# Efficient UQ for Chemical Systems using Active Subspaces

Manav Vohra[†], Sankaran Mahadevan[†]

**Collaborators**: Alen Alexanderian[§], Hailey Guy[§]

[†]Vanderbilt University

[§]North Carolina State University

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# Background & Motivation

- **Idea**: Discover and Exploit a low-dimensional structure in the model.

Active Subspaces

| Parameters | Model Runs | Time (1s/run) |
|---|---|---|
| 1 | 10 | 10 s |
| 2 | $10^2$ | 1.6 min |
| 3 | $10^3$ | 16 min |
| 4 | $10^4$ | 2.7 hours |
| 5 | $10^5$ | 1.1 days |
| 6 | $10^6$ | 1.6 weeks |

- **Definition**: Dominant eigenspace of a matrix derived from the model's gradient.

$$\int \nabla f((x))\nabla f(\boldsymbol{x})^\top \rho(\boldsymbol{x})d\boldsymbol{x} = W\Lambda W^\top$$

$$f(\boldsymbol{x}) = g(w_1^\top x)$$ [P. Constantine, 2015]

# GRADIENT-BASED APPROACH

# GRADIENT-FREE APPROACH

# $H_2/O_2$ Reaction Kinetics

- **Reaction Rate:**

$$k_i(T) = A_i T^{n_i} \exp(-E_{a,i}/RT)$$

$A_i$: Pre-exponent $E_{a,i}$: Activation Energy

- **Uniform Priors:** $A_i \in [0.9A_i^*, 1.1A_i^*]$, $E_{a,i} \in [0.9E_{a,i}^*, 1.1E_{a,i}^*]$

- **Global Reaction:**

$$2H_2 + O_2 \rightarrow 2H_2O$$

- **Equivalence Ratio ($\phi$):**

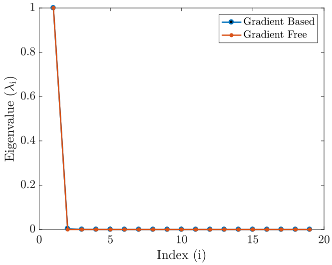
$$\phi = \frac{(M_{H_2}/M_{O_2})_{\text{obs}}}{(M_{H_2}/M_{O_2})_{\text{st}}}$$

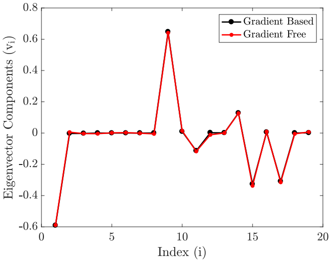
$\phi > 1$ : Rich, $\phi < 1$ : Lean

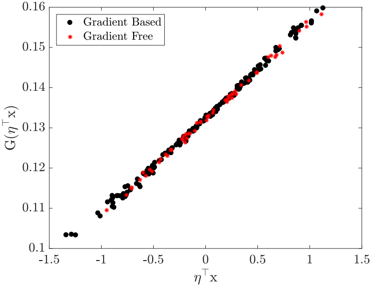
| Reaction # | Reactants | | Products |
|---|---|---|---|
| $\mathcal{R}_1$ | $H + O_2$ | $\rightleftharpoons$ | $O + OH$ |
| $\mathcal{R}_2$ | $O + H_2$ | $\rightleftharpoons$ | $H + OH$ |
| $\mathcal{R}_3$ | $H_2 + OH$ | $\rightleftharpoons$ | $H_2O + H$ |
| $\mathcal{R}_4$ | $OH + OH$ | $\rightleftharpoons$ | $O + H_2O$ |
| $\mathcal{R}_5$ | $H_2 + M$ | $\rightleftharpoons$ | $H + H + M$ |
| $\mathcal{R}_6$ | $O + O + M$ | $\rightleftharpoons$ | $O_2 + M$ |
| $\mathcal{R}_7$ | $O + H + M$ | $\rightleftharpoons$ | $OH + M$ |
| $\mathcal{R}_8$ | $H + OH + M$ | $\rightleftharpoons$ | $H_2O + M$ |
| $\mathcal{R}_9$ | $H + O_2 + M$ | $\rightleftharpoons$ | $HO_2 + M$ |
| $\mathcal{R}_{10}$ | $HO_2 + H$ | $\rightleftharpoons$ | $H_2 + O_2$ |
| $\mathcal{R}_{11}$ | $HO_2 + H$ | $\rightleftharpoons$ | $OH + OH$ |
| $\mathcal{R}_{12}$ | $HO_2 + O$ | $\rightleftharpoons$ | $O_2 + OH$ |
| $\mathcal{R}_{13}$ | $HO_2 + OH$ | $\rightleftharpoons$ | $H_2O + O_2$ |
| $\mathcal{R}_{14}$ | $HO_2 + HO_2$ | $\rightleftharpoons$ | $H_2O_2 + O_2$ |
| $\mathcal{R}_{15}$ | $H_2O_2 + M$ | $\rightleftharpoons$ | $OH + OH + M$ |
| $\mathcal{R}_{16}$ | $H_2O_2 + H$ | $\rightleftharpoons$ | $H_2O + OH$ |
| $\mathcal{R}_{17}$ | $H_2O_2 + H$ | $\rightleftharpoons$ | $HO_2 + H_2$ |
| $\mathcal{R}_{18}$ | $H_2O_2 + O$ | $\rightleftharpoons$ | $OH + HO_2$ |
| $\mathcal{R}_{19}$ | $H_2O_2 + OH$ | $\rightleftharpoons$ | $HO_2 + H_2O$ |

[Yetter et al., 1991]

# COMPARATIVE ANALYSIS



# SENSITIVITY ANALYSIS

- Sobol total effect index

$$\mathcal{T}(\theta_i) = 1 - \frac{\mathbb{V}_{\boldsymbol{\theta}_{\sim i}}(\mathbb{E}_{\theta_i}[\mathcal{G}|\boldsymbol{\theta}_{\sim i}])}{\mathbb{V}(\mathcal{G})}$$

$$= \frac{\frac{1}{N}\sum_{k=1}^{N} f(\boldsymbol{A})_k(f(\boldsymbol{A})_k - f(\boldsymbol{A}_{\boldsymbol{B}}^i)_k)}{\mathbb{V}(\mathcal{G})}$$

  - $\boldsymbol{A}$, $\boldsymbol{B}$: Matrices comprising independent samples of $\boldsymbol{\theta}$.
  - $\boldsymbol{A}_{\boldsymbol{B}}^i$: $i^{\text{th}}$ column of A is replaced by the $i^{\text{th}}$ column of $\boldsymbol{B}$.

- Activity scores

$$\alpha_i(n) = \sum_{j=1}^{n} \lambda_j v_{i,j}^2$$