Generalized Steady-State Method for Stiff Equations

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Theme

THE economical solution of stiff differential equations is usually obtained by the use of implicit methods or special purpose explicit techniques. Implicit techniques, though possessing desirable stability characteristics, usually depend upon matrix operations for solution which become increasingly costly as the number of dependent variables increases. Thus, a trade-off exists between the large increase in step size possible and the expense of many more computer operations at each step, particularly for systems with many variables. Previous explicit methods tend to lack generality because they rely on approximations to the exact equations which exploit the characteristics of a particular set of equations. The technique outlined in this paper is explicit yet general as it solves the exact equations in an approximate manner. The nature of the approximation makes it especially suited to systems describing chemical reactions. The method is based on the steady-state (or quasi-equilibrium) approximation long used in chemical kinetics and is referred to herein as the Generalized Steady State Method (GSSM). A simple yet reliable means for identifying those variables whose values may be approximated and a direct estimate of the resulting error are provided. The method can be interpreted as an application of matched asymptotic expansions which avoids a detailed solution in the inner region. No detailed a priori understanding of the system to be analyzed is necessary; in fact the method can help towards an understanding of the system. Different applications require little modification of the basic technique. The simplicity of the GSSM makes it worthy of consideration in many applications, especially when more sophisticated programs are not readily available.

Content

The characteristic values of a set of ordinary differential equations are determined from the roots of its Jacobian matrix. For weakly coupled systems these values are approximately given by the matrix diagonal elements. Since the equations describing chemically reacting systems are often weakly coupled, this approximation is frequently valid in such applications. Mathematically this is because the diagonal elements of the Jacobian for chemical systems are always negative while contributions to the off-diagonal elements may be positive or negative and hence tend to cancel. It is a simple matter to determine if the diagonal elements are dominant in a given application.

Consideration of the diagonal elements provides a convenient means for sorting out the time scales of each of the dependent variables by defining a set of characteristic times,

$$\tau_i = \left| \frac{\partial^2 y_i}{\partial y_i \partial t}^{-1} \right| \tag{1}$$

If the resulting set of τ_i's contains one or more members which are, say, two orders of magnitude or more smaller than the remaining τ_i's of the system, stiffness is likely to be a problem and use of the GSSM may be profitable.

Those species with small τ_i's, called intermediates, quickly reach a quasi-equilibrium with the remainder of the system. Let the governing differential equations be of the form

$$(\mathrm{d}y_m/\mathrm{d}t) = F(y_m, y_i, y_p) \tag{2}$$

where y_m is a particular intermediate, y_i the other intermediates, and y_p the remaining variables in the system, called principals. The local value of y_m, $y_m^{(0)}$, is obtained by setting the left-hand side of Eq. (2) equal to zero and solving the resulting algebraic equations. This process is applied to the entire set of intermediates using any suitable root finding technique, such as the Newton-Raphson method. Since the previous local values are known and, by definition, not very different from those at the current time, the initial estimates required for such iterative techniques tend to be accurate and convergence is very rapid. Then the values of the principals are easily determined by an explicit integration technique, provided the step size chosen is larger than the largest τ_i among the intermediates, thus "stepping over" the region where they are not in equilibrium with the rest of the system.

Two cautions must be noted. It is possible during part of the transient associated with the intermediates that instead of decreasing exponentially toward an asymptotic steady state, the intermediates increase exponentially. No quasi-equilibrium state then actually exists and use of the GSSM will lead to physically meaningless negative concentrations. If this occurs, it is necessary to transfer that intermediate with the largest τ_i to the set of principals and return the system to the last successful calculation and repeat the time step. Also, for chemical systems the number of intermediates must not exceed $M-E-1$ where M is the total number of active species and E is the number of elements.[1] This rule is a consequence of element conservation and if violated the entire system is likely to jump abruptly to an equilibrium-like composition, followed by rapid spurious oscillations.

An estimate of the errors in the steady-state values for the intermediates may be obtained by differentiating Eq. (2) with respect to time, and using the chain rule to obtain the $(dy_i^{(0)}/dt)$ as a function of the steady-state values. The left-hand side of Eq. (2) is then replaced by $(dy_i^{(0)}/dt)$ and the resulting algebraic equation solved for the next approximation, $y_m^{(1)}$. The difference between $y_i^{(0)}$ and $y_i^{(1)}$ has been suggested by Hirschfelder[2] and Williams[3] to determine the validity of the classical steady-state approximation. Hiestand[1] has shown that to second order in this error, this is equivalent to computing the first two terms in a matched asymptotic expansion solution to Eq. (2). Indeed, the steady-state solution represents the first term in the outer solution and τ_i corresponds to the extent of the inner region. Since the inner region solutions must reach a finite limit for large time, the need for the exponentials to decay in this region is clear.

Because the numerical calculation of the errors just described takes approximately as long to perform as does the calculation of the steady-state result for a given time step,

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Table 1 Results for stoichiometric hydrogen-air reaction, $t = 0.793 \times 10^{-5}$ sec

Mass fraction	H	O	H_2O	OH	O_2	H_2	T, K	Running Time, sec
Exact	3.98×10^{-3}	2.09×10^{-2}	1.55×10^{-1}	1.81×10^{-2}	5.12×10^{-2}	5.98×10^{-3}	2050	40.0
δ max = 0.05								
$z = 2$	4.02×10^{-3}	2.15×10^{-2}	1.57×10^{-2}	1.84×10^{-2}	5.36×10^{-2}	5.98×10^{-3}	2040	7.2
% error	1.00	2.88	1.29	1.66	4.69	0.0	0.49	
δ max = 0.2								
$z = 2$	4.38×10^{-3}	2.50×10^{-2}	1.57×10^{-1}	1.76×10^{-2}	6.75×10^{-2}	5.57×10^{-3}	1950	2.5
% error	12.3	19.6	1.29	2.76	31.9	6.85	4.90	

Table 2 Results for Friedlander-Seinfield photochemical smog model, t 10.4 min

Concentration ppm.	NO_2	NO	O	O_2	O_3	RH	R*	PAN
One intermediate	.424	.757	$.408 \times 10^{-8}$	$.210 \times 10^{-6}$	$.909 \times 10^{-3}$	1.99	$.398 \times 10^{-4}$	$.189 \times 10^{-1}$
3 intermediate	.428	.752	$.412 \times 10^{-8}$	$.210 \times 10^{-6}$	$.926 \times 10^{-3}$	1.99	$.397 \times 10^{-4}$	$.191 \times 10^{-1}$
% error	.95	.66	.98	0.0	1.87	0.0	.25	1.06

error checks are not made at every time step. The choice of maximum normalized error permitted, δ_{max}, directly controls the set of intermediates. Large values of δ_{max} permit rapid, less accurate calculations; smaller values yield increasingly more accurate results but at a slower computation rate. If a δ_{max} is exceeded during a given error check, the intermediate set must be reduced as previously described for negative concentrations.

The success of the GSSM in selecting intermediates and the accuracy of the results were verified by application of the method to two reacting systems. The combustion of a stoichiometric mixture of hydrogen and oxygen studied earlier by Moretti[4] and the simplified model for photochemical smog production proposed by Friedlander and Seinfeld[5] were analyzed on an IBM System 360, model 65 computer. The Improved Euler Method was used for conventional integration in the hydrogen-oxygen system, while the Runge-Kutta method was employed for the photochemical smog system.

Depending upon the δ_{max} permitted, the method automatically makes calculations treating both O and OH or just OH as intermediates in the H_2-O_2 system. Results with the single intermediate OH ($\delta_{max} = 0.05$) are more accurate, as shown in Table 1. There z is the minimum ratio between the smallest τ_i among the principals and the largest τ_i among the intermediates. The method's determination of O and OH as intermediates during the early phase of this reaction is consistent with work done by Bradley[6] and Schott and Kinsey,[7] who also pointed out that the concentration of H grew exponentially during the earliest stages of this reaction. This behavior manifests itself in the present method in negative concentrations when H is treated as an intermediate, a choice otherwise acceptable by virture of its initial τ_i value and the maximum intermediate rule. Bradley also assumed an expression for the characteristic time of the initial reaction phase by assuming that only OH was in steady state, a choice which White and Moore[8] found gives a better fit to experimental data than does using OH plus O.

The equations governing Friedlander and Seinfeld's smog model were also solved using the GSSM. This model consists of eight active species and demonstrates the essential chain-like behavior of more detailed formulations. O, O_3, and R*, an unspecified oxygen-carrying free radical, were automatically selected as intermediates throughout the calculation on the basis of their τ_i values and the maximum intermediate rule, a choice consistent with the set used by Friedlander and Seinfeld based on careful examination of the reacting system. Because of the increase in step-size over a conventional explicit procedure was greater than 10^6, no comparison with exact values was made. Instead the calculation was repeated with only O, the species with by far the smallest τ_i treated as an intermediate. Results of both calculations at $t = 10.4$ min are presented in Table 2.

The GSSM thus provides an attractive and easily applied method for dealing with stiff equations describing chemically reacting systems. It is able to provide accurate solutions at a significant increase in computational speed, with the range of speed and accuracy under the user's control through the choice of several operating parameters. It has been found to reflect the actual chemical behavior of the systems studied and it reduces to ordinary numerical integration if the equations are not stiff.

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