Numerical methods in chemistry. Homework 2

Problem 1

Consider a diatomic molecule AB with the reduced mass μ and the distance of atoms A and B denoted by r. Imagine that the molecule is excited with a laser pulse to a dissociative excited electronic potential energy surface, leading to a dissociation $AB \to A + B$. For short times, this potential can be approximated by an inverted harmonic oscillator,

$$V(r) = V_{\max} - \frac{1}{2}\kappa(r-a)^2, \quad \kappa > 0$$

Set up an ordinary differential equation satisfied by r as a function of time t and use the Laplace transform to solve it to find the explicit dependence of r on t. Assume that at time $t = 0$, the initial distance between A and B is $r_0 > a > 0$ and

$$(dr/dt)|_{t=0} = 0.$$

The answer should be expressed in terms of μ, $V_{\max}$, κ, a, r_0, and t only. Does it depend on all parameters? You can ignore rotations and treat the problem as a one-dimensional system. *Hint*: It is easier to define a variable $x := r - a$, set up an ODE for $x(t)$, solve it, and transform back to $r(t)$. *Warning*: Be aware that in practice, your analytical solution will only be valid for short times when the potential has the shape given above.

Problem 2

Consider the **consecutive reaction**

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C,$$

with the rate constants $k_1 = k_2 = k$ and initial concentrations $[A]_0 = a_0$, $[B]_0 = [C]_0 = 0$. Let us denote the concentrations at time t as $a(t) := [A]_t$, $b(t) := [B]_t$, and $c(t) := [C]_t$. These concentrations satisfy the following system of ordinary differential equations (ODEs):

$$\begin{aligned} \dot{a}(t) &= -k_1 a(t), \\ \dot{b}(t) &= k_1 a(t) - k_2 b(t), \\ \dot{c}(t) &= k_2 b(t). \end{aligned}$$

In contrast to a problem in Exercises 3, the two rate constants k_1 and k_2 are the same and equal to k. Use the Laplace transform to solve this system of ODEs and find explicit expressions for the concentrations of A, B, and C at time t in terms of a_0, k, and t.

Problem 3

Determine the Fourier series for the function $f(x)$ such that

$$\begin{aligned} f(x) &= 0, \quad -\pi \le x \le 0, \\ f(x) &= x, \quad 0 \le x < \pi, \\ f(x) &= f(x + 2\pi), \quad x \in \mathbb{R}. \end{aligned}$$

To what values will the Fourier series converge at $x = -\pi$, 0, and π?

Problem 4

Determine the Fourier series for the function $f(x)$ such that

$$\begin{aligned} f(x) &= -\pi/2, \quad -\pi \le x \le 0, \\ f(x) &= \pi/2, \quad 0 < x < \pi, \\ f(x) &= f(x + 2\pi), \quad x \in \mathbb{R}. \end{aligned}$$

Use the result to find the sum of the series

$$\sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{2n-1}.$$

To what values will the Fourier series converge at $x = -\pi$, 0, and π?

Problem 5

Determine the Fourier series for the function $f(x)$ such that

$$f(x) = |x|, \quad -\pi \leq x \leq \pi,$$
$$f(x) = f(x + 2\pi), \quad x \in \mathbb{R}.$$

Use the result to find the sum of the series

$$\sum_{n=1}^{\infty} \frac{1}{(2n-1)^2}.$$