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To Prof. H. Štěpánková
Faculty of Physics and Mathematics
Charles University, Prague

Report on the Doctoral thesis by Mr. Aurelio Gallardo:

"Theoretical study of charge states in molecular nanostructures on surfaces"

Dear Sirs/Madams,

It is with pleasure that I report on the excellent research work by Mr. Aurelio Gallardo performed in the Department of Condensed Matter Physics of the Charles University under the supervision of Prof. Pavel Jelínek.

The thesis reports on the work done by Mr. Gallardo to understand the theoretical aspects of Kelvin probe force microscopy (FPFM) in the close distance regime and to provide reliable tools for the simulation of KPFM for direct comparison to experimental data. The work is organized in six chapters, the first three focusing on a review of the theoretical and experimental literature pertinent to the research field of Mr. Gallardo and the last three focusing on the novel results obtained by Mr. Gallardo and published on peer reviewed high impact factor international journals.

Chapter 1 introduces the reader to both basic and advanced concepts in scanning probe microscopy (SPM) analyzing experimental and theoretical aspects of scanning tunneling microscopy (STM), atomic force microscopy (AFM) and KPFM together with technicalities needed to adapt theory to simulation strategies. This chapter anticipates the most novel aspect of the research work i.e. the extension of the probe particle model, normally used for "far distance" AFM simulations, to the description of short range contrast in KPFM experiments.

Chapter 2 introduces the reader to the theoretical framework of Density Functional Theory (DFT) that is central to all computational aspects of quantum phenomena in the thesis work.

Chapter 3, on the basis of DFT concepts introduced before, describes some aspects related to advanced methods in molecular dynamics simulations introducing mixed quantum and empirical approaches such as the so called QM/MM method.

Some minor inaccuracies are present in the presentation of the first three chapters and the choice of references from the literature is not always optimal.

Chapter 4 targets a critical issue discussed in the AFM literature, namely the interpretation, the physical origin of sharp contrast in AFM images for non-bonding intermolecular interactions. The chapter provides a clear analysis and an interpretation of the phenomenon that is of crucial relevance for research in this field.

Chapter 5 is devoted to the most important aspect of the thesis. Here the theoretical framework for the tip/sample interaction in KPFM microscopy at short range is derived and two main contributions to the interaction mechanism are identified playing an opposing role in the frequency shift of the tip.

SPM techniques are key to success in research fields where 2D systems have to be characterized microscopically. The increased accuracy of KPFM, when accompanied by adequate theoretical understanding, can provide crucial information on electrostatic phenomena at the nanoscale. Mr. Gallardo, after deriving novel theoretical aspects and

bringing them into simulation tools that are available to the whole scientific community, validates the proposed approach comparing experimental and theoretical results for two systems designed on purpose to highlight the features of KPFM: two molecules (tetrakis(4-fluorophenyl) methane and tetrakis(4-bromophenyl) methane) that adsorbed on a silver substrate, expose to the tip of the probe the halogen atom that is expected to host a so called σ-hole.

Mr. Gallardo analyzed in details the experimental and the simulated KPFM images attributing their features to the interplay of two main contributions, one resembling the electrostatic landscape of the sample and the other related with the electrostatic character of the probe apex.

The work done here is of key importance to the field scanning probe microscopy and is expected to have high impact on correlated research activities.

Chapter 6 finally, nicely demonstrates how the combination of SPM techniques (experiments and simulations) together with QM/MM methods allows to understand complex surface supported chemical reactions as for the case of the formation and subsequent isomerization of a Cu based 1D metal-organic chain.

The content of the thesis, despite several typos that can be easily eliminated in a revised version, is presented clearly with a scientifically accurate language. The results obtained by Mr. Gallardo proves undoubtedly his ability to conduct and inspire creative scientific work.

For the reasons detailed above, it is my pleasure to strongly recommend accepting the work of Mr. Aurelio Jesús Gallardo Caparrós and conferring him the title of Doctor Philosophy

I would have two questions for the candidate:

-How could you imagine to use information extracted from KFPM experiments to improve QM approaches such as DFT in the description of materials?

-Could you discuss more in details the QM/MM approach used to investigate the isomerization reaction? How do you determine when a MD simulation is "long enough"? Which collective variable or variables did you use for the umbrella sampling? Do you know other "less biased" methods to determine the free energy of the reaction? Which was, from the technical point of view, the most difficult part in dealing properly with the QM/MM interface region?

Sincerely yours,

Carlo Antonio Pignedoli

Dübendorf, May 13, 2022