Model Reductions with Special CSP Data

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***Abstract*— Certain reaction-specific CSP data are shown to be especially useful for model reductions.**

I. Statement of the problem

Consider the following general initial-value problem:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y};\epsilon), \quad \mathbf{y}(t=0) = \tilde{\mathbf{y}}, \tag{1}$$

where both $\mathbf{y}$ and $\mathbf{g}$ are N-dimensional column vectors, the components of $\mathbf{g}(\mathbf{y};\epsilon)$ are *given* algebraic functions of $\mathbf{y}$, and ϵ is a small dimensionless parameter. The $\mathbf{y}$ initial value is denoted by $\tilde{\mathbf{y}}$ and is arbitrary. We are interested in the small ϵ case when (1) is known to be *stiff*. We shall show that for general chemical kinetics problems certain reaction-specific data are most useful for doing CSP model reductions, yielding results that are very easy to interpret.

For chemical kinetics problems, $\mathbf{g}(\mathbf{y};\epsilon)$ is usually *given* in the following form:

$$\mathbf{g}(\mathbf{y};\epsilon) = \sum_{r=1}^{R} \boldsymbol{\alpha}_r \Omega^r(\mathbf{y};k_r), \tag{2}$$

where the $\boldsymbol{\alpha}_r$'s are N-dimensional column vectors, and R is the total number of chemical reactions in the reaction system. The physical dimensions of the elements of $\boldsymbol{\alpha}_r$ are the same as that of the corresponding elements of $\mathbf{y}$, while the physical dimensions of all the $\Omega^r(\mathbf{y};k_r)$'s are reciprocal time. For each of the r-th reaction, the elements of $\boldsymbol{\alpha}_r$ are proportional to the *stoichiometric coefficients*, $\Omega^r(\mathbf{y};k_r)$ is the *net reaction rate*, and k_r is the kinetic rate parameter. Usually, $\Omega^r(\mathbf{y};k_r)$ is proportional to k_r and its $\mathbf{y}$ dependence is *nonlinear*. For most real world problems, *the $\boldsymbol{\alpha}_r$'s dependence on $\mathbf{y}$, if any, is weak*, and R is often much bigger than N—so many $\boldsymbol{\alpha}_r$'s are linearly dependent. Equation (1) is stiff when $M > 0$ reactions are much faster than all others. The stiffness of (1) is symbolically represented by the dimensionless parameter ϵ in $\mathbf{g}(\mathbf{y};\epsilon)$. In the present paper, we exploit the fact that both $\boldsymbol{\alpha}_r$ and $\Omega^r(\mathbf{y};k_r)$ are *reaction-specific* entities which are *chemically/physically meaningful* to knowledgeable investigators.

II. The CSP simplified reduced model

When there are M linearly independent fast reactions, CSP [1], [2], [3], [4] introduces a dimensionless $N \times N$ *fast subspace projection matrix* $\mathcal{Q}^{fast}(M)$ as follows:

$$\mathcal{Q}^{fast}(M) \equiv \sum_{m=1}^{M} \mathbf{a}_m \mathbf{b}^m, \tag{3}$$

where the $\mathbf{a}_m$'s and the $\mathbf{b}^m$'s are M pairs of the fast subspace's column and row *basis vectors which are linearly independent* and have been *CSP-refined* at least once. They are—by definition—orthonormal to each other:

$$\mathbf{b}^m \odot \mathbf{a}_{m'} = \delta^m_{m'}, \quad m, m' = 1, \ldots, M, \tag{4}$$

where $\odot$ denotes the inner product operator and $\delta^m_{m'}$ denotes the Kronecker Delta.

CSP provides iterative *refinement procedures* to find *good quality* $\mathbf{a}_m$'s and $\mathbf{b}^m$'s. The right-hand side of (1) is partitioned using a good quality $\mathcal{Q}^{fast}(M)$:

$$\begin{aligned} \mathbf{g}(\mathbf{y};\epsilon) &= \mathbf{g}^{fast}(\mathbf{y};\epsilon) + \mathbf{g}^{slow}(\mathbf{y};\epsilon), && \text{(5a)} \\ \mathbf{g}^{fast}(\mathbf{y};\epsilon) &\equiv \mathcal{Q}^{fast}(M) \odot \mathbf{g}(\mathbf{y};\epsilon), && \text{(5b)} \\ \mathbf{g}^{slow}(\mathbf{y};\epsilon) &\equiv (\mathcal{I} - \mathcal{Q}^{fast}(M)) \odot \mathbf{g}(\mathbf{y};\epsilon), && \text{(5c)} \end{aligned}$$

and $\mathcal{I}$ is the identify matrix. CSP shows that $\mathbf{g}^{fast}(\mathbf{y};\epsilon)$ is dominant only during the initial fast transient. After the fast transient is exhausted (assuming the system is stable), $\mathbf{g}^{fast}(\mathbf{y};\epsilon)$ is $O(\epsilon)$ in comparison to $\mathbf{g}^{slow}(\mathbf{y};\epsilon)$. The CSP-derived simplified reduced model and initial condition for the original given problem in the slow epoch are then:

$$\begin{aligned} \frac{d\mathbf{y}}{dt} &= \mathbf{g}^{slow}(\mathbf{y};\epsilon) + O(\epsilon), && \text{(6)} \\ \mathbf{g}^{fast}(\tilde{\mathbf{y}}^{slow};\epsilon) &= O(\epsilon), \quad \tilde{\mathbf{y}}^{slow} \equiv \mathbf{y}(t = O(\epsilon)). \end{aligned}$$

Any solution $\mathbf{y}(t)$ of the above non-stiff initial-value problem is guaranteed by CSP to *automatically* stay inside the *slow subspace* defined by:

$$\mathbf{g}^{fast}(\mathbf{y}(t);\epsilon) = O(\epsilon), \quad t > O(\epsilon). \tag{7}$$

The quality of the CSP-derived simplified reduced model—as measured by the smallness of the $O(\epsilon)$ terms above—depends on the quality of the $\mathbf{a}_m$'s and $\mathbf{b}^m$'s in $\mathcal{Q}^{fast}(M)$.

III. Reaction-specific CSP Data

Equation (2) clearly associates the column vector $\boldsymbol{\alpha}_r$ with the r-th reaction. We now associate the following row vector $\boldsymbol{\beta}^r$ with the r-th reaction:

$$\boldsymbol{\beta}^r \equiv \tau_r \frac{\partial \Omega^r(\mathbf{y};k_r)}{\partial \mathbf{y}} = \boldsymbol{\beta}^r(\mathbf{y}), \quad r = 1, \ldots, R, \tag{8a}$$

where τ_r, a most interesting **reaction-specific** entity with *time* as its physical dimension, is *defined* by:

$$\tau_r \equiv \frac{1}{\frac{\partial \Omega^r}{\partial \mathbf{y}} \odot \boldsymbol{\alpha}_r} = \tau_r(\mathbf{y}, k_r), \quad r = 1, \ldots, R. \tag{8b}$$

We next *define* $\Gamma^r_{r'}(\mathbf{y})$, a $R \times R$ *dimensionless* matrix, by:

$$\Gamma^r_{r'}(\mathbf{y}) = \boldsymbol{\beta}^r \odot \boldsymbol{\alpha}_{r'}, \quad r, r' = 1, \dots R. \tag{9}$$

Equation (8b)—the formula for $\tau_r(\mathbf{y}, k_r)$—was obtained by setting the diagonal elements of $\Gamma^r_{r'}(\mathbf{y})$ to unity. Note that in general $\Gamma^r_{r'}(\mathbf{y}) \neq 0$ when $r \neq r'$, while $\Gamma^r_r(\mathbf{y}) = 1$ is always honored by definition.

IV. Exploitation of the CSP Data

The $\tau_r(\mathbf{y}, k_r)$ data is most interesting. If the r-th reaction is the only reaction in a reaction system, then it is easy to show that $d\Omega^r/dt = \Omega^r/\tau_r$. Thus $|\tau_r(\mathbf{y}, k_r)|$, with time as its physical dimension, is an *intrinsic time scale* of the r-th reaction. The smaller $|\tau_r(\mathbf{y}, k_r)|$ is, the faster is the intrinsic speed of the r-th reaction. Thus we can, at any time t, order the R reactions in ascending order of their $|\tau_r(\mathbf{y}(t), k_r)|$'s so that $r = 1$ is intrinsically the fastest reaction of them all at that time. Ordering reactions this way is much easier (but less theoretically definitive) than ordering by eigenvalues—which physical dimensions are reciprocal time—of the Jacobian matrix $\partial \mathbf{g}/\partial \mathbf{y}$ [5].

Mathematically, the stiffness of (1) is caused by a large gap in the values of the $\tau_r(\mathbf{y}, k_r)$'s. Such gaps separate the fast and slow reaction subspaces. When the ratio of two successive values of $\tau_r(\mathbf{y}, k_r)$ is small, this ratio is a credible estimate of the small parameter ϵ in $\mathbf{g}(\mathbf{y}; \epsilon)$.

For the sake of simplicity, we assume that the set of M fast $\boldsymbol{\alpha}_1, \dots, \boldsymbol{\alpha}_M$ so identified are linearly independent, and that all M fast $\tau_m(\mathbf{y}, k_m)$'s are negative. In addition, we also assume that the total number of linearly dependent $\boldsymbol{\alpha}_r$'s is not very large. The fast subspace is then M-dimensional (with $M < N$) and stable. It is then *intuitively* obvious that the chemically/physically meaningful $\boldsymbol{\alpha}_m(\mathbf{y})$'s are excellent choices for the $\mathbf{a}_m(\mathbf{y})$'s:

$$\mathbf{a}_m(\mathbf{y}) = \boldsymbol{\alpha}_m(\mathbf{y}) + O(\epsilon), \quad m = 1, \dots, M. \tag{10a}$$

We next choose the $\mathbf{b}^m$'s to be some linear combinations of the fast $\boldsymbol{\beta}^m(\mathbf{y})$'s:

$$\mathbf{b}^m(\mathbf{y}) = \sum_{m'=1}^{M} \Theta^m_{m'}(\mathbf{y}) \boldsymbol{\beta}^{m'}(\mathbf{y}) + O(\epsilon), m = 1, ..., M, \tag{10b}$$

where $\Theta^m_{m"}(\mathbf{y})$, a $M \times M$ dimensionless matrix, is determined by imposing $\mathbf{b}^m \odot \mathbf{a}_{m"} = \delta^m_{m"}$:

$$\Theta^m_{m"}(\mathbf{y}) = \left(\Gamma^{m"}_m(\mathbf{y})\right)^{-1} + O(\epsilon), m, m" = 1, \dots, M. \tag{10c}$$

Thus $\mathcal{Q}^{fast}(M)$ is found. To validate the choices made in (10b), we perform the so-called *step #1 CSP refinement procedure* on the $\mathbf{b}^m(\mathbf{y})$'s as outlined by (6.17a,b) of [3]. Noting that $d\mathbf{b}^m/dt + \mathbf{b}^m \odot \partial \mathbf{g}/\partial \mathbf{y} = \partial(\mathbf{b}^m \odot \mathbf{g})/\partial \mathbf{y}$, we rewrite the original iterative refinement formula as follows:

$$\mathbf{b}^m_o(\mathbf{y}) = \sum_{m'=1}^{M} \tau^m_{m'} \frac{\partial}{\partial \mathbf{y}} (\mathbf{b}^{m'}(\mathbf{y}) \odot \mathbf{g}), \ m = 1, \dots, M, \tag{11}$$

where $\tau^m_{m'}(\mathbf{y})$, a $M \times M$ matrix, is determined immediately below. It is readily demonstrated that $\mathbf{b}^m_o(\mathbf{y}) = \mathbf{b}^m(\mathbf{y}) + O(\epsilon)$. Using (10b) for $\mathbf{b}^m(\mathbf{y})$ on the right-hand side of (11), imposing $\mathbf{b}^m_o \odot \mathbf{a}_{m'} = \delta^m_{m'}$ and taking advantage of (10c), the leading order approximation for $\tau^m_{m'}(\mathbf{y})$ is found to be:

$$\tau^m_{m'}(\mathbf{y}) = \Theta^m_{m'}(\mathbf{y}) \tau_{m'}(\mathbf{y}, k_{m'}) + O(\epsilon), \quad m, m' = 1, \dots, M. \tag{12}$$

The M eigenvalues of $\tau^m_{m'}(\mathbf{y})$—all are expected to be $O(\tau_m)$ and negative—are credible approximations of the time scales of the fast subspace in the small ϵ limit.

The wisdom of the intuitive $\mathbf{a}_m(\mathbf{y})$'s choices made in (10a) can be similarly validated using the step #2 iterative CSP refinement procedure. See §6.5 of [3].

V. The net value of $\Omega^m(\mathbf{y})$ in the slow epoch

After the fast reactions are exhausted, we know $\mathbf{b}^m \odot \mathbf{g} = O(\epsilon)$. Using (10b) for $\mathbf{b}^m$, this equation tells us that in the slow epoch $\Omega^m(\mathbf{y}; k_m) - \Omega^m_\infty(\mathbf{y}) = O(\epsilon)$, where:

$$\begin{aligned} \Omega^m_\infty(\mathbf{y}) &\equiv -\sum_{m"=1}^{M} \Theta^m_{m"} \sum_{r=M+1}^{R} \Gamma^{m"}_r \Omega^r(\mathbf{y}; k_r), \\ m &= 1, \dots, M. \end{aligned} \tag{13}$$

In other words, the forward and reverse reaction rates of the fast reactions are *not* in balance in the slow epoch—their *net* values are given approximately by (13). Note that $\mathbf{g}^{slow}(\mathbf{y}; \epsilon)$ in the slow epoch can also be derived/calculated using the original (2)—*instead* of (5c)—provided the above $\Omega^m_\infty(\mathbf{y})$'s are used for all the needed $\Omega^m(\mathbf{y}; k_m)$'s.

VI. Concluding remarks

Subroutines for $\boldsymbol{\alpha}_r(\mathbf{y})$, $\boldsymbol{\beta}^r(\mathbf{y})$, and $\tau_r(\mathbf{y}, k_r)$ should be included for every reaction in chemical kinetics databases so that—for any reaction system of interest—credible values of M and ϵ can easily be found, and that system data such as $\Gamma^r_{r'}(\mathbf{y})$, $\Theta^m_{m'}(\mathbf{y})$, $\mathbf{b}^m(\mathbf{y})$, $\mathcal{Q}^{fast}(M)$, $\tau^m_{m'}(\mathbf{y})$, etc. can be routinely computed when needed. Such CSP data can provide informative answers to questions such as *what roles does the r-th reaction play at time t*? How to deal with large number of linearly dependent $\boldsymbol{\alpha}_r(\mathbf{y})$'s will be discussed.

References

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