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Assignment 20
Show

(a) by direct minimization,

(b) with the normal equations and

(c) with the QR-factorization

that the least square estimation for the parameter $\theta \in \mathbb{R}$ for the measurements

$$\beta_j = \theta + \varepsilon_j \qquad (j = 1, 2, \ldots, m)$$

is given by $\frac{1}{m}\sum_{j=1}^{m} \beta_j$.

Solution
(a) We have to minimize $f(x) := \sum_{j=1}^{m}(\beta_j - x)^2$. The minimum can be calculated by

$$0 = f'(x) = \sum_{j=1}^{m} 2(\beta_j - x), \quad \text{hence} \quad mx = \sum_{j=1}^{m} \beta_j.$$

(b) With $b = (\beta_1, \ldots, \beta_m)'$ and $A = (1, \ldots, 1)' \in \mathbb{R}^{m\times 1}$ we obtain $f(x) = \|b - Ax\|_2^2$. The normal equations are given by (using $A'A = m$)

$$A'Ax = A'b \quad \Leftrightarrow \quad mx = \sum_{j=1}^{m} \beta_j.$$

(c) A reduced QR-decomposition of A is given by

$$A = \begin{pmatrix} 1 \\ \vdots \\ 1 \end{pmatrix} = \begin{pmatrix} 1/\sqrt{m} \\ \vdots \\ 1/\sqrt{m} \end{pmatrix} \sqrt{m} = QR.$$

We then have

$$Rx = Q'b \quad \Leftrightarrow \quad \sqrt{m}\,x = \frac{1}{\sqrt{m}}\sum_{j=1}^{m} \beta_j \quad \Leftrightarrow \quad x = \frac{1}{m}\sum_{j=1}^{m} \beta_j.$$

Assignment 21 (Arrhenius equation)
The dependence on the temperature T of the reaction rate K of a chemical reaction is modeled by the Arrhenius equation

$$K(T) = C\,\exp(-E/T).$$

Given some measurements (K_j, T_j) the two parameters E (activation energy) and C (normalization) should estimated. Therefor the *nonlinear* model

$$K_j = C\,\exp(-E/T_j) + R_j$$

is used. R_j are independent and normally distributed random variables with standard deviation ΔK_j. Further $|\Delta K_j/K_j| \ll 1$.
In the file `arrhenius.txt` are the measurements in the form $(T_j, K_j, \Delta K_j)$.

(a) Write a Matlab function to visualize the measurements.

(b) Show: The model can be transformed to

$$\ln(K_j) = \ln(C) - \frac{1}{T_j} \cdot E + r_j$$

which is linear w. r. t. $\ln(C)$ and E. Also show: The standard deviation of the r_j are given by $\delta_j = \Delta K_j / K_j$.

(c) Write a Matlab function which

  (a) loads the measurements from the given file,

  (b) uses the transformation in (b) to set up the linear least square problem $\|Ax - b\|_2 = \min!$,

  (c) solves the least square problem and

  (d) returns the estimations for C and E.

(d) Update the visualization of (a): Additionally show the graph $K(T)$ with the estimated parameters.

Solution

(a), (c) & (d) see zip-file.

(b) The model is *nonlinear* w. r. t. the parameters C and E. Using the ln on both sides we infer together with the Taylor series $\log(x+h) = \log(x_0) + h/x + O(h^2)$

$$\begin{aligned}\ln(K_j) &= \ln(C\exp(-E/T_j) + R_j) \doteq \\ &\doteq \ln(C\exp(-E/T_j)) + \underbrace{\frac{R_j}{C\exp(-E/T_j)}}_{=:r_j} = \ln(C) - \frac{1}{T_j} \cdot E + r_j.\end{aligned}$$

There the r_j are also independently normally distributed. Because of

$$r_j = \frac{R_j}{K_j - R_j} \approx \frac{R_j}{K_j}$$

the standard deviation of the r_j is given by $\delta_j := \delta K_j / K_j$.

Now the problem is *linear* in the parameters $\ln(C)$ and E:

$$\ln(K_j) = \ln(C) - \frac{1}{T_j} \cdot E + r_j, \qquad j = 1:m.$$

In order to use the least-squares method, we have to scale the r_j in such a way, that all scaled r_j have the same deviation. So we end up in: find $\ln(C)$ and E such that

$$\sum_{j=1}^{m} \left(\frac{r_j}{\delta_j}\right)^2 = \sum_{i=1}^{m} \left(\frac{-\frac{1}{T_j} \cdot E + 1 \cdot \ln(C) - \ln(K_j)}{\delta_j}\right)^2 = \min!$$

With $D := \operatorname{diag}(\delta_1^{-1}, \ldots, \delta_m^{-1})$,

$$A = D \begin{pmatrix} -1/T_1 & 1 \\ \vdots & \vdots \\ -1/T_m & 1 \end{pmatrix} \qquad \text{and} \qquad b = D \begin{pmatrix} \ln(K_1) \\ \vdots \\ \ln(K_m) \end{pmatrix}$$

we have the form $\|Ax - b\|_2 = \min!$ with $x = (E, \ln(C))^T$.

```
function [E,C,residual]=A21_solve(filename)
% transform, setup linear least square problem and solve
% Input:
%   filename        file with measurements

M=load(filename);m=size(M,1);n=2;  % T_j, K_j, DeltaK_j
D=spdiags(M(:,2)./M(:,3),0,m,m);   % K_j/DeltaK_j

A=D*[-1./M(:,1),ones(m,1)];         % 1. column -1/T_i, 2. column: 1
b=D*log(M(:,2));

R1=triu(qr([A,b]));                 % use "Q-free" method to solve ...
x=R1(1:n,1:n)\R1(1:n,n+1);          % ... least square problem
E=x(1); C=exp(x(2));                % calculate E and C from x
residual=R1(n+1,n+1);
end
```