Electron correlation in strongly orthogonal geminals framework: A quest for polynomial scaling

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Abstract

Arguably, the most important problem of *ab initio* quantum chemistry is accurate description of electron correlation. The exact solution of many-electron Schrödinger equation within a space spanned by the direct product of one-electron basis functions is known as Full Configuration Interaction (FCI). In general, the computation of FCI ground state scales exponentially with the system size. The practical chemical models strive to approximate FCI with methods of low $O(N^5)-O(N^6)$ polynomial scaling. We argue that geminal model offers one of the best ways to approximate FCI.

In order to take advantage of the flexibilities offered by the geminal model, the traditional approach to spin contamination, perturbative corrections, and creation of multireference variational spaces may need to be reconsidered. In particular, we show how the strongly orthogonal geminals can be used to create a computational model that simultaneously (i) yields pure spin wavefunctions, (ii) is strictly size consistent (the energy is a strictly extensive property with respect to the separation to *arbitrary* non-interacting fragments, and (iii) scales polynomially as $O(N^5)$ with the system size.

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