Implementation and Performance of Analytical CD/RI-SA-CASSCF gradients: Cholesky Decomposition in action in Computational Chemistry

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Abstract: The implementation of analytic nuclear gradients of the state-average Complete Active Space SCF method in the framework of the Resolution-of-Identity approximation and auxiliary basis sets based on Cholesky Decomposition is presented. For optimal scaling the implementation is based on explicit and different treatment of the Coulomb, Exchange and Active parts of the two-particle density matrix. Additionally, the difference between the state-specific and state-average CASSCF implementation, due to the inclusion of the orbital relaxation in the two-particle density matrix, require a none standard approach to preserve the scaling benefits of the RI/CD approach. In this presentation details of the implementations will be reviewed. Examples of applications, in which either the RI/CD approach is instrumental to enable large-basis-set SA-CASSCF calculations or will speed up overall CPU times with up to one order of magnitude as compared to conventional integral treatment (see Figure 1), will be demonstrated.

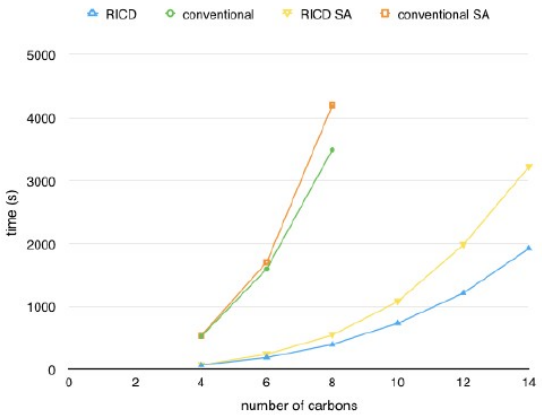

FIG. 1: Comparison of conventional and CD gradient computation time for state-specific and state-averaged calculation of polyenes.