

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Christian Tantardini


PhD Program: Materials Science and Engineering

Title of Thesis: A study of chemical bonding through quantum chemical topology

Supervisor: Prof. Artem Oganov

Date of Thesis Defense: 31 January 2020

Name of the Reviewer: Professor Xavier Gonze

<p>I confirm the absence of any conflict of interest</p> <p>(Alternatively, Reviewer can formulate a possible conflict)</p>	<p>Signature:</p>  <p>Date: 28-12-2019</p>
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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

The PhD thesis presented by Christian Tantardini relies on quantum chemical topology, a powerful approach to analyze bonding in chemical systems, that is applied in different contexts. It includes a new proposal for an equation of states for gases, inspired by van der Waals, as well as a criterion to analyze the frontier between hydrogen bonding and van der Waals bonding, both being of general applicability. It includes also the analysis of bonding (and synthesis) within a family of molecular crystals (oxicam based). The reactivity of a catalyst is then also investigated. Then follows a study of chemical bonding under high pressure, whose result for the first stage (Pauling electronegativity) are presented, that should later be followed by an analysis using quantum chemical topology.

The structure of the thesis is quite clear, with three short preliminary parts (abstract, list of publications, introduction), a useful part on theoretical background (8 pages followed by an appendix and references), and then the major part of the thesis, part 5, with four chapters that directly include 6 publications in international refereed journals. The four chapters relate to the above-mentioned four topics. Each chapter begins with a short summary. Then follows a very short part entitled "Conclusion", and finally the acknowledgments.

As such, I do not have suggestions/criticisms about the structure of the thesis.

The title of the dissertation and its content match very well. Similarly, the methods used in the thesis are adequate to match the objectives. The results are significant and comply with international standards and current state of the art, as most of these have actually been published, which implies refereeing. Actually, the number of actual publications for such a thesis is quite large, and, furthermore, not all results are already published (the last chapter on bonding in high-pressure materials should yield a publication at some stage). As a side comment, I noted that Christian Tantardini has also published five articles that are not presented in the thesis, while being relevant for the global topics of the thesis.

The thesis is scientifically sound. Its orientation is clearly conceptual, and not applied. Indeed, the target of quantum chemical topology is to be able to frame conceptual chemistry, which allows scientists to describe and compare molecules, their properties, their bonding, their reactivity, without being predictive at this stage. Still, quantitative descriptors might be issued from such approach and then would allow to do searches, which might induce discoveries. However, the thesis did not pursue such endeavor, which is a perfectly valid choice.

I appreciate very much that the candidate has addressed important "generic" questions in the field of quantum chemical topology or chemical bonding, and provided new answers, with his studies of the equation of state for gases, the frontier between hydrogen bonding and van der Waals bonding, and chemical bonding under high pressure.

Based on the above arguments, it is clear that the thesis can be presented at a formal thesis defense.

Still, I would like to suggest a few adjustments to the manuscript :

(1) At present, the part entitled "Conclusion and perspective" of the thesis is very short, less than 15 lines. At the end of each publication, there is already a conclusion, but it is obviously focused on the specific topics of the publication. So, I feel there is a lack of high-level thinking, that would transcend the specific collection of six published paper complemented by the study of bonding under high pressure. Such broad, high-level considerations, should be present in such "conclusion or perspective". Of course, this is secondary with respect to the actual scientific achievements, which explains why I do not label such adjustment as "mandatory" for the thesis presentation. I suggest the candidate to take some time to think about the important questions in the field of quantum chemical topology, why the methodology

that he has followed has allowed him to answer the questions, why other conceptual approaches (e.g. other definitions of charges -Hirshfeld is mentioned in the thesis-, natural orbitals) are not as powerful, or on the contrary might have been used. Similarly, what are the currently existing limitations and shortcomings ? Possibly, how to use quantum topology for applications ? The ability to formulate questions is part of the scientific endeavor. This will allow the candidate to enlarge the scope of his thesis.

(2) In the unpublished work Chapter IV, I would have appreciated to see in Fig. 1 the usual Pauling electronegativity scale, simply as a reference. Indeed, in the text it is mentioned that "the results proposed by our computational approach qualitatively fit the previously results obtained in vacuo by Pauling", but the direct comparison would be useful.

(3) In the short summaries that are provided at the beginning of each chapters, as well as in the part "Theoretical background", the standard of English might be improved (miscellaneous typos or inadequate words). I would like to recommend Christian Tantardini to have a very careful reading of these parts. To help in this respect, I have noted some of these and will transmit them to him.

Let me reiterate that the overall impression is positive and the above suggestions are aimed at improving the thesis without constituting an obstacle to public presentation.

As such, I recommend the thesis to public PhD defense.

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