In the previous chapter we presented numerical techniques to solve differential equations of the initial value type, that is, the type where conditions are specified at only one position or time, such as \( t = 0 \) in the time domain. In this chapter we discuss methods to handle ordinary differential equations of the boundary value type, that is, conditions are specified at two different points in the domain, such as conditions at the two ends of a fixed bed reactor or conditions at two sides of a membrane. We start the chapter by discussing general aspects of the underlying basis for the method: weighted residuals. As a subset of this, we pay particular attention to the orthogonal collocation method, which enjoys wide popularity for current applications in chemical engineering research problems. It is particularly attractive for solving nonlinear problems which heretofore have defied analytical treatment.

8.1 THE METHOD OF WEIGHTED RESIDUALS

The method of weighted residuals has been used in solving a variety of boundary value problems, ranging from fluid flow to heat and mass transfer problems. It is popular because of the interactive nature of the first step, that is, the user provides a first guess at the solution and this is then forced to satisfy the governing equations along with the conditions imposed at the boundaries. The left-over terms, called residuals, arise because the chosen form of solution does not exactly satisfy either the equation or the boundary conditions. How these residual terms are minimized provides the basis for parameter or function
selection. Of course, the optimum solution depends on the intelligent selection of a proposed solution.

To illustrate the salient features of the method, we first consider the following boundary value problem in an abstract form, and then later attempt an elementary example of diffusion and reaction in a slab of catalyst material. We shall assume there exists an operator of the type discussed in Chapter 2 (Section 2.5) so that in compact form, we can write

\[ L(y) = 0 \]  \hspace{1cm} (8.1)

where \( L \) is some differential operator. Examples of Eq. 8.1 are

\[ L(y) = \frac{d^2y}{dx^2} - 100y^2 = 0 \]
\[ L(y) = \frac{d}{dx} \left[ (1 + 10y) \frac{dy}{dx} \right] = 0 \]

The differential equation (Eq. 8.1) is subject to the boundary condition

\[ M(y) = 0 \]  \hspace{1cm} (8.2)

These boundary values could be initial values, but any boundary placement is allowed, for example \( dy(0)/dx = 0 \), or \( y(1) = 0 \), where \( M(y) \) is simply a general representation of the operation on \( y \) as \( dy(0)/dx = 0 \) or \( y(1) = 0 \), respectively.

The essential idea of the method of weighted residuals is to construct an approximate solution and denote it as \( y_a \). Because of the approximate nature of the estimated solution, it may not, in general, satisfy the equation and the boundary conditions; that is:

\[ L(y_a) = R \neq 0 \]  \hspace{1cm} (8.3)

and

\[ M(y_a) = R_b \neq 0 \]  \hspace{1cm} (8.4)

where the residuals \( R \) and \( R_b \) are not identically zero. If the approximate solution is constructed such that the differential equation is satisfied exactly (i.e., \( R = 0 \)) the method is called the boundary method. However, if it is constructed such that the boundary conditions are satisfied exactly (i.e., \( R_b = 0 \)) the method is called the interior method. If neither the differential equation nor the boundary conditions are satisfied exactly, it is referred to as the mixed method.

The method of weighted residuals will require two types of known functions. One is called the trial function, and the other is called the test function. The former is used to construct the trial solution, and the latter is used as a basis (criterion) to make the residual \( R \) small (a small residual leads to a small error in the approximate solution). To minimize the residual, which is usually a function of \( x \), we need a means to convert this into a scalar quantity so that a
minimization can be performed. This is done by way of some form of *averaging*, which we call an *inner product*. This can be regarded as a measure of distance between the two functions; that is, between the residual function and the test function, as we show later.

The approximate solution to the governing equation Eq. 8.1 can be written as a polynomial, for example,

$$ y_a(x) = y_0(x) + \sum_{i=1}^{N} a_i \phi_i(x) $$

(8.5)

where $y_0$ is suitably chosen to satisfy the boundary conditions exactly, and generally it is a function of $x$. In the following discussion, we shall use the interior method (i.e., the approximate solution satisfies the boundary conditions exactly). The *trial functions* $\phi_i$ chosen by the analyst must satisfy the boundary conditions, which are usually of the homogeneous type (Chapter 1). The coefficients $a_i$ are unknown and will be determined by the method of residuals to force a close matching of $y_a$ with the proposed equations. Thus, the solution of the governing equation (Eq. 8.1) is reduced to the determination of $N$ coefficients, $a_i$, in the assumed approximate solution (Eq. 8.5).

Substituting this trial solution $y_a$ into the differential equation (Eq. 8.1), we see

$$ R(x) = L \left[ y_0(x) + \sum_{i=1}^{N} a_i \phi_i(x) \right] $$

(8.6)

The residual $R$ is in general nonzero over the whole domain of interest, so that it will be dependent on $x$, in the usual case.

Since the residual $R$ is a function of $x$, we shall need to minimize it over the whole domain of interest. To do this, we need to define some form of averaging. For example, the following integral over the whole domain may be used as a means of averaging

$$ \int_{V} R(x) w_k(x) \, dx $$

(8.7)

where $V$ is the domain of interest, and $w_k$ is some selected set of independent functions ($k = 1, 2, \ldots, N$), which are called the test functions. Such an integral is called an inner product, and we denote this averaging process as

$$ (R, w_k) $$

(8.8a)

This notation is analogous to the dot product used in the analysis of vectors in Euclidean space. The dot product is an operation that maps two vectors into a scalar. Here, in the context of functions, the inner product defined in Eqs. 8.7 or 8.8a will map two functions into a scalar, which will be used in the process of minimization of the residual $R$. This minimization of the residual intuitively implies a small error in the approximate solution, $y_a(x)$. 
Since we have $N$ unknown coefficients $a_i$ in the trial solution (Eq. 8.5), we will take the inner product (defined in Eq. 8.8a) of the residual with the first $N$ test functions and set them to zero, and as a result we will have the following set of $N$ nonlinear algebraic equations

$$(R, w_k) = 0 \quad \text{for} \quad k = 1, 2, 3, \ldots, N \quad (8.8b)$$

which can be solved by using any of the algebraic solvers discussed in Appendix A to obtain the coefficients $a_i$ ($i = 1, 2, \ldots, N$) for the approximate solution (Eq. 8.5).

This completes a brief overview of the approximation routine. To apply the technique, specific decisions must be made regarding the selection of test function and a definition of an inner product (Eq. 8.7 being only one possible choice).

### 8.1.1 Variations on a Theme of Weighted Residuals

There are five widely used variations of the method of weighted residuals for engineering and science applications. They are distinguished by the choice of the test functions, used in the minimization of the residuals (Eq. 8.8). These five methods are

1. The collocation method
2. The subdomain method
3. The least square method
4. The moment method
5. The Galerkin method

Each of these methods have attractive features, which we discuss as follows. Later, we shall concentrate on the collocation method, because it is easy to apply and it can also give good accuracy. The Galerkin method gives better accuracy, but it is somewhat intractable for higher order problems, as we illustrate in the examples to follow.

1. **The collocation method** In this method the test function is the Dirac delta function at $N$ interior points (called collocation points) within the domain of interest, say $0 < x < L$:

$$w_k = \delta(x - x_k) \quad (8.9)$$

where $x_k$ is the $k$th collocation point.

The useful property of the Dirac's delta function is

$$\int_{x_k}^{x} f(x) \delta(x - x_k) \, dx = f(x_k) \quad (8.10)$$

If these $N$ interior collocation points are chosen as roots of an orthogonal Jacobi polynomial of $N$th degree, the method is called the orthogonal collocation method (Villadsen and Michelsen 1978). It is possible to use other orthog-
nal functions, but Jacobi is popular because it is compact and contains only a few terms. Another attractive feature is that the solution can be derived in terms of the dependent variable \( y \) at the collocation points. This will be illustrated in Section 8.4.

2. The subdomain method In this method the domain \( V \) of the boundary value problem is split into \( N \) subdomains \( V_i \); hence, the origin of the name "subdomain method." The test function is chosen such that

\[
w_k = 1
\]

in the subdomain \( V_k \) and is zero elsewhere.

3. The least square method In this method, the test function is chosen as

\[
w_k = \frac{\partial R}{\partial a_k}
\]

With this definition, Eq. 8.8 becomes

\[
\left( R, \frac{\partial R}{\partial a_k} \right) = \frac{1}{2} \frac{\partial}{\partial a_k} (R, R) = 0
\]

Thus, if the inner product is defined as an integral such as in Eq. 8.7, Eq. 8.13 can be written explicitly as

\[
\int_V R \frac{\partial R}{\partial a_k} dx = \frac{1}{2} \frac{\partial}{\partial a_k} \int_V R^2 dx = 0
\]

This means that the coefficients \( a_k \) are found as the minimum of \((R, R)\). The least squares result is the most well-known criterion function for weighted residuals. The test function for this technique is more complicated, owing to the requirement of differentiation in Eq. 8.12.

4. The moment method In this method, the test function is chosen as

\[
w_k = x^{k-1} \quad \text{for} \quad k = 1, 2, \ldots, N
\]

5. The Galerkin method In this method, the weighting function is chosen from the same family as the trial functions, \( \phi_k \), that is:

\[
w_k = \phi_k(x)
\]

For all five methods just discussed, the only restriction on the trial functions is that they must belong to a complete set of linearly independent functions. These functions need not be orthogonal to each other.\(^1\) The trial and test

\(^1\) The definition of orthogonality in the sense used here is discussed in Chapter 10, Section 10.5.
functions must also be chosen as the first $N$ members of that set of independent functions. This will improve the efficiency of the methods of weighted residuals. For the Galerkin method, if the trial and test functions are chosen based on the knowledge of the form of the exact solution of a closely related problem, the efficiency of the method is enhanced (Fletcher 1984). It is noted here that an orthogonal set can always be created from the given set of independent functions.

**EXAMPLE 8.1**

We illustrate the above five variations of weighted residuals with the following example of diffusion and first order chemical reaction in a slab catalyst (Fig. 8.1). We choose the first order reaction here to illustrate the five methods of weighted residual. In principle, these techniques can apply equally well to nonlinear problems, however, with the exception of the collocation method, the integration of the form (8.7) may need to be done numerically.

Carrying out the mass balance over a thin shell at the position $r$ with a thickness of $\Delta r$, we have

$$S J|_r - S J|_{r+\Delta r} - S \Delta r (kC) = 0 \quad (8.17)$$

where $S$ is the cross-sectional area of the catalyst, $J$ is the diffusion flux, defined as moles per unit total area per time, and $kC$ is the chemical reaction rate per unit volume of the catalyst.

![Figure 8.1 Diffusion and reaction in a slab catalyst.](image)
Dividing the equation by $S\Delta r$, we have

$$- \frac{J|_{r+\Delta r} - J|_r}{\Delta r} - kC = 0 \quad (8.18)$$

If we now allow the shell as thin as possible; that is, in the limit of $\Delta r$ approaching zero, we have

$$- \lim_{\Delta r \to 0} \frac{J|_{r+\Delta r} - J|_r}{\Delta r} - kC = 0 \quad (8.19)$$

Using the definition of the derivative, the first two terms in the LHS of Eq. 8.19 become the first derivative of $J$; that is,

$$- \frac{dJ}{dr} - kC = 0 \quad (8.20)$$

The flux into the catalyst particle is taken to be proportional to the concentration gradient

$$J = -D_e \frac{dC}{dr} \quad (8.21)$$

where $D_e$ is the effective diffusivity of the reactant within the catalyst particle, and it is a function of the structure of the catalyst.

Substituting the expression for the diffusion flux (Eq. 8.21) into the mass balance equation (Eq. 8.20) yields

$$D_e \frac{d^2 C}{dr^2} - kC = 0 \quad (8.22)$$

This is a second order differential equation. The boundary conditions for this problem are

$$r = 0; \quad \frac{dC}{dr} = 0 \quad (8.23a)$$

$$r = R; \quad C = C_0 \quad (8.23b)$$

The first condition indicates that there is no flux at the center of the catalyst particle. This condition also says that the reactant concentration profile is symmetrical at the center. This situation is commonly referred to as the symmetry condition. The second boundary condition corresponds to high velocity at the boundary since the reactant concentration at the surface is taken equal to that of the bulk surrounding the particle, which is taken to be invariant in the present problem.

It is convenient to cast the mass balance equation and the boundary conditions into dimensionless form, with the independent variable having the domain
from 0 to 1. By defining the following nondimensional variables and parameters

\[ y = \frac{C}{C_0}; \quad x = \frac{r}{R}; \quad \phi^2 = \frac{kR^2}{D_c} \]  

(8.24)

the mass balance equation and the boundary conditions take the following clean form

\[ \frac{d^2 y}{dx^2} - \phi^2 y = 0 \]  

(8.25a)

\[ x = 0; \quad \frac{dy}{dx} = 0 \]  

(8.25b)

\[ x = 1; \quad y = 1 \]  

(8.25c)

The quantity of interest is the overall reaction rate, which is the observed rate. Starting with the thin shell, the chemical reaction rate in the shell is

\[ \Delta R_{r \times n} = (S \Delta r)(kC) \]  

(8.26)

Thus, the overall reaction rate is obtained by summing all thin elements, which leads to the integral

\[ R_{r \times n} = \int_{-R}^{R} SkC \, dr = 2 \int_{0}^{R} SkC \, dr \]  

(8.27)

Hence, the overall reaction rate per unit volume of the catalyst slab is

\[ \frac{R_{r \times n}}{V_p} = \frac{1}{R} \int_{0}^{R} kC \, dr \]  

(8.28)

Written in terms of the nondimensional variables, the overall reaction rate per unit volume is

\[ \frac{R_{r \times n}}{V_p} = kC_0 \int_{0}^{1} y \, dx \]  

(8.29)

If we denote

\[ \eta = \int_{0}^{1} y \, dx \]  

(8.30)

which is called the effectiveness factor, the overall reaction rate per unit catalyst volume is given by

\[ \frac{R_{r \times n}}{V_p} = kC_0 \cdot \eta \]  

(8.31)

Thus, it is seen now that the overall reaction rate per unit volume is equal to the intrinsic reaction rate per unit volume \((kC_0)\) modified by a factor, called the
effectiveness factor, \( \eta \). The presence of this factor accounts for the fact that the chemical reaction in the catalyst particle is affected by a diffusional resistance. If this diffusional resistance is negligible compared to the reaction rate, the overall reaction rate must be equal to the intrinsic reaction rate. If this resistance is strong, we would expect the overall reaction rate to be less than the intrinsic reaction rate; that is, \( \eta < 1 \).

Let us start the illustration with the situation where \( \phi = 1 \), that is, the rate of reaction is comparable to the rate of diffusion. Using the techniques taught in Chapters 2 and 3, the exact solution to Eqs. 8.25 (which is needed later as a basis for comparison with approximate solutions) is

\[
y = \frac{\cosh(\phi x)}{\cosh(\phi)} \quad \text{(8.32)}
\]

and for \( \phi = 1 \), this yields

\[
y = \frac{\cosh(x)}{\cosh(1)} \quad \text{(8.32a)}
\]

Knowing the dimensionless concentration inside the porous catalyst, the dimensionless reaction rate is given by the integral (Eq. 8.30), which in general is

\[
\eta = \frac{\tanh(\phi)}{\phi} \quad \text{(8.33a)}
\]

and when \( \phi = 1 \) it is

\[
\eta = \int_0^1 y \, dx = \tanh(1) = 0.7616 \quad \text{(8.33b)}
\]

Now we undertake to find approximate solutions using the several variations of weighted residuals. Central to all methods is the choice of the trial solution, \( y_a \). By noting the boundary conditions at \( x = 0 \) and \( x = 1 \), a parabolic function seems to be a good choice so we write our first guess as

\[
y_a = 1 + a_1(1 - x^2) \quad \text{(8.34)}
\]

Here, the function \( y_o(x) = 1 \), which satisfies the boundary conditions (Eqs. 8.25), and the trial function \( \phi_1(x) = 1 - x^2 \), which satisfies the homogeneous boundary conditions

\[
x = 0; \quad \frac{d\phi_1}{dx} = 0 \quad \text{and} \quad x = 1; \quad \phi_1 = 0
\]

Hence, the trial solution \( y_a(x) \) satisfies the boundary conditions (Eqs. 8.25) exactly; that is,

\[
x = 0; \quad \frac{dy_a}{dx} = 0
\]
and
\[ x = 1; \quad y_a = 1 \] (8.35)

Next, substituting the trial function into the differential equation (Eq. 8.25a), we obtain the residual, defined here as
\[ Ly_a = \frac{d^2 y_a}{dx^2} - y_a = R \] (8.36)
or specifically
\[ R(x) = -2a_1 - [1 + a_1(1 - x^2)] \neq 0 \] (8.37)

Note that the residual is a function of \( x \). To find the coefficient \( a_1 \), we need to "transform" this \( x \)-dependent function into a quantity, which is to \( x \) dependent. This is the central idea of the inner product, which we have discussed earlier. Since we are dealing with functions, the inner product should be defined in the form of an integral, to eliminate dependence on \( x \). For the present problem, the inner product between the residual and a test function \( w_1 \) (we only need one, since there is only one coefficient, \( a_1 \), in the trial solution, (Eq. 8.34)) is
\[ (R, w_1) = \int_0^1 Rw_1 \, dx = 0 \] (8.38)

Observing the inner product of Eq. 8.38, we note, following integration, an algebraic relationship is produced, the form and complexity of which depends on the selection of the test function \( w_1 \). This is the only difference among the various methods of weighted residuals. Let us demonstrate this with various methods one by one. We start with the collocation method.

**a) The collocation method** In this method, the test function was stipulated earlier to be
\[ w_1(x) = \delta(x - x_1) \] (8.39)
where \( x_1 \) is a (as yet unknown) collocation point chosen in the domain \([0, 1]\). With one collocation point, the method is called **single point** collocation, a convenient tool for assessing system behavior.

With this test function, Eq. 8.38 can be integrated directly and we obtain the following algebraic equation
\[ (R, w_1) = \int_0^1 [-2a_1 - [1 + a_1(1 - x^2)]] \delta(x - x_1) \, dx \] (8.40)
\[ = -2a_1 - [1 + a_1(1 - x_1^2)] = 0 \]

where we have used the property of the Dirac delta function (Eq. 8.10). Equation 8.40 is simply the residual at \( x = x_1 \), and the collocation method gets
its name from the fact that it forces the residual to be zero at particular points, called collocation points.

From Eq. 8.40, the unknown coefficient \( a_1 \) can be readily determined in terms of the point \( x_1 \) (which is the single collocation point)

\[
a_1 = -\frac{1}{2 + (1 - x_1^2)} \tag{8.41}
\]

We note that \( x_1 \) is unspecified, and it must be chosen in the range: \( 0 < x_1 < 1 \). The trial solution, which approximates the exact solution, is simply

\[
y_a = 1 - \frac{(1 - x^2)}{2 + (1 - x_1^2)} \tag{8.42}
\]

The quantity of interest is the overall reaction rate, and it takes the dimensionless form

\[
\eta = \int_0^1 y \, dx = \int_0^1 y_a \, dx \tag{8.43}
\]

If we substitute the trial solution of Eq. 8.42 into Eq. 8.43, we have

\[
\eta_a = 1 - \frac{2}{3[2 + (1 - x_1^2)]} \tag{8.44}
\]

Thus, if we choose the collocation point as the midpoint of the domain \([0, 1]\) so that \( x_1 = 1/2 \), then the integral of Eq. 8.44 will take the value

\[
\eta_a = 1 - \frac{2}{3[2 + (1 - (0.5)^2)]} = 1 - \frac{8}{33} = 0.7576 \tag{8.45}
\]

We see that the approximate solution obtained by the collocation method agrees fairly well with the exact solution \((\eta = 0.7616)\). Note here that the selection of \( x_1 \) was arbitrary, and intuitive. Other choices are possible, as we shall see.

(b) The subdomain method Here, since we have only one unknown coefficient in the trial solution, only one subdomain is dealt with, and it is the full domain of the problem, that is, \([0, 1]\); hence, the test function is

\[
w_1(x) = 1 \quad \text{for} \quad 0 < x < 1 \tag{8.46}
\]

The inner product is defined as before (Eq. 8.38). Substituting the residual of Eq. 8.37 and the test function (Eq. 8.46) into the inner product (Eq. 8.38) we have

\[
(R, w_1) = \int_0^1 R w_1 \, dx = \int_0^1 \{-2a_1 - [1 + a_1(1 - x^2)]\}(1) \, dx = 0 \tag{8.47}
\]
Integrating the above equation, we finally obtain the following solution for $a_1$

$$a_1 = -\frac{3}{8} \quad (8.48)$$

Hence, the trial solution by the subdomain method is

$$y_a = 1 - \frac{3}{8} (1 - x^2) \quad (8.49)$$

and the approximate nondimensional chemical reaction rate is

$$\eta_a = \int_0^1 y_a \, dx = \int_0^1 \left[ 1 - \frac{3}{8} (1 - x^2) \right] \, dx = \frac{3}{4} = 0.75 \quad (8.50)$$

which also compares well with the exact solution $\eta_{\text{exact}} = 0.7616$.

(c) **The least square method** The test function for the least square approach is

$$w_1 = \frac{\partial R}{\partial a_1} \quad (8.51)$$

The inner product (Eq. 8.38) for this method is

$$(R, w_1) = \int_0^1 R \frac{\partial R}{\partial a_1} \, dx = \frac{1}{2} \frac{\partial}{\partial a_1} \int_0^1 R^2 \, dx = 0 \quad (8.52)$$

that is,

$$(R, w_1) = \frac{1}{2} \left[ -2a_1 - \left[ 1 + a_1(1 - x^2) \right] \right] \, dx = 0 \quad (8.53)$$

Integrating with respect to $x$ and then differentiating with respect to $a_1$ yields

$$(R, w_1) = \frac{1}{2} \left[ 216 \left( \frac{1}{15} a_1 + \frac{16}{3} \right) \right] = 0 \quad (8.54)$$

Hence, solving for $a_1$, we have

$$a_1 = -\frac{10}{27} \quad (8.55)$$

The trial solution for the least square method is

$$y_a = 1 - \frac{10}{27} (1 - x^2) \quad (8.56)$$
and the approximate nondimensional chemical reaction rate is

\[ \eta_a = \int_0^1 y_a \, dx = \int_0^1 \left[ 1 - \frac{10}{27} (1 - x^2) \right] \, dx = \frac{61}{81} = 0.75309 \quad (8.57) \]

compared to the exact solution of tanh(1) = 0.7616.

(d) The moment method The test function for the moment method is

\[ w_1 = x^0 = 1 \quad (8.58) \]

which is identical to the test function of the subdomain method. Thus, the solution of the moment method is the same as that of the subdomain method. This is true because only one term is retained in the trial solution.

(e) The Galerkin method The test function is the same as the trial solution; that is,

\[ w_1 = (1 - x^2) \quad (8.59) \]

Thus, the inner product (Eq. 8.38) becomes

\[ (R, w_1) = \int_0^1 \left( -2a_1 - \left[ 1 + a_1(1 - x^2) \right] \right) (1 - x^2) \, dx = 0 \quad (8.60) \]

that is,

\[ (R, w_1) = -\frac{2}{3} (1 + 2a_1) - \frac{8}{15} a_1 = 0 \quad (8.61) \]

Solving for \( a_1 \) gives

\[ a_1 = -\frac{10}{28} \quad (8.62) \]

Thus, the trial solution obtained by the Galerkin method is

\[ y_a = 1 - \frac{10}{28} (1 - x^2) \quad (8.63) \]

and the approximate nondimensional chemical reaction rate, \( \eta_a \), is

\[ \eta_a = \int_0^1 y_a \, dx = \int_0^1 \left[ 1 - \frac{10}{28} (1 - x^2) \right] \, dx = \frac{64}{84} = 0.7619 \quad (8.64) \]

Table 8.1 provides a summary of the five methods using only one term.

It is seen from Table 8.1 that Galerkin appears to be the most accurate method for this specific problem. However, when more terms are used in the trial solution, the Galerkin method presents more analytical difficulties than the collocation method. As a matter of fact, all the weighted residual procedures
Table 8.1 Comparison of Accuracy for Approximate Solutions

<table>
<thead>
<tr>
<th>Method</th>
<th>$\eta = \int_0^1 y_\alpha , dx$</th>
<th>Relative Percentage Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collocation</td>
<td>$25/33$</td>
<td>0.53</td>
</tr>
<tr>
<td>Subdomain</td>
<td>$3/4$</td>
<td>1.5</td>
</tr>
<tr>
<td>Least square</td>
<td>$61/81$</td>
<td>1.1</td>
</tr>
<tr>
<td>Moment</td>
<td>$3/4$</td>
<td>1.5</td>
</tr>
<tr>
<td>Galerkin</td>
<td>$64/84$</td>
<td>0.041</td>
</tr>
</tbody>
</table>

require an integration of the form of Eq. 8.7 or 8.8 and hence, with the exception of the collocation method, may require numerical evaluation of this integral if analytical integration is impossible. The ease of performing integrals with the Dirac delta function is an enormous advantage for the collocation technique.

All the methods tried so far show very low relative errors, in spite of the fact that only one term was retained in the trial solution (Eq. 8.34). This arises because the diffusion-reaction problem used for illustration has a slow reaction rate. This implies the concentration profile inside the particle is very shallow and can be easily described with only one term in the series of parabolic trial functions.

**Example 8.2**

If we allow higher reaction rates in Eq. 8.25a, one can see that the concentration profile becomes rather steep and the trial solution with only one term obviously will become inadequate, as we shall show.

Let us take $\phi = 10$ (i.e., fast reaction relative to diffusion), hence the exact solution of Eq. 8.25 now becomes

$$y = \frac{\cosh(10x)}{\cosh(10)} \quad (8.65)$$

The nondimensional chemical reaction rate is obtained from the integral

$$\eta = \int_0^1 y \, dx = \int_0^1 \frac{\cosh(10x)}{\cosh(10)} \, dx = \frac{\tanh(10)}{10} = 0.1 \quad (8.66)$$

If we use only one term in Eq. 8.34 and substitute it into Eq. 8.25a with $\phi = 10$, we obtain the following residual

$$R = -2a_1 - 100\left[1 + a_1(1 - x^2)\right] \quad (8.67)$$
We now apply the five variations of the weighted residuals and follow the procedure as presented in the last example.

1. **Collocation method** Using this method, we obtain

\[
a_1 = -\frac{100}{2 + 100(1 - x_1^2)}
\]

\[
\eta_a = \int_0^1 y_a dx = 1 - \frac{200}{3[2 + 100(1 - x_1^2)]}
\]

For \( x_1 = 0.5 \), the nondimensional reaction rate is

\[
\eta_a = 1 - \frac{200}{3[2 + 100(1 - (0.5)^2)]} = 0.1342
\]

Comparing with the exact solution of \( \eta = 0.1 \), the relative error is 34%.

2. **Subdomain method** For this method, we have

\[
a_1 = -\frac{300}{206} \quad \text{and} \quad \eta_a = 0.02913
\]

The relative error between the approximate solution \( \eta_a \) and the exact solution is 71%.

3. **Least square method** We have

\[
a_1 = -\frac{41,200}{33,624} \quad \text{and} \quad \eta_a = 0.183123
\]

The relative error is 83%.

4. **Moment method** same as the subdomain method.

5. **Galerkin method** We have

\[
a_1 = -\frac{1000}{820} \quad \text{and} \quad \eta_a = 0.18699
\]

The relative error is 87%.

We noted that in the case of high reaction rate, the collocation technique seems to be superior to the others. However, the relative errors between all approximate solutions and the exact solution are unacceptably high. The reason for the high error arises from the sharpness of the concentration profiles, as illustrated in Fig. 8.2. Moreover, the approximate solutions yield negative concentration over some parts of the domain \([0, 1]\).

To improve the accuracy in this case, we need to retain more terms in the trial solutions. In general, the more terms retained, the better the accuracy. This
can be carried out in a straightforward way with a computer. To demonstrate how this is done, we shall now retain two terms in the general expansion

\[ y_a = 1 + \sum_{j=1}^{N} a_j x^{2(j-1)}(1 - x^2) \]

which is simply

\[ y_a = 1 + a_1(1 - x^2) + a_2 x^2(1 - x^2) \]  \hspace{1cm} (8.72)

Because of the symmetry property discussed earlier, our trial functions should be chosen to be even functions. This saves time, since a selection of odd functions would ultimately lead to a zero value for the multiplicative coefficient. Inserting \( y_a \) into the defining equation yields the residual

\[ R = -2a_1 - 10a_2 - 100 \]

\[ + (12a_2 - 100a_1)(1 - x^2) - 100a_2 x^2(1 - x^2) \]  \hspace{1cm} (8.73)

We now apply the collocation method to this residual, using the following two test functions

\[ w_1 = \delta(x - x_1) \quad \text{and} \quad w_2 = \delta(x - x_2) \]  \hspace{1cm} (8.74)
where \( x_1 \) and \( x_2 \) are two separate collocation points, chosen in the domain \([0, 1]\).

Next, we evaluate the following two inner products

\[
(R, w_1) = \int_0^1 R w_1 \, dx = 0 \quad \text{and} \quad (R, w_2) = \int_0^1 R w_2 \, dx = 0 \quad (8.75)
\]

to obtain two algebraic equations, solvable for unknowns \( a_1 \) and \( a_2 \)

\[
a_1 = -0.932787 \quad \text{and} \quad a_2 = -1.652576 \quad (8.76)
\]

for two equally spaced collocation points chosen at \( x_1 = 1/3 \) and \( x_2 = 2/3 \).

Knowing the coefficients and the trial solution as in Eq. 8.72, we can now evaluate the integral

\[
\eta_a = \int_0^1 y_a \, dx = 0.1578 \quad (8.77)
\]

This means that the error relative to the exact solution is 58\%, which is even higher than the error when we kept only one term in the trial solution! This is a somewhat surprising result; however, we have made no effort to select the collocation points in any optimum way. Nonetheless, if we retained more terms in the trial solutions (say 10 terms), the accuracy becomes better, as we might expect.

Let us return to the trial solution with two terms and note that we used two collocation points at 1/3 and 2/3, that is, we used equal spacing collocation points. Now, let us try two different collocation points \( x_1 = 0.285231517 \) and \( x_2 = 0.765055325 \), which lead to the coefficients \( a_1 = -0.925134 \) and \( a_2 = -2.040737 \). Knowing these two coefficients, we can evaluate \( \eta_a \) to obtain only 11\% relative error, in contrast to 58\% using equal spacing. This means that the choice of the collocation points is critical, and cannot be undertaken in an arbitrary way. The full potential of the collocation method can only be realized by judicious selection of the collocation points. Moreover, the choice of functions is critical. Orthogonal functions, such as Jacobi polynomials, are particularly attractive, since they are compact and contain only a few terms. One cannot expect good results with any orthogonal polynomial. The last choices of the two collocation points were in fact roots of the Jacobi polynomial. They gave good result because the weighting function of the Jacobi polynomial is

\[
x^\theta(1-x)^\alpha
\]

and the effectiveness factor also has a weighting factor of a similar form.

This previous discussion highlights the essential features of the orthogonal collocation method. The word orthogonal implies the Jacobi polynomials are orthogonal in the sense of the integral shown in Eq. 8.83. We give more detailed discussion in Section 8.2. Also, we again emphasize the origin of orthogonality relates to the Sturm–Liouville equation, discussed in Section 10.5.
Among the many variations of weighted residuals, the collocation is the easiest to use because its formulation is straightforward (owing to the Dirac delta function), the accuracy is good, and if many collocation points are used, the accuracy becomes excellent. With high-speed personal computers, the computation time required for many such terms is minimal. The subdomain and least square methods are more tedious to use. The Galerkin is used by applied mathematicians in some specific cases, but it is not as popular as the orthogonal collocation technique.

Because it has become so widely used, we devote the remainder of the chapter to orthogonal collocation. Before discussing additional details, we introduce a number of preliminary steps, which are needed for further development. These steps include a discussion of Jacobi polynomials (its choice has been explained above) and the Lagrangian interpolation polynomials. The Lagrangian interpolation polynomial is chosen as a convenient vehicle for interpolation between collocation points.

The Jacobi polynomials are important in providing the optimum positions of the collocation points. Since these collocation points are not equally spaced, the Lagrangian interpolation polynomials are useful to effect an approximate solution.

8.2 JACOBI POLYNOMIALS

Since all finite domains can be expressed in the range \([0,1]\) through a linear transformation, we will consider the Jacobi polynomials defined in this domain. This is critical because the orthogonality condition for the polynomials depends on the choice of the domain. The Jacobi polynomial is a solution to a class of second order differential equation defined by Eq. 3.145.

The Jacobi polynomial of degree \(N\) has the power series representation

\[
J_N^{(\alpha,\beta)}(x) = \sum_{i=0}^{N} (-1)^{N-i} \gamma_{N,i} x^i
\]  

(8.78)

with \(\gamma_{N,0} = 1\). Note, the series contains a finite number of terms \((N)\), and is therefore compact (not carried to infinity).

Here, \(\gamma_{N,i}\) are constant coefficients, and \(\alpha\) and \(\beta\) are parameters characterizing the polynomials, as shown in Eq. 8.83. That is, \(J_N^{(\alpha,\beta)}(x)\) is the polynomial orthogonal with respect to the weighting function \(x^\beta (1-x)^\alpha\). The term \((-1)^{N-i}\) is introduced in the series to insure the coefficients \(\gamma\) are always positive. Note that the Jacobi function \(J_N^{(\alpha,\beta)}(x)\) is a polynomial of degree \(N\), since the summation in Eq. 8.78 is bounded and not infinite as with other orthogonal functions, such as Bessel’s.

8.2.1 Rodrigues Formula

The Jacobi polynomials are given explicitly by the Rodrigues formula

\[
J_N^{(\alpha,\beta)}(x) [x^\beta (1-x)^\alpha] = \frac{(-1)^N \Gamma(\beta + 1)}{\Gamma(N + \beta + 1)} \frac{d^N}{dx^N} \left[x^{N+\beta} (1-x)^{N+\alpha}\right]
\]  

(8.79)
where $\Gamma$ is the Gamma function and its definition and properties are detailed in Chapter 4. For many applications, $\alpha = \beta = 0$, and we may conveniently drop the superscripts, that is, $J_N^{(0,0)} = J_N$.

**EXAMPLE 8.3**

For $\alpha = \beta = 0$, we have the following three Jacobi polynomials ($N = 1, 2, 3$) using Eq. 8.79

\[
J_1(x) = -1 + 2x \\
J_2(x) = 6x^2 - 6x + 1 \\
J_3(x) = 20x^3 - 30x^2 + 12x - 1
\]

(8.80) (8.81) (8.82)

The curves for these three Jacobi polynomials are shown in Fig. 8.3 over the domain [0, 1]. It is important to note that $J_1$ has one zero, $J_2$ has two zeros, and $J_3$ has three zeros within the domain [0, 1]; zeros are the values of $x$, which cause $J_N(x) = 0$. These zeros will be used later as the interior collocation points for the orthogonal collocation method.

### 8.2.2 Orthogonality Conditions

Since the Jacobi polynomials belong to a class of orthogonal polynomials, they satisfy the orthogonality condition

\[
\int_0^1 [x^\beta (1-x)^\alpha] J_j^{(\alpha, \beta)}(x) J_N^{(\alpha, \beta)}(x) \, dx = 0 \quad (8.83)
\]

![Figure 8.3 Plots of three Jacobi polynomials.](image)
for \( j = 0, 1, 2, \ldots, (N - 1) \), that is, all Jacobi polynomials are orthogonal to each other except to itself (i.e., when \( j = N \)). This condition arises by consideration of the Sturm–Liouville equation, the detailed discussion of which is given in Section 10.5.1.

The integration is defined in the domain \([0, 1]\). Outside this domain, orthogonality cannot be guaranteed. Any physical systems having a finite domain can be easily scaled to reduce to the domain \([0, 1]\).

The weighting function for this particular orthogonality condition defined with reference to the Sturm–Liouville equation is

\[
W(x) = x^\alpha (1 - x)^\beta
\]  

(8.84)

The exponents \( \alpha \) and \( \beta \) are seen to dictate the nature of the orthogonal Jacobi polynomials.

There are \( N \) equations of orthogonality (Eq. 8.83) because \( j = 0, 1, 2, \ldots, N - 1 \), and there are exactly \( N \) unknown coefficients of the Jacobi polynomial of degree \( N \) to be determined

\[\gamma_{N,1}, \gamma_{N,2}, \gamma_{N,3}, \ldots, \gamma_{N,N}\]

Note that \( \gamma_{N,0} = 1 \).

Solving these \( N \) linear equations for \( N \) unknown coefficients, the following explicit solution is obtained for \( \gamma \) (Villadsen 1970)

\[
\gamma_{N,i} = \binom{N}{i} \frac{\Gamma(N + i + \alpha + \beta + 1)\Gamma(\beta + 1)}{\Gamma(N + \alpha + \beta + 1)\Gamma(i + \beta + 1)}
\]

(8.85a)

where the representation for the lead term is

\[
\binom{N}{i} = \frac{N!}{i!(N - i)!}
\]

(8.85b)

The above equation provides the explicit formula for the coefficients. During computation, it is easier to evaluate coefficients using the following recurrence formula

\[
\frac{\gamma_{N,i}}{\gamma_{N,i-1}} = \frac{N - i + 1}{i} \cdot \frac{N + i + \alpha + \beta}{i + \beta}
\]

starting with \( \gamma_{N,0} = 1 \).

Using the formula obtained above for the coefficients, we can evaluate the first four Jacobi polynomials, with \( \alpha = \beta = 0 \)

\[
J_0 = 1, \quad J_1 = 2x - 1, \quad J_2 = 6x^2 - 6x + 1, \quad J_3 = 20x^3 - 30x^2 + 12x - 1
\]

On inspection of these, we note that (except the first one, which is equal to unity) all have zeros within the domain from 0 to 1 (Fig. 8.3). Here, zeros are used to denote roots of \( J_N(x) = 0 \), so that \( J_N(x) \) has \( N \) values of \( x \) causing it to become zero.
Since the orthogonal collocation method will require roots of the Jacobi polynomial, we shall need to discuss methods for the computation of zeros of $J_{n}^{(\alpha, \beta)}(x)$.

It has been proved by Villadsen and Michelsen (1978), using the orthogonality condition in Eq. 8.83, that $J_{n}^{(\alpha, \beta)}$ has $N$ distinct, real-valued zeros in the domain $[0,1]$.

If the Newton–Raphson method is applied using an initial guess $x = 0$, the first root found will be $x_1$. Once this root is obtained, we can obtain the next root by suppressing the previously determined zero at $x_1$. In general, if $x_1, x_2, \ldots, x_k$ are previously determined zeros, we can suppress these roots by constructing the following function

$$G_{N-k} = \frac{p_N(x)}{\prod_{i=1}^{k} (x - x_i)}$$

(8.86a)

where $p_N(x)$ is the rescaled polynomial

$$p_N(x) = \frac{J_{n}^{(\alpha, \beta)}(x)}{\gamma_{N,N}}$$

(8.86b)

The Newton–Raphson formula to determine the root $x_{k+1}$ at the $i$th iteration is

$$x_{k+1}^{(i)} = x_{k+1}^{(i-1)} - \left[ \frac{G_{N-k}(x)}{G_{N-k}'(x)} \right]_{x_{k+1}^{(i-1)}}$$

(8.87a)

for $i = 1, 2, \ldots$, and the initial guess for $x_{k+1}$ is

$$x_{k+1}^{(0)} = x_k + \varepsilon$$

(8.87b)

where $\varepsilon$ is a small number and a good starting value of $1 \times 10^{-4}$ is recommended.

The function in the bracket of Eq. 8.87a is obtained from Eq. 8.86a and can be written explicitly as

$$\frac{G_{N-k}(x)}{G_{N-k}'(x)} = 1 - \left[ \frac{p_N(x)}{p_N'(x)} \right] \sum_{i=1}^{k} \frac{1}{(x - x_i)}$$

(8.88a)

with $p_N(x)$ and $p_N'(x)$ determined from the following recursive formula for computation

$$p_N(x) = (x - g_N)p_{N-1} - h_Np_{N-2}$$

(8.88b)

$$p_N'(x) = p_{N-1} + (x - g_N)p_{N-1}' - h_Np_{N-2}'$$

(8.88c)
where

\[ g_1 = \frac{\beta + 1}{\alpha + \beta + 2}; \]

\[ g_N = \frac{1}{2} \left[ 1 - \frac{\alpha^2 - \beta^2}{(2N + \alpha + \beta - 1)^2 - 1} \right] \quad \text{for } N > 1 \tag{8.88d} \]

\[ h_1 = 0; \quad h_2 = \frac{(\alpha + 1)(\beta + 1)}{(\alpha + \beta + 2)(\alpha + \beta + 3)} \tag{8.88e} \]

\[ h_N = \frac{(N - 1)(N + \alpha - 1)(N + \beta - 1)(N + \alpha + \beta - 1)}{(2N + \alpha + \beta - 1)(2N + \alpha + \beta - 2)(2N + \alpha + \beta - 3)} \quad \text{for } N > 2 \tag{8.88f} \]

The recursive formula for \( p_N(x) \) and \( p'_N(x) \) are started with \( N = 1 \) and

\[ p_0 = 1; \quad p'_0 = 0; \quad p_{-1} \quad \text{and} \quad p'_{-1} \quad \text{are arbitrary} \]

The choice of \( p_{-1} \) and \( p'_{-1} \) is immaterial because \( h_1 \) is zero in Eq. 8.88b and c.

### 8.3 Lagrange Interpolation Polynomials

We have discussed a class of orthogonal functions called Jacobi polynomials, which have been found to be quite useful in the development of the choice of the interior collocation points for the orthogonal collocation method.

For a given set of data points \((x_1, y_1), (x_2, y_2), \ldots, (x_N, y_N)\) and \((x_{N+1}, y_{N+1})\), an interpolation formula passing through all \((N + 1)\) points is an \(N\)th degree polynomial. We shall call this an interpolation polynomial, and it is expressed as

\[ y_N(x) = \sum_{i=1}^{N+1} y_i l_i(x) \tag{8.89} \]

where \(y_N\) is the \(N\)th degree polynomial, \(y_i\) is the value of \(y\) at the point \(x_i\), and \(l_i(x)\) is called the Lagrange interpolation polynomial. It is defined as

\[ l_i(x_j) = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases} \tag{8.90a} \]

The Lagrange interpolation polynomial is a useful building block. There are \((N + 1)\) building blocks, which are \(N\)th degree polynomials. The building blocks are given as

\[ l_i(x) = \prod_{j=1, j \neq i}^{N+1} \frac{x - x_j}{x_i - x_j} = \frac{p_{N+1}(x)}{(x-x_i)\left[ \frac{dp_{N+1}(x_i)}{dx} \right]} \tag{8.90b} \]
where \( p_{N+1}(x) \) is called the node polynomial. It is a \( N + 1 \) degree polynomial and is defined as

\[
p_{N+1}(x) = (x - x_1)(x - x_2) \cdots (x - x_N)(x - x_{N+1})
\]  \hspace{1cm} (8.91)

where \( x_i \) (\( i = 1, 2, \ldots, N, N + 1 \)) are locations of the data set. The \( p_{N+1}(x) \) is called node polynomial because it passes through all the nodes \( x_i \) (\( i = 1, 2, \ldots, N + 1 \)).

Figure 8.4 shows typical plots of the Lagrangian interpolation polynomials for \( x_1 = 0.044, \ x_2 = 0.35, \ x_3 = 0.76 \). Note that they satisfy Eq. 8.90, for example, \( l_i(x) \) is unity at \( x = x_1 \) and zero at \( x = x_2 \) and \( x = x_3 \).

The construction of the Lagrange interpolation polynomial proceeds as follows. First, the \( N + 1 \) interpolation points are chosen, then the \( N + 1 \) building blocks \( l_i(x) \) can be constructed (Eq. 8.90). If the functional values of \( y \) at those \( N + 1 \) points are known, the interpolation polynomial is given in Eq. 8.89. Hence, the value of \( y \) at any point including the interpolation points, say \( x^* \), is given by

\[
y_N(x^*) = \sum_{i=1}^{N+1} y_i l_i(x^*)
\]  \hspace{1cm} (8.92)

8.4 ORTHOGONAL COLLOCATION METHOD

The previous development on Jacobi and Lagrangian polynomials allows us to proceed directly to computations for the orthogonal collocation method.
Differentiation of a Lagrange Interpolation Polynomial

The interpolation polynomial defined in Eq. 8.89 is a continuous function and therefore can be differentiated as well as integrated.

Taking the first and second derivatives of the interpolation polynomial (Eq. 8.89), we obtain

\[
\frac{dy_N(x)}{dx} = \sum_{i=1}^{N+1} y_i \frac{dl_i(x)}{dx} \quad \text{(8.93)}
\]

\[
\frac{d^2y_N(x)}{dx^2} = \sum_{i=1}^{N+1} y_i \frac{d^2l_i(x)}{dx^2} \quad \text{(8.94)}
\]

In most practical problems, only the first two derivatives are required, so these are presented here. However, if higher derivatives are needed, the Lagrange interpolation polynomial can be differentiated further.

In particular, if we are interested in obtaining the derivative at the interpolation points, we have

\[
\frac{dy_N(x_i)}{dx} = \sum_{j=1}^{N+1} \frac{dl_j(x_i)}{dx} y_j \quad \text{(8.95)}
\]

for \(i = 1, 2, \ldots, N, N + 1\).

Similarly, the second derivative is obtained as

\[
\frac{d^2y_N(x_i)}{dx^2} = \sum_{j=1}^{N+1} \frac{d^2l_j(x_i)}{dx^2} y_j \quad \text{(8.96)}
\]

for \(i = 1, 2, 3, \ldots, N, N + 1\).

The summation format in the RHS of Eqs. 8.95 and 8.96 suggests the use of a vector representation for compactness, as we will show next.

We define the first derivative vector, composed of \((N + 1)\) first derivatives at the \(N + 1\) interpolation points, as

\[
y_N = \begin{bmatrix}
\frac{dy_N(x_1)}{dx}, & \frac{dy_N(x_2)}{dx}, & \ldots, & \frac{dy_N(x_N)}{dx}, & \frac{dy_N(x_{N+1})}{dx}
\end{bmatrix}^T
\quad \text{(8.97)}
\]

Similarly, the second derivative vector is defined as

\[
y''_N = \begin{bmatrix}
\frac{d^2y_N(x_1)}{dx^2}, & \frac{d^2y_N(x_2)}{dx^2}, & \ldots, & \frac{d^2y_N(x_N)}{dx^2}, & \frac{d^2y_N(x_{N+1})}{dx^2}
\end{bmatrix}^T
\quad \text{(8.98)}
\]

The function vector is defined as values of \(y\) at \(N + 1\) collocation points as

\[
y = [y_1, y_2, y_3, \ldots, y_N, y_{N+1}]^T
\quad \text{(8.99)}
\]
With these definitions of vectors \( y \) and derivative vectors, the first and second derivative vectors can be written in terms of the function vector \( y \) using matrix notation

\[
y' = A \cdot y \tag{8.100}
\]

\[
y'' = B \cdot y \tag{8.101}
\]

where the matrices \( A \) and \( B \) are defined as

\[
A = \left\{ a_{ij} = \frac{dl_j(x_i)}{dx} ; \quad i, j = 1, 2, \ldots, N, N + 1 \right\} \tag{8.102a}
\]

and

\[
B = \left\{ b_{ij} = \frac{d^2l_j(x_i)}{dx^2} ; \quad i, j = 1, 2, \ldots, N, N + 1 \right\} \tag{8.102b}
\]

The matrices \( A \) and \( B \) are \((N + 1, N + 1)\) square matrices. Once the \( N + 1 \) interpolation points are chosen, then all the Lagrangian building blocks \( l_j(x) \) are completely known (Eq. 8.90), and thus the matrices \( A \) and \( B \) are also known.

For computation purposes, \( a_{ij} \) and \( b_{ij} \) are calculated from

\[
a_{ij} = \frac{dl_j(x_i)}{dx} = \begin{cases} 1, & j = i \\ \frac{1}{2} p_{N+1}^{(2)}(x_i) & i \neq j \\ \frac{1}{(x_i - x_j)} p_{N+1}^{(1)}(x_i) p_{N+1}^{(1)}(x_j) & i \neq j \end{cases} \tag{8.103a}
\]

and

\[
b_{ij} = \frac{d^2l_j(x_i)}{dx^2} = \begin{cases} 1, & j = i \\ \frac{1}{3} p_{N+1}^{(2)}(x_i) & i \neq j \\ 2a_{ij} \left[ a_{ij} - \frac{1}{(x_i - x_j)} \right] & i \neq j \end{cases} \tag{8.103b}
\]

where \( p_{N+1}^{(1)} \), \( p_{N+1}^{(2)} \) and \( p_{N+1}^{(3)} \) are calculated from the following recurrence formula

\[
p_0(x) = 1
\]

\[
p_j(x) = (x - x_j) p_{j-1}(x); \quad j = 1, 2, \ldots, N + 1
\]

\[
p_j^{(1)}(x) = (x - x_j) p_{j-1}^{(1)}(x) + p_{j-1}(x)
\]

\[
p_j^{(2)}(x) = (x - x_j) p_{j-1}^{(2)}(x) + 2p_{j-1}^{(1)}(x)
\]

\[
p_j^{(3)}(x) = (x - x_j) p_{j-1}^{(3)}(x) + 3p_{j-1}^{(2)}(x)
\]
with

\[ p_0^{(1)}(x) = p_0^{(2)}(x) = p_0^{(3)}(x) = 0 \]

### 8.4.2 Gauss–Jacobi Quadrature

We have discussed the differentiation of the interpolation polynomial. Now, we turn to the process of quadrature.\(^2\) This is often needed in solutions, such as chemical reaction rates obtained as an integration of a concentration profile.

Let \( y_{N-1} \) be the interpolation polynomial of degree \((N - 1)\), passing through \(N\) points \((x_1, y_1), (x_2, y_2), \ldots (x_N, y_N)\) presented as

\[ y_{N-1}(x) = \sum_{j=1}^{N} y_j l_j(x) \quad (8.104) \]

where \( l_j(x) \) is the \((N - 1)\)th degree Lagrange building block polynomial, and it is given by

\[ l_j(x) = \prod_{i=1, i \neq j}^{N} \frac{x - x_i}{x_j - x_i} \]

The interpolation polynomial, \( y_{N-1}(x) \) of Eq. 8.104, is continuous, and therefore we can integrate it with respect to \( x \), using a weighting function \( W(x) \), as

\[ \int_{0}^{1} W(x) y_{N-1}(x) \, dx = \int_{0}^{1} W(x) \left[ \sum_{j=1}^{N} y_j l_j(x) \right] \, dx \quad (8.105) \]

When we interchange the summation sign and the integral sign, the so-called quadrature relation arises

\[ \int_{0}^{1} W(x) y_{N-1}(x) \, dx = \sum_{j=1}^{N} y_j \left[ \int_{0}^{1} W(x) l_j(x) \, dx \right] \quad (8.106) \]

\(^2\) Quadrature defines the process of expressing the continuous integral

\[ \int_{a}^{b} W(x)f(x) \, dx \]

as an approximate sum of terms

\[ \int_{a}^{b} W(x)f(x) \, dx = \sum_{k=1}^{N} w_k f(x_k) \]

where \( x_k \) are suitably chosen.
Next, if we define

\[ w_j = \int_0^1 W(x) l_j(x) \, dx \quad (8.107) \]

which is called the *quadrature weights*, the above quadrature (Eq. 8.106) becomes

\[ \int_0^1 W(x) y_{N-1}(x) \, dx = \sum_{j=1}^{N} w_j y_j \quad (8.108) \]

For a specific choice of weighting function, say the Jacobi weight

\[ W(x) = x^\beta (1 - x)^\alpha \quad (8.109) \]

the quadrature weight then becomes

\[ w_j = \int_0^1 x^\beta (1 - x)^\alpha l_j(x) \, dx \]

If the \( N \) interpolation points are chosen as \( N \) zeroes of the Jacobian polynomial of degree \( N \), the quadrature is called the Gauss–Jacobi quadrature, and \( w_j \) are called the Gauss–Jacobi quadrature weights.

For computational purposes, the following formula for the Gauss–Jacobi quadrature weights can be obtained using the properties of the Lagrangian interpolation polynomials \( l_j(x) \)

\[ w_i = \frac{(2N + \alpha + \beta + 1)c_N^{(\alpha, \beta)}}{x_i(1 - x_i) \left[ \frac{dp_N(x_i)}{dx} \right]^2} \quad (8.110a) \]

where \( dp_N(x_i)/dx \) is calculated from the recurrence formula

\[ p_j^{(1)} = (x - x_j) p_j^{(1)}(x) + p_{j-1}(x) \]

\[ p_j(x) = (x - x_j) p_{j-1}(x) \]

with \( p_0(x) = 1 \) and \( p_0^{(1)}(x) = 0 \). Here, \( c_N^{(\alpha, \beta)} \) is given by Villadsen (1970)

\[ c_N^{(\alpha, \beta)} = \frac{1}{\gamma_{N,N}^2} \frac{\Gamma^2(\beta + 1)N!\Gamma(N + \alpha + 1)}{\Gamma(N + \beta + 1)\Gamma(N + \alpha + \beta + 1)(2N + \alpha + \beta + 1)} \quad (8.110b) \]

where \( \gamma_{N,N} \) is given in Eq. 8.85.

Of practical interest in problem solving, the following situation often arises. Suppose \( x_1, x_2, \ldots, x_N \) are \( N \) roots of an \( N \)th degree Jacobi polynomial \( J_N^{(\alpha, \beta)} \). Now we choose the \((N + 1)\)th point to be the end point of the domain (i.e., \( x_{N+1} = 1 \)). The interpolation polynomial passing through these \( N + 1 \) points is
the $N$th degree polynomial, defined as

$$y_N = \sum_{j=1}^{N+1} y_j l_j(x) \quad (8.111)$$

Now if we need to evaluate the quadrature integral

$$\int_0^1 x^\beta (1 - x)^\alpha y_N(x) \, dx = \sum_{j=1}^{N+1} w_j y_j \quad (8.112)$$

it is found that the first $N$ quadrature weights are identical to the quadrature weights obtained earlier (Eq. 8.110a) and moreover $w_{N+1} = 0$. This means that adding one more point to the interpolation process will not increase the accuracy of the quadrature, if the $N$ interior interpolation points are chosen as zeros of the $N$th degree Jacobian polynomial $J_N^{(\alpha, \beta)}(x)$. For improving the accuracy in the evaluation of the integral (8.112) when one or two boundary points are used as extra interpolation points (in addition to the interior collocation points) we need to use different quadrature formula and this will be addressed in the next section.

### 8.4.3 Radau and Lobatto Quadrature

To improve the accuracy of the quadrature

$$\int_0^1 x^\beta (1 - x)^\alpha y_N(x) \, dx \quad (8.113)$$

when one extra interpolation point is added (say, $x_{N+1} = 1$), the first $N$ interior interpolation points must be chosen as roots of the Jacobi polynomial $J_N^{(\alpha+1, \beta)}(x)$ rather than as roots of $J_N^{(\alpha, \beta)}$.

For practical computations, the following weighting formula was derived by Villadsen and Michelsen (1978)

$$w_i = \frac{(2N + \alpha + \beta + 2)c_N^{(\alpha+1, \beta)}}{x_i \left[ \frac{dp_{N+1}(x_i)}{dx} \right]^2} \cdot K; \quad P_{N+1} = \prod_{j=1}^{N+1} (x - x_j)$$

where $K = 1$ for $i = 1, 2, \ldots, N$, and $K = 1/(\alpha + 1)$ for $i = N + 1$. The coefficient $c_N^{(\alpha+1, \beta)}$ is evaluated using Eq. 8.110b with $\alpha$ being replaced by $\alpha + 1$.

Similarly, when the boundary point at $x = 0$ is added to the $N$ interior interpolation points, the interior points must be chosen as roots of the following $N$th degree polynomial

$$J_N^{(\alpha, \beta + 1)}(x) \quad (8.115)$$
For computations, the formula for \( w_i \) is
\[
\frac{1}{N} \left( \frac{2N + \alpha + \beta + 2}{c_{N}^{(\alpha, \beta+1)}} \right) \cdot K; \quad P_{N} = x \prod_{j=1}^{N} (x - x_j)
\]
where \( K = 1/(\beta + 1) \) for \( i = 0 \), and \( K = 1 \) for \( i = 1, 2, \ldots, N \). The coefficient \( c_{N}^{(\alpha, \beta+1)} \) is evaluated using Eq. 8.110b with \( \beta \) being replaced by \( \beta + 1 \).

Finally, if both the end points (i.e., \( x = 0 \) and \( x = 1 \)) are included in the evaluation of the quadrature (Eq. 8.113), the \( N \) interior interpolation points must be chosen as roots of the following \( N \)th degree polynomial
\[
J_{N}^{(\alpha+1, \beta+1)}(x) \tag{8.116}
\]
The computational formula for \( W_1 \) is
\[
\frac{1}{N} \left( \frac{2N + \alpha + \beta + 3}{c_{N+1}^{(\alpha+1, \beta+1)}} \right) \cdot K; \quad P_{N+2} = x(1 - x) \prod_{j=1}^{N} (x - x_j)
\]
where \( K = 1/(\beta + 1) \) for \( i = 0 \), \( K = 1 \) for \( i = 1, 2, \ldots, N \), and \( K = 1/(\alpha + 1) \) for \( i = N + 1 \). The coefficient \( c_{N+1}^{(\alpha+1, \beta+1)} \) is evaluated using Eq. 8.110b with \( \alpha \) and \( \beta \) being replaced by \( \alpha + 1 \) and \( \beta + 1 \), respectively.

### 8.5 LINEAR BOUNDARY VALUE PROBLEM—DIRICHLET BOUNDARY CONDITION

The diffusion-reaction problem for slab catalyst particles is a classic problem used to illustrate the orthogonal collocation method. We consider this problem next.

**EXAMPLE 8.4**

The problem of a slab catalyst particle, sustaining linear reaction kinetics, was posed earlier and the dimensionless material balance equations were given in Eqs. 8.25.

Note, we must ensure the independent variable \( x \) has a domain from 0 to 1. Here we note that the problem is symmetrical at \( x = 0 \), so the following transformation is convenient
\[
u = x^2 \tag{8.117}
\]

With this transformation, we have
\[
\frac{dy}{dx} = \frac{dy}{du} \cdot \frac{du}{dx} = 2\sqrt{u} \frac{dy}{du} \tag{8.118}
\]
\[
\frac{d^2y}{dx^2} = \frac{d}{dx} \left( 2\sqrt{u} \frac{dy}{du} \right) = \frac{d}{du} \left( 2\sqrt{u} \frac{dy}{du} \right) \cdot \frac{du}{dx} = 2 \frac{dy}{du} + 4u \frac{d^2y}{du^2} \tag{8.119}
\]
Using these relations, the mass balance equation (Eq. 8.25a) and the boundary condition at the catalyst surface (Eq. 8.25c) become

\[ 4u \frac{d^2y}{du^2} + 2 \frac{dy}{du} - \phi^2 y = 0 \quad (8.120) \]

\[ u = 1; \quad y = 1 \quad (8.121) \]

At first glance, it may appear that we have made the problem more difficult. However, the boundary condition at \( x = 0 \) is no longer needed owing to the transformation \( u = x^2 \), which makes \( y \) always an even function.

Since it is our ultimate objective to evaluate the effectiveness factor (Eq. 8.30), we transform the integral in terms of the \( u \) variable, that is,

\[ \eta = \int_0^1 y \, dx = \frac{1}{2} \int_0^1 u^{-1/2} y \, du \quad (8.122) \]

The weighting function for the above integral, by comparison with Eq. 8.109, is simply

\[ W(u) = u^{-1/2} (1 - u)^0 \quad (8.123a) \]

so we conclude

\[ \alpha = 0; \quad \beta = -\frac{1}{2} \quad (8.123b) \]

Now, if we choose \((N + 1)\) interpolation points as \( N \) interior collocation points in the domain \([0, 1]\) and the boundary point at \( u = 1 \) to evaluate the integral of the form of Eq. 8.122, the \( N \) interior collocation points \((u_1, u_2, u_3, \ldots, u_N)\) must be chosen as roots of the Jacobi polynomial \( J_N^{(\alpha+1, \beta)} = J_N^{(1, -1/2)} \) (see Eq. 8.114). The \((N + 1)\)th interpolation point \( u_{N+1} \) is 1.

The interpolation polynomial for this problem is

\[ y_N(u) = \sum_{j=1}^{N+1} y_j l_j(u) = l_{N+1}(u) + \sum_{j=1}^{N} y_j l_j(u) \quad (8.124) \]

where the building blocks \( l_j \) are defined in Eq. 8.90. Comparing Eq. 8.124 with the trial solution formula (8.5), we see the correspondence

\[ l_{N+1} = y_0 \quad \text{and} \quad l_j = \phi_j \]

Since the mass balance equation (Eq. 8.120) is valid at any point inside the domain \([0, 1]\), we evaluate it at the \( i \)th interior collocation point as follows (note, as a reminder, the residual is zero at the collocation points)

\[ R(u_i) = \left[ 4u_i \frac{d^2y}{du^2} \right]_i + \left[ 2 \frac{dy}{du} \right]_i - \left[ \phi^2 y \right]_i = 0 \quad (8.125) \]

for \( i = 1, 2, \ldots, N. \)
But the derivatives at the point $i$ are given by (Eqs. 8.95 and 8.96)

\[
\left[ \frac{dy}{du} \right]_i = \sum_{j=1}^{N+1} A_{ij} y_j
\] (8.126)

and

\[
\left[ \frac{d^2y}{du^2} \right]_i = \sum_{j=1}^{N+1} B_{ij} y_j
\] (8.127)

where $y_j$ is the unknown value of $y$ at the interpolation point $u_j$. Now that the $(N + 1)$ interpolation points are chosen, the matrices $A$ and $B$ are completely known.

Substituting these derivatives (Eqs. 8.126 and 8.127) into Eq. 8.125 yields

\[
4u_i \sum_{j=1}^{N+1} B_{ij} y_j + 2 \sum_{j=1}^{N+1} A_{ij} y_j - \phi^2 y_i = 0
\] (8.128)

for $i = 1, 2, \ldots, N$.

Because we know the value for $y$ at the interpolation point $u_{N+1} = 1$, we can remove the last term from each of the two series as

\[
4u_i \sum_{j=1}^{N} B_{ij} y_j + B_{i,N+1}y_{N+1} + 2 \sum_{j=1}^{N} A_{ij} y_j + A_{i,N+1}y_{N+1} - \phi^2 y_i = 0
\] (8.129)

for $i = 1, 2, \ldots, N$.

But the value of $y$ at the boundary $u = 1$ is $y_{N+1} = 1$, so the above equation becomes

\[
4u_i \sum_{j=1}^{N} B_{ij} y_j + 2 \sum_{j=1}^{N} A_{ij} y_j - \phi^2 y_i = -4u_i B_{i,N+1} - 2A_{i,N+1}
\] (8.130)

for $i = 1, 2, \ldots, N$.

Equation 8.130 represents $N$ coupled algebraic equations, with $N$ unknowns $(y_1, y_2, \ldots, y_N)$, which are functional values of $y$ at $N$ interior collocation points. Techniques for solving large systems of algebraic equations are given in Appendix A. However, in the present problem the algebraic equations are linear and hence they are amenable to solution by matrix methods. By defining the following known matrix $C$ and vector $b$ as

\[
C = \left\{ C_{ij} = 4u_i B_{ij} + 2A_{ij} - \phi^2 \delta_{ij}; \quad i, j = 1, 2, \ldots, N \right\} \quad (8.131a)
\]

\[
b = \left\{ b_i = -4u_i B_{i,N+1} - 2A_{i,N+1}; \quad i = 1, 2, \ldots, N \right\} \quad (8.131b)
\]
Figure 8.5 Concentration profiles for $\phi = 10$, illustrating advantages of additional collocation points.

Figure 8.6 Concentration profiles for $\phi = 100$, with number of collocation points as parameter.
where

\[ \delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \quad (8.132) \]

and the unknown \( y \) as

\[ y = [y_1, y_2, y_3, \ldots, y_N]^T \quad (8.133) \]

then Eq. 8.130 can be put into the following compact vector form

\[ C \cdot y = b \quad (8.134) \]

from which the solution is simply

\[ y = C^{-1} \cdot b \quad (8.135) \]

where \( C^{-1} \) is the inverse of the matrix \( C \).

Since the solution for \( y \) is known, the effectiveness factor, \( \eta \), can be obtained from Eq. 8.122. Substituting Eq. 8.124 into Eq. 8.122, the quadrature for the integral representing effectiveness factor is

\[ \eta = \frac{1}{2} \sum_{j=1}^{N+1} w_j y_j \quad (8.136) \]

Figure 8.5 illustrates the evolution of concentration profiles for \( \phi = 10 \) with the number of collocation points as parameter. It is seen that when the reaction rate is high, the concentration profile inside the particle is very sharp, so that about 5 interior collocation points are needed to get a satisfactory result. Figure 8.6 treats the case for even faster rates, such that \( \phi = 100 \). The extreme

| Table 8.2 Computations Using Orthogonal Collocation: Diffusion in Catalyst Particle |
|-------------------------------|----------|--------------------------|--------|
| Number of Interior Collocation Point, \( N \) | \( \phi \) | \( I \)                | Percentage Relative Error |
| 1        | 10   | 0.186992               | 87     |
| 2        | 10   | 0.111146               | 11     |
| 3        | 10   | 0.100917               | 1      |
| 5        | 10   | 0.100001               | .001   |
| 1        | 100  | 0.166875               | 1569   |
| 2        | 100  | 0.067179               | 572    |
| 5        | 100  | 0.017304               | 73     |
| 7        | 100  | 0.012006               | 20     |
| 10       | 100  | 0.010203               | 2      |
| 15       | 100  | 0.010001               | .01    |
sharpness of the profile requires about 10 or more interior collocation points to yield reasonable accuracy.

Table 8.2 summarizes computation of the effectiveness factor using the orthogonal collocation method. Also shown in the table is the relative error between the calculated effectiveness factor with the exact solution, given by

\[ \eta = \frac{\tanh(\phi)}{\phi} \]

### 8.6 LINEAR BOUNDARY VALUE PROBLEM—ROBIN BOUNDARY CONDITION

#### EXAMPLE 8.5

In this example, we reconsider the catalyst problem in the previous example, but the bulk fluid moves slowly, so that finite film resistance exists. The boundary condition at the catalyst surface (Eq. 8.236) is replaced by

\[ r = R; \quad -\left[ D_e \frac{dC}{dr} \right]_R = k_c (C_R - C_0) \quad (8.137) \]

which is simply a balance of flux to the solid phase and through the film surrounding the exterior surface.

In nondimensional form, this boundary condition becomes

\[ x = 1; \quad \left[ \frac{dy}{dx} \right]_1 = Bi(1 - y_1) \quad (8.138) \]

where \( Bi = \frac{k_c R}{D_e} \).

Thus, the mass balance equation (Eqs. 8.25a and 8.138) written in terms of the variable \( u (u = x^2) \) as before

\[ 4u \frac{d^2 y}{du^2} + 2 \frac{dy}{du} - \phi^2 y = 0 \quad (8.139) \]

\[ u = 1; \quad \left[ \frac{dy}{du} \right]_1 = \frac{Bi}{2} (1 - y_1) \quad (8.140) \]

Again, our objective here is to calculate the overall reaction rate per unit volume, and from this to obtain the effectiveness factor. Therefore, the \( N + 1 \) interpolation points are chosen with the first \( N \) points being interior collocation points in the catalyst particle and the \((N + 1)\)th interpolation point being the boundary point \( (u_{N+1} = 1) \). The \( N \) interior points are chosen as roots of the Jacobian polynomial \( J_N^{(0,-1/2)} \). The optimal choice of \( N \) interior points in this example as well as the last one was studied by Michelsen and Villadsen (1980). This is done by using the quadrature approach to the calculation of the integral (Eq. 8.7) in the Galerkin method. A summary of this approach is presented in Section 8.9.
The mass balance equation is discretized at the \( i \)th interior collocation point as before, and we have

\[
4u_i \left[ \sum_{j=1}^{N} B_{ij} y_j + B_{i,N+1} y_{N+1} \right] + 2 \left[ \sum_{j=1}^{N} A_{ij} y_j + A_{i,N+1} y_{N+1} \right] - \phi^2 y_i = 0
\]

for \( i = 1, 2, \ldots, N \).

In this case, unlike the last example where \( y_{N+1} = 1 \), the value of \( y \) at the boundary point is not equal to unity, but is governed by the boundary condition (Eq. 8.140). At the boundary (i.e., at the point \( u_{N+1} \)), we have

\[
\left[ \frac{dy}{du} \right]_{u=u_{N+1}} = \frac{Bi}{2} (1 - y_{N+1})
\]

The first derivative at the point \( u_{N+1} \) is given by (Eq. 8.95)

\[
\left[ \frac{dy}{du} \right]_{u=u_{N+1}} = \sum_{j=1}^{N+1} A_{N+1,j} y_j
\]

When this is substituted into the boundary equation (Eq. 8.142), we obtain

\[
\sum_{j=1}^{N} A_{N+1,j} y_j + A_{N+1,N+1} y_{N+1} = \frac{Bi}{2} (1 - y_{N+1})
\]

where we removed the last term from the series in the LHS of this equation. Solving for \( y_{N+1} \), we have

\[
y_{N+1} = \frac{1}{1 + \frac{2A_{N+1,N+1}}{Bi}} \left[ 1 - \frac{2}{Bi} \sum_{j=1}^{N} A_{N+1,j} y_j \right]
\]

Thus, we see that when \( Bi \) is extremely large (minuscule film resistance), the above equation reduces to \( y_{N+1} = 1 \) as required.

Next, substitute the equation for \( y_{N+1} \) (Eq. 8.145 into Eq. 8.141), and so obtain the following linear equation in terms of \( y \)

\[
D \cdot y = b
\]

where

\[
D = \begin{cases} 
D_{ij} = C_{ij} - \frac{2}{Bi} C_{i,N+1} A_{N+1,j} & \text{for } i, j = 1, 2, \ldots, N \\
\end{cases}
\]

\[
C = \begin{cases} 
C_{ij} = 4u_i B_{ij} + 2A_{ij} & \text{for } i, j = 1, 2, \ldots, N \\
\end{cases}
\]

\[
b = \begin{cases} 
b_i = -\frac{C_{i,N+1}}{1 + \frac{2}{Bi} A_{N+1,N+1}} & \text{for } i = 1, 2, \ldots, N \\
\end{cases}
\]
Here, we have used a vector-matrix format to achieve compactness. The inverse of Eq. 8.146 will yield the vector $y$, that is, the concentrations $y_i$ at all interior collocation points. Knowing the concentrations at all the interior collocation points, the surface concentration $y_{N+1}$ is calculated from Eq. 8.145. Figure 8.7 presents the concentration profiles for $\phi = 10$, with the number of interior collocation point and the Biot number being parameters.
Table 8.3 Computations Using Orthogonal Collocation: Effect of Boundary Resistance

<table>
<thead>
<tr>
<th>N</th>
<th>$\phi$</th>
<th>Bi</th>
<th>$\eta$</th>
<th>Relative Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td>0.150327</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>10</td>
<td>0.069764</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>10</td>
<td>0.054334</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>10</td>
<td>0.050143</td>
<td>0.3</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>0.050000</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>20</td>
<td>0.166667</td>
<td>150</td>
</tr>
<tr>
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<td>10</td>
<td>20</td>
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</tr>
<tr>
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<td>0.070637</td>
<td>6</td>
</tr>
<tr>
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<td>0.066794</td>
<td>0.2</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>20</td>
<td>0.066667</td>
<td>0</td>
</tr>
</tbody>
</table>

The exact solutions to this problem are

$$y = \frac{\cosh(\phi x)}{\cosh(\phi) + \frac{\phi}{Bi} \sinh(\phi)}$$

$$\eta = \frac{\tanh(\phi)}{\phi \left[1 + \frac{\phi}{Bi} \tanh(\phi)\right]}$$

Table 8.3 compares the numerical solution with the exact solution. Even for sharp profiles, the collocation solutions are comparable to the exact solution using only five collocation points.

8.7 NONLINEAR BOUNDARY VALUE PROBLEM—
DIRICHLET BOUNDARY CONDITION

**Example 8.6**

We wish to consider the catalyst particle for nonlinear conditions so the local reaction rate is given by

$$R_{\text{local}} = g(C) \quad (8.150)$$

where $g(C)$ is some nonlinear function of concentration.

Setting the shell balance at the position $r$, we obtain the following mass balance equation

$$D_e \frac{d^2 C}{dr^2} - g(C) = 0 \quad (8.151a)$$
subject to the boundary conditions

\[ r = 0; \quad \frac{dC}{dr} = 0 \quad (8.151b) \]

\[ r = R; \quad C = C_0 \quad (8.151c) \]

The effectiveness factor for a general nonlinear reaction rate is defined as

\[ \eta = \int g(C) \, dV \int g(C_0) \, dV \quad (8.152a) \]

For the slab geometry, \( dV = A \, dr \), where \( A \) is the cross-sectional area of the catalyst. Hence, Eq. 8.152a becomes for a slab catalyst

\[ \eta = \frac{1}{R g(C_0)} \int_0^R g(C) \, dr \quad (8.152b) \]

Thus, when we know the distribution of \( C \), we replace \( g(C) \) in the integrand of Eq. 8.152b and evaluate the integral numerically. Alternately, we can calculate the effectiveness factor in the following way.

Multiplying Eq. 8.151a by \( dr \) and integrating the result from 0 to \( R \) gives

\[ \int_0^R g(C) \, dr = D_e \frac{dC}{dr} \bigg|_R \]

When we substitute this result into Eq. 8.152b, we obtain

\[ \eta = \frac{D_e}{R g(C_0)} \frac{dC}{dr} \bigg|_R \quad (8.152c) \]

This means that the effectiveness factor can be calculated using the derivative of concentration distribution at the exterior surface of the particle.

By defining the following dimensionless variables and parameters

\[ y = \frac{C}{C_0}; \quad x = \frac{r}{R}; \quad \phi^2 = \frac{g(C_0)R^2}{D_e C_0}; \quad G(y) = \frac{g(C_0 y)}{g(C_0)} \quad (8.153) \]

the mass balance equation (Eqs. 8.151) becomes

\[ \frac{d^2y}{dx^2} - \phi^2 G(y) = 0 \quad (8.154a) \]

\[ x = 0; \quad \frac{dy}{dx} = 0 \quad (8.154b) \]

\[ x = 1; \quad y = 1 \quad (8.154c) \]
In terms of the dimensionless variables and parameters (Eq. 8.153), the effectiveness factor given in Eq. 8.152c becomes

$$\eta = \frac{C_0D_e}{R^2g(C_0)} \frac{dy}{dx} \bigg|_1 = \frac{1}{\phi^2} \frac{dy}{dx} \bigg|_1$$  \hspace{1cm} (8.154d)

Thus, when $y(x)$ is numerically determined from Eqs. 8.154c to c, the effectiveness factor is readily evaluated from Eq. 8.154d.

We introduce the $u$ transformation as before ($u = x^2$), and the mass balance equation now becomes

$$4u \frac{d^2 y}{du^2} + 2 \frac{dy}{du} - \phi^2 G(y) = 0$$  \hspace{1cm} (8.155a)

subject to

$$u = 1; \quad y = 1$$  \hspace{1cm} (8.155b)

The reader is reminded again that when the symmetry transformation ($u = x^2$) is introduced, the boundary condition at $x = 0$ (Eq. 8.154b) is automatically satisfied.

If we now discretize the mass balance equation (Eq. 8.155a) at the interior point $i$, we have

$$4u_i \left[ \sum_{j=1}^{N} B_{ij} y_j + B_{i,N+1} y_{N+1} \right] + 2 \left[ \sum_{j=1}^{N} A_{ij} y_j + A_{i,N+1} y_{N+1} \right] = \phi^2 G(y_i) = 0$$  \hspace{1cm} (8.156)

for $i = 1, 2, \ldots, N$.

Since $y_{N+1} = 1$ (Eq. 8.155b), the above equation becomes

$$4u_i \left[ \sum_{j=1}^{N} B_{ij} y_j + B_{i,N+1} y_{N+1} \right] + 2 \left[ \sum_{j=1}^{N} A_{ij} y_j + A_{i,N+1} \right] = \phi^2 G(y_i) = 0$$  \hspace{1cm} (8.157)

for $i = 1, 2, \ldots, N$. This equation represents a set of $N$ nonlinear coupled algebraic equations in terms of $y_1, y_2, \ldots, y_N$. They can be solved by one of several nonlinear algebraic solvers, such as the Newton–Raphson method (see Appendix A).
To solve Eq. 8.157 by the Newton-Raphson procedure, we define

\[ F_i(y) = 4u_i \sum_{j=1}^{N} B_{ij} y_j + B_{i,N+1} + 2 \left[ \sum_{j=1}^{N} A_{ij} y_j + A_{i,N+1} \right] - \phi^2 G(y_i) = 0 \]  

(8.158)

for \( i = 1, 2, \ldots, N \), and where

\[ y = [y_1, y_2, \ldots, y_N]^T \]  

(8.159)

The iteration scheme for the Newton-Raphson is

\[ y^{(k+1)} = y^{(k)} - d^{(k)} \]  

(8.160a)

where

\[ J(y^{(k)})d^{(k)} = F(y^{(k)}) \]  

(8.160b)

\[ F = [F_1(y), F_2(y), \ldots, F_N(y)]^T \]  

(8.160c)

\[ J = \left\{ \frac{\partial F_i}{\partial y_j} = 4u_i B_{ij} + 2A_{ij} - \delta_{ij}\phi^2 \frac{\partial G(y_j)}{\partial y} ; \ i, j = 1, 2, \ldots, N \right\} \]  

(8.160d)

where \( \delta_{ij} \) represents the Kronecker delta function, defined as

\[ \delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \]  

(8.161)

To solve for the concentration vector \( y \) by the Newton-Raphson technique, we need to select an initial set for \( y^{(0)} \). With this initial guess, the function vector \( F \) and the Jacobian \( J \) can be evaluated (Eqs. 8.160c, d). Using any standard linear equation solver, the vector \( d \) can be calculated from Eq. 8.160b and hence the first iterated solution \( y^{(1)} \) is given in Eq. 8.160a. The process is repeated until a convergence criterion is satisfied. One can choose either of the following criteria for stopping the iteration

\[ \sum_{j=1}^{N} \frac{|y_j^{(k+1)} - y_j^{(k)}|}{|y_j^{(k)}|} < \varepsilon \]

or

\[ \max_j \frac{|y_j^{(k+1)} - y_j^{(k)}|}{|y_j^{(k)}|} < \varepsilon \]
If $y$ is small, the following stopping criterion is recommended

$$
\sum_j \left| y_j^{(k+1)} - y_j^{(k)} \right| < \varepsilon
$$

Figure 8.8 presents computations of concentration profiles for the case of second order chemical kinetics. The first stopping criterion was used to generate these plots, and $\varepsilon$ was 0.001. Again, just as in previous examples, the collocation solutions generated with five or more interior collocation points agree fairly well with the exact solution, which in the present case is taken as the solution generated by using 19 interior collocation points. For this problem of slab geometry, the analytical solution is given as

$$
\int_y^1 \frac{ds}{\left[ 2 \int_{y_0}^s G(m) \, dm \right]^{1/2}} = \phi(1 - x)
$$

where $y_0$ is the value of $y$ at $x = 0$ and is given by

$$
\int_{y_0}^1 \frac{ds}{\left[ 2 \int_{y_0}^s G(m) \, dm \right]^{1/2}} = \phi
$$
Table 8.4 Computations Using Orthogonal Collocation: Nonlinear Reaction Kinetics

<table>
<thead>
<tr>
<th>N</th>
<th>$\phi$</th>
<th>$\eta$</th>
<th>Relative Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>0.230000</td>
<td>109</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>0.130439</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0.117599</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>0.111027</td>
<td>0.61</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>0.110356</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>20</td>
<td>0.110355</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 8.4 shows the numerically calculated effectiveness factor and the relative error as function of the number of interior collocation point.

8.8 ONE-POINT COLLOCATION

The orthogonal collocation method, as we have attempted to illustrate in previous examples, sustains an accuracy, which will increase with the number of points used. Occasionally, one is interested in the approximate behavior of the system instead of the computer intensive exact behavior. To this end, we simply use only one collocation point, and the result is a simplified equation, which allows us to quickly investigate the behavior of solutions, for example, to see how the solution would change when a particular parameter is changed, or to determine whether the solution exhibits multiplicity. Once this is done, detailed analysis can be carried out with more collocation points.

**EXAMPLE 8.7**

We illuminate these attractive features by considering the difficult problems of diffusion and reaction in a slab catalyst sustaining highly nonlinear Hinshelwood kinetics. The mass balance equations written in nondimensional form are taken to be

$$\frac{d^2y}{dx^2} - \frac{\phi^2y}{1 + \delta y + \gamma y^2} = 0 \quad (8.162a)$$

$$x = 0; \quad \frac{dy}{dx} = 0 \quad (8.162b)$$

$$x = 1; \quad y = 1 \quad (8.162c)$$

Noting the symmetry of this problem, we make the usual substitution $u = x^2$, and the mass balance equations become

$$4u \frac{d^2y}{du^2} + 2\frac{dy}{du} - \frac{\phi^2y}{1 + \delta y + \gamma y^2} = 0 \quad (8.163)$$

$$u = 1; \quad y = 1 \quad (8.164)$$
Now we choose one collocation point, $u_1$, in the domain $[0,1]$, and since we know the value of $y$ at the surface of the catalyst, we will use it as the second interpolation point, that is, $u_2 = 1$. For these two interpolation points, we have two Lagrangian interpolation polynomials, $l_1(u)$ and $l_2(u)$, given as

$$ l_1(u) = \frac{u - u_2}{u_1 - u_2}, \quad l_2(u) = \frac{u - u_1}{u_2 - u_1} \tag{8.165} $$

where $u_1$ is the collocation point chosen in the domain $[0,1]$, and $u_2 = 1$.

Using the Lagrangian interpolation polynomials $l_1(u)$ and $l_2(u)$, the approximate solution for $y(u)$ can be written as

$$ y = l_1(u)y_1 + l_2(u)y_2 = l_1(u)y_1 + l_2(u) \tag{8.166} $$

because $y_2 = y(u_2) = y(1) = 1$.

Next, we substitute the approximate solution 8.166 into the differential equation 8.163, and obtain the following residual

$$ R = 4u \frac{d^2y}{du^2} + 2 \frac{dy}{du} - \frac{\phi^2}{1 + \delta y + \gamma y^2} \tag{8.167} $$

We now have only one unknown, which is the value of $y$ at the collocation point $u_1$, and the test function for the collocation method is

$$ w_1 = \delta(u - u_1) \tag{8.168} $$

Averaging the residual with the test function $w_1$ is carried out using the integral

$$ \int_0^1 R(u)w_1(u) \, du = \int_0^1 \left( 4u \frac{d^2y}{du^2} + 2 \frac{dy}{du} - \frac{\phi^2}{1 + \delta y + \gamma y^2} \right) \delta(u - u_1) \, du = 0 $$

that is,

$$ 4u_1 \frac{d^2y}{du^2} \bigg|_{u_1} + 2 \frac{dy}{du} \bigg|_{u_1} - \frac{\phi^2 y_1}{1 + \delta y_1 + \gamma y_1^2} = 0 \tag{8.169} $$

But

$$ \frac{dy}{du} \bigg|_{u_1} = \frac{dl_1(u_1)}{du} y_1 + \frac{dl_2(u_1)}{du} = A_{11}y_1 + A_{12} \tag{8.170a} $$

and

$$ \frac{d^2y}{du^2} \bigg|_{u_1} = \frac{d^2l_1(u_1)}{du^2} y_1 + \frac{d^2l_2(u_1)}{du^2} = B_{11}y_1 + B_{12} \tag{8.170b} $$
When we substitute Eqs. 8.170 into Eq. 8.169, we get

\[ C_{11}y_1 + C_{12} = \frac{\phi^2 y_1}{1 + \delta y_1 + \gamma y_1^2} = 0 \quad (8.171) \]

where

\[ C_{11} = 4u_1 B_{11} + 2A_{11} \quad \text{and} \quad C_{12} = 4u_1 B_{12} + 2A_{12} \]

Equation 8.171 is a cubic equation in terms of \( y_1 \); hence, depending on the values of \( \phi, \delta, \) and \( \gamma \), there may exist three solutions (multiple steady states) for this problem. A knowledge of this will then help the comprehensive computation using more collocation points.

This example serves as a means to allow workers to quickly study the topology of a system before more time is spent on the detailed computation of the governing equations.

**8.9 SUMMARY OF COLLOCATION METHODS**

We have presented a family of approximate methods, called weighted residuals, which are quite effective in dealing with boundary value problems. The name suggests that we need to generate residuals obtained when the approximate solution is substituted into the governing equation. Then, we try to minimize the residuals or force it to be asymptotically close to zero at certain points. A number of methods have appeared, depending on how we minimize this residual.

Among the five methods studied in this chapter, the orthogonal collocation and the Galerkin methods seem to provide the best approximate routes. The Galerkin method provides solution with good accuracy, while the collocation method is easy to apply and to program, owing to its mechanical structure. The accuracy of collocation is comparable to Galerkin if the collocation points are properly chosen. Because of this attribute, the collocation method has found wide applications in chemical engineering and other branches of engineering.

We now summarize the steps taken in the application of the orthogonal collocation procedure.

**Step 1**

For the given problem, normalize the range of the independent variable to \((0, 1)\). Any domain \((a, b)\) can be transformed to a \((0, 1)\) by the transformation

\[ x = \frac{z - a}{b - a} \]

where \( x \) is the new independent variable lying in the domain \((0, 1)\).

**Step 2**

Next, observe the boundary conditions and if there is symmetry at \( x = 0 \), make use of the transformation \( u = x^2 \). Similarly, if the problem is symmetrical at \( x = 1 \), use the transformation \( u = (1 - x)^2 \).
Step 3  Assume an approximate solution of the form in Eq. 8.5, where $y_0(x)$ satisfies the boundary conditions exactly and the trial functions, $\phi_i(x)$, satisfy the homogeneous boundary conditions. The problem at this point is then reduced to the problem of solving for $N$ unknown coefficients. If the trial functions are chosen as the Lagrange interpolation polynomials, $l_i(x)$ (Section 8.3), the coefficients $a_i$ then become the values of $y$ at the interpolation points $x_i$. Interpolation points are those used to generate the Lagrange interpolation polynomials. It is noted here that the Lagrange interpolation polynomial is used here as a convenient vehicle to obtain a solution. Any linearly independent set of trial functions can be used in the collocation method.

Step 4  Substitute the approximate solution prescribed in Step 3 into the governing equation to form a residual $R$ (Eq. 8.6), which is a function of $x$ as well as $N$ coefficients $a_i$.

Step 5  This step is the most crucial step of the orthogonal collocation method. If the Galerkin method is used for minimizing the residual (remember that the Galerkin is the best method among the many weighted residual methods to provide solution of good accuracy), the following function of $N$ coefficients $a_i$ is created

$$\int_0^1 R(a_1, a_2, \ldots, a_N; x) \phi_j(x) \, dx = 0 \quad \text{for} \quad j = 1, 2, \ldots, N$$

These $N$ integrals, in general, cannot be integrated analytically; hence, it must be done numerically by a quadrature method, such as the Gaussian quadrature described in Appendix E. Before doing this, extract a common factor of the form $W(x) = x^\alpha (1 - x)^\beta$ from the integrand of the above integral. This factor must be the same for all values of $j$. The integral can then be written as

$$\int_0^1 R(a_1, a_2, \ldots, a_N; x) \phi_j(x) \, dx = \int_0^1 [x^\beta (1 - x)^\alpha] Q_j(x) \, dx \quad \text{for} \quad j = 1, 2, \ldots, N$$

where

$$Q_j(x) = \frac{R(a_1, a_2, \ldots, a_N; x) \phi_j(x)}{x^\beta (1 - x)^\alpha}$$

If the Gaussian quadrature of $N$ quadrature points is applied to evaluate the above integral approximately, the optimal quadrature formula would be

$$\int_0^1 [x^\beta (1 - x)^\alpha] Q_j(x) \, dx = \sum_{k=1}^{N} w_k Q_j(x_k) \quad \text{for} \quad j = 1, 2, \ldots, N$$
where \( w_k \) are the quadrature weights and \( x_k \) are the quadrature points, which are zeros of the Jacobi polynomial \( J_N^{(\alpha, \beta)}(x) \). Note that the number of quadrature points used is the same as the number of unknown coefficients \( a_i \). It should also be pointed out that the above quadrature approximation will be exact if the polynomial \( Q_j \) is of degree less than or equal to \( 2N - 1 \) (see Appendix E).

**Step 6**

It is then clear from Step 5 that the *optimal approximation* to the Galerkin method is simply to choose

\[
R(a_1, a_2, \ldots, a_N; x_k) = 0 \quad \text{for} \quad k = 1, 2, \ldots, N
\]

Thus, if the collocation method is used, with the collocation points being zeros of the Jacobi polynomial \( J_N^{(\alpha, \beta)}(x) \), then the collocation method will closely approximate the Galerkin method.

These outline the pedagogical steps for undertaking the orthogonal collocation method. They are chosen so that the collocation method closely approximates the Galerkin method. Problem 8.9 illustrates in a practical way how to apply these steps to an engineering problem.

### 8.10 CONCLUDING REMARKS

Boundary value problems are encountered so frequently in modelling of engineering problems that they deserve special treatment because of their importance. To handle such problems, we have devoted this chapter exclusively to the methods of weighted residual, with special emphasis on orthogonal collocation. The one-point collocation method is often used as the first step to quickly assess the behavior of the system. Other methods can also be used to treat boundary value problems, such as the *finite difference* method. This technique is considered in Chapter 12, where we use this method to solve boundary value problems and partial differential equations.

### 8.11 REFERENCES

8.12 PROBLEMS

8.1. The Lagrangian polynomials \( l_j(x) \) defined for \( N + 1 \) interpolation points are given as

\[
l_j(x) = \prod_{k=1, k \neq j}^{N+1} \frac{x - x_k}{x_j - x_k} \quad \text{for} \quad j = 1, 2 \cdots, N + 1
\]

(a) Show that \( l_j(x_j) = 1 \) and \( l_j(x_k) = 0 \) for all \( k \neq j \).
(b) Prove that the definition of the Lagrangian polynomial is equivalent to the expression

\[
l_j(x) = \frac{p_{N+1}(x)}{(x - x_j)p'_{N+1}(x_j)}
\]

where \( p_{N+1}(x) \) is called the node polynomial (it is called node because it becomes zero at the interpolation points) and is defined as

\[
p_{N+1}(x) = (x - x_1)(x - x_2)(x - x_3) \cdots (x - x_N)(x - x_{N+1})
\]

and \( p'_{N+1} = dp_{N+1}/dx \).

8.2. For any set of Lagrangian polynomial \( l_j(x) \) of degree \( N \), defined as in Problem 8.1, show that the sum of these \( N + 1 \) Lagrangian polynomials is unity; that is,

\[
\sum_{j=1}^{N+1} l_j(x) = 1
\]

*Hint:* Start with the following function \( y_N(x) \) representing the polynomial passing through \( N + 1 \) points \( (x_1, y_1), (x_2, y_2), \ldots, (x_N, y_N), (x_{N+1}, y_{N+1}) \)

\[
y_N(x) = \sum_{j=1}^{N+1} l_j(x)y_j
\]

8.3. With the Lagrangian polynomials defined in part (b) of Problem 8.1, show that they are orthogonal to each other with respect to the weighting function \( W(x) = x^\alpha(1-x)^\beta \) if the \( N + 1 \) interpolation points \( x_1, x_2, x_3, \ldots, x_N, x_{N+1} \) are chosen as roots of the Jacobi polynomial \( J_{N+1}^{(\alpha, \beta)}(x) = 0 \); that is,

\[
\int_0^1 x^\beta(1-x)^\alpha l_k(x)l_j(x) \, dx = 0 \quad \text{for} \quad k \neq j
\]
Hint: Use the following orthogonality property of the Jacobi polynomial

\[ \int_0^1 [x^\beta (1 - x)^\alpha] x^j J_{N+1}^{(\alpha, \beta)}(x) \, dx = 0 \quad \text{for} \quad j = 0, 1, 2, \ldots, N \]

8.43. Let \( x_1, x_2, x_3, \ldots, x_N \) be \( N \) interpolation points chosen as roots of the Jacobi polynomial \( J_N^{(\alpha, \beta)}(x) = 0 \) (i.e., \( 0 < x_j < 1 \) for \( j = 1, 2, \ldots, N \)). The ordinates corresponding to these points are denoted as \( y_1, y_2, y_3, \ldots, y_N \), and the polynomial of degree \( N - 1 \), \( y_{N-1}(x) \), passing through these \( N \) points \( (x_1, y_1), (x_2, y_2), \ldots, (x_N, y_N) \), is given by the following Lagrangian formula

\[ y_{N-1}(x) = \sum_{j=1}^{N} l_j(x) y_j \]

where

\[ l_j(x) = \frac{p_N(x)}{(x - x_j)p'_N(x_j)} \]

where \( p_N(x) \) is the scaled Jacobi polynomial defined as

\[ p_N(x) = (x - x_1)(x - x_2)(x - x_3) \cdots (x - x_N) = \frac{J_N^{(\alpha, \beta)}(x)}{\gamma_{N,N}} \]

(a) Show that the integral of the function \( y_{N-1}(x) \) with respect to the weighting function \( W(x) = x^\beta (1 - x)^\alpha \) from 0 to 1 is given by the following quadrature

\[ \int_0^1 [x^\beta (1 - x)^\alpha] y_{N-1}(x) \, dx = \sum_{j=1}^{N} w_j y_j \]

where

\[ w_j = \int_0^1 [x^\beta (1 - x)^\alpha] l_j(x) \, dx \]

(b) Use the results of Problems 8.2 and 8.3 to show that the quadrature weights of part (a) can be written as

\[ w_j = \int_0^1 [x^\beta (1 - x)^\alpha] [l_j(x)]^2 \, dx \]
(c) Starting from the equation in part (b) and the definition of the Lagrangian polynomial \( l_j(x) \), show that

\[
\frac{w_j}{x_j(1-x_j)} = \frac{(2N + \alpha + \beta + 1) c_N^{(\alpha, \beta)}}{d p_N(x_j)}
\]

where

\[
c_N^{(\alpha, \beta)} = \int_0^1 \left[ x^\beta (1-x)^\alpha \right] p_N^2(x) \, dx > 0
\]

8.5. Let \( x_1, x_2, x_3, \ldots, x_N \) be \( N \) interpolation points chosen as roots of the Jacobi polynomial \( J_N^{(\alpha, \beta)}(x) = 0 \) (i.e., \( 0 < x_j < 1 \) for \( j = 1, 2, \ldots, N \)) and the \((N + 1)\)th interpolation point is \( x_{N+1} = 1 \). The ordinates corresponding to these \((N + 1)\) points are denoted as \( y_1, y_2, y_3, \ldots, y_N, y_{N+1} \), and the polynomial of degree \( N \), \( y_N(x) \), passing through these \( N + 1 \) points \((x_1, y_1),(x_2, y_2), \ldots, (x_N, y_N),(x_{N+1}, y_{N+1})\) is given by the Lagrangian formula

\[
y_N(x) = \sum_{j=1}^{N+1} l_j(x) y_j
\]

where

\[
l_j(x) = \frac{p_{N+1}(x)}{(x-x_j)p'_{N+1}(x_j)}
\]

with \( p_{N+1}(x) \) being the node polynomial defined as

\[
p_{N+1}(x) = (x-x_1)(x-x_2)(x-x_3) \cdots (x-x_N)(x-x_{N+1})
\]

\[
= p_N^{(\alpha, \beta)}(x) \cdot (x-1)
\]

where \( p_N^{(\alpha, \beta)}(x) \) is the scaled Jacobi polynomial

\[
p_N^{(\alpha, \beta)}(x) = \frac{J_N^{(\alpha, \beta)}(x)}{\gamma_{N, N}}
\]

(a) Show that the integral of the function \( y_N(x) \) with respect to the weighting function \( W(x) = x^\beta (1-x)^\alpha \) from 0 to 1 is given by the quadrature

\[
\int_0^1 \left[ x^\beta (1-x)^\alpha \right] y_N(x) \, dx = \sum_{j=1}^{N+1} w_j y_j
\]
where
\[ w_j = \int_0^1 [x^\beta (1 - x)^\alpha] l_j(x) \, dx \]

(b) Show that \( w_j \) (for \( j = 1, 2, \ldots, N \)) are identical to the quadrature weights obtained in Problem 8.4, where \( N \) interpolation points are used.

(c) Prove that \( w_{N+1} = 0 \), which implies that the extra interpolation point at \( x_{N+1} \) is not taken into account in the evaluation of the numerical quadrature.

8.6. Similar to Problem 8.5, let \( x_1, x_2, x_3, \ldots, x_N \) be \( N \) interpolation points chosen as roots of the Jacobi polynomial \( J_N^{(\alpha, \beta)}(x) = 0 \) (i.e., \( 0 < x_j < 1 \) for \( j = 1, 2, \ldots, N \)) and \( x_0 = 0 \) is the additional interpolation point. The ordinates corresponding to these \( (N + 1) \) points are \( y_0, y_1, y_2, \ldots, y_N \) and the polynomial of degree \( N \), \( y_N(x) \), passing through these \( N + 1 \) points \( (x_0, y_0), (x_1, y_1), (x_2, y_2), \ldots, (x_N, y_N) \) is given by the Lagrangian formula

\[ y_N(x) = \sum_{j=0}^{N} l_j(x) y_j \]

where
\[ l_j(x) = \frac{p_{N+1}(x)}{(x - x_j) p'_{N+1}(x_j)} \]

with \( p_{N+1}(x) \) being the node polynomial defined as

\[ p_{N+1}(x) = (x - x_0)(x - x_1)(x - x_2) \cdots (x - x_N) = x \cdot p_N^{(\alpha, \beta)}(x) \]

where \( p_N^{(\alpha, \beta)}(x) \) is the scaled Jacobi polynomial

\[ p_N^{(\alpha, \beta)}(x) = \frac{J_N^{(\alpha, \beta)}(x)}{\gamma_{N,N}} \]

(a) Show that the integral of the function \( y_N(x) \) with respect to the weighting function \( W(x) = x^\beta (1 - x)^\alpha \) from 0 to 1 is given by the quadrature

\[ \int_0^1 [x^\beta (1 - x)^\alpha] y_N(x) \, dx = \sum_{j=0}^{N} w_j y_j \]

where
\[ w_j = \int_0^1 [x^\beta (1 - x)^\alpha] l_j(x) \, dx \]
(b) Show that \( w_j \) (for \( j = 1, 2, \ldots, N \)) are identical to the quadrature weights obtained in Problem 8.4, where \( N \) interpolation points are used, and \( w_0 = 0 \). This, like Problem 8.5, means that adding the extra interpolation point either at \( x = 1 \) or \( x = 0 \) does not help to improve the accuracy of the quadrature. Even when \( N \) extra interpolation points are added in addition to the \( N \) collocation points as roots of \( J_N^{(\alpha, \beta)}(x) = 0 \), there is no net effect of this addition. This is because the \( N \) ordinates \( y_j \) at the zeros of \( J_N^{(\alpha, \beta)}(x) = 0 \) are sufficient to integrate a polynomial of degree \( 2N - 1 \) exactly.

8.7*. It is shown in Problems 8.5 and 8.6 that adding an extra interpolation point or even \( N \) interpolation points to the \( N \) interpolation points, which are zeros of \( J_N^{(\alpha, \beta)}(x) = 0 \), does not help to improve the evaluation of the integral by quadrature

\[
\int_0^1 [x^\beta (1-x)^\alpha] y(x) \, dx
\]

Now reconsider Problem 8.5 where \((N + 1)\) interpolation points are used. The \( N \)th degree polynomial passing through \( N + 1 \) points \((x_1, y_1), (x_2, y_2), \ldots, (x_N, y_N), (x_{N+1}, y_{N+1})\) is given by

\[
y_N(x) = \sum_{j=1}^{N+1} l_j(x) y_j
\]

where \( l_j(x) \) is given as in Problem 8.5.

(a) Construct a \( 2N \)th degree polynomial as follows

\[
y_{2N}(x) = y_N(x) + G_{N-1} \cdot (1-x) \cdot p_N^{(\alpha+1, \beta)}(x)
\]

where \( G_{N-1} \) is any \((N - 1)\)th degree polynomial and \( p_N^{(\alpha, \beta)}(x) \) is the scaled Jacobi polynomial

\[
p_N^{(\alpha+1, \beta)}(x) = \frac{J_N^{(\alpha+1, \beta)}(x)}{\gamma_{N, N}}
\]

Evaluate the following integral

\[
\int_0^1 [x^\beta (1-x)^\alpha] y_{2N}(x) \, dx
\]

by the quadrature method and show that it is equal to

\[
\int_0^1 [x^\beta (1-x)^\alpha] y_{2N}(x) \, dx = \sum_{j=1}^{N+1} w_j y_j
\]
where

\[ w_j = \int_0^1 [x^\beta (1 - x)^\alpha] l_j(x) \, dx \]

if the \( N + 1 \) interpolation points are chosen such that the first \( N \) interpolation points are roots of the Jacobi polynomial \( J_N^{(\alpha+1, \beta)}(x) = 0 \) and the \((N + 1)\)th point is \( x_{N+1} = 1 \). This quadrature formula is called the Radau quadrature. It can integrate any polynomial of degree \( 2N \) exactly.

8.8. There are a number of ways to assume the form of the approximate solution. One way, which is used often in the text, is the power law expression

\[ y_N = \sum_{j=0}^{N} a_j x^j \]

where the subscript \( N \) means that the approximate polynomial has the degree \( N \). Another way, also equally useful, is the use of the Jacobi polynomials as the expansion terms, given as

\[ y_N = \sum_{j=0}^{N} b_j J_j^{(\alpha, \beta)}(x) \]

where \( J_j^{(\alpha, \beta)}(x) \) is the Jacobi polynomial of degree \( j \).

(a) Make use of the following orthogonality properties of the Jacobi polynomial

\[ \int_0^1 [x^\beta (1 - x)^\alpha] J_j^{(\alpha, \beta)}(x) J_k^{(\alpha, \beta)}(x) \, dx = 0 \quad \text{for} \ k \neq j \]

to show how the coefficients \( b_j \) are determined in terms of the coefficients \( a_j \).

8.9*. Modelling of a cylindrical catalyst with an \( n \)th order chemical reaction under the isothermal conditions gives rise to the following equation

\[ D_e \frac{1}{r} \frac{d}{dr} \left( r \frac{dC}{dr} \right) - \rho_p k C^n = 0 \]

where \( k C^n \) is the chemical reaction rate per unit mass of the catalyst, and \( D_e \) is the effective diffusivity. Assuming that the fluid surrounding the catalyst is vigorously stirred, the following boundary conditions can be taken

\[ r = 0; \quad \frac{dC}{dr} = 0 \quad \text{and} \quad r = R; \quad C = C_0 \]

where \( C_0 \) is the constant bulk concentration, and \( R \) is the particle radius.
(a) Show that the above dimensional equation can be cast into the following nondimensional form

\[
\frac{1}{x} \frac{d}{dx} \left( x \frac{dy}{dx} \right) - \phi^2 y'' = 0
\]

subject to

\[
x = 0; \quad \frac{dy}{dx} = 0 \quad \text{and} \quad x = 1; \quad y = 1
\]

What are the definitions of \( y, x, \) and \( \phi \) that yield the above form of nondimensional equations?

(b) Because of the symmetry of the problem around the point \( x = 0 \), it is convenient to use the following symmetry transformation \( u = x^2 \). Show that the new equations written in terms of the new variable \( u \) are

\[
4u \frac{d^2 y}{du^2} + 4 \frac{dy}{du} - \phi^2 y'' = 0
\]

\[
u = 1; \quad y = 1
\]

Note that the center boundary condition is not needed because of the symmetry transformation.

(c) To solve the equations in part (b) using the method of weighted residual, assume that the approximation solution has the form

\[
y_a = 1 + a_i (1 - u)
\]

where \( a_i \) is the unknown coefficient to be found. Note that this assumed form is made to satisfy the boundary condition at \( u = 1 \). Use this approximate solution in the governing equation of part (b) to show that the residual is

\[
R(a_i, u) = -4 a_i - \phi^2 [1 + a_i (1 - u)]^n
\]

The residual is a function of both the independent variable \( u \) and the unknown coefficient \( a_i \).

(d) Apply the method of collocation with a test function \( \delta(u - u_1) \) to show that the equation for \( a_i \) is

\[
\int_0^1 R(a_i, u) \delta(u - u_1) \, du = -4 a_i - \phi^2 [1 + a_i (1 - u_1)]^n = 0
\]

where \( u_1 \) is some arbitrary collocation point in the domain \((0, 1)\). The above equation is a nonlinear algebraic equation, which can be solved for \( a_i \) once the collocation point \( u_1 \) is chosen.
(e) Apply the Galerkin method with the test function \((1 - u)\) to show that the equation for \(a_1\) is expressed in the following form of the integral

\[
\int_0^1 R(a_1, u)(1 - u) \, du
\]

\[
= \int_0^1 \{-4a_1 - \phi^2[1 + a_i(1 - u)]\}(1 - u) \, dx = 0
\]

For integer \(n\), the above integral can be analytically integrated, while for noninteger \(n\), it must be evaluated numerically or using some form of numerical quadrature.

(f) Now try the numerical quadrature approach to approximate the integral of part (e) and show that the approximation is

\[
\int_0^1 R(a_1, u)(1 - u) \, du \approx \sum_{j=1}^{M} w_j R(a_1, u_j)
\]

where \(u_j\) are quadrature points, \(w_j\) are the quadrature weights, and \(M\) is the number of such points. Show that the optimal choice of these \(M\) quadrature points are roots of \(J_M^{(1,0)}(u)\).

Now take only one quadrature point, and this point will be the root of the following Jacobi polynomial of degree 1, \(J_1^{(1,0)}(x)\), which is found in Problem 8.14 as

\[
J_1^{(1,0)}(x) = 3u - 1 = 0 \quad \text{i.e.,} \quad u_1 = \frac{1}{3}
\]

Show that the resulting equation for \(a_1\) for the Galerkin method is identical to the equation for \(a_1\) obtained by the collocation method. This means that collocation and Galerkin methods yield the same

---

3 The approximation of the integral

\[
\int_0^1 W(x)f(x) \, dx \quad \text{with} \quad W(x) = x^\alpha(1 - x)^\beta
\]

by the quadrature method is

\[
\int_0^1 W(x)f(x) \, dx = \sum_{k=1}^{M} w_k f(x_k)
\]

where there exists an optimal choice of quadrature points, and those points are roots of the \(M\)th degree Jacobi polynomial \(J_M^{(\alpha, \beta)}(x) = 0\).
answer for \(a_1\), if the collocation point is chosen as a root of the proper Jacobi polynomial, and the quadrature approximation of the integral is exact.\(^4\)

(g) If the chemical reaction is first order \((n = 1)\), show that the quadrature approximation of the integral obtained for the Galerkin method

\[
\int_0^1 R(u_1, u)(1 - u) \, du = w_1 R(u_1, u_1)
\]

is exact. This means that the Galerkin and the collocation methods will yield identical approximate solutions if the collocation point is chosen as root of the Jacobi polynomial \(J_1^{(1,0)} = 0\) (i.e., \(u_1 = 1/3\)). For such a situation, the collocation method is called the orthogonal collocation method because the Jacobi polynomial belongs to a class of orthogonal functions.

(h) Now consider the second order chemical reaction \((n = 2)\), show that the number of quadrature points required to yield exact evaluation of the integral

\[
\int_0^1 R(u_1, u)(1 - u) \, du
\]

by the method of quadrature is 2, with the two quadrature points being roots of \(J_2^{(1,0)}(x) = 0\). Obtain the expression for this Jacobi polynomial of degree 2 and hence derive the solutions for these two quadrature points.

(i) The previous parts (a to h) consider only the one-term approximate solution. Now consider the following \(N\)-terms trial solution

\[
y_a = 1 + \sum_{j=1}^{N} a_j (1 - u) u^{j-1}
\]

where \(a_j\) \((j = 1, 2, \ldots, N)\) are \(N\) unknown coefficients to be found. Show that the residual generated by this choice of approximate solution is

\[
R_N(a_1, a_2, \ldots, a_N; u)
\]

\[
= 4 \sum_{j=1}^{N} a_j [(j - 1)^2 u^{j-2} - j^2 u^{j-1}] - \phi^2 \left[ 1 + (1 - u) \sum_{j=1}^{N} a_j u^{j-1} \right]^n
\]

(j) Now apply the collocation method with the \(N\) test functions \(\delta(u - u_k)\) (for \(k = 1, 2, \ldots, N\)), where \(u_k\) are collocation points to show that

---

\(^4\)Using \(M\) quadrature points (which are roots of the proper Jacobi polynomial) in the numerical quadrature, the quadrature approximation will be exact if the function \(R(u)\) is a polynomial of degree less than or equal to \(2M - 1\).
the \( N \) nonlinear algebraic equations to be solved for \( a_j \)'s are

\[
R_N(a_1, a_2, \ldots, a_N; u_k)
\]

\[
= 4 \sum_{j=1}^{N} a_j [(j - 1)^2 u_k^{j-2} - j^2 u_k^{j-1}] - \phi^2 \left[ 1 + (1 - u_k) \sum_{j=1}^{N} a_j u_k^{j-1} \right] \tag{a}
\]

\[= 0\]

for \( k = 1, 2, 3, \ldots, N \).

(k) Now apply the Galerkin method with the \( N \) test functions \((1 - u)u_k \) (for \( k = 1, 2, \ldots, N \)) to show that the \( N \) equations for \( a_j \)'s written in the form of integral are

\[
\int_0^1 R_N(a_1, a_2, \ldots, a_N; u) [(1 - u)u_k] \, du = 0
\]

for \( k = 1, 2, \ldots, N \),

where \( R_N \) is given in part (i). These integrals must be evaluated numerically or approximated by the following quadrature using \( M \) quadrature points

\[
\int_0^1 [R_N(a_1, a_2, \ldots, a_N; u)u_k^{k-1}] (1 - u) \, du
\]

\[
\approx \sum_{j=1}^{M} w_j [R_N(a_1, a_2, \ldots, a_N; u_j)u_j^{k-1}] = 0
\]

for \( k = 1, 2, \ldots, N \)

The \( M \) quadrature points are roots of the Jacobi polynomial of degree \( M \), \( J_M^{(1,0)}(x) = 0 \). Show that the above quadrature approximation is the exact representation of the integral if

\[
M \geq \frac{N(n + 1)}{2}
\]

(l) Show that one trivial way to satisfy the nonlinear algebraic equations in part (k) is to set

\[
R_N(a_1, a_2, \ldots, a_N; u_j) = 0 \quad \text{for} \quad j = 1, 2, \ldots, M
\]

and hence show that \( a_j \)'s can be determined if the number of quadrature points are chosen the same as the number of coefficient, \( N \), in the trial solution. When this is the case, the Galerkin is "best" approximated by the collocation method if the collocation points are chosen as roots of the \( N \)th degree Jacobi polynomial \( J_N^{(1,0)}(x) = 0 \).
(m) Prove that if the chemical reaction is first order, the collocation method with \( N \) collocation points chosen as roots of \( J_N^{(1,0)}(x) = 0 \) is identical to the Galerkin method.

This example illustrates how collocation points should be optimally chosen so that they can closely match the Galerkin method.

8.10. The Jacobi polynomial can be expressed conveniently as

\[
J_N^{(\alpha, \beta)}(x) = \sum_{j=0}^{N} (-1)^{N-j} \gamma_j x^j \quad \text{with} \quad \gamma_0 = 1
\]

The \( N \) coefficients, \( \gamma_j \) (\( j = 1, 2, \ldots, N \)), are determined from the following \( N \) orthogonality condition equations

\[
\int_0^1 [x^\beta (1-x)^\alpha] J_k^{(\alpha, \beta)}(x) \cdot J_N^{(\alpha, \beta)}(x) \, dx = 0
\]

for \( k = 0, 1, 2, \ldots, N - 1 \)

(a) Show that the above orthogonality condition equations are equivalent to

\[
\int_0^1 [x^\beta (1-x)^\alpha] x^k J_N^{(\alpha, \beta)}(x) \, dx = 0 \quad \text{for} \quad k = 0, 1, 2, \ldots, N - 1
\]

(b) Use the equations of part (a) to then show that the linear equations for solving for \( \gamma_j \)'s are

\[
A \gamma = b
\]

where \( A \) is a coefficient matrix of size \( N \times N \) and \( b \) is a constant vector, taking the form

\[
a_{ij} = \frac{\Gamma(\beta + i + j)\Gamma(\alpha + 1)(-1)^{N-j}}{\Gamma(\beta + \alpha + i + j + 1)}
\]

\[
b_i = -(-1)^{N} \frac{\Gamma(\beta + \alpha + i)\Gamma(\alpha + 1)}{\Gamma(\beta + \alpha + i + 1)}
\]

for \( i, j = 1, 2, \ldots, N \).

8.11. Show that

\[
C_N^{(\alpha, \beta)} = \int_0^1 [x^\beta (1-x)^\alpha] [J_N^{(\alpha, \beta)}(x)]^2 \, dx
\]

\[
= \frac{[\Gamma(\beta + 1)]^2 \Gamma(N + \alpha + 1)(N!)}{\Gamma(N + \beta + 1)\Gamma(N + \alpha + \beta + 1)(2N + \alpha + \beta + 1)}
\]

Hint: Use the Rodrigues formula and apply integration by parts \( N \) times.
8.12. Start with the definition of the Jacobi polynomial to prove that
\[
\frac{dJ_N^{(\alpha, \beta)}(x)}{dx} = \frac{N(N + \alpha + \beta + 1)}{\beta + 1} J_N^{(\alpha+1, \beta+1)}(x)
\]

8.13. Use the orthogonality condition defining Jacobi polynomial to prove that all \( N \) zeros of the Jacobi polynomial \( J_N^{(\alpha, \beta)}(x) = 0 \) are real and that they lie between 0 and 1.

8.14. (a) Use the Newton formula (Eq. 8.87) to determine roots of the following Jacobi polynomials
\[
J_N^{(0,0)}(x), \ J_N^{(1,1)}(x), \ J_N^{(0,1)}(x), \ J_N^{(1,0)}(x)
\]
for \( N = 1, 2, 3, \) and 5.

(b) Write the differential equation satisfied by each polynomial.

8.15. Repeat problem 8.14 using the Jacobi polynomial \( J_N^{(1,-1/2)}(x), \ J_N^{(1,0)}(x) \) and \( J_N^{(1,1/2)}(x) \) for \( N = 1, 2, 3, \) and 5. These roots are used as interpolation points in the orthogonal collocation analysis of a slab, a cylinder, and a spherical particle, respectively.

8.16. Calculate the matrices \( A \) and \( B \) for two collocation points chosen as roots of \( J_N^{(0,-1/2)}(x) \) using the formula (8.103) and show that the sum of all rows is identically zero.

*Hint:* Use the definition of the matrices \( A \) and \( B \) in Eq. 8.102.

8.17. Use the five different methods of weighted residual to obtain approximate solutions for the equation
\[
\frac{d}{dx} \left[ (1 + y) \frac{dy}{dx} \right] = 10y
\]
subject to the following conditions
\[
x = 0; \quad \frac{dy}{dx} = 0
\]
and
\[
x = 1; \quad y = 1
\]

(a) First, try the approximate solution
\[
y_a = 1 + a_1(1 - x^2)
\]
which satisfies the boundary conditions. Substitute this approximate solution to the equation to form a residue, then use the test function appropriate for each method of weighted residual to obtain a solution for \( a_1 \), hence \( y_a \). Compare the approximate solution with the exact solution obtained in part (c).
(b) To improve the accuracy of the approximate solution, use the following trial solution with two unknown coefficients

$$y_a = 1 + a_1(1 - x^2) + a_2 x^2 (1 - x^2)$$

Substitute this approximate solution with yet to be determined coefficients into the governing equation to form a residue, which is then forced to zero in some average sense. For each of the methods of weighted residual, use two test functions to determine the two coefficients, then compare this approximate solution with that in part (a).

(c) To obtain the exact solution of the governing equation, put

$$p = \frac{dy}{dx}$$

then show that the equation will take the form

$$p \frac{d}{dy} [(1 + y)p] = 10y$$

Next, set $$u = (1 + y)$$ to show the new equation is

$$p \frac{d(u p)}{du} = 10(u - 1)$$

To put this equation in separable form, multiply both sides of the equation by $$u$$ and show that the separable form is

$$(up) \frac{d(up)}{du} = 10u(u - 1) \ du$$

Integrate this new separable form with the condition at $$x = 0$$

$$x = 0; \quad y = y_0; \quad p = \frac{dy}{dx} = 0$$

to obtain the equation

$$p = \frac{dy}{dx} = \frac{\sqrt{20}}{1 + y} \left[ \frac{(1 + y)^3 - (1 + y_0)^3}{3} - \frac{(1 + y)^2 - (1 + y_0)^2}{2} \right]^{1/2}$$

where $$y_0$$ is the value of $$y$$ at $$x = 0$$, which is yet to be determined at this stage.
Put the new equation in a separable form and integrate it from $x$ to 1 to show that the solution for $y$ is simply

$$\int_y^1 \frac{(1 + s) \, ds}{\frac{(1 + s)^3}{3} - \frac{(1 + y_0)^3}{3} - \frac{(1 + s)^2}{2} + \frac{(1 + y_0)^2}{2}}^{1/2} = \sqrt{20} \, (1 - x)$$

To find $y_0$, simply put $x = 0$ into the above equation and show an implicit equation for $y_0$ is

$$\int_{y_0}^1 \frac{(1 + s) \, ds}{\frac{(1 + s)^3}{3} - \frac{(1 + y_0)^3}{3} - \frac{(1 + s)^2}{2} + \frac{(1 + y_0)^2}{2}}^{1/2} = \sqrt{20}$$

where $s$ is the dummy integration variable.

**8.18.** Transport of solute through membrane is often limited by the ability of the solute to move (diffuse) through the membrane. If diffusion through the membrane is the rate controlling step, the usual relation to describe such transport is Fick's law (see Problem 6.11). Usually the diffusion coefficient increases with concentration. Set up a material balance of a solute within a thin shell in the membrane to show that the governing equation will take the form at steady state

$$\frac{d}{dr} \left[ D(C) \frac{dC}{dr} \right] = 0$$

where $r$ is the coordinate, taking the origin at the feed side of the membrane. If on the collection side, the solute is swept away quickly with a carrier fluid, then the solute concentrations at both sides of the membrane are $C_0$ and 0, respectively.

(a) By setting $y = C/C_0$, $x = r/L$ and $f(y) = D(C)/D(C_0)$, where $L$ is the membrane thickness, show that the mass balance equation will take the following dimensionless form

$$\frac{d}{dx} \left[ f(y) \frac{dy}{dx} \right] = 0$$

The boundary conditions at two sides of the membrane in nondimensional form are

$$x = 0; \quad y = 1$$

$$x = 1; \quad y = 0$$

For the purpose of computation in this problem, take the following
two forms for \( f(y) \)

\[
f(y) = \begin{cases} 
1 + \sigma(y - 1) \\
\exp[\sigma(y - 1)] 
\end{cases}
\]

(b) Taking note of the asymmetric boundary conditions, use the following equation as a trial solution

\[
y_a = 1 - x + a_1(x - x^2)
\]

Apply the methods of collocation and Galerkin to obtain the approximate solutions.

(c) Repeat part (b) with the following trial solution having two coefficients

\[
y_a = 1 - x + a_1(x - x^2) + a_2(x - x^3)
\]

For \( \sigma = 0.8 \), compare the solutions with those obtained in part (b), and suggest an objective basis for assessing improvement between the two.

Use the following exact solution with which to compare the two approximate solutions.

\[
\frac{\int_0^1 f(s) \, ds}{\int_0^1 f(s) \, ds} = 1 - x
\]

8.19. Problems 8.17 and 8.18 deal with simple diffusion problems with symmetry and asymmetry boundary conditions. The methods of weighted residual can also be applied to cases where a source term appears in the equation and such a source term can be a discontinuous function within the spatial domain, such as the following problem of diffusion of material in a slab with a mass production source. The governing equations are

\[
\frac{d^2 y}{dx^2} + f(x) = 0
\]

where

\[
f(x) = \begin{cases} 
1 & 0 < x < \frac{1}{2} \\
0 & \frac{1}{2} < x < 1
\end{cases}
\]

The boundary conditions at two sides of the slab are taken to be

\[
x = 0; \quad y = 0 \\
x = 1; \quad y = 0
\]
This set of equations can also describe the heat conduction in a slab solid object with a heat source within the slab.

(a) Polynomial trial solutions have been used in Problems 8.17 and 8.18. This time try the following trial solution of trigonometric form

\[ y_a = a_1 \sin(\pi x) \]

and use the collocation method to find the coefficient \( a_1 \). Choose \( x_1 = 1/2 \) (take \( f(1/2) = 1/2 \)).

(b) Improve the trial solution by having two terms in the solution; that is,

\[ y_a = a_1 \sin(\pi x) + a_2 \sin(2\pi x) \]

This problem shows that the trial solutions need not be in the polynomial form used in the text as well as in Problems 8.17 and 8.18, and it also shows that as the number of terms used in the trial solution increases the analysis involving the polynomial is somewhat simpler than that using functions such as trigonometric functions.

**8.20*. The mass and heat balance equations in a catalyst for a first order reaction are

\[ \dot{\phi} + \phi = 0 \]

where \( \phi \) is the Thiele modulus, \( \theta \) is the dimensionless heat of reaction, and \( \gamma \) is the dimensionless activation energy.

Assuming the fluid medium surrounding the catalyst particle is very well stirred, the boundary conditions are

\[ x = 0; \quad \frac{dy}{dx} = \frac{d\theta}{dx} = 0 \]

\[ x = 1; \quad y = 1, \quad \theta = 0 \]

The quantity of interest is the effectiveness factor, which indicates how well a catalyst is utilized by the reactant. It is defined as

\[ \eta = \frac{1}{\phi^2} \frac{dy(1)}{dx} \]

(a) Apply the one-point orthogonal collocation method to solve the above coupled equations. Multiple solutions are possible in this case. Determine the range of \( \phi \) such that more than one steady state is possible.

(b) Another way of solving this problem is to eliminate one variable by first relating it to the other variable. Multiply the equation for \( y \) by \( \beta \)
and add this to the $\theta$ equation to show that
\[ \beta \frac{d^2 y}{dx^2} + \frac{d^2 \theta}{dx^2} = 0 \]

(c) Integrate the above equation once to show that
\[ \beta \frac{dy}{dx} + \frac{d\theta}{dx} = 0 \]

(d) Integrate again and obtain
\[ \beta y + \theta = \beta \]

This shows temperature and composition are linearly related.

(e) Use the result in part (d) to eliminate the temperature from the differential equation for $y$, and show that the final equation is
\[ \frac{d^2 y}{dx^2} - \phi^2 \exp\left( \frac{\gamma \beta (1 - y)}{1 + \beta (1 - y)} \right) y = 0 \]

Now there is only one equation and one unknown, $y$.

(f) Apply the one-point orthogonal collocation to solve the equation in part (e), and compare with the result in part (a).

8.21*. Consider the problem of diffusion and reaction in a spherical catalyst particle. The chemical reaction is assumed to follow the Langmuir–Hinshelwood kinetics
\[ R_{r \times n} = \frac{kC}{1 + KC + K_{1}C^2} \]

The film mass transfer resistance is taken as negligible compared to the internal diffusion resistance.

(a) Derive the mass balance equation for the reactant in the catalyst particle, put it in the nondimensional format, to give the result
\[ \frac{1}{x^2} \frac{d}{dx} \left( x^2 \frac{dy}{dx} \right) - \phi^2 \frac{y}{1 + \beta y + \gamma y^2} = 0 \]

(b) Use the one-point collocation to investigate the behavior of the system.

(c) Choose the parameters such that only one steady-state is possible, and obtain a better approximate solution to the problem using the orthogonal collocation method.

(d) Choose the parameters where multiple steady states occur and solve for all steady-state concentration distributions inside the particle.