MP2 made better and faster? Recent developments in regularization and local correlation

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Rayleigh-Schrodinger perturbation theory, and its ab initio application to many-electron systems via Moller-Plesset (MP) perturbation theory, are not regular order by order, and therefore can exhibit erratic behavior for systems with small HOMO-LUMO gaps. In the first part of this talk, I will discuss a new approach to regularize MP2 theory against divergence in the small gap limit, based on modifying Brillouin-Wigner perturbation theory to be size-consistent as well as regular at second order [1]. The extent to which these advanced regularizers need to be system-specific versus universal will be discussed based on assessment of chemical energy differences [1,2].

My second topic is revisiting the design of local correlation methods at the MP2 level, for its own sake, and as a prototype for higher order methods. In my view, the main challenge for local correlation is to achieve full control over errors such that a user only needs to select a single numerical drop tolerance. To achieve this goal, we have designed a new “single threshold” approach [3] to local MP2, that also avoids use of projected AOs and PNOs to span the virtual space, by instead employing a localized orthogonal virtual basis. Results from a newly completed implementation [4] will be discussed.

[1] “Repartitioned Brillouin-Wigner Perturbation Theory with a Size-Consistent Second-Order Correlation Energy”, K. Carter-Fenk and M. Head-Gordon, J. Chem. Phys. 158, 234108 (2023).
[2] “Optimizing the Regularization in Size-Consistent Second-Order Brillouin-Wigner Perturbation Theory”, K. Carter-Fenk, J. Shee, and M. Head-Gordon, J. Chem. Phys. 159, 171104 (2023).
[3] “Sparsity of the Electron Repulsion Integral Tensor Using Different Localized Virtual Orbital Representations in Local Second Order Moller-Plesset Theory” Z. Wang, A. Aldossary, and M. Head-Gordon, J. Chem. Phys. 158, 064105 (2023).
[4] “Local second order Møller-Plesset theory with a single threshold using orthogonal virtual orbitals: Theory, implementation and assessment”, Z. Wang, A. Aldossary, T. Shi, Y. Liu, X.S. Li, and M. Head-Gordon, J. Chem. Theory Comput. 19, 7577-7591 (2023).