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Date: 2023-08-05

Report on the habilitation thesis of RNDr. Lukáš Grajciar, Ph.D.

It is an honour for me to provide an opinion on the habilitation thesis of RNDr. Lukáš Grajciar, Ph.D. (hereafter referred to as 'author'), entitled "*Towards reliable simulations of nanoporous materials under operando conditions'.* I accepted this assignment with pleasure. I had the opportunity to review the author's Ph.D. thesis in 2013 and I have been closely following his work since then because our research interests overlap to large extent.

The computer-aided simulations based on first principles of physics (co-called ab initio simulations) proved to be an extremely valuable tool of modern chemistry and materials science. However, their reliability critically depends on the following three factors: (i) accuracy of description of interactions between all constituents of the system of interest, (ii) the quality of the structural model used, and (iii) the convergence of an observable with respect to the phase-space sampling. The thesis describes the author's contribution to the development of methods for simulation of nanoporous materials, whereby the three above mentioned factors are addressed. The subject of the thesis is therefore topical and of great scientific importance.

The thesis consists of four chapters. After a brief introduction to the properties of nanoporous materials and the strategies of their simulations in Chapter 1, methods developed by the author and his colleagues are presented in Chapter 2. These involve a correction scheme DFT/CC targeting the well-known problem of DFT with incorrect description of long-range dispersion interactions, CFMM and LMIDF approaches that enable one to accelerate DFT simulations, the global structure optimization techniques, and the development of reactive machine learning and linear scaling potentials for zeolites. Part of the methods from this impressive list are, thanks to their implementation to major codes, such as TURBOMOLE, being actively used by the research community, while some other, more recently developed ones, are likely to find their users in the near future. To this end, it is useful that, in addition to explaining the basic idea behind each method, the author also added his comments on the perspective of its future development. In Chapter 3, the use of the newly developed methods is demonstrated in numerous applications including, e.g., study of sorption of greenhouse gasses in MOF models, or simulation of interaction of zeolitic materials with water. Finally, Chapter 4 offers conclusions and an outlook. The two results Chapters (2 and 3) are based on the material from 14 research papers (provided as an appendix), some of which published in high-profile peer-reviewed journals, including *Nature Communications* and *Advanced Materials*. These papers received a significant number of citations, which is the best demonstration of the importance of the work. The material presented in the thesis is based on original ideals of the author and his

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colleagues and shows no sign of plagiarism. Also, the author clearly indicates his research role in each subsection of the main results Chapters 2 and 3, from which it is clear that his contribution was always essential.

Altogether, the thesis is well and clearly written, the research subject is topical and attractive, and the quality of the results presented leaves the reader with no doubt that Dr. Grajciar is an excellent researcher who has made important contributions to the methodology of simulation of nanoporous materials and its application. **Therefore, I strongly support the acceptance of his habilitation thesis.**

As subjects for scientific discussion, the following points are offered:

1.) In paper 6.5 (presented also in Sec. 2.4), the density functional approximations PBE+D3 and SCAN+D3 were used as target methods for the machine learning (ML) model. Since the cutoff radii typically used for the dispersion correction part (here D3) are typically as large as 50 Å, it may seem paradoxical that an accurate ML model can be based on relatively short-ranged structural descriptors (here SOAPs with cutoff radii of 6 Å), as demonstrated in the above mentioned work. What is the author's explanation for this observation?

2.) Determining a collective variable (CV) representing reaction coordinate for the use in free energy calculations is a challenging task because a suitable CV must fulfil a number of criteria (B. Peters, Annu. Rev. Phys. Chem. 67, 28.1–28.22 (2016), 10.1146/annurev-physchem-040215-112215) that ensure the reversibility of transformation. The author and his coworkers attacked this problem in paper 6.6, where 'a novel method of automatic collective variable identification employing variational autoencoder and pre-trained neural network potential representations' was proposed. It is not clear to me, even after repeated reading of 6.6., how the authors defined their criteria for CV selection and how these were encoded into their procedure. I would therefore appreciate an explanation of that. Does the proposed procedure guarantee improved performance of a candidate CV in the committor test (discussed, e.g., in the above-mentioned paper by Peters)?

3.) In paper 6.9 (results presented also in Sec 3.2), free energies of activation computed using biased MD are reported. The authors mention the calculation of free energy profiles (which are also provided in SI) but, unfortunately, no information nor any relevant reference is given to explain how these were used to obtain free energies of activation (unlike the profiles, the latter are intrinsically independent of the choice of

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CV, see, e.g., J. Chem. Phys. 157, 084113 (2022)). Could the author comment on this point?

Sincerely Yours,

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