

Chemical Model Reduction under Uncertainty

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Abstract—We outline a strategy for chemical kinetic model reduction under uncertainty. We present highlights of our existing deterministic model reduction strategy, and describe the extension of the formulation to include parametric uncertainty in the detailed mechanism. We discuss the utility of this construction, as applied to hydrocarbon fuel-air kinetics, and the associated use of uncertainty-aware measures of error between predictions from detailed and simplified models.

I. INTRODUCTION

Chemical model reduction strategies generally start from a detailed chemical kinetic mechanism as the reference or baseline gold-standard. Given this standard, a specified range of operating conditions or set of state vectors, a select set of quantities of interest (QoIs), and a requisite error threshold, a model reduction strategy produces a simplified mechanism of associated size/complexity [9], [10]. This approach is very useful in generating a spectrum of simplified mechanisms of different sizes, each associated with a given degree of fidelity in predicting chosen QoIs.

This strategy, despite its effectiveness, nonetheless relies on the quality of the starting mechanism. Yet, there is typically significant uncertainty in both the structure of available detailed mechanisms for hydrocarbon fuels, and in their thermodynamic and chemical kinetic rate parameters. Therefore, in principle, the analysis/reduction processes that provide simplified mechanisms starting from the detailed mechanism, and the measures of quality of a simplified mechanism relative to the detailed mechanism, need to account for both model and parametric uncertainties in both mechanisms. This is a challenging, yet highly relevant topic. Overconfidence in the detailed mechanism can lead to a misplaced focus on tight error tolerances in the simplified model, relative to a faulty/uncertain baseline. Simplified model errors ought to be handled along with detailed model uncertainties in the same error budget. Any error norm between simplified and detailed models ought to be weighted appropriately with attendant uncertainties. Moreover, the fact that both the detailed and simplified mechanisms are burdened with uncertainty suggests that any measures of distance between their predictions be done in a probabilistic context. This line of reasoning highlights the need for rethinking of model analysis/reduction strategies for uncertain chemical kinetic models.

The above is a significant undertaking with a range of technical challenges. There has been some work addressing model reduction under uncertainty in the context of proper orthogonal decomposition (POD) [3], albeit for small degrees

of uncertainty. The dynamical analysis of uncertain ordinary differential equation (ODE) systems has also received some attention [7], [8], in a full probabilistic setting. However, the challenge of requisite dynamical analysis and chemical model simplification has yet to receive attention.

We lay out in the following a general strategy for analysis and reduction of uncertain chemical kinetic models, and describe its utilization in the context of ignition of hydrocarbon fuel-air mixtures. The construction is fully probabilistic, allowing for an arbitrary uncertainty structure. It is based on an existing analysis and reduction strategy, using computational singular perturbation (CSP) analysis [2], [4]–[6], that has been used extensively for deterministic models of hydrocarbon fuels [1], [9]–[11].

II. METHOD

Consider a starting chemical mechanism $\mathcal{M}^*(\lambda)$, defined by a set of species $\mathcal{S}^* = \{S_1, \dots, S_N\}$ and elementary reactions $\mathcal{R}^* = \{R_1, \dots, R_M\}$, where λ is the relevant vector of uncertain parameters, *e.g.* the Arrhenius rate parameters of all reactions. Given a chosen physical system of interest, this detailed model is used to generate a database of states. To be specific, consider homogeneous constant pressure ignition of a hydrocarbon fuel-air system, for a range of initial temperature and stoichiometry, which is used to compute a set of ignition trajectories, providing a database of states $D = \{X^{(1)}, \dots, X^{(K)}\}$, where $X \in \mathbb{R}^{N+2}$ is the state vector composed of temperature, mole fractions, and pressure. Given that λ is uncertain, let D_λ denote the database computed for a given value of λ .

For any given D_λ , and considering a given set of QoIs and a tolerance τ on Importance Indices [9], [10], the CSP-based analysis and simplification strategy provides a simplified mechanism $\mathcal{M}_\tau(\lambda)$, being a subset of the starting mechanism with species $\mathcal{S}_\tau(\lambda)$ and reactions $\mathcal{R}_\tau(\lambda)$. In fact, given the starting model specification, the simplified model can be specified compactly in terms of an M -long integer vector $\alpha^\tau(\lambda)$, where, for $r = 1, \dots, M$,

$$\alpha_r^\tau(\lambda) = \begin{cases} 1 & \text{for reaction } R_r \in \mathcal{R}_\tau(\lambda) \\ 0 & \text{otherwise.} \end{cases} \quad (1)$$

Accordingly, we can view the process of database generation, analysis, and model simplification as an input-output map:

$$f_\tau(\lambda) : \lambda \rightarrow \alpha^\tau(\lambda), \quad (2)$$

which provides a convenient abstraction for the use of uncertainty quantification (UQ) methods to account for uncertainty in λ , as follows.

Placing ourselves in a probabilistic UQ setting, uncertain quantities are represented as random variables. Accordingly, λ is defined as a real-valued random vector with a presumed joint probability density function (PDF) $p(\lambda)$. The specification of this PDF is a major challenge, requiring recourse to available data on each parameter in the model, and allowing proper accounting for the correlation among different uncertain parameters. For now, let us consider that λ is composed of the Arrhenius pre-exponential rate constants, $\lambda = (A_1, \dots, A_M)$, and that each A_r is independent and lognormally distributed. The distributions can be specified based on published information on A_r nominal values and uncertainty factors.

Generating J random samples from $p(\lambda)$, $\{\lambda^{(1)}, \dots, \lambda^{(J)}\}$, the above input-output map provides corresponding samples $\{\alpha^{\tau,j}\}_{j=1}^J$, where $\alpha^{\tau,j} = \alpha^\tau(\lambda^{(j)})$, so that we can estimate, $\forall \alpha = (\alpha_1, \dots, \alpha_M)$, the joint probabilities,

$$P_\tau(\alpha) \approx \frac{1}{J} \sum_{j=1}^J \prod_{i=1}^M \delta_{\alpha_i^{\tau,j} \alpha_i} \quad (3)$$

where δ_{pq} is the Kronecker delta. The marginal probabilities are given by

$$P_\tau(\alpha_i) \approx \frac{1}{J} \sum_{j=1}^J \delta_{\alpha_i^{\tau,j} \alpha_i} \quad (4)$$

such that, we define the marginal probability that a reaction is included in the simplified mechanism for a given τ , as

$$\mathcal{P}_i^\tau = P_\tau(\alpha_i = 1) \approx \frac{1}{J} \sum_{j=1}^J \alpha_i^{\tau,j}. \quad (5)$$

In this way, we arrive at a proposed strategy for model reduction under uncertainty, whereby a reaction is included in the simplified mechanism for a given τ , when its marginal probability satisfies $\mathcal{P}_i^\tau > 1 - \epsilon$, where $0 < \epsilon < 1$.

III. DISCUSSION

We have used the above construction for simplification of uncertain methane-air and n-butane-air mechanisms with specified uncertainty in pre-exponential rate constants, based on constant pressure homogeneous ignition computations. We have explored convergence of the results as a function of the size of the database, as well as the number of random samples. We are also exploring requisite means of error estimation, relying *e.g.* on the uncertain prediction of lumped quantities such as ignition-time, or on the comparison of uncertain time-trajectories, given the detailed mechanism and a simplified mechanism. In this last context, whether comparing nominal predictions weighted with uncertainty, or relying on probabilistic measures of difference between uncertain predictions, we employ error estimates that are informed by uncertainty. We will present the above construction, and illustrate its use in the simplification of uncertain detailed kinetics of n-butane.

IV. CONCLUSION

We have outlined a strategy for analysis and simplification of detailed chemical kinetic models under uncertainty. The construction relies on CSP analysis and associated chemical model simplification, along with probabilistic handling of uncertain parameters. The compact representation of a simplified model in terms of a binary vector facilitates the handling of uncertain model space, and the formulation of the model reduction strategy in terms of chance constraints based on sampled statistics. The method is general, and easily applicable to any deterministic chemical model reduction strategy, physical system, and quantities of interest.

ACKNOWLEDGMENT

HNN & MK acknowledge the support of the US Department of Energy (DOE), Office of Basic Energy Sciences (BES) Division of Chemical Sciences, Geosciences, and Biosciences. CS acknowledges the support of the US DOE Advanced Scientific Computing Research (ASCR) Scientific Discovery through Advanced Computing (SciDAC) program. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. MV, PPC, and RMG acknowledge the support of the Italian Ministry of University and Research (MIUR).

REFERENCES

- [1] D.A. Goussis. On the Construction and Use of Reduced Chemical Kinetics Mechanisms Produced on the Basis of Given Algebraic Relations. *J. Comput. Physics*, 128:261–273, 1996.
- [2] D.A. Goussis and S.H. Lam. A study of homogeneous methanol oxidation kinetic using csp. *Proc. Comb. Inst.*, 24:113–120, 1992.
- [3] Chris Homescu, Linda R. Petzold, and Radu Serban. Error estimation for reduced-order models of dynamical systems. *SIAM Review*, 49(2):277–299, 2007.
- [4] S.H. Lam. Using CSP to Understand Complex Chemical Kinetics. *Combustion Science and Technology*, 89:375–404, 1993.
- [5] S.H. Lam and D.A. Goussis. Understanding complex chemical kinetics with computational singular perturbation. *Proc. Comb. Inst.*, 22:931–941, 1988.
- [6] S.H. Lam and D.A. Goussis. Conventional Asymptotics and Computational Singular Perturbation for Simplified Kinetics Modelling. In M.O. Smooke, editor, *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, number 384 in Springer Lecture Notes, chapter 10, pages 227–242. Springer Verlag, 1991.
- [7] M. Salloum, A. Alexanderian, O.P. Le Maître, H.N. Najm, and O.M. Knio. Simplified CSP Analysis of a Stiff Stochastic ODE System. *Computer Methods in Applied Mechanics and Engineering*, 217-220:121–138, 2012.
- [8] B.E. Sunday, R.D. Berry, H.N. Najm, and B.J. Debuschere. Eigenvalues of the Jacobian of a Galerkin-Projected Uncertain ODE System. *SIAM J. Sci. Comp.*, 33:1212–1233, 2011.
- [9] M. Valorani, F. Creta, F. Donato, H.N. Najm, and D.A. Goussis. Skeletal Mechanism Generation and Analysis for n-heptane with CSP. *Proc. Comb. Inst.*, 31:483–490, 2007.
- [10] M. Valorani, F. Creta, D.A. Goussis, J.C. Lee, and H.N. Najm. Chemical Kinetics Simplification via CSP. *Combustion and Flame*, 146:29–51, 2006.
- [11] M. Valorani, F. Creta, A. Li Brizzi, H.N. Najm, and D.A. Goussis. Surrogate Fuel Analysis and Reduction using Computational Singular Perturbation. *AIAA-2008-1009*, 2008. AIAA 46th AIAA Aerospace Sciences Meeting and Exhibit, Reno, NV.