

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

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Perturbative Explicitly-Correlated Coupled-Cluster Methods

We developed a novel perturbative approach, $\text{CCSD}(2)_{\text{R12}}$, that incorporates interelectronic distances r_{ij} into the highly-accurate coupled-cluster wavefunctions. 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.

Our $\text{CCSD}(2)_{\text{R12}}$ method has much smaller, faster-decreasing basis set errors than the conventional CCSD method, at roughly the same cost! The new method has significant technical advantages over the alternatives. Our approach has also produced an R12 version of the CCSD(T) method, the gold-standard of quantum chemistry.

Applications to Predictive Thermochemistry of Radical Species

Using the new $\text{CCSD}(T)_{\text{R12}}$ method in place of the standard CCSD(T) method allows to reduce the basis-set error of the heats of formation of small radicals computed with the standard HEAT model chemistry to the *chemical accuracy* level (1 kcal/mol) using only a triple-zeta basis set. Standard approach requires a much costlier quadruple-zeta basis for such accuracy.

Future Goals

Extend our new approach to treat radicals in electronically-excited states and test its performance for several prototypical hydrocarbon chemistries.

He atom wavefunction

