Numerical Integration of Functions

- Physical meaning of a definite integral is the area of the surface surrounded by \( x=a \) and \( x=b \) on the \( x \)-axis and by \( y=0 \) and \( y=f(x) \) on the \( y \)-axis (see figure).
- MathCAD calculates definite integrals of functions in one easy step:

\[
f(x) := \sin(x) \quad \text{It} := \int_{0}^{\pi} f(x) \, dx = 2
\]

Exercises: Calculate the following definite integrals. Plot the integrands (functions under the integral sign).

\[
\int_{0}^{\infty} e^{-x^2} \, dx
\]

\[
\int_{0}^{5} (1 - x^2)^2 \, dx
\]
Integration of Vector Data

- To integrate vector data
  - Fit the data to an appropriate function
  - Integrate the fitted function.

- Alternative: explicit evaluation
  - Using trapezoidal rule
  - Using Simpson’s rule

### Example 1: Integrate data on page 200 of the textbook from x = 0 to 10

Copy the vectors from page 200† of the book.

Exponential fit to the data

Define the fitted function:

\[
\text{fit}(x) := c_0 \cdot \exp(c_1 \cdot x) + c_2
\]

Integrate the fitted function:

\[
\int_0^{10} \text{fit}(x) \, dx = 97.751
\]

### Example 2: The data set in the table was generated using the function below (with \(a = 4\) and \(b = 0.8\)). Pretend that the values of \(a\) and \(b\) are unknown; fit the data to this functional form in order to recover \(a\) and \(b\). Integrate the fitted function in the range of \(x = 0\) to 9 (solution is given on the next page)

<table>
<thead>
<tr>
<th>(X)</th>
<th>(Y = 4x^2 + 0.8x^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>4.8</td>
</tr>
<tr>
<td>2</td>
<td>22.4</td>
</tr>
<tr>
<td>3</td>
<td>57.6</td>
</tr>
<tr>
<td>4</td>
<td>115.2</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
</tr>
<tr>
<td>6</td>
<td>316.8</td>
</tr>
<tr>
<td>7</td>
<td>470.4</td>
</tr>
<tr>
<td>8</td>
<td>665.6</td>
</tr>
<tr>
<td>9</td>
<td>907.2</td>
</tr>
</tbody>
</table>

Let \(c := \expfit(X, Y)\)

\[
f'(x) = ax^2 + b x^3
\]
**Trapezoidal Rule**

- **Divide the integration interval into equal segments**
  \[ \Delta x = (x_1 - x_0) = (x_2 - x_1) = ... = (x_N - x_{N-1}) \]

- **Calculate the area of each trapezoidal segment**
  \[ \text{Shaded Area} = \frac{y_1 + y_2}{2} \times \Delta x \]

- **Add all the trapezoids together to get the integral**

**Exercise:** Integrate the data set from the previous slide using the trapezoid rule

**Integration of the fitted function**

\[ \int_0^9 f(x) \, dx = 2.284 \times 10^3 \]

**Integration of data by the trapezoidal rule**

\[ \Delta x := 1 \]
\[ \text{length}(X) = 10 \]
\[ \text{Trap} := \sum_{i=0}^{\text{length}(X)-2} \left[ \frac{Y_i + Y_{i+1}}{2} \right] \Delta x = 2.306 \times 10^3 \]
Symbolic Integration of Functions

- MathCAD can perform symbolic integration of certain functions
- Use “evaluate symbolically” symbol: →

**Symbolically evaluated indefinite integral**

\[ \int \left( 2x^2 - 7x^3 + 10 \cdot \sin(x) \right) dx \rightarrow \frac{2}{3}x^3 - \frac{7}{4}x^4 - 10 \cdot \cos(x) \]

**Symbolically evaluated definite integral**

\[ \int_{A}^{B} 2x^2 - 7x^3 \, dx \rightarrow \frac{2}{3}B^3 - \frac{7}{4}B^4 - \frac{2}{3}A^3 + \frac{7}{4}A^4 \]

**Symbolically evaluated double indefinite integral**

\[ \int \int (x + y + x \cdot y) \, dx \, dy \rightarrow \frac{1}{2}x^2 \cdot y + \frac{1}{2}x \cdot y^2 + \frac{1}{4}x^2 \cdot y^2 \]

**Symbolically evaluated triple definite integral**

\[ \int_{0}^{L} \int_{0}^{\pi} \int_{0}^{R} r \cdot s \, dr \, d\theta \, ds \rightarrow \frac{1}{4} \pi \cdot R^2 \cdot L^2 \]

**Exercises:** Use symbolic evaluation of integrals to evaluate indefinite / definite integrals of the following functions:

\[ \int (a + bx + cx^2) \, dx \quad \int \cos(ax) \, dx \quad \int e^{-ax} \, dx \]

\[ \int_{0}^{x} e^{-s/2} \, ds \quad \int_{a}^{b} \ln(x) \, dx \]
Differentiation of Functions

- Physical meaning of **derivative** is the **slope** of the line tangential to function in the point of interest (see figure).

\[ f(x) := \sin(x^2) \]  

**Function definition**

\[
\begin{align*}
\text{t} &:= 1 \\
\frac{d}{dt} f(t) &\approx 1.080605 \quad \text{Numerical calculation of derivative at } x=1. \\
\frac{d}{dx} f(x) &\to 2 \cdot \cos(x^2) \cdot x \quad \text{Symbolic evaluation of derivative} \\
der(x) &:= \frac{d}{dx} f(x) \quad \text{der}(1) = 1.080605 \\
&\quad \text{"Exact" calculation}
\end{align*}
\]

**Exercises:** Plot all functions. Estimate the values of the derivatives at \( x=1 \) by examining the plots. Calculate the derivatives in three ways: symbolically, “exactly”, and numerically at \( x=1 \).

\[ f(x) = x(x + 1)e^{-x^2} \]

\[ f(x) = \frac{x}{1 + x^2} \]

\[ f(x) = x \ln x \]
Differentiation of Vector Data

- To calculate derivatives of vector data
  - Fit the data to an appropriate function
  - Differentiate the fitted function either symbolically or numerically

- Alternative: finite difference approximation
  - Works well only for slowly-varying data sets with sufficiently small spacing between the data points
  - For vector data, $X = [x_1, x_2, x_3, \ldots, x_n]$ and $Y = [y_1, y_2, y_3, \ldots, y_n]$ the finite difference approximation works as follows (e.g., for $x = x_3$):

$$
\frac{dy}{dx}\bigg|_{x=x_3}^{\text{forward}} = \frac{y_4 - y_3}{x_4 - x_3}, \quad \frac{dy}{dx}\bigg|_{x=x_3}^{\text{backward}} = \frac{y_3 - y_2}{x_3 - x_2}, \quad \frac{dy}{dx}\bigg|_{x=x_3}^{\text{central}} = \frac{y_4 - y_2}{x_4 - x_2}
$$

Exercise: This is the same data set as in the exercise on integration of vector data. Find the first and second derivative of $f(x)$, and calculate their values at every X point (provide your answers as 6-element vectors containing first and second derivatives). Also calculate the first derivative using central finite difference approximation for $x = 1$ and 4. Does this method work well in this case?

<table>
<thead>
<tr>
<th>X</th>
<th>Y = 4x^2 + 0.8x^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>4.8</td>
</tr>
<tr>
<td>2</td>
<td>22.4</td>
</tr>
<tr>
<td>3</td>
<td>57.6</td>
</tr>
<tr>
<td>4</td>
<td>115.2</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
</tr>
<tr>
<td>6</td>
<td>316.8</td>
</tr>
<tr>
<td>7</td>
<td>470.4</td>
</tr>
<tr>
<td>8</td>
<td>665.6</td>
</tr>
<tr>
<td>9</td>
<td>907.2</td>
</tr>
</tbody>
</table>
Our function in this example is (obtained by fitting the data):

\[ f(x) := 4 \cdot x^2 + 0.8 \cdot x^3 \]

Let us calculate the first derivative by the central finite difference method. We need to define a range variable that includes all elements of vector \( X \) except for the very first and last ones.

\[
\begin{aligned}
X :=& 
\begin{pmatrix}
0 \\
1 \\
2 \\
3 \\
4 \\
5 \\
6 \\
7 \\
8 \\
9
\end{pmatrix}, \\
Y :=& 
\begin{pmatrix}
0 \\
4.8 \\
22.4 \\
57.6 \\
115.2 \\
200 \\
316.8 \\
470.4 \\
665.6 \\
907.2
\end{pmatrix}
\end{aligned}
\]

We now have two vectors containing the values of the initial \( X \)-vector for which the derivative is calculated, and the estimated derivative.

The exact value of the first and second derivatives:

\[
\text{der1exact}(x) := \frac{d}{dx} f(x) \quad \text{der2exact}(x) := \frac{d}{dx} \text{der1exact}(x)
\]

This is the deviation between the exact and estimated derivatives

\[
\text{deviation}_i := \text{der1appri}_i - \text{der1exact}(X\text{coordinate}_i)
\]
This is an example of a titration of a mixture of a strong acid and weak acid in Chem 151L. The goal is to find the end points as precisely as possible, and determine the concentrations of both acids.

The 1st end point corresponding to the strong acid

The 2nd end point corresponding to the weak acid
Application: Analysis of Titration Data

- At each end point, the first derivative reaches a maximum. One approach is to fit the data $V = [V_1, V_2, V_3, \ldots, V_n]$ and $pH = [pH_1, pH_2, pH_3, \ldots, pH_n]$ to an appropriate function and calculate its derivatives.
- Derivatives can also be evaluated by the finite difference approximation; can be used as follows:

\[
\frac{dpH}{dV} \approx \frac{pH_{i+1} - pH_i}{V_{i+1} - V_i}
\]

Our approach: fit the data to a spline function ($x = \text{added volume}; y = pH$); then find and plot the derivatives.

\[
\begin{align*}
SD := & \text{spline}(V_{\text{NaOH}}, pH) \\
\text{SplineFit}(x) := & \text{interp}(SD, V_{\text{NaOH}}, pH, x) \\
\text{FirstDerSpline}(x) := & \frac{d}{dx}\text{SplineFit}(x)
\end{align*}
\]

![Graph showing the fit and derivatives of titration data.](image-url)
Finding Roots of Functions

- A **root** of a function \( f(x) \) is a value of \( x \) at which \( f(x) = 0 \). A function can have zero, one, or many roots. For example, \( \sin(x) \) has an infinite number of roots, \( x_i = i\pi \) (\( i \) = integer).
- \( N \)-order polynomial functions \( f(x) = \) are known to have exactly \( N \) roots. Some or all of these roots can be complex numbers, \( z = Re + iIm \).
- Function **polyroots(v)** can be used to return all \( N \) roots of a polynomial. Vector \( v \) contains the coefficients \( v = [a_0, a_1, a_2, ..., a_N] \). Example: \( f(x) = 1 - x + x^2 - x^3 \)

\[
\begin{align*}
v &:= \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix} \\
\text{polyroots}(v) &:= \begin{pmatrix} -i \\ 2.213 \times 10^{-9} + i \\ 1 \end{pmatrix}
\end{align*}
\]

For this third order polynomial: we get 3 roots, two of which are complex numbers, and one is a real number.

- Function **root(\( f(x) \), \( x \))** can be used to find a single root of any function \( f(x) \) starting from an initial guess. Example: find roots of \( f(x) = \sin(x^2) \) in the vicinity of \( x = 5 \), \( x = 6 \), and \( x = 7 \):

\[
\begin{align*}
\text{initial guess} & & \text{root found} \\
t_1 := 5 & & \text{root}(f(t), t) = 5.013 \\
t_2 := 6 & & \text{root}(f(t), t) = 6.391 \\
t_3 := 7 & & \text{root}(f(t), t) = 7.09
\end{align*}
\]
Application of Root Finding Functions: Titrating a Weak Acid with a Strong Base

Problem: predict a titration curve for titrating a weak acid HA with known pK_a = 6, initial volume (V_{acid}^{0} = 50 \text{ mL}) , and initial concentration (C_{acid}^{0} = 0.01 \text{ M}) by a strong base NaOH with concentration C_{base}^{0} = 0.01 \text{ M}. The main complication here is that we need to account for the fact that both HA and A^- are present in solution during the titration.

Suppose we are at a point wherein a certain amount of base (V_{base \ added}) was already added to the acid solution. It is convenient to define the following quantities:

Current values of the total volume:

\[ V_{\text{total}} = V_{\text{acid}}^{0} + V_{\text{base \ added}} \]

Effective initial concentrations of the acid and base in the resulting mixture (the ratios of volumes account for the dilution occurring during titration):

\[ C_{\text{initial \ base}} = \frac{C_{\text{base}}^{0} \times V_{\text{base \ added}}}{V_{\text{total}}} \]

\[ C_{\text{initial \ acid}} = \frac{[HA]_{0} \times V_{\text{acid}}^{0}}{V_{\text{total}}} \]
Titrating a Weak Acid with a Strong Base

The following equilibria are to be considered:

\[ \text{HA} \rightleftharpoons \text{A}^- + \text{H}^+ \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]

\[ \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+ \quad K_w = [\text{H}^+][\text{OH}^-] \]

We can write the following mass balance equation:

\[
C_{\text{acid}}^{\text{initial}} = [\text{HA}] + [\text{A}^-] = [\text{A}^-] \times \left( \frac{[\text{H}^+]}{K_a} + 1 \right)
\]

And charge balance equation:

\[
C_{\text{base}}^{\text{initial}} + [\text{H}^+] = [\text{OH}^-] + [\text{A}^-] \quad C_{\text{base}}^{\text{initial}} + [\text{H}^+] = \frac{K_w}{[\text{H}^+]} + \frac{C_{\text{acid}}^{\text{initial}}}{K_a} \left( \frac{[\text{H}^+]}{K_a} + 1 \right)
\]

This results in an equation for \([\text{H}^+]\) which can be solved in MathCAD using the "root" function:

\[
C_{\text{base}}^{\text{initial}} + [\text{H}^+] - \frac{K_w}{[\text{H}^+]} - \frac{C_{\text{acid}}^{\text{initial}}}{\left( \frac{[\text{H}^+]}{K_a} + 1 \right)} = 0
\]
Titrating a Weak Acid with a Strong Base: Solution

Let us define the initial parameters first (using mol and L as units everywhere):

\[ K_a := 10^{-6} \quad K_w := 10^{-14} \quad C_0_b := 0.01 \quad C_0_a := 0.01 \quad V_0_a := 0.05 \]

We are going to treat the volume of the added base as an independent variable. We can then calculate the solution volume \( V \) during any point in the titration process. We can also calculate the effective initial concentrations of the acid and base.

\[
V(V_{\text{added}}) := V_0_a + V_{\text{added}} \quad C_a(V_{\text{added}}) := C_0_a \cdot \frac{V_0_a}{V(V_{\text{added}})} \quad C_b(V_{\text{added}}) := C_0_b \cdot \frac{V_{\text{added}}}{V(V_{\text{added}})}
\]

Defining this function will help us solve this titration problem. Our guess for pH is going to be 5. This was selected by trial and error for this particular problem. Note that the results are sensitive to the value of this guess; the calculations below may collapse for certain combinations of initial conditions and guesses!

\[
f(pH, \text{acid}, \text{base}) := \text{base} + 10^{-pH} - \frac{K_w}{10^{-pH}} - \frac{\text{acid}}{\left(10^{-pH} \frac{K_a}{1 + 1}\right)}
\]

Our guess for pH is going to be 5. This was selected by trial and error for this particular problem. Note that the results are sensitive to the value of this guess; the calculations below may collapse for certain combinations of initial conditions and guesses!

\[
pH(V_{\text{added}}) := \text{root} \left( f(pH_{\text{guess}}, C_a(V_{\text{added}}), C_b(V_{\text{added}}), pH_{\text{guess}}) \right)
\]
Example 2: Titrating $\text{CO}_3^{2-}$ with HCl (Strong Acid)

**Problem:** titrate a given volume (50 mL) containing a solution of $\text{Na}_2\text{CO}_3$ with the initial concentration $[\text{Na}_2\text{CO}_3]_0 = 0.1$ M using a strong acid HCl with a known concentration, $[\text{HCl}] = 0.1$ M.

As we add the acid to the solution of $\text{Na}_2\text{CO}_3$ the total volume increases:

$$V_{\text{total}} = V_{\text{carbonate}}^0 + V_{\text{acid added}}$$

$$C_{\text{HCl}} = \frac{C_{\text{acid}}^0 \times V_{\text{acid added}}}{V_{\text{total}}}$$

$$C_{\text{carbonates}} = \frac{[\text{Na}_2\text{CO}_3]_0 \times V_{\text{carbonate}}^0}{V_{\text{total}}}$$

We are going to calculate pH for a mixture of HCl and $\text{Na}_2\text{CO}_3$ with the following effective initial concentrations (the ratios of volumes account for the dilution occurring during titration)

The following equilibria are to be considered:

$$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.2 \times 10^{-7}$$

$$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.69 \times 10^{-11}$$

$$\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+ \quad K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$$
"Exact Solution": Setting Up the Equations

Mass balance equation:

\[
C_{\text{carbonates}} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = [HCO_3^-] \times \left( \frac{[H^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]} \right)
\]

Charge balance equation:

\[
[Na^+] + [H^+] = [OH^-] + [Cl^-] + [HCO_3^-] + 2\times[CO_3^{2-}]
\]

which is the same as:

\[
2\times C_{\text{carbonates}} + [H^+] = [OH^-] + C_{\text{acid}} + [HCO_3^-] + 2\times[CO_3^{2-}]
\]

This gives us 5 equations and 5 unknowns. They can be solved by a brute force approach using MathCAD (solution is given on the following page). Combining the terms together gives the following equation for us to solve:

\[
\frac{K_w}{[H^+]} + C_{\text{acid}} + \frac{C_{\text{carbonates}}}{\left( \frac{[H^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]} \right)} + \frac{2\times C_{\text{carbonates}}}{1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1} \times K_{a2}}} - 2\times C_{\text{carbonates}} - [H^+] = 0
\]
Solution: Titrating CO$_3^{2-}$ with HCl

Let us define the initial parameters first (using mol and L as units everywhere):

\[ \text{Kw} := 10^{-14} \quad \text{Ka1} := 4.2 \times 10^{-7} \quad \text{Ka2} := 4.69 \times 10^{-11} \]
\[ C_{0\text{carbonate}} := 0.01 \quad C_{0\text{HCl}} := 0.01 \quad V_{0\text{carbonate}} := 0.05 \]

We are going to treat the volume of the added HCl solution as an independent variable. We can then calculate the solution volume (V) during any point in the titration process. We can also calculate the effective initial concentrations of the acid and base.

\[ V(V_{\text{added}}) := V_{0\text{carbonate}} + V_{\text{added}} \]
\[ C_{\text{carbonate}}(V_{\text{added}}) := C_{0\text{carbonate}} \cdot \frac{V_{0\text{carbonate}}}{V(V_{\text{added}})} \]
\[ C_{\text{HCl}}(V_{\text{added}}) := C_{0\text{HCl}} \cdot \frac{V_{\text{added}}}{V(V_{\text{added}})} \]

Defining this function will help us solve this titration problem.

\[
\begin{align*}
\text{f}(pH, \text{HCl}, \text{Carb}) & := \frac{\text{Kw}}{10^{-pH}} + \text{HCl} + \frac{10^{-pH}}{\text{Ka1}} + 1 + \frac{\text{Ka2}}{10^{-pH}} + \frac{1}{1 + \frac{\text{Ka2}}{\text{Ka1} \cdot \text{Ka2}}} \\
\text{pH}(V_{\text{added}}) & := \text{root}(\text{f}(\text{pH}_{\text{guess}}, C_{\text{HCl}}(V_{\text{added}}), C_{\text{carbonate}}(V_{\text{added}})), \text{pH}_{\text{guess}})
\end{align*}
\]

Our guess for pH is going to be 7. This calculation is somewhat less sensitive to the value of this parameter compared to the previous one.