

CHAPTER 10

CONVENTIONAL ASYMPTOTICS AND COMPUTATIONAL SINGULAR PERTURBATION FOR SIMPLIFIED KINETICS MODELLING

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1. Introduction

Generally speaking, the chemical kinetics of any reaction system can potentially be very complex. Even though the investigator may only be interested in a few species, the reaction model almost always involves a much larger number of species. Some of the species involved are often referred to as *radicals* with a special meaning: they are usually reactants of *low* concentrations which are believed to be important *intermediaries* in the whole reaction scheme. A large number of elementary reactions can occur among the species; some of these reactions are fast and some are slow. The aim of simplified kinetics modelling is to derive the simplest reaction system which nevertheless retains the essential features of the full reaction system. The conventional technique [1] is to systematically apply the so-called *steady-state* approximation to the appropriate radicals, the *partial-equilibrium* approximation to the fast reactions, and to ignore the very slow (and therefore unimportant) reactions. The investigator is responsible for identifying what are the appropriate radicals, which are the fast elementary reactions, and which are the very slow ones by making intelligent order of magnitude estimates using information gathered from detailed examination of available data. A skilled and knowledgeable chemical kineticist is usually needed, and the results obtained are expected to be valid only in some limited domain of initial and operating conditions in some limited interval of time. The successful derivation of a simplified chemical kinetics model by conventional methodology thus depends considerably on the experience, intuition and judgement of the investigator.

In the present paper, we present a summary, plus some new recent developments, of the theory of Computational Singular Perturbation [2], [3], [4], [5] (CSP), a general method for non-linear boundary layer type stiff equations particularly appropriate for chemical kinetics problems. A hypothetical reaction system is studied and the appropriate *simplified kinetics models* are derived using both the conventional method and the CSP method, showing clearly their comparative strengths and weaknesses. The goal of the paper is to show that, given the relevant database of elementary reaction rates, the derivation of time-resolved simplified kinetics models for large reaction systems can be routinely accomplished using numerical data generated by CSP.

2. Preliminary Discussions

We are interested in a certain reaction system with initial conditions in a certain temperature and pressure range. A comprehensive and up-to-date database containing all possibly relevant elementary reactions and their rates is assumed available. The *full mechanism* of this reaction system can readily be constructed from this database and consists of R elementary reactions and N species. The species concentrations are represented by the *column* vector \mathbf{y} :

$$\mathbf{y} = [y^1, y^2, \dots, y^N]^T, \quad (2.1)$$

where $[\cdot, \cdot, \dots]$ is a *row* vector and its transpose $[\cdot, \cdot, \dots]^T$ is a *column* vector. For the sake of simplicity, we consider here only isothermal and homogeneous reaction systems. With this qualification, the governing chemical kinetics equations for \mathbf{y} is written formally as follows:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}), \quad (2.2)$$

where the column vector \mathbf{g} is the *global reaction rate* and consists of contributions from each of the R elementary reactions:

$$\mathbf{g} = [g^1, g^2, \dots, g^N]^T = \sum_{r=1}^R \mathbf{S}_r F^r, \quad (2.3)$$

where \mathbf{S}_r and F^r are the *stoichiometric* (column) vector and the *reaction rate* of the r^{th} elementary reactions, respectively. For complex reaction systems [6], Eq.(2.2) is usually stiff, and the values of N and R may be quite large and in general not equal.

The basic idea of CSP is to project the R terms in Eq.(2.3) into N linearly independent *modes*, and group the N modes into a *fast* group and a *slow* group. For most chemical kinetics problems, the fast modes are usually of the boundary layer type, and their amplitudes decay rapidly with time. The appropriate simplified kinetics model is then straightforwardly obtained when the contribution of the fast group becomes “sufficiently small” and is neglected. The process of projecting and grouping of the terms is accomplished by the use of a special set of *basis vectors*.

3. CSP in Summary

Since \mathbf{g} is a N -dimensional vector, it can always be expressed in terms of any set of N linearly independent basis vectors, $(\mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_N)$. For the moment, let us assume that a trial set of N linearly independent basis (column) vectors $(\mathbf{a}_1(t), \mathbf{a}_2(t), \dots, \mathbf{a}_N(t))$ has *somehow* been chosen. The corresponding set of (row) vectors $(\mathbf{b}^1(t), \mathbf{b}^2(t), \dots, \mathbf{b}^N(t))$ satisfying the orthonormal relations:

$$\mathbf{b}^i \bullet \mathbf{a}_k = \delta_k^i, \quad i, k = 1, 2, \dots, N, \quad (3.1)$$

where δ_k^i is the N by N identity matrix, can readily be computed. Eq.(2.3) can be alternatively expressed in terms of these basis vectors:

$$\mathbf{g} = \sum_{i=1}^N \mathbf{a}_i f^i, \quad (3.2)$$

where f^i is the “amplitude” of \mathbf{g} in the “direction” of \mathbf{a}_i . We interpret each of the additive terms in Eq.(3.2) as representing a *reaction mode* or simply a *mode*. Therefore, \mathbf{a}_i and f^i are the *effective stoichiometric vector* and the *effective reaction rate* of the i^{th} mode, respectively. Taking the dot product of \mathbf{b}^k with \mathbf{g} , we obtain, using Eqs.(2.3), (3.1) and (3.2):

$$f^k \equiv \mathbf{b}^k \bullet \mathbf{g} \quad (3.3a)$$

$$\begin{aligned} &= \mathbf{b}^k \bullet \sum_{r=1}^R \mathbf{S}_r F^r \\ &= \sum_{r=1}^R B_r^k F^r, \end{aligned} \quad k = 1, 2, \dots, N, \quad (3.3b)$$

where B_r^k is:

$$B_r^k \equiv \mathbf{b}^k \bullet \mathbf{S}_r, \quad k = 1, 2, \dots, N, \quad r = 1, 2, \dots, R. \quad (3.4)$$

It is seen from Eq.(3.3b) that f^k is some linear combination of the F^r 's. Summarizing: once a full set of basis vectors (either the \mathbf{a}_i 's or the \mathbf{b}^i 's) is somehow chosen, the "other" set of basis vectors and the f^i 's can readily be computed from Eqs.(3.1) and (3.3), respectively. Eq.(3.2) is exact and is an alternative representation of Eq.(2.3).

It is important to note here that each basis vector \mathbf{a}_i may contain an arbitrary time-dependent scale factor. Without loss of generality, we shall assume that all the \mathbf{a}_i vectors have been appropriately scaled such that their orders of magnitude are relatively constant with time. Consequently, the order of magnitude of the contribution of the i^{th} mode in Eq.(3.2) is primarily dependent on the order of magnitude of f^i . How does the choice of the basis vectors influence the time evolution of the f^i 's? To find out, we differentiate Eq.(3.3a) with respect to time to obtain, with the help of Eqs.(3.2) and (2.2):

$$\frac{df^i}{dt} = \sum_{k=1}^N \Lambda_k^i f^k, \quad i = 1, 2, \dots, N, \quad (3.5)$$

where

$$\Lambda_k^i \equiv \Phi_k^i + \frac{d\mathbf{b}^i}{dt} \bullet \mathbf{a}_k = \Phi_k^i - \mathbf{b}^i \bullet \frac{d\mathbf{a}_k}{dt}, \quad i, k = 1, 2, \dots, N, \quad (3.6)$$

$$\Phi_k^i \equiv \mathbf{b}^i \bullet \mathbf{J} \bullet \mathbf{a}_k, \quad i, k = 1, 2, \dots, N, \quad (3.7)$$

and \mathbf{J} is the Jacobian of \mathbf{g} with respect to \mathbf{y} :

$$\mathbf{J} = J_k^i \equiv \frac{\partial g^i}{\partial y^k}, \quad i, k = 1, 2, \dots, N. \quad (3.8)$$

Hence the time evolution of the f^i 's is seen to be controlled solely by Λ_k^i which, according to Eq.(3.6), is completely determined by $\mathbf{a}_i(t)$, $\mathbf{b}^i(t)$ (and their time derivatives) in addition to \mathbf{J} . It is useful to note that J_k^i and Φ_k^i are similar matrices, but Λ_k^i and Φ_k^i are not (unless the \mathbf{a}_i 's and \mathbf{b}^i 's are constant vectors). Note that if Λ_k^i is diagonal, the modes would be completely uncoupled from each other.

If the given problem were linear, \mathbf{J} would be a constant matrix, and the obvious choice for basis vectors would be the (constant) right and left eigen-vectors of \mathbf{J} defined by:

$$\boldsymbol{\beta}^i \bullet \mathbf{J} = \lambda(i) \boldsymbol{\beta}^i, \quad i = 1, 2, \dots, N, \quad (3.9a)$$

$$\mathbf{J} \bullet \boldsymbol{\alpha}_i = \boldsymbol{\alpha}_i \lambda(i), \quad i = 1, 2, \dots, N. \quad (3.9b)$$

The resulting Λ_k^i would be the diagonal matrix (or the Jordan form) of the eigen-values, $\lambda(i)$'s. Consequently, the amplitude of each of the uncoupled modes, f^i , would evolve with its own characteristic time scale. If $\lambda(i)$ is essentially real and negative, the i^{th} mode is said to be of the boundary layer type, and f^i would decay exponentially toward zero and become eventually exhausted for some $t \gg |1/\lambda(i)|$. An obvious algorithm for the linear case is: whenever the amplitude of the currently fastest mode falls below some user-specified threshold, the term representing that mode could be dropped from Eq.(3.2), yielding a less stiff equation to be integrated for larger time. In other words, terms representing exhausted boundary layers can be "neglected" to yield a simplified and less stiff equation for the next boundary layers.

In essence, CSP simply extends the above described algorithm to non-linear problems. Unlike the linear case, it is now not obvious how to choose the basis vectors. However, even though \mathbf{J} is no longer a constant matrix, its left and right eigen-vectors, β^i and α_i , are nevertheless always defined, and can be computed at any time from Eqs.(3.9). Let us denote the reciprocal of the absolute value of $\lambda(i)$ by $\tau(i)$, call the $\tau(i)$'s the current *time scales* of the reaction modes, and order them in ascending magnitudes: $\tau(1) \leq \tau(2) \leq \dots \leq \tau(N)$. These eigen-vectors and eigen-values of \mathbf{J} can either be used directly (provided that \mathbf{J} is non-defective) or serve as a guide for choosing a set of *trial* basis vectors. Note that the main impact of non-linearity is that even if eigen-vectors of \mathbf{J} were used directly as the trial set, the resulting Λ_k^i still would *not* be diagonal. The non-zero off-diagonal elements cause *mixing* of the modes, and as a consequence the fast modes may not decay and become small as in the linear case. In the present paper, we shall focus our efforts to derive a “refinement” algorithm which can generate from any reasonable trial set of basis vectors an improved set which has less mode mixing than before. As shall be demonstrated later in §5, these CSP generated basis vectors and other data can be used in chemical kinetics problems to deduce physically meaningful information such as the global stoichiometry and reaction rates of simplified kinetics models.

We can manipulate Eqs.(3.1), (3.6) and (3.7) to yield:

$$\frac{d\mathbf{b}^i}{dt} + \mathbf{b}^i \bullet \mathbf{J} = \sum_{k=1}^N \Lambda_k^i \mathbf{b}^k, \quad i = 1, 2, \dots, N, \quad (3.10a)$$

$$-\frac{d\mathbf{a}_i}{dt} + \mathbf{J} \bullet \mathbf{a}_i = \sum_{k=1}^N \mathbf{a}_k \Lambda_k^i, \quad i = 1, 2, \dots, N, \quad (3.10b)$$

which may be considered the governing differential equations for the \mathbf{a}_i 's and \mathbf{b}^i 's for any desired Λ_k^i . Since no restriction has been placed on the initial conditions, it is clear that the set of basis vectors corresponding to a given Λ_k^i is not unique. One simple-minded approach would be to choose Λ_k^i to be the diagonal (or the Jordan form) eigen-value matrix of \mathbf{J} , and compute for the corresponding uncoupled \mathbf{a}_i 's and \mathbf{b}^i 's using Eqs.(3.10) with some appropriately chosen initial conditions. It suffices to state here that this approach is fundamentally flawed but a detailed discussion of its shortcomings is beyond the scope of this paper.

Let τ^* be a user-specified time resolution of interest. Thus reaction modes with $\tau(i) < \tau^*$ are considered fast, otherwise they are considered slow. We assume that, for the time interval of interest and guided by the eigen-vectors of \mathbf{J} in some vague sense, the first M basis vectors of the chosen set of trial basis vectors span a M -dimensional fast subspace, and that the rest of the $N - M$ basis vectors span the remaining slow subspace. The left and right eigen-vectors of \mathbf{J} at $t = t_0$ or any other reasonably intelligent choice can be used as the (constant) trial basis vectors for $t \geq t_0$. As mentioned previously, the Λ_k^i computed from any trial set will in general have non-zero off-diagonal elements. We shall presently derive an algorithm which can reduce the amount of mode mixing of any reasonably chosen trial basis vectors.

We shall use indices m and n to refer to the fast subspace ($m, n = 1, \dots, M$), and I and J to refer to the slow subspace ($I, J = M + 1, \dots, N$). Indices i and k shall continue to refer to the whole N -dimensional space ($i, k = 1, 2, \dots, N$).

The right-hand side of Eq.(3.5) can be formally divided into a fast and a slow group.

Writing out the fast and the slow equations separately, we have:

$$\frac{df^m}{dt} = \sum_{n=1}^M \Lambda_n^m f^n + \sum_{J=M+1}^N \Lambda_J^m f^J, \quad m = 1, 2, \dots, M, \quad (3.11a)$$

$$\frac{df^I}{dt} = \sum_{n=1}^M \Lambda_n^I f^n + \sum_{J=M+1}^N \Lambda_J^I f^J, \quad I = M+1, \dots, N. \quad (3.11b)$$

The question is: how do the fast f^m 's behave as time increases? Eq.(3.11a) can be rewritten as follows:

$$\frac{df^m}{dt} = \sum_{n=1}^M \omega_n^m(M)(f^n - f_\infty^n(M)), \quad m = 1, 2, \dots, M, \quad (3.12)$$

where $\omega_n^m(M)$ is the M by M principal submatrix of Λ_k^i :

$$\omega_n^m(M) \equiv \Lambda_n^m, \quad m, n = 1, 2, \dots, M, \quad (3.13)$$

and

$$f_\infty^m \equiv - \sum_{J=M+1}^N p_J^m(M) f^J, \quad m = 1, 2, \dots, M, \quad (3.14)$$

$$p_J^m(M) \equiv \sum_{n=1}^M \tau_n^m(M) \Lambda_J^n, \quad m = 1, 2, \dots, M, \\ J = M+1, \dots, N, \quad (3.15)$$

and $\tau_n^m(M)$ is the inverse of $\omega_n^m(M)$:

$$\sum_{k=1}^M \omega_k^m(M) \tau_n^k(M) = \sum_{k=1}^M \tau_k^m(M) \omega_n^k(M) = \delta_n^m, \quad m, n = 1, 2, \dots, M.$$

The impact of having non-zero off-diagonal elements of the matrix Λ_k^m can be seen from Eq.(3.12): when $\lambda(m)$ is essentially real and negative, f^m no longer decays exponentially to zero as the corresponding boundary layer is exited. Eq.(3.12) shows that f^m decays exponentially with the fast time scale $\tau(m)$ only initially. In a transient period of order $\tau(M)$, f^m tends rapidly toward $f_\infty^m(M)$; thereafter, f^m simply tries to follow the corresponding $f_\infty^m(M)$ which evolves with the slower time scale $\tau(M+1)$ as time increases. At this point, there is no theoretical assurance that $f_\infty^m(M)$ is in any sense small or negligible. Thus, so long as $\Lambda_J^m(M)$ has non-zero elements, there is mixing of the slow modes with the fast modes, and this mixing prevents the amplitude of the fast modes from continuing their rapid decay to become “small” when $t \gg \tau(M)$.

Eq.(3.12) suggests the use of a new f_o^m to replace f^m :

$$f_o^m \equiv f^m - f_\infty^m(M), \quad m = 1, 2, \dots, M. \quad (3.16)$$

We shall show presently that f_o^m is expected to be small in some asymptotic sense when $t \gg \tau(M)$. Eqs.(3.11) can be rewritten as follows:

$$\frac{df_o^m}{dt} = \sum_{n=1}^M \omega_n^m(M)(f_o^n - f_{o,\infty}^n(M)), \quad m = 1, 2, \dots, M, \quad (3.17a)$$

$$\frac{df^I}{dt} = \sum_{J=M+1}^N \Omega_J^I(M) f^J + \sum_{m=1}^M \Lambda_m^I f_o^m, \quad I = M+1, \dots, N, \quad (3.17b)$$

where

$$f_{o,\infty}^n(M) \equiv \sum_{m=1}^M \tau_m^n(M) \frac{df_{\infty}^m(M)}{dt}, \quad n = 1, 2, \dots, M, \quad (3.18)$$

$$\Omega_J^I(M) \equiv \Lambda_J^I - \sum_{m,n=1}^M \Lambda_m^I \tau_n^m(M) \Lambda_J^n, \quad I, J = M+1, \dots, N. \quad (3.19)$$

Note that Eqs.(3.12) and (3.17a) differ only in their forcing term, $f_{\infty}^n(M)$ versus $f_{o,\infty}^n$; hence $f_o^m(M)$ is expected to tend to $f_{o,\infty}^m(M)$ for $t \gg \tau(M)$. Eq.(3.18) clearly shows that $f_{o,\infty}^m(M)$ is smaller than $f_{\infty}^m(M)$ for $t \gg \tau(M)$ by the factor $\varepsilon(M)$:

$$\varepsilon(M) \equiv \frac{\tau(M)}{\tau(M+1)}. \quad (3.20)$$

Thus f_o^m is a “purer” fast mode than f^m . In the asymptotic limit of vanishingly small $\varepsilon(M)$, f_o^m is now theoretically small for $t \gg \tau(M)$.

Inspection of Eq.(3.11b) or (3.17b) indicates that in general there is also mixing of the fast modes with the slow modes so long as $\Lambda_m^I(M)$ has non-zero elements. For obvious reasons, this mixing should be as weak as possible.

The above analysis suggests that the set of basis vectors $\mathbf{a}_i^o(M)$ and $\mathbf{b}_o^i(M)$ defined below is an “improvement” over the original trial set, \mathbf{a}_i and \mathbf{b}^i :

$$\mathbf{b}_o^m(M) \equiv \mathbf{b}^m + \sum_{J=M+1}^N p_J^m(M) \mathbf{b}^J, \quad m = 1, 2, \dots, M, \quad (3.21a)$$

$$\mathbf{a}_J^o(M) \equiv \mathbf{a}_J - \sum_{n=1}^M \mathbf{a}_n p_J^n(M), \quad J = M+1, \dots, N, \quad (3.21b)$$

$$\mathbf{b}_o^I(M) \equiv \mathbf{b}^I - \sum_{n=1}^M q_n^I(M) \mathbf{b}_o^n(M), \quad I = M+1, \dots, N, \quad (3.21c)$$

$$\mathbf{a}_m^o(M) \equiv \mathbf{a}_m + \sum_{J=M+1}^N \mathbf{a}_J^o(M) q_m^J(M), \quad m = 1, 2, \dots, M, \quad (3.21d)$$

where $p_J^m(M)$ was previously given by (3.15), and $q_m^I(M)$ is given by:

$$q_m^I(M) \equiv \sum_{n=1}^M \Lambda_n^I \tau_m^n(M), \quad m = 1, 2, \dots, M, \quad I = M+1, \dots, N. \quad (3.22)$$

Eq.(3.21a) is derived by a conventional singular perturbation analysis on Eq.(3.17a), and Eq.(3.21c) is derived by a similar analysis on Eq.(3.17b). Eqs.(3.21b,d) are derived by insisting that the new set of basis vectors satisfy the orthonormal relation (see Eq.(3.1)):

$$\mathbf{b}_o^i(M) \bullet \mathbf{a}_k^o(M) = \delta_k^i, \quad i, k = 1, 2, \dots, N.$$

Eqs.(3.21) provide an algorithm to generate a new set of basis vectors from an old set. We shall call the new set, $\mathbf{b}_o^i(M)$ and $\mathbf{a}_k^o(M)$, the *refined basis vectors*. Note that the refinement algorithm can be recursively applied. The use of refined $\mathbf{b}_o^m(M)$ and $\mathbf{a}_J^o(M)$

improves (*i.e.* made smaller by $O(\varepsilon(M))$) the order of magnitude of the residual amplitudes of the fast modes. The use of refined $\mathbf{b}_o^I(M)$ and $\mathbf{a}_m^o(M)$ obtained with $q_m^I(M)$ given by Eq.(3.22) purifies the slow modes.

In terms of these new refined basis vectors, a one-parameter family of alternative representation of \mathbf{g} (with M as the parameter) is obtained:

$$\mathbf{g} = \sum_{k=1}^N \mathbf{a}_k^o(M) f_o^k \quad (3.23a)$$

$$= \sum_{m=1}^M \mathbf{a}_m^o f_o^m + \sum_{J=M+1}^N \mathbf{a}_J^o(M) f_o^J \quad (3.23b)$$

where

$$f_o^i = \mathbf{b}_o^i(M) \bullet \mathbf{g}, \quad i = 1, 2, \dots, N. \quad (3.23c)$$

Eq.(3.23b) is exact and is mathematically identical to Eqs.(2.3) or (3.2). It is expected to be “better” because the use of refined basis vectors enables the fast f_o^m 's to asymptote to smaller values for $t \gg \tau(M)$.

When the residual amplitudes of the f_o^m 's become sufficiently small in comparison to some user-specified threshold, their contributions to Eq.(3.23b) may be dropped to yield the leading-order CSP-derived simplified model:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g} \approx \sum_{J=M+1}^N \mathbf{a}_J^o(M) f_o^J, \quad t \gg \tau(M). \quad (3.24)$$

The initial condition for the simplified model must satisfy:

$$f_o^m = \mathbf{b}_o^m(M) \bullet \mathbf{g} \approx 0, \quad m = 1, 2, \dots, M. \quad (3.25)$$

When computing for the numerical solution using the exact formulation, Eqs.(3.23), the mode amplitudes f_o^i 's are most easily evaluated using Eq.(3.23c). However, as the amplitudes of the fast modes decay and become small, the values of the small f_o^m 's so evaluated are likely to be very inaccurate because of possible round-off errors. Fortunately, Eq.(3.17a) provides an alternative route to evaluate them when they are near exhaustion. Applying conventional singular perturbation techniques to Eq.(3.17a), the following analytical approximation is straightforwardly obtained:

$$f_o^m \approx f_{o,asym}^m \equiv f_{o,\infty}^m(M) + \sum_{n=1}^M \tau_n^m(M) \frac{df_{o,\infty}^n(M)}{dt} + O(\varepsilon(M)^3), \quad (3.26)$$

which is valid for $t \gg \tau(M)$. Theoretically, $f_{o,asym}^m$, the particular solution of Eq.(3.17a), is of order $O(\varepsilon(M))$. The two-term representation given above is accurate to order $O(\varepsilon(M)^3)$. Thus, a more accurate CSP-derived simplified model than Eq.(3.24) is obtained by using Eq.(3.26) in Eq.(3.23b):

$$\frac{d\mathbf{y}}{dt} = \mathbf{g} \approx \sum_{m=1}^M \mathbf{a}_m^o f_{o,asym}^m + \sum_{J=M+1}^N \mathbf{a}_J^o(M) f_o^J, \quad t \gg \tau(M). \quad (3.27)$$

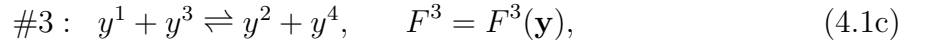
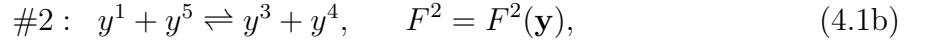
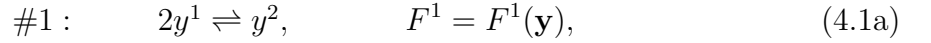
The accuracy of the approximate \mathbf{y} so generated is $O(\varepsilon(M)^3)$. It can be shown that Eqs.(3.25) are approximate *integrals of motion* of Eq.(3.27). Computationally, the time

derivatives needed in the two-term representation of $f_{o,asym}^m$ can be approximately evaluated (*e.g.* by the use of finite differences), and the value of $f_{o,asym}^m$ so computed can be used to assess the accuracy of the CSP model. We have also experimented with the inclusion of the homogeneous solution of Eq.(3.17a) in $f_{o,asym}^m$ and obtained significant improvement in accuracy.

The idea of refining the fast basis vectors was first pointed out in reference [2]. Additional expositions on CSP can be found in references [3], [4] and [5]. An example is worked out in this paper using both the conventional method and CSP in §4 and §5. The derivation of the specific refinement algorithm presented above (Eqs.(3.21)) and other details are beyond the scope of the present paper and will be reported later in a separate paper.

4. The Conventional Method at Work

The following hypothetical chemical reaction system is used as a vehicle for our discussions:



where the reaction rates satisfy the Law of Mass Action:

$$F^1 = k_{1f}y^1y^1 - k_{1b}y^2, \quad (4.2a)$$

$$F^2 = k_{2f}y^1y^5 - k_{2b}y^3y^4, \quad (4.2b)$$

$$F^3 = k_{3f}y^1y^3 - k_{3b}y^2y^4, \quad (4.2c)$$

and k_{rf} and k_{rb} are the forward and backward reaction rates of the r^{th} reaction, respectively. A hypothetical system is used here to more starkly highlight the role of experience and intuition.

The governing equations of the above reaction system are:

$$\frac{dy^1}{dt} = -2F^1 - F^2 - F^3, \quad (4.3a)$$

$$\frac{dy^2}{dt} = F^1 + F^3, \quad (4.3b)$$

$$\frac{dy^3}{dt} = F^2 - F^3, \quad (4.3c)$$

$$\frac{dy^4}{dt} = F^2 + F^3, \quad (4.3d)$$

$$\frac{dy^5}{dt} = -F^2, \quad (4.3e)$$

A conventional analysis would proceed as follows [7], [8]:

- (i) The collection of elementary reactions (Eqs.(4.1)) is examined and found to involve only two atomic species. Let C_1 and C_2 represent the total amount of each atomic species:

$$C_1 \equiv y^1 + 2y^2 + y^3, \quad C_2 \equiv y^3 + y^4 + 2y^5. \quad (4.4)$$

Using Eqs.(4.3) and (4.4), we can easily show that:

$$\frac{dC_1}{dt} = 0, \quad \frac{dC_2}{dt} = 0. \quad (4.5)$$

Eqs.(4.5) indicate that the reaction system respects the physical law of conservation of atomic species.

- (ii) The rate constants and the initial conditions are examined and species y^1 and y^4 are declared radicals (based on experience and/or intuition). The assumptions that $\frac{dy^1}{dt}$ and $\frac{dy^4}{dt}$ are small in some sense are then made. Applying the steady-state approximation to y^1 , we have:

$$g^1(\mathbf{y}) = -2F^1 - F^2 - F^3 \approx 0. \quad (4.6)$$

- (iii) Applying the steady-state approximation to y^4 , we have:

$$g^4(\mathbf{y}) = F^2 + F^3 \approx 0. \quad (4.7)$$

- (iv) Substituting Eqs.(4.6) and (4.7) into Eqs.(4.3), we obtain:

$$\frac{dy^1}{dt} \approx 0, \quad (\text{see Eq.(4.12a) below}) \quad (4.8a)$$

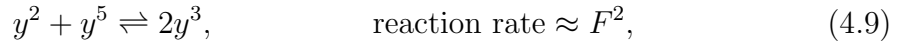
$$\frac{dy^2}{dt} \approx -F^2, \quad (4.8b)$$

$$\frac{dy^3}{dt} \approx 2F^2, \quad (4.8c)$$

$$\frac{dy^4}{dt} \approx 0, \quad (\text{see Eq.(4.12b) below}) \quad (4.8d)$$

$$\frac{dy^5}{dt} \approx -F^2, \quad (4.8e)$$

Eqs.(4.8) represent the following approximate one-step chemical reaction system for large t :



where F^2 depends on y^1 and y^4 in addition to y^3 and y^5 . It is interesting to note that the stoichiometric coefficients appearing in Eq.(4.9) are all rational numbers or integers; this is characteristic of simplified kinetics models derived by the use of steady-state approximations.

- (v) It is well known that Eqs.(4.8a) and (4.8d) do *not* mean y^1 and y^4 are constants; they merely indicate that the net time rate of change of y^1 and y^4 are small in comparison to their forward and reverse contributions. To proceed further, Eqs.(4.6) and (4.7) are solved algebraically for y^1 and y^4 in terms of the other species, y^2 , y^3 and y^5 . In general, this step is not routine, and frequently additional assumptions and restrictions are needed [8] simply to overcome the algebraic difficulties here. For the present problem, straightforward algebraic manipulations yield:

$$y^1 \approx \sqrt{\frac{k_{1b}y^2}{k_{1f}}}, \quad (4.10a)$$

$$y^4 \approx \left(\frac{k_{2f}y^5 + k_{3f}y^3}{k_{2b}y^3 + k_{3b}y^2} \right) \sqrt{\frac{k_{1b}y^2}{k_{1f}}}. \quad (4.10b)$$

Using Eqs.(4.10) in Eq.(4.2b), we obtain F^2 as a function of y^2 , y^3 and y^5 only:

$$F^2 \approx \frac{\sqrt{\frac{k_{1b}y^2}{k_{1f}}}}{k_{2b}y^3 + k_{3b}y^2} (k_{2f}k_{3b}y^2y^5 - k_{3f}k_{2b}y^3y^3) . \quad (4.11)$$

Eq.(4.11) can now be used with Eqs.(4.8b,c,e) to compute for y^2 , y^3 and y^5 ; the values of y^1 and y^4 are then computed from Eqs.(4.10). It is possible to algebraically manipulate Eqs.(4.4) and (4.10) to express all elements of the \mathbf{y} vector in terms of any single species such as y^2 (plus C_1 and C_2) so that F^2 can be expressed as a function of y^2 only. Eq.(4.8b) then becomes a single equation for a single unknown.

The above results can be alternatively presented as follows. Taking the logarithmic time derivatives of Eqs.(4.10) and then solving for $\frac{dy^1}{dt}$ and $\frac{dy^4}{dt}$ with the help of Eqs.(4.8b,c,e), we have:

$$\frac{dy^1}{dt} \approx \frac{y^1}{2y^2} \frac{dy^2}{dt} \approx - \left\{ \frac{y^1}{2y^2} \right\} F^2 \equiv -c_1 F^2, \quad (4.12a)$$

$$\begin{aligned} \frac{dy^4}{dt} &\approx - \left\{ y^4 \left(\frac{k_{2f} - 2k_{3f}}{k_{2f}y^5 + k_{3f}y^3} + \frac{2k_{2b} - k_{3b}}{k_{2b}y^3 + k_{3b}y^2} + \frac{1}{2y^2} \right) \right\} F^2 \\ &\equiv -c_2 F^2. \end{aligned} \quad (4.12b)$$

Eqs.(4.12) can be used to replace Eqs.(4.8a) and (4.8d). Hence, the one-step chemical reaction system represented by Eqs.(4.9) and (4.10) can be alternatively represented by:

$$c_1 y^1 + y^2 + c_2 y^4 + y^5 \rightleftharpoons 2y^3, \quad (4.13a)$$

$$\text{reaction rate} \approx F^2, \quad (4.13b)$$

showing more clearly that y^1 and y^4 are involved in the stoichiometry of this one-step reaction. It is now easy to show that the above approximate results are “slightly” inconsistent with Eqs.(4.5). Differentiating Eq.(4.4) with respect to time and using Eqs.(4.12) and (4.8b,c,e), we obtain:

$$\frac{dC_1}{dt} \approx -c_1 F^2 \neq 0, \quad \frac{dC_2}{dt} \approx -c_2 F^2 \neq 0, \quad (4.14)$$

i.e. this approximate model does not exactly conserve the total amount of atomic species. This “error” can be explained as follows: the steady-state approximation correctly gave the leading approximation to the stoichiometric coefficients of the one-step reaction model as (0, -1, 2, 0, -1), but provided only the small corrections (c_1 and c_2) for the two zeros. To be fully consistent, the other three stoichiometric coefficients also need small corrections (See Eq.(4.20) later). This minor inconsistency does not appear to be widely recognized. Formally, the simplified model derived using the steady-state approximation (Eqs.(4.9), (4.10)) is valid only when c_1 and c_2 as defined above are asymptotically small.

We shall re-analyze the same problem by retaining the steady-state approximation on y^1 but replacing the steady-state approximation on y^4 by the partial-equilibrium approximation on F^1 . We shall show that using the more careful procedure [1] normally reserved for partial-equilibrium approximations, the inconsistency mentioned above can be avoided.

The steps after (ii) are:

- (vi) The steady-state approximation on y^1 again yields Eq.(4.6). Applying the partial equilibrium approximation to F^1 , we have:

$$F^1(\mathbf{y}) = k_{1f}y^1y^1 - k_{1b}y^2 \approx 0. \quad (4.15)$$

Thus Eqs.(4.7) and (4.10) remain valid. Consequently, the starting points of this and the previous analysis are identical.

- (vii) We now rewrite Eqs.(4.3) in the following form:

$$\frac{dy^1}{dt} = g^1, \quad (4.16a)$$

$$\frac{dy^2}{dt} = -g^1 - F^1 - F^2, \quad (4.16b)$$

$$\frac{dy^3}{dt} = g^1 + 2F^1 + 2F^2, \quad (4.16c)$$

$$\frac{dy^4}{dt} = -g^1 - 2F^1, \quad (4.16d)$$

$$\frac{dy^5}{dt} = -F^2. \quad (4.16e)$$

Instead of step (iv) which would have neglected g^1 and F^1 , we algebraically eliminate them:

$$\frac{1}{2} \frac{dy^1}{dt} + \frac{dy^2}{dt} - \frac{1}{2} \frac{dy^4}{dt} = -F^2, \quad (4.17a)$$

$$\frac{dy^3}{dt} + \frac{dy^4}{dt} = 2F^2, \quad (4.17b)$$

$$\frac{dy^5}{dt} = -F^2. \quad (4.17c)$$

No approximation has so far been applied in arriving at Eqs.(4.17). The above three exact differential equations are to be supplemented by the two approximate algebraic relations, Eqs.(4.10) or Eqs.(4.6) and (4.7) or (4.15).

- (viii) Eqs.(4.10) can be used to directly eliminate y^1 and y^4 from Eqs.(4.17). Alternatively, we can differentiate Eqs.(4.6) and (4.7) with respect to time and eliminate the time derivatives of y^1 and y^4 from Eqs.(4.17). Using the latter approach, we obtain, after considerable algebra:

$$\frac{dy^1}{dt} \approx -c_1(1 - c_3)F^2, \quad (4.18a)$$

$$\frac{dy^2}{dt} \approx -(1 - c_3)F^2, \quad (4.18b)$$

$$\frac{dy^3}{dt} \approx (2 + c_1)(1 - c_3)F^2, \quad (4.18c)$$

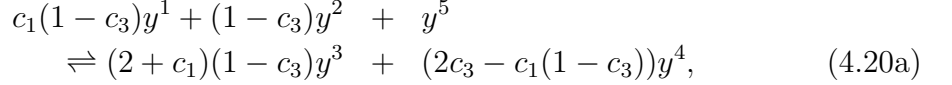
$$\frac{dy^4}{dt} \approx (2c_3 - c_1(1 - c_3))F^2, \quad (4.18d)$$

$$\frac{dy^5}{dt} \approx -F^2, \quad (4.18e)$$

where

$$c_3 \equiv \frac{e_2 - 2e_4 + e_5 + c_1(e_1 + e_3 - e_4)}{(2 + c_1)(e_3 - e_4) + c_1e_1 + e_2}, \quad e_i \equiv \frac{\partial g^4}{\partial y^i}. \quad (4.19)$$

Eqs.(4.18) represent the following approximate one-step chemical reaction system for large t :



$$\text{reaction rate} \approx F^2 = k_{2f}y^1y^5 - k_{2b}y^3y^4. \quad (4.20b)$$

Eq.(4.20a) is seen to be different from both Eq.(4.9) and Eq.(4.13a). It can be shown that when c_1 and c_3 are small in comparison to unity, c_1, c_2 and c_3 are approximately related by:

$$c_3 \equiv \frac{c_1 - c_2}{2}, \quad c_1 \ll 1, \quad c_2 \ll 1. \quad (4.21)$$

Eq.(4.20a) becomes:

$$c_1y^1 + (1 - \frac{c_1}{2} + \frac{c_2}{2})y^2 + c_2y^4 + y^5 \rightleftharpoons (2 + c_2)y^3. \quad (4.22)$$

When both c_1 and c_2 are small, Eqs.(4.9), (4.13a) and (4.22) are competitive approximate reaction models for the same problem, but Eq.(4.22) is clearly the superior model because it alone is consistent with the conservation of atomic species, Eqs.(4.5). When neither c_1 nor c_2 is small, Eq.(4.20a) is the only correct approximate one-step reaction model fully consistent with Eqs.(4.5). In contrast to Eq.(4.9), the stoichiometric coefficients in Eq.(4.20a) and (4.22) are mostly irrational numbers.

In the existing literature [1], a distinction is usually made between the steady-state approximation and the partial-equilibrium approximation. According to the above presentation, partial-equilibrium approximation appears to be the more general procedure: it includes the steady-state approximation as a special case when the approximation of total neglect of the time derivatives of the identified radicals in Eqs.(4.17) can be justified.

5. The CSP Method at Work

We shall work out the same examples with CSP.

1. The eigen-vectors of \mathbf{J} at $t = 0$ can be used as trial basis vectors for $t \geq 0$: $\mathbf{a}_i(t) = \boldsymbol{\alpha}_i(t = 0)$ and $\mathbf{b}^i(t) = \boldsymbol{\beta}^i(t = 0)$. With this choice of constant trial basis vectors, we have $\Lambda_k^i = \Phi_k^i$ which is diagonal only at $t = 0$. In general, the refined basis vectors are not constant and will evolve with time.
2. The CSP computation commences with $M = 0$ at $t = 0$, and any standard (non-stiff) ODE solver can be used. M is incremented whenever the currently fastest active mode in the slow group falls below some user-specified threshold: the mode is promoted into the fast group and declared exhausted at the same time. The integration of Eq.(3.24) or Eq.(3.27) now allows a larger integration time step to be taken.

3. If the refined \mathbf{b}_o^1 is found to be approximately proportional to $[1, 0, 0, 0, 0]$ when $t \gg \tau(1)$, then y^1 is a radical which reaches steady-state first (because $f_o^1 = \mathbf{b}_o^1 \bullet \mathbf{g} \approx g^1(\mathbf{y})$; see Eq.(4.6)). If $f_o^2 \approx (\mathbf{b}_o^2 \bullet \mathbf{S}_1)F^1(\mathbf{y})$ when $t \gg \tau(2)$, then elementary reaction #1 is very fast and reaches partial-equilibrium next (see Eq.(4.15)). If, instead, $f_o^2 \approx (\mathbf{b}_o^1 \bullet \mathbf{S}_1)F^1(\mathbf{y}) + (\mathbf{b}_o^2 \bullet \mathbf{S}_3)F^3(\mathbf{y})$ when $t \gg \tau(2)$, then elementary reactions #1 and #3 quickly reach partial-equilibrium with each other next. Whatever \mathbf{b}_o^1 and \mathbf{b}_o^2 turn out to be, some physically meaningful interpretations for $f_o^1 \approx 0$ and $f_o^2 \approx 0$ may be obtained.
4. When $M = 2$, the effective stoichiometric coefficients of the one-step (see below) simplified kinetics model represented by Eq.(3.24) are given by the elements of \mathbf{a}_3^o , and the corresponding effective reaction rate is $f_o^3 = \mathbf{b}_o^3 \bullet \mathbf{g}$.
5. It can easily be established computationally that the rank of the matrix \mathbf{J} is 3, indicating that there are two zero eigen-values. Thus reaction modes #4 and #5 have identically zero reaction rates, and thus represent some physically interesting conservation laws. Because these modes are never active, the maximum value for M for this problem is 2, at which point the reaction system has an one-step model. It can easily be shown that C_1 and C_2 always satisfy Eqs.(4.5).

What if we were interested in the time interval $\tau(2) \gg t \gg \tau(1)$? The CSP data generated in the time interval with $M = 1$ readily provides the corresponding two-step reaction model. If in the same time interval, it is found numerically that the contribution of f_o^3 (for each component of \mathbf{g}) is below some user-specified accuracy threshold in comparison to that of f_o^2 , then f_o^3 is dormant (*i.e.* reaction mode #2 is not important) and can be neglected to yield a one-step model.

If, at any time, the value of $f_{o,asym}^m$ of one of the M exhausted fast modes rises above the user-specified threshold, that mode can simply be declared active again. If the value of one of the slow eigen-values of \mathbf{J} is positive, then that mode in question is potentially explosive. Interesting information such as ignition delays and chain-branching mechanisms can readily be derived from the CSP data of explosive modes.

In the language of CSP, the conventional method presented in §4 relied on the experience and intuition of the investigator in the sample problem area in certain ranges of initial and operating conditions to choose the following set of trial basis vectors:

$$\mathbf{a}_1 = [1, -1, 1, -1, 0]^T, \quad \mathbf{b}^1 = [1, 0, 0, 0, 0], \quad (5.1a)$$

$$\mathbf{a}_2 = [0, -1, 2, -2, 0]^T, \quad \mathbf{b}^2 = [0, 1, 1, 0, 1], \quad (5.1b)$$

$$\mathbf{a}_3 = [0, 1, -2, 0, 1]^T, \quad \mathbf{b}^3 = [0, 0, 0, 0, 1]. \quad (5.1c)$$

The one-step model given by Eq.(4.9) can be obtained by CSP using the trial set without refinement, while that given by Eqs.(4.20) can be obtained by using the refined set.

6. Discussion

The essential feature of the CSP method is that it is completely algorithmic and programmable. Unlike the conventional method which depends critically on the investigator's experience and intuition in identifying and applying the appropriate approximations and on the success of the subsequent problem-specific algebraic manipulations (*e.g.* to solve for the concentrations of the radicals from highly non-linear algebraic equations), CSP recasts all chemical kinetics problems into a universal standard form. The specifics of the problem are completely contained in the single N by N matrix \mathbf{J} from which all further

results are derived. The reaction system is decomposed into N reaction modes divided into a fast and a slow group using basis vectors refined from an appropriately chosen trial set. With the help of the refined basis vectors, the reaction modes can be classified at any time as being either *exhausted*, *active* or *dormant*. Exhausted reaction modes are fast reaction modes which were once dominant but are now sufficiently spent to be ignored, active reaction modes are slow reaction modes which are mainly responsible for the currently observed activities, and dormant reaction modes are the remaining slow reaction modes which are not contributing significantly. Conventional asymptotic methodology is used to analyze the long time behavior of the f_o^m 's in the fast group, taking advantage of the fact that the relevant equation is in a universal and particularly simple form (Eq.(3.17a)) to obtain the leading approximations.

The left and right eigen-vectors of \mathbf{J} at $t = 0$ are always available to be the initial trial basis vectors for $t \geq 0$. From the programming point of view, *it is straightforward to use the freshly computed set of refined basis vectors at the end of every integration time-step to be the new trial set of constant basis vectors for the next time step*. Recent numerical results have shown that updating of \mathbf{a}_i and \mathbf{b}^i with Eqs.(3.21a,b,c,d) at every time step improves the accuracy of Eqs.(3.24) or (3.27) by nearly another order of $\varepsilon(M)$.

The refined mode amplitude f_o^i is given by:

$$f_o^i = \sum_{r=1}^R B_{o,r}^i(M) F^r(\mathbf{y}), \quad i = 1, 2, \dots, N, \quad (6.1)$$

where

$$B_{o,r}^i(M) \equiv \mathbf{b}_o^i(M) \bullet \mathbf{S}_r, \quad i = 1, 2, \dots, N, \quad r = 1, 2, \dots, R. \quad (6.2)$$

Information on the degree of participation of the r^{th} elementary reaction (and its rate constants) toward the i^{th} mode amplitude can be obtained from Eq.(6.1). The relevance of elementary reactions not included in the original calculation can also be similarly assessed. For the exhausted modes, we have

$$f_o^m = \sum_{r=1}^R B_{o,r}^m(M) F^r(\mathbf{y}) \approx 0, \quad m = 1, 2, \dots, M. \quad (6.3)$$

These are the CSP-derived approximate algebraic relations between the state variables; *i.e.* they are the equations of state of the radicals. For the active modes, the effective stoichiometry of the I^{th} mode is \mathbf{a}_I^o , and its effective reaction rate is f_o^I . These results together is the CSP-derived simplified kinetics model.

The small contribution to \mathbf{g} of the exhausted fast modes can either be ignored (see Eq.(3.24)) or be included with good accuracy (see Eq.(3.26)). Non-stiff integration algorithms can then be used, and the integration time step Δt can be increased each time a fast mode is declared exhausted. Exhausted modes can be declared active again when the user-specified accuracy threshold is breached. The elementary reactions which do not participate significantly in the exhausted and active modes in the time interval of interest can be identified by examining Eq.(6.1); the “reduced mechanism” of the reaction system can then be easily determined [5] by their removal.

The role of CSP in chemical kinetics modelling is clear. For sufficiently simple problems for which the identities of the appropriate radicals and the fast reactions are well known, and the resulting algebraic equations are amendable to the needed manipulations, the conventional analysis is the method of choice because the results are analytical. The minor defect of the steady-state approximation pointed out earlier can easily be remedied.

It should be noted that for sufficiently simple problems the CSP algorithm can be carried out analytically if so desired. For sufficiently large and complex problems for which little is known and few guidelines exist, numerical CSP data can be used to deduce most of the information normally expected from a conventional asymptotic analysis. After using CSP to identify the available simplifications in the time interval of interest, one may follow up with conventional asymptotic analyses to obtain selected additional analytical insights. It is interesting to note that in our sample calculations [5], most of the exhausted reaction modes can indeed be cleanly associated with either the steady-state approximation for radicals or the partial-equilibrium approximation for fast elementary reactions, or both. However, there are also some ambiguous cases when neither seems applicable.

From the point of view of asymptotics, the CSP method removes the need for non-dimensionalization of variables, order of magnitude estimates, identification of small parameters, consistency checks for assumed forms of expansions, and the various labor-intensive and problem-specific manipulations in the derivation of simplified models for boundary-layer type non-linear O.D.E. problems. The myriad asymptotic procedures have been formalized into a straightforward and programmable algorithm. For linear problems, the algorithm reduces to standard eigen-analysis. For non-linear problems of the boundary layer type (*i.e.* when all the fast $\lambda(i)$'s are essentially real and negative), the algorithm "derives" the simplified inner and outer (*i.e.* fast and slow) equations, explicitly accounting for the leading order effects of the "rotation" of the local fast subspace (spanned by the M fast basis vectors) due to the non-linearities of \mathbf{g} .

The CSP user supplies the database of elementary reactions and their rates, specifies the thresholds of accuracy desired for each unknown in the simplified kinetics model, the time scale(s) of interest, τ^* (the desired time resolution of the numerical printouts), and the initial conditions. The main raw data generated by CSP are the refined basis vectors $\mathbf{a}_i^o(M)$'s, $\mathbf{b}_o^i(M)$'s, the time scales $\tau(i)$'s, the number of exhausted reaction modes M , and the number of active and dormant reaction modes (including the identification of conservation laws, if any), all as a function of time. It is a relatively simple matter to deduce from the above raw data most of the information normally expected from a conventional analysis of a reaction system. If the problem under study is insufficiently stiff or if the user-specified threshold of accuracy is too stringent, the contributions of spent fast reaction modes would simply refuse to fall below the threshold.

The CSP algorithm described in this paper has been programmed (CSP8) and tested, and the results have been excellent even when the separation of the fast and slow time scales is only moderate. It is straightforward to include the energy equation by assigning one of the elements of the \mathbf{y} vector to be temperature. However, if spatial diffusive terms are included on the right-hand side of Eq.(2.2) making it into a system of partial differential equations (PDE), many new theoretical issues arise. While discretized PDE systems can be treated as finite dimensional ODE systems by the present CSP algorithm, the formal generalization of CSP concepts to infinite dimensional PDE systems is a significant step and is being explored at the present time.

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