Multireference DFT based on Strongly Orthogonal Geminals

Vitaly A. Rassolov*

Department of Chemistry and Biochemistry,

University of South Carolina, 631 Sumter St, Columbia, SC 29208

Abstract

Our group is among many searching for a practical multireference theory of molecular electronic structure. Electron correlation effects, which are the aim of any multireference theory, can be divided into phenomenologicaly distinct, but theoretically inseparable classes of *static* and *dynamic* correlation. Therefore it is appealing to treat each class with the tools best suited for the job, i.e. multireference (MR) wavefunctions to describe the static part, combined with the density functionals (DFT) for the dynamic part.

The strongly reference geminal model is an appealing multireference theory to use in the combined MR/DFT theory. The model is well defined, size-consistent, variational, and relatively inexpensive computationally. It has a clear physical interpretation, and is flexible enough to include essentially all static correlation. We investigate its use with correlation-only functionals. The simplest approach is to use an existing functional, re-scaled to mitigate double counting of the correlation effects already included in the geminal model. The more advanced approach is to build a functional from scratch. Both approaches are compared and contrasted by applying them to the geometries of diatomic molecules. Possible future modifications of the DFT treatment are also discussed.

*rassolov@mailbox.sc.edu