### Explicitly-Correlated Electronic-Structure Methods for Single-Reference and Multi-Reference Systems

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Predictive computation of energy differences and properties related to them (equilibrium constants, reaction rates, rovibrational spectra) demand convergent series of high-level wave function models in combination with specially-designed basis set sequences. Unfortunately, the use of practical basis sets results in unacceptably-large basis set errors. For example, the mean absolute and maximum basis set error of heats of formations of small closed and open-shell molecules in the HEAT testset are 9.1 and 25.2 kJ/mol when using the correlation-consistent triple-zeta basis set. Reliable predictions of chemical accuracy (defined as 1 kcal/mol = 4.2 kJ/mol) clearly requires more extensive basis sets and computational costs increased by orders of magnitude. The cause of the large basis set errors is fundamental: the qualitatively incorrect behavior of the standard wave functions when electrons approach each other closely. Although carefully designed basis set sequences allow to reduce the basis set error of molecular energies by empirical extrapolation, such approaches are often not reliable and cannot be easily extended to properties. Explicitly correlated R12 wave function methods account for the basis set challenge from first principles. In R12 methods the two-electron basis includes products $f(r_{ij})|ij\rangle$, where $f(r_{ij})$ is a function of an interelectronic distance that models the short-range correlation of the electrons. The many-electron integrals that appear in explicitly correlated methods are simplified by systematic approximations based on the resolution of the identity (RI). At the MP2 level the use of R12 approach allows to reduce the basis set error by an order of magnitude, with a disproportionately-small increase in computational cost. I will first discuss our recent progress in extension of R12 approach to the highly-accurate coupled-cluster (CC) methods for ground and excited states. The rigorous R12 extension of the CC method is formally straightforward but the resulting equations are immensely complex and are not suited for manual implementation. To derive, manipulate, and implement these equations we employed an automated compiler that can handle the more general algebraic structure of the CC-R12 equations, isolate the special R12 intermediates, factorize the resulting tensor expressions, and generate efficient computer codes. Evaluation of the nonstandard two-electron integrals is also carried out by a high-performance computer code produced by a specialized compiler. These developments have allowed us for the first time to investigate a range of unprecedented ground-state CC-R12 methods through CCSDTQ-R12. Application of these novel methods to small polyatomic molecules results in absolute electronic energies of chemical accuracy and without any extrapolation. A more practical approach to R12 coupled-cluster methods is to introduce explicit correlation by perturbation theory. My group has developed a family of CC-R12 methods that treat geminal terms alone (CCSD(2)$_{R12}$), or in conjunction with triple excitations (CCSD(T)$_{R12}$), in a manner similar the workings of the "gold standard" CCSD(T) method. The advantage of the perturbative route is that the standard CC equations are not modified, and technical changes to the MP2-R12 code are minor. We demonstrated that the CCSD(T)$_{R12}$ method is a practical R12 variant of the CCSD(T) method with performance similar to the rigorous CCSD(T)-R12 counterpart. For the aforementioned HEAT example, the