**The Influence of Electron Correlation on the Electronic Structure of Transition Metal Phthalocyanines**

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Transition metal phthalocyanines (TMPcs) are highly symmetric organic molecules with a transition metal atom at their centre. TMPcs have been in the focus of scientific research as possible candidates for applications in spintronics and molecular electronics, where the molecules are typically used when adsorbed on various surfaces [1].

The study of properties of molecules adsorbed on substrates requires the availability of theoretical methods that are accurate enough, but which also have a relatively low computational cost. From this point of view, the description of a TMPc adsorbed on a surface is not straightforward, especially due to the presence of the metal d electrons. A compromise between accuracy and computational cost is achieved by combining Density Functional Theory (DFT) with a Hubbard term exclusively acting on the correlated electrons. Many studies on TMPcs adsorbed on surfaces make use of this approach, but the choice of U is mainly based on previously reported values for similar systems. In this study [2], we provide a detailed analysis of the influence of U on the electronic structure of five TMPcs (Mn-, Fe-,Co-, Ni- and CuPc).

By comparing the calculated valence electronic structures of the single molecules to photoelectron spectroscopy experiments and by computing the Hubbard U term from linear response, we show that U is different for every phthalocyanine. For each TMPc, we provide a range of U values that show good agreement with the experiments. These values represent a safe starting point for DFT+U calculation of physisorbed TMPcs. By calculating a multiple-site linear response U, we also show that the atoms covalently bonded to the metal atom may influence the U value by as much as 1 eV. This point is especially important when estimating the Hubbard U value for chemisorbed molecules.

1. L. Liu et al., Sci. Rep. **3**, 1210 (2013)
2. I.E. Brumboiu, J. Chem. Theory Comput. **12**, 1772 (2016).