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Prague, Aug 20, 2024

Report on the dissertation thesis by Kryštof Březina entitled
Ab initio and path integral molecular dynamics methodology for hydrogen-bonded systems in the condensed phase

The research described in the thesis by Kryštof Březina is concerned with the highly computationally demanding ab initio molecular dynamics calculations and focuses on both implementing and testing new and more accurate methodologies and applications to several specific systems. Overall, the thesis contains very good and state-of-the-art research with important contributions to the field of AIMD simulations and to the structure and dynamics of several interesting systems where hydrogen bonds play crucial role.

The thesis is divided into seven chapters and some computational and experimental details are left to appendices. After quite lengthy Introduction containing already a few results which would be better, in my opinion, to postpone into later chapters devoted to specific applications, the author provides a long chapter on theory where all main approximations used in the work are introduced and explained. Main results, which are also the subjects of five papers attached in the Appendix C (four already published in peer-reviewed journals and one on arXiv), are summarized in Chapters 3-6 where a rather concise exposition of the results from papers is provided. An exception is Chapter 6, the results of which have not been published yet. All main achievements are nicely summarized in the last chapter with conclusions and future prospects.

From my point of view of a theoretical physicist, the most interesting contribution is an implementation of committee neural network models to improve significantly machine learning potentials used in AIMD simulations, described in Chapter 3 and Paper I. Kryštof Březina thoroughly tested this approach on water in various phases and showed that it is superior to previously used methods of obtaining machine learning potentials in both accuracy and efficiency which is very important for ever larger simulations, especially for liquids and solids. This new approach provides a good estimation of the error of the calculated potentials and thus can automatically determine new geometries where *ab initio* calculations should be performed (strategy known as query by committee). A high importance of this work is supported by more than 75 citations of Paper I. In Paper II, this method was further used together with the transition tube sampling, a new efficient sampling of potential energy surface around a suitable

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trajectory using local normal modes, which results in a more efficient way of performing path integral molecular dynamics calculations.

Very interesting and inspiring are also calculations which Kryštof Březina, together with his colleagues, performed for specific systems. He studied benzene radical anion (the results are presented in Chapter 4 and Papers III and IV) confirming stabilization of this anion when inserted into liquid ammonia and getting a deeper insight into the vibrational dynamics and electronic structure of this system. Furthermore, he discusses the π–hydrogen bonding of aromatic compounds in liquid water and ammonia again by a detail study for benzene using path integral molecular dynamics simulations, summarized in Chapter 5 and Paper V. Finally, in Chapter 6, he shows recent results from simulations of proton transfer in a complex molecule DABQDI and its dimers and trimers, both in the gas phase and on the surface of Au(111) showing that quantum effects play an important role at lower temperatures for this process. This last topic is an ongoing research to be supplemented with other large AIMD simulations for molecules on the Au(111) surface and results has not been published yet.

All topics are properly discussed with a lot of insight showing that the author has a very good understanding of the limitations and advantages of used methods and at the same time his capability to analyze the obtained results and make correct, yet cautious, conclusions regarding mechanisms of studied systems and processes.

The thesis is very well and carefully written with very few typos and inaccuracies. The only thing I could slightly criticize is that in some parts the text goes into much detailed exposition of theory, e.g. Schrödinger equation, Born-Oppenheimer approximation, or description of basis sets, which are covered in standard textbooks. On the other hand, I would benefit from a little bit longer discussion of topics like choice of approximate functionals in DFT calculations which are important for this work, although all relevant references are provided, and a reader can find details in the cited literature.

Even though I would have other comments and questions regarding all interesting topics presented in the thesis, I limit myself here only to the following comments/questions, which could be addressed during the thesis defense:

1) Eq. (2.37) is not very informative as it is basically trivial identity. It would be probably better to use a different notation for short- and long-range contributions as they are calculated in a different way.
2) I am not expert on DFT calculations and it seems to me that a proper choice of approximations to exchange–correlation functionals together with a suitable basis set is very important to obtain correct results. Unfortunately, this particular issue is not much discussed in the thesis and results are showed only for one set up. How are particular

functionals chosen for specific calculations? How sensitive are the results to the choice of a functional/basis set?

3) In Figure 6.5, optimized geometries for the DABQDI monomer and dimer on the Au(111) surface show a different position of the monomer and dimer relative to the surface atomic structure. Could this be an artefact of the finite size of used slabs? Are shown configurations global minima?

Despite my few critical remarks above, I consider the thesis to be a high-quality work, which brings important and relevant contributions to the active research area of AIMD simulations and sheds a new light on dynamics of some interesting systems which should trigger further experimental and theoretical investigations.

In my opinion, Kryštof Březina showed that he is able to do research on his own and also within a research group using various available computational tools and, most importantly, he can analyze and interpret the obtained results to get a deeper understanding of the systems under study. **His presented work fulfills all requirements as a dissertation thesis and without hesitation, I can recommend to award him the Ph.D. degree.**

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