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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: Professor Alexei Buchachenko

Name of the Reviewer: Sergey Levchenko

I confirm the absence of any conflict of interest 	**Date: 14-09-2021**

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

- Brief evaluation of the thesis quality and overall structure of the dissertation.

This is one of the most clear and well-organized thesis I've read. Apart from several typos, the English is close to perfect. The scientific quality is outstanding. The thesis combines analytic derivations and ab initio calculations, and can be used as a textbook on physics of weak interatomic/intermolecular interactions containing new advances in the field. There are still several changes that I recommend to improve the readability, as explained below.

- The relevance of the topic of dissertation work to its actual content

The topic exactly conveys the actual content of the thesis.

- The relevance of the methods used in the dissertation

The methods are the main subject of the thesis, and presented applications clearly demonstrate their advantages and limitations.

- The scientific significance of the results obtained and their compliance with the international level and current state of the art

The candidate compares and develops molecular and atomic-fragment approaches to calculating weak inter-molecular/atomic interactions, in particular at long range, with high precision. This is an important topic in the area of atomic-scale modelling in general, and ultracold gases in particular. Developing high-accuracy methods in this area and understanding the remaining challenges is very important for understanding behavior of matter at atomic scale when fine effects associated with long-range interactions become important. The candidate clearly explains how his results can be used for interpretation of novel experimental techniques such as laser resonance chromatography. The presented research is performed at a very high technical level, carefully discussing all approximations that may affect the target accuracy. It is certainly at the highest international level in terms of applied existing methods and analysis of the involved approximations, and extends beyond state of the art by developing novel methodology (highly accurate synthetic potentials and an extended combination rule for homonuclear dipole dispersion coefficients).

- The relevance of the obtained results to applications (if applicable)

The main purpose of the thesis is to develop approaches to accurate modelling of interatomic forces at long range. This is relevant to a wide range of applications, in particular to quantum computing using untracold gases, and spectroscopy of heavy elements in astrophysics.

- The quality of publications

The candidate has 3 first-author publications in peer-reviewed journals. One more first-author publication is in preparation and is available in arXiv. The thesis is based on these publications. All of them are of outstanding technical quality, presenting careful analysis of the methodology and results with an exemplary completeness and clarity.

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

All comments below are meant to be addressed directly by modifying thesis text (correcting typos and re-wording some parts of the text so that the answer to the questions becomes clear). A direct answer is only needed when requested specifically.

"with the long-range coefficients C_n^AB [9,10]" – discuss how the cutoff R between short- and long-range is defined

"and omitted forces of the non-Coulomb origin" – clarify which ones

"However, in the ambit of atomic response properties, atomic approaches, such as that combining Configuration Interaction method and Many-Body Perturbation Theory (CI-MBPT) [23] turned out to be more flexible and more easily customizable for specific systems, having the possibility even to embody empirical corrections (see Ref. [23])." – why is this good? don't we want a black box method without any parameters to get predictive power?

"they are usually empirical, retrieved from first-principles ab initio calculations or from experimental data [24,29]." – if they are retrieved from ab initio calculations, they are not empirical

Equation 2.6 – explain what R_lk(a) is

"the redistribution of charge under application of an external electric field depend on the direction ..." – "...depends..."

"The Thesis will mostly discuss systems where charge distribution is isotropic or, however, anisotropy is negligible." – "however" seems strange in this context

"According to Time-dependent Perturbation Theory, the wave function should be ..." – this form of wave function has nothing to do with perturbation theory, any wave function can be expressed in this way since the basis of psi_k is complete; by the way, please explain in the text what psi_k are

"The frequency \omega is high enough to make the field gradient and the higher derivatives negligible." – you did not introduce \omega; also, explain what \omega_k and \omega_kn are

"In facts" -> "In fact"

Around Eq. 2.51 – please remind what alpha_{alpha gamma}(i omega) are

"Thus, there is no system with the long-range interaction growing faster with the distance." – confusing wording: the interaction is decaying with increasing distance

"When the distance between the interacting species A and B is larger than the wavelength lambda_0, corresponding to the characteristic adsorption frequency of the perturbed species under study" – did you mean absorption frequency for electronic excitations? please clarify this sentence

Eq. 2.62 – it should be a determinant

"It should be noticed" -> "it should be noted"

"finite field CCSD(T) method" – this method was not introduced

"As the difference between scalar relativistic approximations (X2C vs. DKH2) should be very small (See Chapter 3, Section 3.3), This mismatch is due ..." – "..., this mismatch..."

Chapter 5 discusses anisotropic interactions, but no calculations of such interactions were done. It should be clearly discussed why this is so challenging compared to presented tests. Why the combinations rules were not actually tested for anisotropic interactions?

“electric properties of atoms” – I don’t think this is a proper term; the correct one would be “electronic properties”

“yield with” -> “yield”

“Detailed analysis of the long-range interactions of the dimers indicates that, for reasonably heavy atoms,...” – clarify what you mean by “reasonably heavy atoms”

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*