

**TO THE ACADEMIC COUNCIL OF
THE UNIVERSITY OF BELGRADE
FACULTY OF CHEMISTRY**

At the regular meeting of the Academic Council of the University of Belgrade - Faculty of Chemistry held on 12.12.2019. we have been chosen as the Committee members for review, evaluation and defense of the doctoral dissertation of **Filip Ž. Vlahović**, MSc. in chemistry, entitled:

"Теорија функционала густине у проучавању електронских стања аква- и оксо- комплекса прве серије прелазних метала".

"Density functional theory for studying electronic states of aqua- and oxo- first row transition metal complexes".

After reviewing the doctoral dissertation of the candidate, we submit to the Academic Council of the University of Belgrade - Faculty of Chemistry, the following:

R E P O R T

A. Preview of the doctoral dissertation content:

The doctoral dissertation of the candidate **Filip Ž. Vlahović**, is written on 188 pages, A4 (font 12, 1.0 line spacing) with 29 figures and 105 tables (whereas 41 tables are in the main text and 64 tables are in the *Appendix material*). The doctoral dissertation is written in English and contains the 7 chapters (171 pages): After the *Introduction* (2 pages) there is the *General part* divided into 6 subchapters (27 pages): *Theoretical and Methodological Background* contains 7 subchapters (30 pages); and is followed by *Results and discussion* given in 3 subchapters (63 pages). After the *General Conclusion* (1 page) there are *the Appendix material* (30 pages) and the *List of References* (18 pages, 394 citations). In addition, the doctoral dissertation contains *Acknowledgements*, *List of abbreviations* (1 page), *Summary* in English and Serbian languages (2 pages), a *Contents list* (3 pages) and a *Biography* of the author in English and Serbian languages, as well as ethical statements according to the University of Belgrade regulative.

Introduction part describes the subject of the doctoral dissertation as well as its general ideas and aims. The candidate describes the importance of the first row transition metals (TM) and their complex compounds, and pays particular attention to the complicated electronic structure and its relation to the general properties of these compounds, such as catalytic power, photochemical, electrochemical and biochemical properties. Namely, most ions of the first row TMs, with partially filled *d*-orbitals, can have different spin multiplicities in the ground state, thus different spin states. The precise description of the electronic structure and unambiguous

determination of the ground spin state, represent one of the greatest challenges from both experimental and theoretical point of view. This chapter also highlights the importance of theoretical chemistry, as well as Density Functional Theory (DFT) based computational methods used in this dissertation for determination of the ground state and close-lying excited states. Although accurate determination of the ground spin state was not considered during the development of most Density Functional Approximations (DFAs), there are new DFAs specially designed to deal with this type of problem, as highlighted in the introductory part of the dissertation.

Theoretical and Methodological background section presents the theoretical aspects of wave function-based methods, as well as complementary DFT approach. DFT has become one of the most commonly utilized methods for the description of the electronic structure of atoms and molecules. This method is extracting data from the three-dimensional electron density, which is a significant simplification over wave function-based methods, and thus is significantly reducing the required computational time. Like any other method, DFT has some well-known shortcomings, thus the strength and weaknesses of this powerful theoretical tool are discussed in this section. DFT is, in principle, an exact theory, although it is necessary to introduce some approximations. A brief overview of the most important DFAs is followed by a discussion about various possibilities and applicability of DFT techniques for description and investigation of inorganic chemical species. The candidate then focuses on the application of this theoretical method (in its various forms) to calculate the energy of the ground and excited electronic states of aqua- and oxo- complexes of the first row TMs. In this way, the energy of vertical electronic transitions is obtained and utilized for the reproduction and prediction of experimental absorption spectra of hexaaqua complexes. This section describes two different methods, time-dependent density functional theory (TD-DFT) and density functional theory based on ligand field theory (LF-DFT), which are used in this thesis to calculate the excited states. Although it is considered as a more popular method, because of its applicability in all fields of chemistry, TD-DFT has numerous drawbacks. LF-DFT, on the other hand, is based on a multi-determinantal description of electronic states and is specifically designed to treat *d-d* transitions in TM complexes. Finally, the energy decomposition analysis (EDA) technique is described, as well as the computational steps necessary for its effective application for a more detailed understanding of chemical properties and chemical bonding in transition metal complexes.

Results and discussion are divided into three subchapters, each containing an individual conclusion. The first section (Chapter 4.1) contains a systematic performance validation study of two different methods, TD-DFT and LF-DFT, for calculation of the ground and excited states of the first row TM complexes. For this purpose, a series of hexaaqua complexes of the general formula $[M(H_2O)_6]^{2+/3+}$ is considered. This series contains TMs in different oxidation states ($M^{2+/3+} = V^{2+/3+}, Cr^{2+/3+}, Mn^{2+/3+}, Fe^{2+/3+}, Co^{2+/3+}, Ni^{2+}$), and different ground spin states. Although conceptually very different, both methods are based on DFT, which provides a possibility to examine the impact of different DFAs on the obtained results. The geometry of the studied complex ions is optimized using 5 different DFAs, and validation of the two methods mentioned above is performed using 10 different DFAs. The candidate draws attention to the most significant aspect of the LF-DFT method, to which he attributes its good performance for calculation of excited states of first row TM complexes. Namely, LF-DFT combines a complete configuration interaction and Kohn-Sham-DFT, whereas both dynamic and static correlations are being considered. In addition, the shortcomings of the TD-DFT method were also rationalized.

The second part (Chapter 4.2) of the results and discussion is devoted to the validation of various popular DFAs for geometric optimization and then accurate determination of the ground spin state of a series of 18 oxo- (hydroxo-) iron complexes. Studied series contains the central metal ion in different oxidation states ($\text{Fe}^{2+/3+/4+}$), and therefore the whole series is saturated with energetically close-lying spin states. Spin multiplicity differences were not explicitly considered during the development of most DFAs, so this validation study aims to find the most elegant and accurate DFA able to obtain good geometries, as well as to accurately determine the ground spin state. For this purpose, 6 popular DFAs (LDA, PBE-D2, BP86-D3, S12g, S12h, B3LYP-D3) are examined. Modern S12g has proven to be the most effective for geometric optimization, as well as for the unambiguous determination of the ground spin state of all complexes under investigation. In the third part (Chapter 4.3), an EDA analysis of a series of oxo- (hydroxo-) iron model complexes, having a different oxidation state of the central metal ion ($\text{Fe}^{2+/3+/4+}$), is performed. In the first step, the geometry of the model complexes is optimized, and then the energy decomposition of the ground and excited electronic states of these molecular systems is analyzed. The selected model systems have been thoroughly analyzed, with particular attention focused on their complex electronic structure and close-lying spin states. For this purpose, S12g is used, which in the previous study proved to be the best DFA for this type of problem. Oxo- (hydroxo-) complexes of iron represent models (biomimetics) of much larger molecular species present in biological systems, thus their detailed analysis leads to the formation of new insight into different biochemical processes.

In the **General Conclusion**, the candidate summarizes the most important results, gives an analysis of the trends obtained, and proposes computational steps which should be followed in order to obtain good geometries and accurate energy of the spin states of the aqua- and oxo-complexes of the first row TM complexes.

The section **References** (394 citations) includes classical and recent scientific papers in the field of transition metals, spin states, electron transitions, spectroscopy, DFT, and energy decomposition analysis related to this dissertation.

B. A brief description of the achieved results:

Within this doctoral thesis, the complicated electronic structure of the aqua- and oxo-complexes of the first row TM series has been studied. The performance of various DFAs for the unambiguous determination of the ground electronic state was investigated, which is one of the most challenging tasks, from both theoretical and experimental point of view. Using the theoretical methods based on DFT, the energies of the ground and excited electronic states were calculated for the selected TM complexes. The primary challenge was to find an appropriate level of theory, able to explain the interrelationships between structural features and the electronic structure, and thus to rationalize experimentally obtained results.

The first part examines the performance of two different DFT methods (time-dependent density functional theory (TD-DFT) and density functional theory based on ligand field theory (LF-DFT)) for calculation of excited states and reproduction of experimentally obtained absorption spectra of a series of hexaqua complexes, where the central metal ion was $\text{V}^{2+/3+}$, $\text{Cr}^{2+/3+}$, $\text{Mn}^{2+/3+}$, $\text{Fe}^{2+/3+}$, $\text{Co}^{2+/3+}$ and Ni^{2+} . In addition to the performance of the two methods mentioned, the influence of different DFAs was examined. Generally speaking, TD-DFT

calculations agree well with experimentally obtained results at almost all tested theory levels (with minor or major deviations), although considerable discrepancies can be observed in the case of M06L and SAOP approximate density functionals. Also, the unsatisfactory accuracy of TD-DFT was observed in the cases of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ complexes, explained by the absence of orbital relaxation, as well as the inability to include double excitation. The LF-DFT method proved to be significantly superior over the entire series of TM complexes, and reproduced well all experimental spectra. It is important to emphasize that this method does not show any significant dependence on the chosen level of theory, which makes it more reliable for this type of problem. The results obtained by this method are comparable to those obtained with highly accurate *ab initio* calculations, and in some cases even better. Also, the calculations made by the LF-DFT method require less computational time than the *ab initio* calculations. Considered together, the results of this study encourage the researcher to use LF-DFT to compute *d-d* electronic transitions, as a simple yet highly accurate and reliable theoretical technique.

The ground electronic (spin) state, as well as the close-lying excited states, are related to the geometry of the molecule. Changes in the first coordination sphere of a certain complex compound, which can look negligible, can result in significant changes in the energy and arrangement of the electronic states. The influence of the applied level of theory on the obtained geometric parameters of a series of oxo- (hydroxo-) iron complexes was investigated. For this purpose, 18 oxo- (hydroxo-) complexes, formed by the coordination of different ligands, were analyzed. In the investigated series, the central iron ion has a different oxidation state and the electronic (spin) state was experimentally determined. In the first step, the geometry of all electronic states is optimized, whereby all complexes were found to have a high spin or intermediate spin electronic state as the ground state. Of the 7 DFAs used, S12g and BP86-D3 proved to be the best performing for geometrical optimization. The energetics of all electronic states were then examined, and OPBE, S12g, and SSB-D approximate density functionals showed to be the most accurate for the unambiguous determination of the ground electronic (spin) state. Taken together, these results suggest that for successful optimization as well as accurate determination of the ground electronic (spin) state, the S12g approximate density function should be used, since it represents the best way to obtain good geometry and accurate energy.

After the S12g approximate density function is characterized as the best choice for geometric optimizations as well as for the determination of the energy of electronic (spin) states, it is further utilized to analyze the energy decomposition (EDA) of a series of oxo- (hydroxo-) iron model complex. The EDA technique is based on the formation of fragments within a particular molecular species, and the observation of interactions between those fragments. In this way, it is possible to decompose the interaction energy of fragments into chemically meaningful contributions and to rationalize the various aspects and properties of molecular systems. The results show that the most important factor responsible for energy differentiation (as well as the properties of these chemical species) is the excitation energy necessary to bring a metal ion (which represents the first fragment) from the isolated ground electronic state to an electronic state present in a complex compound. The next major contribution originates from orbital stabilization, obtained by establishing a chemical bond between the metal ion and the ligands (second fragment) forming the first coordination sphere (covalent character of the chemical bond).

C. The comparative analysis of the candidate's results with the results from the literature:

The absorption spectra of complex compounds of the first TM series originate from electronic transitions (*d-d* transitions) located at the metal center. DFT methods have become the most commonly used theoretical methods for the description of complicated electronic structure of coordination compounds because of good compromise between the accuracy of obtained results and the computing time requirements. They have found application in determining the energies of electronic states as well as the energies of electronic transitions. DFT techniques, designed to determine and describe electronic transitions (TD-DFT and LF-DFT), have passed a long way to reach the stage where they are now. Although both techniques give very good results, in the case of TD-DFT particular attention must be paid to the choice of the theory level. LF-DFT, on the other hand, performs very well, and the results obtained are comparable, or often better, than those obtained by wave function-based techniques such as CASSCF, SORCI, and MRCI. Problems with the use of DFT for describing electronic (spin) states were first observed in 2001 [1]. It was concluded that older DFAs, based on *Generalized Gradient Approximation* (GGA), favored low spin states, whereas *hybrid functionals*, which have part of the exchange interaction from the *Hartree-Fock* (HF) method included, favor high spin states. Markus Reiher tried to solve this problem by lowering the portion of HF in B3LYP*. In the following years, other DFAs have shown moderate success, but also failures in attempts to describe the problem of close-lying spin states in TM complexes. [2, 3] One of the DFAs that show significant improvements in solving this type of problem was OPBE. Adding the *Grimme-D₂* dispersion energy yielded its successor, SSB-D. Additional improvements in the form of numerical stability, as well as the addition of *Grimme-D₃* dispersion energy, have resulted in the formation of S12g, which has proven to be the most effective DFA for dealing with this topic. The development of these sophisticated DFAs, as well as significant advances in the field of computing power, have made it possible to accurately describe the electronic structure and to relate it to the general properties of molecular species.

Different research groups recommend the use of different DFAs for geometric optimizations [4], as well as for studying the energies of electronic (spin) states and electronic transitions. Since there is no universal functional, validation of existing DFAs for the accurate determination of the ground state and the energy of excited electronic (spin) states is of great importance. All the results presented in this thesis are consistent with the results of experiments and/or *ab initio* calculations, which are considered very accurate. The importance of this topic is well documented in all chapters of the book *Spin States in Biochemistry and Inorganic Chemistry* [5].

[1] Paulsen, H.; Duelund, L.; Winkler, H.; Toftlund, H.; Trautwein, A. X., Free Energy of Spin-Crossover Complexes Calculated with Density Functional Methods. *Inorganic Chemistry* **2001**, 40, 2201-2203.

- [2] Harvey, J. N. DFT Computation of Relative Spin-State Energetics of Transition Metal Compounds. In *Principles and Applications of Density Functional Theory in Inorganic Chemistry I*; Springer Berlin Heidelberg: Berlin, Heidelberg, **2004**, pp 151-184.
- [3] Cramer, C. J.; Truhlar, D. G., Density functional theory for transition metals and transition metal chemistry. *Physical Chemistry Chemical Physics* **2009**, *11*, 10757-10816.
- [4] Moltved, K. A.; Kepp, K. P., Chemical Bond Energies of 3d Transition Metals Studied by Density Functional Theory. *Journal of Chemical Theory and Computation* **2018**, *14*, 3479-3492.
- [5] Swart, M.; Costas, M., *Spin States in Biochemistry and Inorganic Chemistry: Influence on Structure and Reactivity*. Wiley: **2015**.

D. Scientific papers published in the international journals and conference proceedings that are part of the doctoral dissertation:

The results of this doctoral dissertation are published in two scientific papers and one international conference proceeding as an abstract (M64). Both papers were published in renowned international journals, whereby according to the official classification used in the Republic of Serbia for evaluation of results of scientific research, one belongs to the M21 and the other to M22 category. One paper was chosen as the cover of the March 2020 issue of the *International Journal of Quantum Chemistry*.

M21 – Papers published in the top 30% of international journals

1. **Filip Vlahović**, Marko Perić, Maja Gruden-Pavlović, Matija Zlatar, Assessment of TD-DFT and LF-DFT for study of d – d transitions in first row transition metal hexaaqua complexes, *The Journal of Chemical Physics*, **2015**, *142*, 214111, DOI: 10.1063/1.4922111

Link: <https://aip.scitation.org/doi/10.1063/1.4922111>

M22 – Papers published in the top 50% of international journals

2. **Filip Vlahović**, Maja Gruden, Stepan Stepanovic, Marcel Swart, Density functional approximations for consistent spin and oxidation states of oxoiron complexes, *International Journal of Quantum Chemistry*, **2020**, *120*, 5 e26121, DOI: 10.1002/qua.26121

Link: <https://onlinelibrary.wiley.com/doi/abs/10.1002/qua.26121>

M34 - Papers published in the international conference proceedings as abstracts

1. **Filip Vlahovic**, Maja Gruden, Marcel Swart, Density Functional Approximation approach for determination of oxidation states and spin states of oxoiron complexes,

E. Checking the originality of the doctoral dissertation

Candidate **Filip Ž. Vlahović**, completes and will defend his doctoral dissertation in Chemistry on the basis of the Rule on Academic Doctoral Studies of the University of Belgrade - Faculty of Chemistry No. 1557/1 from December 12th 2013, which does not require a plagiarism check. However, due to good research practice and moral code, the plagiarism check was provided. From the report generated by the program "*iThenticate*" which checked the originality of the doctoral dissertation "**Density functional theory for studying electronic states of aqua- and oxo- first row transition metal complexes**", written by **Filip Ž. Vlahović**, we note that the found text match is 14%. This degree of correspondence is due to general places, titles, names of institutions/departments, names of terms in English, as well as the fact that the thesis has been written in English and represents a result of two (public) scientific papers, which is in accordance with point 9 of the Rule on Academic Doctoral studies. On the basis of all the above, and in accordance with point 8, paragraph 2 of the Rule on Academic Doctoral studies, concerning the verification of the originality of doctoral dissertations defended at the University of Belgrade, we declare that the report indicates the originality of the doctoral dissertation and that the prescribed preparation procedure for its defense can be continued.

F. Conclusion (explanation of the scientific contribution of the doctoral dissertation):

Based on all previous statements, it can be concluded that in the submitted dissertation entitled "**Density functional theory for studying electronic states of aqua- and oxo- first row transition metal complexes**", the candidate **Filip Ž. Vlahović**, successfully answered to all tasks related to the investigation of the electronic structure of aqua- and oxo- complexes of the first row transition metals. The results of this doctoral dissertation have been published in two scientific papers in renowned international journals (of M21 and M22 category), whereas the candidate is the first author on both papers, and one international conference proceeding as an abstract (M64). One paper was selected as the cover of a scientific journal, indicating the importance of the obtained results.

The dissertation examines in the detail the complicated electronic structure of aqua- and oxo- complexes of the first TM series, as well as the influence of different DFAs on the obtained results, with the aim of finding the best way to unambiguously determine the ground and excited electronic states. The results suggest that the best DFA for geometry optimizations, as well as for accurate determination of the ground spin state is S12g. As a part of this dissertation, electronic transition energies were also studied, using two different DFT-based methods (TD-DFT and LF-DFT). Obtained results show that both methods agree very well with the experiment, but emphasize the superiority and reliability of the LF-DFT method. It has also been shown that the mentioned methods can be used for fast investigations, as the results are consistent with the results obtained by wave function-based methods. Finally, an energy decomposition analysis was

performed, whereby the interaction energy of metal and ligands is divided into chemically meaningful contributions and related to the properties of the corresponding complex compounds.

The Commission concludes that the scientific research presented in this dissertation is in line with current trends in general and inorganic (theoretical) chemistry and represents a significant scientific contribution to the field. The results of this doctoral dissertation provide appropriate computational protocols for the precise determination of the geometry, energetics of electronic transitions, for aqua- and oxo- complexes of the first TM series.

On the basis of all the above, and in accordance with the Law of the University of Belgrade and the statute of the Faculty of Chemistry, the Commission concludes that the requirements for the defense of the doctoral dissertation are fulfilled. In this regard, the Commission proposes to the Academic council of the Faculty of Chemistry - University of Belgrade to accept the doctoral dissertation of the candidate **Filip Ž. Vlahović**, entitled "**Density functional theory for studying electronic states of aqua- and oxo- first row transition metal complexes**" and approve the public defense.

Belgrade,

06.03.2020.

Commission members

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Dr. Marcel Swart, ICREA Research professor
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