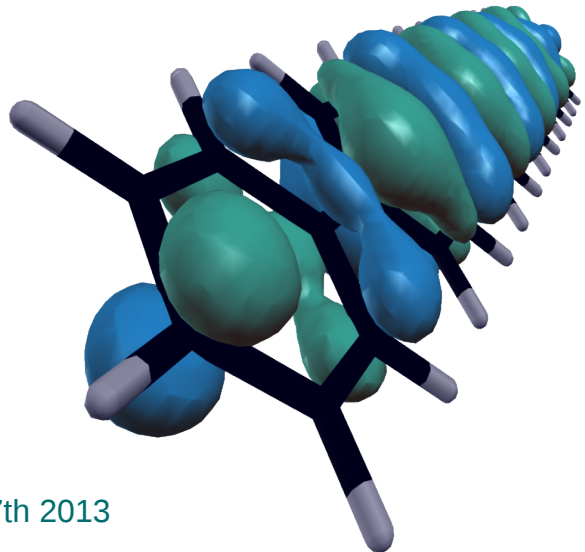
Organic Semiconductors Explored With Ab-initio Electronic Structure Methods



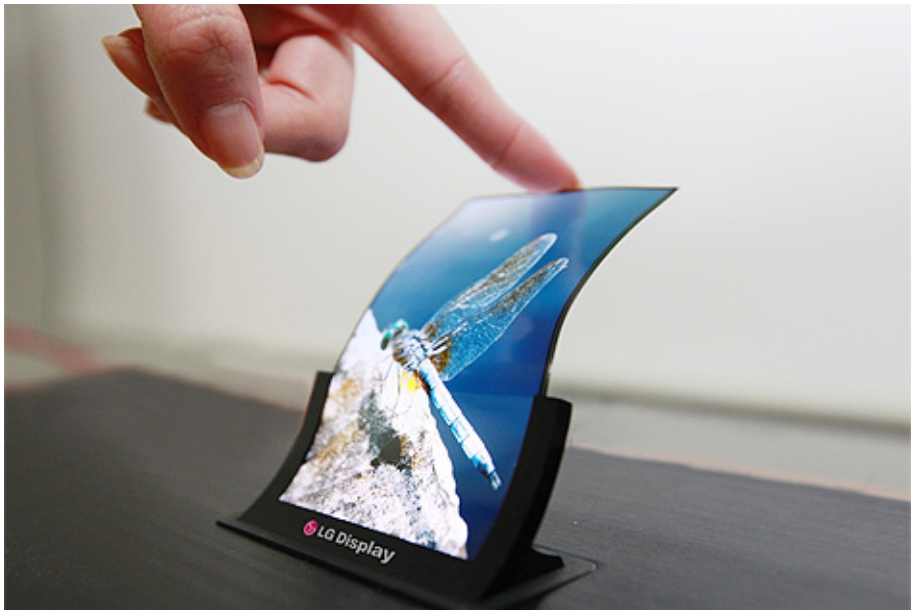
Peter Puschnig, ViCoM Seminar, May 27th 2013

Flexible OLED Displays

May, 26th 2013: http://orf.at/stories/2180119/2180120/

„Die Bildschirmzukunft ist biegsam

Flexible organische Leuchtdioden (Flexible Organic Light Emitting Diode, FOLED) sollen in Zukunft bisherige LCD-Anzeigen in Smartphones ersetzen. Noch in diesem Jahr sollen erste Geräte mit den widerstandsfähigen, dünnen und leichten Displays auf den Markt kommen.“



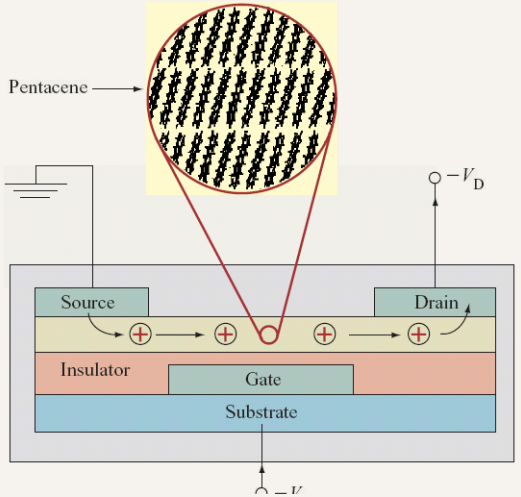
Five inch flexible OLED from LG

Samsung's new smart-phone design

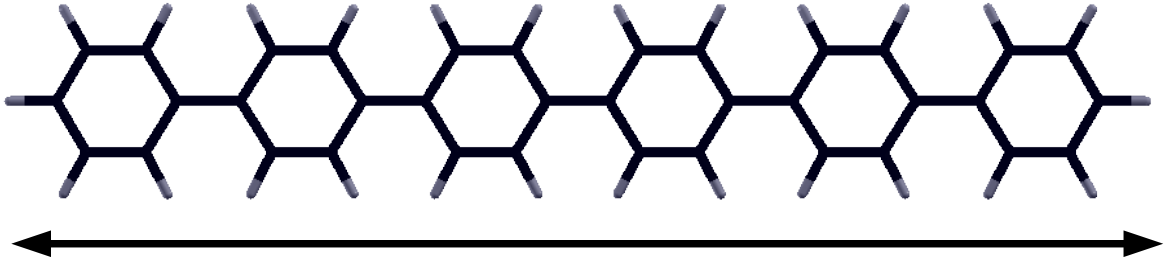
Organic Semiconductors

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

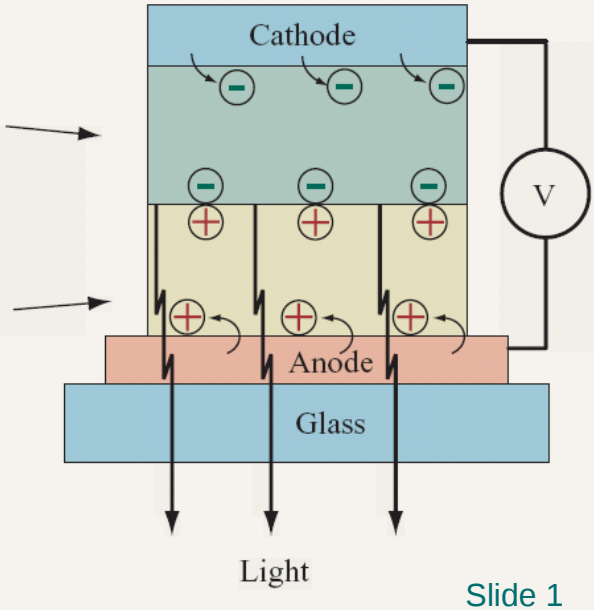
OFET
Organic
Field **E**ffect
Transistor



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



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



Kohn-Sham Equations

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

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

Approximations

Self-consistency

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

Outline

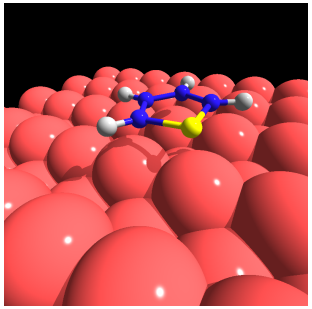
Theory

Density Functional Theory (DFT) in a Nutshell

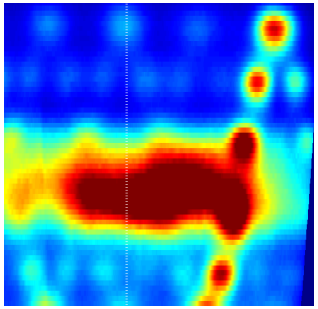
Photoemission Intensity: What angle-resolved PE data tells us about molecular orbitals

Many-Body Perturbation Theory: GW-Approximation, Bethe-Salpeter Equation

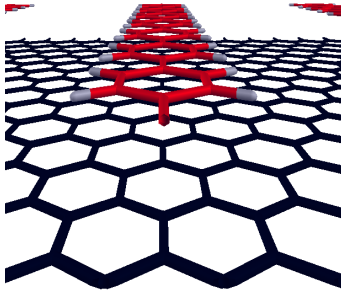
Applications



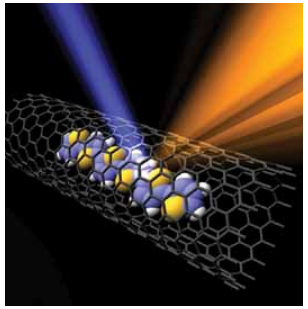
Van der Waals Interactions In DFT



Photoemission from organic molecular films



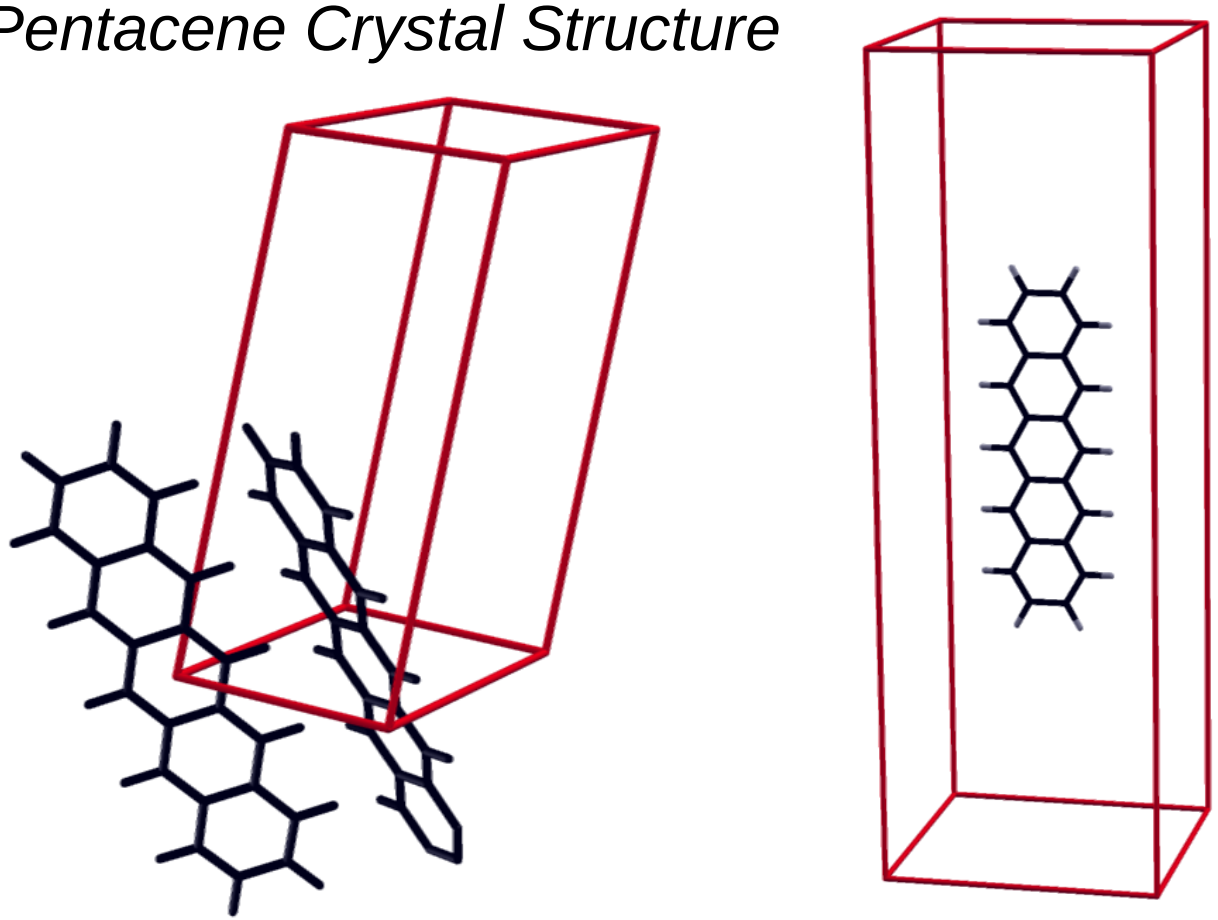
GW-band structure of Polymer / Graphene



Hybrid excitons in Nano-Peapods

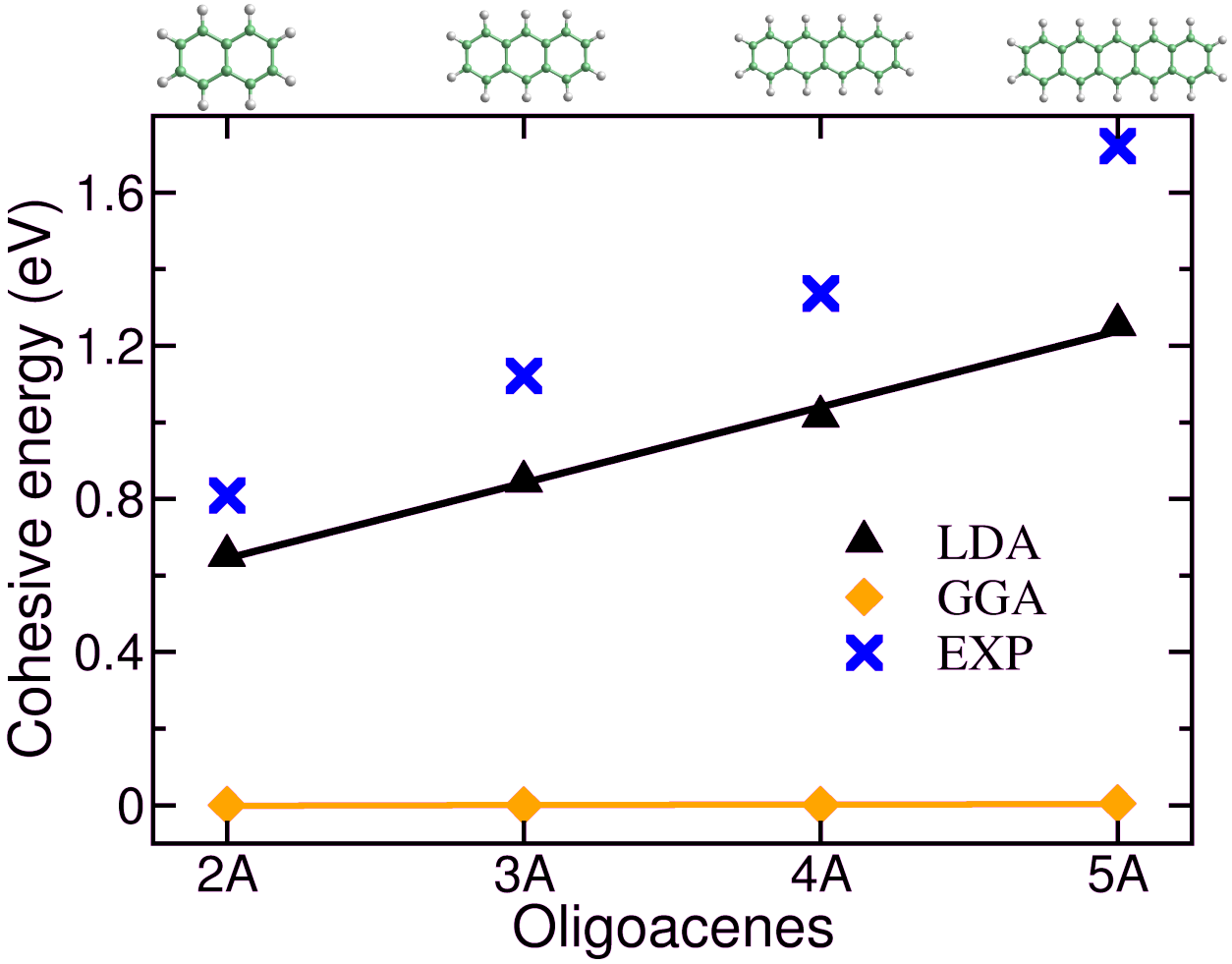
Cohesive Energy of Molecular Crystals

Pentacene Crystal Structure



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

Cohesive Energy of Molecular Crystals



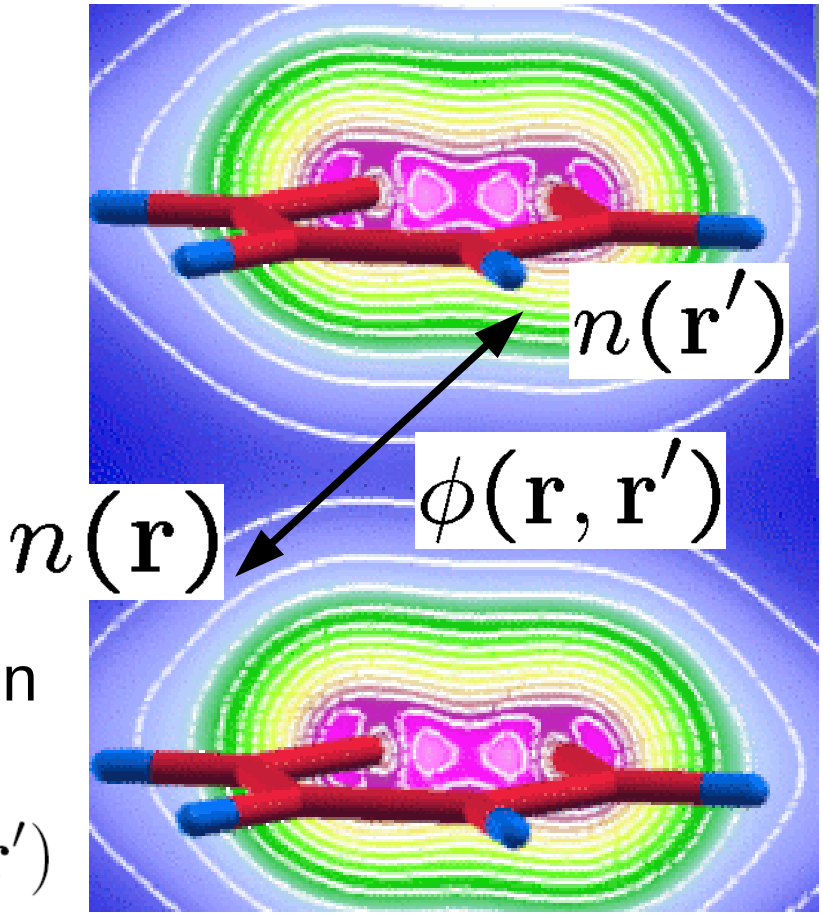
Van der Waals Density Functional

Exchange-Correlation Energy

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

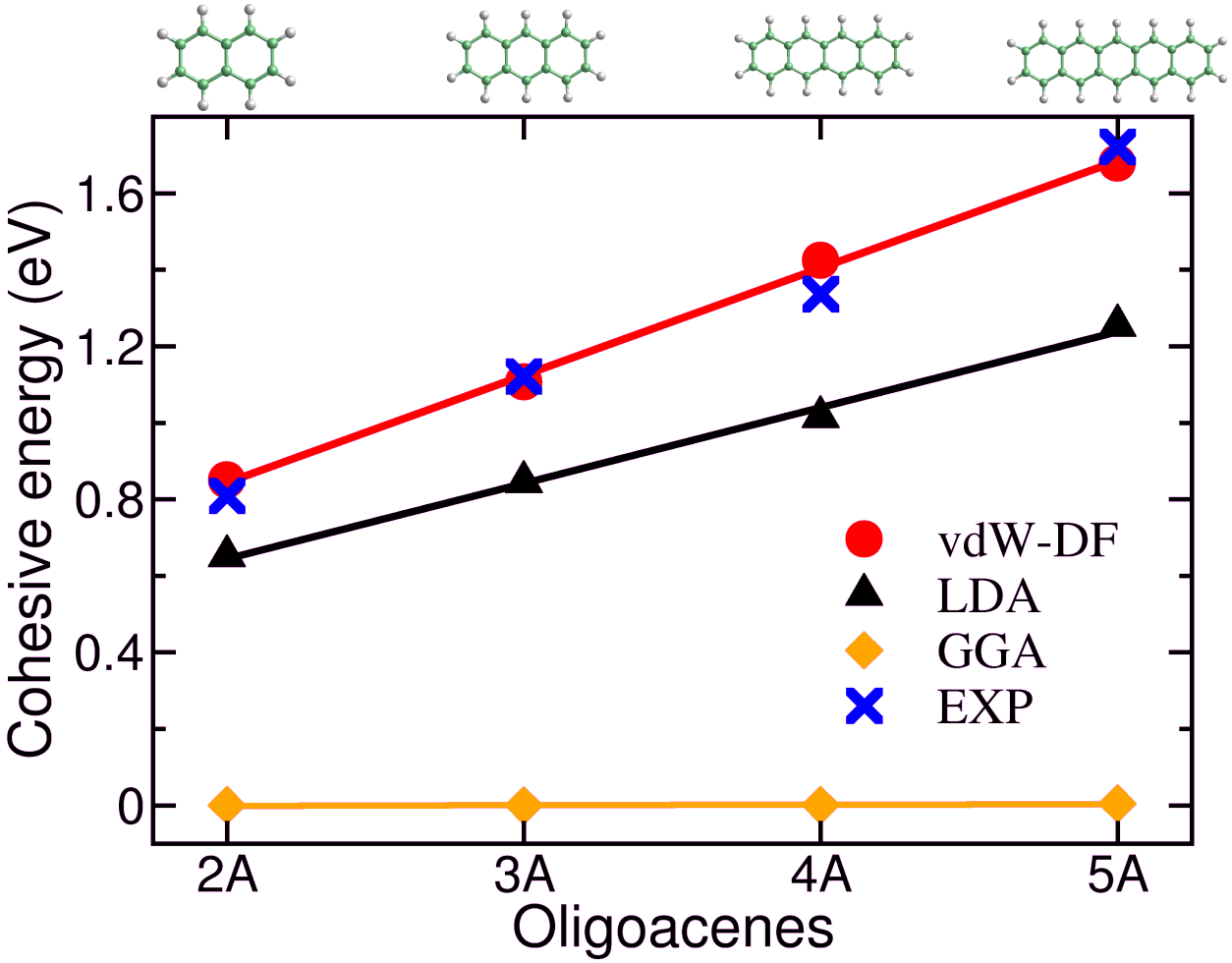
Nonlocal Correlation Energy
leading to van-der-Waals interaction

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



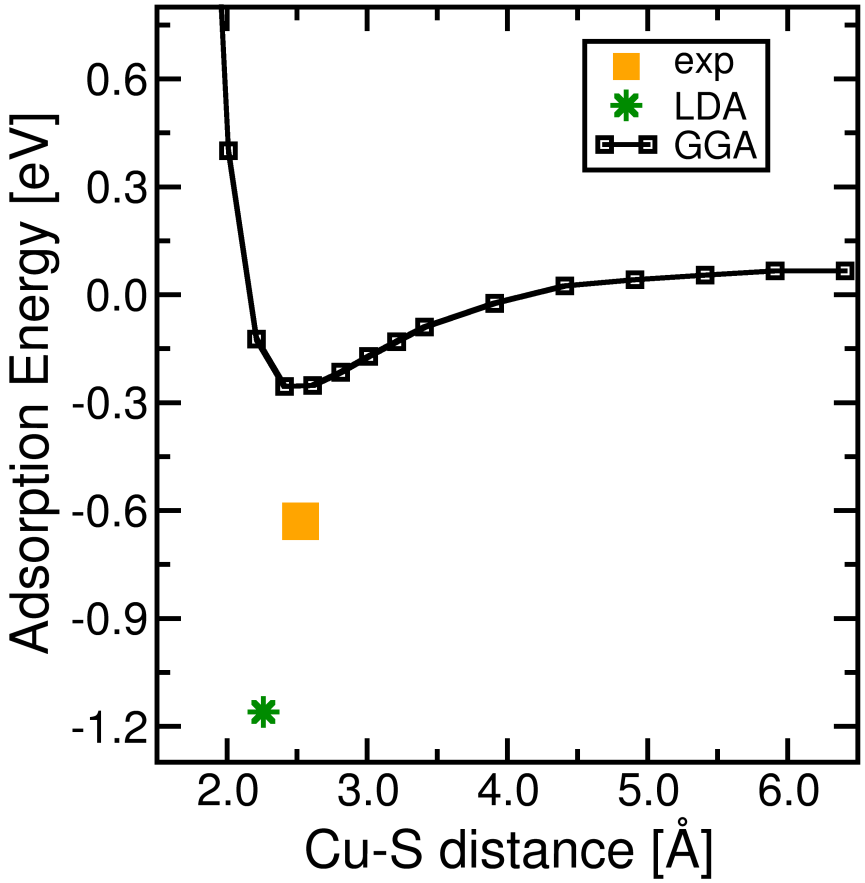
Dion et al, *Phys. Rev. Lett.* ***92****, 246401 (2004).*

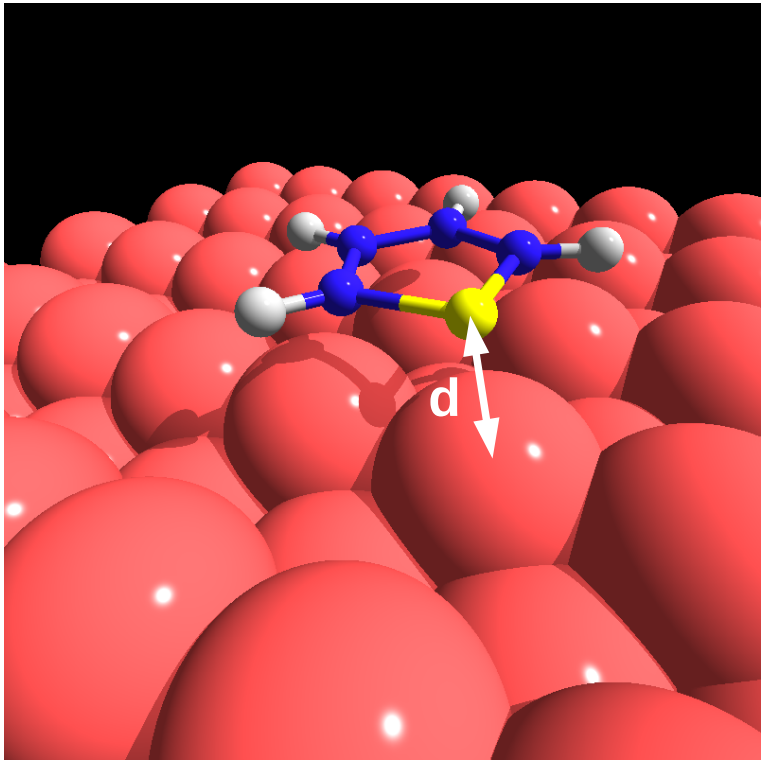
Cohesive Energy of Molecular Crystals



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

Thiophene / Cu(110)





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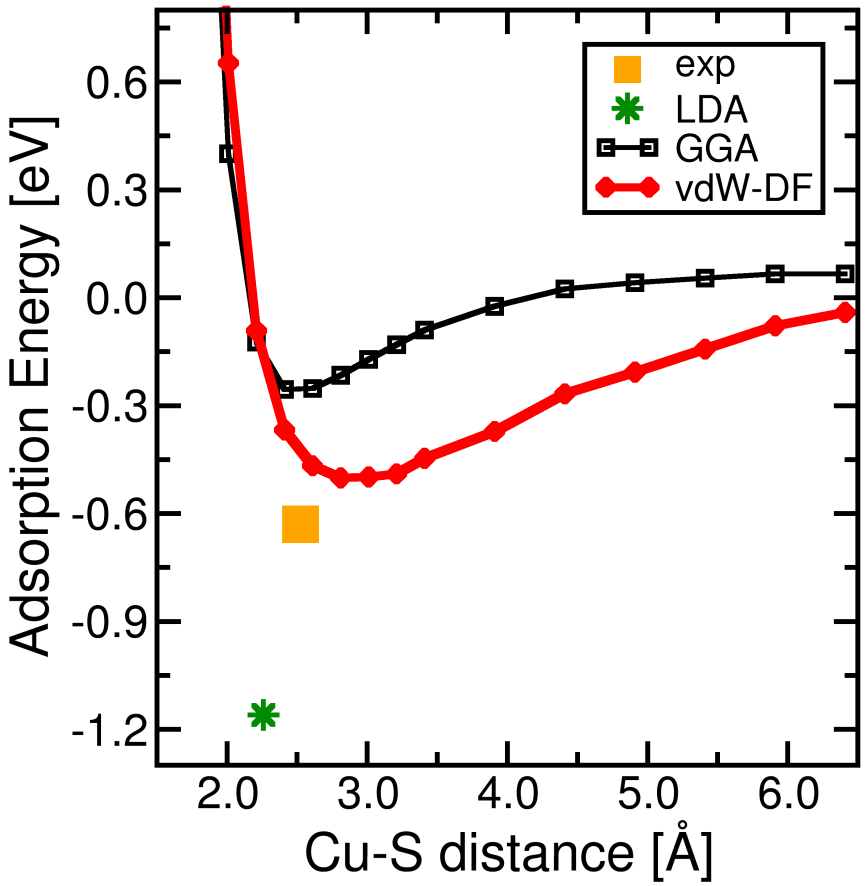
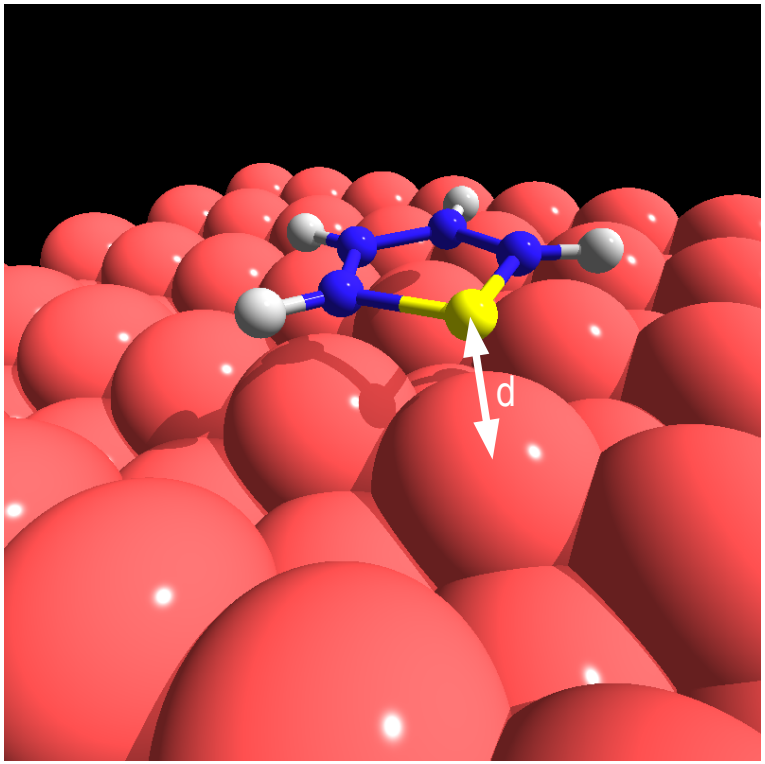
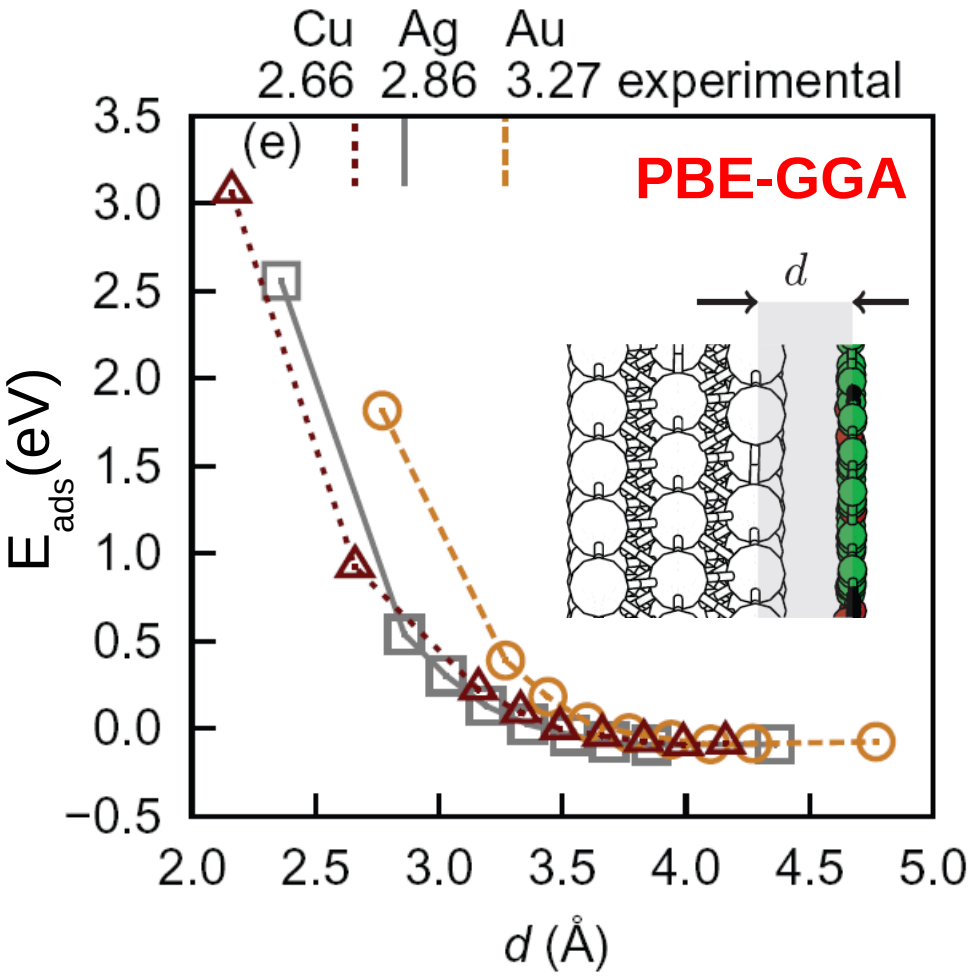


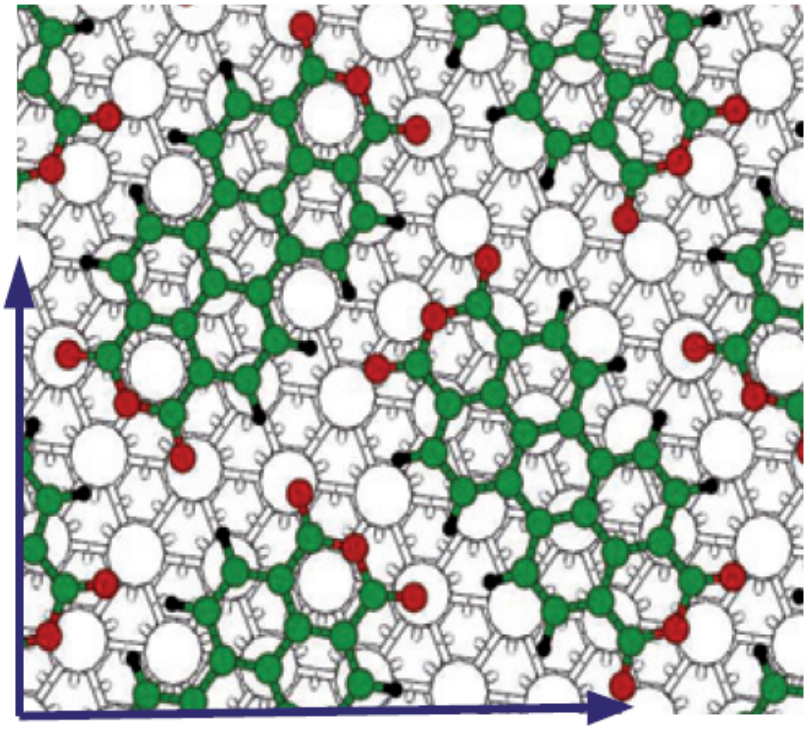


Sony, Puschnig, Nabok, Ambrosch-Draxl, *Phys. Rev. Lett.* ***99****, 176401 (2007).*

Nabok, Puschnig, Ambrosch-Draxl, Comp. *Phys. Comm.* ***182****, 1657 (2011).*

PTCDA / Coinage Metals

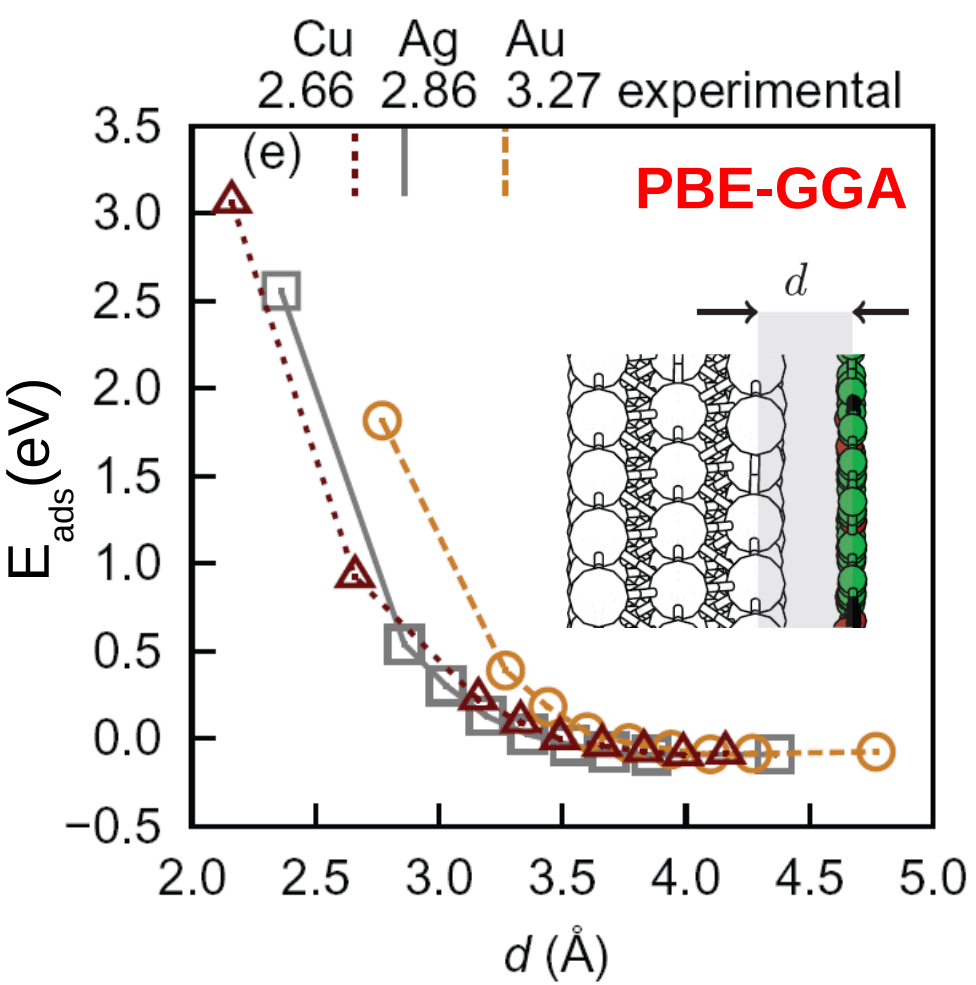


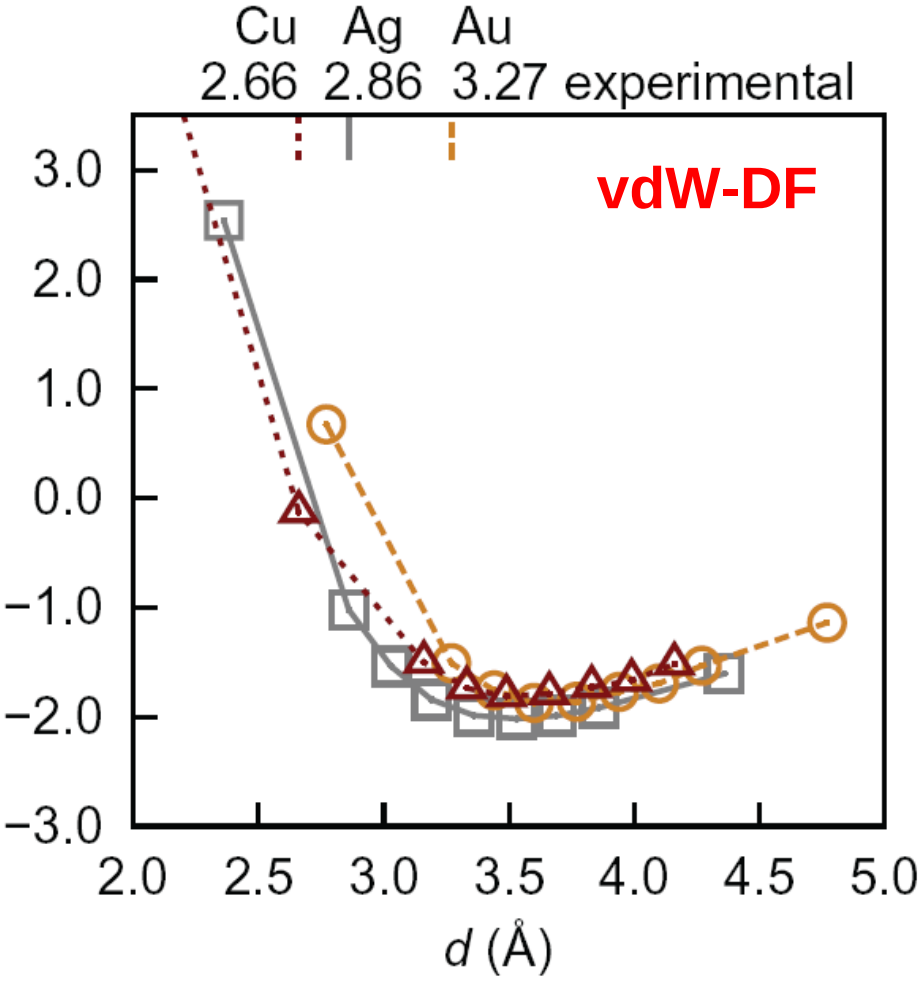


PTCDA / Ag(111)

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

PTCDA / Coinage Metals





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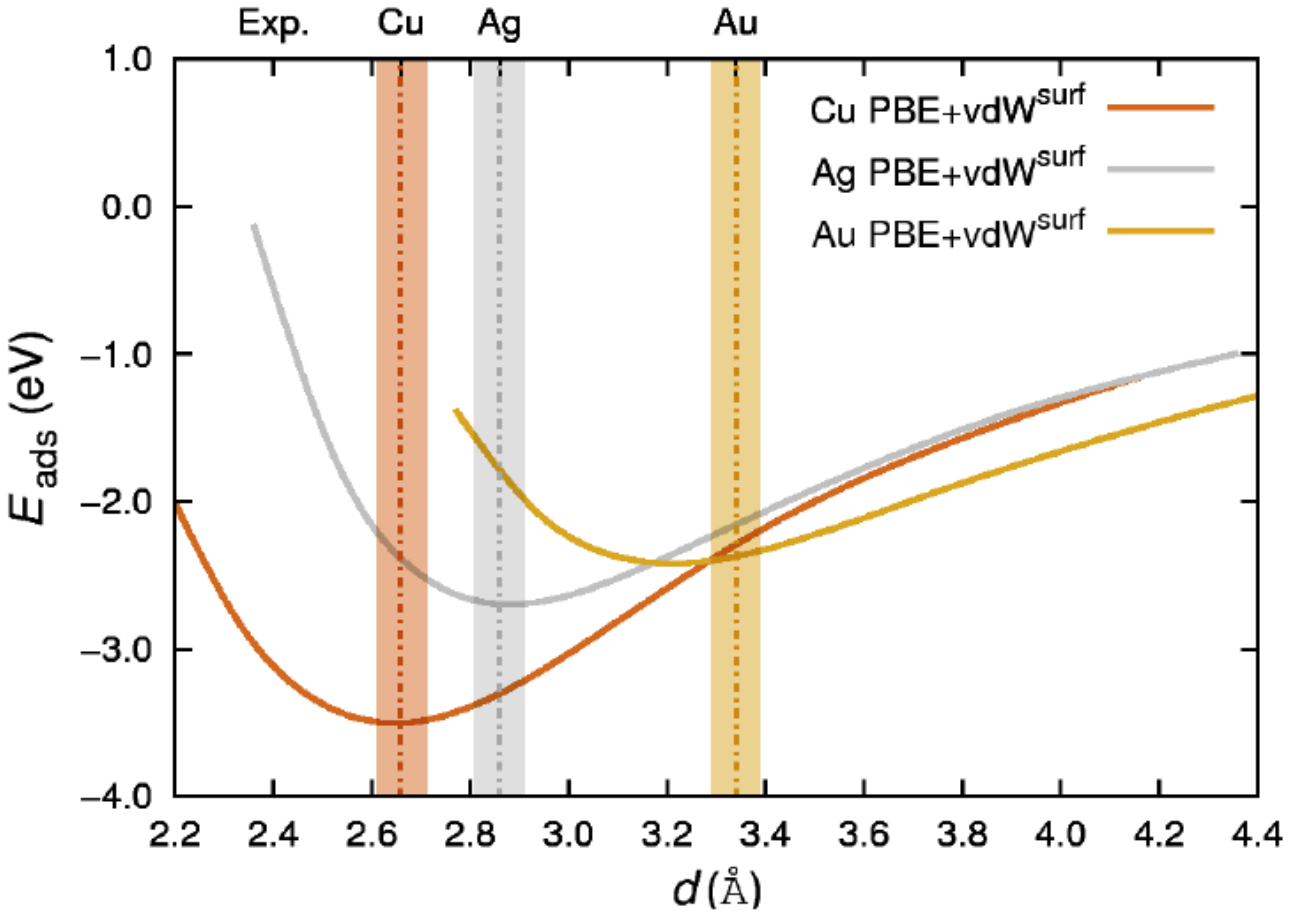

…. inclusion of the many-body collective response of the substrate electrons … by Lifshitz-Zaremba-Kohn theory for the nonlocal Coulomb screening in metals.

Ruiz, Liu, Zojer, Scheffler, Tkatchenko, Phys. Rev. Lett. ***108***, 146103 (2012).

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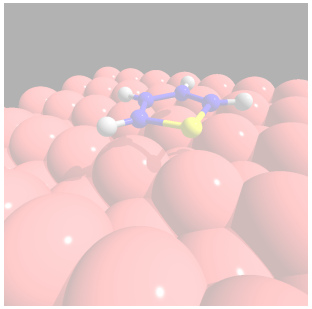

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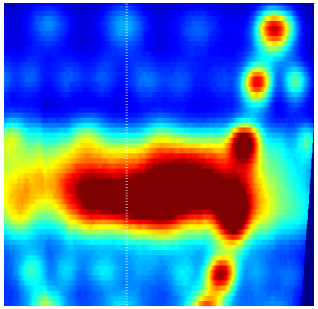

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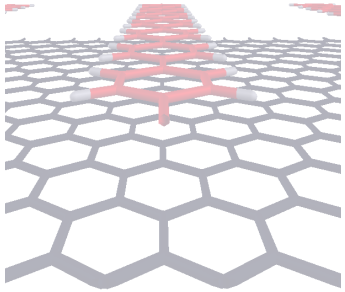

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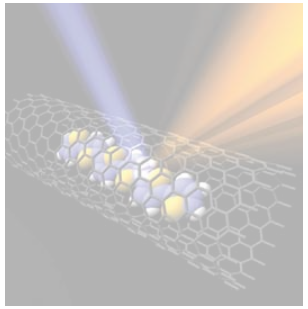
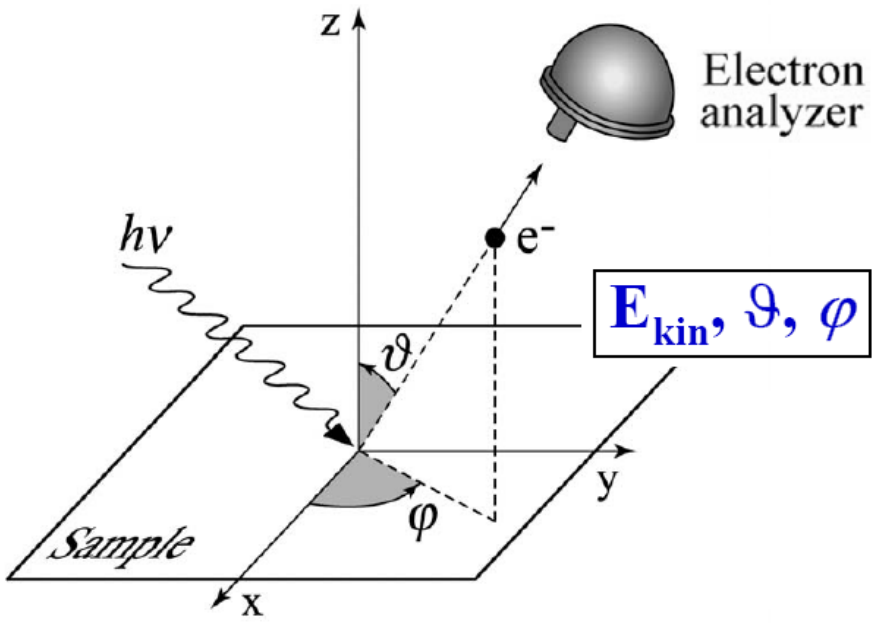


Hybrid excitons in Nano-Peapods

Photoemission Spectroscopy



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

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

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

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

Vacuum

E_{kin}

$\mathbf{K}$

Conservation laws

$$E_f - E_i = h\nu$$

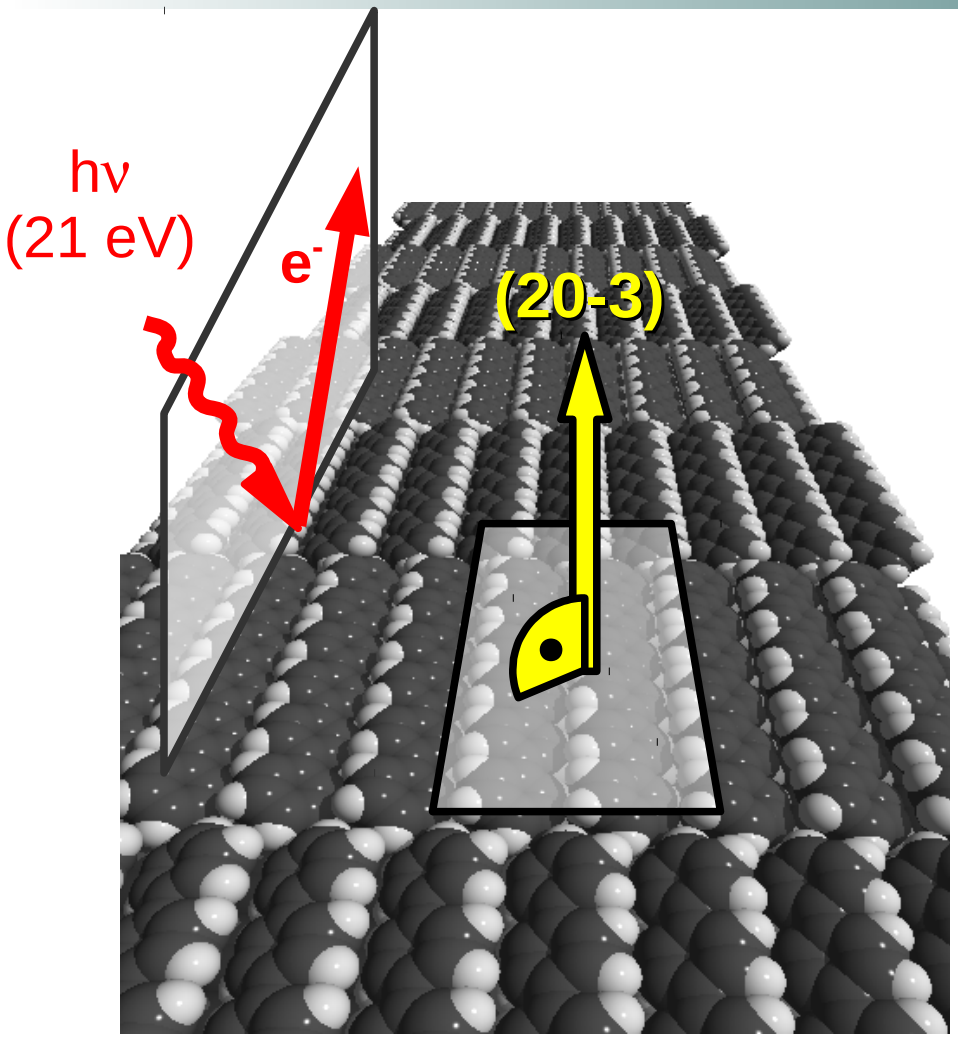
$$\mathbf{k}_f - \mathbf{k}_i = \cancel{\mathbf{k}_{h\nu}}$$

Solid

E_B

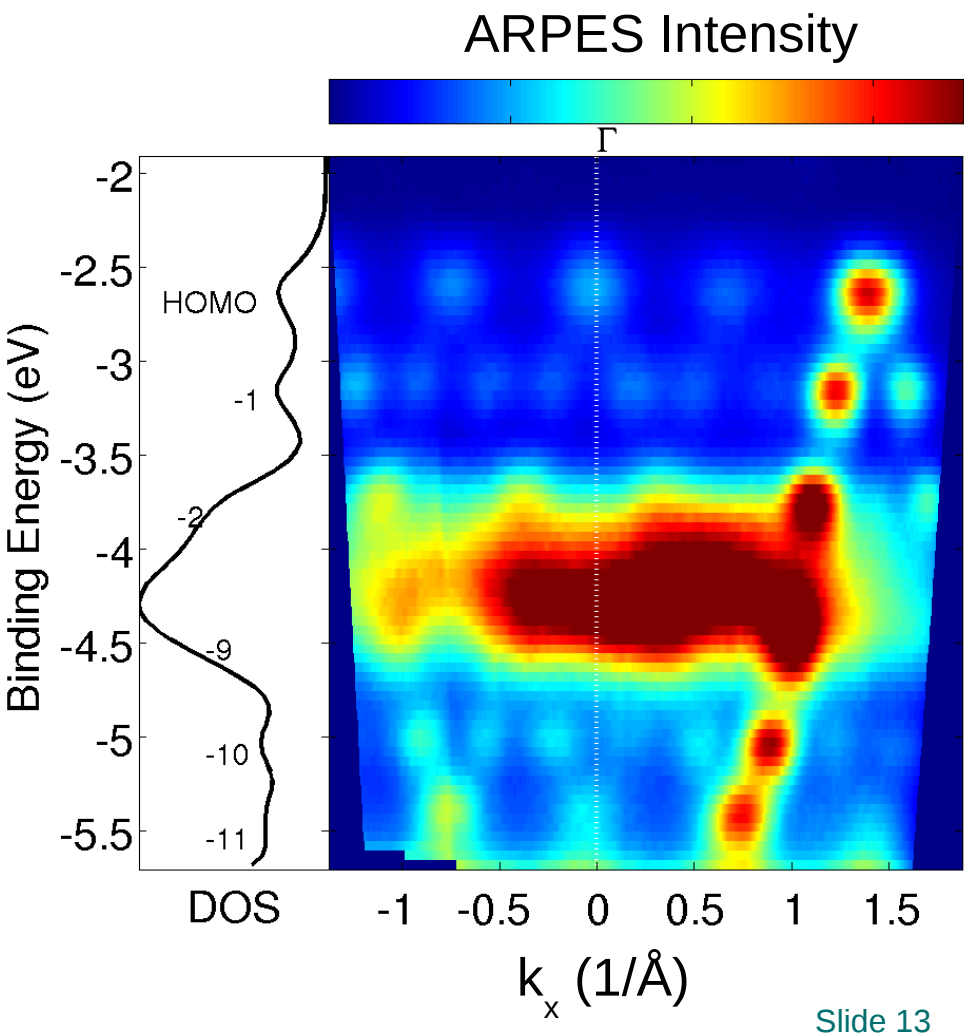
$\mathbf{k}$

Uniaxially Aligned Sexiphenyl

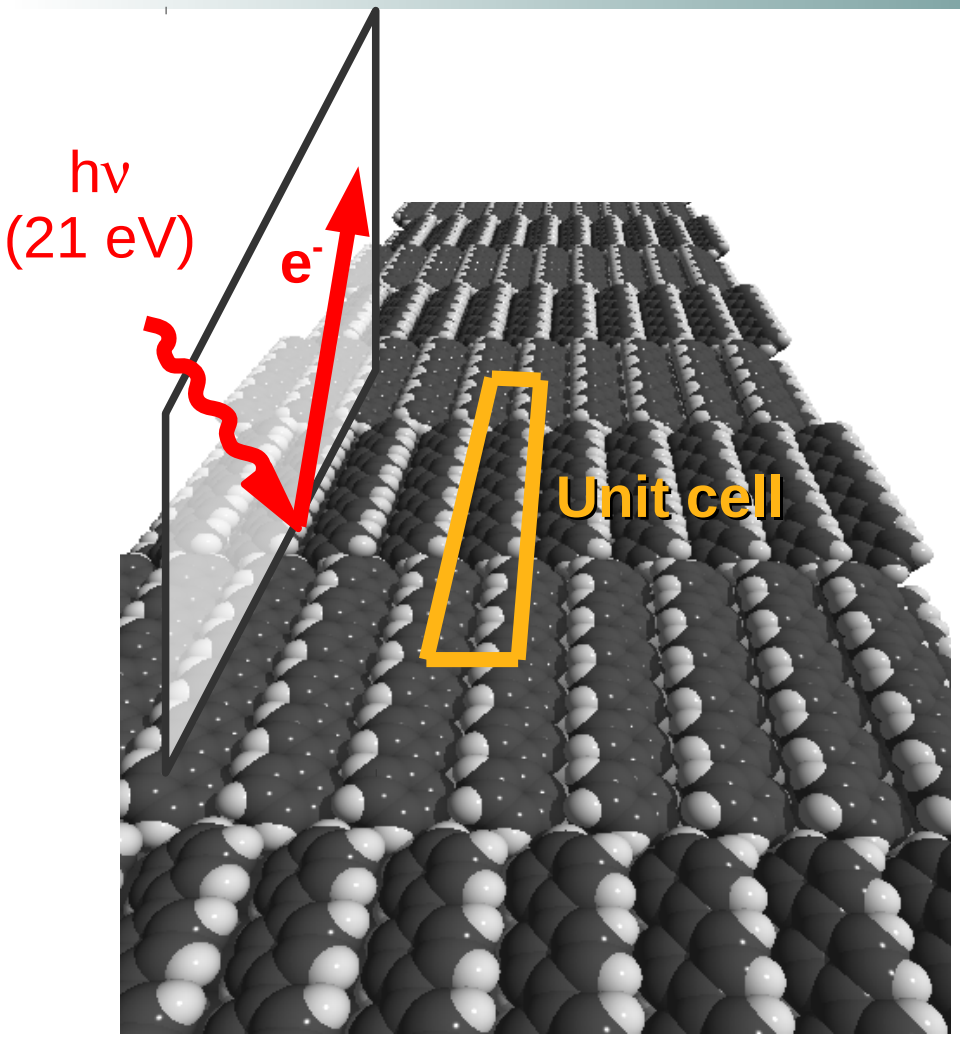


Uniaxially ordered para-sexiphenyl film
on Cu(110)_(2x1)O

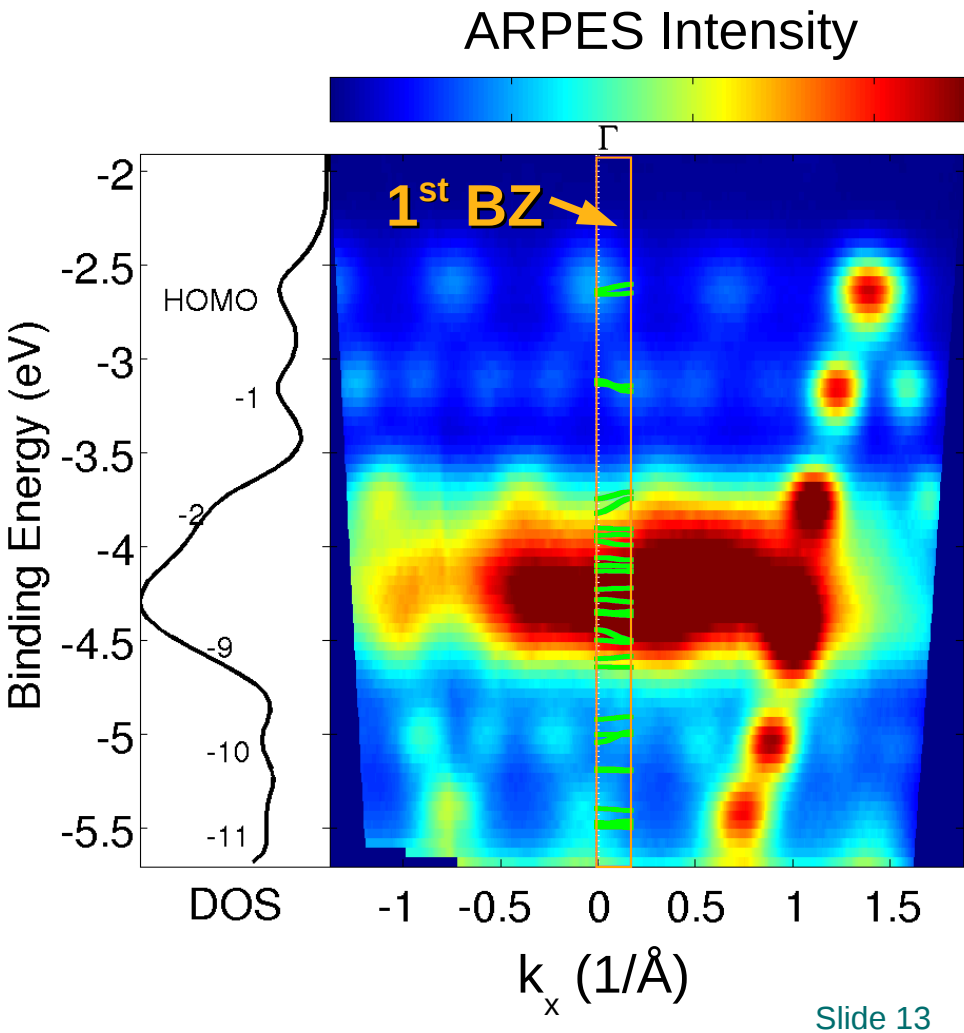
ARPES data from Stephen Berkebile



Uniaxially Aligned Sexiphenyl



Band structure from:
Puschnig et al., *PRB* **60**, 7891 (1999).



Photoemission Intensity

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

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

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

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

Photoemission Intensity

One Step Model

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

- Independent-Particle Picture
- Sudden Approximation

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

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Photoemission Intensity

One Step Model

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

$$H_{int} = \frac{e}{2mc}(\boldsymbol{A} \cdot \boldsymbol{p} + \boldsymbol{p} \cdot \boldsymbol{A}) = \frac{e}{mc}\boldsymbol{A} \cdot \boldsymbol{p}$$

$$[\boldsymbol{p}, \boldsymbol{A}] = -\mathrm{i}\hbar \nabla \cdot \boldsymbol{A} = 0$$

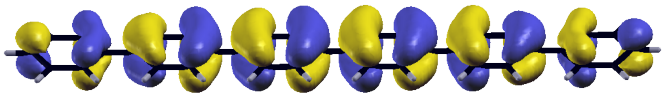
Interaction with the photon field treated as perturbation

Electric dipole approximation
(electric field is constant over atomic dimensions, which holds for the ultra-violet regime)

Photoemission Intensity

One Step Model

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

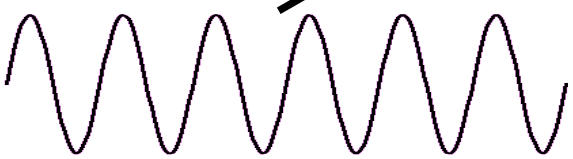


molecular orbital

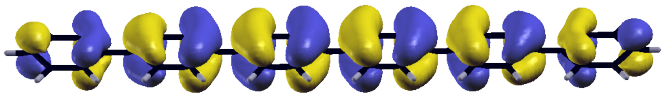
Photoemission Intensity

One Step Model

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



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



molecular orbital

Approximation: final state = plane wave

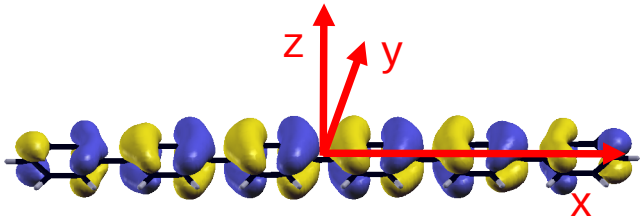
$$I_i(\theta,\phi) \propto \left|(\mathbf{A}\cdot\mathbf{k})\right|^2 \times \left|\tilde{\psi}_i(\mathbf{k})\right|^2$$

Fourier Transform of Initial State Orbital

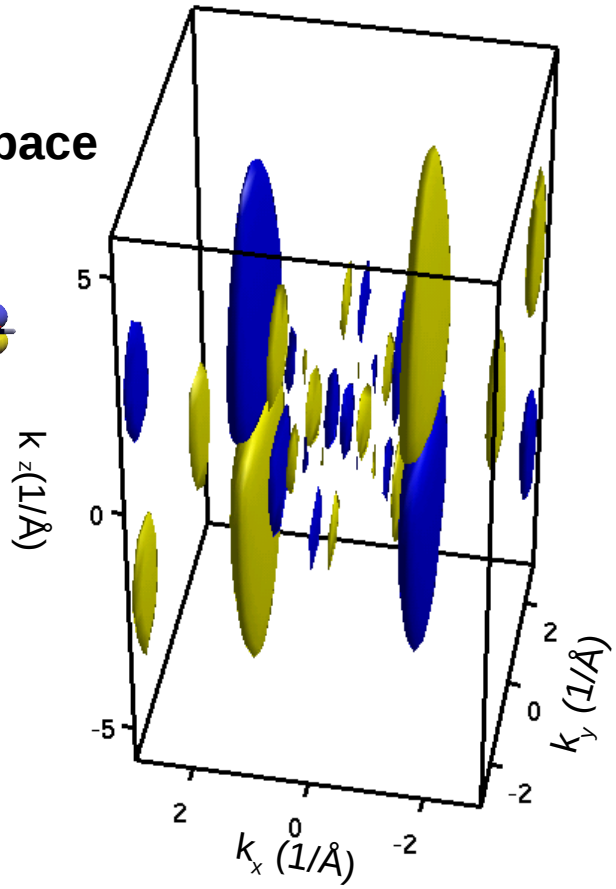
[Feibelman and Eastman, *Phys. Rev. B* **10**, 4932 (1974).]

Fourier Transform of an Orbital

Molecular Orbital in Real Space

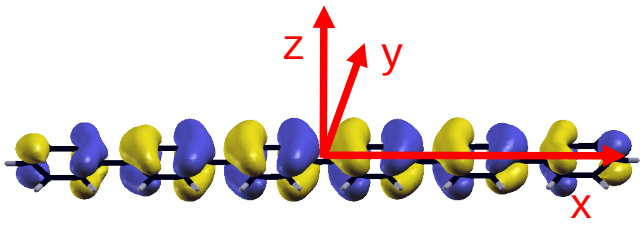


Calculation of the Fourier Transform



Fourier Transform of an Orbital

Molecular Orbital in Real Space



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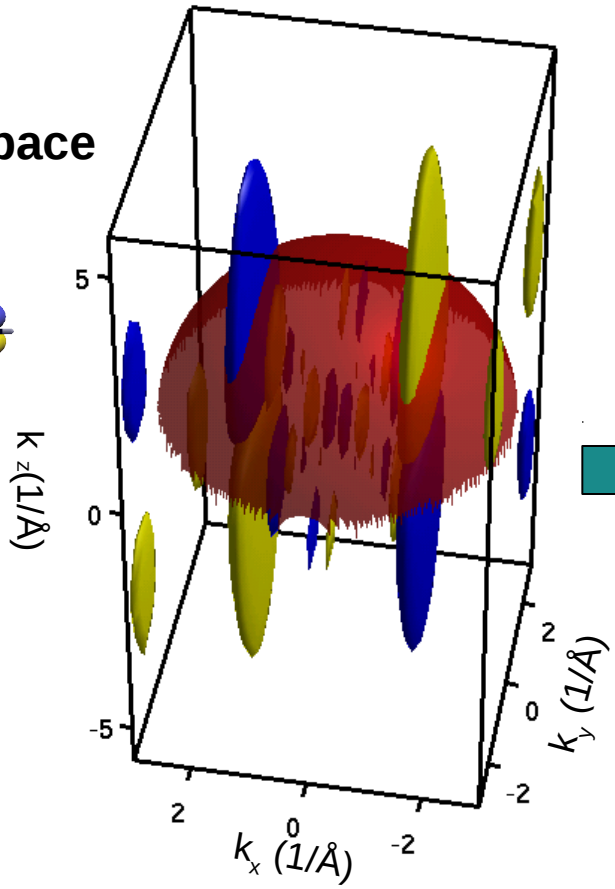
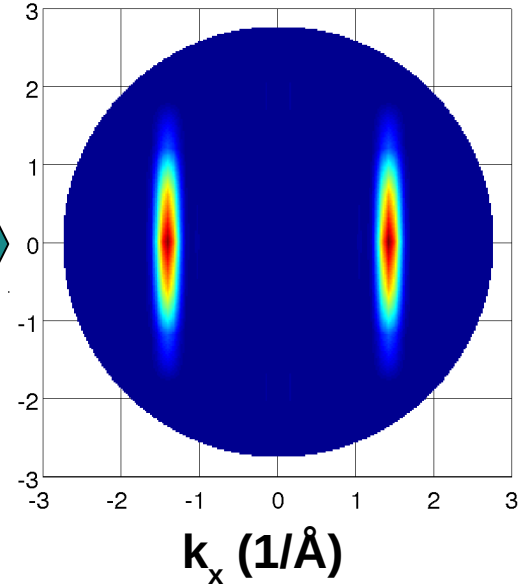
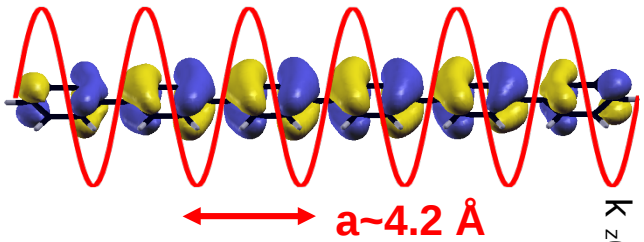


Hemispherical Cut Through 3D Fourier Transform

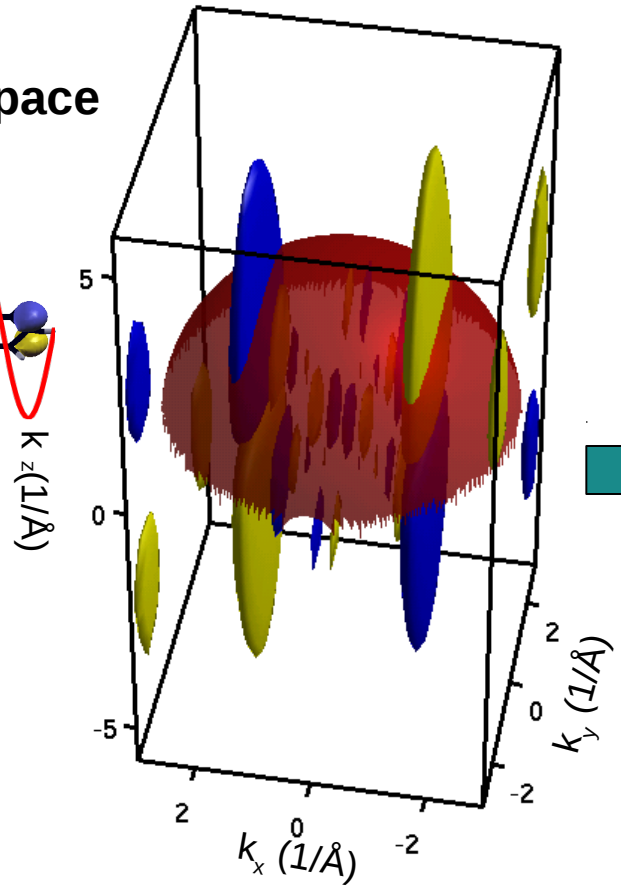


Fourier Transform of an Orbital

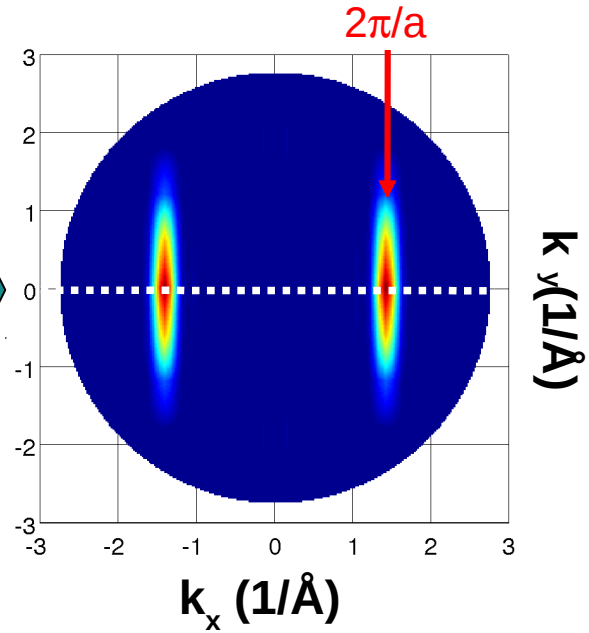
Molecular Orbital in Real Space



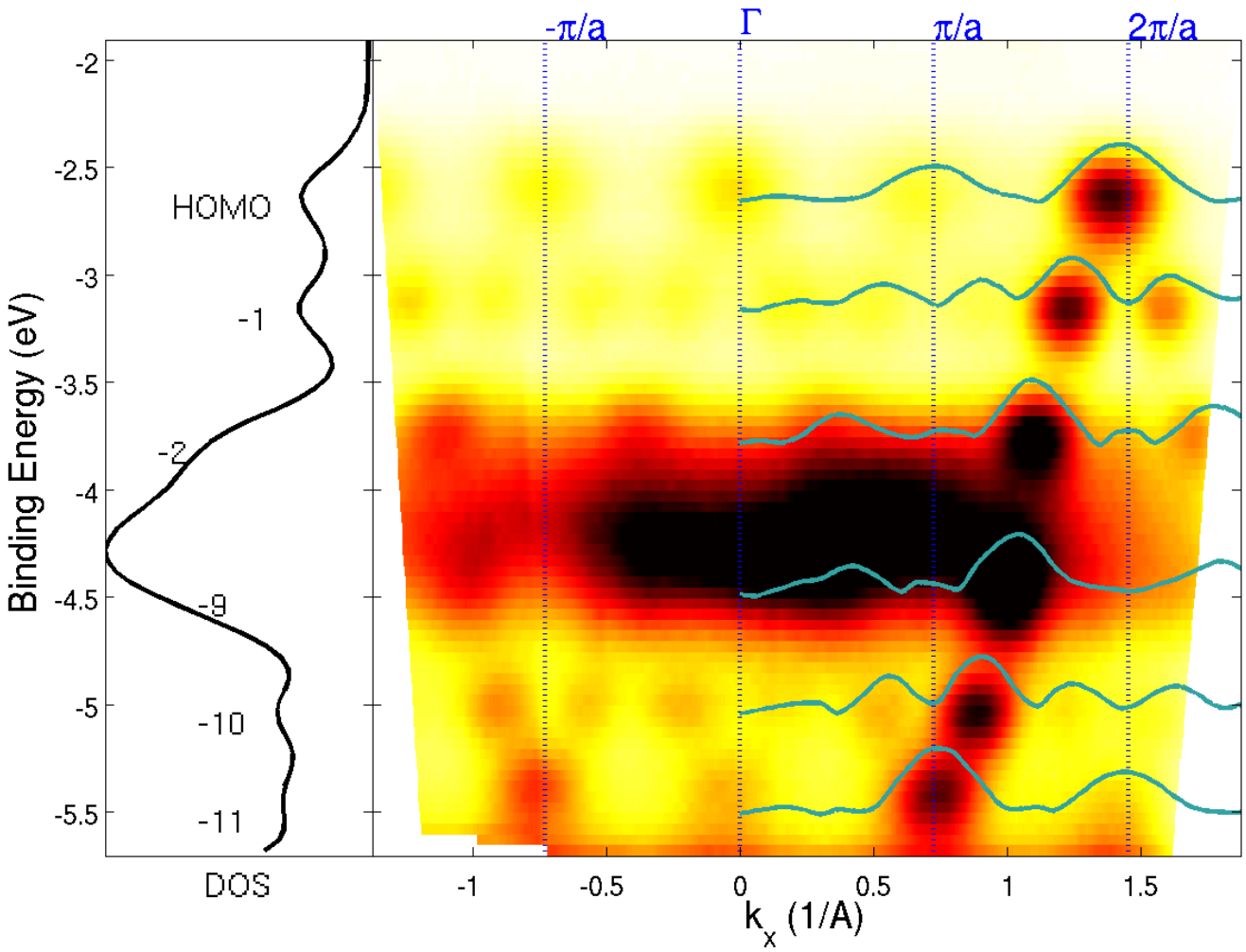
Calculation of the Fourier Transform

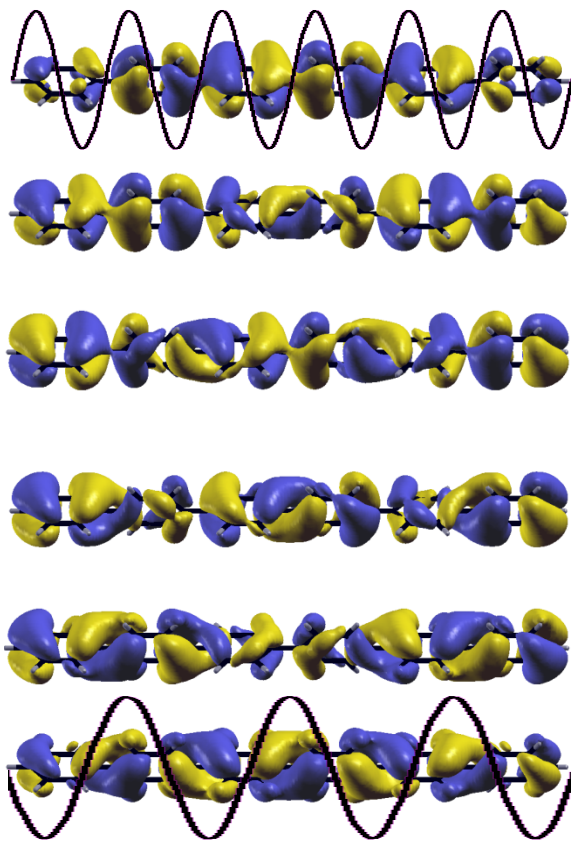


Hemispherical Cut Through 3D Fourier Transform



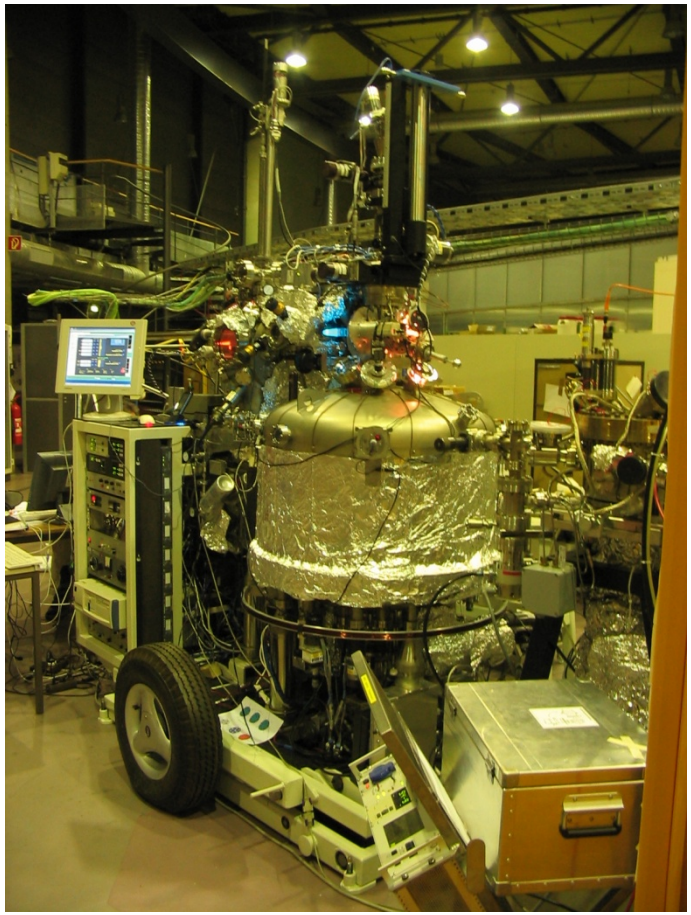
ARPES of *p*-Sexiphenyl

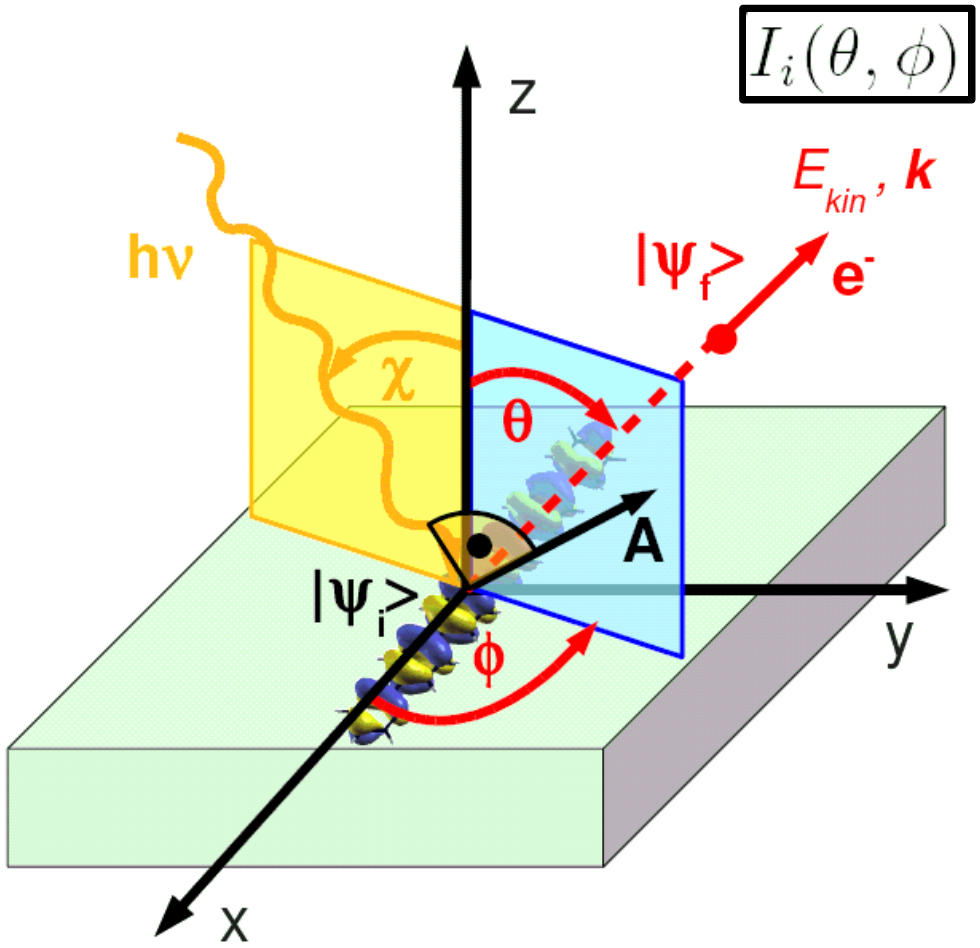




G. Koller et al., *Science* ***317****, 351 (2007).*

Toroidal Electron Energy Analyzer

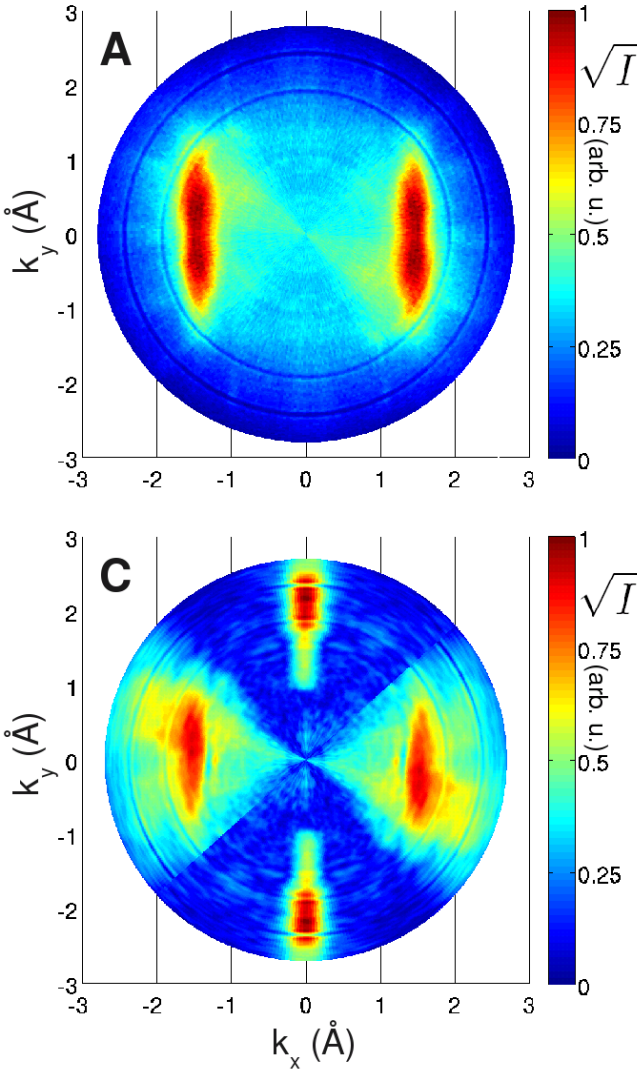


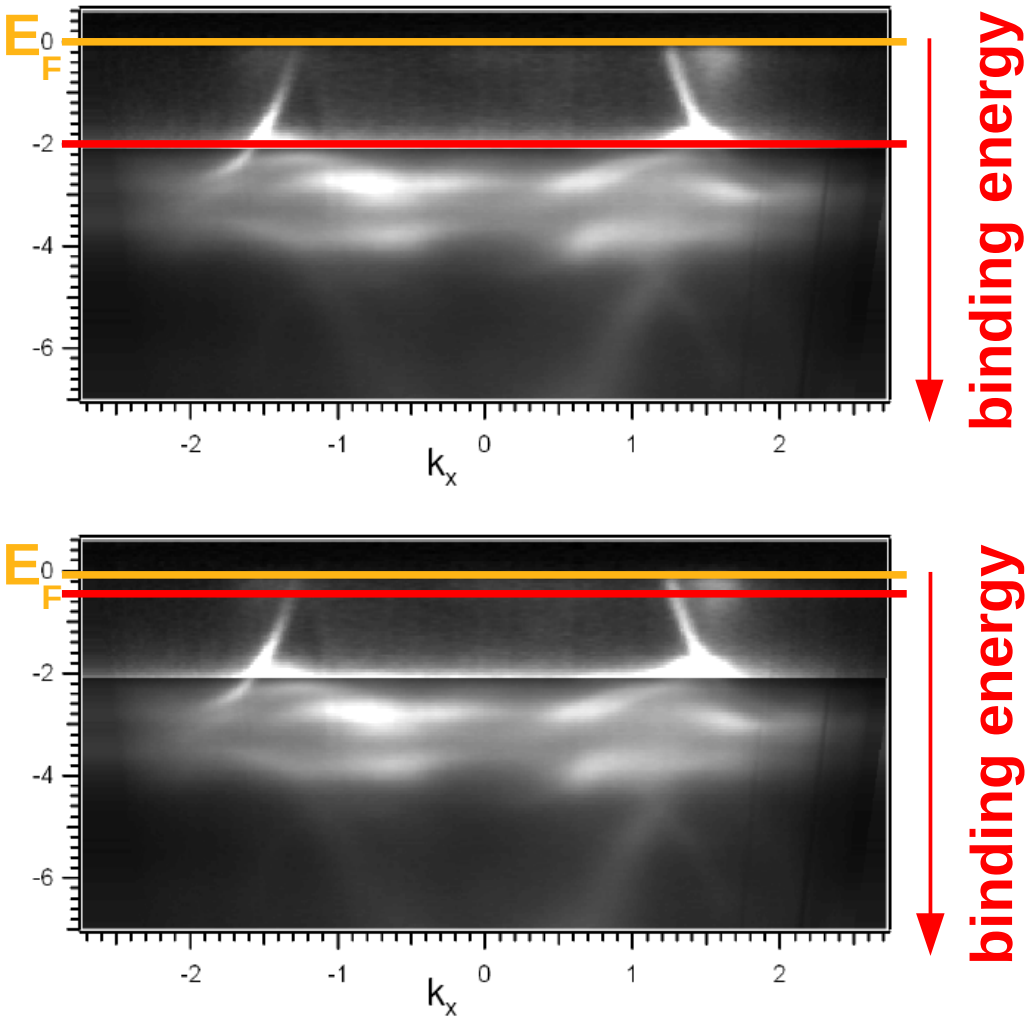


The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II

Sexiphenyl Monolayer on Cu(110)

2D-Momentum Maps

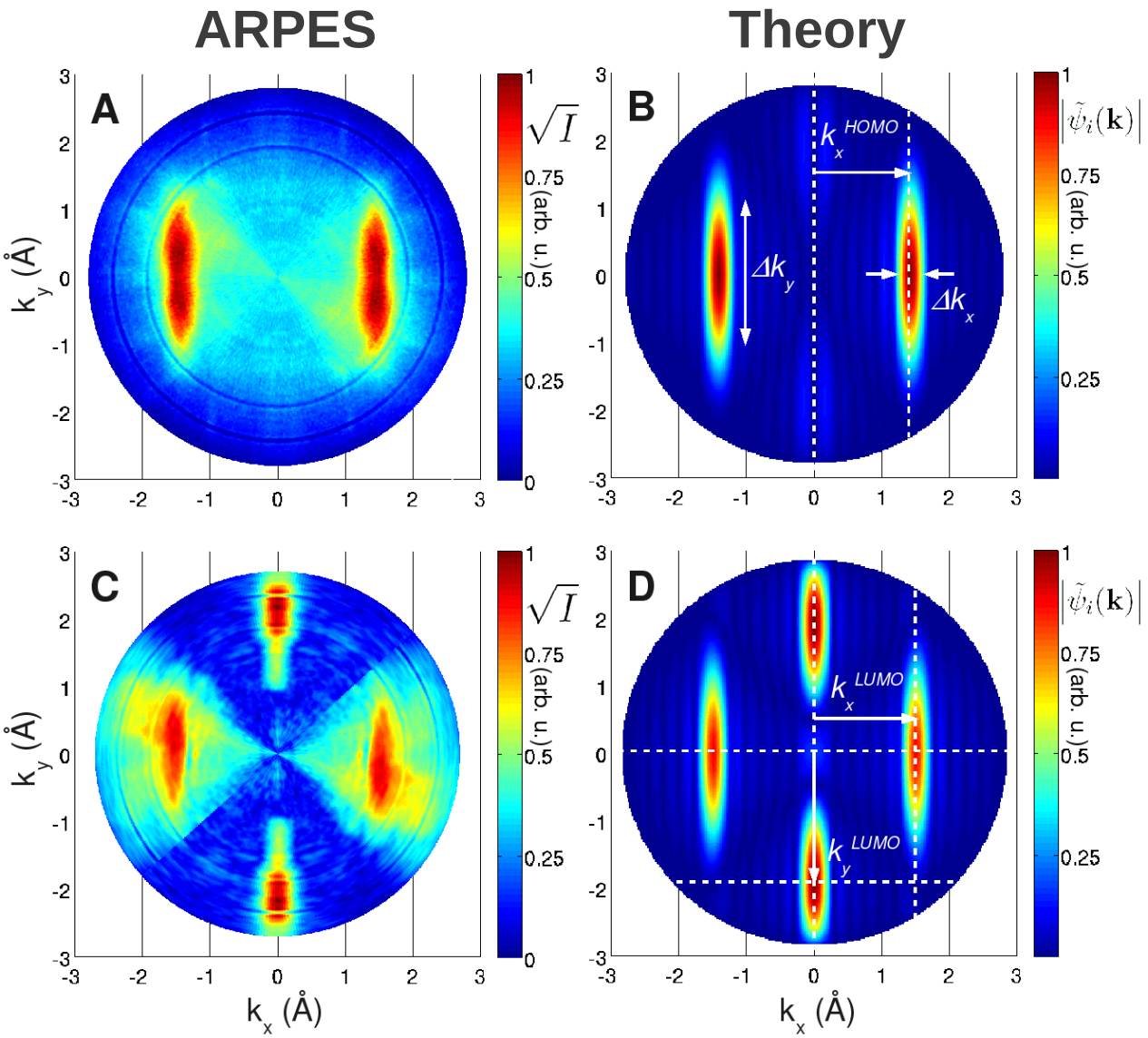




2D-Momentum Maps

HOMO

Filled LUMO

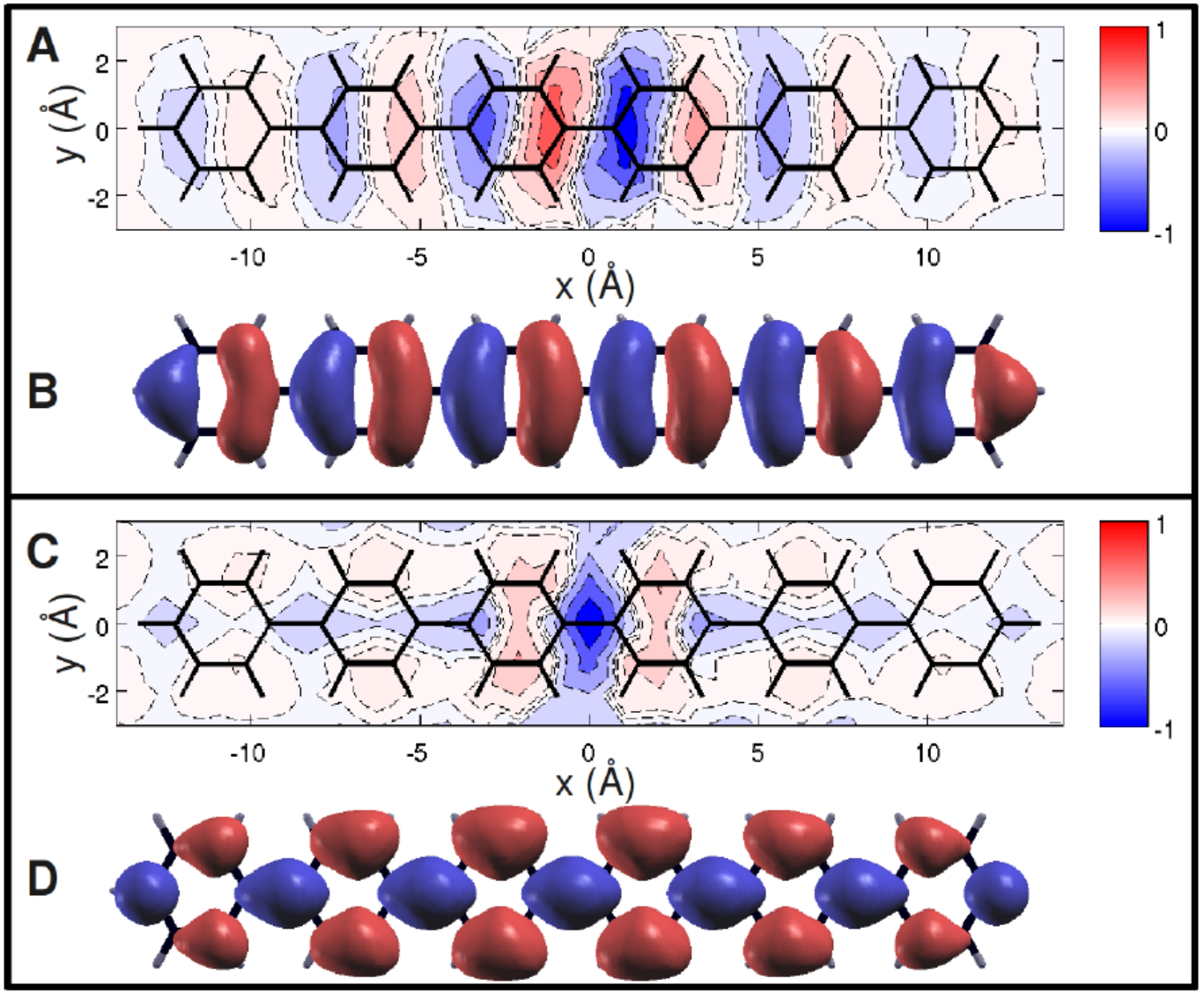


Puschnig et al.,
Science **326**, 702 (2009).

Orbitals from ARPES?

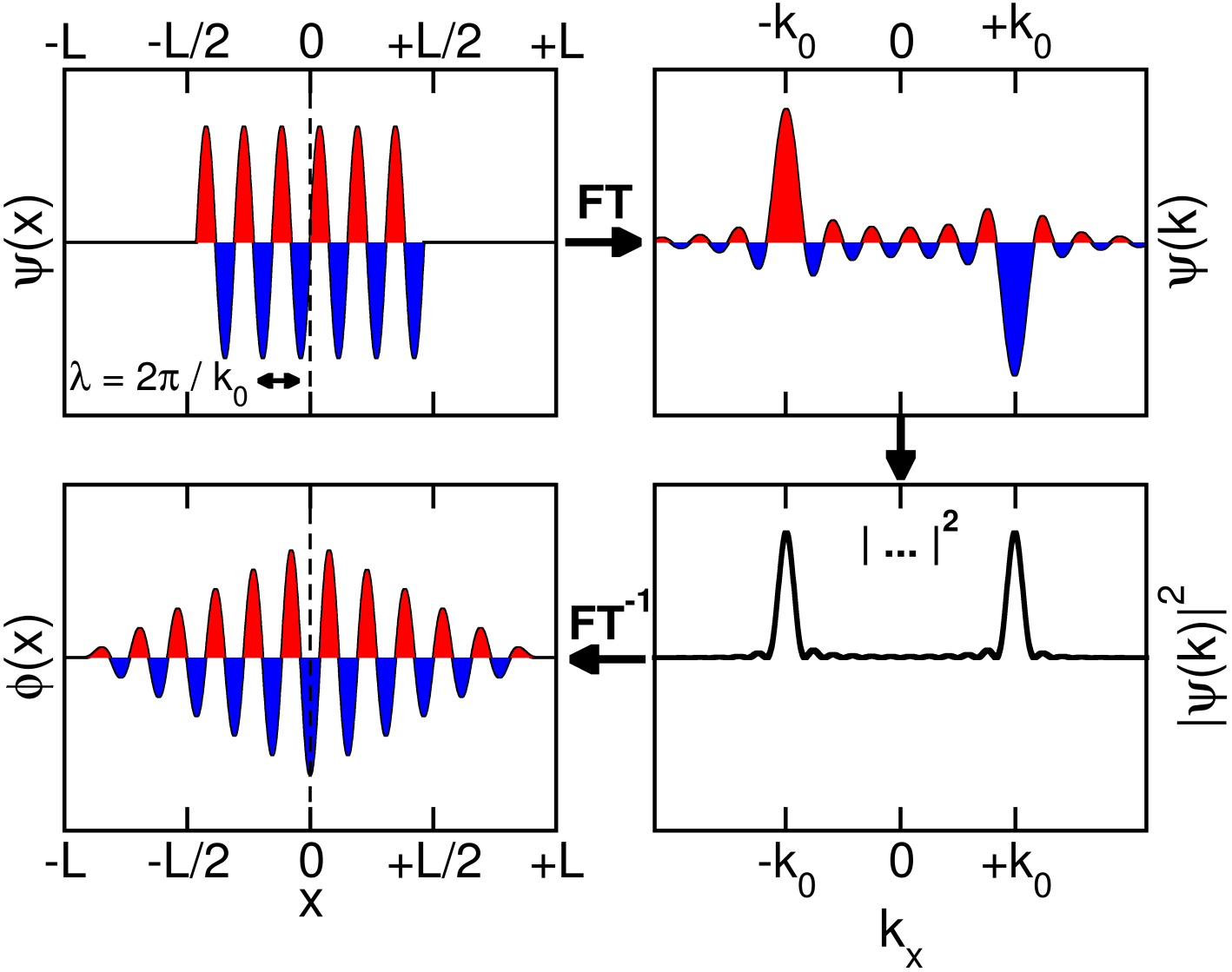
HOMO

Filled LUMO

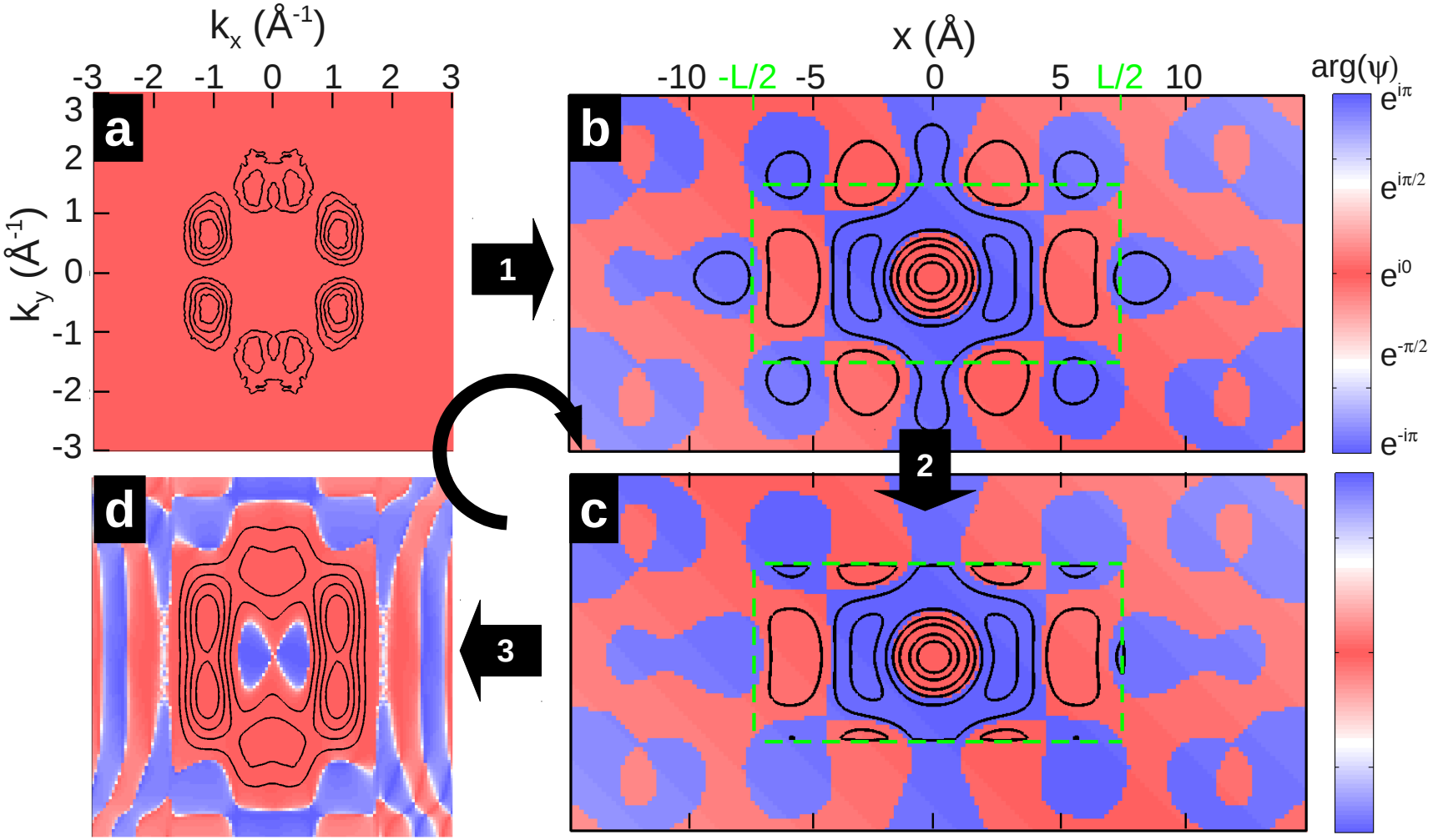


Puschnig et al.,
Science **326**, 702 (2009).

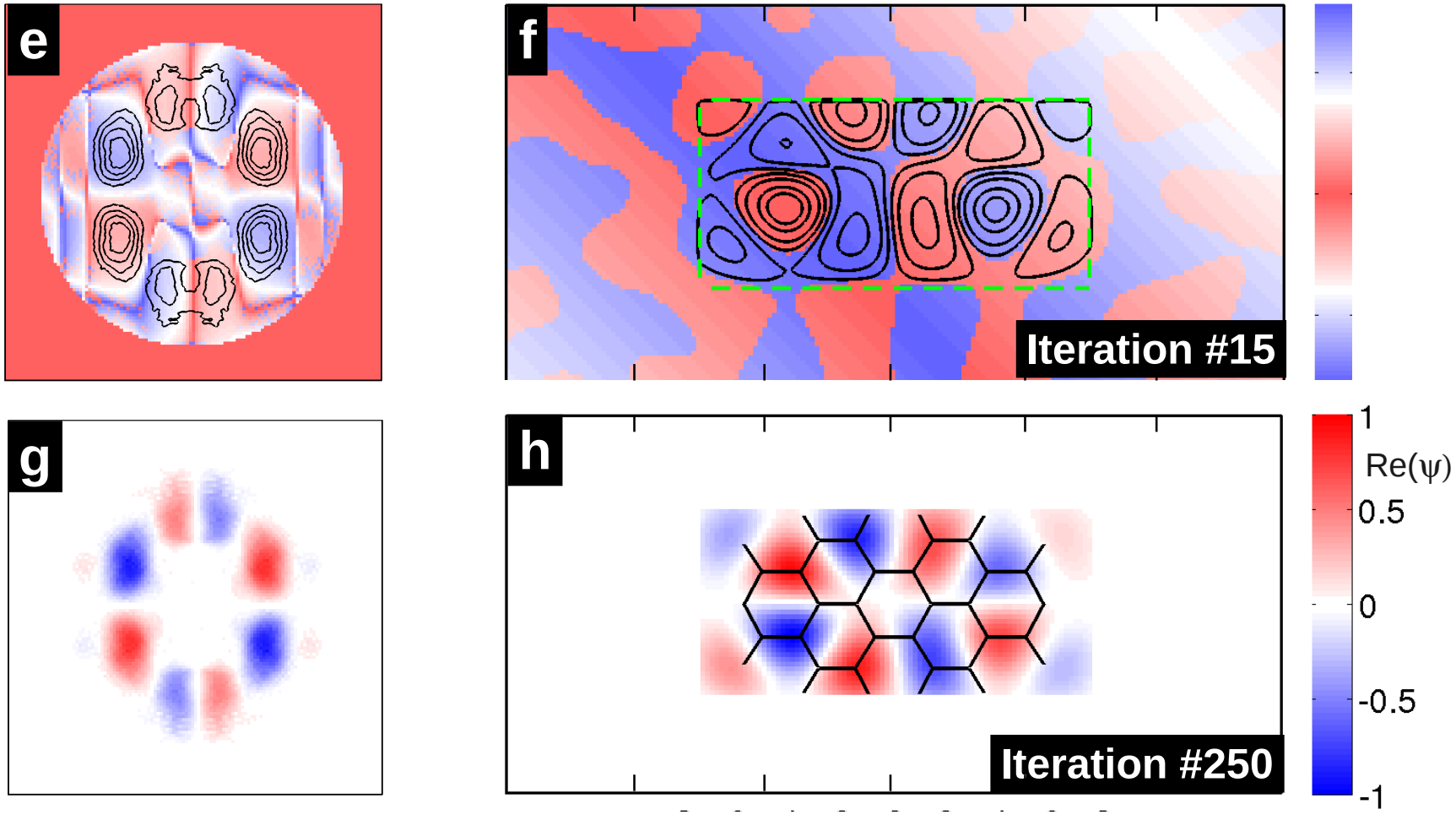
Phase Problem



Iterative Phase Recovery

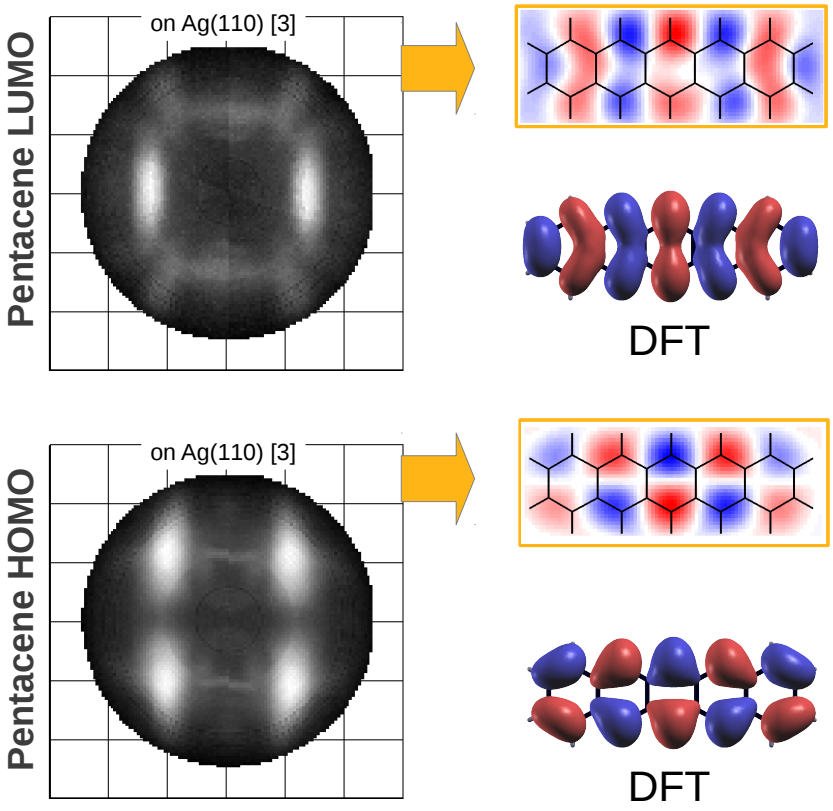


Iterative Phase Recovery

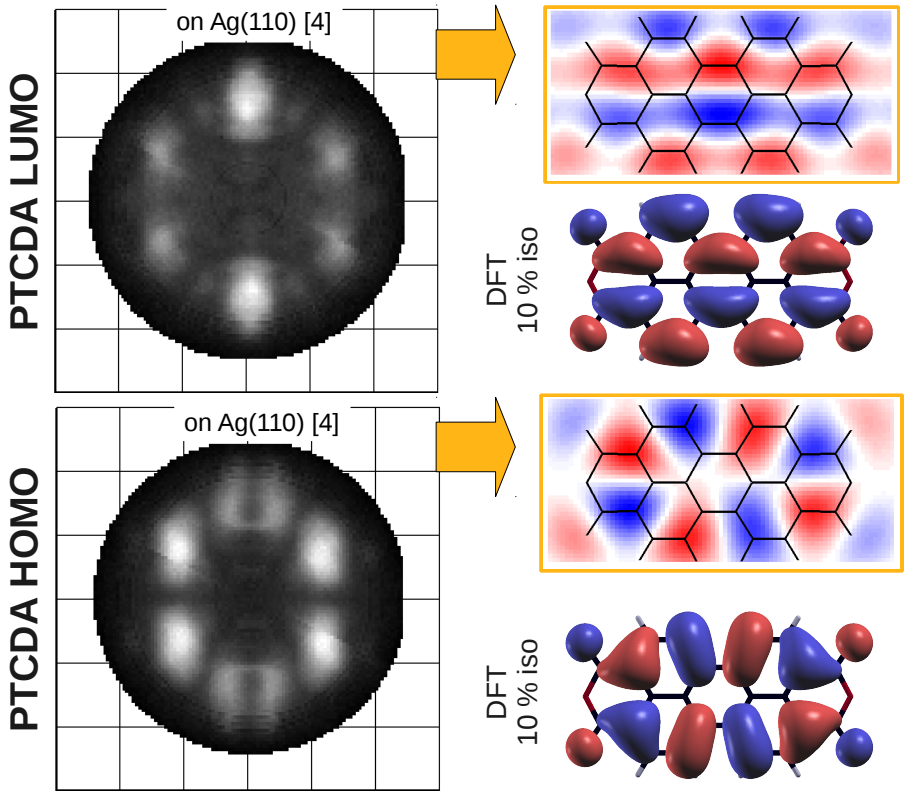


Some Examples

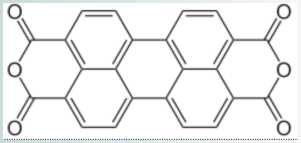
Pentacene: **Reconstructed Orbitals**

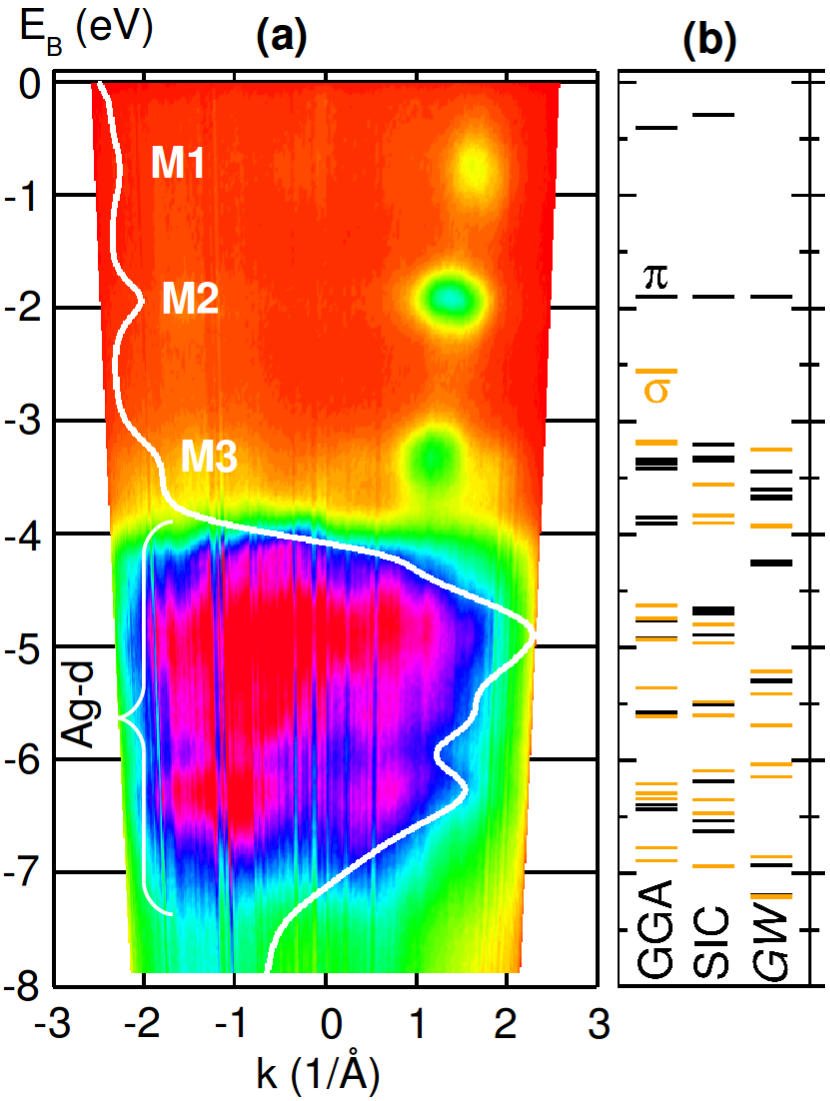


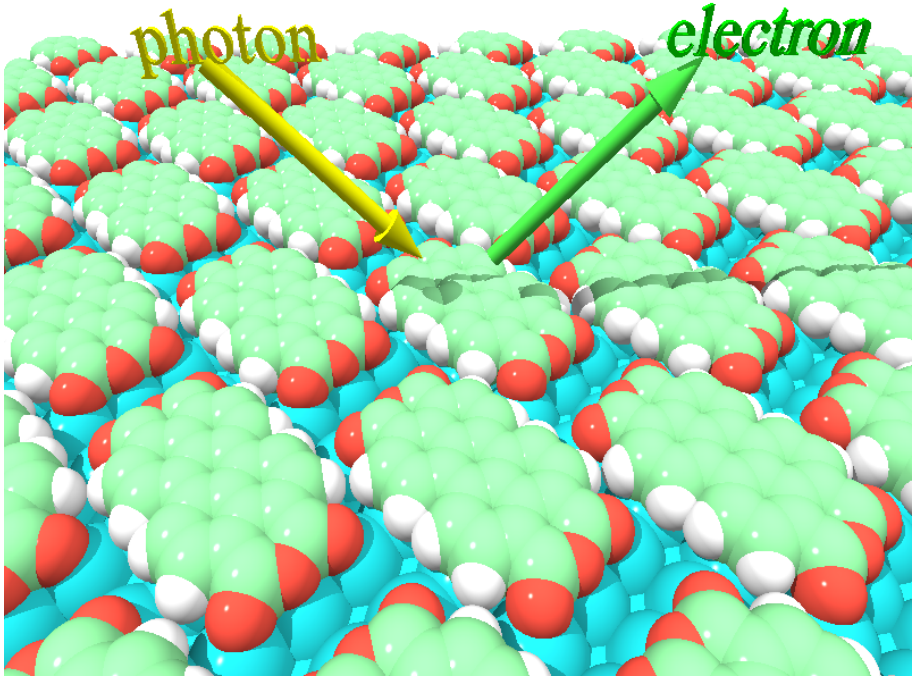
PTCDA: **Reconstructed Orbitals**

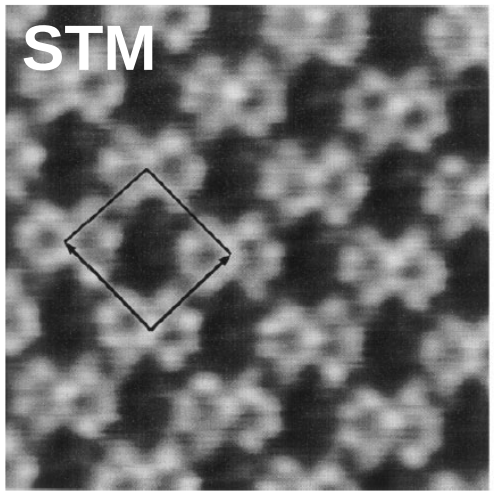


ARPES of PTCDA / Ag(110)

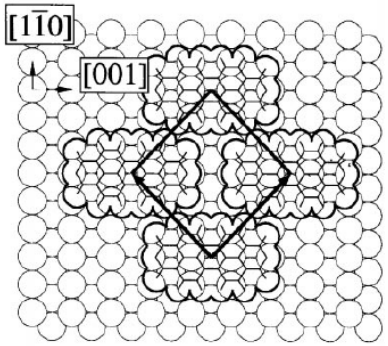




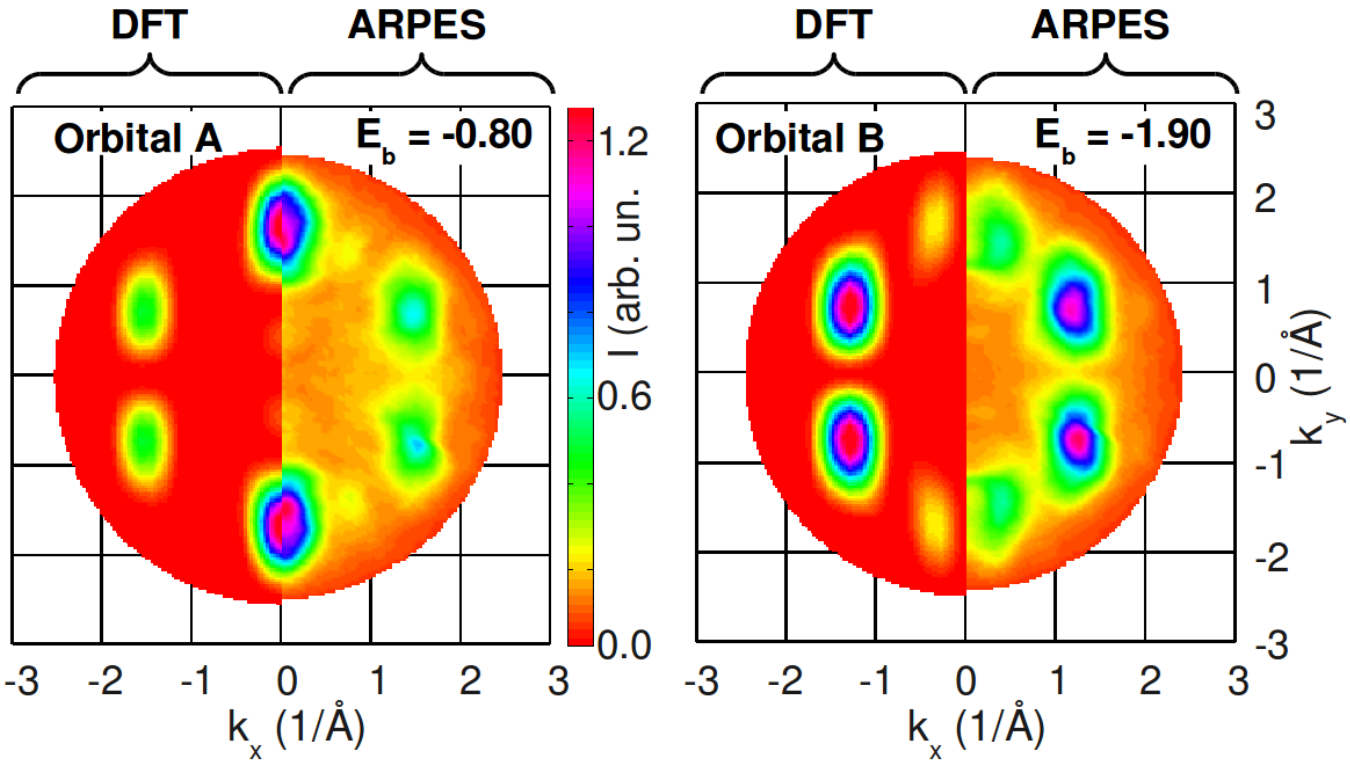




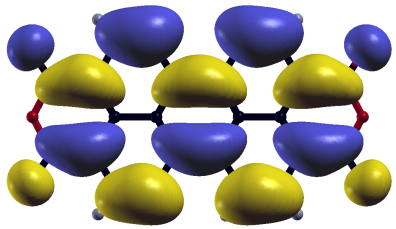
Glöckler et al,
Surf. Sci. **405**, 1-20 (1998).

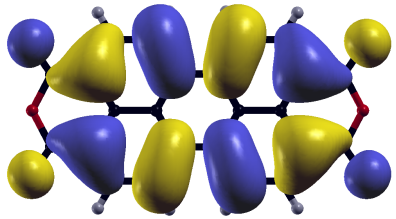


HOMO and Filled LUMO



M1= FLUMO



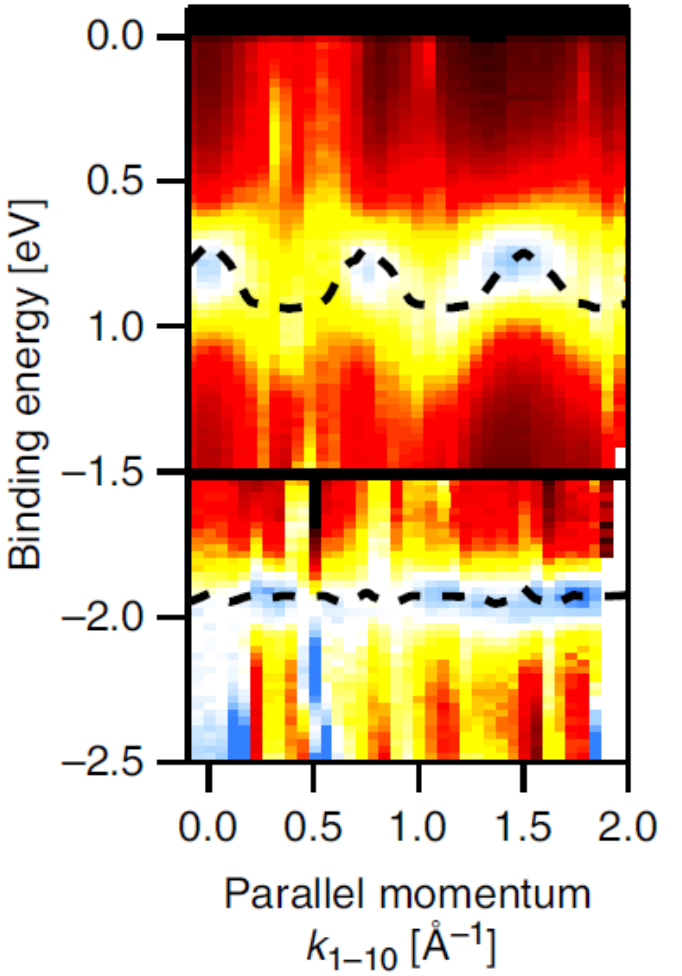


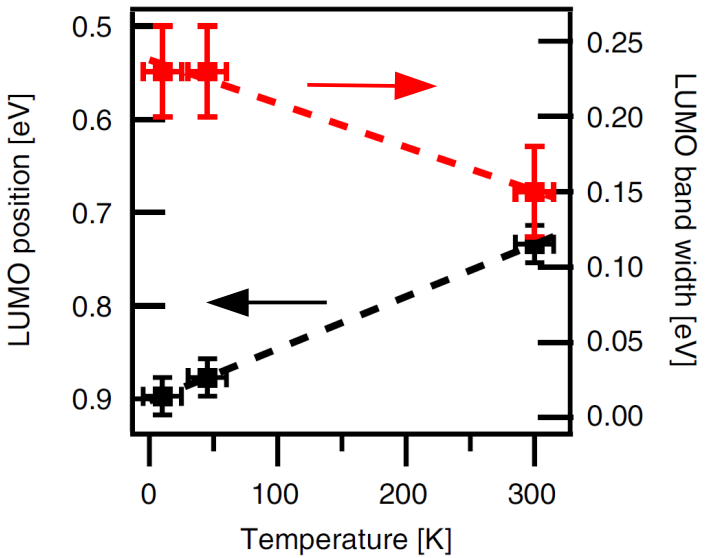
M2= HOMO

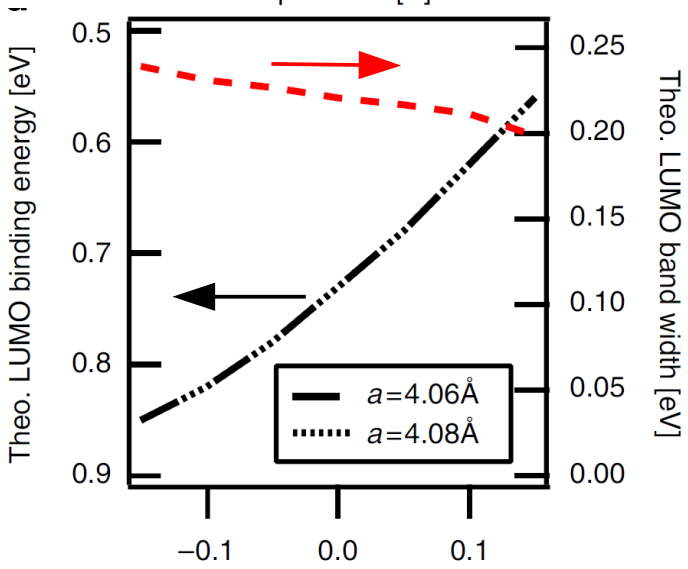
Puschnig et al. PRB **84**, 235427 (2011), Ziroff et al., PRL **104**, 233004 (2010).

Substrate Enhanced Dispersion

LUMO dispersion from ARPES



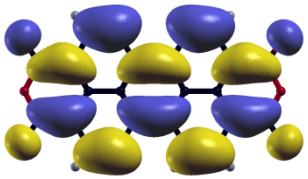




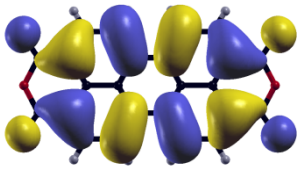
Wießner et al., *Nature Communications* **4**, 1514 (2013).

What is the nature of M3?

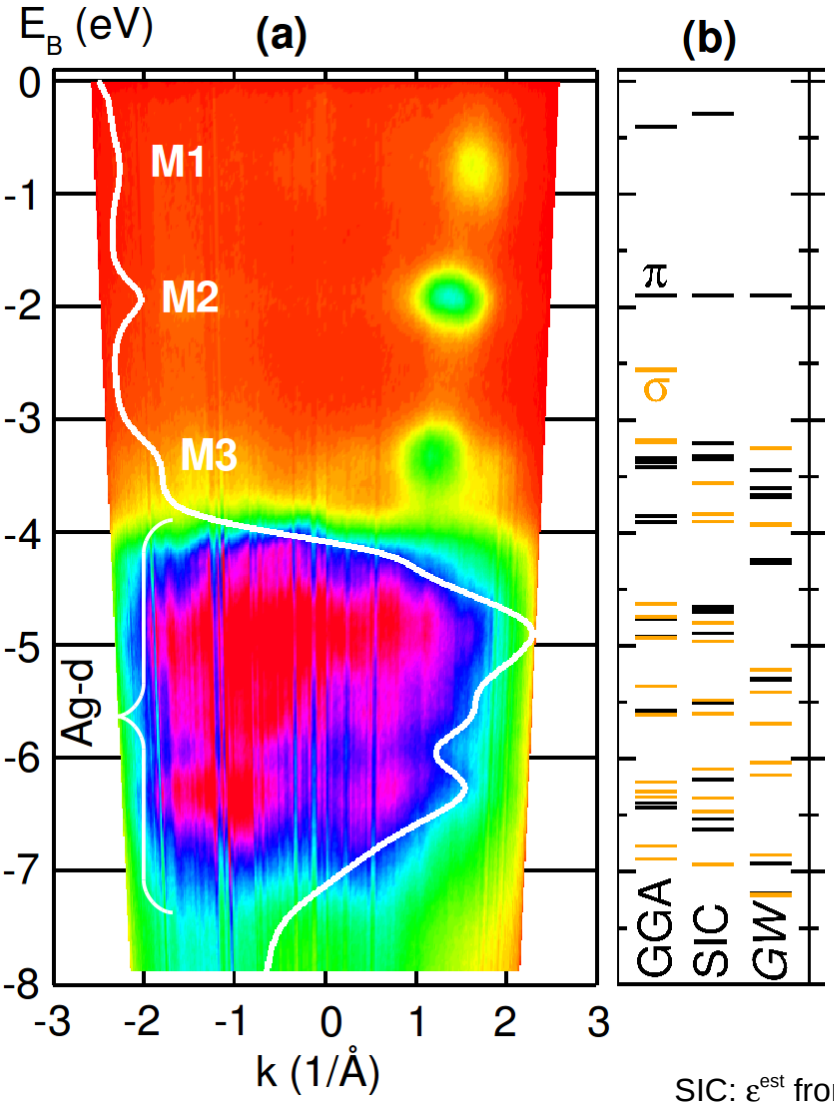
M1= FLUMO



M2= HOMO



?



HOMO aligned with experiment

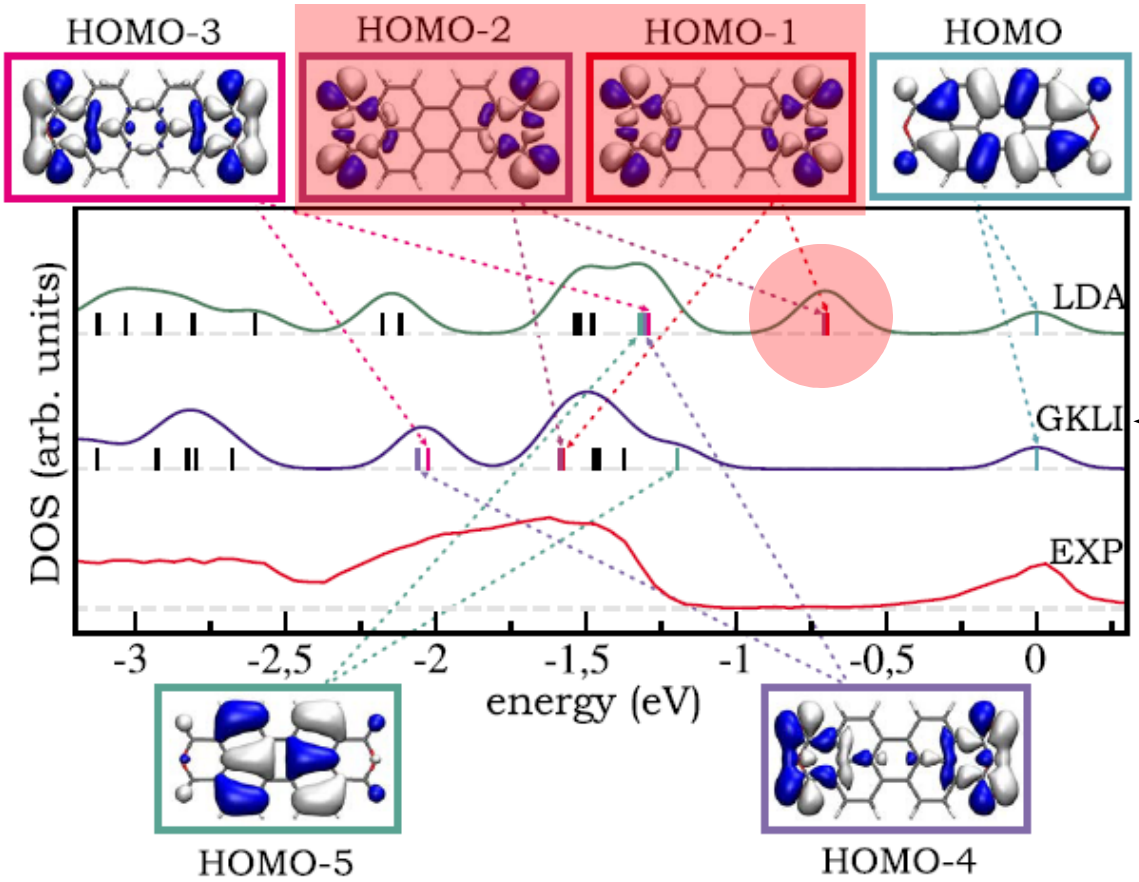
SIC: ε^{est} from Eq. (2) PRB 79, 201205 (R)
GW: G_0W_0@GGA

Identifying Orbitals

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

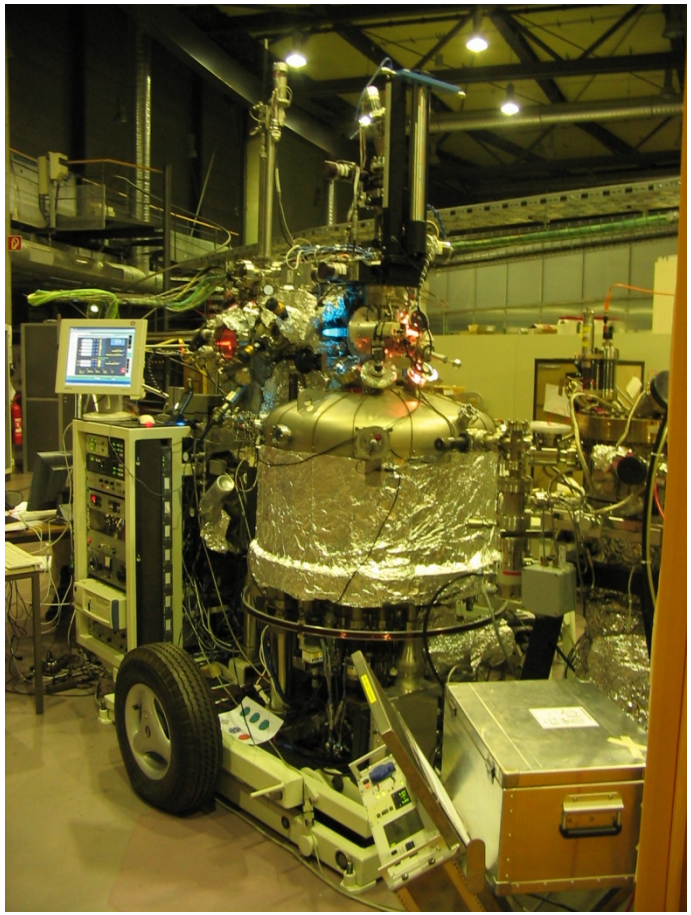
When to trust photoelectron spectra from Kohn-Sham eigenvalues: The case of organic semiconductors

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



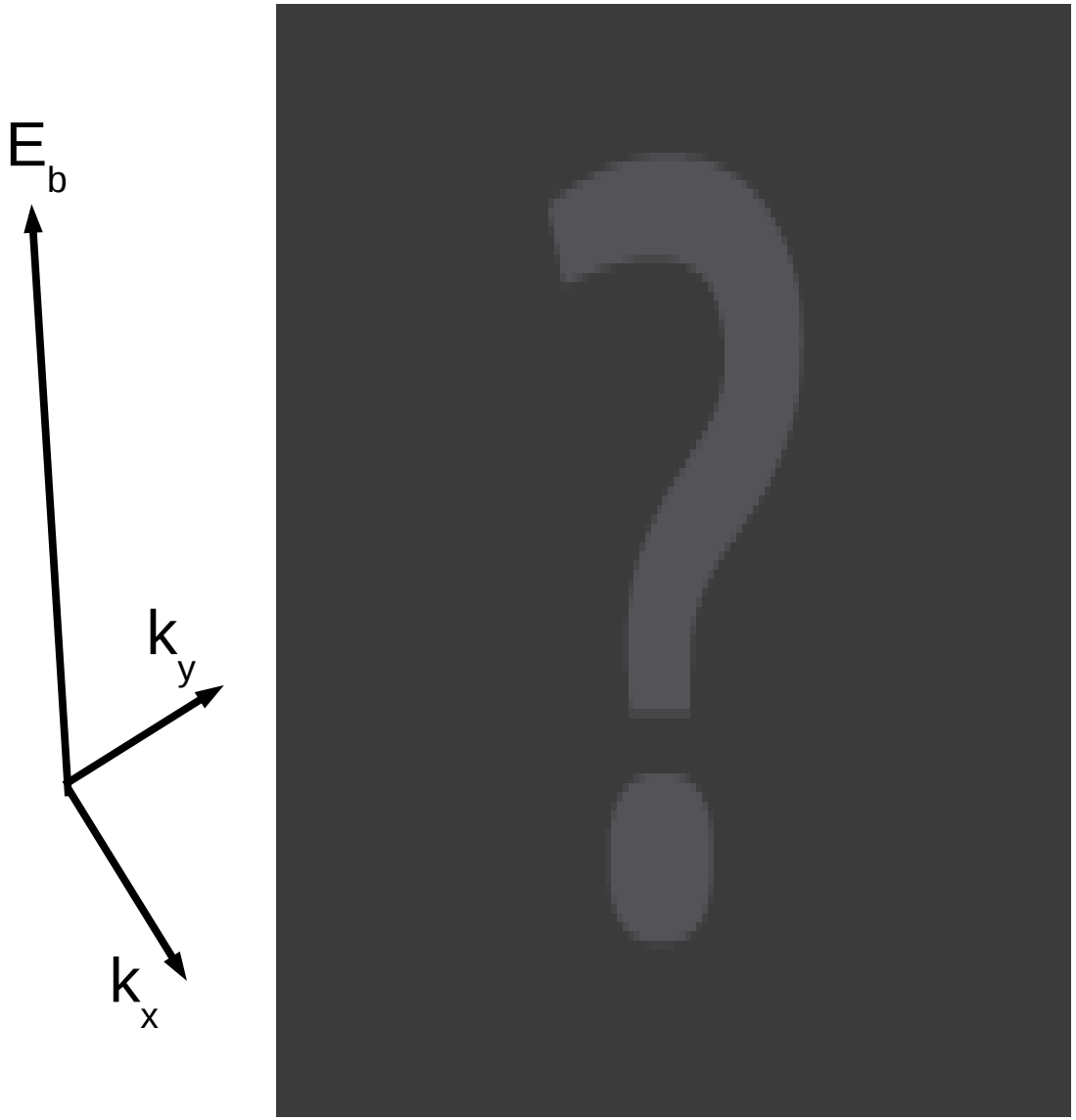
Self-interaction corrected functional

Toroidal Electron Energy Analyzer

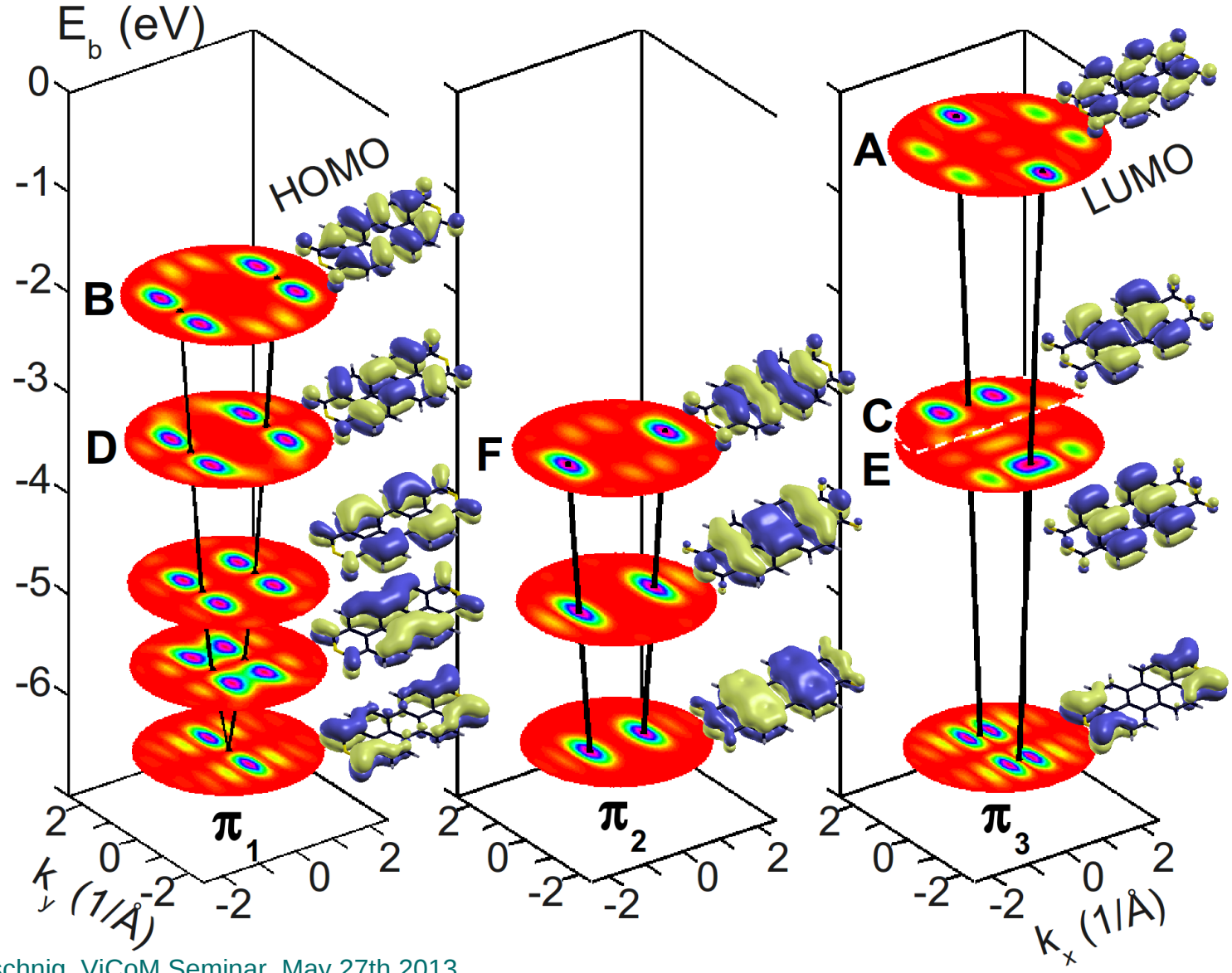


The Toroidal Electron Spectrometer for Angle-Resolved Photoelectron Spectroscopy with Synchrotron Radiation at BESSY II

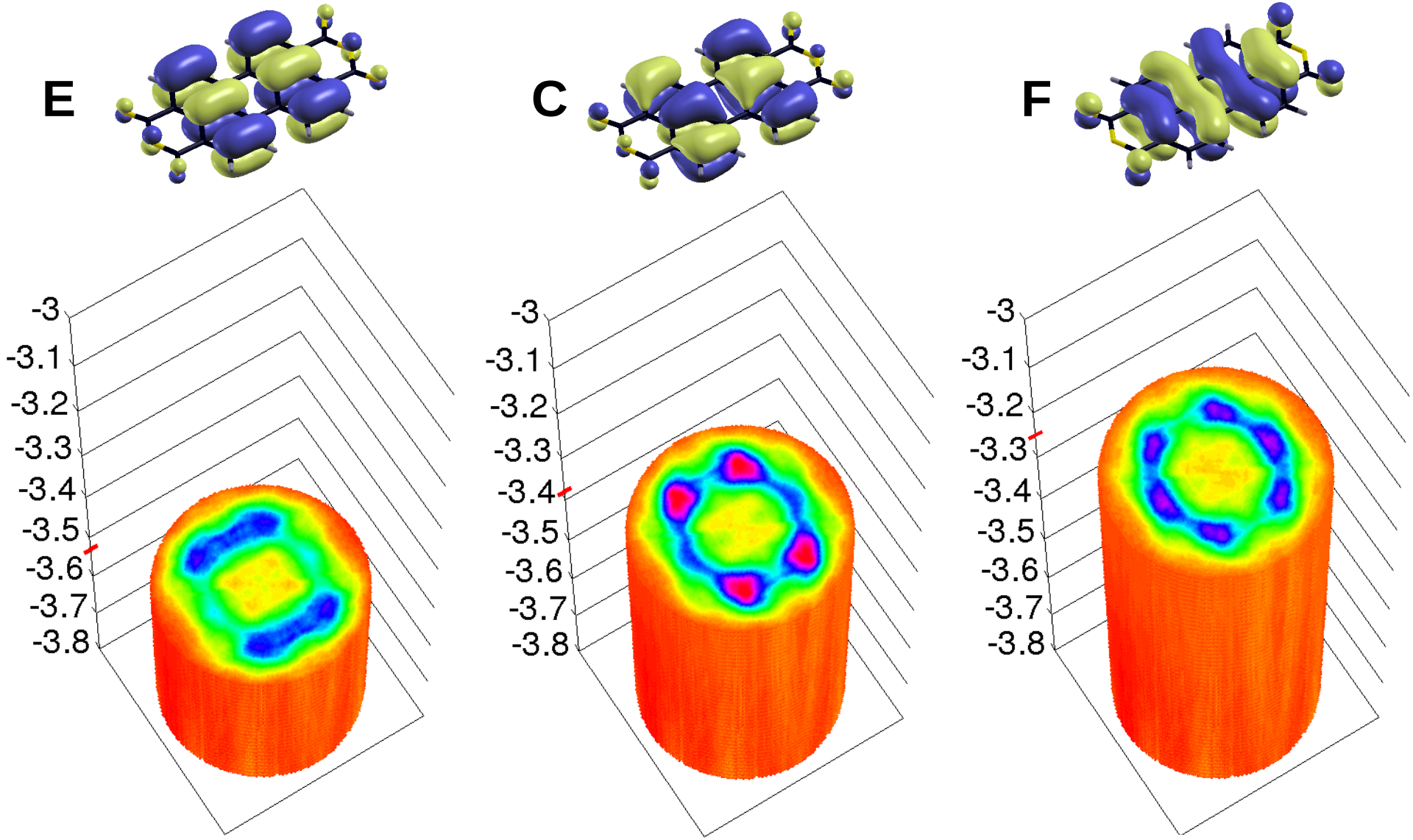
ARPES Data-Cube



Pi-„bands“ of PTCDA

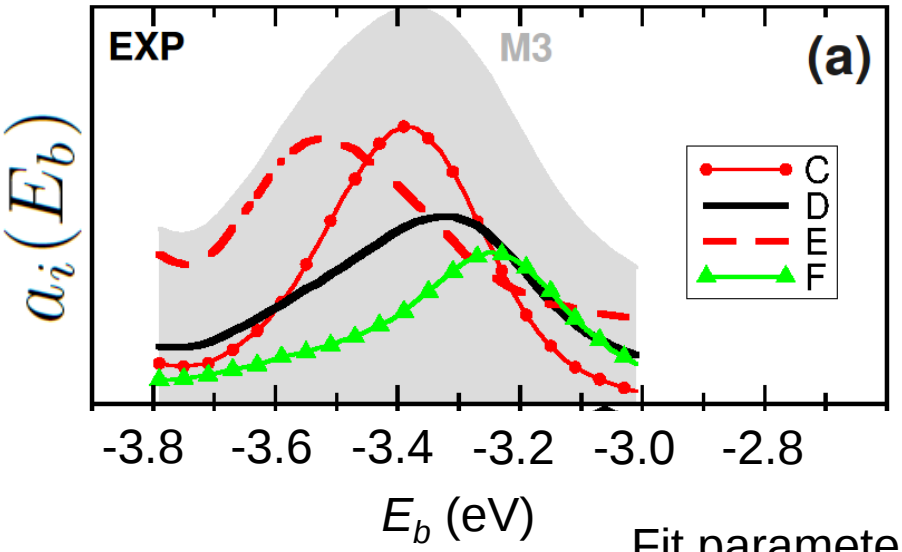


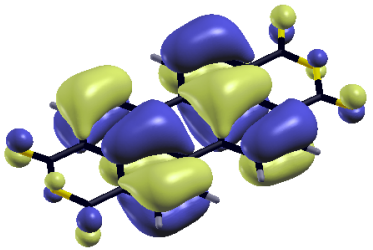
What is the Origin of M3?



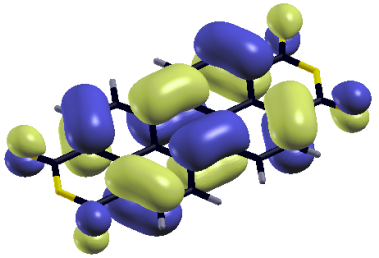
Puschnig et al. PRB **84**, 235427 (2011)

Projected DOS from ARPES!

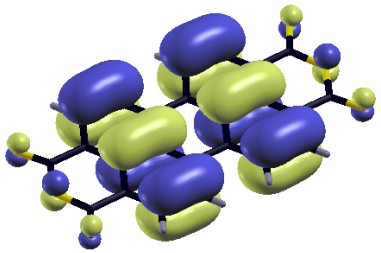




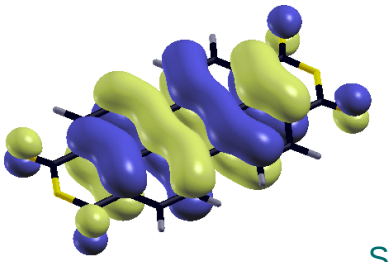
C



D



E



F

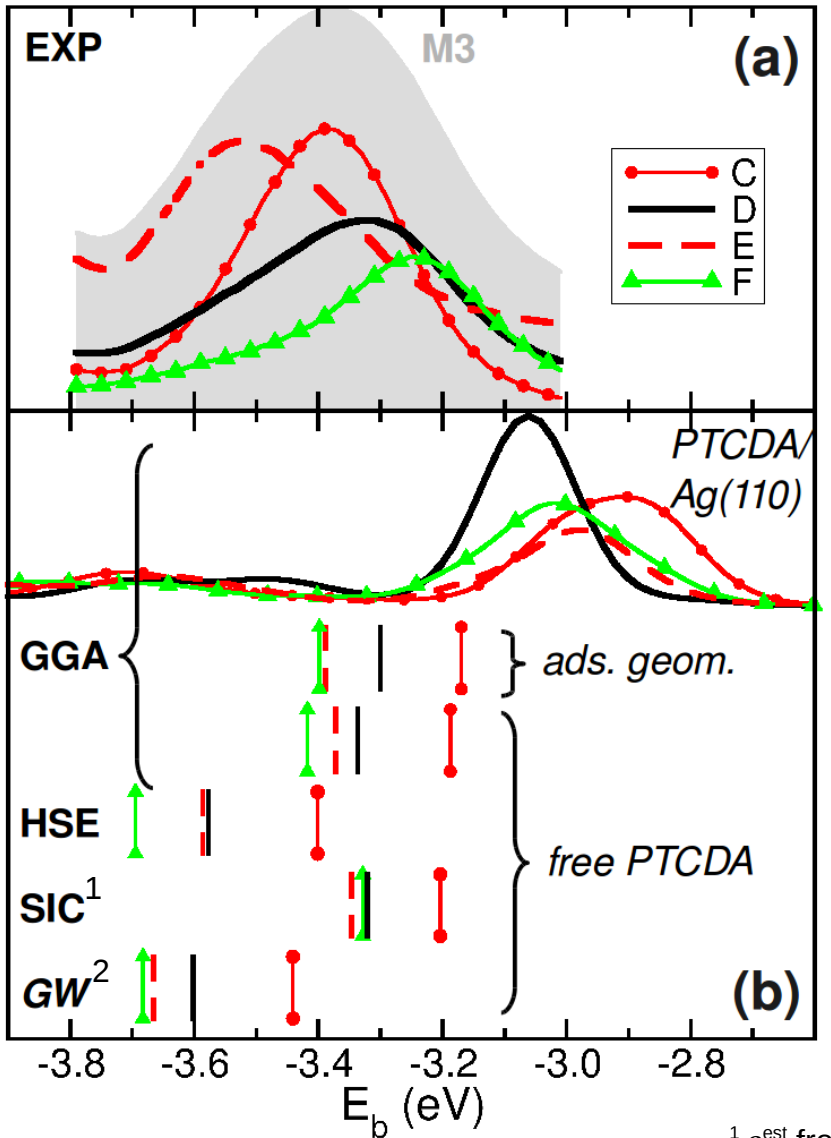
Fit parameters = PDOS

calculated orbitals

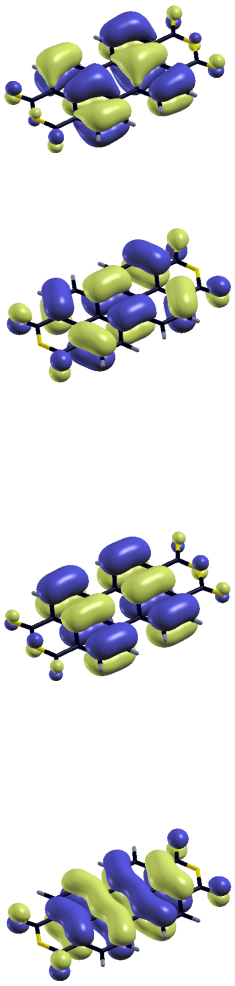
$$\chi^2 = \int dk_x dk_y \left[I(E_b, k_x, k_y) - \sum_i a_i(E_b)\phi_i(k_x, k_y) \right]^2$$

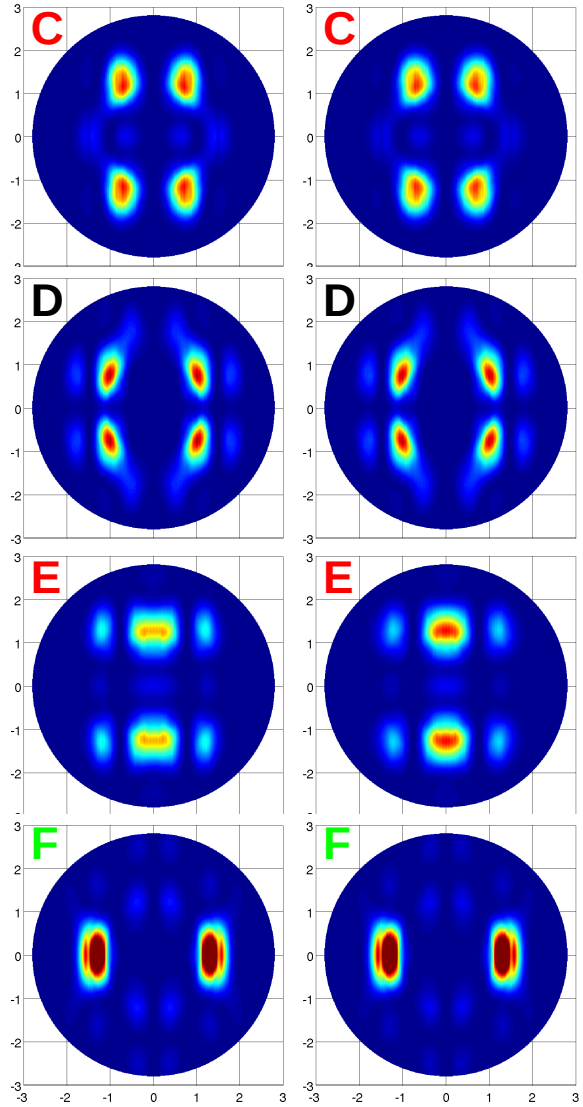
measured photemission data cube

Projected DOS from ARPES!



orbital energies / projected DOS (arb. units)





[1] ε^{est} from Eq. (2) PRB 79, 201205 (R)
[2] G_0W_0@GGA

GGA HSE

Outline

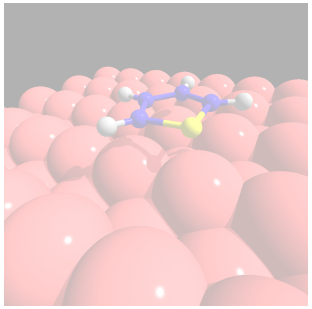
Theory

Density Functional Theory (DFT) in a Nutshell

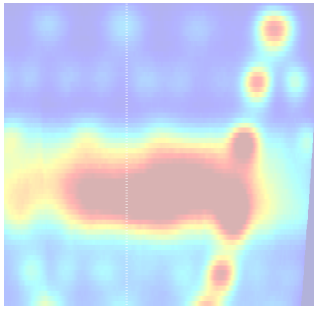
Photoemission Intensity: What angle-resolved PE data tells us about molecular orbitals

Many-Body Perturbation Theory: GW-Approximation, Bethe-Salpeter Equation

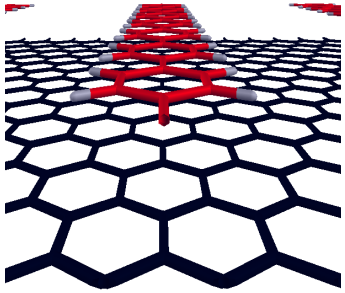
Applications



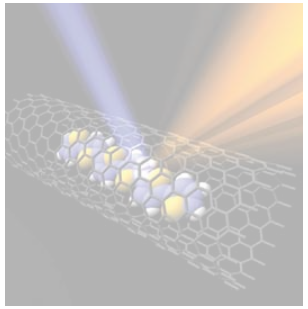
Van der Waals Interactions In DFT



Photoemission from organic molecular films



GW-band structure of Polymer / Graphene



Hybrid excitons in Nano-Peapods

Molecular Level Renormalization

Electron Affinity (A)

$A(N) = E(N) - E(N+1)$

Ionization Potential (I)

$I(N) = E(N-1) - E(N)$

Band Gap (E_g)

$E_g = I(N) - A(N)$

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

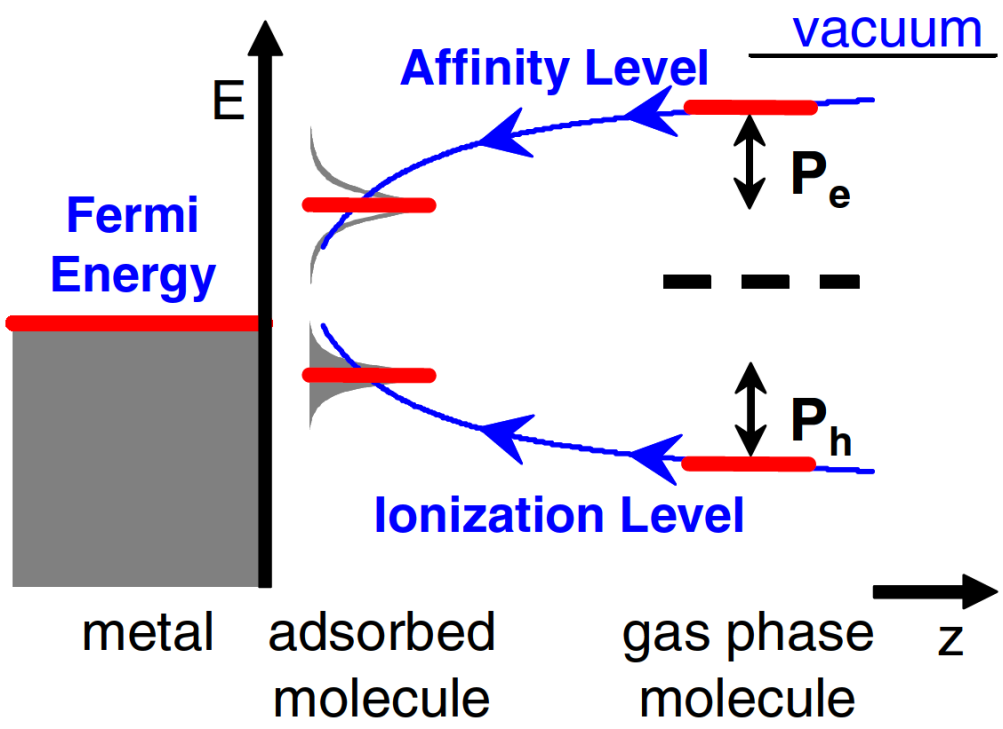
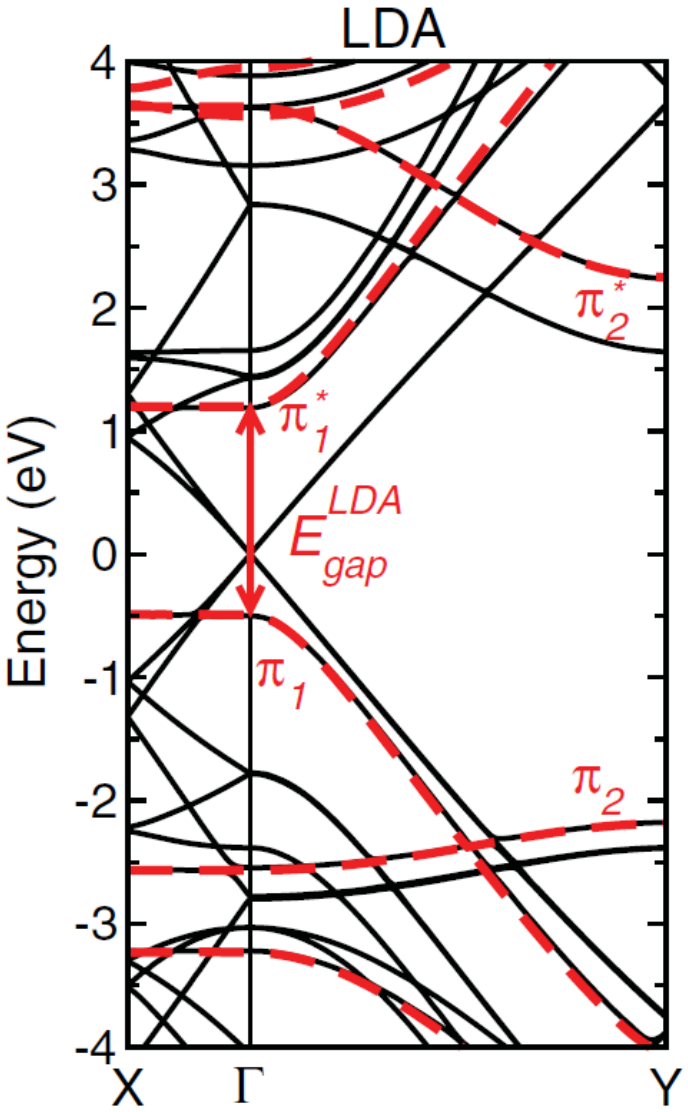
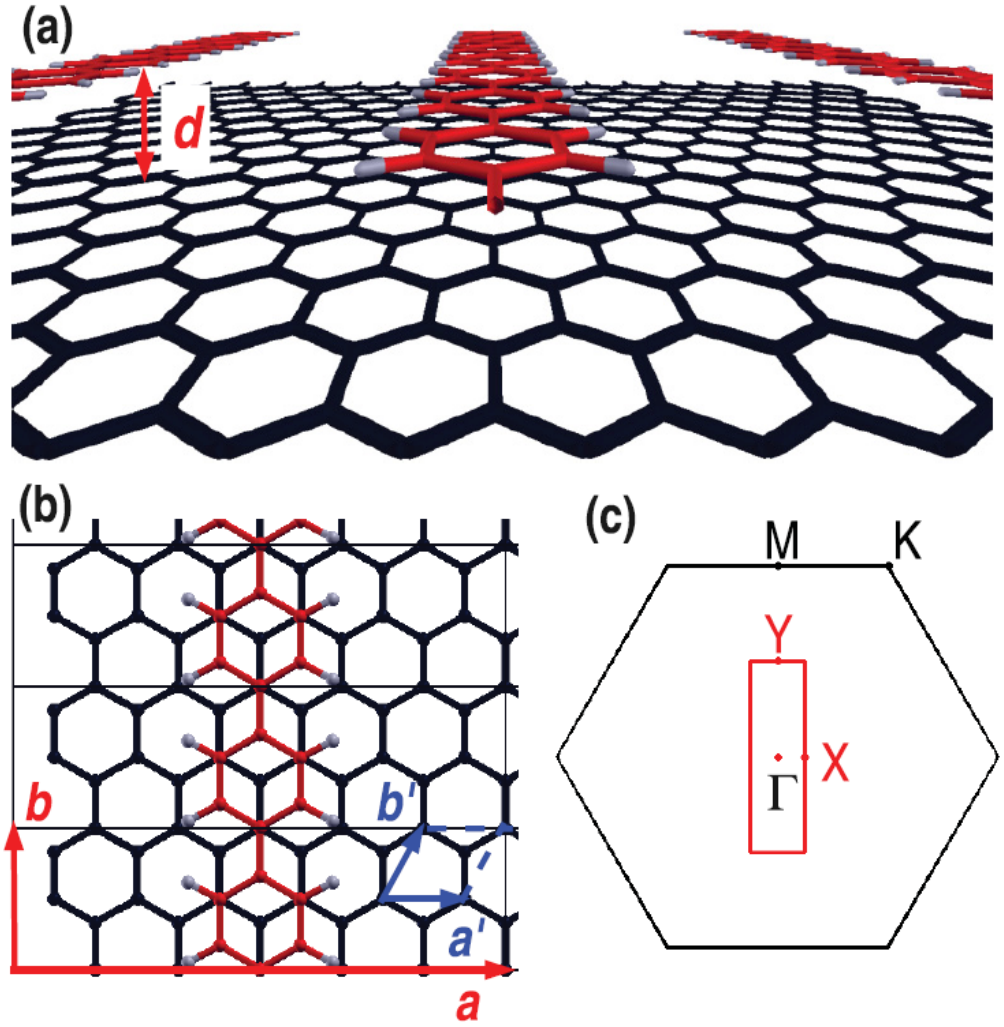


Image potential model: a molecule at a distance *z* from a metallic surface

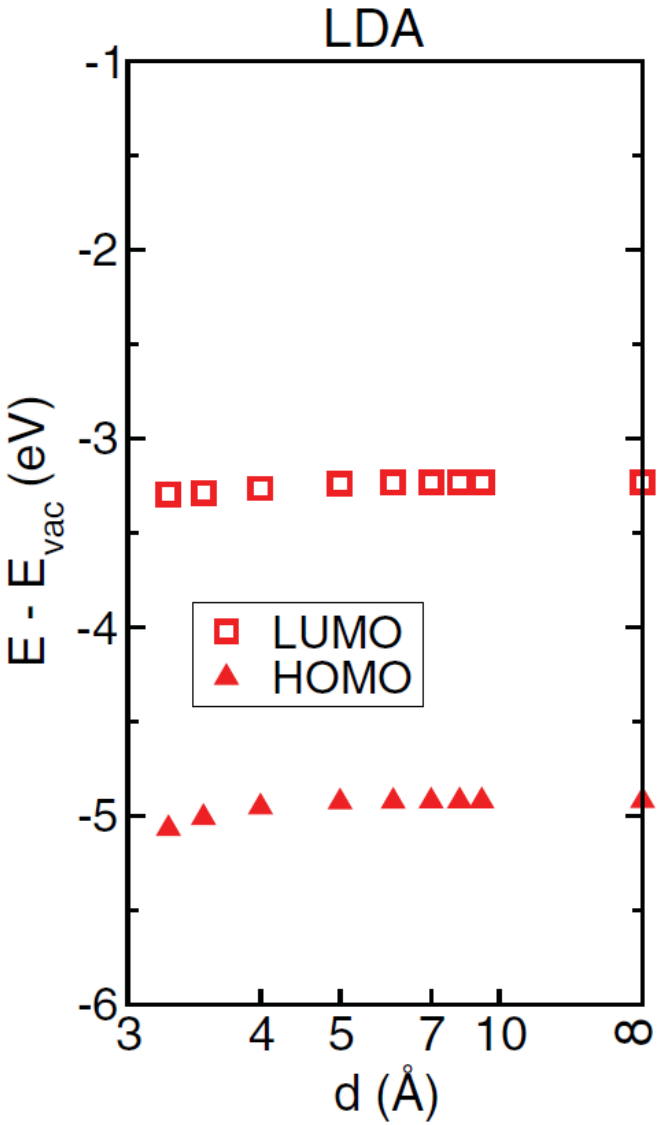
$$I(z) = I(\infty) + \frac{qq'}{4z} \qquad A(z) = A(\infty) - \frac{qq'}{4z}$$

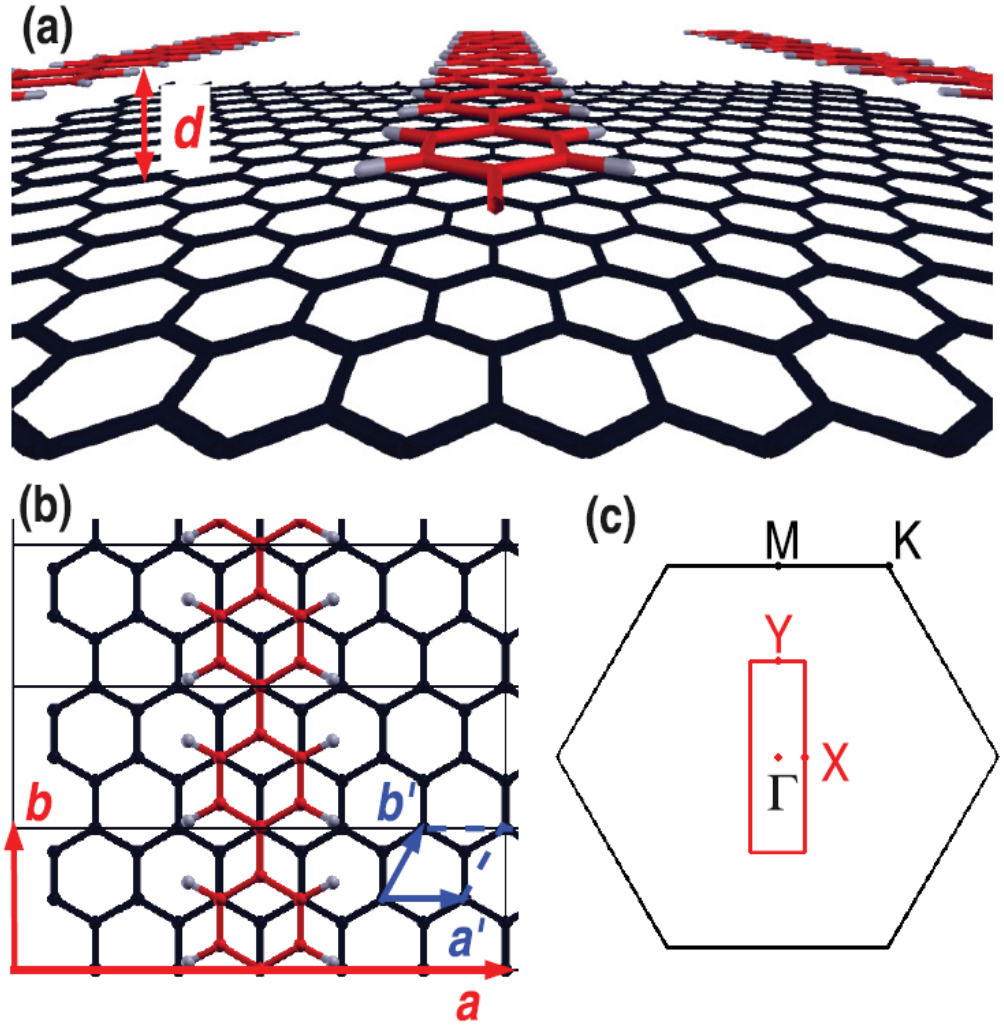
Poly-*para*-Phenylene / Graphene



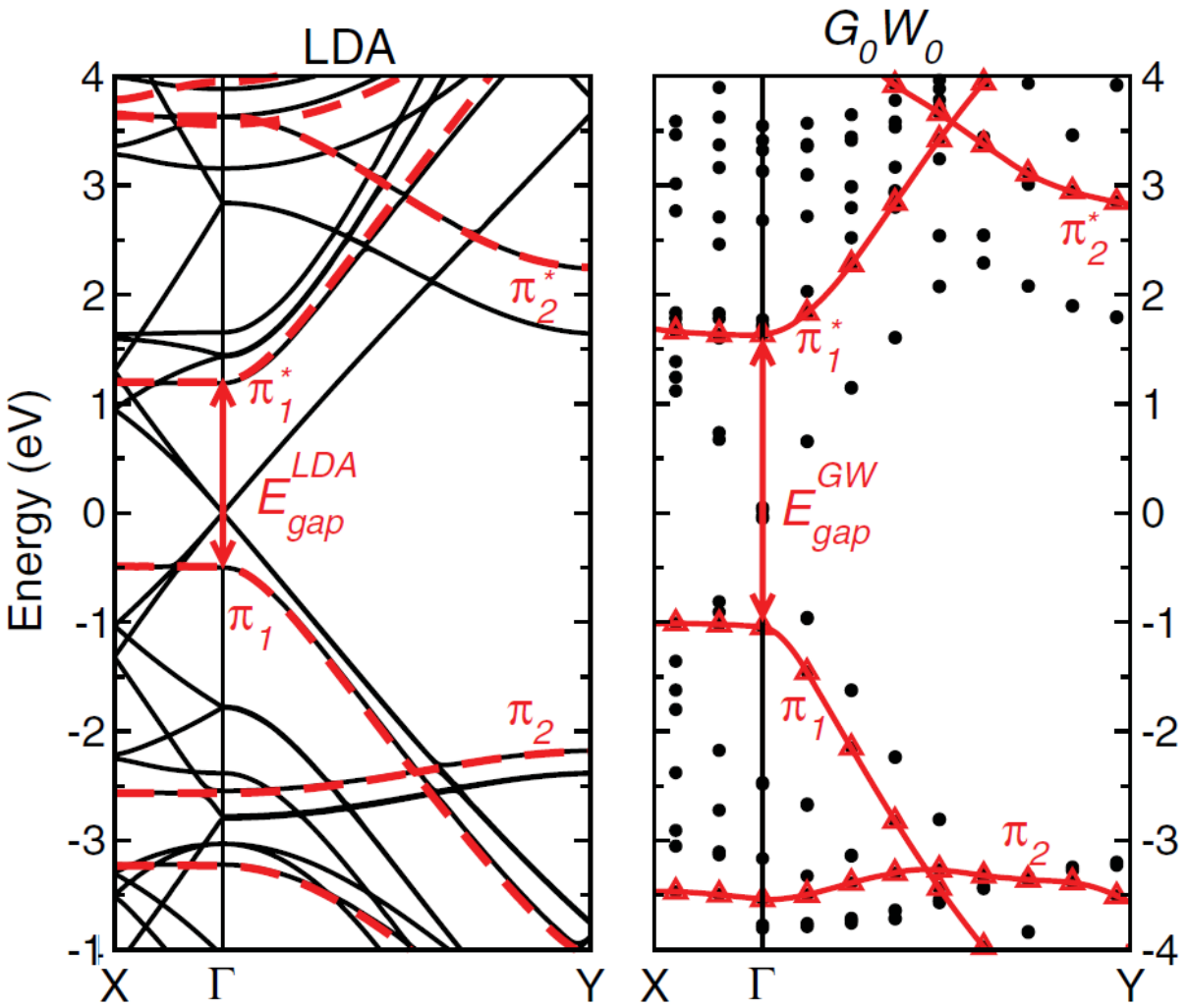


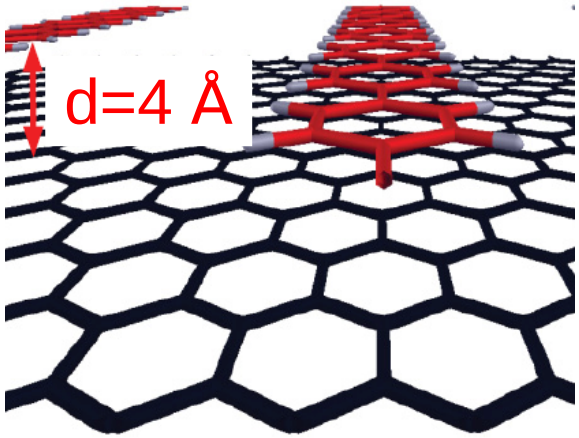
Poly-*para*-Phenylene / Graphene





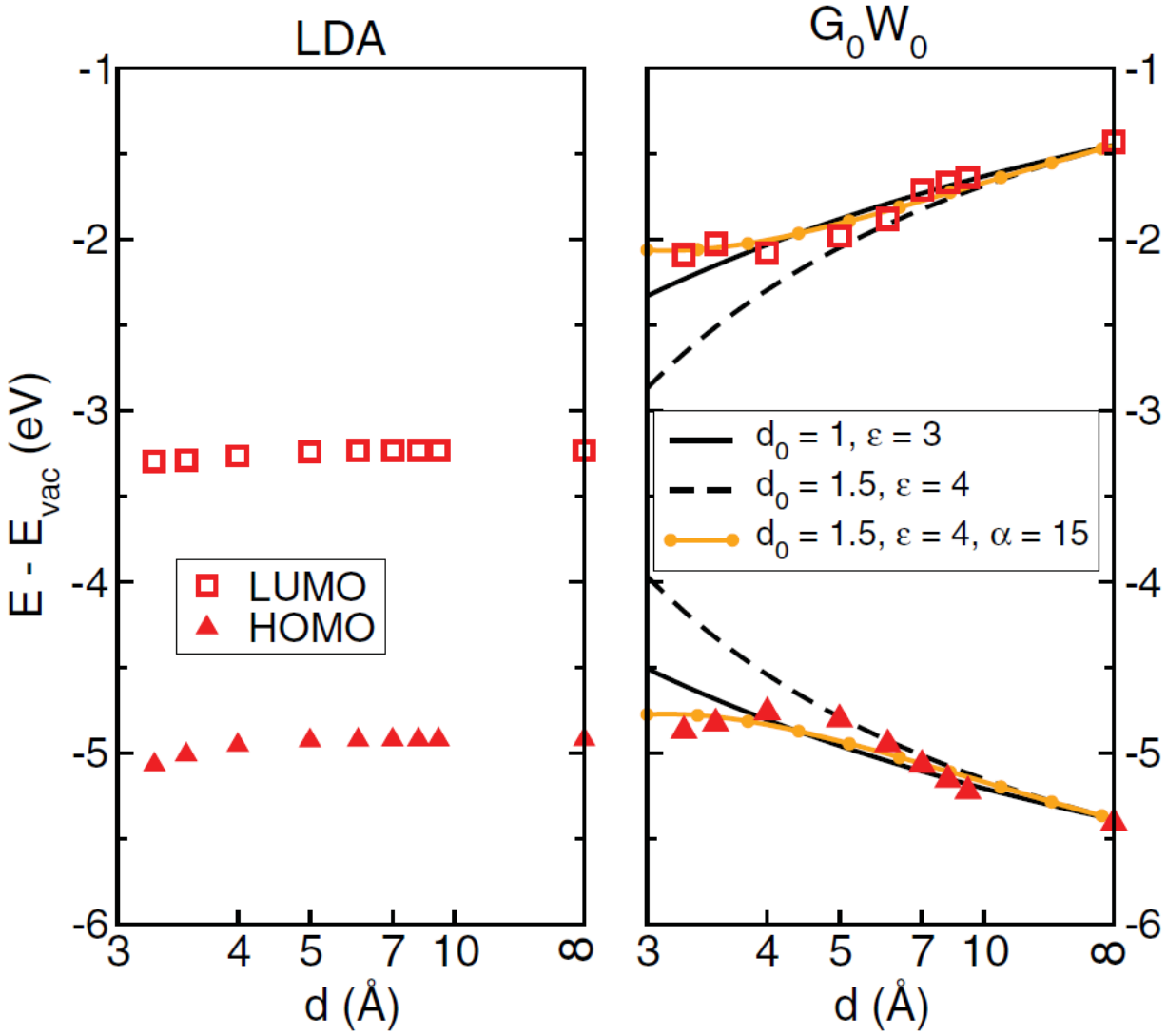
PPP / Graphene



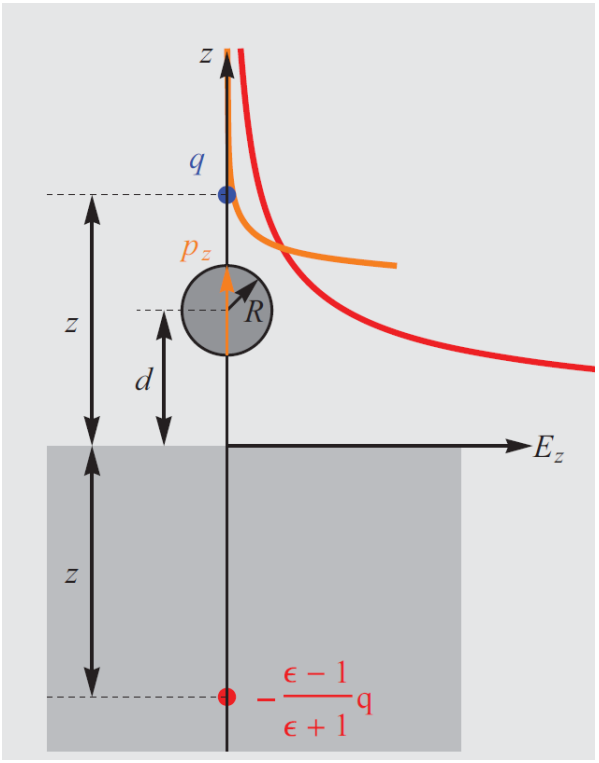


P. Puschnig et al.,
PRB 86, 085107 (2012).

PPP / Graphene



Refined image potential model taking into account the polariz-ability of the adsorbed moelcule.



P. Puschnig et al.,
PRB 86, 085107 (2012).

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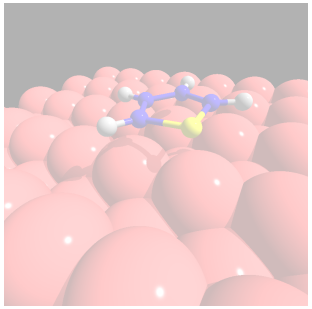
Density Functional Theory (DFT) in a Nutshell

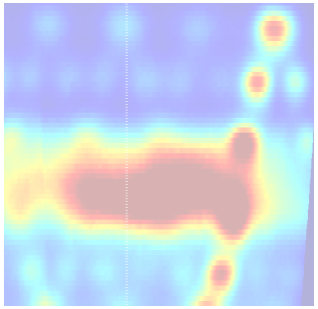
Photoemission Intensity: What angle-resolved PE data tells us about molecular orbitals

Many-Body Perturbation Theory: GW-Approximation, Bethe-Salpeter Equation

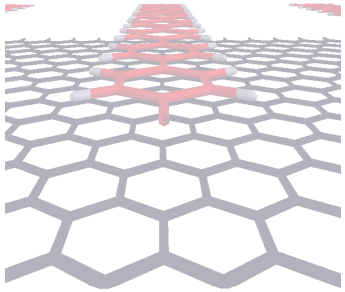
Applications



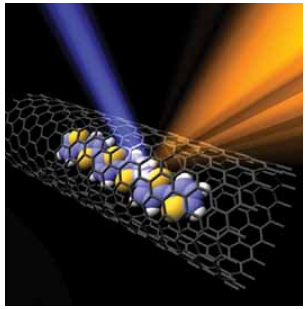
Van der Waals Interactions In DFT



Photoemission from organic molecular films

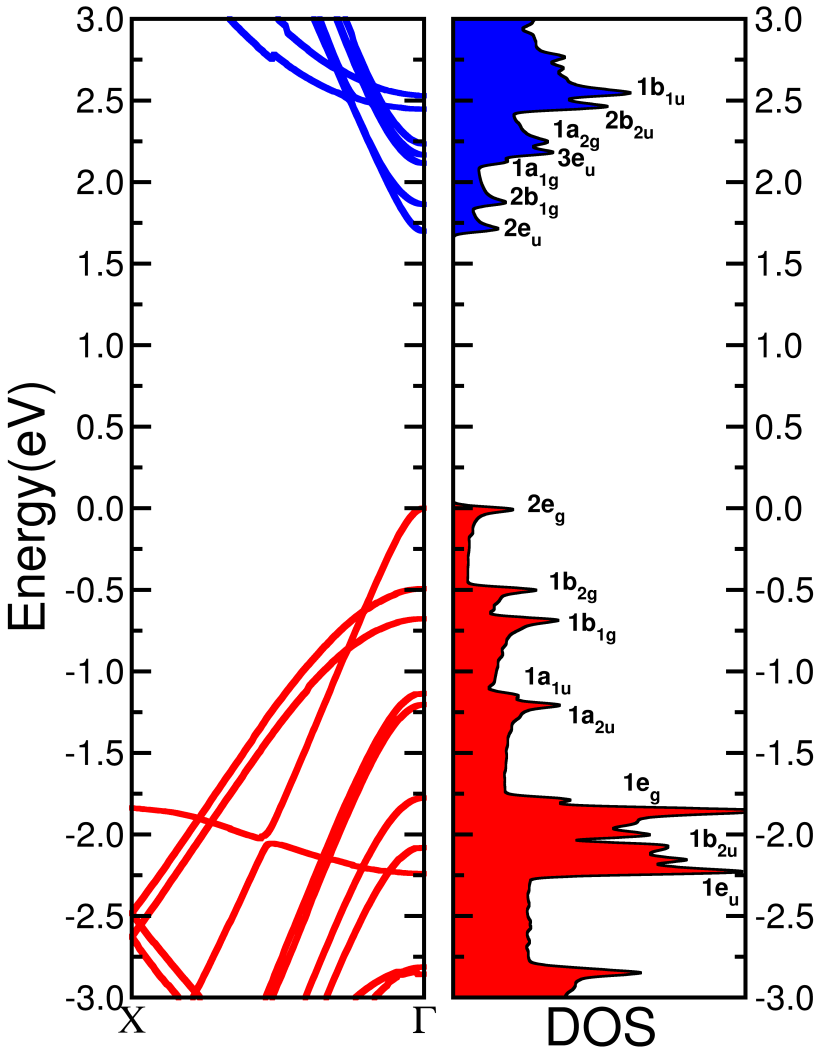


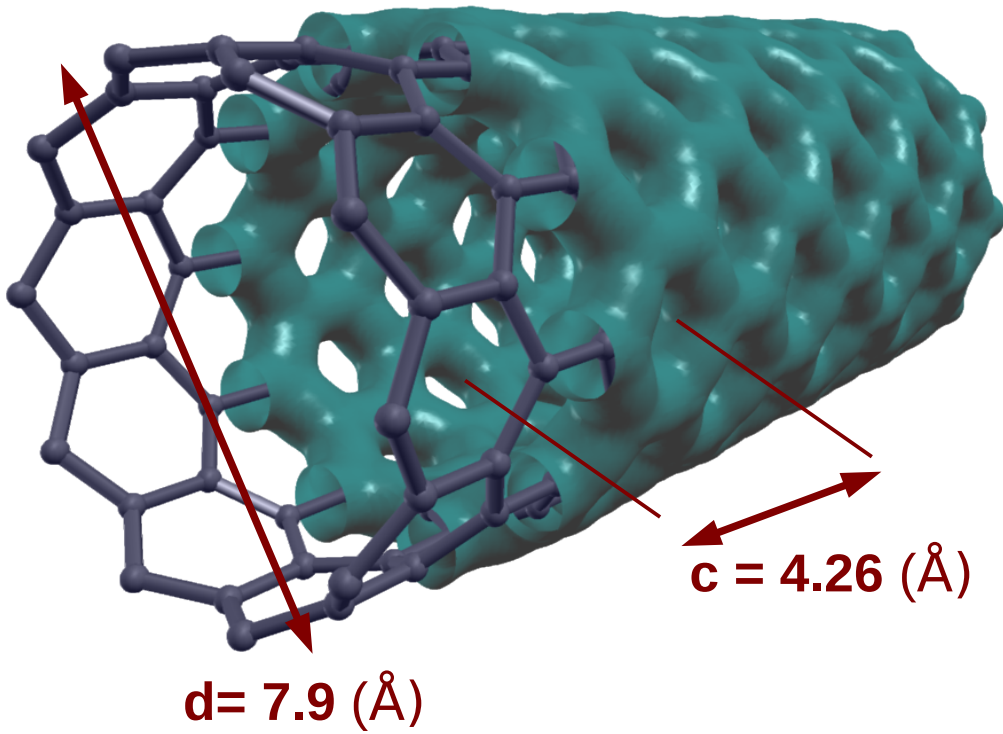
GW-band structure of Polymer / Graphene



Hybrid excitons in Nano-Peapods

(10,0) Carbon Nanotube





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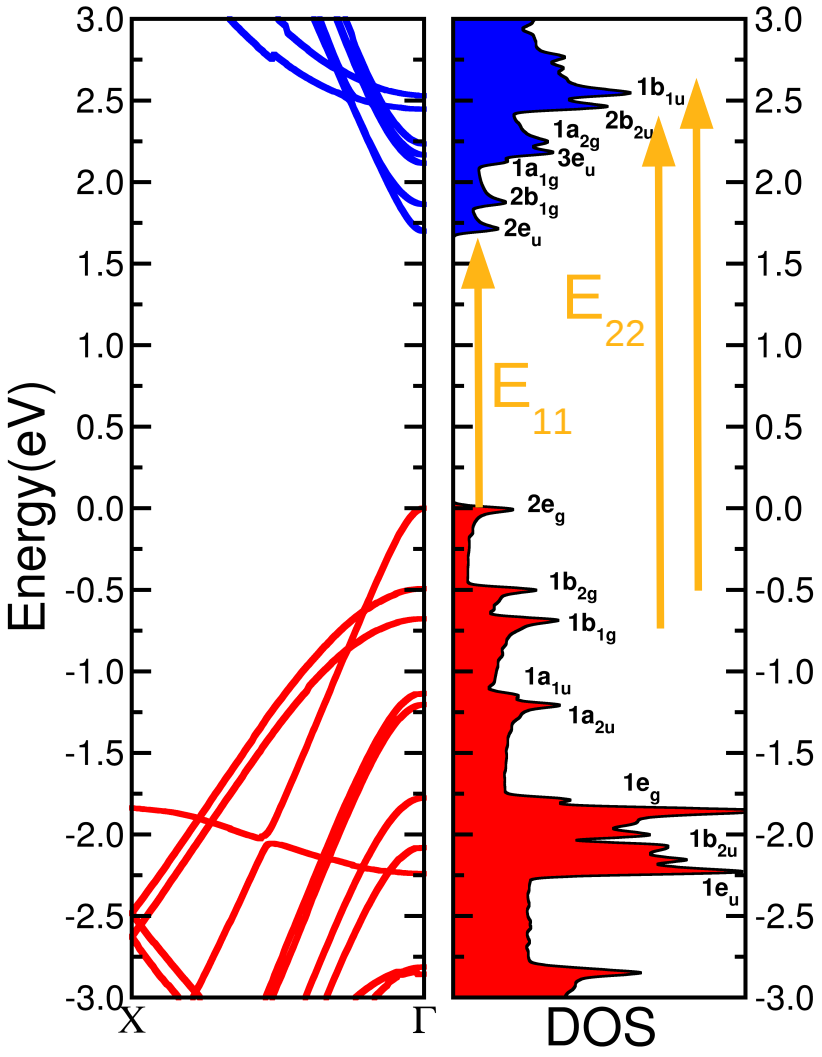
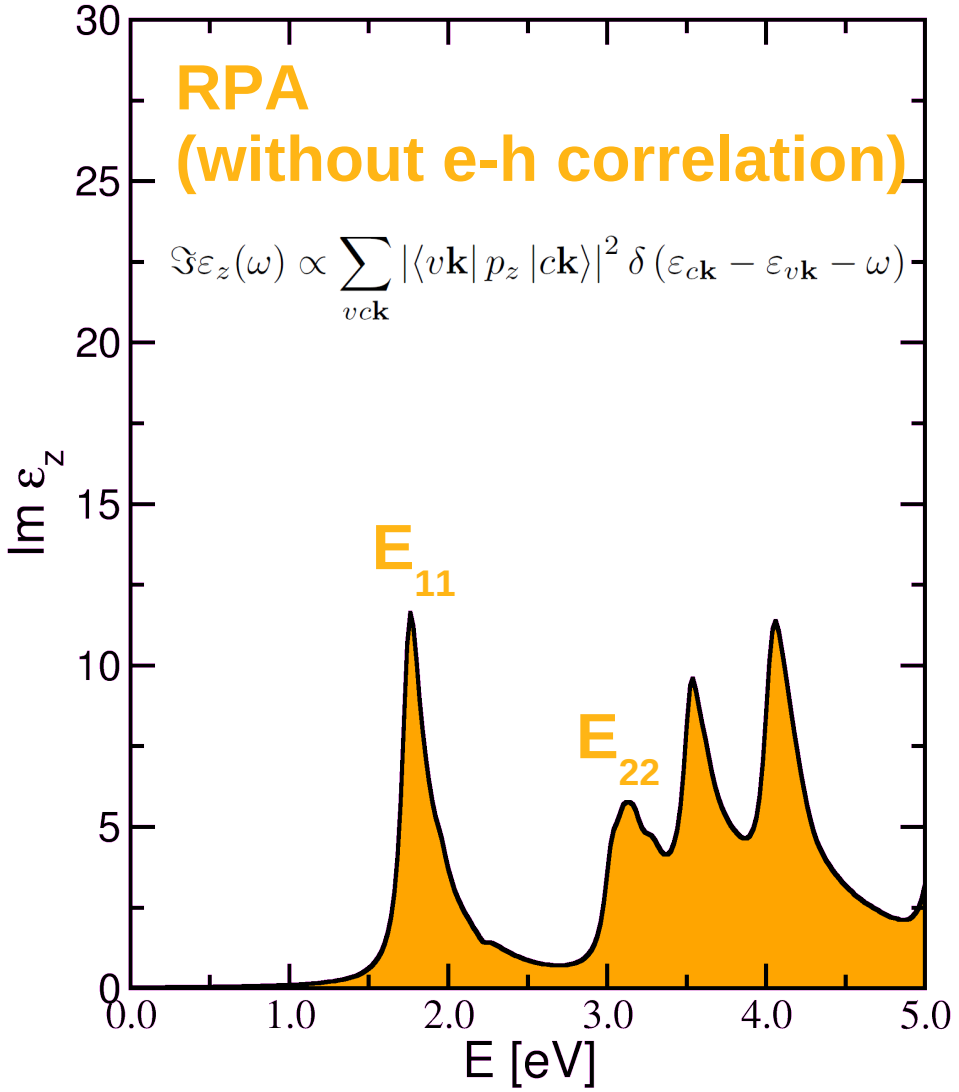
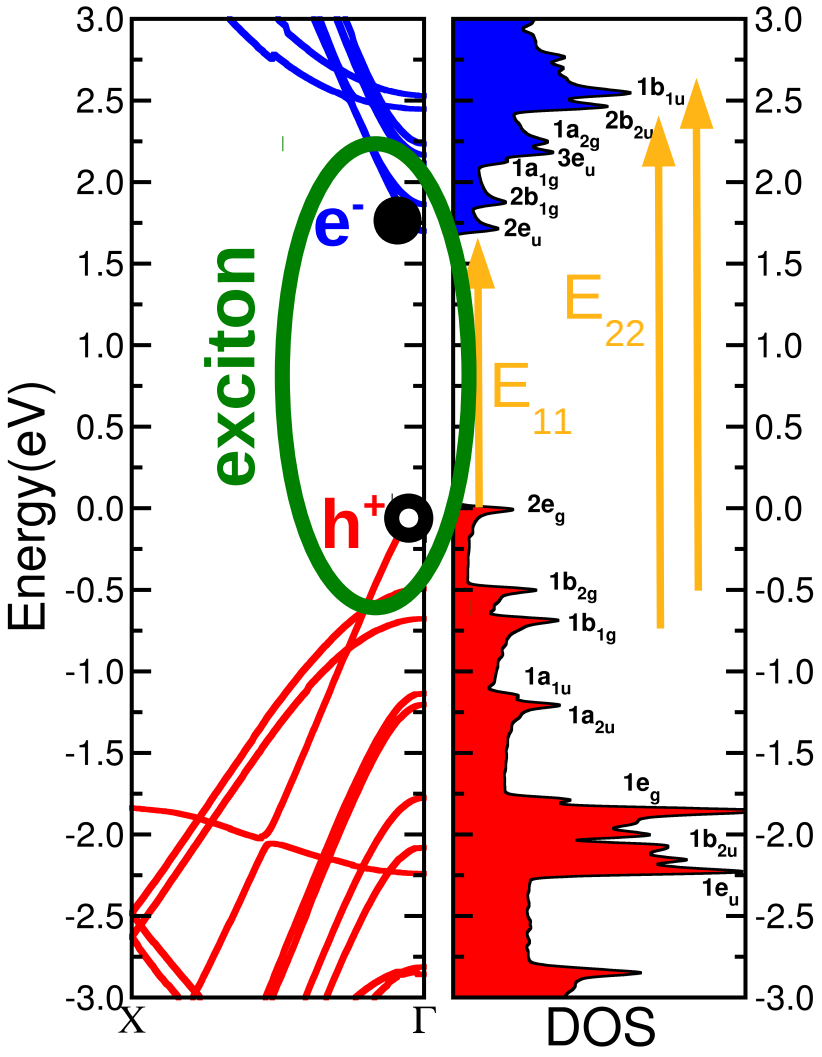
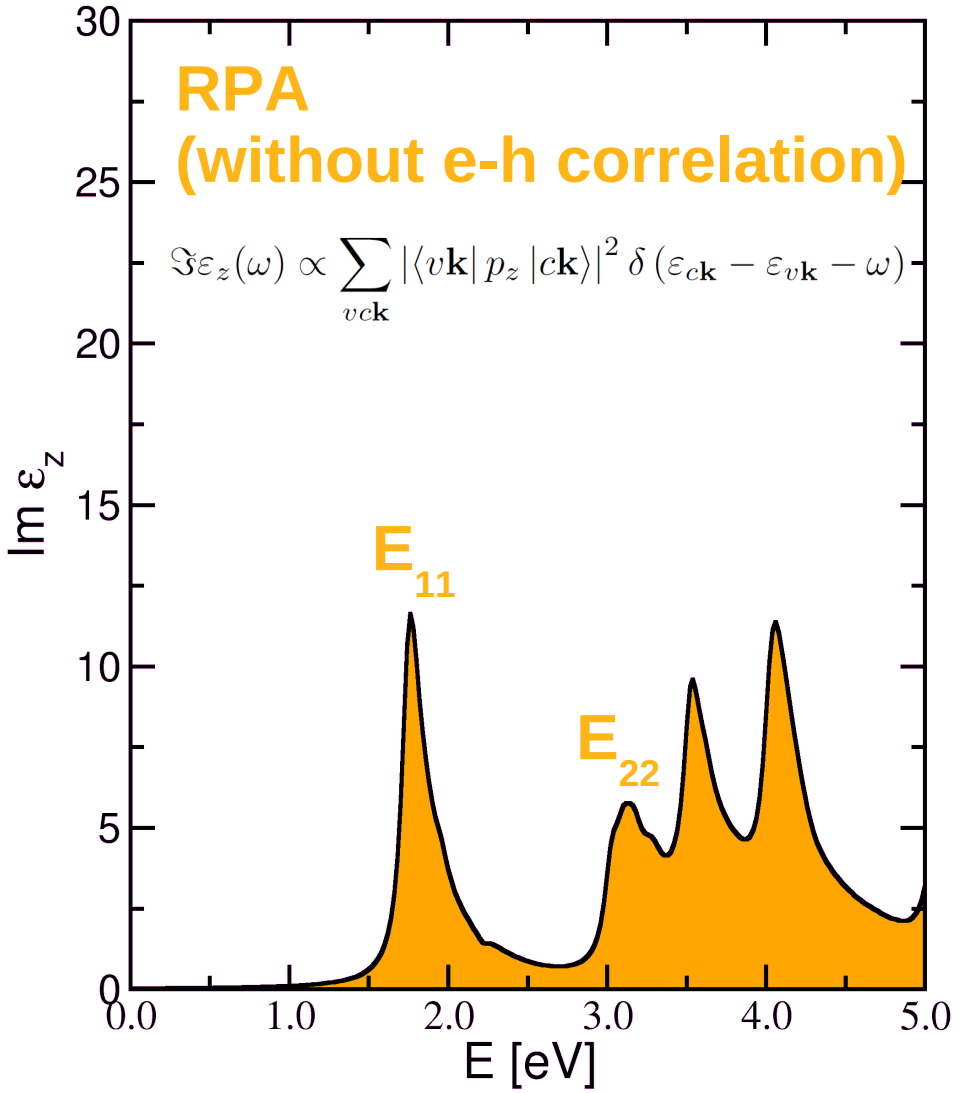




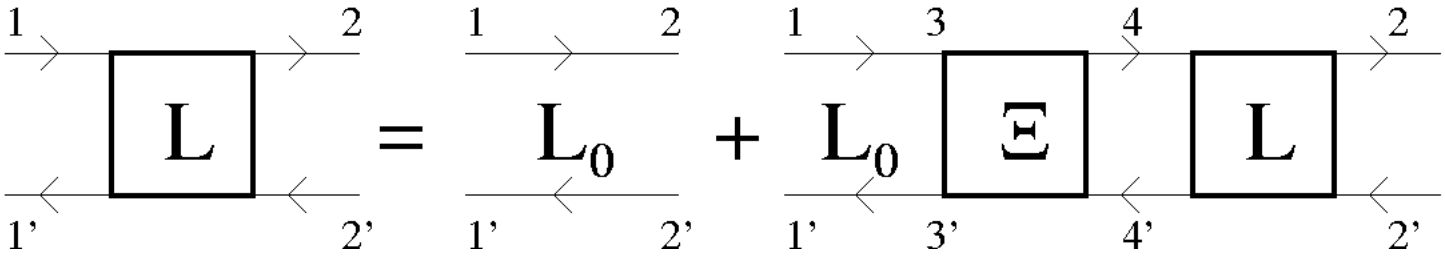
Electron-Hole Correlations?





Electron-Hole Interactions

Bethe-Salpeter-Equation (BSE)



Expansion in a basis of one-particle orbitals leads to ...

$$\sum_{v'c'\mathbf{k}'} H^{e}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E^{\lambda} A^{\lambda}_{vc\mathbf{k}} \qquad H = H^{diag} + H^{dir} + H^{x}$$

... an effective matrix eigenvalue problem for the electron-hole pair

$$H^{dir}_{vc\mathbf{k},v'c'\mathbf{k}'} = -\int\int \mathrm{d}^3r\mathrm{d}^3r' \frac{\psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r}')\varepsilon^{-1}(\mathbf{r},\mathbf{r}')\psi^*_{v'\mathbf{k}'}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

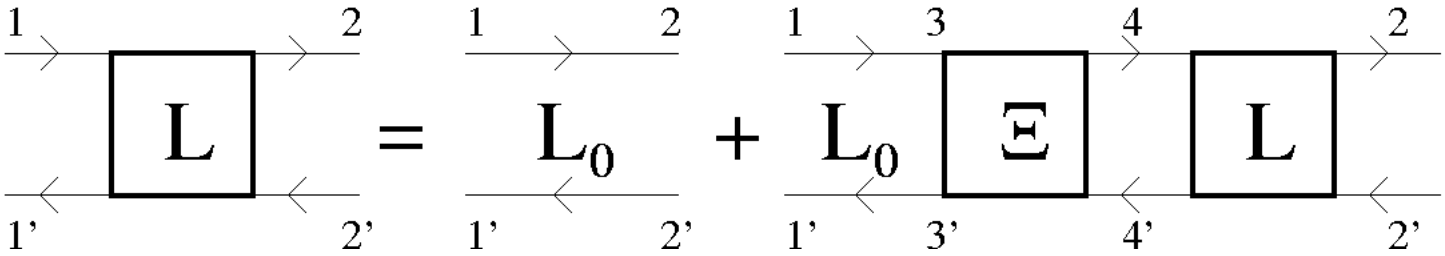
direct screened interaction

$$H^{x}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int\int \mathrm{d}^3r\mathrm{d}^3r' \frac{\psi^*_{v'\mathbf{k}'}(\mathbf{r}')\psi^*_{c\mathbf{k}}(\mathbf{r})\psi_{v\mathbf{k}}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

exchange interaction

Electron-Hole Interactions

Bethe-Salpeter-Equation (BSE)



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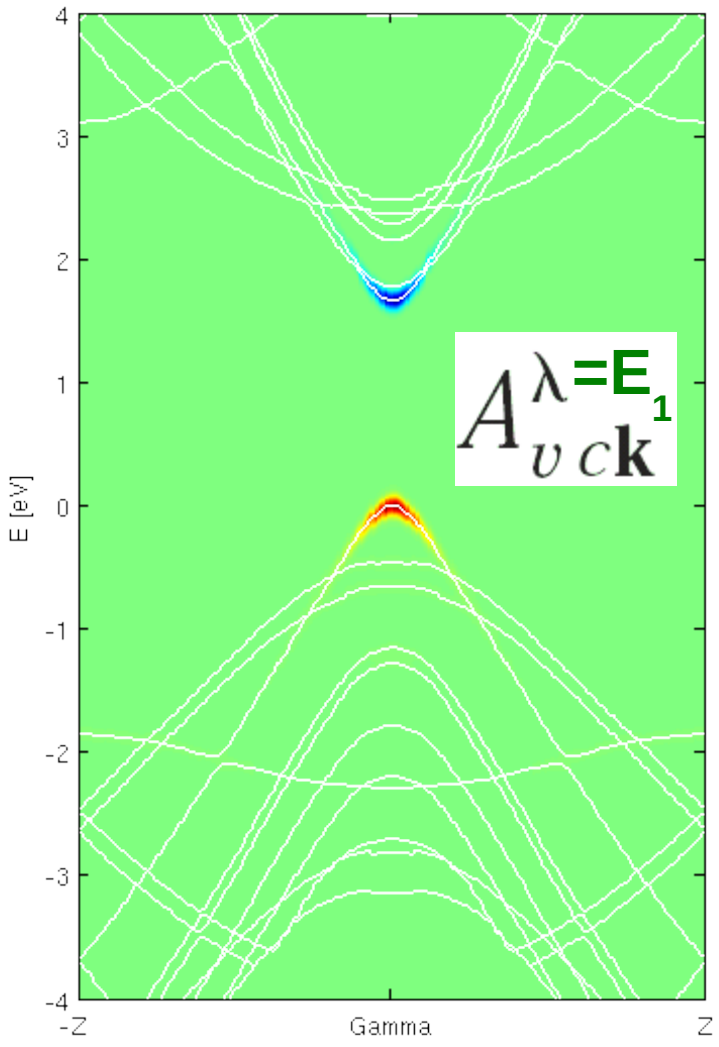
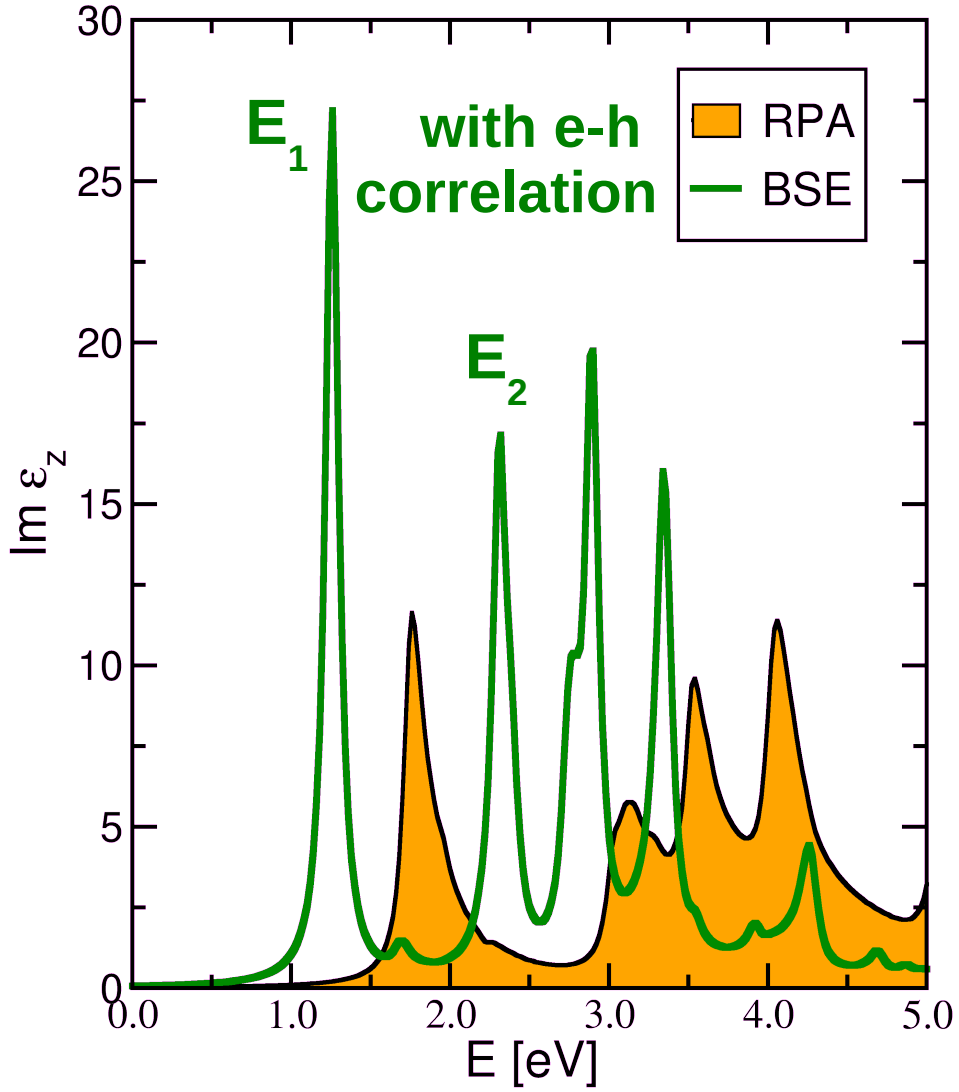
Implementation into LAPW method (WIEN2k code): Puschnig and CAD, *PRB* **66**, 165105 (2002).
Application to trans-polyacetylene: Puschnig and CAD., *PRL* **89**, 056405 (2002).
Application to oligo-acenes: Hummer, Puschnig, and CAD., *PRL* **92**, 147402 (2004).

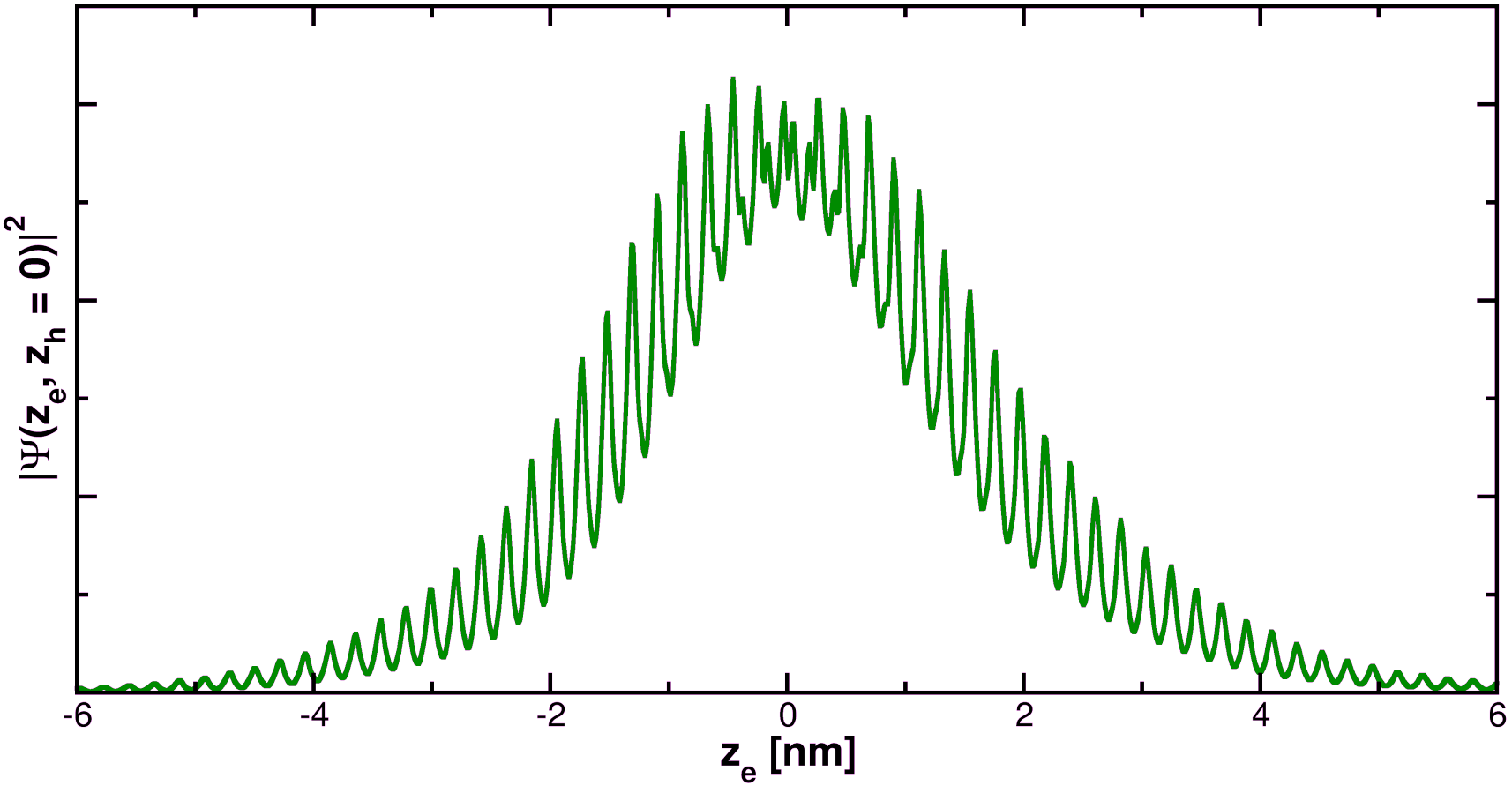
Small diameter SW-CNTs: Spataru, Ismail-Beigi, Benedict, Louie, *PRL* **92**, 077402 (2004).

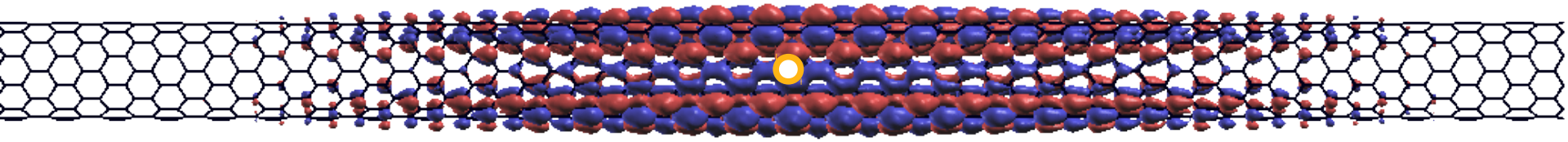
Excitons in (10,0) CNT





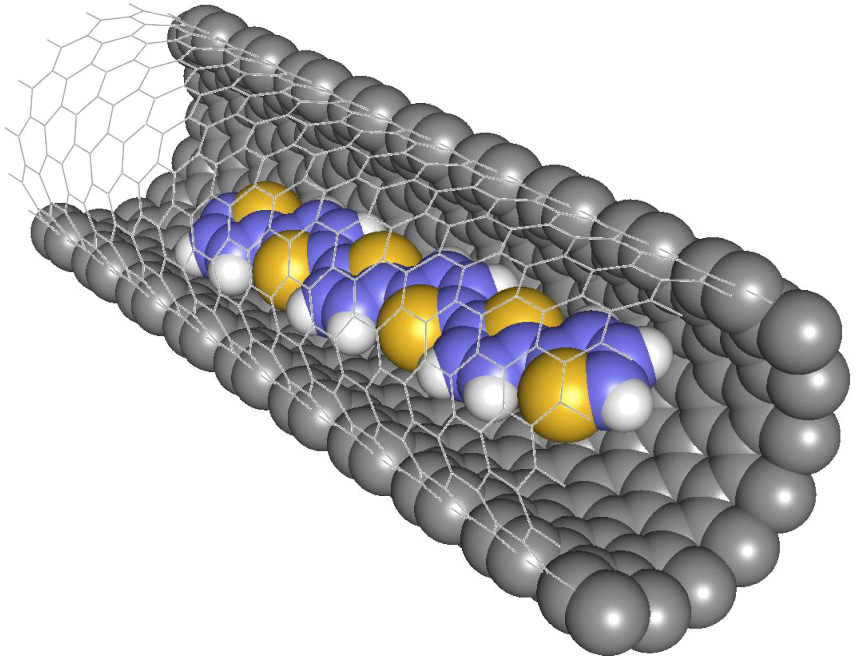
(10,0) CNT – Exciton E_1





Nano-Peapods

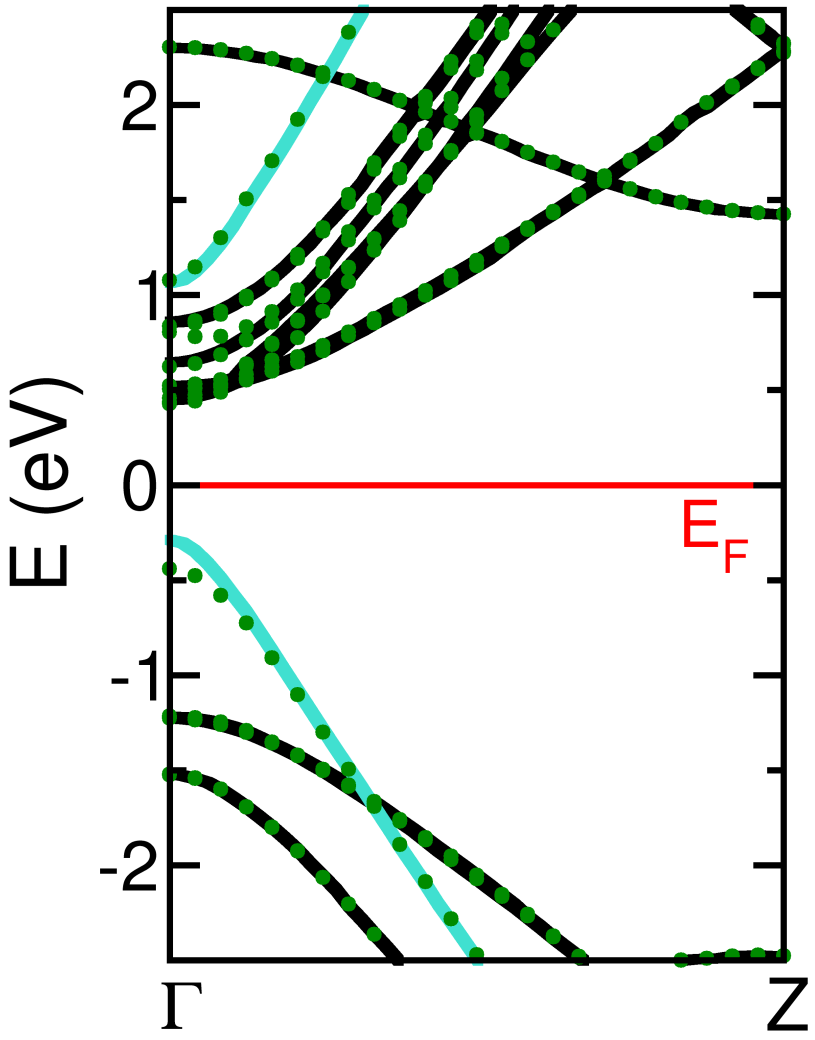
peas in a pod

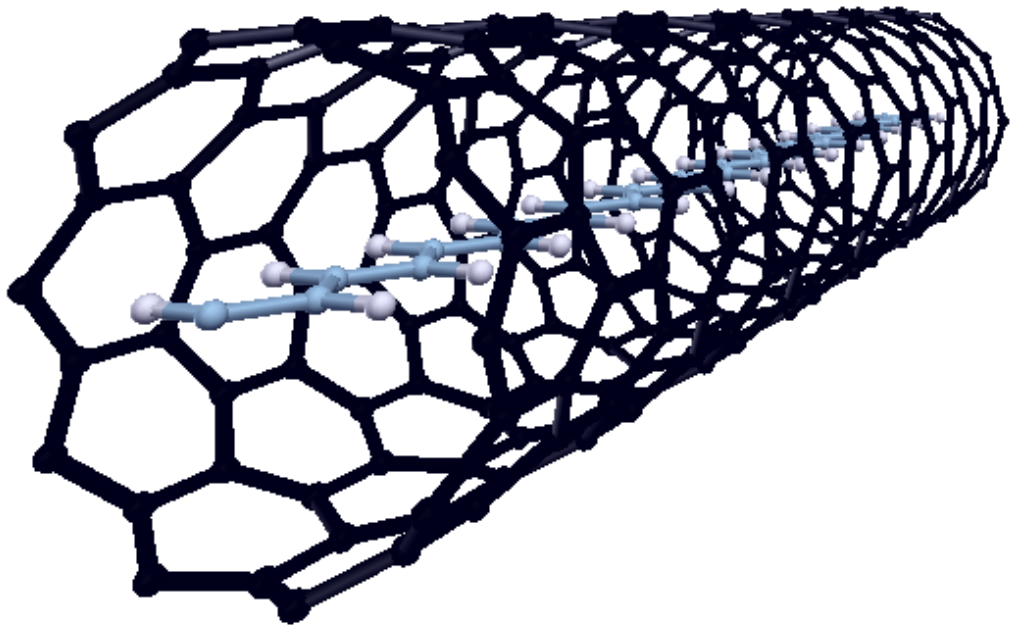


organic molecules in a carbon nanotube

EU-project
Nano-Hybrids for **Pho**tonic **D**evices
C. Draxl

Model System

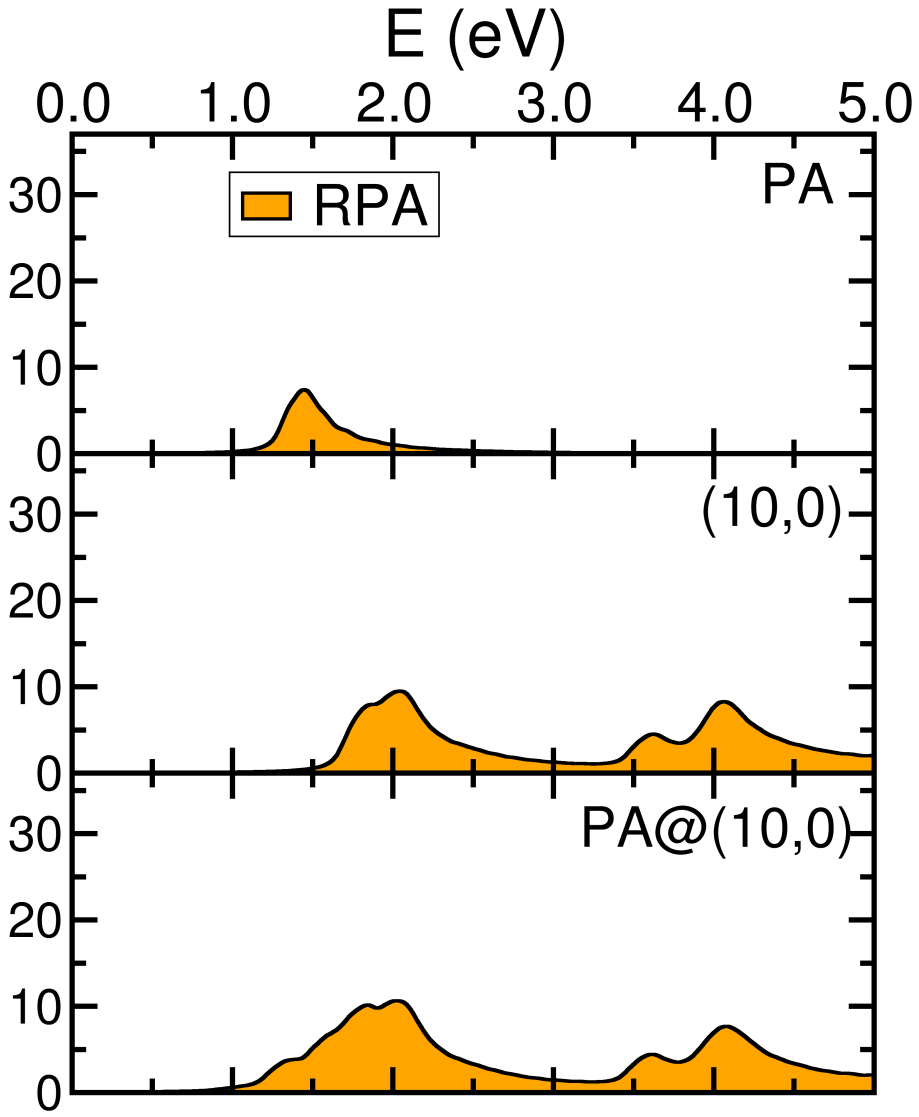


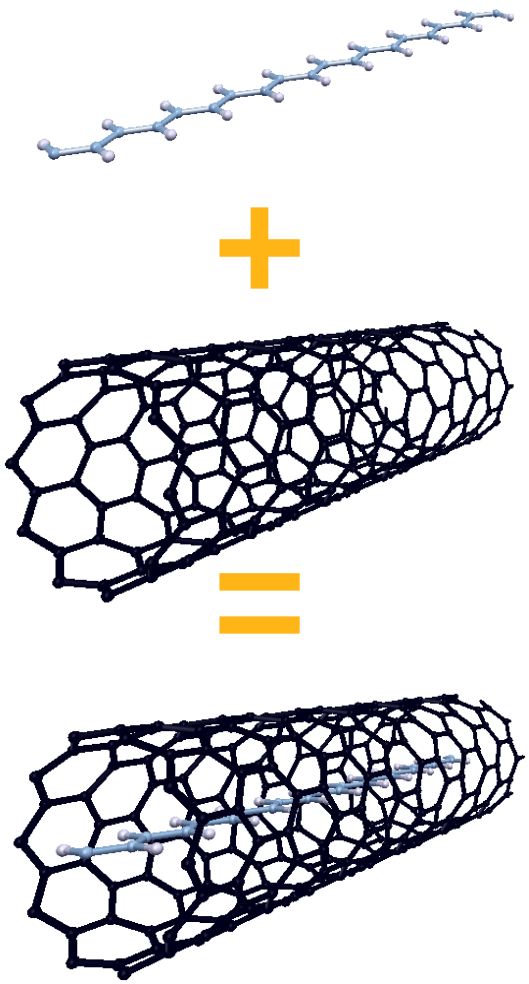


trans-polyacetylene
inside a
(10,0) CNT

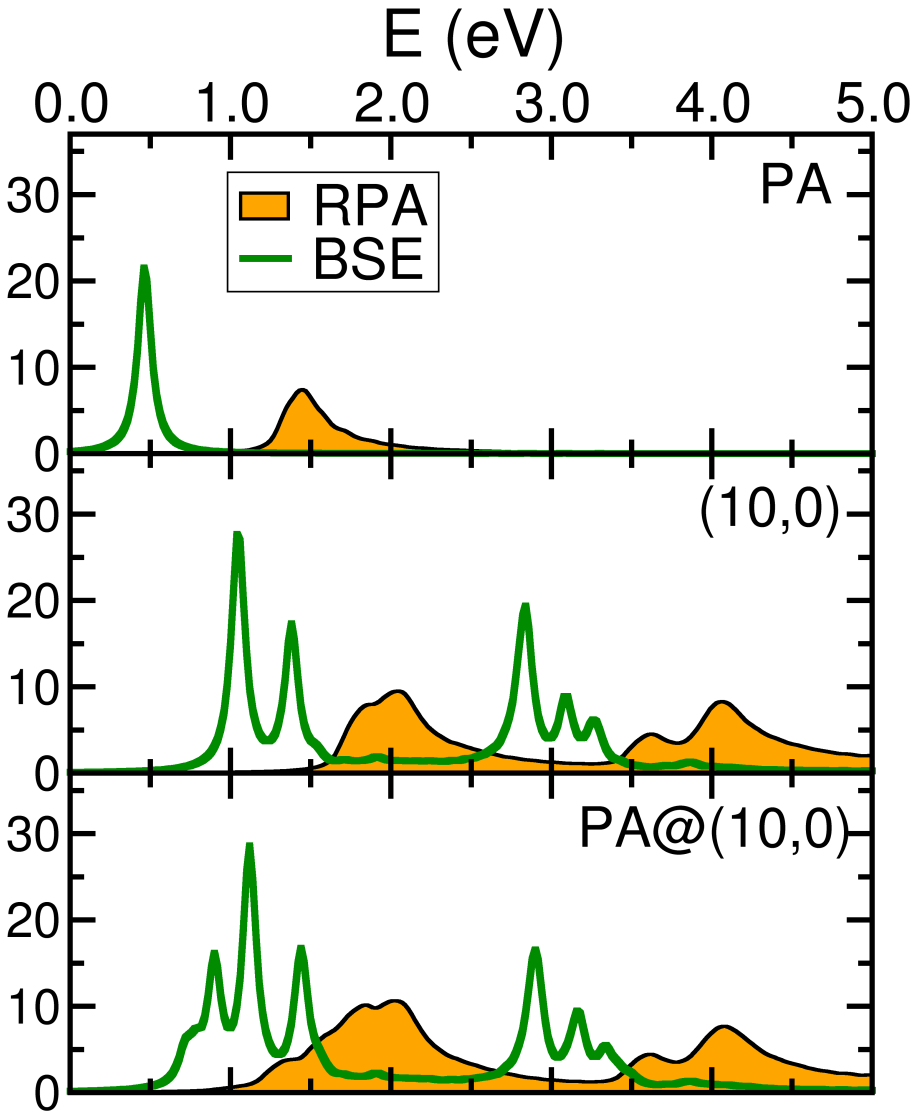
Milko et al., PRB 86, 155416 (2012).

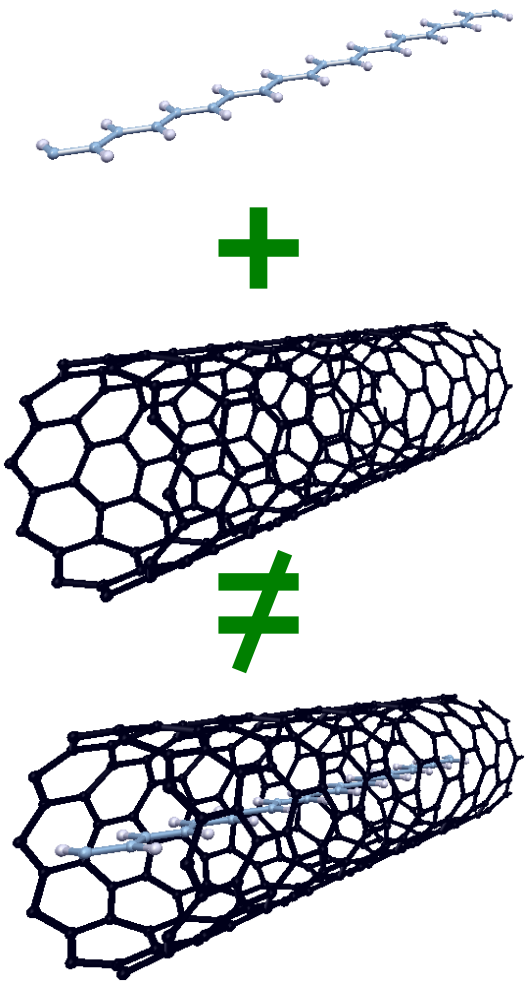
Polyacetylene @ (10,0) CNT



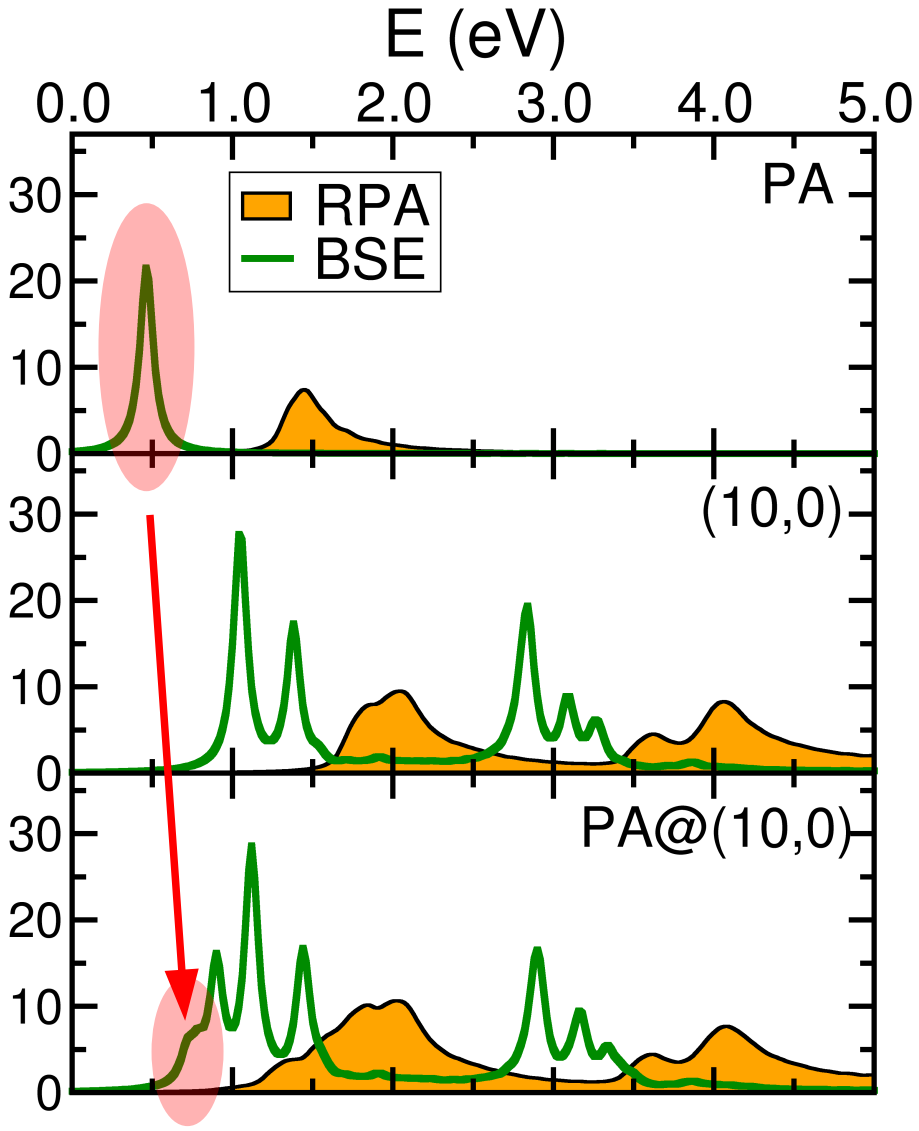


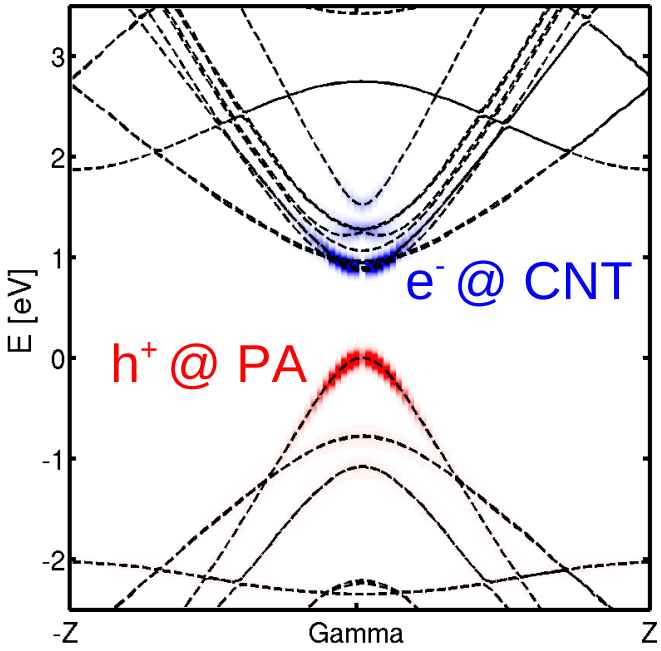
Polyacetylene @ (10,0) CNT

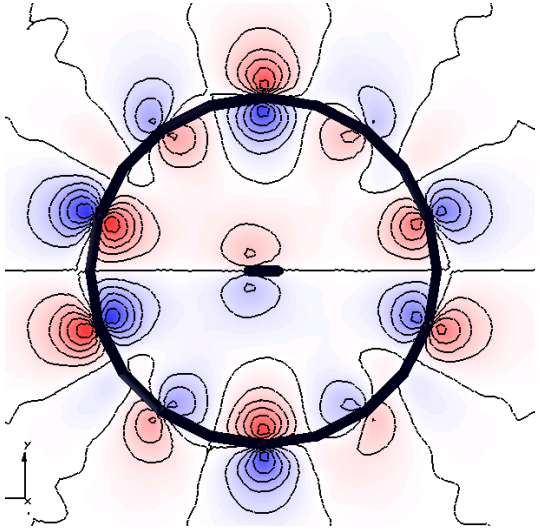




Polyacetylene @ (10,0) CNT







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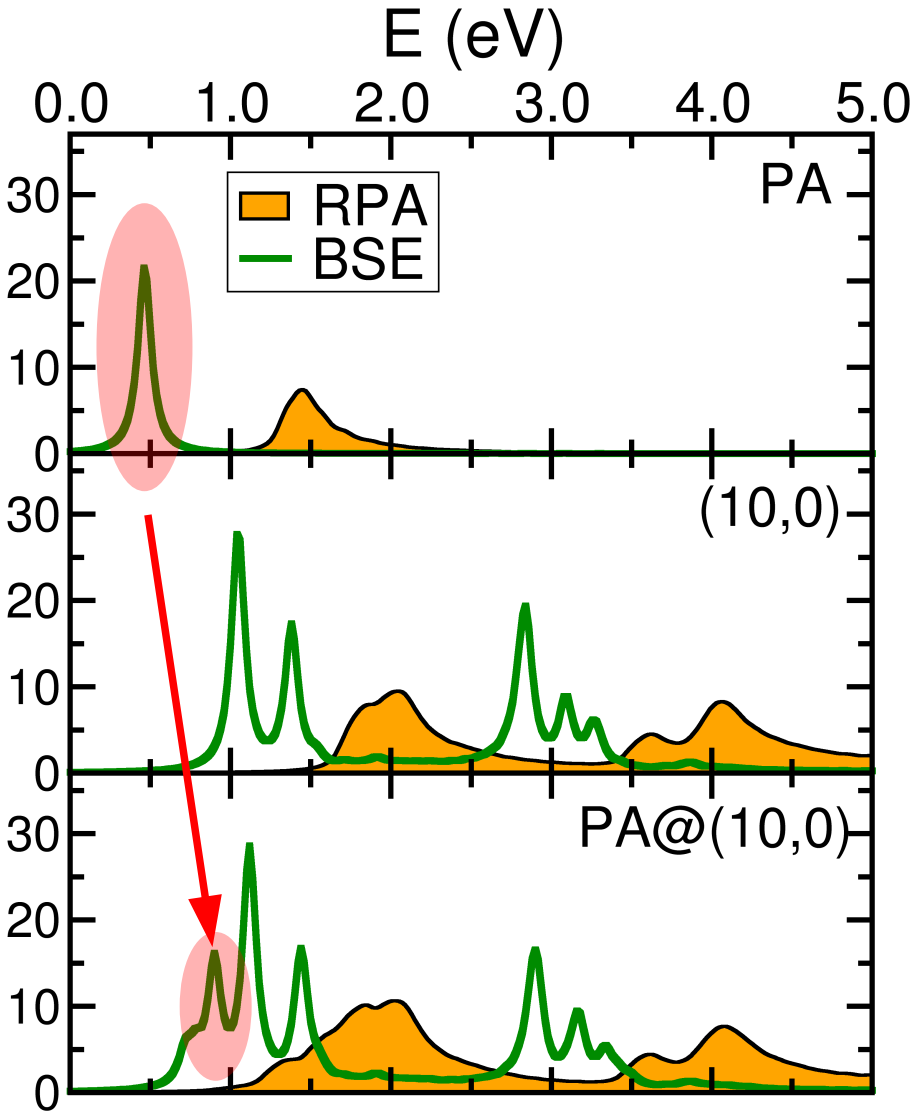
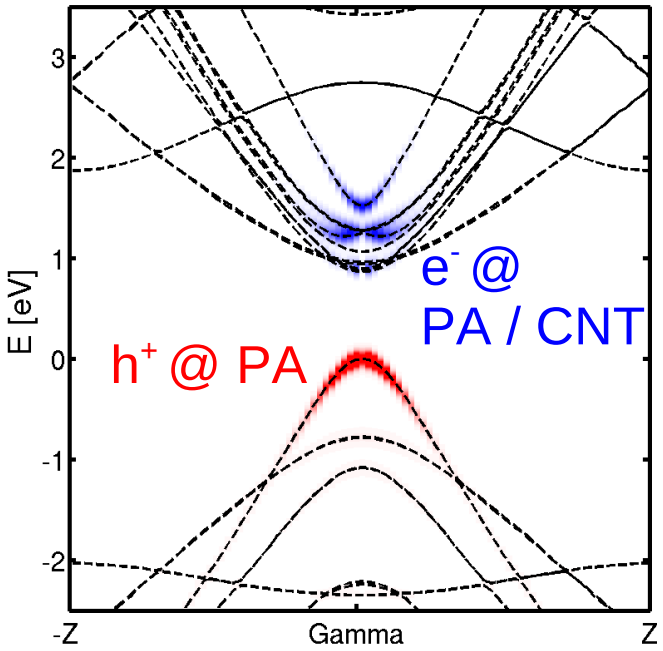
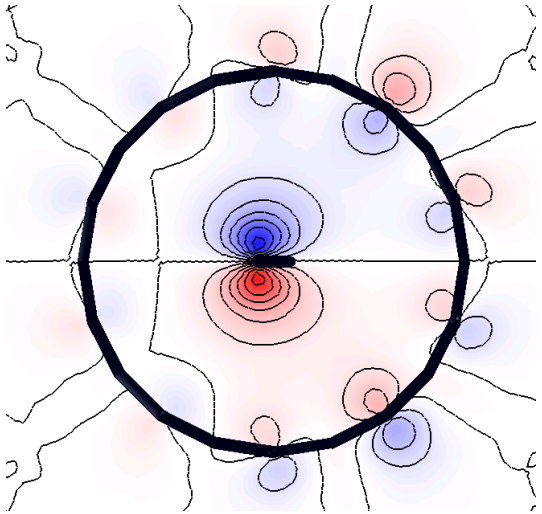
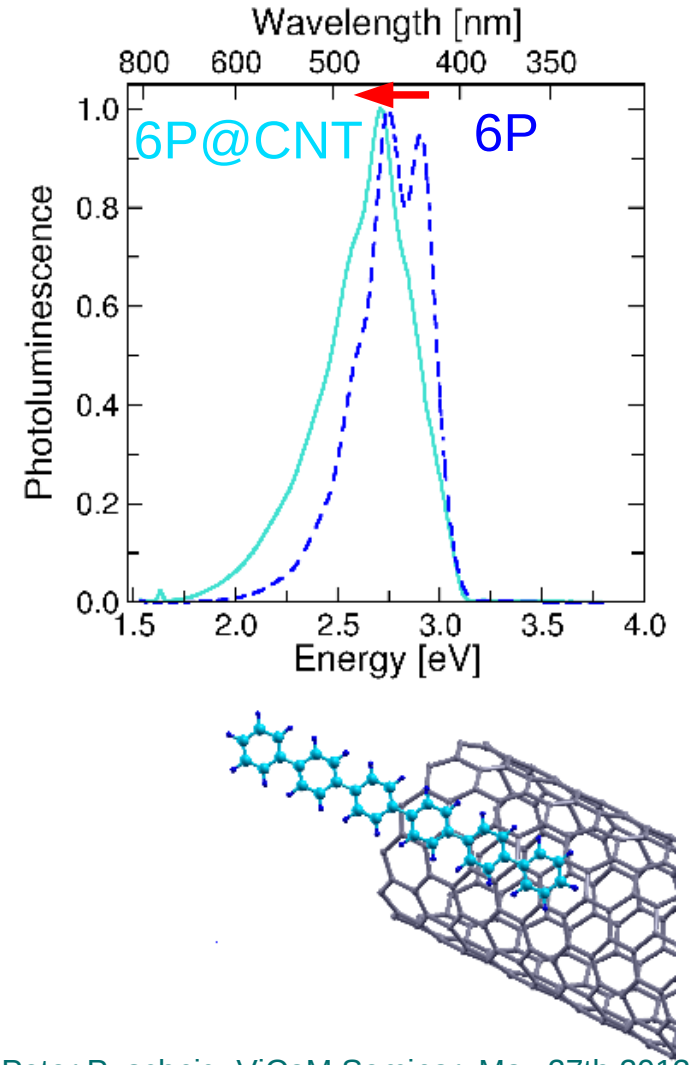






Real Peapods

Photoluminescence: Sexiphenyl @ CNT



HRTEM: Sexithiophene @ CNT

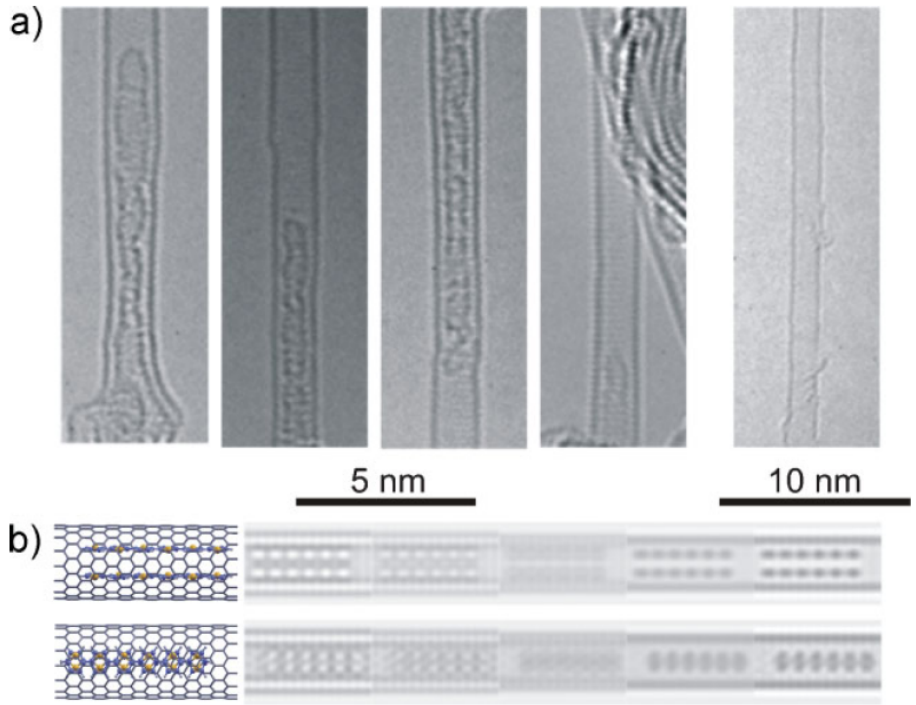
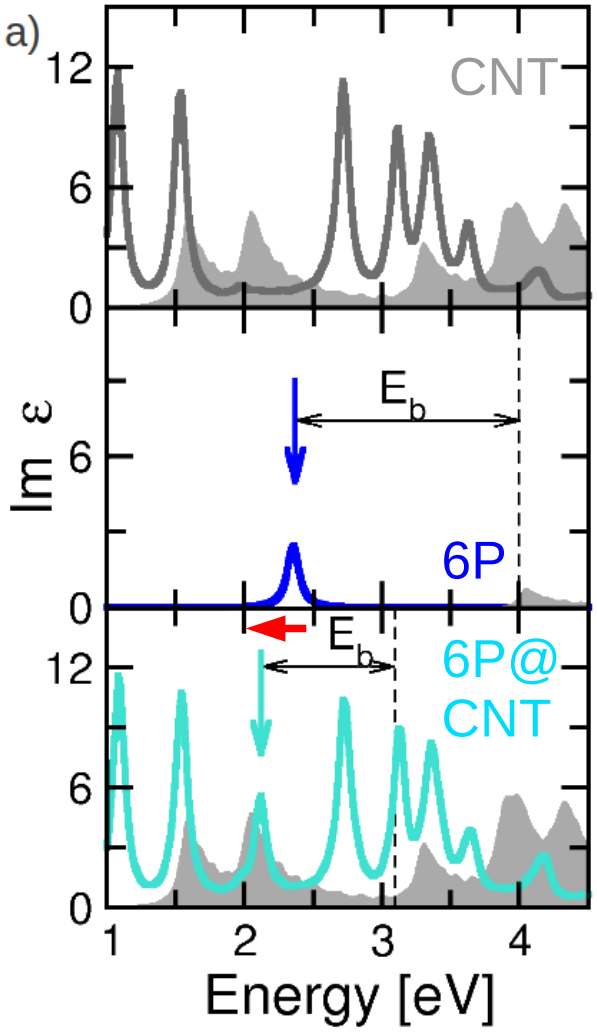
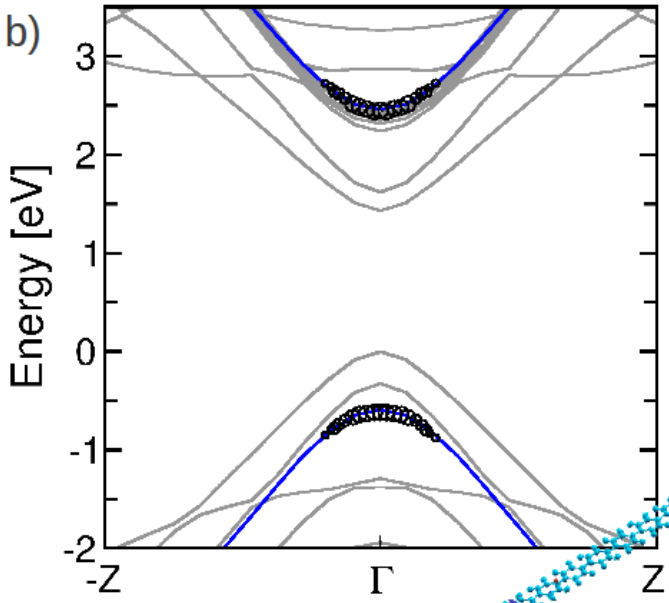


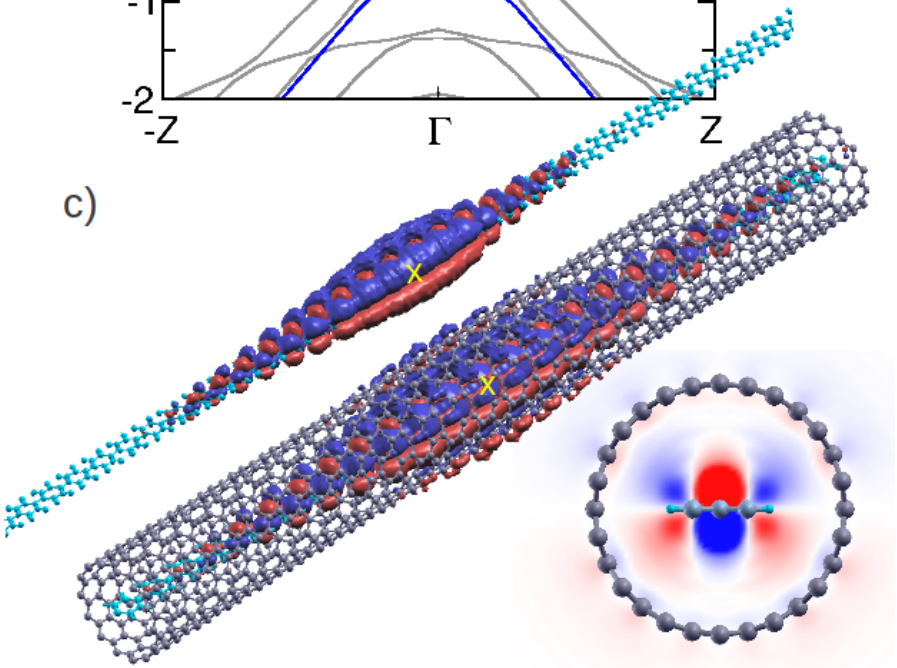
Figure 2. HRTEM images and simulations. a) Measured TEM images of 6T@SWNT (four images on the left); pristine nanotube (right). b) Atomic model of 6T molecules inside a (15,0) SWNT in two different projections (left) together with multi-slice simulations (right). The electron beam is assumed to be parallel (top) and perpendicular (bottom) to the molecular plane. The defocus varies between −4 to +4 nm in steps of 2 nm (from left to right).

M. A. Loi, Adv. Mater. 22, 1635 (2010).

Sexiphenyl @ (14,0)CNT







Milko et al., submitted

Summary

Theory

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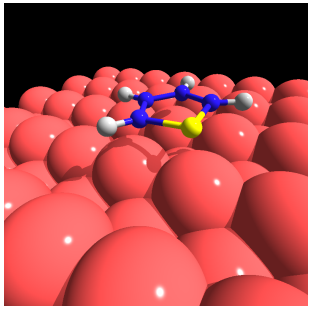
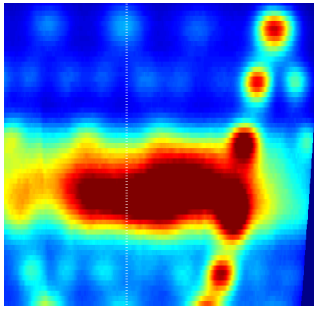
Photoemission Intensity: What angle-resolved PE data tells us about molecular orbitals

Many-Body Perturbation Theory: GW-Approximation, Bethe-Salpeter Equation

Applications



Van der Waals Interactions In DFT



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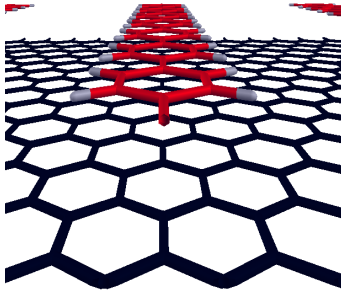

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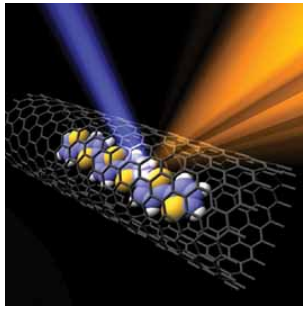

Hybrid excitons in Nano-Peapods

Collaborations and Funding

Theoretical Physics – University Graz, Austria
Daniel Lüftner, Matus Milko

Dmitrii Nabok, Priya Sony, Lorenz Romaner,
Claudia Draxl: formerly at Chair of Atomistic Modelling, MU Leoben, now at HU Berlin

Experimental Surface Science Group – University Graz, Austria
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Georg Koller, Mike Ramsey

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

Peter Grünberg Institut (PGI-3), JARA, Forschungszentrum Jülich,
Sergey Soubatch, Benjamin Stadtmüller, Martin Willenbockel
Stefan Tautz

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„Interface controlled and functionalized organic films“
and the single project P23190-N16 „Understanding photoemission of organic thin films“