CY40014 Introduction to Computational Chemistry
Autumn 2010-2011

Worksheet 7

Module 2: Introduction to Numerical Analysis

Solution of non-linear equations: Newton-Raphson method

Aim

To find the root of a complex polynomial. This method can also be extended to solve a set of non-linear equations such as

$$f(x) = a_n x^n + a_{n-1}x^{n-1} + a_{n-2}x^{n-2} + ... + a_2 x^2 + a_1 x + a_0 = 0$$

In this exercise, we shall primarily concentrate on the solution of a cubic equation.

Outline of method

- This process involves an iterative search for the root of the polynomial *f(x)*, i.e. the value of $x = x_p$ such that $f(x_p) = 0$.
- The search starts with an initial guess value of $x = x_0$.
- The Taylor series expansion of *f(x)* around $x = x_0$ may be written as

$$f(x) = f(x_0) + (x - x_0) f^{'}(x_0) + \frac{1}{2!} f^{''}(x_0) + ...$$

where $f^{'}(x)$ and $f^{''}(x)$ are the first and second derivatives of the function *f(x)*, respectively. If $(x - x_0)$ is small, i.e. the initial guess lies close to the actual root, then the above series can be truncated at the second term and a new guess value for the root would be obtained as

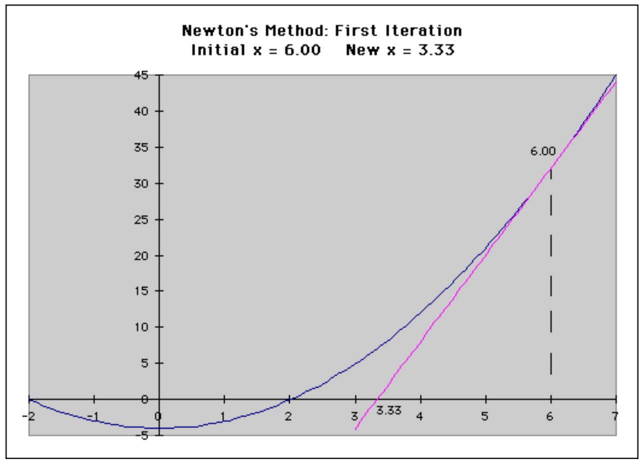
$$x_1 = x_0 - \frac{f(x_0)}{f^{'}(x_0)}$$

Thus the NR method finds the tangent to the function $f(x)$ at $x = x_0$ and extrapolates it to intersect the x axis to get x_1. x_1 can then be taken as the new approximation to the root and the above procedure repeated until convergence is reached.

In summary, if $x = x_i$ at the end of the i-th iteration, then next value of x is given by $x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)}$. If $|x_{i+1} - x_i| \le \delta$, where δ is a small number chosen from outside convergence is reached and $x_p = x_{i+1}$. Typically, $\delta \approx 10^{-3} - 10^{-8}$ depending on the level of accuracy desired.

Example:

Let us solve $f(x) = x^2 - 4 = 0$ with $x_0 = 6$. The steps of iteration are shown in the table below and the tangent line from 1st iteration step shown in the figure above.



Iterat-ion step	x_i	$f(x_i)$	$f'(x_i)$	x_{i+1}	$\lvert x_{i+1} - x_i \rvert$
1	6.0	32	12	3.33333333	
2	3.33333333	7.11111111	6.66666667	2.26666667	1.06666667
3	2.26666667	1.13777778	4.53333333	2.01568627	0.250980392
4	2.01568627	0.0629911572	4.03137255	2.00006104	0.0156252384
5	2.00006104	0.000244148076	4.00012207	2.	6.10351563E-05

Note: An online interactive tool for the solution of simple non-linear equations using NR method is available at http://www.shodor.org/UNChem/math/newton/index.html.

Worksheet problems

W7_1. Write a program to use the Newton-Raphson method to search for the root of $f(x) = x^2 - 4 = 0$ starting with an initial guess value of $x_0 = 6$. The output should be given as a table similar to the one shown above.

W7_2. Recall simple Huckel Theory. For linear conjugated systems such as unsaturated hydrocarbons with alternate double and single bonds, the molecular orbital is written as $\psi = \sum_i C_i \phi_i$ where ϕ_i is a $2p_z$ atomic orbital of the atom *i* and the summation is over all $2p_z$ atomic orbitals. The coefficients and energies of these orbitals are obtained by solving the secular equations

$$\sum_i C_i (H_{ij} - S_{ij}E) = 0$$

Assume $H_{ii} = \alpha;\ S_{ij} = \delta_{ij};\ H_{ij} = \beta$ if atoms i and j are directly bonded, and zero otherwise. Then the secular equation takes up the following form:

$$\begin{vmatrix} \alpha - E & \beta & 0...... & 0 \\ \beta & \alpha - E & \beta...... & 0 \\ .. & ... & .. & 0 \\ 0 & 0 & ...... & \alpha - E \end{vmatrix} = 0$$

For an $(N \times N)$ determinant, expansion yields a polynomial equation of degree N giving N roots that correspond to N energy eigen values.

(i) Consider the ethylene molecule. Here the secular equation is given by

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \;\Rightarrow\; x^2 - 1 = 0 \text{ where } \quad x = \frac{\alpha - E}{\beta}.$$

Solve the secular equation iteratively to obtain x.

(ii) Derive the energies of bonding and antibonding orbitals in terms of α and β.

W7_3. Consider the allyl fragment ($-CH_2-CH=CH_2$). Set up the cubic secular equation for this system and solve it using NR method

(i) Analytically and
(ii) using a simple program.

Assignment on Newton-Raphson method

A7_1. The exact pH of a mono-protic acid solution can be determined from the following exact expression:

$$[H^+]^3 + K_a [H^+]^2 - (K_w + K_a C_a)[H^+] - K_a K_w = 0$$

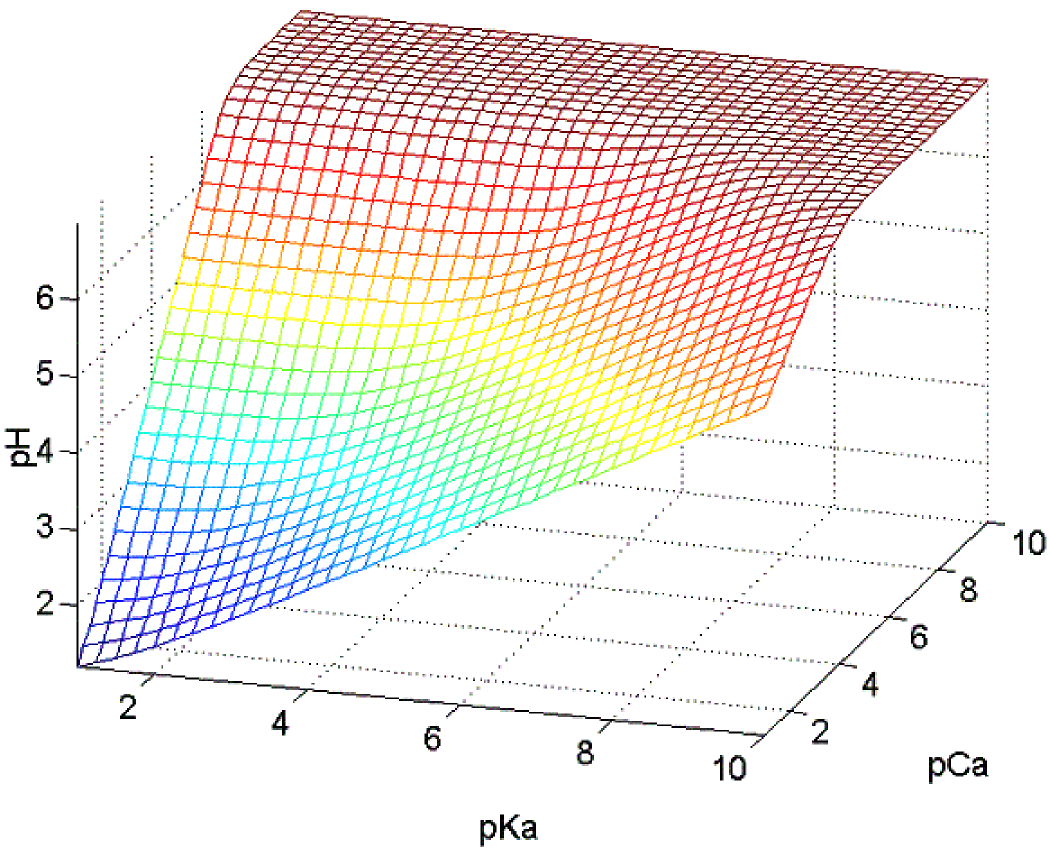
where C_a is the initial concentration of the acid in mole L^{-1} and K_a is the acid dissociation constant. K_w is the ionic product of water.

(i) Of the three roots, only one is going to be relevant chemically. Using $pK_a=4.0$ and $pC_a=6.0$, obtain the pH of this solution.

(ii) Calculate and plot the dependence of pH on pC_a by varying it from 0 to 10 at an interval of 1 keeping $pK_a=4.0$.

Note: A concise description of the determination of pH of monoprotic acid solutions is available online at http://www.chem.sc.edu/faculty/morgan/resources/acidbase/exact.html

A7_2. Solve the cubic equation as in **A6_2** varying both pK_a and pC_a from 0 to 10 using the Newton-Raphson method. The output should contain pK_a, pC_a and pH as three columns in the output file. Plot the resultant variation using gnuplot. The three-dimensional plot should look as follows:



Ref.: http://www.chem.sc.edu/faculty/morgan/resources/acidbase/exact.html

[The assignment in blue is optional].