Pentacene/Ag(110): A comparison of DFT and GW results with photoemission data

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Abstract

We present a combined experimental and theoretical study of the electronic structure of a highly ordered monolayer of pentacene on Ag(110). Experimentally, the valence electronic structure is studied by angle-resolved photoemission spectroscopy. Using a toroidal electron energy analyzer, the complete k_x, k_y dependence of the photocurrent I in the binding energy range from the Fermi level to 3.5 eV is measured. By comparing this data cube $I(kx, ky, Eb)$ with momentum maps of various pentacene molecular orbitals calculated by density functional theory (DFT), we unambiguously identify four molecular states between the Fermi level and the top of the Ag d-band. This allows us to investigate in detail their energetic positions, broadenings, and modifications in orbital shapes upon adsorption. Moreover, we have calculated the electronic structure of different geometric arrangements of pentacene molecules within the framework of density functional theory (DFT) and -- on top of that -- the G_0W_0 approximation. We show that G_0W_0 gaps strongly depend on the local environment, an effect which is absent in DFT orbital energies. Finally, we compare the orbital energies from DFT and G_0W_0 calculations to the experimental values obtained for the pentacene monolayer on Ag(110).

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): KohnSham orbitals of an isolated 5A molecule (c): KohnSham and GW-bandstructure 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.

Density of states

Fig.2:(a): DOS as obtained from photoemission experiment (b): Partial DOS from DFT calculations including Orbital-resolved DOS.

The orbital-resolved DOS is calculated by minimization of

$$\sum_{i,j}\left[I_{i,j}(E_b) - \sum_{n=1}^{4} a_n(E_b)\Phi_{i,j}^n\right]^2$$

with respect to a_n, wherein $I_{i,j}$ represents the intensity in the E, k_x, k_y-space for the whole system: molecule plus substrate and $\Phi_{i,j}$ the intensity in k_x, k_y for the isolated molecule.
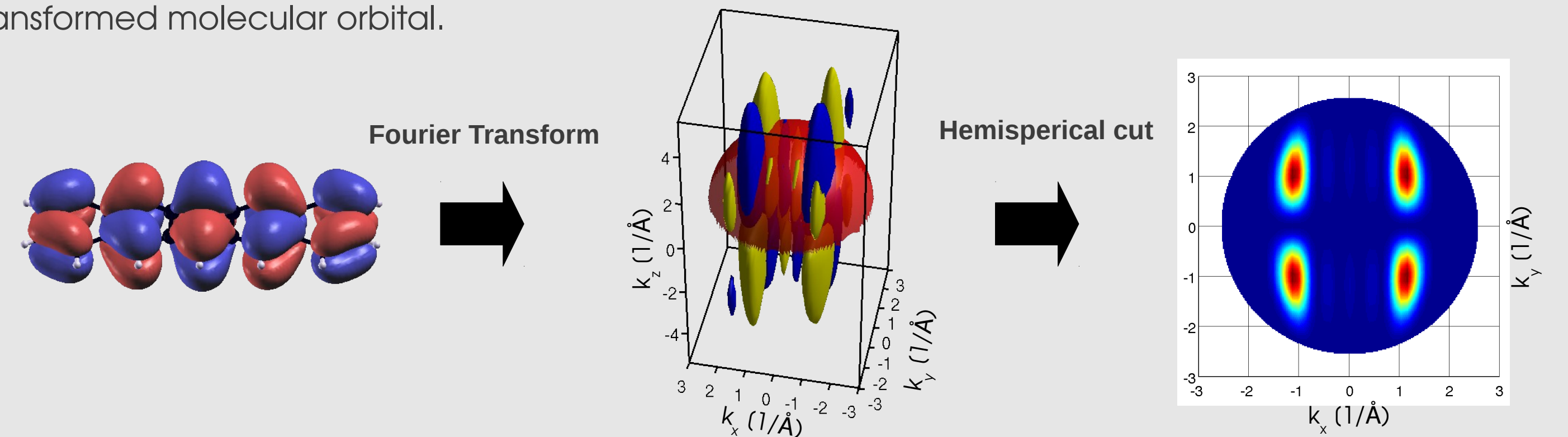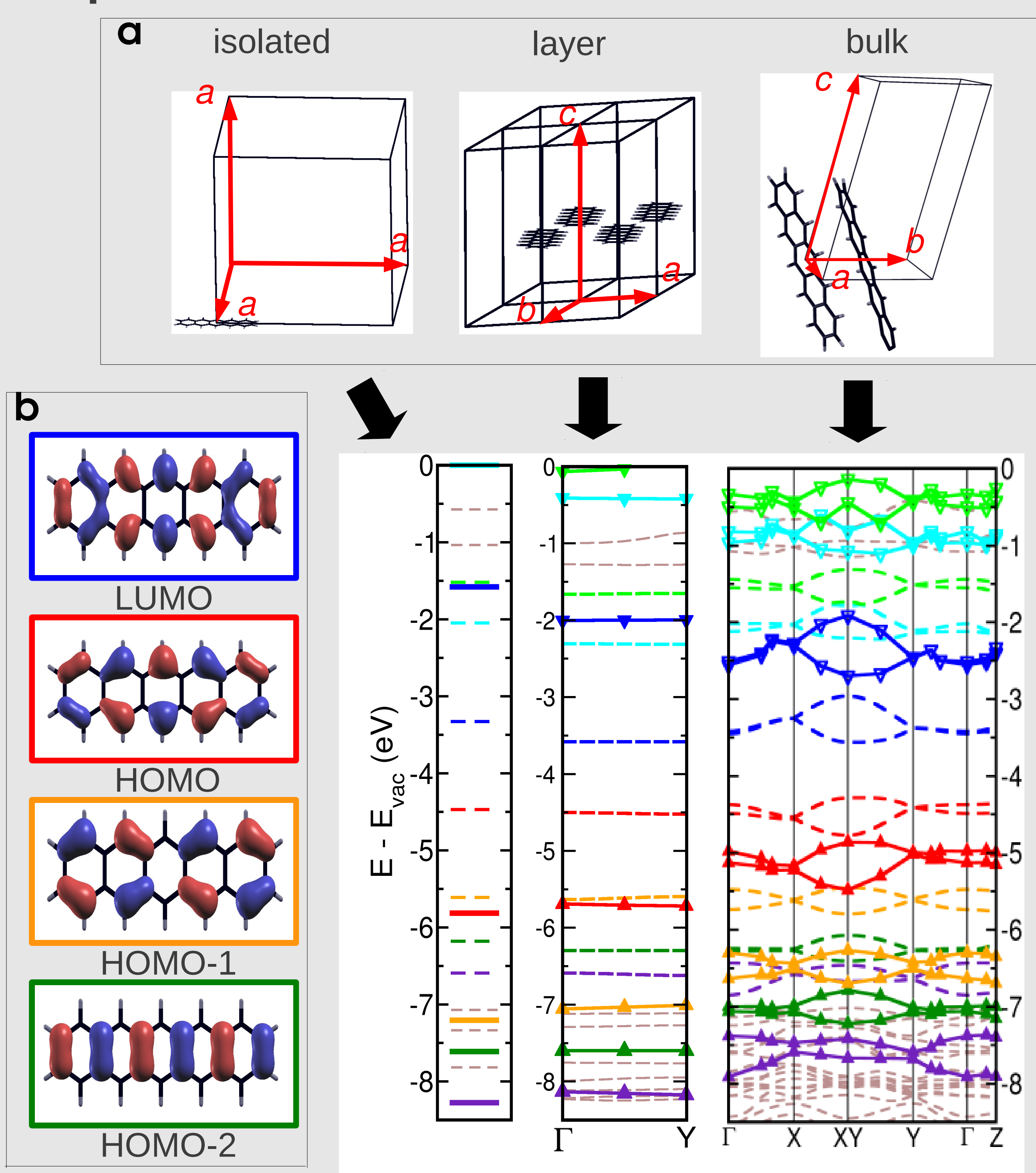
Acknowledgments

Computation of Photoemission Intensity

We use the so called one-step-model, whereat the excitation occurs in a single step from initial Bloch state in 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 (1):

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

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 (2). 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.
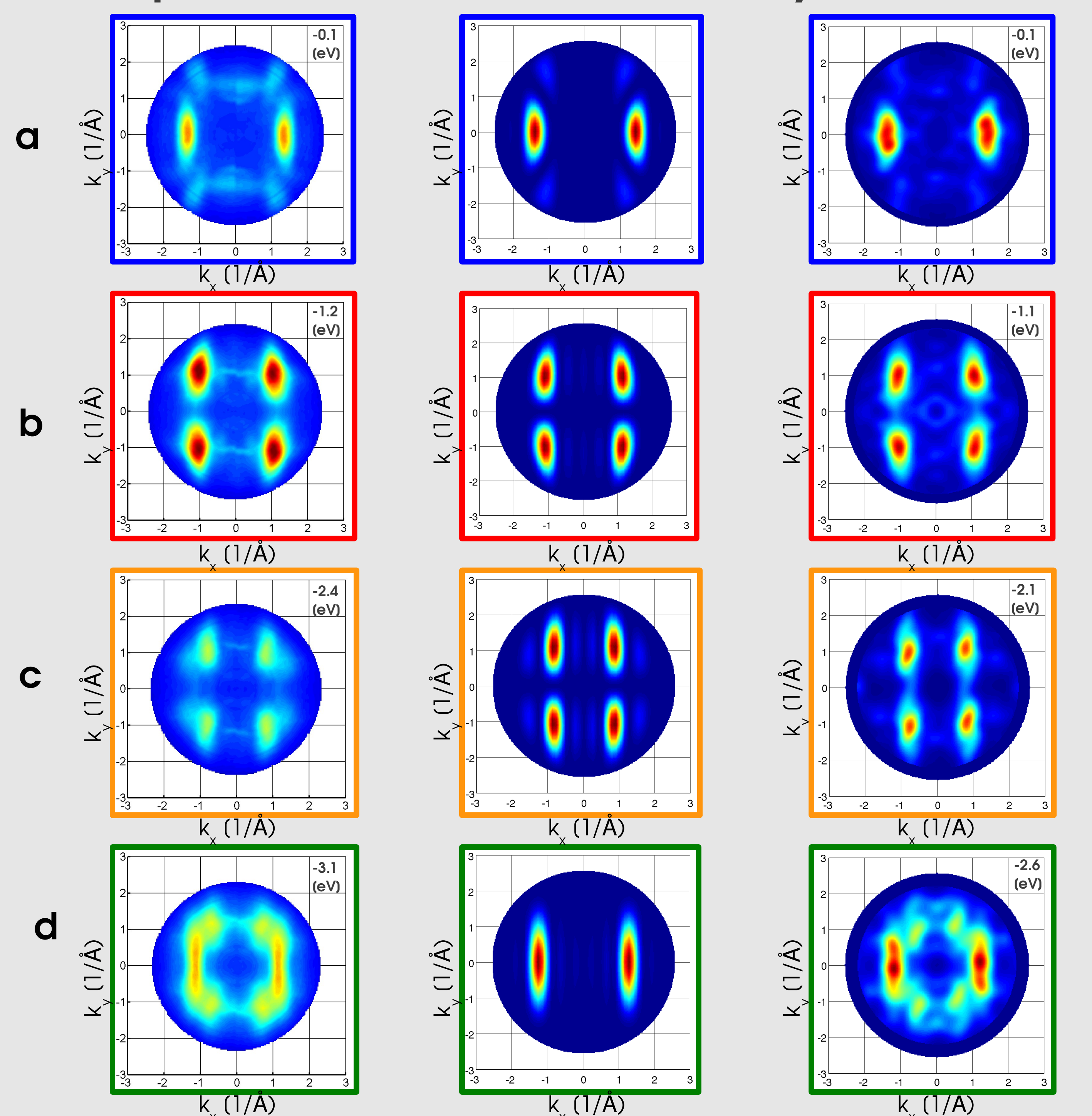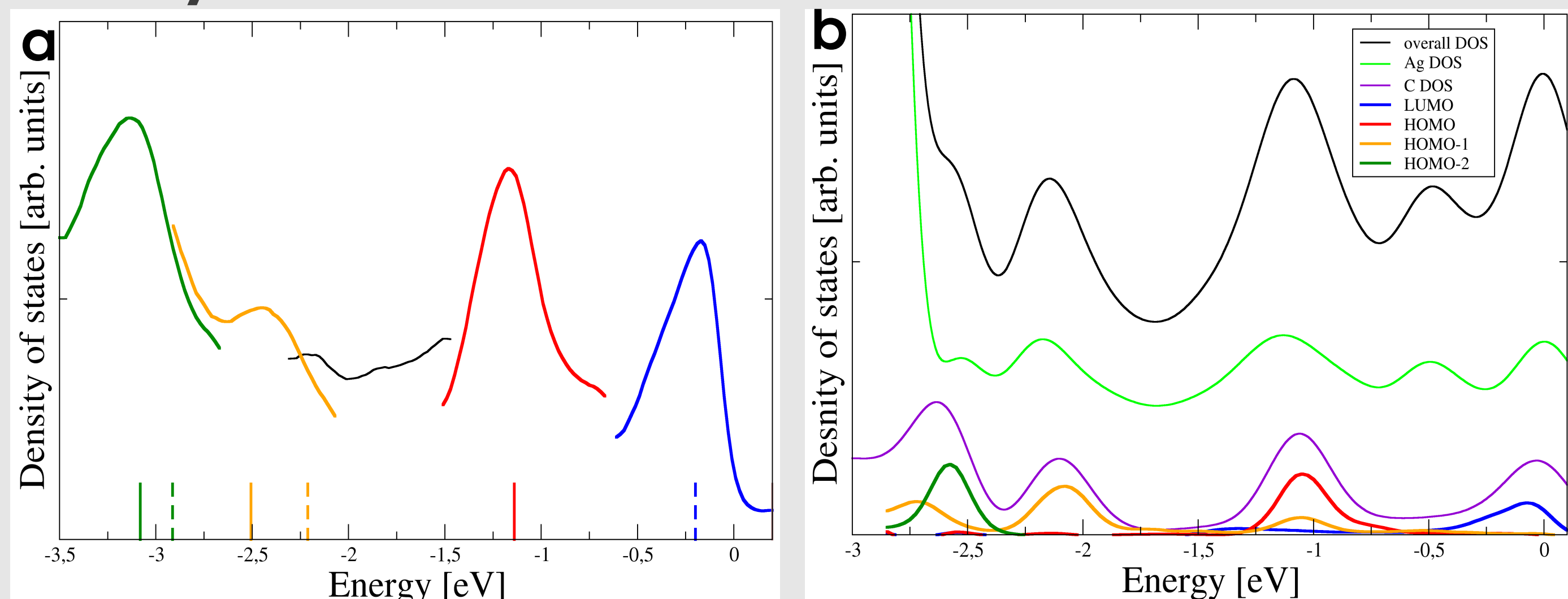

Experiment vs. Theory

Fig.2: Various molecular orbitals in reciprocal space as obtained in ARPES (left) and from DFT, for an isolated molecule (middle) and including the substrate (right) (a): LUMO (b): HOMO (c): HOMO-1 (d): HOMO-2

Computational Details

We utilize the ABINIT code (3) 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 the computation of the photoemission intensity including the substrate we used the VASP code (6) including the DFT-D2 method of Grimme (7) to describe van-der-Waals interaction during geometry relaxation.

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