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Inference of reaction rate parameters based on summary statistics from experiments

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Abstract

We present the results of an application of Bayesian inference and maximum entropy methods for the estimation of the joint probability density for the Arrhenius rate parameters of the rate coefficient of the H_2/O_2-mechanism chain branching reaction $H + O_2 \rightarrow OH + O$. Available published data is summary statistics in terms of nominal values and error bars of the rate coefficient of this reaction at a number of temperature values obtained from shock-tube experiments. Our approach relies on generating data, in this case OH concentration profiles, consistent with the given summary statistics, using Approximate Bayesian Computation methods and a Markov chain Monte Carlo procedure. The approach permits the forward propagation of parametric uncertainty through the computational model in a manner that is consistent with the published statistics. A consensus joint posterior on the parameters is obtained by pooling the posterior parameter densities given each consistent data set. To expedite this process, we construct efficient surrogates for the OH concentration using a combination of Padé and polynomial approximants. These surrogate models adequately represent forward model observables and their dependence on input parameters and are computationally efficient to allow their use in the Bayesian inference procedure. We also utilize Gauss–Hermite quadrature with Gaussian proposal probability density functions for moment computation resulting in orders of magnitude speedup in data likelihood evaluation. Despite the strong non-linearity in the model, the consistent data sets all result in nearly Gaussian conditional parameter probability density functions. The technique also accounts for nuisance parameters in the form of Arrhenius parameters of other rate coefficients with prescribed uncertainty. The resulting pooled parameter probability density function is propagated through stoichiometric hydrogen–air auto-ignition computations to illustrate the need to account for correlation among the Arrhenius rate parameters of one reaction and across rate parameters of different reactions.

Keywords: Uncertainty quantification; Bayesian inference; Reaction rates; Arrhenius parameters; Shock tube experiments

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1. Introduction

Chemical kinetic models for hydrocarbon fuels commonly involve $\mathcal{O}(10^2 - 10^4)$ elementary reactions. Experimentalists have traditionally reported nominal elementary reaction rates with uncertainty estimates in the form of error bars or uncertainty factors assigned to rate coefficients, with the original experimental data not published. In order for modelers to make reliable computational predictions with these chemical kinetic models, the various sources of uncertainty including reaction rates must be characterized accurately and then propagated using uncertainty quantification (UQ) methods (see [1–3] for a review). This issue has received increased attention from the modeling community in a variety of contexts in recent years. Frenklach [4] discusses the role of uncertainty analysis and reduction in the context of model development. You et al. [5] developed an approach for the calibration of combustion models by constraining the optimization to both parameter uncertainties and uncertainties in experimental data. Nagy and Turányi [6] developed a method for characterizing the uncertainty in the Arrhenius parameters from the information available in kinetic databases. Sheen et al. [7] calibrated a model for the oxidation of unsaturated hydrocarbons against a range of measurements of the H atom attack process in single-pulse shock tubes using the method of uncertainty minimization by polynomial chaos expansion. Xin et al. [8] used the same methodology in providing reduced kinetic models for n-butane and iso-butane. Goldsmith et al. [9] perform global sensitivity analysis for the phenomenological rate constants for O_2 + n-propyl. Tomlin [10] provides an overview of the available methodologies for local and global sensitivity and uncertainty analysis for kinetic mechanisms. Hakim et al. [11] apply Bayesian inference in the calibration of simple Arrhenius mechanisms for simulation of Diesel engine combustion with uncertainties.

Often, modelers interpret the uncertainty factors in the reaction rates, as reported by experimentalists, as uncertainties in the pre-exponential factor of the Arrhenius rate expression. This approach is limiting, as it ignores uncertainty in the temperature exponent and activation energy, resulting in uncertainties in reaction rates that are constant in temperature. As an improvement on this approach, Nagy and Turányi [6] proposed a procedure for fitting a truncated multivariate normal distribution for the Arrhenius parameters to temperature-dependent uncertainty factors. The method, however, considers data only in the form of uncertainty factors on the rate coefficients in providing a joint Arrhenius parameter PDF but does not consider the fit model (reaction mechanism) used by the experimentalists, the detailed experimental conditions, or the statistical representation of measurement uncertainty to further inform the joint posterior parameter PDF. Turányi et al. [12] proposed a framework for the optimization of Arrhenius parameters of rate coefficients for multiple reactions using direct (e.g. rate coefficient) and indirect (e.g. ignition delay and flame speed) data and providing a covariance matrix to characterize the joint uncertainty of these parameters. The method provides a joint Gaussian distribution on the unknown Arrhenius parameters and was applied for joint characterization of the Arrhenius parameters of the rate coefficients of $H + O_2 \rightarrow OH + O$ and $H + O_2 + M \rightarrow HO_2 + M$. The method was recently utilized to provide an optimized hydrogen combustion mechanism [13]. The technique used in this investigation is fully Bayesian in that no Gaussian approximation is assumed for the Arrhenius parameters. It also considers the fit model as well as experimental conditions used by the experimentalists in obtaining the direct data on rate coefficient, which in tandem greatly inform the joint distribution (e.g. correlation) of the Arrhenius parameters. Furthermore, the proposed method incorporates prescribed marginal uncertainty in the Arrhenius parameters of rate coefficients for other reactions, acting as nuisance parameters in the inference process.

For a probabilistic forward UQ analysis, a joint PDF on the Arrhenius parameters is needed. Bayesian inference methods [14] can be used for estimating these joint PDFs given experimental data. For example, Miki et al. [15] applied Bayesian inference to quantify the uncertainty in the rate coefficient of $H + O_2 \rightarrow OH + O$ using shock-tube experimental data. Mosbach et al. [16] applied Bayesian inference to estimate the Arrhenius parameters in a chemical kinetic mechanism for n-propylbenzene oxidation using shock-tube experimental data. In the context of experimental chemical kinetics in combustion, however, the experimental data used in obtaining the nominal reaction rates and uncertainty factors is typically unavailable. The only information available that could inform a posterior PDF on the parameters are the published nominals and uncertainty factors, which can be regarded as summary statistics of the missing data. Berry et al. [17] developed a framework capable of handling such problems. The method, dubbed Data Free Inference (DFI), uses the maximum entropy (MaxEnt) principle to enforce the given summary statistics and relevant experimental parameters using Approximate Bayesian Computation (ABC) [18]. It provides a joint posterior density on both data and model parameters consistent with the published summary statistics. The implicit marginalization of this joint posterior provides the sought-after posterior on the parameters of interest. The resulting construction involves the solution of a nested pair of Bayesian inference problems, an outer one on the data-space and an inner one on the