Model Reductions with Special CSP Data

Harvey S. H. Lam
Princeton University

Full length paper available at
http://www.princeton.edu/~lam

Model reductions for stiff problems

- Consider the general initial-value problem:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y};\varepsilon)$$

$$\mathbf{y}(t=0) = \hat{\mathbf{y}}$$

Where **y** and **g** are N dimensional column vectors. The initial condition is arbitrary.

The problem is **stiff** when ε is asymptotically small.

For chemical kinetics …

$$\mathbf{y} = \begin{bmatrix} H_2O \\ O \\ OH \\ \vdots \\ T \end{bmatrix} \qquad \mathbf{g}(\mathbf{y};\varepsilon) = \sum_{r=1}^{R} \alpha_r \Omega^r(\mathbf{y}, k_r)$$

Where the α_r's are the **stoichiometric** column vectors, and the $\Omega^r(\mathbf{y};\varepsilon)$'s are the **kinetic rates** of the r–th reaction, respectively.

R is number of reactions. Usually, R >> N.

The issues of interest…

- Some of the reactions are very, very fast…
- We are interested in a much coarser time scale … (the **stiffness** issue)
- We want to know who is doing what to whom at time t … (the **insight** issue)
- Which kinetic rate parameters do we need to know accurately … and which can we accept sloppiness …(the **sensitivity** issue)
- Can we reduce the value of N … (the **size** issue)

Paper/pencil vs computer

- When N is small (e.g. less than 10), one could use paper/pencil to do singular perturbation asymptotics. But **Quasi-steady approximation** (QSA) and/or **Partial Equilibrium approximation** (PEA) require insights and mathematical skills…
- When N is large, such problems are beyond the reach of classical paper/pencil analysis.
- Computational singular perturbation (CSP) is **programmable paper/pencil analysis**…

Chemical kinetics data

r-th reaction: $H_2O + O \Leftrightarrow 2OH$

$$\mathbf{y} = \begin{bmatrix} H_2O \\ O \\ OH \\ \vdots \\ T \end{bmatrix} \qquad \alpha_r = \begin{bmatrix} -1 \\ -1 \\ +2 \\ 0 \\ \Delta h_r \end{bmatrix}$$

$$\Omega^r(\mathbf{y}) = k_r([H_2O][O] - K_r[OH]^2)$$

A reaction is **fast** if k_r is very, very large...

Special CSP data $\alpha_r, \beta^r, \tau^r$.

$\Omega^r(\mathbf{y}; k_r), \alpha_r$ Given data of the r-th reaction.

$H_2O + O \Leftrightarrow 2OH$

These data are **reaction-specific**!

Row vector

$$\beta^r(\mathbf{y}) \equiv \tau^r \frac{\partial \Omega^r}{\partial \mathbf{y}} = \tau^r \left[\frac{\partial \Omega^r}{\partial [H_2O]}, \frac{\partial \Omega^r}{\partial [O]}, \frac{\partial \Omega^r}{\partial [OH]}, \cdots, \frac{\partial \Omega^r}{\partial T} \right]$$

scalar

$$\tau^r(\mathbf{y}) \equiv \frac{1}{\frac{\partial \Omega^r}{\partial \mathbf{y}} \otimes \alpha_r} = \frac{1}{-\frac{\partial \Omega^r}{\partial [H_2O]} - \frac{\partial \Omega^r}{\partial [O]} + 2\frac{\partial \Omega^r}{\partial [OH]} + \ldots + \Delta h_f \frac{\partial \Omega^r}{\partial T}}$$

Note physical dimension of τ^r is **time**, and it is **defined** $\beta^r \otimes \alpha_r = 1$ so that

More special CSP data

$$\Gamma^{r}_{r'}(\mathbf{y}) = \beta^{r} \otimes \alpha_{r'}$$

r, r'=1, …, R.

All elements of this matrix are **dimensionless** O(1) numbers.

The diagonal elements are unity by definition.

Fast-slow partitioning

- Once we have the $\tau^r(\mathbf{y})$'s on the fly, we can **tentatively** rank the R reactions on the fly.
- The reactions can be partitioned into **fast** and **slow** groups on the fly:

Fast reactions

Slow reactions

$$\mathbf{g}(\mathbf{y};\varepsilon) = \sum_{m=1}^{M} \alpha_m \Omega^m(\mathbf{y};k_m) + \sum_{n=M+1}^{R} \alpha_n \Omega^n(\mathbf{y};k_n) \qquad \varepsilon \equiv \frac{|\tau^M|}{|\tau^{M+1}|} << 1$$

???

Question:

what happens to the fast reaction group after the fast reactions are exhausted?

$$\mathbf{g}(\mathbf{y};\varepsilon) = \sum_{m=1}^{M} \alpha_m \Omega^m(\mathbf{y};k_m) + \sum_{n=M+1}^{R} \alpha_n \Omega^n(\mathbf{y};k_n)$$

- We are given explicit algebraic formulas for $\Omega^m(\mathbf{y};k_m)$
- Differentiate it with respect to time:

$$\frac{d\Omega^m}{dt} = \frac{\partial \Omega^m}{\partial \mathbf{y}} \frac{d\mathbf{y}}{dt} = \frac{\beta^m}{\tau^m} * \mathbf{g} = \frac{1}{\tau^m} \left(\sum_{m'=1}^{M} \Gamma^m_{m'} \Omega^{m'} + \sum_{n=M+1}^{R} \Gamma^m_n \Omega^n \right)$$

- Define

$$\Theta^{m^*}_m \equiv \left[\Gamma^m_{m^*} \right]^{-1} \qquad \tau^{m^*}_m \equiv \Theta^{m^*}_m \tau^m \qquad m, m^* = 1, \ldots, M.$$

- **Exact** differential equations for the Ω^{m^*}'s are obtained:

$$\sum_{m=1}^{M} \tau^{m^*}_m \frac{d\Omega^m}{dt} = \Omega^{m^*} - \Omega^{m^*}_\infty \left(\mathbf{y};k_{slow} \right) \qquad \Omega^{m^*}_\infty \left(\mathbf{y};k_{slow} \right) \equiv - \sum_{n=M+1}^{R} \left(\sum_{m=1}^{M} \Theta^{m^*}_m \Gamma^m_n \right) \Omega^n \left(\mathbf{y};k_n \right)$$

These two equations are the foci of this paper!

CSP refinement procedures

- The leading order **converged CSP-refined** fast basis vectors can be obtained analytically in terms of the CSP data!

$$\mathbf{a}_m = \alpha_m, m = 1, \ldots, M.$$

They must be linearly independent.

$$\mathbf{b}^m = \sum_{m'=1}^{M} \Theta_{m'}^{m} \beta^{m'}, m = 1, \ldots, M.$$

These **converged** fast CSP-refined basis vectors are most useful for model reductions.

Exact reformulation of the problem

$$\frac{d\mathbf{y}}{dt} = \sum_{m=1}^{M} \alpha_m \Omega^m + \sum_{n=M+1}^{R} \alpha_n \Omega^n\left(\mathbf{y}; k_n\right)$$

$$\sum_{m'=1}^{M} \tau_{m'}^{m}\left(\mathbf{y}\right) \frac{d\Omega^{m'}}{dt} = \Omega^m - \Omega_\infty^m\left(\mathbf{y}; k_{slow}\right)$$

Where $\tau_{m'}^{m}(\mathbf{y})$ and $\Omega_\infty^m\left(\mathbf{y}; k_{slow}\right)$ are CSP data.

negative and small

What happens when $\tau_{m'}^{m}(\mathbf{y})$ is asymptotically small?

how small is small?

The classical paper/pencil strategy

Neglect "higher order" terms:

$$\frac{d\mathbf{y}}{dt} = \sum_{m=1}^{M} \alpha_m \Omega^m + \sum_{n=M+1}^{R} \alpha_n \Omega^n(\mathbf{y}; k_n)$$

$$\Omega^m = \Omega_\infty^m(\mathbf{y}; k_{slow}) + \sum_{m'=1}^{M} \tau_{m'}^{m}(\mathbf{y}) \frac{d\Omega^{m'}}{dt} \approx \Omega_\infty^m(\mathbf{y}; k_{slow})$$

negligible

The classical paper/pencil **reduced model** is:

$$\frac{d\mathbf{y}}{dt} \approx \sum_{m=1}^{M} \alpha_m \Omega_\infty^m(\mathbf{y}; k_{slow}) + \sum_{m=M+1}^{R} \alpha_n \Omega^n(\mathbf{y}; k_n)$$

Note: the above equation does not depend on the fast k_m's. It is no longer stiff.

A new strategy

Consider $\Omega^m, m = 1, \ldots, M,$ also as depending variables!

$$\frac{d\mathbf{y}}{dt} = \sum_{m=1}^{M} \alpha_m \Omega^m + \sum_{n=M+1}^{R} \alpha_n \Omega^n \left(\mathbf{y}; k_n \right)$$

$$\sum_{m'=1}^{M} \tau_{m'}^{m} \left(\mathbf{y} \right) \frac{d\Omega^{m'}}{dt} = \Omega^m - \Omega_\infty^m \left(\mathbf{y}; k_{slow} \right)$$

- Use any credible **implicit** finite difference scheme to integrate the second equation.

This NEW reduced model is exact---
weaknesses of implicit schemes are tolerated.

Example: backward finite difference

Do **not** neglect anything:

$$\frac{d\mathbf{y}}{dt} = \sum_{m=1}^{M} \alpha_m \Omega^m + \sum_{n=M+1}^{R} \alpha_n \Omega^n (\mathbf{y}; k_n)$$

$$\Omega^m = \Omega_\infty^m (\mathbf{y}; k_{slow}) + \sum_{m'=1}^{M} \tau_{m'}^{m} (\mathbf{y}) \frac{d\Omega^{m'}}{dt}$$

use backward finite difference

where

$$\Omega_\infty^{m^*} (\mathbf{y}; k_{slow}) \equiv - \sum_{n=M+1}^{R} \left(\sum_{m=1}^{M} \Theta_m^{m^*} \Gamma_n^m \right) \Omega^n (\mathbf{y}; k_n)$$

$$\tau_{m'}^{m} \equiv \Theta_{m'}^{m} \tau^{m'}$$

Th solutions are exact.

Insight extractions...

- All "answers" are expressed in terms of

$$\alpha_r, \beta^r, \tau^r(\mathbf{y}), \tau^m_{m'}(\mathbf{y}), \Omega^n(\mathbf{y}; k_n), \Omega^m_\infty(\mathbf{y}; k_{slow}), \Theta^m_{m'}(\mathbf{y}), \Gamma^r_{r'}(\mathbf{y}), \ldots.$$

  These are physically/chemically meaningful to knowledgeable investigators.

- Laminar/turbulent **diffusion terms can be handled**…
- **Effective stoichiometries** of the slow reactions are obtained…
- Reduced models are **not** unique.
- What happens at a different pressure? What happens if some rate data were wrong?

The slow invariant manifold

$$\Omega^m\left(\mathbf{y};k_m\right)=\Omega^m_{forward}\left(\mathbf{y};k_m\right)-\Omega^m_{reverse}\left(\mathbf{y};k_m\right)\approx\Omega^m_{\infty}\left(\mathbf{y};k_{slow}\right)$$

Negligible

So

$$\Omega^m_{forward}\left(\mathbf{y};k_m\right)\cong\Omega^m_{reverse}\left(\mathbf{y};k_m\right)+\Omega^m_{\infty}\left(\mathbf{y};k_{slow}\right)$$

provides M algebraic equations which can replace M differential equations (of the CSP radicals). Note: the above is independent of k_m.

$$H_2O+O\Leftrightarrow 2OH$$

$$[H_2O][H]=K_m[OH]^2+\frac{\Omega^m_{\infty}\left(\mathbf{y};k_{slow}\right)}{k_m}$$

negligible…

What can we learn from the CSP numbers?

- The issues:
  stiffness, **insights**, **sensitivities, size**.
- All important results are **analytically** expressed in terms of the CPS data. The most informative CSP data is $\Theta_m^{m*} \equiv \left[\Gamma_{m*}^{m}\right]^{-1}$.
- Provide guidance on how to **intelligently** exploit $\Omega^m(\mathbf{y};k_m)=\Omega^m(t), m=1,\ldots,M.$

  These provide M algebraic equations for the N components of **y** on the fly.

- Conservation of atomic elements and very slow reactions (i.e. large $\tau^n(\mathbf{y};k_n)$'s) are not exploited...but may be exploited if so desired.

Computational Singular Perturbation

- Do not need to neglect things...
- Identify unimportant terms...in the derived analytical formulas...
- Take advantage of numerical algorithms being involved...
- Use dimensionless numbers...
- Remember...the important issue is: what can we learn from the computed numbers?

Special CSP Data

$$\alpha_r, \beta^r(\mathbf{y}), \tau^r(\mathbf{y}), \Theta^m_{m'}(\mathbf{y}), \tau^m_{m'}(\mathbf{y}), \ldots$$

Leading order converged CSP-refined fast basis vectors are analytically found for chemical kinetics problems ...

$$\sum_{m'=1}^{M} \tau^m_{m'}\left(\mathbf{y}; k_{m'}\right) \frac{d\Omega^{m'}}{dt} = \Omega^m - \Omega^m_\infty\left(\mathbf{y}; k_{slow}\right), \; m = 1, \ldots, M.$$

Full length paper available at:
http://www.princeton.edu/~lam