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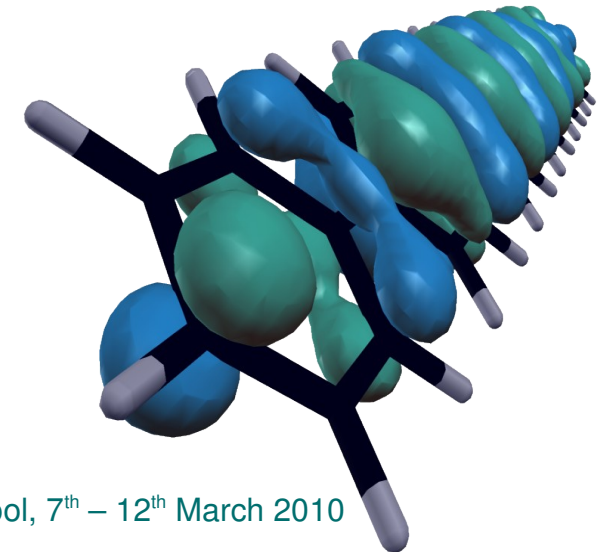
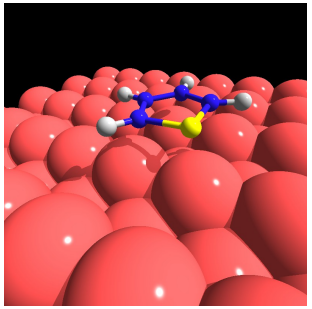
Fundamental Properties of Organic Semiconductors from Density Functional Theory



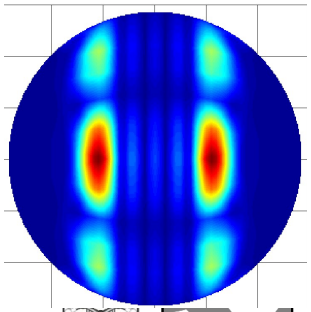
Overview

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

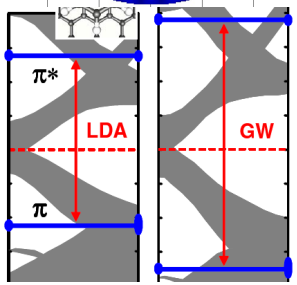
Density Functional Theory



Structural Properties

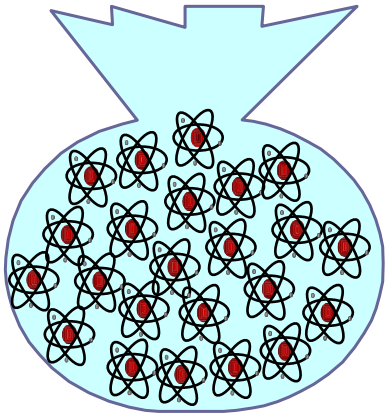


Electronic Structure



Problems in DFT

From First-Principles



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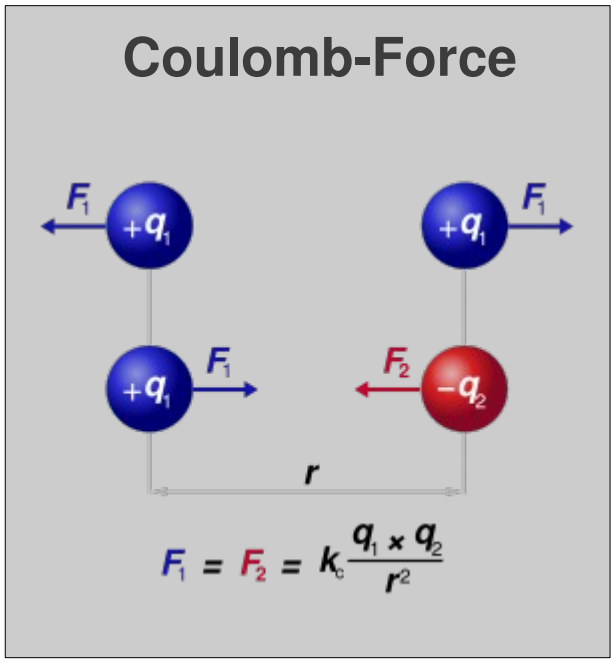

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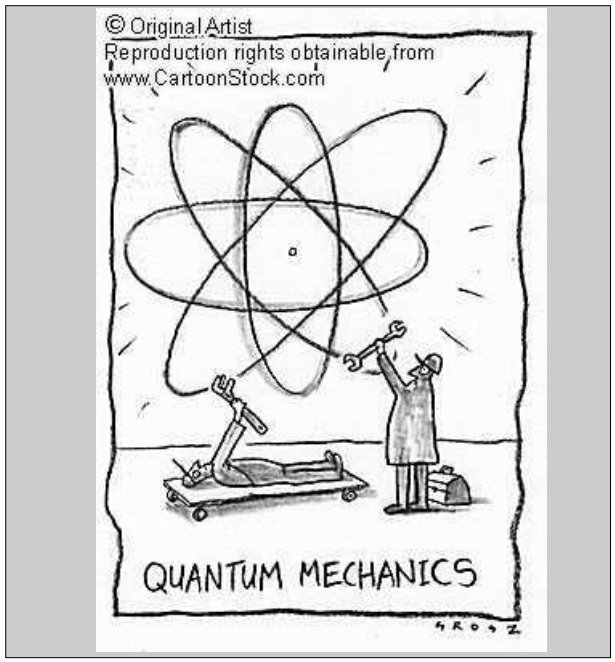


type of bonding

crystal structure

elastic constants

lattice vibrations

band structure

Many-Electron-Problem

Many-Electron Schrödinger Equation

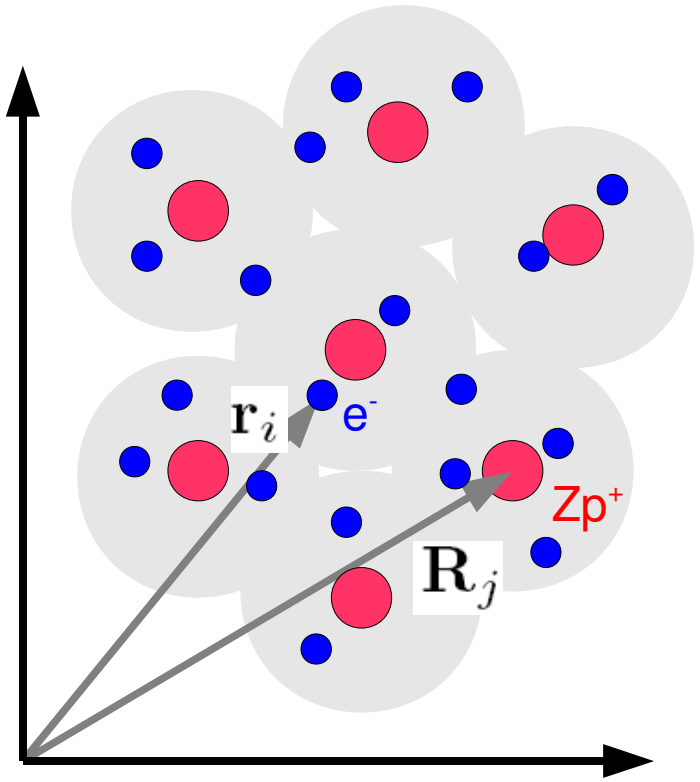
$$H\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_n) = E\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_n)$$

Total Electronic Hamiltonian

$$H = \sum_{i=1}^{n} h_i + V_{e-e}$$

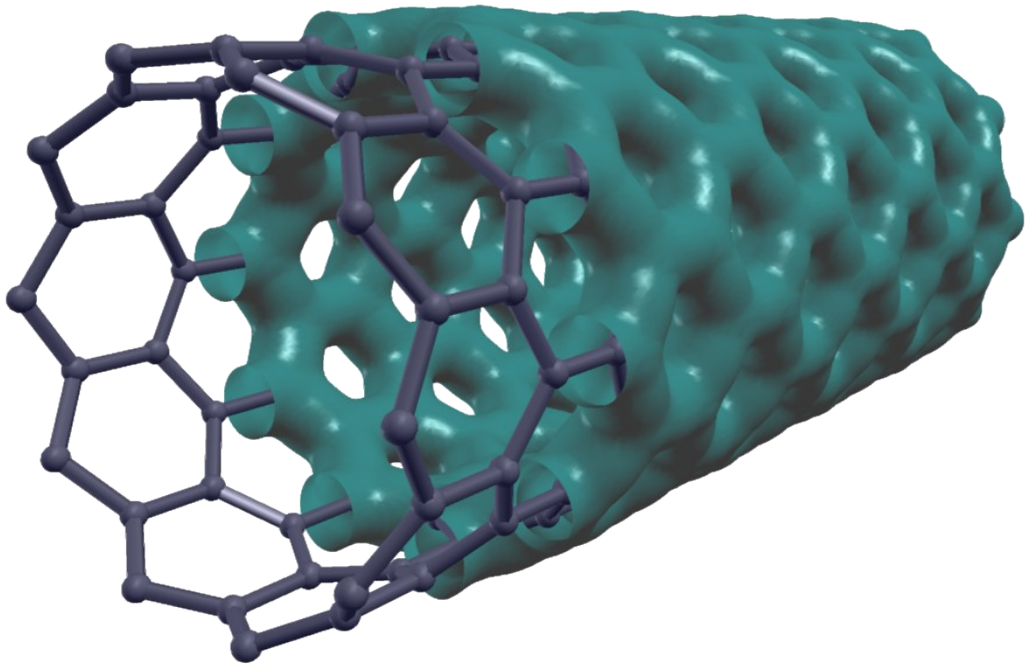
$$h_i = -\frac{\hbar^2}{2m_e}\Delta_i + \sum_{j=1}^{N} \frac{1}{4\pi\epsilon_0} \frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|}$$

$$V_{e-e} = \sum_{i=2}^{n} \sum_{j=1}^{i-1} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$



Electron Density Distribution

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



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

Hohenberg-Kohn Theorem

universal functional of the electron density

external potential due to atomic nuclei

$$E = F[n(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}^3 r$$

- The total energy of a system of interacting electrons is a functional of the density.
- The energy takes its minimum at the ground state density.

Hohenberg-Kohn Theorem

universal functional of the electron density

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$$E = F[n(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}^3 r$$

- The total energy of a system of interacting electrons is a functional of the density.
- The energy takes its minimum at the ground state density.

Suggestion of Kohn and Sham:

exchange-correlation energy

$$F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}^3 r \mathrm{d}^3 r' + E_{xc}[n(\mathbf{r})]$$

Kohn-Sham Equations

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

- Replace the system of interacting electrons by a fictitious system of non-interacting electrons with the *same* density
- Single-electron Schrődinger equations with an *effective* potential

Kohn-Sham Equations

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

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

Atomic nuclei

Kohn-Sham Equations

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

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

Atomic nuclei

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

Hartree potential

Kohn-Sham Equations

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

$-\frac{Z}{r}$ — Atomic nuclei

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

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

classical electro-static interactions

Quantum-mechanical effects

Kohn-Sham Equations

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

$$-\frac{Z}{r} \qquad \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r' \qquad \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Self-consistency

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

Kohn-Sham Equations

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

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Approximations

Self-consistency

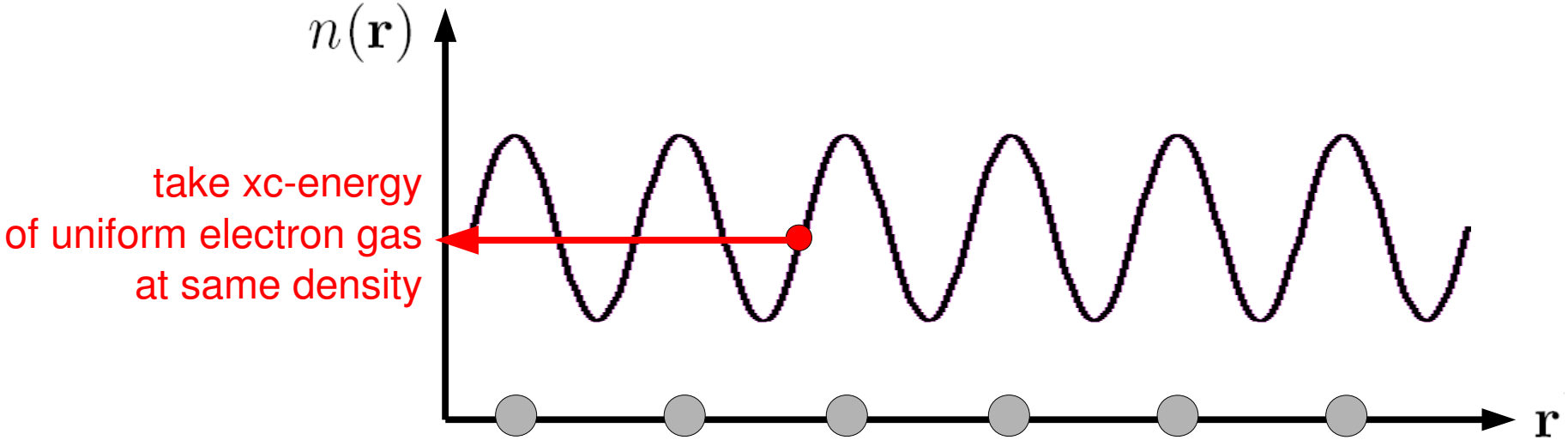
$$n(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2$$

Exchange-Correlation Functionals

First Generation (1980)

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r}) e_{xc}^{\text{uniform}}(n(\mathbf{r}))\, \mathrm{d}^3 r$$

Local Density Approximation (LDA)



Exchange-Correlation Functionals

First Generation (1980)

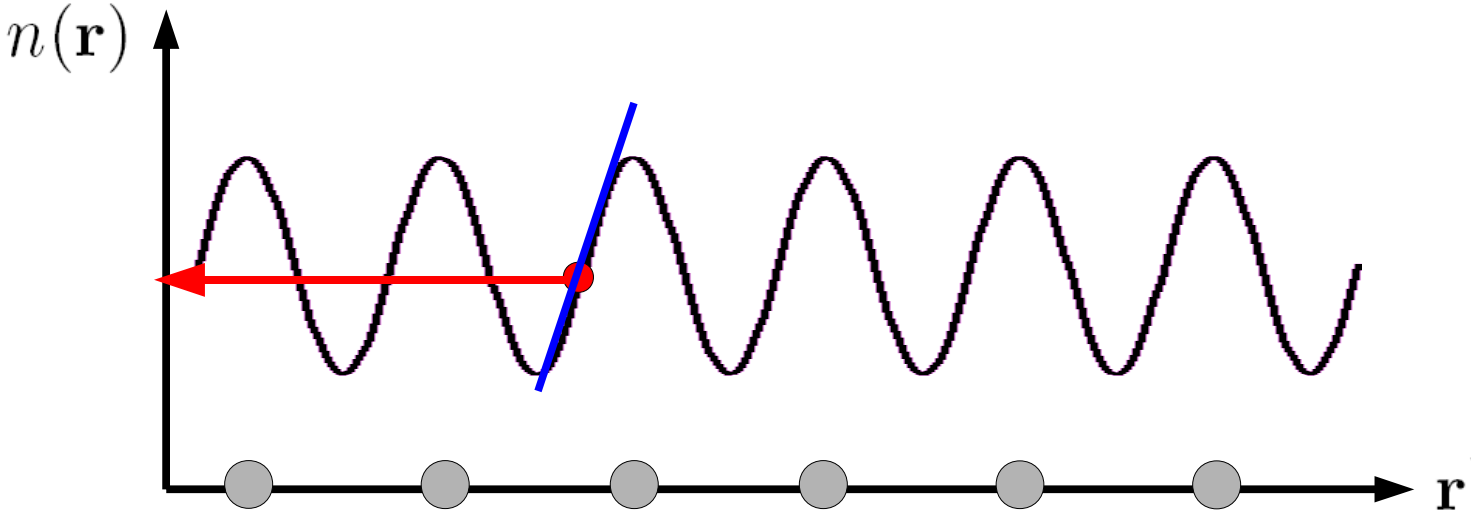
$$E_{xc}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r}) e_{xc}^{\text{uniform}}(n(\mathbf{r}))\, \mathrm{d}^3 r$$

Local Density Approximation (LDA)

Second Generation (1996)

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int n(\mathbf{r}) f(n(\mathbf{r}), |\nabla n(\mathbf{r})|)\, \mathrm{d}^3 r$$

Generalized Gradient Approximation (GGA)



Content

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Cohesive Energies of Molecular Crystals

Adsorption Energies of Molecules at Metal Surfaces

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PTCDA / Coinage Metal (111) Surfaces

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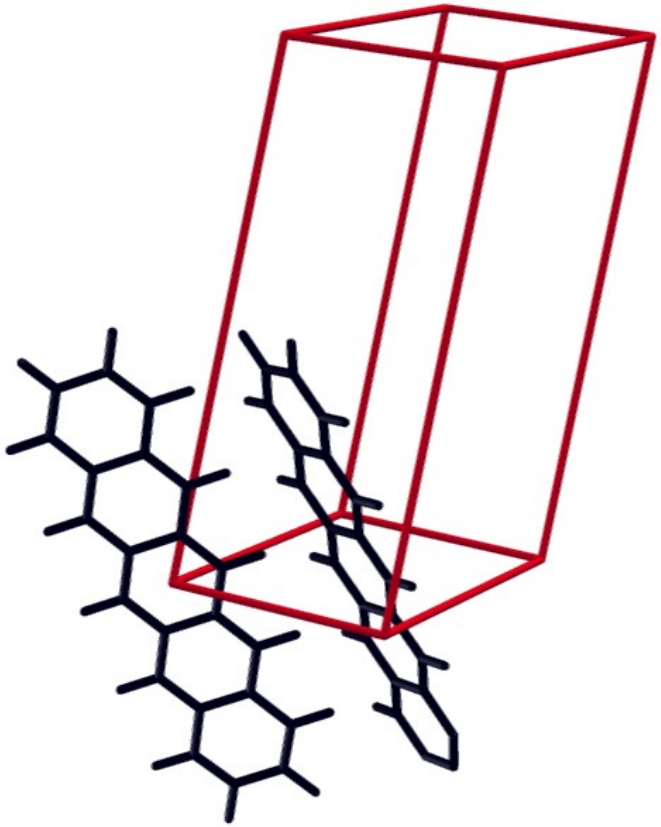
Cohesive Energy of Molecular Crystals

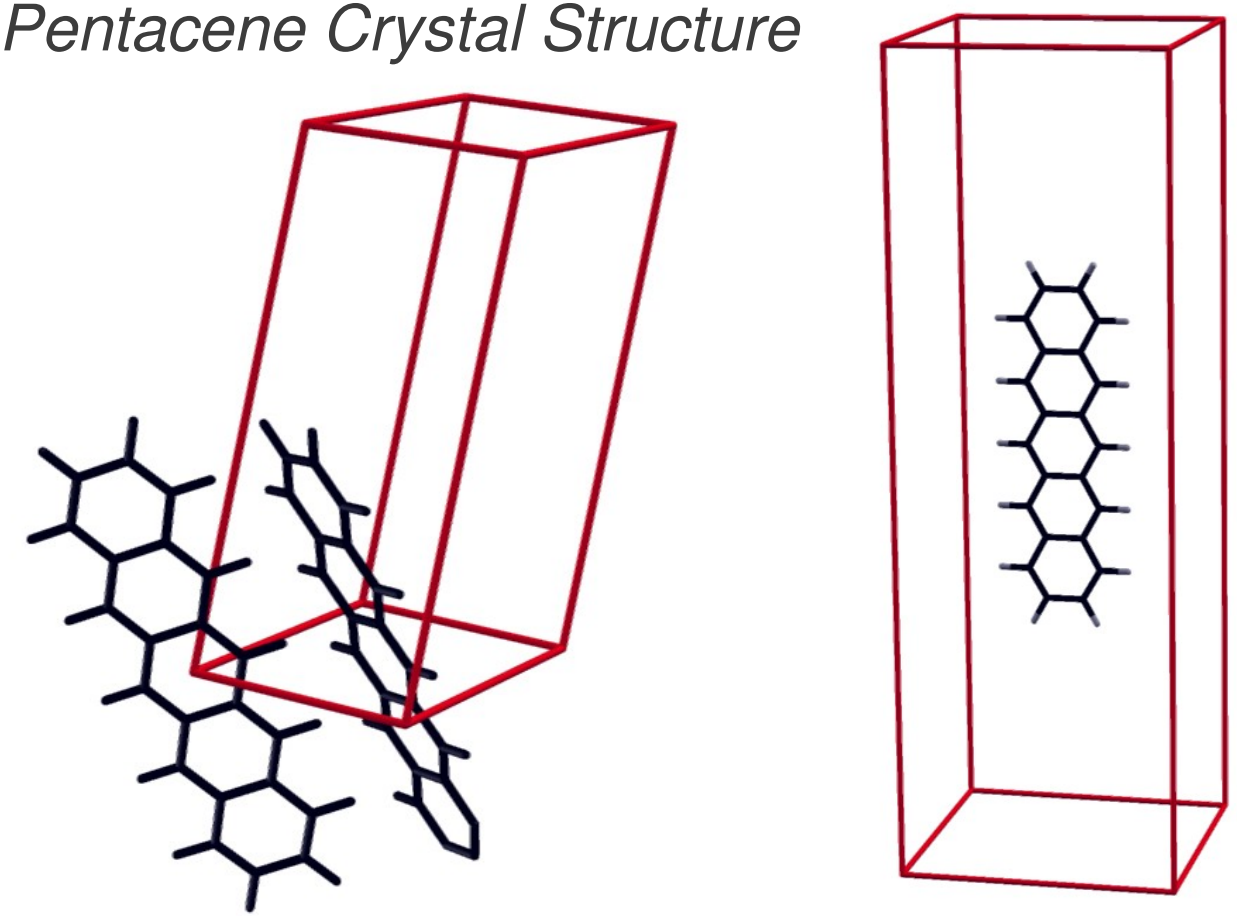
Pentacene Crystal Structure



$E_{crystal}$

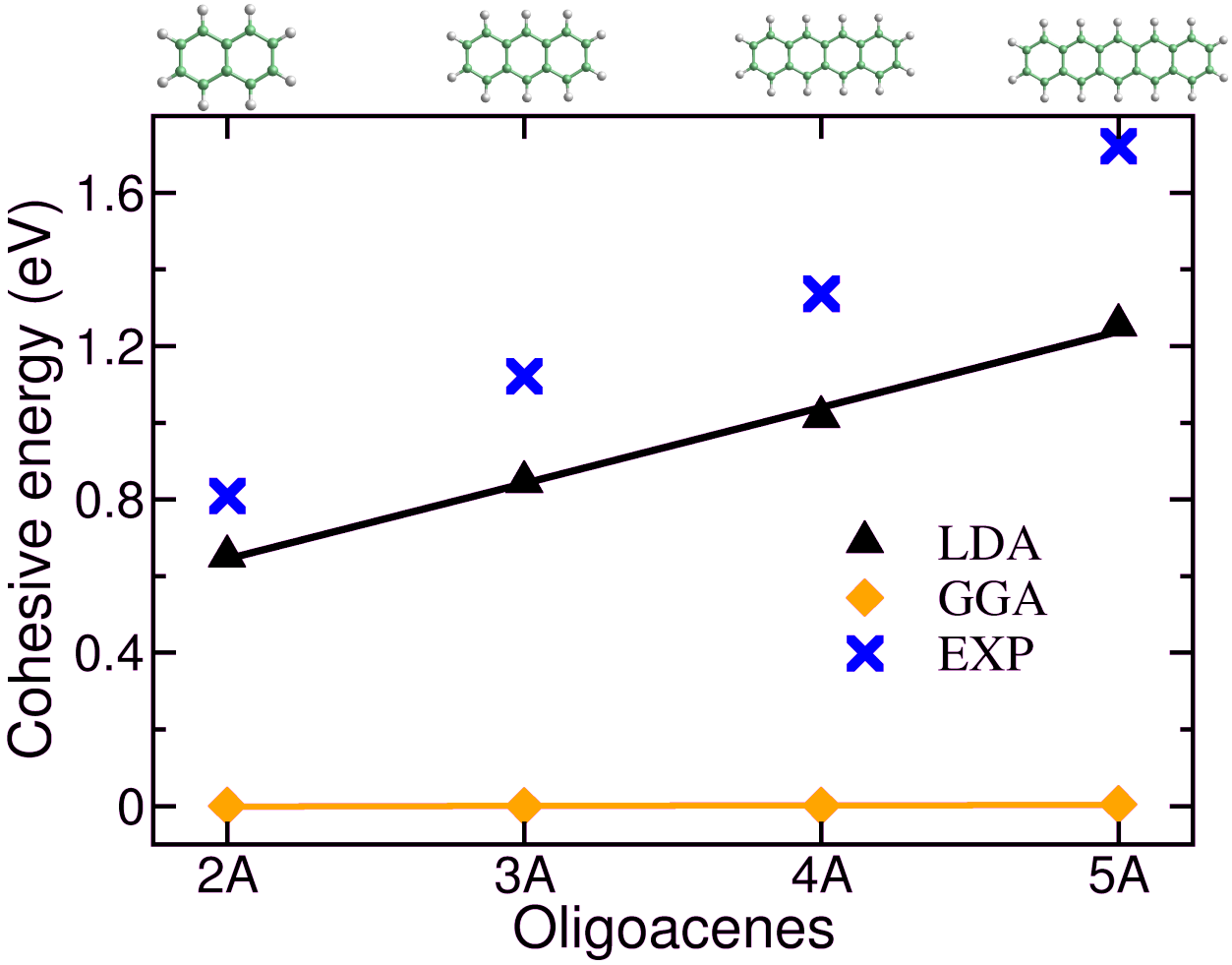
Cohesive Energy of Molecular Crystals

Pentacene Crystal Structure



$$E_{cohesive} = -[\ (1/2)E_{crystal} - E_{molecule}\ ]$$

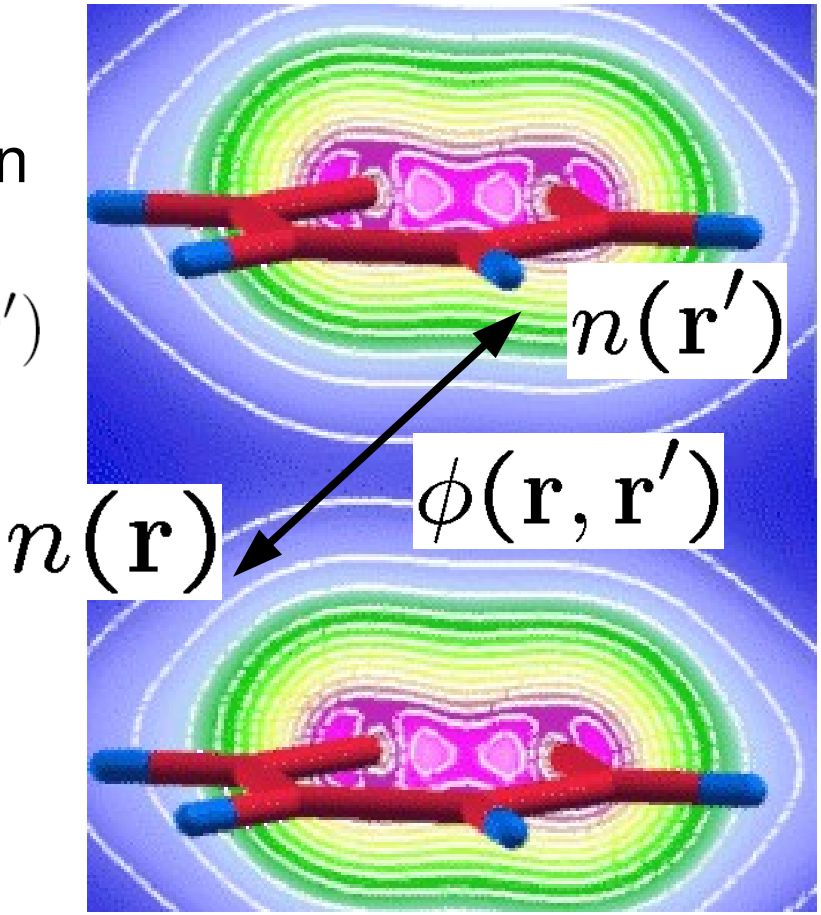
Cohesive Energy of Molecular Crystals



Van der Waals Density Functional

Nonlocal Correlation Energy
leading to van-der-Waals interaction

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

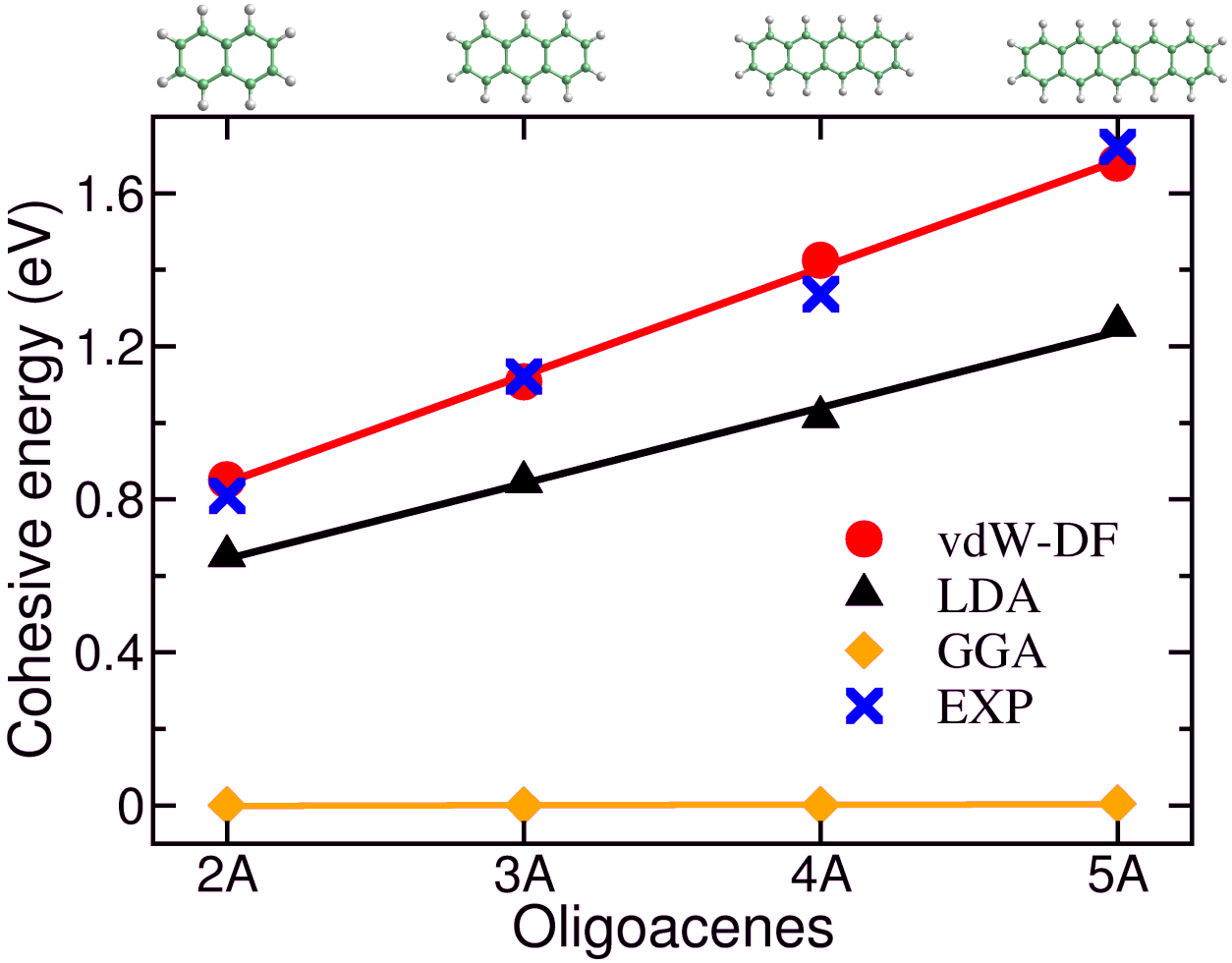


Exchange-Correlation Energy

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

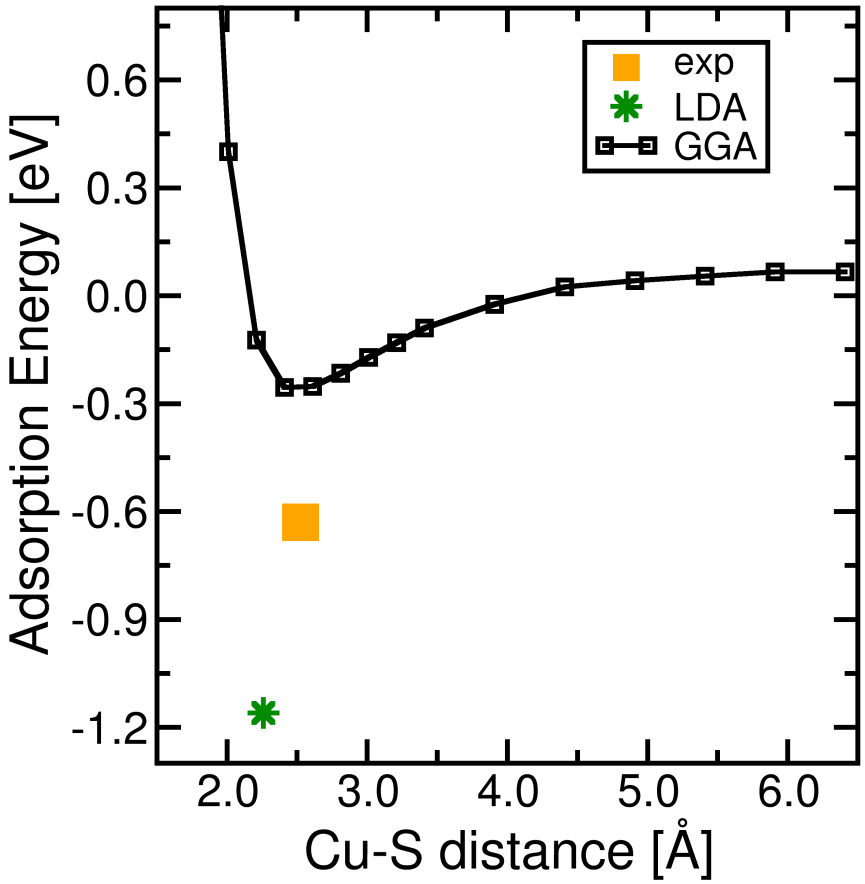
Dion et al, *Phys. Rev. Lett.* ***92****, 246401 (2004).*

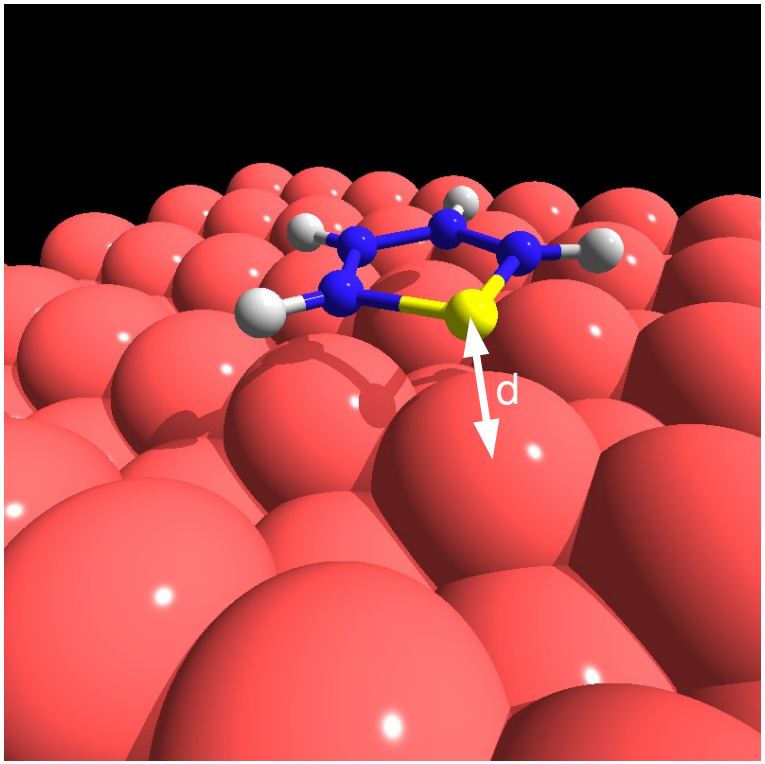
Cohesive Energy of Molecular Crystals



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

Thiophene / Cu(110)





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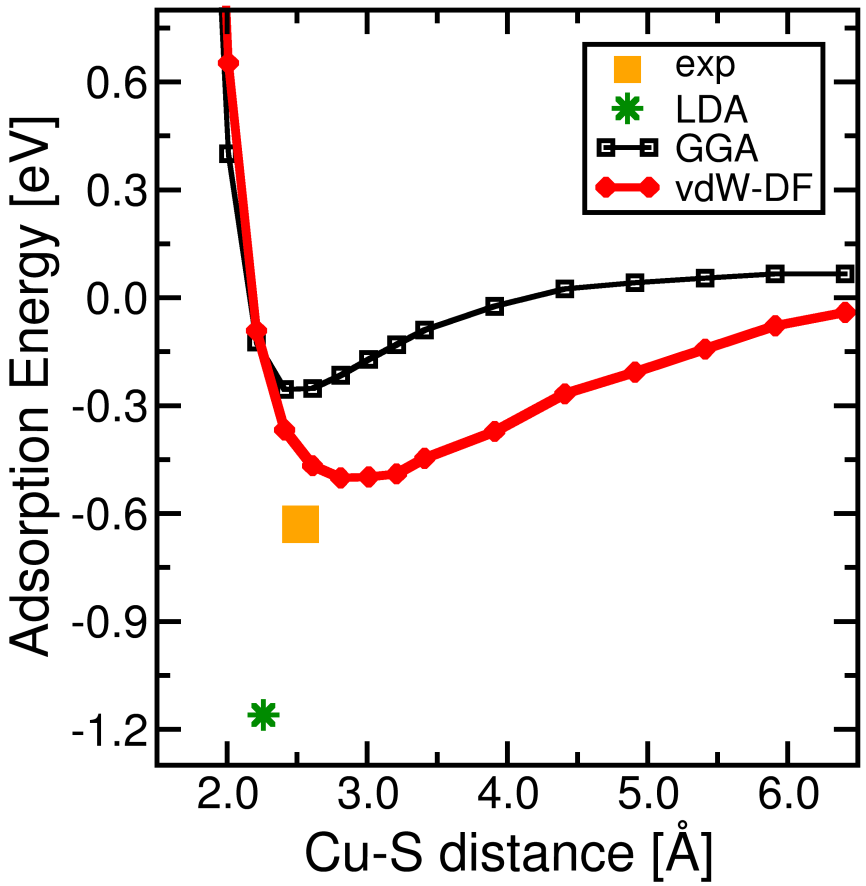
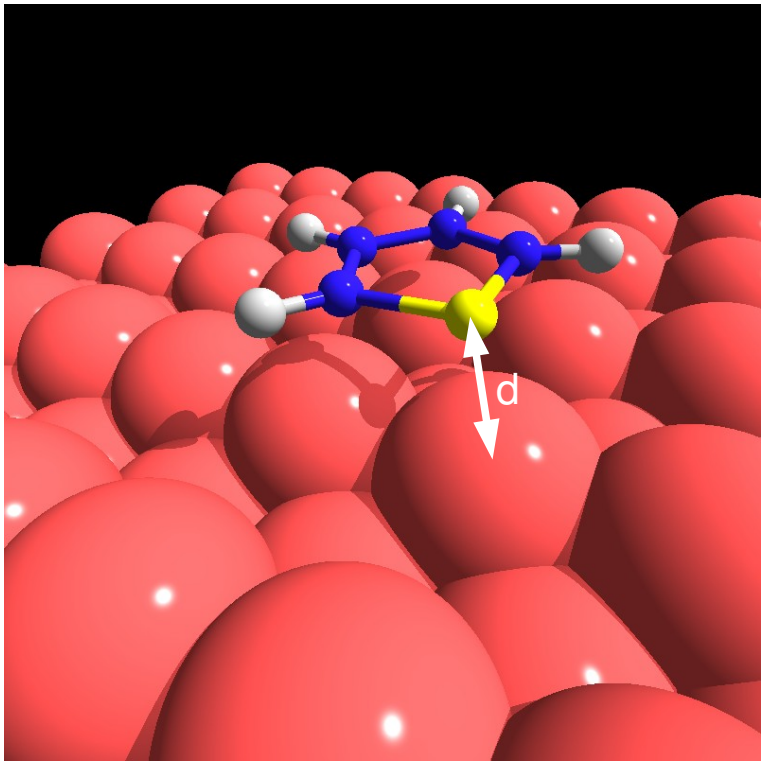
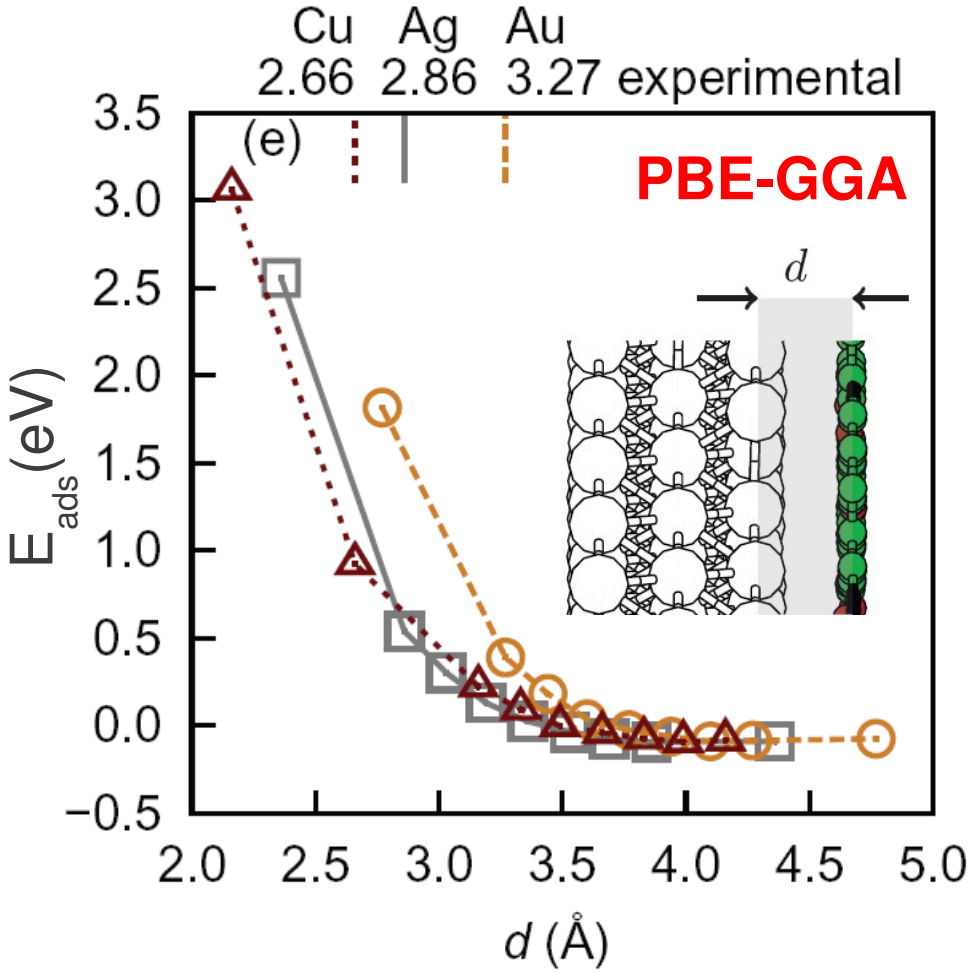
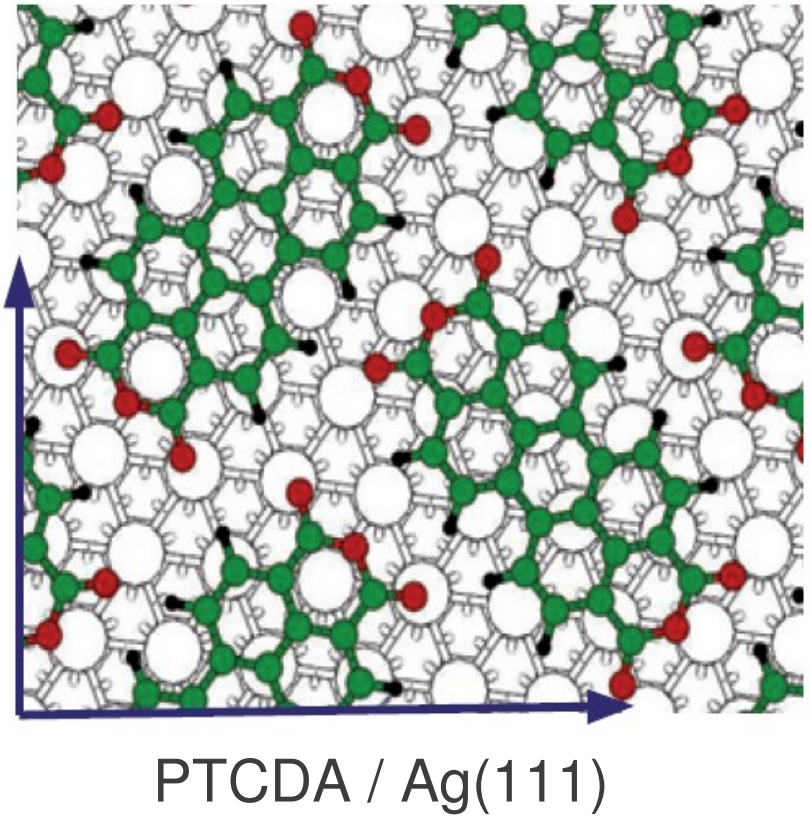




Sony, Puschnig, Nabok, Ambrosch-Draxl, *Phys. Rev. Lett.* ***99****, 176401 (2007).*

PTCDA / Coinage Metals

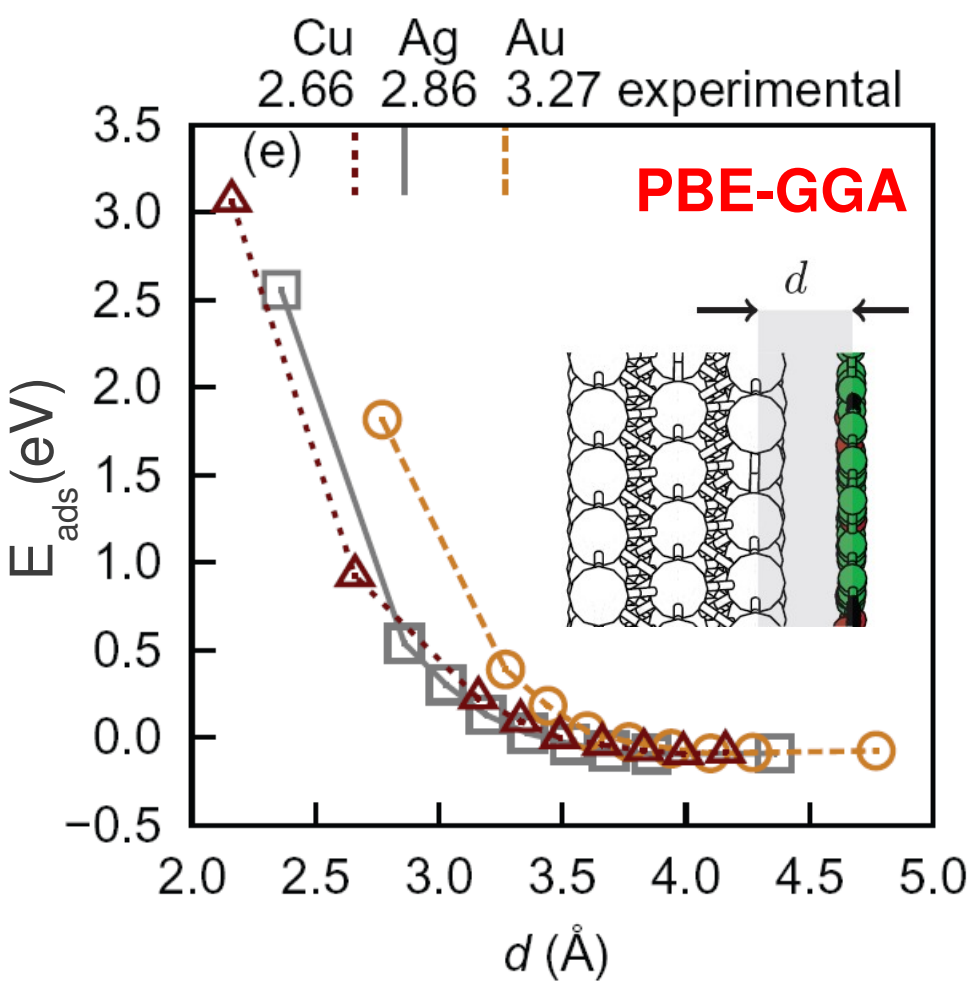


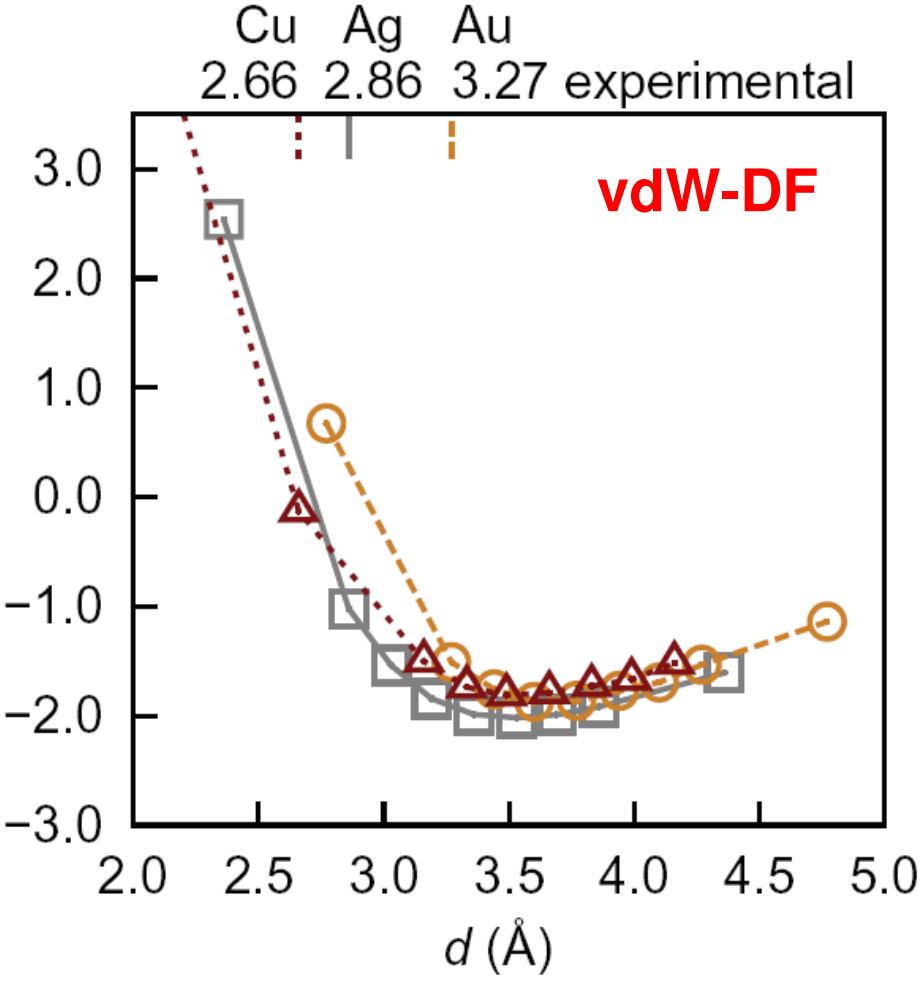


PTCDA / Ag(111)

Romaner, Nabok, Puschnig, Zojer, Ambrosch-Draxl, *New. J. Phys.* **11**, 053010 (2009).

PTCDA / Coinage Metals





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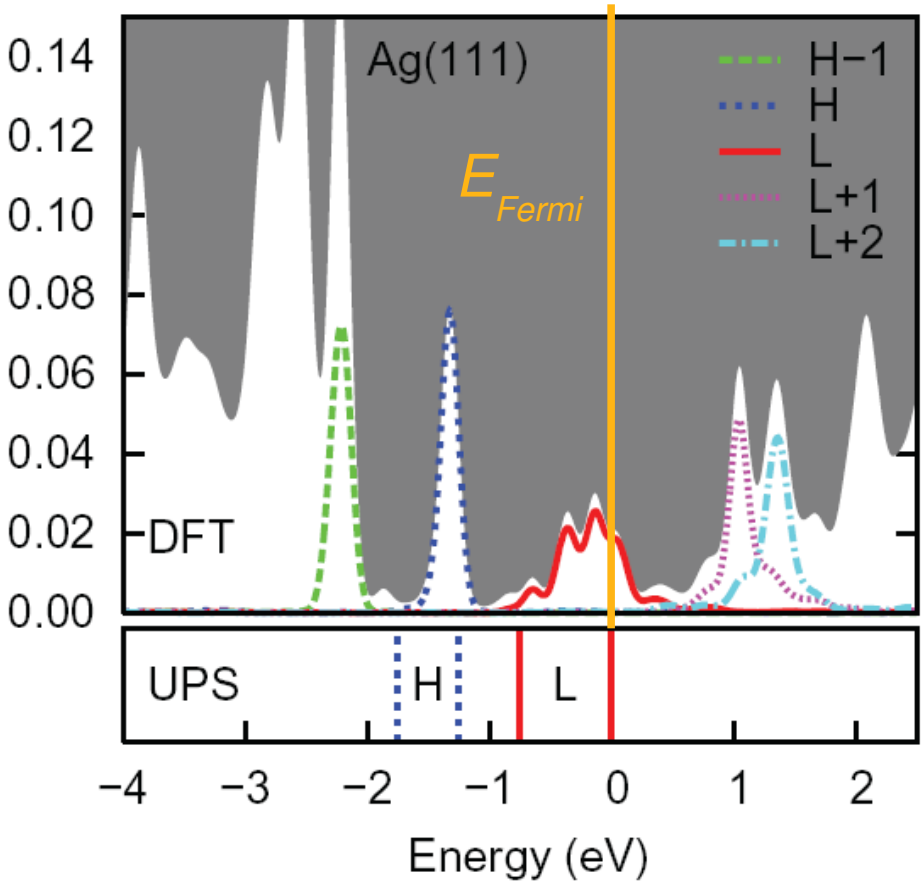
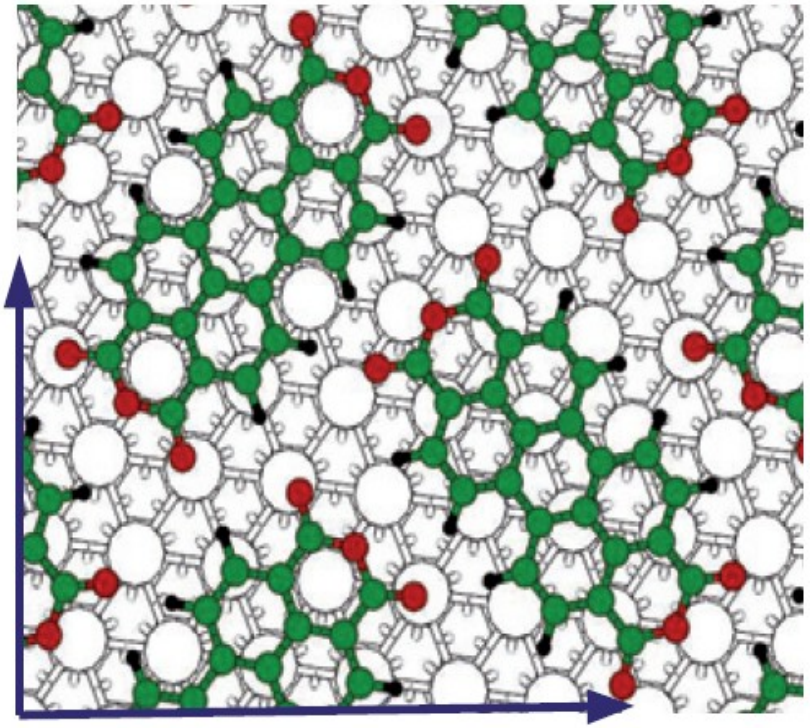
PDOS @ exp. distance



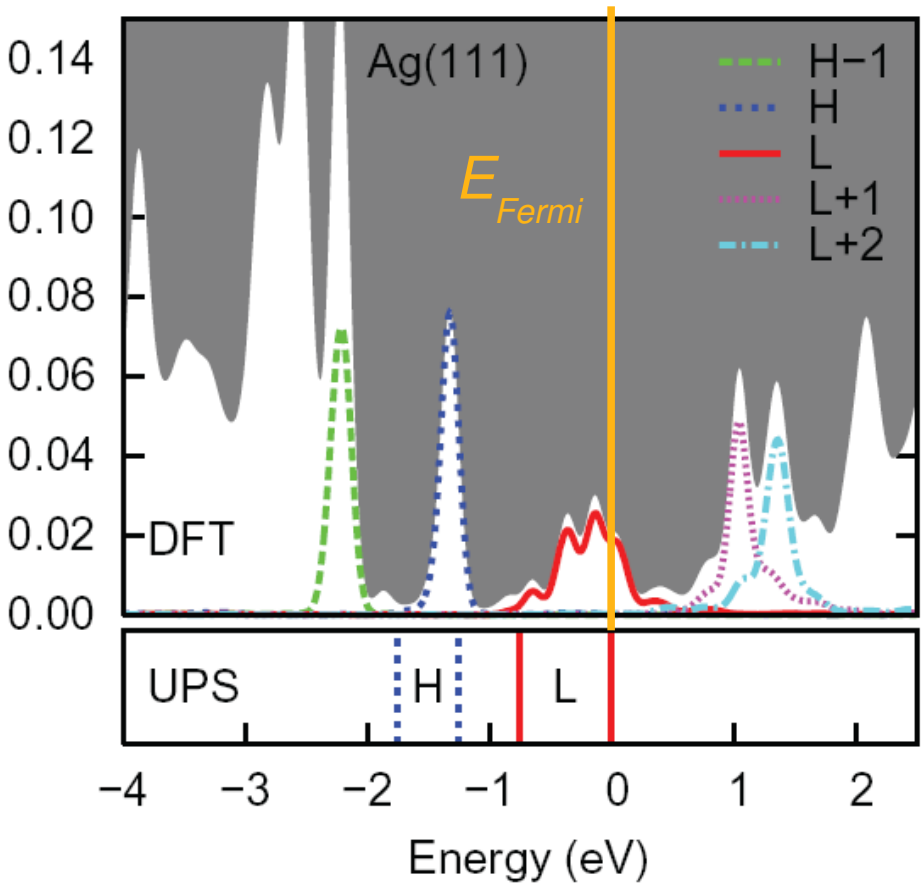


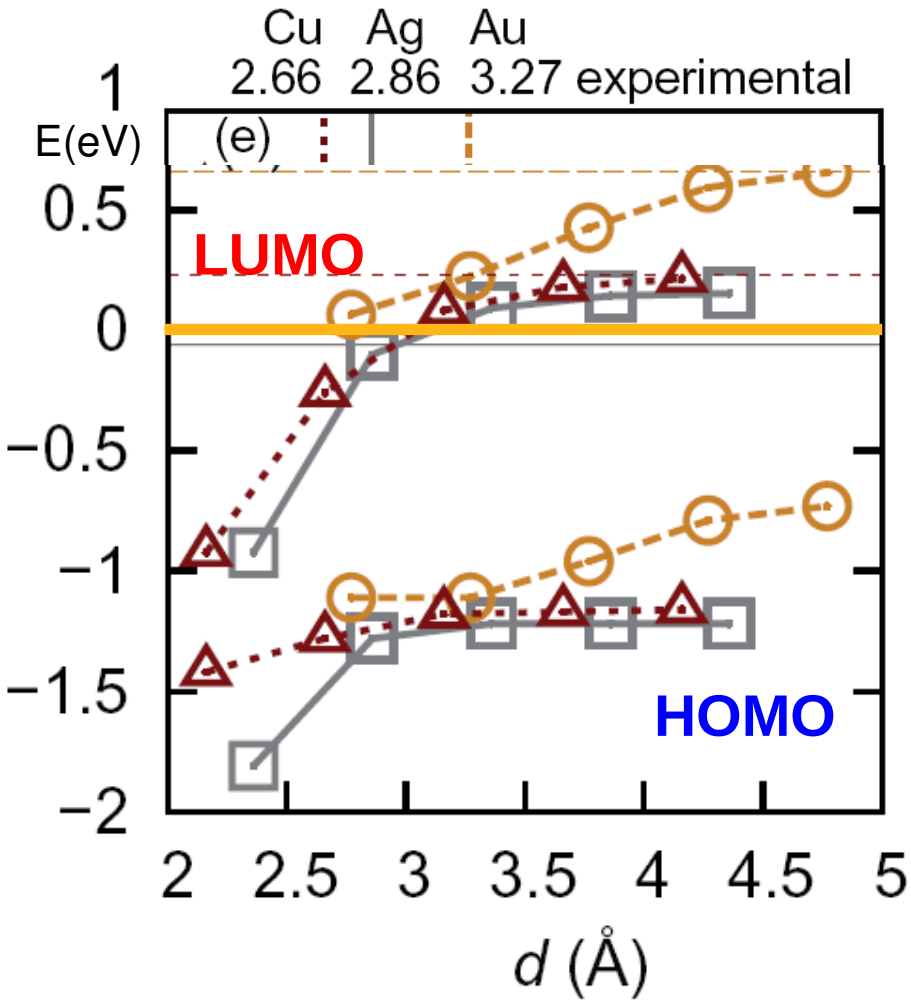
PTCDA / Ag(111)

Romaner, Nabok, Puschnig, Zojer, Ambrosch-Draxl, *New. J. Phys.* **11**, 053010 (2009).

Level Alignment

PDOS @ exp. distance

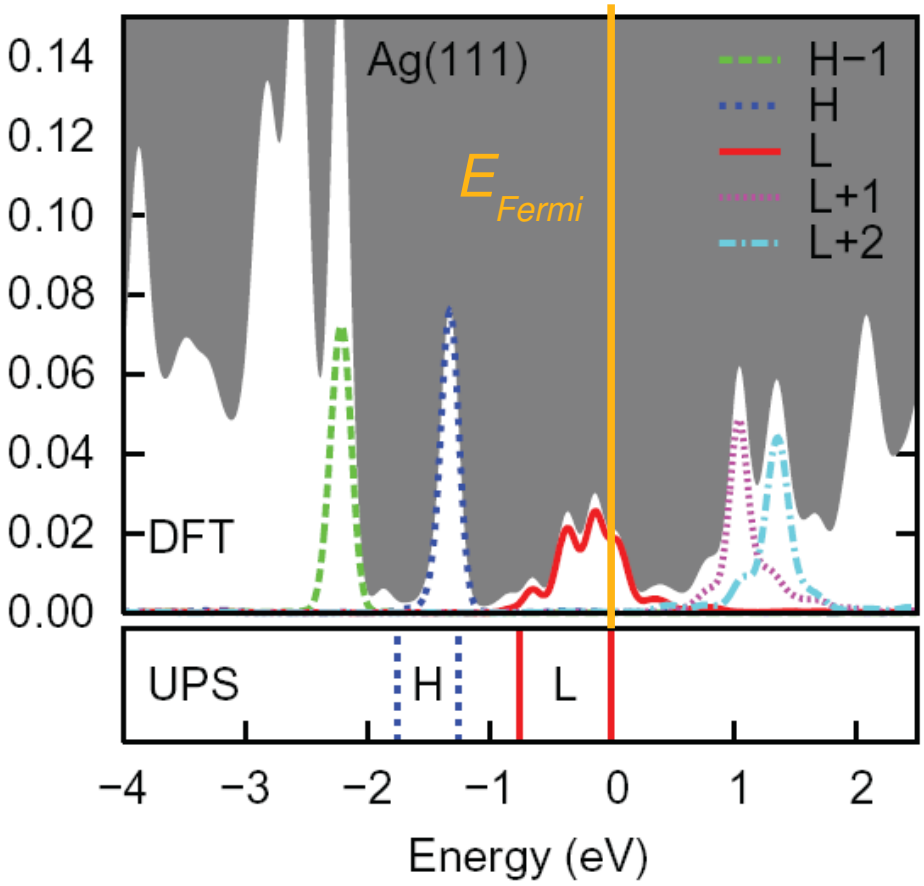




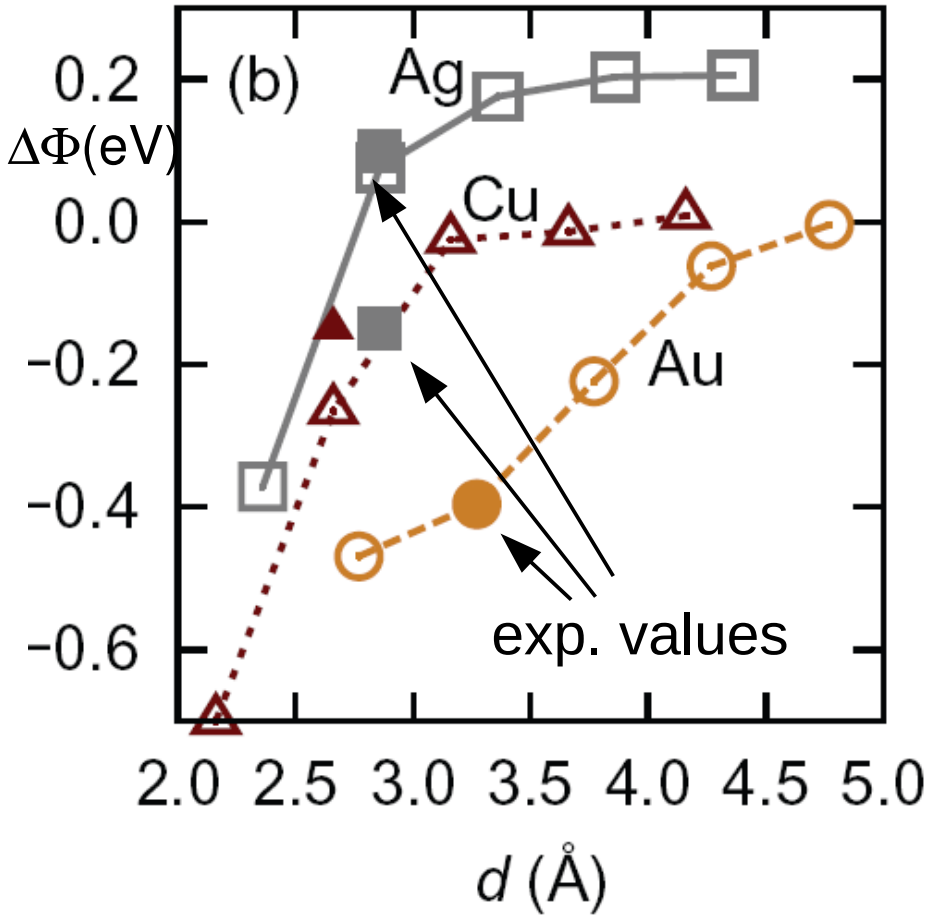
Romaner, Nabok, Puschnig, Zojer, Ambrosch-Draxl, *New. J. Phys.* **11**, 053010 (2009).

Work Function Change

PDOS @ exp. distance

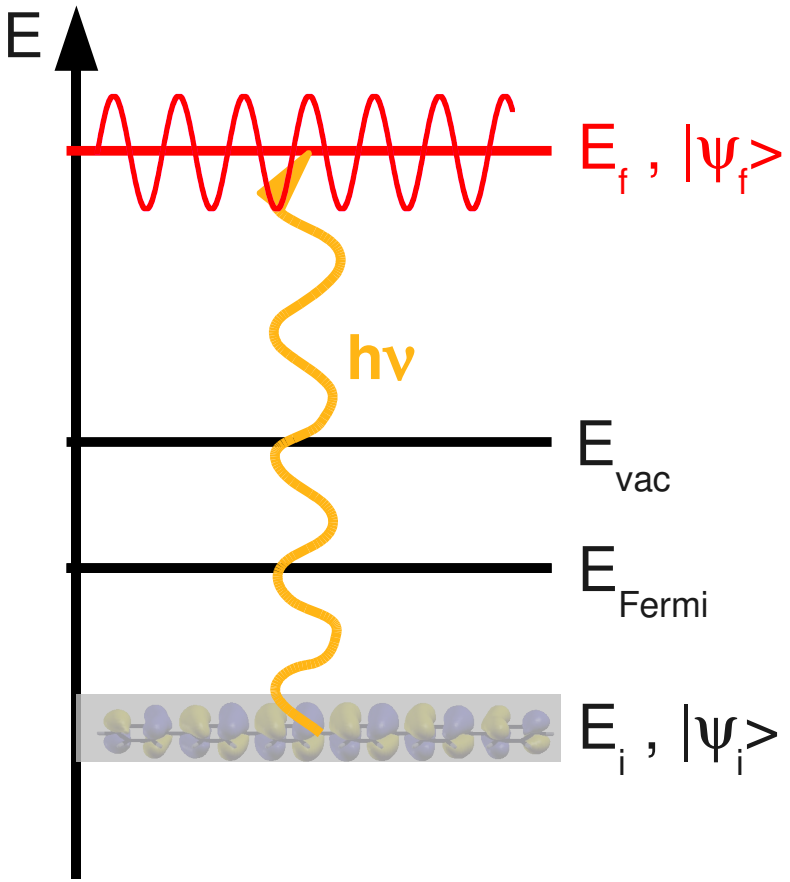


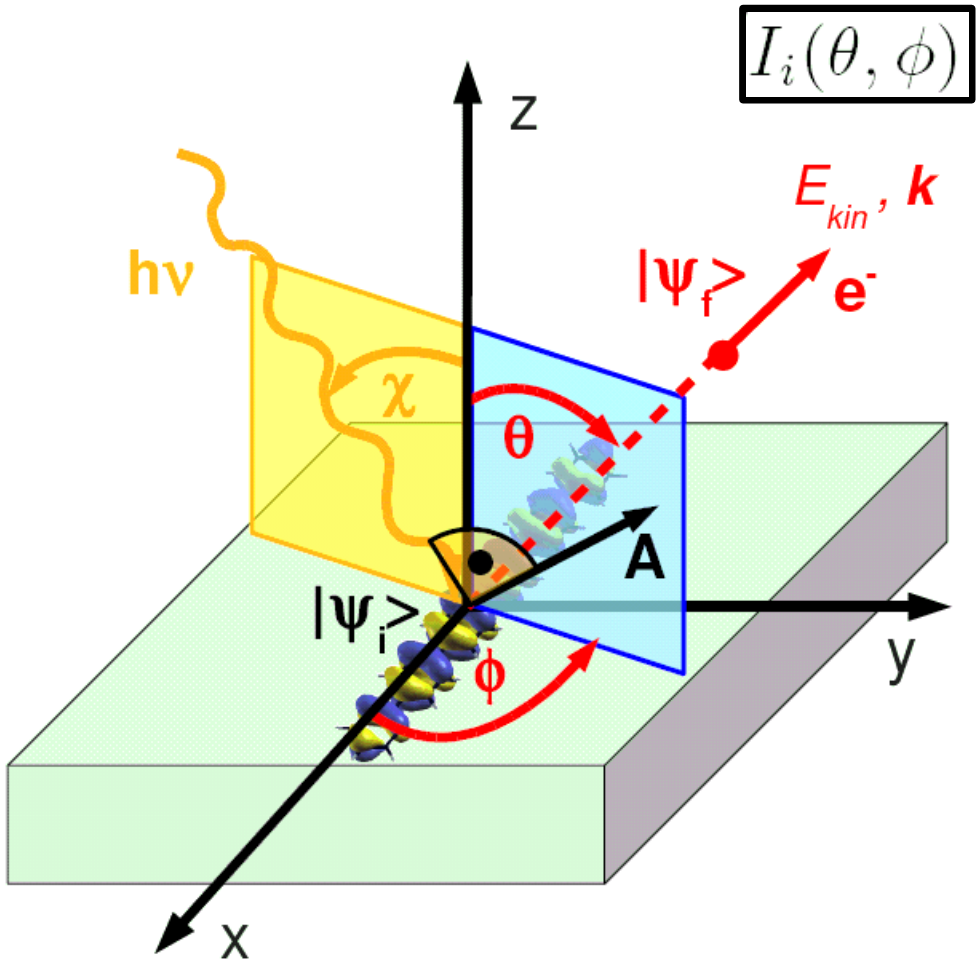
Work function change ΔΦ



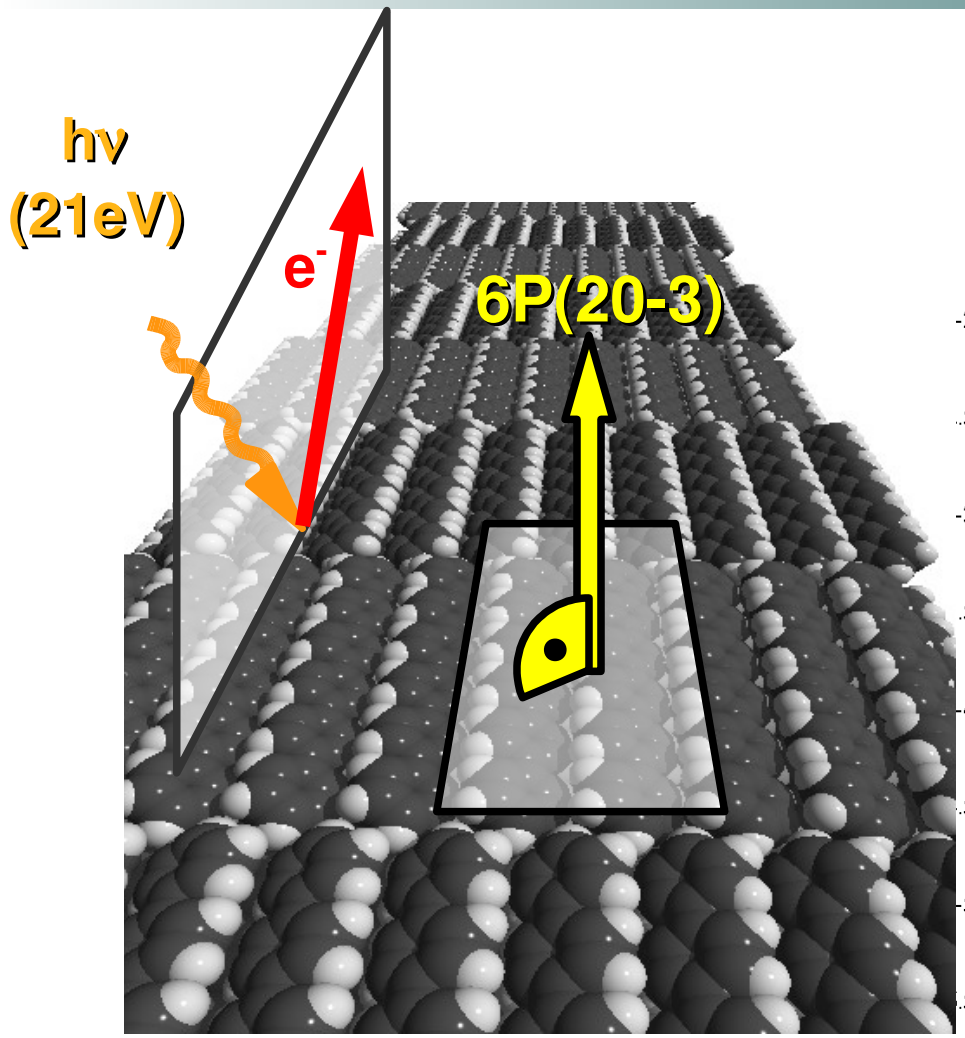
Romaner, Nabok, Puschnig, Zojer, Ambrosch-Draxl, *New. J. Phys.* **11**, 053010 (2009).

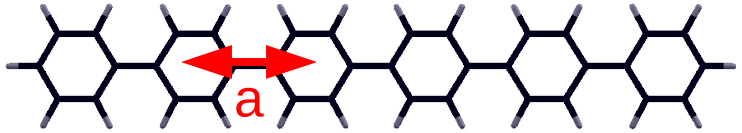
Angle-Resolved Photoemission

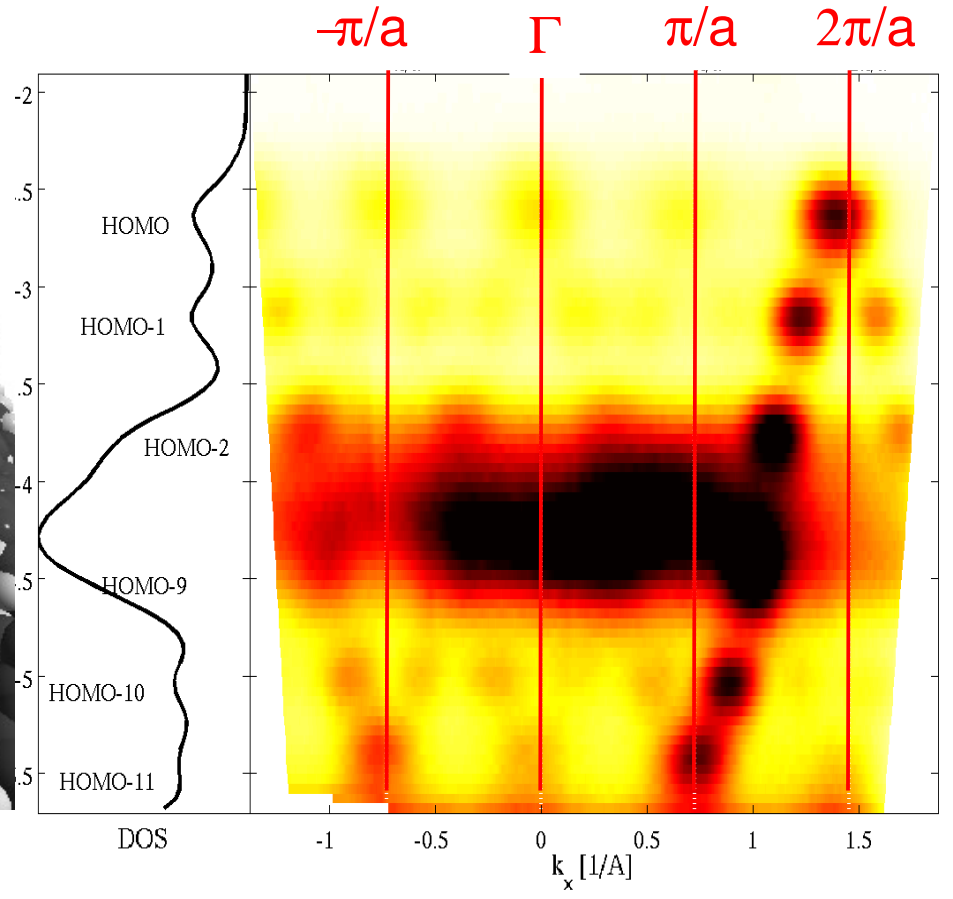




Uniaxially Aligned Sexiphenyl





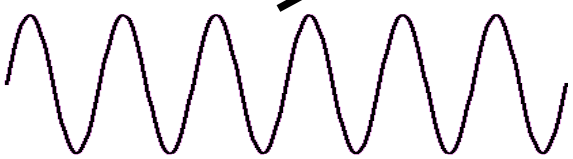


Uniaxially ordered para-sexiphenyl film
on Cu(110)_(2x1)O

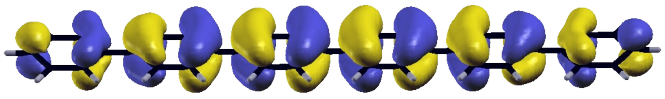
Photoemission Intensity

A simple approach (one-step model + final state = plane wave)

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



plane wave



molecular orbital

... leads to a simple result

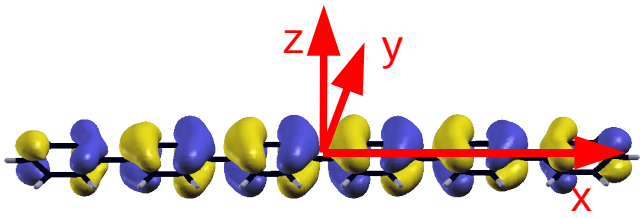
$$I_i(\theta,\phi) \propto \left|(\mathbf{A}\cdot\mathbf{k})\right|^2 \times \left|\tilde{\psi}_i(\mathbf{k})\right|^2$$

Fourier Transform of Initial State Orbital

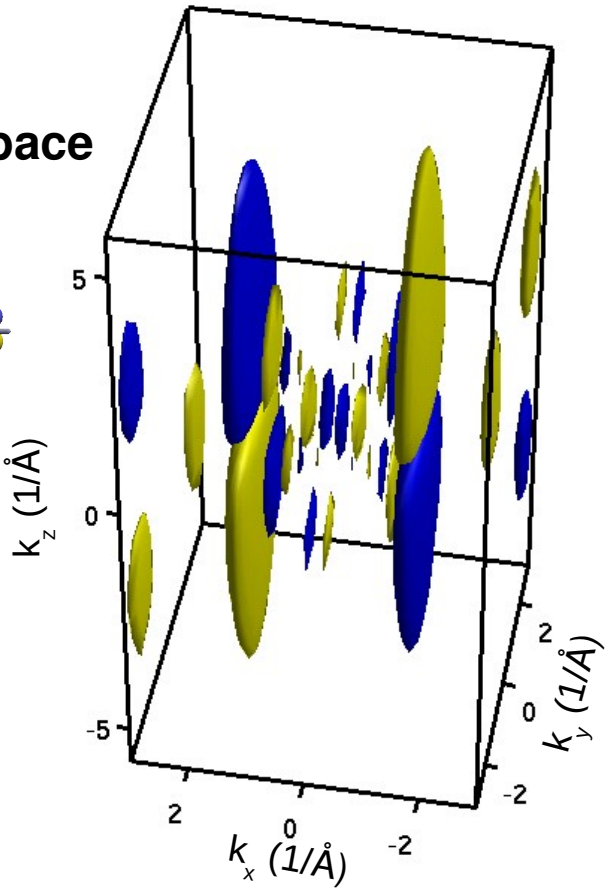
[Feibelman and Eastman, *Phys. Rev. B* **10**, 4932 (1974).]

Comparison with DFT

Molecular Orbital in Real Space

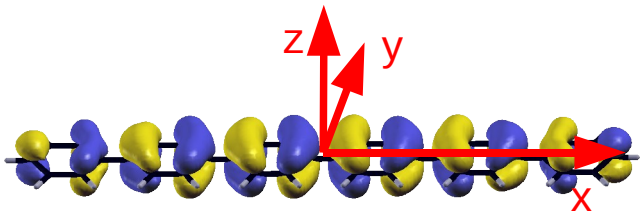


Calculation of the Fourier Transform

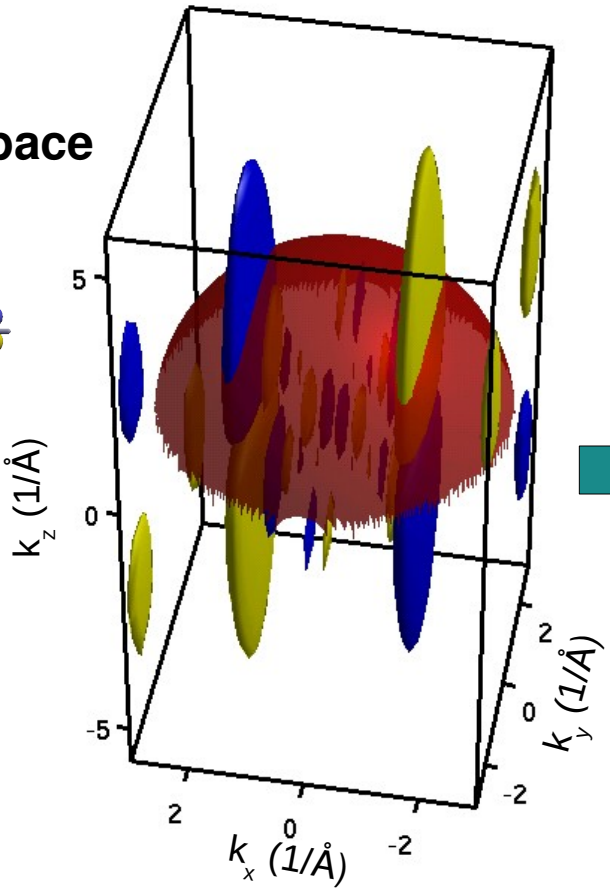


Comparison with DFT

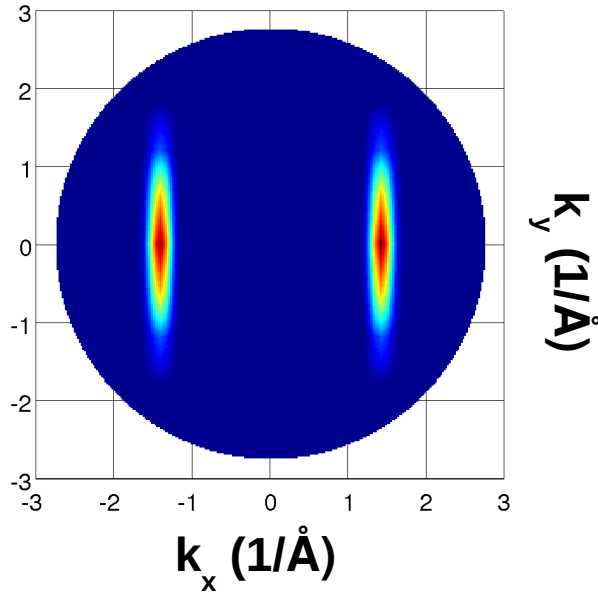
Molecular Orbital in Real Space



Calculation of the Fourier Transform

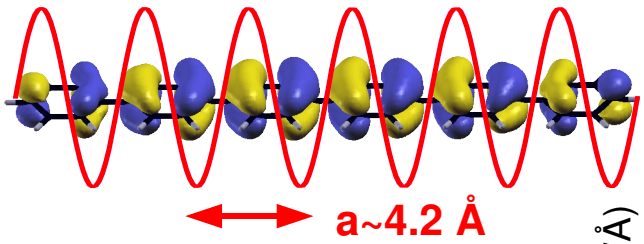


Hemispherical Cut Through 3D Fourier Transform

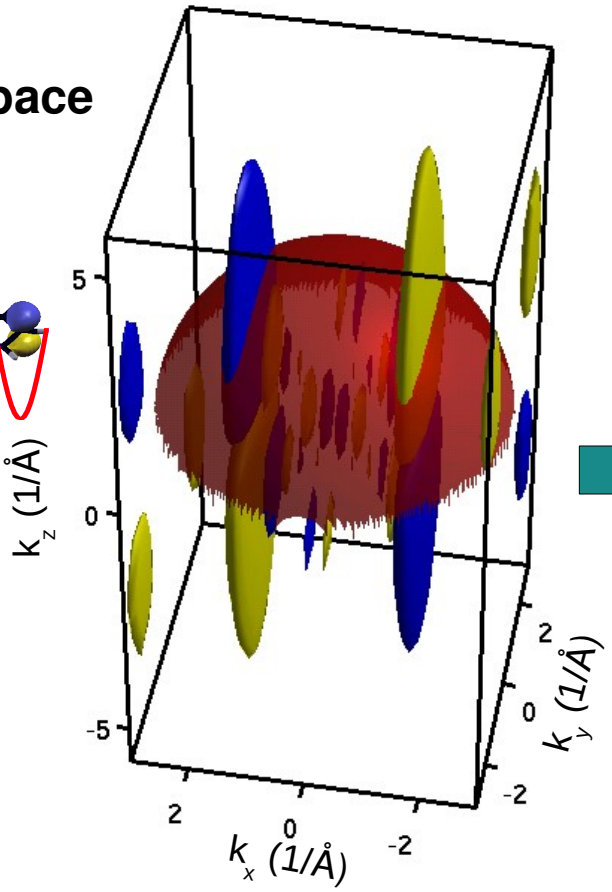


Comparison with DFT

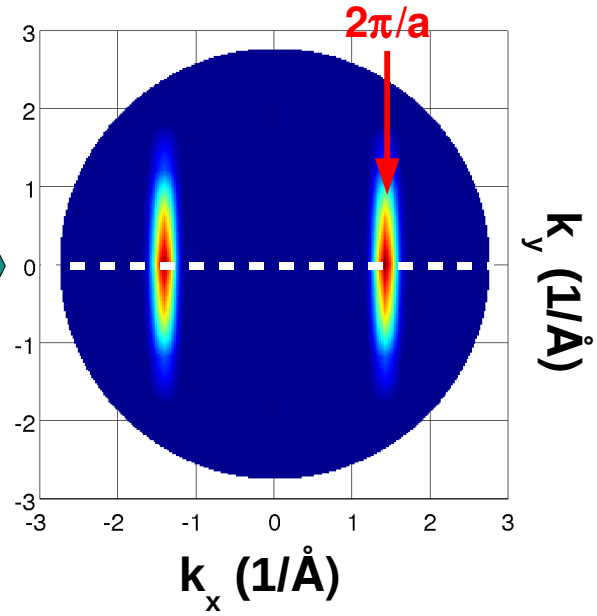
Molecular Orbital in Real Space



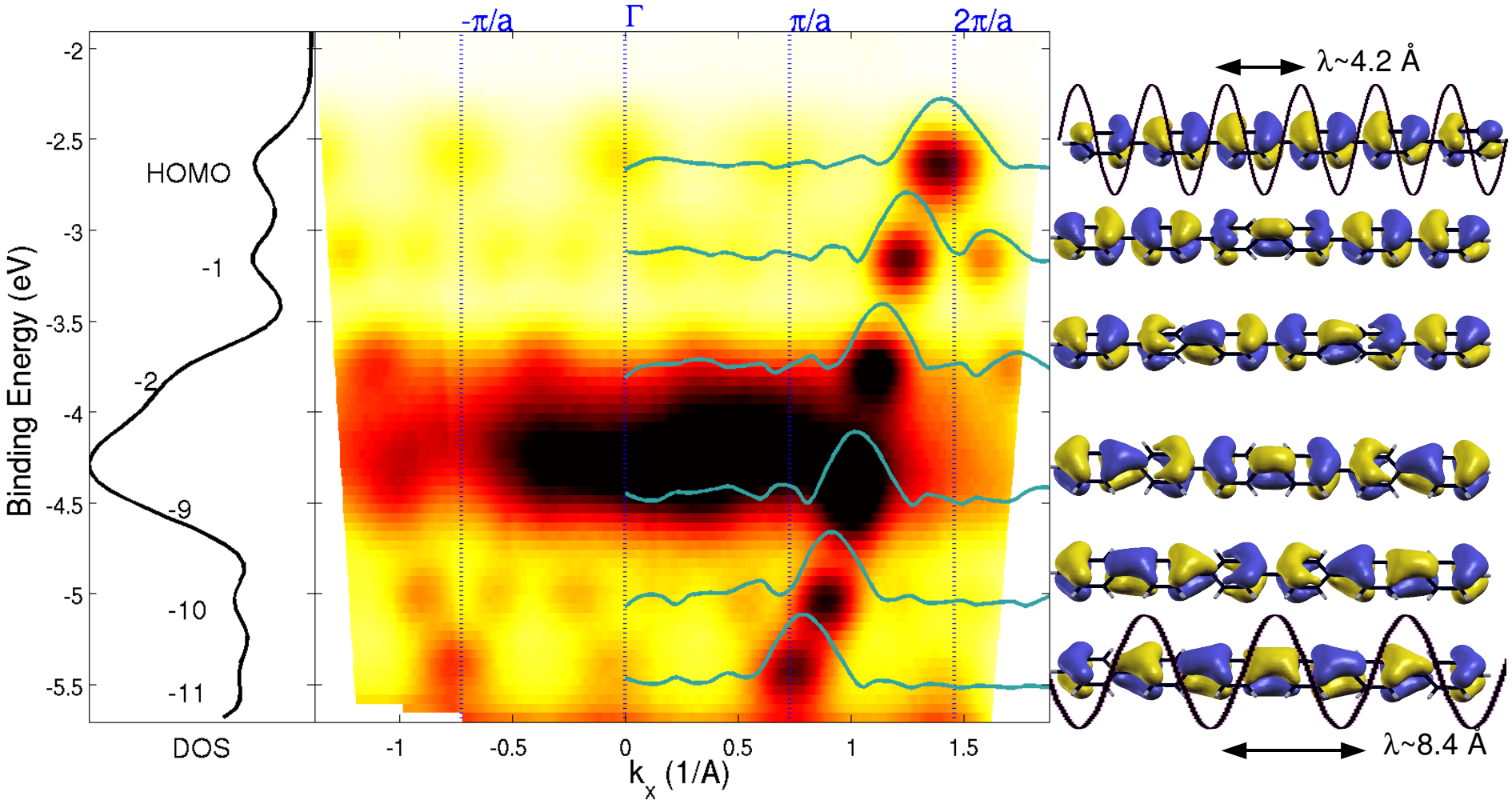
Calculation of the Fourier Transform



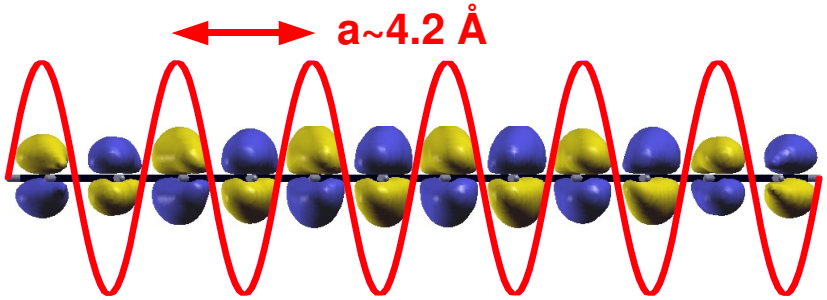
Hemispherical Cut Through 3D Fourier Transform

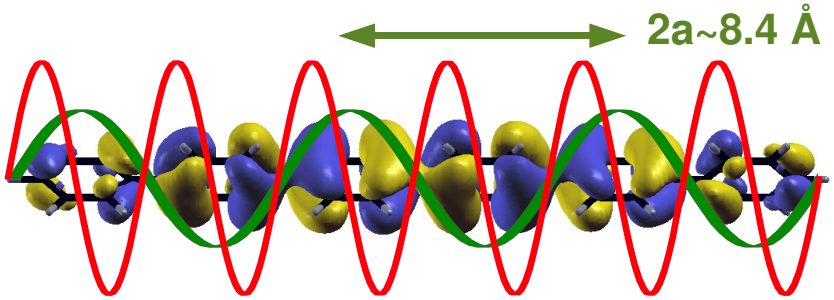


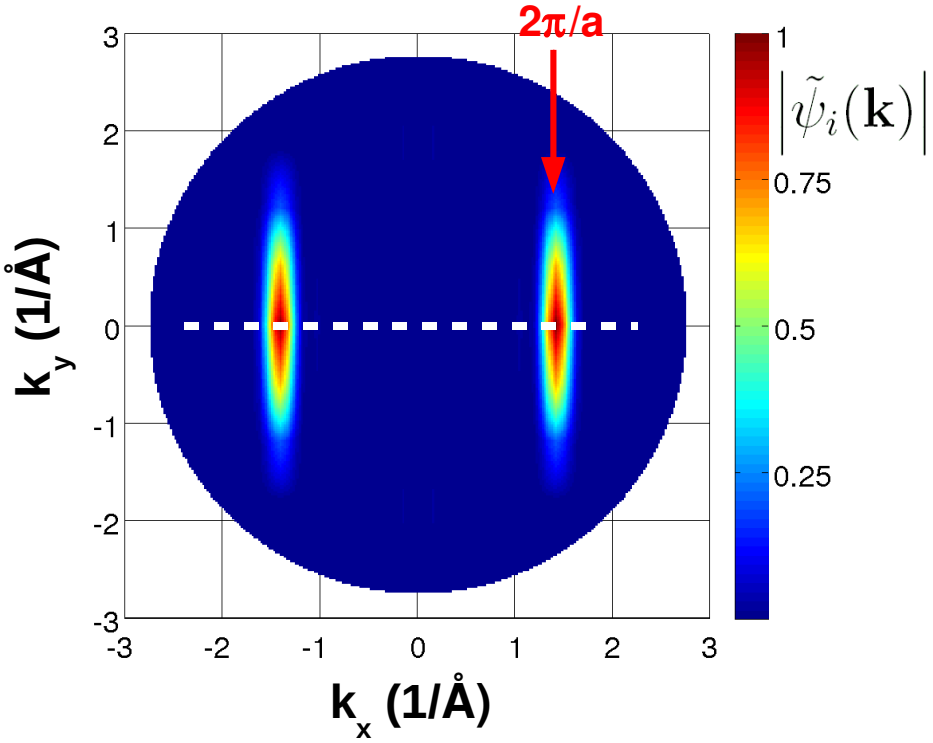
*Intra*molecular Band Structure

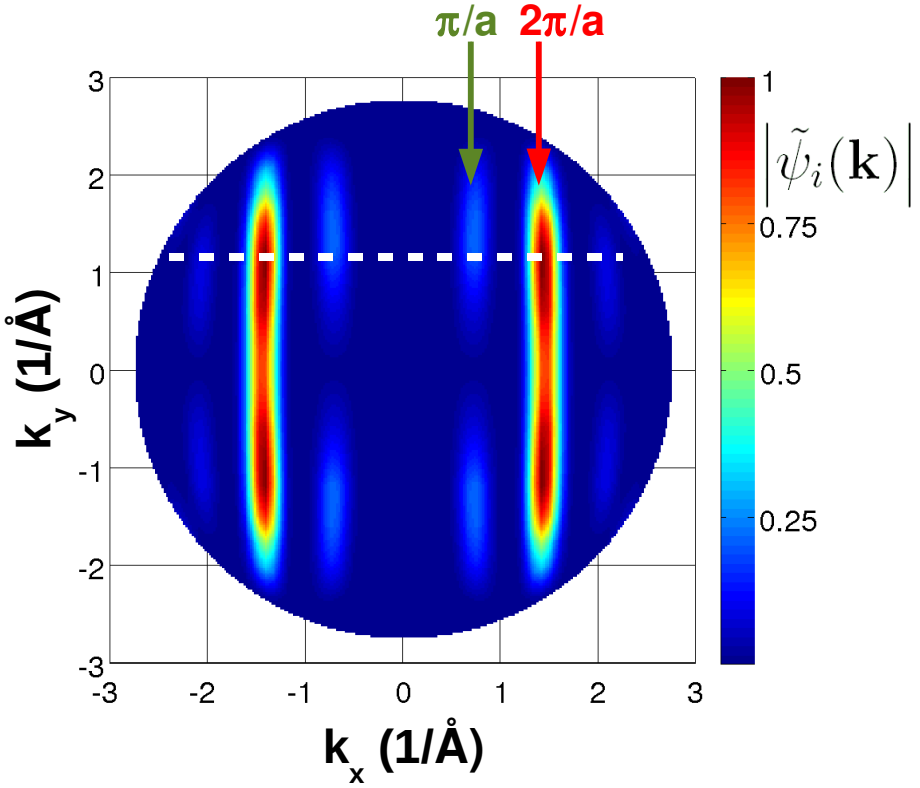


Planar vs. Twisted

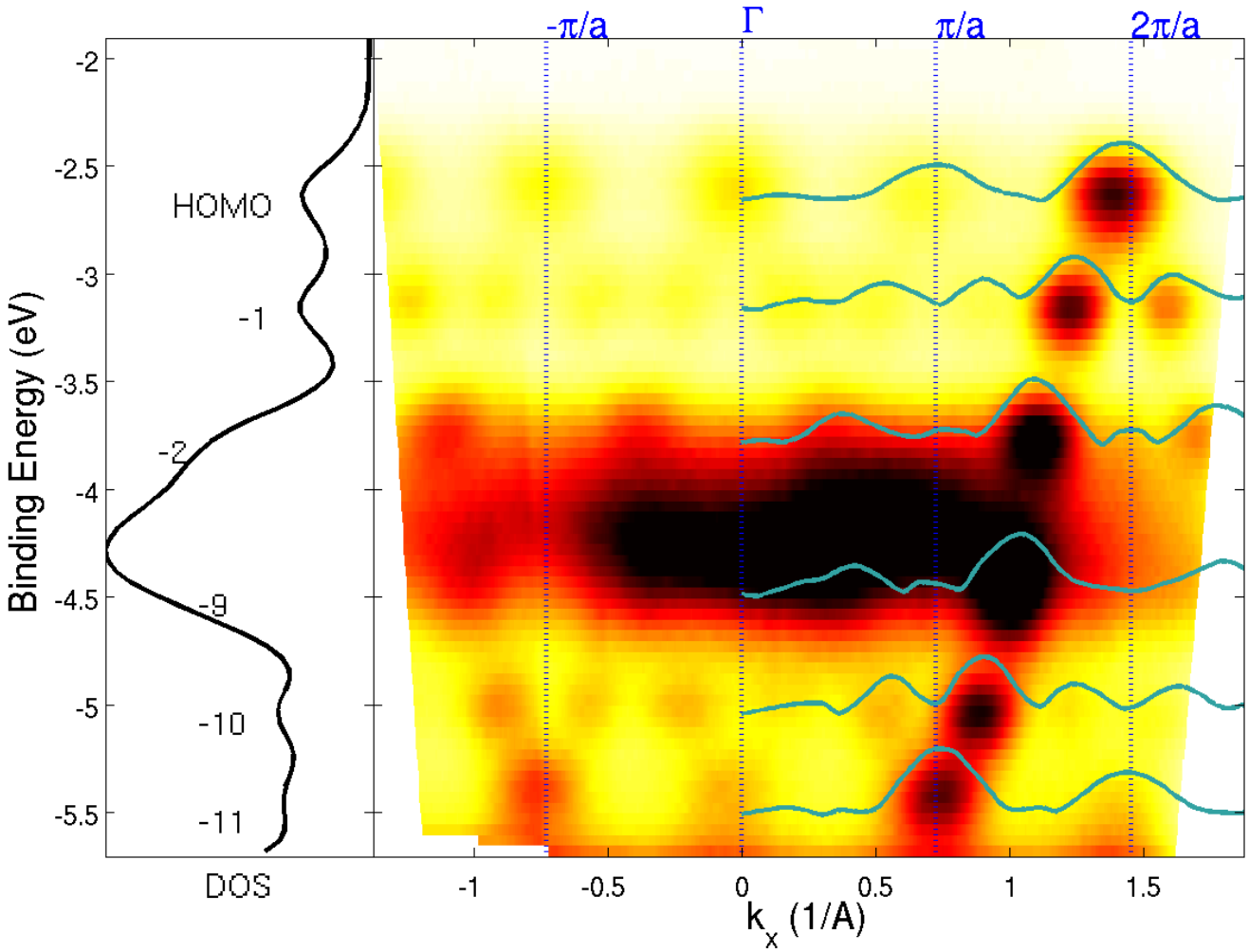


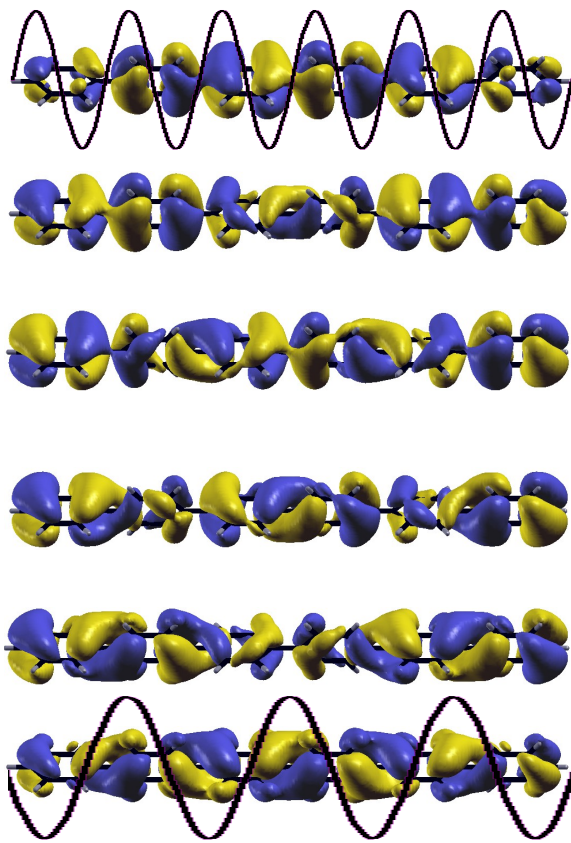






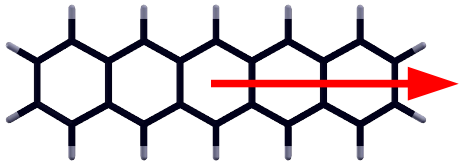
Twisted Sexiphenyl

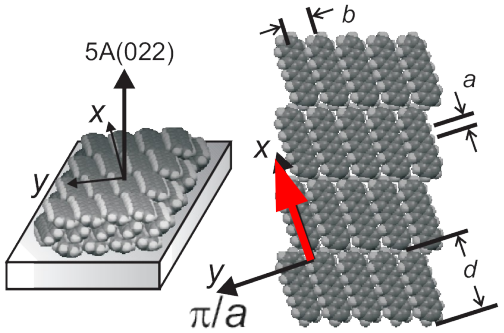




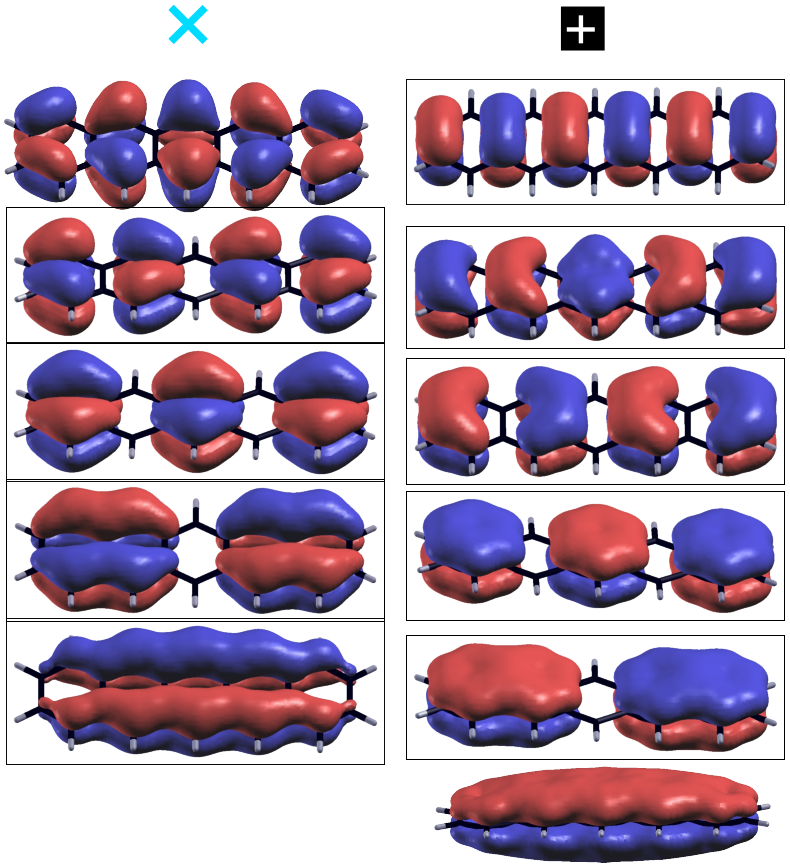
G. Koller et al., *Science* ***317****, 351 (2007).*

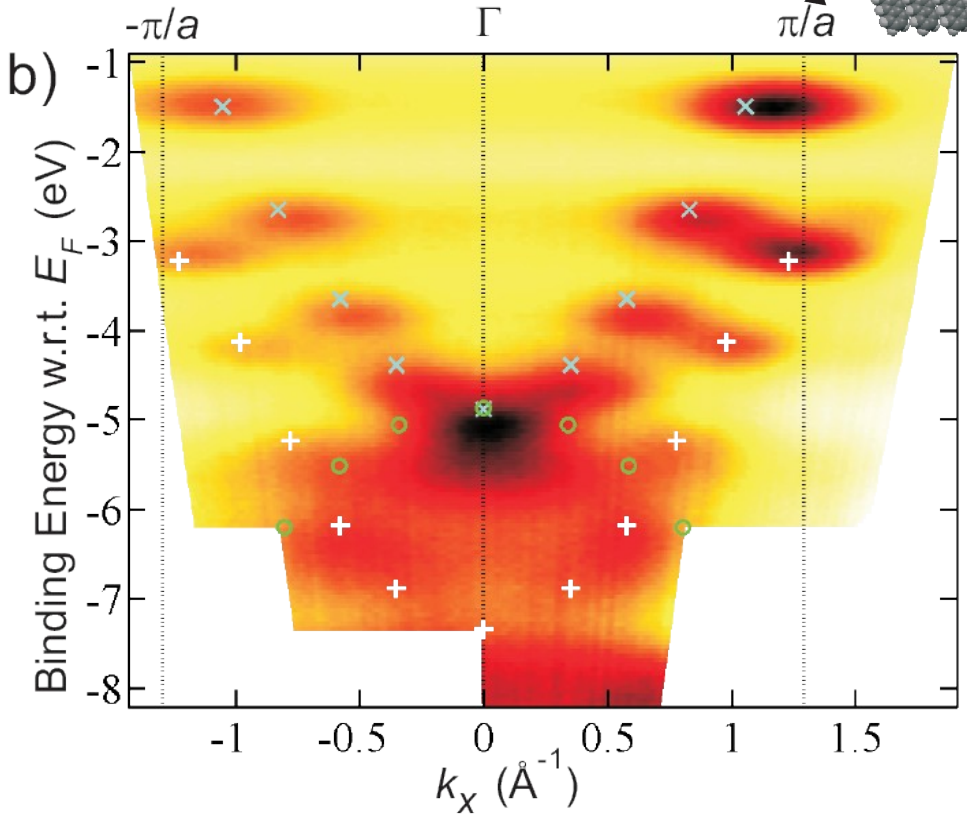
Pentacene





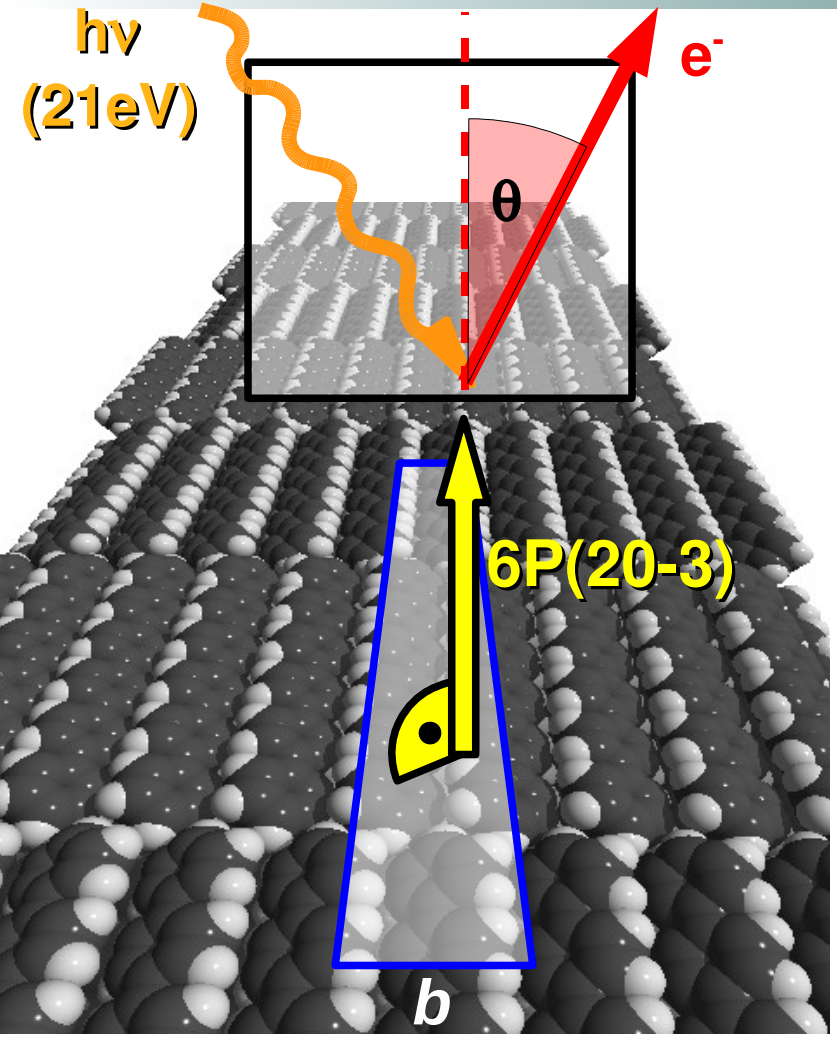
22 Carbons lead to
11 occupied π orbitals



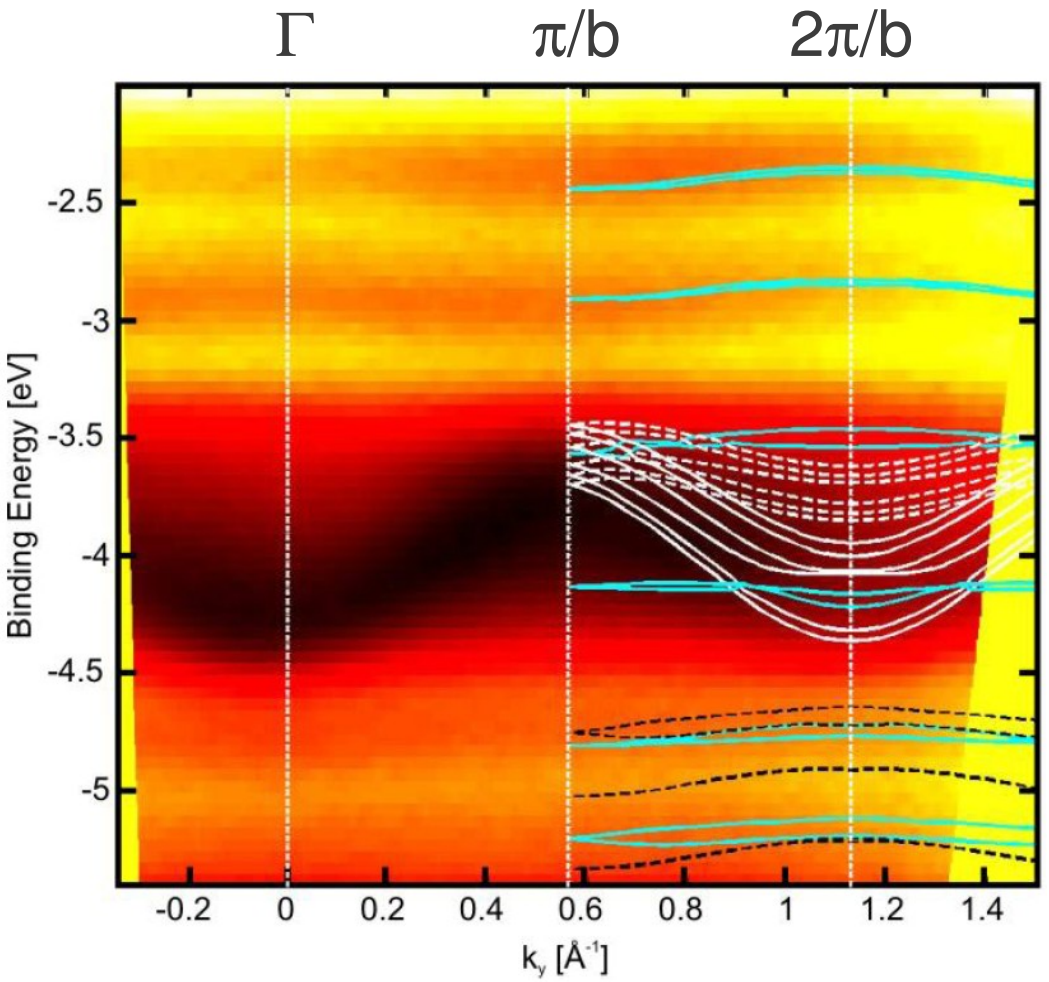


Stephen Berkebile, et al., PRB 77, 115312 (2008)

Sexiphenyl: *Inter*-molecular Dispersion

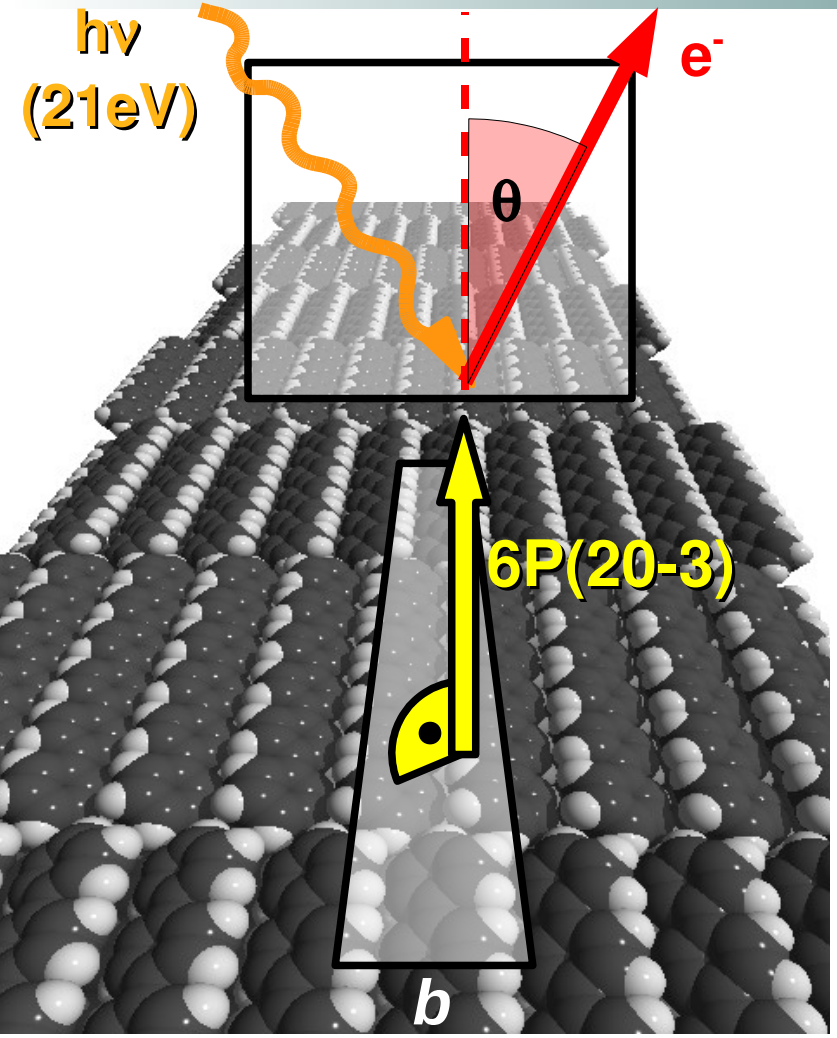


Uniaxially ordered para-sexiphenyl film
on Cu(110)_(2x1)O



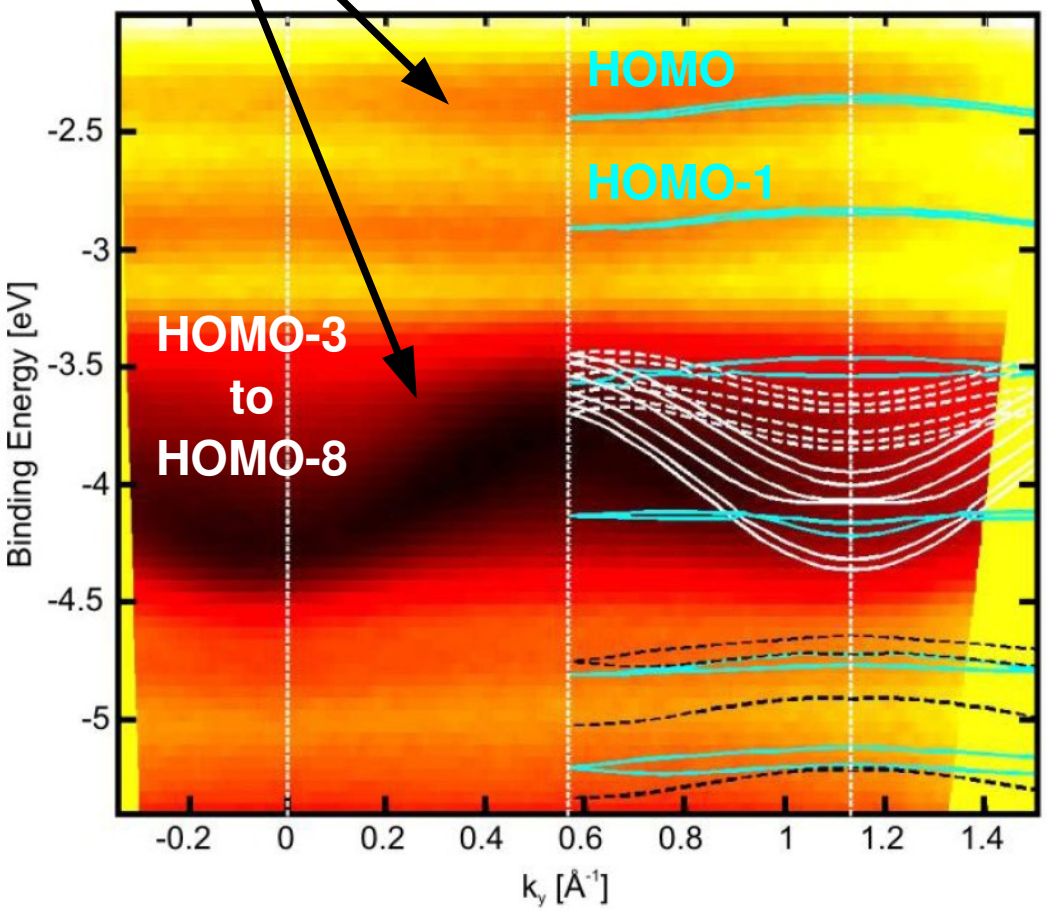
G. Koller et al., *Science* ***317****, 351 (2007).*

Sexiphenyl: *Inter*-molecular Dispersion



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

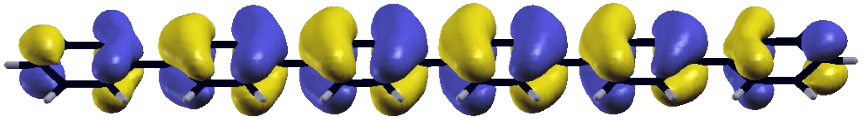
1. Why is the dispersion so different?
2. Why is the PE intensity so different?



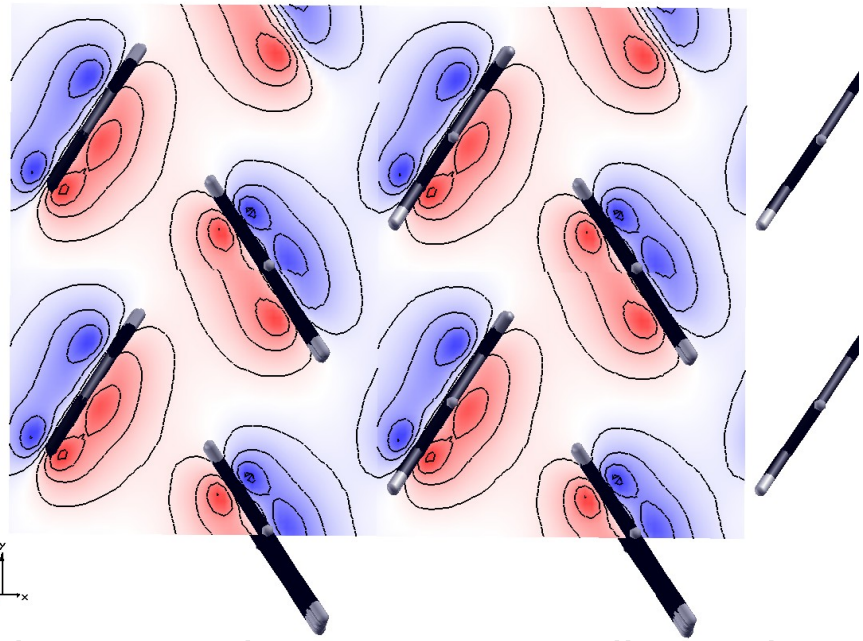
G. Koller et al., *Science* ***317****, 351 (2007).*

1. Dispersion

HOMO

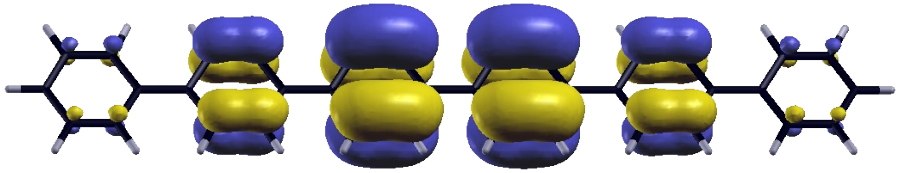


de-localized over a molecule

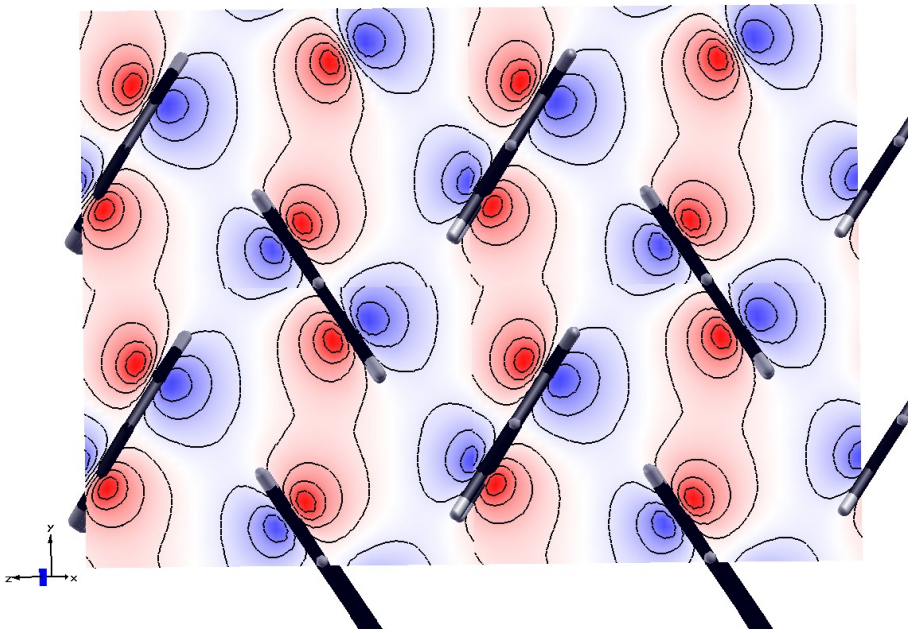


... but small intermolecular dispersion

HOMO-8

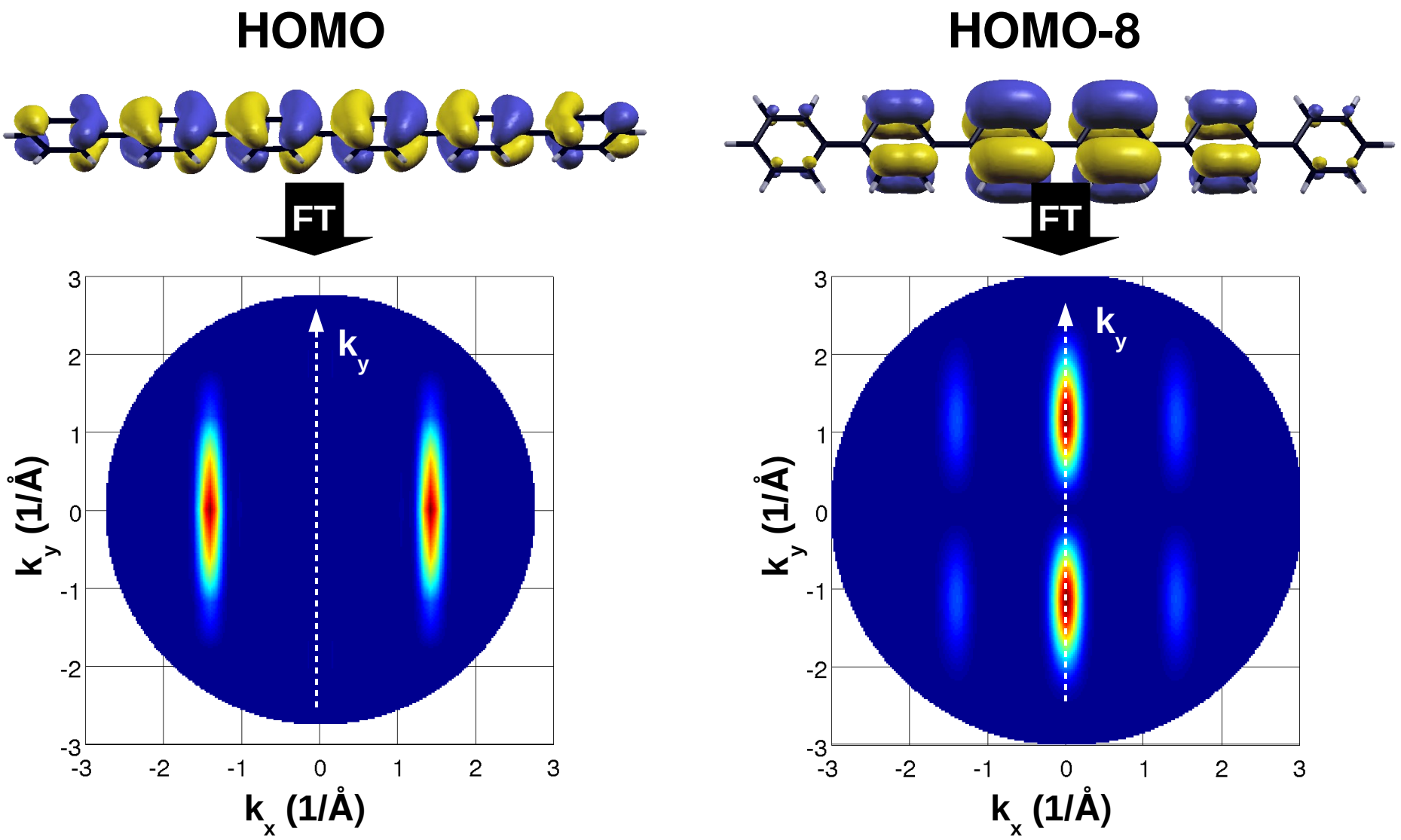


localized on rings

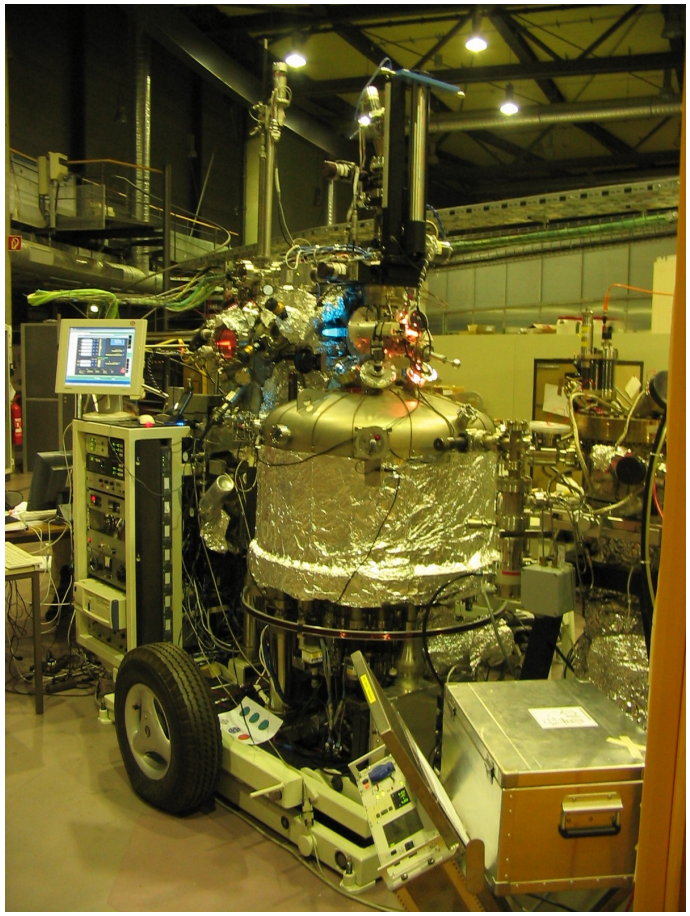


... and sizeable intermolecular dispersion

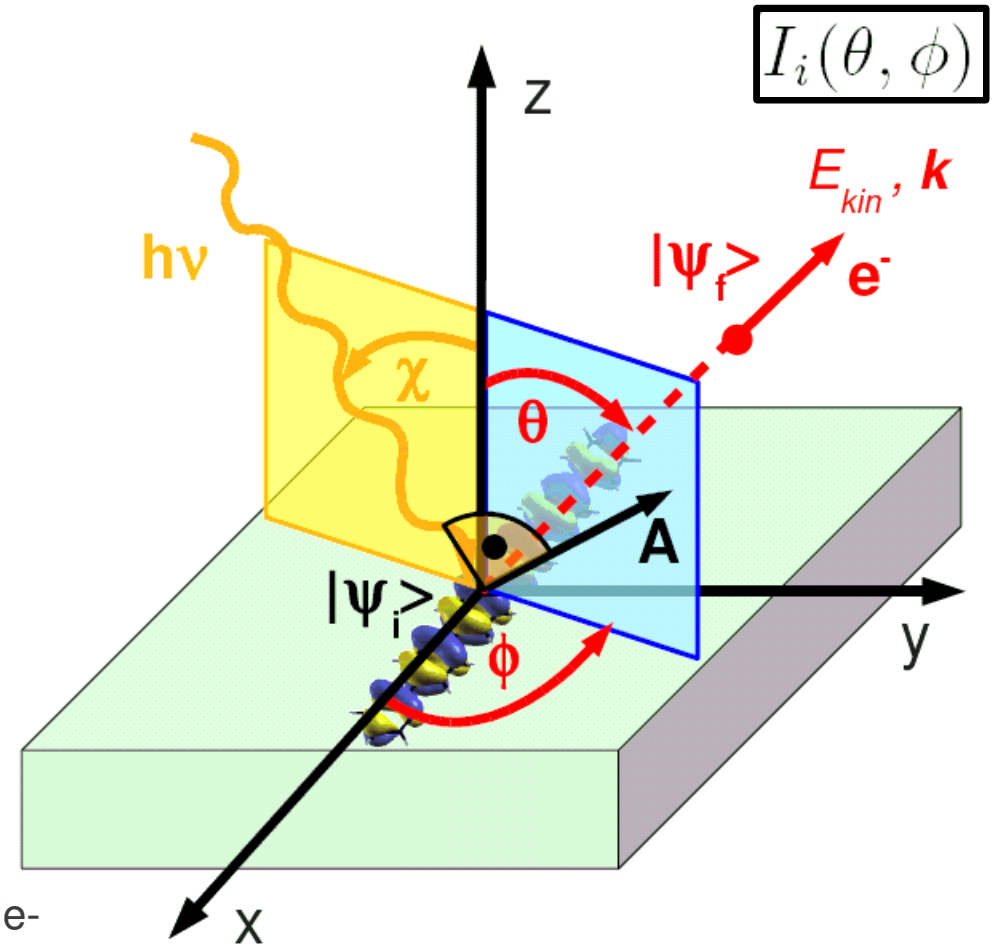
2. Photoemission Intensity



Orbital Tomography

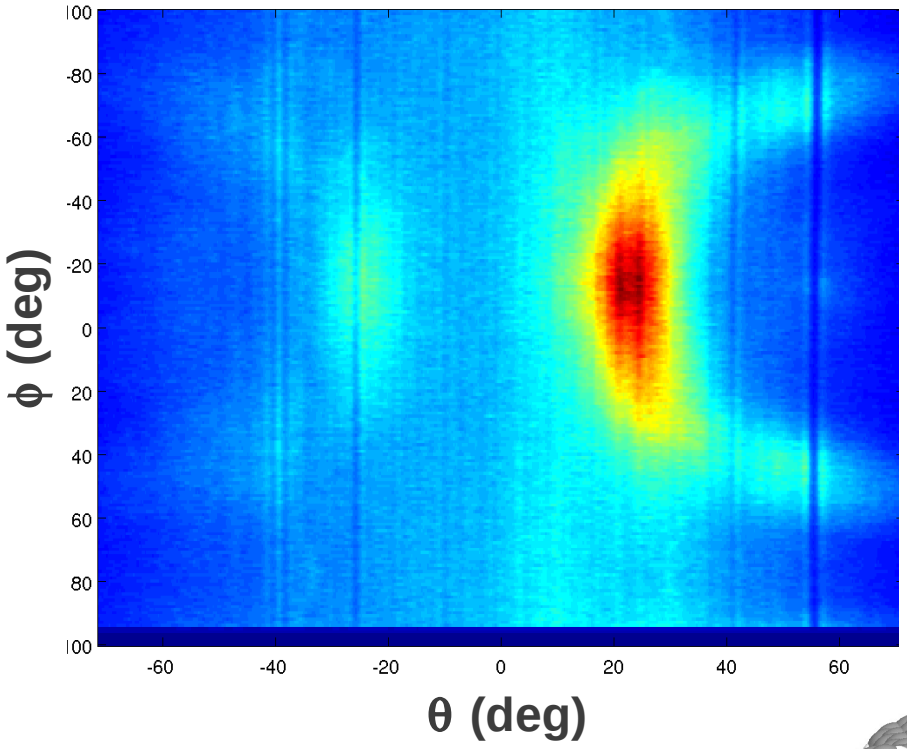


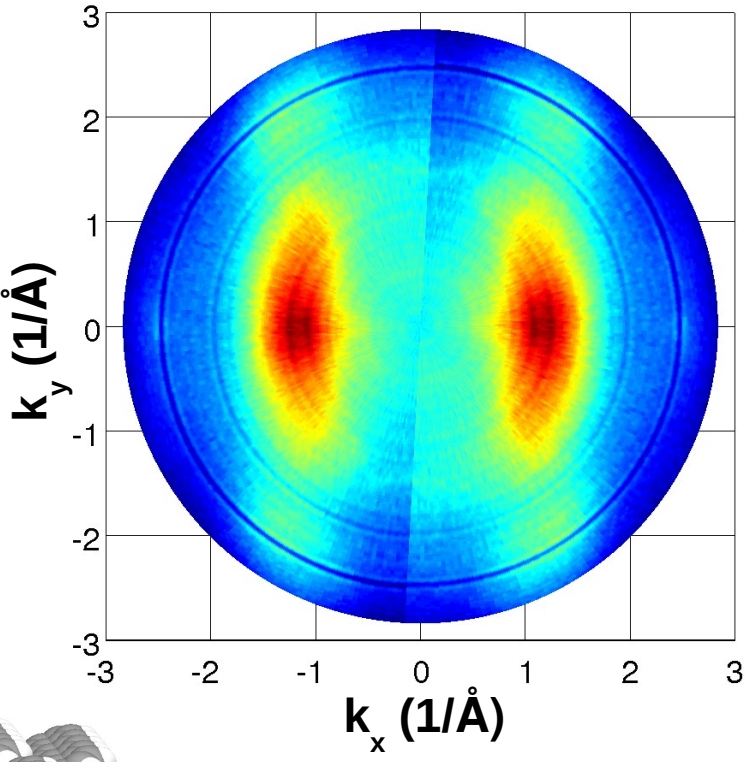
The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II



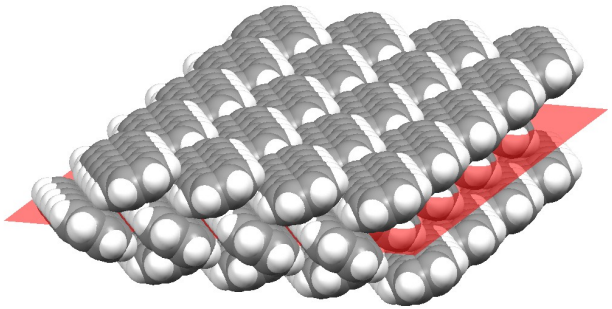
Pentacene HOMO

k_x-k_y scans at constant photon energy and constant kinetic energy





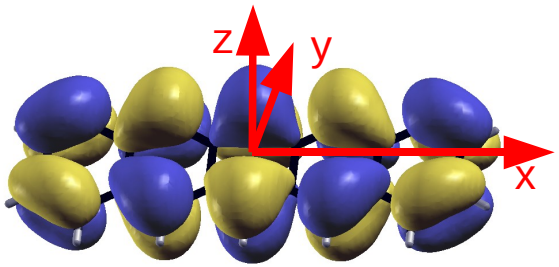
Multilayer of
Pentacene/Cu(110)_(2x1)O



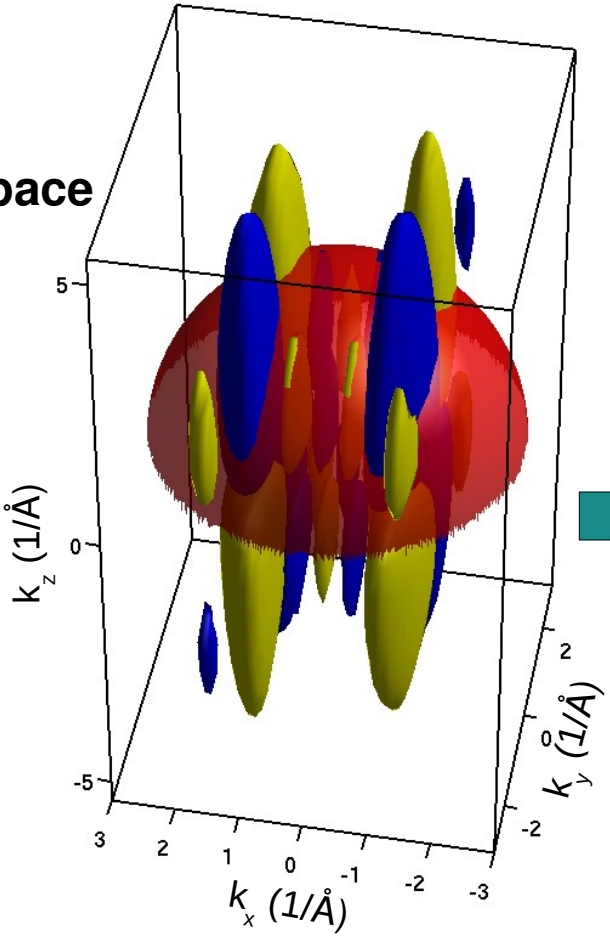
$$k_{\parallel} = \sqrt{\frac{2m}{\hbar^2} E_{\mathrm{kin}}} \sin\theta$$

Pentacene HOMO

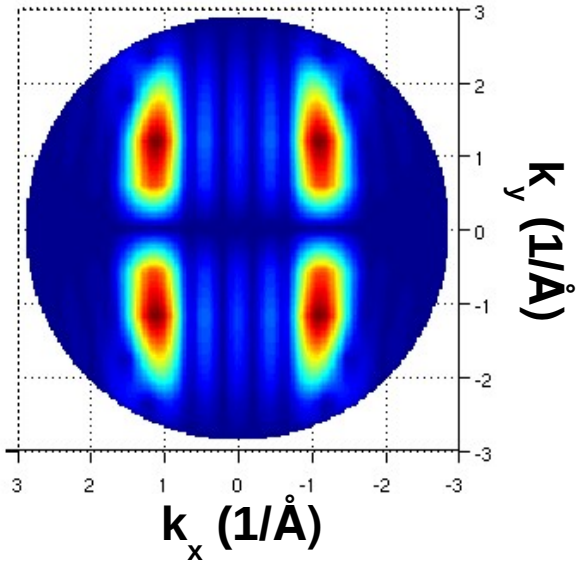
Molecular Orbital in Real Space



Calculation of the Fourier Transform

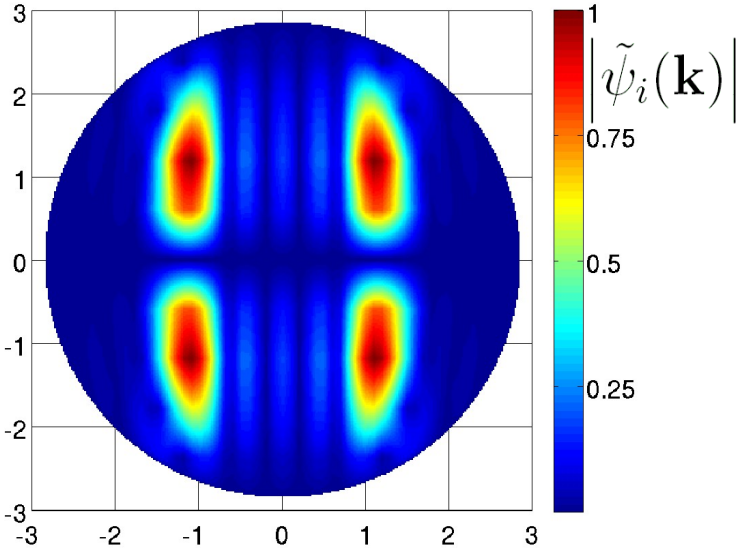


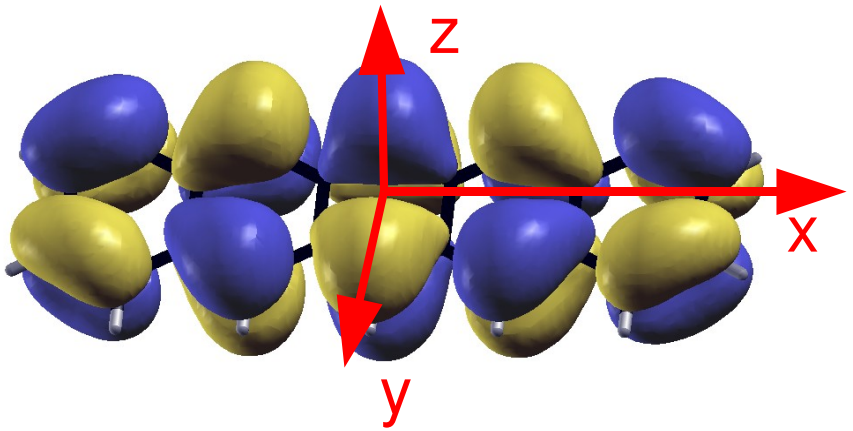
Hemispherical Cut Through 3D Fourier Transform



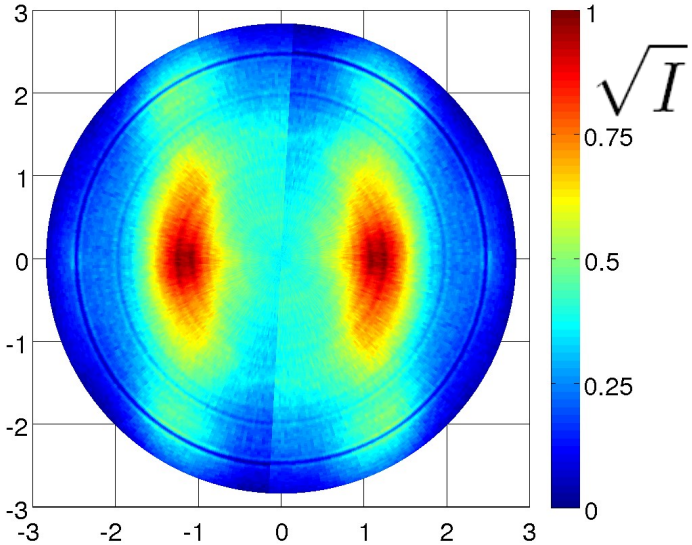
Theory vs. Experiment

Theory





ARPES



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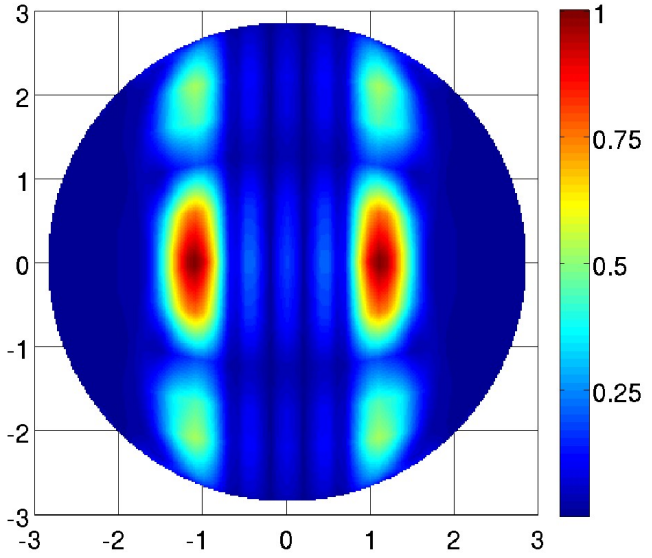
Theory vs. Experiment

Theory



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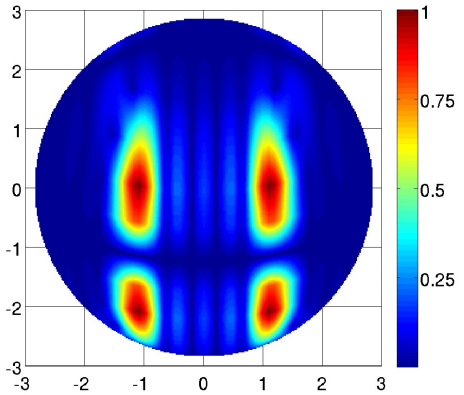
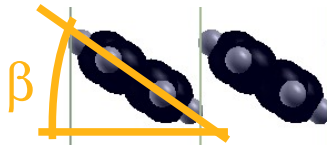
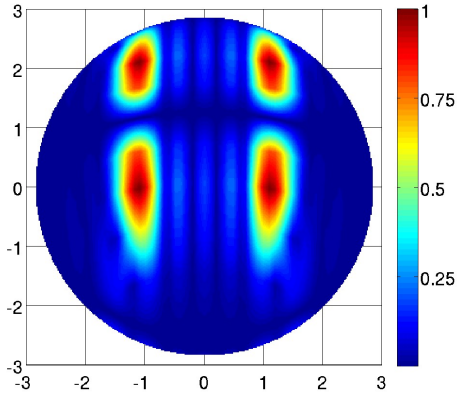
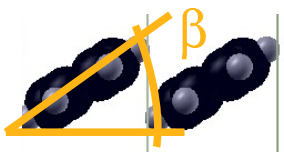




+26 deg tilt

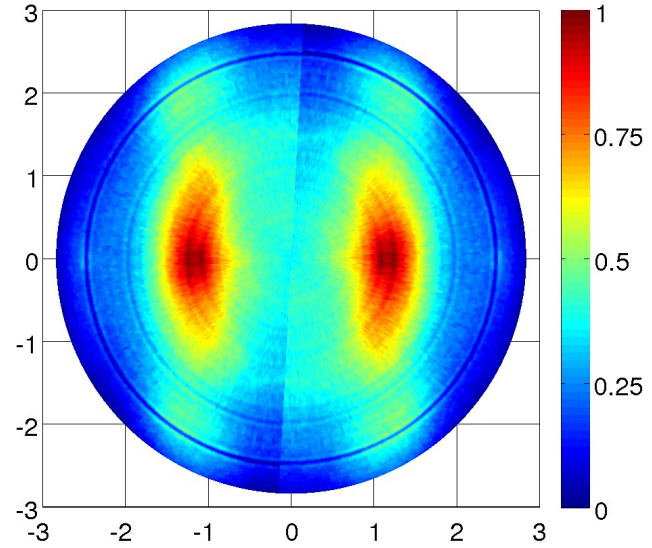
+

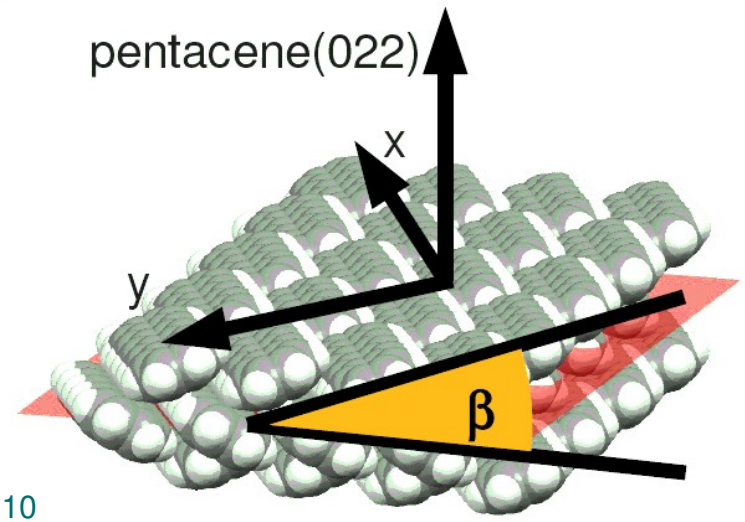




–26 deg tilt

ARPES

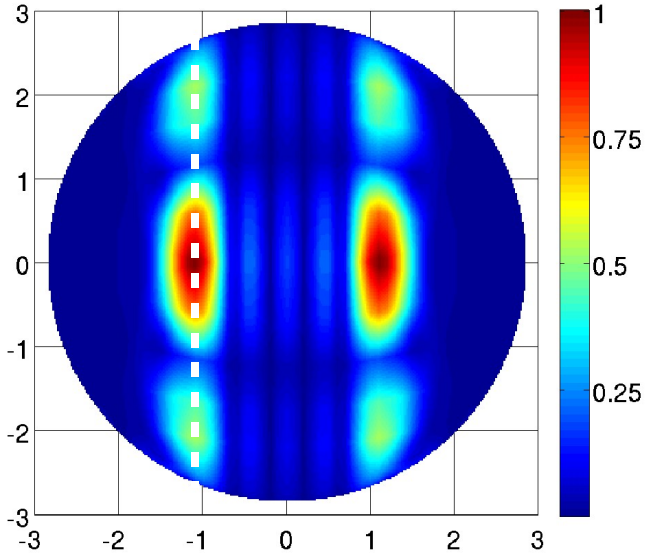




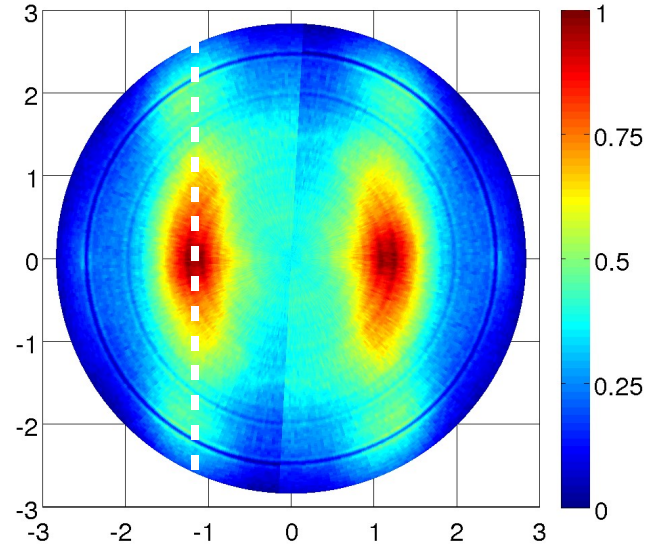
Puschnig et al., *Science* **326**, 702 (2009).

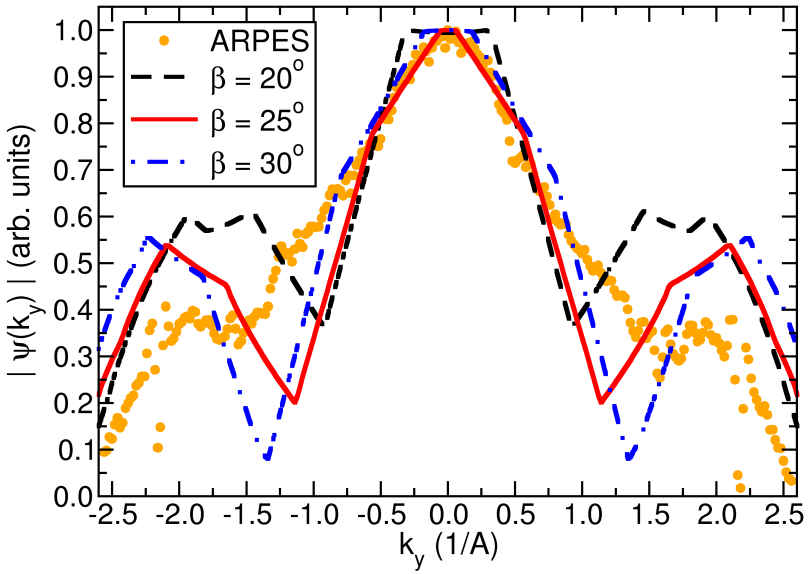
Theory vs. Experiment

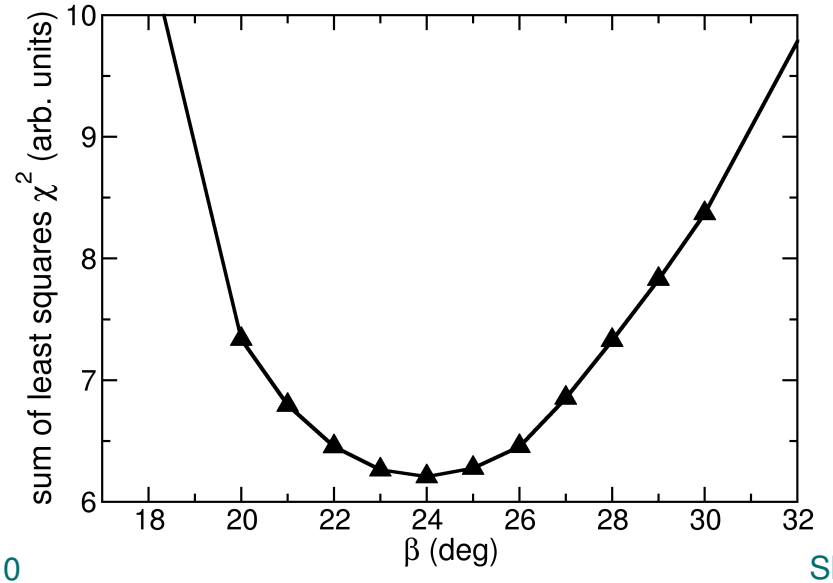
Theory



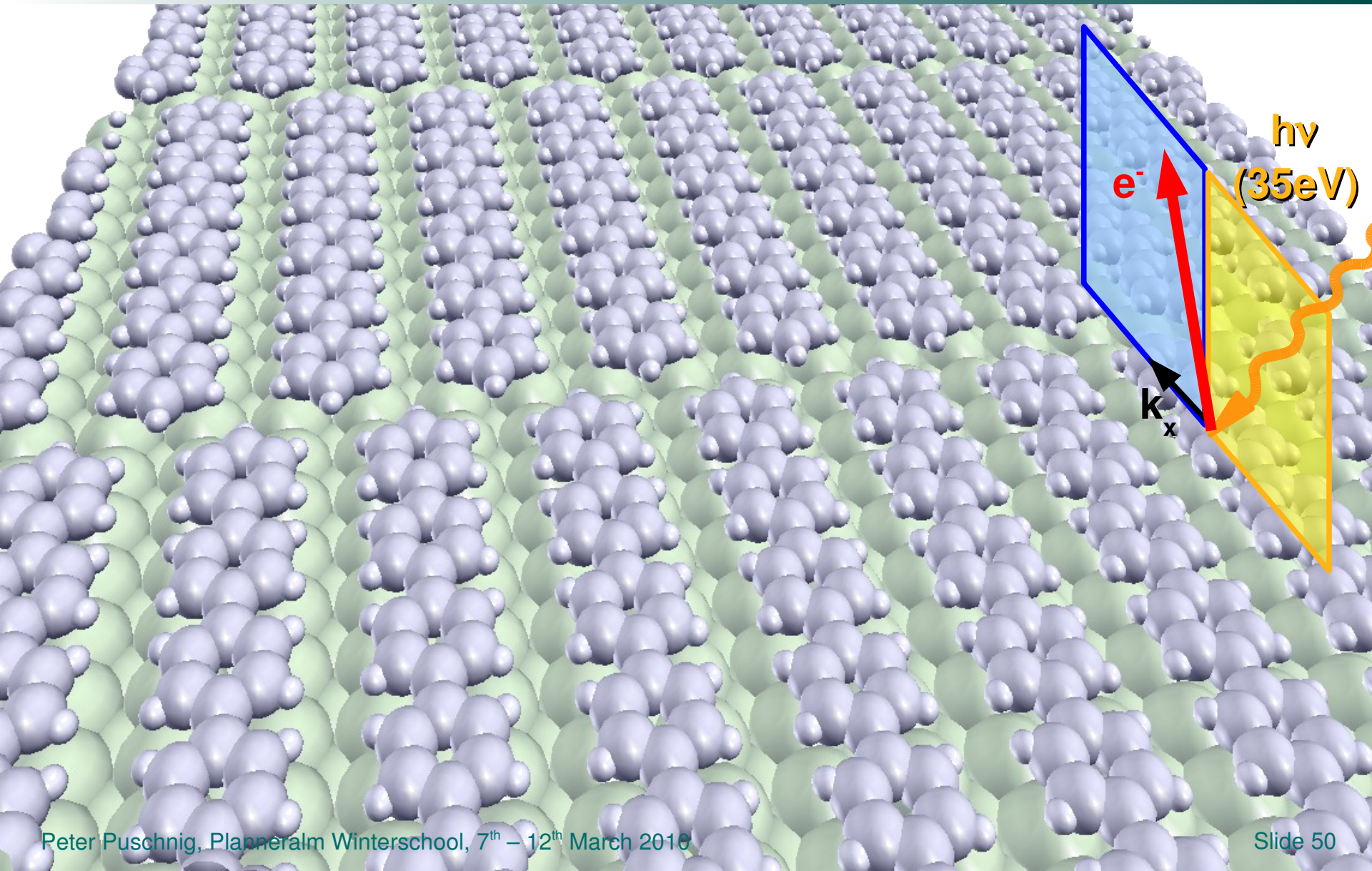
ARPES



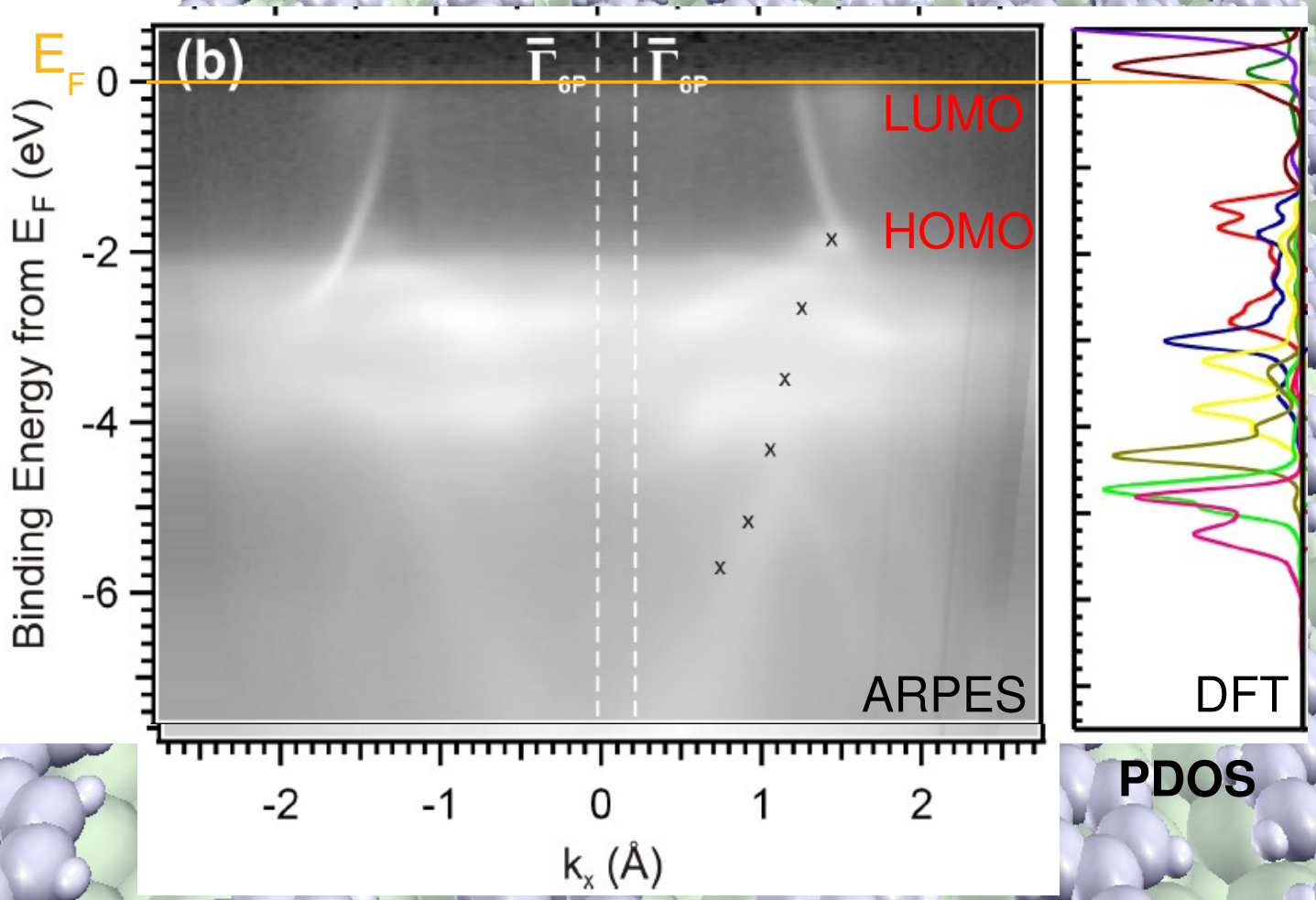




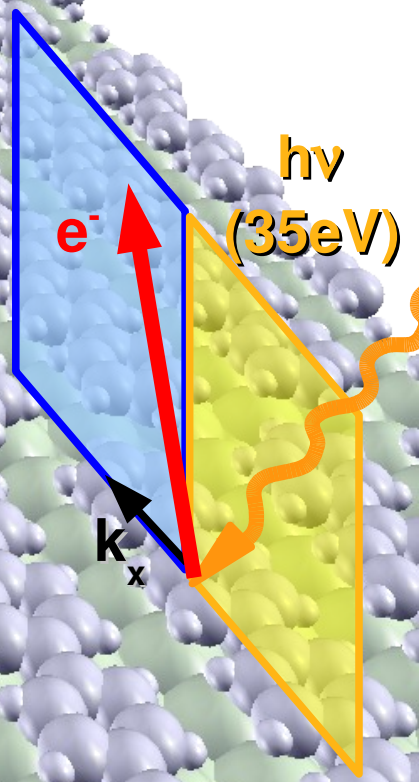
Sexiphenyl Monolayer on Cu(110)



Sexiphenyl Monolayer on Cu(110)



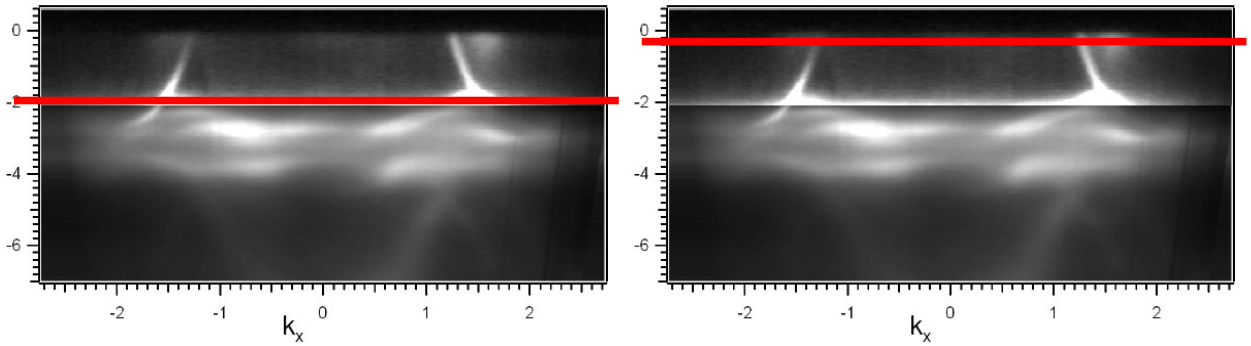
PDOS



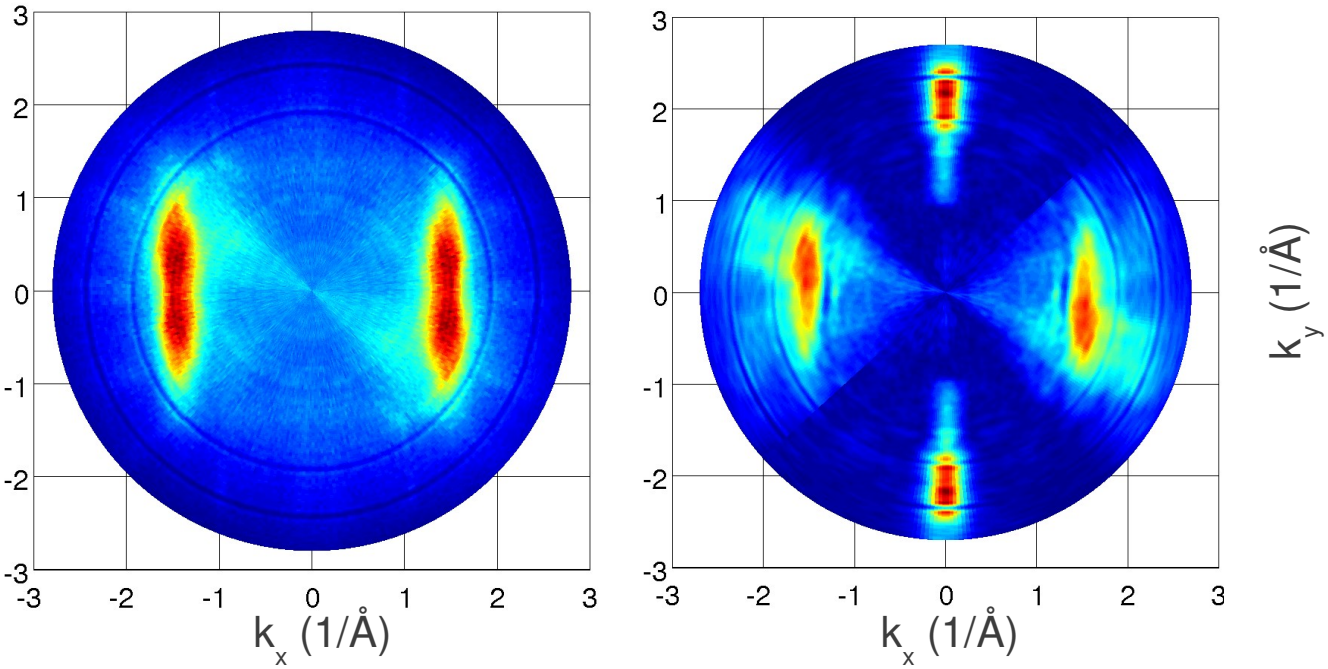
Berkebile et al. (submitted to PNAS)

2D-Momentum Maps

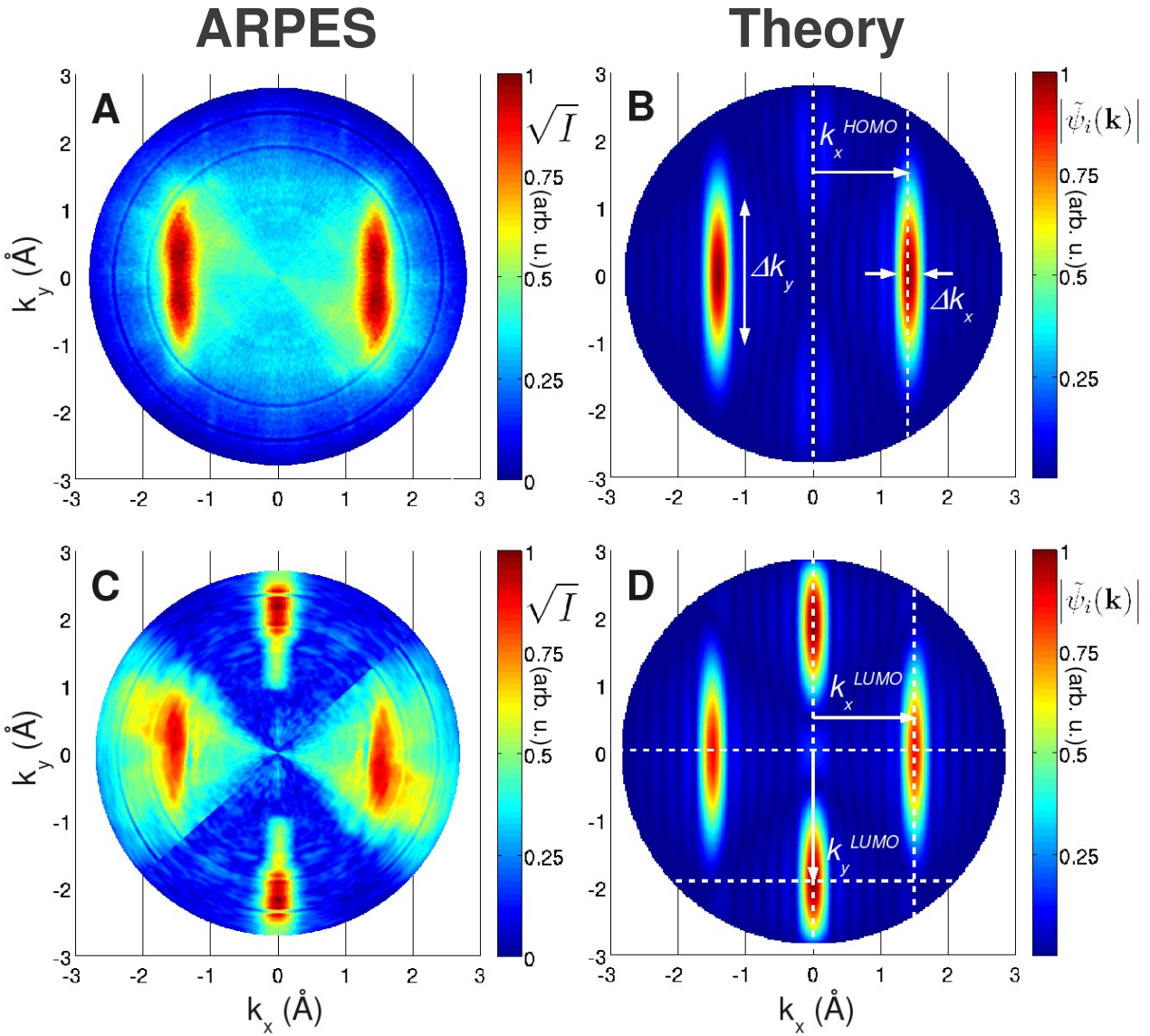
ARPES data for a monolayer of 6P / Cu(110)



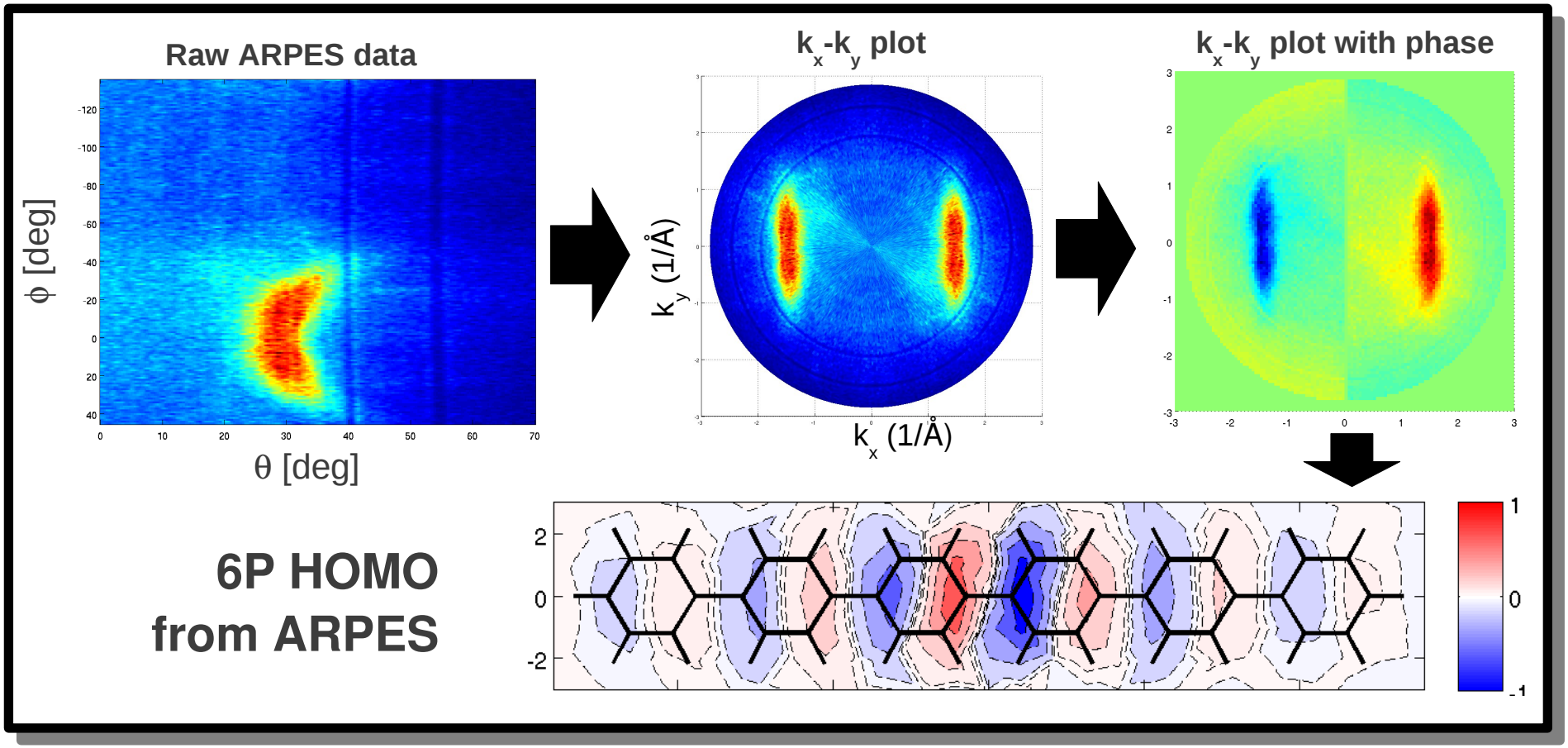
HOMO **filled LUMO**



2D-Momentum Maps



Reconstruction of Orbitals

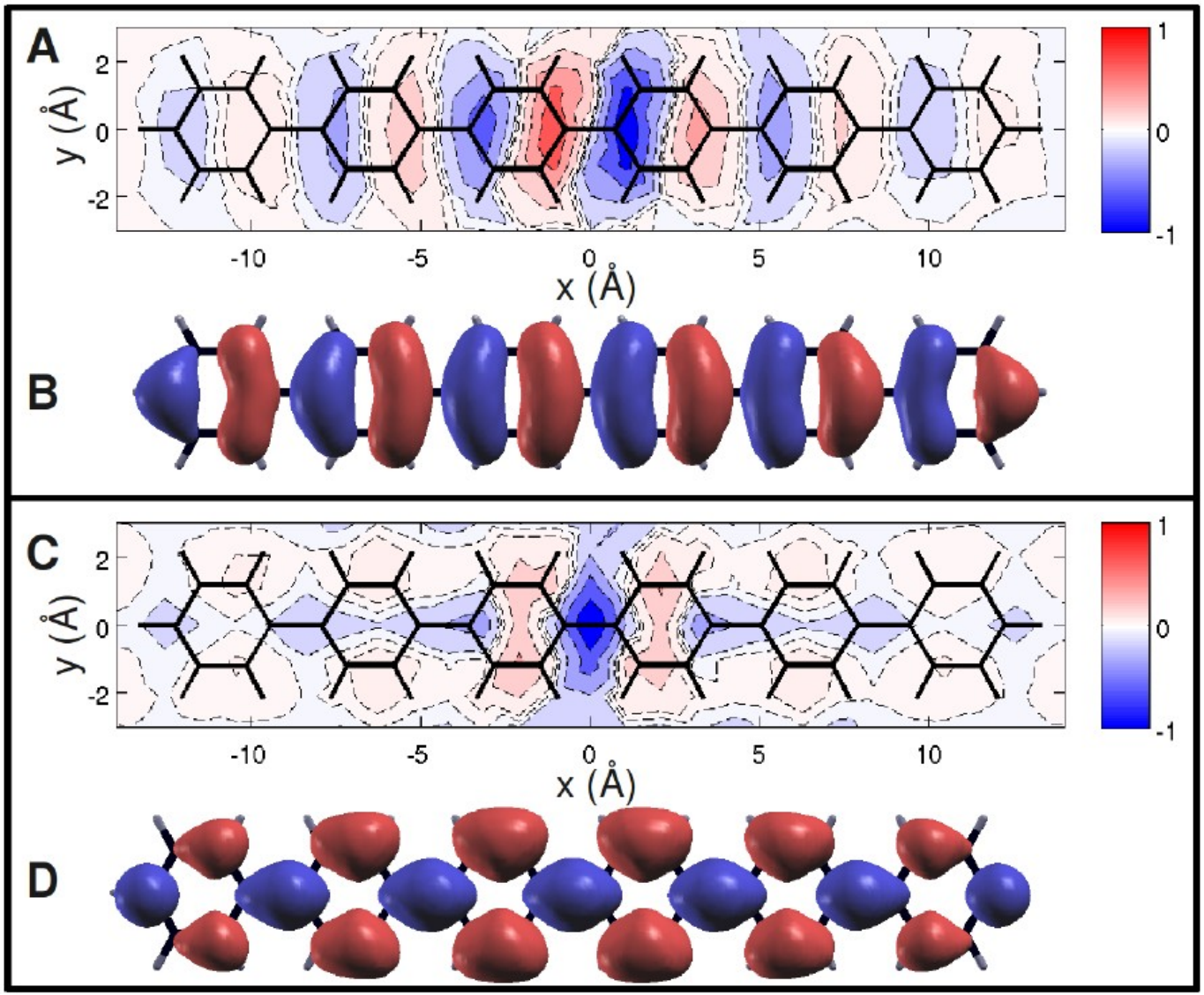


Puschnig et al., *Science* **326**, 702 (2009).

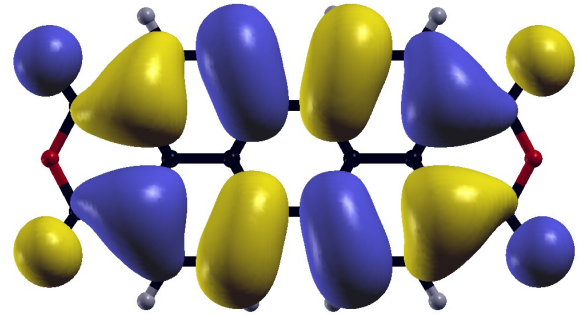
Reconstruction of Orbitals

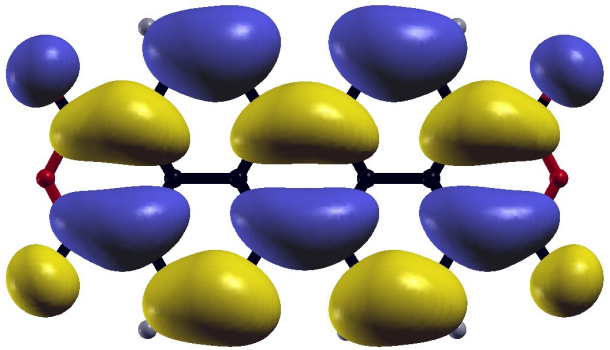
HOMO

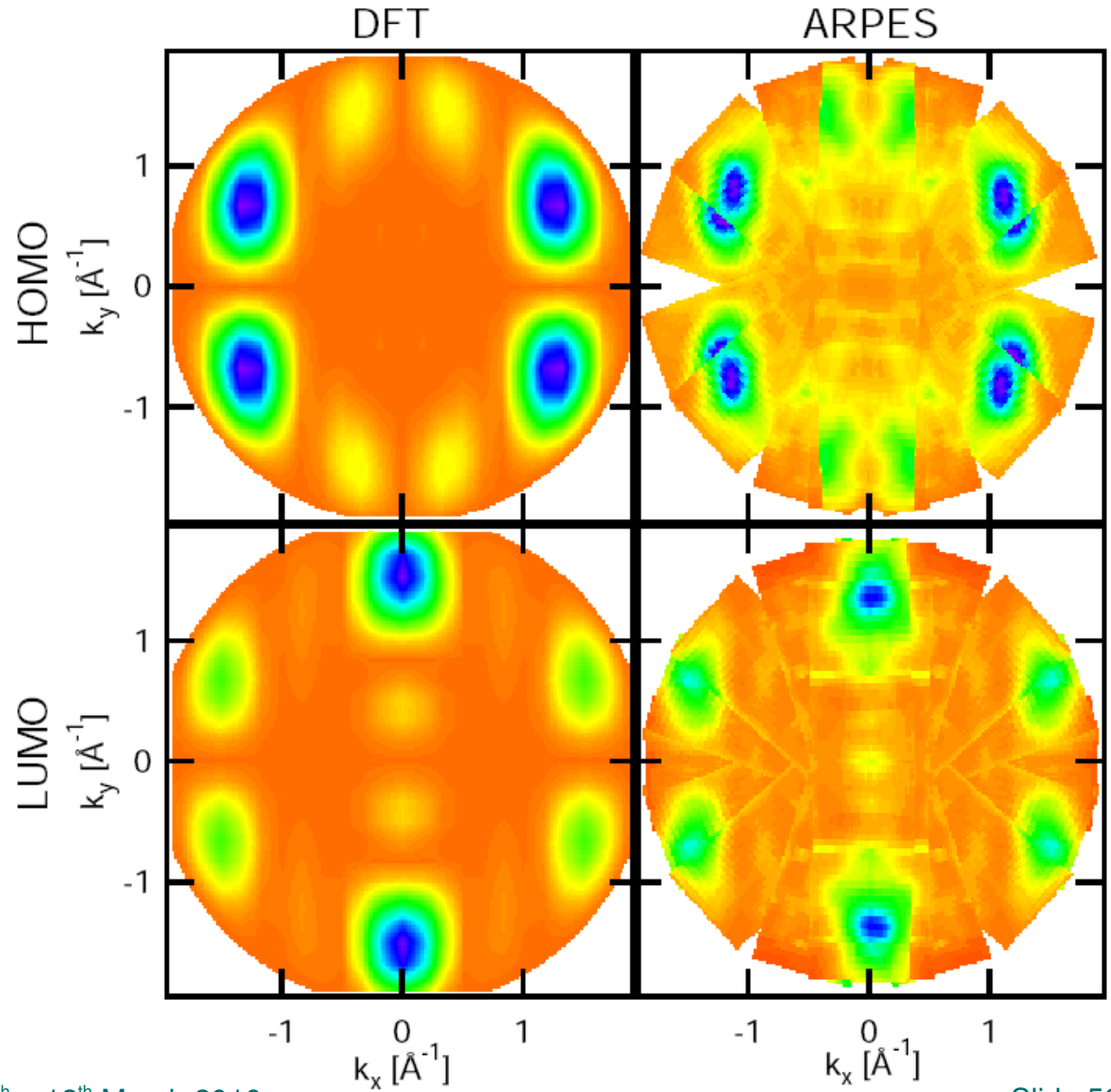
Filled LUMO



Monolayer PTCDA / Ag(110)







Ziroff et al. (submitted to PRL)

Content

I. Density Functional Theory

II. Structural Properties

Cohesive Energies of Molecular Crystals

Adsorption Energies of Molecules at Metal Surfaces

III. Electronic Structure

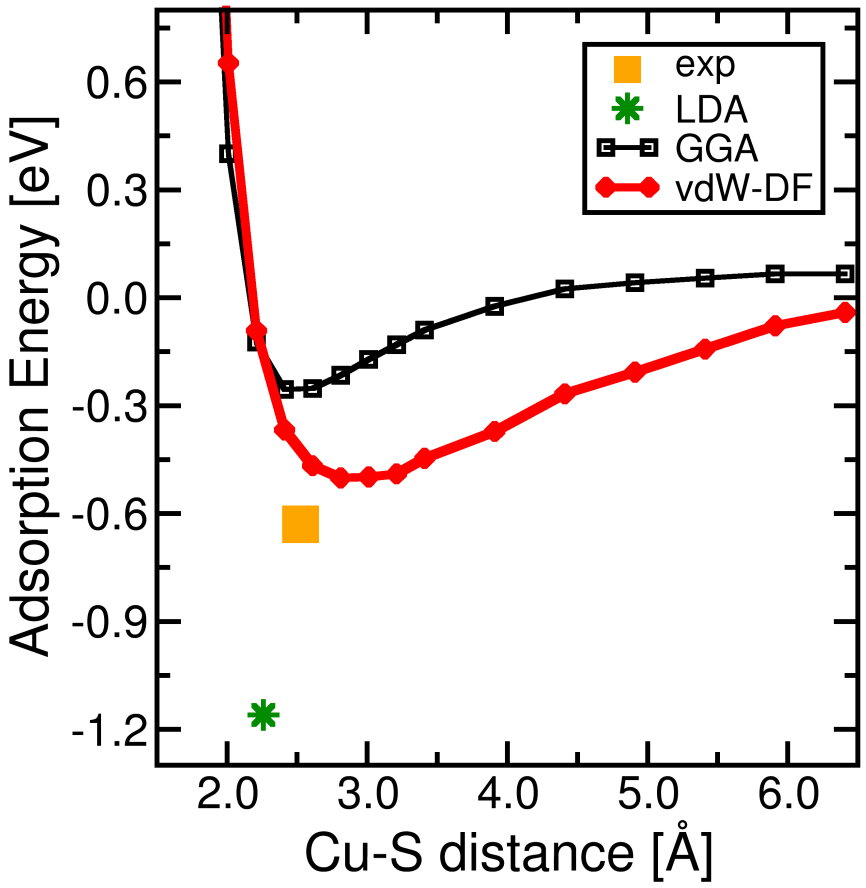
PTCDA / Coinage Metal (111) Surfaces

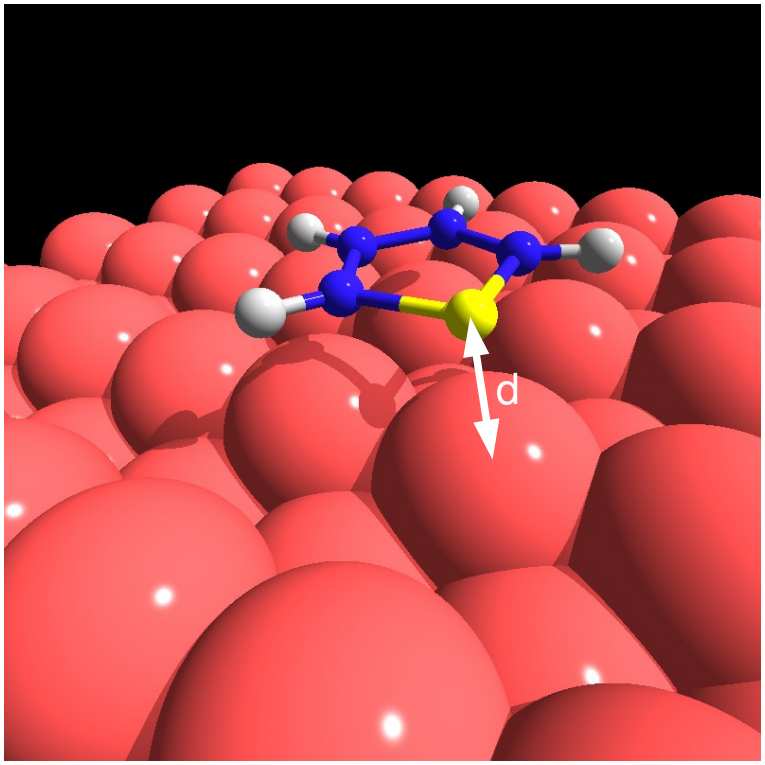
Inter- and Intramolecular band structure of chain-like molecules

Can ARPES tell us something about the molecular orbital structure?

IV. Problems in DFT

Van der Waals Interactions



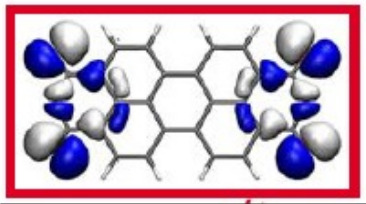


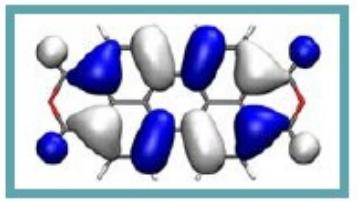
Total Energy: Further improvements in E_{xc} required!

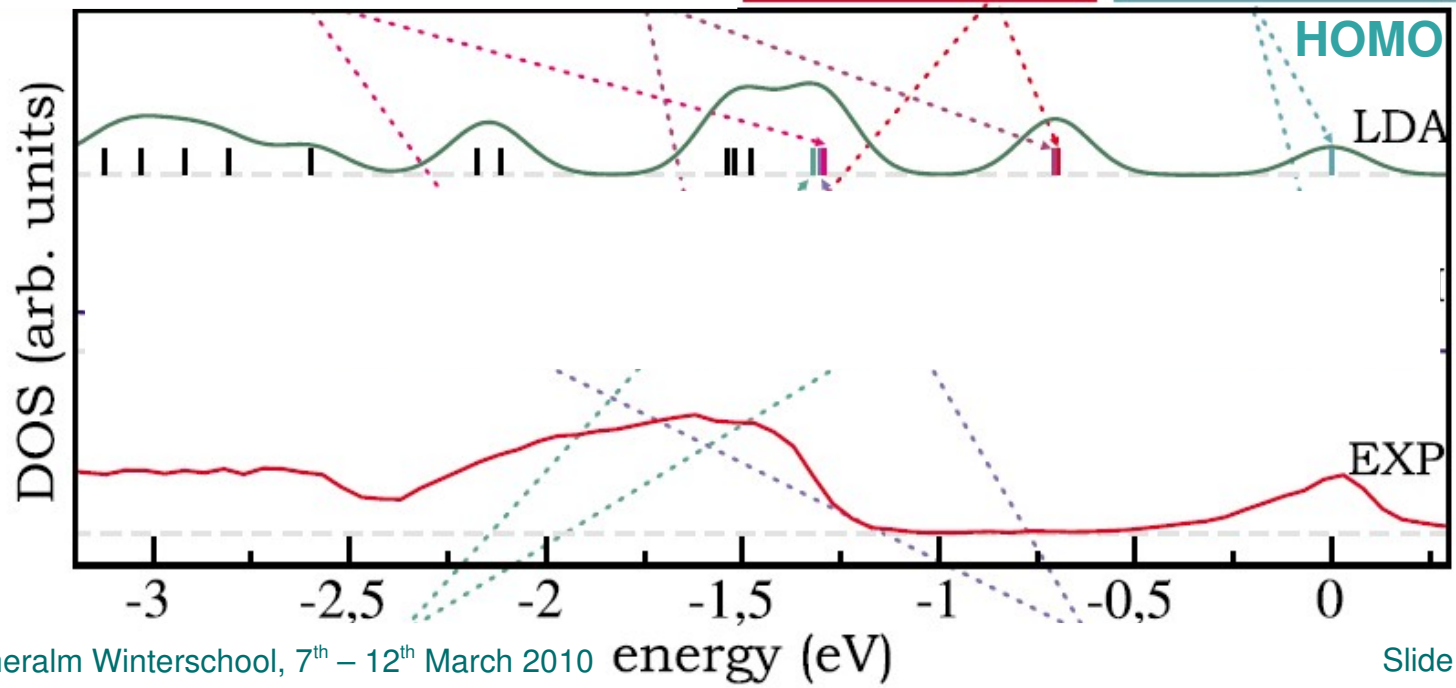
What about Band Energies?

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

HOMO-1







Körzdörfer et al., *PRB* **79**, 201205(R) (2009).

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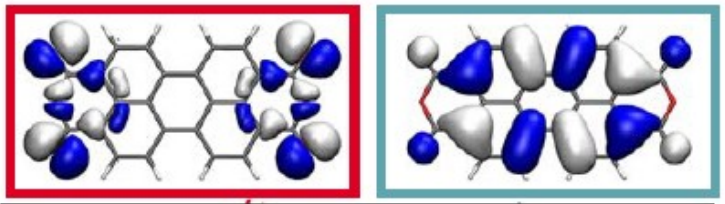
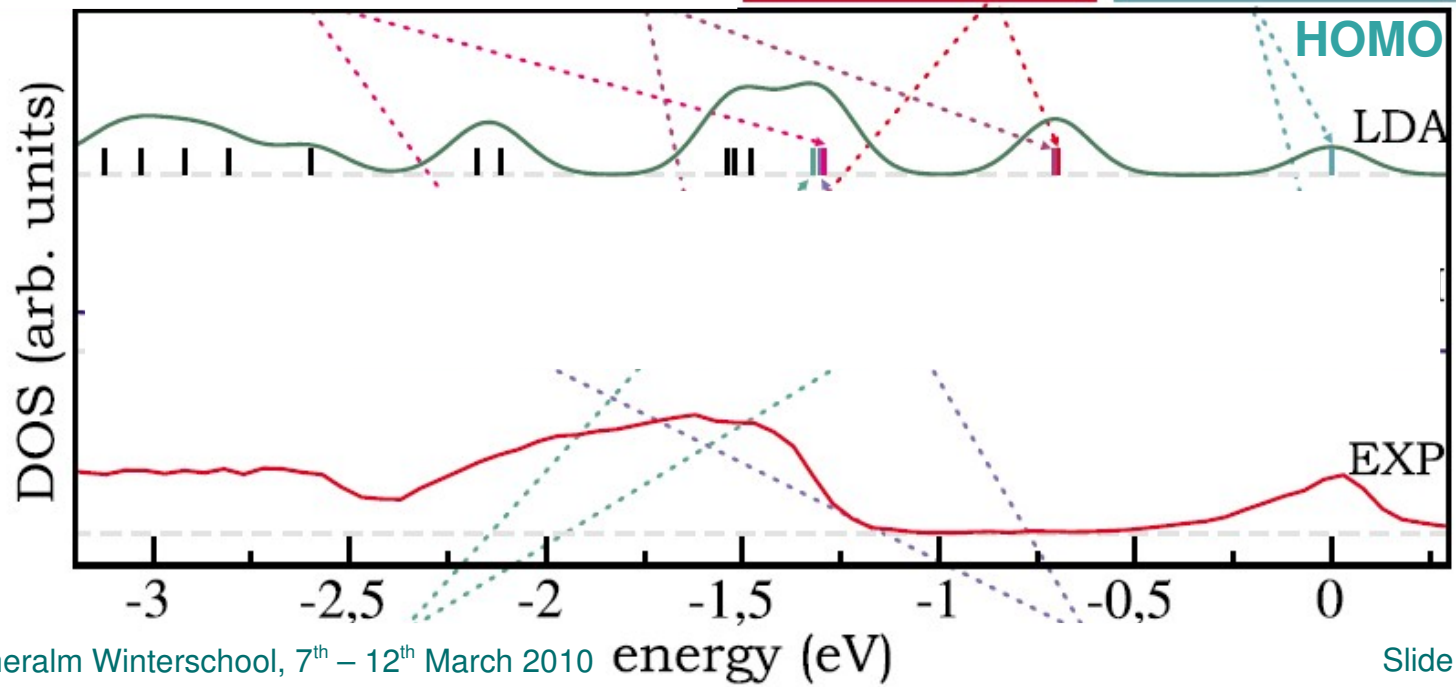
Incomplete cancellation of self-interaction !!

HOMO-1





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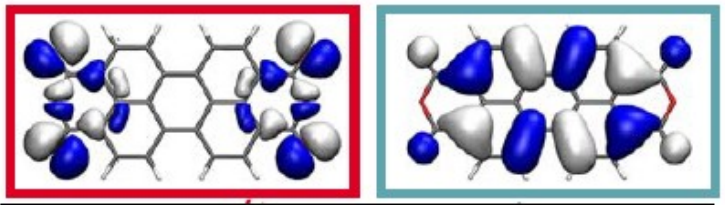
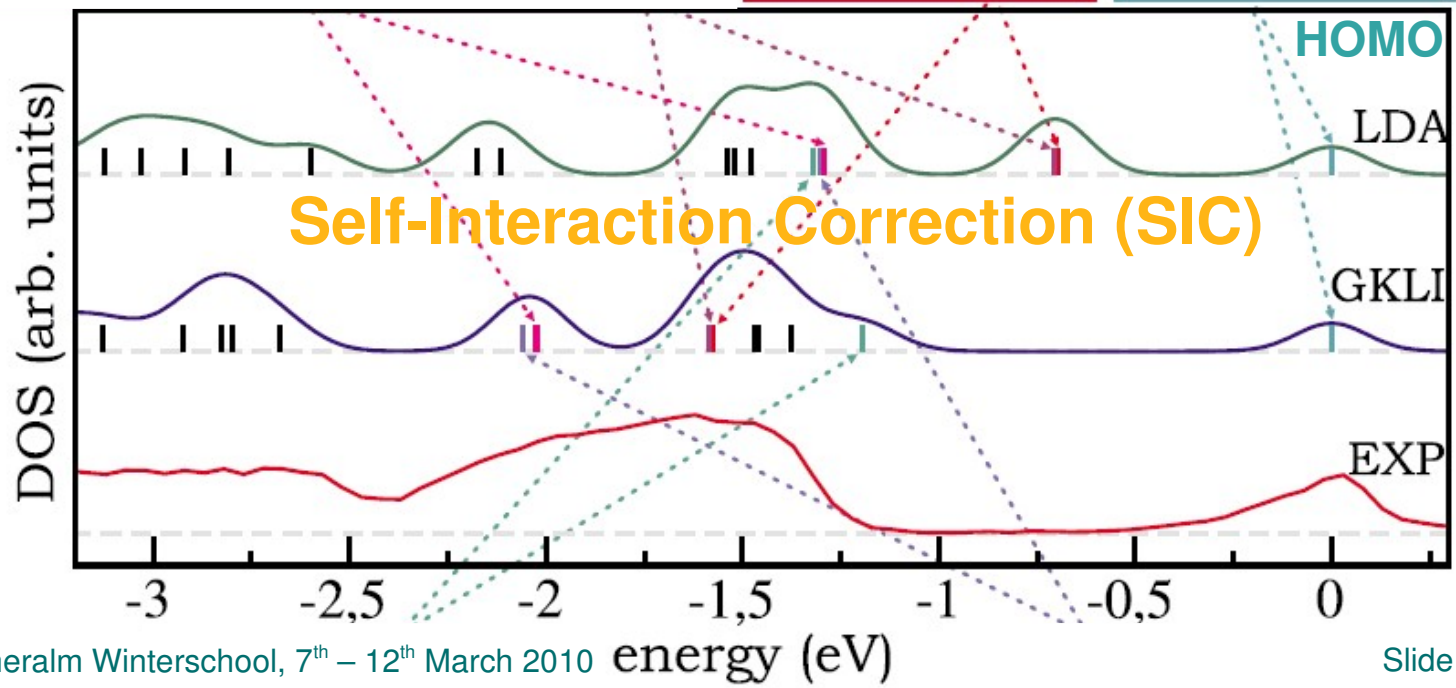
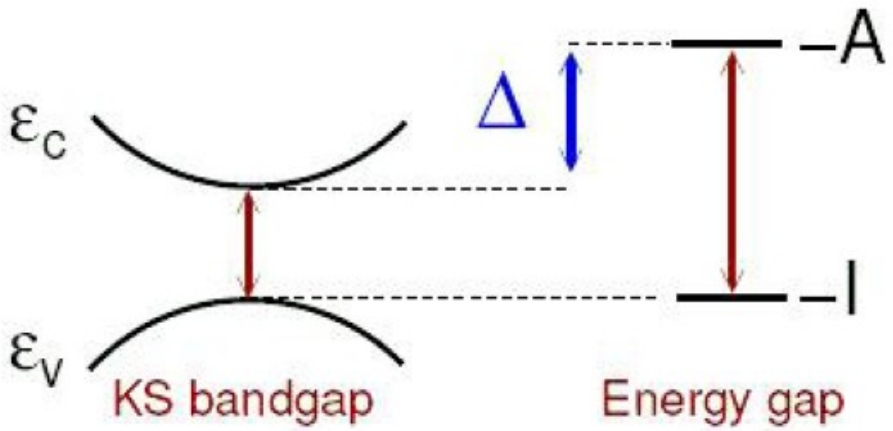




Körzdörfer et al., *PRB* **79**, 201205(R) (2009).

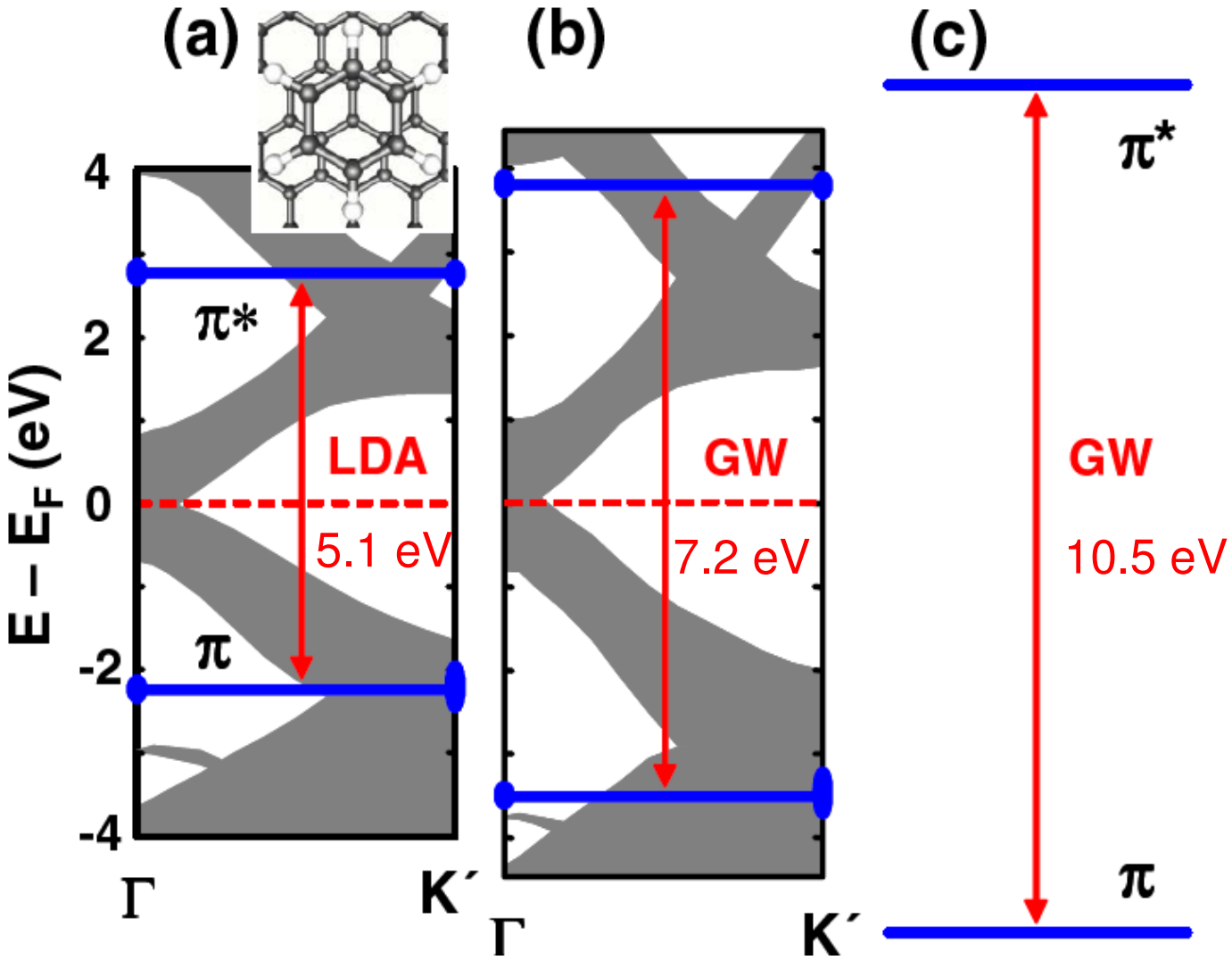
Band Gap Problem

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



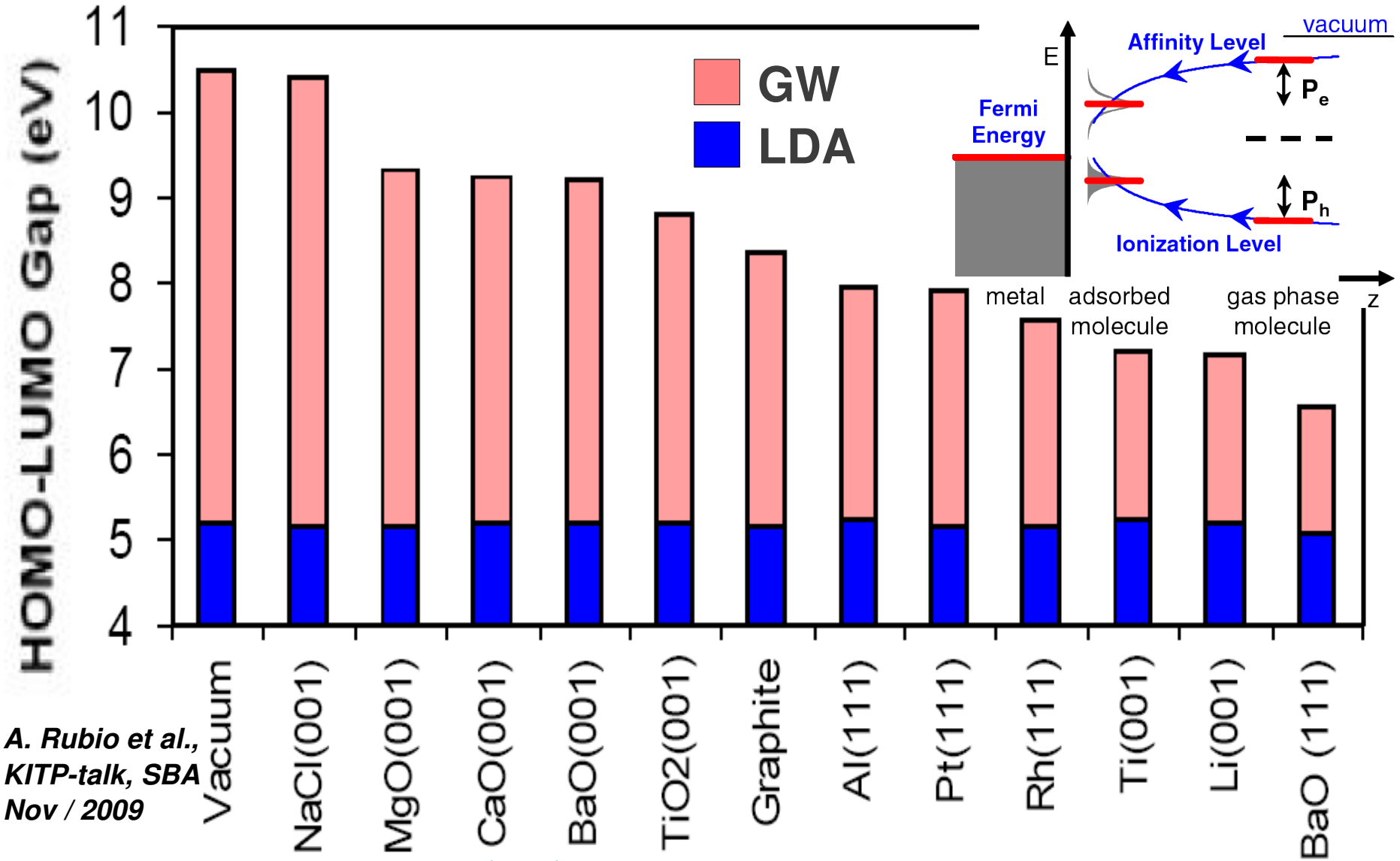
- $E_{\text{gap}} = \varepsilon_{\text{gap}}^{\text{KS}} + \Delta_{\text{xc}}$
- $\Delta_{\text{xc}} = v_{\text{xc}}^{+} - v_{\text{xc}}^{-}$
- How large is Δ_{xc}?

Benzene / Graphene



Neaton et al., *PRL* **97**, 216405 (2006).

Physisorbed Benzene

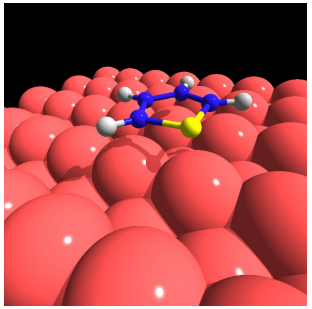


A. Rubio et al., KITP-talk, SBA Nov / 2009

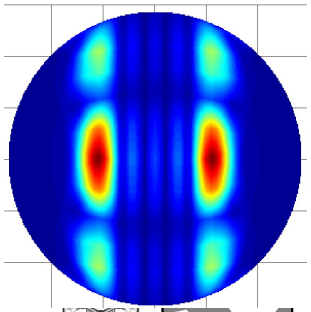
Summary

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

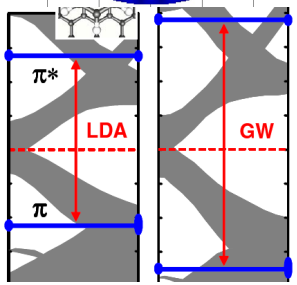
Density Functional Theory



Structural Properties



Electronic Structure



Problems in DFT

Collaborations and Funding

Atomistic Modelling Group – University Leoben, Austria
- Dmitrii Nabok
- Priya Sony
- Lorenz Romaner
- 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, Germany
- Thomas Seyller
- Konstantin Emtsev

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„Interface controlled and functionalized organic films“

Thank You!

2007 Winterschool of the NFN
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