
APPLICATION OF ADVANCED ATOMIC-SCALE TOOLS TO MULTI-FUNCTIONAL HYBRID ORGANIC-INORGANIC MATERIALS

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Hybrid organic-inorganic materials are at the forefront research in the field of multi-functional systems [1,2]. Among these materials, layered inorganic systems are particularly under focus because of their ability to be organically modified by different approaches (intercalation, grafting, exfoliation and so on). Such a modification can be used to build hybrid nano-structures with tuneable physico-chemical properties. The experimental team at IPCMS is particularly interested in layered hydroxides and oxides in view of their peculiar opto-electronic and magnetic properties. This, in turn, discloses new possibilities to functionalize them with a wide range of molecules [1-3]. Yet, the chemical modification of inorganic layered structures by large flexible adducts induces structural disorder and the precise structure of these materials is often largely unknown. For instance, regarding hydroxides, the structure of the cobalt hydroxy-acetate phase $(\text{Co}_2(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O})$ is only deduced on the basis of its analogy with the one of zinc hydroxy nitrate [1]. Regarding the hybridization of layered oxide materials, such as $\text{Bi}_2\text{SrTa}_2\text{O}_9$, the structure of the starting compound is known,[4] but the one of the acidic reactive phase $\text{H}_{1.8}\text{Bi}_{0.2}\text{Sr}_{0.8}\text{Ta}_2\text{O}_7$ is under debate [5].

Given this scenario, a precise understanding of chemical bonding among all constitutive units involved is essential to guide the synthesis of new materials bearing tunable magnetic properties. Also, current experimental studies do not always have access to the full set of properties (structural, electronic, magnetic) calling for invaluable complementary contribution from theory. In recent works, issued from a synergy between the experimental group and the computational materials science team of the DCMI department, density functional theory (DFT) based molecular dynamics simulations have been done on the copper hydroxide acetate [6,7]. This has shown how different spin topologies can be realised and even controlled by applying an external pressure along the crystallographic axis orthogonal to the planes containing the layered hydroxides.

To get a deeper insight into the structure and reactivity of these solids, in this thesis, we wish to focus both on methodological issues and on applications related to **a)** accuracy and performance of exchange-correlation functionals and **b)** linear scheme approaches. By referring explicitly to the involvement of issue **a)** and or issue **b)** as sketched above, we can mention here: 1) the need of controlling the exchange-correlation functional in systems for which DFT XC approaches have proved to be not fully satisfactory (issue **a)**) , 2) the lack of quantitative power in the prediction of magnetic coupling constants evaluated within DFT XC [8] approaches (issue **a)**) 3) the search of the optimized structure of hybrid organic-inorganic materials and the characterization of their electronic and magnetic properties (issue **a)** and issue **b)**), 4) the simulation of large systems (in between, 500 and 1000 atoms) [9] to be able to describe changes induced in the global properties of the hybrid system according to the different chemical composition and morphology of the organic molecules inserted between the hydroxide and oxide layers (issue **b)**). In this latter case, particular attention will be given to the reaction pathway [10,11] for the functionalization process.

This PhD thesis project will be carried out by exploiting local HPC cluster at IPCMS, computational resources of the University of Strasbourg under the EQUIP@MESO initiative and national computational resources. Moreover it will take advantage of the experience acquired within the team in the development, testing and use of the most advanced computational techniques and codes oriented to atomic scale modeling.

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