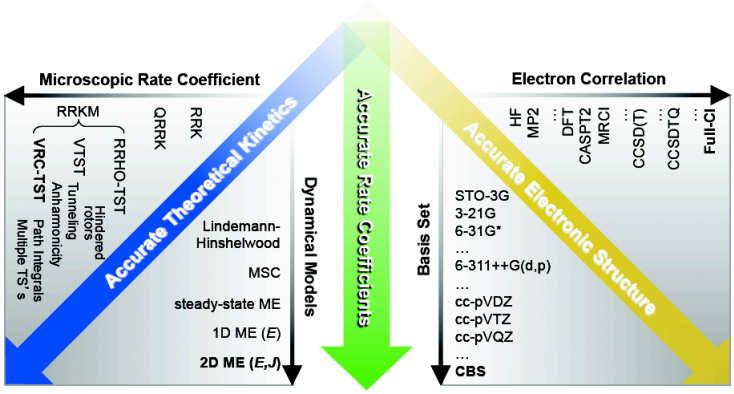
Uncertainties in *ab initio* rate coefficient calculations

Judit Zádor

Combustion Chemistry Department, Sandia National Laboratories, Livermore, California, USA

jzador@sandia.gov

Modern chemical mechanisms describing the combustion of a single-component fuel often consist of thousands of chemical reactions. Unfortunately, only a relatively small number of rate coefficients are known experimentally, especially under conditions relevant to combustion. As the pace of the experimental investigations clearly cannot keep up with the pace of mechanism development, modelers increasingly rely on theoretical approaches to determine rate coefficients. Theoretical kinetics has a clear path to increase accuracy in the calculations, which entails accurate electronic structure methods and an accurate treatment of microscopic transition probabilities coupled to a rigorous dynamic model to describe the probabilities with which the microscopic populations evolve.



The components of theoretical kinetics, arranged in order of increasing accuracy [1].

Advances in electronic structure methods and transition state theory allow accurate *ab initio* determination of elementary gas-phase reaction rate coefficients involving several heavy atoms. Exactly how accurate these calculations are, what accuracy we need, and where most of the uncertainties lie is just beginning to unfold through the recent studies directed towards this problem. In this talk these issues will be illustrated through several examples, and the possibilities that lie in Bayesian inference [2] will be highlighted.

[1] Zádor, J., Taatjes, C. A., Fernandes, R. X. *Prog. Energ. Combust. Sci.*, 37:371-421, 2011.
[2] Prager, J., Najm, H. N., Zádor, J. *Proc. Combust. Inst.*, 34:583-590, 2013.