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Review of Ph.D. Thesis "Advancement of the pair coupled cluster doubles-based molecular property calculations with quantum embedding" by Rahul Chakraborty

It was my pleasure to review the Ph.D. thesis referenced above, submitted by Rahul Chakraborty, and conducted under the supervision of Professor Paweł Tecmer. I was not involved in the research presented in this thesis, but my research group made our PyADF software available to Rahul Chakraborty and provided support in connection with its use in Publication 1. Neither I nor any of my group members contributed scientifically to the project. Our support is acknowledged in the publication.

Over the past decade, the groups of Tecmer and Boguslawski have developed the pair Coupled Cluster Doubles (pCCD) method, into a practical tool for describing strongly correlated molecular systems, and have put forward post-pCCD methods for capturing dynamical correlation. The present thesis fits into these lines of research and addresses two related scientific problems in this context:

First, while the computational effort for pCCD is comparable to the mean-field calculation, the computational cost of post-pCCD corrections needed for high accuracy is often prohibitive. This challenge is addressed in this thesis by applying quantum embedding methods that partition chemical systems into an active region [treated accurately with (post-)pCCD methods] and an approximately treated environment, thereby extending the applicability of (post-)pCCD-based methods to larger and more complex systems while managing computational expense.

Second, the evaluation of molecular properties is particularly relevant in molecular physics. The existing approaches for computing molecular properties that are based on response theory have been found to be inadequate in many cases. As an alternative the present thesis introduces an expectation-value-based method for computing molecular properties with pCCD and post-pCCD approaches.

Chapter 1 of the thesis presents an introduction and lays out the theoretical background of the thesis. It offers a comprehensive and well-structured overview of the theoretical foundations underlying pCCD-based methodologies. For me, Section 1.2 served as an excellent primer into this area of quantum chemistry. Beginning with the concept of seniority number and its role in classifying electronic configurations, the chapter systematically builds up the theoretical framework through geminal-based methods before introducing the pCCD ansatz itself. The subsequent sections thoughtfully expand on this base, covering dynamic correlation corrections, extensions to excited-state modeling through the equation-of-motion (EOM) formalism, and approaches for molecular property calculations as well as to quantum embedding methods.

Throughout, the discussion is characterized by remarkable clarity and didactic care, with each subsection carefully motivating the need for the next theoretical development, making the chapter accessible even to readers less familiar with the technical intricacies of coupled cluster theory (such as myself). This thorough presentation not only provides essential context for the original contributions of the thesis, but also reflects the author's strong command of the subject matter and his general theoretical knowledge in quantum chemistry and molecular physics.

The core of the thesis is formed by four publications that are summarized in Section 2 and contained in the Appendix of the thesis, which I will discuss in the following.

Publication 1 (*Phys. Chem. Chem. Phys.* **25**, 25377, 2023, DOI: 10.1039/d3cp02502k) applies pCCD-based methods (specifically the EOM-pCCD-LCCSD approach) for the active subsystem in the density-based WFT-in-DFT scheme previously developed by Andre Gomes and myself. The method uses a static embedding potential, derived from a DFT-in-DFT calculation, which is incorporated as an effective one-electron term into the pCCD-based Hamiltonian. In line with our previous work, the authors consider the calculation of electronic excitation energies, but apply pCCD-type methods.

The methodology is validated on three representative systems of increasing complexity: the hydrogen-bonded water-ammonia complex, micro-solvated thymine surrounded by six explicit water molecules, and the uranyl tetrahalide series ($UO_2X_4^{2-}$, X = F, Cl, Br), the latter posing a particularly demanding test case due to closely spaced excited states and open-shell/relativistic effects associated with actinide chemistry. It is found that the EOM-pCCD-LCCSD-in-DFT embedding reliably reproduces supramolecular excitation energies and their environmental shifts across all test systems, consistently outperforming the simpler point-charge model. A nice aspect of this paper is the complementary orbital entanglement and correlation analysis, which provides a novel, quantitative diagnostic for assessing the quality of the embedding potential.

Publication 4 (arXiv preprint, DOI: 10.48550/arXiv.2604.14904) builds on this work and addresses its most important limitation: In Publication 1, the embedding potential is generated using DFT densities, not the actual pCCD densities. The key methodological innovation is the use of pCCD response one-particle reduced density matrices, obtained inexpensively via the associated Λ-equations, to generate subsystem electron densities. From these, the density-based embedding potential is constructed. A self-consistent freeze-and-thaw (FT) protocol is implemented alongside a cheaper single-step "non-FT" variant, and dynamic correlation is incorporated a posteriori via fpCCSD/fpLCCSD corrections, including excited-state modeling through EOM-fpLCCSD. The method is validated on the dipole moments of weakly bound $CO_2\cdots Rg$ (Rg = He, Ne, Ar, Kr) complexes, which were chosen for their high sensitivity to subtle electron density changes. I particularly appreciate the use of this test case, which goes back to the first publication from my own Ph.D. thesis. Additional tests are performed for the vertical excitation energies of the $H_2O\cdots NH_3$ complex and for microsolvated uracil.

The most important finding is that pCCD-in-pCCD, particularly when combined with the expectation-value-based dipole moment approach (XfpLCCSD-in-pCCD), reproduces supramolecular CCSD(T) reference dipole moments within 1–12% error and accurately captures both the magnitude and correct ordering of localized excitations relative to supramolecular EOM-fpLCCSD calculations, in several cases outperforming even the corresponding supramolecular pCCD-based results. These results confirm that a fully pCCD-based embedding scheme is a viable, self-contained alternative to the previously developed pCCD-in-DFT method, thus reinforcing that pCCD-based embedding constitutes a promising route toward large-scale simulations of complex systems.

Publication 2 (*J. Chem. Theory Comput.* **20**, 4689, 2024, DOI: 10.1021/acs.jctc.4c00471) addresses the calculation of dipole moments with pCCD-based methods. The authors systematically benchmark pCCD, pCCD-LCCD, and pCCD-LCCSD dipole moments, using both canonical Hartree-Fock and pCCD-optimized (localized) orbitals, against CCSD(T) and experimental reference values for a diverse set of main-group diatomics, as well as selected weakly bound complexes. The response 1-RDM formalism (obtained via the pCCD Λ-equations) is used throughout, allowing a consistent, low-cost route to relaxed and unrelaxed density matrices for both pCCD and its extensions.

Notably, the analysis is extended to the pCCD-in-DFT embedding scheme developed in Publication 1, showing that static embedding reliably reproduces supramolecular dipole moments and their trends for weakly interacting hydrogen-bonded and noble-gas complexes, though some discrepancies remain for heavier noble-gas atoms due to the limitations of the approximate kinetic-energy functional.

Publication 3 (*J. Phys. Chem. A* **129**, 6713, 2025, DOI: 10.1021/acs.jpca.5c03859) directly addresses the shortcomings of the response-based approach identified in Publication 2 by implementing an expectation-value formalism for computing one-electron properties with pCCD and post-pCCD (fpCC/fpLCC) methods. Building on the explicitly connected S-operator expansion of Jeziorski and Moszyński, the authors derive expectation-value one-particle density matrices directly from the cluster amplitudes, thereby avoiding the costly Λ-equations required in the response formalism.

The approach is benchmarked extensively against relaxed CCSD(T) reference dipole and quadrupole moments for a large and chemically diverse set of 50 molecules (28 small inorganic/diatomic species and 22 organic molecules), using both canonical Hartree-Fock and pCCD-optimized orbitals. Altogether, this publication establishes the expectation-value approach as a computationally cheaper and, in many cases, more reliable alternative for one-electron properties.

Altogether, I consider this an excellent thesis that fulfills all the requirements of the Polish law on academic degrees. First, the thesis clearly demonstrates the candidate’s general theoretical knowledge in many-body physics and quantum chemistry. Chapter 1 demonstrates the candidate's command of this field with particular clarity, systematically developing the theoretical apparatus from the second-quantized formalism and the seniority concept through geminal-based and coupled-cluster wave function models to the theory of embedding potentials and molecular response properties, thereby exhibiting the breadth and depth of theoretical understanding required at the doctoral level.

Second, concerning the requirement of an original solution to a scientific problem, the thesis clearly meets this standard: the pCCD-in-pCCD embedding scheme constitutes a genuinely new, self-consistent formulation, while the expectation-value-based formulation of one- and two-particle density matrices for pCCD and post-pCCD wave functions provides a previously unavailable, computationally efficient alternative to the response (Λ-equation) formalism. Both contributions are non-trivial extensions of the theoretical machinery of many-body quantum theory rather than incremental applications of existing tools, and both have been independently implemented, tested, and published in international peer-reviewed journals, which supports the assessment that the candidate is capable of independently for-

mulating a research problem, deriving and implementing the required theory, and critically analyzing the resulting data.

I only have a few minor points that might be addressed in a revised version of the thesis:

- On the pCCD-in-pCCD embedding scheme, the abstract states: *"[It] shows significantly better performance, as it does not depend on approximated density functionals*." I do not agree with the second part of this statement, because the density-based embedding potential still requires non-additive kinetic energy and exchange-correlation functionals. (Even though I understand the point that the densities themselves are not dependent on approximated functionals). I would appreciate if this could be rephrased.
- There is a typesetting error (*"the 'glsfci wavefunction"*) before Eq. (1.9).
- In the second paragraph in Section 1.6, the author uses the term *"fragmentation approach"*. In my optinion, this term should be reserved for methods that treat the fragments on an equal footing, and *"embedding approach"* would be more appropriate here.

In summary, I conclude that in accordance with Art. 191 of the Act of July 20, 2018, on Higher Education and Science, the condition for admitting a candidate for a doctoral degree to the defense, apply for admission to further procedural stages of the dissertation.

Sincerely,