Sensitivity analysis of state-specific multireference perturbation theory

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Quantum chemical methods often contain certain parameters (cluster amplitudes, linear expansion coefficients, ...). A sensitivity analysis with respect to them may be interesting to monitor (or sometimes to detect) theoretical problems in the model formulated.

In this study we examine state-specific multireference perturbation theory (SS-MRPT), an electronic structure method which has been successful in describing molecules in the challenging situation of far from equilibrium. It has been observed earlier, that non-physical kinks may appear on the potential energy surface obtained by SS-MRPT while related coupled-cluster methods may face convergence difficulties.

Sensitivity analysis is used as a tool for detecting which parameter of the theory is responsible. By monitoring the singular values of sensitivity matrices, orders of magnitude increase is found in the largest value, in the vicinity of the problematic geometry point on the potential energy surface.

The ill-effect can be removed by resolving certain type of redundancy which appears in the spin-adapted version of the theory. Redundancy is eliminated by selecting a linearly independent set of spin-adapted, excited functions. By this step, non-physical kinks are elminiated. Parallel to this, sensitivities are decreased by orders of magnitude.