This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Reacting Flow Modeling with Detailed Chemical Kinetics

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Sandia National Laboratories
Livermore, CA

BES Contractors Meeting
Leesburg, VA
May 31 – June 3, 2016

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Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE

Outline of Research Program

General focus on Predictive modeling with combustion chemistry

- Quality of models, data, and computational predictions
- Uncertainty quantification in computational combustion

Specific areas of work:

- Inference of uncertain chemical rate constants given available information/missing-data – H_2-O_2 mechanism
- Global sensitivity analysis and forward UQ in ignition & flames
- Bayesian estimation of model error in chemical systems
- Intrusive forward UQ methods in chemical systems – stability
- Reduction of stochastic chemical models
- **Chemical model reduction under uncertainty – CSP & UQ**

UQ has broad applicability in science

General Utility

- Estimation of uncertainty in experimental measurements and computational predictions
- Model comparison, selection, and validation
- Hypothesis testing
- Design optimization under uncertainty
- Decision support

SciDAC-Partnership Applications of UQ – examples

- Multiscale atmospheric transport
- Fusion: ITER reactor modeling; fusion plasma surface damage
- Climate: Ice sheet dynamics
- Chemistry: Quantum chemistry computations

Partnerships with other BES projects

Efficient representation of potential energy surfaces & estimation of high dimensional quantum chemistry integrals

- with So Hirata, UIUC
- with Ahren Jasper, SNL

UQ in Large Eddy Simulation of turbulent combustion

- with Joe Oefelein, SNL

UQ in tomographic Particle Imaging Velocimetry measurements in flames

- with Jonathan Frank, SNL

Chemical Model Reduction under Uncertainty

with Riccardo Malpica-Galassi & Mauro Valorani, Sapienza Univ. of Rome

Outline:

1. Introduction
2. Deterministic Chemical Mechanism Simplification with CSP
3. Uncertain Chemical Mechanism Simplification with CSP
4. Demonstration on an Uncertain n-butane Mechanism
5. Closure

Uncertainty in Reacting Flow Modeling

- Chemical models involve much empiricism
- Model uncertainties: choice of species and reactions
- Parametric uncertainties:
  - Chemical rate constants
  - Thermodynamic parameters
  - turbulence/subgrid models
  - mass/energy transport and fluid constitutive laws
  - geometry and initial/boundary conditions
- Present focus on parametric uncertainty
  - kinetic rate coefficients

Uncertainty and Chemical Model Reduction

- Typical ingredients in chemical model reduction
  - A detailed starting chemical kinetic mechanism M^*
  - Operating conditions of interest
  - Quantities of interest (QoIs) desired with specified accuracy

$$\mathcal{E} \equiv \|\Phi - \Phi^*\| < \alpha$$

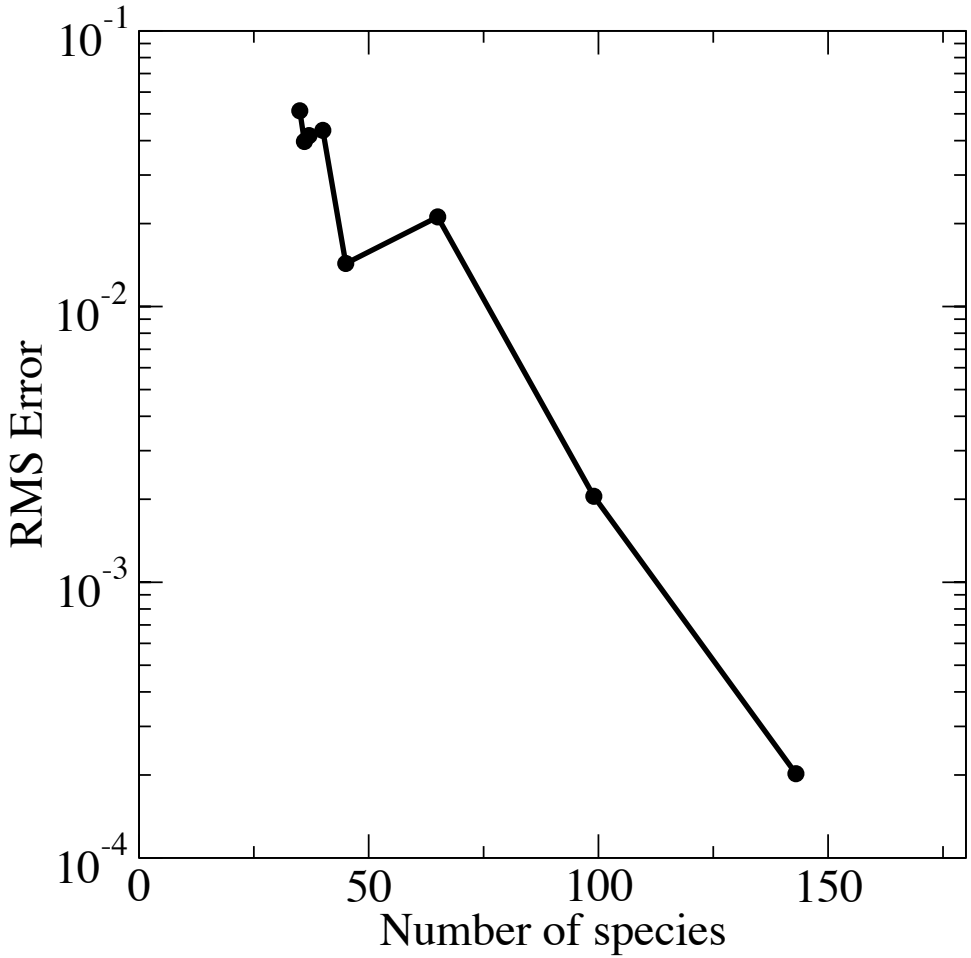
- Consequences of uncertainty in the detailed model?
  - Errors in QoIs: acceptable over range of uncertainty
  - QoIs are uncertain – $\Phi(\omega)$ – error measure definition
  - Probabilistic measures of model fidelity

$$\begin{aligned} \mathcal{E}(\omega) \equiv \|\Phi - \Phi^*\| \quad &\Rightarrow \quad \text{Prob}[\mathcal{E} < \alpha] < \epsilon \\ \mathcal{E} \equiv \|\mathcal{S}(\Phi) - \mathcal{S}(\Phi^*)\| \quad &\Rightarrow \quad \mathcal{E} < \alpha \\ \mathcal{E} \equiv \mathcal{D}_{\text{KL}}[p(\Phi), p(\Phi^*)] \quad &\Rightarrow \quad \mathcal{E} < \alpha \end{aligned}$$

Deterministic Chemical ODE System Analysis

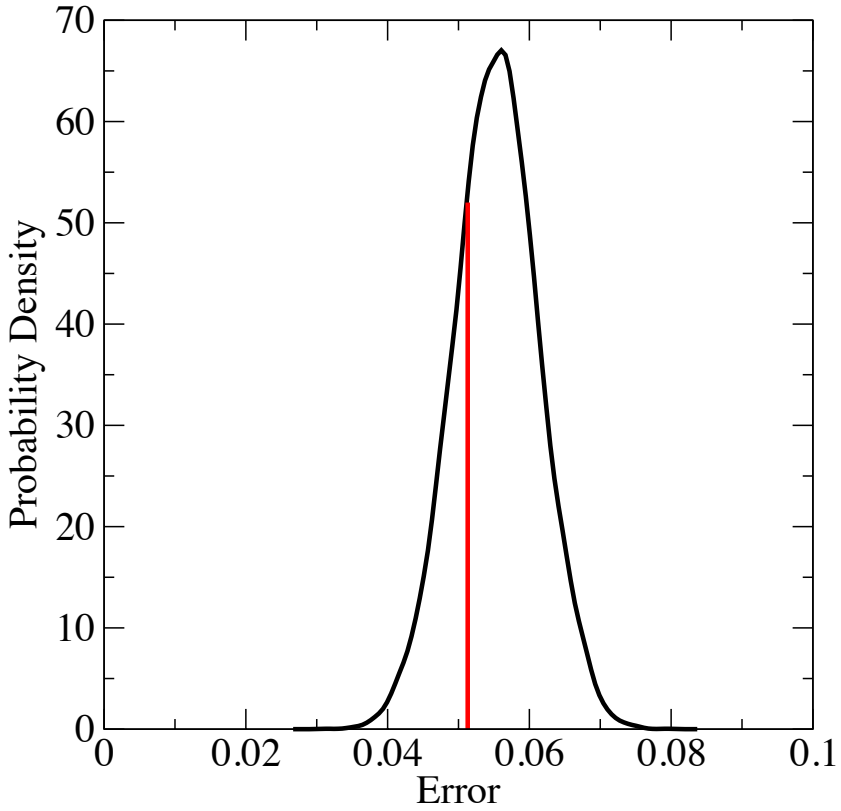
- Computational Singular Perturbation (CSP) analysis
- Jacobian eigenvalues provide first-order estimates of the time-scales of system dynamics: $\tau_i \sim 1/\lambda_i$
- Jacobian eigenvectors provide first-order estimates of the vectors that span the fast/slow tangent spaces
- With chosen thresholds, have M "fast" modes
  - M algebraic constraints define a slow manifold
  - Fast processes constrain the system to the manifold
  - System evolves with slow processes along the manifold
- CSP Importance indices provide estimates of "importance" of a given reaction to a given species in each of the fast/slow subspaces – Importance Index threshold : $\tau \in [0, 1]$

Determ. Kinetic Model Simplification with CSP: n-butane



Relative *a posteriori* error in ignition time vs. simplified model sizes
Control using τ-threshold on CSP importance indices

Deterministic Reduction Challenged with Uncertainty



- Model chosen based on a 5% *a posteriori* error threshold
- Employing it, allowing for uncertainty in its pre-exponentials, results in 75% probability of exceeding the threshold

Reduction Strategy under Uncertainty

- Deterministic strategy:
  - Given
    - Detailed starting chemical model M^*, with parameters λ
    - Solution database D of state vectors generated with $M^*(\lambda)$
    - Quantities of interest Q – mole fractions of target species
    - Specified thresholds τ on CSP Importance Indices
  - Discover a simplified model $M(M^*(\lambda), D, Q, \tau) := M(\lambda)$
- Probabilistic strategy:
  - Given uncertainty in λ, we model this parameter vector as a random vector with a given joint density $p(\lambda)$.
  - As a result, the resulting model structure $M(\lambda)$ is a random object, with a probability for any given M, denoted by $P(M)$.
  - Each $M \in \mathcal{M}$ is defined by a network of species/reactions
  - The set $\mathcal{M}$ is not easy to work with

Convenient coordinates on model space

- Given the starting detailed model M^*, any simplifed model M is uniquely defined by the set of retained reactions
  - Retained species are those involved in retained reactions
- Set of elementary reactions in M^*: $\mathcal{R}_{M^*} = \{R_1, \cdots, R_K\}$
- Define the bit vector $\boldsymbol{\alpha} = (\alpha_1, \cdots, \alpha_K) \in \{0,1\}^K$
- A model M is specified by $\boldsymbol{\alpha}(M)$ where, for $r = 1, \ldots, K$,

$$\alpha_r(M) = \begin{cases} 1 & \text{if } R_r \in \mathcal{R}_M \\ 0 & \text{otherwise} \end{cases}$$

clearly: $\boldsymbol{\alpha}(M^*) = (1, \cdots, 1)$

- Thus, given M^*, we have the mapping: $\lambda \rightarrow \boldsymbol{\alpha}(\lambda)$

Uncertain Simplified Model Specification

- For uncertain λ: $p(\lambda) \rightarrow P(\boldsymbol{\alpha}) \equiv P_{\boldsymbol{\alpha}}$
- Clearly, $P_{\boldsymbol{\alpha}} \geq 0$, and $\sum_{\boldsymbol{\alpha}} P_{\boldsymbol{\alpha}} = 1$
- Illustrative example: M^*: A $\underset{2}{\overset{1}{\rightleftarrows}}$ B
  - $K = 2$, such that $\boldsymbol{\alpha} = (\alpha_1, \alpha_2)$
  - Set of possible values of $\boldsymbol{\alpha}$: $\{(1,1),(1,0),(0,1),(0,0)\}$
  - Set of possible models M: $\{M_{(1,1)}, M_{(1,0)}, M_{(0,1)}, M_{(0,0)}\}$
  - Uncertain simplified model specification:

$$\{P_{(1,1)}, P_{(1,0)}, P_{(0,1)}, P_{(0,0)}\}$$

where $P_{(i,j)} \equiv P(\boldsymbol{\alpha} = (i,j))$

Uncertain Reduction Strategy – 1

- Generate N random samples of λ from $p(\lambda)$
- For each λ^i, $i = 1, \ldots, N$
  - Analyze resulting $M^*(\lambda^i)$ for ignition – range of (T, P, Φ) ICs
  - Get simplified model $M^i(\mathcal{S}^i, \mathcal{R}^i)$
  - Evaluate $\boldsymbol{\alpha}^i = \boldsymbol{\alpha}(M^i)$:

$$\alpha_k^i = \begin{cases} 1 & \text{for } R_k \in \mathcal{R}_{M^i} \\ 0 & \text{otherwise} \end{cases} \qquad k = 1, \ldots, K$$

- Estimate Model probabilities: $$P_{\boldsymbol{\alpha}} = \frac{1}{N} \sum_{i=1}^{N} \delta_{\boldsymbol{\alpha}, \boldsymbol{\alpha}^i}$$
- Marginal reaction probabilities:

$$P_{\alpha_k} = \frac{1}{N} \sum_{i=1}^{N} \delta_{\alpha_k, \alpha_k^i}, \qquad k = 1, \ldots, K$$

Uncertain Reduction Strategy – 2

- Marginal reaction inclusion probability

$$P_k := P_{\{\alpha_k=1\}} = \frac{1}{N}\sum_{i=1}^{N} \alpha_k^i, \qquad k = 1, \ldots, K$$

- Include reaction k if:

$$P_k > \theta$$

- Resulting model $M_{\tau,\theta}(\lambda)$ is the CSP-simplified model given
  - the starting detailed model $M^*(\lambda)$
  - the database of solution state vectors
  - the CSP Importance Index tolerance τ
  - for $\lambda \sim p(\lambda)$

  with marginal reaction inclusion probability $> \theta$

Computational Considerations

- Efficient **Tchem** based thermochemistry
  - In-memory manipulation of Arrhenius parameters
  - Fast evaluation of source term and analytical Jacobian
  - www.sandia.gov/tchem
  - Contact: C. Safta: csafta@sandia.gov
- Fast **CVODE** based stiff time integration
  - computation.llnl.gov/casc/sundials
- Versatile **UQTk** sampling and statistics capabilities
  - www.sandia.gov/uqtoolkit
  - Contact: B. Debusschere: bjdebus@sandia.gov
- Efficient **CSPTk** analysis and reduction
  - Minimal I/O; efficient dynamical analysis
  - Contact: M. Valorani: mauro.valorani@uniroma1.it

Demo on n-butane ignition

- Detailed chemical mechanism for n-butane/air combustion, with specified uncertainty factors in the pre-exponentials
  E. Hebrard, A.S. Tomlin, R. Bounaceur, F. Battin-Leclerc, Proc. Comb. Inst. **35**(1):607-616, 2015.
- $N = 1111$ reactions
- Temperature-dependent uncertainty factors
  - Mechanism specificies (f_r, g_r) for each reaction r
  - Uncertainty factor: $\ln A = \ln A_{\text{nom}} \pm \ln F$

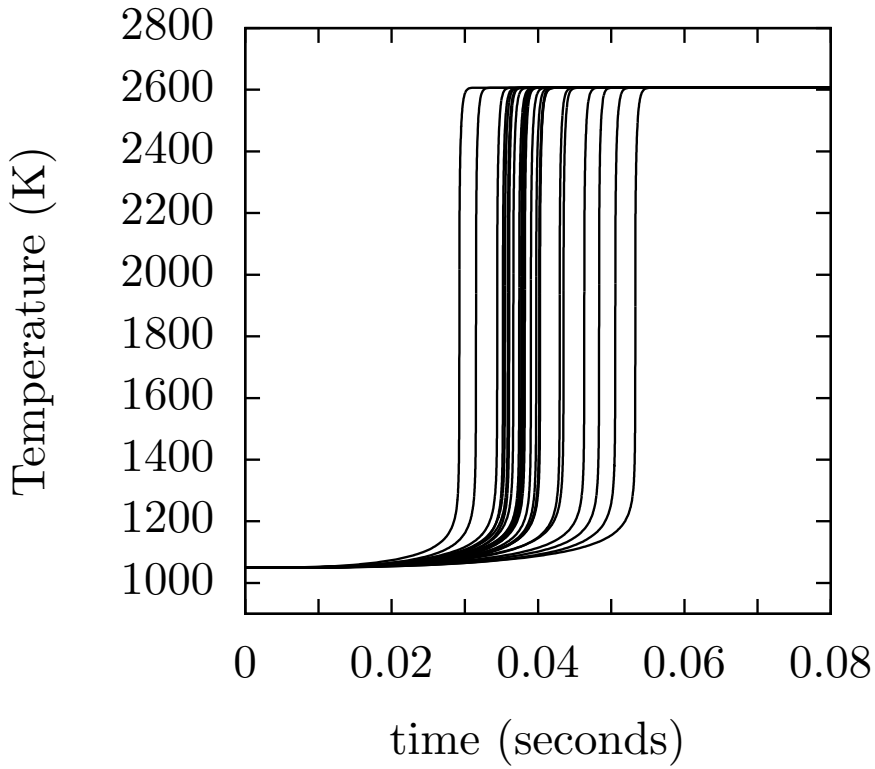
$$F_r(T) = f_r \exp\left(\left| g_r \left(\frac{1}{T} - \frac{1}{300}\right)\right|\right)$$

- For now, we employ a temperature-independent F_r:

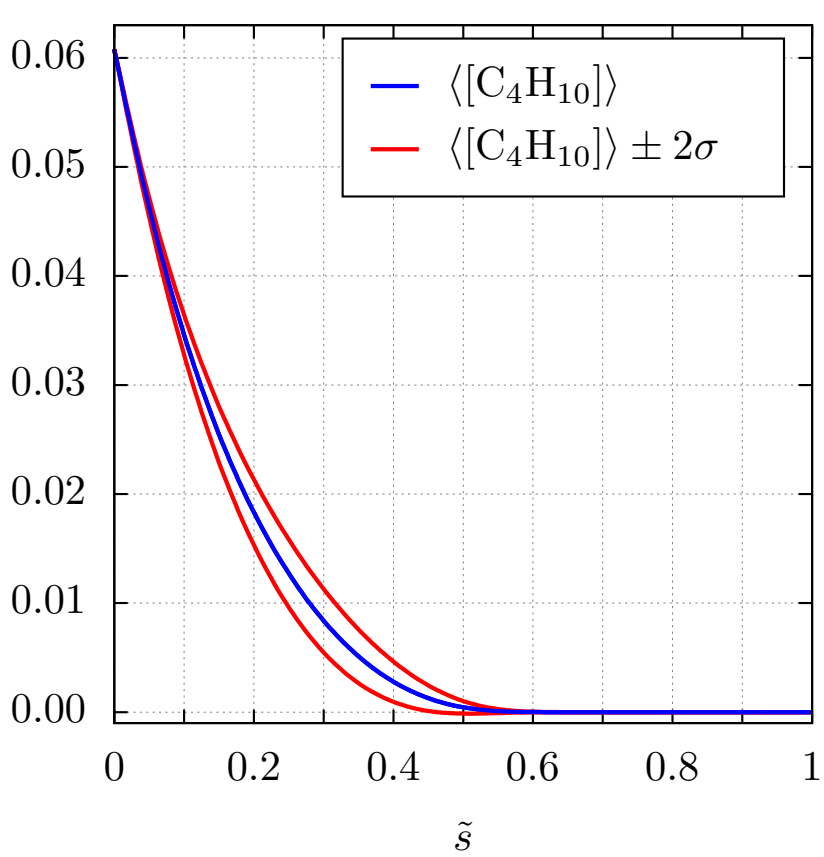
$$F_r := F_r(T)|_{T=1500\ \text{K}}$$

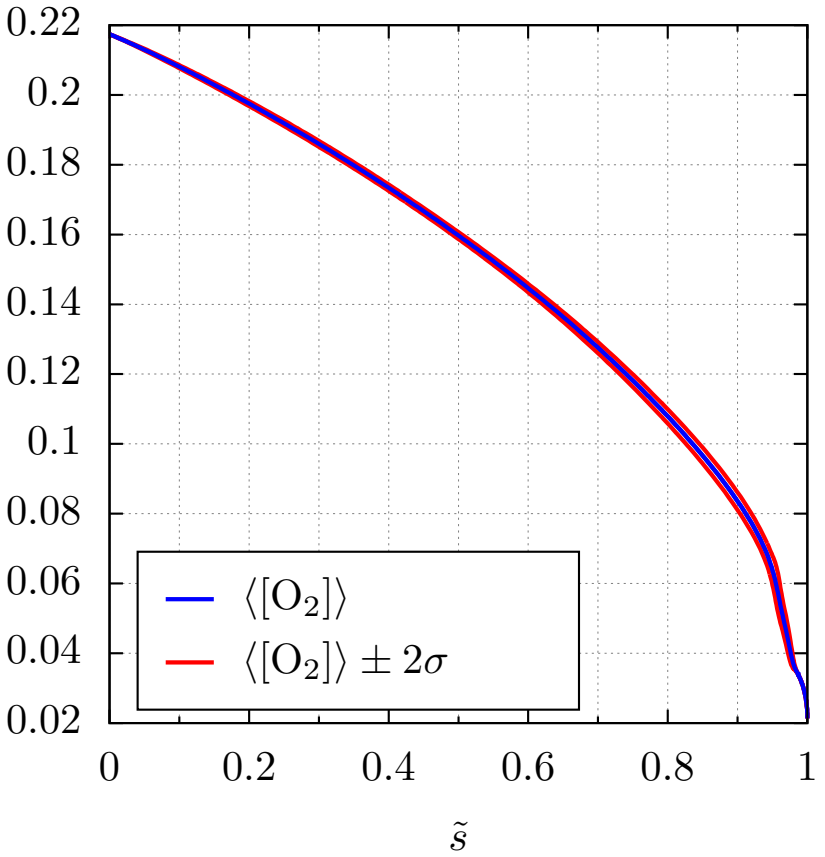
Sampled ignition trajectories – detailed mechanism

- Significant uncertainty in ignition time
- Large range of state-variable uncertainty vs time
  - fast ignition transient
- Examine trajectory errors and uncertainty in an alternate progress-variable phase space
  - Entropic phase space



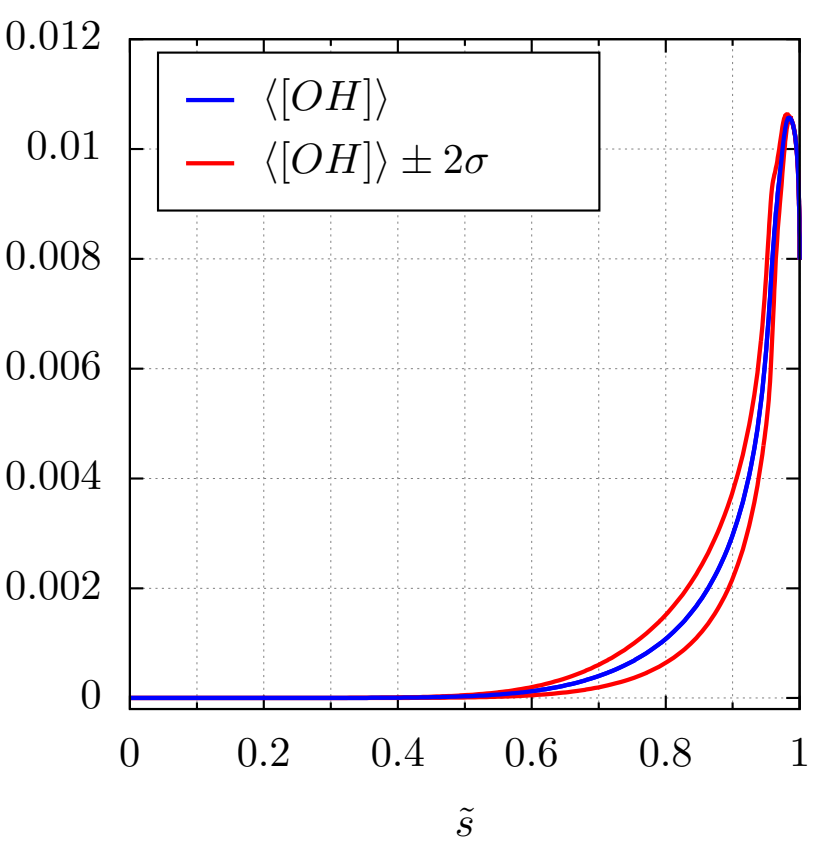
Uncertain trajectories in the entropy phase space

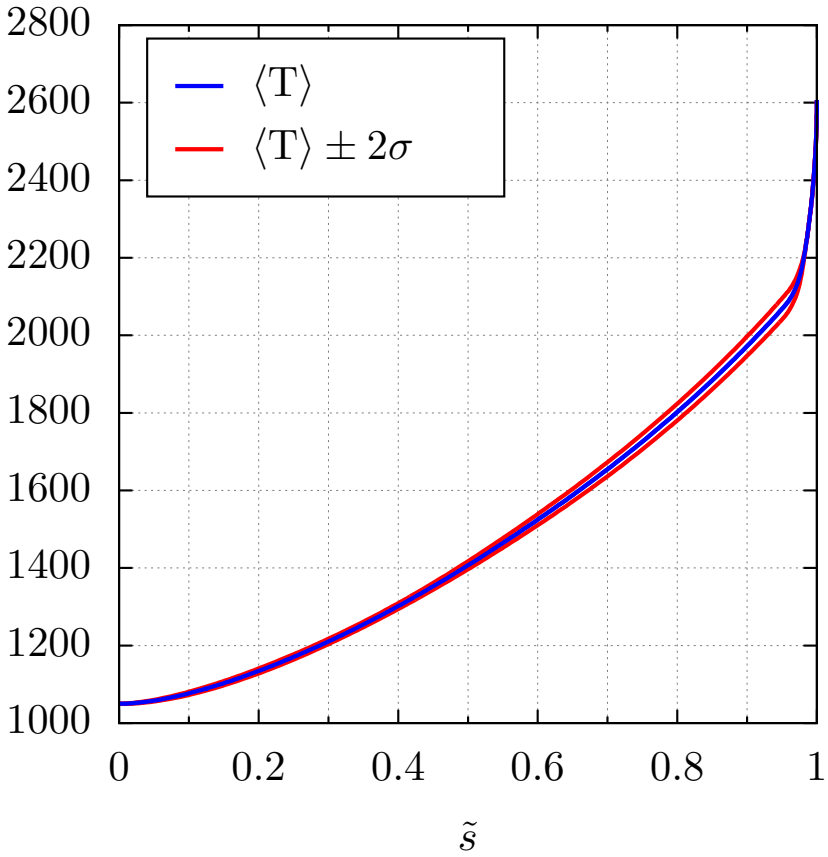




- Mean and Mean$\pm 2\sigma$ trajectories for select state variables
- No uncertainty at equilibrium
  - Rate parameters, not thermodynamic properties, are uncertain
- Coefficient of variation can be large when the mean is low

Uncertain trajectories in the entropy phase space





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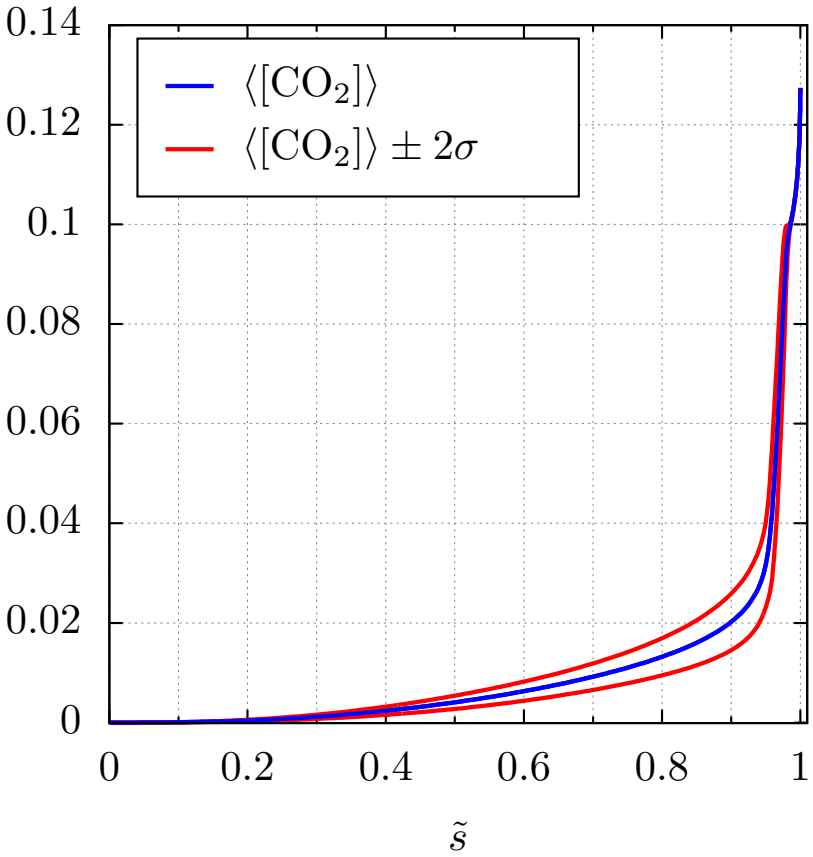
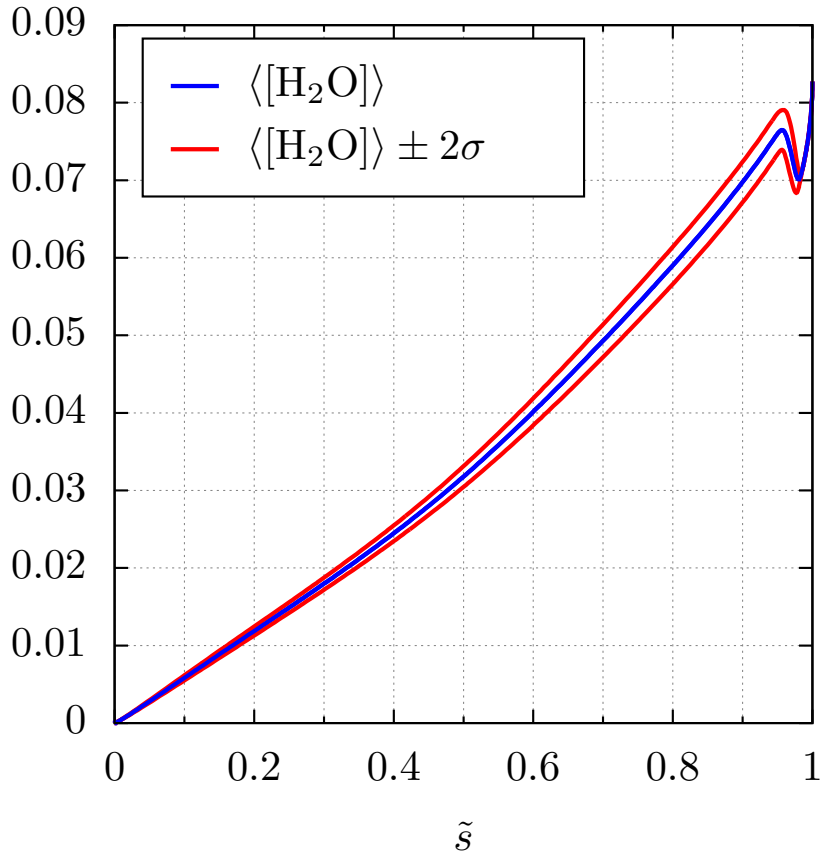
Uncertain trajectories in the entropy phase space





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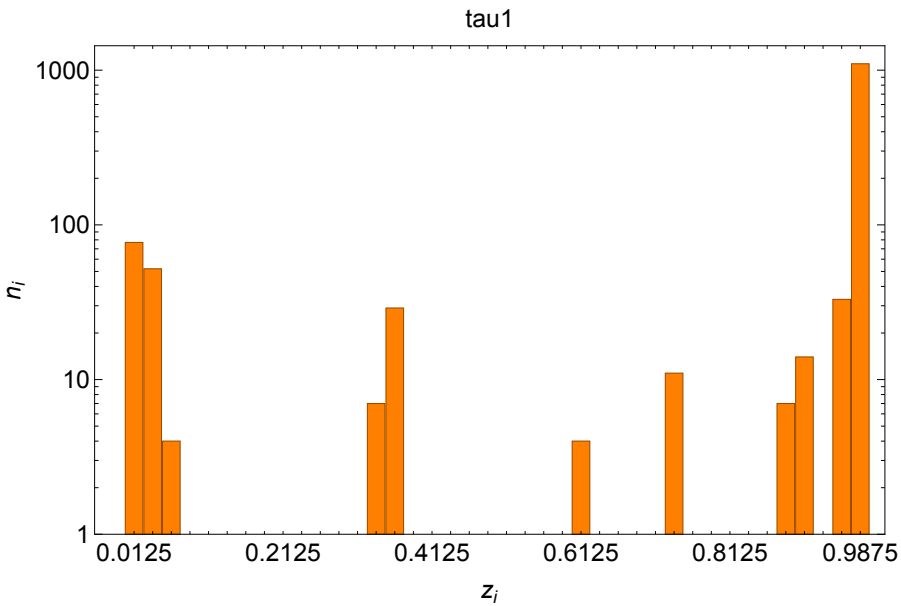
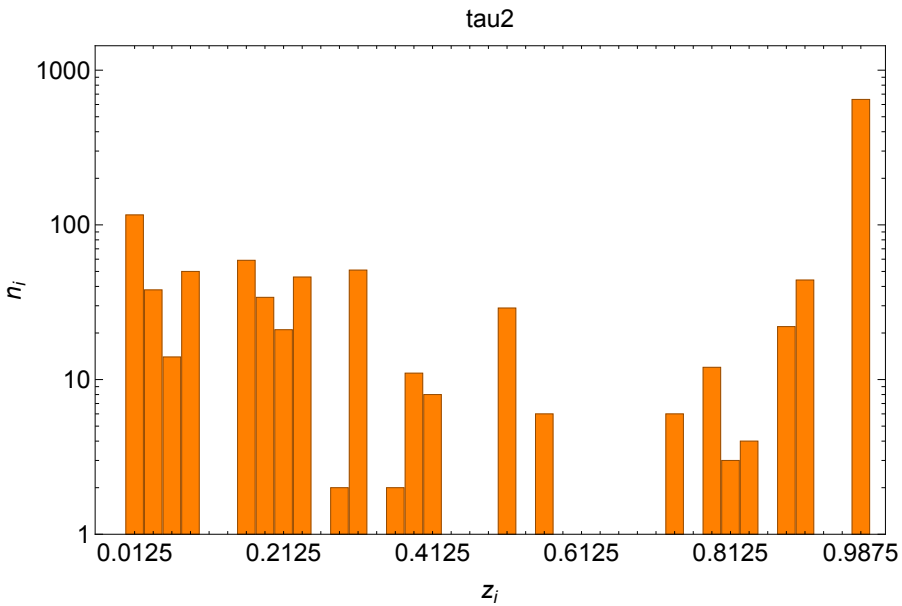
Distribution of Marginal Reaction Probabilities



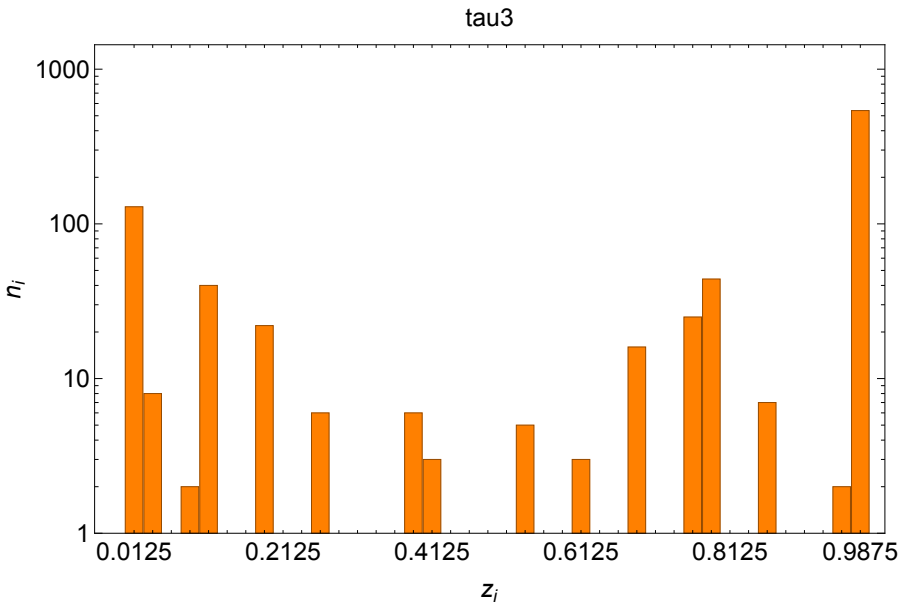
$\tau = 0.020$



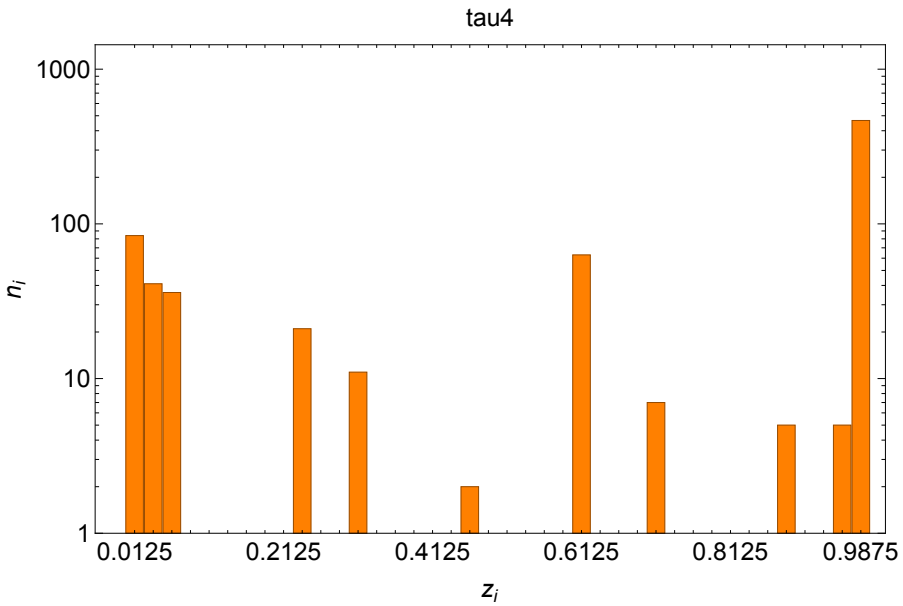
$\tau = 0.047$

- # reactions versus Marginal Reaction Probability
  - $p(P_k)$ ... modulo normalization
  - for different values of the CSP Importance Index threshold τ
- Choice of reaction probability threshold θ selects for reactions with $P_k > \theta$

Distribution of Marginal Reaction Probabilities



$\tau = 0.075$



$\tau = 0.103$

- # reactions versus Marginal Reaction Probability
  - $p(P_k)$ ... modulo normalization
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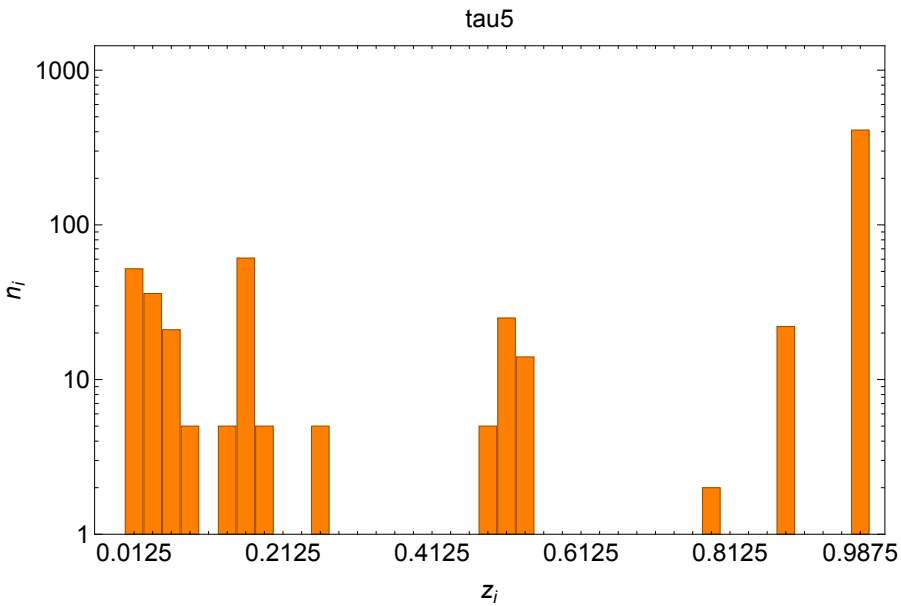
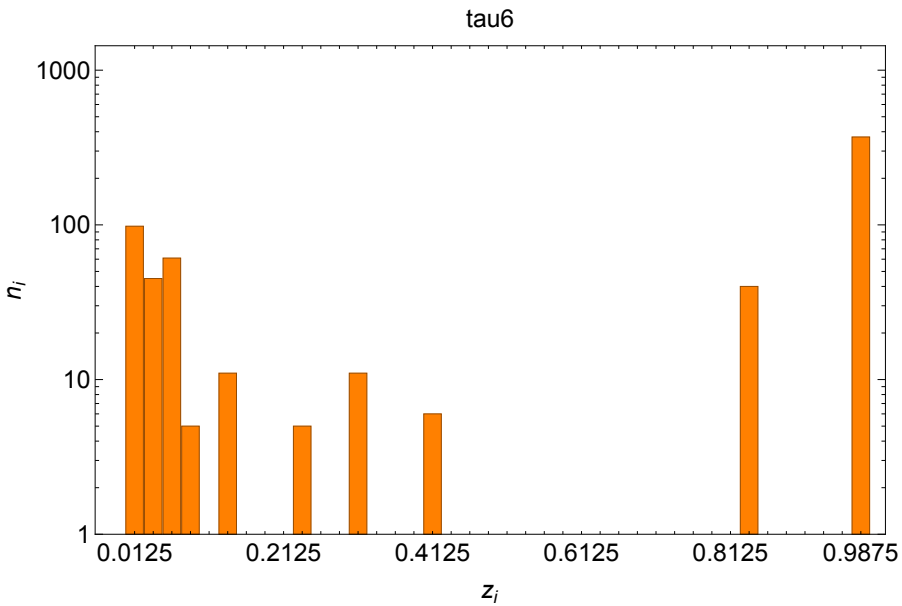
Distribution of Marginal Reaction Probabilities



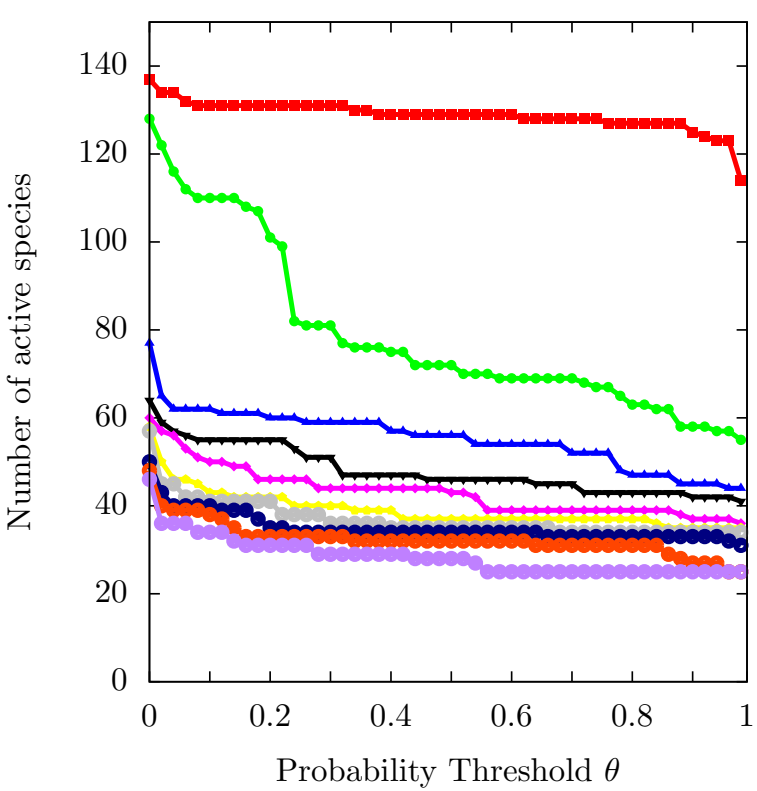
$\tau = 0.131$

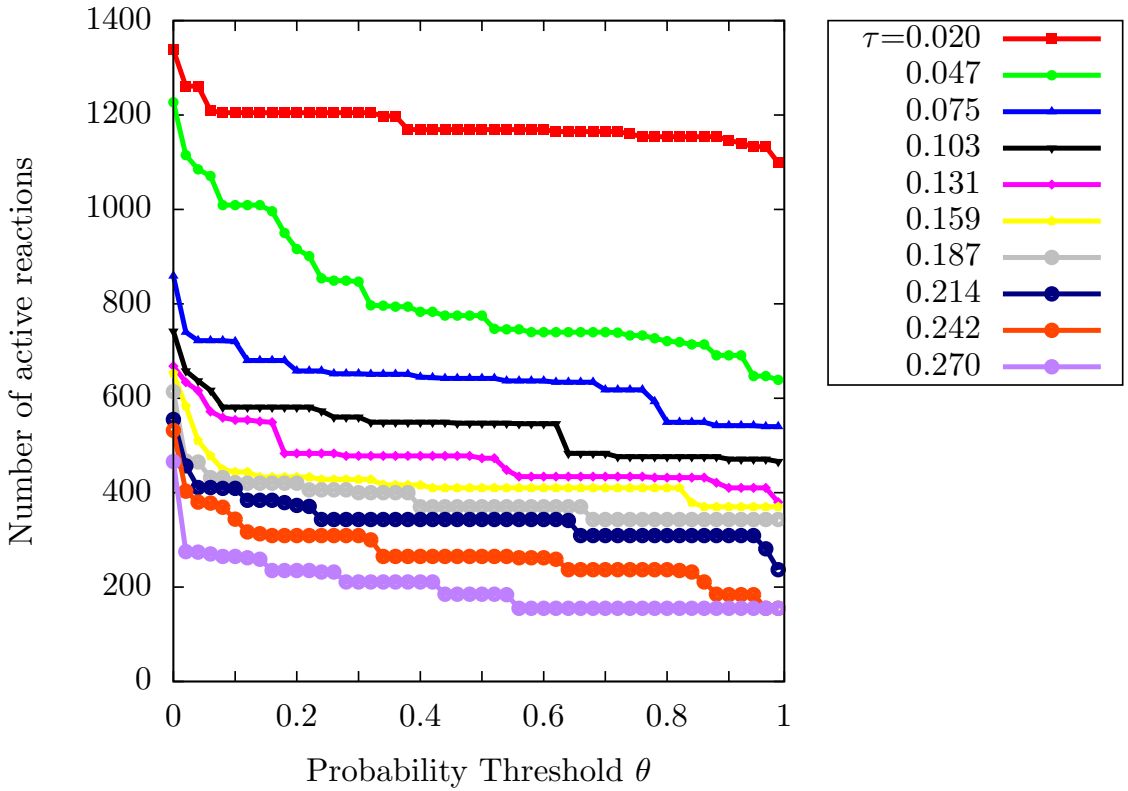


$\tau = 0.159$

- # reactions versus Marginal Reaction Probability
  - $p(P_k)$ ... modulo normalization
  - for different values of the CSP Importance Index threshold τ
- Choice of reaction probability threshold θ selects for reactions with $P_k > \theta$

of active reactions/species varies inversely with (τ, θ)





- Number of active reactions/species goes down monotonically with:
  - increasing threshold θ on P_k
  - increasing Importance Index threshold τ

A posteriori error estimation

For any quantity of interest $\phi(\mathfrak{s}, \cdot)$, define the trajectory error norm over time steps $t_k : k = 1, \ldots, K$, with $\mathfrak{s}_k = \tilde{s}(t_k)$,

$$\mathcal{E}_\phi^{p,w} = \frac{\|\phi - \phi_d\|_{p,w}}{\|\phi_d\|_{p,w}} = \frac{\left(\frac{1}{K} \sum_{k=1}^{K} w_k |\phi(\mathfrak{s}_k, \cdot) - \phi_d(\mathfrak{s}_k, \cdot)|^p \right)^{1/p}}{\left(\frac{1}{K} \sum_{k=1}^{K} w_k |\phi_d(\mathfrak{s}_k, \cdot)|^p \right)^{1/p}}$$

where

- ϕ_d refers to the detailed model
- $w_k = w(\mathfrak{s}_k)$ is a weight function *e.g.* $w_k = 1$ or $w_k = 1/\sigma_d(\mathfrak{s}_k)$

A posteriori error estimation

Example quantities of interest for trajectory error estimation

- A per-trajectory error that is random

$$\phi(\mathfrak{s},\lambda) := X_i(\mathfrak{s},\lambda) \qquad \Rightarrow \qquad \mathcal{E}^{p,w}_{X_i}(\lambda;\tau,\theta)$$

- An error in the mean of uncertain trajectories

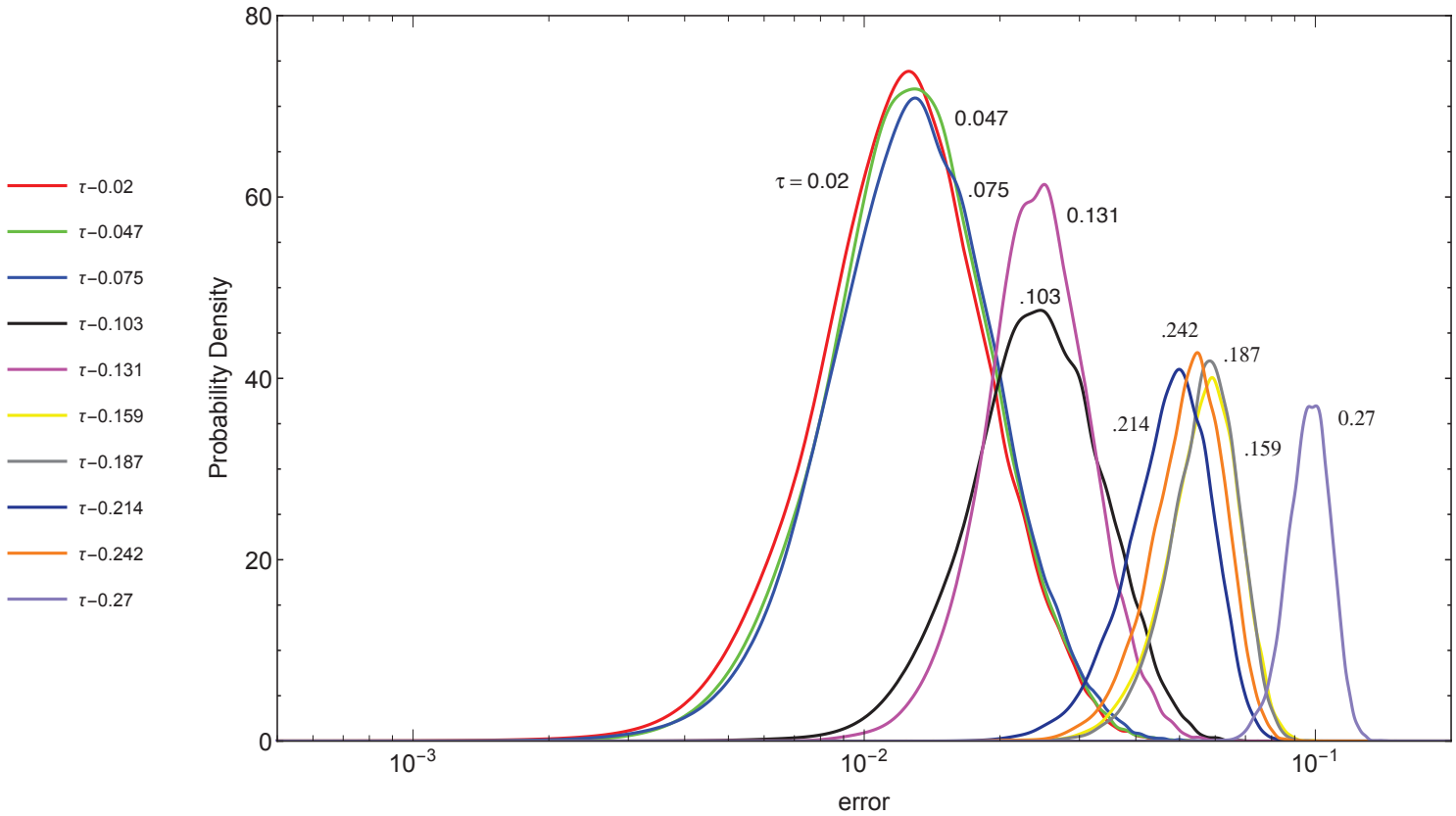
$$\phi(\mathfrak{s}) := \mu_i(\mathfrak{s}) = \mathsf{E}_\lambda[X_i(\mathfrak{s},\lambda)] \qquad \Rightarrow \qquad \mathcal{E}^{p,w}_{\mu_i}(\tau,\theta)$$

- An error in the standard deviation of uncertain trajectories

$$\phi(\mathfrak{s}) := \sigma_i(\mathfrak{s}) = (\mathsf{V}_\lambda[X_i(\mathfrak{s},\lambda)])^{1/2} \qquad \Rightarrow \qquad \mathcal{E}^{p,w}_{\sigma_i}(\tau,\theta)$$

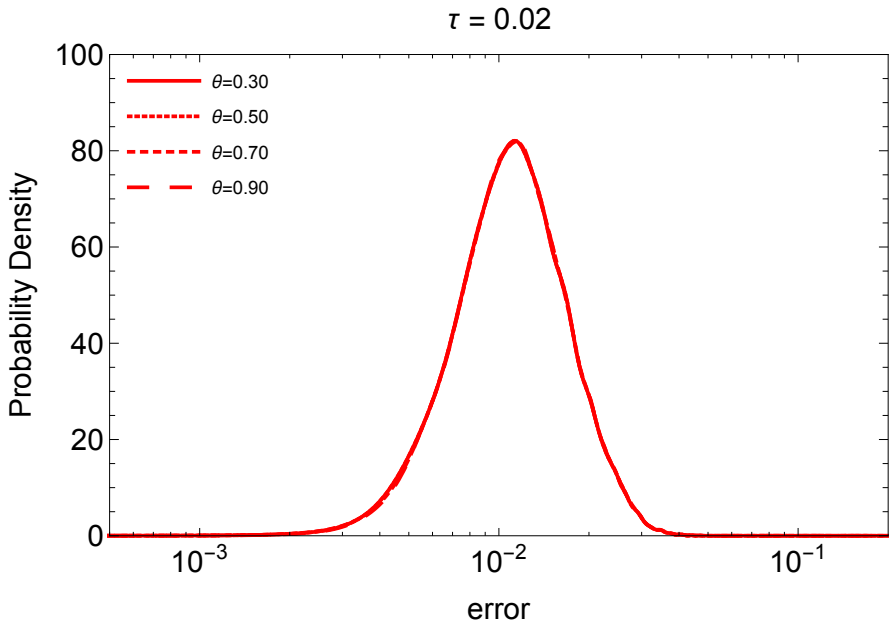
Trajectory error statistics

- PDF of trajectory error, averaged over target species, $\theta = 0.30$

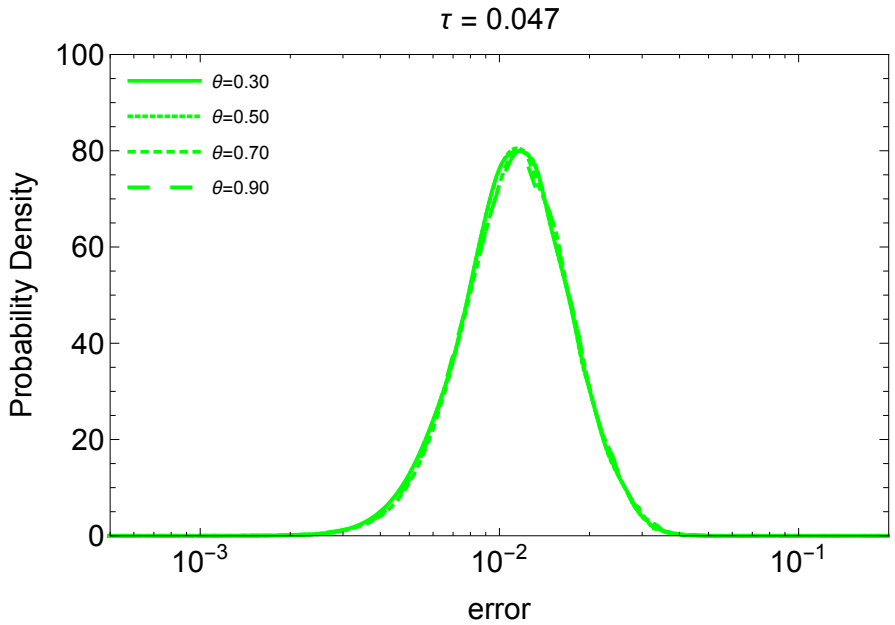


- PDF generally shifts towards larger errors with increasing τ
- Localized non-monotonic behavior with variation in τ

Distribution of a posteriori Error – dependence on θ



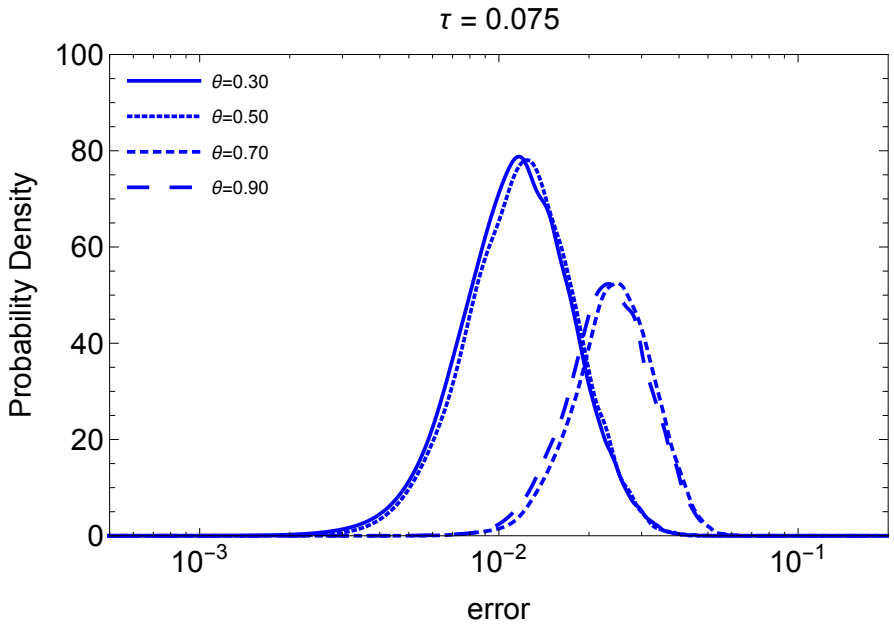
$\tau = 0.020$



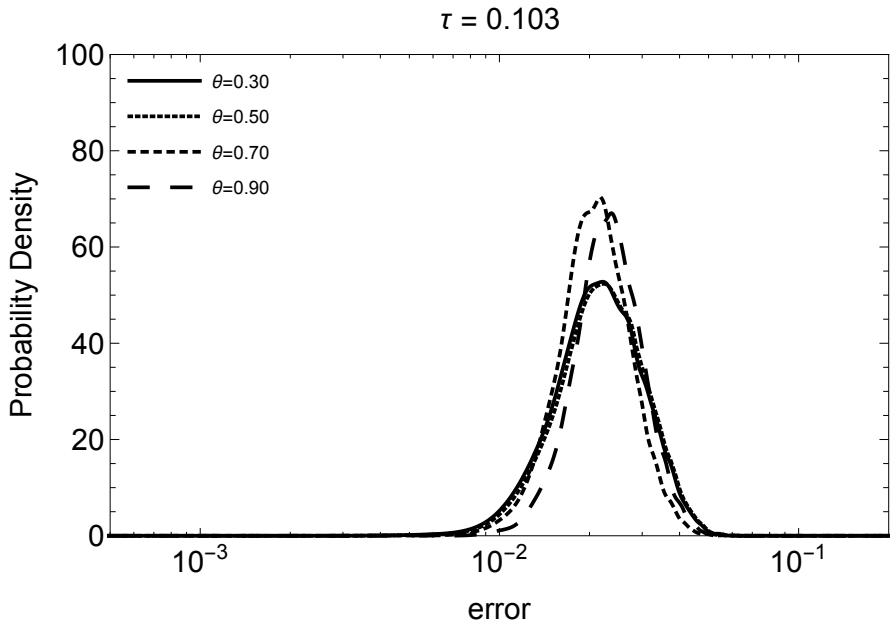
$\tau = 0.047$

- Trajectory error statistics exhibit occasional non-monotonic local dependence on θ
- Global trend towards higher error with larger (τ, θ)

Distribution of a posteriori Error – dependence on θ



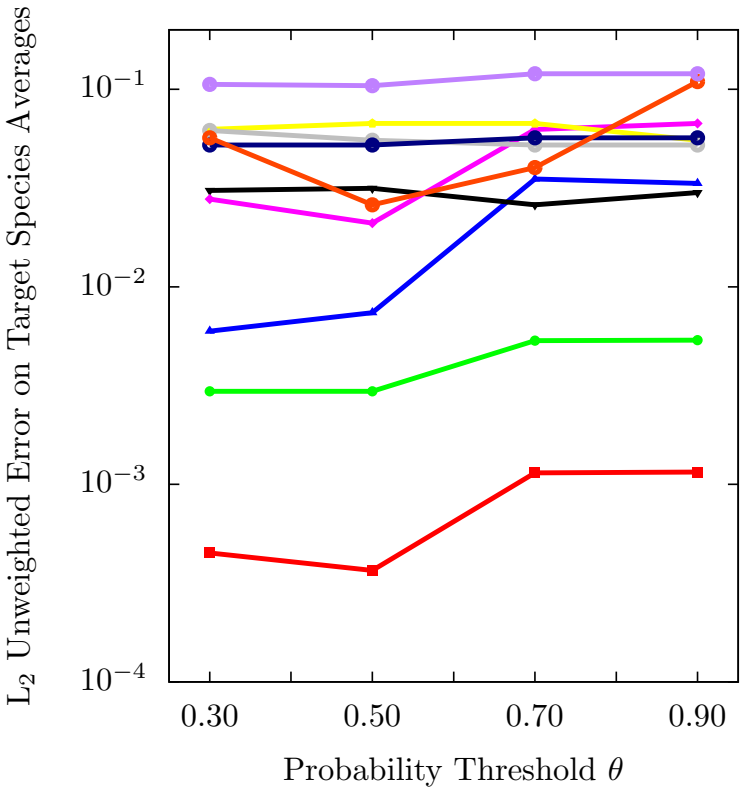
$\tau = 0.075$



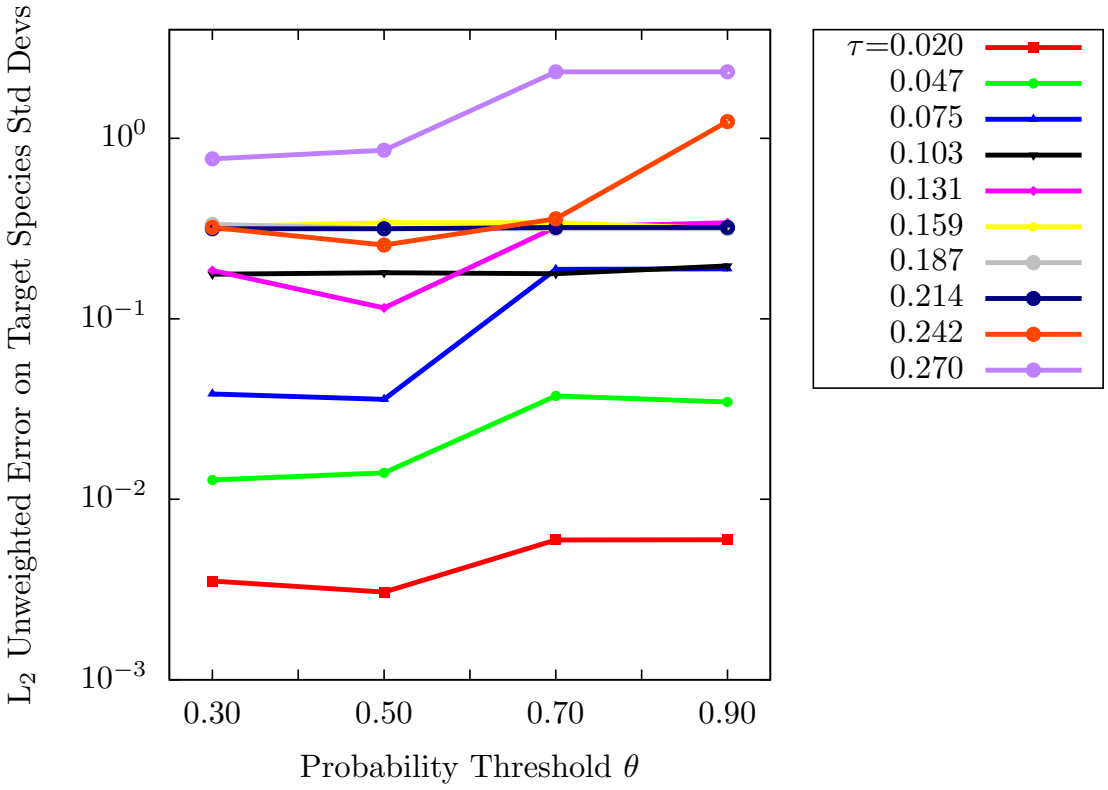
$\tau = 0.103$

- Trajectory error statistics exhibit occasional non-monotonic local dependence on θ
- Global trend towards higher error with larger (τ, θ)

Error in mean & stdv, avg on target species



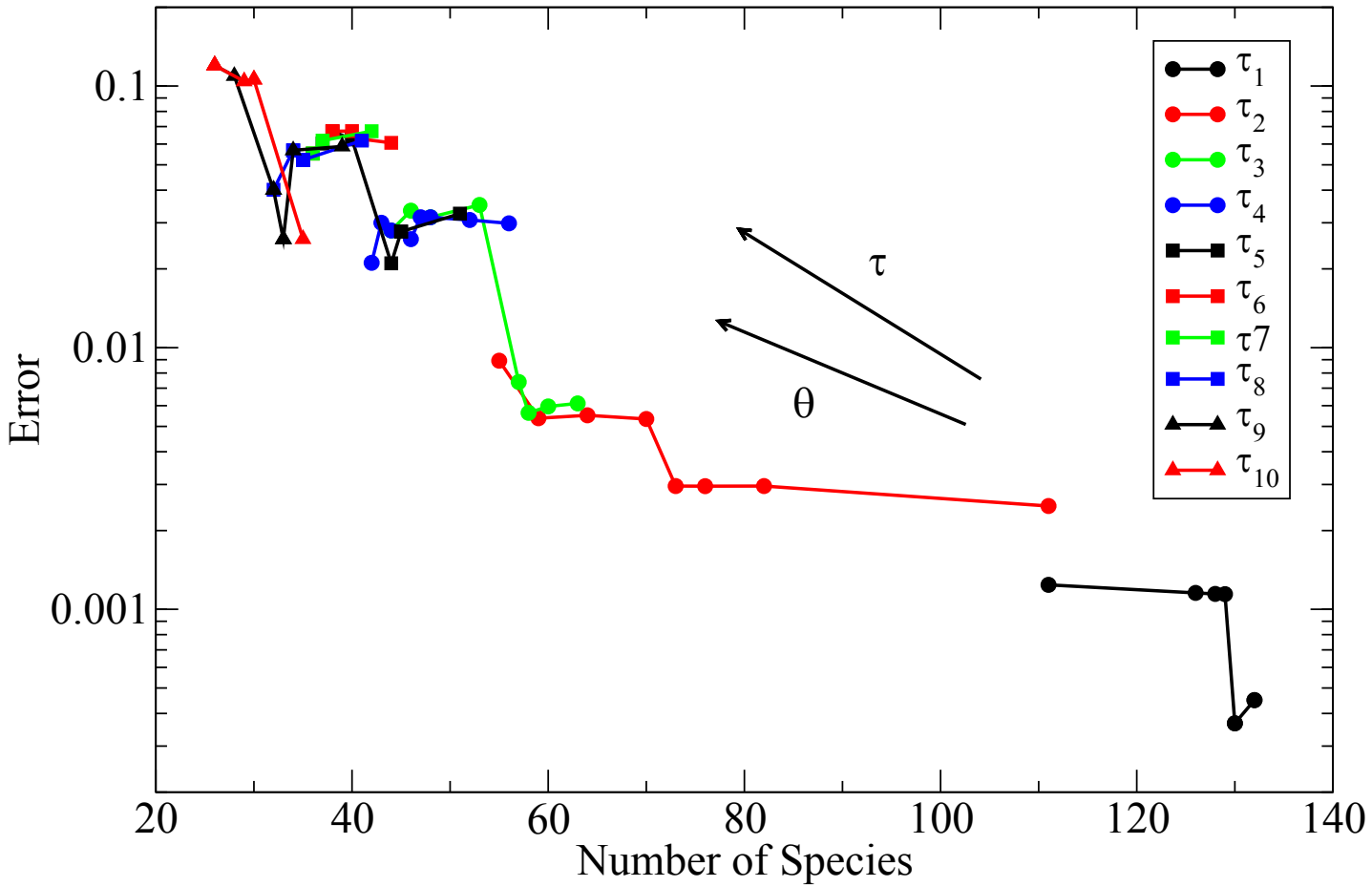
Mean



Standard Deviation

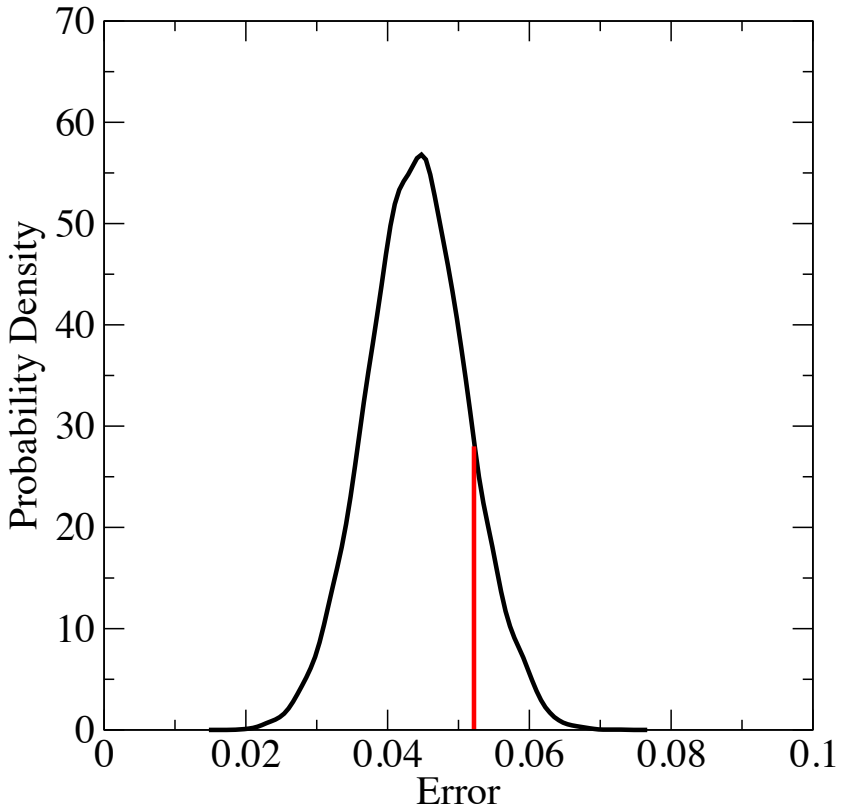
- Non-monotonic trend towards higher error with increasing τ, θ
- Trend is more evident at low τ

Error vs. N



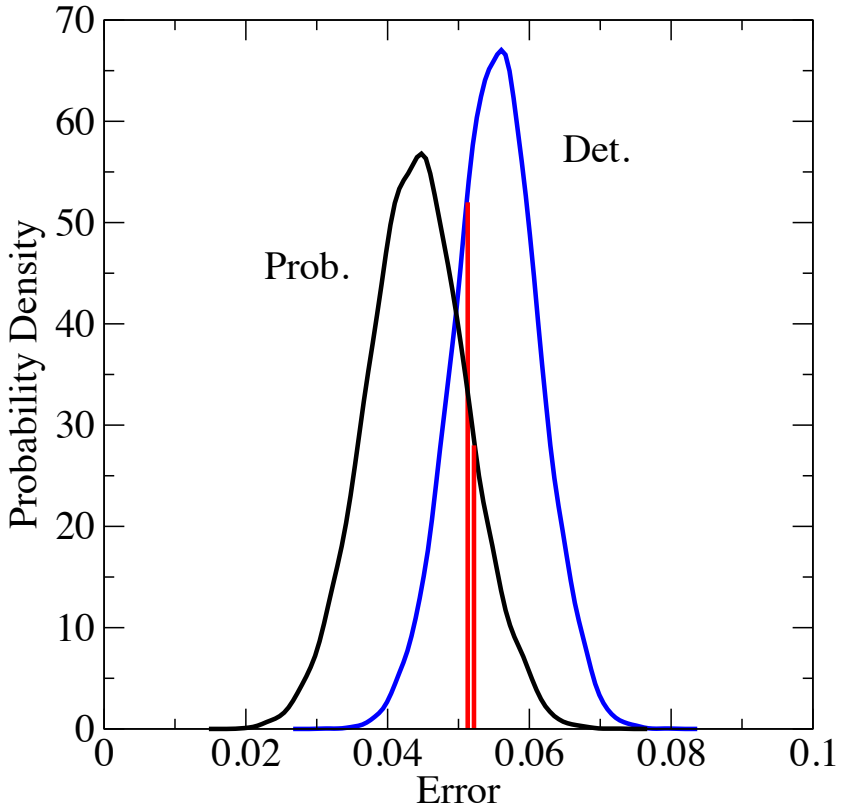
- Globally monotonic trend with increasing (τ, θ)
- Local non-monotonic trends towards higher error, τ, θ

Probabilistic Reduction Advantage



- Probabilistic-reduction with a 5% *a posteriori* error threshold
- Allowing for uncertainty in its pre-exponentials, results in 88% probability of being below threshold

Probabilistic Reduction Advantage



- Accounting for uncertainty in the reduction strategy reduces the probability of exceeding stated threshold from 75% to 12%

Closure

- Predictive modeling of combustion with detailed kinetics
- Highlighted chemical model reduction under uncertainty
- A probabilistic framework for analysis and reduction of chemical models under uncertainty
  - Employs the deterministic analysis/reduction strategy as a black box
  - CSP analysis ensures models with consistent dynamical fidelity
  - Use both dynamical and probabilistic thresholds
- Demo with an uncertain n-butane mechanism
- Resulting mech satisfies, with high probability, requested error tolerance