

Active Thermochemical Tables: Uncertainty Quantification in Thermochemistry

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The accepted standard for expressing uncertainties attached to thermochemical values, such as enthalpies of formation, bond dissociation energies, etc., which is followed by virtually all thermochemical tabulations (such as CODATA, Gurvich et al., JANAF, etc.), is to provide the best estimate of a 95% confidence interval [1]. This is in contrast to the ubiquitous mean absolute deviation (MAD), which is frequently used in benchmarking electronic structure computational approaches, and which leads to an underestimate of the recommended thermochemical uncertainty by a factor of 2-3.

Active Thermochemical Tables (ATcT) [2] have garnered wide recognition for delivering benchmarks of unprecedented accuracy, and were successfully used in developing and benchmarking two of the most accurate electronic structure methods in existence, W4 [3] and HEAT III [4], both of which achieve sub-kJ/mol accuracy and otherwise could not have been evaluated in earnest. ATcT are currently involved in developing and benchmarking additional high-level theoretical methods [5, 6].

As opposed to the sequential approach underlying traditional thermochemical tabulations, ATcT are based on constructing, analyzing, correcting, and solving a Thermochemical Network (TN), and represent a new paradigm for obtaining accurate, reliable, and internally consistent thermochemical values, accompanied by uncertainties that adhere to the accepted standard. In addition to increased accuracy and statistically sound uncertainties, both of which are highly relevant to benchmarking state-of-the-art electronic structure methods, ATcT introduces a number of new commodities to the field of thermochemistry. Inter alia, the ATcT uncertainties are accompanied by a complete set of covariances. Though covariances are completely ignored in traditional tabulations, thus leaving no choice but to treat the tabulated values as if they were entirely uncorrelated, the enthalpies of formation that are obtained via a sequential approach are in fact very highly correlated. The TN approach of ATcT softens this correlation, and the superior accuracy achieved by ATcT is related to TN features that lower the inter-species correlation. In general, covariances influence the propagation of the uncertainties of the enthalpies of formation to reaction enthalpies, and thus affect, for example, the correct propagation of thermochemical uncertainties through models of complex chemical environments, such as simulations of combustion processes or atmospheric chemistry, whose chemical mechanisms involve a large number of species and reactions. Another valuable ATcT feature that is related to the treatment of uncertainties is the ability to perform variance decomposition, which allows, for example, an explicit quantification of the influence of each and every thermochemically-relevant determination present in the TN.

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- [1] F. D. Rossini, "Assignment of Uncertainties to Thermochemical Data", Chapter 14 in: "Experimental Thermochemistry", F. D. Rossini, Ed., Interscience: New York 1956
- [2] B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. Bittner, S. G. Nijssure, K. A. Amin, M. Minkoff, and A. F. Wagner, *J. Phys. Chem. A* 108:9979-9997, 2004; B. Ruscic, R. E. Pinzon, G. von Laszewski, D. Kodeboyina, A. Burcat, D. Leahy, D. Montoya, and A. F. Wagner, *J. Phys. Conf. Ser.* 16:561-570, 2005
- [3] A. Karton, E. Rabinovich, J. M. L. Martin, and B. Ruscic, *J. Chem. Phys.* 125:144108/1-17, 2006
- [4] M. E. Harding, J. Vazquez, B. Ruscic, A. K. Wilson, J. Gauss, and J. F. Stanton, *J. Chem. Phys.* 128:114111/1-15, 2008
- [5] W. Klopper, B. Ruscic, D. P. Tew, F. A. Bischoff, and S. Wolfsegger, *Chem. Phys.* 356:14-24, 2009
- [6] S. J. Klippenstein, L. B. Harding, and B. Ruscic, *J. Phys. Chem. A*, to be submitted