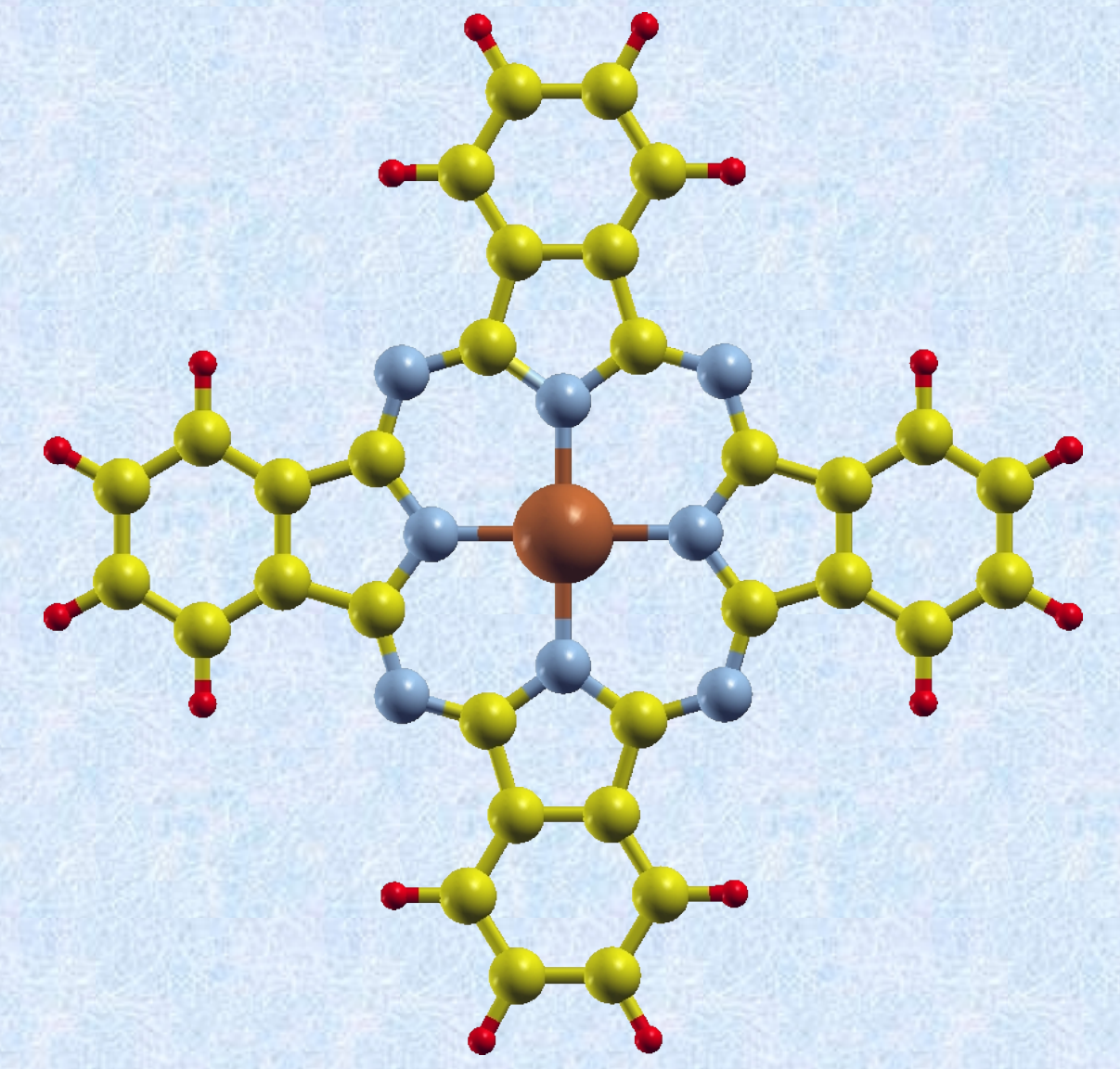
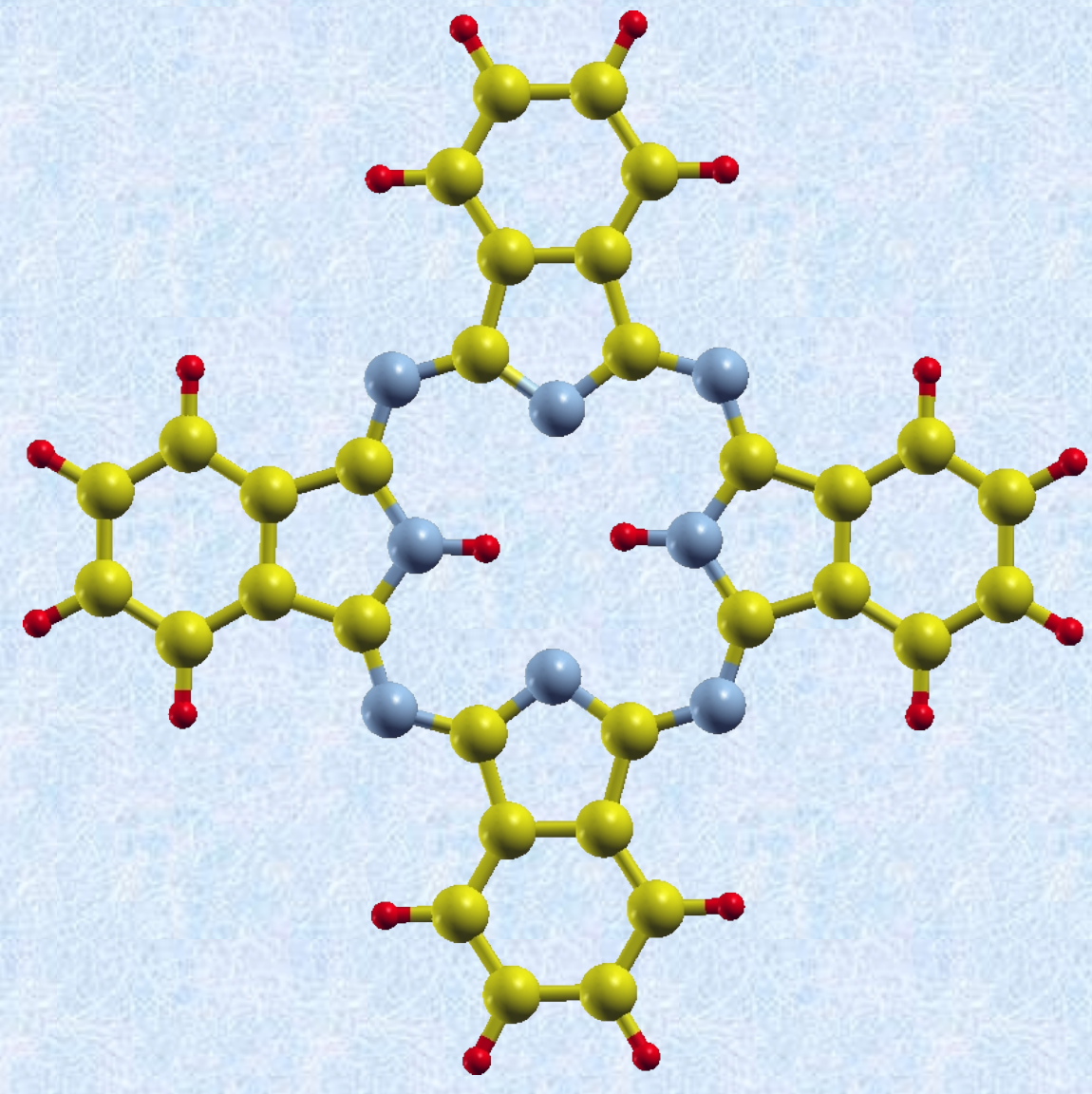


Electronic structure and photoemission spectra of H_2Pc and $CuPc$

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Motivation

Photoemission spectroscopy is a unique experimental technique that provides detailed data of the electronic structure of the probed materials. By measuring the kinetic energy of the photoemitted electrons in dependence of their angular distribution, not only the information about the orbital energy levels can be extracted, but also the corresponding orbitals in the reciprocal space [1]. This way, one obtains very valuable physical picture of the explored objects. Moreover, the outcome of this study resembles very much to what one can obtain from a quantum mechanical computation which makes the comparison between theory and experiment straightforward. On the other hand, theoretical investigation substantially facilitates the interpretation of such experiments. Motivated by those facts, we modelled the photoemission experiment of two organic/organometallic molecules copper pthalocyanine ($CuPc$) and hydrogen pthalocyanine (H_2Pc). The modelling is based to a great extent on DFT and DFT+G0W0 calculations, which provide the electronic structure of these compounds as well as input parameters for the evaluation of photoemission intensities from which the orbital maps are constructed.

Methodology

For the simulation of the photoemission, we treat the photoexcitation as a single coherent process from a molecular orbital to the final state within the so called plane-wave final state model. Here, the intensity is given by the a Fermi golden rule formula [2]:

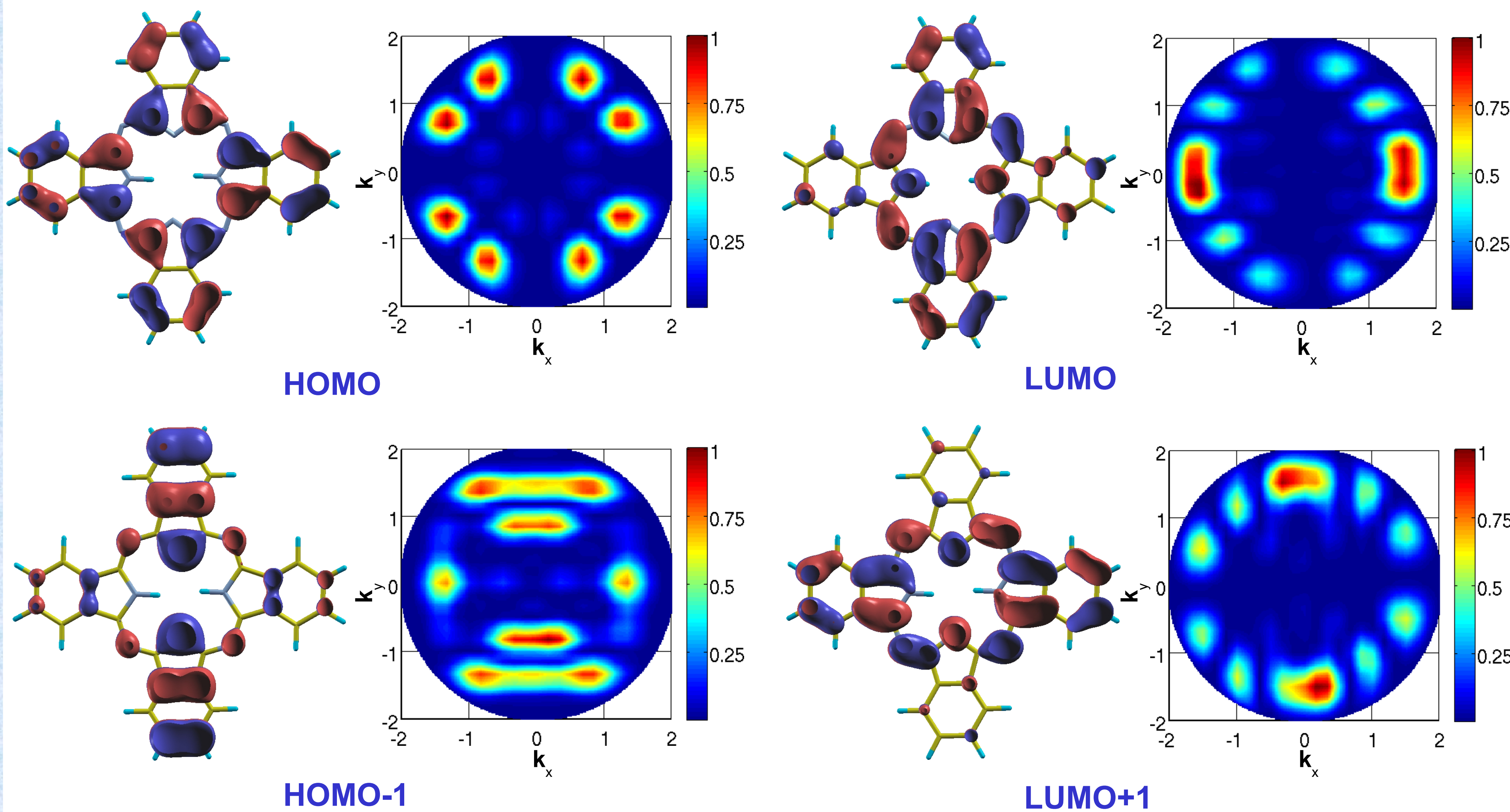
$$I(\theta, \phi; E_{kin}, \omega) \propto \sum_i |\langle \psi_f(\theta, \phi; E_{kin}) | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle|^2 \times \delta(E_i + \Phi + E_{kin} - \hbar\omega)$$

Angular dependent intensity Final state – a plane wave Photon Initial state

As ψ_i we use Kohn-Sham orbitals, for calculation of which we use the code ABINIT [3]. The results presented in this work were obtained using the pseudopotential approach in connection with the PBE functional. To obtain more refined results G0W0 approach.

H_2Pc

Orbitals and their photoemission maps



Electronic structure

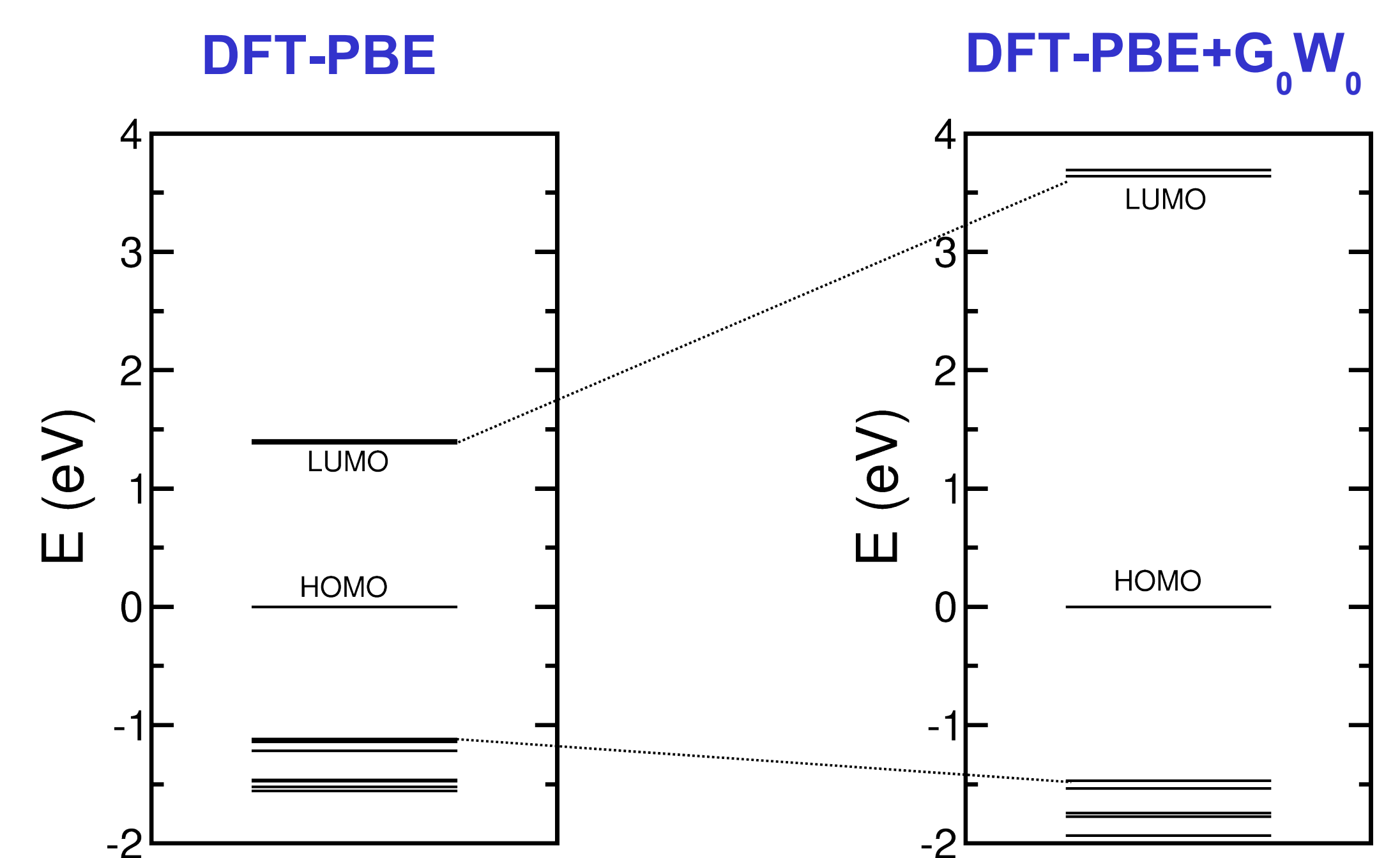
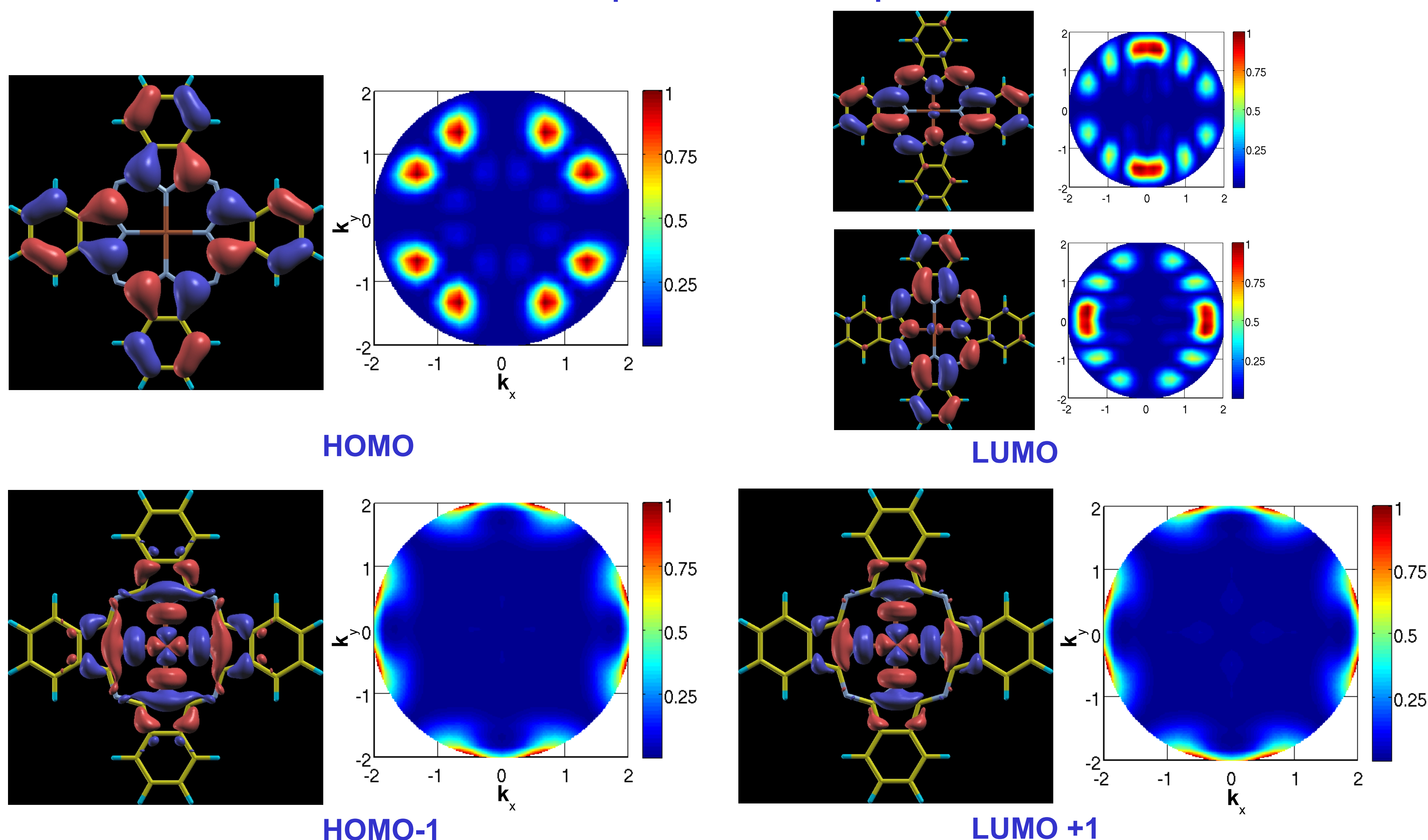


Fig.1. Left: The HOMO, HOMO-1, LUMO and LUMO+1 orbitals together with the corresponding photoemission maps for the H_2Pc molecule. For the photoemission simulation, the kinetic energy of 15.8 eV was used.

Above: The electronic structure of the H_2Pc molecule within DFT-PBE and DFT-PBE+G0W0 approach.

$CuPc$

Orbitals and their photoemission maps



Electronic structure

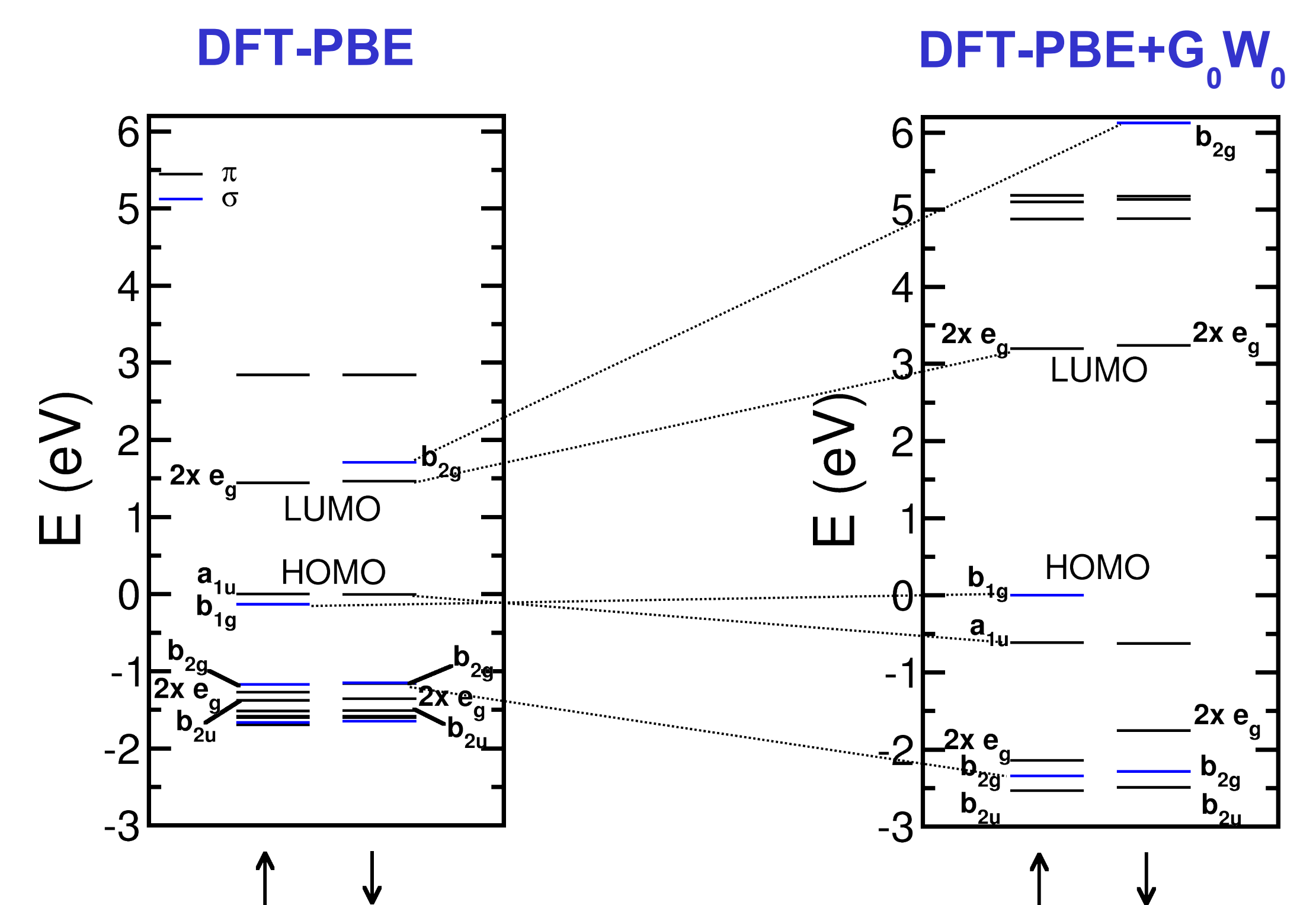


Fig.2. Left: The HOMO, HOMO-1, LUMO and LUMO+1 orbitals together with the corresponding photoemission maps for the $CuPc$ molecule. For the photoemission simulation, the kinetic energy of 15.8 eV was used.

Above: The electronic structure of the $CuPc$ molecule within DFT-PBE and DFT-PBE+G0W0 approach. The arrows show the spin polarization of the corresponding orbitals.