Opponent's review of the dissertation of Andrés Pinar Solé with the title

Study of Molecular Systems on Surfaces Investigated by Means of Scanning Probe Microscopy

The doctoral thesis by Andrés Pinár Solé is focused on functionalization of an STM tip by niclocene or cobaltocene molecules for measurements of magnetic properties of single atoms or molecules on surfaces. Such challenging topic requires not only solid skills of experimental physics to achieve the data, but also a theoretical background for the data interpretation. The thesis meets both needs, applicant first of all conducted the experiments, but also used the theory to simulate tunneling between the niclocene and the magnetic atoms. Such combination is indeed commendable.

The first chapter is dealing with background of the experiments, principles of STM, AFM, STS etc. together with some technical aspects, such as reduction of vibrations. I am not sure, if such detailed introduction to SPM is needed in a PhD thesis. Furthermore, many erroneous details appear in this part (e.g. inconsistent naming of variables on p.12, wrong Eq. 1.4, some incorrect statements such as "we can assume that the tunneling probability is inversely proportional to the tip-sample distance d and the tunneling barrier ϕ", etc.) On the other hand, background of some more specific features important for the study are not given, such as e.g. of the Kondo effect.

The second chapter covers the properties of niclocene and cobaltocene, from STM experiments to the theoretical background based on the Heisenberg/co-tunneling theory. I consider this part crucial for understanding of later presented own results, unfortunately reading is a little bit complicated by some typesetting errors (e.g. some paragraphs appear twice).

The own results are presented in Chapter 3, showing outcomes of nice experiments using the functionalized tip to measure magnetic properties of various systems (graphene nanoribbons, polyradical nanographene, 1D molecular chains and 2D layers of transition metal dichlorides). Some of these results have already been published in top-quality journals (Nature Chemistry, ACS Nano), I believe that publication of the other results is to be expected soon. The data are always interpreted using the theoretical approach and nice agreement between the experiments and simulation is usually found.

Despite the stated objections, I am convinced that the author proofed his ability to perform creative work on his own. The work in my opinion very well meets the requirements for a doctoral dissertation, and I recommend accepting it for the defense.

I ask the author to answer the following questions during the defense:

Q1. Part 1.4.3 Noise management seems somewhat confused. Could you find out what I don't like?

Q2. In some cases (figs. 2.10, 2.16) the z distance is different in experiment (from literature) and the simulation using the Heisenberg/co-tunneling theory. What is the reason for the difference?

Q3. For simulations of the $d^2I/dV^2(z)$ spectra, a "Python script" has been used, which has been developed by the author and created by his "colleagues from the theory department". Could you give details about your contribution to the script?

In Prague on May 2nd, 2024 Doc. RNDr. Pavel Kocán, Ph.D.

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