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Review of the PhD thesis of Rahul Chakraborty titled
"Advancement of the pair coupled cluster doubles-based molecular property calculations with quantum embedding"

The PhD dissertation of Rahul Chakraborty has been prepared under the supervision of Prof. Paweł Tecmer. The work was conducted at the Institute of Physics of Nicolaus Copernicus University in Toruń.

The research problems undertaken in the thesis are related to extending the applicability of the pair-coupled cluster doubles (pCCD) method. The two main goals have been to develop embedding methods that allow pCCD-based methods to be applied to large systems and to develop a methodology for obtaining accurate molecular properties using expectation-value methods with pCCD.

First, it must be stressed that the developments undertaken in the thesis are of high potential value for electronic structure method development. The pCCD ansatz, with extensions for capturing dynamic correlation, remains an attractive method for electronic structure predictions for systems featuring static correlation, particularly in view of its relatively low computational cost. The developments presented in the thesis have the potential to equip computational chemists with new tools for modelling novel materials.

Thus, the topic of the thesis is important and timely.

Turning to the evaluation of the thesis itself, I am not entirely convinced by its unconventional format, compared with similar PhD theses submitted in Poland. The first chapter provides an extensive introduction to pCCD-based methods for calculating energies and molecular properties, as well as to quantum chemical embedding methods.

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The core of the dissertation consists of a collection of four papers co-authored by Mr. Rahul Chakraborty, which are included in the thesis together with their supplementary information.

Including papers that constitute an integral part of a thesis is not unusual. However, it is customary for such papers to be preceded by chapters describing the main assumptions, results, and conclusions of the research presented in each paper, often including additional unpublished results. Instead, Chapter 2 contains only very brief descriptions of the four papers, approximately half a page for each.

Three of the included papers have already been published and have undergone peer review. The fourth has been submitted to arXiv. According to Tables 2.1–2.4, which describe the contributions of the co-authors, the role of the PhD candidate consisted of performing calculations, participating in the implementation of the new methods in the PyBEST code, and contributing to the writing of the articles.

The contributions of the PhD candidate, as described above, are appropriate for a doctoral dissertation and demonstrate his substantial involvement in the research underlying the included publications.

While reading the abstract, I was puzzled by the statement that “pCCD produces reliable results for strongly correlated chemical systems and performs better than other traditional quantum chemical methods.” It is not clear to me which methods are meant by “traditional quantum chemical methods” in this context. For strongly correlated systems, I would typically consider multiconfigurational methods such as CASSCF or MRCI to be the relevant traditional approaches.

If the number of strongly correlated electrons is modest and the choice of the active space is "natural" (e.g., CAS(6,6) for N_2), traditional multiconfigurational methods such as CASSCF would generally be expected to provide more reliable results than pCCD. I would therefore appreciate it if the author could clarify this statement and comment on the comparison between pCCD and traditional multiconfigurational methods during the discussion part of the defense.

In the first part of the Introduction, the geminal-based and related pCCD methods are reviewed. The author does not mention the work of Shuhua Li and co-workers, who have developed the GVB block-correlated coupled cluster (GVB-BCCC) methods, including

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their EOM extensions. Similarly to the pCCD ansatz, in GVB-BCCCn inter-pair correlations are accounted for. The good accuracy, attractive computational cost, and applicability to large active spaces make (EOM-)GVB-BCCCn a competing approach to pCCD-based methods. Could the author briefly discuss these methods and their relation to the pCCD approach?

The Introduction chapter is overall well written and uses appropriate scientific language and a high degree of rigor. Occasionally, however, I have encountered a few issues that could be corrected in the thesis, if possible, or clarified during the defense.

On p. 32, one finds the following sentence: “However, analysis of electron correlation using single-orbital entropy and orbital-pair mutual information based on pCCD density matrices shows that the pCCD ansatz tends to overestimate correlation effects.”

Is this statement correct? My understanding is that the pCCD ansatz generally underestimates the correlation energy, so I wonder what is meant here by “overestimate correlation effects.”

Chapter 1.6 is devoted to embedding methods. I was surprised not to see any mention of the projection-based embedding method of Müller and co-workers. This method is generally considered superior to FDET for embedding subsystems whose electron density strongly overlaps with that of the environment, including systems in which the subsystems are covalently bonded. For such systems, FDET is not applicable with the currently available approximations to the nonadditive kinetic energy functional, as these approximations generally fail in this regime. Unfortunately, this limitation is not mentioned in the thesis.

More importantly, in the paragraph below Eq. (1.118), there is an incorrect statement that the subsystem orbitals are Kohn–Sham orbitals and that they are not orthogonal. In fact, the subsystem orbitals are not Kohn–Sham orbitals, and they are not expected to be orthogonal. The inaccuracies of the DFT embedding procedure discussed in this paragraph arise from the insufficient accuracy of the nonadditive kinetic energy potential, rather than from the lack of orthogonality of the orbitals.

In Eqs. (1.115)–(1.118), the symbols (V^I_{\mathrm{nuc}}) and (V^{II}_{\mathrm{nuc}}) are not defined. It would also be preferable to use lowercase (v) for these quantities, in accordance with the usual notation for external potentials.

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In Paper 1, included as part of the dissertation, EOM-fpLCCSD-in-DFT has been applied to calculate vertical excitation energies of uranyl halides. The active subsystem comprised the uranyl fragment, while the tetrahalide fragment was assigned to the environment. The results are rather poor, particularly for the F and Br halides. The authors speculate that the embedding potential obtained for the ground state may not be appropriate for use in the EOM equations. I wonder, however, whether an alternative explanation could be the strong overlap between the halide and uranyl fragments and the resulting inadequacy of the approximation to the nonadditive kinetic energy potential, which is a component of the embedding potential.

I have also noticed what appears to be an incorrect factor in Eq. (2) of Paper 1: there should be no factor of (1/2) in front of the fourth term in the expression for the interaction energy, (E_{\mathrm{int}}). I assume that this is simply a typo.

In Paper 2, dipole moments of 20 diatomic molecules have been calculated using pCCD, fpLCCD, and fpLCCSD. The goal was to investigate the effects of including dynamic correlation and orbital rotations on the calculated dipole moments. The study of the accuracy of pCCD-based methods for predicting molecular response properties, with dipole moments as a specific example, was continued in Paper 3. In that work, the expectation-value approach of Jeziorski and Moszynski was adapted to pCCD, fpCC, and fpLCC. The corresponding "X" methods were shown to be not only more efficient than their response-theory counterparts, but also to yield more reliable results.

In Paper 4, an embedding method, pCCD-in-pCCD, is proposed. The author claims that it "removes any dependence on DFT" (p. 58). I would disagree with this statement. The embedding potential is constructed from the nonadditive exchange-correlation and kinetic potentials, and the approximations used for these quantities can therefore influence the overall accuracy of the embedding method. In this context, I am puzzled as to why the relatively poor local approximation was used for the nonadditive potentials. Could the author comment on this choice and on its possible impact on the results?

The embedding method was applied to the calculation of dipole moments and vertical excitation energies of noncovalently bound dimers.

I have also noticed mistakes on p. 173 (the first page of Paper 4), in the notation below Eq. (3). The symbol (\nu^i_{\mathrm{nuc}}(\mathbf r)) does not denote a "nuclear charge"; rather, it denotes the potential generated by the nuclei assigned to subsystem (i).

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Also, the second term in this equation is not "the Coulomb potential". It is the Coulomb (Hartree) energy.

In summary, I find the research presented in the dissertation to be of high scientific value. Three of the papers constituting the main body of the dissertation have already been published in renowned journals, namely Physical Chemistry Chemical Physics, Journal of Chemical Theory and Computation, and The Journal of Physical Chemistry A, while the fourth paper has been submitted for publication. The contributions of the PhD candidate to these works, as described in the thesis, are substantial and fully satisfactory for a doctoral dissertation. In addition to the four papers included in the dissertation, Rahul Chakraborty is a co-author of three other publications, further demonstrating his involvement in research.

The dissertation demonstrates that M.Sc. Rahul Chakraborty has a good command of advanced electronic structure methods and has acquired strong computational and programming skills. The research presented in the thesis addresses relevant and timely problems in the development and application of electronic structure methods, and the results contribute to the advancement of pCCD-based approaches and their applicability to molecular systems.

In conclusion, I find that the dissertation of M.Sc. Rahul Chakraborty meets the requirements for a doctoral thesis of the Article 187 of the Act on Higher Education and Science of July 20, 2018 (as amended) necessary to obtain the academic degree of Doctor.

I therefore recommend that Mr. Rahul Chakraborty be admitted to the subsequent stages of the doctoral procedure.

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