Multi-reference Brillouin–Wigner CCSD — Analytic Gradient of Energy

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Abstract

The analytic energy gradient for the multi-reference Brillouin–Wigner CCSD method has been proposed and is being implemented into the ACES II program package. The derivation is based on the generalized Hellman–Feynman theorem and is performed by the Lagrangian technique.

The gradient of the general MR BW CCSD involves quite complicated reference-coupling derivatives that are, however, omitted in the variant that iteratively corrects the size-extensivity. The first step is therefore the implementation of the gradient for this variant of the method.

In this case the resulting equations are very analogous to the single-reference CCSD gradient formulae. Much of the single-reference code can thus be reused and, moreover, the final formula as well as the lambda equations are reference-independent so the program can easily be parallelized.