Series solutions for boundary value problems using a symbolic successive substitution method

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Abstract

This paper presents a method for obtaining series solutions for boundary value problems (BVPs). The technique consists of converting the given two point BVP into an initial value problem (IVP). This IVP is then solved using the successive substitution method (SSM) with the boundary condition at the other endpoint as an additional constraint. The series solutions obtained by this process depend on both the independent variable and the parameters (such as reaction rate constants) that appear in the governing equations. The method is illustrated for both linear and nonlinear problems. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

We present here a series solution technique for solving systems of linear and nonlinear BVPs. We start by converting the given BVP to an IVP and subsequently integrate the resulting system of equations by finding the matrizant (Amundson, 1966, pp. 199–203) of the coefficient matrix. For matrices with a constant coefficient matrix the matrizant simplifies to the exponential of the matrix. Solving IVPs by finding the matrix exponential is well known (Varma and Morbidelli, 1997, pp. 56–57). In some cases, even though the IVP is linear the matrix is a function of the independent variable. For such problems, where the coefficient matrix varies with the independent variable the successive substitution method (SSM) is used for determining the matrizant (Taylor and Krishna, 1993, pp. 524–529). Finally, we extend this technique to nonlinear BVPs by quasi-linearizing the nonlinear terms and iterating for the unknown initial condition (Haran and White, 1996) to develop a series solution.

The first objective of this paper is to describe the method of successive substitution for linear, two point boundary value problems. The technique is illustrated for a simple linear problem from chemical engineering namely,

determining the effectiveness of a rectangular cooling fin (Davis, 1984, pp. 72–75). Next, the methodology for problems with a variable coefficient matrix is illustrated by solving the classical problem of diffusion and reaction in a cylindrical catalyst pellet (Villadsen and Michelsen, 1978, pp. 68–73). Finally, we demonstrate the methodology for nonlinear BVPs by solving the coupled equations for the steady state analysis of a gas-fed porous electrode in a fuel cell (White et al., 1984). The technique has been implemented using Maple® (a copy of the Maple code (on a diskette) is available from the authors [Ralph E. White] upon request).

2. Method of successive substitution

We demonstrate the technique for linear problems first by solving a simple example from chemical engineering. Consider the conduction of heat in a rectangular cooling fin. The governing differential equation (Davis, 1984, pp. 72–75) in dimensionless form is,

$$\frac{d^2\theta}{dx^2} = H^2\theta, \tag{1}$$

subject to the following boundary conditions:

$$\theta(0) = 1, \quad \frac{d\theta}{dx}(1) = 0, \tag{2}$$

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where θ is the dimensionless temperature, x is the dimensionless distance and H is the dimensionless heat transfer coefficient.

The rectangular cooling fin is chosen because it is linear, and has an analytical solution:

$$\theta = \frac{\cosh H(1-x)}{\cosh H}. \tag{3}$$

Eq. (1) can be written in the form of a vector differential equation (Krishna and Taylor, 1993, p. 524),

$$\frac{d\mathbf{y}}{dx} = \mathbf{A}\mathbf{y}, \tag{4}$$

where

$$\frac{d\mathbf{y}}{dx} = \begin{bmatrix} \dfrac{dy_1}{dx} \\ \dfrac{dy_2}{dx} \end{bmatrix} = \begin{bmatrix} \dfrac{d\theta}{dx} \\ \dfrac{d^2\theta}{dx^2} \end{bmatrix}, \tag{5}$$

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} \theta \\ \dfrac{d\theta}{dx} \end{bmatrix}, \tag{6}$$

$$\mathbf{A} = \begin{bmatrix} 0 & 1 \\ H^2 & 0 \end{bmatrix} \tag{7}$$

and

$$\mathbf{y}_0 = \begin{bmatrix} y_{10} \\ y_{20} \end{bmatrix} = \begin{bmatrix} 1 \\ y_{20} \end{bmatrix}. \tag{8}$$

The solution to Eq. (4) can be written as follows,

$$\mathbf{y} = [\Omega(\mathbf{A})]\mathbf{y}_0, \tag{9}$$

where $\Omega(\mathbf{A})$ is defined as the matrizant of matrix $\mathbf{A}$ and is given by,

$$\Omega(\mathbf{A}) = [\mathbf{I}] + \int_0^x [\mathbf{A}(x_1)\,dx_1]$$
$$\times \int_0^x [\mathbf{A}(x_1) \int_0^{x_1} [\mathbf{A}(x_2)]\,dx_2]\,dx_1$$
$$+ \int_0^x \left[\mathbf{A}(x_1) \int_0^{x_1} \left[\mathbf{A}(x_2)\right.\right.$$
$$\left.\left.\times \int_0^{x_2} [\mathbf{A}(x_3)]\,dx_3\right]dx_2\right]dx_1 + \cdots. \tag{10}$$

For this heat transfer example, the coefficient matrix $\mathbf{A}$ (Eq. (7)) is constant since H is constant and the matrizant $\Omega(\mathbf{A})$ simplifies to the matrix exponential (Varma and Morbidelli, 1997, pp. 56–57):

$$\Omega(\mathbf{A}) = [\mathbf{I}]x + [\mathbf{A}] + \tfrac{1}{2}[\mathbf{A}]^2 x^2 + \tfrac{1}{6}[\mathbf{A}]^3 x^3 + \cdots = \exp[\mathbf{A}]x$$

$$= \begin{bmatrix} \left(\dfrac{(\exp(Hx) + \exp(-Hx))}{2}\right) & \left(\dfrac{(\exp(Hx) - \exp(-Hx))y_{20}}{2H}\right) \\ \left(\dfrac{H(\exp(Hx) - \exp(-Hx))}{2}\right) & \left(\dfrac{(\exp(Hx) + \exp(-Hx))y_{20}}{2}\right) \end{bmatrix}. \tag{11}$$

Hence, by substituting the expression for the matrizant (Eq. (11)) and $\mathbf{y}_0$ from Eq. (8) into Eq. (9) we get,

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} \theta \\ \dfrac{d\theta}{dx} \end{bmatrix} = \begin{bmatrix} \left(\dfrac{(\exp(Hx) + \exp(-Hx))}{2} + \dfrac{(\exp(Hx) - \exp(-Hx))y_{20}}{2H}\right) \\ \left(\dfrac{H(\exp(Hx) - \exp(-Hx))}{2} + \dfrac{(\exp(Hx) + \exp(-Hx))y_{20}}{2}\right) \end{bmatrix}. \tag{12}$$

The constant y_{20} is obtained by using the known boundary at $x = 1$ namely, $d\theta/dx = 0$ or $y_2(1) = 0$:

$$y(1) = \begin{bmatrix} y_1(1) \\ y_2(1) \end{bmatrix} = \begin{bmatrix} \theta(1) \\ 0 \end{bmatrix} = \begin{bmatrix} \left(\dfrac{(\exp(H) + \exp(-H))}{2} + \dfrac{(\exp(H) - \exp(-H))y_{20}}{2H}\right) \\ \left(\dfrac{H(\exp(H) - \exp(-H))}{2} + \dfrac{(\exp(H) + \exp(-H))y_{20}}{2}\right) \end{bmatrix}. \tag{13}$$

From the second row of the matrix Eq. (13) y_{20} is obtained as,

$$y_{20} = -\frac{H(\exp(H) - \exp(-H))}{(\exp(H) + \exp(-H))}. \tag{14}$$

This value for the unknown initial condition is then substituted back into Eq. (12) to get the complete solution to the BVP, which is the same as Eq. 3. Similar BVPs arise in the diffusion and reaction in rectangular and spherical coordinates. In these cases, the matrizant reduces to the exponential of the matrix which is directly calculated and used.

However, for diffusion and reaction problems in cylindrical coordinates the matrizant does not reduce to the matrix exponential. Fortunately, an analytical solution can still be obtained by writing the second-order governing equation as a system of first order equations and using the method of successive substitution, as before. In this case Eq. (10) is used for evaluating the matrizant. This can be illustrated by considering diffusion and reaction in a cylindrical catalyst pellet. The reaction is assumed to be isothermal, irreversible and of first order. The dimensionless concentration, c, obeys the governing equation (Villadsen and Michelsen, 1978, pp. 68–73),

$$\frac{d^2 c}{dx^2} + \frac{1}{x}\frac{dc}{dx} - \Phi^2 c = 0, \tag{15}$$

where Φ is the Thiele parameter and x is the dimensionless radial distance. The boundary conditions are,

$$\frac{dc}{dx}(0) = 0, \quad c(1) = 1. \tag{16}$$

We convert this into an IVP of the form of Eq. (4) of the previous example, where,

$$\frac{d\mathbf{y}}{dx} = \begin{bmatrix} \dfrac{dy_1}{dx} \\ \dfrac{dy_2}{dx} \end{bmatrix} = \begin{bmatrix} \dfrac{dc}{dx} \\ \dfrac{d^2 c}{dx^2} \end{bmatrix}, \tag{17}$$

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} c \\ \dfrac{dc}{dx} \end{bmatrix} \tag{18}$$

and

$$\mathbf{A}(x) = \begin{bmatrix} 0 & 1 \\ \Phi^2 & \dfrac{-1}{x} \end{bmatrix}. \tag{19}$$

As before, only one of the initial conditions is known i.e., $dc/dx(0) = 0$. Thus,

$$\mathbf{y}_0 = \begin{bmatrix} y_{10} \\ y_{20} \end{bmatrix} = \begin{bmatrix} y_{10} \\ 0 \end{bmatrix} \tag{20}$$

The initial condition for the concentration in Eq. (20) is obtained using the boundary at the other end namely, $c(1) = 1$ or $y_1(1) = 1$. The final solution is given by Eq. (9). For this case, since the coefficient matrix $\mathbf{A}$ (Eq. (9)) is not constant the matrizant $\Omega(\mathbf{A})$ is calculated using Eq. (10). However, a singularity is encountered at the origin $(x = 0)$ since the matrix $\mathbf{A}$ involves the $1/x$ term. This singularity is avoided by making use of the independent variable transformation (Rice and Do, 1995, p. 59):

$$t = \ln(x). \tag{21}$$

When this transformation is applied the given BVP is converted to,

$$\frac{d^2 c}{dt^2} = \exp(2t)\Phi^2 c \tag{22}$$

with the boundary conditions

$$\frac{dc}{dt}(-\infty) = 0, \quad c(0) = 1. \tag{23}$$

Converting this into an IVP of the form of Eq. (4) we have,

$$\frac{d\mathbf{y}}{dx} = \begin{bmatrix} \dfrac{dy_1}{dt} \\ \dfrac{dy_2}{dt} \end{bmatrix} = \begin{bmatrix} \dfrac{dc}{dt} \\ \dfrac{d^2 c}{dt^2} \end{bmatrix}, \tag{24}$$

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} c \\ \dfrac{dc}{dt} \end{bmatrix} \tag{25}$$

and

$$\mathbf{A}(t) = \begin{bmatrix} 0 & 1 \\ \exp(2t)\Phi^2 & 0 \end{bmatrix}. \tag{26}$$

The initial conditions are changed to

$$\mathbf{y}_0 = \begin{bmatrix} y_{10} \\ y_{20} \end{bmatrix} = \begin{bmatrix} 1 \\ y_{20} \end{bmatrix}. \tag{27}$$

The initial condition for the derivative of the concentration i.e., y_{20} is obtained by using $dc/dt(-\infty) = 0$. The solution is given by Eq. (9). In this case, the matrizant $\Omega(\mathbf{A})$ is obtained from Eqs. (10) and (26) as

$$\Omega(\mathbf{A}) = \begin{bmatrix} \begin{array}{l} 1 - \frac{1}{4}\Phi^2 - \frac{5}{64}\Phi^4 - \frac{5}{1152}\Phi^6 - \cdots \\ \quad - (\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4 + \frac{1}{384}\Phi^6 + \cdots)\,t \\ \quad + (\frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4\exp(2t) +)\exp(2t) \\[1em] - (\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4 + \frac{1}{384}\Phi^6 + \cdots) \\ \quad + (\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4\exp(2t) + \cdots)\exp(2t) \end{array} & \begin{array}{l} \frac{1}{4}\Phi^2 + \frac{3}{128}\Phi^4 + \cdots \\ (1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \cdots)\,t \\ \quad - (\frac{1}{4}\Phi^2 + \frac{3}{128}\Phi^4\exp(2t) + \cdots)\exp(2t) \\ \quad + t(\frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4\exp(2t) + \cdots)\exp(2t) \\[1em] 1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \frac{1}{2304}\Phi^6 \\ \quad - (\frac{1}{4}\Phi^2 + \frac{5}{64}\Phi^4\exp(2t) + \cdots)\exp(2t) \\ \quad + t(\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4\exp(2t) + \cdots)\exp(2t) \end{array} \end{bmatrix}. \tag{28}$$

Now, by substituting the expression for the matrizant (Eq. (28)) and $\mathbf{y}_0$ from Eq. (27) into Eq. (25) we get,

$$
\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} c \\ \dfrac{dc}{dt} \end{bmatrix} = \left[\begin{array}{c} \left(\begin{array}{c} \left(\begin{array}{c} 1 - \frac{1}{4}\Phi^2 - \frac{5}{64}\Phi^4 - \frac{5}{1152}\Phi^6 - \cdots \\ - (\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4 + \frac{1}{384}\Phi^6 + \cdots)t \\ + (\frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 \exp(2t) + \cdots)\exp(2t) \end{array} \right) \\ + y_{20} \left(\begin{array}{c} \frac{1}{4}\Phi^2 + \frac{3}{128}\Phi^4 + \cdots \\ (1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \cdots)t \\ - (\frac{1}{4}\Phi^2 + \frac{3}{128}\Phi^2 \exp(2t) + \cdots)\exp(2t) \\ + (\frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^2 \exp(2t) + \cdots)t\exp(2t) \end{array} \right) \end{array} \right) \\ \left(\begin{array}{c} \left(\begin{array}{c} - (\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4 + \frac{1}{384}\Phi^6 + \cdots) \\ + (\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4 \exp(2t) + \cdots)\exp(2t) \end{array} \right) \\ + y_{20} \left(\begin{array}{c} 1 + \frac{1}{4}\Phi^2 + \frac{5}{64}\Phi^2 + \frac{1}{2304}\Phi^6 \\ - (\frac{1}{4}\Phi^2 + \frac{5}{64}\Phi^4 \exp(2t) + \cdots)\exp(2t) \\ + (\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4 \exp(2t) + \cdots)t\exp(2t) \end{array} \right) \end{array} \right) \end{array} \right]. \tag{29}
$$

The constant y_{20} in Eq. (29) is obtained by using the known, transformed boundary condition, as $t \to -\infty$, dc/dt or $y_2(-\infty) = 0$:

$$
\mathbf{y}(-\infty) = \begin{bmatrix} y_1(-\infty) \\ y_2(-\infty) \end{bmatrix} = \begin{bmatrix} c(-\infty) \\ 0 \end{bmatrix} = \left[\begin{array}{c} \left(\begin{array}{c} \left(\begin{array}{c} 1 - \frac{1}{4}\Phi^2 - \frac{5}{64}\Phi^4 - \frac{5}{1152}\Phi^6 - \cdots \\ - (\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4 + \frac{1}{384}\Phi^6 + \cdots)t \end{array} \right) \\ + y_{20} \left(\begin{array}{c} \frac{1}{4}\Phi^2 + \frac{3}{128}\Phi^4 + \cdots \\ + (1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \cdots)t \end{array} \right) \end{array} \right) \\ \left(\begin{array}{c} - (\frac{1}{2}\Phi^2 + \frac{1}{16}\Phi^4 + \frac{1}{384}\Phi^6 + \cdots) \\ + y_{20}(1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \frac{1}{2304}\Phi^6 + \cdots) \end{array} \right) \end{array} \right]. \tag{30}
$$

In the first row of Eq. (30) the limit of $t \to -\infty$ is not applied because 't' will be cancelled in a subsequent step, as seen below. From the second row of the matrix Eq. (30), y_{20} is obtained as

$$
y_{20} = \frac{\frac{1}{2}\Phi^2(1 + \frac{1}{8}\Phi^2 + \frac{1}{192}\Phi^4 + \frac{1}{9216}\Phi^6 + \frac{1}{737\,280}\Phi^8 + \cdots)}{(1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \frac{1}{2304}\Phi^6 + \frac{1}{147\,456}\Phi^8 + \frac{1}{14\,745\,600}\Phi^{10} + \cdots)} \tag{31}
$$

When this value of y_{20} is substituted into the first row of Eq. (30), we see that the coefficient of the 't' term vanishes, removing the singularity. Next y_{20} from Eq. (31) is substituted into Eq. (29) to get the complete solution to the BVP in terms of the transformed independent variable t as

$$
y = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} c \\ \dfrac{dc}{dt} \end{bmatrix} = \left[\begin{array}{c} \dfrac{\left(\begin{array}{c} 1 + \frac{1}{4}\Phi^2 \exp(2t) + \frac{1}{64}\Phi^4 \exp(4t) + \frac{1}{2304}\Phi^6 \exp(6t) \\ + \frac{1}{147\,456}\Phi^8 \exp(8t) + \frac{1}{14\,745\,600}\Phi^{10} \exp(10t) + \cdots \end{array} \right)}{(1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \frac{1}{2304}\Phi^6 + \frac{1}{147\,456}\Phi^8 + \frac{1}{14\,745\,600}\Phi^{10} + \cdots)} \\ \\ \dfrac{\frac{1}{2}\Phi^2 \exp(2t) \left(\begin{array}{c} 1 + \frac{1}{8}\Phi^2 \exp(2t) + \frac{1}{192}\Phi^4 \exp(4t) \\ + \frac{1}{9216}\Phi^6 \exp(6t) + \frac{1}{737\,280}\Phi^8 \exp(8t) + \cdots \end{array} \right)}{(1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \frac{1}{2304}\Phi^6 + \frac{1}{147\,456}\Phi^8 + \frac{1}{14\,745\,600}\Phi^{10} + \cdots)} \end{array} \right] \tag{32}
$$

Substitution of Eq. (21) into Eq. (32) transforms the solution back to the original independent variable x:

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} c \\ \dfrac{dc}{dx} \end{bmatrix} = \begin{bmatrix} \left(\dfrac{(1 + \frac{1}{4}\Phi^2 x^2 + \frac{1}{64}\Phi^4 x^4 + \frac{1}{2304}\Phi^6 x^6 + \frac{1}{147\,456}\Phi^8 x^8 + \frac{1}{14\,745\,600}\Phi^{10} x^{10} + \cdots)}{(1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \frac{1}{2304}\Phi^6 + \frac{1}{147\,456}\Phi^8 + \frac{1}{14\,745\,600}\Phi^{10} + \cdots)} \right) \\ \left(\dfrac{\frac{1}{2}\Phi^2 x (1 + \frac{1}{8}\Phi^2 x^2 + \frac{1}{192}\Phi^4 x^4 + \frac{1}{9216}\Phi^6 x^6 + \frac{1}{737\,280}\Phi^8 x^8 + \cdots)}{(1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \frac{1}{2304}\Phi^6 + \frac{1}{147\,456}\Phi^8 + \frac{1}{14\,745\,600}\Phi^{10} + \cdots)} \right) \end{bmatrix} \qquad (33)$$

From the first row of the matrix Eq. (33), the concentration profile is obtained as

$$c = \frac{(1 + \frac{1}{4}\Phi^2 x^2 + \frac{1}{64}\Phi^4 x^4 + \frac{1}{2304}\Phi^6 x^6 + \frac{1}{147\,456}\Phi^8 x^8 + \frac{1}{14\,745\,600}\Phi^{10} x^{10} + \cdots)}{(1 + \frac{1}{4}\Phi^2 + \frac{1}{64}\Phi^4 + \frac{1}{2304}\Phi^6 + \frac{1}{147\,456}\Phi^8 + \frac{1}{14\,745\,600}\Phi^{10} + \cdots)} \qquad (34)$$

The series expansions in Eq. (34) are the modified Bessel functions of zeroth order (Villadsen and Michelsen, 1978, p. 69). Thus, Eq. (34) can be rewritten as,

$$c = \frac{I_0(\Phi x)}{I_0(\Phi)} \qquad (35)$$

which is the same as the analytical solution given by Villadsen and Michelsen.

3. Nonlinear BVPS

Nonlinear BVPs can also be solved with the method presented above. This is done by quasi-linearizing the nonlinear term in the ODE by Newton's method (Haran and White, 1996). For a nonlinear ODE with only one dependent variable we have,

$$y'(x) = f(x, y) + b(x) \qquad (36)$$

Quasi-linearization of the nonlinear function $f(x, y)$ gives,

$$f(x, y^k) = f(x, y^{k-1}) + \left(\frac{df}{dy} \right)_{y=y^{k-1}} (y^k - y^{k-1}), \qquad (37)$$

where k represents the iteration number. Rewriting Eq. (36) by using Eq. (37) we have,

$$\frac{dy^k}{dx} = f(x, y^{k-1}) + \left(\frac{df}{dy} \right)_{y=y^{k-1}} (y^k - y^{k-1}) + b(x)^{k-1}. \qquad (38)$$

The initial condition remains the same as for the linear case. Eq. (38) is linear in y^k and we can integrate this by using the successive substitution method as described earlier. Repeating the same procedure, we can solve Eq. (38) by iterating until the required convergence is obtained. The same approach can also be used for solving systems of coupled non-linear differential equations.

4. Example

In this example, we solve two coupled non-linear differential equations using quasi-linearization and successive substitution. This example involves the steady state analysis of a gas-fed porous electrode in a fuel cell (White et al., 1984). The ODEs describing the Molar fractions of the gas and liquid reactants within a gas-fed porous electrode of a fuel cell are,

$$\frac{d^2 c_1}{dx^2} = k_1 c_1^2, \qquad (39)$$

$$\frac{d^2 c_2}{dx^2} = k_2 c_1^2, \qquad (40)$$

with boundary conditions,

$$c_1(0) = 0.21, \frac{dc_2}{dx}(0) = 0 \qquad (41)$$

and

$$c_2(1) = 0.127, \frac{dc_1}{dx}(1) = 0, \qquad (42)$$

where c_1 and c_2 are the dimensionless concentration of species 1 and 2, respectively, x is the dimensionless distance, and k_1 and k_2 are the rate constants for the reactions. The non-linearity in the ODEs arises because of the c_1^2 terms. Quasi-linearization of this term by Newton's method (Bala and White, 1996) yields,

$$(c_1^2)^k = (c_1^2)^{k-1} + 2c_1^{k-1}(c_1^k - c_1^{k-1}), \qquad (43)$$

where k is the iteration counter. Substituting Eq. (43) into Eqs. (39) and (40) gives,

$$\frac{d^2 c_1^k}{dx^2} = k_1 [(c_1^2)^{k-1} + 2c_1^{k-1}(c_1^k - c_1^{k-1})], \qquad (44)$$

$$\frac{d^2 c_2^k}{dx^2} = k_2 [(c_1^2)^{k-1} + 2c_1^{k-1}(c_1^k - c_1^{k-1})], \qquad (45)$$

Eqs. (44) and (45) are linear and give rise to the vector differential equation,

$$\left(\frac{d\mathbf{y}}{dx}\right)^k = \mathbf{A}(x))^{k-1}\mathbf{y}^k + (\mathbf{b}(x))^{k-1}, \tag{46}$$

where,

$$\frac{d\mathbf{y}}{dx} = \begin{bmatrix} \dfrac{dy_1}{dx} \\ \dfrac{dy_2}{dx} \\ \dfrac{dy_3}{dx} \\ \dfrac{dy_4}{dx} \end{bmatrix} = \begin{bmatrix} \dfrac{dc_1}{dx} \\ \dfrac{d^2c_1}{dx^2} \\ \dfrac{dc_2}{dx} \\ \dfrac{d^2c_2}{dx^2} \end{bmatrix}, \tag{47}$$

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \end{bmatrix} = \begin{bmatrix} c_1 \\ \dfrac{dc_1}{dx} \\ c_2 \\ \dfrac{dc_2}{dx} \end{bmatrix}, \tag{48}$$

$$(\mathbf{A}(x))^{k-1} = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 2k_1c_1^{k-1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 2k_2c_1^{k-1} & 0 & 0 & 0 \end{bmatrix} \tag{49}$$

and

$$(\mathbf{b}(x))^{k-1} = \begin{bmatrix} 0 \\ -k_1(c_1^2)^{k-1} \\ 0 \\ -k_2(c_1^2)^{k-1} \end{bmatrix} \tag{50}$$

For this case a forcing function (Eq. (50)) arises out of the quasi-linearization process. Only two of the initial conditions are known i.e., $c_1(0) = 0.21$; $dc_2/dx(0) = 0$. Thus,

$$\mathbf{y}_0 = \begin{bmatrix} y_{10} \\ y_{20} \\ y_{30} \\ y_{40} \end{bmatrix} = \begin{bmatrix} 0.21 \\ y_{20} \\ y_{30} \\ 0 \end{bmatrix}, \tag{51}$$

The initial conditions for the derivative of the first species, $dc_1/dx(0)$ or y_{20} and concentration of the second

species $c_2(0)$ or y_{30} are obtained simultaneously by using the constraints at the other boundary, $c_2(1)$ [i.e., $y_3(1)$] = 0.127 and $dc_1/dx(1)$ [i.e., $y_2(1)$] = 0, as described in more details below. Since the governing equations are coupled, we need to solve for the two initial conditions simultaneously for each iteration. This is done by iterating for the initial conditions using the two boundaries given above as constraints.

For the first iteration the value of variable $c_1^{k-1}(x)$ with $k = 1$ is assumed to be equal to the boundary value for all x (i.e., $c_1^{k-1}(x) = c_1(0) = 0.21$). Thus,

$$(\mathbf{A}(x))_{k=1}^{k-1} = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 2k_1c_1^{k-1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 2k_2c_1^{k-1} & 0 & 0 & 0 \end{bmatrix}_{k=1}$$

$$= \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0.42k_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0.42k_2 & 0 & 0 & 0 \end{bmatrix} \tag{52}$$

and

$$(\mathbf{b}(x))_{k=1}^{k-1} = \begin{bmatrix} 0 \\ -k_1(c_1^2)^{k-1} \\ 0 \\ -k_2(c_1^2)^{k-1} \end{bmatrix}_{k=1} = \begin{bmatrix} 0 \\ -k_1(0.21)^2 \\ 0 \\ -k_2(0.21)^2 \end{bmatrix}. \tag{53}$$

The solution for Eq. (46) can be written as (Taylor and Krishna, 1993, p. 528),

$$\mathbf{y} = [\Omega(\mathbf{A})]\left(\mathbf{y}_0 + \int_0^x [\Omega(\mathbf{A})]^{-1}(\mathbf{b}(x_1))\,dx_1\right). \tag{54}$$

In this case, the matrizant $\Omega(\mathbf{A})$ obtained from Eq. (10) with $\mathbf{A}$ from Eq. (52) simplifies to,

$$\Omega(\mathbf{A}) = \begin{bmatrix} 1 + 0.21k_1x^2 + \cdots & x + 0.07k_1x^3 + \cdots & 0 & 0 \\ 0.42k_1x + 0.0294k_1^2x^3 + \cdots & 1 + 0.21k_1x^2 + \cdots & 0 & 0 \\ 0.21k_2x^2 + 0.00735k_2k_1x^4 + \cdots & 0.07k_2x^3 + 0.00147k_2k_1x^5 + \cdots & 1 & x \\ 0.42k_2x + 0.0294k_2k_1x^3 + \cdots & 0.21k_2x^2 + 0.00735k_2k_1x^4 + \cdots & 0 & 1 \end{bmatrix} \tag{55}$$

Now by substituting the expression for the matrizant (Eq. (55)), $\mathbf{b}(x)$ from Eq. (53) and $\mathbf{y}_0$ from Eq. (51) into Eq. (54) we get,

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \end{bmatrix} = \begin{bmatrix} c_1 \\ \dfrac{dc_1}{dx} \\ c_2 \\ \dfrac{dc_2}{dx} \end{bmatrix},$$

$$
= \begin{bmatrix}
\begin{pmatrix} (0.21 + 0.0221k_1x^2 + 0.0000663k_1^3x^5 + \cdots) \\ + y_{20}(x + 0.07k_1x^3 + 0.00147k_1^2x^5 + \cdots) \end{pmatrix} \\
\begin{pmatrix} (0.0441k_1x + 0.00311k_1^2x^3 + 0.0000663k_1^3x^5) \\ + y_{20}(1 + 0.21k_1x^2 + 0.00735k_1^2x^4 + \cdots) \end{pmatrix} \\
\begin{pmatrix} (0.0221k_2x^2 + 0.000781k_2k_1x^4 + \cdots) \\ + y_{20}(0.07k_2x^3 + 0.00147k_2k_1x^5 + \cdots) + y_{30} \end{pmatrix} \\
\begin{pmatrix} (0.0441k_2x + 0.00311k_2k_1x^3 + 0.0000667k_2k_1^2x^5) \\ + y_{20}(0.21k_2x^2 + 0.00735k_2k_1x^4 + \cdots) \end{pmatrix}
\end{bmatrix}
\tag{56}
$$

The constants y_{20} and y_{30} in Eq. (56) are obtained by first applying the constraints at the other boundary ($x = 1$), $c_2(1) = 0.127$ or $(y_3(1) = 0.127)$ and $dc_1/dx(1) = 0$ (or $y_2(1) = 0$), which yields,

$$
\mathbf{y}(1) = \begin{bmatrix} y_1(1) \\ y_2(1) \\ y_3(1) \\ y_4(1) \end{bmatrix} = \begin{bmatrix} c_1(1) \\ 0 \\ 0.127 \\ \dfrac{dc_2}{dx}(1) \end{bmatrix},
$$

$$
= \begin{bmatrix}
\begin{pmatrix} (0.21 + 0.0221k_1 + 0.0000663k_1^3 + \cdots) \\ + y_{20}(1 + 0.07k_1 + 0.00147k_1^2 + \cdots) \end{pmatrix} \\
\begin{pmatrix} (0.0441k_1 + 0.00311k_1^2 + 0.0000663k_1^3) \\ + y_{20}(1 + 0.21k_1 + 0.00735k_1^2 + \cdots) \end{pmatrix} \\
\begin{pmatrix} (0.0221k_2 + 0.000781k_2k_1 + \cdots) \\ + y_{20}(0.07k_2 + 0.00147k_2k_1 + \cdots) + y_{30} \end{pmatrix} \\
\begin{pmatrix} (0.0441k_2 + 0.00311k_2k_1 + 0.0000667k_2k_1^2) \\ + y_{20}(0.21k_2 + 0.00735k_2k_1 + \cdots) \end{pmatrix}
\end{bmatrix}
\tag{57}
$$

From the second and third rows of the matrix Eq. (57), the constants y_{20} and y_{30} are solved simultaneously as series expansions in k_1 and k_2 as,

$$
y_{20} = -0.0442k_1 + 0.00618k_1^2 - 0.0104k_1^3 + 0.000173k_1^4 - \cdots
\tag{58}
$$

and

$$
y_{30} = 0.127 - 0.0221k_2 + 0.00231k_2k_1 - 0.000347k_2k_1^2 + 0.0000671k_2k_1^3 - \cdots.
\tag{59}
$$

These values of the unknown initial conditions (Eqs. (58) and (59)) are then substituted back into Eq. (56) to get the

concentration of both the species as follows,

$$
\begin{aligned}
y_1 = c_1 = {} & 0.21 + (-0.0442k_1 + 0.00618k_1^2 - 0.0104k_1^3 \\
& + 0.000173k_1^4 - \cdots)x + 0.0221k_1x^2 \\
& + 0.07(-0.0442k_1 + 0.00618k_1^2 \\
& - 0.0104k_1^3 + \cdots)k_1x^3 + 0.000781k_1^2x^4 \\
& + \cdots
\end{aligned}
\tag{60}
$$

and

$$
\begin{aligned}
y_3 = c_2 = {} & 0.127 - 0.0221k_2 + 0.00231k_2k_1 \\
& - 0.000347k_2k_1^2 + \cdots + 0.0221k_2x^2 \\
& + 0.07(-0.0442k_1 + 0.00618k_1^2 \\
& - 0.0104k_1^3 + \cdots)k_2x^3 \\
& + 0.000781k_2k_1x^4 + \cdots.
\end{aligned}
\tag{61}
$$

Hence we have obtained a series solution for the concentration of each species after the first iteration.

For the second iteration ($k = 2$), the expression for c_1 given by Eq. (60) is used in both $\mathbf{A}$ and $\mathbf{b}$ in Eqs. (49) and (50). Thus,

$$
\begin{aligned}
c_{1k=2}^{k-1} = c_{1k=1}^{k} = {} & 0.21 + (-0.0442k_1 + 0.00618k_1^2 \\
& - 0.0104k_1^3 + 0.000173k_1^4 - \cdots)x \\
& + 0.0221k_1x^2 + 0.07(-0.0442k_1 \\
& + 0.00618k_1^2 - 0.0104k_1^3 + \cdots)k_1x^3 \\
& + 0.000781k_1^2x^4 + \cdots.
\end{aligned}
\tag{62}
$$

The same procedure that was used for finding the unknown initial conditions y_{20} and y_{30} in the first iteration is repeated until three digit convergence is obtained for the unknown initial conditions. For this case only two iterations were required to achieve three digit accuracy for the range of values used here for k_1 and k_2, as described later.

The final solutions for the concentration profiles for both species are:

$$
\begin{aligned}
c_1(x) = {} & 0.210 - (0.0441k_1 - 0.00615k_1^2 + \cdots)x \\
& + 0.0221k_1x^2 - (0.0031k_1^2 - 0.000430k_1^3 + \cdots)x^3 \\
& + (0.00073k_1^2 + 0.000162k_1^3 + \cdots)x^4 \\
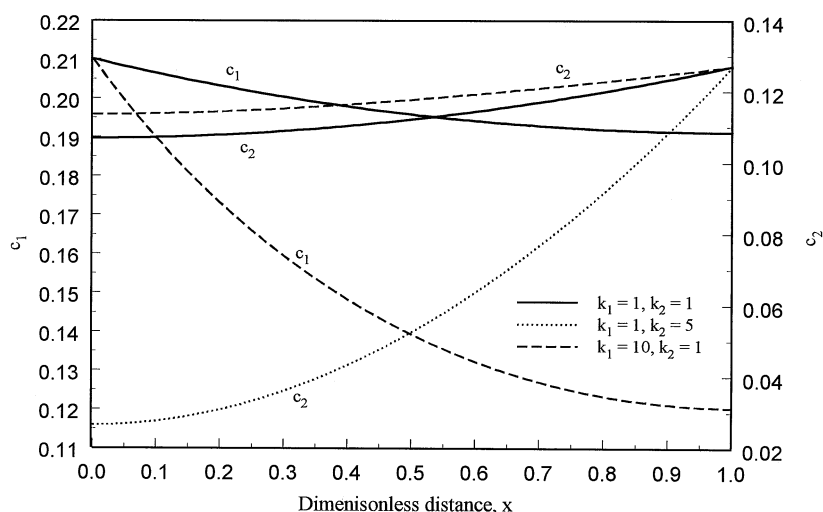& - (0.000163k_1^3 - 0.000022k_1^4 + \cdots)x^5 + \cdots
\end{aligned}
\tag{63}
$$

Fig. 1. Predicted concentration profiles in a fuel cell electrode.

and

$$c_2(x) = 0.127 - 0.0222k_2 + 0.00234k_2k_1$$
$$- 0.000458k_2k_1^2 + \cdots + 0.0221k_2x^2$$
$$- (0.0031k_2k_1 - 0.000430k_2k_1^2 + \cdots)x^3$$
$$+ (0.0007k_2k_1 + 0.000162k_2k_1^2 + \cdots)x^4$$
$$- (0.000163k_1^3 - 0.000022k_1^4 + \cdots)x^5 + \cdots. \quad (64)$$

The concentration profiles given by Eqs. (63) and (64) are plotted for various values of the reaction constants in Fig. 1. We did not check for the convergence of the series solutions given by Eqs. (63) and (64). Instead, we set the values of k_1 and k_2 and then added constant terms to the coefficients of the x^2 and higher-order x terms until the predicted values for $c_1(x)$ and $c_2(x)$ did not change in the third digit. This process required three terms for $k_1 = k_2 = 1$ and eight terms for $k_1 = 1$, $k_2 = 5$, and 22 terms for $k_1 = 10$, and $k_2 = 1$.

A generalized methodology is given in the Appendix. These series solutions (Eqs. (63) and (64)) may be more convenient than numerical solutions. For example, it may be efficient to use these series solutions with nonlinear parameter estimation techniques to obtain values for k_1 and k_2, for a given set of data for c_1 and c_2. This may be possible because the values of $c_1(x)$ and $c_2(x)$ would be obtained from series evaluation as opposed to numerical integration of the governing equations.

5. Conclusions

A technique for solving BVPs is presented for both linear and nonlinear problems. The methodology developed herein is simple and general and should be applicable for any class of BVPs. By including more terms in the successive substitution step greater accuracy can be obtained. Further, for problems where one is only interested in the results at a particular x, this method offers a quick solution, compared to numerical techniques where one needs to integrate from the origin to that particular x. In general, numerical IVP solvers for BVP problems (e.g., shoot and correct, Davis, pp. 54–55) require an initial guess for the unknown condition. However, we have proposed here an alternate scheme, which does not require an initial guess for the unknown initial condition and results in a series solution. Three sample problems from classical chemical engineering are solved and discussed. For linear BVPs the technique yields a fast and accurate analytical solution. For nonlinear BVPs, an iterative algorithm coupled with Newton's quasi-linearization yields series solutions. For both linear and nonlinear BVPs parameter estimation may be possible with the series solutions obtained here because the parameters (k_1 and k_2) appear explicitly.

Appendix A. Generalized methodology for linear BVPs

The successive substitution method, which was discussed in this paper is generalized here. Consider the two-point BVP of a single dependent variable y of nth

order in the domain $[a, b]$ as,

$$\frac{d^n y}{dx^n} + \gamma_{n-1} \frac{d^{n-1} y}{dx^{n-1}} + \cdots \gamma_1 \frac{dy}{dx} + \gamma_0 y = f(x), \quad (A.1)$$

where $\gamma_0, \gamma_1, \ldots, \gamma_{n-1}$ are the coefficients of the dependent variable and it's derivatives and $f(x)$ is the forcing function. This is a nth order inhomogeneous equation in the independent variable x subject to the following boundary conditions at the ends of the interval, i.e. at $x = a$ and $x = b$:

$$g[y(a), y'(a), \ldots, y^{n-2}(a), y^{n-1}(a)] = \alpha, \quad (A.2)$$

$$f[y(b), y'(b), \ldots, y^{n-2}(b), y^{n-1}(b)] = \beta. \quad (A.3)$$

Eq. (A.1) can be reduced to n linear first-order coupled differential equations (Rice and Do, 1995, p. 61) by defining,

$$y_1 = y, y_2 = \frac{dy}{dx}, y_3 = \frac{d^2 y}{dx^2}, y_n = \frac{d^{n-1} y}{dx^{n-1}}. \quad (A.4)$$

Eq. (A.4) can be written in vector form as (Taylor and Krishna, 1993, p. 524),

$$\frac{d\mathbf{y}}{dx} = \mathbf{A}(x)\mathbf{y} + \mathbf{b}(x). \quad (A.5)$$

For a second-order differential equation the vectors are,

$$\frac{dy}{dx} = \left[\frac{dy_1}{dx}, \frac{dy_2}{dx}\right]^T,$$

$$\mathbf{y} = [y_1, y_2]^T, \quad \mathbf{b} = [0, f(x)]^T \quad (A.6)$$

and the coefficient matrix is,

$$\mathbf{A} = \begin{bmatrix} 0 & 1 \\ -\gamma_0 & -\gamma_1 \end{bmatrix}. \quad (A.7)$$

The new problem requires the solution of a system of IVPs with appropriate initial conditions. Eqs. (A.2) and (A.3) become,

$$g[y_1(a), y_2(a)] = \alpha, \quad y_2(a) = \lambda. \quad (A.8)$$

The second condition arises due to the fact that the initial condition at $x = a$ is not known for y_2. The alternate that y_1 is unknown and y_2 is known at $x = a$ is also possible. Here λ is the unknown initial condition for y_2. The value of λ is subject to the constraint of the boundary at the other end,

$$g[y_1(b), y_2(b)] = \beta. \quad (A.9)$$

The solution for Eq. (A.5) can be written as (Taylor and Krishna, 1993, p. 528)

$$\mathbf{y} = [\Omega(\mathbf{A})]\left(\mathbf{y}_0 + \int_0^x [\Omega(\mathbf{A})]^{-1}(\mathbf{b}(x_1)) \, dx_1\right) \quad (A.10)$$
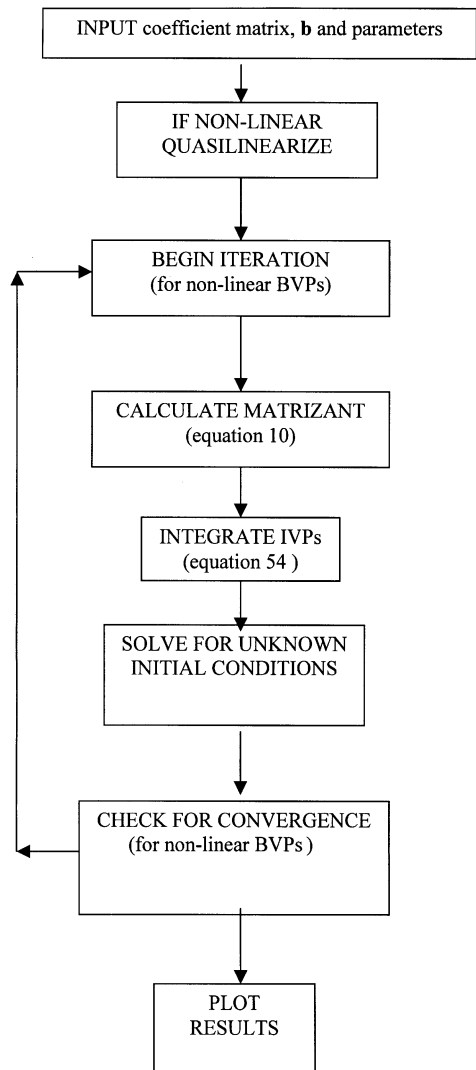

Fig. 2. General solution scheme for two-point boundary value problem.

However, conversion of linear BVPs in some cases gives rise to sets of equations where the matrix $\mathbf{A}$ varies with the independent variable, x. Eq. (A.10) along with Eq. (10) for the matrizant represents a general solution to a system of IVPs irrespective of whether the coefficient matrix $\mathbf{A}$ is constant or varying. For further details on the derivation of the matrizant the reader is advised to refer to the pertinent literature (Taylor and Krishna, 1993, pp. 524–529; Amundson, 1966, pp. 199–203). The vector y_0 in Eq. (A.10) consists of the initial conditions at $x = a$ including the unknown λ.

$$\mathbf{y}_0 = [g[y_1(a), y_2(a)] = \alpha, y_2(a) = \lambda]^T. \quad (A.11)$$

A general algorithm for solving two-point boundary value problems is given in Fig. 2. The given linear BVP is first converted into a set of IVPs. These IVPs are then integrated by the successive substitution method. The

unknown initial condition is then obtained by using the known boundary condition. The same procedure is used for nonlinear BVPs after quasi-linearizing the nonlinear terms and iterating for the required convergence. The technique as shown for one dependent variable can be used for solving any number of coupled differential equations.

The input given to the maple code consists of the coefficient matrix (obtained by quasi-linearization for nonlinear BVPS) and the parameter values (only for determining 3 digits accuracy as described in Section 4). Then the Maple code finds the matrizant by the successive substitution method and gives the final series solution required. We used Maple® for implementing the solution scheme outlined in Fig. 2. Though we implemented the technique in Maple®, it may be possible to use other symbolic solvers to implement our procedure.

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