Error-Propagation by Increments

Thomas Weymuth[a] and Markus Reiher[a]

[a] *Laboratory for Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland*
markus.reiher@phys.chem.ethz.ch

For many practical applications, it is crucial to know how large the error of a given quantum chemical method is [1]. Unfortunately, it is often not possible to compare to a reference calculation of high reliability, in particular for large molecules. To tackle this problem, we propose an approach based on the Bethe–Goldstone equation [2]. With this equation, any molecular property can be cast in terms of a many-body expansion, the bodies being fragments of the original molecule. Many popular approaches in quantum chemistry are based on this idea such as the method of increments [3], the kernel energy method [4], many-body expanded full configuration interaction [5], and the fragment molecular orbital method [6].
In our specific case, we do not rely on a fragmentation of the orbital space (as is done, for example, in the method of increments) but instead directly partition the molecular structure. Then, for each of the smaller fragments, a reliable but computationally demanding reference calculation is carried out (our approach is not tailored towards a specific method, but general enough to allow for any quantum chemical method). To be flexible with regard to the choice of fragmentation, it is often necessary to separate strongly interacting parts (*e.g.*, cutting through covalent bonds). We rely on the embedding approach proposed by Manby, Miller, and coworkers [7] to take such parts into account by a computationally less expensive method (see also Ref. [8]). It is found that our many-body expansion is quickly converging for the cases studied; in fact, it is often sufficient to truncate it at third order. Therefore, this method provides a viable way to reliably propagate errors calculated on smaller fragments to larger molecules [9].

References

1. G. N. Simm, J. Proppe, and M. Reiher, *Chimia* **71** (2017), 202.
2. R. K. Nesbet, *Adv. Chem. Phys.* **14** (1969), 1.
3. H. Stoll, *Phys. Rev. B* **46** (1992), 6700.
4. L. Huang, L. Massa, and J. Karle, *Int. J. Quantum Chem.* **103** (2005), 808.
5. J. J. Eriksen, and J. Gauss, *J. Chem. Theory Comput.* **14** (2018), 5180.
6. D. G. Fedorov, and K. Kitaura, *J. Phys. Chem. A* **111** (2007), 6904.
7. F. R. Manby, M. Stella, J. D. Goodpaster, and T. F. Miller, III, *J. Chem. Theory Comput.* **8** (2012), 2564.
8. A. H. Mühlbach, and M. Reiher, *J. Chem. Phys.* **149** (2018), 184104.
9. T. Weymuth, and M. Reiher, *in preparation.*