

Assessing *ab initio* methods by analyzing their wave functions

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The quality of wave-function-based quantum-chemical approaches are assessed by comparing the obtained *wave functions* – rather than *energies* or *properties* – with reference data. This is applied to wave-functions from full configuration interaction (FCI) and coupled-cluster (CC) theory up to quadruple excitations as well as to the following first-order wave-functions of the perturbation-theory (PT) approaches: Møller-Plesset (MP)-PT, the related S2-MP-PT [1], which is a correctly spin-adapted PT incorporating spin-component-scaled MP at second order (SCS-MP2) [2], and retaining-the-excitation-degree (RE)-PT [3, 4].

It is shown that MP theory provides relatively poor first-order wave-functions. However, the MP2 energy profits from a fortuitous error compensation as the absolute contribution of the opposite-spin components to the correlation energy are underestimated while the same-spin contributions are overestimated. This trend is explained on the basis of the CI matrix-elements of the respective configurations. It is shown that the systematic error of MP2 energies increases the robustness of this method by stabilizing the opposite-spin contribution which is error-prone due to small energy denominators. We demonstrate that the SCS-MP2 parameterization of Grimme tends to correct the errors of the first-order MP wave function but overshoots. Thus, it generally underestimates the absolute value of the opposite spin contribution to the correlation energy.

CCSD and the first order RE-PT wavefunctions are rather well balanced. However, CCSD tends to underestimate the absolute value of the correlation energy which means that the doubles contributions of the CCSD wave function are consistently too small. An analysis based on the full CI matrix shows that in particular unlinked-triple excitations are systematically increasing the absolute value of the correlation energy.

In the first order RE-PT wave function this effect is partially included by neglecting exclusion principle violating terms which is a consequence of using Rayleigh-Schrödinger perturbation theory. RE-PT is the perturbation theory which provides the by far best first-order wave function. However, its total performance is not equally good as near degeneracy effects are frequently not well described. Options for improving this behavior are discussed.

[1] Fink, R. F., *J. Chem. Phys.*, 133:174113, 2010.

[2] Grimme, S., *J. Chem. Phys.*, 118:9095, 2003.

[3] Fink, R. F., *Chem. Phys. Lett.*, 428:461, 2006.

[4] Fink, R. F., *Chem. Phys.*, 356:39, 2009.