

# Local and global uncertainty analysis in automated reaction mechanism generation

Connie W. Gao<sup>1,\*</sup> and William H. Green<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

\* Corresponding author: [connieg@mit.edu](mailto:connieg@mit.edu)

Due to the nonlinearity of chemical reaction systems, uncertainties in a few input parameters can become exaggerated while others are suppressed. Uncertainty analysis is useful for model refinement because it can efficiently identify the greatest contributors of error in a detailed kinetic model. In automatic (and also manual) reaction mechanism generation, where mechanisms are constructed through group-based estimation schemes such as kinetics rate rules and Benson group additivity, uncertainties in the inputs are often correlated. These correlations can have a large impact on the uncertainties in the model outputs. Local and global uncertainty analysis were used to analyze several kinetic models built by the Reaction Mechanism Generator (RMG),<sup>1</sup> an open-source software package capable of automatically constructing detailed kinetic mechanisms. A framework for propagating local uncertainties evaluated at nominal parameter values was implemented using Cantera<sup>2</sup> as a backend. We compare the propagation of thermodynamic and kinetic parameter uncertainties considered as either independent or correlated random variables. We show that correlated uncertainties based on kinetics rate rules and group additivity estimates of thermochemistry drastically reduce a model's degrees of freedom and can have a large impact on the model outputs. Global uncertainty analysis was implemented using adaptive Smolyak pseudospectral approximations<sup>3</sup> to efficiently compute and construct polynomial chaos expansions (PCEs) which approximate the dependence of outputs of interest on a subset of uncertain input parameters. These approximations were constructed using the MIT Uncertainty Quantification Library (MUQ),<sup>4</sup> which allows global uncertainty propagation to be performed using either a user-specified total computation time or error tolerance. Global sensitivity indices are compared against local uncertainties for several kinetic models. The results show that similar qualitative insights can be gathered from both methods. This study highlights the necessity of uncertainty analysis in the mechanism generation workflow.

## References

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