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An Effective Numerical Integration Method for Typical Stiff Systems

There is an equivalence between stiff and singularly perturbed systems of ordinary differential equations. This feature is exploited in this paper by numerically employing recent singular perturbation methods to attack troublesome boundary layer stage of the solution in which some variables have very short response times. The numerical method affords a means of essentially determining the thickness of this boundary layer. The algorithm is capable of high stability and accuracy for the commonly occurring stiff system, whether or not it is in singularly perturbed form. Application to a singularly perturbed reaction system and a highly stiff reactor system not in singularly perturbed form demonstrate the effectiveness and utility of this approach.

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SCOPE

Many commonly occurring physical and chemical dynamic systems have widely separated time constants. These systems are often represented by sets of initial-value ordinary differential equations which possess variables that rapidly change during time intervals much smaller than the duration of the phenomenon of interest (Lapidus et al., 1973). This presents the numerical integration difficulties associated with such stiff systems. Thus even integration routines stable for any step size (so-called "A-stable" methods) have accuracy problems in following the eigenvalues large in absolute value which damp out early in the solution. This error can easily propagate to destroy the remainder of the transient.

It is of major importance that the practitioner be able to identify the occurrence of a stiff problem. Otherwise, confusion can arise as to why the commonly available integration routines require inordinately small step sizes to obtain an insignificant fraction of the transient (at great expense in computation time). Even when the nature of the difficulty is realized, the popular decision to turn to complex analytical asymptotic methods (MacMillan, 1968) or pseudo steady state hypotheses (Gelinas, 1972) must be viewed with caution as the degree of error introduced is unknown. A number of viable alternatives for the direct numerical integration have been emerging rather recently, however (Lapidus et al., 1973; Seinfeld et al., 1970), and knowledge of these would prove valuable to the general user.

The present study, based on an extension of Miranker (1972), offers one such technique capable of high numerical stability and accuracy. It is particularly effective for systems having some variables with very short initial response times, as frequently occurs within chemical engineering contexts.

Details of the numerical algorithm are presented here as well as the use of the algorithm for two examples of direct interest to the chemical engineer. These examples are the thermal decomposition of ozone and the dynamic behavior of a catalytic fluidized bed. Many other stiff problems are also identified.

CONCLUSIONS AND SIGNIFICANCE

Recognition of the equivalence of stiff and singularly perturbed equations makes available new tools for the solution of both forms of equations. In this study, use is made of singular perturbation methods to develop a numerical technique capable of high stability and accuracy. A unique feature present is the ability to monitor the contribution of the stiff component to assess when the solution is out of the boundary layer. Thereafter the bulk of the transient may be obtained without the accuracy problems associated with this initial section. The numerical approach is applicable to numerous problems in chemical engineering and other disciplines where currently inadequate solution procedures are employed.

OCCURRENCE AND NUMERICAL DIFFICULTY OF STIFF SYSTEMS

Qualitatively, strong requirements on the numerical stability of a method (that is, on the step size h) for an accurate solution is referred to as stiff. Thus all systems possess a degree of stiffness and can benefit increased stability bounds, but the problems of primary concern here are those practically unsolvable by standard techniques.

Such problems abound in chemical engineering. Stiff characteristics have long been the motivation for the pseudo steady state hypothesis in chemical kinetics (Curtiss and Hirschfelder, 1952) although this approximation may not always be desirable (Edelson, 1973). A wide variety of kinetic mechanisms from chain reactions (Creighton, 1971) to autocatalysis (Schneider, et al., 1972) and to enzyme reactions (Garfinkel, 1973) are typically stiff. Chemical reaction coupled with transport phenomenon are further examples as in reactor dynamics (Schneider et al., 1973; O'Malley, 1969; Amundson, 1965), combustion processes (De Groat, 1965), and boundary layer flows (Riley, 1972). Stiff systems arise in all the classic areas of heat (Descloux, 1970) and mass transfer (Distefano, 1968), fluid mechanics (Ackerberg, 1973; 1971), and control (Yackel, 1973; O'Malley, 1972).

The stability limitations in most standard techniques for an n-dimensional system is that they require $\max_i |h\lambda_i|$, $i = 1, 2, \ldots, n$, where λ_i's are the local eigenvalues, be bounded by a single small number, typically in the 1 to 10 range. Thus if a single eigenvalue is large in absolute value, severe restrictions are placed on the step size. Depending upon the length of the solution interval of interest, this can demand a great deal of computation time. In addition to the requirement of stable integration is accurate integration. If the fast modes significantly contribute to the solution in a finite region, the accuracy of approximating this contribution is poorer the larger $|h\lambda_i|$. Thus although these errors will eventually decay with a stable method, they may destroy the reliability of much of the computed transient. Further, there are limits on how small h can be before roundoff errors accumulate and render this calculation worthless.

In order to make the nature of the problem clearer, consider a specific linear time invariant system:

$$\begin{bmatrix} \dot{x} \\ \dot{y} \end{bmatrix} = \begin{bmatrix} \lambda_1 & 0 \\ \kappa & \lambda_2 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}, \begin{bmatrix} x(0) \\ y(0) \end{bmatrix}$$

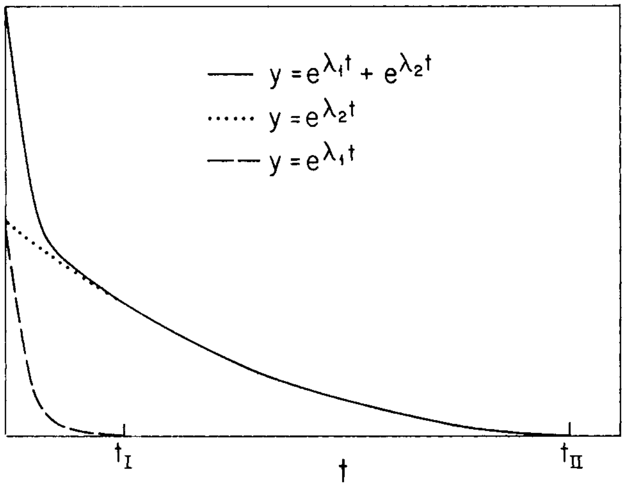

Fig. 1. Illustration of boundary layer contribution for the two variable example having widely separated eigenvalues.

with the analytic solution

$$x(t) = x(0) \exp(\lambda_1 t)$$

$$y(t) = C_1 \exp(\lambda_1 t) + C_2 \exp(\lambda_2 t)$$

where

$$C_1 = \frac{\kappa x(0)}{\lambda_1 - \lambda_2}, \quad C_2 = y(0) - C_1$$

Suppose $\lambda_2 << \lambda_1 < 0$ and $C_1 = C_2 = 1$. Then the solution for $y(t)$ may apear as in Figure 1.

It is evident from Figure 1 that the contribution to the solution from the term involving λ_1 is negligible after t_I (the boundary layer), yet its presence will fix the maximum allowable step size through the domain of interest by the bound on $\max_i |h\lambda_i|$. Stiff stability requirements arise when the domain of interest is much larger than t_I. This domain is usually determined by min $|\lambda_i|$ ($\lambda_i < 0V_i$) until a steady state has essentially been reached (t_{II} in Figure 1) although for some nonlinear problems this may be difficult to assess. A spread in eigenvalue magnitudes then defines the stiff problem. For some applications, however, the domain of concern is the boundary layer itself (Patterson and Cresswell, 1971), so that small time steps are desirable; in this domain the problem is not stiff even with very large eigenvalues. On the other hand, the domain may be so large as to make the problem stiff even if all eigenvalues are of moderate magnitude. For example, some iterative schemes involved with solving the two point boundary value problem of a tubular reactor with axial dispersion (Corbo and Lapidus, 1972) require continuation of the solution down the entire length of the reactor for each iteration, while the process variables may reach values constant for practical purposes near the entrance. Thus one may suggest the qualitative statement of the following:

Definition: An n-dimensional system of initial-value ordinary differential equations,

$$\frac{dz(t)}{dt} = \mathbf{F}(\mathbf{z}); \ \mathbf{z}(t_0)$$

is called stiff if the local Jacobian $(\partial \mathbf{F}/\partial \mathbf{z})$ contains at least one eigenvalue that does not contribute significantly over most of the domain of interest.

EQUIVALENCE OF STIFF AND SINGULARLY PERTURBED DIFFERENTIAL EQUATIONS

Consider a two variable set of first-order ordinary differential equations with a small parameter ϵ multiplying the derivative of one of the variables, the type of system for which singular perturbation methods have been developed:

$$\begin{aligned} \frac{dx}{dt} &= f(x, y, \epsilon), \ x(0) = \zeta \\ \epsilon \frac{dy}{dt} &= g(x, y, \epsilon), \ y(0) = \eta \end{aligned} \tag{1}$$

where $f(0, 0, \epsilon) = g(0, 0, \epsilon) = 0$. If (1) is linearized along its trajectory, it may be expressed as

$$\begin{bmatrix} \dfrac{dx}{dt} \\ \dfrac{dy}{dt} \end{bmatrix} = \begin{bmatrix} f_x & f_y \\ g_x/\epsilon & g_y/\epsilon \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}, \begin{bmatrix} x(0) \\ y(0) \end{bmatrix} = \begin{bmatrix} \zeta \\ \eta \end{bmatrix} \tag{2}$$

Examination of the Jacobian eigenvalues indicates that their spread increases the smaller ϵ becomes, one approaches zero while the other grows larger in absolute value. The occurrence of an eigenvalue large in absolute value indicates a stiff problem; thus (2) can be regarded as the linearized representation of a stiff system with widely separated eigenvalues. It then follows that such a stiff system and the singular perturbation form of (1) are at least locally equivalent.

It will be shown subsequently that the parameter ϵ is introduced into the general stiff system (13) merely as a bookkeeping device to systematically group terms of comparable degrees of accuracy. Use of the artificial parameter ϵ has demonstrated its convenience in many common solution approximation schemes of classical implicit function theory (Bellman, 1964). Thus (1) should be viewed as identically equivalent to the general stiff system form of (13).

This equivalence will allow recent developments in singular perturbation theory to be used in obtaining an effective procedure for the numerical integration of either equation type. It will be shown that the resulting algorithm does not require identification of the perturbing parameter ϵ, and hence is quite applicable to the general stiff system.

FORMAL PERTURBATION METHOD

In this section, latest advancements in the theory for obtaining the solution properties of ordinary differential equations with small parameters as presented by Hoppensteadt (1971) are used to develop first-order asymptotic expansions for the entire domain of interest.

Consider initial value problems of the form of (1) with the perturbing parameter ϵ small. First assume the solution may be approximated by the simple first-order expansion in the (outer) variables, obtained by truncation from the full infinite power series ϵ expansion:

$$\begin{aligned} x^{\star} &= x_0 + \epsilon x_1 \\ y^{\star} &= y_0 + \epsilon y_1 \end{aligned} \tag{3}$$

Substitute $(x^{\star}, y^{\star})$ into (1) for (x, y) and expand about $(x_0(t), y_0(t))$. Matching terms with like powers of ϵ results in

$$\frac{dx_0}{dt} = f(x_0, y_0, \epsilon),\ x_0(0) = \zeta \tag{4a}$$

$$0 = g(x_0, y_0, \epsilon) \tag{4b}$$

and

$$\frac{dx_1}{dt} = f_x(x_0, y_0)x_1 + f_y(x_0, y_0)y_1,\ x_1(0) = 0 \tag{5a}$$

$$\frac{dy_0}{dt} = g_x(x_0, y_0)x_1 + g_y(x_0, y_0)y_1 \tag{5b}$$

An inconsistency can arise when (4b) is not satisfied by (ζ, η). To alleviate this, additional (inner) variables are introduced which are particularly important in the very early stages of the transient. Expanding these variables to first order in ϵ and adding them to (3) gives the new composite solution approximation (x^*, y^*):

$$\begin{aligned} x^*(t) &= x_0(t) + \epsilon x_1(t) + X_0(t/\epsilon) + \epsilon X_1(t/\epsilon) \\ y^*(t) &= y_0(t) + \epsilon y_1(t) + Y_0(t/\epsilon) + \epsilon Y_1(t/\epsilon) \end{aligned} \tag{6}$$

A boundary layer type characteristic is required of the inner variables:

$$\lim_{t/\epsilon \to \infty} X_0 = X_1 = Y_0 = Y_1 = 0 \tag{7}$$

Let $\tau = t/\epsilon$ and make this variable change in (1):

$$\begin{aligned} \frac{dx}{d\tau} &= \epsilon f(x, y, \epsilon),\ x(0) = \zeta \\ \frac{dy}{d\tau} &= g(x, y, \epsilon),\ y(0) = \eta \end{aligned} \tag{8}$$

a set of regularly perturbed equations. Now substitute (x^*, y^*) into (8) and expand about $(x_0(\epsilon\tau) + X_0(\tau), y_0(\epsilon\tau) + Y_0(\tau))$. Matching terms with like powers in ϵ results in the following as $\epsilon \to 0$:

$$\begin{aligned} \frac{dX_0}{d\tau} &= 0 \\ \frac{dY_0}{d\tau} &= g(x_0(0) + X_0(\tau),\ y_0(0 + Y_0(\tau)) \end{aligned} \tag{9}$$

and

$$\begin{aligned} \frac{dX_1}{d\tau} &= f(x_0(0) + X_0(\tau),\ y_0(0 + Y_0(\tau)) \\ &\qquad - f(x_0(0),\ y_0(0)) \\ \frac{dY_1}{d\tau} &= g_x X_1(\tau) + g_y y_1(0) + g_y Y_1(\tau) - g_x(x_0, y_0)x_1(0) \\ &\qquad - g_y(x_0, y_0)\, y_1(0) + g_x x_1(0) \end{aligned} \tag{10}$$

Equations (4) and (9) share the initial conditions

$$\begin{aligned} x_0(0) + X_0(0) &= \zeta \\ y_0(0) + Y_0(0) &= \eta \end{aligned} \tag{11}$$

while (5) and (10) share

$$\begin{aligned} x_1(0) + X_1(0) &= 0 \\ y_1(0) + Y_1(0) &= 0 \end{aligned} \tag{12}$$

Note that as a result of (7) and (9), $X_0(\tau) = 0$. The conditions under which (6) may be expected to be a valid solution representation over the domain of interest may be found in the Hoppensteadt article.

NUMERICAL PROCEDURE

It will now be shown that the perturbation method of the last section is entirely applicable to the general stiff system for which the perturbing parameter ϵ may not be directly identifiable. This leads to a novel approach to the numerical integration of such systems. Miranker (1972) was the first to recognize and detail the possibilities of such an approach. His treatment, however, is not as computationally feasible as the present [mainly in the vital outer variable condition (21)] and, most importantly, does not include any information on the inner terms. It will be demonstrated in the examples following this section that knowledge of these inner terms, thus the length of the boundary layer, is of paramount concern.

Consider the system

$$\frac{dx}{dt} = f(x, y),\ x(0) = \zeta \tag{13a}$$

$$\frac{dy}{dt} = w(x, y),\ y(0) = \eta \tag{13b}$$

in which $w(x, y)$ is very large and thus stiff. For convenience, introduce the small parameter ϵ into (13b):

$$\epsilon \frac{dy}{dt} = g(x, y),\ y(0) = \eta \tag{14}$$

where $g \equiv \epsilon w$ is of the same order as f in (13a). Equations (13a) and (14) are now in the same form as (1).

Zeroth Order Approximation

Equation (4) may be written as

$$\frac{dx_0}{dt} = f(x_0, y_0), \quad x_0(0) = \zeta \tag{15a}$$

$$0 = w(x_0, y_0) \tag{15b}$$

Equation (15b) can be written since no assumption has been made on the magnitude of ϵ. Equations (15), the zeroth-order outer expansion, correspond to the pseudo steady state approximation often used in chemical kinetics, but now written for the general stiff system. The common procedure of setting ϵ to zero, if this quantity is identified, may mechanically produce the pseudo steady state approximation, but no such restriction was placed on the magnitude of ϵ in deriving (15). This may have interesting consequences (Ray, 1969). Equation (15) may be simultaneously solved to yield $y_0(0)$, $x_0(h)$, and $y_0(h)$, where h is the chosen time step size. This will require some extraneous numerical integration routine for (15a). Since the equation will be non-stiff, no particular difficulties should be encountered.

From (9):

$$\frac{dY_0}{d\tau} = g(x_0, y_0 + Y_0), \quad Y_0(0) = \eta - y_0(0)$$

$$\simeq g(x_0, y_0) + g_y(x_0, y_0)Y_0(\tau)$$

a linear equation with the solution

$$Y_0(\tau) = Y_0(0)e^{g_y(x_0,y_0)y_0\tau}$$

or (16)

$$Y_0(h/\epsilon) = Y_0(0)e^{w_y(x_0,y_0)h}$$

This linearization should be a good approximation since the boundary layer will decay with a large exponential over most of $Y_0(\tau)$. Equation (16) may be visualized as the linearization of (13b) for the scalar w linear in y, where $x_0(0) = \eta$ and $y_0(0)$ does not appear in w_y; the interpretation for the vector version where $y_0(0)$ appears in the Jacobian w_y is not as obvious.

First-Order Approximation

Rewrite (5) as

$$\epsilon\frac{dx_1}{dt} = f_x(x_0, y_0)\epsilon x_1 + f_y(x_0, y_0)\epsilon y_1,$$

$$\epsilon x_1(0) + \epsilon X_1(0) = 0 \tag{17a}$$

$$\epsilon\frac{dy_1}{dt} = g_x(x_0, y_0)\epsilon x_1 + g_y(x_0, y_0)\epsilon y_1 \tag{17b}$$

Take the total derivative of (15b) to be used in solving (17b) for ϵy_1. After substitution into (17a):

$$\epsilon\frac{dx_1}{dt} = \left(f_x(x_0, y_0) - \frac{f_y(x_0, y_0)w_x(x_0, y_0)}{w_y(x_0, y_0)}\right)\epsilon x_1 - \frac{f_y(x_0, y_0)w_x(x_0, y_0)}{w_y(x_0, y_0)^2}$$

$$\equiv \alpha\epsilon x_1 - \beta$$

a linear equation with the solution

$$\epsilon x_1(h) = [(\alpha\epsilon x_1(0) - \beta)e^{\alpha h} + \beta]/\alpha \tag{18a}$$

and thus

$$\epsilon y_1(h) = -\left(\frac{w_x(x_0, y_0)}{w_y(x_0, y_0)}\epsilon x_1(h) + \frac{w_x(x_0,y_0)}{w_y(x_0, y_0)^2}f\right) \tag{18b}$$

The crucial condition $\epsilon x_1(0)$ is still unknown. From (7) and (12)

$$\epsilon x_1(0) = -\epsilon X_1(0) = \epsilon\int_0^\infty \frac{dX_1(\tau)}{d\tau}d\tau \tag{19}$$

A crude evaluation of this integral may proceed as follows. Suppose the region of influence of X_1 is essentially determined by the behavior of its derivative initially (see Figure 2a). The integral of (19) is then given by the shaded area in this figure or

$$\int_0^\infty X_1(\tau)d\tau \simeq \frac{1}{2}\tau_I X_1(0) \tag{20}$$

Now take τ_I as that time after which Y_1 is negligible in addition to X_1 (see Figure 2b). Thus

$$\tau_I = Y_0(0)/\dot{Y}_0(0)$$

Since

$$\dot{X}_1(0) = f(\zeta, \eta) - f(\zeta, y_0(0))$$

and

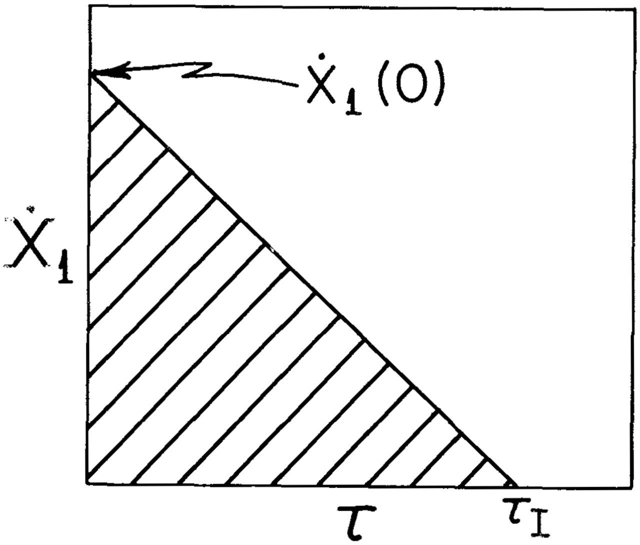

Fig. 2a. Evaluation of an integral in (20) by crude linear boundary layer approximation.

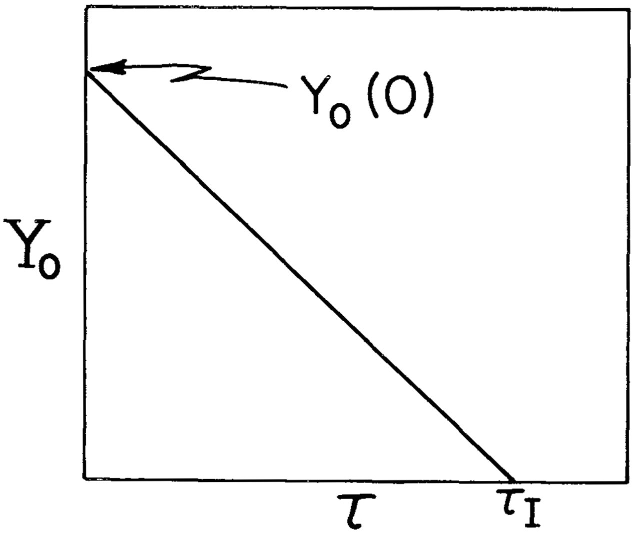

Fig. 2b. Estimate of the region of boundary layer influence τ_I.

$$\dot{Y}_0(0) = \epsilon w(\zeta, \eta)$$

(19) becomes

$$\epsilon x_1(0) = \frac{Y_0(0)}{2w(\zeta, \eta)} \left(f(\zeta, \eta) - f(\zeta, y_0(0))\right) \quad (21)$$

This allows rather simple computation of $\epsilon x_1(h)$, $\epsilon y_1(h)$, and $\epsilon y_1(0)$.

We note from (10) that $\dot{X}_1(\tau)$ is functionally dependent only on known arguments, so that immediately

$$\epsilon X_1(h/\epsilon) = \epsilon X_1(0) + h\dot{X}_1(h/\epsilon),\ \epsilon X_1(0) = -\epsilon x_1(0) \quad (22)$$

From (10):

$$\epsilon \dot{Y}_1(\tau) = g_y \epsilon Y_1(\tau) + \gamma$$

where

$$\gamma = g_x \epsilon X_1(\tau) + (g_x - g_x(x_0, y_0))\epsilon x_1(0) - (g_y - g_y(x_0, y_0))\epsilon y_1(0)$$

a linear equation with the solution

$$\epsilon Y_1(\tau) = [(g_y \epsilon Y_1(0) + \gamma)e^{g_y \tau} - \gamma]/g_y$$

which yields

$$\begin{aligned}\epsilon Y_1(h/\epsilon) = \{&[w_x \epsilon X_1(h/\epsilon) + (w_x - w_x(x_0, y_0))\epsilon x_1(0) \\ &- (w_y - w_y(x_0, y_0))\epsilon y_1(0) + w_y \epsilon Y_1(0)]e^{w_y h} \\ &- w_x \epsilon X_1(h/\epsilon) + (w_x - w_x(x_0, y_0))\epsilon x_1(0) \\ &- (w_y - w_y(x_0, y_0))\epsilon y_1(0)\}/w_y \quad (23)\end{aligned}$$

Finally, we may join all of the above results for the numerical approximation $(x^*(h), y^*(h))$ to $(x(h), y(h))$,

$$x(h) \sim x_0(h) + \epsilon x_1(h) + X_0(h/\epsilon) + \epsilon X_1(h/\epsilon)$$

$$y(h) \sim y_0(h) + \epsilon y_1(h) + y_0(h/\epsilon) + \epsilon Y_1(h/\epsilon)$$

A step-by-step summary of the algorithm with comments appears in Table 1.

EXAMPLE APPLICATIONS

This numerical procedure was programmed and tested on numerous examples using the IBM 360/91 at the Princeton University Computer Center. No attempt was made toward achieving an optimally efficient algorithm. The Runge-Kutta-Gill fourth-order (RKG4) routine was used to integrate the non-stiff Equation (15a). RKG4 was further used on the examples that follow to provide a benchmark comparison of stability, accuracy, and computation time with the singular perturbation approach. Here we quote results from two examples previously appearing in the literature selected from a much larger number. The first example was chosen mainly for its mildly stiff characteristics and its singularly perturbed form, hence clearly illustrating the importance of the boundary layer length and providing a severe accuracy test on the truncated first-order partial sum (6). The second example is very stiff, of dimensionality greater than two, and contains the highly nonlinear Arrhenius temperature dependence.

First Example: The Thermal Decomposition of Ozone

This problem was used by Bowen et al. (1963) as an important system in singularly perturbed form with which to derive an analytical solution approximation via matched asymptotic expansions. The accepted kinetic steps involved for a dilute ozone-oxygen mixture are

$$O_3 + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O + 2O_2$$

$$O_3 + O \overset{k_3}{\rightarrow} 2O_2$$

If the following dimensionless variables are defined:

$$x = [O_3]/[O_3]_0,\ y = [O]/\epsilon[O_3]_0$$

$$\kappa = 2k_2[O_2]_0/k_1,\ \epsilon = k_1[O_2]_0/2k_3[O_3]_0$$

and the time scale divided by $2/k_1[O_2]_0$, then the transient behavior may be described by

$$\frac{dx}{dt} = -x - xy + \epsilon\kappa y,\ x(0) = 1$$

$$\epsilon\frac{dy}{dt} = x - xy - \epsilon\kappa y, \quad y(0) = 0$$

with $\epsilon = 1.0/98.0$, $\kappa = 3.0$.

The authors expended considerable effort in obtaining the inner, outer, and far out solutions which, when combined, appear as in Figure 3. Also drawn in the figure is the numerical solution from RKG4 and the present perturbation algorithm. The analytical approximation is seen to be considerably in disagreement once past the initial boundary layer. Since the analytical solution is accurate only to $0(\epsilon)$ in the far out portion of the curve

Table 1. Summary of Singular Perturbation Algorithm Sequence

Variable	Equation	Comments
$x_0(h), y_0(h)$	(15a), (15b)	Simultaneous solution by any accurate integration and root finding procedures
$X_0(h/\epsilon)$	(7), (9)	Always equal to zero
$Y_0(h/\epsilon)$	(16)	Boundary layer importance to accuracy indicated by $Y_0(0) = \eta - y_0(0)$; linear integration
$\epsilon x_1(h)$	(18a)	$\epsilon x_1(0)$ from (21); w_y may not be singular; linear integration
$\epsilon y_1(h)$	(18b)	Follows directly from $\epsilon x_1(h)$
$\epsilon X_1(h/\epsilon)$	(22)	$\epsilon X_1(0)$ from (19); simple function evaluations for the integration
$\epsilon Y_1(h/\epsilon)$	(23)	$\epsilon Y_1(0) = -\epsilon y_1(0)$ obtained from (18b) with $h = 0$; w_y may not be singular; linear integration

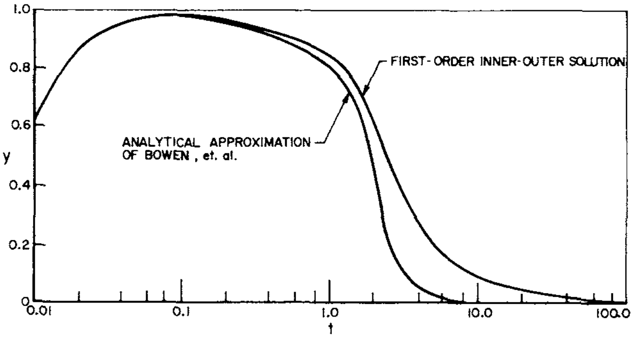

Fig. 3. Transient behavior of dimensionless oxygen atom concentration.

TABLE 2A. OZONE, EXACT AND FIRST-ORDER SOLUTIONS: NON-STIFF VARIABLE

t	x	X_0	ϵX_1	x_0	ϵx_1	x^*
0.01	0.986615	0.0	−0.001231	0.980787	0.004559	0.984115
0.02	0.969778	0.0	−0.000450	0.965216	0.001665	0.966430
0.04	0.933960	0.0	−0.000062	0.930135	0.000225	0.930298
0.07	0.881443	0.0	−0.000003	0.877917	0.000005	0.877919
0.10	0.831826	0.0	7×10^{-7}	0.828503	−0.000008	0.828495
0.50	0.389468	0.0	0.000005	0.387841	−0.000022	0.387824
0.90	0.189700	0.0	0.000020	0.188700	−0.000045	0.188675
5.00	0.006656	0.0	−0.000028	0.006470	0.000213	0.006655
10.00	0.002582	0.0	−0.000007	0.002657	0.000069	0.002719
20.00	0.001148	0.0	−0.000002	0.001257	0.000019	0.001275
50.00	0.000428	0.0	-3×10^{-7}	0.000499	0.000003	0.000502
100.00	0.000208	0.0	-7×10^{-8}	0.000251	9×10^{-7}	0.000252

TABLE 2B. OZONE, EXACT AND FIRST-ORDER SOLUTIONS: STIFF VARIABLE

t	y	Y_0	ϵY_1	y_0	ϵy_1	y^*
0.01	0.692814	−0.353401	−0.002720	0.969733	0.000685	0.614298
0.02	0.837530	−0.131524	−0.000578	0.969260	0.000620	0.837778
0.04	0.949530	−0.018846	−0.000245	0.968137	0.000619	0.949664
0.07	0.965869	−0.000933	−0.000275	0.966306	0.000681	0.965779
0.10	0.965161	0.000216	−0.000322	0.964368	0.000759	0.965021
0.50	0.929962	0.001792	−0.001955	0.926847	0.002965	0.929647
0.90	0.869663	0.006708	−0.007525	0.860417	0.009351	0.868952
5.00	0.192618	0.003348	−0.003362	0.174480	0.021907	0.196373
10.00	0.080713	0.000892	−0.001058	0.079862	0.006025	0.085720
20.00	0.036792	0.000224	−0.000288	0.039471	0.001607	0.041014
50.00	0.013872	0.000037	−0.000050	0.016050	0.000278	0.016316
100.00	0.006787	0.000009	−0.000013	0.008143	0.000072	0.008212

while the inner and outer expansions are accurate to $0(\epsilon^3)$ and since the RKG4 and the perturbation algorithm agree, the conclusion is that the analytical approximation is in error for $t > 0.12$.

Table 2 contains a detailed account of all inner and outer terms for both variables, along with the exact solution. The inner terms are seen to make a substantial contribution up to $t \sim 0.07$, corresponding to the length of the boundary layer, after which their effect is much smaller. The first-order outer terms are seen to contribute as much as 10% for the stiff variable y^* but is always very small for the non-stiff variable x^*; in fact with the small variation of x^* within the boundary-layer, the zeroth-order outer approximation x_0 is adequate for 0.1% accuracy through the entire transient.

The maximum step size that could be run with RKG4 for 0.1% accuracy was 0.01; for the perturbation routine step sizes as large as 1.0 could be taken for an agreement within 1% of RKG4. This gave a decrease in computation time by a factor of 25. A step of 1.0 actually leaps over the boundary layer so that, in this case, the outer terms would suffice for the same accuracy. If a step is taken within the boundary layer with only the outer terms however, errors incurred there can propagate and considerably lower accuracy. For example, a step size of 0.01 using outer terms only can cause as much as a 70% deviation from the inner plus outer solution within the boundary layer and 35% deviation thereafter.

Second Example: Transient Behavior of a Catalytic Fluidized Bed

Luss and Amundson (1968) have examined a simplified model for the dynamics of a catalytic fluidized bed in which mixing is complete and heat and mass transfer resistances are lumped at the particle surfaces. One irreversible gas phase reaction $A \rightarrow B$ is assumed to occur within the uniform porous catalysts, each of which are at the same partial pressure and temperature. The details for setting up the mass and heat balances will be omitted here and only the equations with parameters numerically specified presented:

$$\frac{dx}{dt} = 1.30(y_2 - x) + 1.04 \times 10^4 k y_1, \quad x(0) = 759.167$$

$$\frac{dy_1}{dt} = 1.88 \times 10^3 [y_3 - y_1(1 + k)], \quad y_1(0) = 0.0$$

$$\frac{dy_2}{dt} = 1752 - 269 y_2 + 267 x, \quad y_2(0) = 600.$$

$$\frac{dy_3}{dt} = 0.1 + 320 y_1 - 321 y_3, \quad y_3(0) = 0.1$$

where $k = 0.0006 \exp(20.7 - 15000/x)$ and x, y_1, y_2, and y_3 represent the temperature (°R) and partial pressure (atm.) of the catalyst and interstitial fluid, respectively. With this selection of parameters, Luss and Amundson report the existence of three possible steady states. The eigenvalues at each of these states differ by six orders of magnitude so that the system is very stiff. As expected, severe numerical stability problems were encountered using RKG4, leading Luss and Amundson to state that the use of the assumption $x = y_2$ and $y_1 = y_3$ "might be the only feasible way to carry out the transient computations." Actually, there are undoubtably numerous numerical methods now available for this type of system, as illustrated here using the singular perturbation approach.

Note that while previous developments were of two dimensions for simplicity, the multi-dimensional case naturally follows. Now, for example, the initial condition on (21) becomes

$$\epsilon \mathbf{x}_1(0) = \frac{||\mathbf{Y}_0(0)||}{2||\mathbf{w}(\boldsymbol{\zeta}, \boldsymbol{\eta})||} \{\mathbf{f}(\boldsymbol{\zeta}, \boldsymbol{\eta}) - \mathbf{f}[\boldsymbol{\zeta}, \mathbf{y}_0(0)]\}$$

where the Euclidean norm $|| \cdot ||$ is used.

From our knowledge of the model, it is anticipated that the solution behavior of all variables is dictated by that of the particle, its heat capacity being the main obstacle to change. For this reason, we chose the relatively slowly varying catalyst temperature to be the non-stiff variable x and put all other into $y = [y_1\, y_2\, y_3]^T$.

Table 3 contains the individual zeroth and first-order inner and outer terms for the temperature x^* and concentration y_1^* of the catalyst as computed by our algorithm. Also given is the exact solution computed by RKG4 early in the transient; later in the transient another method, that of Gear (1971), generally accepted as the best all purpose optimized stiff package available, was used to allow judgment of the reliability of results. That method automatically adjusts the step size (and the order) as the calculation proceeds to achieve specific accuracy requirements so that the solution at precise values of the independent variable is not available. Thus we present in the table for the exact solution only those digits known to be correct at the listed times. Inner terms are found not significant beyond a time of 5.0 to 7.0, corresponding to the length of the boundary layer. Within the boundary layer, however, they have a substantial influence even for the first-order terms. The zeroth-order outer terms are by far the dominant variables through the entire solution domain (the steady state is reached at $t \sim 2200$). The first-order outer terms contribute within the boundary layer and to a varying extent thereafter.

While we display the solution at early points in the transient from use of small steps, this is done only to examine the size of the various terms in all regions of the solution. If the purpose is to quickly obtain the trend of the solution outside the boundary layer, step sizes as large as 50 can be taken with the same accuracy as in the table and about four orders of magnitude faster than RKG4.

REMARKS

It should be mentioned that the perturbation approach is useful only when not all variables are substantially influenced by the large eigenvalues, namely, there must be a differentiation possible between the non-stiff and stiff variables. This is true for a very large number of stiff physical and chemical systems. Ideally, this differentiation may be accomplished from a knowledge of the physical phenomena or by examination of the equation set for small perturbing quantities. If this is not possible, integration of the stiff set with standard routines will require computation steps within the boundary layer and the slowly varying non-stiff variables will become evident. Automatic programming criteria for this has not yet been developed but would make particular use of our small-parameter independent algorithm. For the relatively rare systems in which the stiff and non-stiff variables may change during the course of the integration, as in certain branched free radical mechanisms, such criteria would be required throughout the transient.

Monitoring the inner terms allows an indication of the extent of the boundary layer; after these terms are negligible either the outer terms alone may be used for efficiency in computation (assuming no later quick changes in the solution) or an A-stable technique (Lapidus and Seinfeld,

TABLE 3A. FLUIDIZED BED, EXACT AND FIRST-ORDER SOLUTIONS: NON-STIFF VARIABLE

t	x	X_0	ϵX_1	x_0	ϵx_1	x^*
0.001	758.986	0.0	0.226	759.167	−0.383	759.010
0.005	758.601	0.0	0.076	758.730	−0.129	758.677
0.010	758.455	0.0	0.020	758.563	−0.033	758.550
0.020	758.407	0.0	0.001	758.510	−0.002	758.509
0.100	758.404	0.0	−0.009	758.508	0.009	758.508
0.500	758.510	0.0	−0.004	758.499	0.004	758.499
2.00	758.610	0.0	-10^{-4}	758.571	3×10^{-4}	758.571
5.00	758.610	0.0	7×10^{-7}	758.563	3×10^{-8}	758.563
7.00	758.600	0.0	10^{-7}	758.563	10^{-7}	758.563
100.0	758.170	0.0	10^{-7}	757.910	10^{-4}	757.910
500.0	748.700	0.0	10^{-8}	746.024	10^{-4}	746.024
1000.0	701.700	0.0	10^{-8}	699.881	0.002	699.883

TABLE 3B. FLUIDIZED BED, EXACT AND FIRST-ORDER SOLUTIONS: STIFF VARIABLE

t	y_1	y_0	ϵY_1	y_0	ϵy_1	y_1^*
0.001	0.075062	0.008775	−0.000277	0.066927	0.000220	0.075645
0.005	0.085154	0.017719	−0.000111	0.067181	0.000072	0.084861
0.010	0.085048	0.017390	−0.000026	0.067280	0.000017	0.084660
0.020	0.084825	0.017111	6×10^{-7}	0.067302	0.000001	0.084413
0.100	0.083140	0.015569	0.000009	0.067415	−0.000007	0.082986
0.500	0.076000	0.009781	0.000005	0.067415	−0.000004	0.077197
2.00	0.069001	0.001485	0.000002	0.067371	−0.000002	0.068856
5.00	0.067300	0.000025	0.000002	0.067382	−0.000002	0.067407
7.00	0.067267	−0.000004	0.000002	0.067382	−0.000002	0.067377
100.0	0.067510	-10^{-11}	10^{-11}	0.067749	-10^{-6}	0.067745
500.0	0.072700	-10^{-11}	10^{-11}	0.074213	−0.000030	0.074184
1000.0	0.091100	-10^{-11}	10^{-11}	0.091517	−0.000015	0.091503

1971) employed without the accuracy problems associated with the initial stiff section. This unique feature could be used to advantage in conjunction with other highly stable methods since the dominate of the inner terms Y_0 is rather easily calculated via (16).

Further study has been directed toward development of an effective scheme for estimating the boundary layer length after which the pseudo steady state approximation (15) may be used. Checks on the accuracy by occasional calculation of the first-order outer terms (18) would then provide complete information on the applicability of the easily implemented pseudo steady state approximation for general stiff systems.

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NOTATION

$f(x, y, \epsilon)$ = a general function of dependent variables x, y, and parameter ϵ
$g(x, y, \epsilon)$ = a general function of dependent variables x, y, and parameter ϵ
h = step size increment in t
k, k_1, k_2, k_3 = kinetic rate coefficients
$[O]_0$ = initial concentration of oxygen atom
$[O_2]_0$ = initial concentration of oxygen molecule
$[O_3]_0$ = initial concentration of ozone
RKG4 = fourth-order Runge-Kutta-Gill integration routine
t = independent variable
w = a general function of x and y with ϵ as a pole
x = regularly perturbed (non-stiff) variable
x_0, x_1 = non-stiff outer variables
X_0, X_1 = non-stiff inner variables
y = singularly perturbed (stiff) variable
y_0, y_1 = stiff outer variables
Y_0, Y_1 = stiff inner variables
z = general dependent variable

Greek Letters

$\alpha, \beta, \gamma, \epsilon$ = constants defined for convenience
η = initial condition on non-stiff variable
κ = dimensionless constant
λ_i = ith eigenvalue
ζ = initial condition on stiff variables
τ = expanded inner t scale, t/ϵ

Subscripts

x = partial derivative with respect to x
y = partial derivative with respect to y
0 = zeroth-order expansion in ϵ
1 = first-order expansion in ϵ

Superscripts

$\star$ = first-order approximation in outer variable
$*$ = first-order approximation in both outer and inner variables
I = domain of boundary layer
II = entire domain of interest

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