Linear scaling open-shell local correlation methods

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The local correlation methods as originally proposed by Pulay [1, 2] and implemented previously for closed-shell methods in our group [3, 4, 5] have been generalized and implemented for spin-restricted high-spin open-shell MP2 (RMP2) and unrestricted coupled cluster (UCCSD) theory, using ROMP2 orbitals. Two different localization schemes are compared and discussed. In the first case localization is performed separately in the closed-shell and open-shell orbital spaces. In the second case localization is performed separately for the alpha and beta spin orbitals. The excitations are restricted to domains, and only strong pairs are treated at the highest level. Local density fitting approximations [6] are used to compute all integrals. Provided that the orbitals can be well localized, this leads to linear scaling of the computational effort with molecular size and extends the applicability of the local RMP2 and UCCSD methods to systems with 100-150 correlated orbitals and 2000-4000 basis functions. The methods are tested for computing ionization potentials, electron affinities and reaction energies. The accuracy is found to be comparable to the corresponding canonical methods.

References

[1] P. Pulay, Chem. Phys. Lett. **100**, 151 (1983).

[2] S. Saebø and P. Pulay, J. Chem. Phys. **88**, 1884 (1988).

[3] C. Hampel and H.-J. Werner, J. Chem. Phys. **104**, 6286 (1996).

[4] M. Schütz and H.-J. Werner, Chem. Phys. Lett. **318**, 370 (2000).

[5] M. Schütz and H.-J. Werner, J. Chem. Phys. **114**, 661 (2001).

[6] H.-J. Werner, F. R. Manby, and P.J. Knowles, J. Chem. Phys. **118**, 8149 (2003).