

ME 451C  
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Week # 8

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**Abstract**

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## 1 Toy Problems

Consider the following the slightly modified toy problem (it makes no chemistry sense) with  $N = 2$  and  $R = 3$  that was your homework assignment last week:

$$\frac{DX_1}{Dt} = W_1 + W_2, \quad (1)$$

$$\frac{DX_2}{Dt} = -2W_1 + W_3, \quad (2)$$

$$W_1 = \frac{X_2^2 - X_1}{\epsilon}, \quad W_2 = X_2(X_1, X_2), \quad W_3 = W_3(X_1, X_2), \quad (3)$$

where  $W_2(X_1, X_2)$  and  $W_3(X_1, X_2)$  are some differentiable functions of their arguments and are independent of  $\epsilon$ . The initial conditions are:

$$X_1(0) = c_1, \quad X_2(0) = c_2. \quad (4)$$

It is known that  $\epsilon$  is a very small positive number, and  $c_1$  and  $c_2$  are two (arbitrary) positive numbers. Specifically,  $c_1 \neq c_2^2$ . We are interested in the solution for  $t = O(1)$  in the limit of very small  $\epsilon > 0$ .

It is easily verified that this toy problem has no conserved scalars ( $A = 0$ ). In order to utilize the QSSA approximation, we would have to choose either  $X_1$  or  $X_2$  to be a “radical.” And it is not clear which should have the honor. But in the small  $\epsilon$  limit it is clear that reaction #1 is the fast reaction. So we will use the PE approximation.

In the small  $\epsilon$  limit, we rewrite  $W_1$  to obtain:

$$X_1 = X_2^2 - \epsilon W_1 = X_2^2 + O(\epsilon) \quad (5)$$

where the second equality merely assumes that  $W_1$  is finite (*i.e.*  $O(1)$ ) in the time domain of interest ( $t = O(1)$ ). This algebraic equation relating  $X_1$  and  $X_2$  allows us to conclude that  $X_1$  can be approximated by  $X_2^2$ —with error  $O(\epsilon)$  in the small  $\epsilon$  limit.

We can use Eq.(5) to approximately evaluate  $W_2(X_1, X_2)$  as  $W_2(X_2^2, X_2)$ , and similarly to approximately evaluate  $W_3(X_1, X_2)$  as  $W_3(X_2^2, X_2)$ . But we can't use Eq.(5) to approximately evaluate  $W_1$ . The reason is, of course, obvious. Eq.(5) was derived by assuming  $W_1$  to be some unknown  $O(1)$  thing. If you use Eq.(5) to evaluate  $W_1$ , you are going backwards, and you can only recover what you assumed—that  $W_1$  is some unknown  $O(1)$  thing.

This is the reason the PE procedure requires that you manipulate the original ODEs so that  $W_1$  does not appear. In this toy problem, inspection of Eq.(1) and Eq.(2) tells us how to achieve this goal:

$$\frac{D}{Dt}(2X_1 + X_2) = 2W_2(X_1, X_2) + W_3(X_1, X_2). \quad (6)$$

This equation is exact. It can replace either of the two original ODEs, Eq.(1) or Eq.(2).

## 1.1 The rapid initial transient

At the initial instant, our initial condition is supposed to be arbitrary ( $c_1$  is not anywhere close to  $c_2^2$ ). So there is no question that  $W_1$  is a huge number in the beginning, and by comparison  $W_2$  and  $W_3$  are minor players. Inspection of the two ODEs in Eq.(1) and Eq.(2) tells us that both  $X_1$  and  $X_2$  will have a rapid transient, while inspection of Eq.(6) tells us that  $(2X_1 + X_2)$  hardly changes at all in this brief transient period. In other words, during the brief transient period,  $(2X_1 + X_2)$  behaves approximately as a conserved scalar. So, in this brief transient period  $t = O(\epsilon)$ , we have:

$$2X_1 + X_2 = 2c_1 + c_2 + O(\epsilon). \quad (7)$$

At the tail end of this brief period, we expect  $W_1$  to rapidly decay to something (*i.e.*  $O(1)$ ). Of course, at the tail end of the initial transient, we expect  $X_1 = X_2^2$  to be a good approximation. Using it in Eq.(7), we have the following equation

$$2X_2^2 + X_2 = 2c_1 + c_2 + O(\epsilon) \quad (\text{tail end of initial transient}) \quad (8)$$

which must be satisfied by the value of  $X_2$  near the tail end of the rapid transient. Discarding the negative root, we have:

$$X_2 = \frac{-1 + \sqrt{1 + 8(2c_1 + c_2)}}{4} \quad (\text{tail end of initial transient}). \quad (9)$$

This shall serve as the “initial condition” for the following slow evolutionary period.

## 1.2 The slow evolution there after

After the initial rapid transient, the system no longer evolve with time “rapidly.” The governing equations are Eq.(6)—which is exact and is independent of  $\epsilon$ , and Eq.(5), which is approximate with error  $O(\epsilon)$ .

Using Eq.(5) to get rid of  $X_1$  in Eq.(6), we obtain:

$$\frac{D}{Dt}(2X_2^2 + X_2) = 2W_2(X_2^2, X_2) + W_3(X_2^2, X_2) + O(\epsilon) \quad (10)$$

or

$$\frac{DX_2}{Dt} = \frac{2W_2(X_2^2, X_2) + W_3(X_2^2, X_2)}{1 + 4X_2} + O(\epsilon). \quad (11)$$

The initial condition for  $X_2$  is given by Eq.(9)—which is independent of  $\epsilon$ . Once  $X_2$  is found,  $X_1$  in the slow evolutionary period is immediately given by Eq.(5).

## 2 Comments

When we have a “tractable” problem which contains a few (asymptotically) small parameters, the above analysis is standard fare in the *singular perturbation* community. Professor Milton Van Dyke of Stanford University is one of the pioneers of this methodology [1] (he called it *Method of Matched Asymptotic Expansions*).

For this toy problem, the mathematical validity of the approach should be convincing. It is a relatively simple matter to verify the

answers by brute force numerical simulation. It should be clear that the approach can be used for any reasonable  $W_2$  and  $W_3$  one may dream up.

How about the case when  $W_2$  and/or  $W_3$  include diffusion terms?

### 3 Diffusion coupling

Suppose we have:

$$W_2 = w_2(X_1, X_2) + \nabla \cdot (D_{11} \nabla X_1), \quad (12)$$

$$W_3 = w_3(X_1, X_2) + \nabla \cdot (D_{22} \nabla X_2). \quad (13)$$

where  $w_2$  and  $w_3$  now represent the “slow” chemistry terms while the other terms represent diffusion. What happens in the small  $\epsilon$  limit to this PDE problem?

If  $w_3 = -2w_2$ , then it can readily be verified that in the absence of diffusion this chemistry problem has a true conserved scalar (which most probably represent the amount of some atomic element),  $2X_1 + X_2$ , which remains unchanged from its initial condition for all time. However, once diffusion is present, no unequivocal statement about  $2X_1 + X_2$  can now be made. So we immediately lose the simplifications usually available in the pure chemistry problems.

We can repeat the mathematical development in the previous sections, and find that the diffusion term is rather passive and accommodating. Obviously, Eq.(5) remains valid in the small  $\epsilon$  limit (away from initial transients and side boundaries). The PDE for  $X_2$  derived is:

$$\frac{DX_2}{Dt} = \frac{2w_2(X_2^2, X_2) + w_3(X_2^2, X_2) + \nabla \cdot (4X_2 D_{11} + D_{22}) \nabla X_2}{1 + 4X_2} + O(\epsilon). \quad (14)$$

Look at what happens to the diffusion term (it is no longer a divergence, and both  $D_{11}$  and  $D_{22}$  are involved)!

We just derived the theoretical conclusion that chemical reaction affects the diffusion of species. Does this conclusion make physical sense? When you think about it, of course it does. In the absence of chemical reaction, a species diffuses from here to there by bumping around, always keeping its identity during the trip. When the species can react, it can become some other species, and bump around with that identity, and eventually react to become its old identity again when it gets here. So its “effective” diffusion coefficient should depend

not only on its own diffusion coefficient but it should also depend on all the other diffusion coefficients when it was masquerading as some other species during the trip.

Most importantly, the following PDE for  $X_2$  would be incorrect:

$$\frac{DX_2}{Dt} = \frac{2w_2(X_2^2, X_2) + w_3(X_2^2, X_2)}{1 + 4X_2} + \nabla \cdot (D_{22}\nabla X_2) + O(\epsilon). \quad (15)$$

Unfortunately, many people do not realize this is wrong.

## 4 Some preliminaries and notations

We shall use  $\mathbf{x}, \mathbf{w}$  and  $\mathbf{d}$  to denote  $N$ -dimensional column vectors, representing the dependent variables, the chemistry term, and the diffusion term, respectively:

$$\mathbf{x} = \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix}, \quad \mathbf{w} = \begin{pmatrix} \mathcal{W}_1 \\ \mathcal{W}_2 \\ \vdots \\ \mathcal{W}_N \end{pmatrix} = \mathbf{w}(\mathbf{x}), \quad \mathbf{d} = \begin{pmatrix} \nabla \cdot \mathbf{j}_1^* \\ \nabla \cdot \mathbf{j}_2^* \\ \vdots \\ \nabla \cdot \mathbf{j}_N^* \end{pmatrix} \quad (16)$$

where the  $\mathbf{j}_n^*$ 's are diffusion fluxes. So the generic PDE we are dealing with can be written as follows:

$$\frac{D\mathbf{x}}{Dt} = \mathbf{w} + \mathbf{d}. \quad (17)$$

The question being addressed is: how to simplify the right hand side when  $\mathbf{w}(\mathbf{x})$  is very nonlinear, messy and contains lots of reactions, when you are interested only in some specific time interval (your choice). Without loss of generality, we assume that time  $t$  has been normalized so that our time interval of interest is  $t = O(1)$ .

Let's first derive a PDE for  $\mathbf{w}$ . Taking its substantial derivative, we obtain:

$$\frac{D\mathbf{w}}{Dt} = \mathbf{J} \cdot (\mathbf{w} + \mathbf{d}) \quad (18)$$

where

$$\mathbf{J} \equiv \frac{\partial \mathbf{w}}{\partial \mathbf{x}} \quad (19)$$

is the square  $N \times N$  Jacobian matrix.

## 4.1 Basis vectors

Let us choose a set of  $N$  linearly independent (column) basis vectors,  $\mathbf{a}_n(t)$ , to “span” the  $N$ -dimensional  $\mathbf{x}$  or  $\mathbf{w}$  (column vector) space. Your choice. The only request is that the “magnitude” of each of these vectors do not change much over time. Once they are chosen, we can find the set of  $N$  linearly independent row vectors,  $\mathbf{b}^n(t)$ , which by definition honors the following orthonormal relations:

$$\mathbf{b}^n \mathbf{a}_{n'} = \delta_{nn'}, \quad n, n' = 1, \dots, N, \quad (20)$$

where  $\delta_{nn'}$  is the Kronecker Delta. In addition, the following is an identity:

$$\sum_{n=1}^N \mathbf{a}_n \mathbf{b}^n = \mathbf{I} \quad (21)$$

where  $\mathbf{I}$  is the identity matrix.

## 4.2 Decomposing $\mathbf{w}$

Even though  $\mathbf{w}$  is usually a sum of  $R$  terms with  $R$  possibly larger than  $N$ , we can always decompose it into a sum of no more than  $N$  terms. This is straightforward linear algebra:

$$\mathbf{w} = \mathbf{I} \cdot \mathbf{w} = \sum_{n=1}^N \mathbf{a}_n \mathbf{b}^n \cdot \mathbf{w} = \sum_{n=1}^N \mathbf{a}_n f^n \quad (22)$$

where

$$f^n \equiv \mathbf{b}^n \cdot \mathbf{w}. \quad (23)$$

We may remember that  $\mathbf{w}$ , when formulated by a chemical kineticist, came with the stoichiometric vectors of the  $R$  elementary reactions playing the role of the  $\mathbf{a}_n$ 's here. Hence, we can “interpret” the  $\mathbf{a}_n$ 's we chose as “alternative” stoichiometric vectors. If we switched to our new alternative stoichiometric vectors, the corresponding reaction rates of these alternative reactions are the  $f^n$ 's. Since the magnitude of the  $\mathbf{a}_n(t)$ 's do not change much over time, the contribution by the  $n$ -th mode to  $\mathbf{w}$  is then controlled by the magnitude of  $f^n(t)$  as time evolves.

We can find the PDEs for the  $f^n$ 's. Taking the substantial derivative of the  $f^n$ 's, we obtain:

$$\frac{Df^n}{Dt} = \mathbf{b}^n \cdot \frac{D\mathbf{w}}{Dt} + \frac{D\mathbf{b}^n}{Dt} \cdot \mathbf{w} = \sum_{n'=1}^N \mathcal{L}_{n'}^n f^{n'} + \mathbf{b}^n \cdot \mathbf{J} \cdot \mathbf{d} \quad (24)$$

where

$$\mathcal{L}_{n'}^n \equiv \left( \frac{D\mathbf{b}^n}{Dt} + \mathbf{b}^n \cdot \mathbf{J} \right) \cdot \mathbf{a}_{n'}. \quad (25)$$

Note that this  $\mathcal{L}_{n'}^n$  matrix depends strongly on the choice of  $\mathbf{a}_n$ 's (and the associated  $\mathbf{b}^n$ 's) you made.

Now you can see what happens when you use the physically meaningful stoichiometric vectors for your  $\mathbf{a}_n$ 's (never mind that less than  $N$  of them are linearly independent). You have a messy (non-diagonal)  $\mathcal{L}_{n'}^n$  matrix, and all the reaction rates of your  $N$  modes are all messed up with each other—through the non-diagonal elements of  $\mathcal{L}_{n'}^n$ .

The physical dimension of  $\mathcal{L}_{n'}^n$  is reciprocal time. Hence, the physical dimension its eigenvalues is reciprocal time. What is the physical meaning of the reciprocal of the eigenvalues? They are the *time scales of the eigenmodes* of the problem (we are talking loosely). Remember, our time interval of interest is  $t = O(1)$ . Now, how do we decide whether a mode is fast or slow? The answer should be obvious: if the magnitude of its eigenvalue is large (in comparison to unity), the mode is fast; if the magnitude of its eigenvalue is small (in comparison to unity), the mode is dormant. Modes with  $O(1)$  eigenvalues are the modes controlling the behavior of the reacting system.

### 4.3 The ideal basis vectors

Since the choice of the basis vectors is up to you, the question is: what is the smartest choice? The answer is obvious. You want  $\mathcal{L}_{n'}^n$  to be diagonal. Speaking loosely again, a diagonal  $\mathcal{L}_{n'}^n$  is wonderful because each of the  $f^m$ 's are uncoupled from the others. Each has their own private time scale.

### 4.4 Consequences of non-ideal basis vectors

Suppose we somehow managed to get  $\mathcal{L}_{n'}^n$  more or less diagonal, and order the modes in descending magnitude of the diagonal elements. So mode #1 is the fastest, and mode #N is the slowest. Of course we should not be surprised (for chemistry problems) to find  $A$  “conservation” modes—they have zero  $f^n$ 's and are tied for last place.

An obvious approach is to choose  $\mathbf{a}_n$ 's to be the right eigenvectors of  $\mathbf{J}$  (thus the  $\mathbf{b}^n$ 's are the left eigenvectors of  $\mathbf{J}$ ). But this won't get us a diagonal  $\mathcal{L}_{n'}^n$ : we have  $D\mathbf{b}^n/Dt$  in  $\mathcal{L}_{n'}^n$  to ruin our diagonalization attempt. The obvious strategy should be obvious. Just ignore

this term as a first approximation [3]. But the true  $\mathcal{L}_{n'}^n$  which used (local—time dependent) eigenvectors of  $\mathbf{J}$  as basis vectors will have off-diagonal terms. We shall need to prove that it is negligible “as a first approximation.”

What does the off-diagonal terms do? Well, when there is no off-diagonal terms, each mode evolves with its private time scale,  $t_n = 1/|\text{Real } \mathcal{L}_n^n|$ . Each mode are independent of the other modes. But once there are off-diagonal terms in  $\mathcal{L}_{n'}^n$ , different modes are now coupled. The most important impact of this “mode mixing” is that the fast decaying modes no longer decays “rapidly” (with timescale  $t_n$ ) all the way to zero (as would be the case for diagonal  $\mathcal{L}_{n'}^n$ )—they decay rapidly (with their private time scale) for a while, then they evolve with slower time scales at some non-zero level. In order for us to obtain a legitimate “reduced chemistry model,” we need assurance that the fast modes when it evolves slowly at the non-zero level are negligible. In other words, we want to remove, as much as possible, the fast-slow mode mixing—which comes about by the  $\mathcal{L}_{n'}^n$  matrix not being “block-diagonal” enough.

Suppose we find that in the time interval of interest ( $t = O(1)$ ), the first  $M$  modes are considered fast—*i.e.*  $|t_m| \gg 1$ ,  $m = 1, \dots, M$ —and that they are decaying modes. So the  $f^m(t)$ 's will decay toward some non-zero values. Let's find these non-zero values. We rewrite Eq.(24) as follows:

$$\frac{Df^m}{Dt} = \sum_{m=1}^M \mathcal{L}_{m'}^m f^{m'} + \sum_{n'=M+1}^N \mathcal{L}_{n'}^m f^{n'} + \mathbf{b}^m \cdot \mathbf{J} \cdot \mathbf{d}, \quad m = 1, \dots, M. \quad (26)$$

We further rewrite it as follows:

$$\frac{Df^m}{Dt} = \sum_{m'=1}^M \mathcal{L}_{m'}^m (f^{m'} - f_{\infty}^{m'}), \quad m = 1, \dots, M. \quad (27)$$

where

$$f_{\infty}^m \equiv - \sum_{m'=1}^M \tau_{m'}^m \left( \sum_{n'=M+1}^N \mathcal{L}_{n'}^{m'} f^{n'} + \mathbf{b}^{m'} \cdot \mathbf{J} \cdot \mathbf{d} \right), \quad (28)$$

$$\tau_{m'}^m \equiv [\mathcal{L}_{m'}^{m'}]^{-1}. \quad (29)$$

It should be clear from Eq.(27) that the fast  $f^m(t)$ 's rapidly approach  $f_{\infty}^m(t)$ 's—which evolve slowly with time—as time marches on. Note that the  $M$  fast modes had been classified as fast *because* the  $\tau_{m'}^m$ ,

matrix is “small.” However, the magnitude of  $f_\infty^m$  is also controlled by the magnitude of the  $M \times (N - M)$  matrix elements in  $\mathcal{L}_n^{n'}$  above—they are responsible for the mixing of the slow modes in the fast modes. If we want the chemistry contribution to  $f_\infty^m$  to be small, we need to make this upper-right block of the  $\mathcal{L}_n^{n'}$  matrix as small as possible. Certainly we don’t want this block to be “big.”

It is important and interesting to note that  $f^m \approx f_\infty^m$  is now *not* an algebraic equation relating the  $X_n$ ’s—as was the case for the pure chemistry case. It now provides  $M$  PDEs (depending on the number of spatial dimensions involved). It will accommodate “side wall” boundary layers.

If you chose a set of non-ideal basis vectors, and the fast  $f_\infty^m(t)$ ’s turn out to be not small enough to be neglected, the sensible thing to do is to improve the set of fast  $\mathbf{b}^m$  vectors.

#### 4.5 Computing the decaying $f^{M+1}(t)$ ’s

The  $(M + 1)$ -th mode is the fastest active mode. Assuming it is a decaying mode, the computer can readily compute  $f^{M+1} = \mathbf{b}^{M+1} \cdot \mathbf{w}$  (where  $\mathbf{w}$  is the sum of the contributions from  $R$  elementary reactions) and monitor its rapid decay. However, it should be clear that this way of computing  $f^{M+1}$  necessarily involves a lot of near cancellations of big numbers. Consequently, when  $f^{M+1}$  is decayed to be “small” very severe cancellation errors is to be expected, and the accuracy of the resulting value of  $f^{M+1}$  is suspect. In fact, whenever  $f^{M+1}$  so computed is losing significant figures,  $f_\infty^{M+1}$  computed from Eq.(28) is the better way to go.

We are reminded that if we had chosen “good” basis vectors then the fast  $f_\infty^m$ ’s are expected to be “small.”

#### 4.6 Projection matrices

We can define a *fast subspace projection matrix*,  $\mathbf{Q}_{fast}$ , by:

$$\mathbf{Q}_{fast} \equiv \sum_{m=1}^M \mathbf{a}_m \mathbf{b}^m. \quad (30)$$

The *slow subspace projection matrix*,  $\mathbf{Q}_{slow}$ , is the complement of  $\mathbf{Q}_{fast}$  (see Eq.(21)):

$$\mathbf{Q}_{slow} \equiv \mathbf{I} - \mathbf{Q}_{fast}. \quad (31)$$

The original PDE for  $\mathbf{x}$ , Eq.(18), can now be rewritten as:

$$\frac{D\mathbf{x}}{Dt} = \mathbf{Q}_{fast} \cdot (\mathbf{w} + \mathbf{d}) + \mathbf{Q}_{slow} \cdot (\mathbf{w} + \mathbf{d}). \quad (32)$$

## 4.7 The fast subspace components

The first term on the right hand side can be rewritten as follows:

$$\mathbf{Q}_{fast} \cdot (\mathbf{w} + \mathbf{d}) = \sum_{m=1}^M \mathbf{a}_m (f^m + \mathbf{b}^m \cdot \mathbf{d}). \quad (33)$$

As time marches on, we expect  $f^m \rightarrow f_\infty^m$ . Using Eq.(28) for  $f_\infty^m$ , we obtain:

$$\begin{aligned} \mathbf{Q}_{fast} \cdot (\mathbf{w} + \mathbf{d}) = & - \sum_{m=1}^M \mathbf{a}_m \sum_{m'=1}^M \sum_{k=M+1}^N \tau_{m'}^m \mathcal{L}_k^{m'} f^k \\ & + \sum_{m=1}^M \mathbf{a}_m \left( \mathbf{b}^m - \sum_{m'=1}^M \tau_{m'}^m \mathbf{b}^{m'} \cdot \mathbf{J} \right) \cdot \mathbf{d}. \end{aligned} \quad (34)$$

Remember, the  $M$  modes are consider fast because the magnitude of the elements in the  $\tau_{m'}^m$  matrix (particularly the diagonal elements) are *small* in comparison to the time scales of your interest. In other words, we can *loosely* consider the  $\tau_{m'}^m$  matrix as our small parameter in a singular perturbation exercise.

## 4.8 Reduced chemistry model in the slow subspace

When the problem has no diffusion terms and the basis vectors used are “good,” we know  $\mathbf{Q}_{fast} \cdot (\mathbf{w})$  will be small as time marches on. If we decompose  $\mathbf{d}$  into its fast and slow subspace components, it can be shown that  $\mathbf{Q}_{fast} \cdot (\mathbf{d})$  has the same order of magnitude as  $\mathbf{Q}_{fast} \cdot (\mathbf{w})$  in terms of its dependence on  $\tau_{m'}^m$ . Thus we conclude that when  $\mathbf{Q}_{fast} \cdot (\mathbf{w} + \mathbf{d})$  is small enough to be neglected, the reduced chemistry PDE for  $\mathbf{x}$  (under this hypothesis) is:

$$\frac{D\mathbf{x}}{Dt} \approx \mathbf{Q}_{slow} \cdot (\mathbf{w} + \mathbf{d}). \quad (35)$$

Note that  $N$  ODEs are provided for the  $N$  dependent variables.

Most importantly, the investigator has the right (and responsibility) to decree the criterion to “neglect” a term.

The quality of this reduced chemistry model depends entirely on how “good” the chosen basis vectors are. So what we need is a (programmable) way to get a set of good basis vectors—use the computer instead of pen-and-paper if there is a choice.

## 5 Refinement of basis vectors

Instead of finding an algorithm to find the ideal basis vector, Lam [2, 4, 5] proposed a set of *refinement procedures* which is designed to improve the “goodness” of any trial basis vector set. In other words, an iteration procedure is provided so that each iteration will make the basis vector set better and better. The converged result is the ideal basis vector set.

The following are the CSP refinement procedures:

$$\mathbf{b}_o^m = \sum_{m'=1}^M \tau_{m'}^m \left( \frac{D\mathbf{b}^{m'}}{Dt} + \mathbf{b}^{m'} \cdot \mathbf{J} \right), \quad (36)$$

$$\mathbf{a}_m^o = \sum_{m'=1}^M \left( -\frac{D\mathbf{a}_{m'}}{Dt} + \mathbf{J} \cdot \mathbf{a}_{m'} \right) \tau_{om'}^{m'}. \quad (37)$$

It is clearly programmable on a computer. The refined basis vectors are marked by either a subscript or a superscript *o*. Eq.(36) is called *step one* refinement, and Eq.(37) is called *step two* refinement (and  $\tau_{om'}^{m'}$  is the  $\tau_{m'}^m$  matrix which uses  $\mathbf{a}_m$  and  $\mathbf{b}_o^m$  as basis vectors). Step one refinement reduces the magnitude of  $\mathbf{Q}_{fast} \cdot (\mathbf{w} + \mathbf{d})$  each time it is applied. One may begin with any arbitrary basis vector set (respecting the orthonormal condition), repeat these iterative steps as many times as patience permits. Step two refinement is a cosmetic one. Its role is to make the theory pretty (and guard against really dumb initial  $\mathbf{a}_m$  choices), but does not do much otherwise. It can be skipped (if the chosen  $\mathbf{a}_m$ 's are the actual stoichiometric vectors of the elementary reactions) without degrading the answers.

In the absence of diffusion ( $\mathbf{d} = 0$ ), it can be shown that:

$$\mathbf{b}_o^m \cdot \mathbf{w} = f^m - f_\infty^m \equiv f_o^m \quad (38)$$

and that  $|f_o^m| \ll |f_\infty^m|$  at the tail end of the  $m$ -th mode decay.<sup>1</sup> Most importantly, the  $\mathcal{L}_{n'}^m$  of the refined basis vectors has a smaller upper-right block than before, thus providing improved decoupling of the fast-slow modes. I shall provide some of the proofs in class, including what happens when  $\mathbf{d} \neq 0$ .<sup>2</sup>

## 5.1 What happens to the atomic elements?

For chemistry problems, there usually (nearly always for properly formulated problems) exist  $A$  linearly independent constant row vectors  $\alpha_a$  ( $a = 1, \dots, A$ ) such that:

$$\alpha_a \cdot \mathbf{w} = 0, \quad a = 1, \dots, A. \quad (40)$$

And  $\alpha_a \cdot \mathbf{x}$  are called conserved scalars—they represent the amount of atomic elements—when diffusion is absent. When diffusion is present, these  $A$  entities are no longer constants strictly determined by initial conditions. They diffuse according to the following PDE:

$$\frac{D(\alpha_a \cdot \mathbf{x})}{Dt} = \alpha_a \cdot \mathbf{d}, \quad a = 1, \dots, A. \quad (41)$$

These PDEs are not independent from Eq.(35). They are included in Eq.(35).

## 6 Remarks

The above procedures developed for reduced chemistry modeling is called *computational singular perturbation* (CSP) by Lam. The work of Maas and Pope [3] is called *Intrinsic Low-Dimensional Manifolds* (ILDM), and it uses the same theoretical reasonings. Instead of refinements, it simply advocates the use of eigenvectors of  $\mathbf{J}$  for the basis vectors *and* advocates the tabulation of the reduced-chemistry

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<sup>1</sup>In other words, a step one refinement makes the magnitude of the new  $f_\infty^m$  smaller than its old (pre-refined) value.

<sup>2</sup>It is easy to show that the governing equations for the  $f_o^m$ 's are:

$$\frac{Df_o^m}{Dt} = \sum_{m'=1}^M \mathcal{L}_{m'}^m(f_o^{m'}) - \sum_{m''=1}^M \tau_{m''}^{m'} \frac{Df_\infty^{m''}}{Dt}. \quad (39)$$

when  $\mathbf{d} = 0$ .

terms to be used as table-lookup files (hence, it is limited to low dimensional models). In essence, these methodologies recast the conventional paper and pencil singular perturbation analysis in terms of programmable algorithms and exploit the power of the computer. One does not need properly non-dimensionalized formulations, or identify asymptotic parameters, or worry about “matching” of solutions between different time epochs. The computer now carries the whole load—the simplifications of the modeling, and the generation of the numerical answers. With the help of the basis vectors, it is possible to extract detailed insights on the problem, in addition to information on sensitivity of the solutions to parameters.

It is useful to point out that the CSP methodology is applicable to any nonlinear (actually we need quasi-linearity) system of first order ODEs or parabolic PDEs. Its applicability is not restricted to chemical kinetics in diffusion problems. The main caveat is that none of the eigenvalues of  $\mathcal{L}_{n'}$  are purely imaginary with high frequencies. Such problems are usually called WKB problems. Turbulence belongs to this more difficult class of problems.

## 7 homework

1. For the toy problem ( $N = 2$ ) in §1, use the following as your trial set of fast basis vectors ( $M=1$ ):

$$\mathbf{a}_1 = \begin{vmatrix} \alpha_1 \\ \alpha_2 \end{vmatrix}, \quad \mathbf{b}^1 = [\beta_1, \beta_2] \quad (42)$$

Pick two random numbers for  $\alpha_1$  and  $\alpha_2$ , find  $\beta_1$  and  $\beta_2$ .

2. Do one CSP refinement (step one) for  $\mathbf{b}^1$ —get  $\mathbf{b}_o^1$ —to leading order in  $\epsilon$ .<sup>3</sup> Do one more CSP refinement (step two) for  $\mathbf{a}_1$ —get  $\mathbf{a}_1^o$  to leading order in  $\epsilon$ . Now use  $(\mathbf{a}_1^o, \mathbf{b}_o^1)$  as your chosen pair of fast basis vectors.
3. Find  $\mathbf{Q}_{fast}$ .
4. Find  $\mathbf{Q}_{slow}$ .
5. Find  $\mathbf{Q}_{fast} \cdot (\mathbf{w} + \mathbf{d})$ —use  $\mathbf{Q}_{fast}$  from #3, and keep all terms.
6. Find the reduced chemistry model (by neglecting  $\mathbf{Q}_{fast} \cdot (\mathbf{w} + \mathbf{d})$ —use  $\mathbf{Q}_{slow}$  from #4, and keep all terms

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<sup>3</sup>Note: Only  $W_1$  explicitly depends on  $\epsilon$ ;  $W_2$  and  $W_3$  do not.

7. Find  $(\mathbf{a}_2, \mathbf{b}^2)$  to accompany the above refined  $(\mathbf{a}_1^o, \mathbf{b}_o^1)$  to form a complete basis vector set for our 2-dimensional vector space. (I am not asking for a step two refinement. Just to get the complement of the fast subspace—it is the slow subspace).
8. Find  $f_\infty^1$  obtained from the refined set  $(\mathbf{a}_1, \mathbf{b}_o^1)$ , then compare it to  $f_\infty^1$  obtained from the un-refined set  $(\mathbf{a}_1, \mathbf{b}^1)$ . What happens in the small  $\epsilon$  limit in the slow evolutionary period (did refinement drop the magnitude of  $f_\infty^1$ )? Does the use of  $\mathbf{a}_1$  or  $\mathbf{a}_1^o$  make any difference? Ignore the diffusion term.
9. This is not directly related to the toy problem. Derive Eq.(39). It is totally straightforward.

## References

- [1] Milton D. van Dyke, “Perturbation Methods in Fluid Mechanics,” Parabolic Press, Stanford, CA, 1975.
- [2] S. H. Lam and D. A. Goussis, in *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, Chapter 10: “Conventional asymptotics and computational singular perturbations for simplified kinetics modeling,” *Lecture Notes in Physics 384*, M. Smooke, Ed., Springer-Verlag, 1991.
- [3] U. Maas and S. B. Pope, “Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space,” *Combust. Flame*, **88**, pp. 239-262, 1992.
- [4] “Using CSP to understand complex chemical kinetics,” *Combust. Sci. and Tech.*, **89**, pp. 375-404, 1993.
- [5] S. H. Lam and D. A. Goussis, “The CSP Method for Simplifying Kinetics,” *International Journal of Chemical Kinetics*, **26**, pp. 461-486, 1994.