Accurate Bond Dissociation Curves at Mean-Field Computational Cost: Describing Strongly Correlated Systems with Nonorthogonal Geminals

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Antisymmetrized product of electron pairs (geminals) have been recognized as conceptually interesting and highly accurate wavefunctions since the early days of quantum chemistry.[1] In contrast to the conventional orbital approach, geminals make explicit use of the two-particle nature of the Hamiltonian. It was shown in the past that such geminal methods are a particular kind of one-electron reduced density matrix functionals.[2] Although very appealing from a fundamental point of view, until recently there were no computationally tractable approaches that did not impose severe restrictions on the geminals (*e.g.* strong orthogonality).[3] Applying a different, milder set of approximations, it was possible to surmount these bounds and use *non*-orthogonal geminals without sacrificing the mean-field like computational cost.[4]

We could show that this method is highly reliable for bond dissociations and accurately models all effects of strong electron correlation, yet is computationally very inexpensive. Although the nonorthogonal geminal method fails to fully describe weak (dynamical) correlation, the bond dissociation curves for this method are certainly highly parallel to accurate multireference calculations.

The symmetric H_2O bond dissociation, shown below, is one of the hard problems for DFT (and even coupled-cluster is running into some convergence problems at long distances). Our quartic scaling geminal method shows a very small non-parallelity error on such systems and in fact is also in very good agreement with the results of the factorially scaling doubly-occupied CI method (a CI including all possible closed-shell determinants).
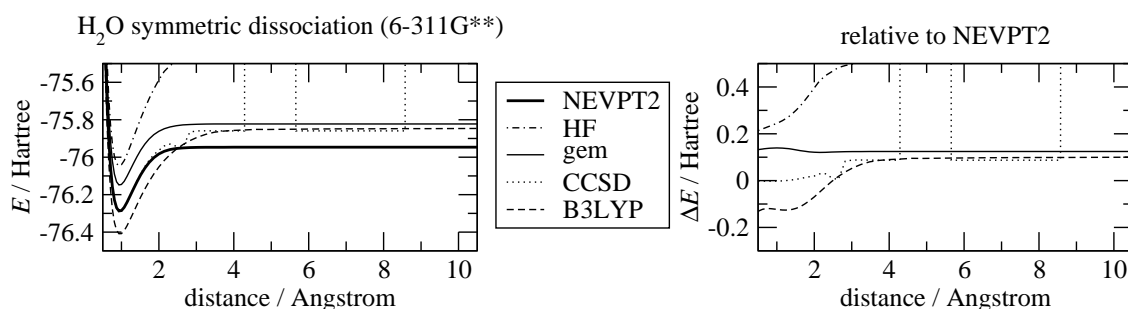
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