COURSE · LECTURE & APPLICATION WORKSHOP HANDOUT

Fixed-Point Iteration Method
& Applications in Chemistry

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Research domain: Mathematical Chemistry · Quantum Chemistry

Class introduction script

Learning objectives

During this lecture, we will cover:

1. How to transform a root-finding problem $f(x) = 0$ into an equivalent fixed-point relation $x = g(x)$.
2. The contraction mapping principle and the mathematical condition $|g'(x)| < 1$ required for guaranteed convergence.
3. Two complete chemical applications: one modelling steady-state reactor conversion involving polynomial and exponential terms, and another modelling laser-induced molecular dipole alignment involving trigonometric terms.

1 Theoretical foundation

1.1 From $f(x) = 0$ to $g(x) = x$

In physical chemistry, non-linear algebraic equations often take the form:

$$f(x) = 0 \tag{1}$$

The **Fixed-Point Iteration Method** transforms this equation into an equivalent fixed-point equation, by an algebraic rearrangement such that $g(x) = x \iff f(x) = 0$:

$$x = g(x) \tag{2}$$

A value α such that $\alpha = g(\alpha)$ is called a **fixed point** of the function $g(x)$; it is then a root of f.

1.2 Iterative scheme

1. **Initial guess (x_0):** choose a physically meaningful starting value (e.g., ideal gas volume, preliminary conversion estimate, or initial orientation angle).
2. **Recurrence relation:** generate successive approximations using

Fixed-point recurrence

$$x_{k+1} = g(x_k), \qquad k = 0, 1, 2, \ldots \tag{3}$$

3. **Stopping criterion:** stop the iterations when the absolute change or relative error falls below a pre-specified tolerance ε:

$$|x_{k+1} - x_k| \leq \varepsilon \quad \text{or} \quad \frac{|x_{k+1} - x_k|}{|x_{k+1}|} \leq \varepsilon \tag{4}$$

1.3 Convergence criterion (fixed-point theorem)

Fixed-Point Theorem

Let $g(x)$ be a continuously differentiable function on an interval $I = [a, b]$, and assume that:

1. $g(x) \in I$ for all $x \in I$ (self-mapping);
2. there exists a constant $L < 1$ such that $|g'(x)| \leq L < 1$ for all $x \in I$.

Then g has a **unique** fixed point $\alpha \in I$, the scheme $x_{k+1} = g(x_k)$ converges to α for **every** $x_0 \in I$, and

$$|x_k - \alpha| \leq \frac{L^k}{1 - L} |x_1 - x_0| \qquad \text{and} \qquad |x_k - \alpha| \leq \frac{L}{1 - L} |x_k - x_{k-1}| \tag{5}$$

(*a priori* and *a posteriori* error estimates).

Practical rule

Near the root α, the mean value theorem gives $e_{k+1} = g'(\xi_k)\, e_k$ with $e_k = x_k - \alpha$ and ξ_k between x_k and α. Hence the error is multiplied at each step by a factor close to $g'(\alpha)$, and the magnitude of this derivative at the solution must be strictly less than 1 for local convergence:

$$|g'(\alpha)| < 1 \tag{6}$$

- If $|g'(\alpha)| \ll 1$, the method converges rapidly.
- If $|g'(\alpha)| > 1$, the iterations move away from α (divergence); the case $|g'(\alpha)| = 1$ is inconclusive.
- If $g'(\alpha) > 0$ the iterates approach α monotonically; if $g'(\alpha) < 0$ they alternate on both sides of α.

1.4 Error control and stopping test

The stopping test $|x_{k+1} - x_k| \leq \varepsilon$ measures the *change* between two iterates, not the error itself. For a decreasing function g, both coincide up to a bound:

Certifying the stopping test when $g' < 0$

Suppose g is decreasing on I and $x_k \in I$. If $x_k < \alpha$, then $x_{k+1} = g(x_k) > g(\alpha) = \alpha$; if $x_k > \alpha$, then $x_{k+1} < \alpha$. The iterates therefore alternate on both sides of α, so that α lies **between** x_k and x_{k+1} and

$$|x_{k+1} - \alpha| \;\leq\; |x_{k+1} - x_k| \tag{7}$$

The test $|x_{k+1} - x_k| \leq \varepsilon$ then guarantees an error of at most ε. Both exercises below fall in this case.

2 Exercise 1: chemical reaction kinetics (polynomial & exponential)

2.1 Problem statement

In a non-isothermal batch reactor, the dimensionless steady-state conversion $x \in [0, 1]$ of a first-order irreversible exothermic reaction is modelled by balancing the reaction rate against heat removal, yielding the non-linear equation:

$$f(x) = x^3 + 0.5\,x - 0.2\,e^{-x} = 0 \tag{8}$$

1. Transform $f(x) = 0$ into a suitable fixed-point form $x = g(x)$ that guarantees convergence.
2. Prove that the chosen function $g(x)$ satisfies the convergence conditions (self-mapping and $|g'(x)| < 1$) on a suitable interval I containing the root.
3. Starting with an initial guess of $x_0 = 0.3$, perform fixed-point iterations to find the conversion x accurate to 4 decimal places ($\varepsilon = 10^{-4}$).

2.2 Detailed solution

Step 1 · Formulating $g(x)$

Existence and uniqueness of the root. Since $f'(x) = 3x^2 + 0.5 + 0.2\,e^{-x} > 0$, f is strictly increasing; moreover $f(0) = -0.2 < 0$ and $f(1) \approx 1.426 > 0$. Hence f has exactly one root $\alpha \in (0, 1)$.
Fixed-point form. Isolating x from the linear term $0.5x$:

$$0.5\,x = 0.2\,e^{-x} - x^3 \quad\Longrightarrow\quad x = 2\,(0.2\,e^{-x} - x^3) = 0.4\,e^{-x} - 2x^3$$

Thus, we define (the rearrangement is equivalent to $2f(x) = 0$):

$$\boxed{g(x) = 0.4\,e^{-x} - 2x^3}$$

Step 2 · Checking the convergence conditions

We compute the derivative of $g(x)$:

$$g'(x) = -0.4\,e^{-x} - 6x^2 \quad \Longrightarrow \quad |g'(x)| = 0.4\,e^{-x} + 6x^2 \quad (x \geq 0)$$

Let us take the interval $I = [0.23,\ 0.31]$, which contains the expected root.

- **Bound on $|g'|$.** On I, $\dfrac{d}{dx}|g'(x)| = 12x - 0.4\,e^{-x} > 0$, so $|g'|$ is increasing and its maximum is reached at $x = 0.31$:

$$|g'(0.23)| \approx 0.3178 + 0.3174 = 0.6352 < 1$$
$$|g'(0.31)| \approx 0.2934 + 0.5766 = 0.8700 < 1$$

  Hence $|g'(x)| \leq L = 0.87 < 1$ on I.

- **Self-mapping.** Since $g'(x) < 0$, g is decreasing on I, so $g(I) = [\,g(0.31),\ g(0.23)\,] \approx [\,0.2338,\ 0.2935\,] \subset I$.

Both conditions of the fixed-point theorem hold: convergence is guaranteed for any $x_0 \in I$, in particular $x_0 = 0.3$.

Why not the whole interval $[0, 1]$?

The conditions cannot hold on all of $[0, 1]$: $|g'(x)|$ exceeds 1 as soon as $x \gtrsim 0.345$ (for instance $|g'(1)| \approx 6.15$), and $g(1) \approx -1.85 \notin [0, 1]$. The interval must therefore be chosen around the root.

Step 3 · Fixed-point iterations ($x_0 = 0.3$)

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

$$x_1 = g(x_0) = 0.4\,e^{-0.3} - 2(0.3)^3 = 0.4(0.740818) - 2(0.027) = \mathbf{0.242327}$$

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

$$x_2 = g(x_1) = 0.4\,e^{-0.242327} - 2(0.242327)^3 = 0.313920 - 0.028460 = \mathbf{0.285460}$$

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

$$x_3 = g(x_2) = 0.4\,e^{-0.285460} - 2(0.285460)^3 = 0.300667 - 0.046523 = \mathbf{0.254145}$$

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

$$x_4 = g(x_3) = 0.4\,e^{-0.254145} - 2(0.254145)^3 = 0.310232 - 0.032830 = \mathbf{0.277402}$$

Table 1. *Iterative convergence table for Exercise 1 (stopping criterion $\varepsilon = 10^{-4}$).*

Iteration k	x_k	$x_{k+1} = g(x_k)$	$\lvert x_{k+1} - x_k \rvert$
0	0.300000	0.242327	0.057673
1	0.242327	0.285460	0.043132
2	0.285460	0.254145	0.031315
3	0.254145	0.277402	0.023257
4	0.277402	0.260407	0.016994
5	0.260407	0.272978	0.012571
⋮	⋮	⋮	⋮
20	0.267765	0.267639	0.000126
21	0.267639	0.267732	0.000093

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

Final result

The tolerance $|x_{k+1} - x_k| \leq 10^{-4}$ is first satisfied at $k = 21$ (**22 iterations**). The steady-state conversion is

$$x \approx \mathbf{0.2677} \quad (\text{or } 26.77\,\%)$$

Rigour: error certification and speed of convergence

- Since g is decreasing, α lies between $x_{21} = 0.267639$ and $x_{22} = 0.267732$, hence $|x_{22} - \alpha| \leq 9.3 \times 10^{-5} \leq \varepsilon$. The actual error is $|x_{22} - \alpha| \approx 3.9 \times 10^{-5}$, the exact root being $\alpha = 0.267692$ (it rounds to 0.2677).
- Near the root, the error is multiplied at each step by about $|g'(\alpha)| \approx 0.74$, which explains the 22 iterations; the iterates alternate on both sides of α because $g'(\alpha) < 0$.
- The *a priori* estimate with the global constant $L = 0.87$ only guarantees $|x_k - \alpha| \leq 10^{-4}$ for $k \geq 61$: it is a safe but pessimistic bound.

3 Exercise 2: photochemical spectroscopy (trigonometric cos)

3.1 Problem statement

In molecular spectroscopy, the dipole alignment angle θ (in radians) of a polar molecule under a combined laser and electric field satisfies the non-linear transcendental equation:

$$f(\theta) = \theta - 0.8\cos(\theta) - 0.2 = 0 \tag{9}$$

1. Formulate the fixed-point iteration function $g(\theta)$.
2. Show mathematically that the fixed-point scheme converges for any initial guess $\theta_0 \in [0, \pi/2]$.
3. Compute the alignment angle θ starting from $\theta_0 = 0.5\,\text{rad}$ with a tolerance $\varepsilon = 10^{-4}\,\text{rad}$.

3.2 Detailed solution

Step 1 · Formulating $g(\theta)$

Existence and uniqueness of the root. On $[0, \pi/2]$, $f'(\theta) = 1 + 0.8\sin(\theta) > 0$, so f is strictly increasing; moreover $f(0) = -1 < 0$ and $f(\pi/2) = \pi/2 - 0.2 \approx 1.371 > 0$. Hence f has exactly one root in $(0, \pi/2)$.
Fixed-point form. Isolating θ:

$$\theta = 0.8\cos(\theta) + 0.2 \quad \Longrightarrow \quad \boxed{g(\theta) = 0.8\cos(\theta) + 0.2}$$

Step 2 · Proving convergence

We calculate the derivative of $g(\theta)$:

$$g'(\theta) = -0.8\sin(\theta)$$

Taking the absolute value on $I = [0, \pi/2]$, where $\sin(\theta) \geq 0$:

$$|g'(\theta)| = 0.8\sin(\theta) \quad \Longrightarrow \quad \max_{\theta \in [0, \pi/2]} |g'(\theta)| = 0.8 < 1$$

Moreover, g is decreasing on I with $g(0) = 1.0$ and $g(\pi/2) = 0.2$, so $g(I) = [0.2,\ 1.0] \subset [0, \pi/2]$ (self-mapping).
Because both conditions of the fixed-point theorem hold ($|g'(\theta)| \leq L = 0.8 < 1$ everywhere on the domain), the fixed-point method is **guaranteed to converge** for any $\theta_0 \in [0, \pi/2]$.

Step 3 · Fixed-point iterations ($\theta_0 = 0.5\,\text{rad}$)

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

$$\theta_1 = g(\theta_0) = 0.8\cos(0.5) + 0.2 = 0.8(0.877583) + 0.2 = \mathbf{0.902066}\,\text{rad}$$

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

$$\theta_2 = g(\theta_1) = 0.8\cos(0.902066) + 0.2 = 0.8(0.619990) + 0.2 = \mathbf{0.695992}\,\text{rad}$$

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

$$\theta_3 = g(\theta_2) = 0.8\cos(0.695992) + 0.2 = 0.8(0.767418) + 0.2 = \mathbf{0.813934}\,\text{rad}$$

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

$$\theta_4 = g(\theta_3) = 0.8\cos(0.813934) + 0.2 = 0.8(0.686644) + 0.2 = \mathbf{0.749315}\,\text{rad}$$

Table 2. *Iterative convergence table for Exercise 2 (stopping criterion* $\varepsilon = 10^{-4}$ rad*).*

Iteration k	θ_k (rad)	$\theta_{k+1} = g(\theta_k)$ (rad)	$\lvert\theta_{k+1} - \theta_k\rvert$
0	0.500000	0.902066	0.402066
1	0.902066	0.695992	0.206074
2	0.695992	0.813934	0.117942
3	0.813934	0.749315	0.064620
4	0.749315	0.785725	0.036410
5	0.785725	0.765501	0.020224
⋮	⋮	⋮	⋮
14	0.772710	0.772817	0.000107
15	0.772817	0.772757	0.000060

Final result

The tolerance is first satisfied at $k = 15$ (**16 iterations**): the difference drops from 1.07×10^{-4} to 6.0×10^{-5}. The equilibrium alignment angle is

$$\theta \approx \mathbf{0.7728}\,\text{rad} \quad (\text{approximately } 44.28^\circ)$$

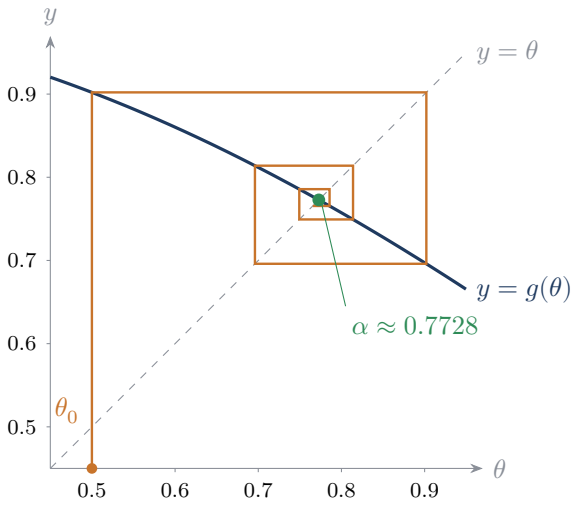


Figure 1. *Cobweb diagram for Exercise 2: starting from $\theta_0 = 0.5\,\text{rad}$, the iterates spiral towards the fixed point $\alpha \approx 0.7728\,\text{rad}$. Since $g'(\alpha) < 0$, they alternate on both sides of α.*

Rigour: error certification and speed of convergence

- Since g is decreasing, α lies between $\theta_{15} = 0.772817$ and $\theta_{16} = 0.772757$, hence $|\theta_{16} - \alpha| \leq 6.0 \times 10^{-5} \leq \varepsilon$. As both endpoints round to 0.7728, this value is correct to 4 decimal places; the actual error is $|\theta_{16} - \alpha| \approx 2.1 \times 10^{-5}$, the exact root being $\alpha = 0.772779$.
- Near the root, the error is multiplied at each step by about $|g'(\alpha)| = 0.8\sin(\alpha) \approx 0.56$, against ≈ 0.74 in Exercise 1: this smaller contraction factor explains why 16 iterations suffice here instead of 22.
- The *a priori* estimate with the global constant $L = 0.8$ only guarantees $|\theta_k - \alpha| \leq 10^{-4}$ for $k \geq 45$: it is a safe but pessimistic bound.

Summary of the two applications

Exercise	Root α	Iterations	$\lvert g'(\alpha)\rvert$	A priori bound
1. Reactor kinetics	0.267692	22	0.736	$k \geq 61$
2. Dipole alignment	0.772779 rad	16	0.559	$k \geq 45$

Iterations are counted for $\varepsilon = 10^{-4}$. The a priori bound is the number of iterations guaranteed by the fixed-point theorem with the global constant L (0.87 and 0.8 respectively).