

PHYSICAL REVIEW B **84**, 235427 (2011)



## Orbital tomography:

# Deconvoluting photoemission spectra of organic molecules

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C. Ambrosch-Draxl,<sup>1</sup> and M. G. Ramsey<sup>2</sup>



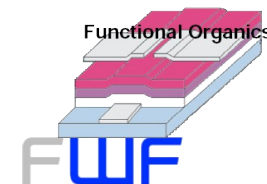
Austria



Austria

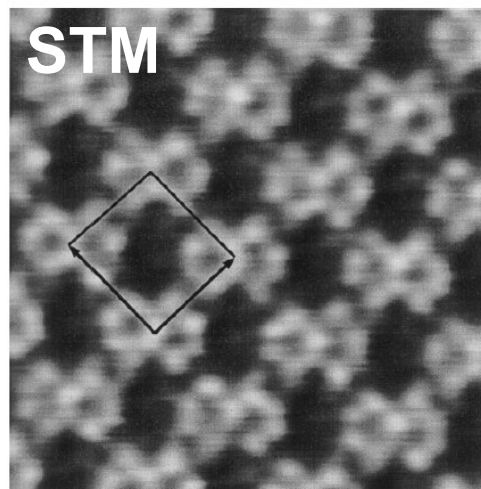
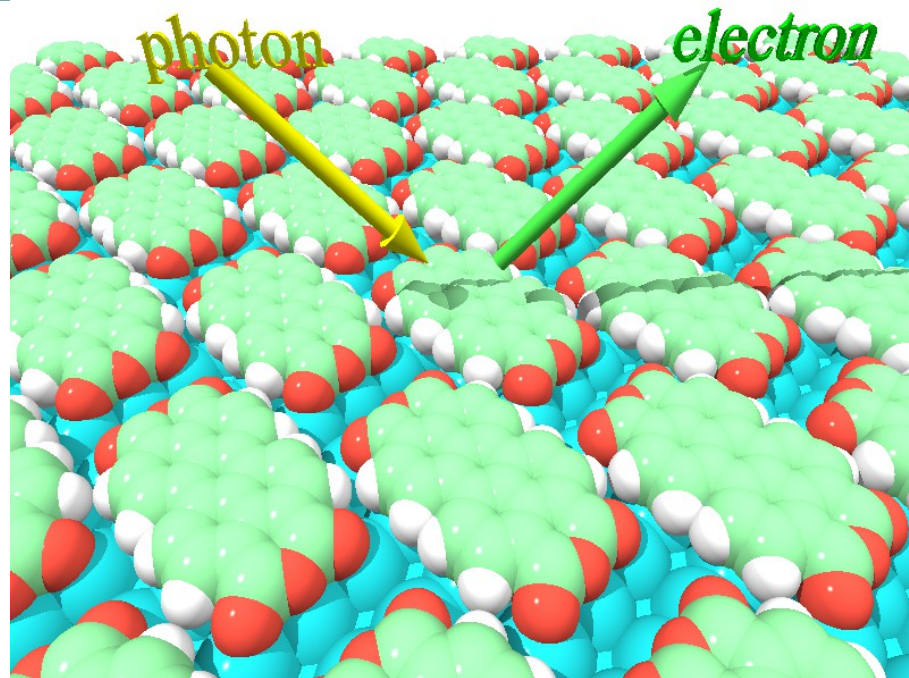
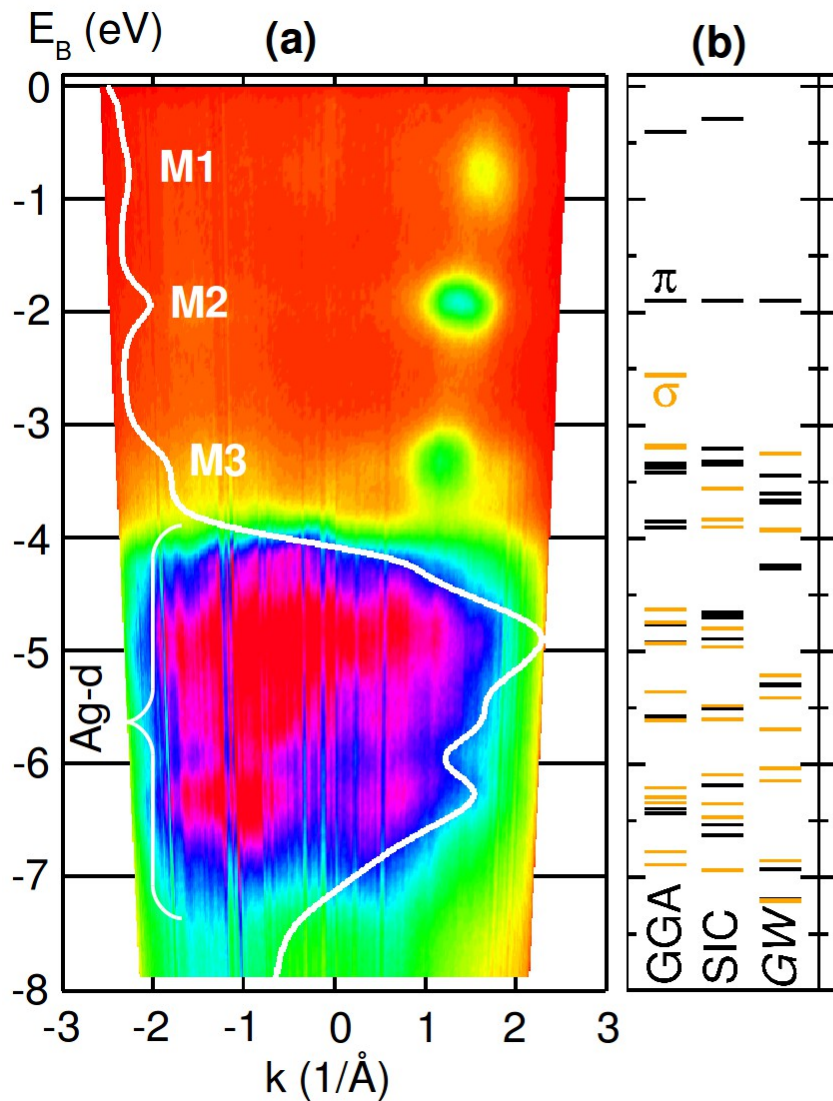


Germany

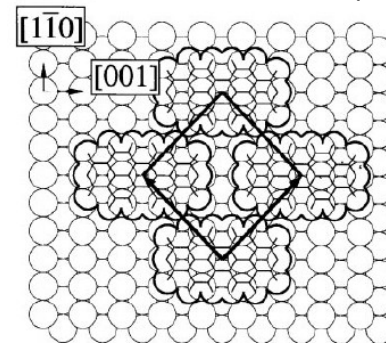


Austrian Science Fund  
P23190-N16

# ARPES of PTCDA / Ag(110)



Glöckler et al,  
*Surf. Sci.* **405**, 1-20 (1998).

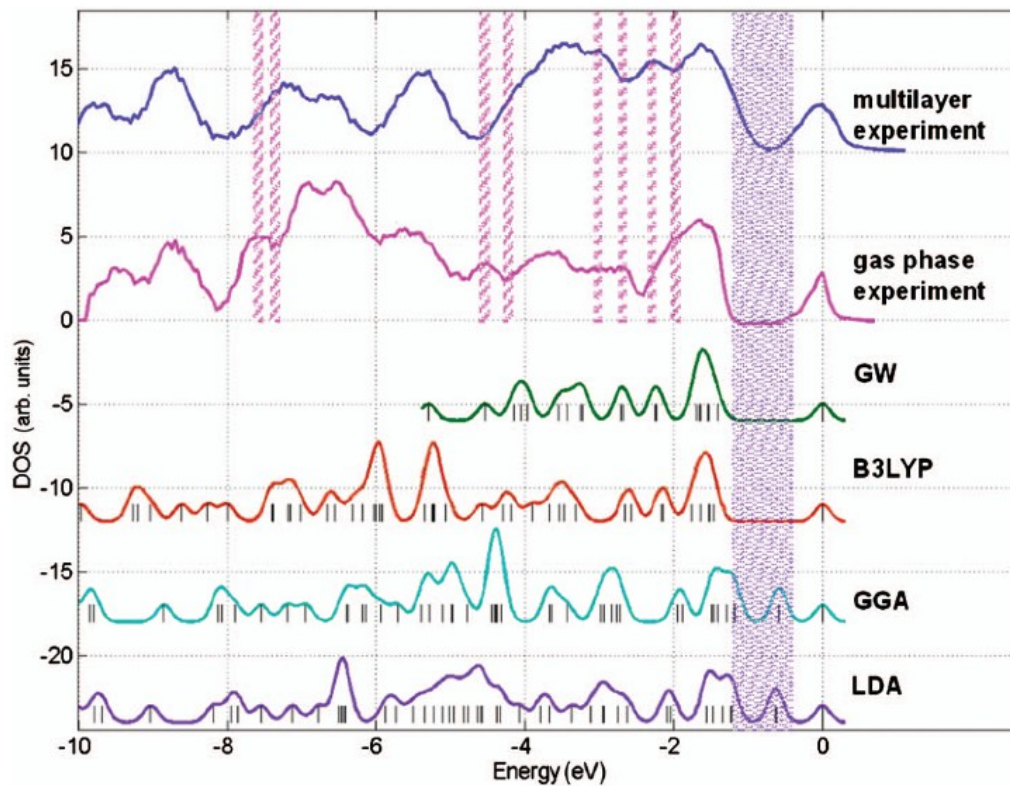


# Identifying Orbitals

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,<sup>1,\*</sup> Mahesh Menon,<sup>1,\*</sup> Lennart Kilian,<sup>2</sup> Moritz Sokolowski,<sup>2,3</sup> Leeor Kronik,<sup>1,†</sup> and Eberhard Umbach<sup>2</sup>



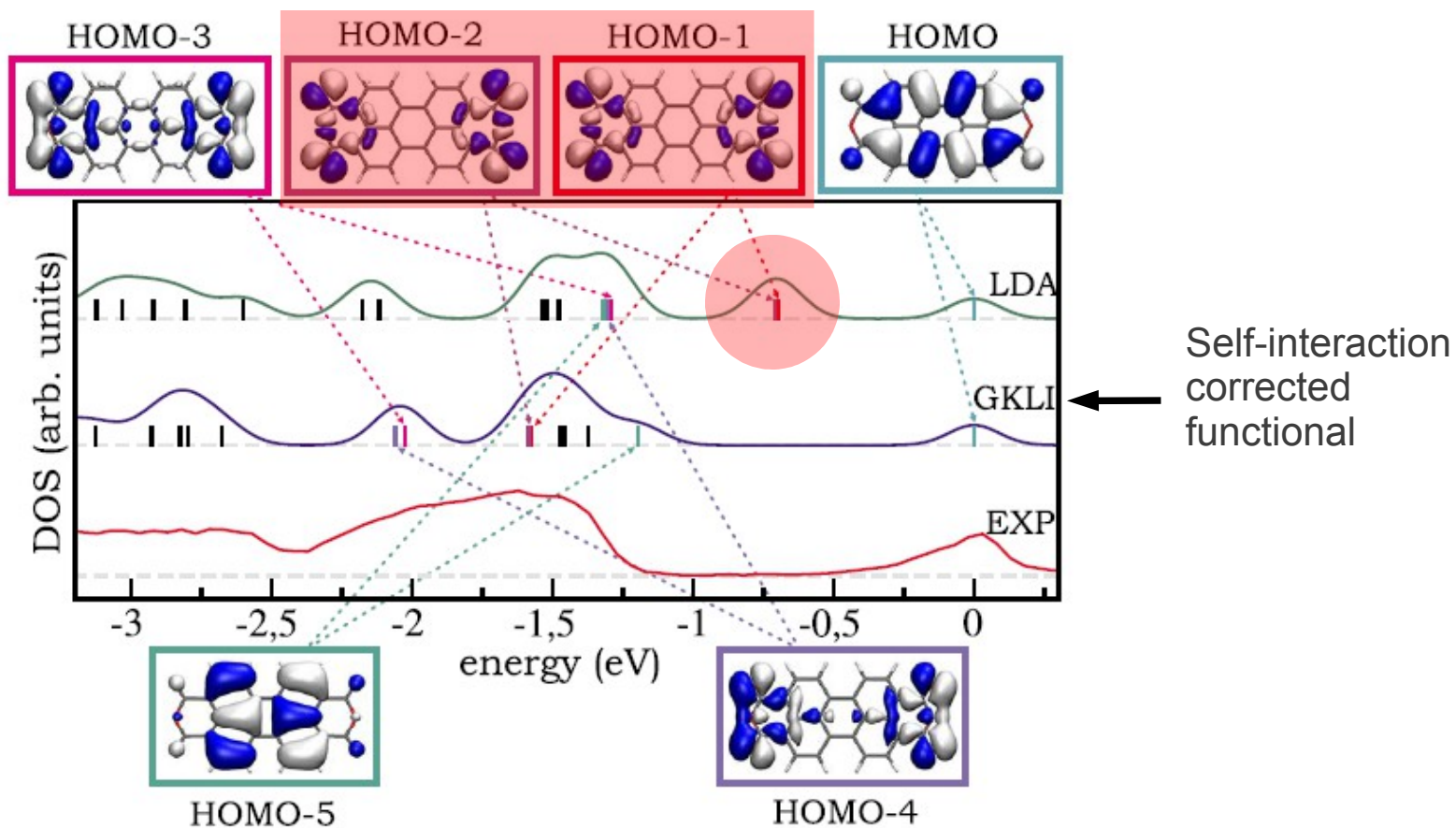


# Identifying Orbitals

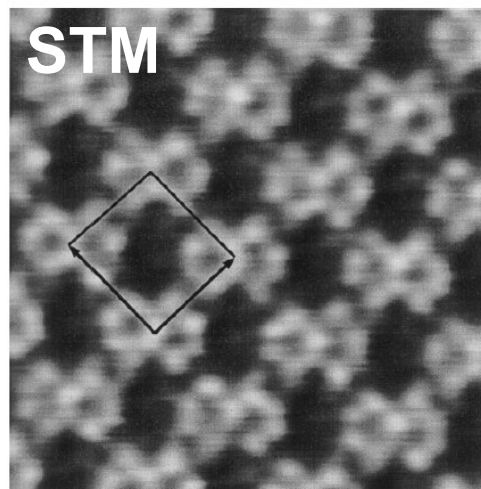
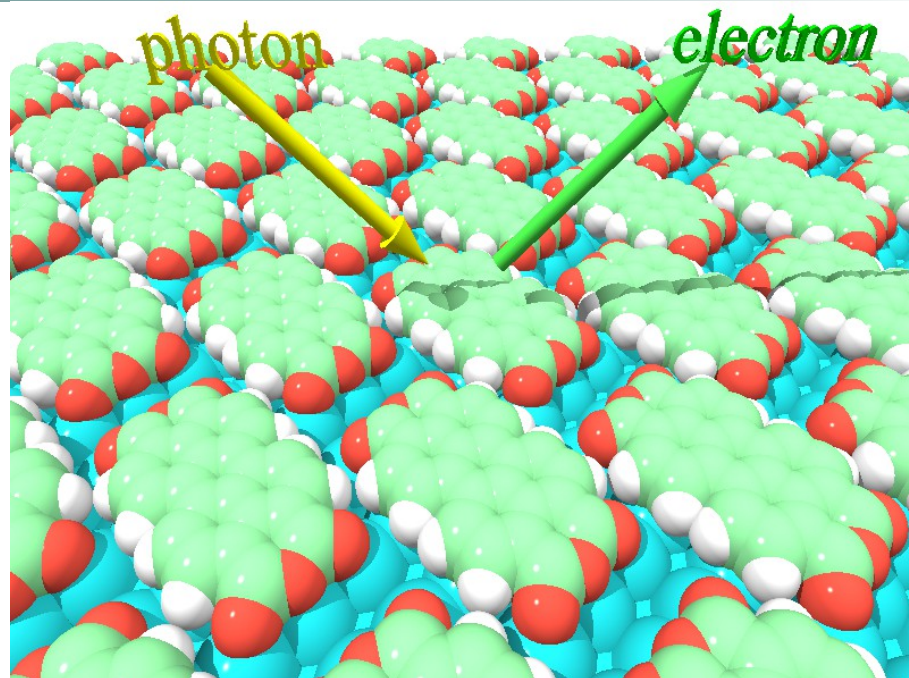
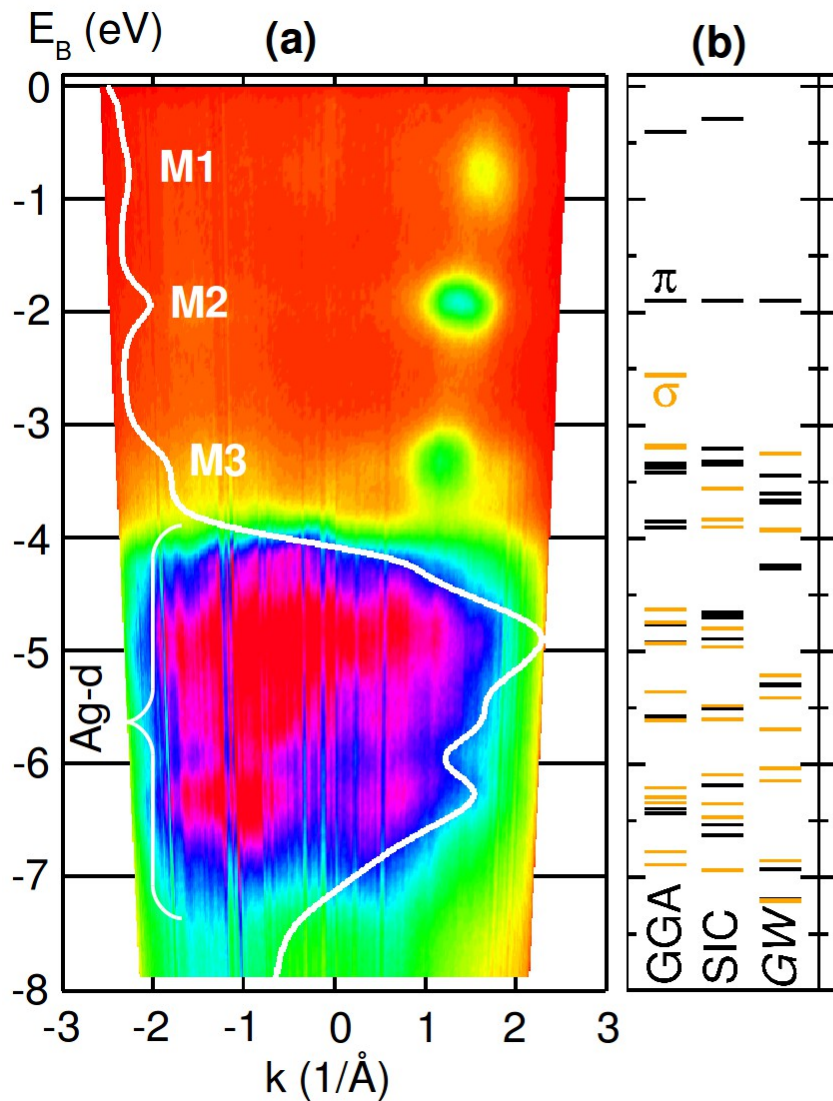
PHYSICAL REVIEW B 79, 201205(R) (2009)

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

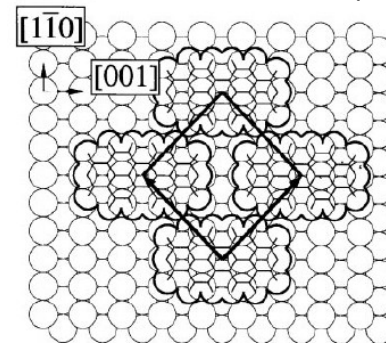
T. Körzdörfer and S. Kümmel      N. Marom and L. Kronik



# ARPES of PTCDA / Ag(110)



Glöckler et al,  
*Surf. Sci.* **405**, 1-20 (1998).



# Photoemission Intensity

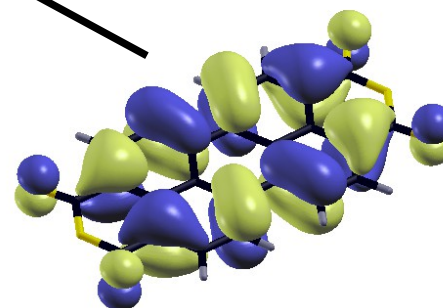
## One Step Model

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

# Photoemission Intensity

## One Step Model

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

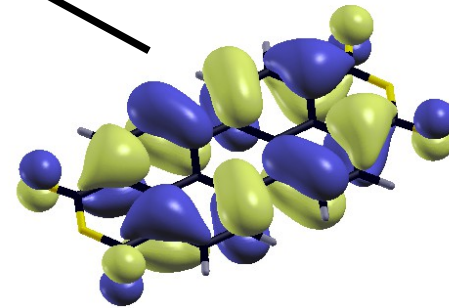
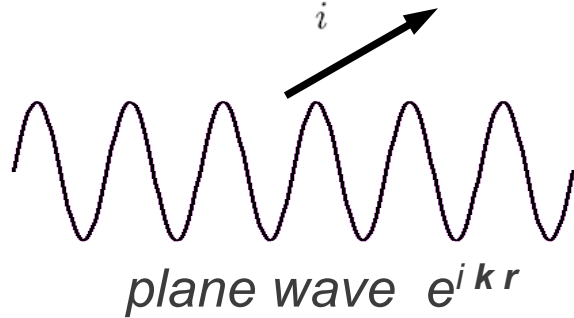


*molecular orbital*

# 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<sub>2</sub>

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

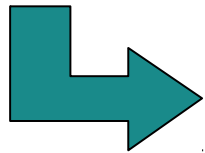
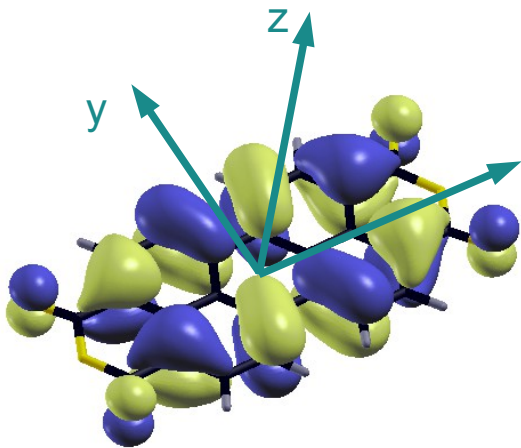
Fourier Transform of Initial State Orbital

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

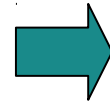
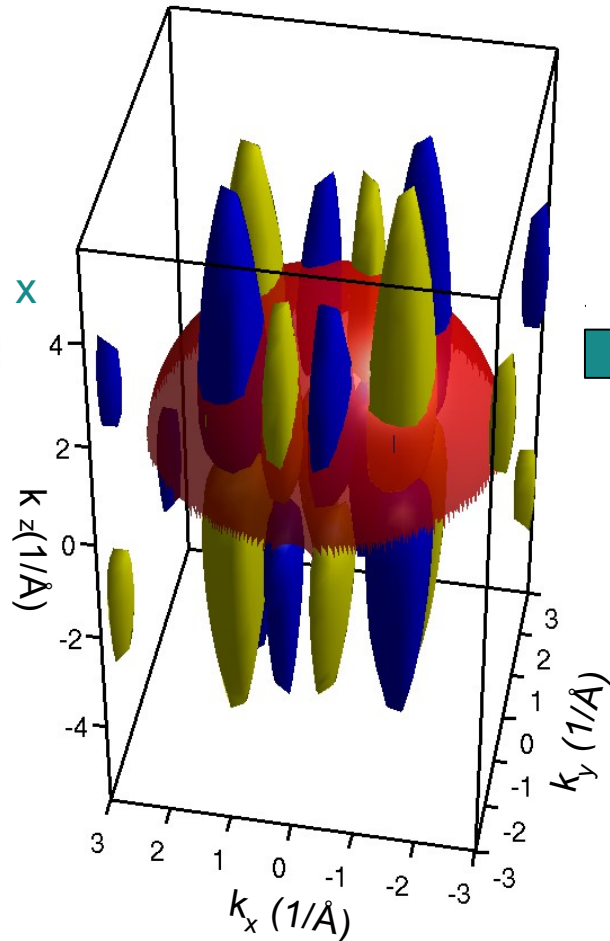


# Comparison with DFT

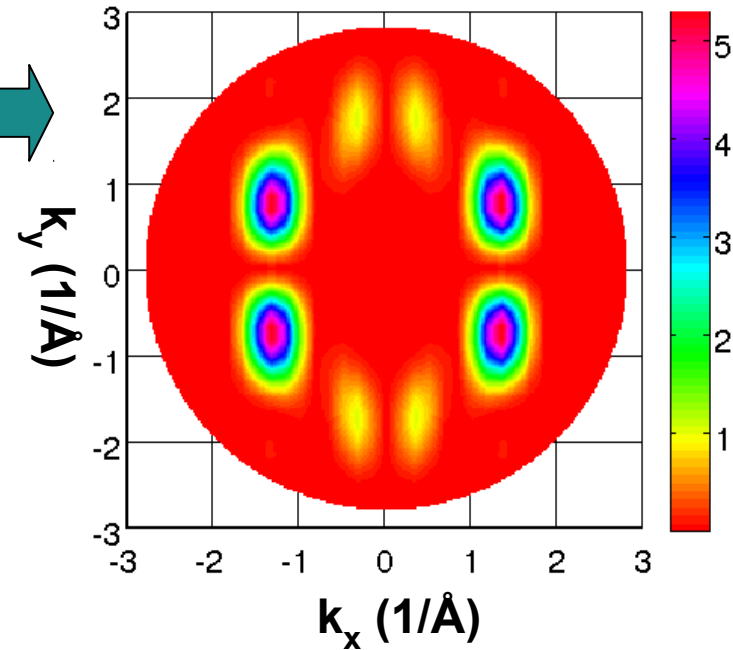
Molecular Orbital  
in Real Space



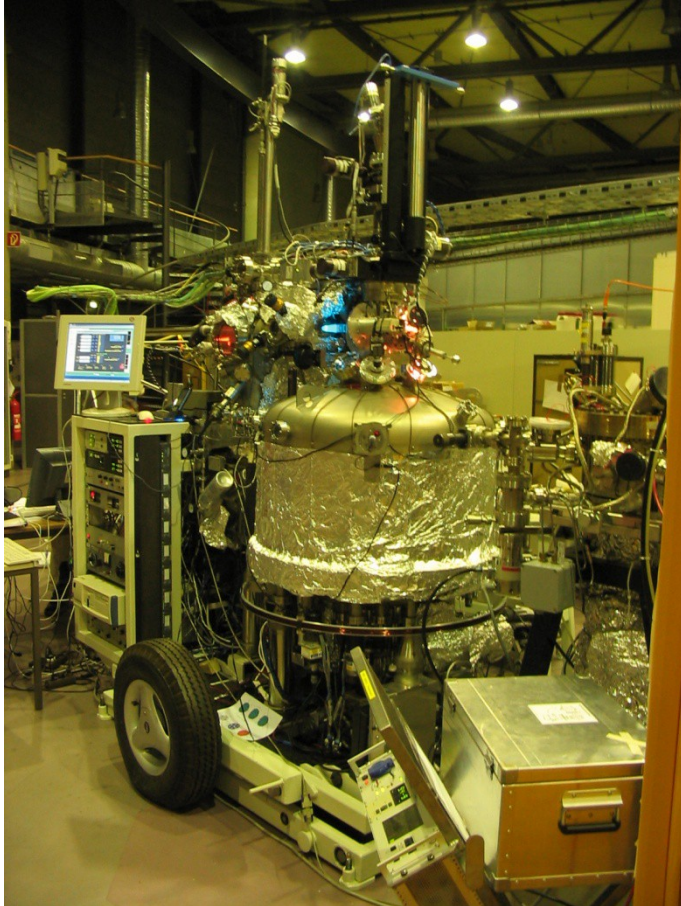
Calculation of  
the Fourier Transform



Hemispherical Cut Through  
3D Fourier Transform

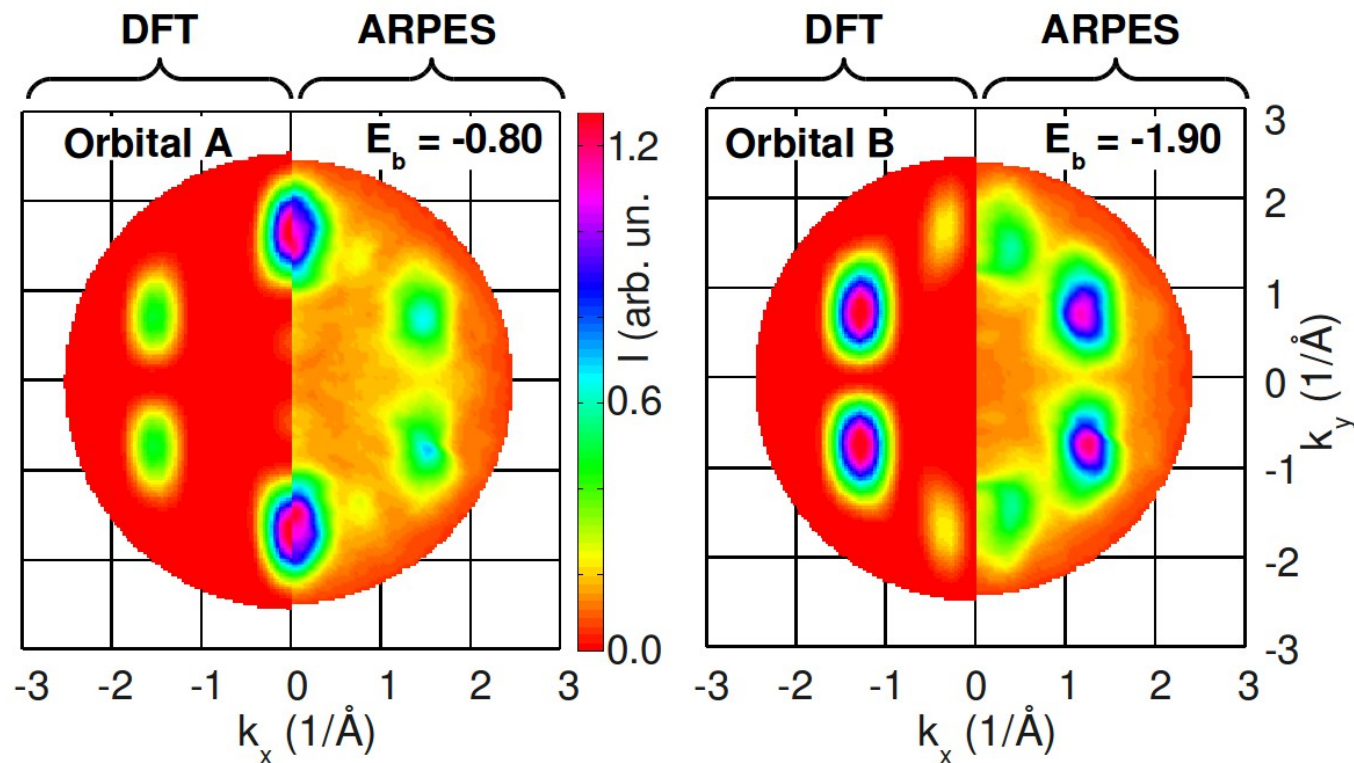


# Toroidal Electron Energy Analyzer

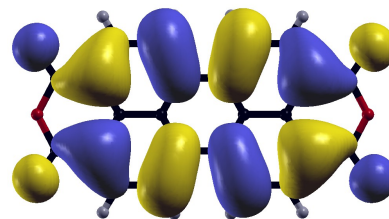
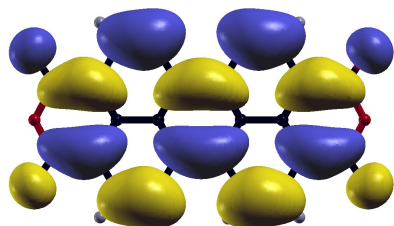


The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II

# HOMO and Filled LUMO



**M1=**  
**FLUMO**

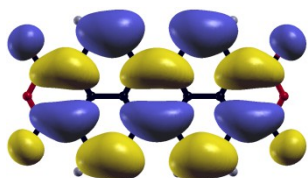


**M2=**  
**HOMO**

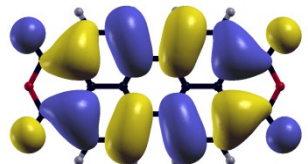
Puschnig et al. PRB **84**, 235427 (2011), Ziroff et al., PRL **104**, 233004 (2010).

# What is the nature of M3?

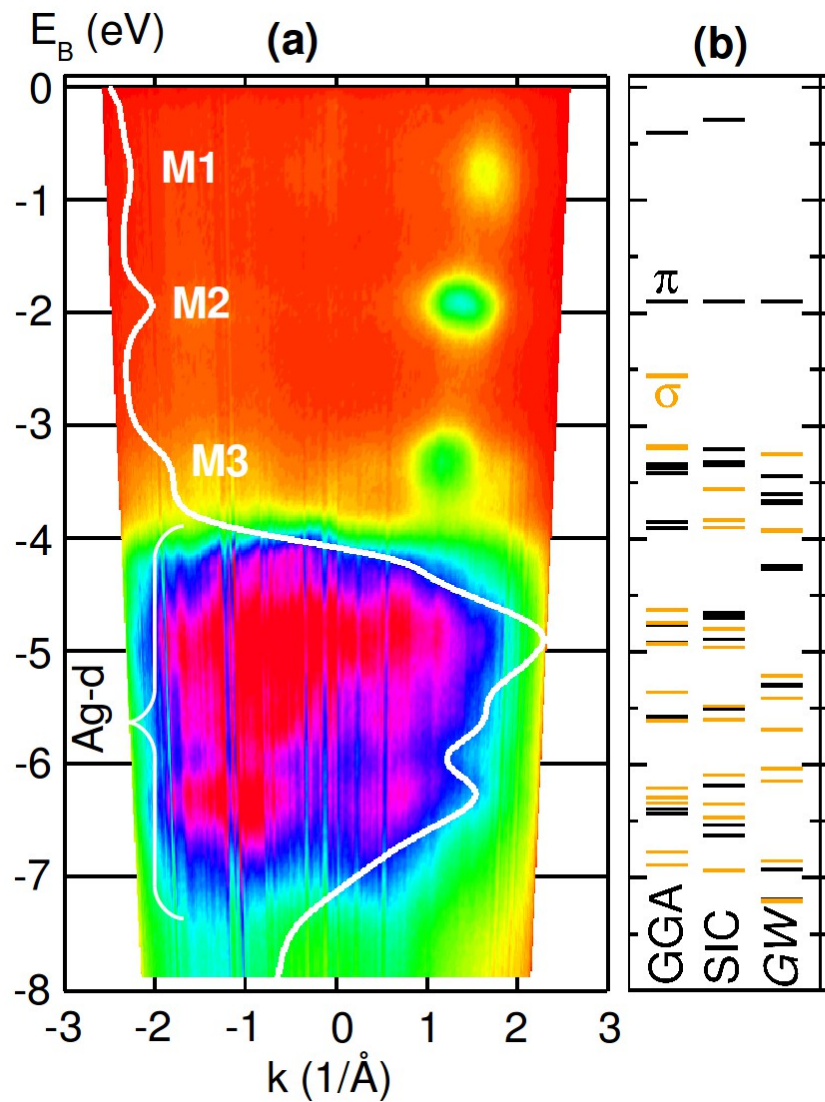
M1=  
FLUMO



M2=  
HOMO

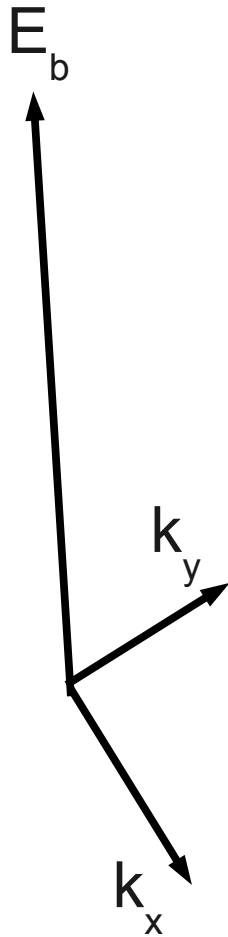


?

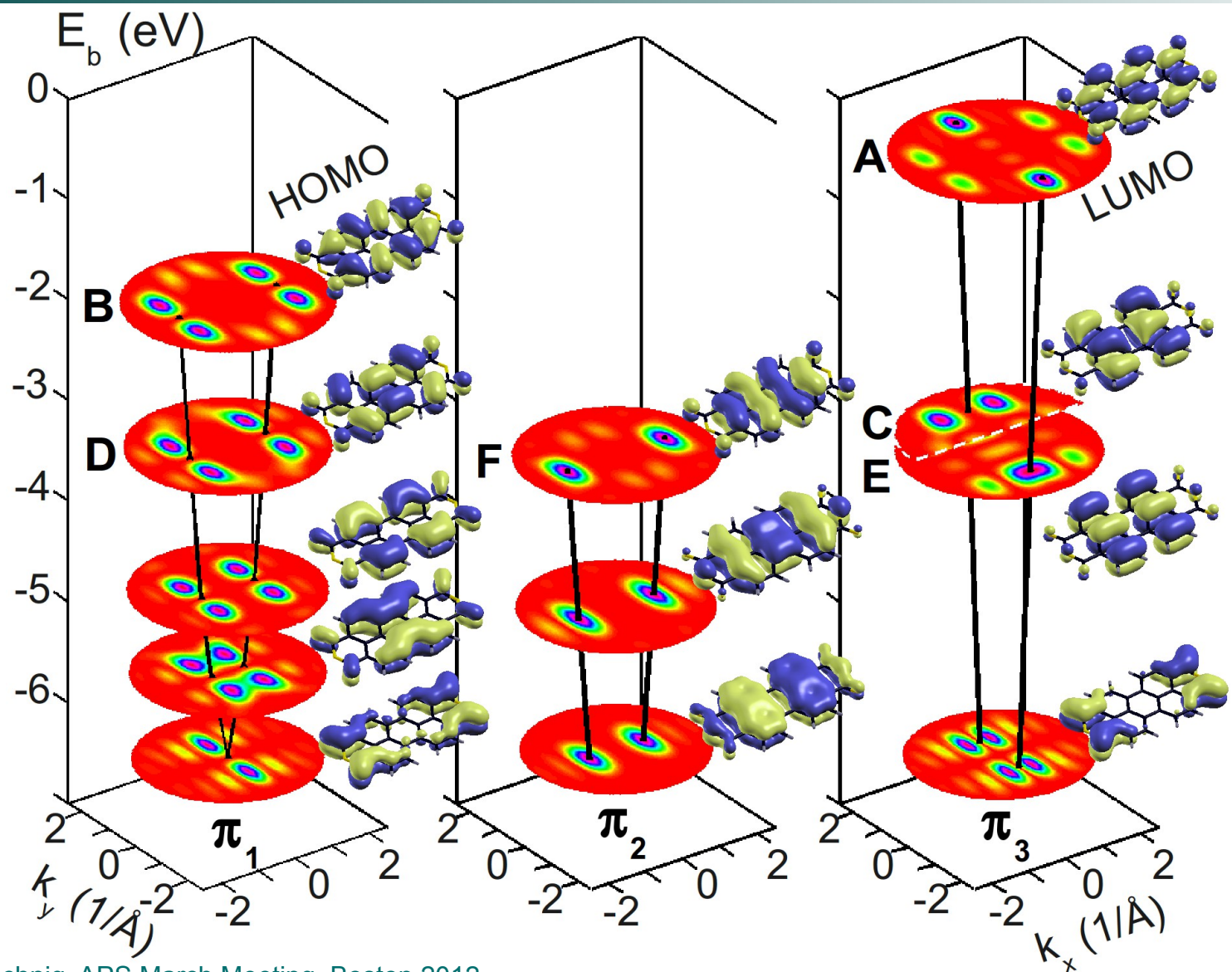




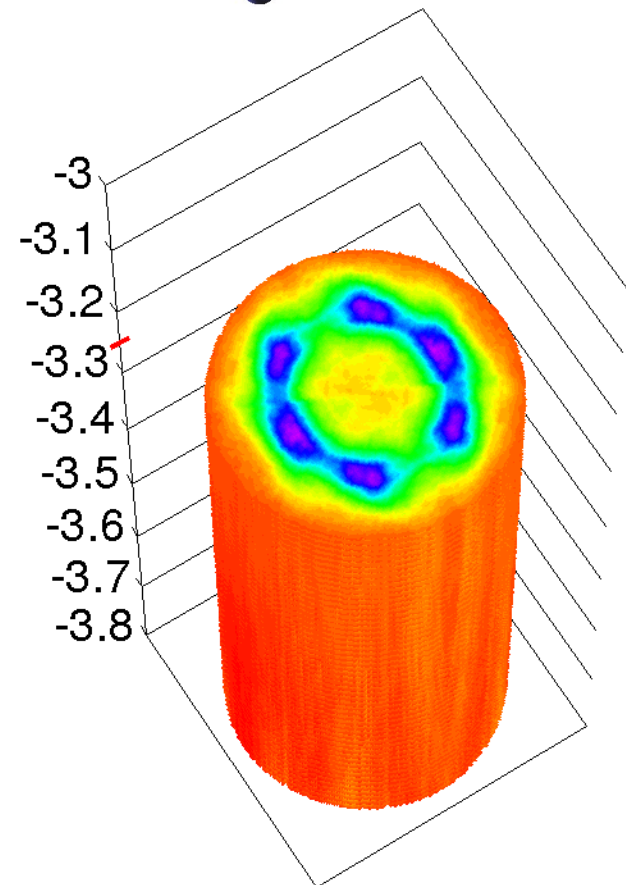
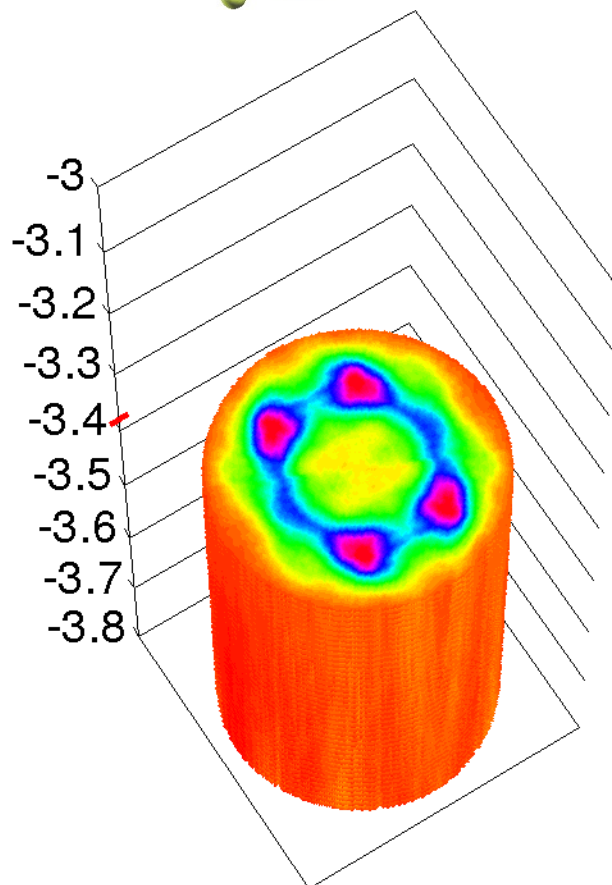
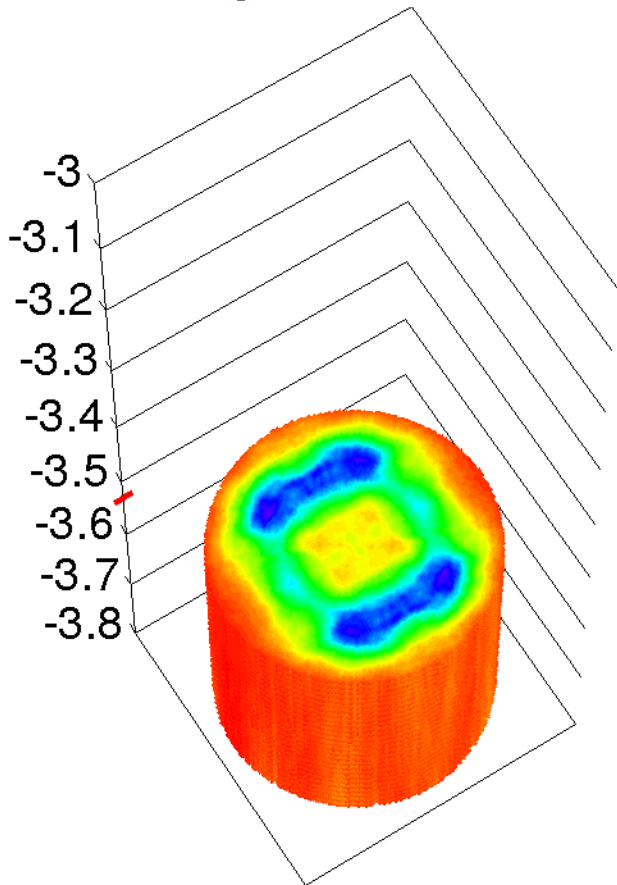
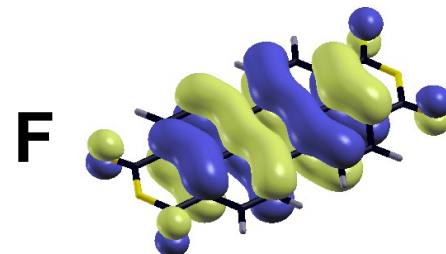
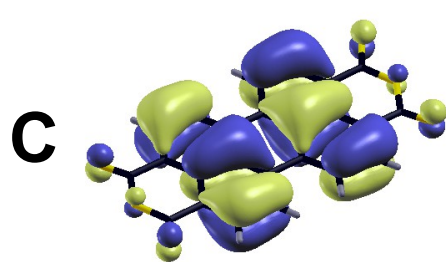
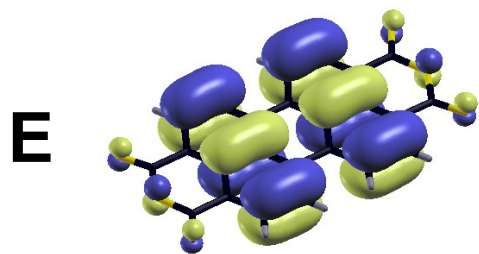
# ARPES Data-Cube



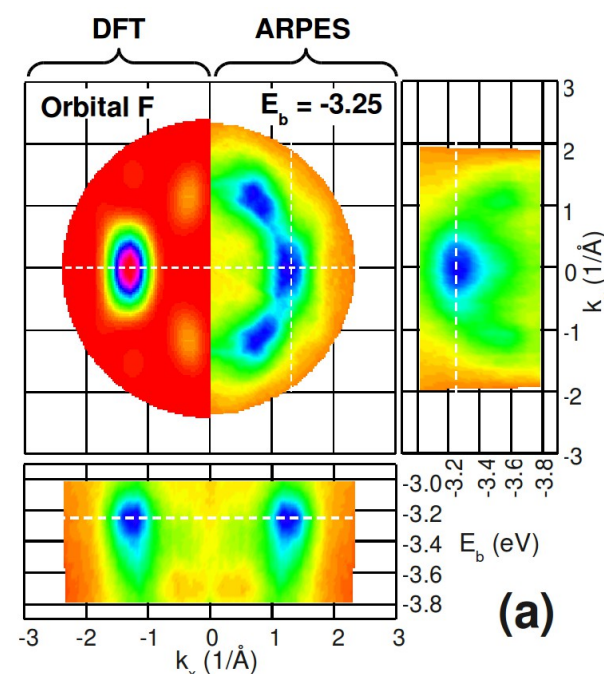
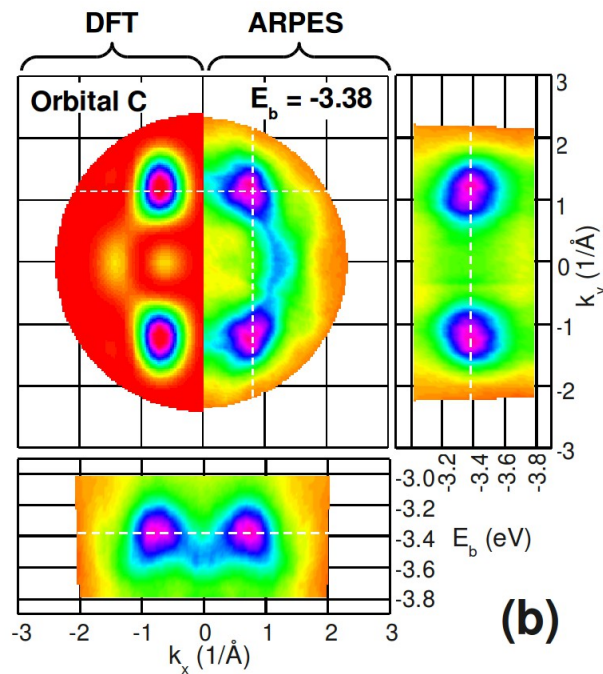
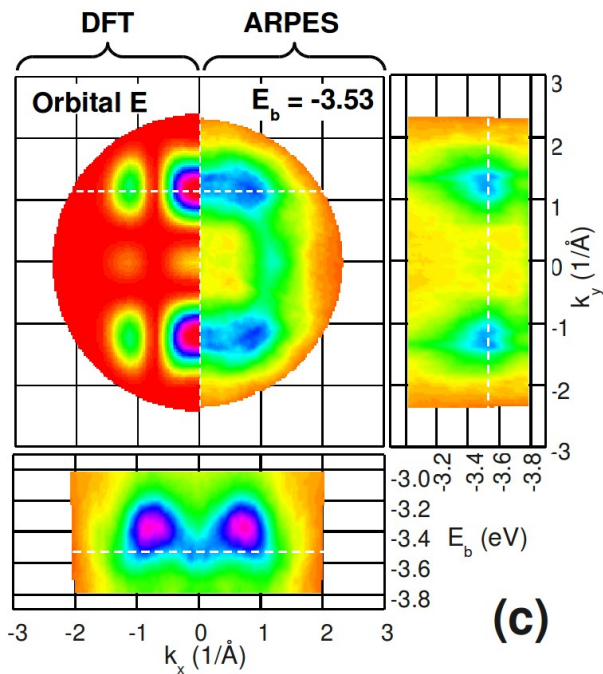
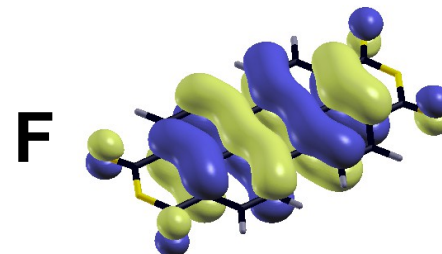
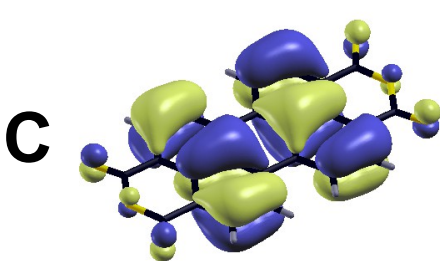
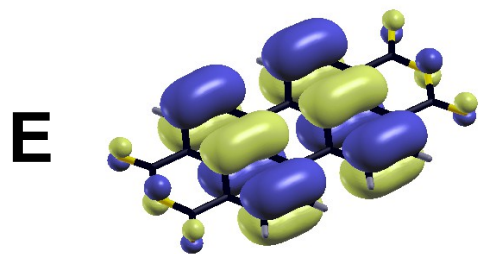
# $\pi$ -bands of PTCDA



# What is the Origin of M3?



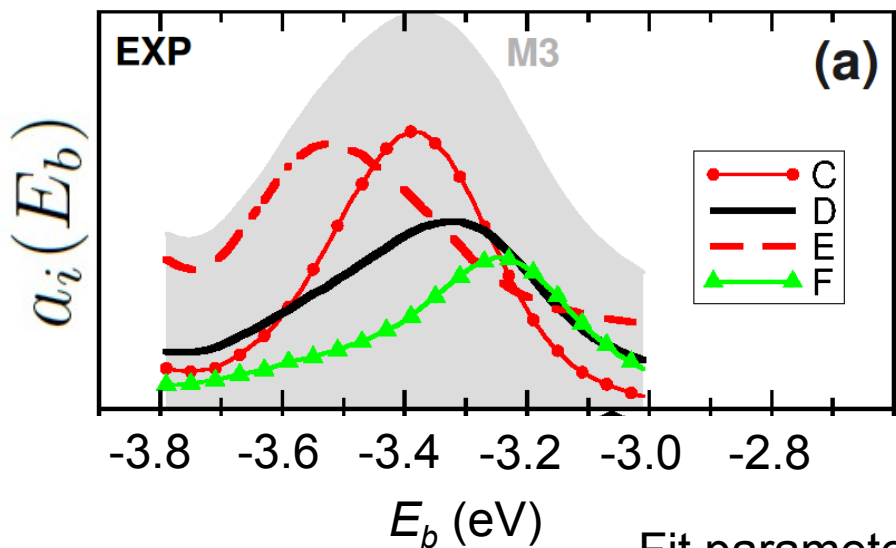
# What is the Origin of M3?



Puschnig et al. PRB **84**, 235427 (2011), see also: Dauth et al., PRL **107**, 193002 (2011).



# Projected DOS from ARPES!

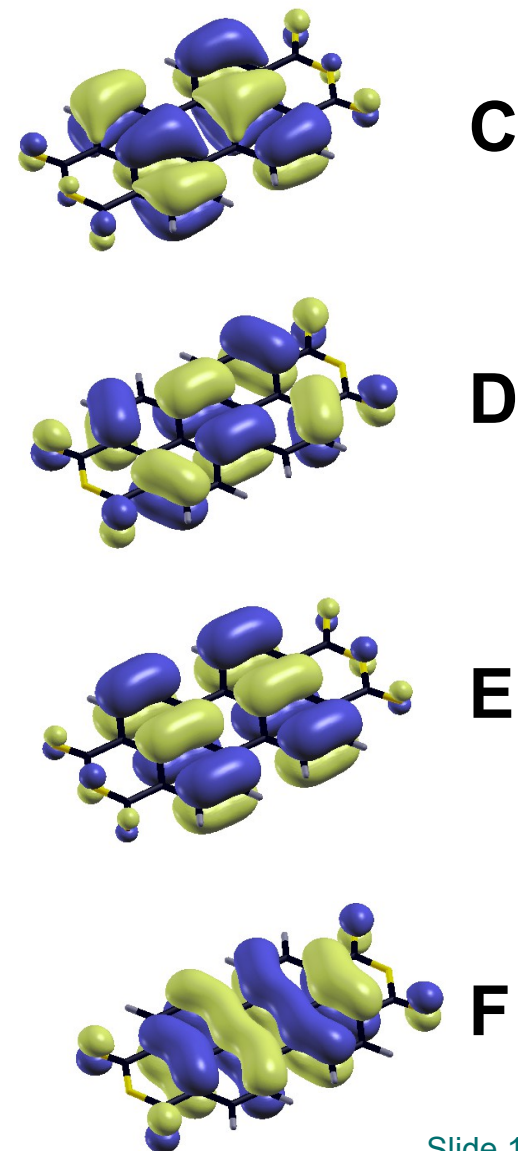


Fit parameters  
= PDOS

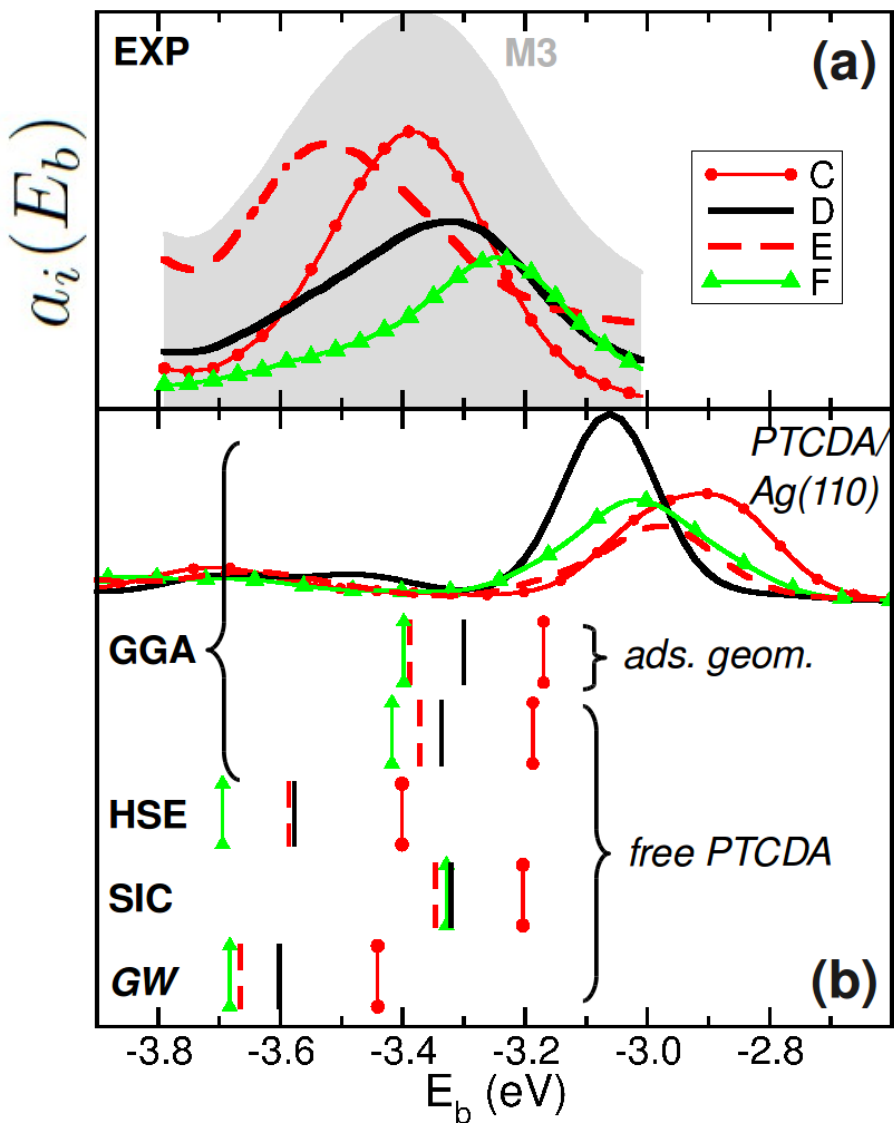
calculated  
orbitals

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

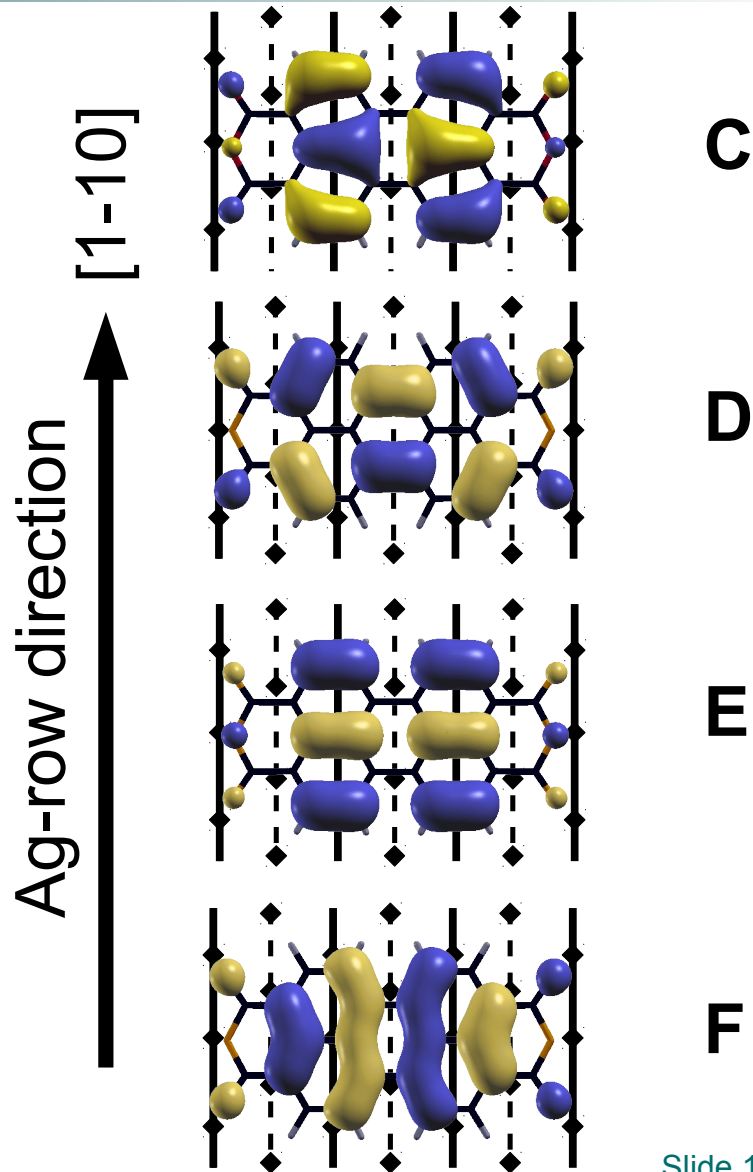
measured  
photoemission  
data cube



# Benchmark for Theory



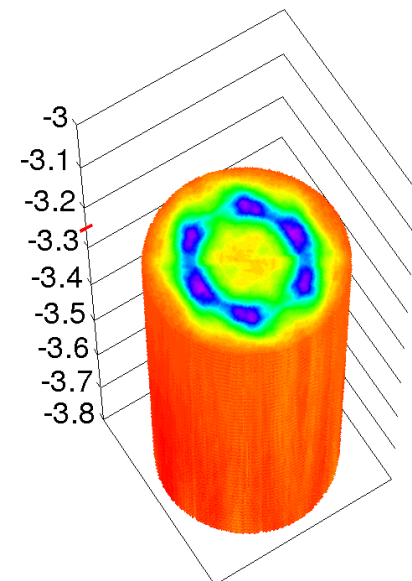
orbital energies / projected DOS (arb. units)



# Conclusion

## Orbital Tomography

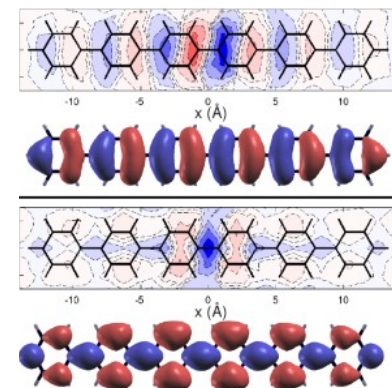
- Make use of characteristic momentum space patterns
- Unambiguous identification of molecular features
- Density of states projected onto molecular orbitals
- Deconvolution beyond limits of energy resolution



## Other Applications

### Real space reconstruction of molecular orbital densities

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



### Hybridization of molecular orbitals mit metallic states

Ziroff et al., *Phys. Rev. Lett.* **104**, 233004 (2010).

Berkebile et al., *Phys. Chem. Chem. Phys.* **13**, 3604 (2011).