Explicitly Correlated Electronic Structure Methods for Predictive Energetics and Kinetics of Radical Reactions

Edward Valeev
Department of Chemistry, Virginia Tech, Blacksburg, VA 24060

High-Rank Explicitly-Correlated Coupled-Cluster Methods

We developed novel accurate electronic structure methods that incorporate interelectronic distances r_{ij} without undue extra cost. Unlike conventional counterparts, such *explicitly-correlated* wavefunctions behave like the **exact** wavefunction when electrons approach each other closely and, as a consequence, do not suffer from the ubiquitous basis-set problem that plagues accurate quantum-chemical methods.

Using the novel CCSDTQ-R12 method were were able to solve the electronic Schrodinger equation for water molecule with an 0.004 % accuracy (2 kcal/mol) without any empirical corrections. The extra cost of the R12 terms in the practical formulations of such methods, such as our CCSD(T)$_{R12}$, are almost negligible.

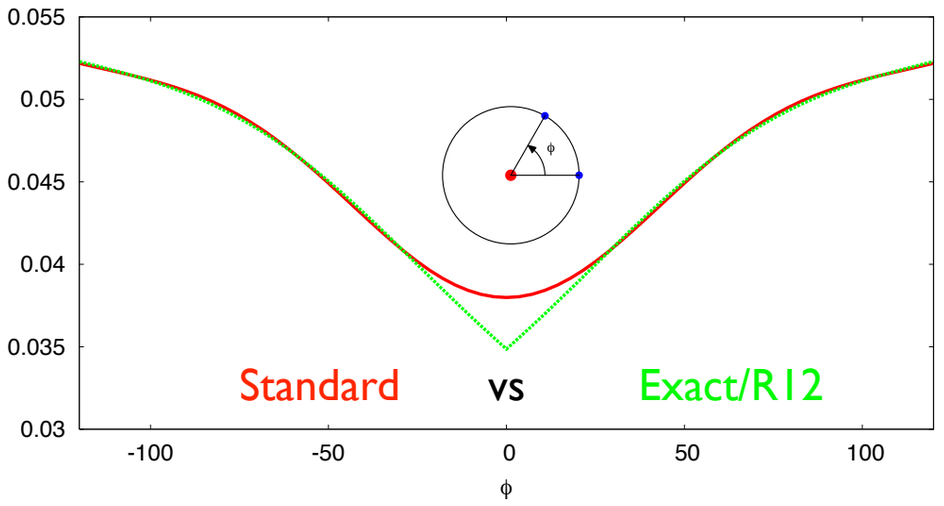
Universal Explicitly-Correlated Methods

We developed a universal R12 method that can be used to improve *any* wave function, single- or multi-reference. In an initial application to the dissociation of the triple bond in N_2 only a double-zeta basis was required with the R12 method to match the accuracy of the standard quadruple-zeta result.

Future Goals

Benchmark the performance of the efficient CC-R12 methods for computing reaction barriers and extend the universal R12 method to treat excited states.

He atom wavefunction



dissociation of N_2 molecule