Development of Multiconfigurational Perturbation-adapted Perturbation Theory

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In 2022, a new approach in single-reference many body perturbation theory was introduced by P. Knowles [1]. The essence of the idea is to derive the zero-order Hamiltonian of a quantum many-body system from a model by requiring that the zero-order is as close to the exact Hamiltonian as possible. The procedure was termed perturbation-adapted perturbation theory. One of the conclusions of a recent analysis [2] of the formulation of the method as proposed by Knowles, was that the efficieny of the single-reference method for weakly correlated systems encourages towards the extension of the theory to the multi-reference approach. The single-but-multi version of projected multiconfigurational perturbation theory [3] serves as the basis for the formulation of the multi-reference working formulae of perturbation-adapted perturbation theory as it requires the least alteration of the original approach introduced by Knowles. The TDK work entailed derivation, implementation and debugging of the extended approach in order to improve the description of strongly correlated systems by perturbation theory. Currently, the performance of the new method is still under assessment. The computational cost when optimally coded, is expected to scale in accordance with the single-reference version, introducing a linear increase with the number of determinants in the CI expansion of the arbitrary reference function. Preliminary results of a few tests performed with a parallelized working code indicate that the inherent pivot dependence of the projected multiconfigurational method itself is enlarged by this formulation of the perturbation-adapted approach. Nonetheless, the multi-reference adaptation of the Knowles-partitioning is observed to be able to account for a significantly greater part of the correlation than that of the Moller-Plesset partitioning in strongly correlated cases. While it maintains the advance of the original single-reference version in the weakly correlated regime. Additionally, the inherent slight size-inconsistency of the framework used for the formulation is not observed to be enlarged. Publication of the results are currently in progress. As for future research topics, it is found that the reformulation of the partitioning technique with reduced pivot-dependence might be a promising study. Further considerations to completely abandon the concept of the pivot using a suitable framework to formulate another version of the multi-reference extension is among future plans.

References:

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