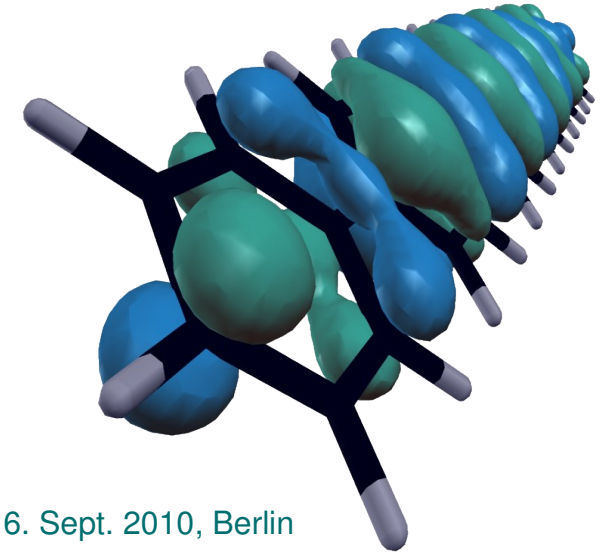
MONTAN UNIVERSITÄT
WWW.UNILEOBEN.AC.AT

The Electronic Structure of Organic Molecular Layers:

Theoretical Insight into Photoemission Experiments



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

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

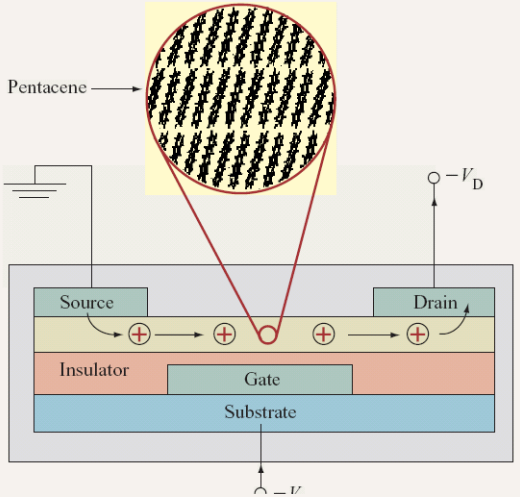
Experimentelle Physik VII – Universität Würzburg, Germany
Johannes Ziroff, Frank Forster,
Achim Schöll, Friedrich Reinert

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

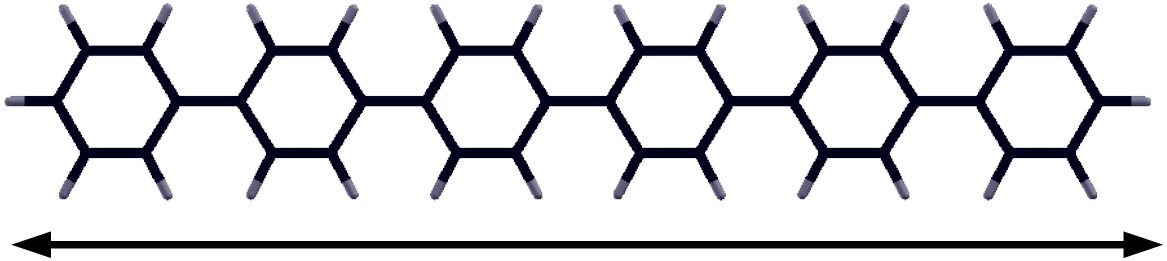
Organic Semiconductors

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

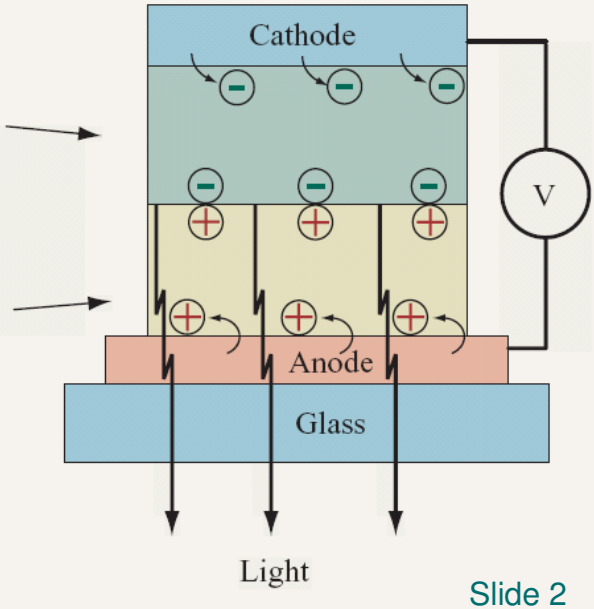
OFET
Organic
Field **E**ffect
Transistor



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

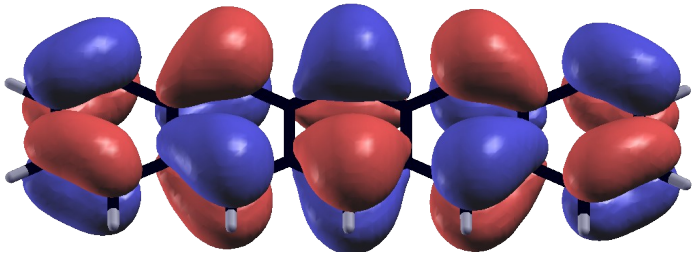


OLED
Organic
Light **E**mitting **D**iode

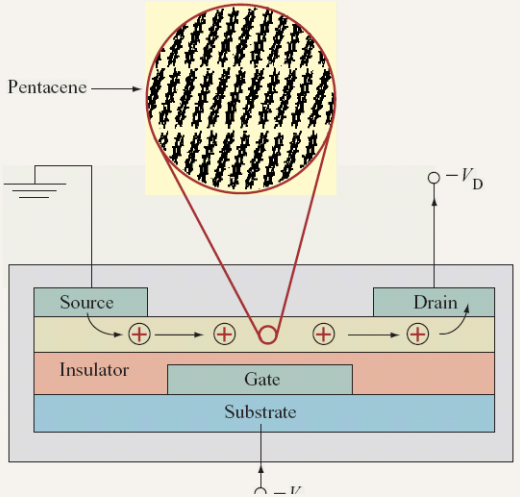


Organic Semiconductors

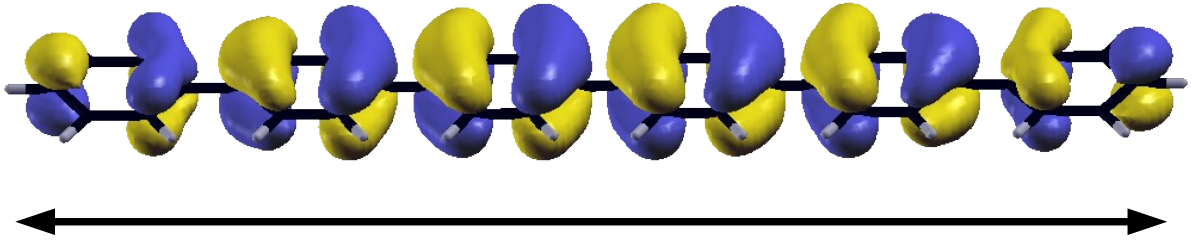
Pentacene ($C_{22}H_{14}$)



OFET
Organic
Field **E**ffect
Transistor

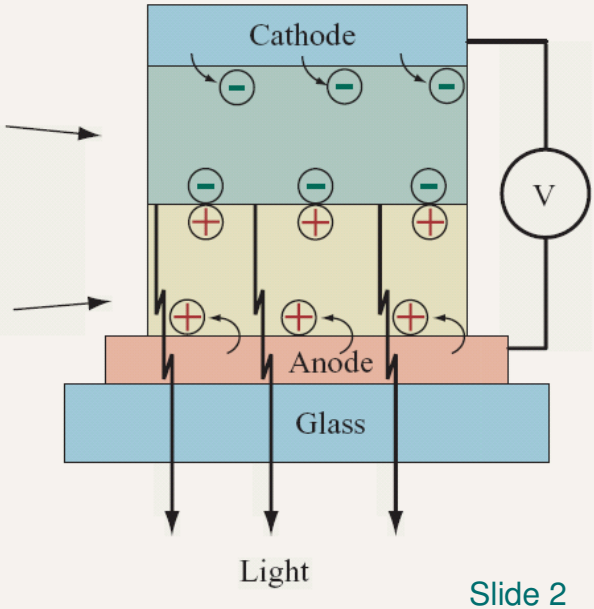


Para-Sexiphenyl ($C_{36}H_{26}$)

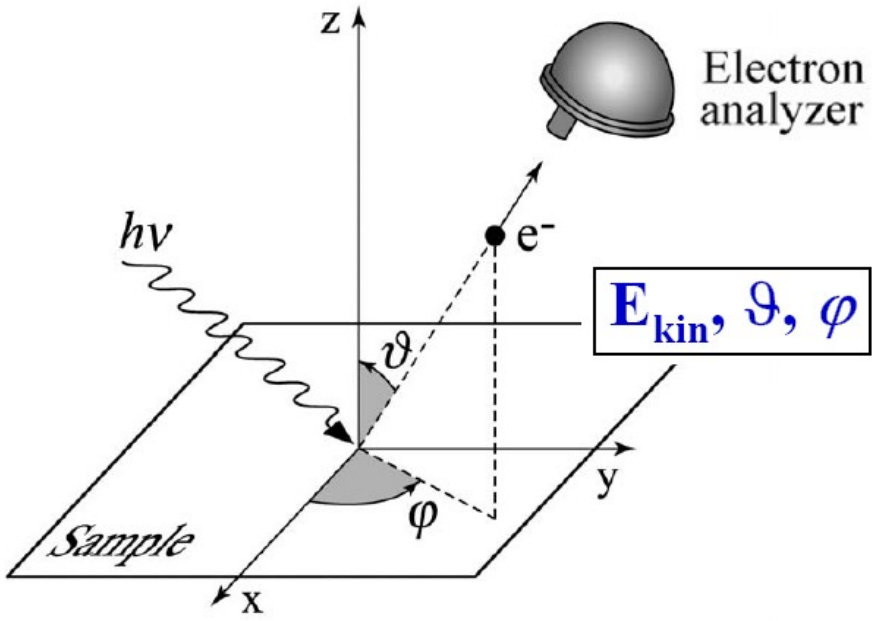


2.6 nm

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

E_{kin}

$\mathbf{K}$

Conservation laws

$$E_f - E_i = h\nu$$

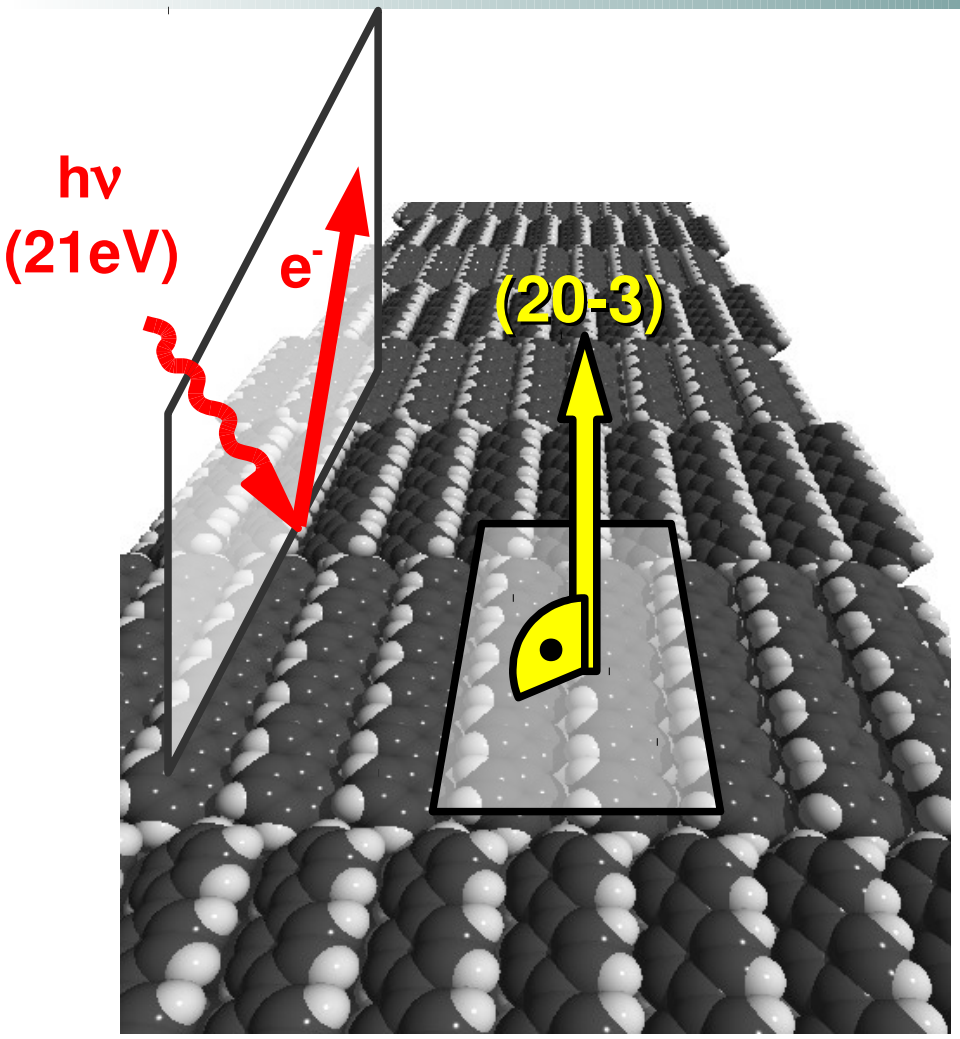
$$\mathbf{k}_f - \mathbf{k}_i = \cancel{\mathbf{k}_{h\nu}}$$

Solid

E_B

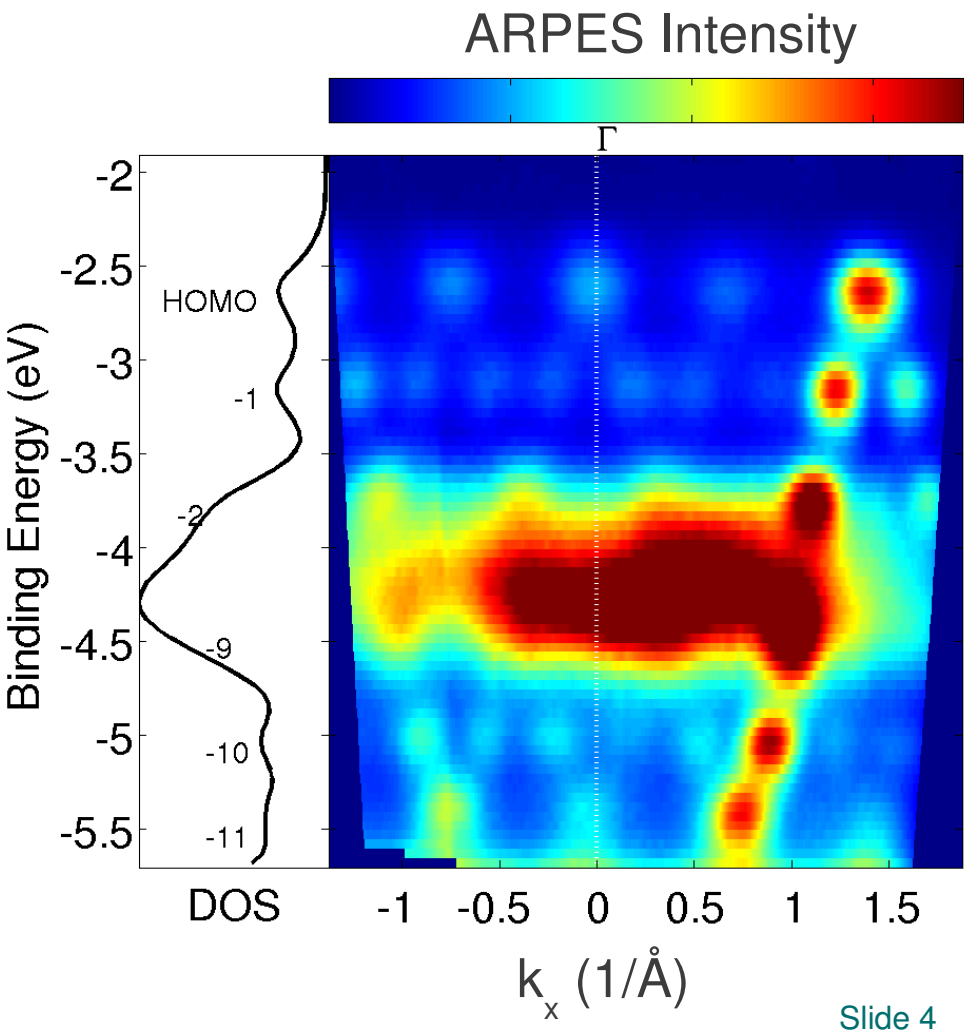
$\mathbf{k}$

Uniaxially Aligned Sexiphenyl

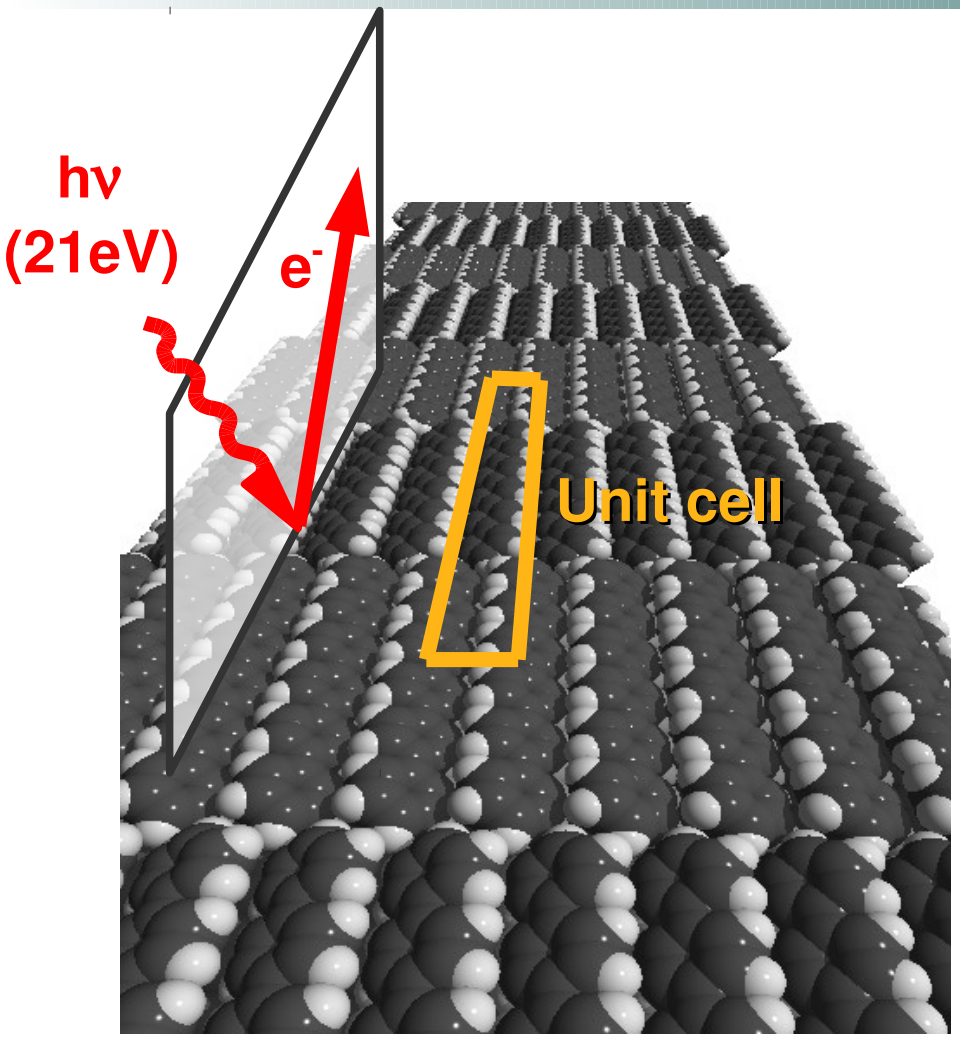


Uniaxially ordered para-sexiphenyl film
on Cu(110)_(2x1)O

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

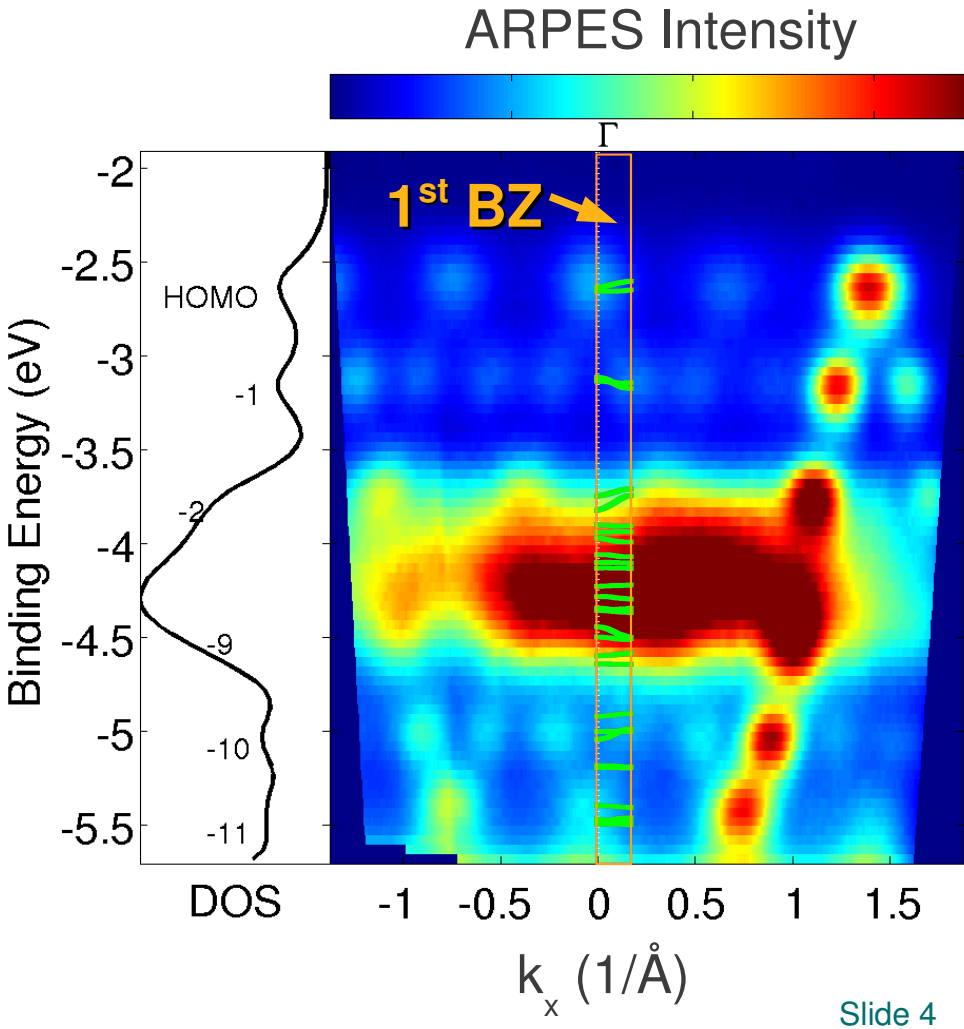


Uniaxially Aligned Sexiphenyl

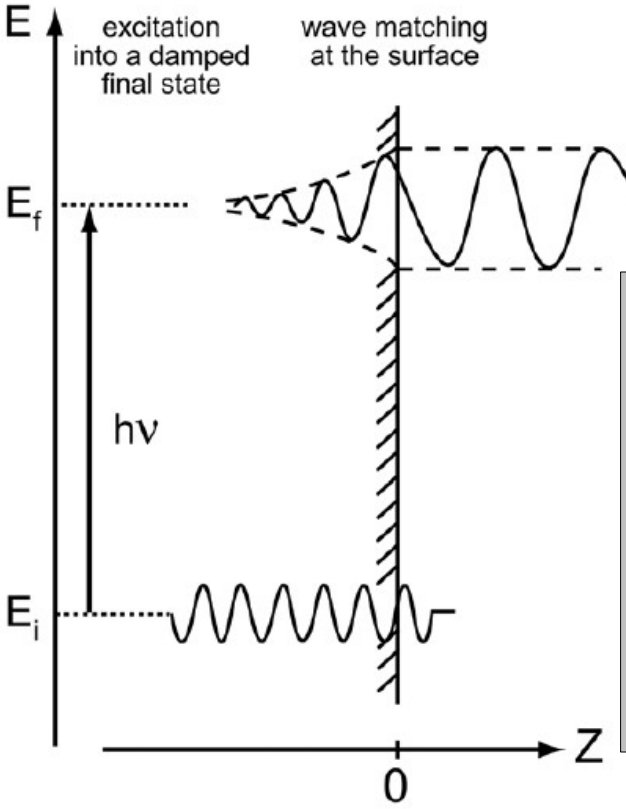


Uniaxially ordered para-sexiphenyl film
on Cu(110)_(2x1)O

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



Photoemission Intensity



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

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

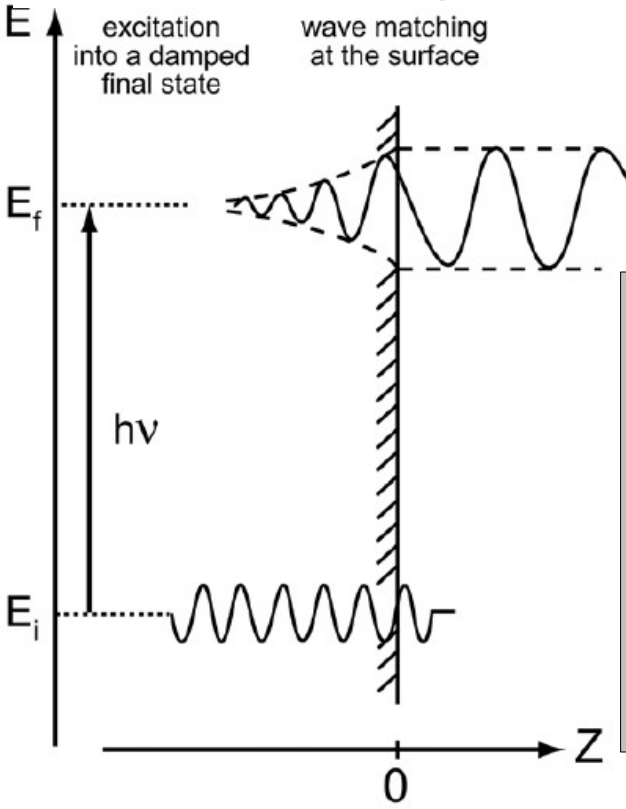
Spectral Function
(energy renormalzation and life time due to many-body effects)

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

Photoemission Intensity

One Step Model

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



- Independent-Particle Picture
- Sudden Approximation

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

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

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

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

Photoemission Intensity

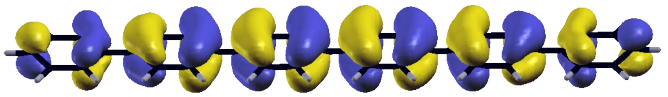
One Step Model

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

Photoemission Intensity

One Step Model

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

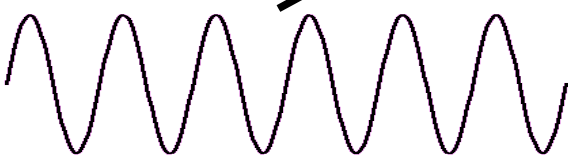


molecular orbital

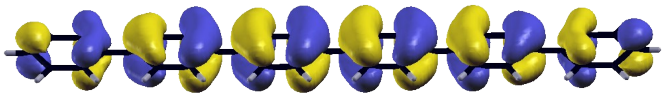
Photoemission Intensity

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

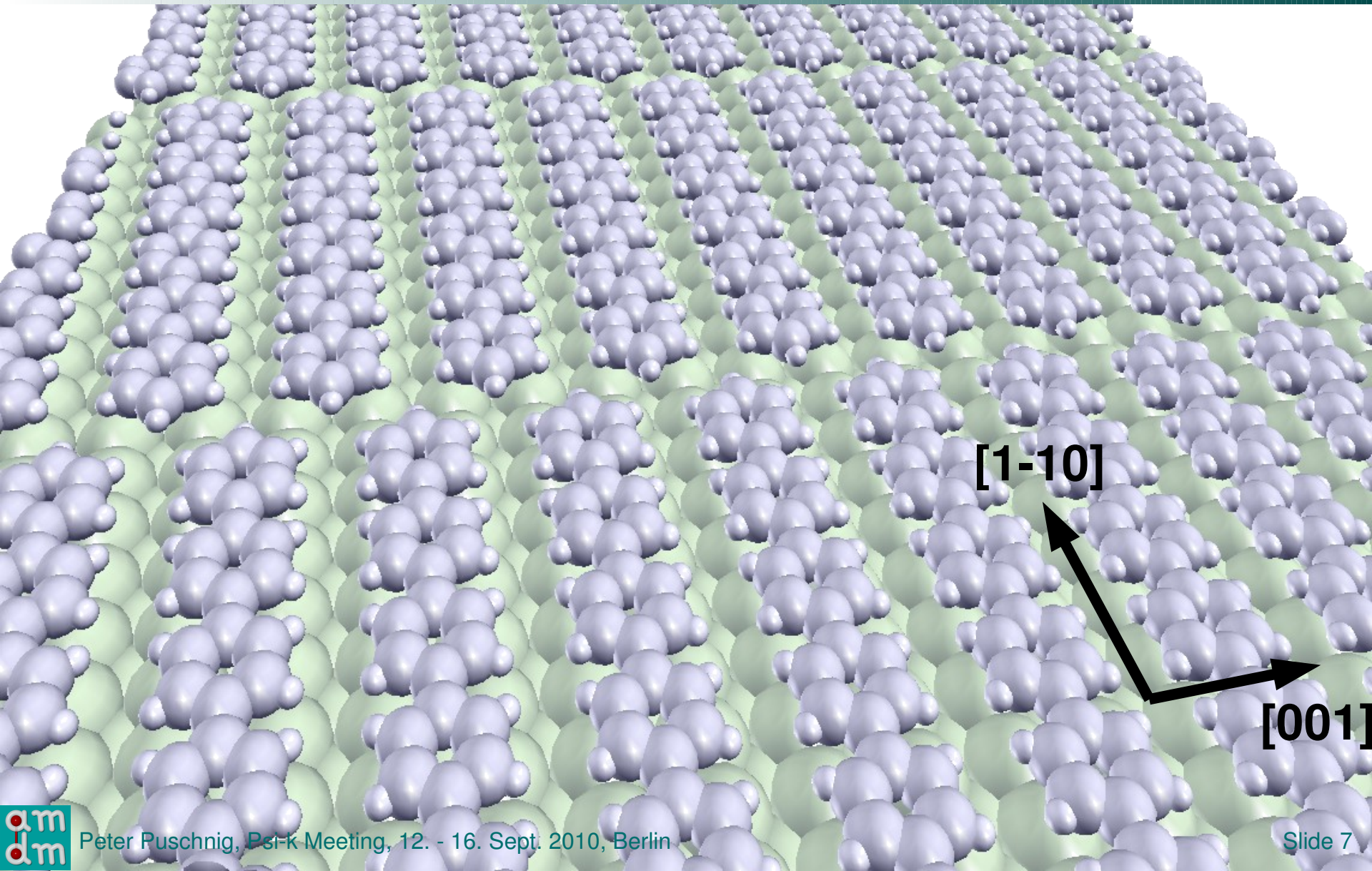
Approximation: final state = plane wave

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

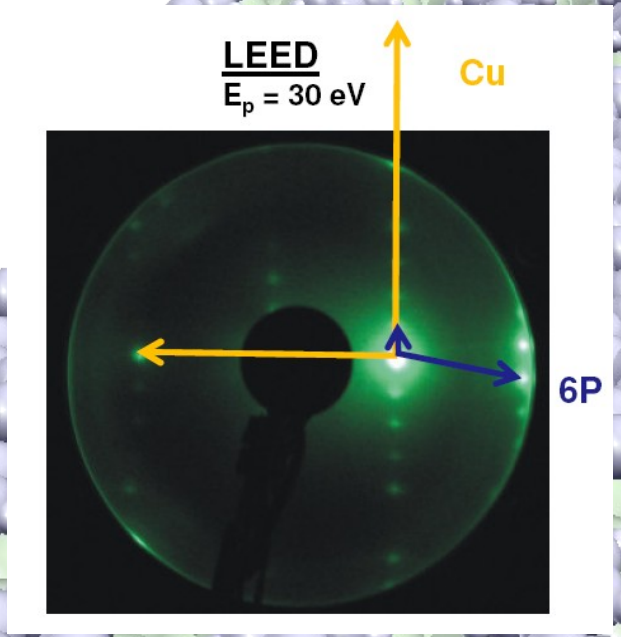
Fourier Transform of Initial State Orbital

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

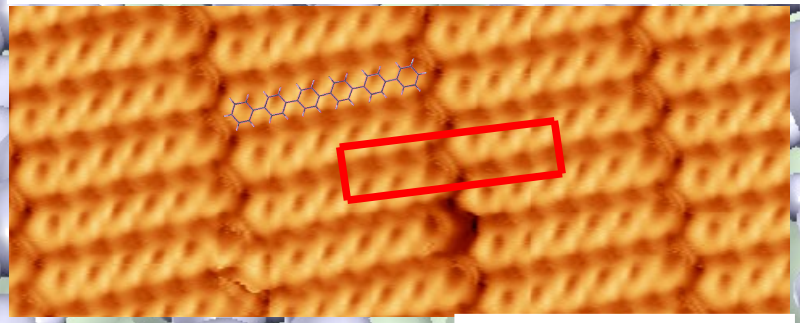
Sexiphenyl Monolayer on Cu(110)



Sexiphenyl Monolayer on Cu(110)



Low-T STM by courtesy of Stephen Berkebile



-130 mV / 0.38 nA

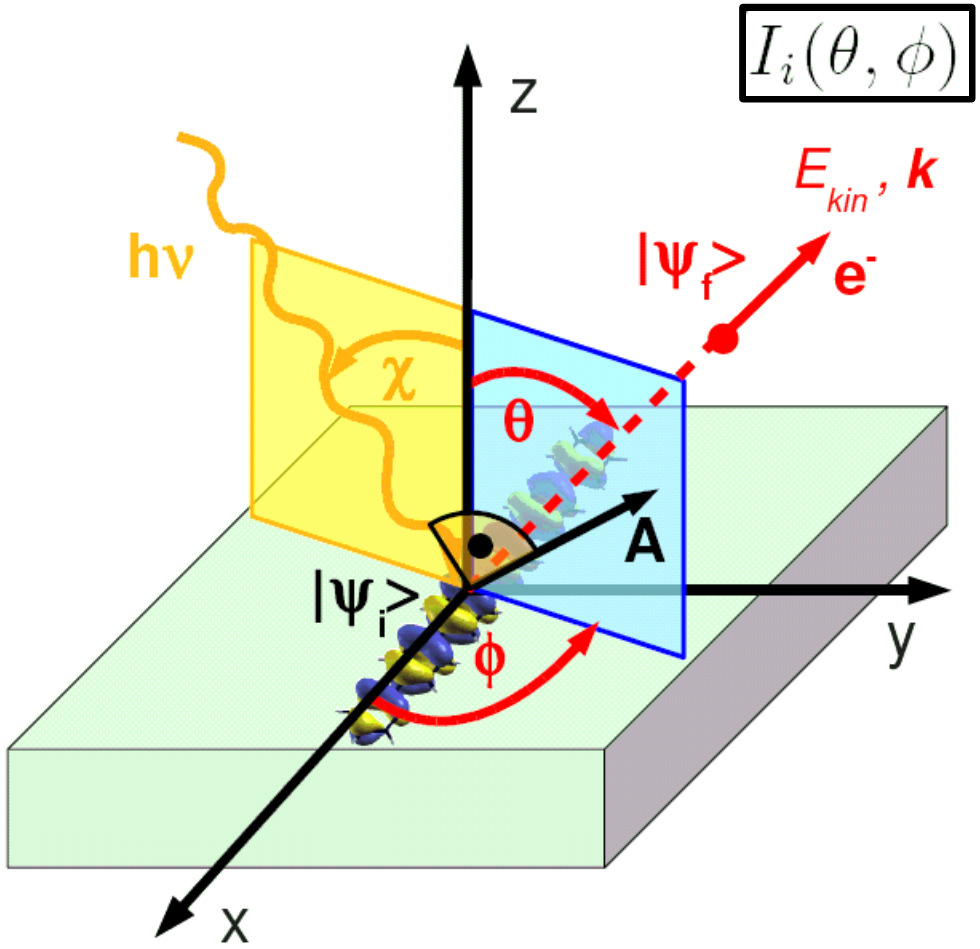
11 a_{Cu} / sqrt(2)

2 a_{Cu}

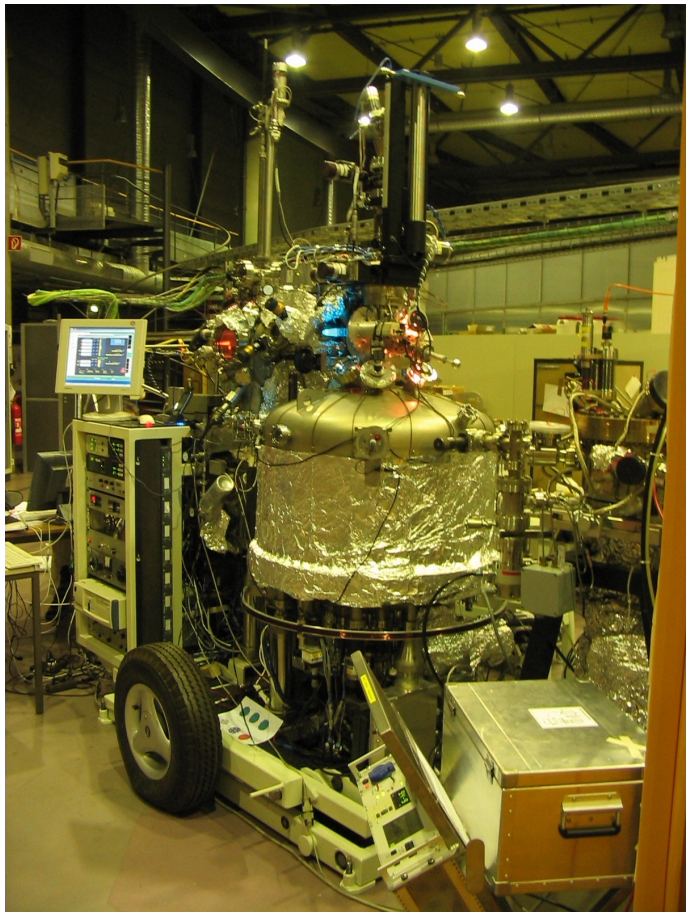
[1-10]

[001]

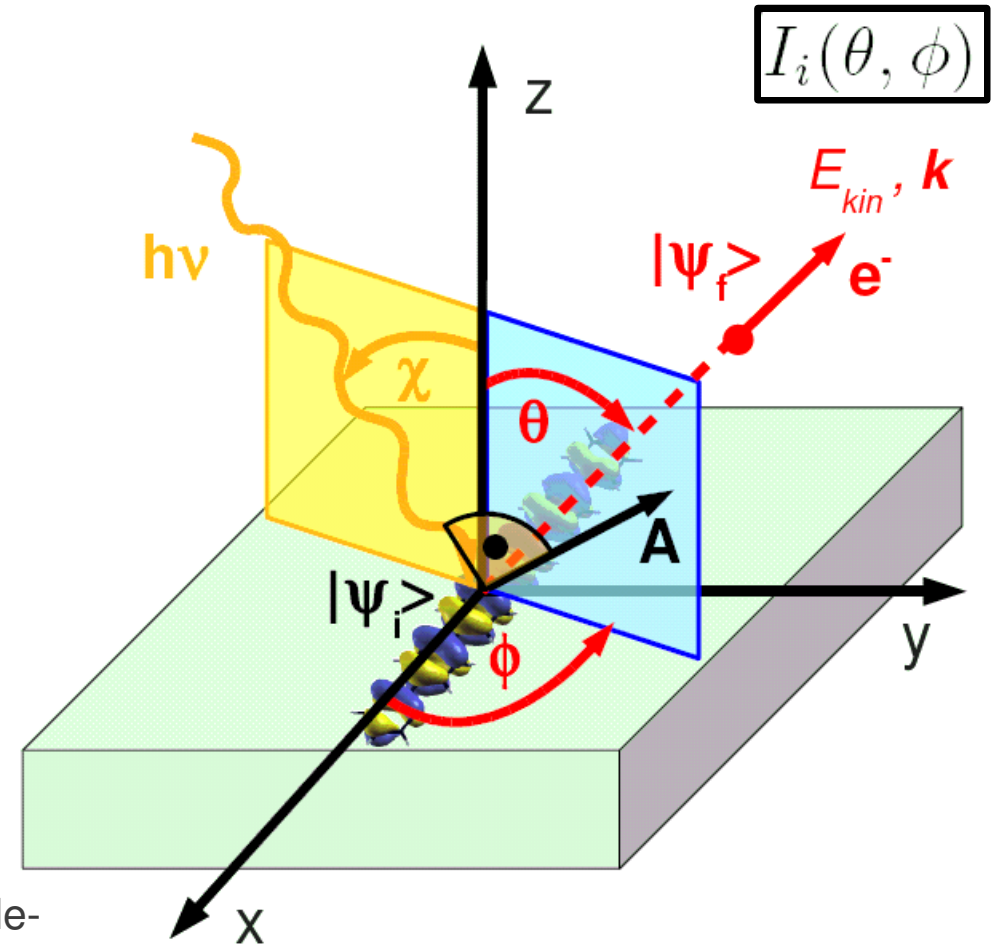
2D Momentum Maps



2D Momentum Maps

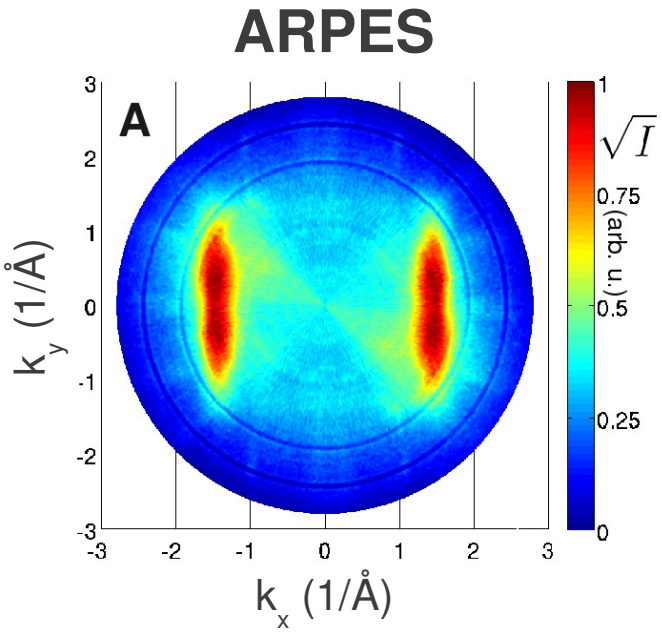


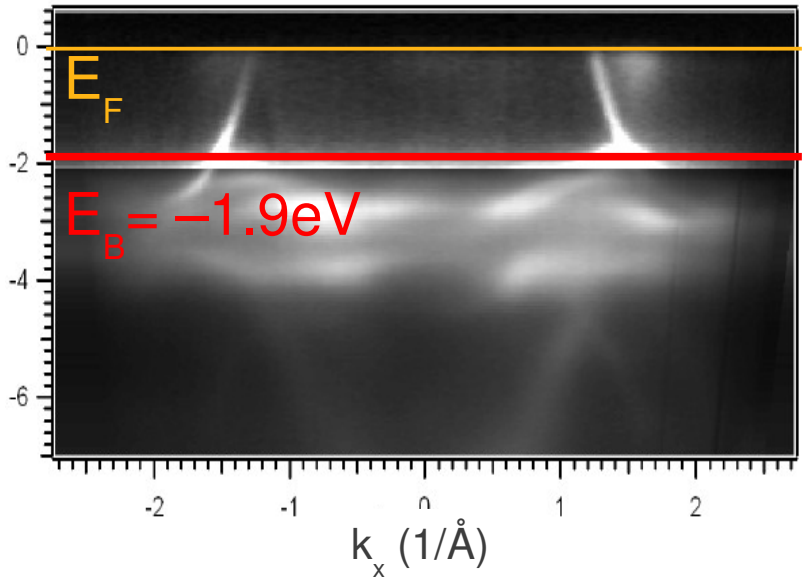
The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II



2D-Momentum Maps

HOMO

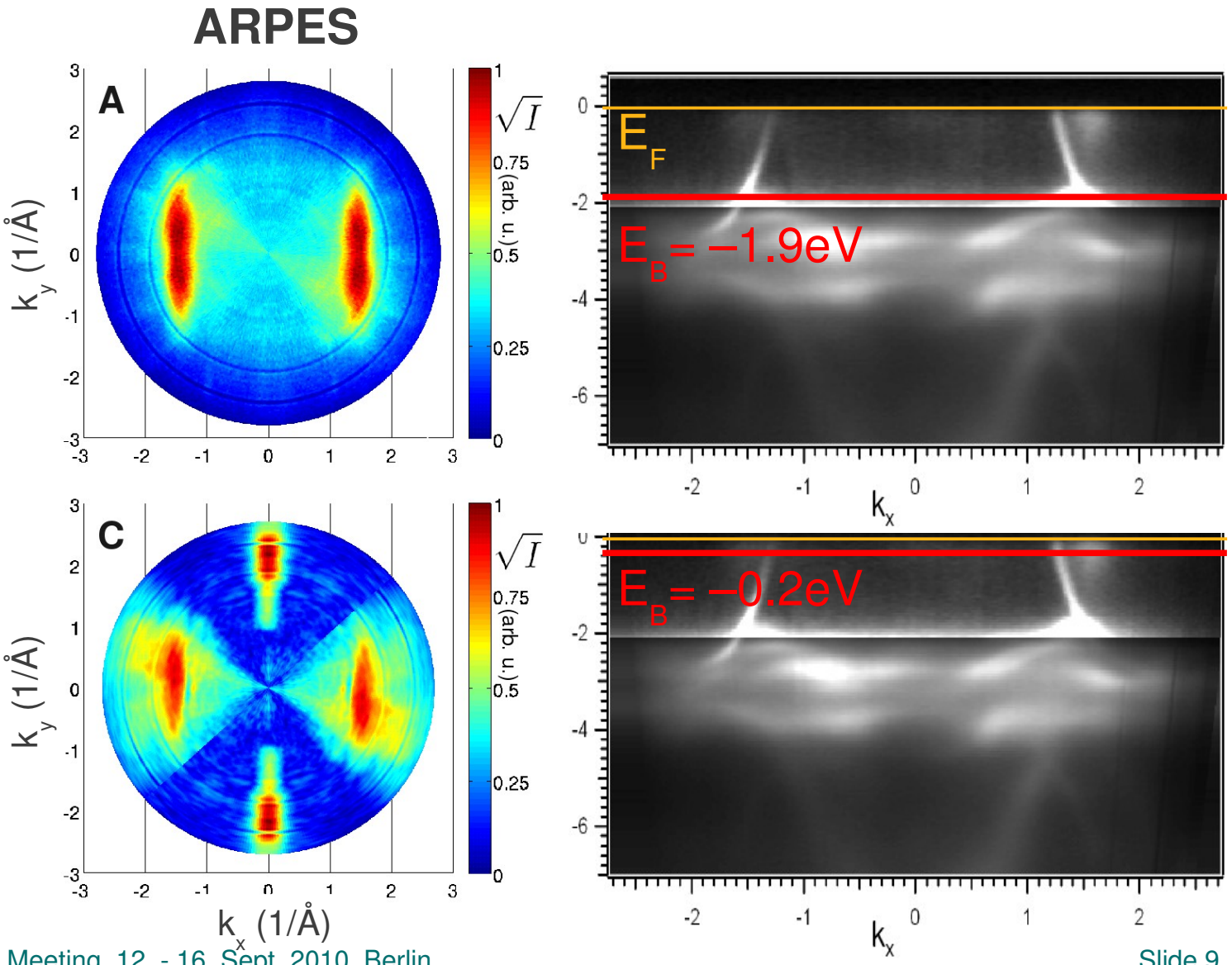




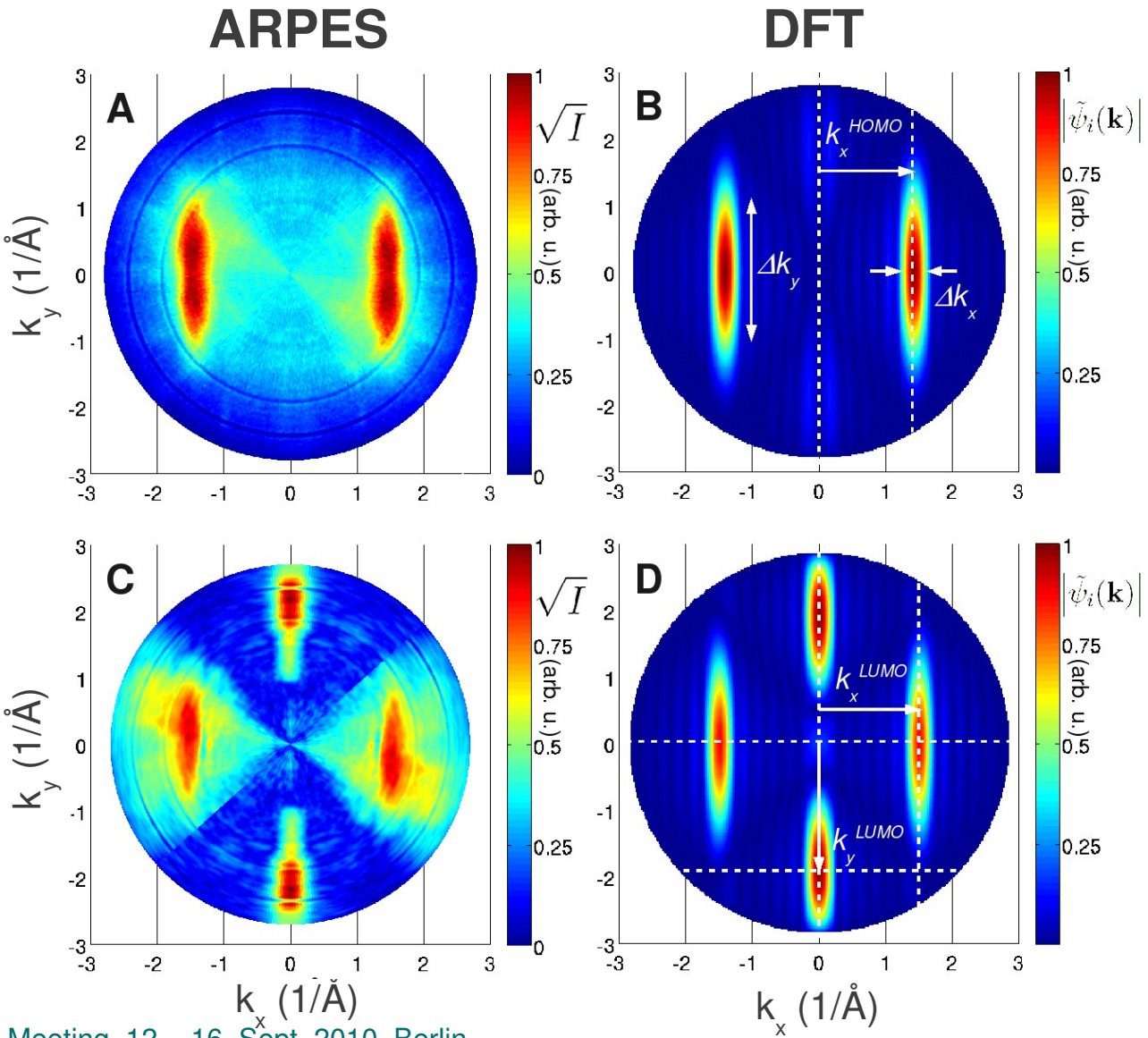
2D-Momentum Maps

HOMO

Filled LUMO



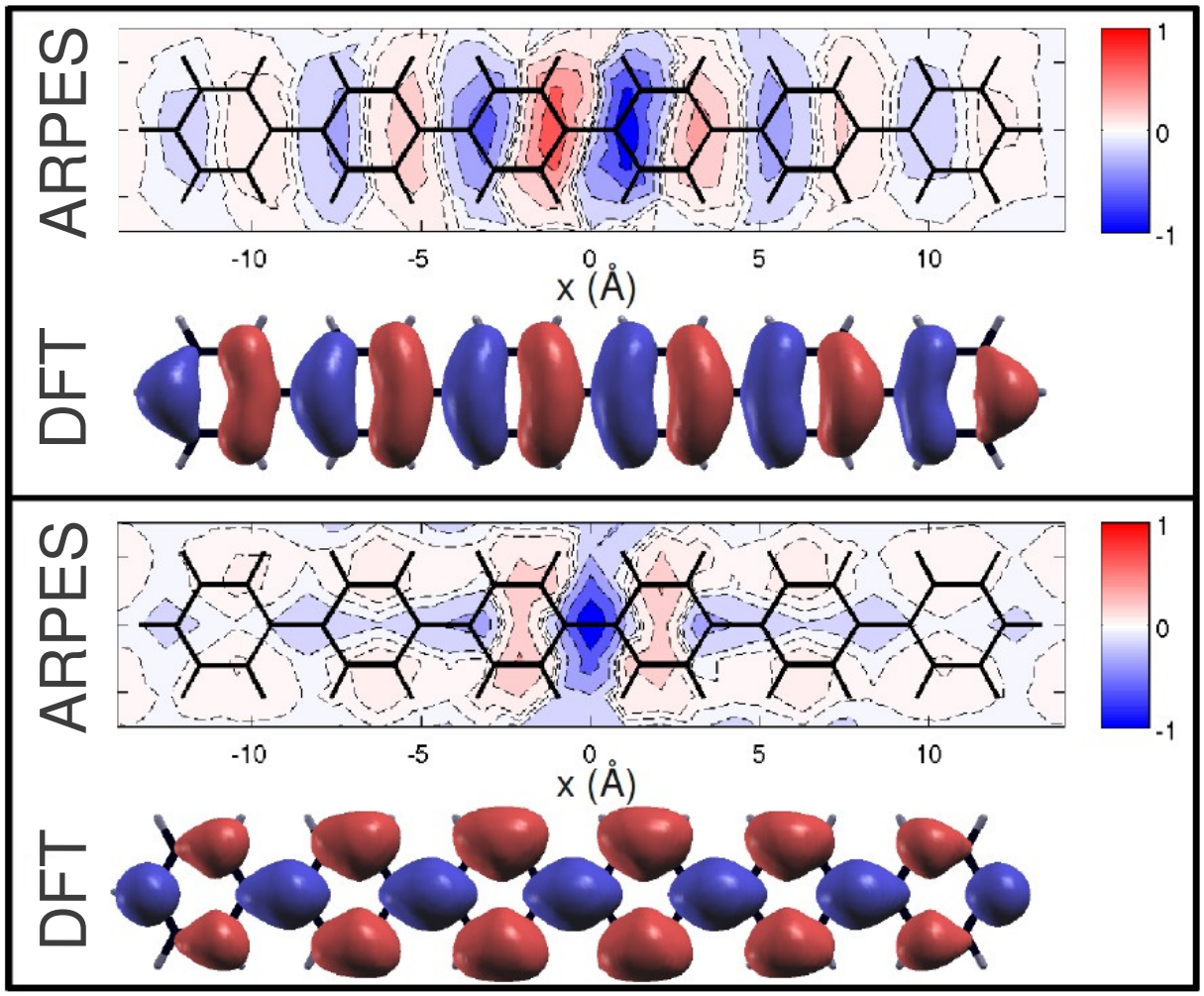
2D-Momentum Maps



Reconstruction of Orbitals

HOMO

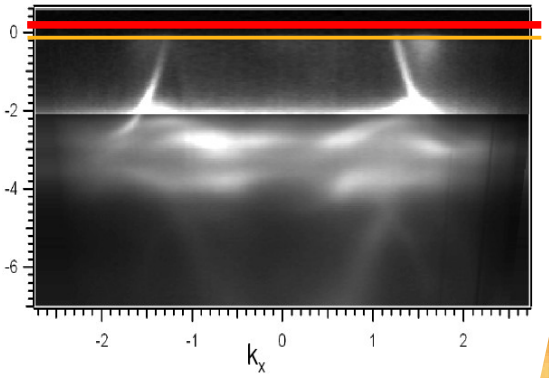
Filled LUMO



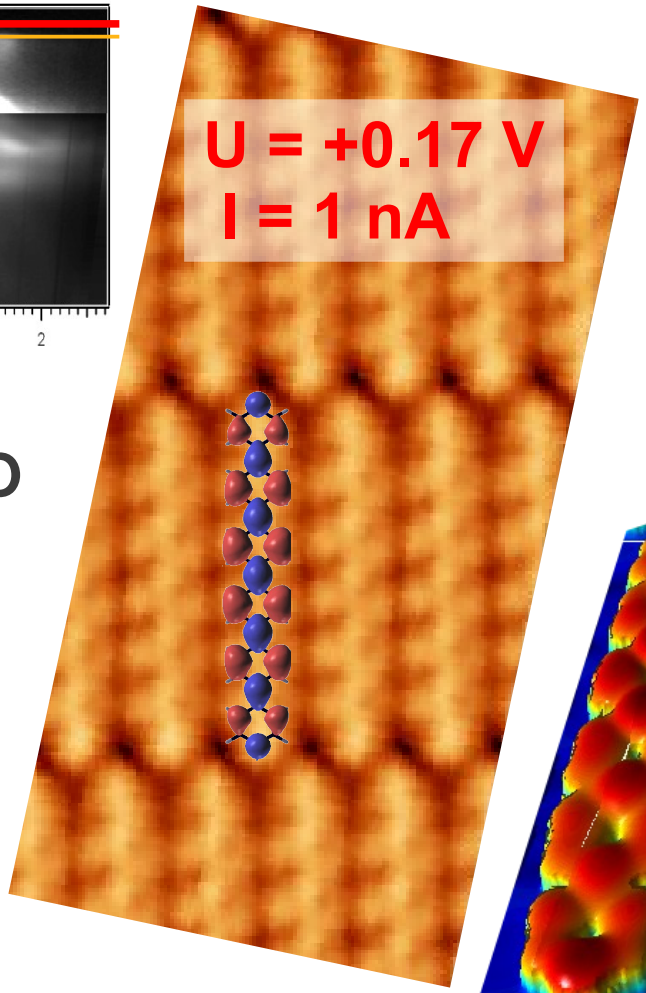
Puschnig et al., Science **326**, 702 (2009)

What about STM?

ARPES

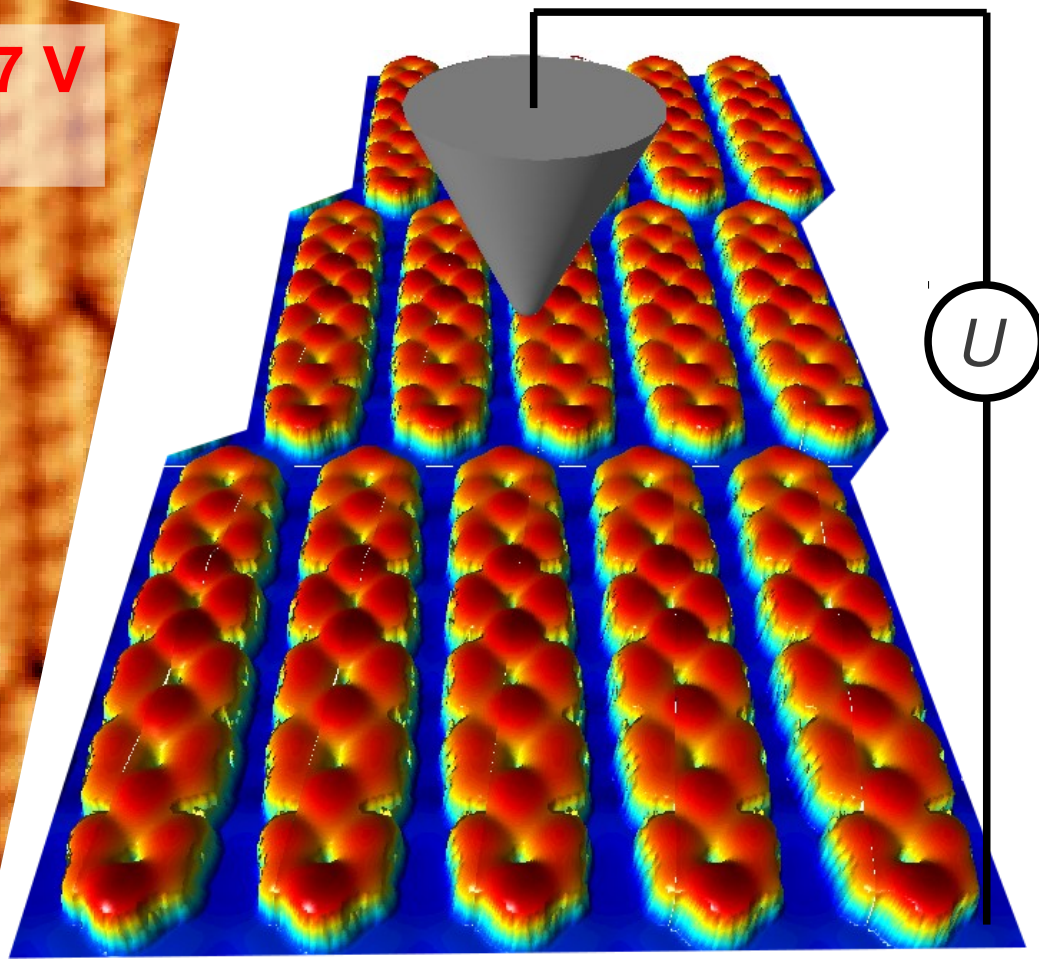


low-T-STM

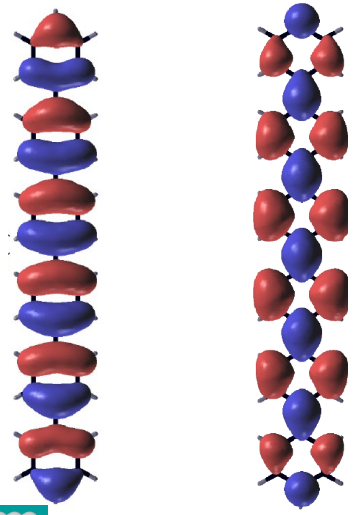


STM – Simulation

(Tersoff-Hamann approximation)

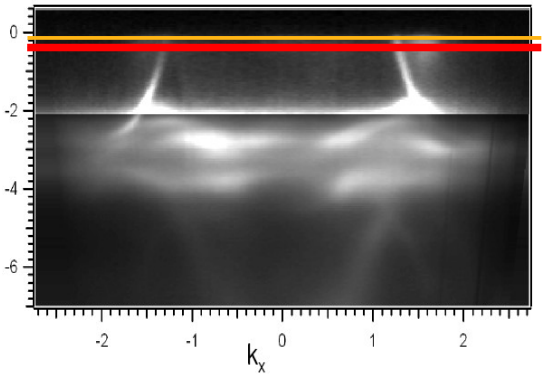


HOMO **LUMO**

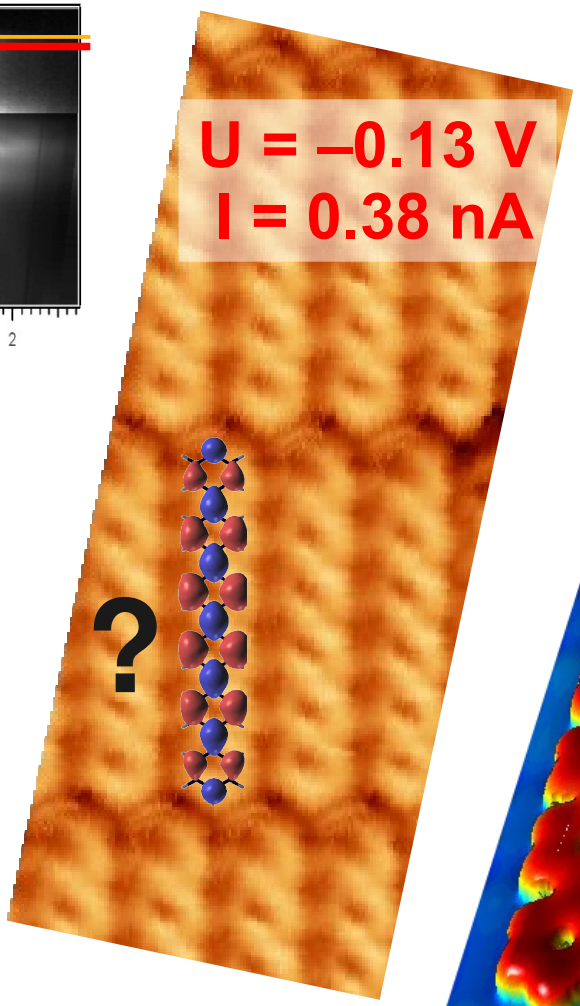


What about STM?

ARPES

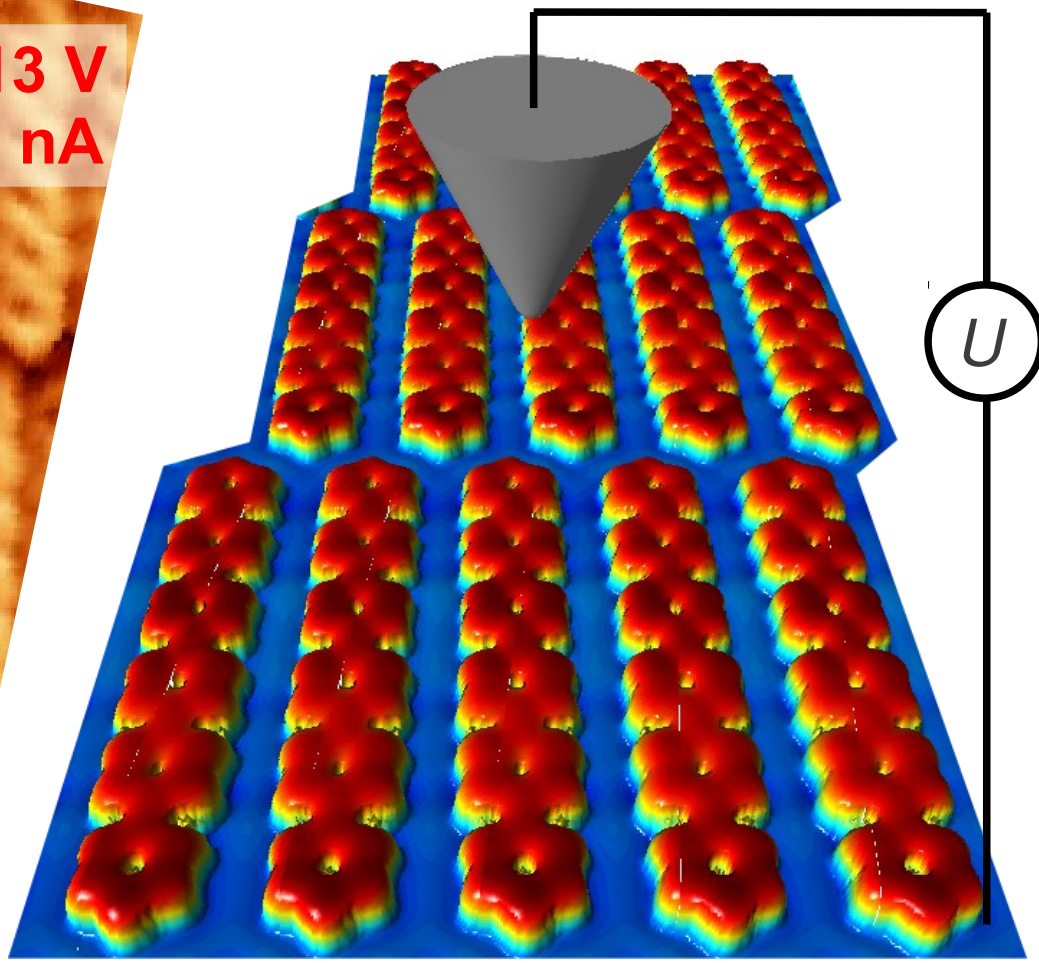


low-T-STM

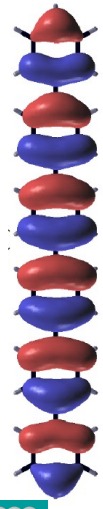


STM – Simulation

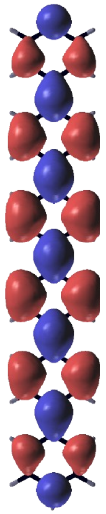
(Tersoff-Hamann approximation)



HOMO



LUMO

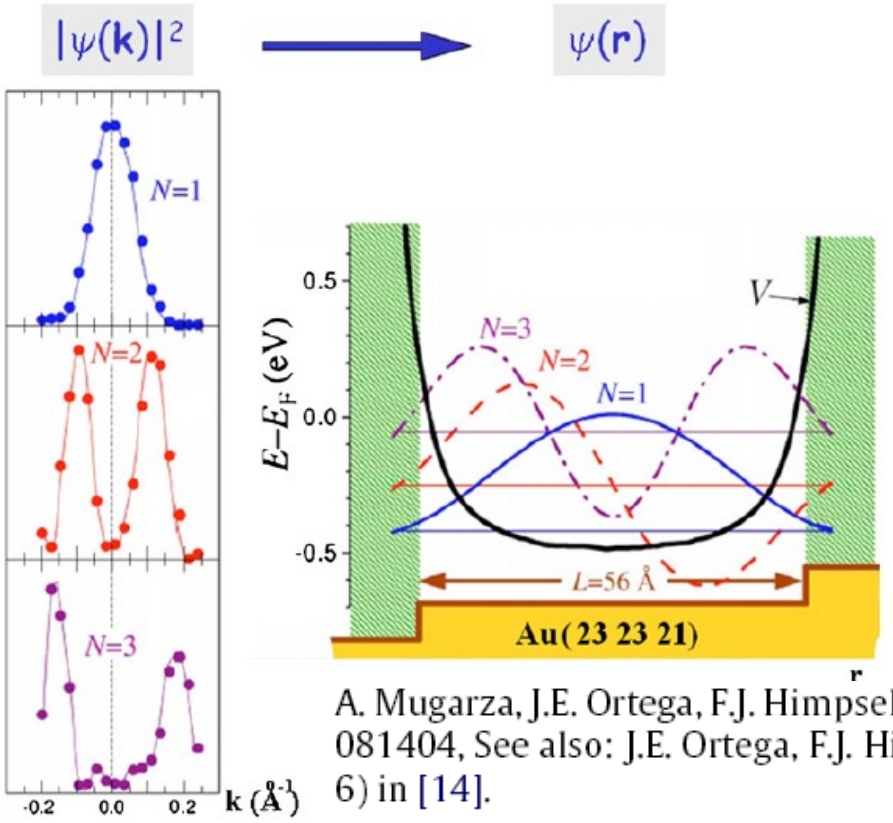


Conclusion and Outlook

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

- **1D and 2D orbital mapping 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].

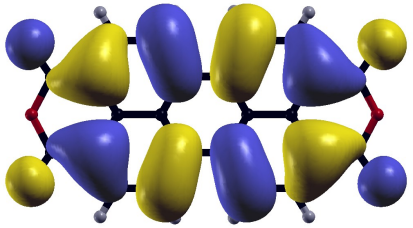
Conclusion and Outlook

Angle-resolved photoemission: From reciprocal space to real space

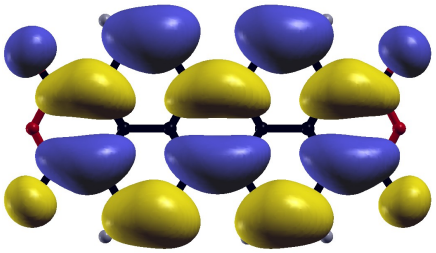
F.J. Himpsel, J. Electron Spectrosc. Relat. Phenom. (2010), doi:10.1016/j.elspec.2010.03.007

- **1D and 2D orbital mapping demonstrated**

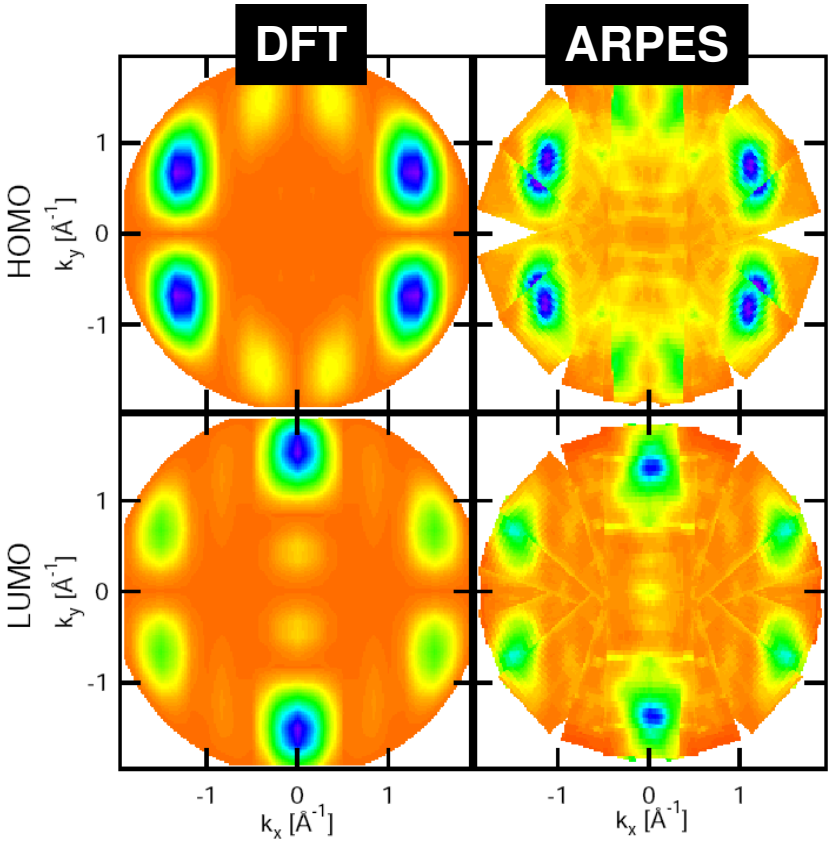
HOMO of PTCDA



LUMO of PTCDA



Ziroff et al. PRL 104, 233004 (2010)

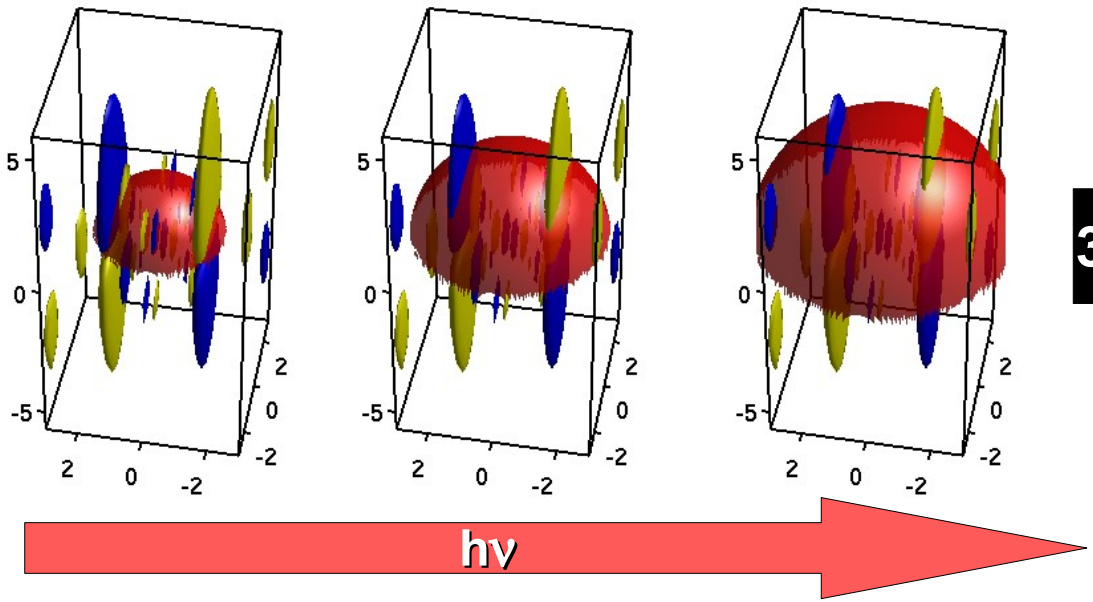


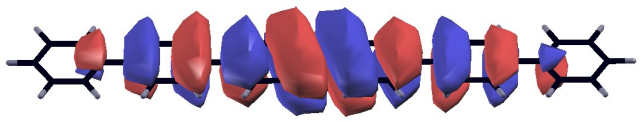
Conclusion and Outlook

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





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

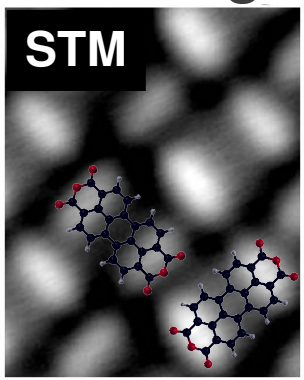
- 1D and 2D orbital mapping demonstrated
- Prospect of 3D imaging through scans of the photon energy
- **Desireable to do PE experiments on individual nano-objects (goal is to reach the focussing limit of soft x-rays 25 nm)**

Conclusion and Outlook

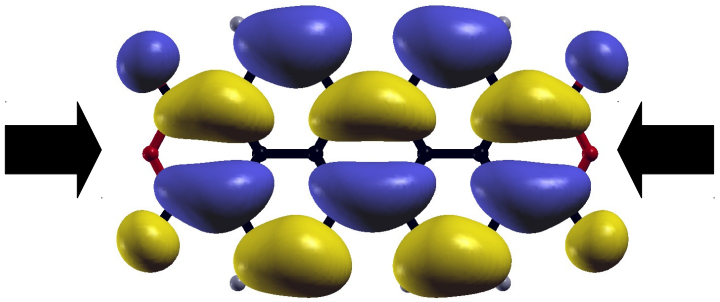
Angle-resolved photoemission: From reciprocal space to real space

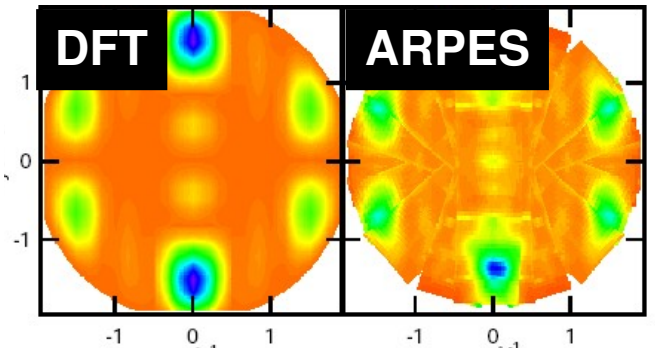
F.J. Himpsel, J. Electron Spectrosc. Relat. Phenom. (2010), doi:10.1016/j.elspec.2010.03.007

- 1D and 2D orbital mapping demonstrated
- 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**



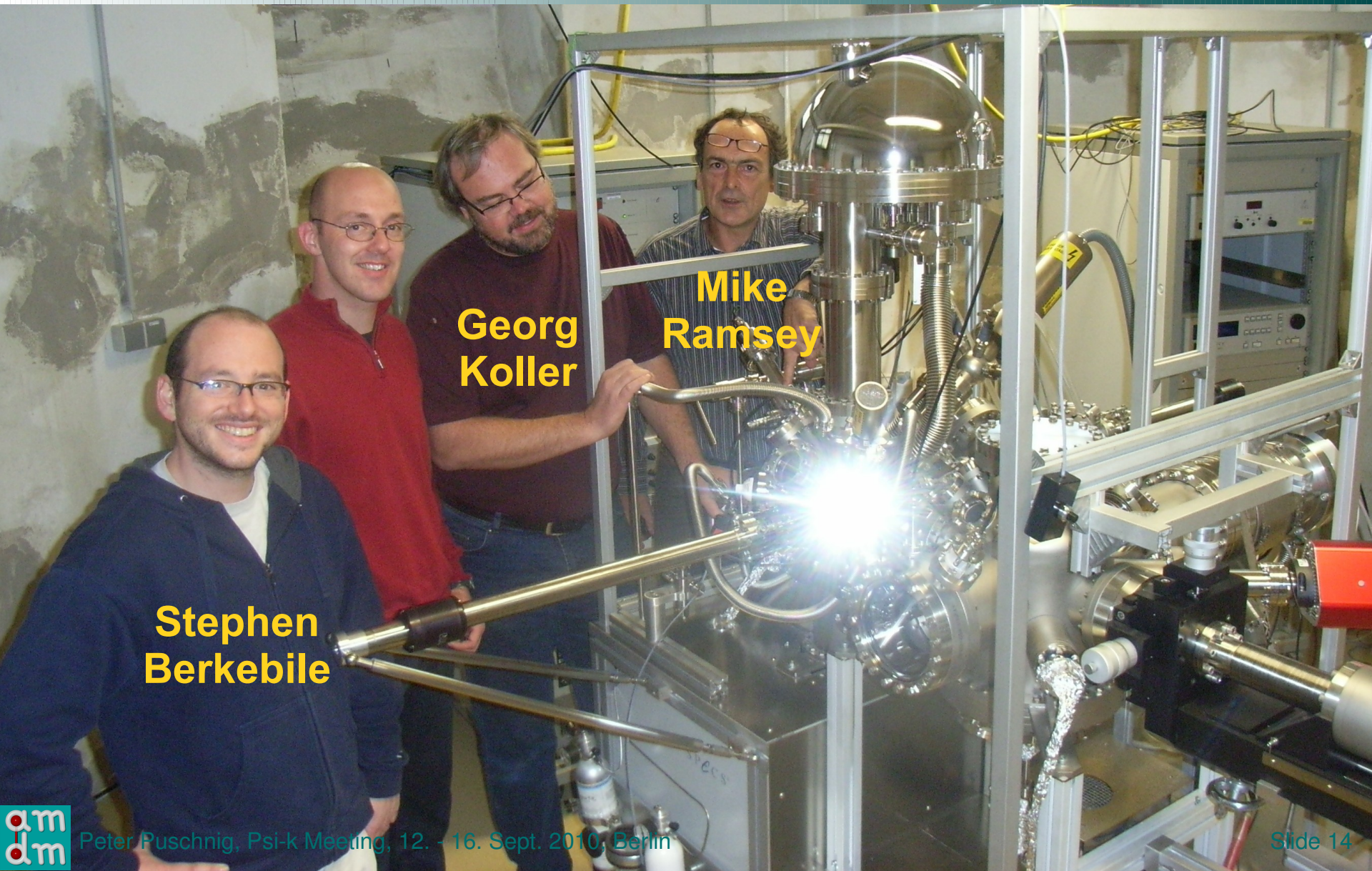
Rohlfing et al. PRB 76 (2007)





Ziroff et al. PRL 104, 233004 (2010)

Thank You for Your Attention!



Additional Slides ...

Plane Wave Final State

The **I**ndependent **A**tomic **C**entre approximation (IAC)

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

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

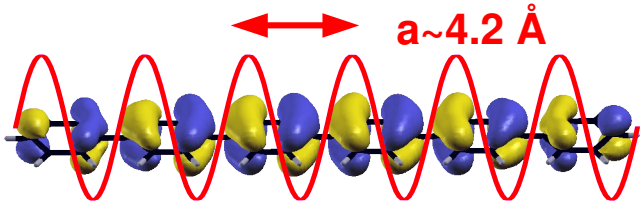
Reduces to the PW final state result, if

- 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

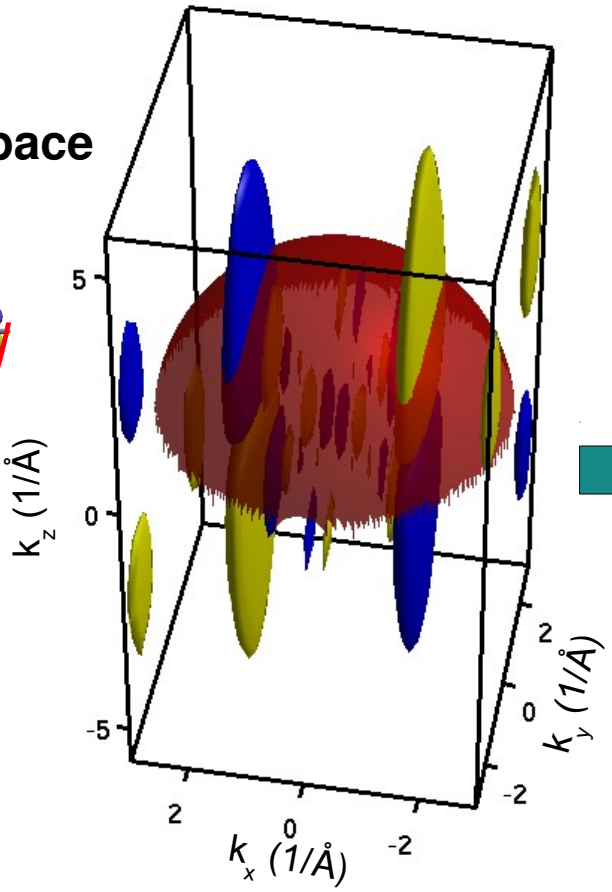
[Goldberg et al, Solid State Commun. **28**, 459-463 (1978),
Puschnig et al., supporting online material to Science **326**, 702 (2009)]

Photoemission Intensity in Pictures

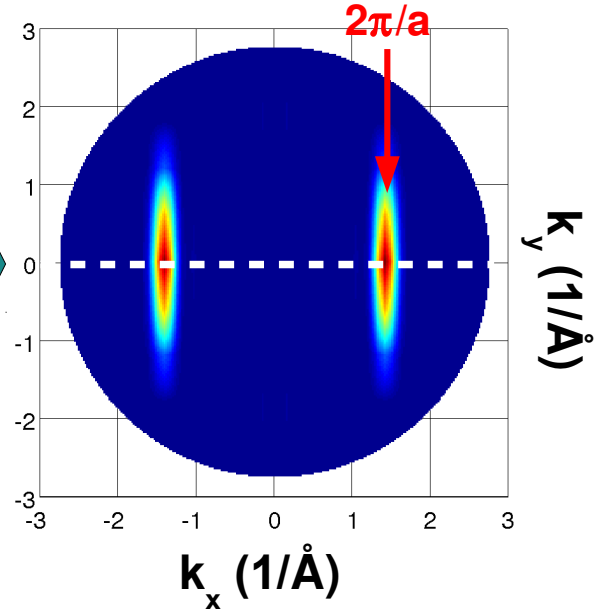
Molecular Orbital in Real Space



Fourier Transform

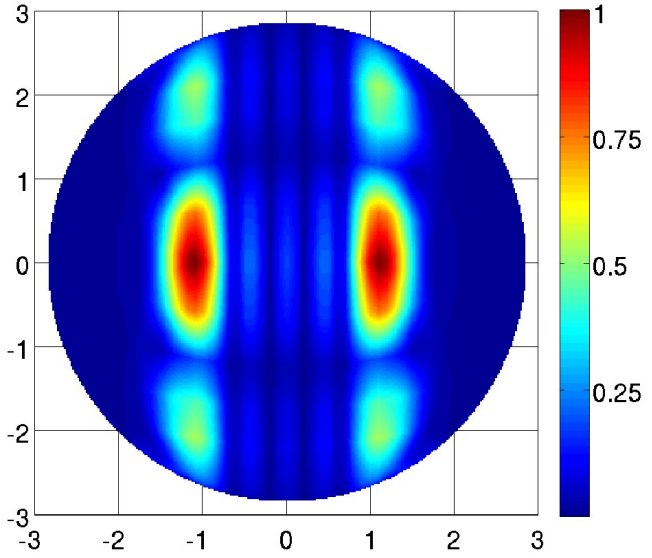


Hemispherical Cut Through 3D Fourier Transform

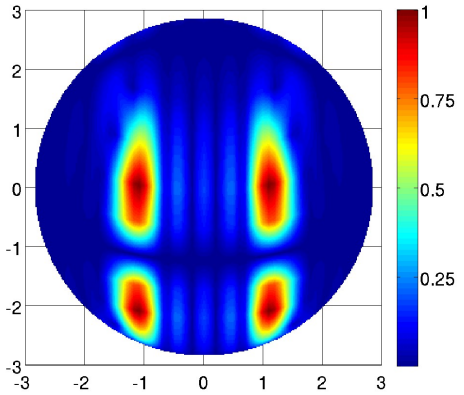


HOMO of Pentacene Multilayer

Theory

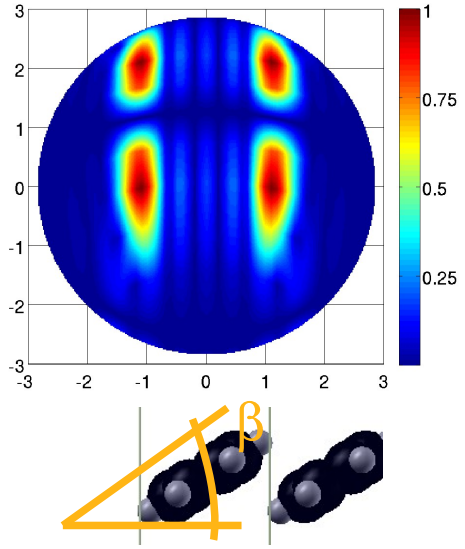


=



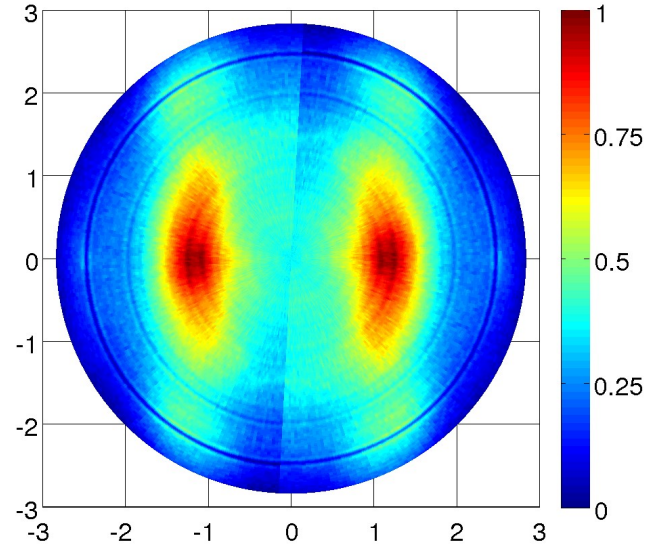
+26 deg tilt

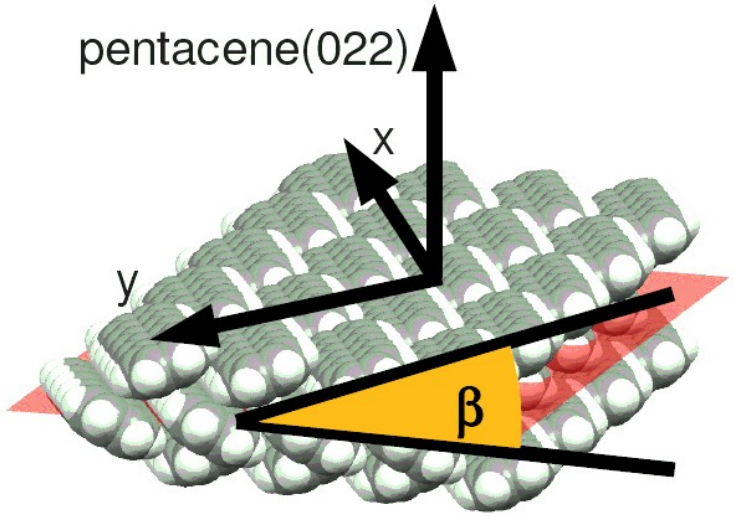
+



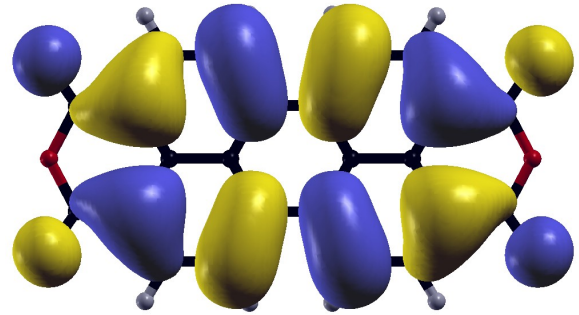
–26 deg tilt

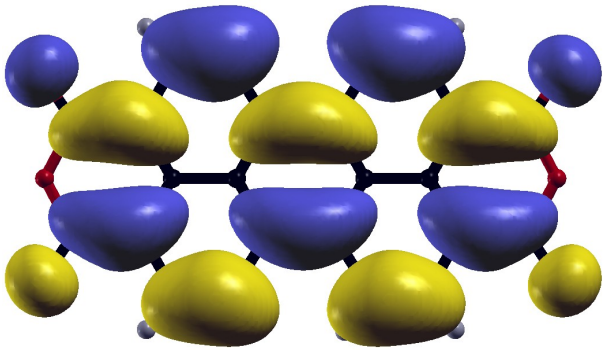
ARPES

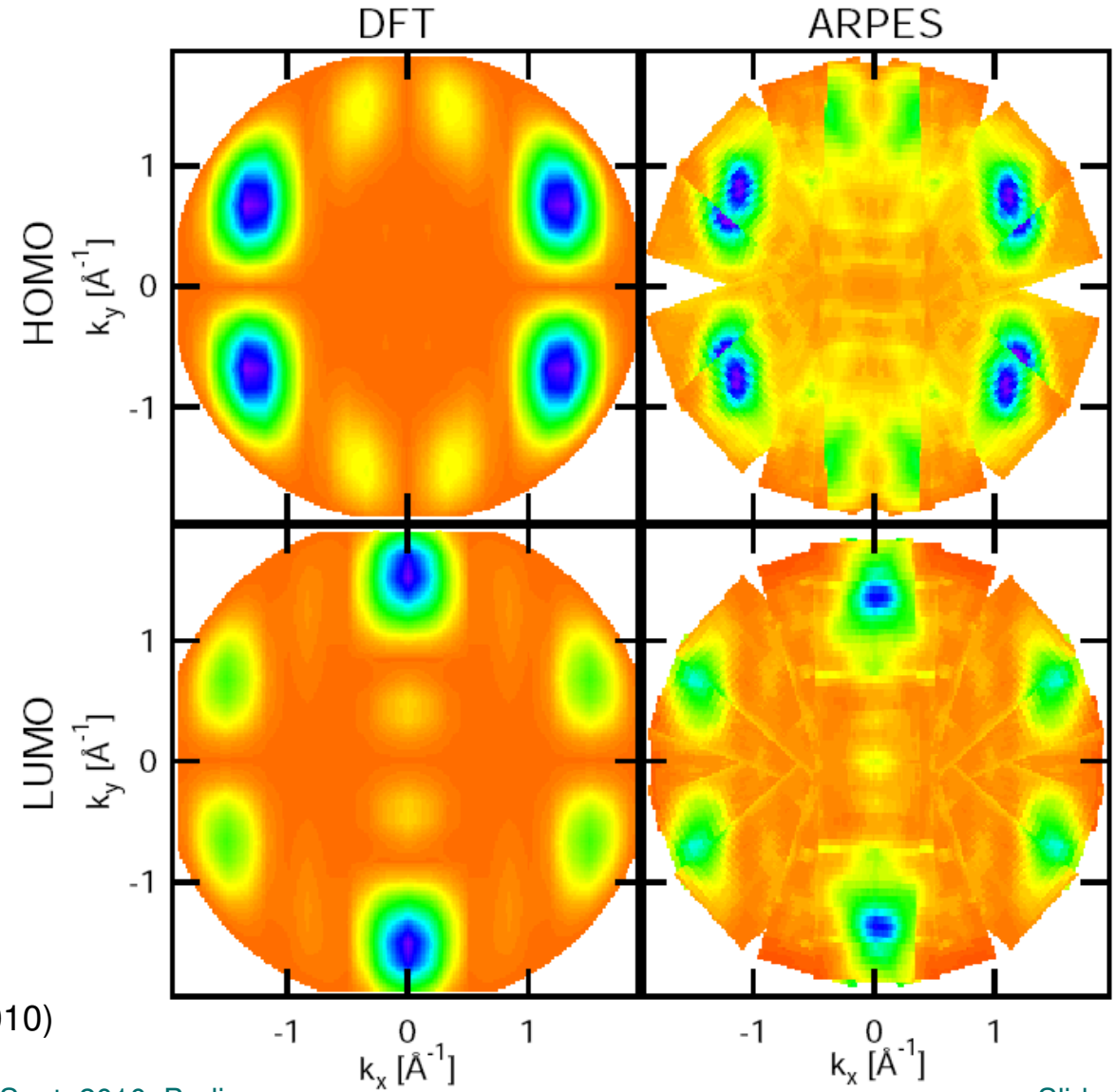




PTCDA Monolayer on Ag(110)



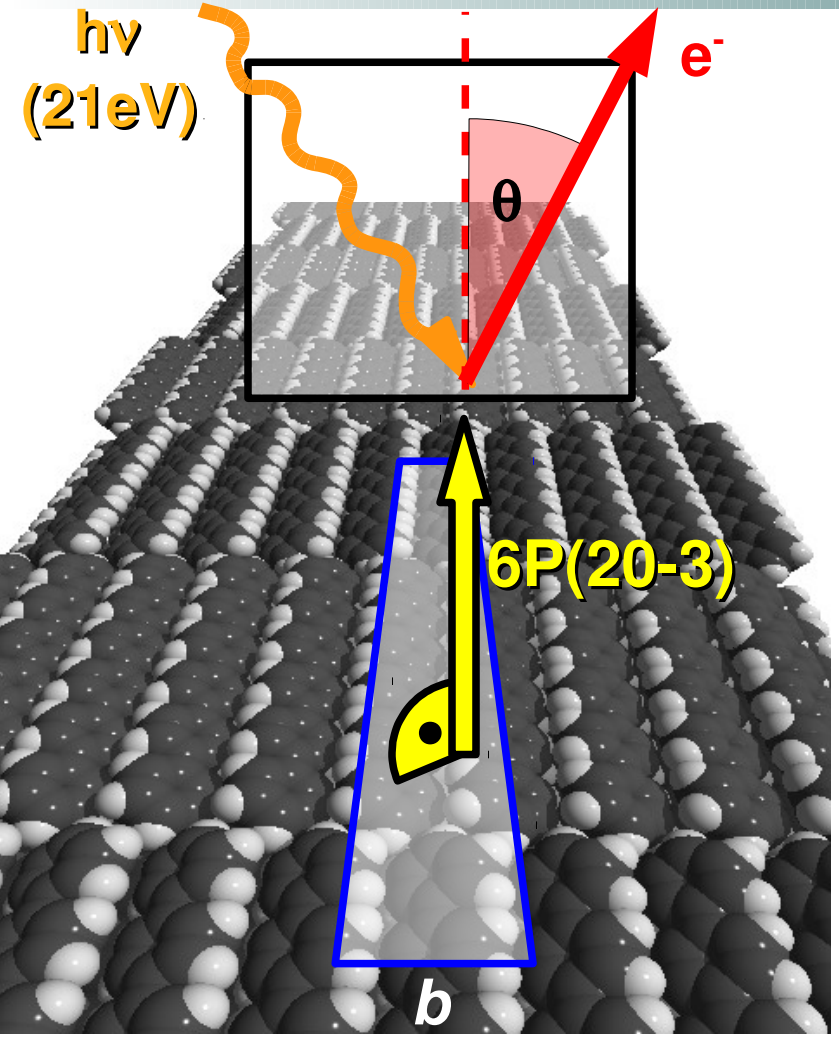




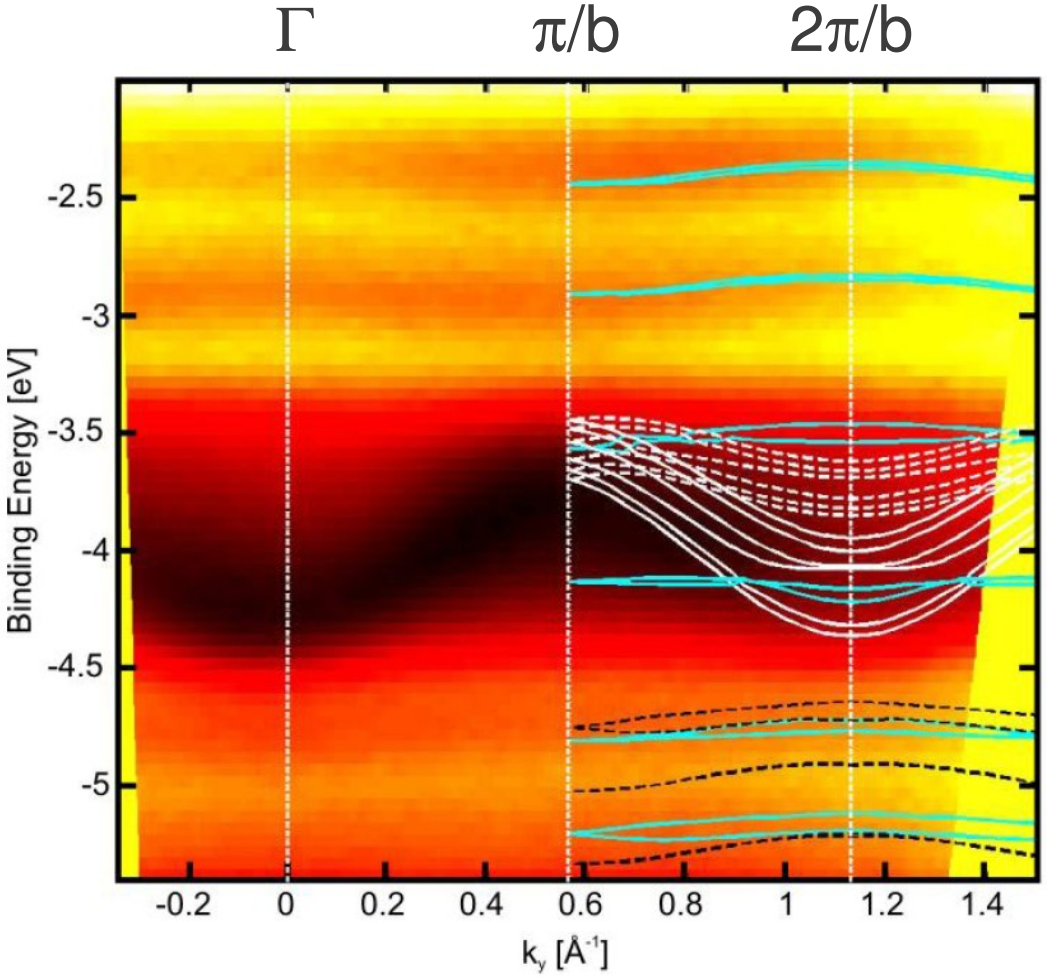
Ziroff et al., *Phys. Rev. Lett.* (June, 2010)

Ziroff et al., *Phys. Rev. Lett.* (June, 2010)

Intermolecular Dispersion



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



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