Thesis Changes Log

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. Dr. Artem R. Oganov

Chair of PhD defense Jury: Prof. Dr. Xavier Gonze   *Email:* X.Gonze@skoltech.ru

Date of Thesis Defense: 31 January 2020

The thesis document includes the following changes in answer to the external review process.

I would like to thank referees for their valuable comments and suggestions that allowed to increase the quality of PhD thesis. Hereafter, all replies are reported to their comments.

Reviewer: Prof. Dr. Alexander Shapeev

1) The quality of the English is sufficient to understand the results of the thesis, although it could be improved. For example, the first sentence of the Introduction:
«The PhD thesis is mainly devoted to studies of fundamental insight of chemical bonding in the field of Quantum Chemical Topology using first-principles simulations on different state of matter with both local basis set and plane wave basis set calculations.».
Should be corrected to read:
«The PhD thesis is mainly devoted to the study of fundamental insights on/into chemical bonding within the field of Quantum Chemical Topology using first-principles simulations of different states of matter with both local basis set and plane wave basis set calculations.».

As he suggested in the Introduction the sentence was modified.

2) The last section "CONCLUSION AND FUTURE PROSPECTIVES" is missing future perspectives as well as a discussion of the relevance of the obtained results to applications. Can the PhD candidate comment on that?

The last section numerated "6.0" was reformulated as written below taking into account all raised questions by the referee:
«The human mind gets information from experiences, and collection of those can be described by the same abstracted model in the same group. In case an experience cannot be connected by anyone to an already present model, then the human mind will create a new model. The human mind is constantly looking for an explanation of the surrounding environment and this is achieved through abstracted models to catalogue the information.
Scientists, more than everyone, are driven by this ancestral need and, through continuous research and the creation of new definitions, want to describe the physical phenomena. In fact, even if the definitions change over time, they change or become obsolete thanks to continuous research. It is remarkable that for a period have allowed us to describe the physical reality for which they were created.
So, looking the IUPAC definition for an H-bond, a lacuna was found about the "energy border" between H-bond and vdW interaction. It seems a simple concept, because the presence of H-bond should be represented by a sufficient stretch of X–H···Y observed under the given experimental conditions, but the quantification

of this stretch is not defined. In the present work, the "energy border" between H-bond and vdW interaction as the limit of long range interactions was defined through the topological descriptor source function [1-2], that was shown earlier to stem from the description of the electron density in the field of quantum theory of atoms in molecule [3] (QTAIM). This approach depends only on the method used to describe the charge density, which can be density functional theory [4-7] (DFT), Møller−Plesset perturbation theory [8-20] (MP) and coupled cluster [21-26] (CC). CC calculations are time demanding albeit they give back results that agree with experimental ones. For big systems DFT exchange/correlation functionals with different semiempirical corrections as DFT-D [27,28], Tkatchenko-Scheffler [29,30] or exchange-hole dipole moment [31-36] (XDM) dispersion model are able to estimate with a certain accuracy the dispersion energies generated by non-covalent interactions and the intermolecular charge density. Thus, the proposal to discriminate between a blurry H-bond and vdW interaction can fail, making this definition useless if there is not a very accurate description of charge density. This becomes easier with the increase of system size and should always be kept in mind during the study of non-covalent interactions. Albeit the defined "energy border" through a topological approach is characterized by obstacles that limit its applications, actually the present work is the first endeavor to estimate it. Such definition could be used in crystal structure prediction of molecular crystals in order to evaluate in presence of X–H⋯Y interactions if they are H-bonds or vdW interactions with the consequence that a larger presence of the first ones determine a better stability of the structure. This concept expressed by "energy border" for molecular crystal is similar to the concept expressed by crystal orbital Hamilton population [37] (COHP) for metal crystal structures, for which if such indicator is further away from the Fermi energy then the crystal structure is more stable.

Another improvement of theory with possible future perspective is the new proposal of an equation of state for real gases. It represents an advance in theory of gases in that atoms are no more considered like spheres, but as asymmetric atomic units in agreement with QTAIM. The spherical approximation can be feasible for monoatomic gas (i.e., He) due to the only presence of nuclear spin that generates a slight ellipsoidal distortion of atoms. However, the spherical approximation fails for diatomic and triatomic gases, being characterized by interatomic and inter-molecular interactions, which affect considerably the shape of the atoms. Specially for strong conditions (i.e., high pressure and high temperature) such interactions are extremely modified, with consequent impact on the shape of atoms, that cannot be neglected. The classical physics is seen to arise from quantum physics through an equation of state for real gases that considers the deformation of atoms induced by interatomic and inter-molecular interactions. The atomic partition made in the field of QTAIM can be considered a right choice due to previous theoretical and experimental works [38-41]. In the next future it will be necessary to compare the Van der Waals coefficients a and b calculated in the field of QTAIM with semiempirical coefficients extrapolated for P and T equal to 0 by potential curves built from experimental data of infra-red (IR) spectroscopy for several gases. This will allow us to finally validate the new equation of state for real gases with subsequently possible applications. For example, a and b coefficients calculated for a certain pressure, temperature and volume from the new equation of state for real gases will correspond to the interaction energy and average molecular/atomic volume at such conditions. Such calculated coefficients will be compared with those extrapolated through the Dunham's rules[42] by Tang-Tonnies [43] potential curve specific for Van der Waals (vdW) interactions and Lippincot–Schroeder [44] potential curve specific for hydrogen bonds (H-bonds). This will allow us to understand what kind of inter-molecular/atomic interaction exists within particles of a gas by a and b coefficients and what dimension associated to such particles. This information can give us the possibility to identify possible molecular compounds with specific functional groups that can interact with the particles of a gas for at specific conditions using one or another type of non-covalent interactions. Furthermore, different crystal structures with enough empty space could be considered as host for the particles of gas at predetermined conditions with relevant consequences in the crystal structure prediction of storage materials. The crystal structure prediction of molecular crystals is strongly affected by the non-covalent interactions as said before, and a deep study of such interactions within very well-known compounds as oxicams allowed us to better understand the mechanism of synthon formations. Such synthons as seen for oxicams are affected not only by H-bonds, but sulphur bonds (S-bonds) and π…π interactions between aromatic fragments, and affects the presence of one or another conformer generating a one or another polymorph during the crystallization. Thus, for the future prospective in the field of crystal structure prediction, it is necessary to consider them especially when we are interested to obtain new co-crystals structures. First, the molecular structures with different functional groups that allow them to make non-covalent interactions should be searched as well as the molecular structure with aromatic fragments should be searched with the possibility to make between them π…π interactions. All possible dimeric combinations should be optimized in *vacuo* and subsequently used by USPEX [45-47] evolutionary algorithm to generate the first population. USPEX

[45-47] evolutionary algorithm will create different periodical structures from the most stable molecular dimers in *vacuo* to consider the non-covalent interactions during the generation of subsequently populations until a certain number of structures stable under predetermined conditions are obtained. Thus, the tuning of non-covalent interaction should be reflected on the crystal structure prediction allowing us to obtain one or another polymorph of the considered molecular crystal.

Also in the field of crystal structure prediction the study of chemical bond through the investigation of electronegativity at high pressure gave important information for future prediction of new structures knowing *a priori* the type of bond and consequent oxidation number. This will allow us to reduce the number of possible structures that characterize the populations generated by USPEX [45-47] evolution algorithm other that the possibility to tune the entire process of crystal structure prediction focusing on a desired specific bond between two atoms to obtain different physical, chemical and mechanical proprieties. Everything correlated with the explanation of chemical bonding can be traced to the properties of a molecule and subsequently to the properties of its periodical structure as explained by QTAIM [3].

Furthermore, in order to explain a specific chemical propriety as the reactivity of a molecule a catalyst as Dess-Martin periodinane [48,49] (DMP) was investigated. DMP is very important in organic chemistry for the oxidation of alcohols into ketones [48,49]. As DMP, many other organic compounds are used by industry as catalysts without knowing the causes of their high reactivity. The possibility of a topological study with different tools allowed to investigate the causes and also the possibility of tuning of reactivity. The tuning of reactivity plays an important role into the design of new catalysts. In the optic of future prospective the *a priori* knowledge of the intrinsic causes within molecular structure that affect the reactivity will allow to go ahead in investigating how the reactivity is affected by environment (i.e., solvents). All these information will allow one to develop an new genetic algorithm within USPEX [45-47] code to predict new crystal structures of catalysts with high reactivity for predetermined environments.

The study of chemical bonding within this work can be considered a first step for the subsequent crystal structure prediction of new materials with different properties.

6.1 References

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3) In the first work "A new equation of state for real gases…" could the new equations be validated against experimental data? (for such gases as H2 or He or H2O it should be known experimentally?) Also, how large would zero-point energy effects be compared to the corrections made by the author?

The spectroscopic data from IR can give the frequencies of oscillations. The specific oscillation frequency associated to diatomic interaction for two atoms of He and to bimolecular interaction between two molecules of H_2 are fitted by potential curve of Tang-Tonnies[1] specific for Van der Waals interactions. While, the oscillation frequency associated to hydrogen bond between two molecule of water can be fitted by Lippincot–Schroeder[2] potential curve. The Van der Waals coefficients *a* and *b* can be obtained by potential curves by Dunham's rules [3]. *a* is function of depth of the potential hole, while *b* describe the variation of repulsive part of potential curve. The validation of new equation for real gases will be validated by experimental data from IR spectroscopy in a subsequently work with several gases. The calculation of the complexation energy consisting in the dissociation energy corrected for the basis set superposition error[4,5] taken into account the zero point energy of the dimer and the zero point energy of each monomer:

$$D_0^{CC} = -V_{AB}^{CC}(\mathbf{G}) - ZPE_{AB}^{CC}(\mathbf{G}) + ZPE_A^{CC}(\mathbf{G}) + ZPE_B^{CC}(\mathbf{G})$$

References:
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.**Reviewer:** Prof. Dr. Xavier Assfeld

4) I would ask to enhance a little bit the fourthchapter with references on these new phenomena induced by very high pressure. It is also not perfectly clear to me how the different values of the external pressure are fixed by the simulation protocol.

As suggested by the Referee in the Chapter IV the section "Computational Details" was modified to cleary explain how the calculations were performed. Here below is reported such section:
«A model fcc structure of He was fully optimized at hydrostatic pressures equal to 0, 50, 100, 200 and 300 GPa. Based on this relaxed structure, we created, at each pressure, a 3x3x3 supercell (i.e. the final supercell contained 108 helium atoms), and then replacing two nearest-neighbor helium atoms by different atoms, re-relaxed to find optimal geometries of μ—F and μ—μ dimers at each given pressure. The helium matrix acted as an inert pressure-transmitting medium.

The calculations were carried out with norm-conserving (NC) Vanderbilt [8] pseudopotentials for all elements except for lanthanoids and actinoids using Quantum Espresso code [9,10]. The calculations for the latters were carried out with projector-augmented wave [11] (PAW) potentials using the VASP code [12-16].

All calculations were performed using density functional theory with PBE [17] exchange-correlation functional and Monkhorst-Pack [18] *k*-points grid for He unit cell equal to 8 x 8 x 8, while for supercells it was equal to 1 x 1 x 1. The plane wave kinetic energy cut-off for NC pseudopotentials was chosen equal to 160 Ry, which gave excellent convergence, and calculations proceeded until self-consistency with energy and force convergence thresholds equal to 10^{-8} Ry. The large kinetic energy cut-off used can be considered enough to achieve the converged solution as reported in literature [19]. The kinetic energy cut-off for PAW calculations was chosen equal to 1000 eV, and with energy and force convergence thresholds were equal to 10^{-8}.

For comparison, we also computed Pauling's electronegativities for Li and Cs using Li—F, Cs—F, Li—Li, Cs—Cs and F—F dimers in an empty box with dimensions 10 x 10 x 10 Å.».

References from PhD thesis:
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**Reviewer:** Prof. Dr. Xavier Gonze

5) 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

The same request was done by Prof. Dr Alexander Shapeev and the answer is written at the point 2.

6) 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.

As suggested by the Referee in the Chapter IV was added the Pauling electronegativity scale as reference ad we have compared with all our values, as now written in the chapter:

«*In primis*, we have compared our results on electronegativity in *vacuo* with those tabulated by Pauling to see how much our results are aligned with his scale. At the first glance our values agree with Pauling values (Figure 2), except a very large discrepancy for the 1st and 2nd group: Pauling's scale shows very low values and the trend of the electronegativity is to decrease when going down the Periodic Table, but this is not what we see. Then we decided to make a test, where we extracted the electronegativities for Li and Cs from the enthalpies of their dimers with fluorine (i.e., Li—F and Cs—F) within empty box to confirm that the quality of our results are absolutely unaffected by the helium matrix. Pauling's scale reported 0.98 $eV^{-1/2}$ for Li and 0.79 $eV^{-1/2}$ for Cs, but they disagree with our computed results: 1.94 $eV^{-1/2}$ for Li and 1.97 $eV^{-1/2}$ for Cs. To evaluate if our inversed electronegativity trend respect that proposed by Pauing's scale was due to helium matrix we have calculated the electronegativity of Li and Cs from their energy dimers in *vacuo* (within empty box, see "Computational Details" section) obtaining 1.98 $eV^{-1/2}$ for Li and 2.05 $eV^{-1/2}$ for Cs. Indeed, if we directly apply Pauling's definition, eq.(1), to our results (both in helium matrix and *in vacuo)* and to experimental dissociation energies at 298K [20], we find, to our surprise, that the resulting values come out to be very far from Pauling's values and very close to our values. This showed that the presence of the helium matrix does not distort the results to any significant extent. Unfortunately, Pauling died many years ago and we cannot know how exactly he generated his scale of electronegativity. Thus, if we are unable to reproduce such results we cannot use his scale as *vademecum* for all chemists, but it is necessary to recalculate all electronegativity values giving values that are truly aligned with experimental dissociation energies.
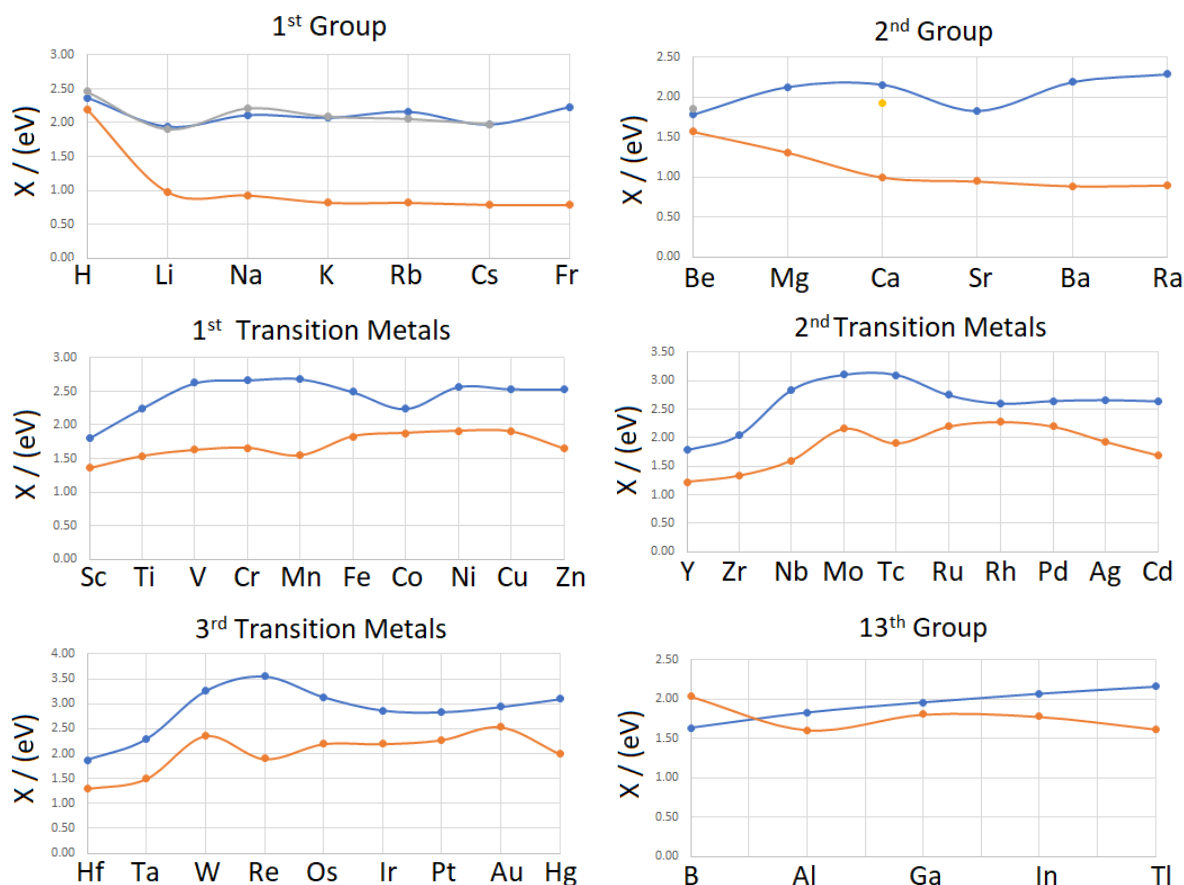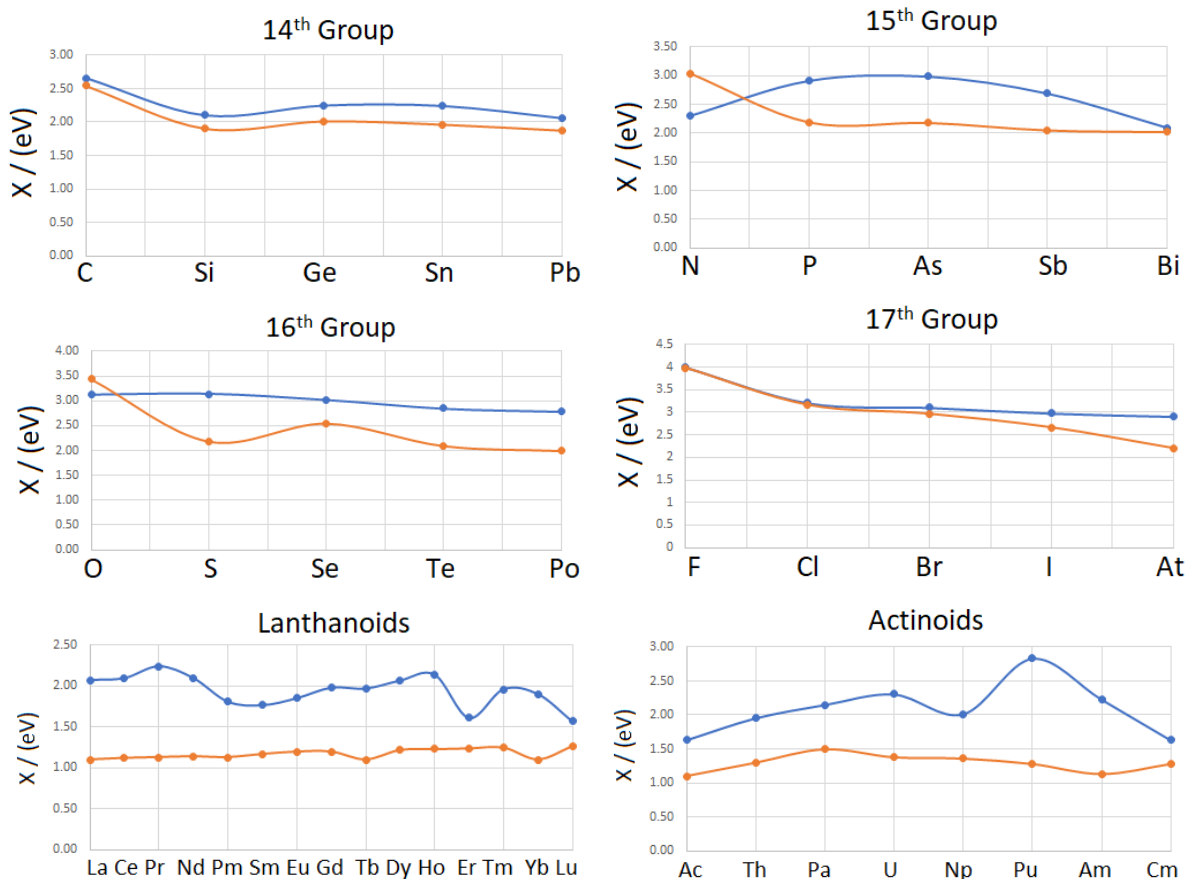
Figure 2. Electronegativity values tabulated by Pauling (orange), computed by helium matrix method here (blue) and calculated by us from experimental dissociation energies (grey, yellow) for 91 different elements.».

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.

As suggested by the Referee the quality of the English of all thesis was improved removing miscellaneous typos and changing inadequate words.