

IS CCSD (T)/CBS REALLY THE *GOLD STANDARD*?

The *gold standard* in quantum chemistry is the method that is considered to be the best, the one that gives accurate reproduction of experimental results. The CCSD (T) method is often referred to as the *gold standard*, especially when a complete basis set (CBS) extrapolation is utilized. But is this method truly accurate, or simply the highest level method that is within our reach today?

Řezáč and Hobza¹ address the question of the accuracy of CCSD(T)/CBS by examining 24 small systems that exhibit weak interactions, including hydrogen bonding (e.g. in the water dimer and the water...ammonia complex), dispersion (e.g. in the methane dimer and the methane...ethane complex) and π -stacking (e.g. as in the stacked ethene and ethyne dimers). Since weak interactions result from quantum mechanical effects, these are a sensitive probe of computational rigor.

A CCSD(T)/CBS computation, a *gold standard* computation, still entails a number of approximations. These approximations include (a) an incomplete basis set dealt with by an arbitrary extrapolation procedure; (b) neglect of higher order correlations, such as complete inclusion of triples and omission of quadruples, quintuples, etc.;

(c) usually the core electrons are frozen and not correlated with each other nor with the valence electrons; and (d) omission of relativistic effects. Do these omissions/approximations matter?

Comparisons with calculations that go beyond CCSD(T)/CBS to test these assumptions were made for the test set. Inclusion of the core electrons within the correlation computation increases the non-covalent bond, but the average omission is about 0.6% of the binding energy. The relativistic effect is even smaller, leaving it off for these systems involving only first and second row elements gives an average error of 0.1%. Comparison of the binding energy at CCSD(T)/CBS with those computed at CCSDT(Q)/6-311G** shows an average error of 0.9% for not including higher order configuration corrections. The largest error is for the formaldehyde dimer (the complex with the largest binding energy of $4.56 \text{ kcal mol}^{-1}$) is only $0.08 \text{ kcal mol}^{-1}$. If all three of these corrections are combined, the average error is 1.5%. It is safe to say that the current gold standard appears to be quite acceptable for predicting binding energy in small non-covalent complexes. This certainly gives much support to our notion of CCSD(T)/CBS as the universal *gold standard*.

Source: <http://comporgchem.com/blog/?p=2688>