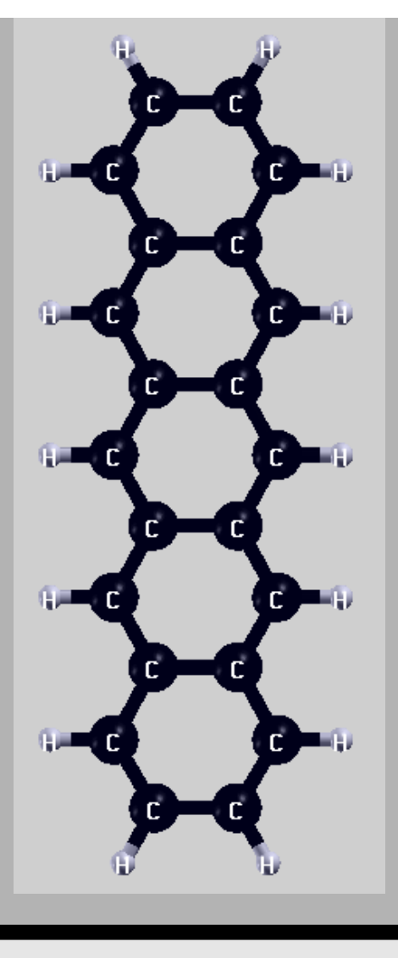

The electronic structure of pentacene monolayers on Cu(110) and Ag(110) surfaces: DFT and GW results vs. photoemission data

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Abstract

We present a combined theoretical and experimental study of ordered monolayers of pentacene (5A) on Ag(110) and Cu(110) surfaces. Theoretically, we have performed ab initio calculations within the framework of density functional theory using GGA and a hybrid functional for the adsorbed monolayers. We analyze the electronic structure in terms of projected density of states and photoemeission cross sections within the plane-wave final-state approximation. In addition, we have also undertaken GW-calculations for isolated pentacene, bulk pentacene and a freestanding layer of pentacene to emphasizing that G_0W_0 corrections greatly improve DFT band gaps. Thereby we also demonstrate that the G_0W_0 gaps are strongly dependent on the local environment of the pentacene molecule, an effect which is absent in DFT orbital energies. Experimentally, the valence electronic structure of pentacene monolayers are studied by angle-resolved photoemission spectroscopy. Thereby, an extensive data set of the photocurrent as a function of parallel momenta and binding energy has been obtained. This data cube is compared with simulated momentum maps of various pentacene molecular orbitals of an isolated molecule calculated. Thereby we can unambiguously identify four molecular states between the Fermi level and the top of the Ag *d*-band. By including the substrate in momentum map calculations, we are able to detect possible modifications of molecular states due to the interaction with the substrate. On comparing monolayer on Ag(110) and Cu(110), we find that 5A is oriented parallel to the (1-10) direction of the substrate on Cu(110) and perpendicular an Ag(110). We unambiguously identify four (two) molecular states above the (Ag(Cu) d-states, and for instance, observe a significant downward shift of the LUMO on Cu(110) as compared to Ag(110).

Comparison: DFT vs. GW

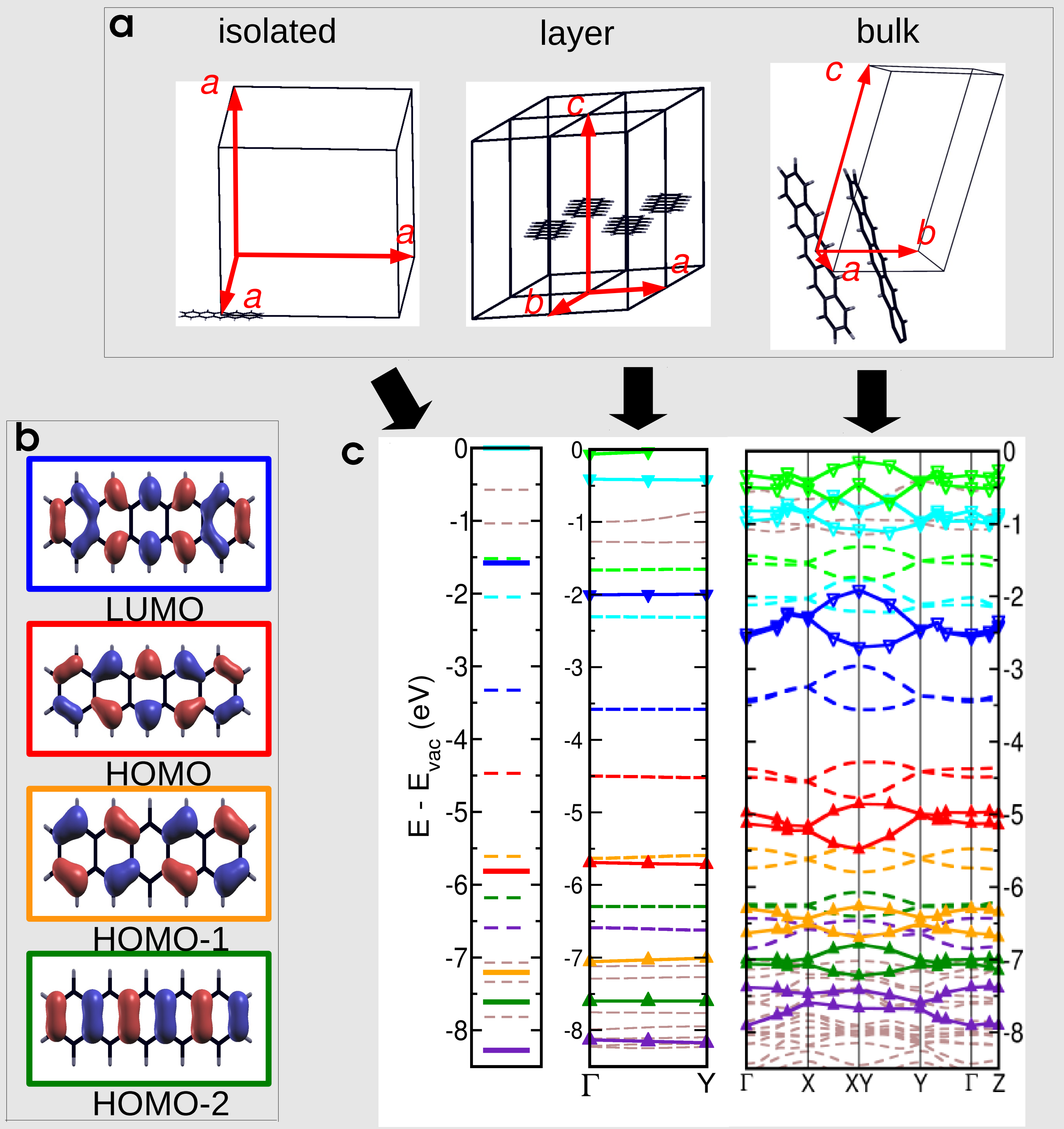


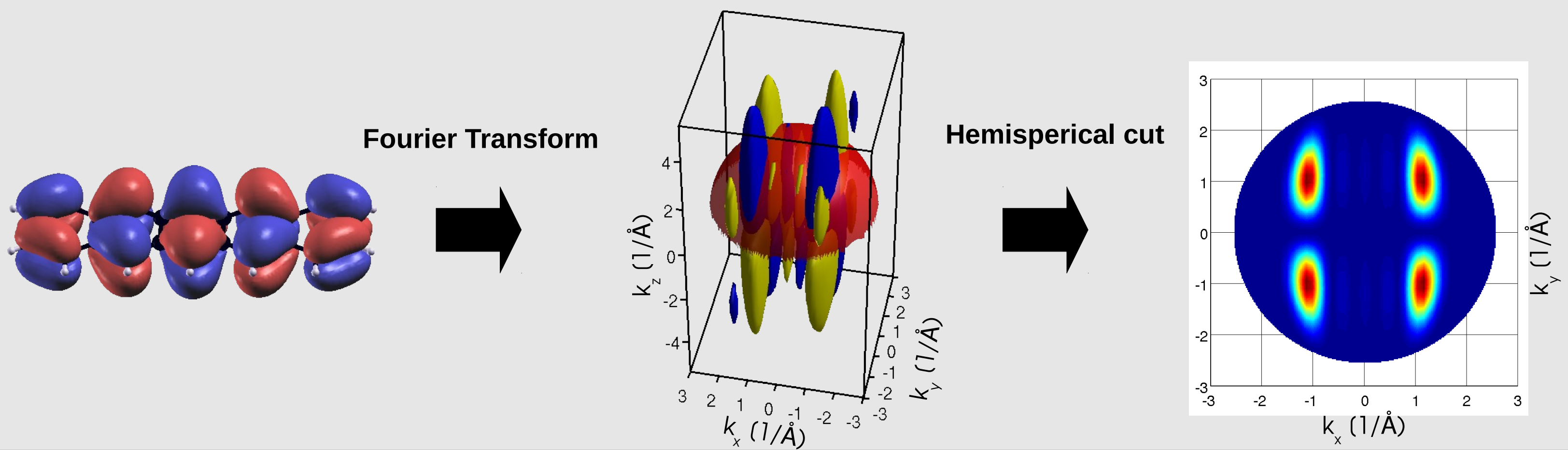
Fig.1: (a): Unit cells used for GW calculations of an isolated molecule (left) a layer of molecules (middle) and the bulk crystal structure of 5A (right) (b): Kohn Sham orbitals of an isolated 5A molecule (c): Kohn Sham and GW-bandstructure for isolated (left) layered (middle) and bulk (right) pentacene.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

Computation of Photoemission Intensity

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

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

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 through the Fourier transformed molecular orbital with a radius proportional to the square root of the kinetic energy .



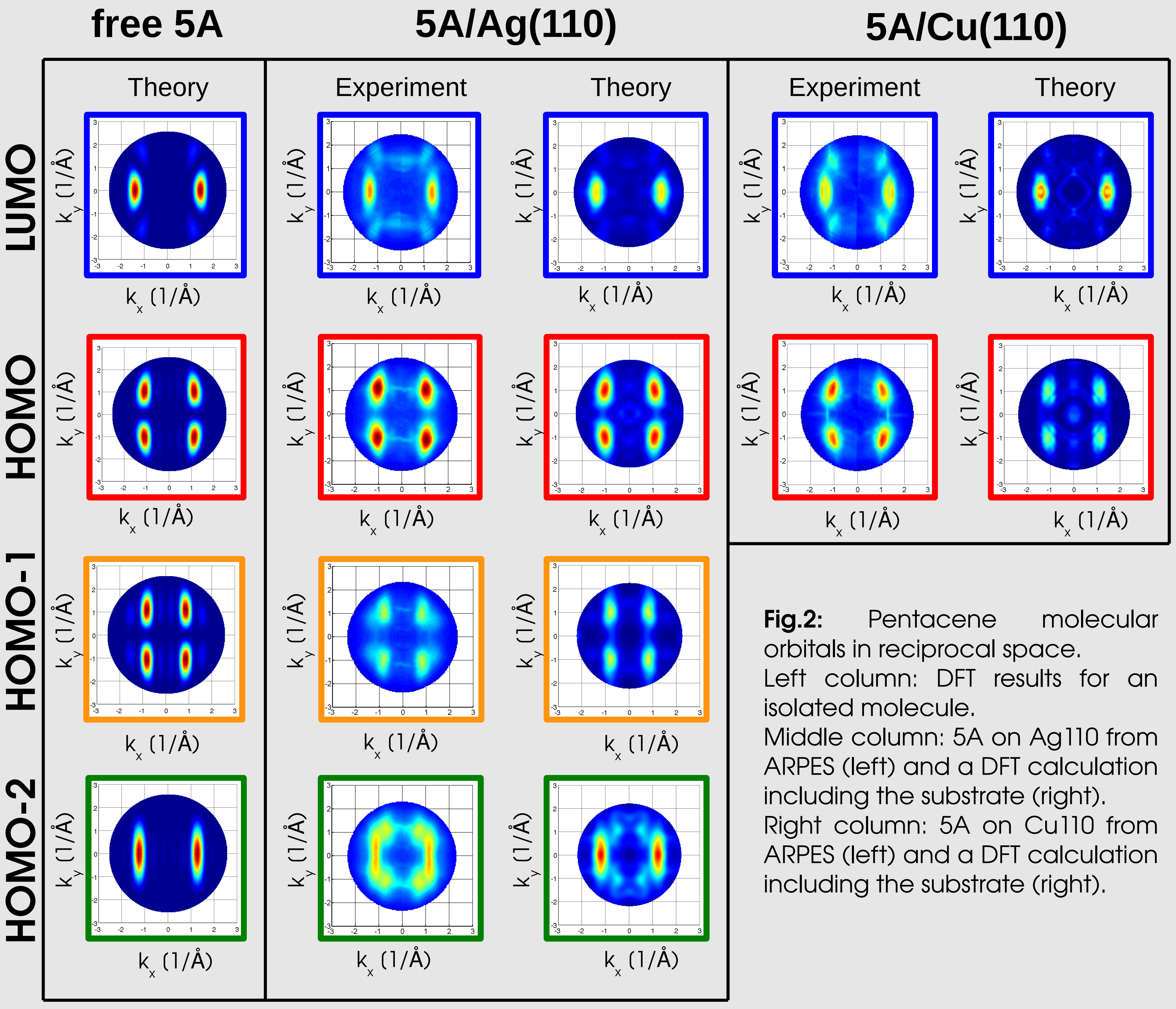


Fig.2: Pentacene molecular orbitals in reciprocal space.
Left column: DFT results for an isolated molecule.
Middle column: 5A on Ag110 from ARPES (left) and a DFT calculation including the substrate (right).
Right column: 5A on Cu110 from ARPES (left) and a DFT calculation including the substrate (right).

Density of states

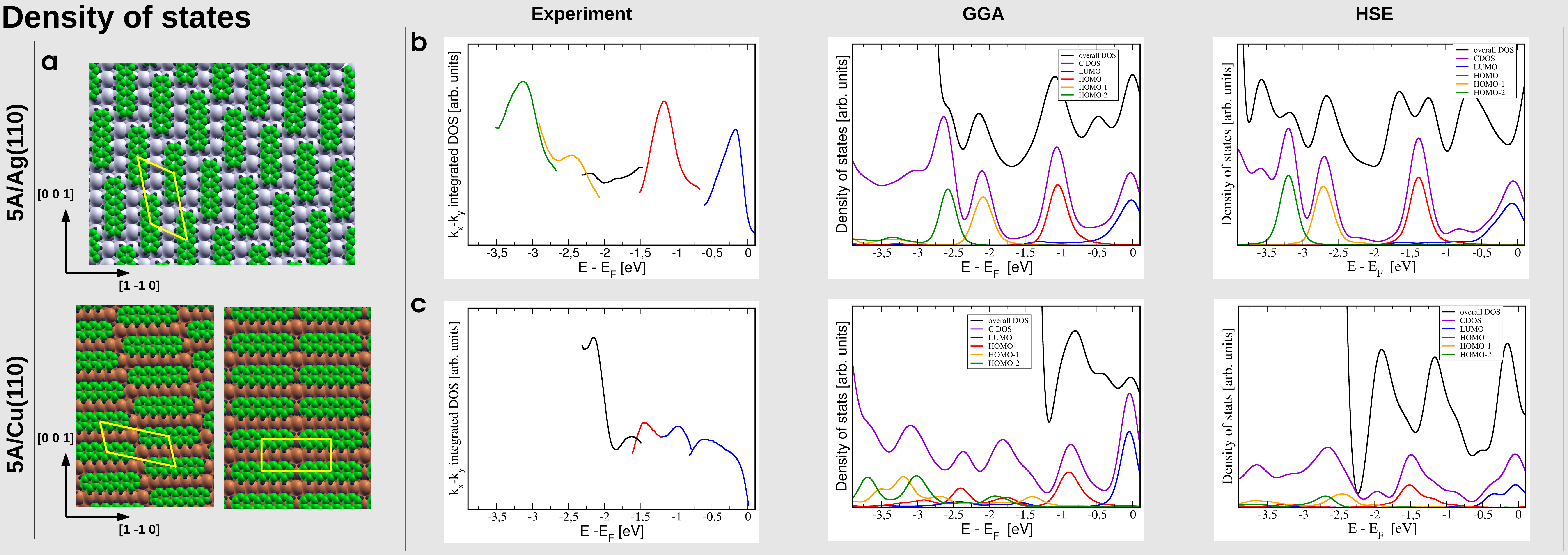


Fig.3: (a): Adsorbed monolayer structure of 5A on Ag110 (top), on Cu110 (bottom left) and as used in calculation (bottom right) (b): DOS for 5A/Ag(110) as obtained from photoemmision experiment (left), calculated with a GGA functional (middle) and calculated with a hybrid functional (right) (c): DOS for 5A/Cu(110) as obtained from photoemmision experiment (left), calculated with a GGA functional (middle) and calculated with a hybrid functional (right).
The calculated spectra include a DOS projected onto molecular orbitals calculated via $\rho_{\Phi_i}(E)=\sum_n |\langle \Phi_i | \psi_{n\vec{k}} \rangle|^2 \delta(E-\epsilon_n)$ for the respective orbital.

Computational Details

We utilize the ABINIT code (3) for 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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