

# Electronic Structure of Pentacene: A comparison of DFT and GW results with photoemission data

Daniel Lüftner<sup>1</sup>, Thomas Ules<sup>2</sup>, Georg Koller<sup>2</sup>, Michael G. Ramsey<sup>2</sup> and Peter Puschnig<sup>1</sup>

<sup>1</sup>Chair of Atomistic Modelling and Design of Materials, Montanuniversität Leoben, Austria

<sup>2</sup>Institute of Physics, Surface and Interface Physics, Karl-Franzens Universität Graz, Austria

UNI  
GRAZ

## Abstract

Pentacene (5A) is of great interest due to its application as organic semiconductor in thin films devices such as organic field-effect transistor. Here we investigate the electronic structure of different arrangements of 5A molecules within the framework of density functional theory (DFT) (1). We also calculate corrections to the Kohn-Sham (KS) orbital energies by many-body perturbation theory using the  $G_0W_0$  approximation. We show that  $G_0W_0$  corrections greatly improve KS band gaps and demonstrate that the  $G_0W_0$  gaps are strongly dependent on the local environment of the 5A molecule, an effect which is absent in the KS orbital energies. Moreover, we have simulated the angular dependence of the photocurrent resulting from a angle-resolved photoemission spectroscopy (ARPES). By treating the final state of the photoemission process as plane wave(2), we obtain excellent agreement between our simulated  $k_x k_y$ -momentum maps and experimental results obtained for a highly oriented monolayer of pentacene on Ag(110).

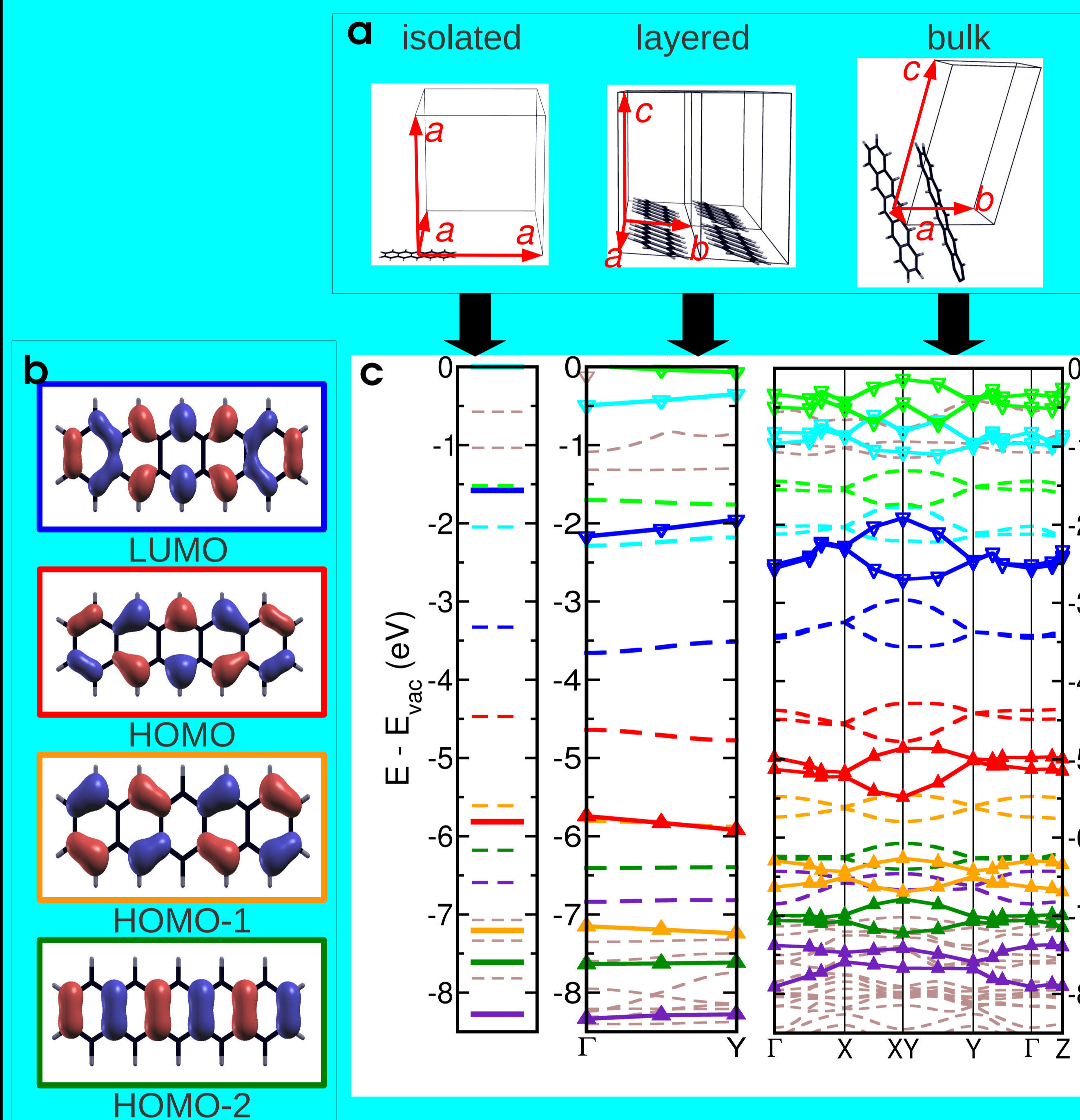
## Computation of Photoemission Intensity

We use the so called one-step-model, whereat the excitation occurs in a single step from the initial Bloch state into a so called "time reversed LEED state" final state. The ARPES intensity  $I(\theta, \phi; E_{kin})$  is then given by a Fermi golden rule formula(3)

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

By approximating the final state by a free electron state, the evaluation of the matrix elements is greatly simplified and turns out to be proportional to the Fourier transform of the initial state wave function. Thus, the square root of the measured photocurrent is proportional to the absolute value of the orbital in reciprocal space. Thereby, we have to take a hemispherical cut with a reciprocal radius proportional to the square root of the kinetic energy through the Fourier transformed molecular orbital.

## Comparison: DFT vs. GW

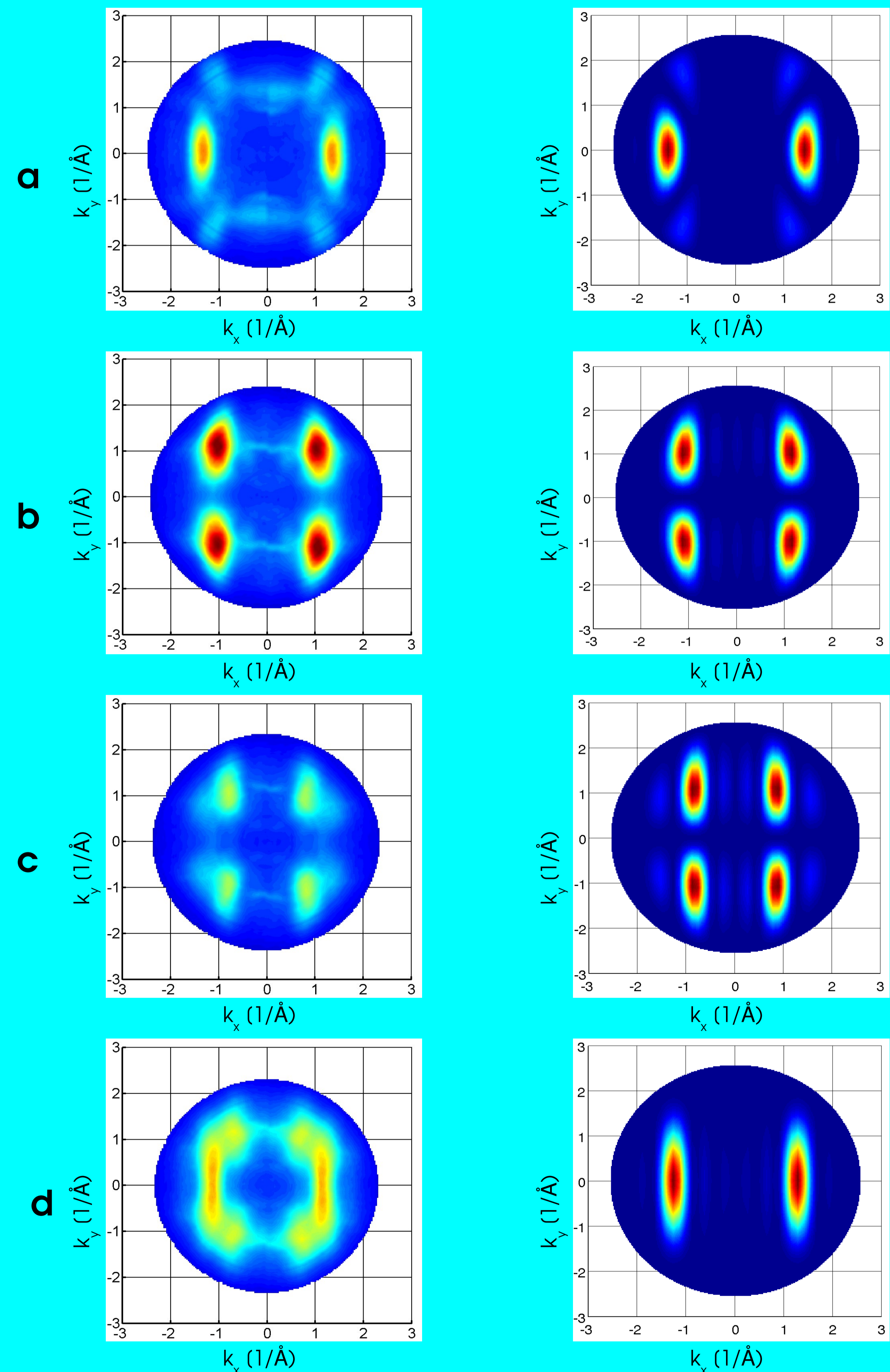


**Fig.1:** (a): Unit cells used for GW calculations of an isolated molecule (left) a layer of molecules (middle) and the bulk crystal structure of 5A (right) (b): Kohn-Sham orbitals of an isolated 5A molecule (c): Kohn-Sham and GW-band structure for isolated (left) layered (middle) and bulk (right) pentacene. Dashed line shows the KS result and the continuous lines the correspond to the GW results.

### Computational Details

We utilize the ABINIT code for both the self-consistent KS and the non-self consistent  $G_0W_0$  calculations. We employ the plasmon-pole model according to Hybertson and Louie(4) and use the energy-effective technique to circumvent the summation over empty states(5). For the isolated molecule and the pentacene layer, we cut off the Coulomb potential within the sphere and slab geometries, respectively. For slab (bulk) calculations a k-mesh of  $4 \times 4 \times 1$  ( $4 \times 4 \times 3$ ) turned out to lead converged  $G_0W_0$  corrections within 0.1 eV.

## Comparison: Theory vs. Experiment



**Fig.2:** Various molecular orbitals in reciprocal space as obtained in ARPES (left) and from DFT (right), respectively (a): LUMO (b): HOMO (c): HOMO-1 (d): HOMO-2

## Acknowledgments

This work is supported by the Austrian Science Fund (FWF), Project S97, Nationales Forschungsnetzwerk (NFN) „Interface Controlled and Functionalized Organic Films“, and project P23190-N16, “Understanding photoemission of organic molecular films”.

FWF

## References

- (1) X. Gonze et al., First-principles computation of material properties: the ABINIT software project, *Comput. Mater. Sci.* **25**, 478 (2002).
- (2) P. Puschnig, S. Berkebile, A. J. Flemming, G. Koller, K. Emtsev, T. Seyller, J. D. Riley, C. Ambrosch-Draxl, F. P. Netzer and M. G. Ramsey, *Science* **326**, 702 (2009).
- (3) P. J. Feibelman and D. E. Eastman, *Phys. Rev. B* **10**, 4932 (1974).
- (4) M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986).
- (5) Berger et al., *Phys. Rev. B* **82**, 041103 (2010)