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Mgr. Miriam Delongová
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Dear Mgr. Delongová,

As agreed, I am sending the report on the Habilitation thesis of Mgr. Piotr Błoński, Ph.D, titled *Atomic clusters and graphene: many faces of nanomagnetism*, submitted at the Palacký University Olomouc, CZ.

Sincerely Yours,

Cesare Franchini

REPORT HABILITATION THESIS

Title: *Atomic clusters and graphene: many faces of nanomagnetism*
Habilitation Thesis: Mgr Piotr Błoński, Ph.D

General Comments

The topic of the thesis is the application of first principles approaches in the framework of DFT to study magnetic interactions in clusters, thin films and 2D materials (primarily graphene). Before commenting the results and analysis discussed in the various chapters I would like to start with some general considerations. The thesis begin with a comprehensive phenomenological introduction on the importance of magnetism in low-dimensional materials and a brief review of the main concepts of DFT and its spin-polarized extensions. The main part of thesis is dedicated to the presentation of the most important results obtained by Dr. Błoński in the last 10 years, supported by the reprints of 16 published articles and an excellent review. The research collected in this set of articles is of exceptionally high scientific quality from many points of view: (i) The first set of papers represents probably the first application of the PAW-scheme to non-collinear and relativistic spin-structures, and are still cited nowadays by the experts in the field. (ii) The set of seminal papers on non-collinear magnetism are extremely solid works, well detailed and provides a comprehensive technical and conceptual description of both, technicalities and theoretical interpretations; (iii) by following the careers path of Dr. Błoński from the sequence of published papers one recognizes a clear vision. The papers are not only thematically related but one sees continuous improvements (or better a progression) in terms of complexity (from isolated clusters to adatoms/clusters on surfaces), innovation (from classical magnetic materials to magnetism in graphene) and interdisciplinary (from purely computational works to joint theory-experiment research). (iv) All this work culminates with an excellent review which summarizes the state of the art in magnetic graphene and reviews the most promising applications (spintronics and biomedical).
In a scientific world often shaken by scientific bubbles and mainstream fashions, the capability and strength to follow a clear scientific path and to progressively develop/envision new ideas and application on top of the previously acquired experience is a rare and highly appreciable attitude. Overall this thesis is a very good piece of work and the candidate deserve to obtain the Habilitation without any hesitation.

I move now to analyze and comment each chapter of the thesis. The thesis is structured in four chapters and three Appendices.

The first chapter offers a brief (and pleasant) introduction on the history of magnetism followed by an overview (Sec. 1.2) on the importance of magnetic information storage, how this can be realized in practice in tapes and disks and which routes can be explored to miniaturized further the dimensions of storage devices, for example via bit pattern media and single-atom magnetic bit. After reviewing the most important aspects of classical magnetic materials based on transition metal on spin-orbit coupled substrate, the discussion turns on the possibility to engineering magnetism in graphene, an important topic discussed in more details in Sec. 1.3. Sec. 1.2 reads very well. In this part the candidate has decided to adopt a phenomenological perspective, which is unusual for a computational physicist and clearly demonstrates the ability of the candidate to bridge first principles calculations at the quantum mechanical level with technology and experiments. This is an excellent (but unfortunately rare) characteristic for a modern computational materials scientists. Said that, from a theoretical physicist I would have expected a more detailed description of the quantum-mechanical aspects of magnetism (spin, different types of exchange and different form of MAE, energy scales, etc.) supported by a more extended formalism. But I understand that this was a deliberated choice of the author, who has preferred to make the thesis more easily readable. A second aspect that could have been mentioned is that

the computational study of magnetism in low-dimensional systems is not only achieved using DFT but also by other powerful approaches such as Green's function based methods and spin dynamics (In this part of Sec. 1.2, pages 19 and 20, the candidate has preferred to focus on his on contributions in the field).
In Sec. 1.3 virtually all ways to make graphene magnetic are comprehensively reviewed and explained in great details (point defects, adatoms, hydrogenation, oxidation etc). The only alternative one could think of is twisted bilayer graphene which have been just reported to exhibit magnetism (Science10.1126/science.aaw3780 Science). this section is very clear, instructive and well organized. It shows the excellent familiarity of the candidate on this subject and his ability to bring the readers easily through this path. Also in this section there is a nice balance between computational results and experimental observations, and it is remarkable to realize that important results have been anticipated by the theory and only later confirmed by the measurements.

The second chapter summarizes the theoretical basis of the computational scheme (DFT+PAW) used to obtain the results discussed in the remaining part of the thesis. This is a rather standard part, common of many reports and thesis. Still, some caution should be taken in updating text-book like composition. For instance at p.45, in discussing the benefits of meta-GGA functionals, it is claimed that "a systematical improvement of the properties compared to those obtained with GGA has not been obtained". This statement could have been somehow valid 4 years ago, before the advent of the SCAN meta-GGA functional (PRL 115, 036402 (2015), which has proved to be superior to other local, semilocal and meta- functionals. Also, I find inappropriate to cite Ref. 94 as main reference for the Jacob's Ladder (self-citing is important but should not be overused, in particular out of turn). Finally, I have the impression that the last paragraph of sec. 2.1.2 (p.47) is a repetition of the LDA part discussed in 2.1.1. The psedupotential part (including the relativistic extension) is written very well, clear and compact.

The third chapter is the central part of this thesis, where the candidate reports his major scientific achievements. It incorporates five coherently linked sections, which in some way follows the chronological evolution and progressive improvements of Błoński career.
Sec. 3.1 set the basis of the forthcoming studies. In fact, isolated clusters can be considered as a test case to assess the methods and acquire reference information for more complex structures. For instance, the candidates reveals the crucial role of SOC in splitting the orbital levels in dimers, which favors the onset of a large MAE. With increasing cluster-size the determination of the optimal structure is of great importance and it is strongly coupled with the arrangement of both spin (and orbital) moments. By studying light and heavy elements (Pt, Pd, Ni) the candidate has shown that magneto-structural effects are present also for 3d and 4d elements. This is nowadays an accepted paradigm but at the time of the publication of the seminal works of Błoński and Hafner (e.g. Refs. 19 & 20, year 2011) this results came as an unexpected outcome which has stimulated further thinking and additional conceptual works. Another important result that was raveled in the earlier articles of Błoński was that the spin moment is not necessary isotropic. The next level of complexity, discussed in Sec. 3.1.4, is the study of magnetic anisotropy in mixed clusters, in which the interplay between reduced symmetry, orbital and spin anisotropy, and additional structural changes is extremely difficult to rationalize.
In Sec. 3.2 the author moves to discuss the first possible scenario with practical relevance, small clusters on graphene. The additional issues to consider in this configuration, which the authors have addressed with the usual care, are the adsorption configuration and the interaction between the adsorbed clusters and substrate, which can also induced structural changes in the substrate. As a consequence, the spin arrangements within the supported cluster is more inhomogeneous as compared to the isolated cluster and this ultimately leads to a decrease of the magnetic anisotropy, also due to the formation of noncollinear spin orderings. While somehow expected, to my knowledge this work (Ref. 25) is the first unambiguous demonstration of the role of substrate-cluster interaction in deteriorating the MAE.
Sec. 3.3 and 3.4 push the limits to the thin film regime, specifically TM clusters on graphene on Ni(111) (chemisorbed) and on Cu(111) (physisorbed), where graphene-TM interaction and dispersion forces are necessary to achieve a proper description. Probably, the most important result of this study is that the presence

of Ni(111) increases the interaction between Pt and graphene. This influences the orientation of the adsorbates (competition between flat and upright geometries), and directly affects the mechanism which promotes magnetic anisotropy as well as its strength.
Finally, Sec. 3.5 deals with the most recent works of the candidate, imprinting magnetism in graphene. Here the candidate and his research team explore and discuss many different routes to induce magnetism in graphene, ranging from spatial confinement, doping with foreign atoms, and sp3 functionalization. This set of works show a turn in Błoński's career from fundamental reference theoretical works to applied studies, often in cooperation with experimentalists. Besides being technically impeccable the articles related to this part are of great applicative importance and are published in high-impact journals. Considering the collaborative character of these studies, the candidate could have added a statement for each article specifying his own contribution (this is only done for Refs 68 $ 69, as explicitly required by the journal policy). Howveer, by reading the papers it is clear that the contribution of theory in these works were essential to understand and interpret the observations. For instance in Ref. 75 DFT finds that S act as n-donor pushing the Dirac cone below the Fermi level. What remains somehow to be understood is the link between dopant concentration and magnetism both in S-doped graphene and N-doped graphene (Ref. 76), but these are admittedly very difficult issues. The DFT results in Ref. 91 are particularly interesting and computationally rather challenging. Here Błoński and coworkers map DFT magnetic energies onto a spin Hamiltonian and compute the Curie temperature as a function of the morphology and size of many graphene flakes. They found that magnetism is enhanced by the sharp angles between edges, loosely speaking triangular flakes are more favorable, in apparent agreement with measurements. This is definitely an impressive result. Finally, Sec. 3.5.3 summarizes the results published in Refs. 68 and 69 on room temperature magnetism in graphene achieved via incorporation of F/OH groups (hydroxofluorographenes). The works are impressive, even though the specific contribution of the candidate is probably less crucial.

The conclusions are a concise but precise summary of the discussion developed in the first and third chapters and sketch the future plans of the candidate which aim to find alternative and innovative ways to promote high-T magnetism in graphene. This appears to be a key area of research for the Palacký University in Olomouc which has the great merit to have established a very successful research plan with excellent scientists of international caliber. I am sure that Dr. Błoński will continue to contribute to this outstanding research with his capability to conduct technically challenging calculations and to help the experimental colleagues to decipher the observations at microscopic level. Moreover, I am also certain that Dr. Błoński will contribute to growth a new generation of researchers expert in computational magnetism, if he will have the chance to teach to students and supervise young researchers. I underline once more that the Habilitation meets all international standards of quality and innovation and therefore I fully support a positive conclusion of the Habilitation process and wish Dr. Błoński a brilliant scientific future.