

## Jury Member Report – Doctor of Philosophy thesis.

**Name of Candidate:** Giorgio Visentin

**PhD Program:** Materials Science and Engineering

**Title of Thesis:** Accurate ab initio evaluation of the interatomic potentials and long-range coefficients

**Supervisor:** Prof. Alexei Buchachenko

**Name of the Reviewer:** Dr. Andrey Stolyarov

I confirm the absence of any conflict of interest	<b>Date:</b> Oct 14, 2021
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*The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.*

*If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.*

### Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

PhD research work by Giorgio Visentin addresses the applications of the state-of-the-art ab initio approaches to interatomic interactions at long range and the problem of merging the results of molecular and atomic ab initio calculations. This topic can hardly be regarded as novel, being quite well known and notorious for molecular spectroscopy. However, an interest to construction of the global interatomic potentials has been revitalized during the last decade due to the development of experimental methods for probing near-threshold molecular bound levels in ultracold atomic ensembles. Photoassociation spectroscopy, as well as ultracold scattering measurements, is extremely sensitive to the long range tail of interaction potential, but poorly assess the region of the potential well. Even if for a certain system it is possible to combine the molecular and ultracold atomic spectroscopic data on bound energy levels, they may not overlap, leading to a problem in the global potential characterization. In fact, theory mirrors the experimental dilemma – powerful methods of interatomic interaction theory make it possible to describe the long range limit with very high accuracy, while the state-of-the-art ab initio approaches can reasonably well reproduce the potential minimum and repulsive wall. But still, direct merging and balancing the accuracies of these approaches, regarded in the thesis as monomeric and dimeric, are indeed the problems worthy of special investigation.

The thesis consists of seven chapters. Two first provide an introduction to the work and very detailed account of the theoretical concepts and methods used or referred to in the work. The rest is devoted to four particular tasks addressed in the thesis and overall conclusions. As such, the thesis does not contain traditional literature review. Rather, small literature reviews are given for each task. Four tasks are not always directly related to each other. Also, general conclusions are not formulated. To me, the thesis looks a bit fragmentary, but it should not undermine of course the essence of the research.

Each of the tasks presented in the thesis features the material of the published paper or submitted manuscript and has its own idea and interesting result.

Chapter 3 presents the assessment of the ab initio schemes, usually applied to molecular calculations, in the calculation of the response properties of alkaline-earth atoms and Yb. It is instructive to see that standard recipes of improving the accuracy of molecular calculations work for the long-range dispersion coefficients equally well. The fact that the CCSD propagator technique can be made competitive with the special atomic methods like CI-MBPT or extended state summation is somewhat unexpected. Its importance lies in the possibility to accurately tune the coupled cluster methods for molecular calculations to frequently known parameters of the long range tail.

The study of the global interaction potential of ytterbium dimer is presented in the Chapter 4. Existence of ultraprecise photoassociation spectroscopy data for a variety of isotopes makes this molecule very interesting for studying mass-dependent effects beyond the Born-Oppenheimer approximation. New scalar relativistic calculations presented in the thesis set the new benchmark for the ground state Yb dimer potential, explain quite large discrepancies between previous results and provide the reference for improved spectroscopic models. Alas, the main result – no direct matching of the molecular and atomic approaches is possible – looks

pessimistic. Unfortunately, no assessment of the scalar-relativistic approximation accuracy was made through the relativistic calculations on Yb dimer, but I understand that it goes beyond the scope of the thesis.

New combination rule presented in Chapter 5 is a nice piece of the analytical theoretical work. One can seldom see nowadays formulations and solutions of such physical problems.

Chapter 6 stays a bit apart from the preceding content dealing with ion-atom interactions. Still, one can trace the connection: tuning of an ab initio scheme to the long-range properties (in this case – known atomic polarizabilities) promises higher accuracy of the global potentials. Unfortunately, little can be said on such accuracy at present, as virtually no experimental data on actinide ion mobility exists. The references to the lanthanide cases are, however, quite convincing.

The results of the thesis are presented in three papers published in high-level international journals suitable for the particular scientific field. The results on Yb dimer constitutes submitted manuscript.

Overall, the research work presented in the thesis is solid, interesting and original. It certainly indicates the PhD level of its author.

**Provisional Recommendation**

I recommend that the candidate should defend the thesis by means of a formal thesis defense

I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report

The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense

*Stolyarov AM*