Precious metal standards of intermolecular interaction energy calculations
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High-accuracy ab initio interaction energies are indispensable as data points for potential energy surfaces and as benchmark values for improving and testing more approximate approaches. The preferred algorithm (the gold standard) for computing these energies has been the coupled-cluster method with singles, doubles, and perturbative triples (CCSD(T)) converged to the complete basis set (CBS) limit. However, gold-standard calculations are expensive as correlated interaction energies converge slowly with the basis set size, and establishing the CBS limit to better than 0.05 kcal/mol typically requires a CCSD(T) calculation in a basis set of at least triple-zeta quality. If an even higher accuracy is required (for example, for the assignment of complicated high-resolution spectra), establishing a consistently superior platinum standard requires both a precisely converged CCSD(T)/CBS limit and the corrections for the core correlation, relativistic effects, and higher-order coupled-cluster terms at least through the perturbative quadruple excitations, CCSDT(Q). On the other hand, if a triple-zeta CCSD(T) calculation is not feasible but a double-zeta one is, it is worthwhile to look for a silver standard that provides the most accurate and consistent approximation to the gold standard at a reduced computational cost. I will present some recent developments, from my group and others, aimed at (i) increasing the breadth and diversity of the available collection of gold-standard benchmark interaction energies [1], (ii) evaluating best computational strategies for platinum-standard calculations [2] and producing beyond-CCSD(T) potential energy surfaces for spectroscopic and scattering applications of the highest precision [3], and (iii) improving the accuracy of the silver-standard, double-zeta-level CCSD(T)/CBS estimates through the combined use of explicit correlation and midbond functions [4].