"KS-HEAT" part I : construction of a recipe targeting "semi-spectroscopic" accuracy

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First developed in 2004, HEAT, or High-Accuracy Extrapolated *ab initio* Thermochemistry, is one of a number of so-called "composite methods" designed to predict experimental enthalpies of formation to within 1 kJ mol^{-1}. This endeavor has been largely successful for well-behaved molecules containing a small number of heavy atoms; that the various flavors of these high-accuracy composite methods (HEAT[1], Wn[2], FPA[3], FPD[4]) are so similar suggests that the protocol for obtaining this level of accuracy is fairly well established. However, given modern advances in both hardware and software, one might consider to what degree of accuracy these composite-methods can be pushed, and whether a target of "semi-spectroscopic" accuracy (10 cm^{-1}) can be achieved.

To this end, the development of an extension to the HEAT protocol, currently termed "KS-HEAT", is reported. The first iteration of KS-HEAT, recently published in JCP [5], is considerably more expensive than the usual HEAT model chemistries, and also more accurate: it reproduces the ATcT (TN v. 1.124 [6]) 0K enthalpies of formation of HF, CO, N$_2$, and H$_2$O to within 13 cm^{-1}.

In part I, we report on the details of these calculations, suggest some routes for approximating components of KS-HEAT in order to extend the range of molecules to which it can be applied, and investigate the cancellation of errors hidden within HEAT which are responsible for the latter method's usually excellent performance.

References

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