

Non-iterative coupled cluster triples models: Error cancellations and the role of amplitude relaxation

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In two recent papers [J. Chem. Phys. **140**, 064108 (2014); *ibid.* **140**, 174114 (2014)], we proposed a novel Lagrangian-based perturbation series, the CCSD(T- n) series, which systematically corrects the coupled cluster singles and doubles (CCSD) energy in orders of the Møller-Plesset fluctuation potential for effects due to triple excitations. In a follow-up paper [J. Chem. Phys., <http://dx.doi.org/10.1063/1.4904754>], we presented numerical results for the CCSD(T- n) series up through fourth order (the CCSD(T-4) model). As relaxation effects to the CCSD singles and doubles amplitude spaces start to enter the CCSD(T- n) series at fourth order, we were able to demonstrate the crucial importance of these in perturbative coupled cluster calculations, cf. Figure 1. In this talk, we will present the first numerical results for the fifth-order CCSD(T-5) model, which confirm the predicted convergence trend throughout the series towards the energy of its target, the coupled cluster singles, doubles, and triples (CCSDT) model. A comparison of the CCSD(T- n) models will be made to the Λ CCSD[T]/(T) and CCSD[T]/(T) models, which in slightly different manners augment the CCSD energy by the [T] and (T) corrections rationalized from many-body perturbation theory (MBPT).

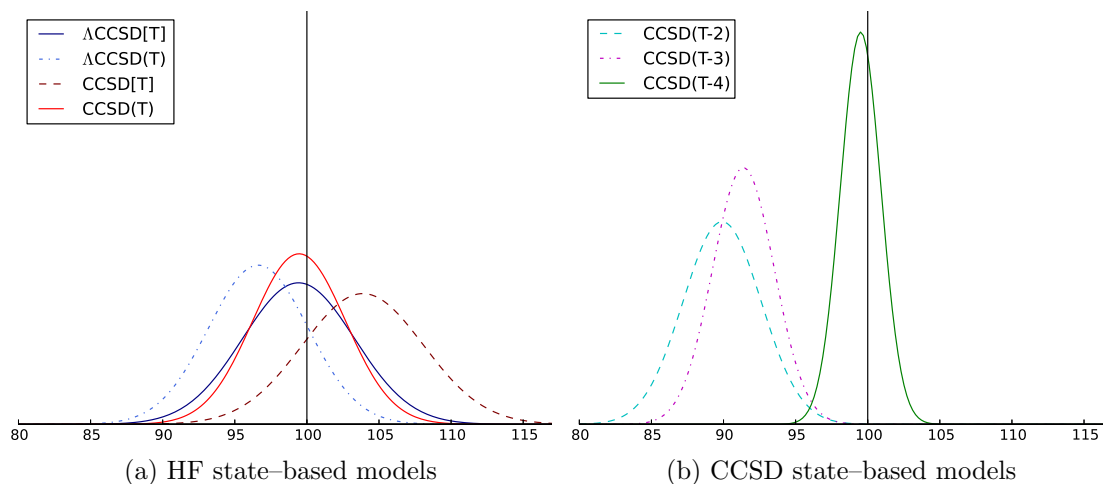


Figure 1: Normal distributions of the all-electron CCSDT/cc-pCVQZ triples correlation energy ($E_{\text{CCSDT}} - E_{\text{CCSD}}$) recovery in percent (%) for Λ CCSD[T]/(T) and CCSD[T]/(T) calculations (Figure 1a) and CCSD(T- n) ($n = 2 - 4$) calculations (Figure 1b) on a test set of 17 small closed-shell molecules at their equilibrium geometries.