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Review of the PhD dissertation by Rahul Chakraborty

On June 9, 2026, the doctoral dissertation by **Rahul Chakraborty**, entitled *"Advancement of the pair coupled cluster doubles-based molecular property calculations with quantum embedding"*, was submitted to me for review. It was prepared under the supervision of dr hab. Paweł Tecmer, prof. UMK, at the Department of Quantum Physics, Institute of Physics, Nicolaus Copernicus University in Toruń, Poland.

The doctoral thesis submitted by Rahul Chakraborty investigates the advancement of pair-coupled cluster doubles (pCCD) theory, aiming to expand its applicability to strongly correlated chemical systems via quantum embedding and novel property evaluation techniques. The thesis is organized in a mixed structure. The core of the thesis comprises three articles that have already been published in the scientific literature and one preprint which is not yet published, but is available on `arXiv` and is fully aligned with the overall objectives and topic of the thesis. These four documents (together with the corresponding supplemental material) are included in the thesis as Appendix B. Additionally, the thesis comprises an extended introduction, summary of each publication and discussion of its importance, and conclusions together with a broader outlook on possible future work. Moreover, Appendix A provides details on the more technical side of evaluation of the expectation values with the so-called S-operator formalism.

Chapter 1 provides a comprehensive theoretical background, encompassing configuration interaction (CI), standard coupled cluster (CC) frameworks, seniority-based partitioning, and geminal methods, ultimately leading to the pCCD ansatz. The thesis explores dynamic correlation corrections, such as the frozen pair LCC (fpLCC) method,

and covers excited-state modeling using equation-of-motion (EOM) extensions. Furthermore, the author implements two quantum embedding formulations: pCCD-in-DFT and pCCD-in-pCCD, based on frozen density embedding (FDE) to model large supramolecular systems like uranyl tetrahalides and micro-solvated thymine. A significant methodological contribution of the work is the derivation and implementation of an expectation-value-based approach using the $\hat{S}$-operator to estimate one-electron properties. This approach successfully evaluates dipole and quadrupole moments while bypassing the computationally demanding Λ-equations required in traditional response theory. Chapter 1 is written carefully and pedagogically and is accessible to non-experts. I have found only a couple of typos and editorial problems, all of them extremely minor:

1. the abbreviation CC is given before it is introduced;
2. "on-relativistic" on page 4;
3. Eq. (1.6) and (1.7) refer to the spin-orbital basis;
4. the term "glsfci" on page 5 is likely a typo;
5. the typo "f0" instead of "f^0" is used on page 27;
6. spacing is missing in "inRef." on page 32;

Chapter 2 of the dissertation presents a summary of the publications included in the thesis, as well as other papers published by the author. While the number of papers included in the thesis is already substantial, it is worth pointing out that Rahul Chakraborty has also published several other papers in the literature. This level of scientific activity is very high for this stage of the career, especially considering that some of the papers are devoted to completely different problems which is even more impressive. Chapter 2 concludes with the statements regarding the contribution of the author to each publication of the thesis. They confirm that the author has indeed made the major contribution to each of the papers, and especially large contribution in the case of data generation, performing calculations, analysis of the results, data verification and analysis, and implementation. In my opinion, inclusion of these papers in the dissertation is therefore fully justified.

Chapter 3 is short but informative. It provides a brief summary of the main results of the thesis which are the most important from the point of view of the author. Next, an extended set of conclusions follows, together with an outlook that also points out some possible avenues of future work. Finally, the bibliography of the thesis is extensive (about 200 positions) and covers practically all relevant work in the field. Moreover, it is prepared very carefully. I have encountered only a handful of typos and editorial issues, which are not even worth mentioning, and that is clearly impressive

for a bibliography of this size.

In the next part of the review, I discuss each paper included in the thesis in turn. However, these papers have already been reviewed by several experts in the field in the course of the journal submission. It is therefore not surprising that also during the present review, no fundamental methodological or numerical problems were found within them. As a result, the questions and comments provided above are mostly driven by the curiosity of the reviewer.

Moving on to the first paper included in the thesis, the authors present a novel wave function theory in density functional theory (WFT-in-DFT) quantum embedding scheme. The embedded active subsystem is described using the frozen-pair linearized coupled cluster singles and doubles (EOM-pCCD-LCCSD) approach on top of an orbital-optimized pair-coupled cluster doubles (pCCD) reference. The environment's static embedding potential is constructed via a preceding DFT-in-DFT calculation utilizing the PW91 exchange-correlation and PW91k kinetic energy functionals within freeze-and-thaw cycles. After reading the text of the paper, I have a follow-up question. Given the discrepancy between the orbital mutual information assessment and the actual excitation energy accuracy for $UO_2F_4^{2-}$ versus $UO_2Cl_4^{2-}$, how reliable the entanglement spectrum is as a predictive tool for evaluating embedding quality *prior to* calculating the excitation energies?

The second paper included in the thesis evaluates the accuracy of electronic dipole moments computed using pair coupled cluster doubles (pCCD) and its linearized dynamic correlation corrections (pCCD-LCC). The study rigorously benchmarks these methods across 20 main-group diatomics, dipole moment surfaces (DMS), and embedded weakly-interacting complexes. The authors convincingly demonstrate that orbital-optimized pCCD with a linearized doubles correction (oo-pCCD-LCCD) yields CCSD-quality dipole moments for singly bonded molecules. The work establishes a clear, computationally efficient use-case for geminal-based methods in predicting specific electrostatic properties without requiring full single excitations, which is a huge achievement that many believed to be impossible. However, the inclusion of linearized single excitations (oo-pCCD-LCCSD) drastically overcorrects and worsens dipole moments for multiply bonded molecules such as SiO, PN, and CS. While the manuscript identifies this empirical failure, it lacks a rigorous theoretical explanation for why the linearized singles so severely over-polarize the electron density in these specific bonding environments. Can such an effect be analyzed using some simple toy model?

The third paper explores the formulation and implementation of the expectation-value coupled-cluster (XCC) approach based on the connected $\hat{S}$-operator commutator expansion (originally formulated by Jeziorski and Moszyński, and adapted by Korona)

for the pair-coupled cluster doubles (pCCD) family of methods. The central premise is to bypass the computationally demanding Λ-equations required in traditional response theory, evaluating properties directly from cluster amplitudes at significant computational savings. The performance is systematically benchmarked across about 50 molecules against linear response CCSD(T) references, obtaining satisfactory agreement for XfpCCSD dipole and quadrupole moments in the canonical HF orbital basis. This leaves me wondering whether the author considered extending this formalism to static and dynamic polarizabilities? Are the pCCD family of methods and their extensions expected to provide reliable values of such quantities?

The final paper included in the thesis is a preprint that has not yet been published in the literature (at the time of completing the review). This manuscript introduces a wave-function-in-wave-function (WFT-in-WFT) frozen density embedding (FDE) framework utilizing pair-coupled-cluster doubles (pCCD) electron densities. By extracting 1-particle reduced density matrices (1-RDMs) directly from the computationally inexpensive pCCD Λ-equations (which scale as $\mathcal{O}(N^4)$), the authors generate static embedding potentials to capture environmental effects without relying on Density Functional Theory (DFT) for the base subsystem densities. The coupling between the active and environment subsystems is iteratively resolved using freeze-and-thaw (FT) cycles. I wonder if, since the non-additive correlation potential is entirely neglected by the use of the Slater $X\alpha$ and Thomas-Fermi LDA approximations, it is reasonable to anticipate that explicitly including a parameterized correlation functional would resolve the overpolarization observed in the $H_2O\cdots NH_3$ FT cycles?

In conclusion, the remarks presented in the above review are of a supplementary nature and in no way affect the **unequivocally positive** evaluation of the doctoral dissertation by Rahul Chakraborty. The thesis addresses an important research topic and provides a solution to a scientific problem with broad applicability that is situated at the current forefront of research. It is written in excellent academic language, and the analysis of the results and their quality raise no objections. The dissertation comprises three papers published in respected peer-reviewed journals, one yet-unpublished preprint, as well as a proper introduction, discussion, and bibliography. The dissertation also demonstrates that the doctoral candidate is capable of independently conducting scientific research utilizing modern theoretical and numerical techniques.

Taking these arguments into consideration, I conclude that the dissertation **undoubtedly meets the requirements** set for doctoral dissertations by the Act of July 20, 2018, the Law on Higher Education and Science (consolidated text: Journal of Laws of 2024, item 1571, as amended), as well as the customary standards expected of doctoral dissertations in its discipline. Therefore, with full conviction, I petition the Esteemed Physical Sciences Discipline Council of the Nicolaus Copernicus University

in Toruń **to admit** Rahul Chakraborty to the further stages of the doctoral proceedings. Furthermore, due to the high quality and significance of the results contained in the dissertation, I submit a motion to **award the dissertation with distinction**.

Michał Lesiuk