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Prof. Monika Musiał Katowice, September 6 2019

Evaluation of the PhD Thesis entitled

Multireference coupled cluster methods with local pair natural orbital approach

presented by Mr. Jakub Lang

The dynamic progress in the development of the computer hardware observed over the last decades creates hopes that the research performed *in silico* can replace that done *in vitro*. Although in the last 40 years an enormous advancement in the application of the computational chemistry into the chemical research is observed there is still a feeling that many important chemical processes are beyond the access of the theory. Of course, the quantum chemistry is capable to treat relatively large chemical structures, e.g. with the DFT (Density Functional Theory) method, however, the results are in many cases inconclusive. The desired situation would occur if the methods based on the wave function theory (WFT) could be used for that range of molecules which now are available only to the DFT approach.

One of the active research areas within the WFT segment going in that direction is a development of the local correlation methods in which number of correlated orbitals is limited to those localized and strongly interacting. A localization can be applied at the various level of the WFT approach. One of the most demanding realization of the local approach is that connected with the exponential parameterization of the wave function used in the coupled cluster (CC) approaches.

The CC methods have proven very successful in the *ab initio* description of the atomic and molecular systems, however their implementation requires cumbersome procedures and rather complicated formal derivations. Of particular importance and usefulness in the studies of difficult chemical structures are multirefence (MR) variants of the CC approach.

The scope of the research presented by Mr. Jakub Lang in his PhD dissertation is to incorporate a multireference realization of the CC method into the framework of the local approach. Basically, one employs the MR formalism in two cases: first - when the ground state of the system is degenerate or quasidegenerate; second - when the objective is the evaluation of the energies of the excited states. Within the CC theory there are two principal variants, i.e. Hilbert-Space MRCC approach and the Fock-Space MRCC approach. In the first one the wave-operator is a sum of the operators defined independently for each model function. The second MRCC approach assumes the wave-operator to be of the same form for all reference determinants, i.e., is defined universally with respect to the whole model space and due to that this version of the MRCC theory is often called a Valence Universal MRCC approach.

The aim of the research contributing to the refereed PhD thesis is to study the large challenging systems using the newly developed multireference CC methods in Hilbert-Space formalism via Mukherjee's state-selective form (MkCC) with the domain-based local pair natural orbital (DLPNO) approach which allows to study large, interesting systems at a highly accurate level, presently dominated by DFT methods. Thus, the main objective of the research is to develop new computational schemes based on the MRCC theory. The principal element of the research relies on the incorporation of the DLPNO into the MRCC methods which is crucial in high level calculations for large systems. I consider the topic of the doctoral dissertation of Mr. Jakub Lang as very interesting and well chosen. The supervisor has long experience in the development of the quantum chemistry methods used in the correlational calculations and in the construction of new variants of the coupled cluster method. The methods developed in the dissertation can be divided into three groups.

The first one is focused on realization of the DLPNO-MkCC approach at the singles and doubles level (DLPNO-MkCCSD). The study includes implementation of the MkCCSD method with the domain-based local pair natural orbital approximation. As a result Author obtained the powerful computational scheme capable to treat systems with more than 2000 basis functions.

The second group is devoted to the study of perturbative triples correction to the DLPNO-MkCCSD (DLPNO-MkCCSD(T)) method in order to significantly improve the results with the computational cost comparable to the variant with singles and doubles. Moreover, the newly developed methods were implemented within the ORCA package and tested on the rotational barrier of tetramethyleneethane and isomers of napthynes. Mr. Lang also has calculated the larger systems, e.g. $[Be(^{Me}L)_2]$ complex, triangulene or dynemicin.

The last group is devoted to the tailored coupled cluster method at the CCSD level with DLPNO, i.e. DLPNO-TCCSD. This is new implementation of the DLPNO-CCSD method and also canonical MkCCSD one tailored by matrix product state wave functions. New computational schemes provide better results than regular ones, i.e. Mk-CCSD or TCCSD. The benchmark tests were done for TME, oxo-Mn(salen) and porphyrin.

The results have been presented in three papers published in *Molecular Physics*, *Journal of Chemical Theory and Computation*, *Physical Chemistry Chemical Physics* in which Mr. Jakub Lang is a coauthor.

Speaking in general terms I am impressed by the professionalism and high skill of the Author of the dissertation. The performed calculations are done with the state of the art technique. Also I appreciate his well thought out comments and mature opinions on the studied subject. I would like to compliment the Author as well as his supervisor for selecting an attractive topic of the research which in many aspects shows strong ties with the experimental chemistry.

Just a few words concerning an editorial aspect of the dissertation. It is composed of seven chapters and a bibliography plus a list of figures and tables. In the Introduction Author describes the content of the PhD thesis and the dissertation is finished by an overview that summarizes the work. The doctoral dissertation is written in English, in a clear and understandable language.

Coming to the conclusion I want to state that Mr. Jakub Lang is a well educated, knowledgeable and skilled person capable of doing research in the field of quantum chemistry. He has a good orientation in the modern quantum chemical methods being — at the same time — aware of the current limitations of the theory particularly in cases when the large molecules come into play.

Thus judging on the basis of his dissertation I am stating that his knowledge, competence and proficiency in the field of quantum chemistry merits - beyond any doubt - the degree of Doctor of Philosophy.

Thus giving my high evaluation of his dissertation I conclude that **I recommend to grant Mr. Jakub Lang the degree of Doctor of Philosophy.**

If it is in accordance with the local customs or regulations I suggest to grant the degree with the distinction **summa cum laude**.

M. Muriel