COURSE · LECTURE & APPLICATION WORKSHOP HANDOUT

The Newton-Raphson Method

Numerical Analysis for Chemists

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Research domain: Mathematical Chemistry · Quantum Chemistry

Class introduction script

Why this lecture?

Last time, we explored the Fixed-Point Iteration Method and learned how to transform non-linear equations $f(x) = 0$ into $x = g(x)$. While fixed-point iteration is versatile, its convergence speed is linear and strongly dependent on our choice of $g(x)$.
Today, we are introducing one of the most powerful and widely used root-finding techniques in science and engineering: **the Newton-Raphson Method**. By leveraging localized tangent lines and first-order derivative information, Newton's method achieves **quadratic convergence**: the number of correct decimal places roughly doubles with every single iteration.

In this lecture, we will:

1. Derive the Newton-Raphson formula directly using a first-order Taylor series expansion.
2. Rigorously prove why its convergence rate is quadratic ($e_{k+1} \approx C\, e_k^2$).
3. Solve three practical chemical problems step by step: finding acid-base equilibrium pH (polynomial), modelling non-isothermal reactor conversion (exponential), and determining laser-induced dipole alignment angles (trigonometric).

1 Theoretical derivation

1.1 Derivation via Taylor series

Let $f(x)$ be a continuously differentiable function on an interval containing the true root α, such that $f(\alpha) = 0$.

Suppose x_k is our current approximation of the root. We approximate $f(x)$ near x_k using a first-order Taylor series expansion:

$$f(x) \approx f(x_k) + f'(x_k)\,(x - x_k) \tag{1}$$

Setting this linear approximation to zero to estimate the next candidate root x_{k+1}:

$$f(x_k) + f'(x_k)\,(x_{k+1} - x_k) = 0 \tag{2}$$

Assuming $f'(x_k) \neq 0$, solving for x_{k+1} yields the fundamental recurrence:

Newton-Raphson recurrence formula

$$x_{k+1} = x_k - \frac{f(x_k)}{f'(x_k)}, \qquad k = 0, 1, 2, \ldots \tag{3}$$

Geometrically, x_{k+1} represents the x-intercept of the tangent line drawn to the curve $y = f(x)$ at the point $(x_k, f(x_k))$.

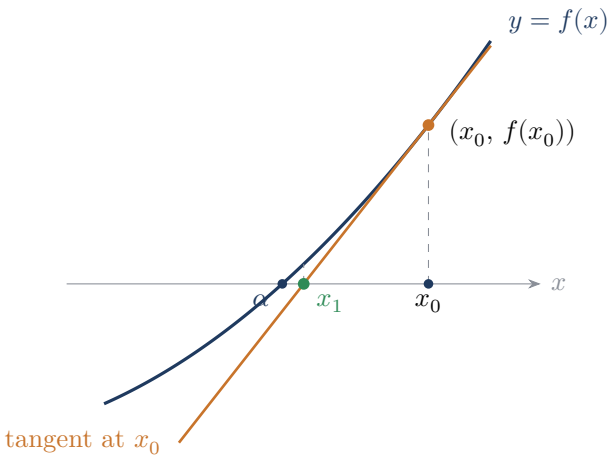


Figure 1. *Geometric interpretation of one Newton-Raphson step (illustrated on $f(x) = x^2 - 2$): the next iterate x_1 is the x-intercept of the tangent at $(x_0, f(x_0))$ and lies closer to the root α.*

1.2 Connection to fixed-point iteration

The Newton-Raphson method can be viewed as a special case of fixed-point iteration $x_{k+1} = g(x_k)$, where

$$g(x) = x - \frac{f(x)}{f'(x)} \tag{4}$$

Differentiating $g(x)$ using the quotient rule gives:

$$g'(x) = 1 - \frac{[f'(x)]^2 - f(x)\,f''(x)}{[f'(x)]^2} = \frac{f(x)\,f''(x)}{[f'(x)]^2} \tag{5}$$

Why convergence is so fast

At the exact root α, since $f(\alpha) = 0$ (and assuming $f'(\alpha) \neq 0$):

$$g'(\alpha) = \frac{0 \cdot f''(\alpha)}{[f'(\alpha)]^2} = 0 \tag{6}$$

Because $|g'(\alpha)| = 0 < 1$, the Newton-Raphson method is guaranteed to converge extremely rapidly near simple roots.

2 Proof of quadratic convergence

To evaluate the rate of convergence, let the error at iteration k be defined as:

$$e_k = x_k - \alpha \quad \Longrightarrow \quad x_k = \alpha + e_k \tag{7}$$

Expanding $f(\alpha)$ around x_k using a second-order Taylor expansion with remainder:

$$0 = f(\alpha) = f(x_k) + f'(x_k)\,(\alpha - x_k) + \frac{f''(\xi_k)}{2}\,(\alpha - x_k)^2 \tag{8}$$

where ξ_k lies between x_k and α. Substituting $\alpha - x_k = -e_k$:

$$f(x_k) = f'(x_k)\,e_k - \frac{f''(\xi_k)}{2}\,e_k^2 \tag{9}$$

Substitute $f(x_k)$ into the Newton-Raphson error expression $e_{k+1} = x_{k+1} - \alpha$:

$$\begin{aligned} e_{k+1} &= x_k - \frac{f(x_k)}{f'(x_k)} - \alpha = e_k - \frac{f'(x_k)\,e_k - \frac{1}{2}f''(\xi_k)\,e_k^2}{f'(x_k)} \\ &= e_k - e_k + \frac{f''(\xi_k)}{2f'(x_k)}\,e_k^2 = \frac{f''(\xi_k)}{2f'(x_k)}\,e_k^2 \end{aligned} \tag{10}$$

Taking the limit as $k \to \infty$ (where $x_k \to \alpha$ and $\xi_k \to \alpha$):

Quadratic convergence

$$\lim_{k\to\infty} \frac{|e_{k+1}|}{|e_k|^2} = \left|\frac{f''(\alpha)}{2f'(\alpha)}\right| = C \tag{11}$$

This proves that the Newton-Raphson method exhibits **quadratic convergence** (order $p = 2$), provided $f'(\alpha) \neq 0$.

3 Exercise 1: acid-base equilibrium (polynomial equation)

3.1 Problem statement

The hydronium ion concentration $x = [\mathrm{H_3O^+}]$ (in M) of a weak diprotic acid solution is governed by the cubic equilibrium polynomial equation:

$$f(x) = x^3 + 10^{-4}x^2 - 10^{-7}x - 10^{-11} = 0 \tag{12}$$

1. Compute the derivative $f'(x)$.
2. Using an initial guess $x_0 = 10^{-3}$ M, apply Newton-Raphson iterations to find $[\mathrm{H_3O^+}]$ accurate to 6 significant figures.
3. Calculate the resulting solution pH $= -\log_{10}([\mathrm{H_3O^+}])$.

3.2 Detailed solution

Step 1 · Derivative calculation

$$f'(x) = 3x^2 + 2 \times 10^{-4}\, x - 10^{-7}$$

The recurrence updates follow:

$$x_{k+1} = x_k - \frac{x_k^3 + 10^{-4}x_k^2 - 10^{-7}x_k - 10^{-11}}{3x_k^2 + 2 \times 10^{-4}x_k - 10^{-7}}$$

Step 2 · Iterations ($x_0 = 1.000000 \times 10^{-3}$)

- **Iteration 1 ($k = 0$):**

$$f(x_0) = (10^{-3})^3 + 10^{-4}(10^{-3})^2 - 10^{-7}(10^{-3}) - 10^{-11} = 9.900000 \times 10^{-10}$$
$$f'(x_0) = 3(10^{-3})^2 + 2 \times 10^{-4}(10^{-3}) - 10^{-7} = 3.100000 \times 10^{-6}$$
$$x_1 = 10^{-3} - \frac{9.900000 \times 10^{-10}}{3.100000 \times 10^{-6}} = \mathbf{6.806452 \times 10^{-4}}$$

- **Iteration 2 ($k = 1$):**

$$f(x_1) = 2.835911 \times 10^{-10}, \qquad f'(x_1) = 1.425963 \times 10^{-6}$$
$$x_2 = 6.806452 \times 10^{-4} - \frac{2.835911 \times 10^{-10}}{1.425963 \times 10^{-6}} = \mathbf{4.817682 \times 10^{-4}}$$

- **Iteration 3 ($k = 2$):**

$$f(x_2) = 7.685193 \times 10^{-11}, \qquad f'(x_2) = 6.926555 \times 10^{-7}$$
$$x_3 = 4.817682 \times 10^{-4} - \frac{7.685193 \times 10^{-11}}{6.926555 \times 10^{-7}} = \mathbf{3.708156 \times 10^{-4}}$$

Iterations 4 to 7 follow the same procedure and are collected in Table 1.

Table 1. *Newton-Raphson convergence table for the acid-base equilibrium (Exercise 1).*

k	x_k (M)	$f(x_k)$	$f'(x_k)$	$\lvert x_{k+1} - x_k \rvert$
0	1.000000×10^{-3}	9.900000×10^{-10}	3.100000×10^{-6}	3.1935×10^{-4}
1	6.806452×10^{-4}	2.835911×10^{-10}	1.425963×10^{-6}	1.9888×10^{-4}
2	4.817682×10^{-4}	7.685193×10^{-11}	6.926555×10^{-7}	1.1095×10^{-4}
3	3.708156×10^{-4}	1.765757×10^{-11}	3.866757×10^{-7}	4.5665×10^{-5}
4	3.251506×10^{-4}	2.433086×10^{-12}	2.821988×10^{-7}	8.6219×10^{-6}
5	3.165287×10^{-4}	7.930485×10^{-14}	2.638769×10^{-7}	3.0054×10^{-7}
6	3.162281×10^{-4}	9.477426×10^{-17}	2.632463×10^{-7}	3.6002×10^{-10}
7	3.162278×10^{-4}	1.36×10^{-22}	2.632456×10^{-7}	5.16×10^{-16}

Step 3 · pH calculation

After 6 iterations, $x_6 = 3.16228 \times 10^{-4}\,\mathrm{M}$ already carries the six requested significant figures, and x_7 confirms it (relative change $\approx 1.1 \times 10^{-6}$). Therefore:

$$[\mathrm{H_3O^+}] = \mathbf{3.16228 \times 10^{-4}\ M} \quad \Longrightarrow \quad \mathrm{pH} = -\log_{10}\left(3.162278 \times 10^{-4}\right) = \mathbf{3.50000}$$

Exact check

The polynomial factorises as $f(x) = (x + 10^{-4})\,(x^2 - 10^{-7})$. Its only positive root is therefore exactly $\alpha = \sqrt{10^{-7}} = 10^{-3.5} = 3.162278 \times 10^{-4}\,\mathrm{M}$, i.e. pH = 3.5, which confirms the numerical result.

Remark: when does the convergence become quadratic?

The starting value $x_0 = 10^{-3}$ is more than three times larger than the root. Far from α, the cubic term dominates and the error shrinks only by a factor of about 2 per iteration (Table 1, $k = 0, \ldots, 3$). The quadratic regime only sets in close to the root: the errors are $e_5 \approx 3.0 \times 10^{-7}$, $e_6 \approx 3.6 \times 10^{-10}$ and $e_7 \approx 5 \times 10^{-16}$, so that $e_{k+1}/e_k^2 \approx 3.98 \times 10^3\,\mathrm{M^{-1}}$. This matches the theoretical constant $C = |f''(\alpha)/2f'(\alpha)| \approx 3.98 \times 10^3\,\mathrm{M^{-1}}$.

4 Exercise 2: reactor kinetics (polynomial & exponential)

4.1 Problem statement

Revisiting the non-isothermal batch reactor conversion problem $x \in [0, 1]$:

$$f(x) = x^3 + 0.5\,x - 0.2\,e^{-x} = 0 \tag{13}$$

1. Derive the analytical expression for $f'(x)$.
2. Perform Newton-Raphson iterations starting from $x_0 = 0.3$ to achieve a tolerance of $\varepsilon = 10^{-6}$.
3. Compare the number of iterations required by Newton-Raphson versus Fixed-Point Iteration

(22 iterations for $\varepsilon = 10^{-4}$).

4.2 Detailed solution

Step 1 · Derivative formulation

$$f'(x) = 3x^2 + 0.5 + 0.2\,e^{-x}$$

Recurrence relation:

$$x_{k+1} = x_k - \frac{x_k^3 + 0.5\,x_k - 0.2\,e^{-x_k}}{3x_k^2 + 0.5 + 0.2\,e^{-x_k}}$$

Step 2 · Iterations ($x_0 = 0.3$)

- **Iteration 1 ($k = 0$):**

$$f(0.3) = (0.3)^3 + 0.5(0.3) - 0.2\,e^{-0.3} = 0.027 + 0.15 - 0.148164 = \mathbf{0.028836}$$
$$f'(0.3) = 3(0.3)^2 + 0.5 + 0.2\,e^{-0.3} = 0.27 + 0.5 + 0.148164 = \mathbf{0.918164}$$
$$x_1 = 0.3 - \frac{0.028836}{0.918164} = \mathbf{0.268593}$$

- **Iteration 2 ($k = 1$):**

$$f(x_1) = 0.019377 + 0.134297 - 0.152891 = \mathbf{7.829\times10^{-4}}$$
$$f'(x_1) = 3(0.268593)^2 + 0.5 + 0.2\,e^{-0.268593} = 0.216427 + 0.5 + 0.152891 = \mathbf{0.869318}$$
$$x_2 = 0.268593 - \frac{7.829\times10^{-4}}{0.869318} = \mathbf{0.267693}$$

- **Iteration 3 ($k = 2$):**

$$f(x_2) = \mathbf{5.908\times10^{-7}}, \qquad f'(x_2) = \mathbf{0.868007}$$
$$x_3 = 0.267693 - \frac{5.908\times10^{-7}}{0.868007} = \mathbf{0.267692}$$

Table 2. *Newton-Raphson convergence table for reactor kinetics (Exercise 2).*

k	x_k	$f(x_k)$	$f'(x_k)$	$\lvert x_{k+1} - x_k\rvert$
0	0.300000	2.8836×10^{-2}	0.918164	3.1407×10^{-2}
1	0.268593	7.8291×10^{-4}	0.869318	9.0061×10^{-4}
2	0.267693	5.9081×10^{-7}	0.868007	6.8065×10^{-7}
3	0.267692	3.4×10^{-13}	0.868006	3.9×10^{-13}

Intermediate terms are rounded to 6 decimals; iterates and steps are computed with full precision.

Comparison with fixed-point iteration

The step $|x_3 - x_2| = 6.8 \times 10^{-7}$ is already below $\varepsilon = 10^{-6}$: Newton-Raphson reaches $x \approx \mathbf{0.267692}$ in just **3 iterations**, whereas Fixed-Point Iteration required **22 iterations** for the weaker tolerance $\varepsilon = 10^{-4}$.

Quadratic convergence check

The errors are $e_1 \approx 9.0 \times 10^{-4}$ and $e_2 \approx 6.8 \times 10^{-7}$, so $e_2/e_1^2 \approx 0.837$, in agreement with $C = |f''(\alpha)/2f'(\alpha)| \approx 0.837$, where $f''(x) = 6x - 0.2\,e^{-x}$.

5 Exercise 3: molecular spectroscopy (trigonometric cos)

5.1 Problem statement

The laser-induced molecular dipole orientation angle $\theta \in [0, \pi/2]$ satisfies:

$$f(\theta) = \theta - 0.8\cos(\theta) - 0.2 = 0 \tag{14}$$

1. Derive $f'(\theta)$.
2. Starting with $\theta_0 = 0.5\,\text{rad}$, perform Newton-Raphson iterations to achieve $\varepsilon = 10^{-6}\,\text{rad}$.

5.2 Detailed solution

Step 1 · Derivative calculation

$$f'(\theta) = 1 + 0.8\sin(\theta)$$

Recurrence formula:

$$\theta_{k+1} = \theta_k - \frac{\theta_k - 0.8\cos(\theta_k) - 0.2}{1 + 0.8\sin(\theta_k)}$$

Step 2 · Iterations ($\theta_0 = 0.5\,\text{rad}$)

- **Iteration 1 ($k = 0$):**

$$f(0.5) = 0.5 - 0.8\cos(0.5) - 0.2 = 0.5 - 0.702066 - 0.2 = \mathbf{-0.402066}$$
$$f'(0.5) = 1 + 0.8\sin(0.5) = 1 + 0.383540 = \mathbf{1.383540}$$
$$\theta_1 = 0.5 - \frac{-0.402066}{1.383540} = \mathbf{0.790607}\,\text{rad}$$

- **Iteration 2 ($k = 1$):**

$$f(\theta_1) = 0.790607 - 0.8\cos(0.790607) - 0.2 = \mathbf{0.027875}$$
$$f'(\theta_1) = 1 + 0.8\sin(0.790607) = \mathbf{1.568624}$$
$$\theta_2 = 0.790607 - \frac{0.027875}{1.568624} = \mathbf{0.772836}\,\text{rad}$$

- **Iteration 3** ($k = 2$)**:**

$$f(\theta_2) = \mathbf{8.938\times10^{-5}}, \qquad f'(\theta_2) = \mathbf{1.558535}$$
$$\theta_3 = 0.772836 - \frac{8.938\times10^{-5}}{1.558535} = \mathbf{0.772779}\,\text{rad}$$

- **Iteration 4** ($k = 3$)**:**

$$f(\theta_3) = 9.4\times10^{-10}, \qquad \theta_4 = \mathbf{0.772779}\,\text{rad}$$

Table 3. *Newton-Raphson convergence table for the dipole alignment angle (Exercise 3).*

k	θ_k (rad)	$f(\theta_k)$	$f'(\theta_k)$	$\lvert\theta_{k+1}-\theta_k\rvert$
0	0.500000	-4.0207×10^{-1}	1.383540	2.9061×10^{-1}
1	0.790607	2.7875×10^{-2}	1.568624	1.7771×10^{-2}
2	0.772836	8.9382×10^{-5}	1.558535	5.7350×10^{-5}
3	0.772779	9.4×10^{-10}	1.558502	6.0×10^{-10}

Final result

The equilibrium alignment angle is

$$\theta \approx \mathbf{0.772779}\,\text{rad} \quad (\text{or } 44.277^\circ)$$

After 3 iterations, $\theta_3 = 0.772779$ is already correct to 6 decimal places ($|\theta_3 - \alpha| \approx 6\times10^{-10}$). The stopping test $|\theta_{k+1} - \theta_k| \le 10^{-6}$ is formally satisfied at $k = 3$, i.e. after **4 iterations**.

Quadratic convergence check

The errors are $e_1 \approx 1.78 \times 10^{-2}$ and $e_2 \approx 5.7 \times 10^{-5}$, so $e_2/e_1^2 \approx 0.180$, close to $C = |f''(\alpha)/2f'(\alpha)| \approx 0.184$, where $f''(\theta) = 0.8\cos(\theta)$.

Summary of the three applications

Exercise	Root α	Iterations	C
1. Acid-base equilibrium	3.162278×10^{-4} M (pH = 3.5)	6 (+1 to confirm)	$3.98 \times 10^{3}\ \text{M}^{-1}$
2. Reactor kinetics	0.267692	3	0.837
3. Dipole alignment	0.772779 rad	3 (+1 to confirm)	0.184

Here $C = |f''(\alpha)/2f'(\alpha)|$ is the asymptotic error constant of Section 2.