A general analysis of approximate nonlinear lumping in chemical kinetics. II. Constrained lumping

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A general analysis of approximate constrained nonlinear lumping is presented for a chemical kinetic system described by an n-dimensional set of first order ordinary differential equations $d\mathbf{y}/dt=\mathbf{f}(\mathbf{y})$. There is a one-to-one relation between the differential equation system and the linear partial differential operator $A=\Sigma_{i=1}^{n} f_i(\mathbf{y})(\partial/\partial y_i)$. The algebraic method in nonlinear perturbation theory for lumping is extended to include constrained nonlinear lumping, in which the operator A is only transformed to a partially canonical form and some variables are left unlumped. A singular perturbation method is used to provide approximate analytical expressions for the solutions of the lumped variables. The resulting expressions can then be substituted into the equations describing the unlumped species, leading to a low dimensional system. The method is illustrated by application to a simple model describing the nonisothermal oxidation of hydrogen in a closed vessel. The results show that the method of constrained lumping leads to an accurate representation of the ignition features and maximum temperature rise given by the full model. The singular perturbation technique is proved to be only a special case of a general constrained lumping approach based on the algebraic method in nonlinear perturbation theory when the equations are linear in the deleted variables. Consequently the quasisteady-state approximation (QSSA) is the zeroth order approximation within the slow invariant manifold of the constrained approach. In cases where QSSA is not a good approximation, the first order correction generally provides significant improvement of the results.

I. INTRODUCTION

In a previous article, the authors presented a technique for the approximate unconstrained nonlinear lumping of an arbitrary chemical kinetic system, based on the application of the algebraic method in nonlinear perturbation theory.[1] Using this approach, the corresponding linear partial differential operator of the original kinetic equation system can be approximately transformed to a canonical form by a nonlinear transformation of the original variables to a new set of lumped variables. In this canonical form, the new lumped variables are partly separated, and a lower dimensional differential equation system for some lumped variables can be easily derived. The approximate solutions of other lumped variables, called purely fast variables, can be given explicitly by exponential functions in terms of the first set of lumped variables and time t. The concentration profiles of the original variables are available from the purely fast variables and the solution of the lumped differential equation system by the inverse transformation.

For unconstrained lumping, the choice of nonlinear transformation is not influenced by any previously imposed restrictions and is determined only by the method. However, in practice, dimension reduction is often not the only goal, and some restrictions on the choices of the lumping transformations are required. For example, we may require that some species, such as important products or initial reactants, remain unlumped in the system. In the present paper, we therefore extend previous work to provide a technique for approximate constrained nonlinear lumping, where the lumped system may still contain some of the original variables.

For constrained lumping, we wish to transform only some of the variables leaving others unlumped. We will show that by using the algebraic method in nonlinear perturbation theory, this goal can be achieved by approximately transforming the corresponding linear partial differential operator to a partially canonical form. For the lumped variables, the resultant operator is diagonal or Jordan. Moreover, the lumped variables are purely fast variables and their approximate analytical solutions can be obtained by the singular perturbation method. Combined with the inverse transformation, these solutions can then be employed to delete the corresponding original variables from the differential equations of the remaining unlumped variables leading to a lower dimensional system.

The paper is organized as follows: in Sec. II, we briefly summarize the algebraic method in nonlinear perturbation theory and its application to unconstrained lumping. In Sec. III, we show how it may be extended to include constrained lumping by only approximately transforming the linear partial differential operator to some partially canonical form. In Sec. IV, we present a simple example from combustion which illustrates the application of the constrained lumping

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approach to nonisothermal systems. Finally, in Sec. V, we present conclusions and a discussion.

II. THE ALGEBRAIC METHOD IN NONLINEAR PERTURBATION THEORY AND ITS APPLICATION TO UNCONSTRAINED LUMPING

In order to understand the basic idea of approximate constrained nonlinear lumping, we first briefly summarize the theoretical basis of the algebraic method in nonlinear perturbation theory and its application to unconstrained lumping.[1,2]

The kinetics of a reaction system with n species can be described by an n-dimensional ordinary differential equation system

$$\frac{d\mathbf{y}}{dt}=\mathbf{f}(\mathbf{y}), \quad \mathbf{y}\in\mathscr{R}^n, \tag{1}$$

where $\mathbf{y}$ is an n-dimensional vector, $\mathbf{f}(\mathbf{y})$ is an n-dimensional and $\mathscr{C}^2$ (twice continuously differentiable) function vector with $\mathbf{f}(\mathbf{0})=\mathbf{0}$. There exists a one-to-one relation between this system and the linear partial differential operator

$$A=\sum_{i=1}^{n} f_i(\mathbf{y})\frac{\partial}{\partial y_i}. \tag{2}$$

For different bases, A possesses different forms. For example, suppose there exists a basis consisting of eigenfunctions $\varphi_i(\mathbf{y})$ and invariants $\omega_j(\mathbf{y})$ of A, i.e.,

$$\varphi_1(\mathbf{y}),\varphi_2(\mathbf{y}),\ldots,\varphi_k(\mathbf{y}), \quad \omega_1(\mathbf{y}),\omega_2(\mathbf{y}),\ldots,\omega_m(\mathbf{y}),$$

for $k+m=n$,

where the eigenvalues $\lambda_i(\omega)$ corresponding to $\varphi_i(\mathbf{y})$ are not identically equal to zero and are required to be functions of the invariant vector $\omega=(\omega_1,\omega_2,\ldots,\omega_m)^T$ only. Within this basis, the operator A possesses the form

$$A=\sum_{i=1}^{k}\lambda_i(\omega)\varphi_i(\mathbf{y})\frac{\partial}{\partial\varphi_i(\mathbf{y})}=(\Lambda\varphi,\nabla_\varphi), \tag{3}$$

where Λ is a $k\times k$ diagonal matrix with $\lambda_i(\omega)$ as its ith diagonal element, and

$$\varphi=(\varphi_1\varphi_2\cdots\varphi_k)^T,$$

$$\nabla_\varphi=\left(\frac{\partial}{\partial\varphi_1}\frac{\partial}{\partial\varphi_2}\cdots\frac{\partial}{\partial\varphi_k}\right)^T.$$

This is referred to as a diagonal canonical form. The coefficients for $\partial/\partial\varphi_i(\mathbf{y})$ will be therefore linear in $\varphi_i(\mathbf{y})$. Similarly, we have defined other canonical forms such as Jordan, blockwise diagonal, and quasilinear.[1] We have shown that the algebraic method in nonlinear perturbation theory can be employed to approximately transform a general form of A to a canonical form M.

The new dependent variables, called lumped variables, are partly or completely separated in the corresponding differential equations for M. The differential equations for the separated lumped variables compose a lower dimensional differential equation system. Moreover, the differential equations for some lumped variables, called *purely fast variables*, are linear with respect to themselves, and can be approximately solved by a singular perturbation method.[3] Approximate analytical solutions in the form of an exponential function in terms of the other lumped variables and time t can therefore be obtained. Hence, the determination of nonlinear lumping schemes is equivalent to transforming A to a canonical form M.

A. Canonical form and the change of variable operator

For chemical kinetic systems, the operator A can have a special form due to the separation in time scales between competing reaction rates. It can be expressed as

$$A=A_0+\epsilon A_1+\epsilon^2A_2+\cdots, \tag{4}$$

where ϵ is a small positive parameter and all $A_i(i=0,1,\ldots)$ are defined in a common basis. The magnitudes of the coefficients for all A_i are comparable to one another. In systems where no time scale separation exists, it may still be possible to use the above form by finally setting $\epsilon=1$. In this case, there is no guarantee of the convergence of the terms of M_i but we may still make use of the approximation by a finite number of terms in many cases. For the application of the algebraic method in nonlinear perturbation theory, the *leading operator* A_0 should be of a diagonal, Jordan, or quasilinear canonical form.

For unconstrained lumping, we used the algebraic method in nonlinear perturbation theory to find a transformation operator S such that the resultant operator

$$M=\epsilon^{-S}Ae^{S}, \tag{5}$$

where

$$S=\epsilon S_1+\epsilon^2S_2+\cdots \tag{6}$$

and all S_i are linear partial differential operators, is blockwise diagonal and its diagonal size and location are the same as the Jordan blocks of A_0 as long as the eigenvalues are distinct. When some Jordan blocks have the same eigenvalue, the corresponding diagonal block of M is an extended one whose size includes all these Jordan blocks. We say that M possesses a canonical form similar to A_0. The dependent variables in the corresponding differential equation system for a blockwise diagonal operator are partly separated, and the differential equations for the separated variables only contain these variables. Since there is a one-to-one relation between an operator and its corresponding differential equation system, we can simply write down the corresponding differential equation system after we obtain the canonical form M.

According to Eqs. (5) and (6), it can be readily verified that

$$M=M_0+\epsilon M_1+\epsilon^2M_2+\cdots \tag{7}$$

and

$$M_0=A_0, \quad M_1=[A_0,S_1]+A_1,$$

$$M_2=[A_0,S_2]+A_2+[A_1,S_1]+\tfrac{1}{2!}[[A_0,S_1],S_1],\ldots, \tag{8}$$

where $[X,Y]$ is the *commutator* of operators X and Y defined as

$$[X,Y]=XY-YX. \tag{9}$$

The formulas in Eq. (8) are recursive

$$M_i=[A_0,S_i]+Y_i \quad (i=1,2,\ldots), \tag{10}$$

where $Y_1=A_1$ and Y_i for $i>1$ are known if $S_1,\ldots,S_{i-1}$ are known. By appropriate choices of S_i's, M_i and consequently M will possess a canonical form similar to A_0.

Necessary and sufficient conditions for M being of a canonical form similar to A_0 have been obtained,[2] i.e., M transforms a Jordan basis function $\varphi_\lambda(\mathbf{y})$ corresponding to the eigenvalue λ of A_0 to a Jordan basis function $\phi_\lambda(\mathbf{y})$ corresponding to the same eigenvalue of A_0. As typically one will only take a limited number (usually only the first one or two) of terms in Eq. (7), the lumping is approximate.

B. Determination of S_i and M_i

There are different ways to choose S_i. In particular, we presented a method for the selection of S_i and M_i using the mapping property of Jordan basis functions when the following conditions are satisfied:

(1) For any Jordan basis function $\varphi_\lambda(\mathbf{y})$ corresponding to the eigenvalue $\lambda(\mathbf{y})$ of A_0 which is used in the basis, we have

$$Y_i\varphi_\lambda(\mathbf{y})=\sum_k \phi_k(\mathbf{y}), \tag{11}$$

where $\phi_k(\mathbf{y})$ is a Jordan basis function corresponding to the eigenvalue $\mu_k(\mathbf{y})$ of A_0.

(2) Either $\mu_k(\mathbf{y})\equiv\lambda(\mathbf{y})$ or $\mu_k(\mathbf{y})\neq\lambda(\mathbf{y})$ for all $\mathbf{y}$ in the considered domain of $\mathbf{y}$.

If these two conditions hold, then Eq. (10) is solvable, where M_i possesses a canonical form similar to A_0.

Suppose A_0 is diagonal with the form given by Eq. (3). For invariants $\omega_j(\mathbf{y})$ of A_0, Eq. (10) becomes

$$\begin{aligned} M_i\omega_j(\mathbf{y}) &= A_0S_i\omega_j(\mathbf{y})-S_iA_0\omega_j(\mathbf{y})+Y_i\omega_j(\mathbf{y}) \\ &= A_0S_i\omega_j(\mathbf{y})+\phi_0(\mathbf{y})+\sum_{k\in I_{i,j}}\phi_k(\mathbf{y}), \end{aligned} \tag{12}$$

where $I_{i,j}$ is a set of positive integers and ϕ_0 is an invariant and can be zero. By choosing

$$S_i\omega_j(\mathbf{y})=-\sum_{k\in I_{i,j}}\phi_k(\mathbf{y})/\mu_k(\mathbf{y}), \tag{13}$$

we have a solution of Eq. (12) and

$$M_i\omega_j(\mathbf{y})=\phi_0(\mathbf{y}). \tag{14}$$

Equation (14) shows that M_i transforms an invariant to still be an invariant of A_0.

For eigenfunctions $\varphi_\lambda(\mathbf{y})$ of A_0, the quantity $M_i\varphi_\lambda(\mathbf{y})$ can be represented as follows:

$$M_i\varphi_\lambda(\mathbf{y})=A_0S_i\varphi_\lambda(\mathbf{y})-\lambda S_i\varphi_\lambda(\mathbf{y})+\phi_\lambda(\mathbf{y})+\sum_{k\in I_{i,\lambda}}\phi_k(\mathbf{y}), \tag{15}$$

where $\phi_\lambda(\mathbf{y})$ and $\phi_k(\mathbf{y})$ are eigenfunctions of A_0 corresponding to eigenvalues λ and μ_k with $\lambda-\mu_k\neq0$, respectively, and $I_{i,\lambda}$ is a set of positive integers. Setting

$$S_i\varphi_\lambda(\mathbf{y})=\sum_{k\in I_{i,\lambda}}\frac{\phi_k(\mathbf{y})}{\lambda-\mu_k}, \tag{16}$$

we obtain

$$M_i\varphi_\lambda(\mathbf{y})=\phi_\lambda(\mathbf{y}). \tag{17}$$

It may also be the case that $M_i\varphi_\lambda(\mathbf{y})=0$ when $\phi_\lambda(\mathbf{y})$ is absent in Eq. (15). This shows that M_i transforms an eigenfunction $\varphi_\lambda(\mathbf{y})$ of A_0 corresponding to eigenvalue λ, to an eigenfunction of A_0 with the same eigenvalue, or to 0. Thus M_i is of a canonical form similar to A_0, and Eqs. (13) and (16) present a method for the selection of S_i.

Notice that even though A and M use the same symbols for the variables, they are not identical. Actually, the lumped variables in M are nonlinear functions of the original variables in A. If we use y_i and $\hat{y}_i$ to represent the variables for A and M, respectively, it can be verified that

$$\hat{y}_i=e^Sy_i \quad (i=1,2,\ldots,n). \tag{18}$$

Naturally, e^S is referred to as a *change of variable operator*. Since

$$A=e^SMe^{-S}, \tag{19}$$

similarly we have

$$y_i=e^{-S}\hat{y}_i \quad (i=1,2,\ldots,n). \tag{20}$$

If we express e^S and e^{-S} by

$$e^S=I+S+\tfrac{1}{2}S^2+\cdots=I+\epsilon S_1+\epsilon^2(S_2+\tfrac{1}{2}S_1^2)+\cdots \tag{21}$$

and

$$e^{-S}=I-S+\tfrac{1}{2}S^2-\cdots=I-\epsilon S_1-\epsilon^2(S_2-\tfrac{1}{2}S_1^2)-\cdots, \tag{22}$$

then

$$\hat{y}_i=y_i+\epsilon S_1\ y_i+\epsilon^2(S_2+\tfrac{1}{2}S_1^2)y_i+\cdots \tag{23}$$

and

$$y_i=\hat{y}_i-\epsilon S_1\hat{y}_i-\epsilon^2(S_2-\tfrac{1}{2}S_1^2)\hat{y}_i-\cdots. \tag{24}$$

In Eqs. (23) and (24), the operators S_i are defined in the bases $\mathbf{y}=\{y_1,y_2,\ldots,y_n\}$ and $\hat{\mathbf{y}}=\{\hat{y}_1,\hat{y}_2,\ldots,\hat{y}_n\}$, respectively.

III. CONSTRAINED LUMPING

The algebraic method in nonlinear perturbation theory can also be used for approximate *constrained* nonlinear lumping, where some variables are left unlumped. The first stage of the process is to select an appropriate leading operator A_0 which can be easily transformed into a canonical form. Suppose the kinetic equations of a reaction system with n species are of the following form:

$$\frac{d\mathbf{y}}{dt}=\epsilon\mathbf{f}(\mathbf{y},\mathbf{z}), \tag{25}$$

$$\frac{d\mathbf{z}}{dt}=B(\mathbf{y})\mathbf{z}+\epsilon\mathbf{g}(\mathbf{y},\mathbf{z}), \tag{26}$$

where $\mathbf{y}$ and $\mathbf{f}$, and $\mathbf{z}$ and $\mathbf{g}$ are m- and k-dimensional vectors and function vectors with $m+k=n$, respectively, and $\mathbf{g}(\mathbf{y},\mathbf{z})$ may be absent in some cases; B is a $k\times k$ diagonal or Jordan matrix whose eigenvalues have negative real parts. A canonical leading operator can then easily be chosen. Although reaction rate equations are not generally of the above form, it is always possible to transform them to this form provided some purely fast variables exist for the given system.

If ϵ is a small positive parameter, Eqs. (25) and (26) show that the rates of z_j's are much faster than those of y_i's. However, for the application of the algebraic method, it is not necessary for ϵ to be present explicitly in the equations. These conditions may be satisfied even if the kinetic equations do not contain ϵ. In this case, the reaction system exhibits time scale separation, but $\mathbf{f}(\mathbf{y},\mathbf{z})$, $\mathbf{g}(\mathbf{y},\mathbf{z})$, and $B\mathbf{z}$ are not comparable in magnitudes. The convergence of the terms in the approximation will therefore depend on the fact that ϵ remains "hidden." In many cases, $\mathbf{z}$ represents the concentration vector of radicals or complexes composed of reactants and catalysts. Their initial values $\mathbf{z}(0)$ are usually zero. In the following, we consider B to be diagonal. For the case that B is of a Jordan form, the discussion is similar.

For such a system, we wish to find a lumped model in which the variables y_i are unlumped. The linear partial differential operator corresponding to the system given by Eqs. (25) and (26) is as follows:

$$A=A_0+\epsilon A_1, \tag{27}$$

where

$$A_0=\sum_{i=1}^{k}\lambda_i(\mathbf{y})z_i\frac{\partial}{\partial z_i}, \tag{28}$$

$$A_1=\sum_{i=1}^{m}f_i(\mathbf{y},\mathbf{z})\frac{\partial}{\partial y_i}+\sum_{i=1}^{k}g_i(\mathbf{y},\mathbf{z})\frac{\partial}{\partial z_i}, \tag{29}$$

and $\lambda_i(\mathbf{y})$ is the ith diagonal element of B. Notice that all y_i's are invariants and z_i is an eigenfunction with eigenvalue $\lambda_i(\mathbf{y})$ of A_0, whose real part is negative. Hence, A_0 is of a diagonal canonical form. For unconstrained lumping, one can use the algebraic method in nonlinear perturbation theory to transform A into a canonical form similar to A_0 by selecting an appropriate operator S. Now we wish to keep the y_i's unlumped. In order to do so, we can employ the same approach as in unconstrained lumping to transform A into a partially canonical form

$$M=e^{-S}Ae^{S} \tag{30}$$

under the condition that

$$Sy_i=0 \quad (i=1,2,\ldots,m), \tag{31}$$

i.e., all $S_jy_i=0$ for $j=1,2,\ldots$. Then the lumped variables

$$\hat{y}_i=e^{S}y_i=(I+S+\tfrac{1}{2}S^2+\cdots)y_i=y_i \tag{32}$$

remain the same as the original variables y_i. The other coefficients S_jz_i $(i=1,2,\ldots,k;\ j=1,2,\ldots)$ are determined by the same procedure as in unconstrained lumping.

As A_0 is diagonal, the differential equation for $\hat{z}_i$ corresponding to M will possess the form

$$\frac{d\hat{z}_i}{dt}=\omega_i(\mathbf{y},\epsilon)\hat{z}_i \quad (i=1,2,\ldots,k), \tag{33}$$

where $\omega_i(\mathbf{y},\epsilon)$ are some functions of $\mathbf{y}$ and ϵ with negative values. If $\omega_i(\mathbf{y},\epsilon)$ is complex, then its real part is negative. Therefore, the lumped variables $\hat{z}_i$ are referred to as purely fast variables and Eq. (33) can be solved by a singular perturbation method.[3,4] Since $\hat{z}_i$ decays quickly to zero, its solution only consists of an initial layer solution near $t=0$, i.e.,

$$\begin{aligned}\hat{z}_i(t)&\approx\hat{z}_i[\mathbf{y}(0),\mathbf{z}(0)]\exp\{\omega_i[\mathbf{y}(0),\epsilon]t\}\\&=\hat{z}_i[\mathbf{y}(0)]\exp\{\omega_i[\mathbf{y}(0),\epsilon]t\}.\end{aligned} \tag{34}$$

Here we used the condition $\mathbf{z}(0)=\mathbf{0}$ and the initial values $\hat{z}_i[\mathbf{y}(0),\mathbf{z}(0)]$ are determined by Eq. (23). As the $y_i(t)$'s change on a much slower time scale than the $\hat{z}_i(t)$'s, we can simply replace $\mathbf{y}(0)$ with $\mathbf{y}$ without introducing a significant error. Thus

$$\hat{z}_i(t)\approx\hat{z}_i(\mathbf{y})\exp[\omega_i(\mathbf{y},\epsilon)t]. \tag{35}$$

The original variables z_i can be obtained by

$$z_i=\hat{z}_i-\epsilon S_1\hat{z}_i-\epsilon^2(S_2-\tfrac{1}{2}S_1^2)\hat{z}_i-\cdots. \tag{36}$$

As the coefficients of S_i are functions of y_i and $\hat{z}_i$, so are the original variables z_i. Substituting these expressions of z_i into Eq. (25) and considering Eq. (35) yields

$$\frac{d\mathbf{y}}{dt}=\epsilon\mathbf{f}[\mathbf{y},\mathbf{z}(\mathbf{y},\hat{\mathbf{z}})]=\epsilon\mathbf{f}[\mathbf{y},\mathbf{z}(\mathbf{y},t,\epsilon)]=\epsilon\mathbf{F}(\mathbf{y},t,\epsilon). \tag{37}$$

The resultant lumped differential equation system for $\mathbf{y}$ is only functions of the original variables $\mathbf{y}$ and independent variable t. In some cases, the purely fast variables approach zero in such a short time that we can even discard the terms containing exponential functions of t in $\mathbf{F}(\mathbf{y},t,\epsilon)$ without introducing a significant error. We then have the approximation of $d\mathbf{y}/dt$ in the slow invariant manifold as follows:

$$\frac{d\mathbf{y}}{dt}=\epsilon\tilde{\mathbf{F}}(\mathbf{y},\epsilon). \tag{38}$$

This is the basic idea of constrained lumping. The approach will be illustrated by an example below.

IV. THE DETERMINATION OF CONSTRAINED LUMPING SCHEMES IN A COMBUSTION SYSTEM

A simple mechanism describing the oxidation of hydrogen in oxygen will be utilized for illustration of the method of constrained approximate nonlinear lumping to nonisothermal combustion schemes. We wish to provide a lumped

model which reproduces the maximum temperature rise and main ignition features of the starting model. The starting mechanism is as follows:

$$H_2+O_2 \xrightarrow{k_1} H+HO_2,$$

$$H_2+OH \xrightarrow{k_2} H+H_2O,$$

$$O_2+H \xrightarrow{k_3} OH+O,$$

$$H_2+O \xrightarrow{k_4} H+OH,$$

$$O_2+H+M \xrightarrow{k_5} M+HO_2,$$

$$H \xrightarrow{k_6} \text{wall},$$

where

$$M=H_2+0.4O_2+6H_2O.$$

The rate constant for each reaction is in the form $k_i=AT^n \exp(-E/RT)$ with units $(\text{molecule cm}^{-3})^{1-m}\text{s}^{-1}$ for an mth order reaction, and the data for each reaction are given in Table I. The sources for the data can be found in Ref. 5.

We stress that the above skeleton scheme is in no way a comprehensive scheme for hydrogen oxidation. It does, however, contain the key reactions which lead to ignition in the system, and therefore we use it here as an illustration of how the algebraic method may be applied to general combustion schemes. We model the system in a closed vessel for selected ambient temperatures and pressures in the region of the second explosion limit, i.e., at ambient temperatures between 800 and 1000 K and at pressures of ~20 Torr. We require the lumped scheme to reproduce the ignition profiles of the skeleton scheme over the chosen range of temperatures and pressures.

The dynamics in a closed system is described by the following set of equations.

mass balance

$$\frac{dy_i}{dt}=f_i(\mathbf{y},\mathbf{k})=-\sum_j \upsilon_{ij}R_j \tag{39}$$

and energy balance

$$\sigma C_p \frac{dT}{dt}=\sum_j R_j(-\Delta H_j)-\frac{\chi S}{V}(T-T_a), \tag{40}$$

where y_i represents the concentration of species i, $\mathbf{k}$ is the rate constant vector, υ_{ij} is the stoichiometric coefficient of species i in reaction j, and R_j is the rate of reaction j, where j signifies the reaction number. The total heat loss term describes the loss via Newtonian cooling through the walls. T_a is the ambient temperature, $-\Delta H_j$ is the heat of reaction j, χ is the heat transfer coefficient, S is the surface area, V is the volume, and σ is the molar density. C_p is the specific heat at constant pressure and T is the temperature of the gas mixture. A constant value for $(\chi S)/V$ of 0.8×10^{-3} $\text{W cm}^{-3}\text{K}^{-1}$ was chosen. The temperature dependence and thermochemical data are described by polynomial fits developed by the NASA thermodynamics group.[6]

We define the species concentrations to be

$$y_1=[H_2],\quad y_2=[O_2],\quad y_3=[H_2O],$$

$$y_4=[H],\quad y_5=[OH],\quad y_6=[O],\quad y_7=[HO_2].$$

The mass balance equations then become

$$\frac{dy_1}{dt}=-k_1y_1y_2-k_2y_1y_5-k_4y_1y_6,\quad \frac{dy_2}{dt}=-k_1y_1y_2-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3),$$

$$\frac{dy_3}{dt}=k_2y_1y_5,\quad \frac{dy_4}{dt}=-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)-k_6y_4+k_1y_1y_2+k_2y_1y_5+k_4y_1y_6, \tag{41}$$

$$\frac{dy_5}{dt}=-k_2y_1y_5+k_3y_2y_4+k_4y_1y_6,\quad \frac{dy_6}{dt}=-k_4y_1y_6+k_3y_2y_4,\quad \frac{dy_7}{dt}=k_1y_1y_2+k_5y_2y_4(y_1+0.4y_2+6y_3).$$

For this reaction system, we are usually only concerned with the temperature changes and the evolution of the main species such as H_2, O_2, and H_2O. Therefore, we wish to eliminate as many radicals as possible. As $[HO_2]$ does not influence the changes of concentrations of other species, we need not consider the last equation.

Strictly the application of the algebraic method in nonlinear perturbation theory requires the existence of a small parameter ϵ in the equations, and this can be revealed by a nondimensionalization procedure. However, even for such a simple set of equations, this is a complicated process which can be avoided by carrying out a numerical investigation of the time scales present in the problem. By examining the eigenvalues of a linear approximation to the system, it becomes clear that there are two negative fast modes in the above equations over all conditions tested. These are indi-

TABLE I. Rate constants.

Reaction no.	Reaction	A [(cm^3 molecule^{-1})$^{1-m}$s^{-1}]	n	(E/R) (K)
1	$H_2+O_2\rightarrow H+HO_2$	2.40×10^{-10}	0	28 500
2	$H_2+OH\rightarrow H+H_2O$	1.70×10^{-16}	1.60	1 660
3	$O_2+H\rightarrow OH+O$	3.30×10^{-10}	0	8 460
4	$H_2+O\rightarrow H+OH$	8.50×10^{-20}	2.67	3 160
5	$O_2+H+M\rightarrow M+HO_2$	1.37×10^{-32}	0	−500
6	$H\rightarrow$ wall	75	0	0

cated by the presence of two large negative eigenvalues in the spectrum over the whole of each trajectory. In fact, there are two purely fast variables related to y_5 and y_6 which can be eliminated. Such fast modes can also be identified using techniques such as computational singular perturbation theory[7] (CSP). For some combustion systems, the fast modes may not correspond directly to species, and a more detailed comparison of reaction fluxes will have to be carried out in order to select an appropriate A_0.

For the above system, we set $\epsilon=1$ and choose A to be the following:

$$A=A_0+A_1, \tag{42}$$

where

$$A_0=(-k_2y_1y_5+k_3y_2y_4+k_4y_1y_6)\frac{\partial}{\partial y_5}+(-k_4y_1y_6+k_3y_2y_4)\frac{\partial}{\partial y_6}, \tag{43}$$

$$A_1=(-k_1y_1y_2-k_2y_1y_5-k_4y_1y_6)\frac{\partial}{\partial y_1}+[-k_1y_1y_2-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)]\frac{\partial}{\partial y_2}+k_2y_1y_5\frac{\partial}{\partial y_3}$$
$$+[-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)-k_6y_4+k_1y_1y_2+k_2y_1y_5+k_4y_1y_6]\frac{\partial}{\partial y_4}. \tag{44}$$

In the nonisothermal condition, A should contain a term representing the differential equation of T, i.e., A_1 has a term $g(T,\mathbf{y})\partial/\partial T$, where $g(T,\mathbf{y})$ is given by Eq. (40). As $g(T,\mathbf{y})$ is an exponential function of T through the rate constants, the treatment for this case by the algebraic method will become very complicated. Fortunately, in many cases, we can omit this term without introducing a significant error. We will discuss it later.

Notice that although Eq. (41) possesses the form given in Eqs. (25) and (26), we did not simply use the terms which are linear in the deleted variables of the fifth and sixth equations in Eq. (41) to construct A_0. This is because the more terms contained in A_0, the less terms in Eq. (7) are needed to reach the same accuracy. Therefore, we choose all terms in these two equations to construct A_0 and first transform A_0 into a canonical form. It is easy to prove that the two eigenfunctions of A_0 are as follows:

$$\varphi_1=\frac{2k_3y_2y_4}{k_2y_1}+\frac{k_3y_2y_4}{(k_4-k_2)y_1}-y_5-\frac{k_4y_6}{k_4-k_2}, \tag{45}$$

$$\varphi_2=\frac{k_3y_2y_4}{k_4y_1}-y_6, \tag{46}$$

corresponding to the eigenvalues

$$\lambda_1=-k_2y_1, \tag{47}$$

$$\lambda_2=-k_4y_1. \tag{48}$$

The inverse relations for y_5 and y_6 are

$$y_5=\frac{2k_3y_2y_4}{k_2y_1}-\varphi_1+\frac{k_4\varphi_2}{k_4-k_2}, \tag{49}$$

$$y_6=\frac{k_3y_2y_4}{k_4y_1}-\varphi_2. \tag{50}$$

We use y_i ($i=1$, 2, 3, and 4) and φ_j ($j=1$ and 2) as a new basis. With respect to this basis, the operator A_0 is diagonal and the y_i's are its invariants

$$A_0=-k_2y_1\varphi_1\frac{\partial}{\partial\varphi_1}-k_4y_1\varphi_2\frac{\partial}{\partial\varphi_2}. \tag{51}$$

Operator A_1 possesses the form

$$A_1=\left[-k_1y_1y_2-3k_3y_2y_4+k_2y_1\varphi_1+\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}\varphi_2\right]\frac{\partial}{\partial y_1}+[-k_1y_1y_2-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)]\frac{\partial}{\partial y_2}$$
$$+\left(2k_3y_2y_4-k_2y_1\varphi_1+\frac{k_2k_4y_1}{k_4-k_2}\varphi_2\right)\frac{\partial}{\partial y_3}+\left(k_1y_1y_2+2k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)-k_6y_4-k_2y_1\varphi_1\right.$$
$$\left.-\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}\varphi_2\right)\frac{\partial}{\partial y_4}+\left(\frac{2k_4-k_2}{k_2(k_4-k_2)}\alpha-\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\varphi_1\right.$$
$$\left.-\frac{k_3k_4(k_4-2k_2)(2k_4-k_2)(y_1y_2+y_2y_4)}{k_2(k_4-k_2)^2y_1}\varphi_2\right)\frac{\partial}{\partial\varphi_1}+\left[\frac{\alpha}{k_4}-\frac{k_2k_3(y_1y_2+y_2y_4)}{k_4y_1}\varphi_1\right.$$
$$\left.-\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\varphi_2\right]\frac{\partial}{\partial\varphi_2}, \tag{52}$$

where

$$\alpha=\frac{k_3y_2}{y_1^2}[k_1y_1(y_1y_2-y_1y_4+y_2y_4)+k_3y_4(2y_1y_2-y_1y_4$$
$$+3y_2y_4)-k_5y_1y_4(y_2+y_4)(y_1+0.4y_2+6y_3)$$
$$-k_6y_1y_4]. \tag{53}$$

Compared to the other terms in the square brackets of the above equation, the first and the last ones are relatively small and then α can be approximately represented as

$$\alpha=\frac{k_3y_2}{y_1^2}[k_3y_4(2y_1y_2-y_1y_4+3y_2y_4)-k_5y_1y_4(y_2+y_4)$$
$$+(y_1+0.4y_2+6y_3)]. \tag{54}$$

Now we return to consider the error introduced by omitting the term $g(T,\mathbf{y})\partial/\partial T$ in A_1. As $g(T,\mathbf{y})=dT/dt$, this gives that $g(T,\mathbf{y})\partial/\partial T=(dT/dt)\partial/\partial T$. If A_1 contains the term $(dT/dt)\partial/\partial T$, the coefficient $A_1\phi_i$ in A_1 will contain another term $(dT/dt)\partial\phi_i/\partial T$. Notice that ϕ_i is a function of T through rate constants $k_j=A_jT^{n_j}\exp(-E_j/RT)$ and

$$\frac{\partial\phi_i}{\partial T}=\sum_j\frac{\partial\phi_i}{\partial k_j}\frac{dk_j}{dT}=\sum_j\frac{\partial\phi_i}{\partial k_j}\left(\frac{n_jk_j}{T}+\frac{E_jk_j}{RT^2}\right). \tag{55}$$

Then we have

$$\frac{dT}{dt}\frac{\partial\phi_i}{\partial T}=\sum_j\frac{\partial\phi_i}{\partial k_j}\left(\frac{n_jk_j}{T}+\frac{E_jk_j}{RT^2}\right)\frac{dT}{dt}$$
$$=\sum_j\frac{\partial\phi_i}{\partial k_j}\left(n_jk_j\frac{d(\ln T)}{dt}-\frac{E_jk_j}{R}\frac{d(1/T)}{dt}\right). \tag{56}$$

Compared to dy_i/dt, $d(\ln T)/dt$ and $d(1/T)/dt$ are all small. Omitting $g(T,\mathbf{y})\partial/\partial T$ will not introduce a significant error provided that the other terms in Eq. (56) are not very large.

The corresponding differential equation system for A is the following:

$$\frac{dy_1}{dt}=-k_1y_1y_2-3k_3y_2y_4+k_2y_1\varphi_1+\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}\varphi_2,\quad \frac{dy_2}{dt}=-k_1y_1y_2-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3),$$
$$\frac{dy_3}{dt}=2k_3y_2y_4-k_2y_1\varphi_1+\frac{k_2k_4y_1}{k_4-k_2}\varphi_2,\quad \frac{dy_4}{dt}=k_1y_1y_2+2k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)-k_6y_4-k_2y_1\varphi_1$$
$$-\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}\varphi_2,$$
$$\frac{d\varphi_1}{dt}=\frac{2k_4-k_2}{k_2(k_4-k_2)}\alpha-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]\varphi_1-\frac{k_3k_4(k_4-2k_2)(2k_4-k_2)(y_1y_2+y_2y_4)}{k_2(k_4-k_2)^2y_1}\varphi_2,$$
$$\frac{d\varphi_2}{dt}=\frac{\alpha}{k_4}-\frac{k_2k_3(y_1y_2+y_2y_4)}{k_4y_1}\varphi_1-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]\varphi_2 \tag{57}$$

which is of the form given in Eqs. (25) and (26).

Now we employ the algebraic method in nonlinear perturbation theory to transform A into a partially canonical form M similar to A_0. First we determine M_1 by using

$$M_1=[A_0S_1]+A_1 \tag{58}$$

under the condition that y_i ($i=1$, 2, 3, and 4) are left unlumped. In order to do so, we set

$$S_1y_i=0 \quad (i=1,2,3, \text{ and } 4) \tag{59}$$

and $S_1\varphi_i$ ($i=1$ and 2) can be determined by

$$M_1\varphi_i=A_0S_1\varphi_i-S_1A_0\varphi_i+A_1\varphi_i=A_0S_1\varphi_i-\lambda_iS_1\varphi_i+A_1\varphi_i. \tag{60}$$

Notice that all terms of $A_1\varphi_i$ are eigenfunctions of A_0 corresponding to eigenvalues 0, λ_1, or λ_2, respectively. By using Eqs. (16) and (17), we obtain

$$S_1\varphi_1=-\frac{2k_4-k_2}{k_2^2(k_4-k_2)y_1}\alpha-\frac{k_3k_4(k_4-2k_2)(2k_4-k_2)}{k_2(k_4-k_2)^3y_1^2}\times(y_1y_2+y_2y_4)\varphi_2, \tag{61}$$

$$S_1\varphi_2=-\frac{\alpha}{k_4^2y_1}+\frac{k_2k_3}{k_4(k_4-k_2)y_1^2}(y_1y_2+y_2y_4)\varphi_1, \tag{62}$$

and

$$M_1y_i=A_1y_i \quad (i=1,2,3, \text{ and } 4), \tag{63}$$

$$M_1\varphi_1=-\frac{k_3(2k_4-k_2)}{(k_4-k_2)y_1}(y_1y_2+y_2y_4)\varphi_1, \tag{64}$$

$$M_1\varphi_2=-\frac{k_3(k_4-2k_2)}{(k_4-k_2)y_1}(y_1y_2+y_2y_4)\varphi_2. \tag{65}$$

If we only consider the first order approximation, we have

$$M\approx A_0+M_1. \tag{66}$$

The corresponding lumped differential equation system for M is

$$\frac{dy_1}{dt}=-k_1y_1y_2-3k_3y_2y_4+k_2y_1\varphi_1+\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}\varphi_2, \quad \frac{dy_2}{dt}=-k_1y_1y_2-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3),$$

$$\frac{dy_3}{dt}=2k_3y_2y_4-k_2y_1\varphi_1+\frac{k_2k_4y_1}{k_4-k_2}\varphi_2, \quad \frac{dy_4}{dt}=k_1y_1y_2+2k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)-k_6y_4-k_2y_1\varphi_1-\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}\varphi_2,$$

$$\frac{d\varphi_1}{dt}=-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]\varphi_1 \quad \frac{d\varphi_2}{dt}=-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]\varphi_2. \tag{67}$$

All φ_i in these equations are lumped variables. The last two equations can be solved by the singular perturbation method[3] and the solutions consist of only those for the initial layer. After approximately treating y_i as constants, the integration gives

$$\hat{\varphi}_1(t)=\hat{\varphi}_1(0)\exp\left\{-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}, \tag{68}$$

$$\hat{\varphi}_2(t)=\hat{\varphi}_2(0)\exp\left\{-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}. \tag{69}$$

Here we used $\hat{\varphi}_i$ to distinguish them from the original φ_i. The initial values $\hat{\varphi}_i(0)$ will be given by

$$\hat{\varphi}_i(0)=\varphi_i(0)+S_1\varphi_i(0). \tag{70}$$

Suppose the initial values $y_5(0)$ and $y_6(0)$ are zero. From Eqs. (45), (46), (61), and (62), we know that $\hat{\varphi}_i(0)$ are only functions of $y_i(0)$($i=1$, 2, 3, and 4). As $\hat{\varphi}_i$ are purely fast variables, which vanish on a much faster time scale than the changes in y_i, we can use y_i instead $y_i(0)$ in the expressions of $\hat{\varphi}_i(0)$ without introducing a significant error. Thus we write $\hat{\varphi}_i(0)\approx\hat{\varphi}_i(\mathbf{y})$, where $\mathbf{y}=(y_1,y_2,y_3,y_4)^T$. Then we have

$$\hat{\varphi}_1(t)=\hat{\varphi}_1(\mathbf{y})\exp\left\{-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}, \tag{71}$$

$$\hat{\varphi}_2(t)=\hat{\varphi}_2(\mathbf{y})\exp\left\{-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}. \tag{72}$$

From Eq. (24), we know that the zeroth and first order approximations of the original variables are as follows:

$$\varphi_i=\hat{\varphi}_i, \tag{73}$$

$$\varphi_i=\hat{\varphi}_i-S_1\hat{\varphi}_i. \tag{74}$$

Substituting these expressions for φ_i into the first four equations of the original differential equation system (57) yields the lumped differential equation system for y_1, y_2, y_3, and y_4. For the zeroth order approximation of φ_i, the resultant lumped differential equation system is

$$\frac{dy_1}{dt}=-k_1y_1y_2-3k_3y_2y_4+k_2y_1\hat{\varphi}_1(\mathbf{y})\exp\left\{-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}+\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}\hat{\varphi}_2(\mathbf{y})$$
$$\times\exp\left\{-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\},$$

$$\frac{dy_2}{dt}=-k_1y_1y_2-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3),$$

$$\frac{dy_3}{dt}=2k_3y_2y_4-k_2y_1\hat{\varphi}_1(\mathbf{y})\exp\left\{-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}+\frac{k_2k_4y_1}{k_4-k_2}\hat{\varphi}_2(\mathbf{y})$$
$$\times\exp\left\{-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\},$$

$$\frac{dy_4}{dt}=k_1y_1y_2+2k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)-k_6y_4-k_2y_1\hat{\varphi}_1(\mathbf{y})\exp\left\{-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}$$
$$-\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}\hat{\varphi}_2(\mathbf{y})\exp\left\{-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}. \tag{75}$$

This lumped differential equation system is nonautonomous. If we only consider the solutions within the slow invariant manifold, the exponential terms are discarded giving

$$\frac{dy_1}{dt}=-k_1y_1y_2-3k_3y_2y_4\quad\frac{dy_2}{dt}=-k_1y_1y_2-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3),\quad\frac{dy_3}{dt}=2k_3y_2y_4,$$
$$\frac{dy_4}{dt}=k_1y_1y_2+2k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)-k_6y_4. \tag{76}$$

Actually, this system can be obtained by using the quasisteady-state assumption for y_5 and y_6 in Eq. (41).

For the first order approximation of φ_i, the resultant lumped differential equation system is

$$\frac{dy_1}{dt}=-k_1y_1y_2-3k_3y_2y_4+\frac{2(k_2+k_4)}{k_2k_4}\alpha+\left[k_2y_1-\frac{k_2k_3(k_4-2k_2)}{(k_4-k_2)^2y_1}(y_1y_2+y_2y_4)\right]\hat{\varphi}_1(\mathbf{y})$$
$$\times\exp\left\{-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}+\left[\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}+\frac{k_3k_4(k_4-2k_2)(2k_4-k_2)}{(k_4-k_2)^3y_1^2}(y_1y_2\right.$$
$$\left.+y_2y_4)\right]\hat{\varphi}_2(\mathbf{y})\exp\left\{-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\},$$

$$\frac{dy_2}{dt}=-k_1y_1y_2-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3),$$

$$\frac{dy_3}{dt}=2k_3y_2y_4-\frac{k_2+2k_4}{k_2k_4}\alpha-\left[k_2y_1+\frac{k_2^2k_3(y_1y_2+y_2y_4)}{(k_4-k_2)^2y_1}\right]\hat{\varphi}_1(\mathbf{y})\exp\left\{-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}-\left[\frac{k_2k_4y_1}{k_2-k_4}\right.$$
$$\left.+\frac{k_3k_4(k_4-2k_2)(2k_4-k_2)}{(k_4-k_2)^3y_1}(y_1y_2+y_2y_4)\right]\hat{\varphi}_2(\mathbf{y})\exp\left[-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right],$$

$$\frac{dy_4}{dt}=k_1y_1y_2+2k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)-k_6y_4-\frac{2(k_2+k_4)}{k_2}\alpha-\left[k_2y_1-\frac{k_2k_3(k_4-2k_2)}{(k_4-k_2)^2y_1}(y_1y_2+y_2y_4)\right]$$
$$\times\hat{\varphi}_1(\mathbf{y})\exp\left\{-\left[k_2y_1+\frac{k_3(2k_4-k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}-\left[\frac{k_4(k_4-2k_2)y_1}{k_4-k_2}+\frac{k_3k_4(k_4-2k_2)(2k_4-k_2)}{(k_4-k_2)^3y_1}(y_1y_2+y_2y_4)\right]$$
$$\times\hat{\varphi}_2(\mathbf{y})\exp\left\{-\left[k_4y_1+\frac{k_3(k_4-2k_2)(y_1y_2+y_2y_4)}{(k_4-k_2)y_1}\right]t\right\}. \tag{77}$$

Similarly, the differential equation system for the solutions within the slow invariant manifold can be obtained by omitting the exponential terms

$$\frac{dy_1}{dt}=-k_1y_1y_2-3k_3y_2y_4+\frac{2(k_2+k_4)}{k_2k_4}\alpha,\quad \frac{dy_2}{dt}=-k_1y_1y_2-k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3),$$
$$\frac{dy_3}{dt}=2k_3y_2y_4-\frac{k_2+2k_4}{k_2k_4}\alpha,\quad \frac{dy_4}{dt}=k_1y_1y_2+2k_3y_2y_4-k_5y_2y_4(y_1+0.4y_2+6y_3)-k_6y_4-\frac{2(k_2+k_4)}{k_2k_4}\alpha. \tag{78}$$

Comparing Eqs. (76) and (78), we see that the first approximation contains more terms than the zeroth order one. Actually, Eqs. (76) and (78) can be obtained from Eq. (41) by substituting the zeroth and first order approximations for y_5 and y_6 within the slow invariant manifold into the first four equations, respectively, as follows:

$$y_5=\frac{2k_3y_2y_4}{k_2y_1}, \tag{79}$$

$$y_6=\frac{k_3y_2y_4}{k_4y_1}, \tag{80}$$

$$y_5=\frac{2k_3y_2y_4}{k_2y_1}-\frac{k_2+2k_4}{k_2^2k_4y_1}\alpha, \tag{81}$$

$$y_6=\frac{k_3y_2y_4}{k_4y_1}-\frac{\alpha}{k_4^2y_1}. \tag{82}$$

For the calculation of ignition profiles, it is necessary to calculate the temperature change from the energy balance equation (40). Substituting the above expressions for y_5 and y_6 into Eq. (40) and using the heats of formation ΔH_f^0 for all species, the first order approximation gives

$$\sigma C_p\frac{dT}{dt}=\sum_{i=1}^{4}\frac{dy_i}{dt}(-\Delta H_f^0)_i+\frac{2\alpha}{k_2}(-\Delta H_f^0)_5$$
$$+\frac{\alpha}{k_4}(-\Delta H_f^0)_6+[k_1y_1y_2+k_5y_2y_4(y_1+0.4y_2$$
$$+6y_3)](-\Delta H_f^0)_7-\frac{\chi S}{V}(T-T_a), \tag{83}$$

where $(\Delta H_f^0)_i$ represents the heat of formation for species y_i, $dy_i/dt(i=1, 2, 3, \text{and } 4)$ are given by Eq. (78), although we must neglect the term k_6y_4 in the equation for dy_4/dt, since $-\Delta H_6$ for reaction (6) was treated as zero in the full model. For the zeroth order approximation, one only needs to omit all the terms containing α. The results show that the first order approximation within the slow invariant manifold provides a good accuracy.

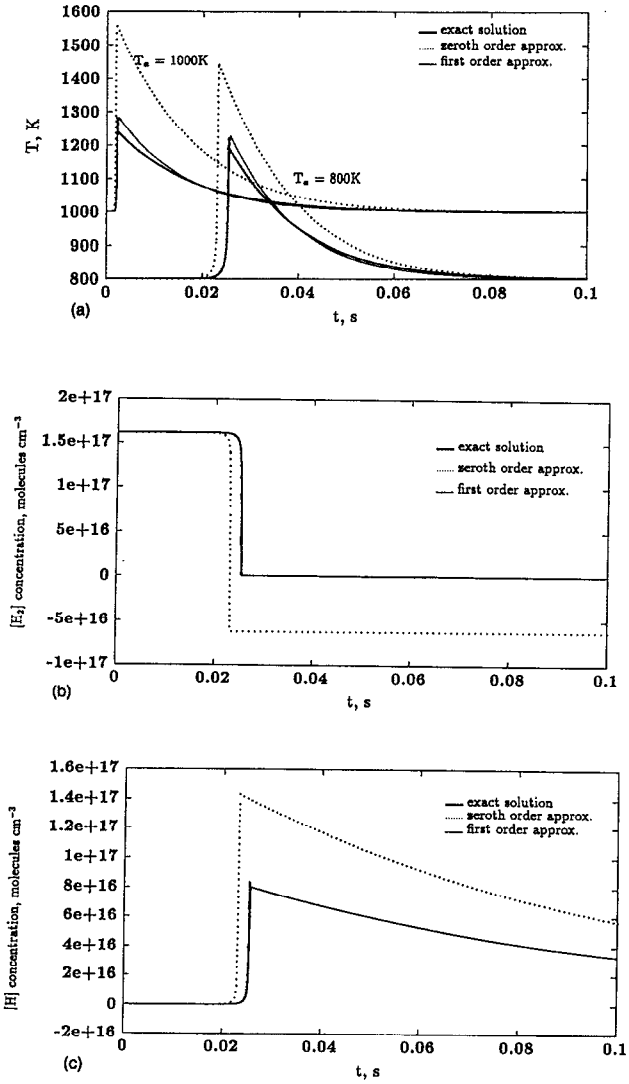

FIG. 1. Initial mixture H_2:O_2=2:1, pressure=20 Torr, and T_a=800 and 1000 K. (a) Temperature profiles; (b) concentration of H_2 at 800 K; and (c) concentration of H at 800 K.

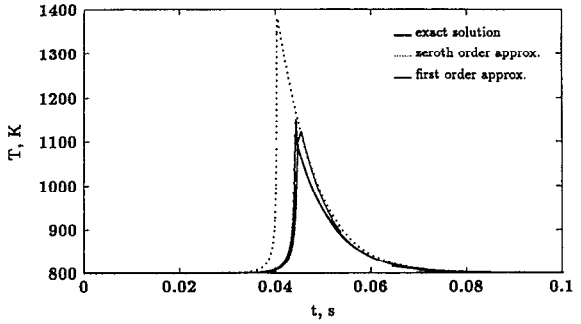

FIG. 2. Initial mixture H_2:O_2=2:1, pressure=10 Torr, T_a=800 K.

In Figs. 1–3, we present a comparison of the full equation system with the zeroth and first order lumped systems within the slow invariant manifold for a range of temperatures, pressures, and reaction mixtures. The zeroth order approximation fails to reproduce the maximum temperature rise even at 800 K, and we can see from Fig. 1(b) it even leads to negative steady-state concentrations in hydrogen when the ignition has taken place. The first order lumped scheme gives a very good approximation to the exact solution for both the temperature profile and the species concentrations at 20 Torr for both 800 and 1000 K as shown in Fig. 1. The maximum temperature rise and the time to ignition are both well reproduced. At a lower pressure of 10 Torr in Fig. 2, the accuracy of the lumped schemes is slightly less satisfactory in describing the maximum temperature rise, although the first order scheme gives an accurate description of the time to ignition. For a 1:1 initial mixture of hydrogen to oxygen shown in Fig. 3, the shape of the ignition peak is not so well represented by the lumped schemes. However, the inclusion of the first order term results in a significant improvement, which could be predicted from the fact that the extra term in the first order equations depends on the ratio y_2/y_1. In terms of the QSSA, this shows that the higher the initial concentration of oxygen compared to hydrogen, the larger the error in the QSSA.

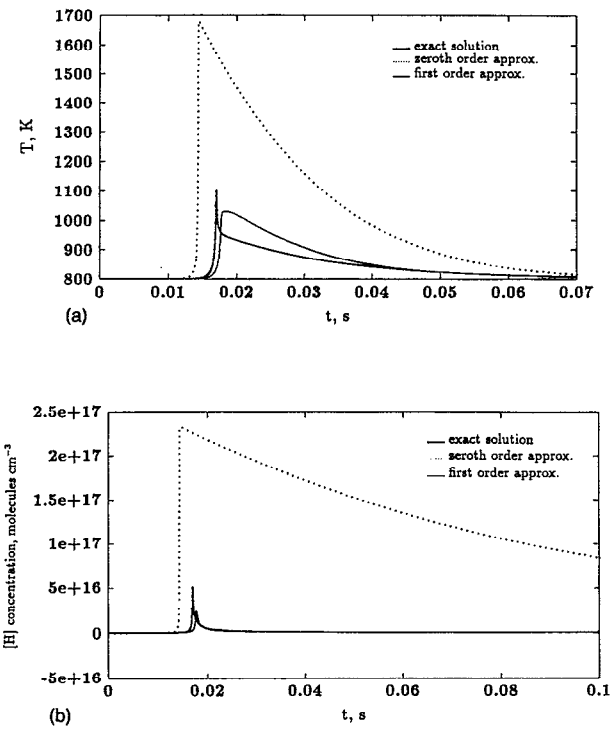

FIG. 3. Initial mixture H_2:O_2=1:1, pressure=20 Torr, T_a=800 K. (a) Temperature profile; (b) concentration of H.

The use of this model clearly shows the advantages of the algebraic approach in that it can reach any desired accuracy by using higher order approximations to form the lumped equations. Zeroth order approximations such as that given in the slow invariant manifold corresponding to the QSSA can be seen to lead to significant errors. Although we have only included up to first order terms in the present example, we can see that they provide a significant improvement in the solution. We again point out that we use the reaction scheme chosen here purely to illustrate the method. The lumped model in this case has all the limitations of the full reaction scheme, which is by no means comprehensive. We have, however, shown that it is possible to choose a single nonlinear transformation vector which produces a low dimensional model applicable over a range of parameters, temperatures, and initial conditions, reproducing many of the important reaction features of the full model.

V. CONCLUSIONS AND A DISCUSSION

A method for approximate constrained nonlinear lumping by the algebraic method in nonlinear perturbation theory has been presented. There is a one-to-one relationship between an n-dimensional ordinary differential equation system $d\mathbf{y}/dt=\mathbf{f}(\mathbf{y})$ and the linear partial differential operator $A=\Sigma_{i=1}^{n} f_i(\mathbf{y})(\partial/\partial y_i)$. Constrained lumping involves the reduction of the operator A to some partially canonical form, leaving some variables unlumped. The lumped variables are purely fast variables and their approximate analytical solutions can be obtained by a singular perturbation method. The inverse transformation can be used to return to the corresponding original variables. A reduced scheme can be derived by substituting the approximate expressions of these variables into the remaining differential equations for the unlumped variables.

The advantage of using constrained lumping is that some variables in the lumped scheme can remain as the original variables. The form of equations describing the dynamics of the original species can therefore be investigated without having to make the inverse transformation. In combustion calculations, this can provide advantages, since the thermodynamic or transport properties of lumped species would be hard to define. Further, although the lumped scheme will not in general be of kinetic form,[8] it may be possible in certain cases to make simplifications of the lumped equations in order to provide a kinetic scheme. The use of constrained lumping will then lead to simplified reaction schemes in terms of real chemical species rather than lumped species. The disadvantage of constrained lumping compared to un-

constrained lumping is that the form of the resulting equations is in general more complicated. The calculation of the right-hand sides is therefore more computationally time consuming. For unconstrained lumping, it is possible to use a simpler form for the equations and to use the inverse transformation at only specified output times, making the calculation more efficient. The choice of constrained lumping is only advantageous when it is necessary to keep some variables unlumped and is therefore problem specific.

Previously the authors have presented a singular perturbation method to determine nonlinear lumping schemes.[3] It can be proven that the singular perturbation approach is only a special case of constrained lumping by the algebraic method in nonlinear perturbation theory when the equations are linear in the deleted variables (see the Appendix). We have also illustrated that the quasisteady-state approximation (QSSA) can be derived as the zeroth order approximation of the algebraic method in nonlinear perturbation theory, when considered in the slow invariant manifold. The present method is therefore a much more general method than other approaches and can be applied to any form of equations. Both the QSSA and the singular perturbation approach depend on the original equations being linear in the deleted variables, which restricts the approach to only certain types of systems. For the QSSA, this restriction stems from the difficulty in solving sets of coupled nonlinear algebraic equations. Using the algebraic method in nonlinear perturbation theory, the original equations may take any form. Furthermore, zeroth order approximations such as the QSSA can clearly lead to errors both in species concentrations and temperature profiles.

Assuming that the sequence of M_i is convergent, then using the algebraic method, the lumped equations can be derived to any desired accuracy by adding more terms in the approximation. The main problem, however, is the complexity of the resulting equations. The greater accuracy achieved by using more terms in the lumped equations may be outweighed by the computational effort needed to compute the right-hand sides at each time step. For some systems, the second and higher order terms may even be too complicated to handle, although the calculations can be aided with the use of algebraic manipulation packages such as MATHEMATICA or REDUCE. The investigation of techniques to simplify the expressions for higher order terms would be of great benefit to the application of this approach and may be a topic for future study.

We have shown that the approach can be used to investigate systems where time scale separation exists between the species reaction fluxes. An eigenvalue investigation of a linear approximation of the system or CSP can reveal such time scales and therefore the number of fast modes. Since the approach results in the decoupling of purely fast variables, the fastest time scales are inevitably removed in the lumped scheme. Significant savings can therefore be made due to the decrease in time step allowed by the reduction in stiffness of the problem. For combustion systems, the time scale separation can be large enough that we do not need to consider the initial exponential decay of the fast variables. The exponential terms in time can therefore be removed from the lumped equations providing simplifications of the right-hand sides. In this case, the lumped system describes the dynamics in the slow invariant manifold.

For other systems, such as those found in biochemistry, there may not be such a time scale separation between the variables. In such cases, reduced schemes obtained by approaches such as the QSSA or global center manifold theories will not adequately describe the dynamics of the system, since the solution will not quickly reach the slow invariant manifold. The algebraic approach can still provide accurate lumped models, however, since it provides a method for the calculation of the exponential terms describing the collapse onto the manifold. The existence of a small parameter in the original equation system is not therefore necessary.[3]

The potential complexity of higher order terms may lead one to consider a numerical approach to finding reduced models, such as the CSP.[7] Certainly, such an approach can be applied more automatically than the algebraic method described here. However, since it provides transformations which are linear in the reaction rates, CSP cannot provide global reduced models for nonlinear systems. The reduced mechanism provided by CSP is local and therefore changes at points along each trajectory. This means that even though each reduced mechanism is of low dimension, there is a decrease in computational efficiency caused by updating the resulting equations. This updating also makes such mechanisms difficult to use in spatially inhomogeneous calculations since the reduced chemistry may change at each grid point. Using the algebraic method, it is possible to provide a more global lumped model which can be used over a whole trajectory, and over a range of initial conditions and parameter values. Caution should be used, however, in applying such models in parameter regions outside those tested during the lumping process.

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APPENDIX

Suppose a kinetic system can be described by a set of first order ordinary differential equations of the following form:

$$\frac{d\mathbf{y}}{dt} = \mathbf{a}(\mathbf{y}) + A(\mathbf{y})\mathbf{z}, \tag{A1}$$

$$\epsilon \frac{d\mathbf{z}}{dt} = \mathbf{b}(\mathbf{y}) + B(\mathbf{y})\mathbf{z}, \tag{A2}$$

where $\mathbf{y}$, $\mathbf{a}(\mathbf{y})$ and $\mathbf{z}$, $\mathbf{b}(\mathbf{y})$ are m- and k-dimensional vectors and function vectors with $m+k=n$, respectively; $A(\mathbf{y})$ and $B(\mathbf{y})$ are $m\times k$ and $k\times k$ function matrices and $B(\mathbf{y})$ is a matrix whose eigenvalues have negative real parts and the inverse $B^{-1}(\mathbf{y})$ can be given explicitly.

For such a system, we can prove that when ϵ is a small positive scalar, the lumped differential equation system of $\mathbf{y}$

given by the singular perturbation method[3] can be obtained by the constrained approximate lumping approach of the algebraic method in nonlinear perturbation theory.

The singular perturbation method gives a lumped differential equation system for $\mathbf{y}$ as follows:

$$\frac{d\mathbf{y}}{dt}=\mathbf{a}(\mathbf{y})-A(\mathbf{y})\mathbf{h}(\mathbf{y})+A(\mathbf{y})\phi(t), \tag{A3}$$

where

$$\mathbf{h}(\mathbf{y})=\sum_{i=0}^{\infty}\epsilon^i\mathbf{h}_i(\mathbf{y}) \tag{A4}$$

with

$$\mathbf{h}_0(\mathbf{y})=B^{-1}(\mathbf{y})\mathbf{b}(\mathbf{y}), \tag{A5}$$

$$\mathbf{h}_1(\mathbf{y})=B^{-1}(\mathbf{y})\mathbf{h}_{0\mathbf{y}}(\mathbf{y})[\mathbf{a}(\mathbf{y})-A(\mathbf{y})\mathbf{h}_0(\mathbf{y})], \tag{A6}$$

$$\ldots,$$

$$\phi(t)=\sum_{i=0}^{\infty}\epsilon^i\phi_i(t) \tag{A7}$$

with

$$\phi_0(t)=\exp\{B[\mathbf{y}(0)]t/\epsilon\}\phi_0(0), \tag{A8}$$

$$\phi_1(t)=\exp\{B[\mathbf{y}(0)]t/\epsilon\}\mathbf{h}_1[\mathbf{y}(0)] + \int_0^t \exp\{\epsilon^{-1}B[\mathbf{y}(0)](t-s)\}\epsilon^{-1}\mathbf{h}_{0\mathbf{y}}[\mathbf{y}(0)]A[\mathbf{y}(0)] \times\exp\{\epsilon^{-1}B[\mathbf{y}(0)]s\}ds\,\phi_0(0), \tag{A9}$$

Now we can prove that under the condition that y_i $(i=1-m)$ is left unlumped, the constrained approximate lumping approach by the algebraic method in nonlinear perturbation theory will give the same result.

Set

$$\tau=t/\epsilon. \tag{A10}$$

Then Eqs. (A1) and (A2) become

$$\frac{d\mathbf{y}}{d\tau}=\epsilon[\mathbf{a}(\mathbf{y})+A(\mathbf{y})\mathbf{z}], \tag{A11}$$

$$\frac{d\mathbf{z}}{d\tau}=\mathbf{b}(\mathbf{y})+B(\mathbf{y})\mathbf{z}. \tag{A12}$$

Let us introduce a new variable vector

$$\phi=B^{-1}(\mathbf{y})\mathbf{b}(\mathbf{y})+\mathbf{z}, \tag{A13}$$

which gives

$$\mathbf{z}=\phi-B^{-1}(\mathbf{y})\mathbf{b}(\mathbf{y}). \tag{A14}$$

For the new dependent variable set $\{\mathbf{y},\phi\}$, the corresponding differential equation system is the following:

$$\frac{d\mathbf{y}}{d\tau}=\epsilon[\mathbf{a}(\mathbf{y})-A(\mathbf{y})B^{-1}(\mathbf{y})\mathbf{b}(\mathbf{y})+A(\mathbf{y})\phi], \tag{A15}$$

$$\frac{d\phi}{d\tau}=\frac{d}{d\mathbf{y}}[B^{-1}(\mathbf{y})\mathbf{b}(\mathbf{y})]\frac{d\mathbf{y}}{d\tau}+\frac{d\mathbf{z}}{d\tau}=B(\mathbf{y})\phi + \epsilon\frac{d}{d\mathbf{y}}[B^{-1}(\mathbf{y})\mathbf{b}(\mathbf{y})][\mathbf{a}(\mathbf{y})-A(\mathbf{y})B^{-1}(\mathbf{y})\mathbf{b}(\mathbf{y}) +A(\mathbf{y})\phi]. \tag{A16}$$

Setting

$$\mathbf{h}_0(\mathbf{y})=B^{-1}(\mathbf{y})\mathbf{b}(\mathbf{y}), \tag{A17}$$

$$\mathbf{h}_{0\mathbf{y}}(\mathbf{y})=\frac{d}{d\mathbf{y}}[B^{-1}(\mathbf{y})\mathbf{b}(\mathbf{y})], \tag{A18}$$

gives

$$\frac{d\mathbf{y}}{d\tau}=\epsilon[\mathbf{a}(\mathbf{y})-A(\mathbf{y})\mathbf{h}_0(\mathbf{y})+A(\mathbf{y})\phi], \tag{A19}$$

$$\frac{d\phi}{d\tau}=B(\mathbf{y})\phi+\epsilon\mathbf{h}_{0\mathbf{y}}(\mathbf{y})[\mathbf{a}(\mathbf{y})-A(\mathbf{y})\mathbf{h}_0(\mathbf{y})+A(\mathbf{y})\phi]. \tag{A20}$$

The corresponding linear partial differential operator of Eqs. (A19) and (A20) is defined as follows:

$$A=A_0+\epsilon A_1 \tag{A21}$$

with

$$A_0=(B(\mathbf{y})\phi,\nabla_\phi), \tag{A22}$$

$$A_1=(a(\mathbf{y})-A(\mathbf{y})\mathbf{h}_0(\mathbf{y})+A(\mathbf{y})\phi,\nabla_{\mathbf{y}})-(\mathbf{h}_{0\mathbf{y}}(\mathbf{y})[\mathbf{a}(\mathbf{y}) -A(\mathbf{y})\mathbf{h}_0(\mathbf{y})+A(\mathbf{y})\phi],\nabla_\phi). \tag{A23}$$

Notice that A_0 is of a quasilinear canonical form. Now we employ the algebraic method in nonlinear perturbation theory to transform A into a canonical form M similar to A_0 by

$$M=e^{-S}Ae^{S}=A_0+\epsilon M_1+\cdots, \tag{A24}$$

where

$$S=\epsilon S_1+\epsilon^2 S_2+\cdots. \tag{A25}$$

For constrained lumping, we set

$$S_1\mathbf{y}=\mathbf{0}, \tag{A26}$$

$$S_1\phi=B^{-1}(\mathbf{y})\mathbf{h}_{0\mathbf{y}}(\mathbf{y})[\mathbf{a}(\mathbf{y})-A(\mathbf{y})\mathbf{h}_0(\mathbf{y})]. \tag{A27}$$

For the sake of simplicity, we have used the vector form for the coefficients of S_1. Then we have

$$M_1\mathbf{y}=A_0S_1\mathbf{y}-S_1A_0\mathbf{y}+A_1\mathbf{y}=A_1\mathbf{y}, \tag{A28}$$

$$M_1\phi=A_0S_1\phi-S_1A_0\phi+A_1\phi=-B(\mathbf{y})S_1\phi+A_1\phi =-\mathbf{h}_{0\mathbf{y}}(\mathbf{y})[\mathbf{a}(\mathbf{y})-A(\mathbf{y})\mathbf{h}_0(\mathbf{y})]+\mathbf{h}_{0\mathbf{y}}(\mathbf{y}) \times[\mathbf{a}(\mathbf{y})-A(\mathbf{y})\mathbf{h}_0(\mathbf{y})+A(\mathbf{y})\phi] =\mathbf{h}_{0\mathbf{y}}(\mathbf{y})A(\mathbf{y})\phi. \tag{A29}$$

If we only consider the first order approximation, i.e.,

$$M\approx A_0+\epsilon M_1, \tag{A30}$$

the resultant $M\mathbf{y}$ and $M\phi$ are as follows:

$$M\mathbf{y}=A_1\mathbf{y}, \tag{A31}$$

$$M\phi=[B(\mathbf{y})+\epsilon\mathbf{h}_{0\mathbf{y}}(\mathbf{y})A(\mathbf{y})]\phi. \tag{A32}$$

The corresponding differential equation system of ϕ is

$$\frac{d\phi}{d\tau}=[B(\mathbf{y})+\epsilon\mathbf{h}_{0\mathbf{y}}(\mathbf{y})A(\mathbf{y})]\phi. \tag{A33}$$

As ϕ vanishes much faster than the changes of $\mathbf{y}$, the above system can be approximately solved by the singular perturbation method. The solution is only composed of the initial boundary layer solution for $\mathbf{y}=\mathbf{y}(0)$. Set

$$\phi=\sum_{i=0}^{\infty}\epsilon^i\phi_i, \tag{A34}$$

where ϕ_i are all k-dimensional vectors. Substituting ϕ into Eq. (A33) and comparing the terms with the like powers of ϵ on both sides gives the equations to determine ϕ_i. For ϕ_0, we have

$$\frac{d\phi_0}{d\tau}=B[\mathbf{y}(0)]\phi_0. \tag{A35}$$

Notice that ϕ_0 is the zeroth order approximation of the lumped variable ϕ. Its initial value is equal to the initial value of the original variable $\phi(0)$, i.e.,

$$\begin{aligned}\phi(0)&=B^{-1}[\mathbf{y}(0)]\mathbf{b}[\mathbf{y}(0)]+\mathbf{z}(0)\\&=B^{-1}[\mathbf{y}(0)]\mathbf{b}[\mathbf{y}(0)]=\mathbf{h}_0[\mathbf{y}(0)].\end{aligned} \tag{A36}$$

Its solution is

$$\phi_0=\exp\{B[\mathbf{y}(0)]\tau\}\phi_0(0)=\exp\{B[\mathbf{y}(0)]t/\epsilon\}\phi_0(0). \tag{A37}$$

For $\phi_1(\tau)$, we have

$$\begin{aligned}\frac{d\phi_1}{d\tau}&=B[\mathbf{y}(0)]\phi_1+\mathbf{h}_{0\mathbf{y}}[\mathbf{y}(0)]A[\mathbf{y}(0)]\phi_0\\&=B[\mathbf{y}(0)]\phi_1\\&\quad+\mathbf{h}_{0\mathbf{y}}[\mathbf{y}(0)]A[\mathbf{y}(0)]\exp\{B[\mathbf{y}(0)]\tau\}\phi_0(0).\end{aligned} \tag{A38}$$

As ϕ_1 is the first order approximation of the lumped variable ϕ, its initial value is

$$\begin{aligned}\phi_1(0)=S_1\phi(0)=B^{-1}[\mathbf{y}(0)]\mathbf{h}_{0\mathbf{y}}[\mathbf{y}(0)]\{\mathbf{a}[\mathbf{y}(0)]\\-A[\mathbf{y}(0)]\mathbf{h}_0[\mathbf{y}(0)]\}.\end{aligned} \tag{A39}$$

Set

$$\mathbf{h}_1(\mathbf{y})=B^{-1}(\mathbf{y})\mathbf{h}_{0\mathbf{y}}(\mathbf{y})[\mathbf{a}(\mathbf{y})-A(\mathbf{y})\mathbf{h}_0(\mathbf{y})]. \tag{A40}$$

Then

$$\phi_1(0)=\mathbf{h}_1[\mathbf{y}(0)]. \tag{A41}$$

The solution is

$$\begin{aligned}\phi_1(\tau)&=\exp\{B[\mathbf{y}(0)]\tau\}\mathbf{h}_1[\mathbf{y}(0)]\\&\quad+\int_0^{\tau}\exp\{B[\mathbf{y}(0)](\tau-s)\}\mathbf{h}_{0\mathbf{y}}[\mathbf{y}(0)]A[\mathbf{y}(0)]\\&\quad\times\exp\{B[\mathbf{y}(0)]s\}ds\ \phi_0(0).\end{aligned} \tag{A42}$$

Substituting $\tau=t/\epsilon$ into Eq. (A42) will give Eq. (A9).

Since we only consider the first order approximation, the original variable ϕ can be given by

$$\phi=\phi-\epsilon S_1\phi=\phi_0+\epsilon\phi_1-\epsilon\mathbf{h}_1(\mathbf{y}). \tag{A43}$$

Here for convenience we do not use different symbols for the original and lumped variables. Substituting Eq. (A43) into Eq. (A19) yields

$$\frac{d\mathbf{y}}{d\tau}=\epsilon\{\mathbf{a}(\mathbf{y})-A(\mathbf{y})[\mathbf{h}_0(\mathbf{y})+\epsilon\mathbf{h}_1(\mathbf{y})]+A(\mathbf{y})(\phi_0+\epsilon\phi_1)\}, \tag{A44}$$

or

$$\frac{d\mathbf{y}}{dt}=\mathbf{a}(\mathbf{y})-A(\mathbf{y})[\mathbf{h}_0(\mathbf{y})+\epsilon\mathbf{h}_1(\mathbf{y})]+A(\mathbf{y})(\phi_0+\epsilon\phi_1). \tag{A45}$$

The results of $\mathbf{h}_0$, $\mathbf{h}_1$ and ϕ_0, ϕ_1 are the same as those given by the singular perturbation method. A similar proof for higher order $\mathbf{h}_i$ and ϕ_i can be given. To save space, we will not give it here. This shows that the singular perturbation method is only a special case of the constrained lumping approach given by the algebraic method in nonlinear perturbation theory when the equations are linear in the deleted variables. Consequently, the QSSA is the zeroth order approximation in the invariant manifold for this case.

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