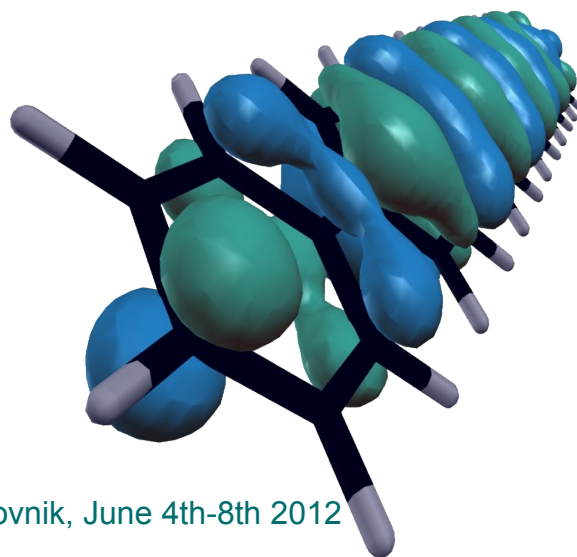
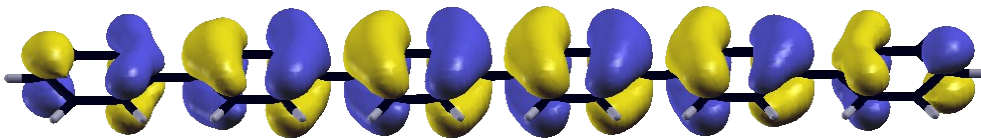
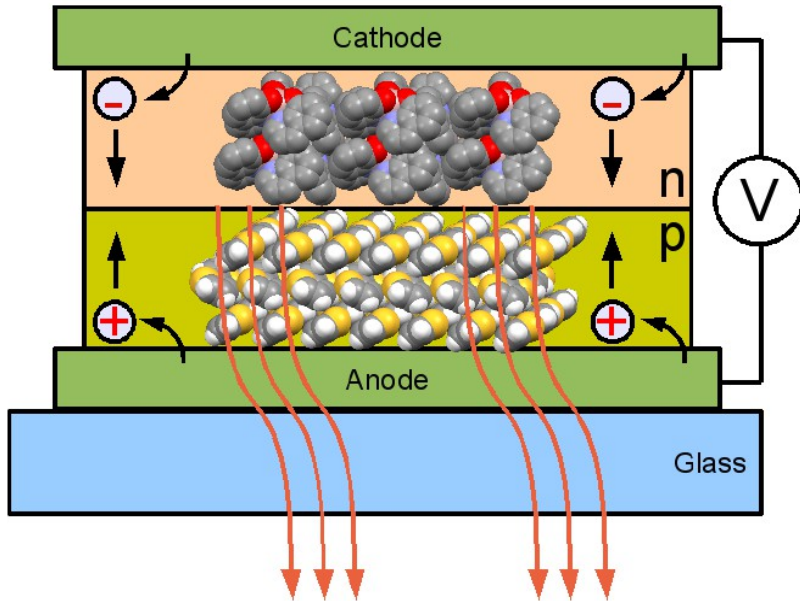


Growth and Electronic Structure of Organic Molecular Layers Studied by Density Functional Theory



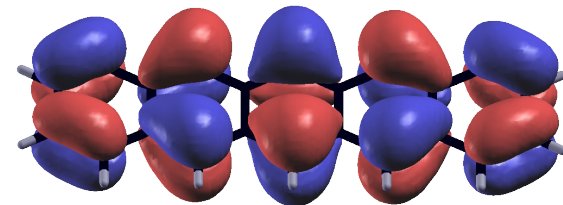
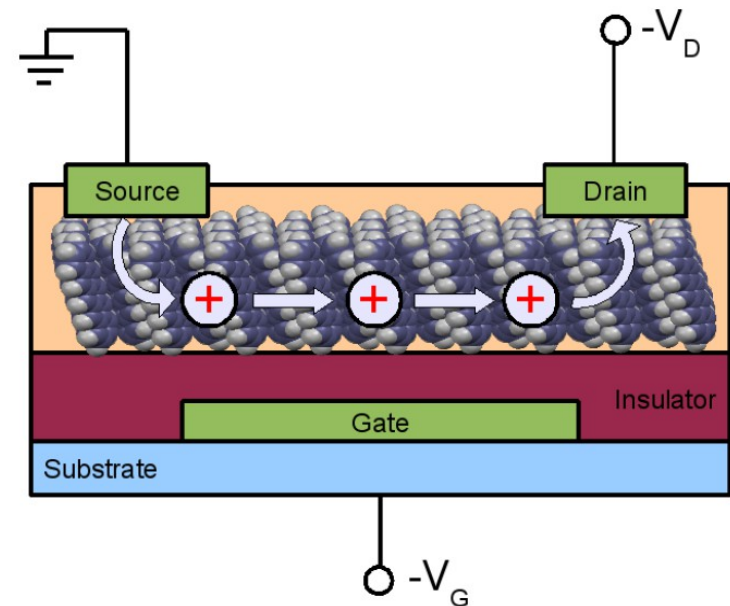
Motivation

OLED



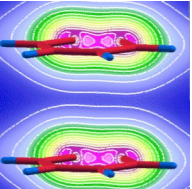
para-Sexiphenyl (6P) ($C_{36}H_{26}$)

OFET

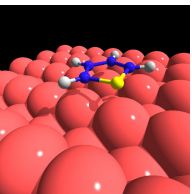


Pentacene (5A) ($C_{22}H_{14}$)

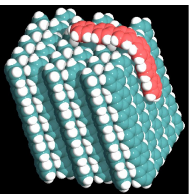
Outline



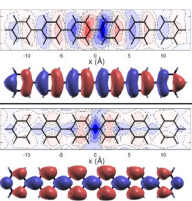
1. Density Functional Theory in a Nutshell



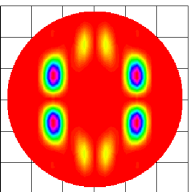
2. Van der Waals Forces: Surface / Adsorption Energies



3. Step-Edge Barrier in Organic Thin Film Growth



4. Orbital Densities from Angle-Resolved Photoemission



5. Dissecting Orbitals: Tomography in Reciprocal Space

Outline



1. Density Functional Theory in a Nutshell



2. Van der Waals Forces: Surface / Adsorption Energies



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Density Functional Theory in a Nutshell

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

$$-\frac{Z}{r}$$

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

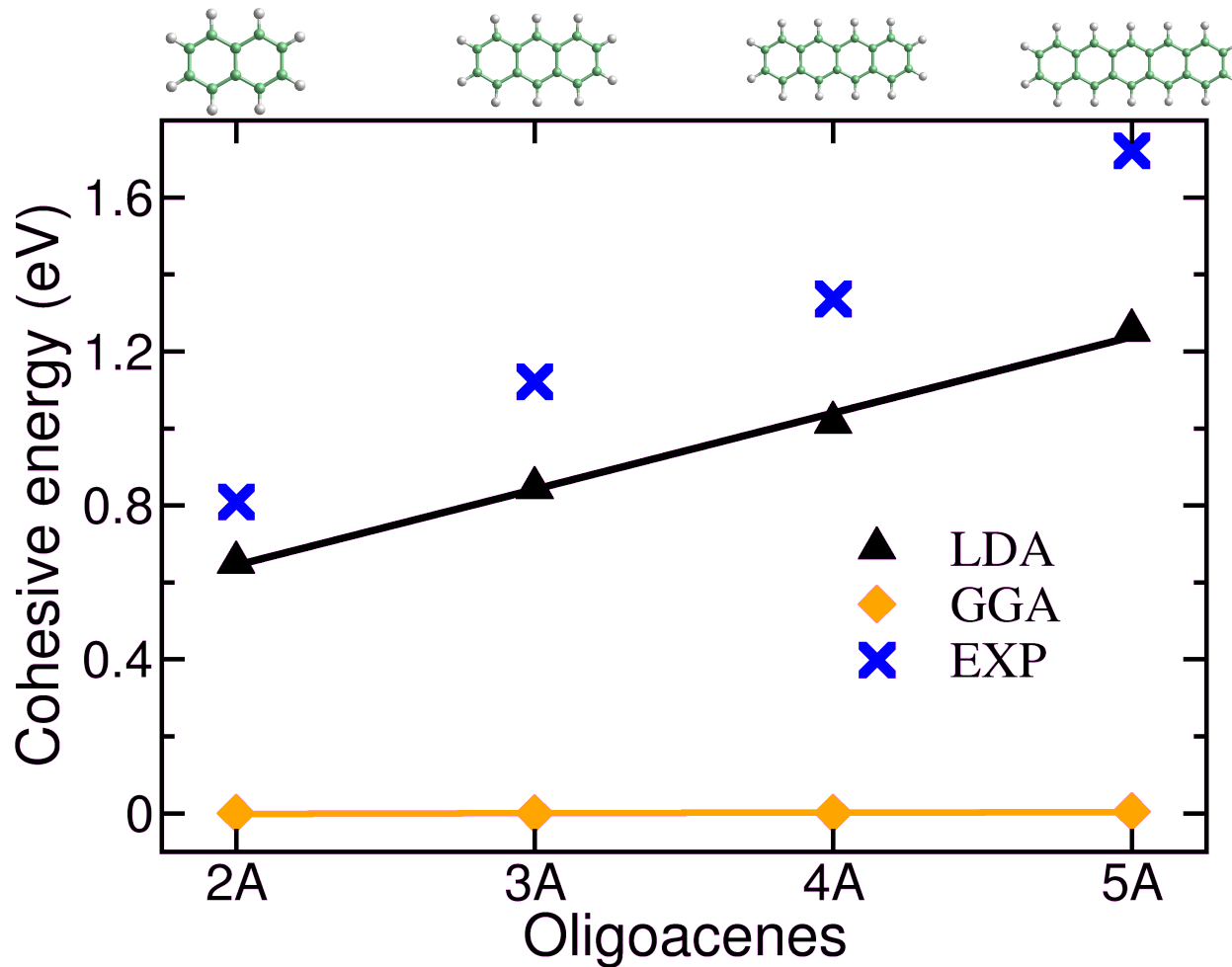
$$\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Self-consistency

Approximations:
e.g.: LDA, GGA, ...

$$n(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2$$

Cohesive Energy of Molecular Crystals



Van der Waals Density Functional

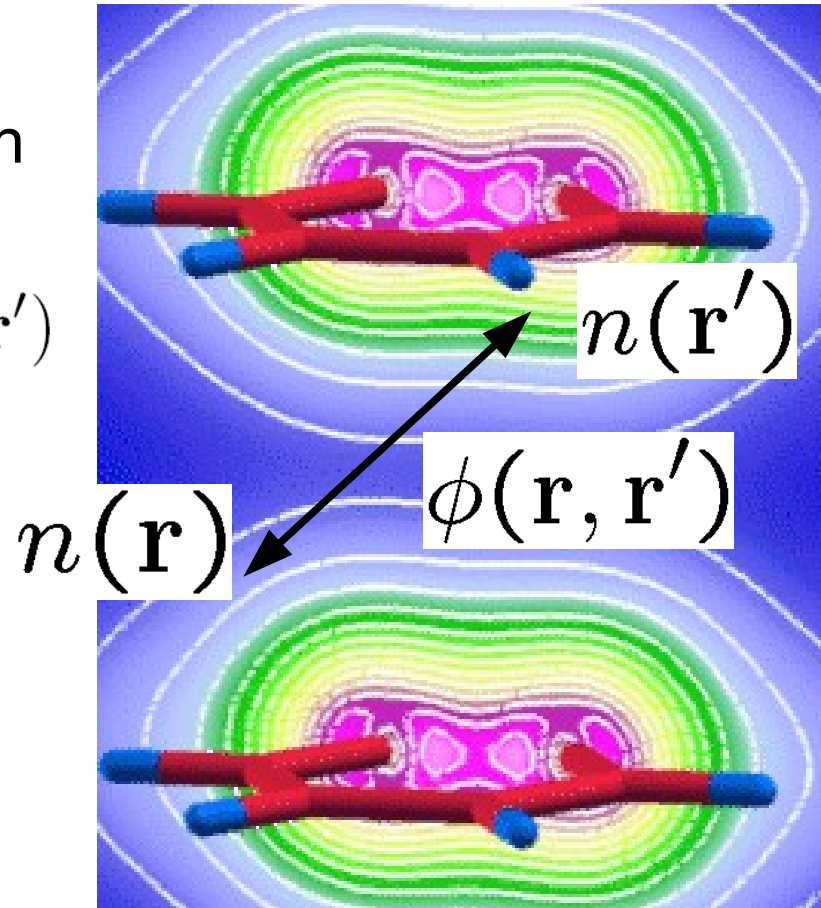
Nonlocal Correlation Energy
leading to van-der-Waals interaction

$$E_c^{\text{nl}} = \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$

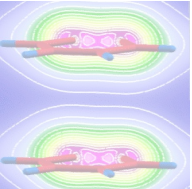
Exchange-Correlation Energy

$$E_{xc}^{\text{vdWDF}} = E_x^{\text{GGA}} + E_c^{\text{LDA}} + E_c^{\text{nl}}$$

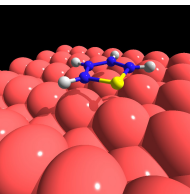
Dion et al, *Phys. Rev. Lett.* **92**, 246401 (2004).



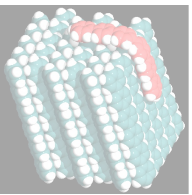
Outline



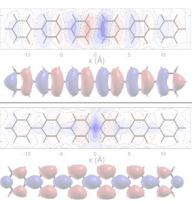
1. Density Functional Theory in a Nutshell



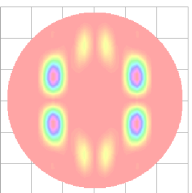
2. Van der Waals Forces: Surface/Adsorption Energies



3. Step-Edge Barrier in Organic Thin Film Growth

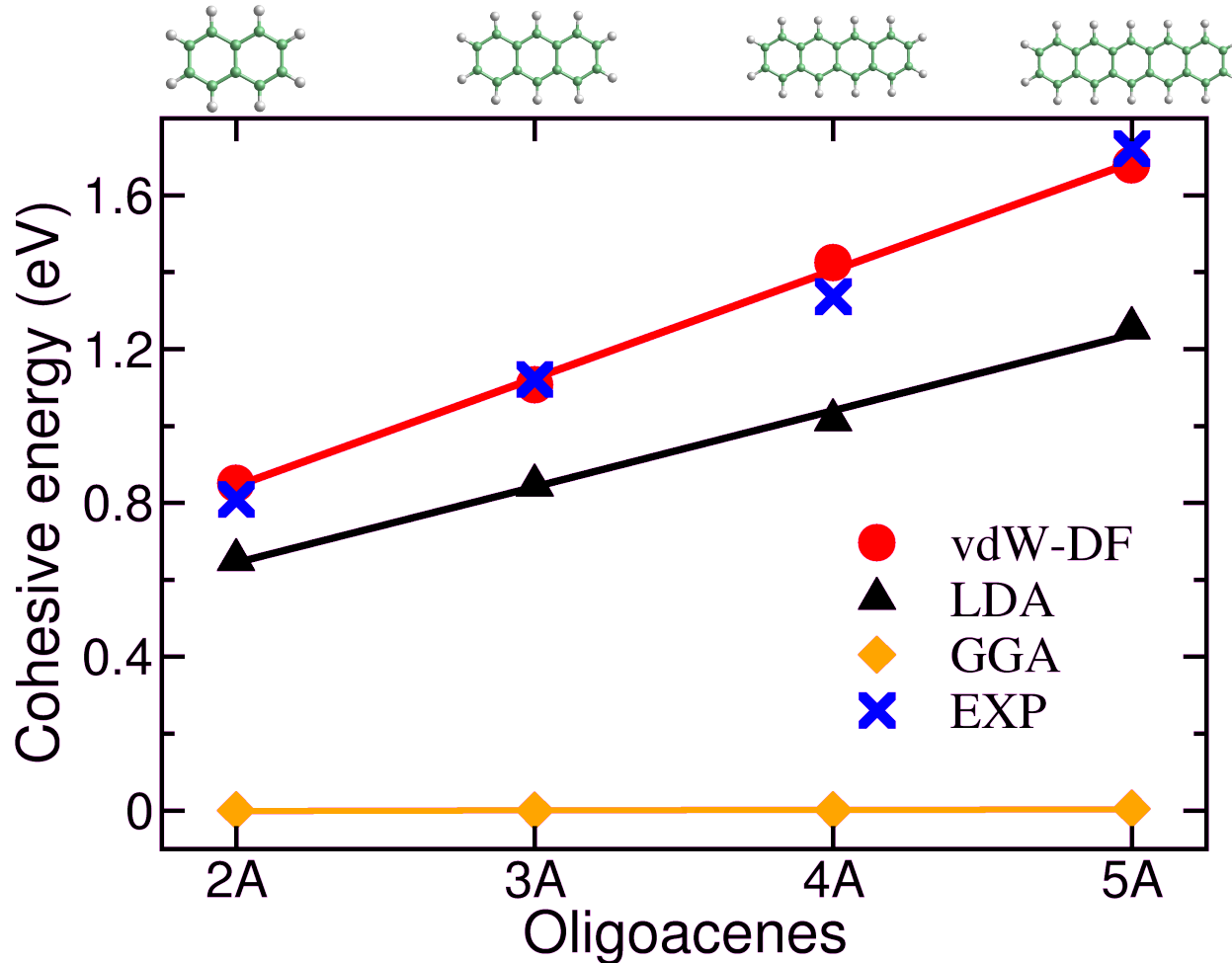


4. Orbital Densities from Angle-Resolved Photoemission



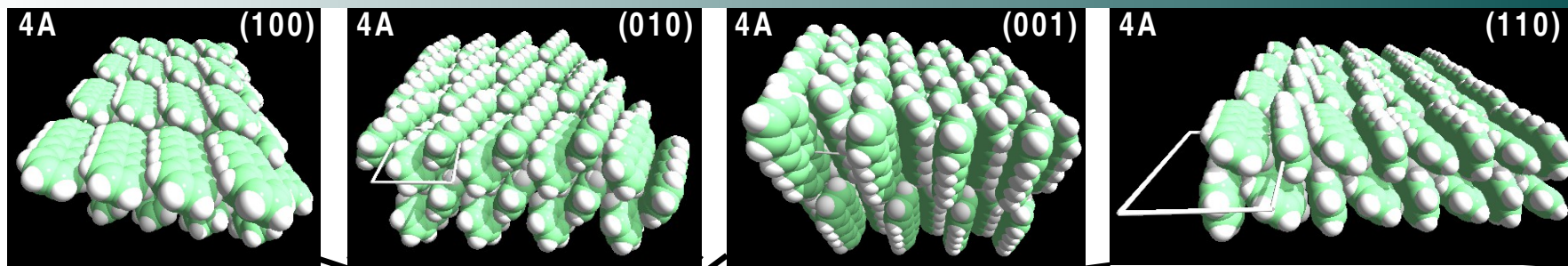
5. Dissecting Orbitals: Tomography in Reciprocal Space

Cohesive Energy of Molecular Crystals



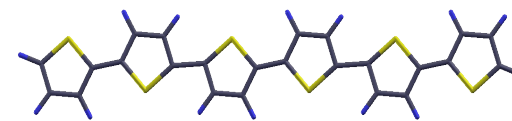
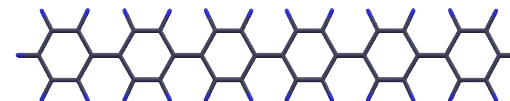
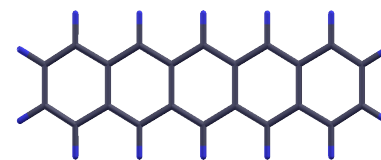
Nabok, Puschnig, Ambrosch-Draxl, *Phys. Rev. B* **77**, 245316 (2008).

Surface Energies of Molecular Crystals



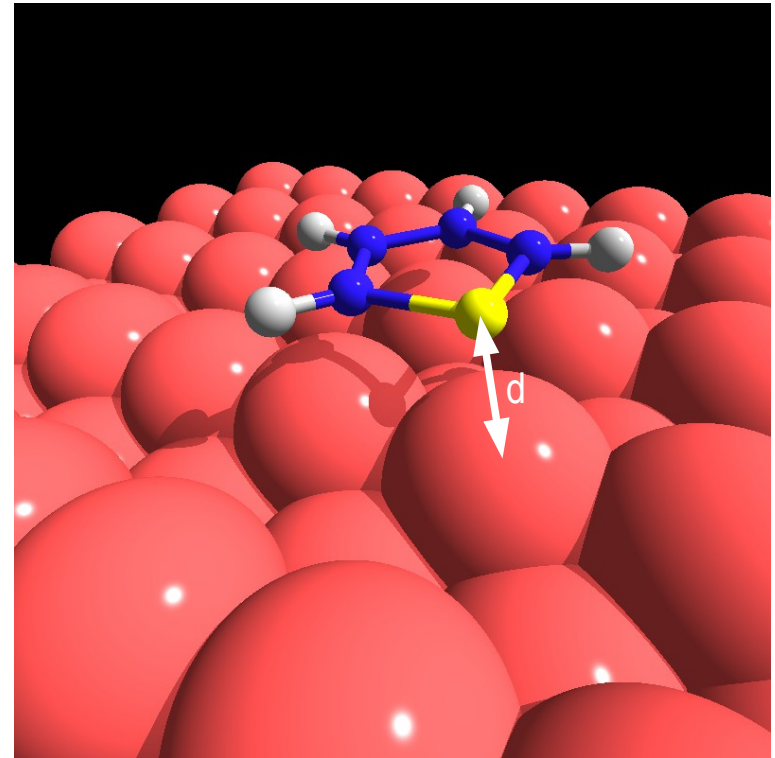
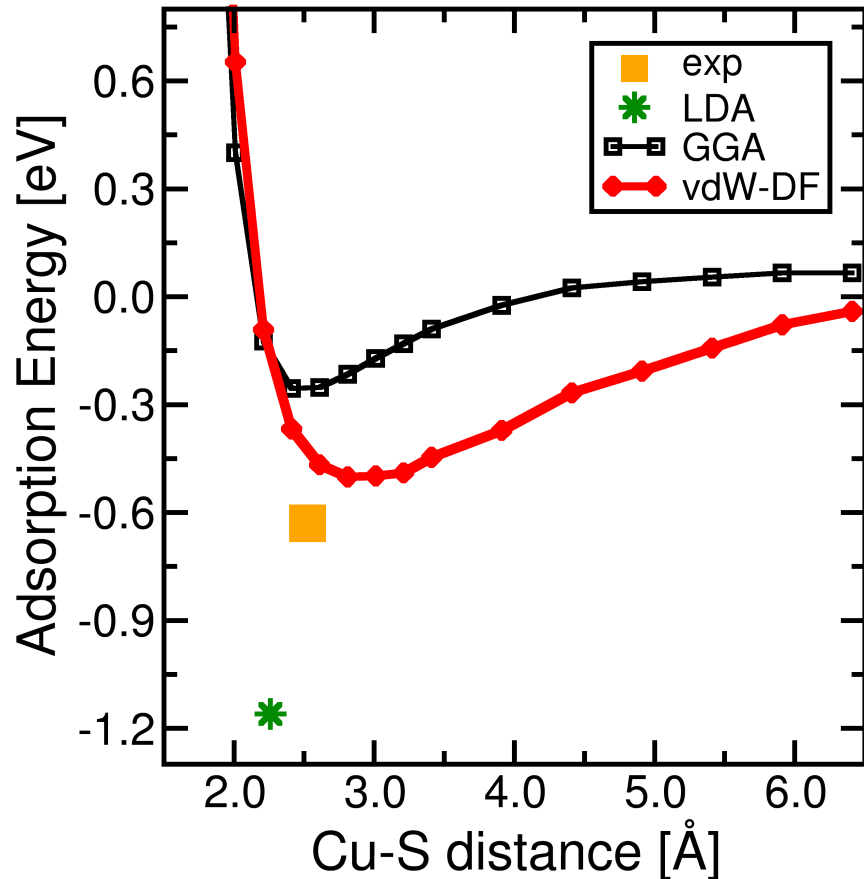
γ [mJ/m^2]

	(100)	(010)	(001)	(110)
2A	102	107	90	120
3A	100 (88 ^a) [66 ^b]	115 (118 ^a) [91 ^b]	81 (76 ^a) [53 ^b]	108 (90 ^a)
4A	109	124	84	106
5A	107 [77 ^b]	130 [103 ^b {140 ^c }	82 [50 ^b {76 ^c }	113 [75 ^b {150 ^c }
2P	122	129	97	118
3P	124	136	99	123
4P	124	140	96	124
6P	142	142	107	135
2T	147	123	110	121
4T	134	133	102	125
6T	176	128	115	146



Nabok et al. *Phys. Rev. B* **77**, 245316 (2008); Ambrosch-Draxl et al., *New J. Phys.* **11**, 125010 (2009).

Thiophene / Cu(110)



Thiophene@Cu(110): Sony et al., *Phys. Rev. Lett.* **99**, 176401 (2007).

PTCDA@Cu,Ag,Au(111): Romaner et al., *New. J. Phys.* **11**, 053010 (2009).

Van-der-Waals-Bibliography

Ab-initio vdW-Density Functional

Theory

- Dion et al, *Phys. Rev. Lett.* **92**, 246401 (2004).
Thonhauser et al., *Phys. Rev. B*, **76**, 125112 (2007)
Vydrov et al., *Phys. Rev. Lett.*, **103**, 063004 (2009)
Lee et al. *Phys. Rev. B* **82**, 081101 (2010)

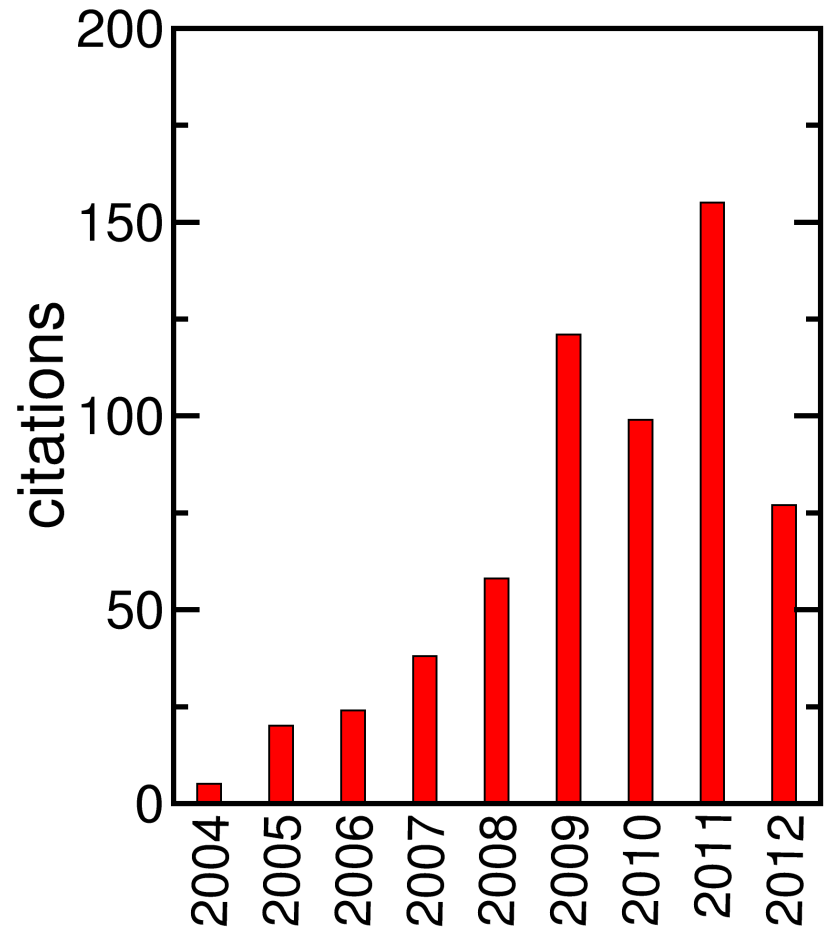
Efficient Implementations

- Roman-Perez et al. *Phys. Rev. Lett.* **103**, 096102 (2009).
Vydrov et al., *J. Chem. Phys.* **132**, 164113 (2010).
Lazic et al. *Comp. Phys. Commun.* **181**, 371 – 379 (2010).
Nabok et al. *Comp. Phys. Commun.* **182**, 1657-1662 (2011).

Applications

... huge number ...

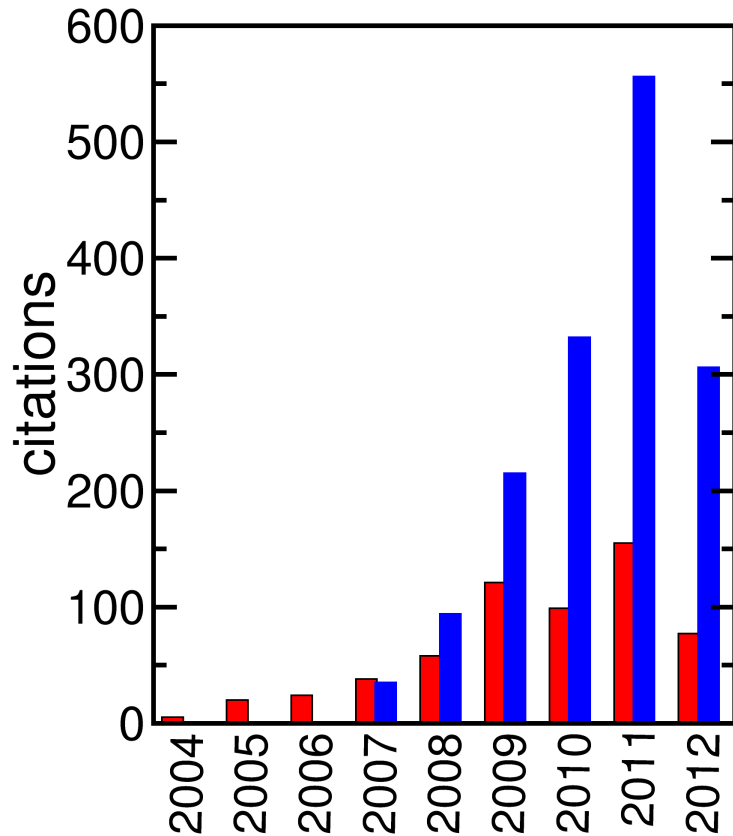
- Brief Review see e.g.:
Langreth et al., *J. Phys.: CM* **21**, 084203 (2009)



Van-der-Waals-Bibliography

Ab-initio vdW-DF

Dion et al, *Phys. Rev. Lett.* **92**, 246401 (2004).

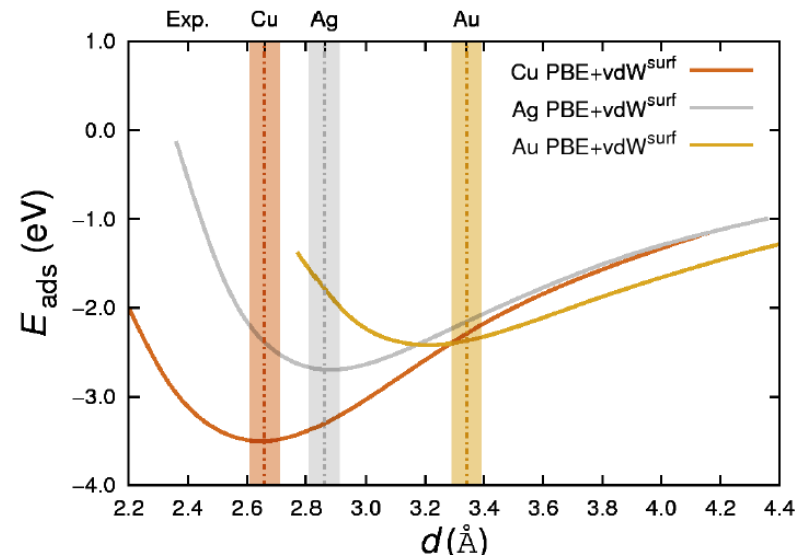


Semi-Empirical Correction

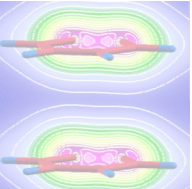
Grimme, *J. Comput. Chem.*, **25**, 1463 (2004).
Grimme, *J. Comput. Chem.*, **27**, 1787 (2006).
Tkatchenko et al. *PRL* **102**, 073005 (2009).

Ruiz et al. *PRL* **108**, 146103 (2012):

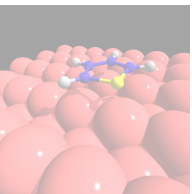
PTCDA / Coinage-Metal(111)-Surfaces



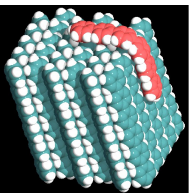
Outline



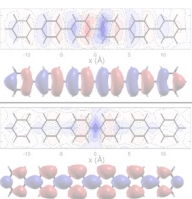
1. Density Functional Theory in a Nutshell



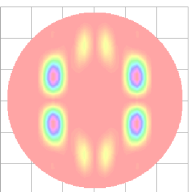
2. Van der Waals Forces: Surface / Adsorption Energies



3. Step-Edge Barrier in Organic Thin Film Growth



4. Orbital Densities from Angle-Resolved Photoemission

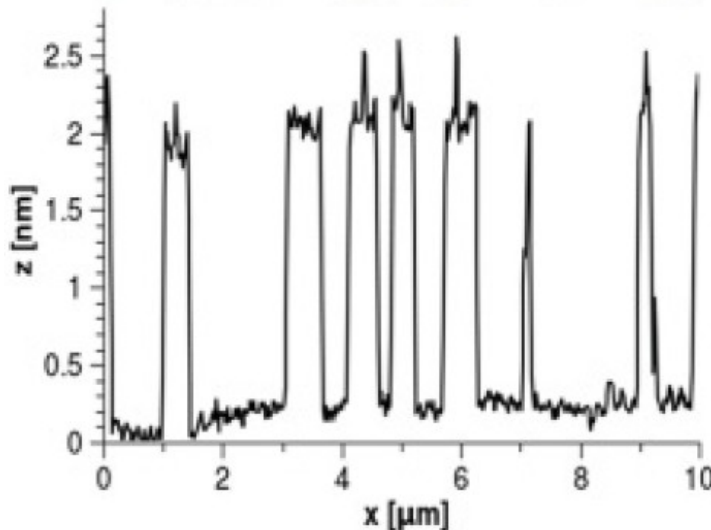
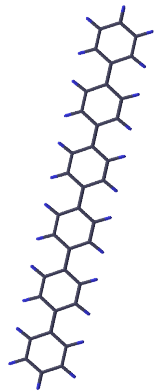
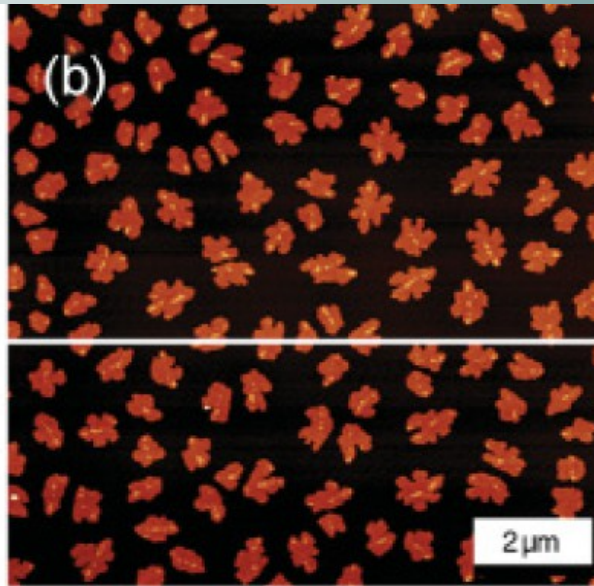


5. Dissecting Orbitals: Tomography in Reciprocal Space

Island Growth on Amorphous Mica

AFM-image

10 x 10 μm^2
T = 300 K
 $\theta = 0.32$ ML
F = 0.02 ML/min



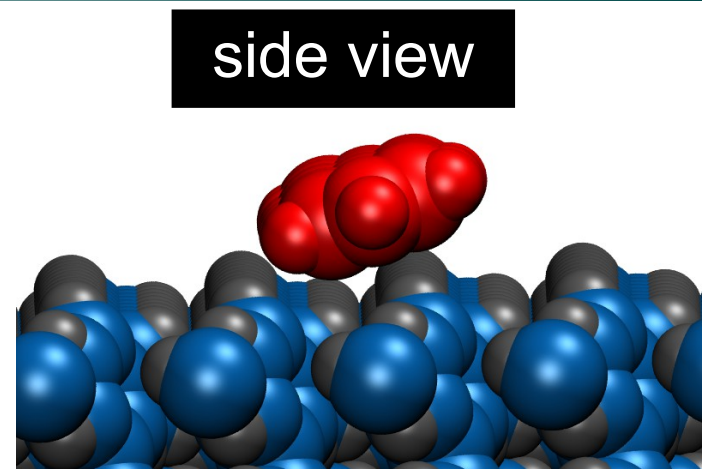
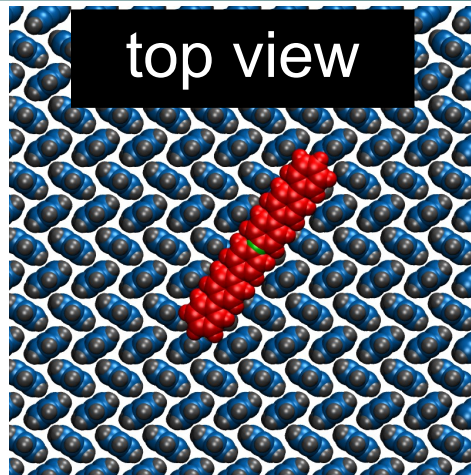
- Amorphous Mica (ion bombarded)
- Observation of islands consisting of standing p-6P
- What is the critical cluster size?
- Transition from lying-to-standing p-6P?

Potocar et al., *PRB* **83**, 075423 (2011).
→ talk by A. Winkler, Tue 10:20-10:40

p-6P / p-6P(001)

p-6P(001) as model
substrate with weak
Interactions

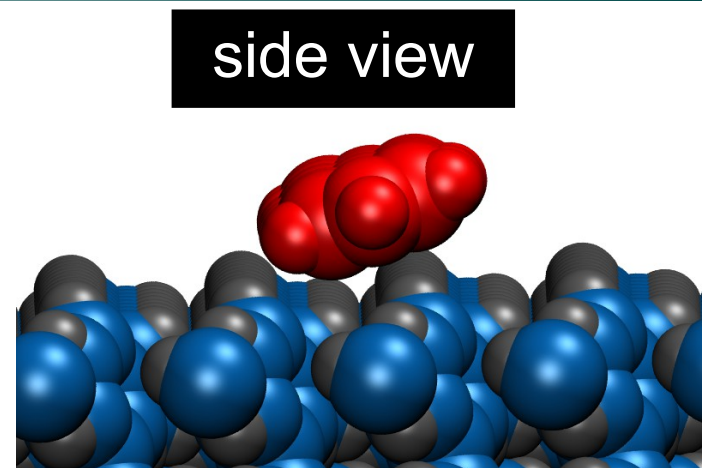
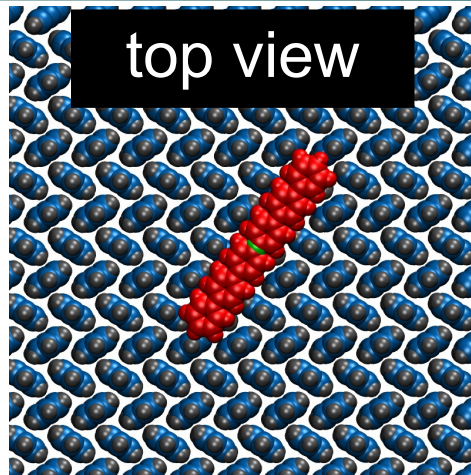
Adsorption geometry:



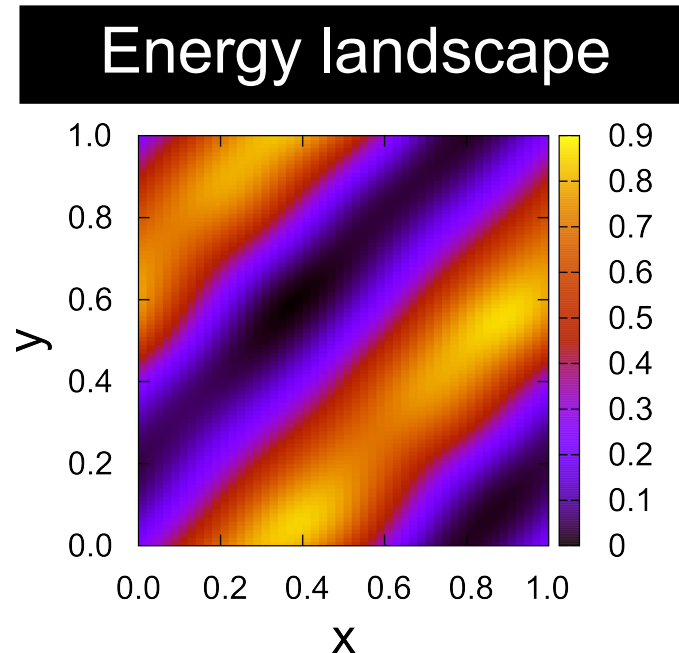
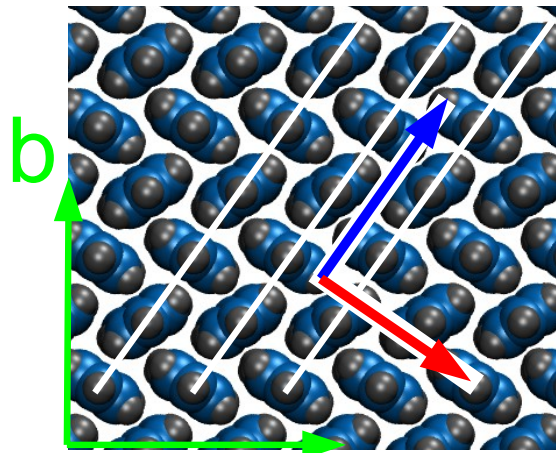
p-6P / p-6P(001)

p-6P(001) as model substrate with weak interactions

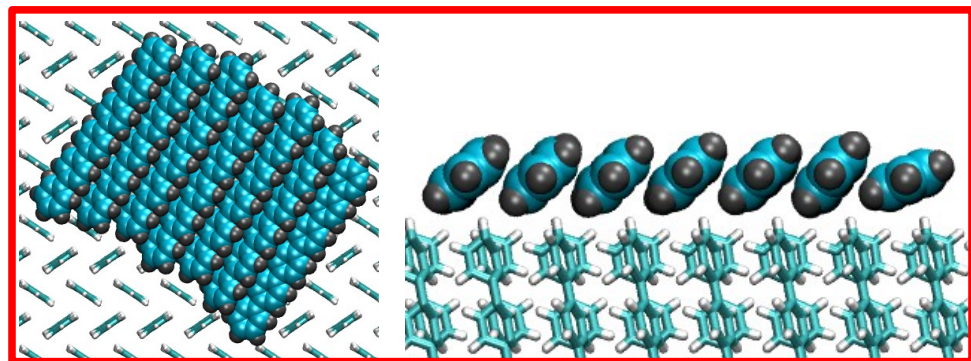
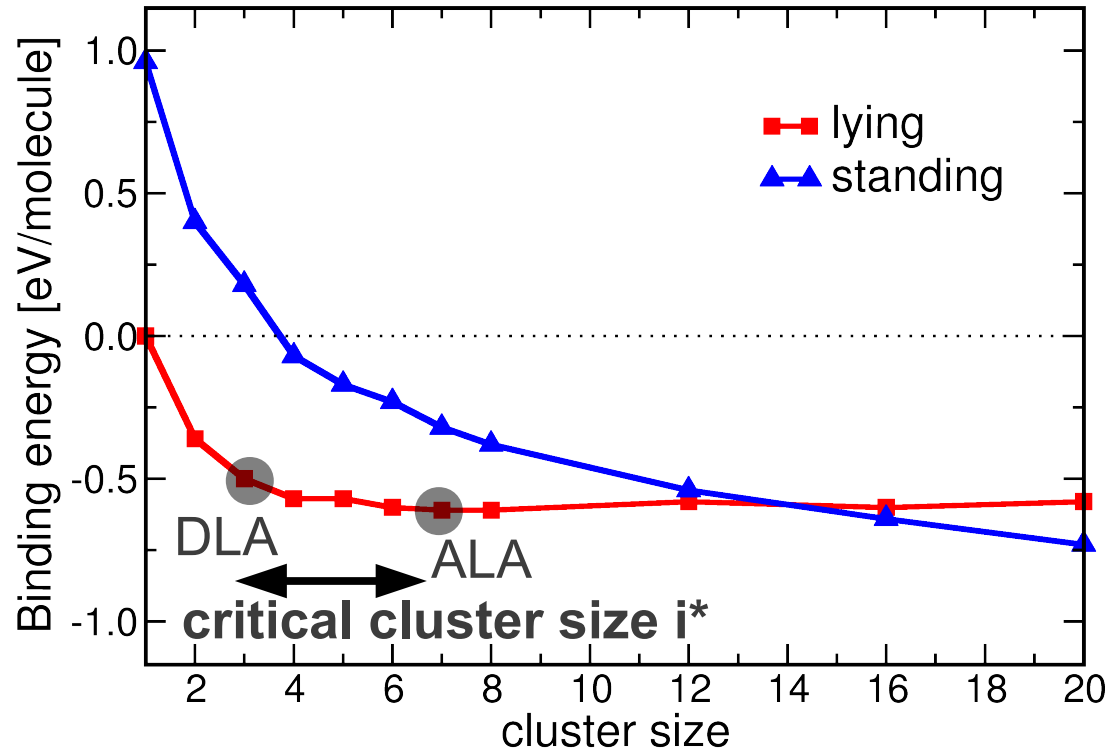
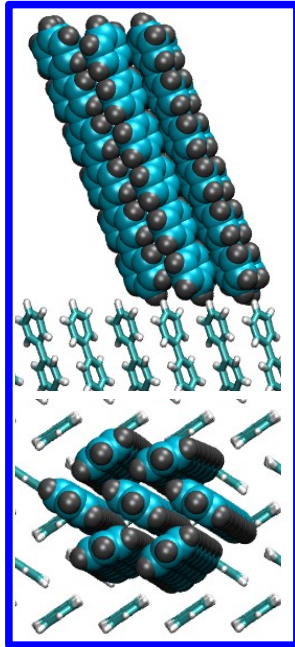
Adsorption geometry:



Diffusion path:

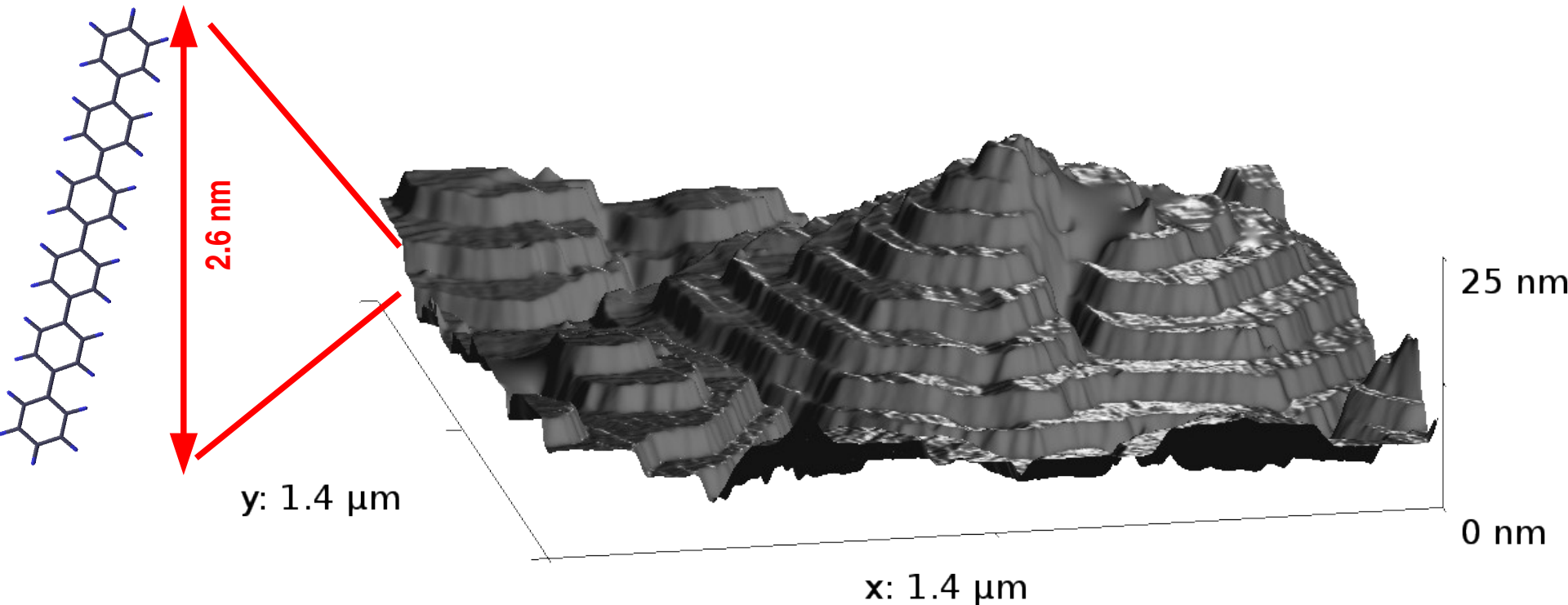


Lying vs. Standing p-6P



$$E_{\text{binding}} = E_{\text{cluster}}^n / n - E_{\text{lying molecule}}$$

Terraced Mounds



AFM image: Sexiphenyl grown on a disordered mica surface

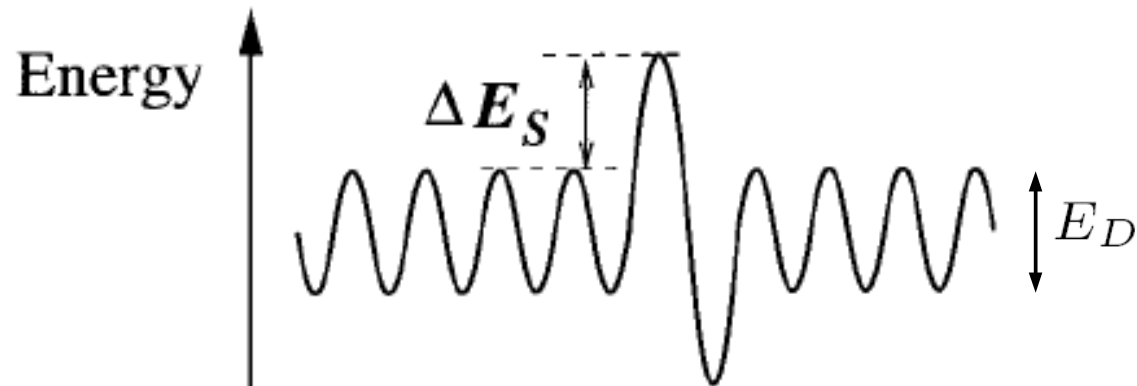
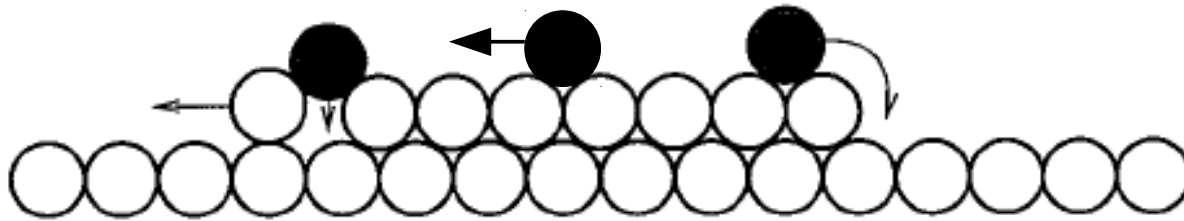
Ehrlich-Schwöebel Barrier (ESB)

Diffusion on a terrace

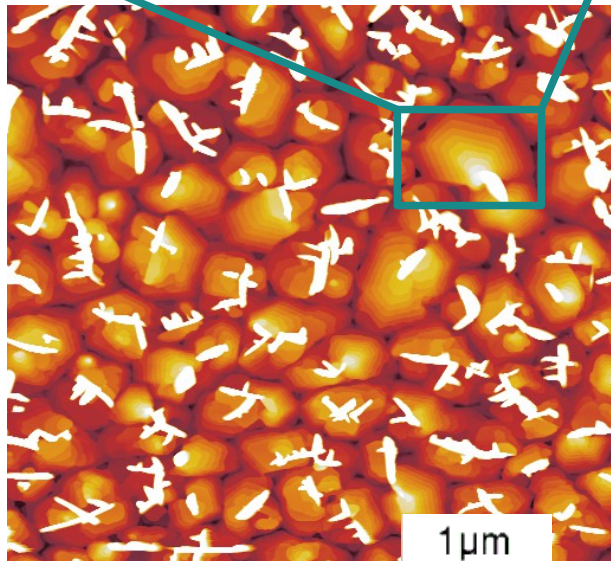
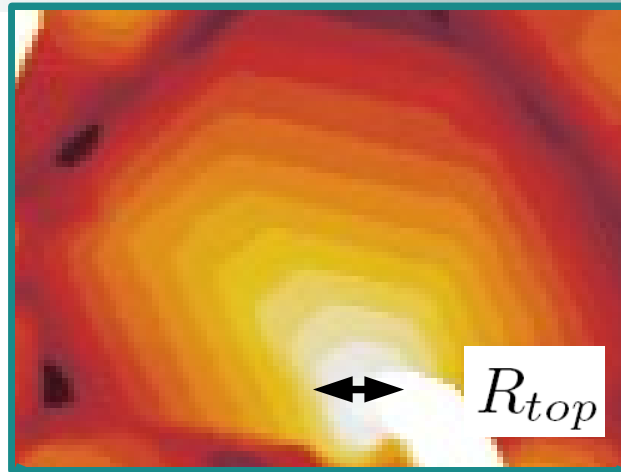
$$\nu = \nu_0 e^{-E_D/k_B T}$$

Interlayer jump rate

$$\nu' = \nu'_0 e^{-E_S/k_B T}$$



Sexiphenyl on Mica



AFM image: Film thickness = 30 nm

Ehrlich-Schwoebel Barrier = 0.67 eV

$$R_{top} \propto \left(\frac{\nu'}{F} \right)^{1/5} \approx 20 - 50 \text{ nm}$$

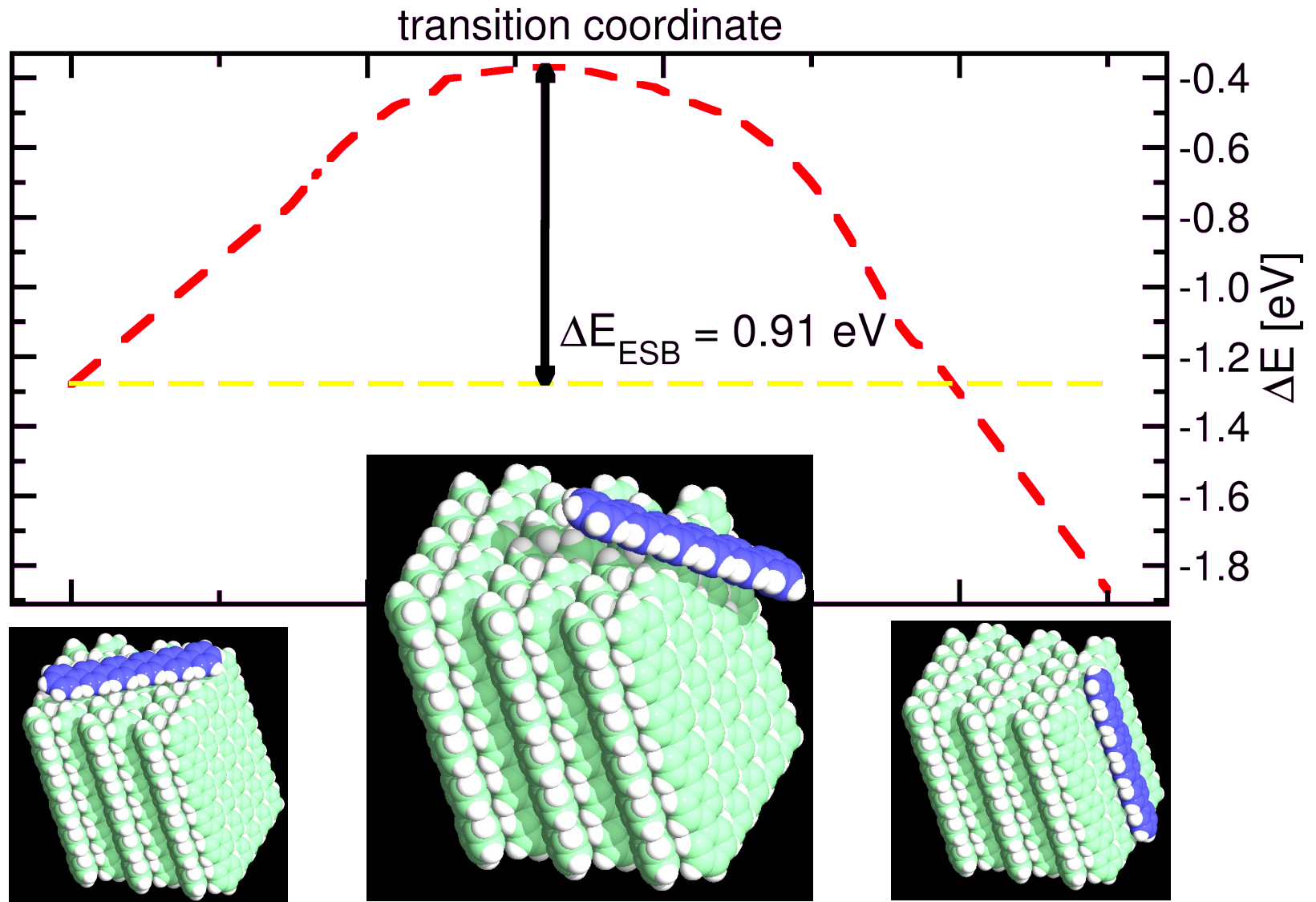
↑

$$\omega = \frac{\tau}{(\Delta t)^2} = \frac{\text{residence time}}{(\text{deposition time})^2}$$

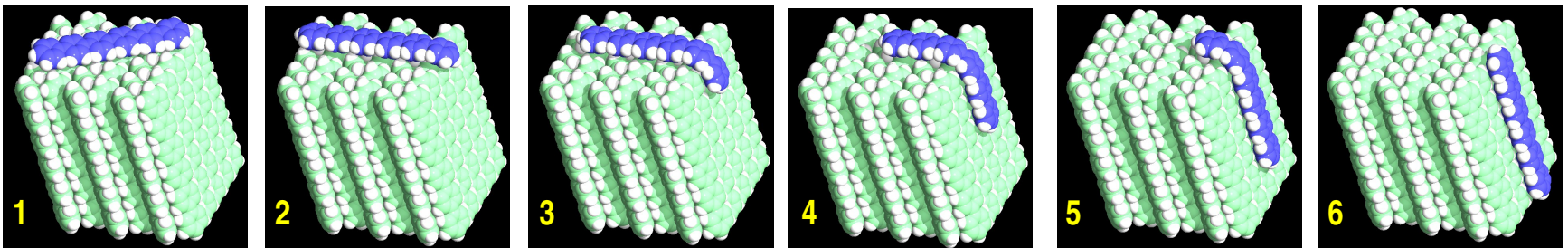
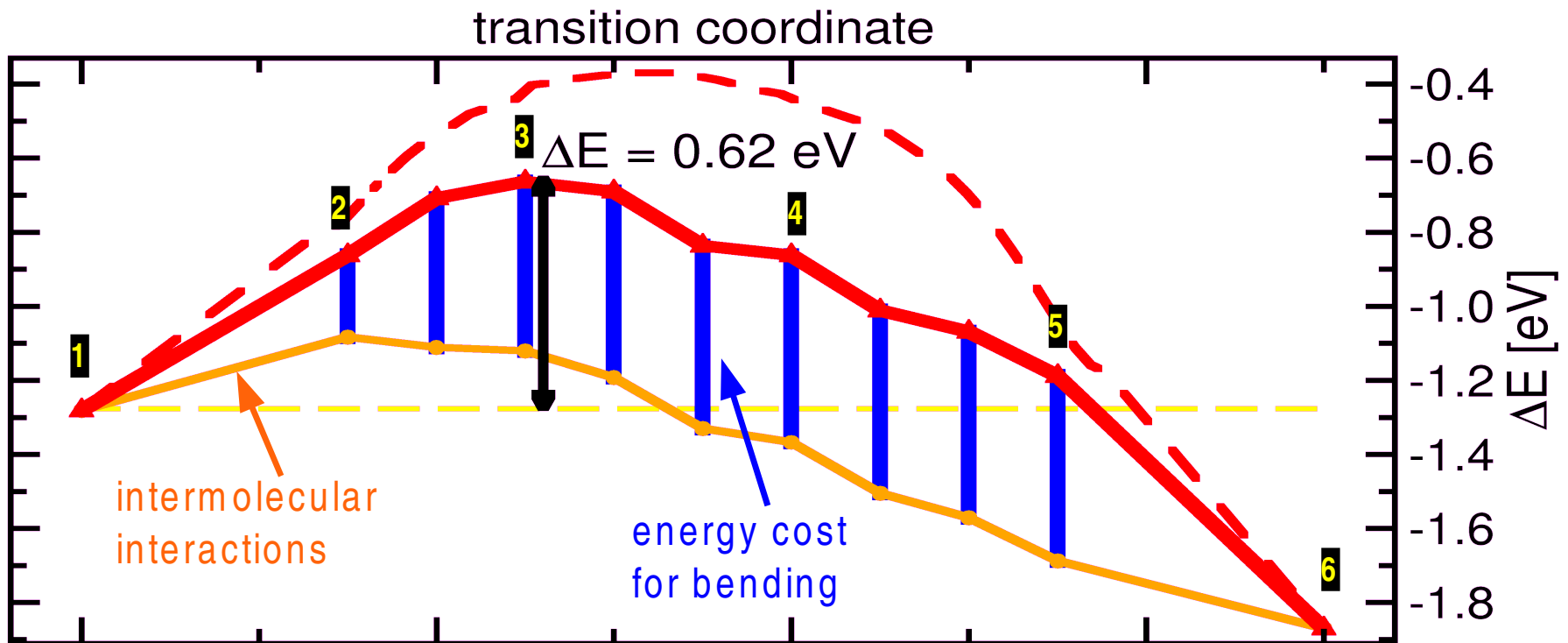
↑

2nd layer nucleation rate

Step-Edge Barrier



Step-Edge Barrier

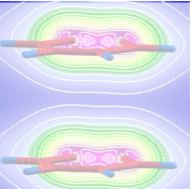


G. Hlawacek et al., *Science* **321**, 108 (2008).

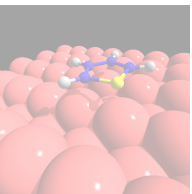
Step-Edge Barrier



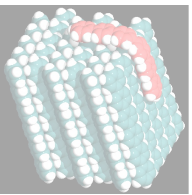
Outline



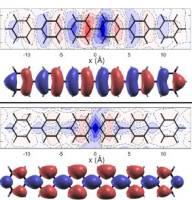
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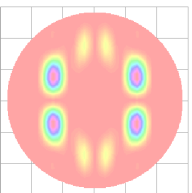
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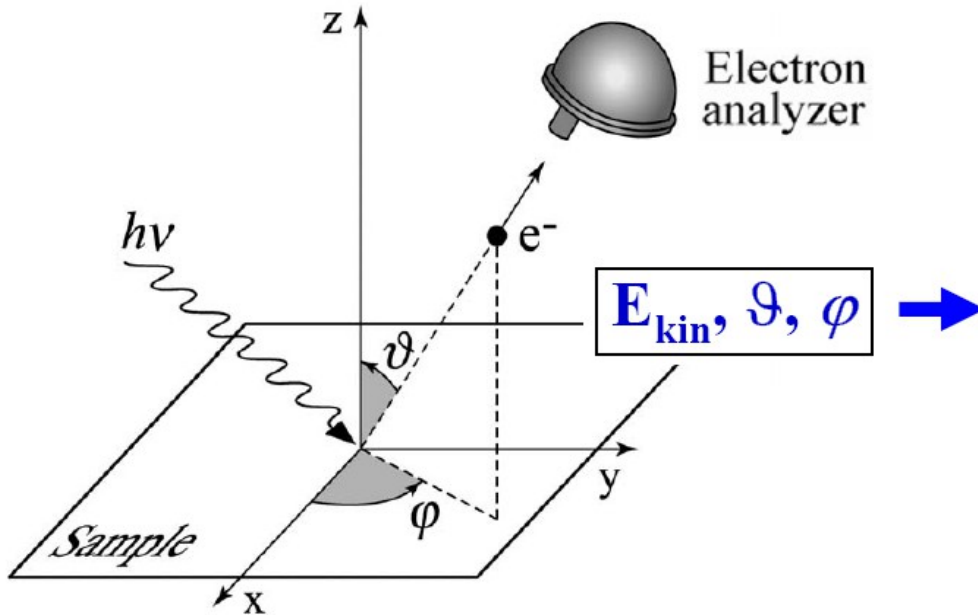


4. Orbitals from Angle-Resolved Photoemission



5. Dissecting Orbitals: Tomography in Reciprocal Space

Photoemission Spectroscopy



$$\mathbf{K} = \mathbf{p} / \hbar = \sqrt{2mE_{kin}} / \hbar$$

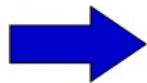
$$K_x = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \vartheta \cos \varphi$$

$$K_y = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \vartheta \sin \varphi$$

$$K_z = \frac{1}{\hbar} \sqrt{2mE_{kin}} \cos \vartheta$$

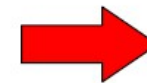
Vacuum

$$\begin{matrix} E_{kin} \\ \mathbf{K} \end{matrix}$$



Conservation laws

$$\begin{matrix} E_f - E_i = h\nu \\ \mathbf{k}_f - \mathbf{k}_i = \cancel{\mathbf{k}_{h\nu}} \end{matrix}$$



Solid

$$\begin{matrix} E_B \\ \mathbf{k} \end{matrix}$$

Photoemission Intensity

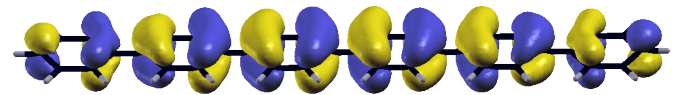
One Step Model

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

Photoemission Intensity

One Step Model

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

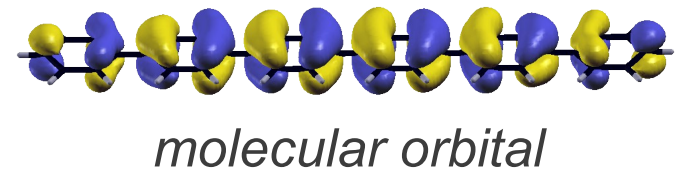
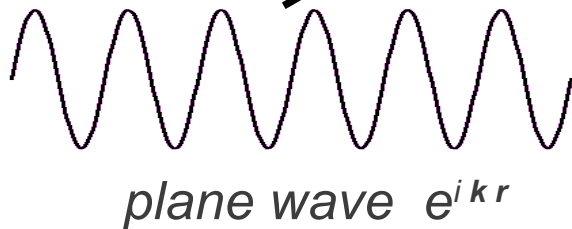


molecular orbital

Photoemission Intensity

One Step Model

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



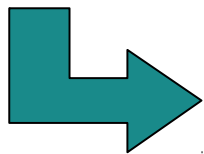
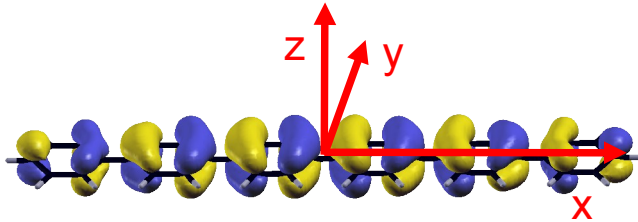
Approximation: final state = plane wave

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

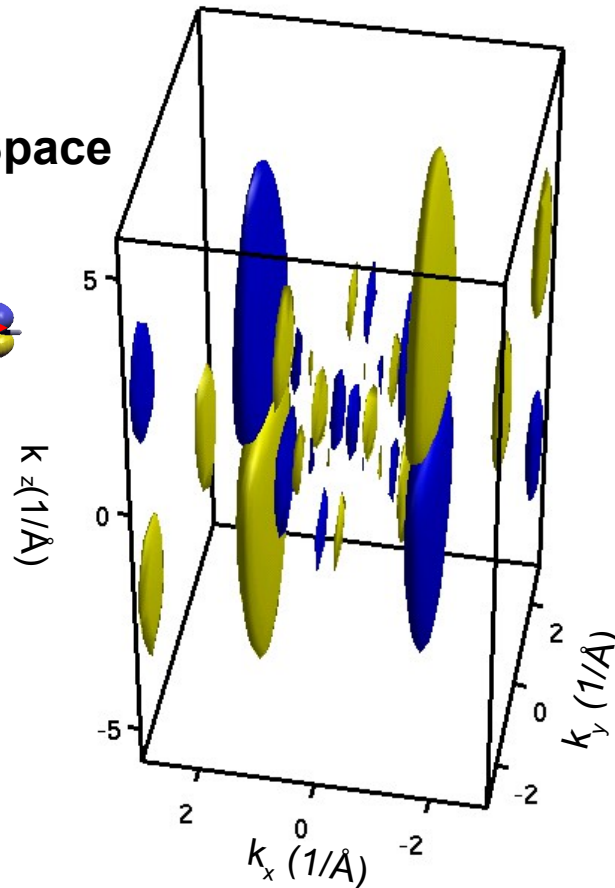
Fourier Transform of Initial State Orbital

Comparison with DFT

Molecular Orbital in Real Space

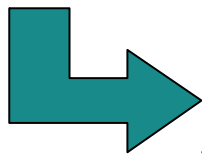
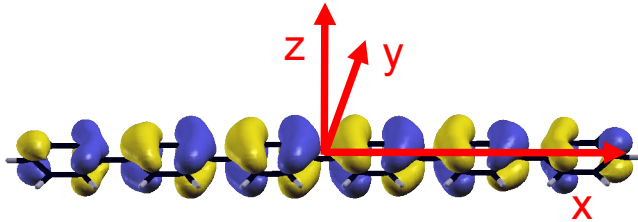


**Calculation of
the Fourier Transform**

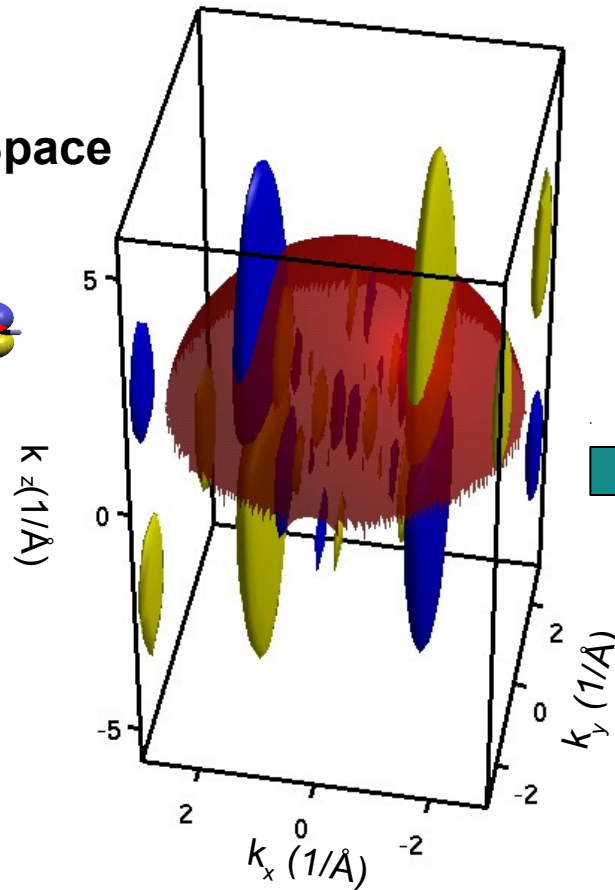


Comparison with DFT

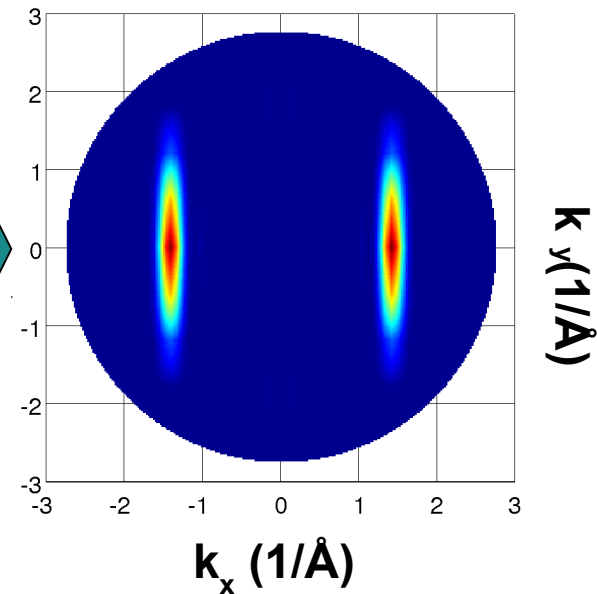
Molecular Orbital in Real Space



Calculation of
the Fourier Transform

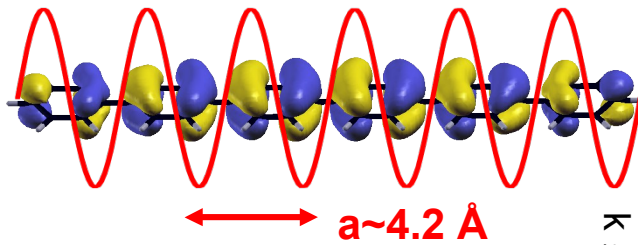


Hemispherical Cut Through
3D Fourier Transform

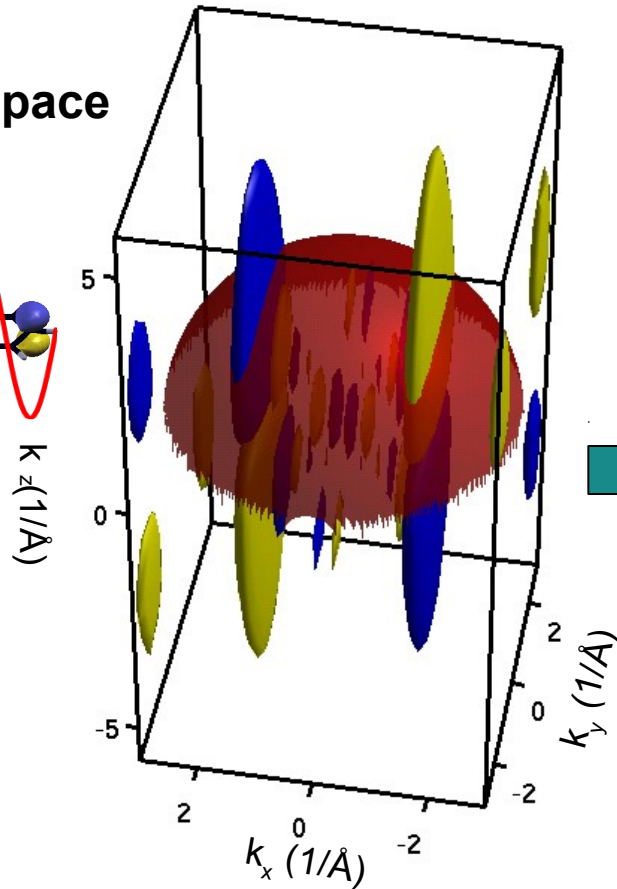
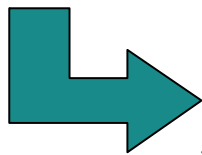


Comparison with DFT

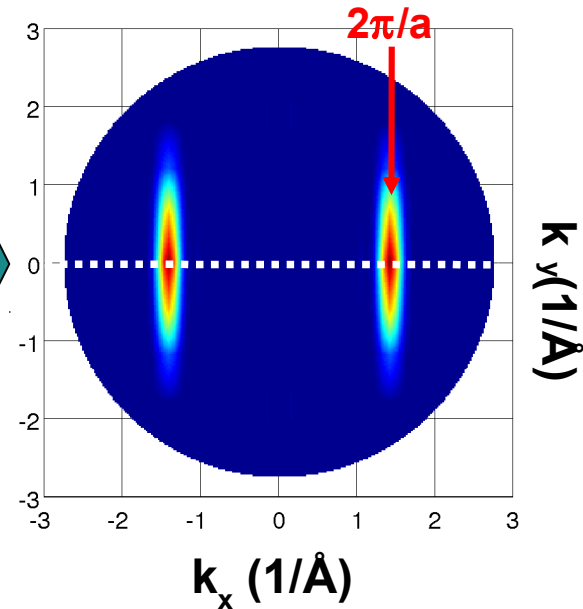
Molecular Orbital in Real Space



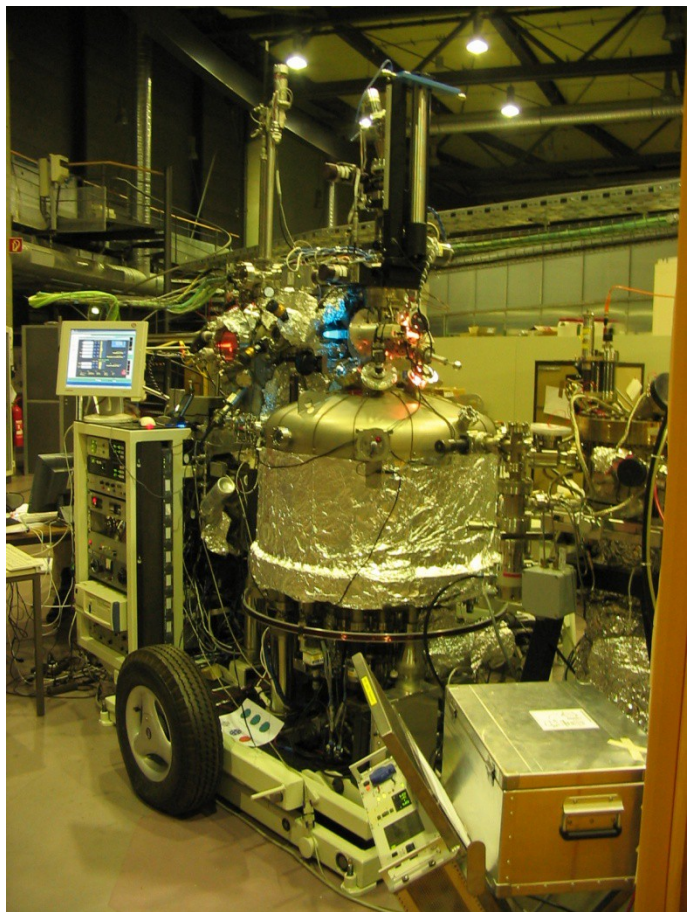
Calculation of
the Fourier Transform



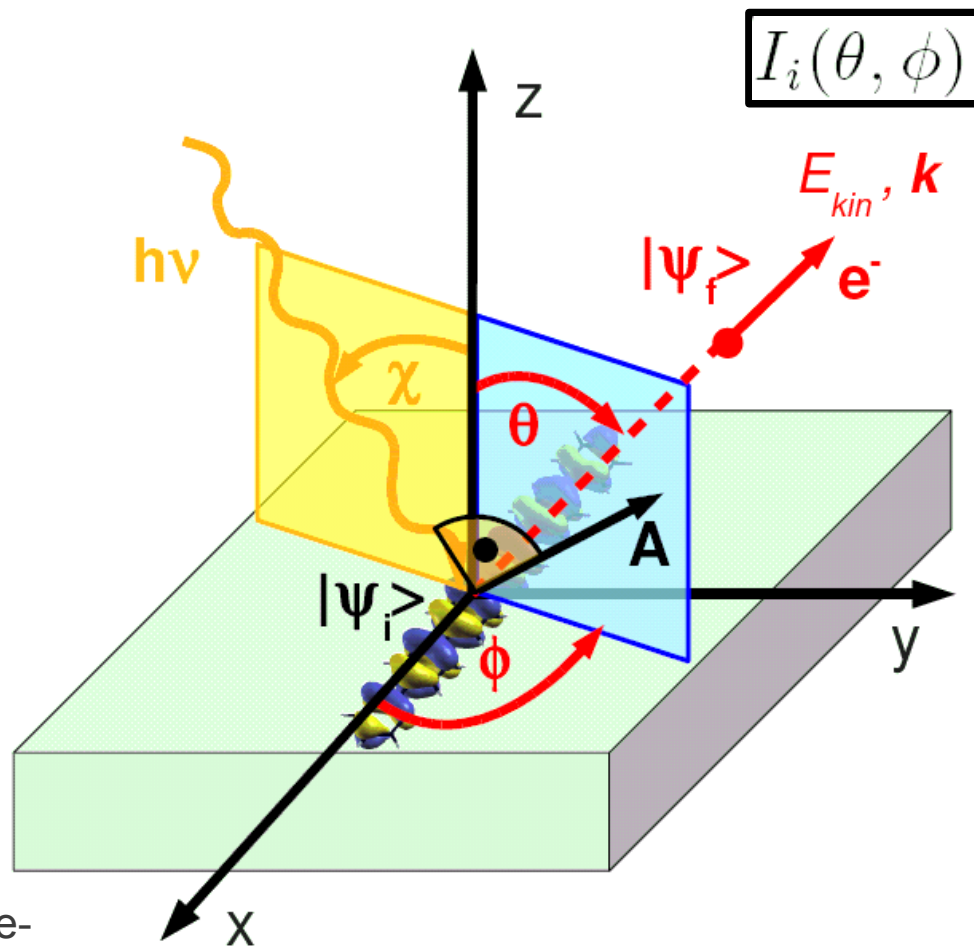
Hemispherical Cut Through
3D Fourier Transform



Toroidal Electron Energy Analyzer



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

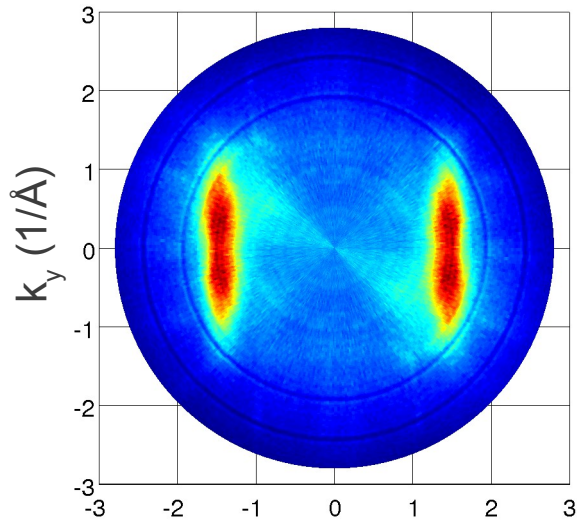


Sexiphenyl Monolayer on Cu(110)

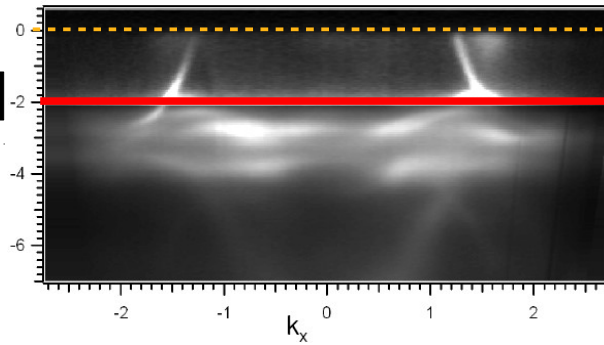


2D-Momentum Maps

Constant Binding Energy Scans

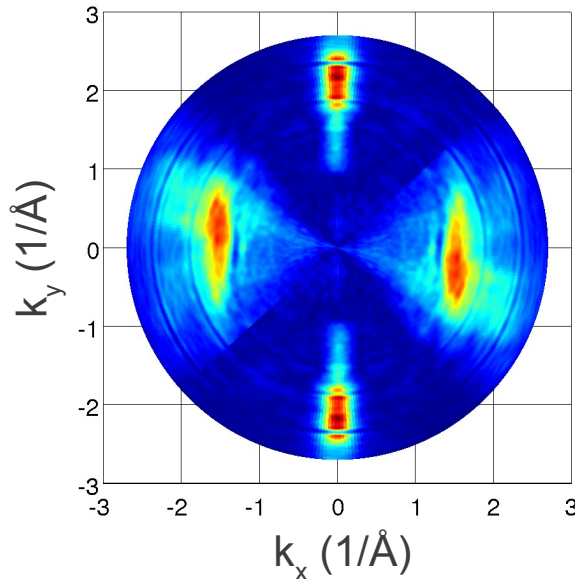


CBE

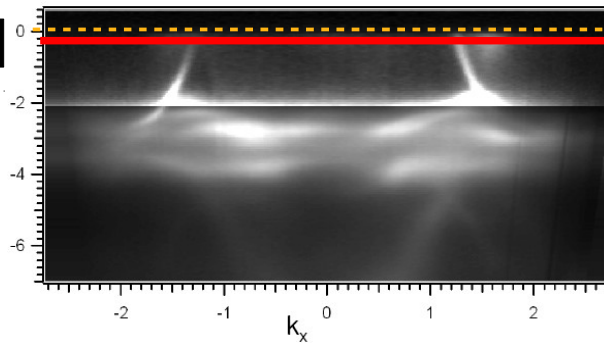


E_F

$E_{\text{HOMO}} = -1.9$ eV



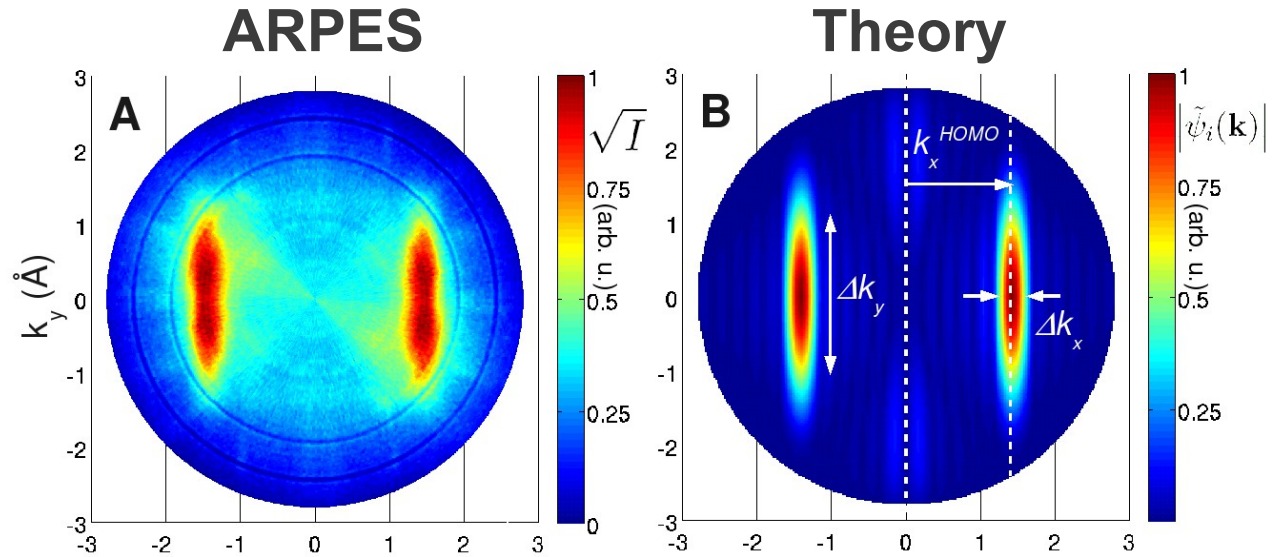
CBE



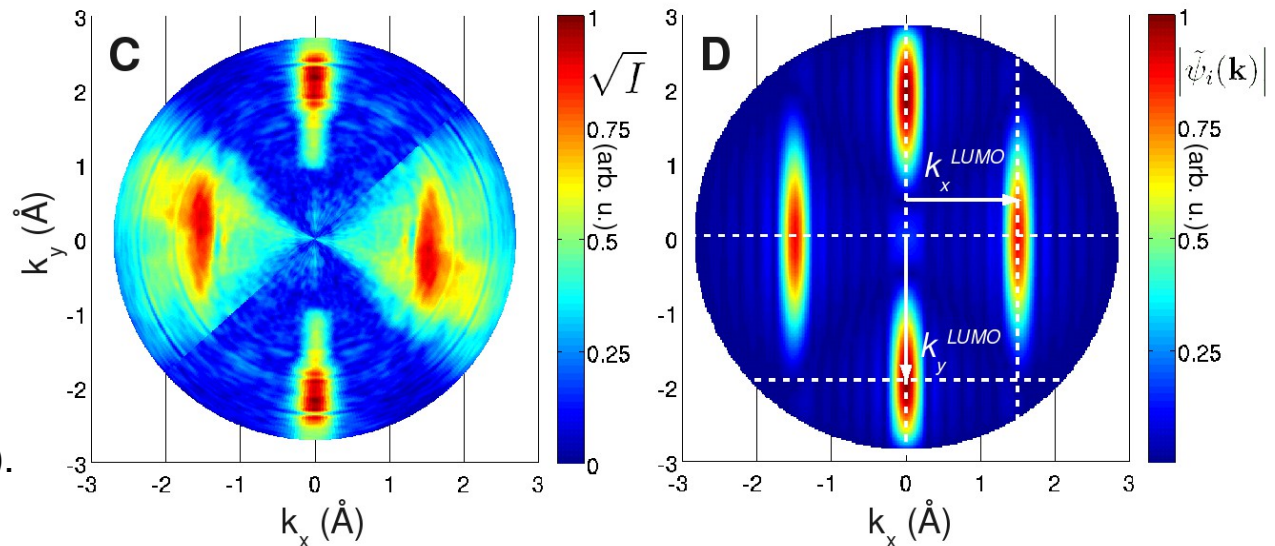
$E_{\text{LUMO}} = -0.4$ eV

2D-Momentum Maps

HOMO



Filled
LUMO



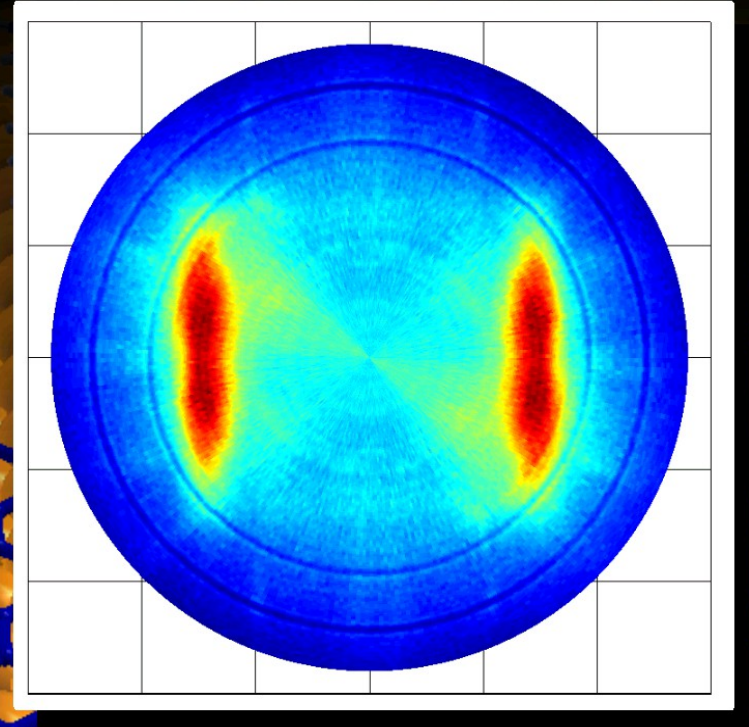
Puschnig et al.,
Science **326**, 702 (2009).

Reconstruction of Orbitals

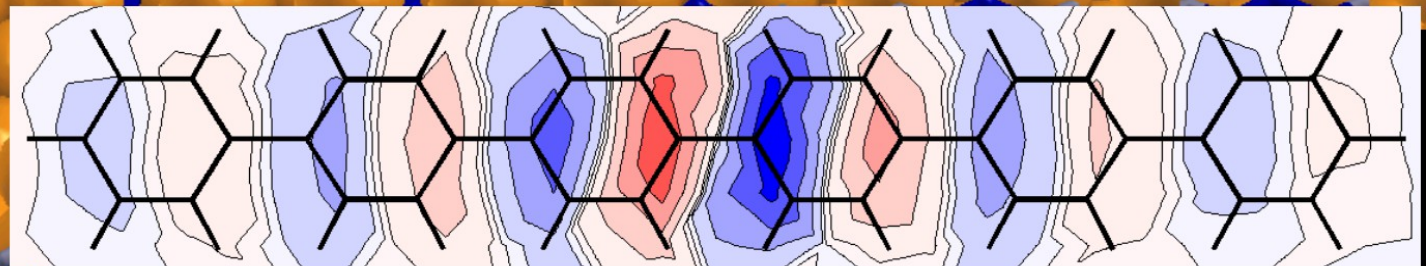
UV light

electrons

ARPES

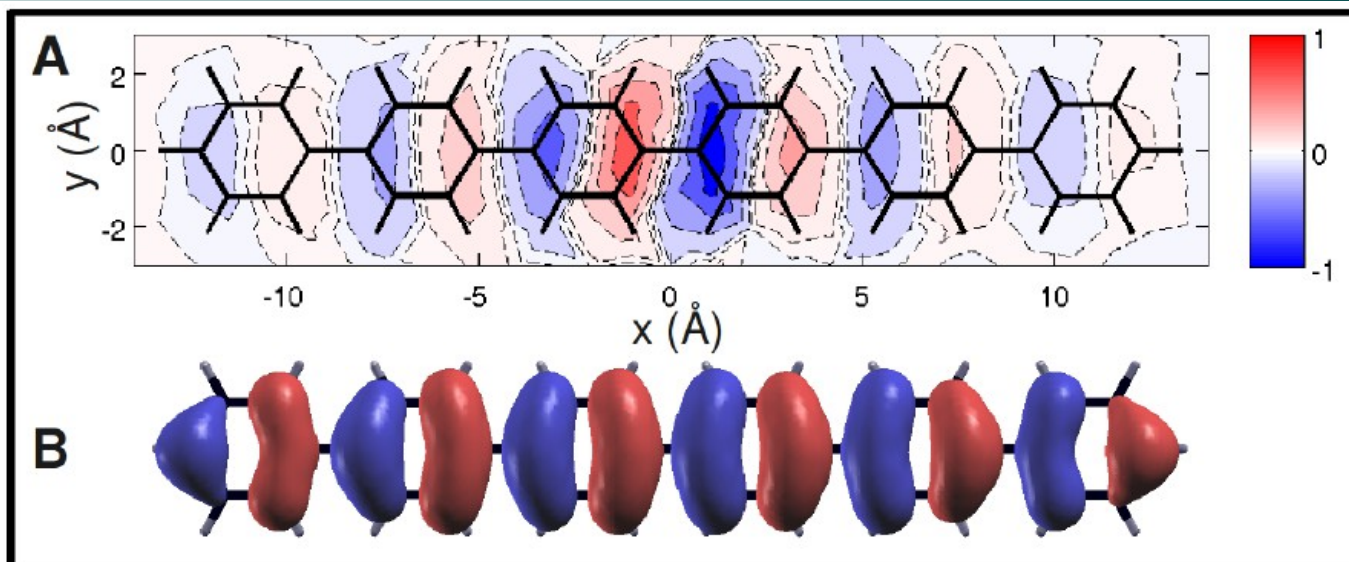


IFT

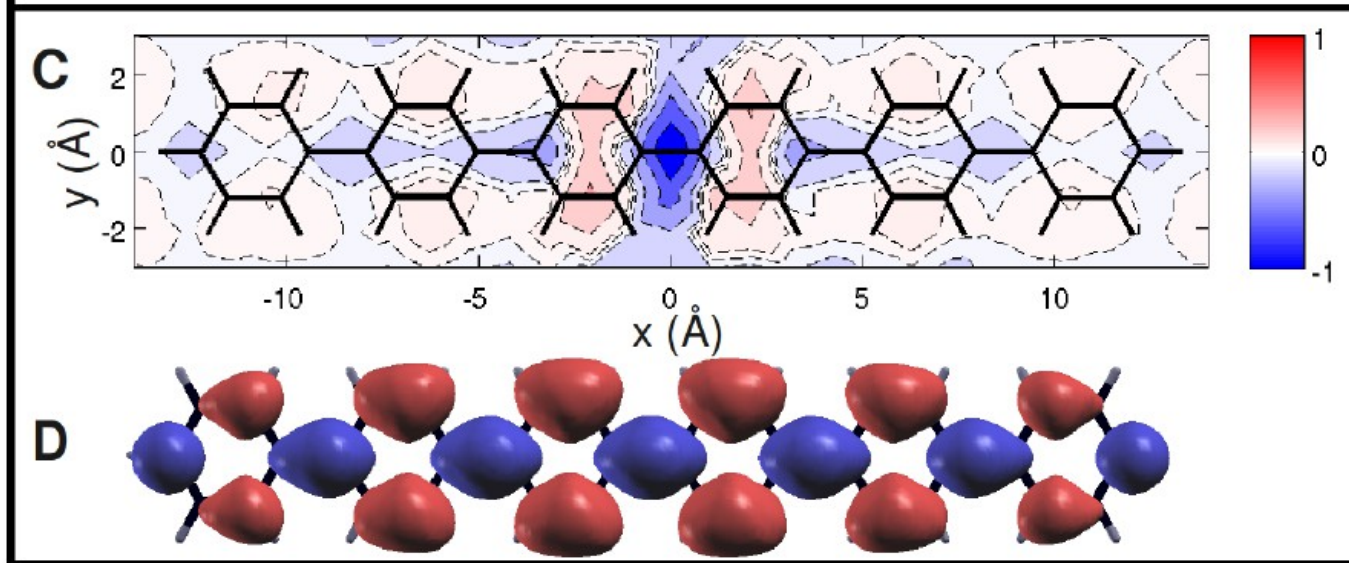


Reconstruction of Orbitals

HOMO

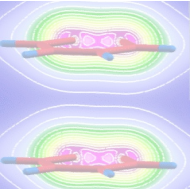


Filled
LUMO

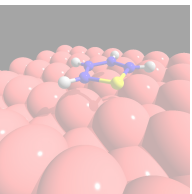


Puschnig et al.,
Science **326**, 702 (2009).

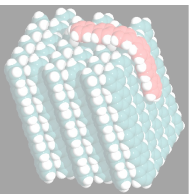
Outline



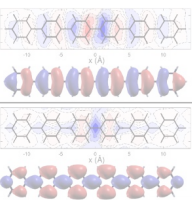
1. Density Functional Theory in a Nutshell



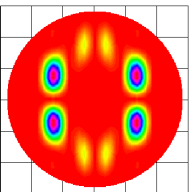
2. Van der Waals Forces: Surface / Adsorption Energies



3. Step-Edge Barrier in Organic Thin Film Growth

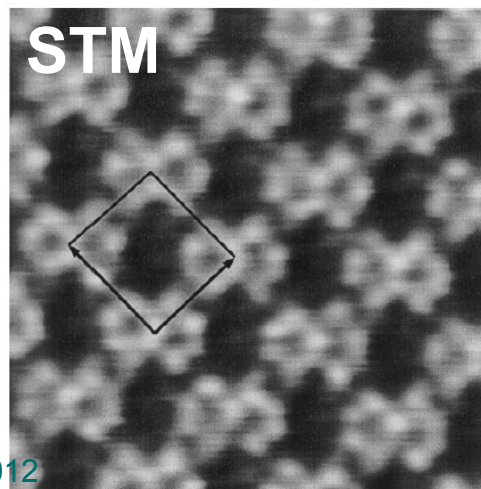
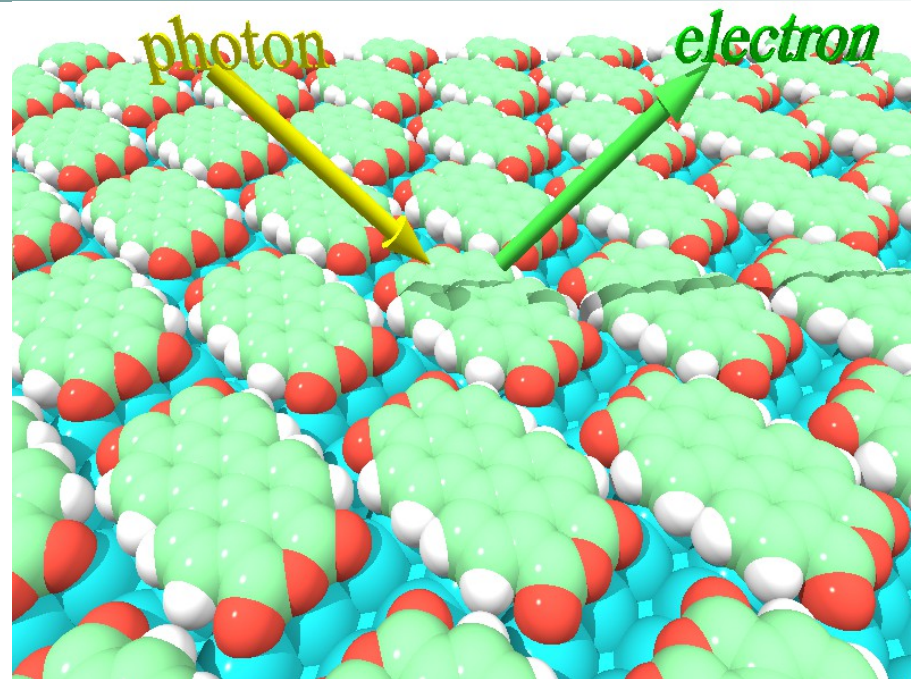
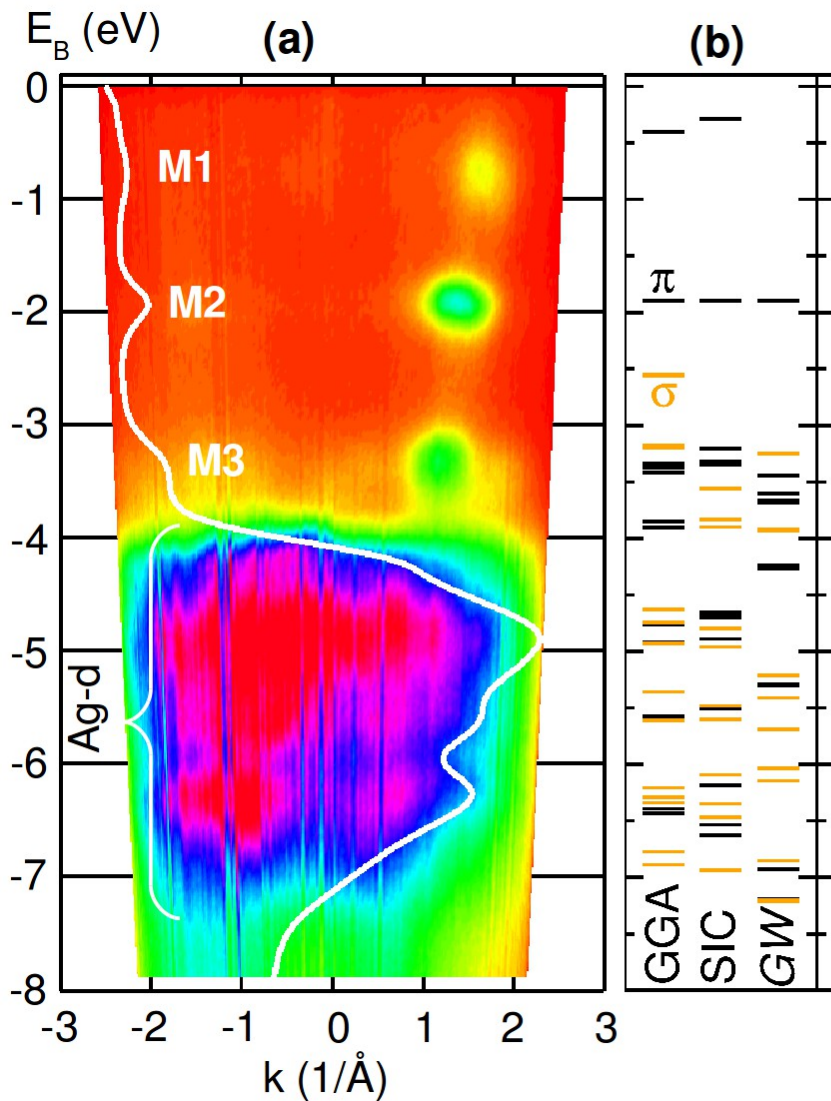


4. Orbital Densities from Angle-Resolved Photoemission

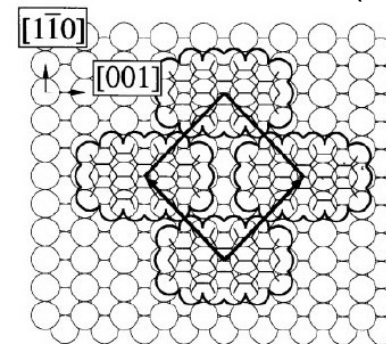


5. Dissecting Orbitals: Tomography in Fourier Space

ARPES of PTCDA / Ag(110)



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

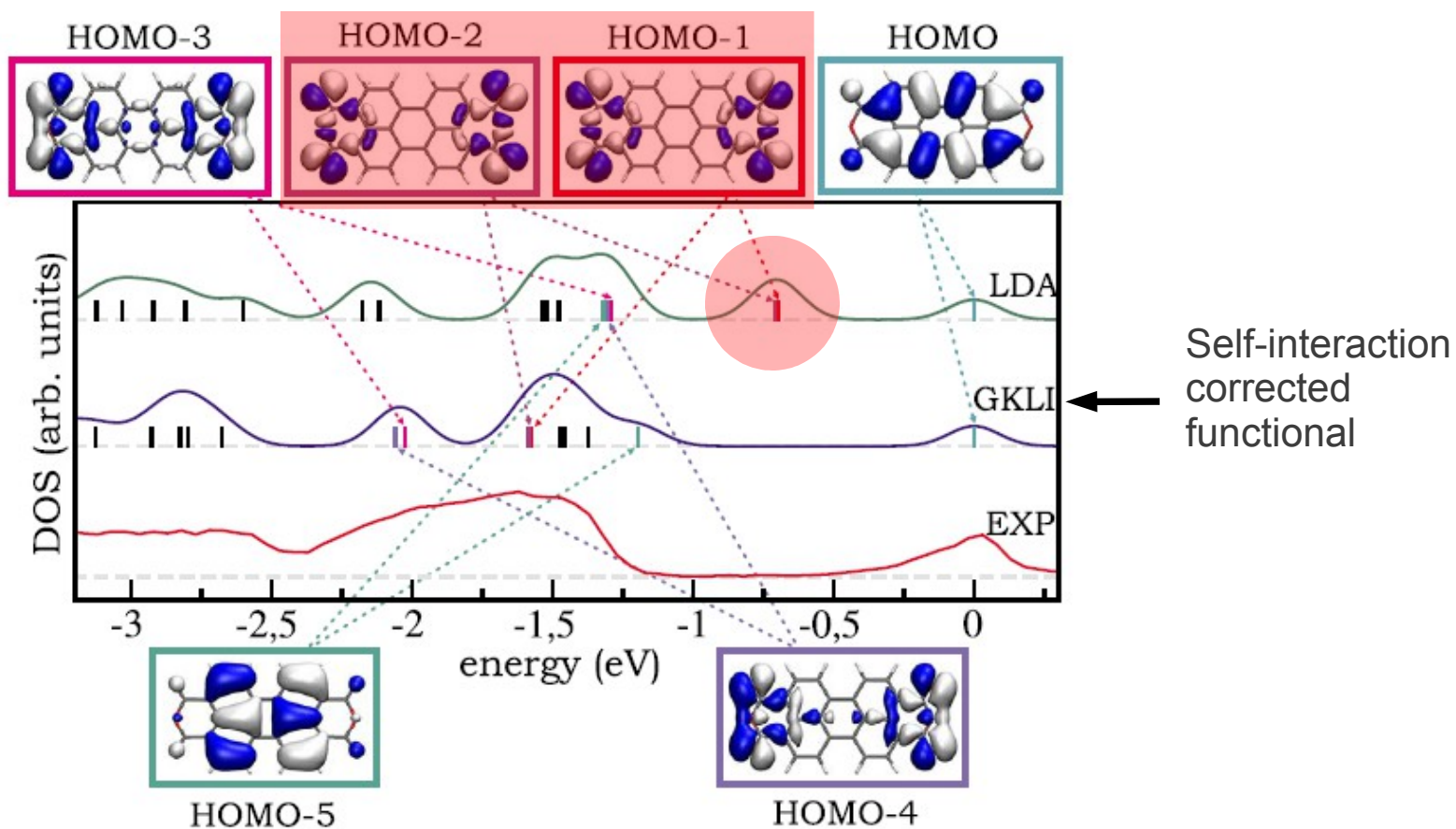


Identifying Orbitals

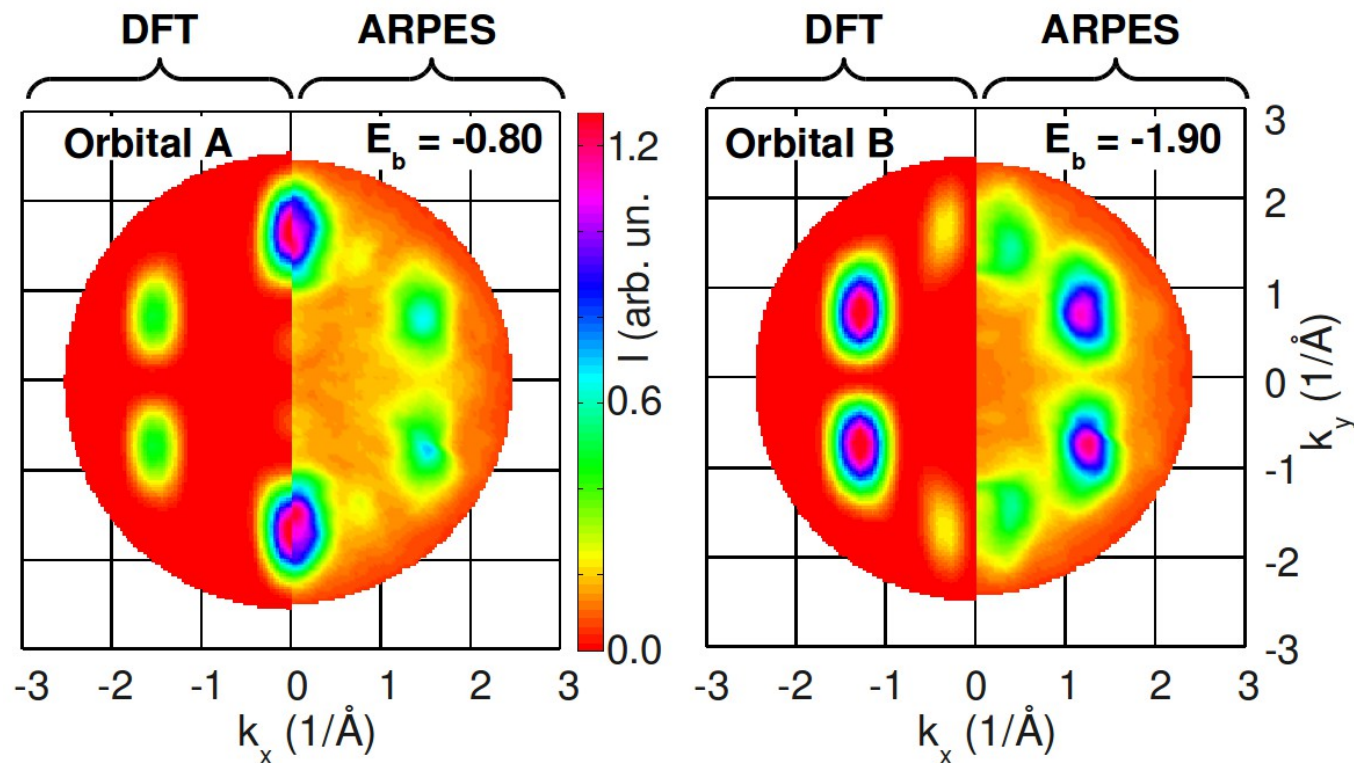
PHYSICAL REVIEW B 79, 201205(R) (2009)

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

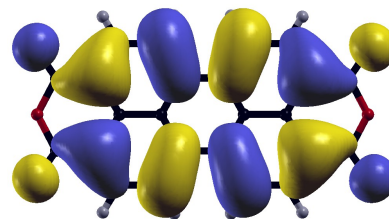
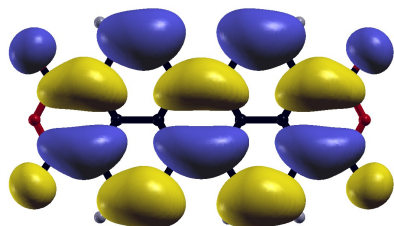
T. Körzdörfer and S. Kümmel N. Marom and L. Kronik



HOMO and Filled LUMO



M1=
FLUMO

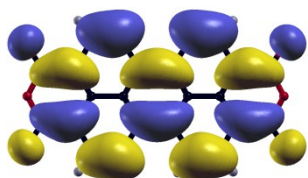


M2=
HOMO

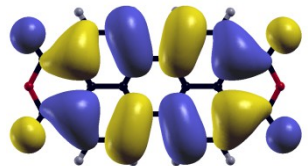
Puschnig et al. PRB **84**, 235427 (2011), Zirotto et al., PRL **104**, 233004 (2010).

What is the nature of M3?

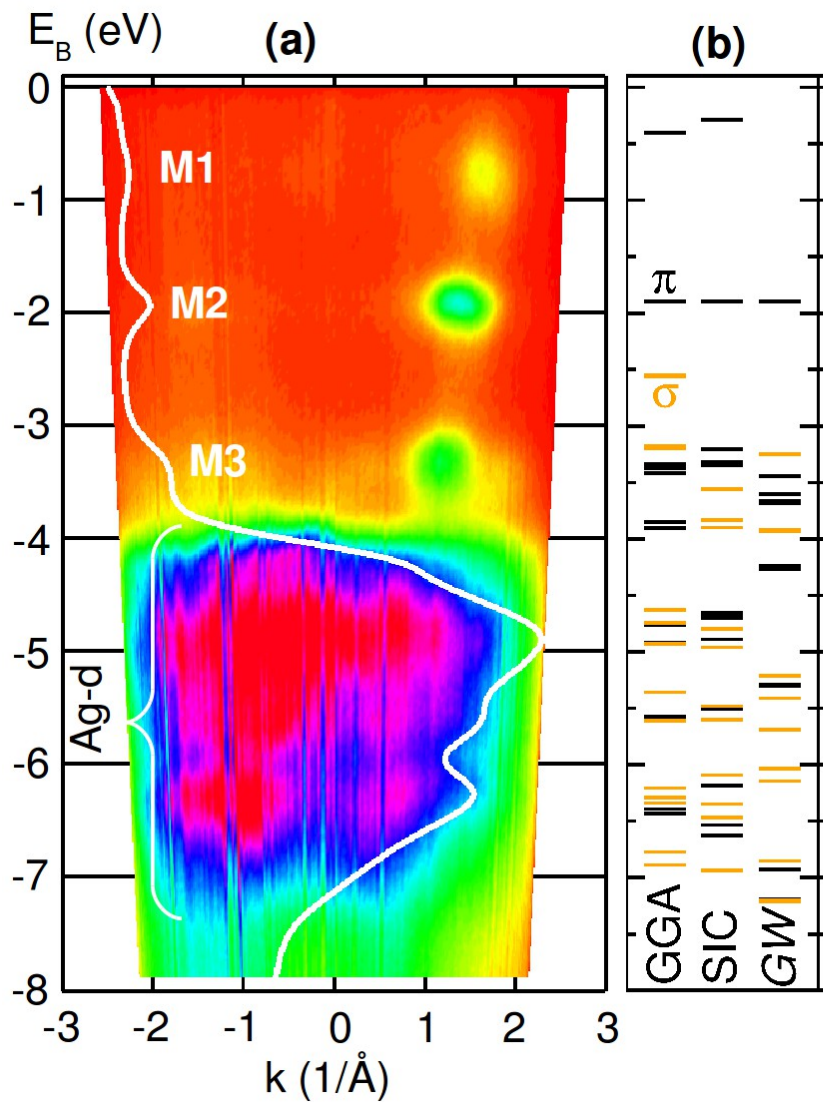
M1=
FLUMO



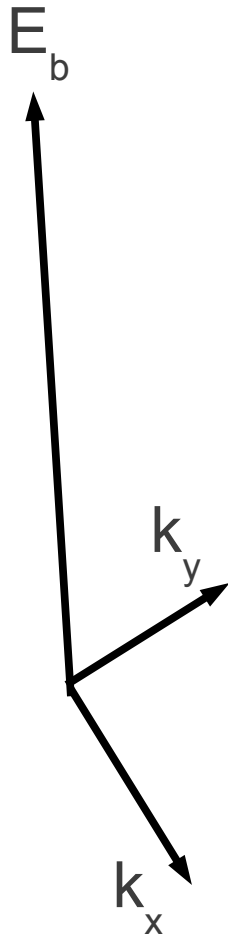
M2=
HOMO



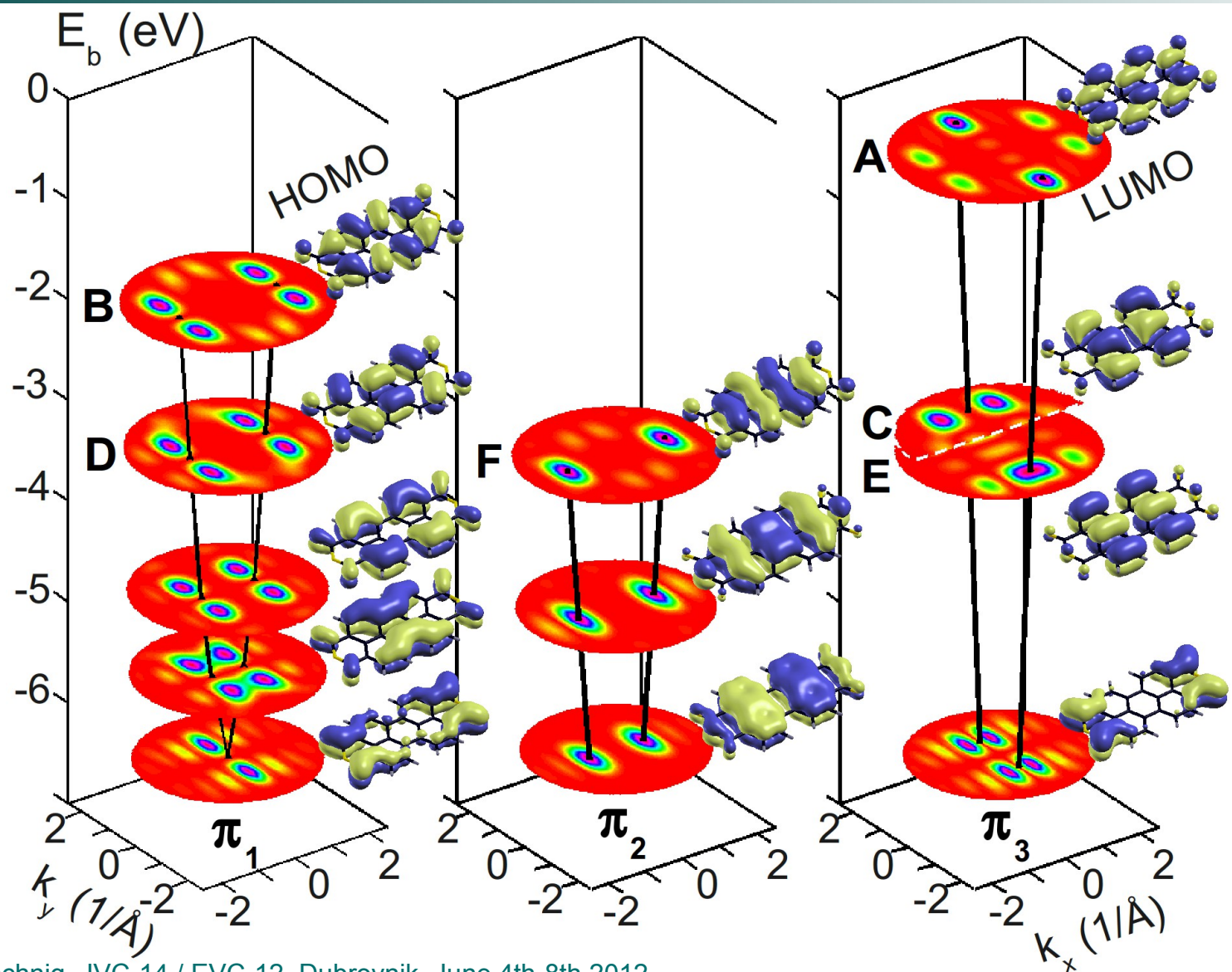
?



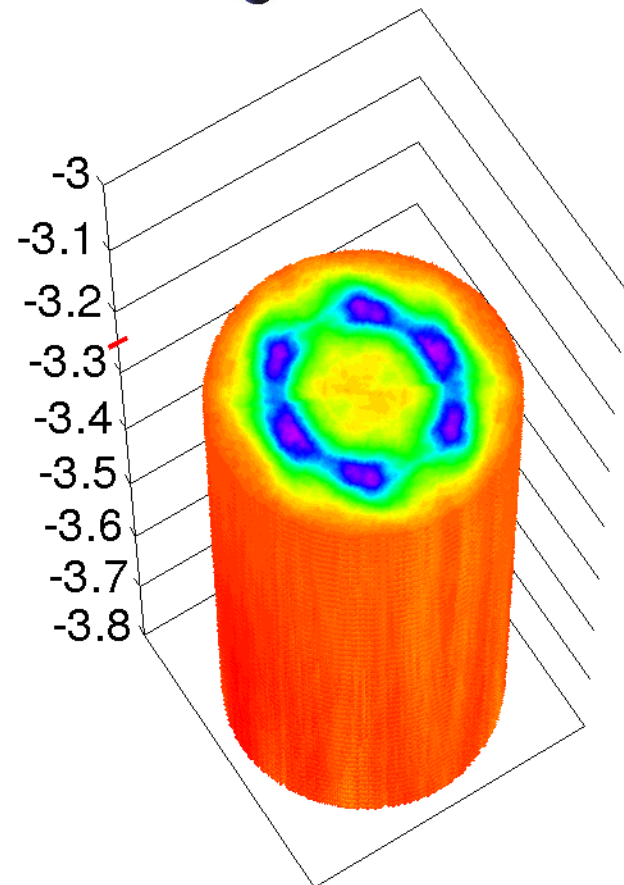
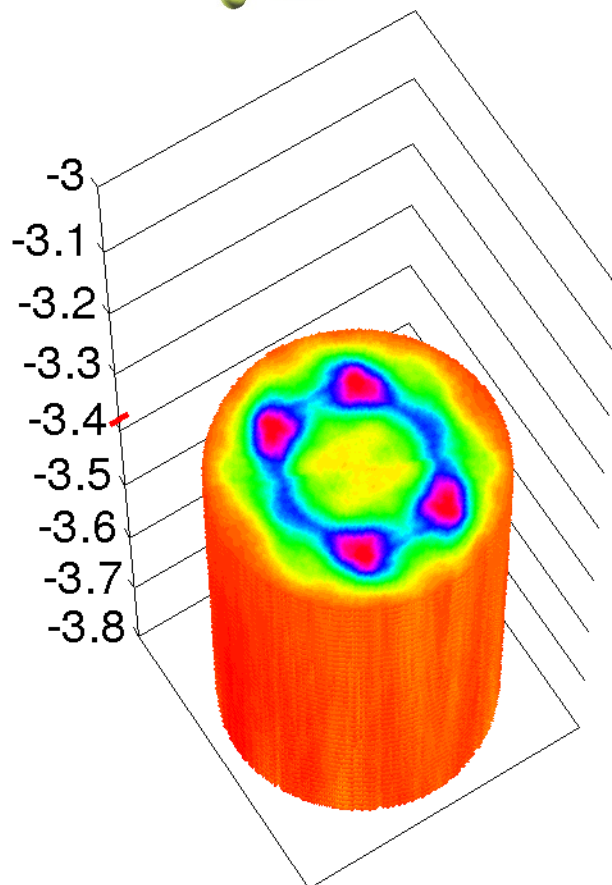
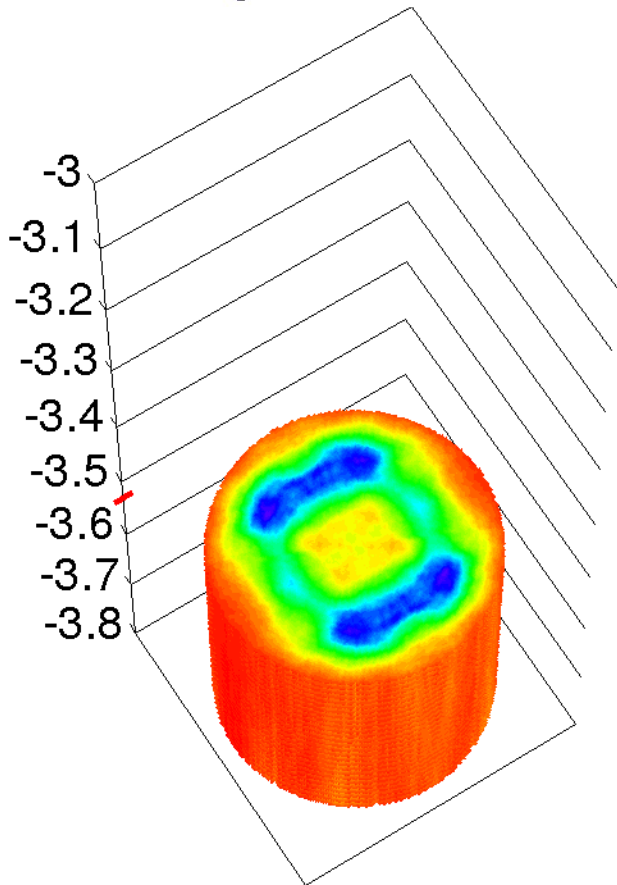
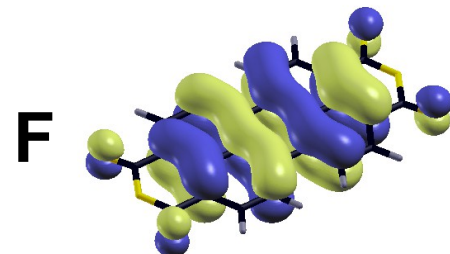
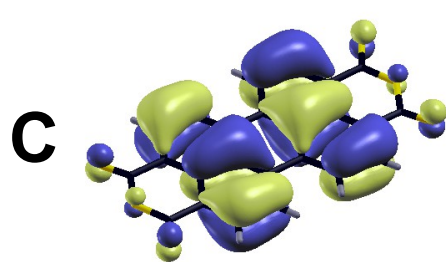
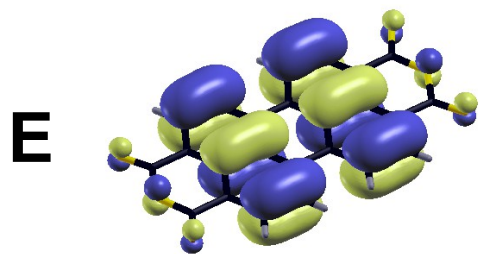
ARPES Data-Cube



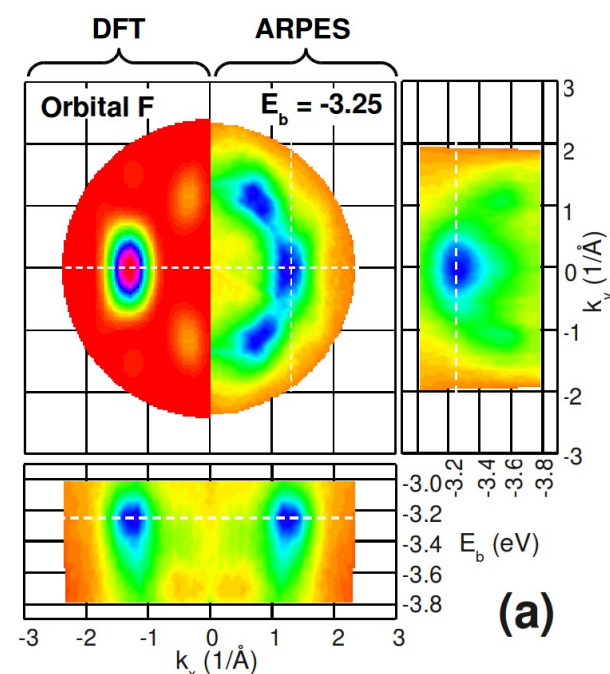
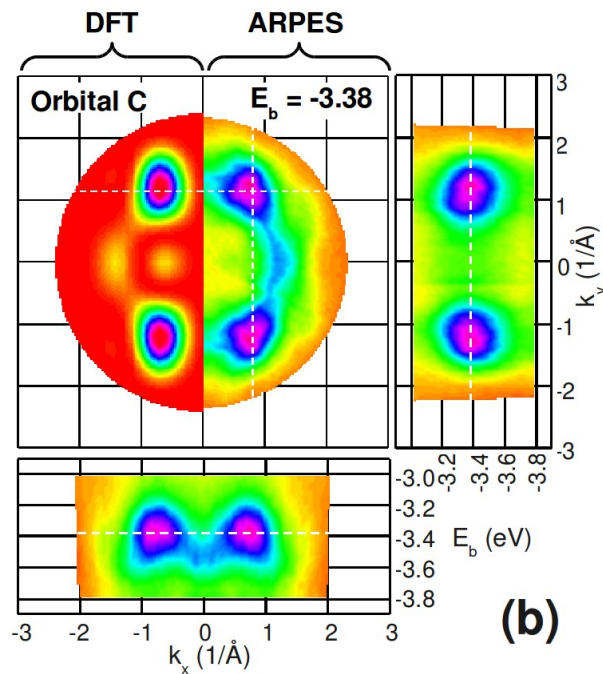
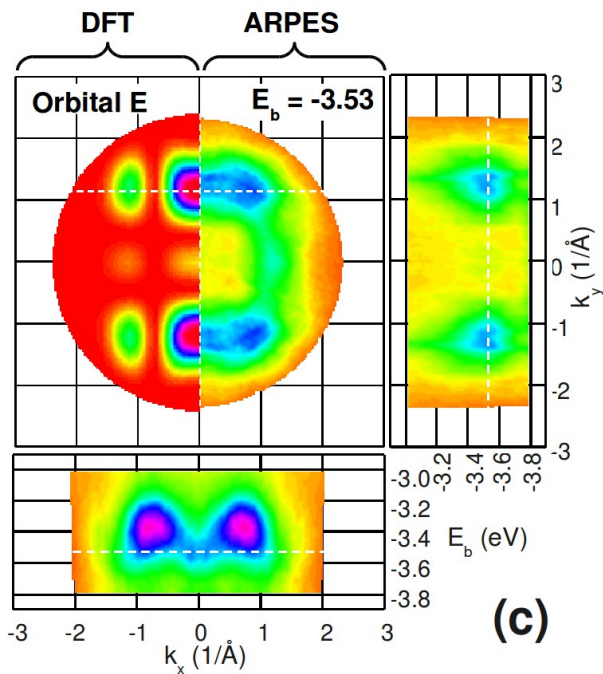
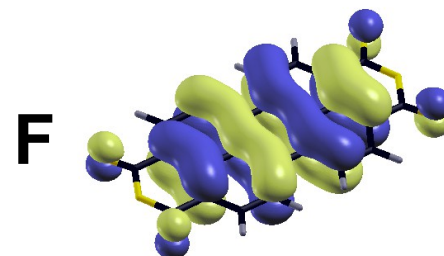
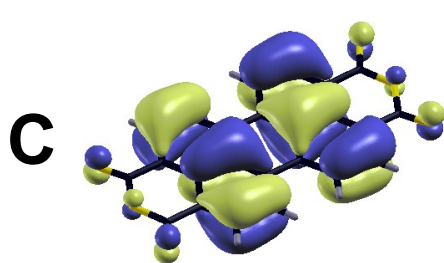
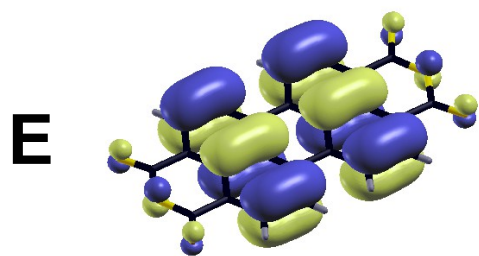
π -„Bands“ of PTCDA



What is the Origin of M3?

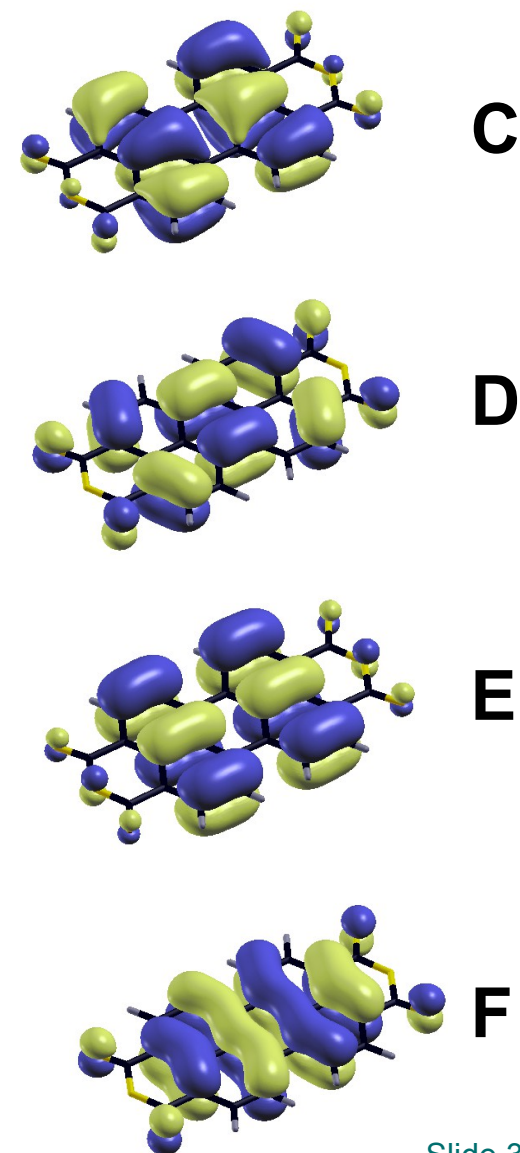
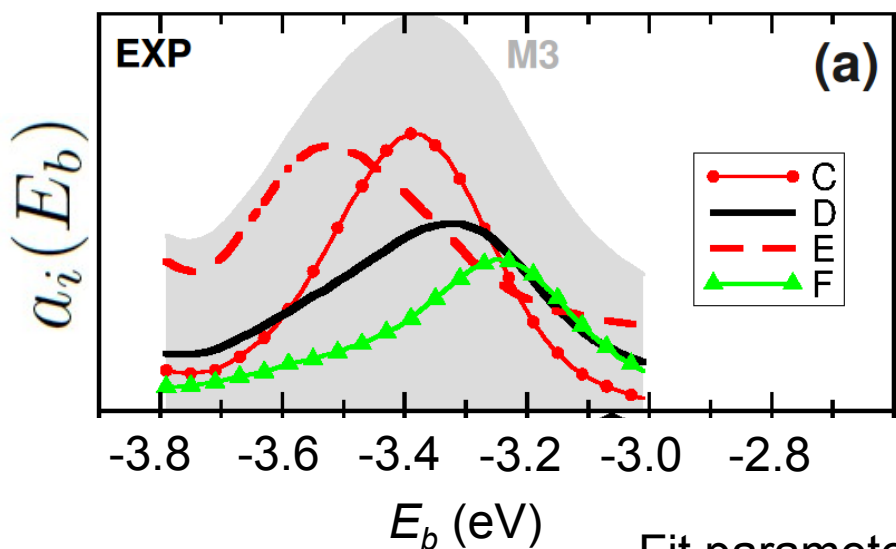


What is the Origin of M3?



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

Projected DOS from ARPES!



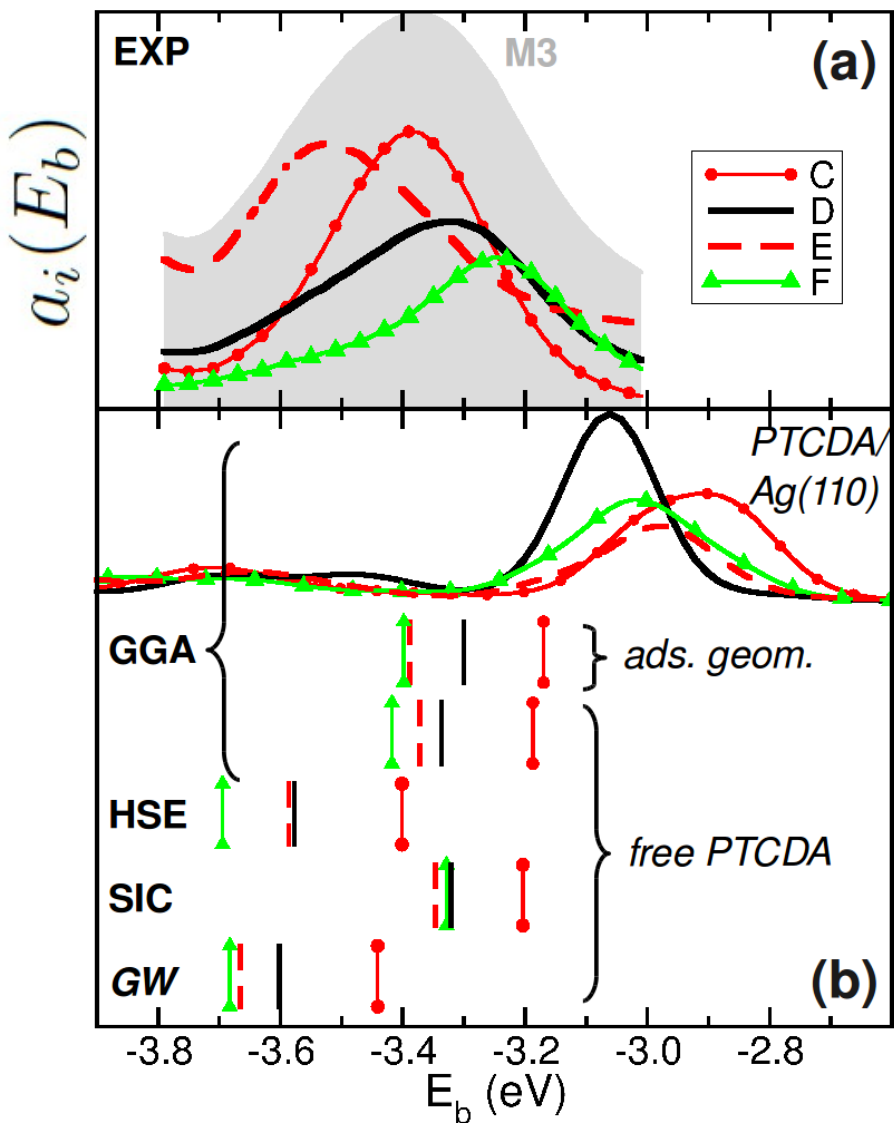
Fit parameters
= PDOS

calculated
orbitals

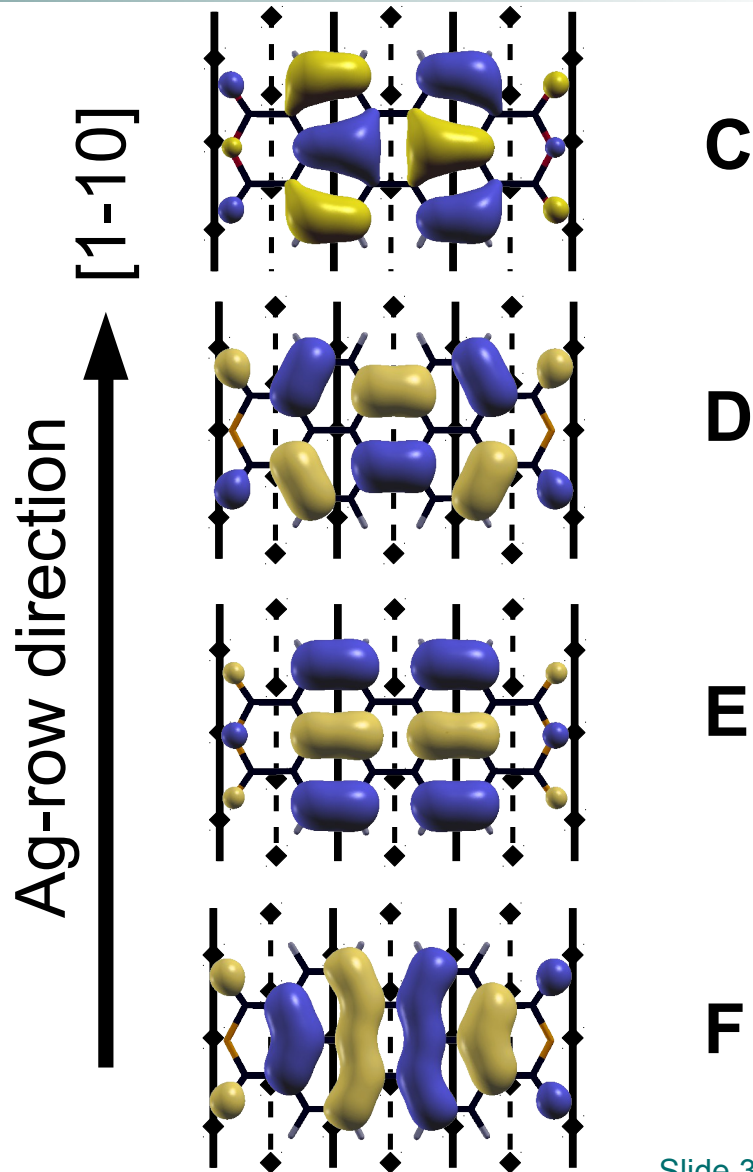
$$\chi^2 = \int dk_x dk_y \left[I(E_b, k_x, k_y) - \sum_i a_i(E_b) \phi_i(k_x, k_y) \right]^2$$

measured
photoemission
data cube

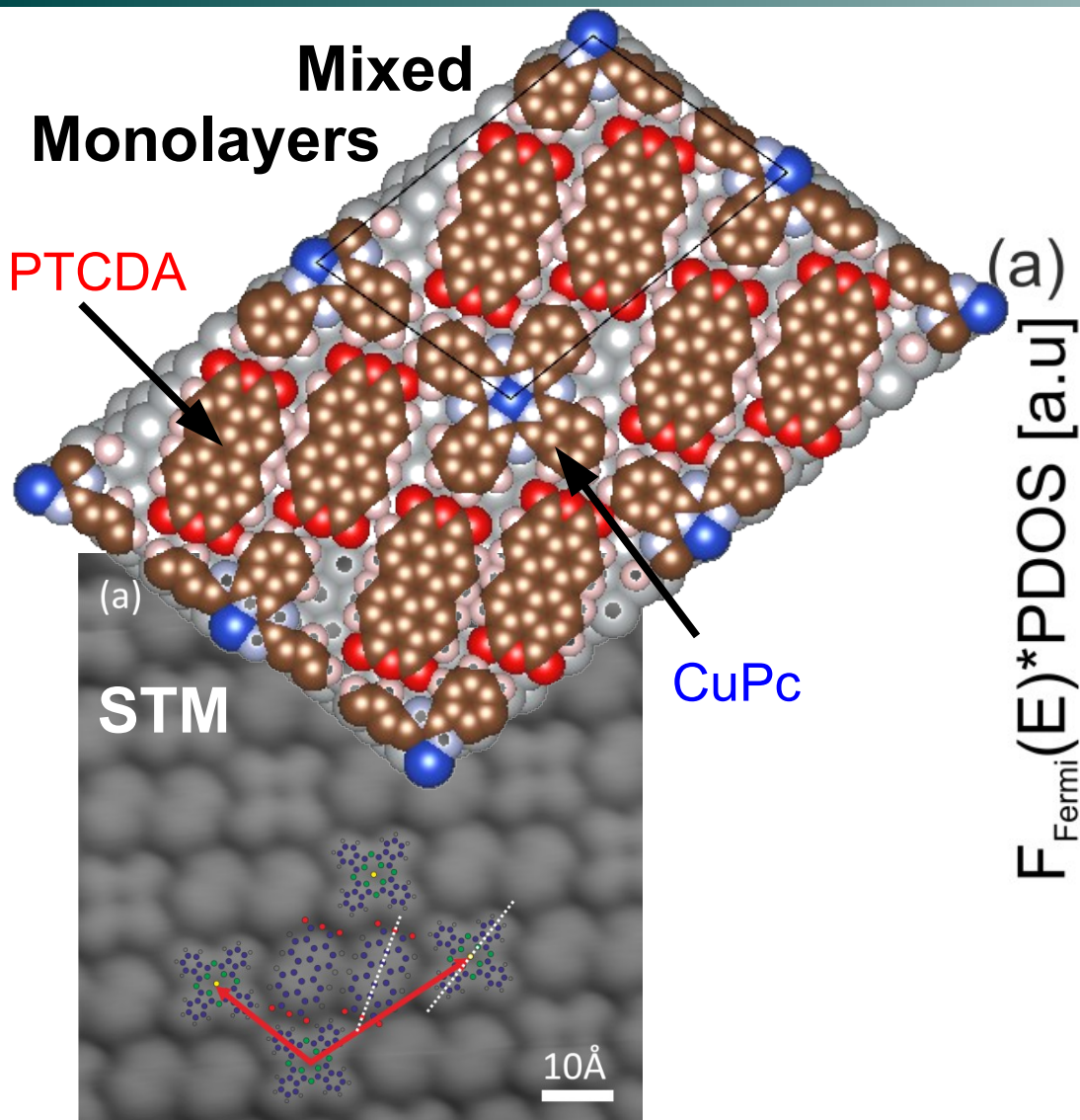
Benchmark for Theory



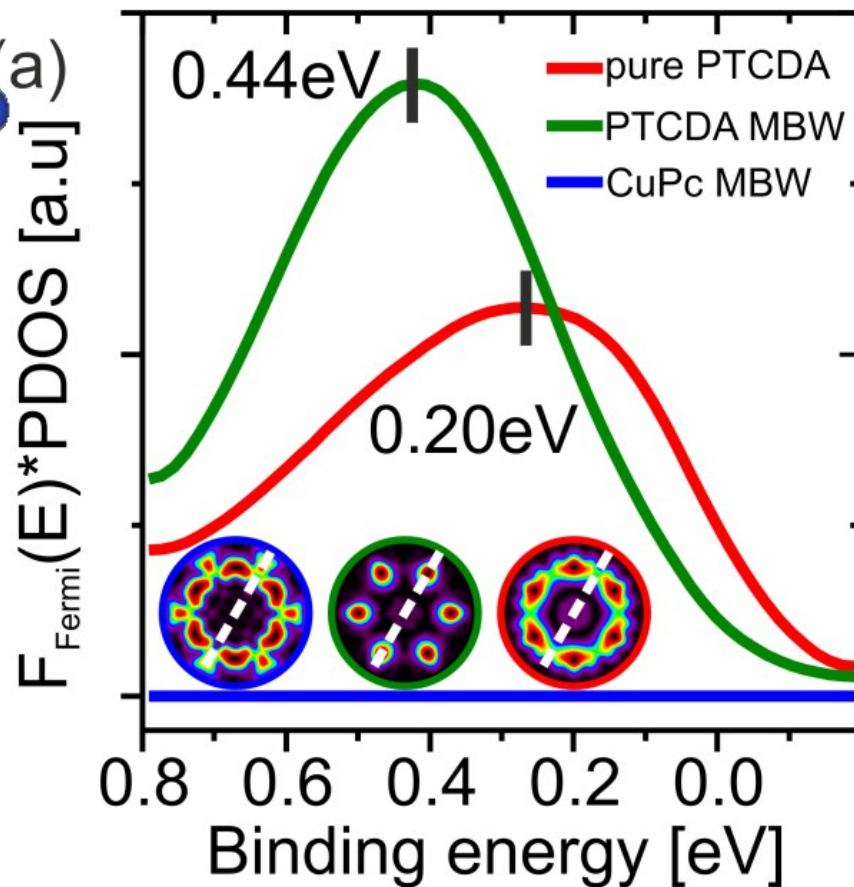
orbital energies / projected DOS (arb. units)



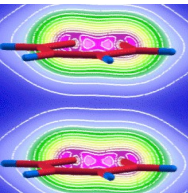
Identification of Orbitals



ARPES Tomography



Conclusion



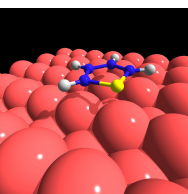
Van der Waals Interactions within DFT

Organic / organic works fine; organic / metal interactions more problematic

Nabok et al., PRB 77, 245316 (2008).

Sony et al., PRL. 99, 176401 (2007).

Romaner et al., NJP 11, 053010 (2009).



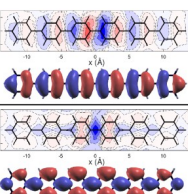
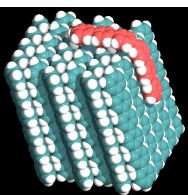
Island Growth and Step-Edge Barriers

Critical cluster = 2-3, Transition lying \rightarrow standing p-6P about 15 molecules

Potocar et al., PRB 83, 075423 (2011).

Some success in understanding certain kinetic barriers,
but still a lot of work to do ...

G. Hlawacek et al., Science 321, 108 (2008); see also: Goose et al., PRB 81, 205310 (2010).



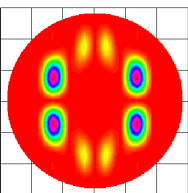
Orbital Densities and Hybridization with Metallic States

Puschnig et al., Science 326, 702 (2009); Zirotto et al., Phys. Rev. Lett. 104, 233004 (2010).

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

Orbital Tomography [Puschnig et al. PRB 84, 235427 (2011)]

- 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



Collaborations and Funding

Lehrstuhl für Atomistic Modelling and Design of Materials – MU Leoben

Dmitrii Nabok, Priya Sony, Lorenz Romaner, Claudia Ambrosch-Draxl

Institut für Physik, Montanuniversität Leoben, Austria

Gregor Hlawacek, Stefan Lorbek, Quan Shen, Christian Teichert



Theoretical Physics – University Graz, Austria

Daniel Lüftner, Matus Milko, Peter Puschnig

Experimental Surface Science Group – University Graz, Austria

Thomas Ules, Eva-Maria Reinisch, Stephen Berkebile, Alexander Fleming

Georg Koller, Mike Ramsey



Institut für Festkörperphysik, TU Graz, Austria

Thomas Potocar, Paul Frank, Adolf Winkler



Peter Grünberg Institut (PGI-3), JARA, Forschungszentrum Jülich,

Sergey Soubatch

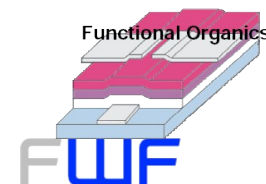
Stefan Tautz



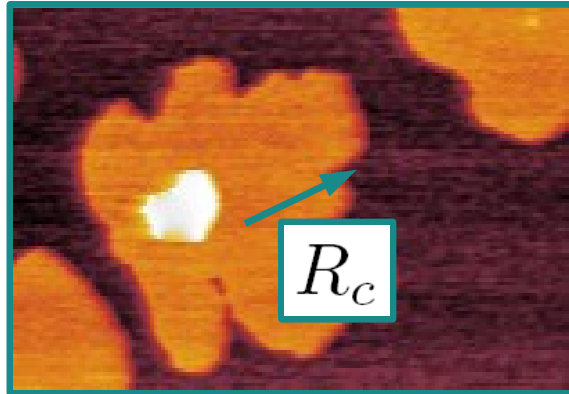
The work is part of the National Research Network

„**Interface controlled and functionalized organic films**“

and the single project P 23190-N16 „Understanding photoemission of organic thin films“

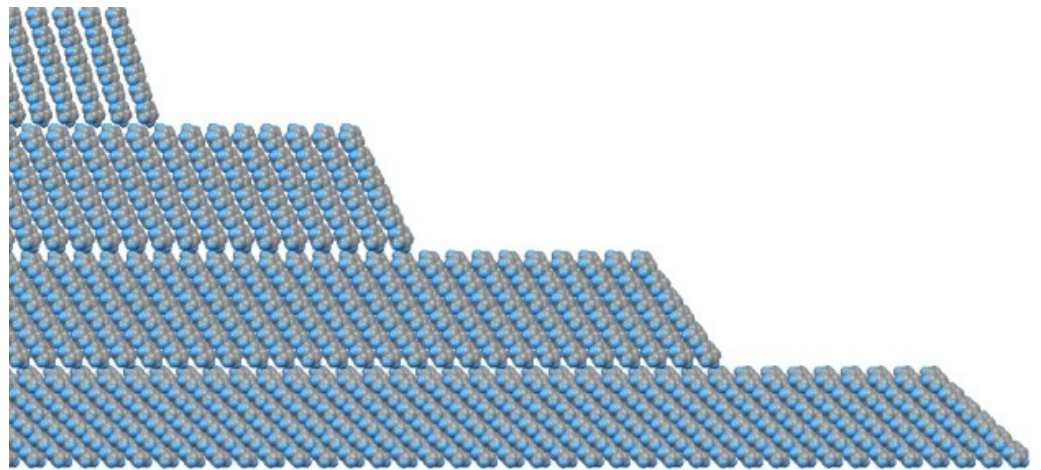
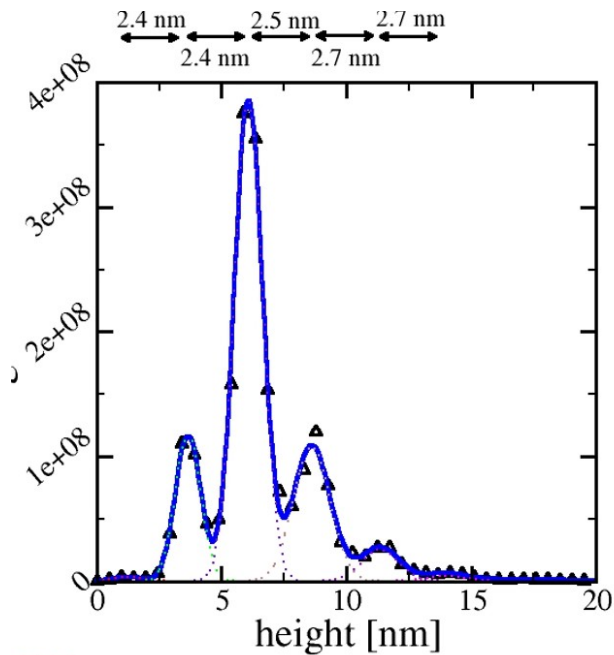
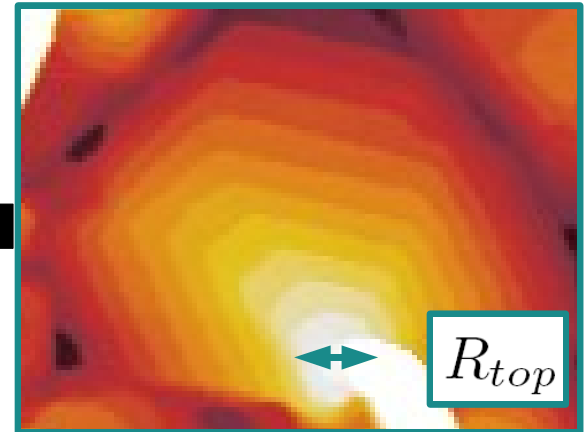


Layer-Dependent ESB

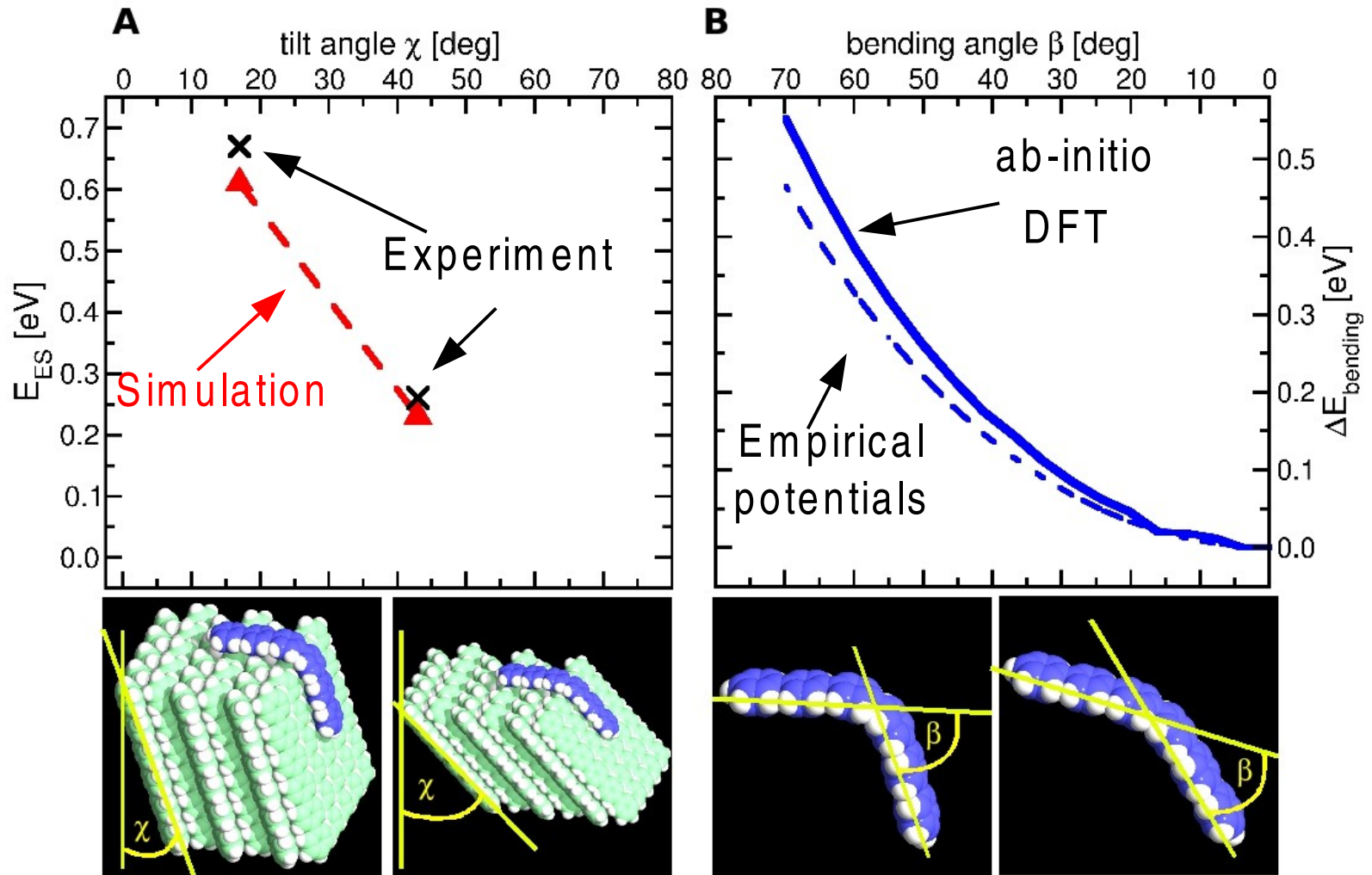


ESB

0.26 vs. 0.67



Layer-Dependent ESB



G. Hlawacek et al., *Science* **321**, 108 (2008).

ARPES Map of σ -Orbital

