Report on the thesis

„Multireference State-Specific Mukherjee’s Coupled Cluster Method With Iterative and Non-iterative Triexcitations“

submitted by Kiran Bhaskaran Nair
to the Faculty of Science, Charles University, Prague
for the defend in order to obtain the degree of Ph.D.

To start, let me mention that during the whole period of the doctoral study of Kiran Bhaskaran Nair I had a pleasure to follow his personal engagement in the development related to the subject of this thesis that is very close to my own scientific interests. As the title indicates, the work has been to a great extent methodological, and, from the candidate, it was expected to introduce a new method within the framework of the multi-reference (MR) coupled cluster (CC) theory. In particular, he had to include the contribution from the triexcited configurations in combination with a fairly successful state-specific MR CC concept introduced more than a decade ago by Prof. Debashis Mukherjee [J. Chem. Phys. 110, 6171 (1999) - MR MkCC]. The main advantage with respect to the Brillouin-Wigner (BW) MR-CC approach is its property of size extensivity, at the same time preserving an inherent property of being exempt of the intruder states problem. Since MR BW-CC has been developed and extensively investigated in the group of the thesis supervisor so far, the main implemental task was to adopt the existing code to MkCC theory, including some new variants. Furthermore, the newly implemented approaches had to be thoroughly tested, as far as the performance is concerned.

The goal of the thesis is highly topical. The subject itself required a deep understanding of the theoretical background of the MR-CC methods in general, together with understanding many subtle technical details of MkCC, in particular. To achieve this, the doctoral fellow had to manage with perfect use of the second quantization and diagrammatic techniques starting from the single reference CC approaches. A brief overview on this topic is given in the first two chapters of the thesis together with a summary related to the multi-reference CC theories with the main focus on the fundamentals of the Hilbert-space MR-CC approaches, and BWCC method, in particular.

Chapter 3 is devoted to the MR MkCC scheme, including its “linked” formulation that enables simplification of the working equations that are briefly presented for the amplitudes up to triexcitations. An “uncoupled” MkCC method is also mentioned, as a fairly successful approximation to the full variant. One has to note that the doctoral fellow has been involved in the course of this theoretical development, too. Briefly, though sufficiently, the author analyses the subtle differences in perturbative triples corrections in MR-BWCC and in different MkCC schemes, among them two approaches that directly profited from the author’s contribution. All the novel features of the MR MkCC have been implemented within the ACES II program package.

Testing applications including lowest three electronic states of O₂, singlet-triplet gap in cyclobutadiene, CH₂ and BeH₂ are presented in Chapter 5. Beside showing the performance of different (BW and Mk) variants of the MRCC, a critical analysis is given focussed on the performance of the (approximate) uncoupled variant, as well as to the sensitivity of the results with respect to rotations of orbitals within the active space. In the
case of BeH$_2$ it has been verified, that the singularities on the potential energy curve present in MkCCSD(T$_a$) were removed by the new MkCCSD(T$_u$) method. An important conclusion was that for small model spaces, the uncoupled approximation for triexcitations does not significantly deteriorate the accuracy of MkCC, and the MkCCSD(T$_u$) method can thus save a significant part of the computational cost needed to iterate the triples equation in the previously proposed MkCCSD(T$_i$). The main body of the thesis is finished by the general conclusions in Chapter 6. Main text of the thesis comprises 59 pages with 115 references that reflect the scientific scope of the candidate. The text is clearly written so that the reader is nicely introduced into the four published papers that are attached as appendices to this thesis.

As aforementioned, main part of the work has been already published and underwent a serious reviewing process in the the highly ranked scientific journal in the field (Journal of Chemical Physics).

I do not have any objections or serious critical comments to the submitted work. The following questions are meant to prompt the discussion:

i) I was somewhat puzzled by the wiggled energy difference curves between the uMkCC and MkCC (see Fig. 5.1 and 5.2). Does the candidate have a plausible explanation for such a behavior?

ii) The non-invariance with respect to rotations of orbitals in the active space seems to be a serious drawback. It is interesting to see that the same rotations cause substantial decreasing of the energy at the MkCCSD level, on the other hand increasing of the total energy when the triples are switched on. Is there an explanation for that?

**Based upon the judgment of the submitted thesis, but also on my personal experience related to the scientific quality of the candidate, I suggest the thesis for a public defense and afterwards awarding the candidate the title of PhD.**

Bratislava, 9. 06. 2011

Prof. RNDr. Jozef Noga, DrSc.