



**Claudia**

**the Dirac point**

**Graphene off**

**Draxl**



# Who killed the Dirac point?

PHYSICAL REVIEW B **80**, 235431 (2009)

## Band-structure topologies of graphene: Spin-orbit coupling effects from first principles

M. Gmitra,<sup>1</sup> S. Konschuh,<sup>1</sup> C. Ertler,<sup>1</sup> C. Ambrosch-Draxl,<sup>2</sup> and J. Fabian<sup>1</sup>

<sup>1</sup>*Institute for Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany*

<sup>2</sup>*Chair of Atomistic Modeling and Design of Materials, University of Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria*

(Received 26 November 2009; published 28 December 2009)

The electronic band structure of graphene in the presence of spin-orbit coupling and transverse electric field is investigated from first principles using the linearized augmented plane-wave method. The spin-orbit coupling opens a gap of  $0.4 \mu\text{eV}$  ( $0.25 \text{ K}$ ) at the  $K/K'$  point. It is shown that the previously accepted value of  $1 \mu\text{eV}$ , coming from the  $\sigma$ - $\pi$  mixing, is incorrect due to the neglect of  $d$  and higher orbitals whose contribution is dominant due to symmetry reasons. The transverse electric field induces an additional (extrinsic) Bychkov-Rashba-type splitting of  $10 \mu\text{eV}$  ( $0.11 \text{ K}$ ) per  $\text{V/nm}$ , coming from the  $\sigma$ - $\pi$  mixing. A “miniripple” configuration with every other atom shifted out of the sheet by less than 1% differs little from the intrinsic case.

**Spin-orbit coupling opens a gap**

**Dirac!**

# Can we “see” orbitals?

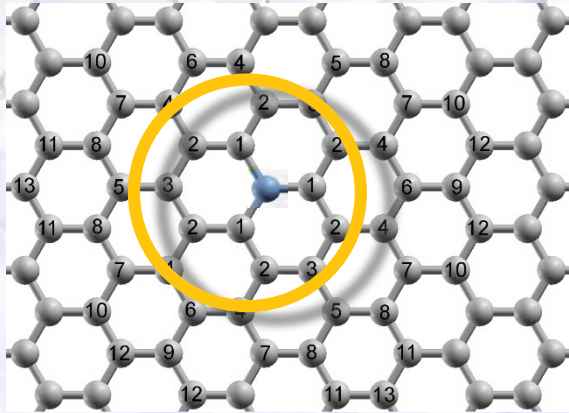


**L. Pardini, S. Löffler, G. Biddau, R. Hambach, U. Kaiser, CD, and P. Schattschneider, Phys. Rev. Lett. 117, 036801 (2016).**

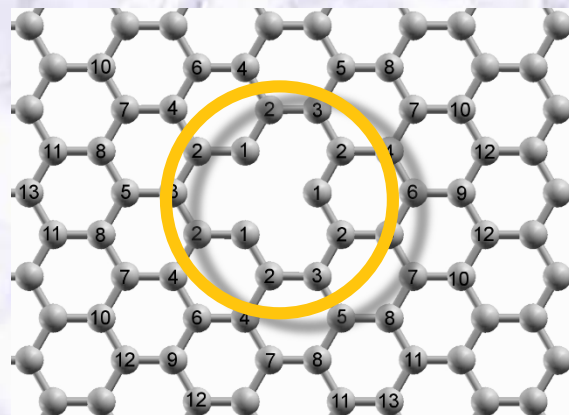
S. Löffler, V. Motsch, and P. Schattschneider, Ultramicroscopy 131, 39 (2013).

# Orbital mapping in the EFTEM

What should we see in the microscope?



N-doped

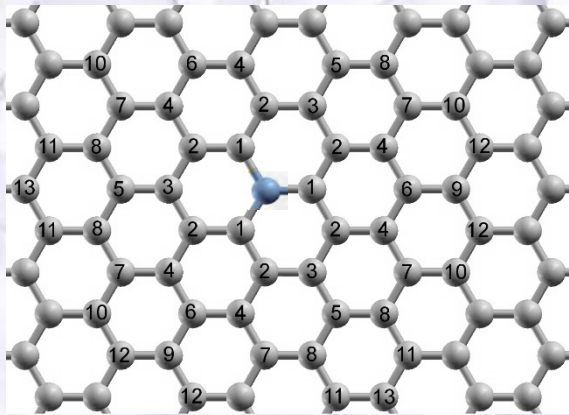


Vacancy

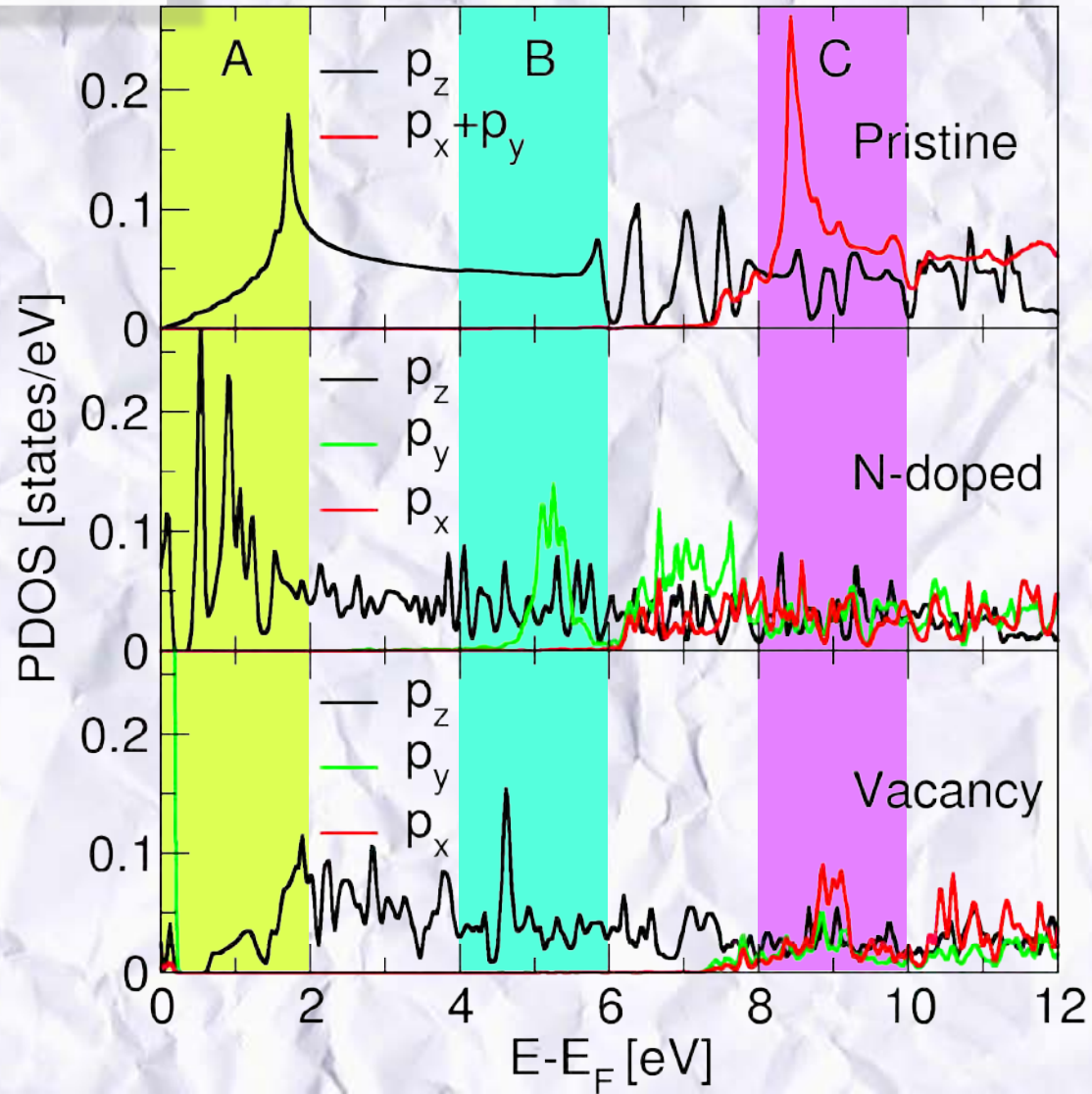
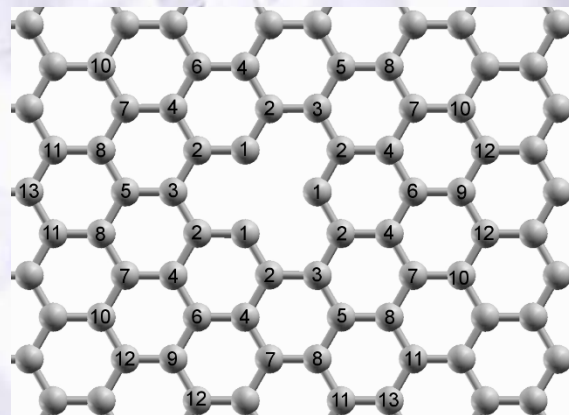
# Orbital mapping in the EFTEM

DOS of first nearest neighbors

N-doped



Vacancy



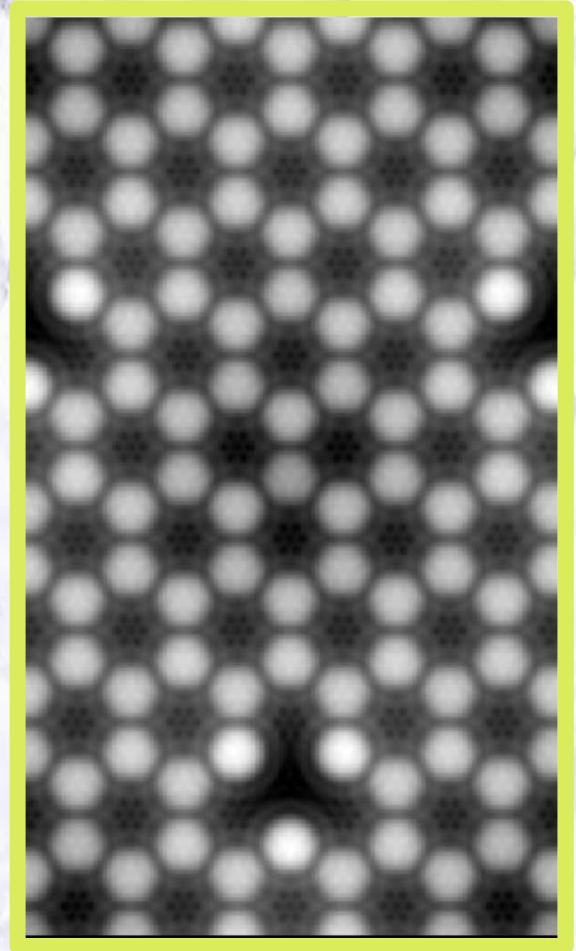
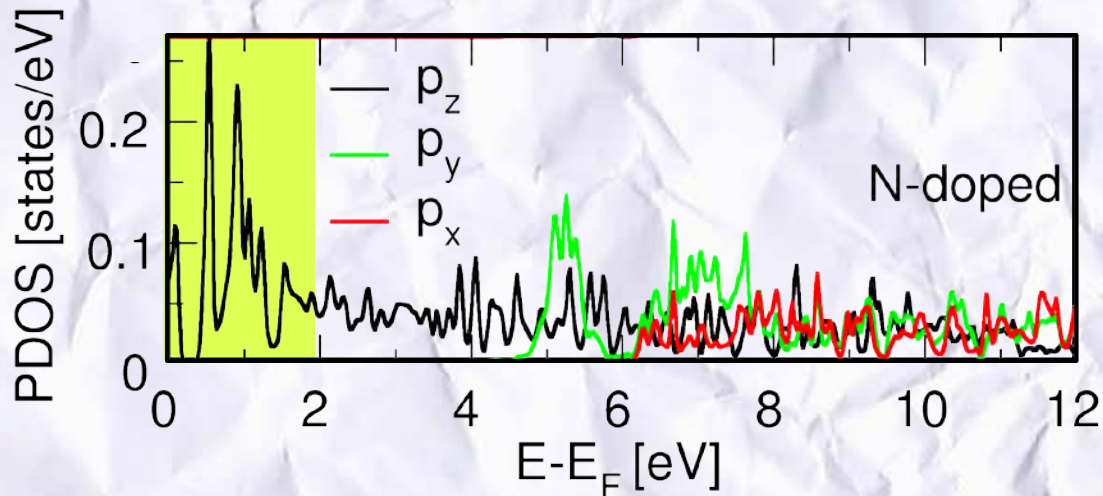
# Orbital mapping in the EFTEM

N-doped graphene

Mixed dynamic form factor

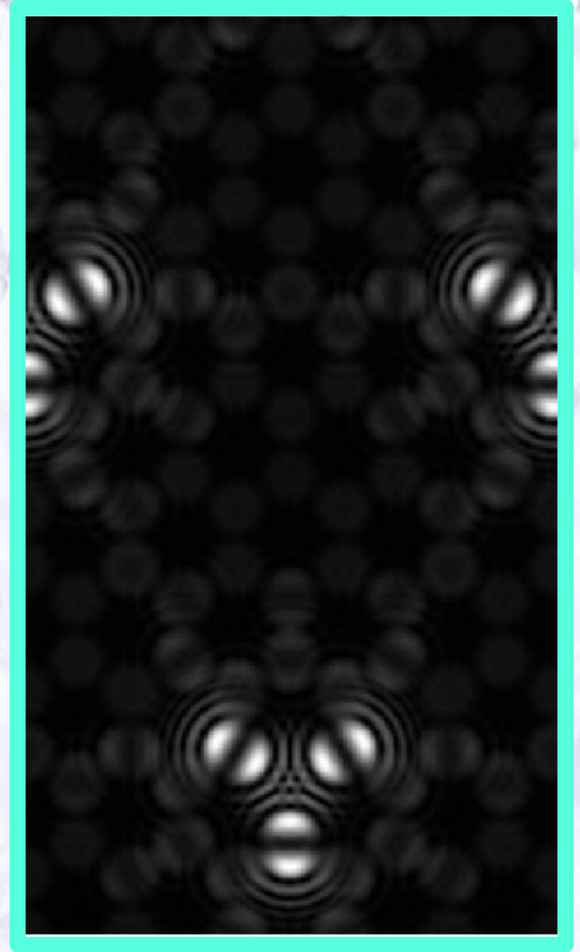
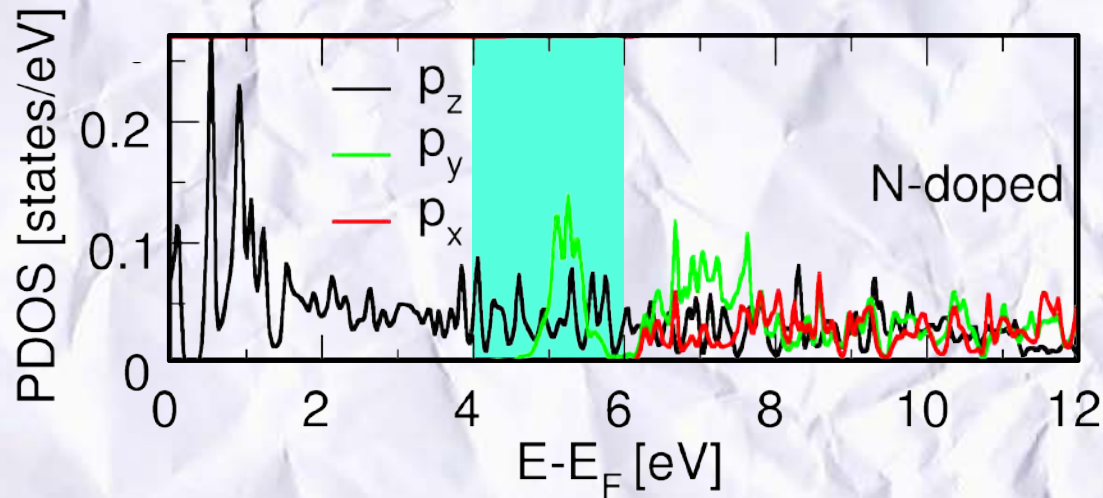
$$S(\mathbf{q}, \mathbf{q}'; E) \propto \sum_{n\mathbf{k}} D_{LM}^{n\mathbf{k}} (D_{L'M'}^{n\mathbf{k}})^* \delta(E_n(\mathbf{k}) - E)$$

Cross-density of states



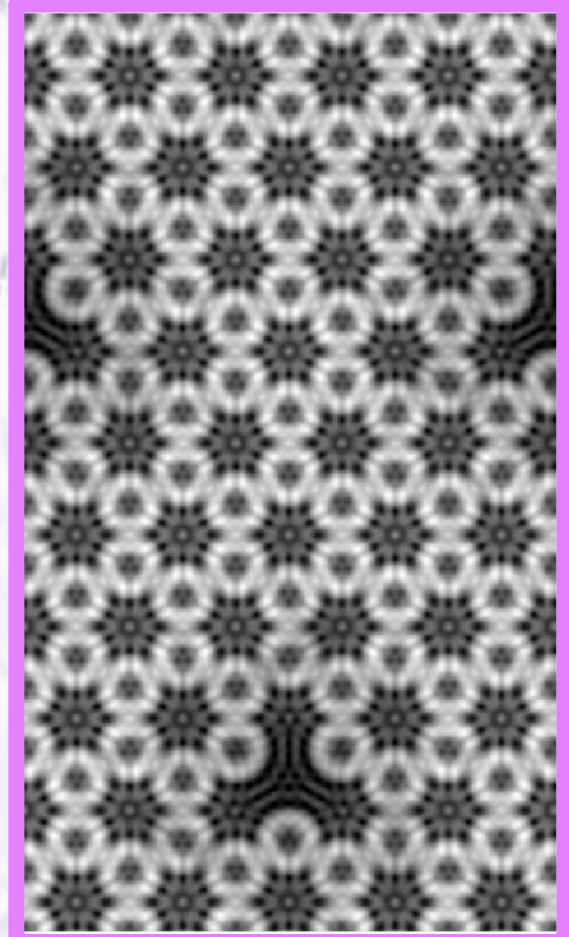
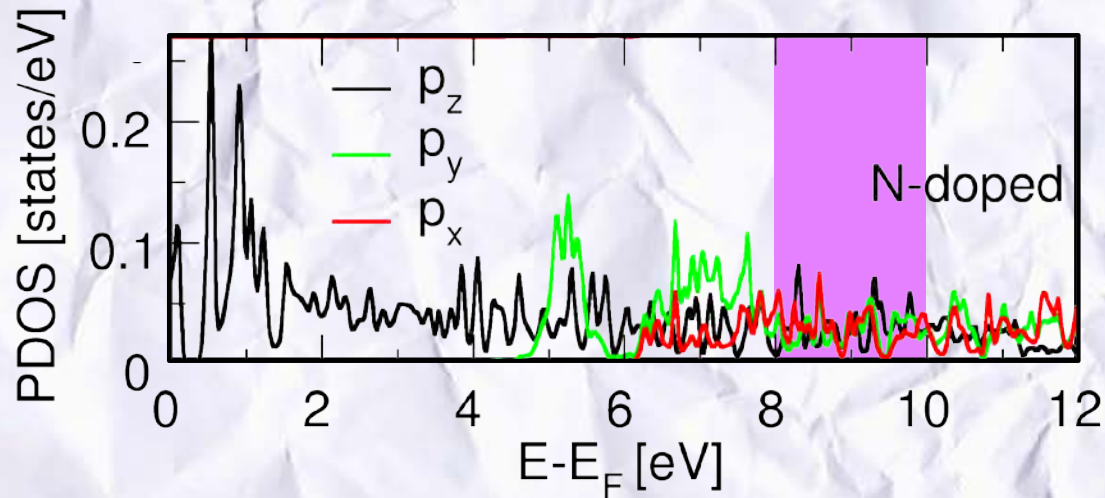
# Orbital mapping in the EFTEM

N-doped graphene



# Orbital mapping in the EFTEM

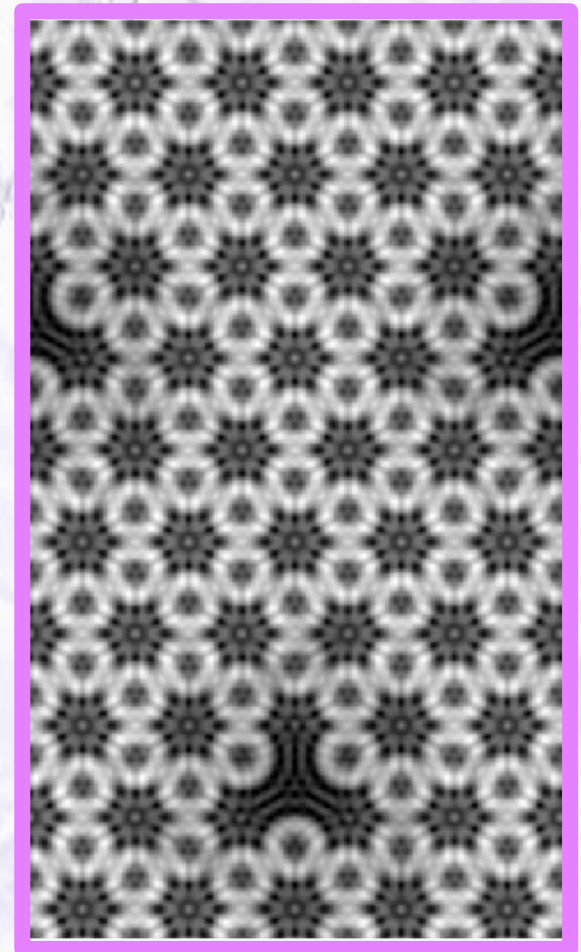
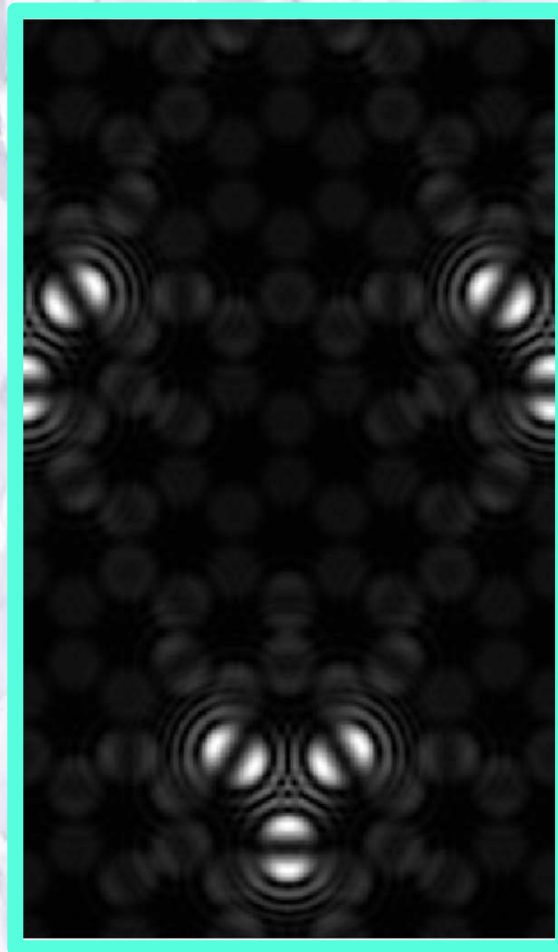
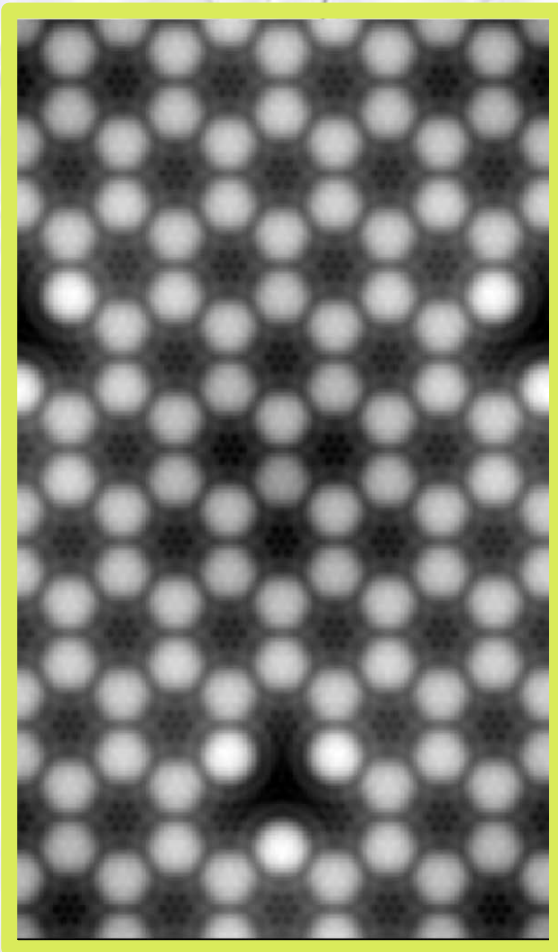
N-doped graphene





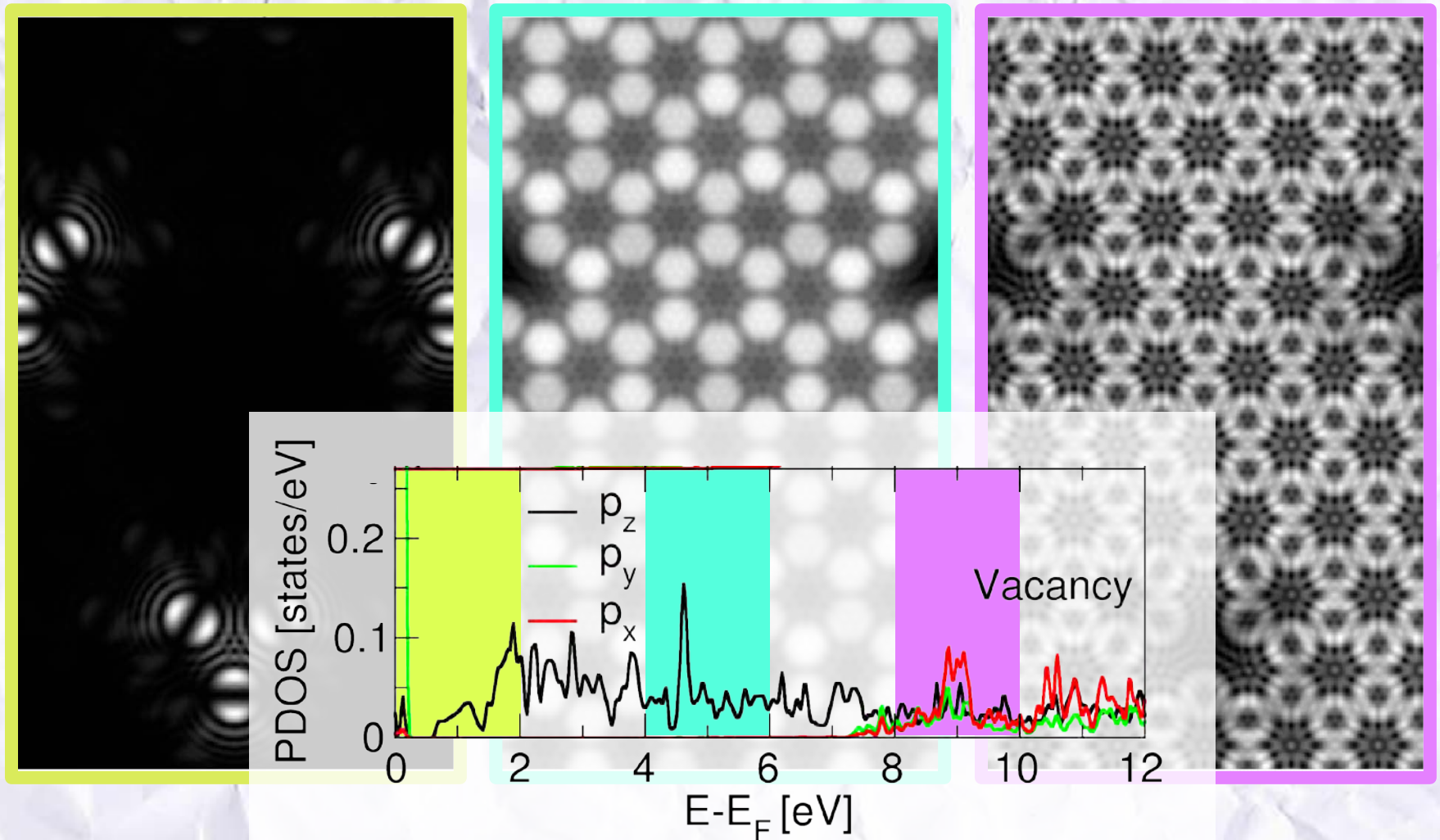
# Orbital mapping in the EFTEM

N-doped graphene



# Orbital mapping in the EFTEM

Graphene with vacancy

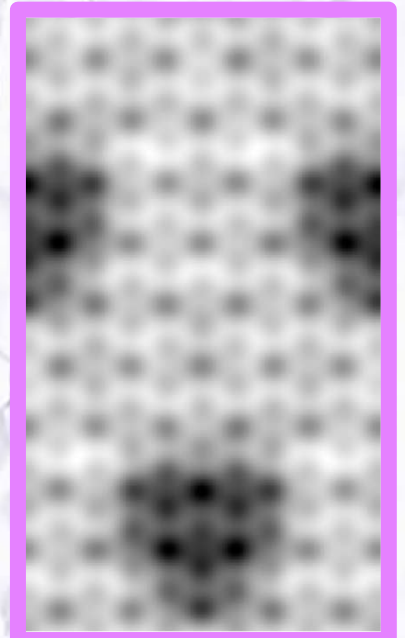
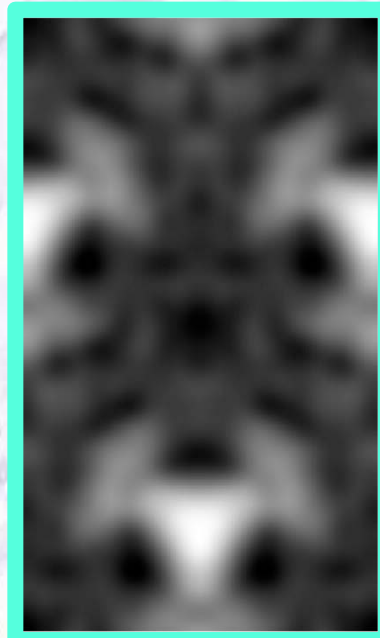
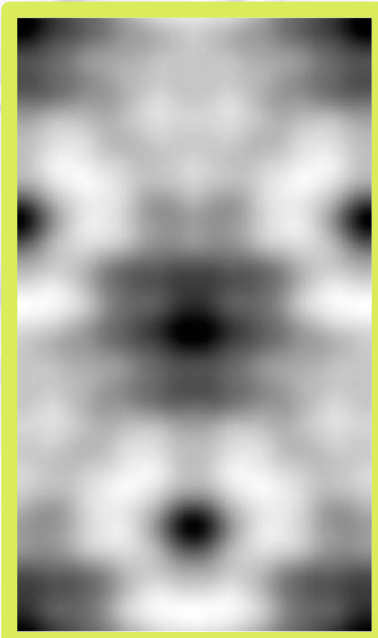
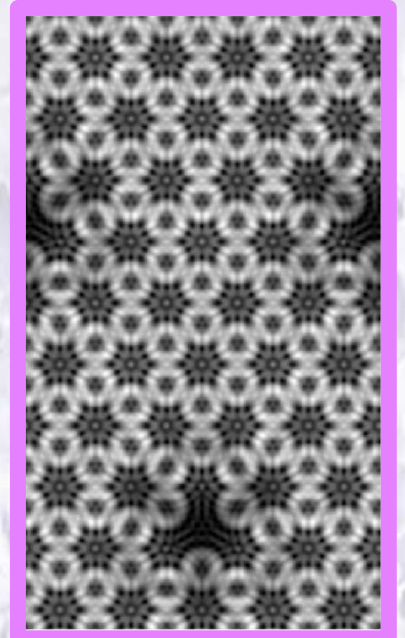
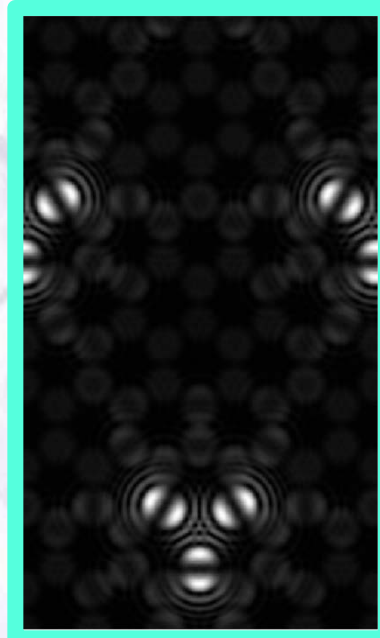
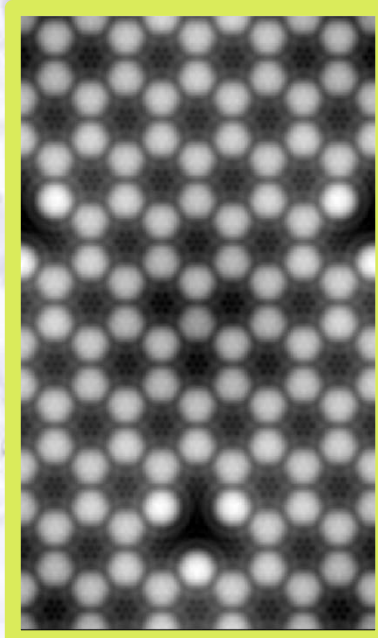


# Reality?

Theory

N-doped  
graphene

Tecnai G<sup>2</sup> F20  
80 keV

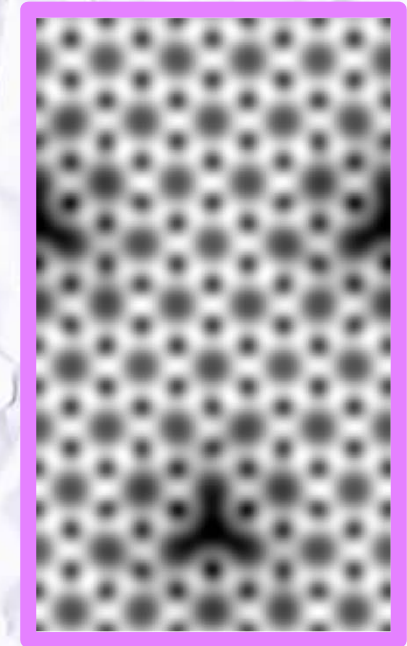
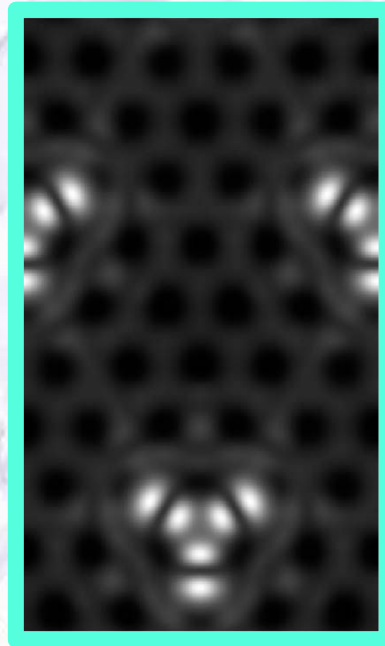
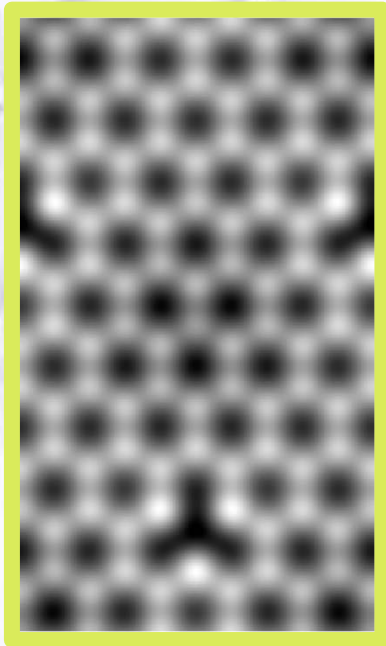
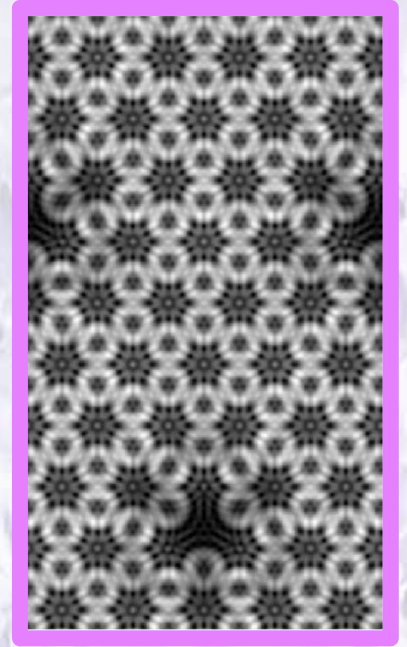
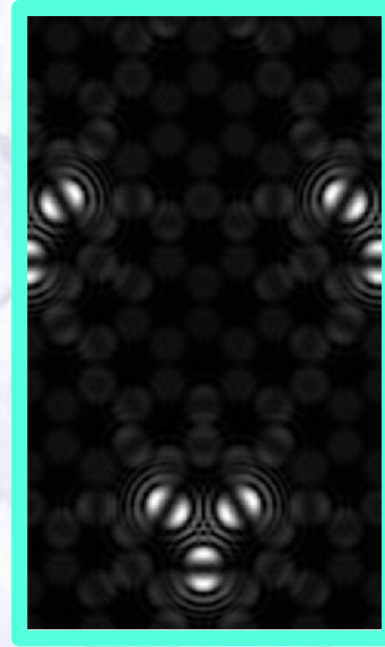
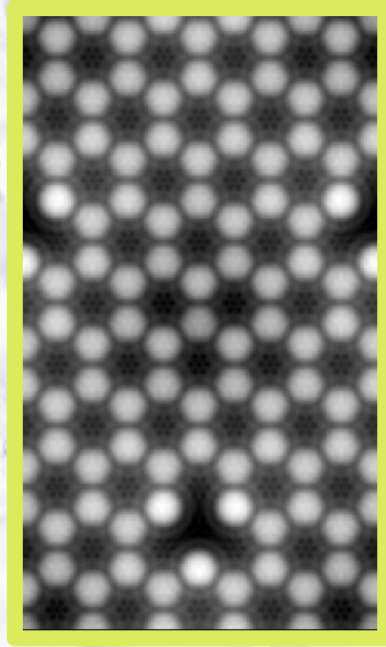


# Reality?

Theory

N-doped  
graphene

Titan G<sup>2</sup> 60-300  
80 keV



L. Pardini, et al.,  
PRL 117, 036801 (2016).

Graphene as substrate ...

# Polarization effect

FWF



$G_0W_0@LDA$

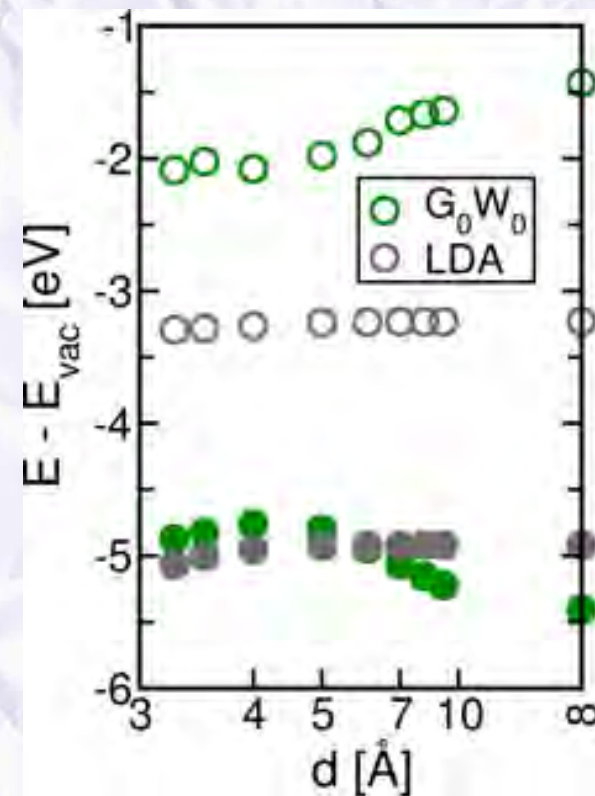
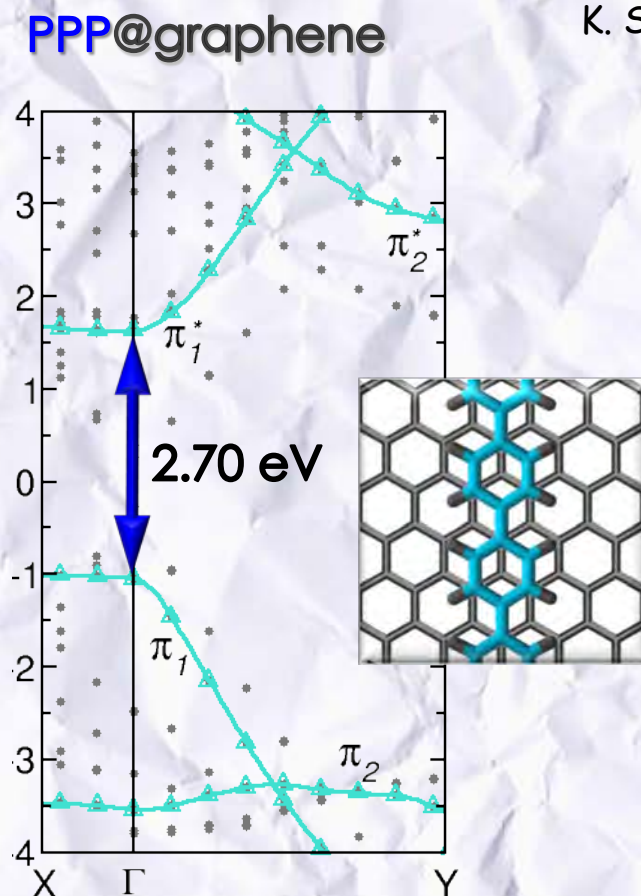
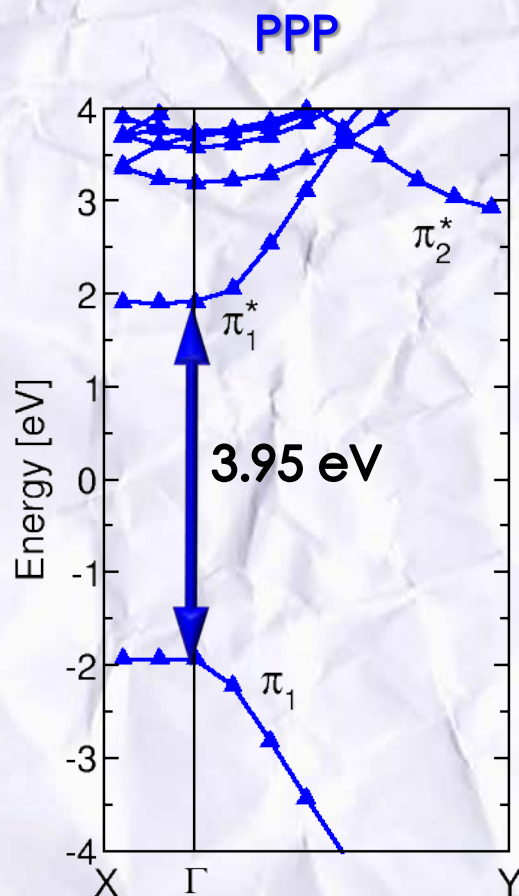
Decrease of gap on adsorption

P. Puschnig, P. Amiri & CD  
PRB 86, 085107 (2012).

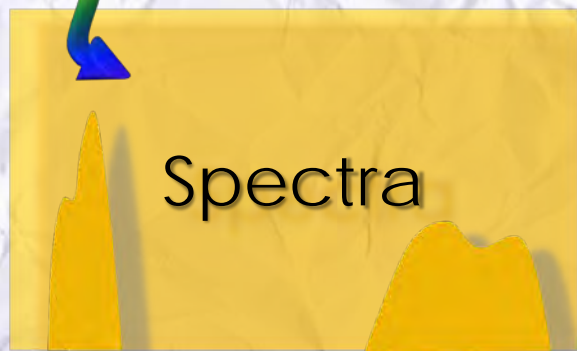
see also

J. Neaton, et al., PRL (2006).

K. S. Thygesen and A. Rubio, PRL (2009).



# State of the art methodology



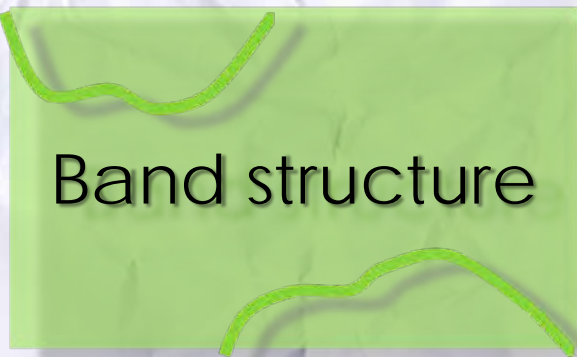
$$\left[ H_{el} + H_{hole} + H_{el-hole} \right] A_{\lambda} = E_{\lambda} A_{\lambda}$$

**Bethe-Salpeter equation**

Many-body perturbation theory

**$G_0W_0$  approximation**

$$\epsilon_{nk}^{QP} = \epsilon_{nk}^{KS} + \langle nk | \Sigma - V_{xc}^{KS} | nk \rangle$$



Density-functional theory

**Kohn-Sham equation**



$$\left[ T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS} \psi_i^{KS}(\mathbf{r})$$

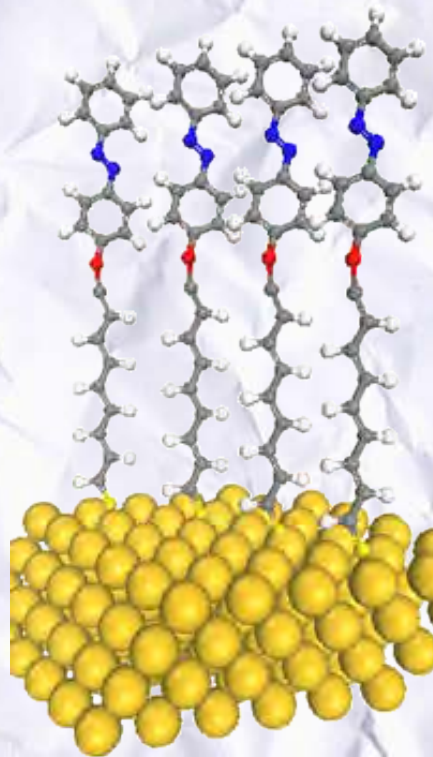
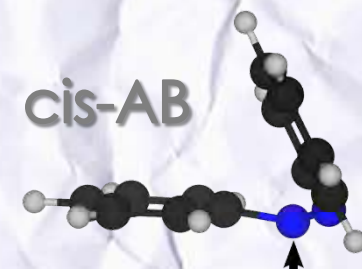
# Molecular switches ...

## Azobenzene SAMs on metals

Switching hampered

Intermolecular coupling in excited state

Interaction with substrate

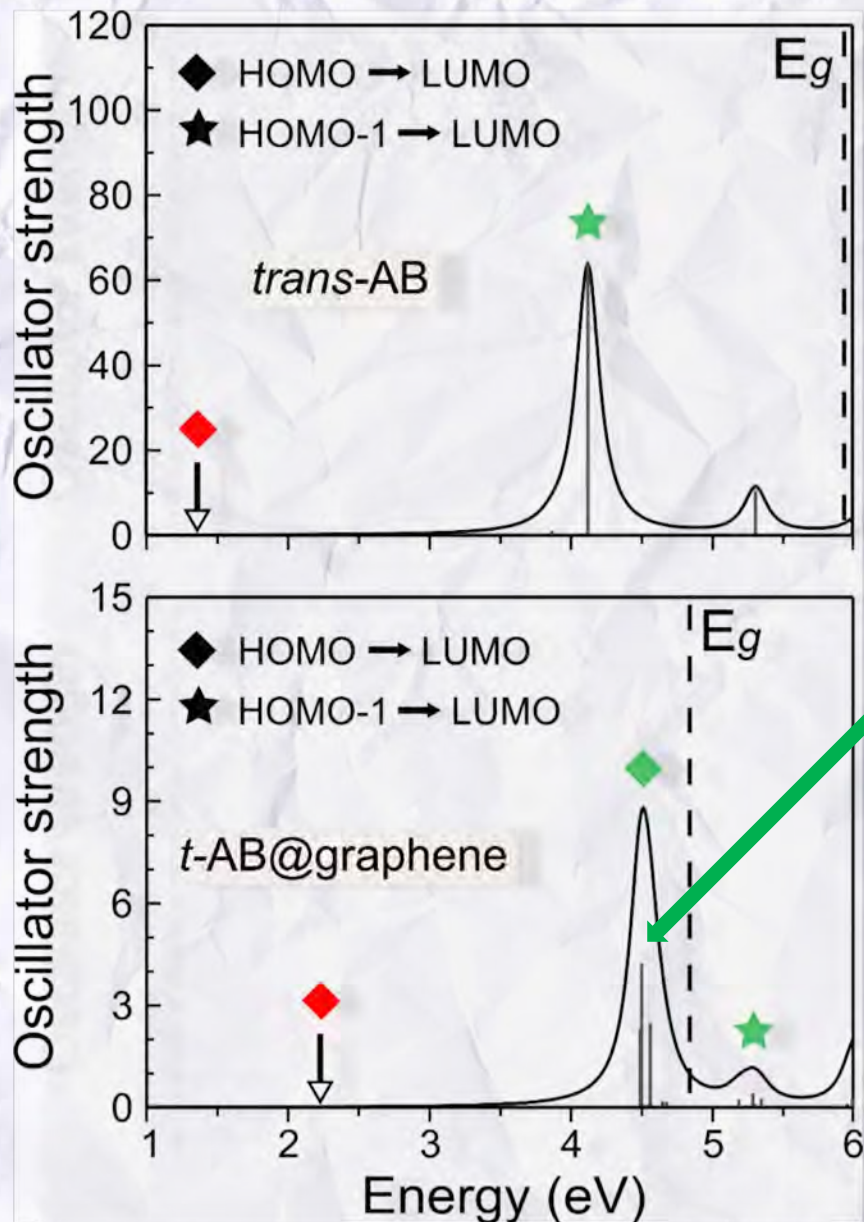


C. Cocchi and C. Draxl  
PRB **92**, 205105 (2105).

C. Cocchi, T. Moldt, C. Gahl,  
M. Weinelt, and C. Draxl  
JCP **145**, 234701 (2016).



# Azobenzene / graphene



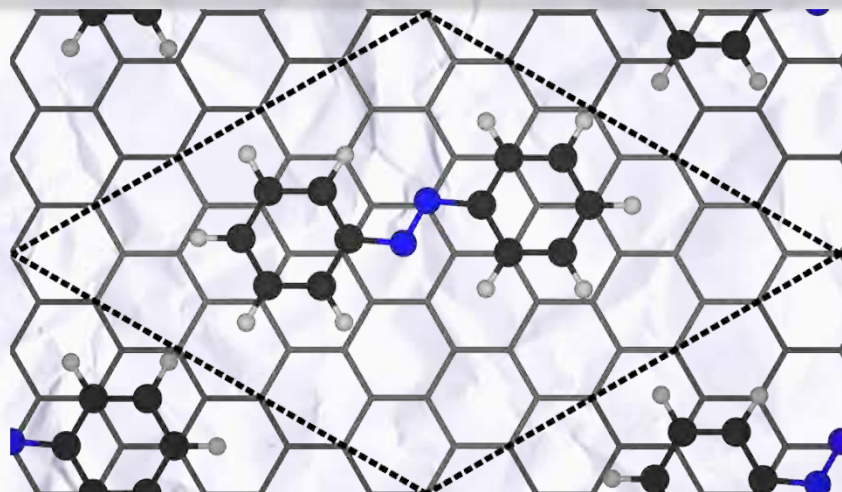
Blue-shift upon adsorption

Polarization reduces gap  
by 1.1 eV

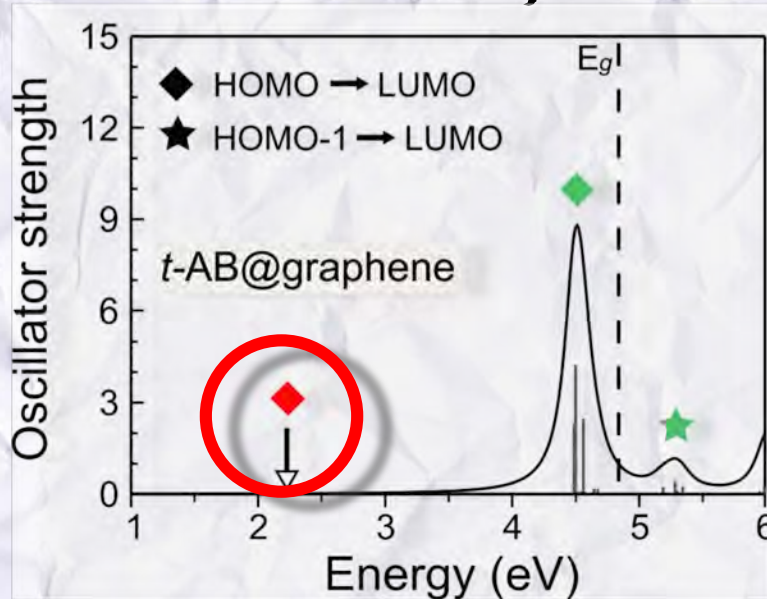
Screening reduces exciton  
binding energy by 2eV

Effects on switching behavior

Loss of symmetry makes  
forbidden transitions allowed



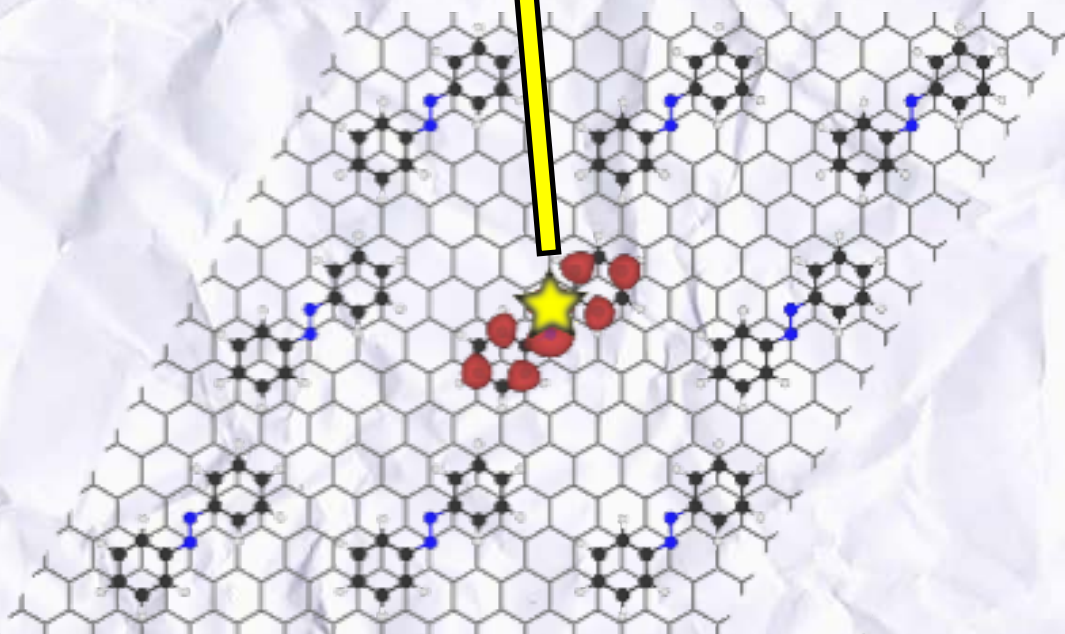
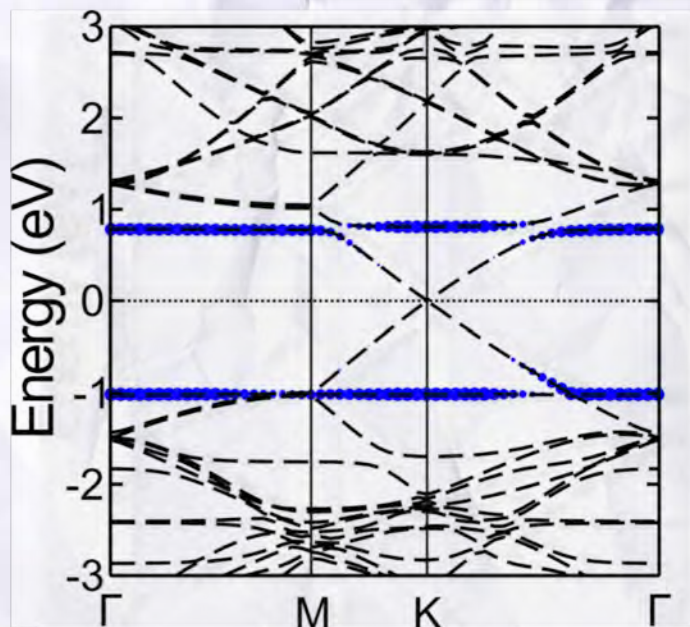
# Azobenzene / graphene



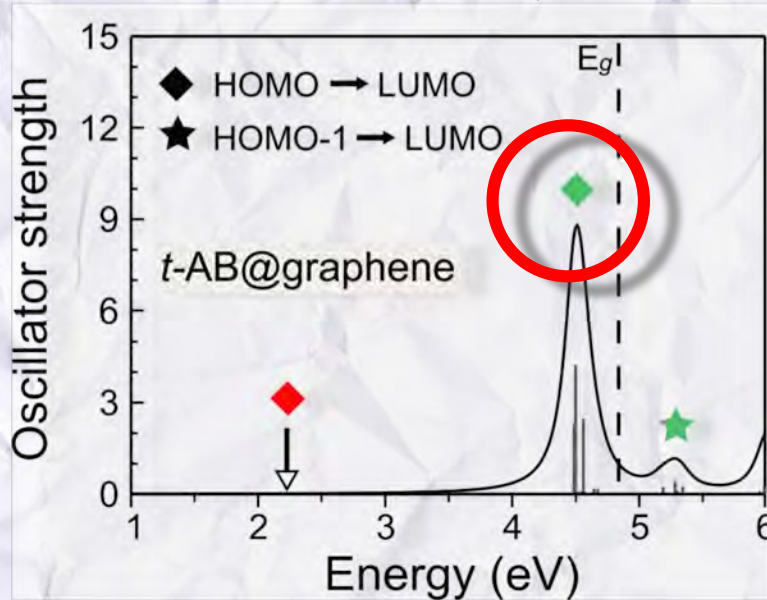
Q. Fu, C Cocchi, D. Nabok,  
A. Gulans, and CD,  
PCCP 19, 6196 (2017).

Exciton wavefunction

$$\phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_e) \psi_v(\mathbf{r}_h)$$



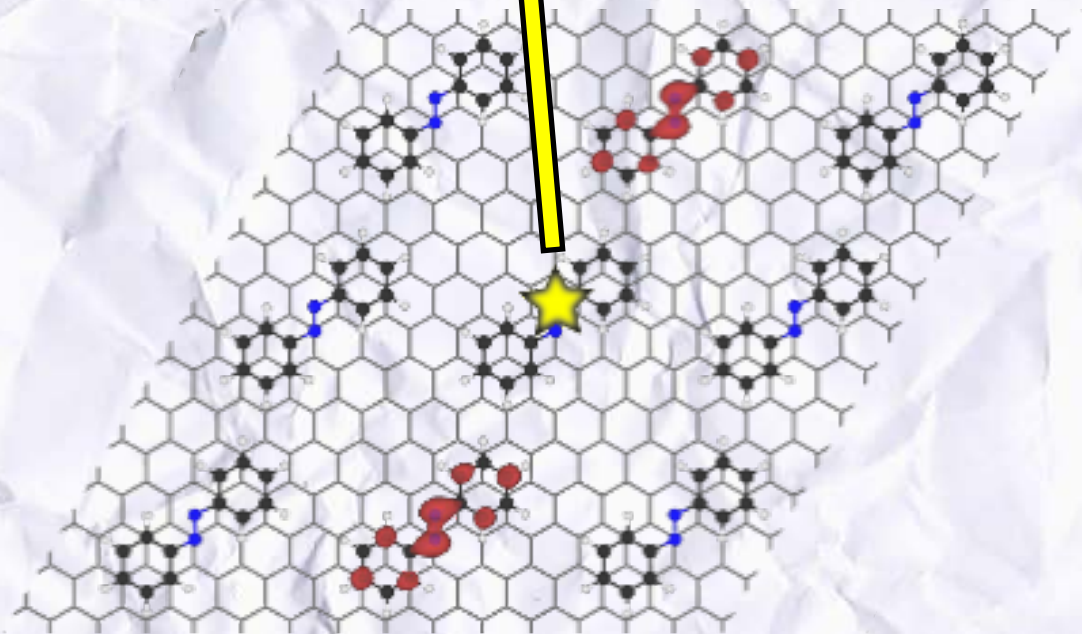
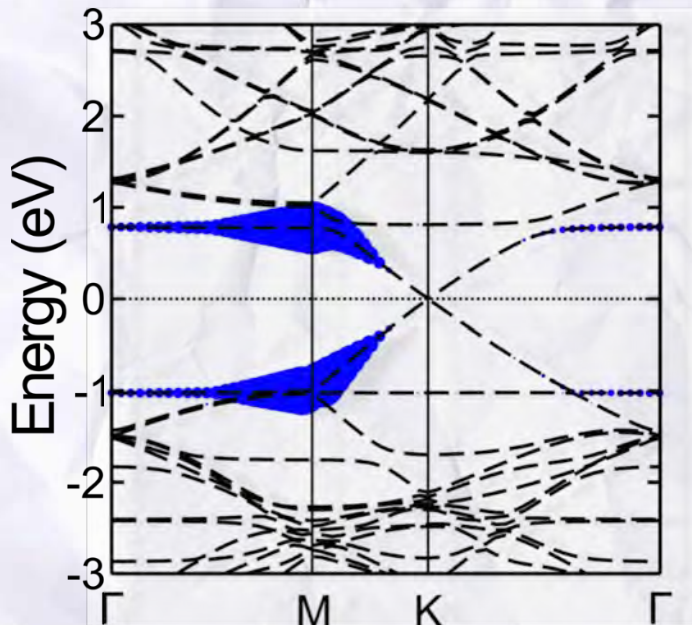
# Azobenzene / graphene



Q. Fu, C Cocchi, D. Nabok,  
A. Gulans, and CD,  
PCCP 19, 6196 (2017).

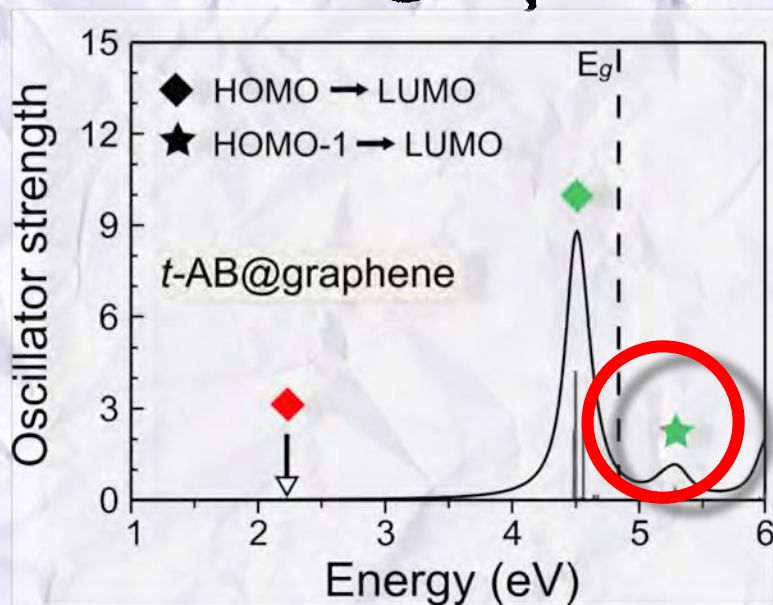
Exciton wavefunction

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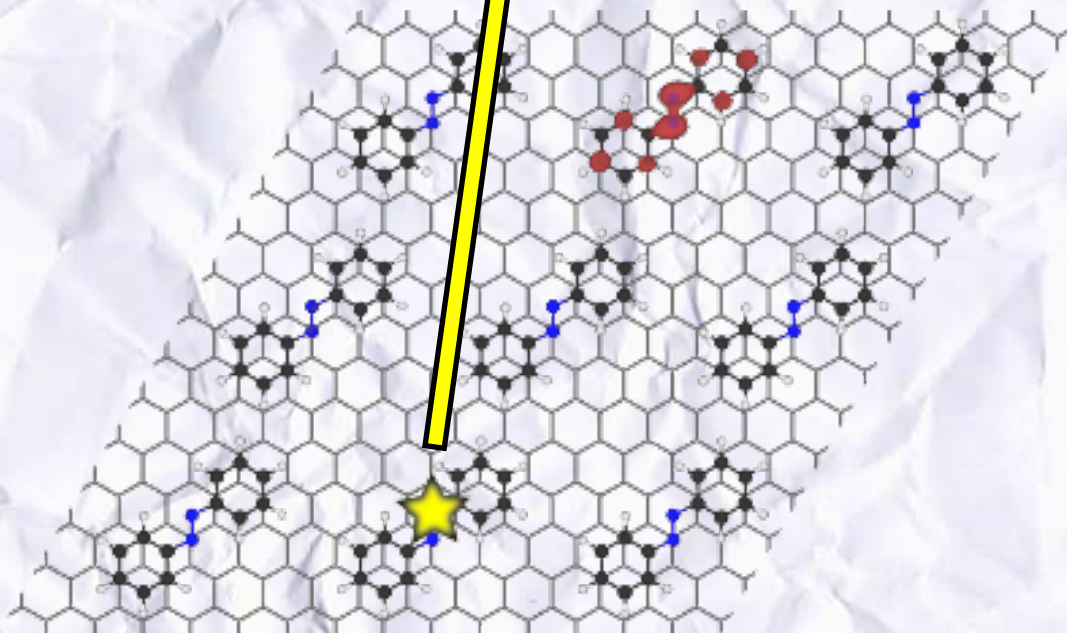
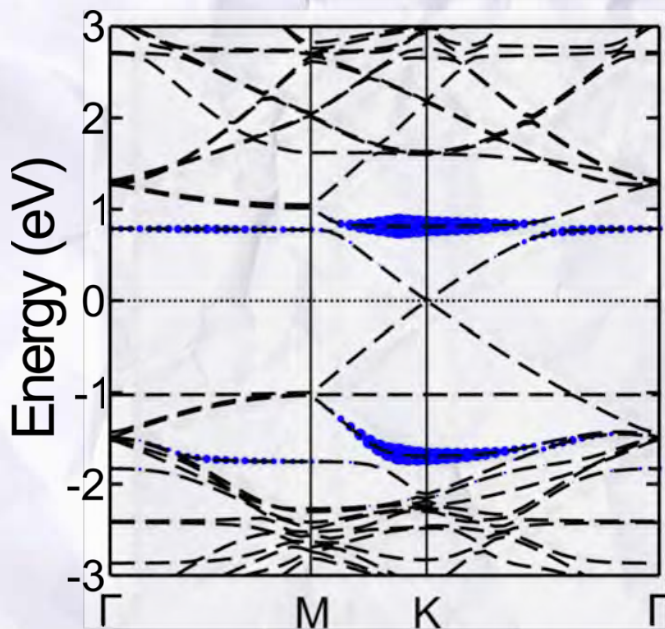
# Azobenzene / graphene

Q. Fu, C Cocchi, D. Nabok,  
A. Gulans, and CD,  
PCCP 19, 6196 (2017).

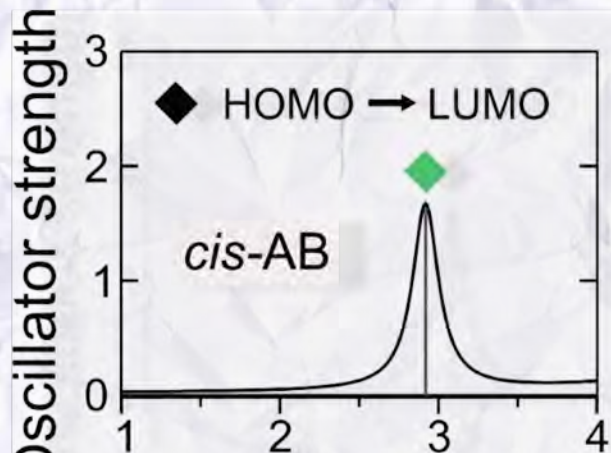
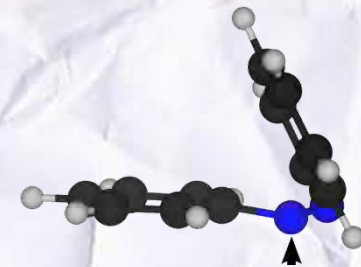


Exciton wavefunction

$$\phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_e) \psi_v(\mathbf{r}_h)$$



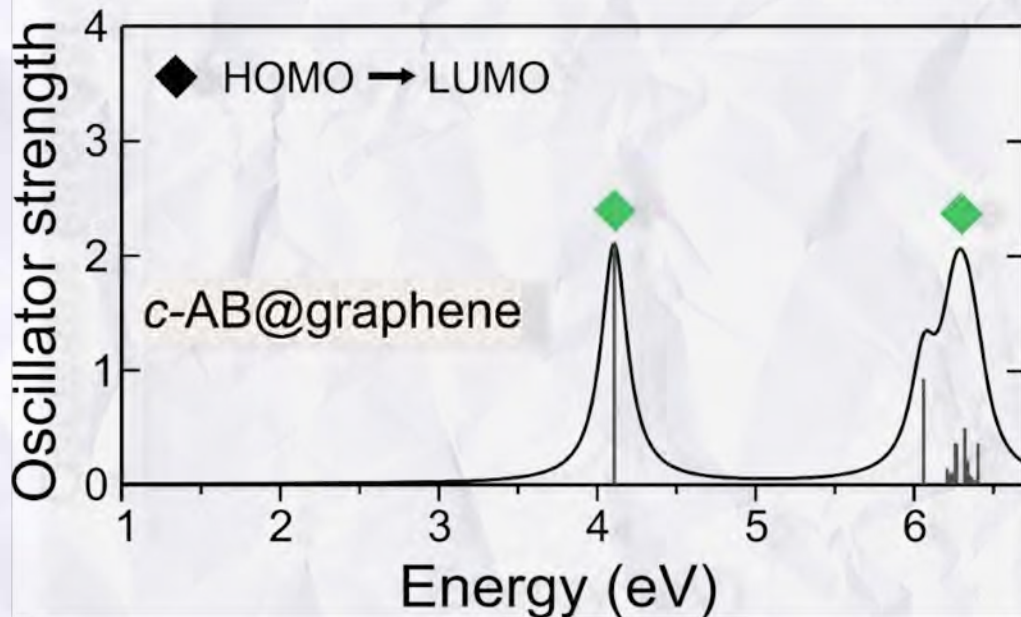
# Azobenzene / graphene



Blue-shift of HOMO-LUMO transition

New features at higher energies

Mediated by graphene substrate



Q. Fu, C Cocchi, D. Nabok,  
A. Gulans, and CD,  
PCCP 19, 6196 (2017).

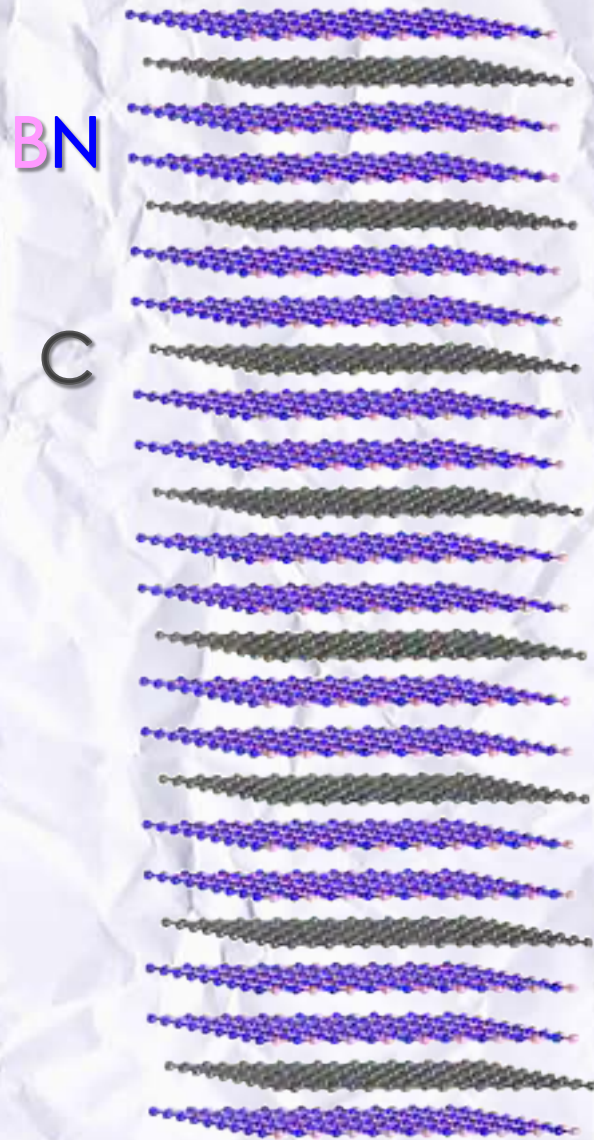
# C/BN heterostructures

Several patterns open  
a gap in graphene

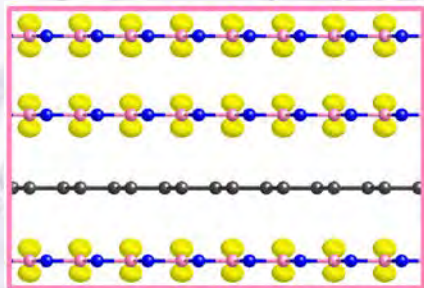
see also R. Quhe *et al.*,  
NPG Asia Materials (2012)



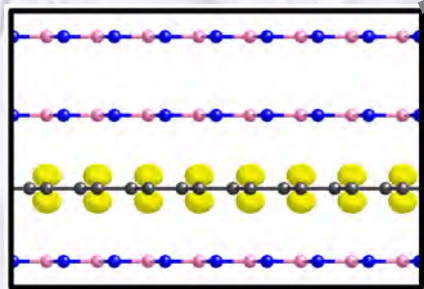
**W. Aggoune, C. Cocchi, K. Rezouali, M. Belkhir, and CD,**  
J. Phys. Chem. Lett. 8, 1464 (2017).



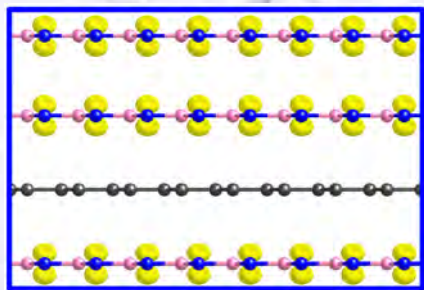
# C/BN heterostructures



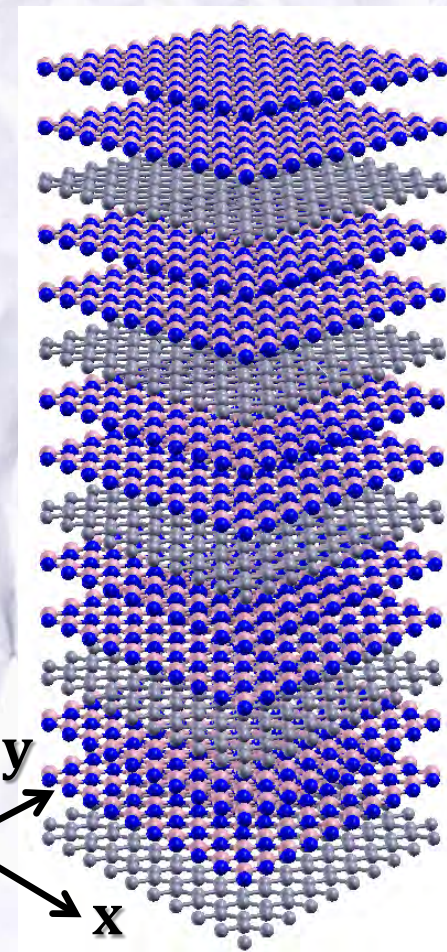
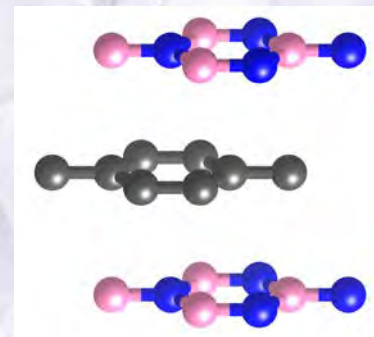
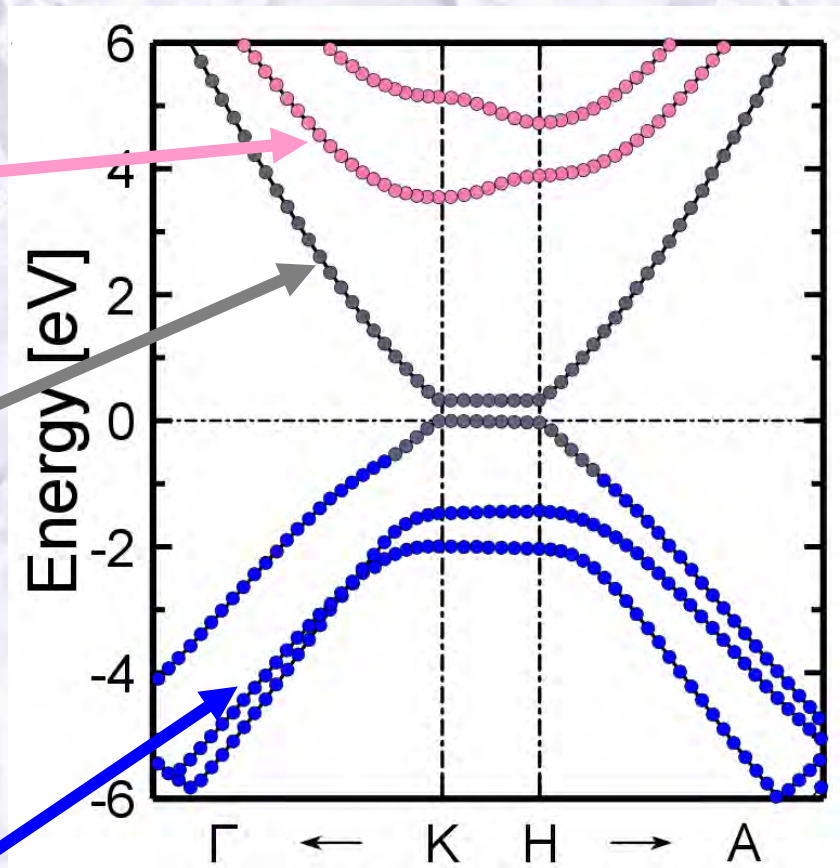
Boron



Carbon



Nitrogen

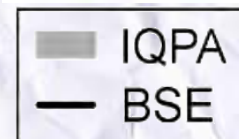
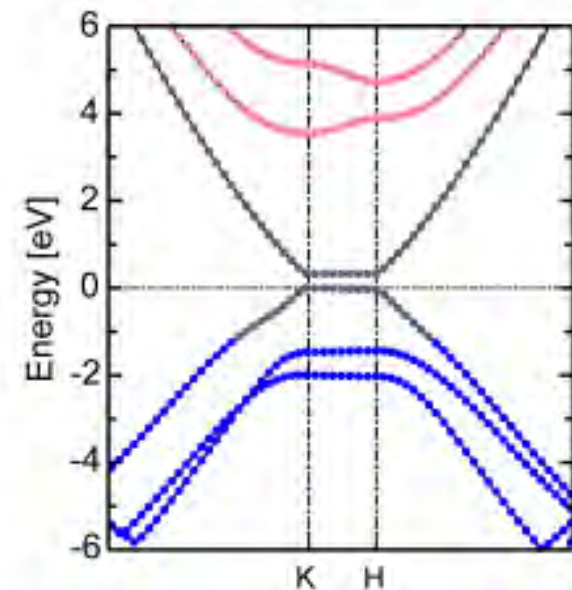
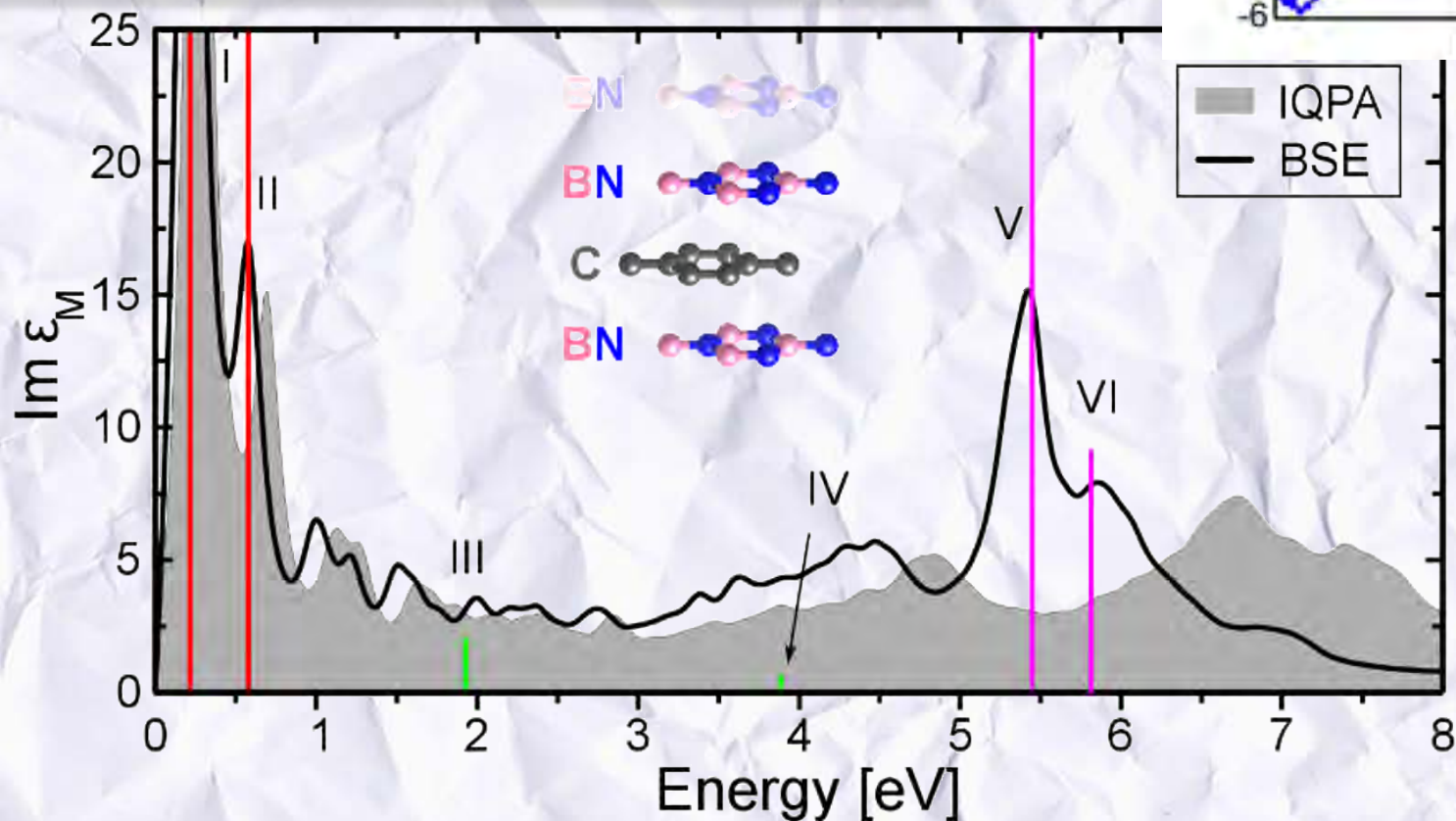


# C/BN heterostructures

Intense peaks in the IR region

Finite absorption in the visible

Excitons in the near-UV range



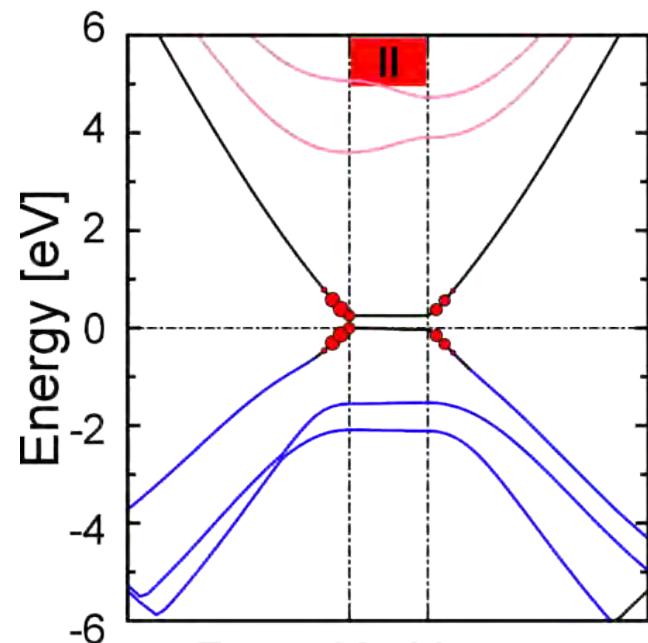
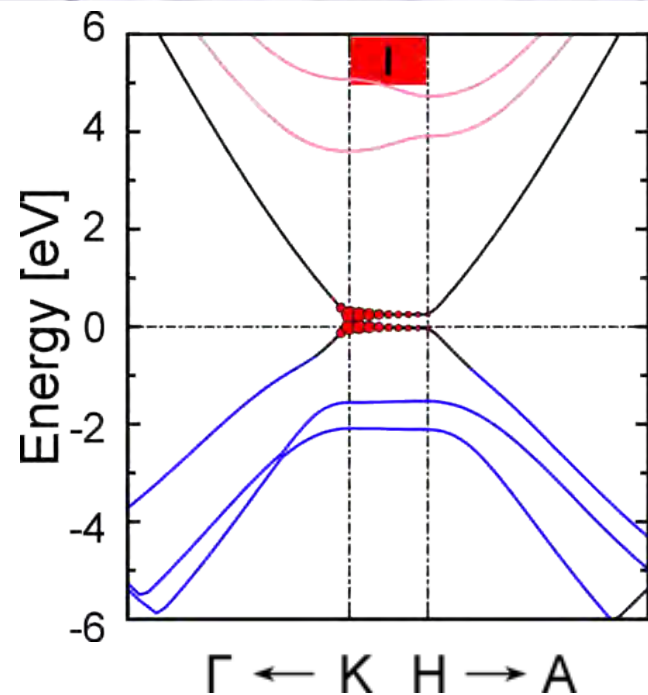
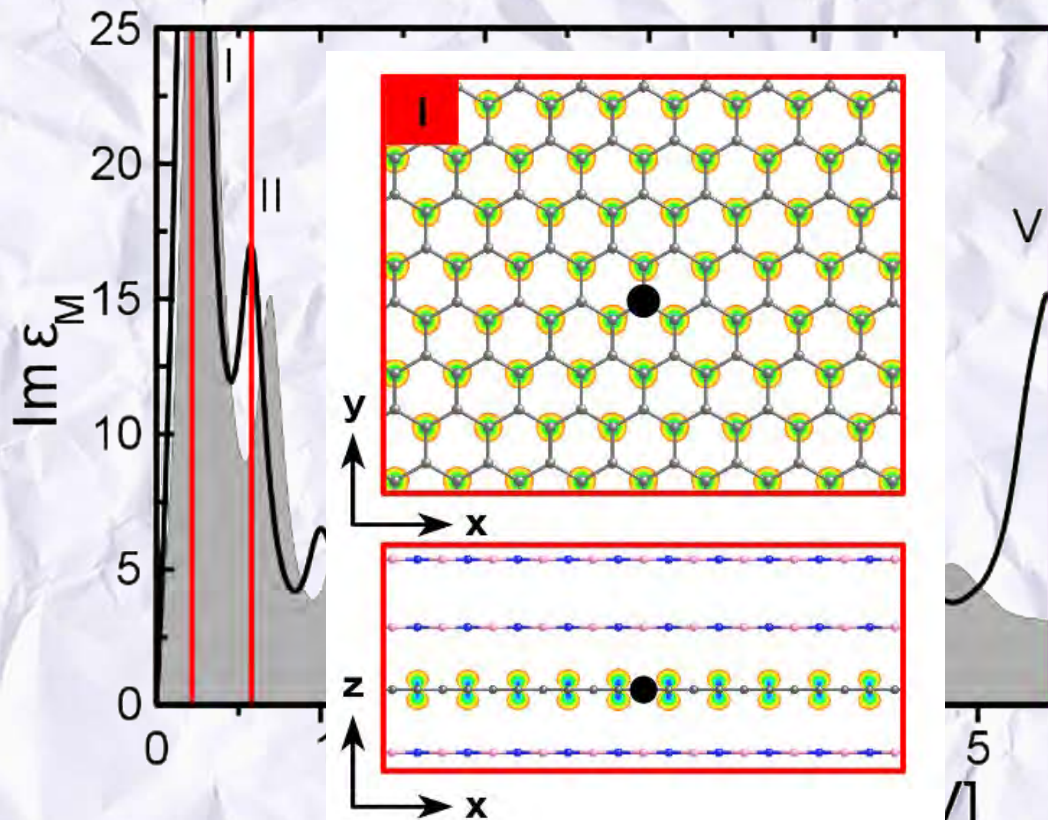


# C/BN heterostructures

I, II: graphene  $\leftrightarrow$  graphene

Weakly bound  $\pi$ - $\pi^*$  excitations

Min  Max

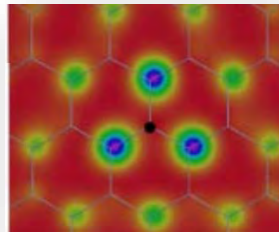
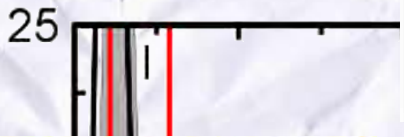


# C/BN heterostructures

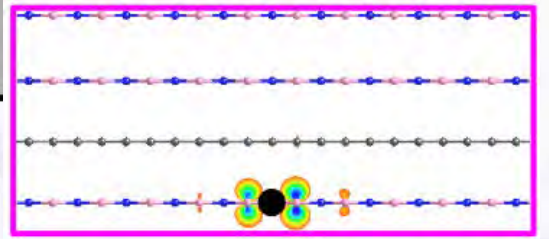
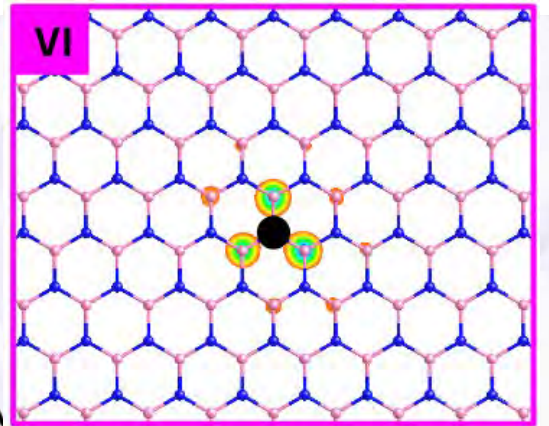
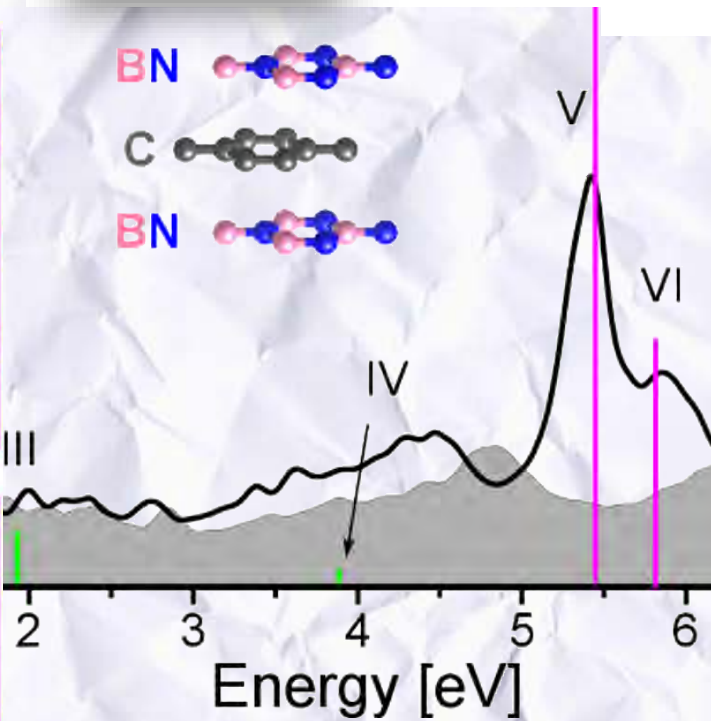
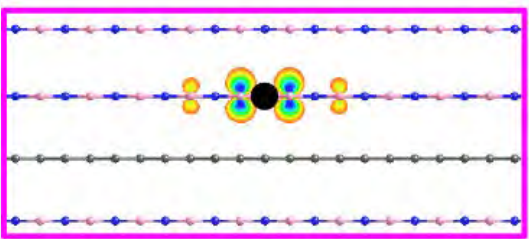
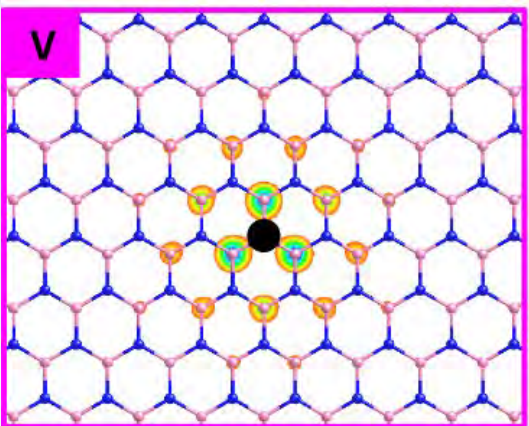
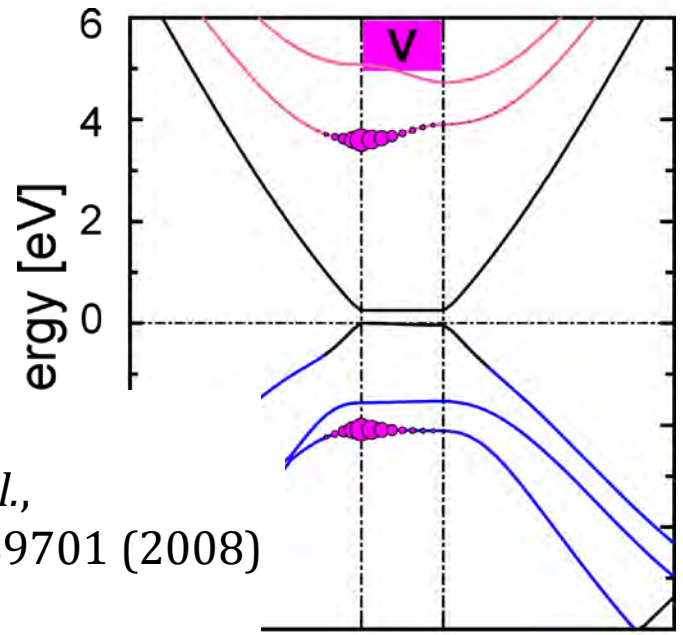
V, VI: BN  $\leftrightarrow$  BN

Strongly bound intralayer exciton

Like in h-BN bulk



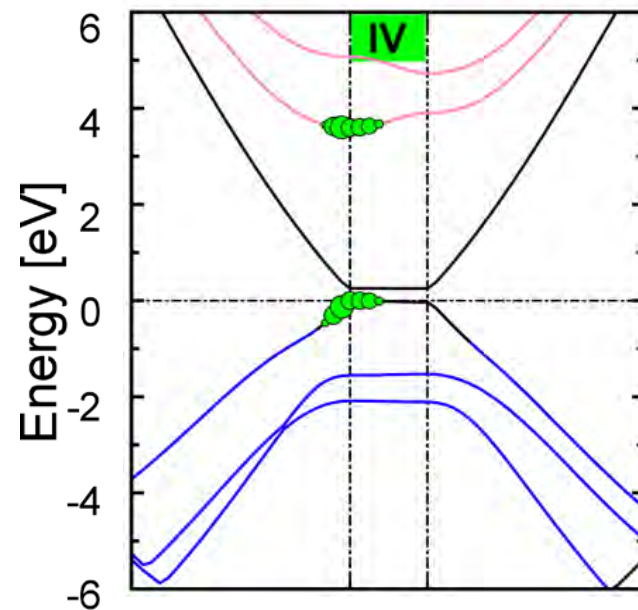
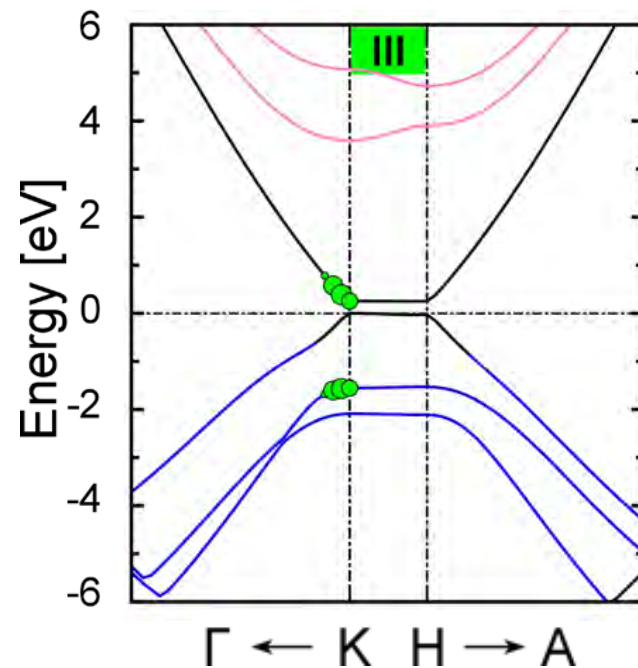
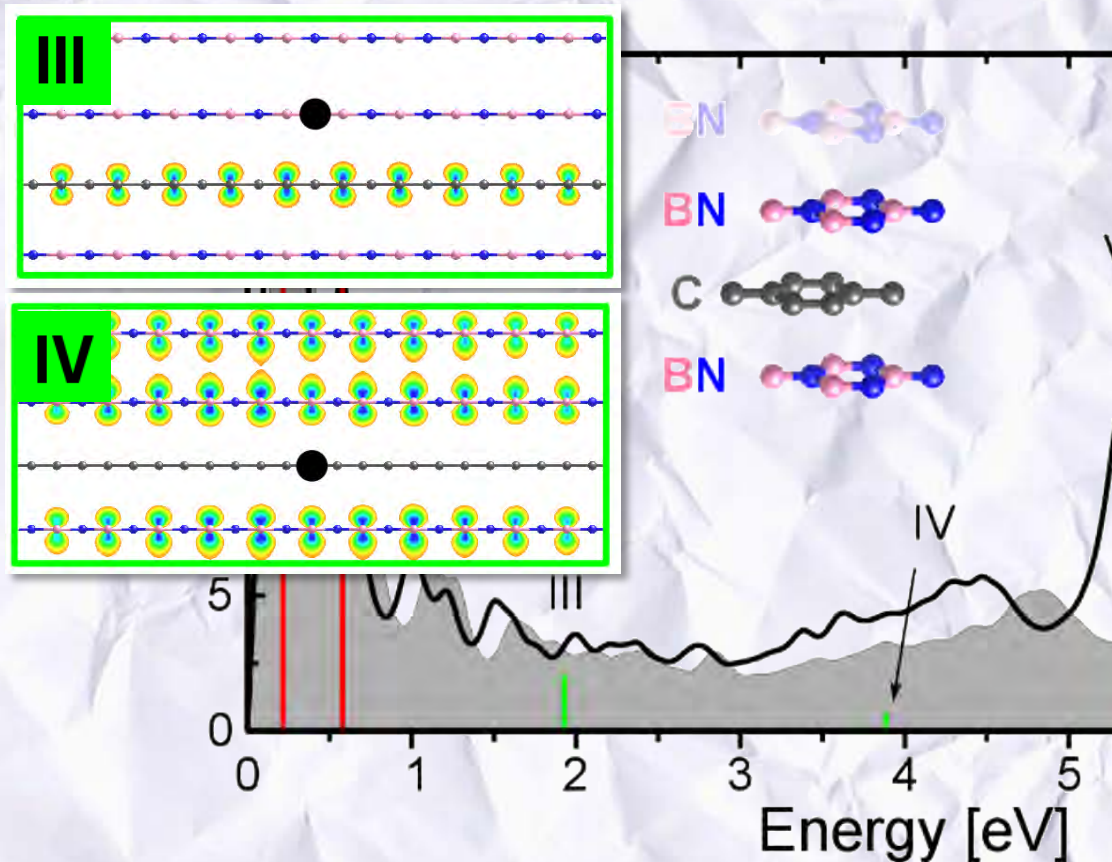
L. Wirtz *et al.*,  
PRL **100**, 189701 (2008)



# C/BN heterostructures

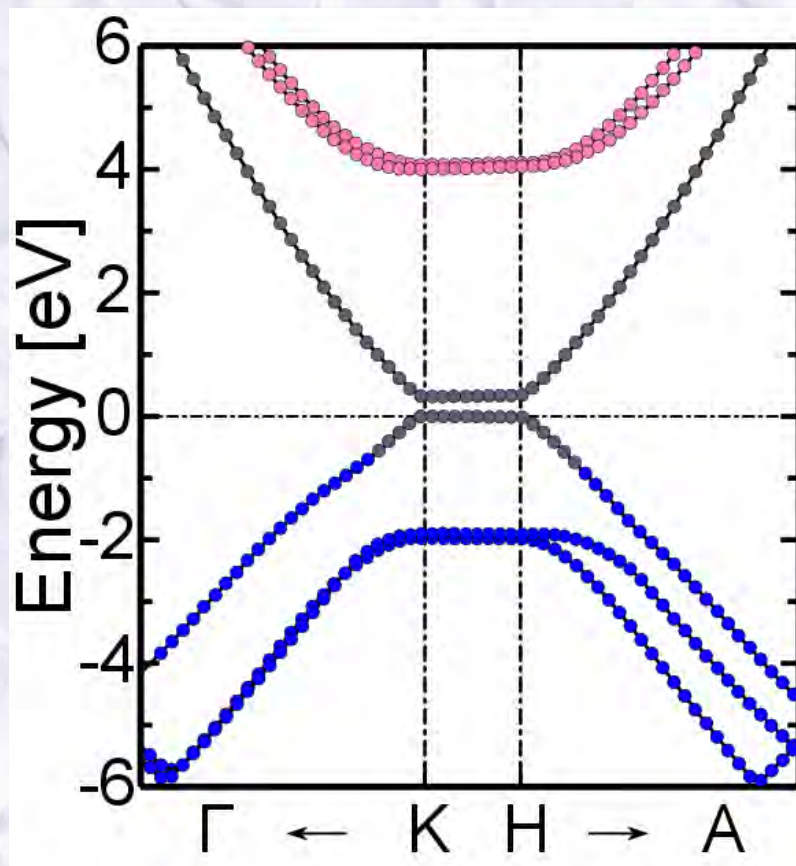
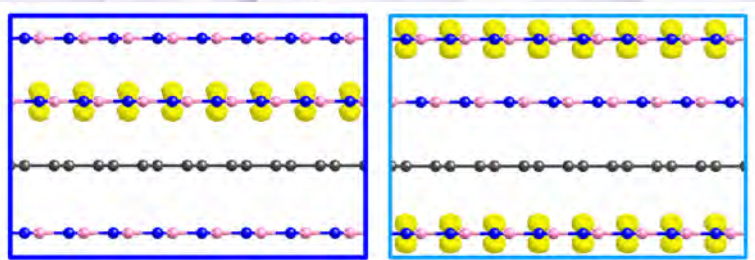
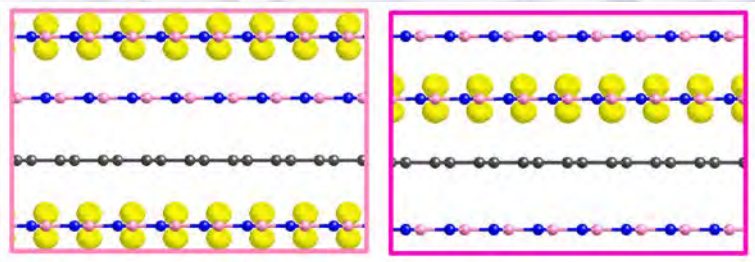
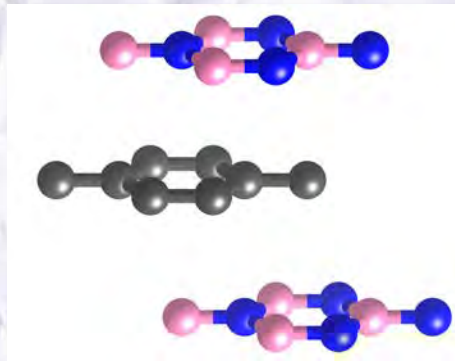
III, IV: graphene  $\leftrightarrow$  BN

Weakly bound CT excitations



# C/BN heterostructures

Tuning the spectrum by stacking

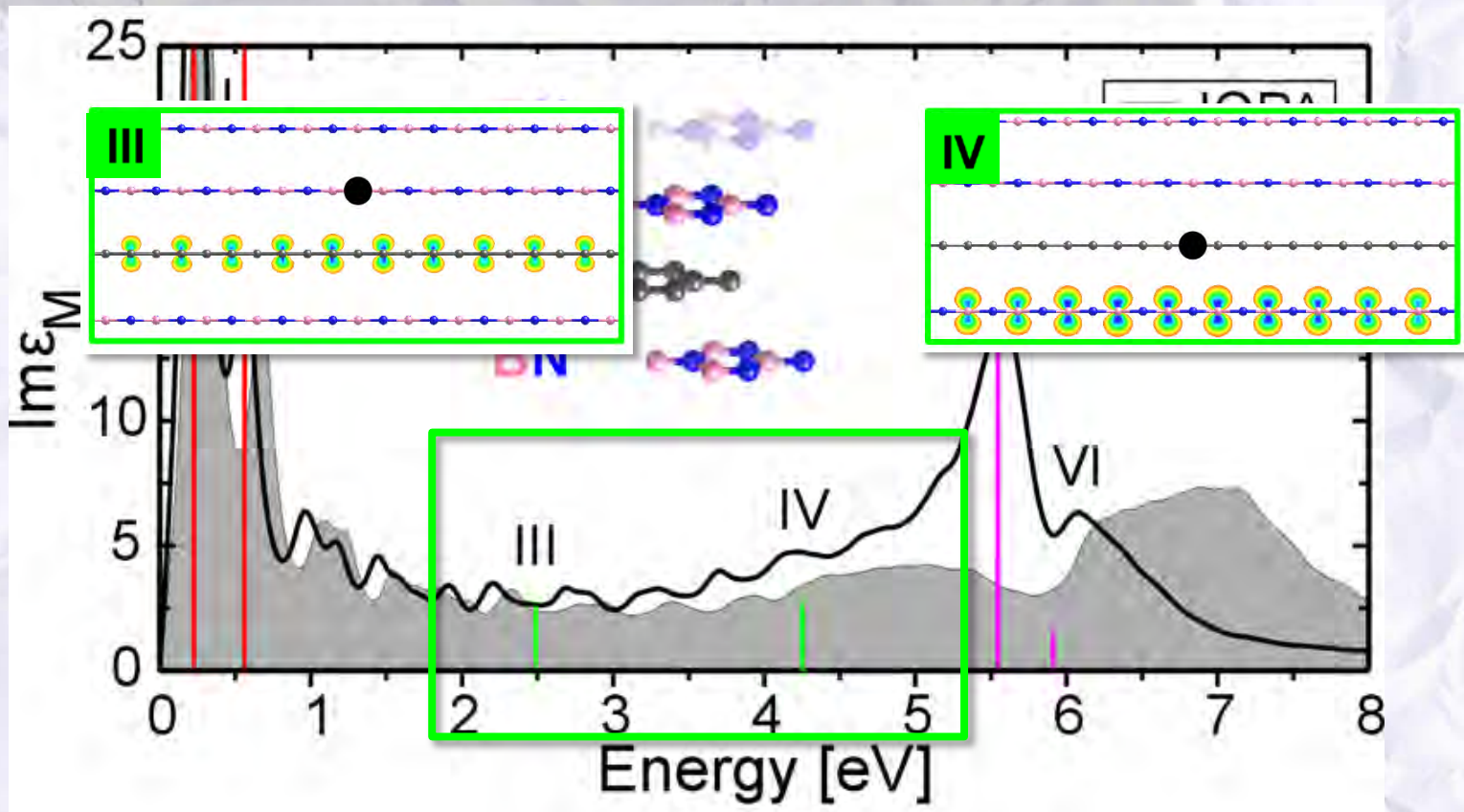


# C/BN heterostructures

## Tuning the spectrum by stacking

Main spectral features preserved

Most significant differences in the UV-visible



# Our instrument ...

<http://exciting-code.org>

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl

**exciting**: a full-potential all-electron package implementing density-functional theory and many-body perturbation theory  
J. Phys: Condens. Matter 26, 363202 (2014).

The logo for the 'exciting' software package, featuring the word 'exciting' in a lowercase, sans-serif font. The letter 'i' is stylized with a yellow and orange flame-like graphic behind it.

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## The exciting Code

## Download exciting

**exciting** is a full-potential all-electron density-functional-theory package implementing the families of linearized augmented planewave methods. It can be applied to all kinds of materials, irrespective of the atomic species involved, and also allows for exploring the physics of core electrons. A particular focus are excited states within many-body perturbation theory.

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl, "exciting – a full-potential all-electron package implementing density-functional theory and many-body perturbation theory", J. Phys.: Condens. Matter **26**, 363202 (2014)



Documentation page  
**How exciting! Hands-on with exciting**

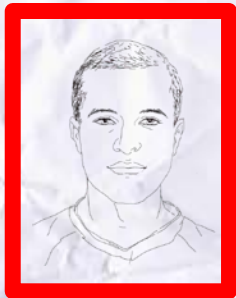
## Developers Team

- [exciting hub at the Humboldt Uni](#)
- [Current developers](#)

## Events

# Teamwork

Thanks!



Wahib Aggoune



Lorenzo Pardini



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