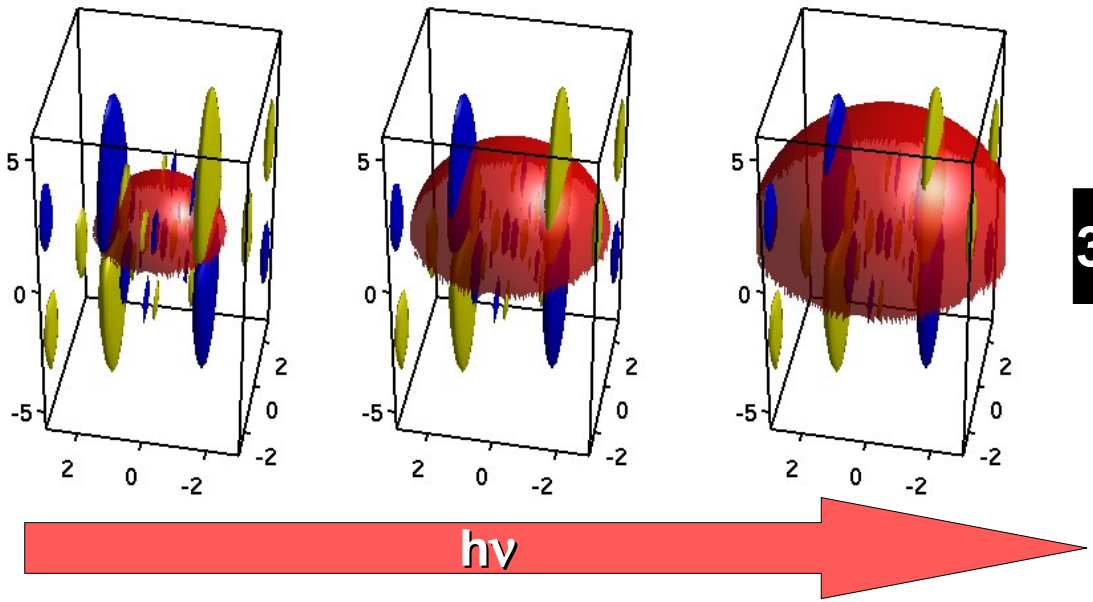
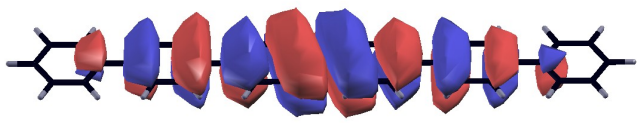
- **Prospect of 3D imaging through scans of the photon energy**





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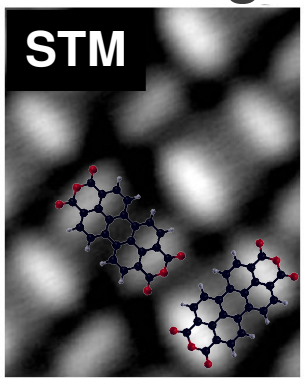
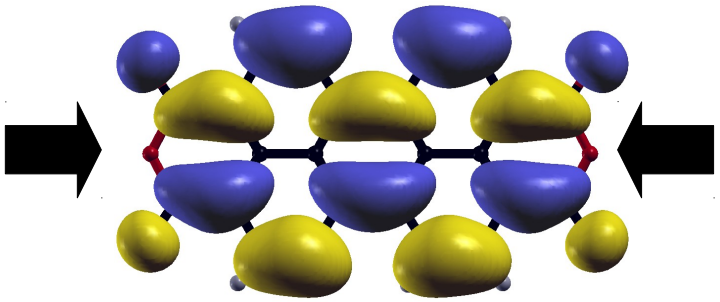
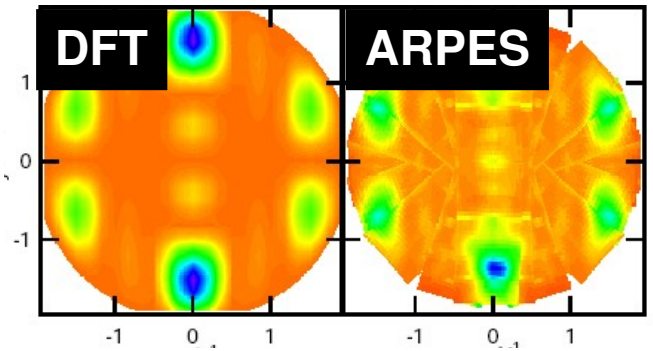
- Prospect of 3D imaging through scans of the photon energy
- Desireable to do PE experiments on individual nano-objects (goal is to reach the focussing limit of soft x-rays 25 nm)
- **Scanning tunneling microscopy and PE complement each other**







Rohlfing et al. PRB 76 (2007)

Ziroff et al. PRL (2010)

Thank You for Your Attention!