

CY40014 Introduction to Computational Chemistry
Autumn 2010-2011

Worksheet 6

Module 2: Introduction to Numerical Analysis

Topic 3: Numerical solution of ordinary differential equation

Aim

To solve ordinary differential equations (ODE) like $\frac{d^n y}{dx^n} = f(x, y)$ involving the n -th order derivative of y , that is a function of an independent variable x . For the sake of simplicity, we shall primarily focus on first order ODE, where $n=1$.

Solving differential equations using the Runge-Kutta Method

This method was devised by Runge (1895) and extended later by Kutta (1901). Let us demonstrate the Runge-Kutta method for the solution of the following first order differential equation:

$$\frac{dy}{dx} = f(x, y),$$

where the initial values of x and y are given as x_0 and y_0 , respectively. This belongs to the class of problems known as the *initial value problem*.

The solution:

Let h be the interval between equidistant values of x and $x_{n+1} = x_n + h$.

Then, the value of y at the point $n+1$ can be determined using the set of formulae given here.

Note that for the determination of the solution at any point $n+1$, the values of x and y at the point n are the only pre-requisites.

$$\begin{aligned} k_1 &= f(x_n, y_n) h \\ k_2 &= f\left(x_n + \frac{h}{2}, y_n + \frac{k_1}{2}\right) h \\ k_3 &= f\left(x_n + \frac{h}{2}, y_n + \frac{k_2}{2}\right) h \\ k_4 &= f(x_n + h, y_n + k_3) h \\ \Delta y &= \frac{1}{6} (k_1 + 2k_2 + 2k_3 + k_4) \\ x_{n+1} &= x_n + h, \quad y_{n+1} = y_n + \Delta y, \end{aligned}$$

Worksheet problem

W6_1. Write a fortran program to solve the following ordinary differential equation

$$\frac{dy}{dx} = 2.0 \text{ at } x = 5.0 \text{ with the initial condition } x=0.0, y=0.0.$$

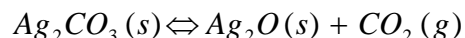
W6_2. Write a Fortran program to solve the above equation for $x = 1.0, 2.0, 3.0, \dots, 9.0$ and 10.0 . Present in an output file the values of x and y .

W6_3. An ideal gas is enclosed in a heated chamber with a small hole in one wall. Due to effusion, the pressure of the gas varies with time and is given by

$$\frac{dp}{dt} = -\frac{p}{\tau}$$

Using the Runge-Kutta method, (i) calculate the value of pressure at time $t = \tau$, (ii) write a fortran program to obtain the values of the pressure, p as a function of time t by varying time from zero to 5τ . Plot the output of your program.

W6_4. The equilibrium constant, K of the reaction



is found to be 3.98×10^{-4} at 350 K. The standard reaction enthalpy, ΔH_{rxn}^o of the decomposition is known to be $+80 \text{ kJ mol}^{-1}$.

(a) Write a program that numerically solves van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^o}{RT^2}$$

using Runge-Kutta 4th order method to estimate K at 10 different temperatures between 350 K and 400 K.

(b) Obtain the solution of the above equation analytically and calculate the expected value of K at 360 K.

Assignment on Runge-Kutta method

A6_1. (a) Write a short note on the predictor-corrector method of solving an ordinary differential equation.

(b) Solve the problem of W6_1 using the predictor-corrector method and compare your results with those obtained from the Runge-Kutta method discussed above.