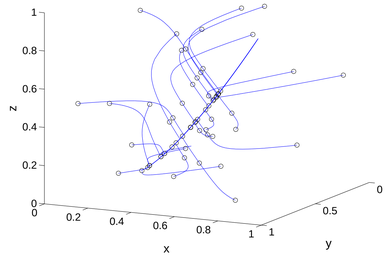
Model Simplification of Chemical Kinetic Systems Under Uncertainty

Tom Coles and Youssef Marzouk

Aerospace Computational Design Laboratory, MIT

Slow Manifolds Arising from Timescale Separation

The wide range of dissipative timescales found in chemical kinetics problems result in convergence to low dimensional manifolds. This representative 3D system rapidly converges to a 2D plane and then a 1D line. The distance moved along the line is negligible in the time span associated with movement to the line.



○ = initial condition and convergence to a lower dimensional manifold.

Model Simplification vs. Model Reduction

There are two complementary approaches to reducing the computational expense of chemical kinetics simulations:

- Remove unimportant species and reactions — sometimes termed **simplification**.
- Decrease the chemical source term stiffness or otherwise improve computational efficiency — sometimes termed **reduction**.

This work focuses on model simplification.

Computational Singular Perturbation (CSP)

Physical representation of ODE for state $\mathbf{y}$ in terms of reaction rates $R_i(\mathbf{y})$ and stoichiometric vectors $\mathbf{s}_i(\mathbf{y})$:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \sum_{i=1}^{N_R} \mathbf{s}_i(\mathbf{y}) R^i(\mathbf{y})$$

CSP fast/slow representation in terms of new basis vectors $\mathbf{a}_i$:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}^{\text{fast}}(\mathbf{y}) + \mathbf{g}^{\text{slow}}(\mathbf{y}) \qquad \mathbf{g}^{\text{fast}}(\mathbf{y}) = \sum_{i=1}^{M} \mathbf{a}_i f^i(\mathbf{y}) \qquad \mathbf{g}^{\text{slow}}(\mathbf{y}) = \sum_{i=M+1}^{N} \mathbf{a}_i f^i(\mathbf{y})$$

where mode amplitudes are found using dual basis vectors $\mathbf{b}_i$:

$$f^i(\mathbf{y}) = \mathbf{b}^i \cdot \mathbf{g}(\mathbf{y}) \qquad \mathbf{b}^i \cdot \mathbf{a}_j = \delta^i_j$$

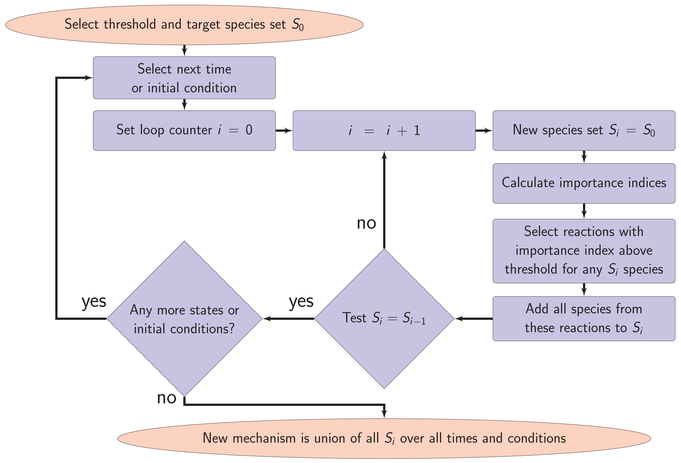
Importance Indices

These projections of stoichiometric vectors in fast and slow directions can be used to understand the impact of reactions on different species.

$$(I^i_k)_{\text{slow}} = \left| \frac{\sum_{s=M+1}^{N-N_c} [\mathbf{a}_s]_i (\mathbf{b}^s \cdot \mathbf{s}_k) F^k}{\sum_{j=1}^{N_R} \left| \sum_{s=M+1}^{N-N_c} [\mathbf{a}_s]_i (\mathbf{b}^s \cdot \mathbf{s}_j) F^j \right|} \right| \qquad (I^i_k)_{\text{fast}} = \left| \frac{\sum_{s=1}^{M} [\mathbf{a}_s]_i (\mathbf{b}^s \cdot \mathbf{s}_k) F^k}{\sum_{j=1}^{N_R} \left| \sum_{s=1}^{M} [\mathbf{a}_s]_i (\mathbf{b}^s \cdot \mathbf{s}_j) F^j \right|} \right|$$

Valorani CSP Deterministic Simplification Algorithm - 2006

This state of the art scheme uses target species and thresholds on importance indices.



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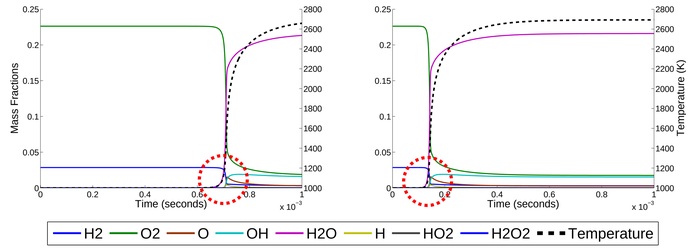
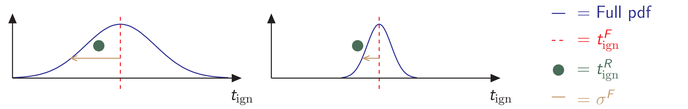
Uncertainty in Arrhenius parameters

Previous simplification schemes have been entirely deterministic; we have investigated the impact of uncertainty in Arrhenius rate parameters. Even low uncertainty can result in large variations in ignition time, as shown with this 5% change to E_A for one reaction in a hydrogen-oxygen mechanism.



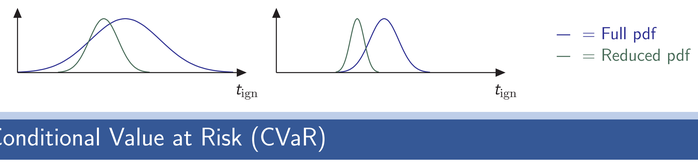
Two Possible Objectives Under Uncertainty

- Use uncertainty as an opportunity to allow more error when using nominal parameter values.
  Error criterion is: $\frac{\left|t^F_{\text{ign}} - t^R_{\text{ign}}\right|}{\sigma^F}$



- Simplify while ensuring that the pdf remains reasonable or even reproduces the full model pdf. Error criterion is Kullback-Leibler divergence:

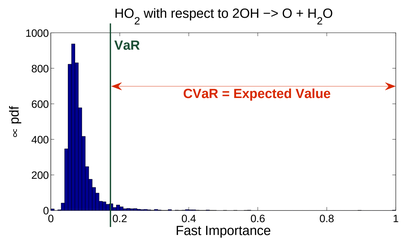
$$D_{KL}(P|Q) = \int_0^\infty p(t_{\text{ign}}) \log \frac{p(t_{\text{ign}})}{q(t_{\text{ign}})} \, dt_{\text{ign}} \qquad \text{where} \begin{cases} p \text{ is full pdf} \\ q \text{ is reduced pdf} \end{cases}$$



Conditional Value at Risk (CVaR)

- Uncertain rate parameters yield a distribution of importance indices.
- Threshold selection is somewhat arbitrary and sensitive to the quality of sampling.
- Even a small risk of exceeding the threshold by a large amount could be undesirable.

We addressed these issues by modifying the Valorani algorithm to applying thresholds to the CVaR of importance indices.



For confidence level α:

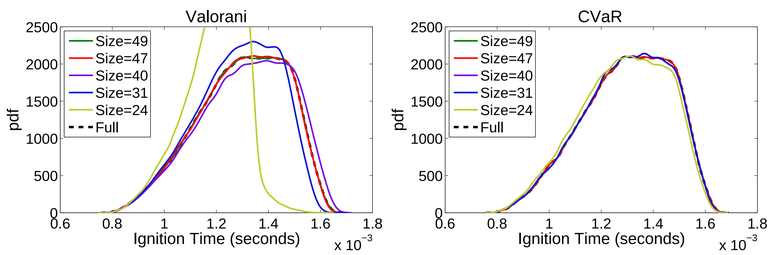
$\text{CVaR} = \mathbb{E}(I^i_k \,|\, I^i_k > \eta)$

η (the VaR) satisfies:

$P(I^i_k > \eta) = \alpha$

CVaR results

The CVaR algorithm often gives better pdf reproduction for small reduced mechanisms than the original Valorani algorithm when applied to the GRIMech-3.0 mechanism.



This example is for uncertainty only in the reactions directly involving methane.

References

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Diagnostics

Detailed diagnostics may give insight into techniques to more fully take advantage of uncertainty and develop uncertainty-aware algorithms that are more predictable than the heuristic CVaR modification, while also potentially decreasing computational cost. Some initial investigations are presented here.

Global Sensitivity Analysis

This variance-based sensitivity analysis determines components of the output variance that are explained by different input parameters $\boldsymbol{\xi}$. Of particular interest are:

- First order sensitivity S_i is the variance explained by ξ_i when acting alone:

$$S_i = \frac{\text{var}_{\xi_i}\left(\mathbb{E}_{\boldsymbol{\xi}_{\sim i}}[u \,|\, \xi_i]\right)}{\text{var}_{\boldsymbol{\xi}}(u)}$$

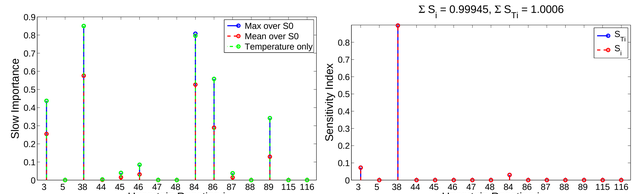
- Total effect sensitivity S_{T_i} is the variance explained by ξ_i when acting both alone and in combination with other variables:

$$S_{T_i} = 1 - \frac{\text{var}_{\boldsymbol{\xi}_{\sim i}}\left(\mathbb{E}_{\xi_i}[u \,|\, \boldsymbol{\xi}_{\sim i}]\right)}{\text{var}_{\boldsymbol{\xi}}(u)}$$

Sensitivity and Importance

The output is insensitive to most reactions, even those that are important. An uncertainty-aware simplification scheme therefore need only consider the small number of sensitive reactions, making the problem more tractable.

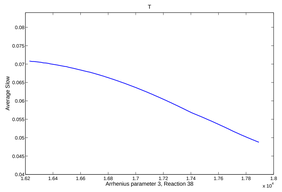
These figures demonstrate importance and output sensitivity for the GRI-Mech 3.0 mechanism with uncertainty only in the hydrogen-oxygen reactions.



Near unity sums of S_i and S_{T_i} indicate negligible impact on the output from the combined effects of uncertain inputs acting together. A simplification scheme may therefore be able to consider a series of 1D uncertainty models rather than a single high-dimensional model.

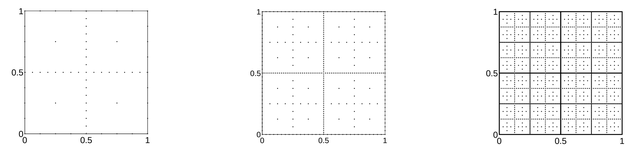
Specific Sensitivity and Importance Examples

Two important reactions from the above are shown; the output is only sensitive to one.



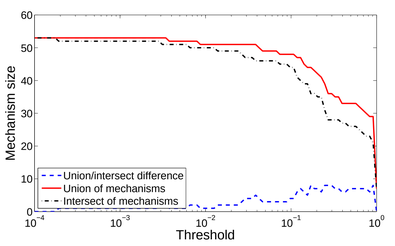
Dimension-Adaptive Sparse Quadrature

Sparse quadrature techniques can be used to explore parameter space without resorting to tensor products of 1D quadrature rules. Nested grids can be refined as shown until the desired level of accuracy is attained; axes here represent different rate parameters.



Dimension-adaptive sparse quadrature improves on this approach by anisotropically refining the grid in directions of greatest non-linearity.

Reduction at Quadrature Points



How do deterministic simplified models vary over parameter space?

The difference in size of the intersection and union of these mechanisms gives an indication of the number of degrees of freedom in the choice of simplified mechanism - this is generally relatively low.

tcoles@mit.edu, ymarz@mit.edu