Local spin by the antisymmetric product of strongly orthogonal geminals (APSG) and its perturbative corrections

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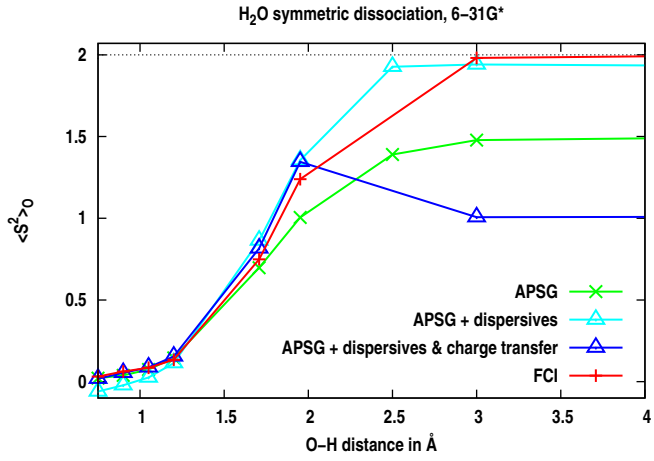
Geminals are among the simplest multireference wavefunctions, providing potential energy curves which are qualitatively correct. In spite of the apparent good shape of the energy profile, spin-state of the fragment(s) may be incorrect when dissociating multiple bonds with singlet-coupled geminals.

In the present work we explore the error in describing local spins in numerical terms. Spins of molecular fragments are computed following a spin decomposition scheme suggested recently[1]. Besides the geminal wavefunction, its perturbative (PT) corrections[2] are also examined.

Charge transfer and dispersive excitations are found to have an antagonistic role in correcting the local spin of APSG. Possibilities are explored to improve upon energy and local spin, simultaneously.



[1] E. Ramos-Cordoba, E. Matito, P. Salvador and I. Mayer, Phys. Chem. Chem. Phys., **14** 15291 (2012).

[2] T. Zoboki, Á. Szabados, P. R. Surján, J. Chem. Theory Comput., **6** 2602 (2013).