Skoltech
Skolkovo Institute of Science and Technology

Prof. Andriy Zhugayevych
Skolkovo Institute of Science and Technology
3 Nobel St, Moscow 143026, Russia
Phone: +7-495-2801481ext3343
Email: a.zhugayevych@skoltech.ru

*January 29, 2020*

**Review of PhD thesis of Christian Tantardini**
**"A STUDY OF CHEMICAL BONDING THROUGH QUANTUM CHEMICAL TOPOLOGY"**

Dr. Andriy Zhugayevych[1]

*Skolkovo Institute of Science and Technology*

In the reviewed PhD thesis, the author presents his results on application of chemical bonding analysis to multiple problems in physical chemistry from equation of state of molecular gases to structural analysis of molecular crystals and molecular reactivity. The results are published as contributions to six peer-reviewed articles, including two articles as the first author and another two as the only author. Most of the articles are published in top international journals in theoretical and computational chemistry. Therefore the overall scientific outcome of the work is evidently significant and the scholar quality of presentation of the work is high. For this reason I have no any critical concerns with Tantardini's work.

On Thesis Defense I would like to discuss orally the following questions:

1) In all the reported articles only one type of bonding analysis is actively used: the analysis of electronic density, whereas use of orbital population analysis is rather scarce and not covered in Section 4 of the Thesis. For example, Natural Bond Orbital (NBO) analysis is complementary to the analysis of electronic density, and can be used to explain intricate through-space interactions in crowded atomic environments for which the latter approach gives contradictory results as we demonstrated in Ref. [J Phys Chem C 118, 15610; Fig.2].

2) *The role of S-bond in tenoxicam keto-enolic tautomerization*. It is written that NBO analysis has been applied to analyze S-O interaction, but no details of this analysis are given in the article – only a few selected orbital interactions are mentioned which is not enough to understand bonding in such a crowded atomic environment where multiple interactions of similar strength compete.

3) *New equation of state for real gases*. Methodologically it is unclear why the author is limited to "fixed-accuracy" van der Waals equation, whereas more systematic (with respect to accuracy improvement) approaches exist, e.g. virial expansion.

4) *When Does a Hydrogen Bond Become a van der Waals Interaction?* Hydrogen atom tunneling is an important part of the hydrogen bond, but this aspect of bonding is missed in the author's analysis and thus it is unclear how it influences the conclusions.

5) *Chemical Bonding at High-Pressure*. The goal of this work is unclear: a formal "electronegativity" has been calculated by formula whose original context does not suppose application of pressures with pV term comparable with energy of interatomic interaction, and then no any examples of meaningful use of thus calculated quantity are given.

To summarize, the reviewed PhD thesis shows that Christian Tantardini is an experienced researcher with solid knowledge and good technical skills in computational and theoretical chemistry, having excellent publication record in top professional journals in various author combinations from contributing author to sole author. For all the above reasons I strongly recommend that Tantardini should defend his Thesis by means of a formal thesis defense. No changes to Thesis are requested by this review.

Sincerely yours,
Andriy Zhugayevych

[1] Candidate of Physical-Mathematical Sciences by the specialty "Solid State Physics" (Ukraine)