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.

$$k_1 = f(x_n, y_n)\,h$$

$$k_2 = f\left(x_n + \frac{h}{2}, y_n + \frac{k_1}{2}\right)h$$

$$k_3 = f\left(x_n + \frac{h}{2}, y_n + \frac{k_2}{2}\right)h$$

$$k_4 = f(x_n + h, y_n + k_3)\,h$$

$$\Delta y = \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4)$$

$$x_{n+1} = x_n + h, \quad y_{n+1} = y_n + \Delta y,$$

Worksheet problem

W6_1. Write a fortran program to solve the following ordinary differential equation $\frac{dy}{dx} = 2.0$ at x= 5.0 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,……,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

$$Ag_2CO_3\,(s) \Leftrightarrow Ag_2O\,(s) + CO_2\,(g)$$

is found to be $3.98x10^{-4}$ at *350* K. The standard reaction enthalpy, ΔH^o_{rxn} of the decomposition is known to be +*80* kJ mol^{-1}.

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

$$\frac{d\ln K}{dT} = \frac{\Delta H^o_{rxn}}{RT^2}$$

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.