Calculation of Parametric Dependence and Finite-Difference Methods

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INTRODUCTION

The algorithm for calculating the parametric dependence of the solution of a particular nonlinear boundary value problem has been proposed by Goldberg et al. (1963, 1965), Rubberts and Landahl (1967), and independently rediscovered by Kubíček and Hlavacek (1971).

Several authors have used this technique for solution of nonlinear differential equations arising in hydrodynamics (Kubíček et al., 1976a; Nath, 1973; Rubberts and Landahl, 1967; Sivaneri and Harris, 1980, combustion theory (Marathe and Jain, 1977) and civil engineering (Goldberg et al., 1963, 1965) or nonlinear difference equations in chemical engineering rectification problems (Jelínek et al., 1973; 1976).

In order to overcome certain inherent difficulties associated with this parametric differentiation technique (mainly the problem of parameter continuation if limit points exist), Kubíček and Hlavacek (1972, 1973) proposed a new technique, General Parameter Mapping (GPM), which is capable of overcoming these difficulties. The GPM algorithm deals with parametric differentiation problems most happily, when the governing equations do not exhibit stiff character. For problems which feature boundary layers (narrow intervals where the solution varies rapidly), the algorithm fails.

The purpose of the present paper is:

i) To propose an algorithm, based on the finite-difference approach for calculation of parametric dependences, which can also easily handle stiff problems

ii) To suggest a number of improvements in a general parameter continuation algorithm published by Kubíček (1976)

iii) To illustrate the superiority of the algorithm proposed on nonlinear boundary value problems (diffusion-reaction, diffusion-convection-reaction problems)

iv) To convince the chemical engineers that the parametric differentiation via the finite-difference approach is both a very powerful and elegant procedure for calculation of parametric dependences

THEORETICAL BACKGROUND

We present the background information which is necessary to understand the parametric continuation via finite-difference method.

Let us consider a set of algebraic equations

$$F(x,\alpha) = 0. \tag{1}$$

Here x is a vector of variables and α is a parameter. In a scalar form Eq. 1 reads:

$$\begin{aligned} f_1(x_1,\ldots,x_n,\alpha) &= 0 \\ &\cdots\cdots \\ f_n(x_1,\ldots,x_n,\alpha) &= 0. \end{aligned} \tag{2}$$

Suppose that for some x_0 and α_0

$$F(x_0,\alpha_0) = 0. \tag{3}$$

Assuming that $F(x,\alpha)$ is continuously differentiable and Γ^{-1} exists, we may write:

$$\frac{\partial F}{\partial x}dx + \frac{\partial F}{\partial \alpha}d\alpha = 0, \tag{4}$$

or

$$\frac{dx}{d\alpha} = -\Gamma^{-1}(x,\alpha)\frac{\partial F}{\partial \alpha} \tag{5}$$

Here Γ is a Jacobian matrix, $n \times n$,

$$\Gamma = \frac{\partial F}{\partial x} = \left\{\frac{\partial f_i}{\partial x_j}\right\}$$

and

$$\frac{\partial F}{\partial \alpha} = \left(\frac{\partial f_1}{\partial \alpha},\ldots\frac{\partial f_n}{\partial \alpha}\right)^T$$

If Γ is a regular matrix, the parametric dependence $x(\alpha)$ can be calculated by integration of Eq. 5 subject to initial conditions

$$\alpha = \alpha_0,\ x = x_0. \tag{6}$$

For the case that Γ may become singular, Kubíček (1976) and Keller (1977) suggested a parametrization of the problem. A most obvious choice of the parameter is the arc-length t. Differentiation of Eq. 2 with respect to t yields:

$$\frac{df_i}{dt} = \sum_{j=1}^{n}\frac{\partial f_i}{\partial x_j}\frac{dx_j}{dt} + \frac{\partial f_i}{\partial \alpha}\frac{d\alpha}{dt} = 0. \quad i = 1,2,\ldots,n \tag{7}$$

The condition for the arc-length is

$$\sum_{j=1}^{n}\left(\frac{dx_j}{dt}\right)^2 + \left(\frac{d\alpha}{dt}\right)^2 = 1. \tag{8}$$

The initial conditions for Eqs. 7 and 8 are

$$t = 0\text{: } x = \hat{x}_0,\ \alpha = \hat{\alpha}_0 \tag{9}$$

where $\hat{x}_0$ and $\hat{\alpha}_0$ are the values of x and α for which the Jacobian matrix is regular. Equations 7 and 8 represent a set of $n + 1$ ordinary differential equations for $n + 1$ unknowns, $x_1, \ldots, x_n, \alpha$. However, numerical solution of Eq. 7 and 8 cannot be calculated in a straightforward way because of the implicit character of Eq. 8. In order to use the standard ordinary differential equation packages, it is necessary to transform Eqs. 7 and 8 to $y' = G(\alpha,y)$. The gist of this transformation is the calculation of the kernel of a matrix Γ', $n \times (n + 1)$,

$$\Gamma' = \begin{pmatrix} \frac{\partial f_1}{\partial x_1},\ldots\frac{\partial f_1}{\partial x_n},\frac{\partial f_1}{\partial \alpha} \\ \vdots \\ \frac{\partial f_n}{\partial x_1},\ldots\frac{\partial f_n}{\partial x_n},\frac{\partial f_n}{\partial \alpha} \end{pmatrix} \tag{10}$$

which has a full rank. This operation should be performed as precisely as possible, for the calculation of the kernel the Householder reflection (Businger-Golub, 1965) is recommended. If the matrix Γ' is sparse, the Golub and Plemmons (1980) technique can be used.

PATH TRACING ALGORITHM

To integrate Eqs. 5, we can use a path-tracing algorithm which can be constructed in a similar way as a program published by

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Kubíček (1976). Watson (1979b) recommended not to use this program because "the numerical linear algebra and ordinary differential equations techniques in that program are primitive compared to current technology."

Obviously, to integrate Eqs. 7, we must find a kernel of a matrix which has full rank. Finding the kernel of the $n \times (n+1)$ matrix should be done very accurately; Watson (1979a, 1979b) recommended using the Householder reflection (Businger-Golub, 1965). This matrix Γ' has full rank at limit points, however, loses its rank at bifurcation points. In the neighborhood of bifurcation points, some additional calculations are required to switch from one branch to another. Keller (1977) recommended using a new tangent vector in place of the old tangent while Rheinboldt (1978) advocated for the singular chord method.

Evidently, the integration of Eqs. 7 and 8 is associated with the substantial portion of the computer time expenditure. Watson (1979a) suggested adopting the subroutines STEP and INTRP described in the book by Shampine and Gordon (1975).

For a number of technical problems, we may expect a regular behavior of the Jacobian matrix; however, the matrix is sparse and the dimension of this matrix can be very large. In this particular case, it is not necessary to make use of the arc-length transformation but in order to improve the economy of the calculation the subroutine GAUSE in Kubíček's algorithm should be replaced by an appropriate sparse matrix procedure (Lawson and Hanson, 1974; Golub and Plemmons, 1980). While the former modifications are important for parametric study of nonlinear differential equations, the latter modifications can be used for parametric calculation on separation processes.

PARAMETRIC DEPENDENCE AND FINITE-DIFFERENCE METHOD

We illustrate here the advantages of the finite-difference method over the shooting (or more generally decomposition approach) on two examples.

Example 1

Enzymatic reaction occurring in a plate may result in a spectrum of symmetric and asymmetric profiles (Kubíček and Marek, 1977).

The governing equations are:

$$\frac{d^2x}{dz^2} = \frac{L^2}{D_x}\left[\alpha xy - \frac{\beta x}{1+x}\right] = g_1(x,y) \tag{11}$$

$$\frac{d^2y}{dz^2} = \frac{L^2}{D_y}[1 - \alpha xy] = g_2(x,y) \tag{12}$$

subject to boundary conditions

$$z = 0: x = \bar{x},\ y = \bar{y} \tag{13}$$

$$z = 1: x = \bar{x},\ y = \bar{y} \tag{14}$$

Here x and y are concentrations of components X and Y, z is a space coordinate, D_x and D_y are the diffusion coefficients, L is the characteristic length of the system and α,β are the kinetic constants.

Kubíček and Marek (1977) solved this problem by the GPM approach. This approach is based on the shooting method. The unknown values of $x'(0)$ and $y'(0)$ are denoted

$$x'(0) = \eta_1,\ y'(0) = \eta_2 \tag{15}$$

The initial conditions 13 along with 15 provide the sufficient information to integrate Eqs. 11 and 12 across. At $z = 1$ we have:

$$F_1(\eta_1,\eta_2,L) = x(1) - \bar{x} \tag{16a}$$

$$F_2(\eta_1,\eta_2,L) = y(1) - \bar{y}. \tag{16b}$$

The unknown values η_1 and η_2 should be manipulated in such a way that

$$F_1(\eta_1,\eta_2,L) = 0 \tag{17a}$$

$$F_2(\eta_1,\eta_2,L) = 0. \tag{17b}$$

Equations 17a and 17b represent two nonlinear algebraic equations; using the formula 5 we get

$$\frac{d\eta}{dL} = -\Gamma^{-1}\frac{\partial F}{\partial L}. \tag{18}$$

Here

$$\Gamma = \begin{pmatrix} \frac{\partial F_1}{\partial \eta_1} & \frac{\partial F_1}{\partial \eta_2} \\ \frac{\partial F_2}{\partial \eta_1} & \frac{\partial F_2}{\partial \eta_2} \end{pmatrix} \text{ and } \frac{\partial F}{\partial L} = \begin{pmatrix} \frac{\partial F_1}{\partial L} \\ \frac{\partial F_2}{\partial L} \end{pmatrix} \tag{19}$$

The elements of the Jacobian matrix are

$$\frac{\partial F_1}{\partial \eta_1} = \frac{\partial x(1)}{\partial \eta_1} = p_1(1),\quad \frac{\partial F_1}{\partial \eta_2} = \frac{\partial x(1)}{\partial \eta_2} = p_2(1),$$

$$\frac{\partial F_1}{\partial L} = \frac{\partial x(1)}{\partial L} = p_3(1) \tag{20}$$

$$\frac{\partial F_2}{\partial \eta_1} = \frac{\partial y(1)}{\partial \eta_1} = q_1(1),\quad \frac{\partial F_2}{\partial \eta_2} = \frac{\partial y(1)}{\partial \eta_2} = q_2(1),$$

$$\frac{\partial F_2}{\partial L} = \frac{\partial y(1)}{\partial L} = q_3(1)$$

The values of the variational variables can be calculated from variational equations (Kubíček and Hlavacek, 1972). For instance, the variational variable p_1 is governed by the variational equation

$$p_1'' = \frac{L^2}{D_x}\left[\left(\alpha y - \frac{\beta}{(1+x)^2}\right)p_1 + \alpha x q_1\right]$$

$$p_1(0) = 0,\ p_1'(0) = 1. \tag{21}$$

Evidently, in order to calculate the information necessary for integration of Eq. 18 we must integrate two second-order equations (Eqs. 11 and 12) along with six second order variational equations for $p_i, q_i,\ i = 1, 2, 3$.

For the finite-difference method we may take advantage of the Stφrmer-Numerov formula (Hildebrandt, 1968) which has $O(h^4)$ accuracy. For a differential equation

$$\frac{d^2w}{d\xi^2} + G(\xi,w) = 0$$

we can write

$$w_{k+1} - 2w_k + w_{k-1} + h^2\left(G_k + \frac{1}{12}\delta^2 G_k\right) = 0 \tag{22}$$

where

$$\delta^2 G_k = \frac{G_{k-1} - 2G_k + G_{k+1}}{h^2}$$

We can note that the occurrence matrix for this $O(h^4)$ schema is tridiagonal. Using the Størmer-Numerov formula for approximation of Eqs. 11 and 12, we get a six diagonal matrix if using Eq. 5 and a six diagonal with one column if adopting the arc-length transformation (Eqs. 7 and 8).

For calculation of a parametric dependence we recommend the following procedure:

i) Integrate Eq. 5 as long as the matrix Γ is regular.

ii) If the matrix Γ approaches singularity (which can be easily discovered by comparing the last two diagonal elements in the factorization process of Γ) switch over to the arc-length continuation. At bifurcation points we must perform some extra computation to jump from one branch to another (Keller, 1977).

iii) Being at the new branch switch back to integration of Eq. 5.

Let us compare roughly the number of necessary operations. Assume that for integration of the variational equations we use a Runge-Kutta of the 4th order having $O(h^4)$ accuracy. Using N internal mesh points we must perform for the finite difference

schema $2N \times 6 + 2N = 14N$ function evaluations and $2N \times 5 \times (5 + 5 + 1) = 110N$ multiplications. The GPM method, on the other hand, requires $4 \times 8 \times (N + 1) = 32(N + 1)$ function evaluations and $(6 \times 16) \times (N + 1) = 96(N + 1)$ multiplication. As a result the number of multiplications is of the same order of magnitude, however, the GPM method requires by far more function evaluations.

Since the GPM algorithm is of the shooting type it suffers from all shortcomings typical for marching procedures. The most severe is the problem of the "boundary value character" of the particular initial value problem. For instance, for the nonisothermal-nonadiabatic dispersion model (Kubíček et al., 1979) the algorithm was not capable of calculating the parametric dependences in a certain domain of higher values of Peclet numbers. For calculation of long packed bed reactors (Pe $\gg$ 100), the algorithm failed completely.

The same conclusions are valid also for a number of boundary value problems in hydrodynamics (Holodniok et al., 1977); Wang and Watson, 1979a, 1979b). On the other hand, the GPM algorithm may be superior for problems where the corresponding initial value problem is not stiff, however, a very steep oscillating profile exists along the space coordinate (e.g., problems of calculation of dissipative structures for higher values of the space coordinate (Herschkowitz-Kaufman, (1975).

So far, we have discussed the finite-difference method only for the case of the diffusion equation in the form $y'' = f(\xi,y)$. However, in chemical engineering there is an important class of problems referred to as the diffusion-convection equations. As a typical representative of this class of problems consider a description of a nonadiabatic nonisothermal packed bed:

$$\frac{1}{\mathrm{Pe}_H}\frac{d^2\theta}{d\xi^2} - \frac{d\theta}{d\xi} = \psi_1(\theta,y) \tag{23}$$

$$\frac{1}{\mathrm{Pe}_M}\frac{d^2y}{d\xi^2} - \frac{dy}{d\xi} = \psi_2(\theta,y) \tag{24}$$

subject to boundary conditions

$$\mathrm{Pe}_H\theta(0) - \theta'(0) = 0, \quad \mathrm{Pe}_M y(0) - y'(0) = 0 \tag{25}$$

$$\theta'(1) = y'(1) = 0. \tag{26}$$

Here θ and y are dimensionless temperature and conversion, Pe_H and Pe_M are Peclet numbers for heat and mass transfer respectively. In order to eliminate the first derivative the following substitutions may be used:

$$\theta = t \exp\left(\frac{\mathrm{Pe}_H}{2}\xi\right) \quad y = y\exp\left(\frac{\mathrm{Pe}_H}{2}\xi\right). \tag{27a, 27b}$$

After simple algebraic manipulations we have

$$\frac{d^2t}{d\xi^2} = \frac{\mathrm{Pe}_H^2}{4}t + \mathrm{Pe}_H \exp\left(-\frac{\mathrm{Pe}_H}{2}\xi\right)\psi_1 \times \left[t\exp\left(\frac{\mathrm{Pe}_H}{2}\xi\right), Y\exp\left(\frac{\mathrm{Pe}_M}{2}\xi\right)\right]$$

$$\frac{d^2Y}{d\xi^2} = \frac{\mathrm{Pe}_M^2}{4}Y + \mathrm{Pe}_M \exp\left(-\frac{\mathrm{Pe}_M}{2}\xi\right)\psi_2 \times \left[t\exp\left(\frac{\mathrm{Pe}_H}{2}\xi\right), Y\exp\left(\frac{\mathrm{Pe}_M}{2}\xi\right)\right] \tag{29}$$

subject to boundary conditions

$$\xi = 0: \frac{1}{2}\mathrm{Pe}_H t - \frac{dt}{d\xi} = 0, \quad \frac{1}{2}\mathrm{Pe}_M Y - \frac{dY}{d\xi} = 0 \tag{30}$$

$$\xi = 1: \frac{1}{2}\mathrm{Pe}_H t + \frac{dt}{d\xi} = 0, \quad \frac{1}{2}\mathrm{Pe}_M Y + \frac{dY}{d\xi} = 0 \tag{31}$$

Evidently for the transformed problem we can easily adopt the Stǿrmer-Numerov formula.

For problems where we cannot perform such a transformation (e.g., problems in the boundary layer theory) we must use a better approximation of the space derivatives, e.g., a five-point centered difference scheme of fourth order. Of course, as a result, the band in the Jacobian matrix is of higher dimension and the number of necessary operations to solve Eq. 5 is higher. The other possibility is to use the Padé approximation (Hlavacek, in press).

Example 2

The problem we are going to deal with here is the calculation of the parametric dependence of a rectification column. Parametric study of a column may be required for changing, for example, heat loads, amount of the side stream, concentration of the key components etc. Evidently, a suboptimalization of such a column is performed via a set of parametric dependences. Jelínek et al. (1973) proposed using the method of parametric differentiation for this problem.

The GPM approach, tested by Kubíček et al. (1974), could not be easily generalized for a parametric calculation of a column, however, the parametric differentiation proved to be very reliable. The authors feel, however, that it did not find a common acceptance. Apparently the reason is that the majority of chemical engineers believe that it is associated with a great deal of analytic and programming effort. In fact, this conclusion was correct a decade ago. Presently it is a general consensus that the Newton-Raphson method yields the most general and flexible code for calculation of rectification equipment and programs based on this approach are common.

However, ten years ago a general curve tracing algorithm was not developed. As we can infer from Eq. 5 the most complicated problem associated with implementing the parametric differentiation approach is the construction of the Jacobian matrix and the appropriate sparse matrix procedure. Since presently this information is easily available, we can use it in a general curve tracing program, in the Kubíček's (1976) program we replace only the subroutine GAUSE by an appropriate sparse matrix procedure which is used in the Newton-Raphson code (Kubíček et al., 1976b). As a result, using a curve tracing algorithm we must add only the vector $\partial f_i/\partial\alpha$. The work associated with the construction of this vector is usually minimal since it contains a number of zero elements. Using multistep integration procedure the economy of calculation is increased in comparison with the Newton-Raphson method.

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A Note on Diffusion Limitations for Multiple Reaction Systems in Porous Catalysts

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Diffusion of species through the pores of solid catalysts is very often the rate-limiting step in catalytic reactions. Diffusion limitations also have a very important effect on the selectivity in multiple reaction systems. Since the kinetic rate expressions are usually nonlinear, it is usually very difficult to determine the effect of transport processes on the observed rates by solving the controlling differential equations of the model.

A number of criteria were derived to predict the importance of diffusion limitations on the overall rate of catalytic reactions (Weisz and Prater, 1954; Peterson, 1964; Hutchings and Carberry, 1966; Schneider and Mitschka, 1966; Bischoff, 1967; Narshimhan and Guha, 1972). The criterion developed by Hudgins (1968) is applicable for reactions having other than power-type rate expressions. Dogu and Dogu (1980) extended the criterion derived by Hudgins to bidisperse systems. Effect of diffusion on the observed rate in bidisperse systems was also investigated by Ors and Dogu (1979). In all of these studies a single independent reaction is considered. A detailed review of diffusion and reaction processes in porous catalysts is given by Aris (1975).

More often than not, solid-catalyzed reactions are multiple reactions. Reactions occur in parallel and the products of these decompose further. A general consecutive reaction system is investigated by Van De Vusse (1966). Luss and Golikeri (1971) and Roberts (1972) investigated multiple reaction systems under isothermal conditions and obtained asymptotic solutions. In stoichiometrically complex systems it is usually impossible to derive analytical expressions for the observed rates. In this work, a very general criterion is developed for detecting the presence of significant intraparticle mass transport effects for multiple fluid-porous solid reaction systems. The criterion is applicable to any multiple reaction system and to reactions conforming to any rate law.

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