Matlab for Chemists

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PREFACE

MATLAB is an interactive program package for numerical computation and visualization. It originated in the middle of the 1980s as a user interface to matrix manipulation packages written in FORTRAN. Hence its name: "Matrix Laboratory". Over the years the system has been extended, it now includes a programming language, extensive visualization tools, and many numerical methods.

These are notes accompanying a course in MATLAB for chemistry and natural science students at the University of Nijmegen. The course has the following objectives:

- Offering of practical exercises supporting an obligatory course in linear algebra.
- Offering of practical exercises supporting an obligatory course in quantum mechanics.
- A first introduction to programming (loops, if then else constructs, functions).
- A tool for fitting and plotting data obtained in the chemical laboratory.

Although no new mathematical concepts are introduced in the present lectures, the mathematical knowledge necessary to do the MATLAB exercises, is briefly reviewed.

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Contents

1. Vectors and their operations

1.1 Scalars and vectors

Variables, assignments, scalars, row and column vectors, echoing of input, transposition, length versus norm of vector, inner products. Difference between vector- and dot- operations.

All internal operations in MATLAB are performed with floating point numbers 16 digits long, as e.g., 3.141592653589793 or 0.3141592653589793e-1 (e-1 indicates 10^{-1}). The simplest data structure in MATLAB is the scalar (handled by MATLAB as a 1×1 matrix). Scalars can be given names and assigned values, e.g.,

```
>> num_students = 25;
>> Temperature  = 272.1;
>> Planck       = 6.6260755e-34;
```

It is important to understand fully the difference between the mathematical equality $a = b$ (which can be written equally well as $b = a$) and the MATLAB assignment `a=b`. In the latter statement it is necessary that the right hand side has a value at the time that the statement is executed. The right hand side is first fully evaluated and then the result is assigned to the left hand side. Example:

```
>> a = 33.33;
>> a = 3*a - a
a =
66.6600
```

First the expression `3*a-a` is fully evaluated. The value of `a`, which it has just before the statement, is substituted everywhere. Only at the end of the evaluation `a` is assigned a new value by means of the assignment symbol `=`.

A variable name must start with a lower- or uppercase letter and only the first 31 characters of the name are used by MATLAB. Digits, letters and underscores are the only allowed characters in the name of a variable. MATLAB is case sensitive: the variable `temperature` is another than `Temperature`. Scalars can be added: `a+b`, subtracted: `a-b`, multiplied: `a*b`, divided: `a/b` and taken to a power: `a^b`. The usual priority rules hold (multiplication

before addition, etc.), but it is better not to rely on this and to force the priority by brackets. Do not write `a/b^3`, but `(a/b)^3`, or `a/(b^3)`, whatever your intention is.

The second simplest data structure in MATLAB is the vector, which is simply a sequence of floating point numbers. Vectors come in two flavors: *row vectors* and *column vectors*. Row vectors are entered either space delimited or comma delimited, as

```
>> a=[1 2 3 -2 -4]
a =
     1     2     3    -2    -4

>> b=[1,2,3,-2,-4]
b =
     1     2     3    -2    -4
```

The sequence is delimited by square brackets. Notice that the vectors `a` and `b` are indeed equal. After they have been entered at the MATLAB prompt (`>>`), MATLAB echoes the input. This echoing of input is suppressed when the statement is ended by a semicolon (`;`). The vector is shown by typing its name, thus,

```
>> a=[1 2 3 -2 -4]; % No output
>> a                % echo the vector a
a =
     1     2     3    -2    -4
```

Note that comments may be entered preceded by a % sign, they run until end of line. The rules for naming vectors are the same as for scalars. (Case sensitive, starting with letters, length ≤ 31, only digits, letters and underscores in the name). Column vectors are entered either semicolon delimited or end of line delimited.

```
>> a=[1;2;3]
a =
     1
     2
     3
>> a=[
1
2
3]
```

```
a =
     1
     2
     3
```

A row vector can be turned into a column vector and vice versa (transposition) by the transposition operator (')

```
>> a=[1 2 3];
>> b=a'
b =
     1
     2
     3
>> c=b'
c =
     1     2     3
```

Note
Experience shows that the most common error in MATLAB *is forgetting whether a vector is a row or a column vector. We adhere strictly to the convention that a vector is a column.*

The easiest way to enter a column vector is as a row plus immediate transposition, thus,

```
>> a=[5 4 3 2]'
a =
     5
     4
     3
     2
```

A single element of a row or column vector can be retrieved as e.g., `a(4)`, this gives the fourth element of `a` (the number 2 in the example). A range can be returned by the use of a colon (`:`). For instance, `b=a(2:3)` returns a column vector `b` with the digits 4 and 3 as elements. The word `end` gives the end of a vector: `b=a(2:end)` creates a column vector `b` containing 4, 3, 2.

In mathematics and physics the *norm* and the *length* of a vector are often used as synonyms. In MATLAB the two concepts are different, `length(a)` returns the number of components of `a` (the dimension of the vector), while `norm(a)` returns the norm of `a`. Remember that the norm $|\boldsymbol{a}|$ of $\boldsymbol{a}$ is by definition $|\boldsymbol{a}| = \sqrt{\boldsymbol{a} \cdot \boldsymbol{a}}$.

The usual mathematical operations can be performed on vectors: addition and subtraction of two vectors (provided the vectors are of the same length) and multiplication and division by a number.

```
>> a=[1 2 3 4 5]';
>> b=[5 4 3 2 1]';
>> 2*a+3*b
ans =
    17
    16
    15
    14
    13
```

In mathematics the following operation is *not* defined: $s + \boldsymbol{a}$, where s is a scalar (number) and $\boldsymbol{a}$ is a vector. However, in MATLAB the following happens,

```
>> a     % show the present value of vector a
a =
    0.5028
    0.7095
    0.4289
    0.3046
>> a=a+1
a =
    1.5028
    1.7095
    1.4289
    1.3046
```

The inner (dot) product of two real vectors consisting of n elements is mathematically defined as

$$\boldsymbol{a} \cdot \boldsymbol{b} \equiv a_1 b_1 + a_2 b_2 + \cdots + a_n b_n = \begin{pmatrix} a_1 & a_2 & \cdots & a_n \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix} = \sum_{i=1}^{n} a_i \, b_i$$

In MATLAB:

```
>> a =[ 0.4225    0.8560    0.4902    0.8159    0.4608]';
>> b =[ 0.4574    0.4507    0.4122    0.9016    0.0056]';
>> a'*b
ans =
    1.5193
```

Recalling the definition of the norm of a vector, we see that `sqrt(a'*a)` gives the very same answer as `norm(a)`. Both `sqrt` and `norm` are functions known to MATLAB.

Recall that the set of all column vectors with n real components forms a vector space commonly denoted by $\mathbb{R}^n$. The geometric meaning of the inner product in $\mathbb{R}^n$ is well-known in $\mathbb{R}^3$. It is the following: it gives the angle between two vectors,

$$\boldsymbol{r}_1 \cdot \boldsymbol{r}_2 = r_1\, r_2\, \cos\phi.$$

Here $r_i \equiv |\boldsymbol{r}_i| \equiv \sqrt{\boldsymbol{r}_i \cdot \boldsymbol{r}_i}$ is the norm of vector $\boldsymbol{r}_i$ $(i = 1, 2)$ and ϕ is the angle between the two vectors. We give an example of the computation of ϕ:

```
>> % Introduce two column vectors for the example:
>> a=[23 0 -21]';
>> b=[0 10 0]';
>> % Compute their lengths:
>> la = norm(a);
>> lb = norm(b);
>> % Now the cosine of the angle
>> cangle = (a'*b)/(la*lb);
>> % the angle itself
>> phi = acos(cangle)
phi =
    1.5708
>> % Radians, convert to degrees:
>> phi*180/pi
ans =
    90
```

Explanation:
Division of two numbers is by the slash (`/`). MATLAB knows the inverse cosine (`acos`), which gives results in radians. MATLAB knows $\pi = 3.14\ldots$, it is simply the variable `pi`. *Do not use the name pi for anything else!*

MATLAB has lots of elementary mathematical functions that all work elementwise on vectors and matrices. In Table 1.1 we show the most important mathematical functions.

We end this section, by introducing the *dot operations*, which are not defined as such in linear algebra. It often happens that one wants to divide all the individual elements of vectors. Suppose we have measured 5 numbers as a function of a certain quantity and that we also made a fit of the measured values. To compute the percentage error of the fit we proceed as follows:

Table 1.1: *Elementary mathematical functions. All operate on the elements of matrices.*

abs	Absolute value and complex magnitude
acos, acosh	Inverse cosine and inverse hyperbolic cosine
acot, acoth	Inverse cotangent and inverse hyperbolic cotangent
acsc, acsch	Inverse cosecant and inverse hyperbolic cosecant
angle	Phase angle
asec, asech	Inverse secant and inverse hyperbolic secant
asin, asinh	Inverse sine and inverse hyperbolic sine
atan, atanh	Inverse tangent and inverse hyperbolic tangent
atan2	Four-quadrant inverse tangent
ceil	Round toward infinity
complex	Construct complex data from real and imaginary components
conj	Complex conjugate
cos, cosh	Cosine and hyperbolic cosine
cot, coth	Cotangent and hyperbolic cotangent
csc, csch	Cosecant and hyperbolic cosecant
exp	Exponential
fix	Round towards zero
floor	Round towards minus infinity
gcd	Greatest common divisor
imag	Imaginary part of a complex number
lcm	Least common multiple
log	Natural logarithm
log2	Base 2 logarithm and dissect floating-point numbers into exponent and mantissa
log10	Common (base 10) logarithm
mod	Modulus (signed remainder after division)
nchoosek	Binomial coefficient or all combinations
real	Real part of complex number
rem	Remainder after division
round	Round to nearest integer
sec, sech	Secant and hyperbolic secant
sign	Signum function
sin, sinh	Sine and hyperbolic sine
sqrt	Square root
tan, tanh	Tangent and hyperbolic tangent

```
>> % Enter the observed values:
>> obs = [ -0.3012  -0.0999   0.0527   0.1252   0.2334]';
>> % Enter the fitted values:
>> fit = [ -0.3100  -0.1009   0.0531   0.1263   0.2479]';
>> % Percentage error: (put result into vector error
>> % and transpose for typographical reasons)
>> error=[100*(obs-fit)./obs]'
error =
   -2.9216   -1.0010   -0.7590   -0.8786   -6.2125
```

Note the operation `./`, this is pointwise division, i.e., it computes

$$\text{error}(i) = 100 * (\text{obs}(i) - \text{fit}(i))/\text{obs}(i) \quad \text{for} \quad i = 1, \ldots, 5,$$

successively. Suppose we forgot the dot in the division, then MATLAB does not give an error, but the following unexpected result[1] (a 5×5 matrix):

```
>> error=[100*(obs-fit)/obs]'
error =
   -2.9216   -0.3320    0.1328    0.3652    4.8141
         0         0         0         0         0
         0         0         0         0         0
         0         0         0         0         0
         0         0         0         0         0
```

Also pointwise multiplication is possible, example:

```
>> [1 2 3 4]'.*[24 12 8 6]'
ans =
    24
    24
    24
    24
```

1.2 Linear independent and orthogonal vectors

Linear dependence, orthogonality

Returning to linear algebra, we recall the following two definitions:

[1] The reason is that if MATLAB meets an expression of the type $s/\boldsymbol{a}$, where $\boldsymbol{a}$ is a column vector, it tries to solve the equation $\boldsymbol{x} \cdot \boldsymbol{a} = s$, and obviously one of the possible solutions is the row vector $\boldsymbol{x} = (s/a_1, 0, 0, \ldots, 0)$. We do not get a matrix of five of these row vectors, because there is a prime on the result, but the transposed matrix.

1. The set of n non-null vectors $\boldsymbol{r}_1,\ \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n$ is linearly dependent if one of the vectors can be written as a linear combination of the others, i.e., if expansion coefficients c_j can be found so that the following is true for some i

$$\boldsymbol{r}_i = c_1\boldsymbol{r}_1 + \cdots c_{i-1}\boldsymbol{r}_{i-1} + c_{i+1}\boldsymbol{r}_{i+1} + \cdots c_n\boldsymbol{r}_n,$$

where $\boldsymbol{r}_i$ does not appear on the right hand side. If a set of vectors is not linearly dependent it is (not surprisingly) called linearly independent.

2. Two vectors $\boldsymbol{r}_i = (r_{1i}\ r_{2i}\ \cdots\ r_{ni})$ and $\boldsymbol{r}_j = (r_{1j}\ r_{2j}\ \cdots\ r_{nj})$ are orthogonal if

$$\boldsymbol{r}_i \cdot \boldsymbol{r}_j \equiv r_{1i}\, r_{1j} + r_{2i}\, r_{2j} + \cdots + r_{ni}\, r_{nj} = 0.$$

Remember further that orthogonal vectors are linearly independent.

A basis of $\mathbb{R}^n$ is a maximum set of linearly independent real vectors of dimension n. A set of nonzero vectors $\boldsymbol{r}_i$ forms an orthogonal basis of $\mathbb{R}^n$ if

$$\boldsymbol{r}_i \cdot \boldsymbol{r}_j = 0 \quad \text{for} \quad i, j = 1, \ldots, n, i \neq j.$$

This is usually compactly written as follows

$$\boldsymbol{r}_i \cdot \boldsymbol{r}_j = r_i^2\, \delta_{ij} \ \text{ with } \ \delta_{i,j} = \begin{cases} 1 & \text{if} \quad i = j \\ 0 & \text{if} \quad i \neq j \end{cases} \ \text{ and } \ r_i^2 \equiv \boldsymbol{r}_i \cdot \boldsymbol{r}_i. \tag{1.1}$$

An arbitrary real vector $\boldsymbol{a}$ of dimension n can be written as a linear combination of the n orthogonal vectors $\boldsymbol{r}_i$

$$\boldsymbol{a} = a_1\boldsymbol{r}_1 + a_2\boldsymbol{r}_2 + \cdots + a_n\boldsymbol{r}_n = \sum_{i=1}^{n} a_i\, \boldsymbol{r}_i,$$

because this is a maximum set of linearly independent vectors in $\mathbb{R}^n$. It is easy to compute the expansion coefficients a_i:

$$\boldsymbol{r}_j \cdot \boldsymbol{a} = \sum_{i=1}^{n} a_i\, \boldsymbol{r}_j \cdot \boldsymbol{r}_i = \sum_{i=1}^{n} a_i\, r_i^2 \delta_{i,j} = a_j\, r_j^2,$$

so that $a_j = \boldsymbol{r}_j \cdot \boldsymbol{a}/r_j^2$ for all $j = 1, \ldots, n$.

As a geometric application we remember that we learned in our linear algebra course about a plane in the space $\mathbb{R}^3$. Consider a certain fixed vector $\boldsymbol{x}$ with norm x. All vectors $\boldsymbol{r}$ orthogonal to $\boldsymbol{x}$ form a plane, i.e., all vectors $\boldsymbol{r}$ in the plane satisfy $\boldsymbol{r} \cdot \boldsymbol{x} = 0$. An orthogonal basis of the plane can be constructed as follows.

1. Choose a vector $\tilde{\boldsymbol{y}}$ that is not a multiple of $\boldsymbol{x}$, $\boldsymbol{x}$ and $\tilde{\boldsymbol{y}}$ are linearly independent.

2. Orthogonalize $\tilde{\boldsymbol{y}}$ onto $\boldsymbol{x}$ by the following equation,

$$\boldsymbol{y} = \tilde{\boldsymbol{y}} - \boldsymbol{x}(\boldsymbol{x} \cdot \tilde{\boldsymbol{y}})/x^2.$$

   clearly $\boldsymbol{y} \neq 0$, we check the orthogonality:

$$\boldsymbol{x} \cdot \boldsymbol{y} = \boldsymbol{x} \cdot \tilde{\boldsymbol{y}} - (\boldsymbol{x} \cdot \boldsymbol{x})(\boldsymbol{x} \cdot \tilde{\boldsymbol{y}})/x^2 = \boldsymbol{x} \cdot \tilde{\boldsymbol{y}} - \boldsymbol{x} \cdot \tilde{\boldsymbol{y}} = 0,$$

   since $x^2 = \boldsymbol{x} \cdot \boldsymbol{x}$. Hence $\boldsymbol{y}$ (with norm y) is in the plane orthogonal to $\boldsymbol{x}$.

3. To obtain the second basis vector of the plane we can choose a third vector which is linearly independent of $\boldsymbol{x}$ and $\boldsymbol{y}$ and orthogonalize. Or, we can form the vector product $\boldsymbol{z} = \boldsymbol{x} \times \boldsymbol{y}$, which is less general as it only works in $\mathbb{R}^3$, but is easier. [The cross product in MATLAB is `r3=cross(r1,r2)`].

The vectors $\boldsymbol{x}$, $\boldsymbol{y}$ and $\boldsymbol{z}$ form a right-handed orthogonal frame (set of axes) of $\mathbb{R}^3$. An arbitrary vector $\boldsymbol{a}$ in this space can be decomposed as follows

$$\boldsymbol{a} = \boldsymbol{x}(\boldsymbol{x} \cdot \boldsymbol{a})/x^2 + \boldsymbol{y}(\boldsymbol{y} \cdot \boldsymbol{a})/y^2 + \boldsymbol{z}(\boldsymbol{z} \cdot \boldsymbol{a})/z^2.$$

If we want to reflect $\boldsymbol{a}$ in the y-z plane (which is orthogonal to the given vector $\boldsymbol{x}$), we simply keep the y and z components of $\boldsymbol{a}$ unchanged and change the sign of its component vector along $\boldsymbol{x}$.

1.3 Exercises

Exercise 1.

Try to reproduce the examples above to get acquainted with MATLAB.

Exercise 2.

Type in the column vector `a` containing the six subsequent elements: 1, -2, 3, -4, 5, -6. Normalize this vector. That is, determine its norm and divide the vector by it. Check your result by computing the norm of the normalized vector.

Exercise 3.

Type in the column vector `b` containing the subsequent elements: -1, 2, -3, 4, -5, 6. Determine the angle (in degrees) of this vector with the vector of the previous exercise. The answer is very simple, explain why.

Exercise 4.

A root (or zero) of a polynomial $P(x) = a_0 + a_1 x + \cdots + a_n x^n$ is a solution of the equation $P(x) = 0$. The main theorem of algebra states that this equation has exactly n roots, which may be complex.

Determine the roots of the 4^{th} degree polynomial

$$x^4 - 11.0x^3 + 42.35x^2 - 66.550x + 35.1384.$$

Hint:
Put the coefficients of powers of x into a column array `c` (in decreasing power of x) and issue the command `roots(c)` (a call to the MATLAB function `roots`, use the MATLABhelp function to see the syntax).

Exercise 5.

In the USA the curious temperature scale Fahrenheit[2] is in daily use.

To convert to the Celsius scale use the formula C = 5(F - 32)/9. Prepare a table `F` starting at -20 °C, ending at 100 °C with steps of 5 °C that contains Celsius converted to Fahrenheit.

Hint: A row vector containing the Celsius steps can be prepared by the command: `C=[-20:5:100]`. To get a nice table on the screen use `[C' F']`.

Compute in degrees Celsius the points: 0, 32, 96, and 212 °F by interpolation with the MATLAB function `interp1`. For instance, `interp1(F,C,104)` returns 40.

Exercise 6.

Consider the methane molecule CH_4. The four protons are on the 4 alternating corners of a cube, with one CH bond pointing into the $(1, 1, 1)$ direction and the other bonds pointing to other corners in agreement with methane being tetrahedral. All C–H bondlengths are 1.086 Å. Compute the 6 H–C–H angles and the 6 H–H distances (all should be equal due to the high symmetry of methane).

Exercise 7.

Compute

```
[1 2 3 4]'.*[24 12 8 6]'
[1 2 3 4]'*[24 12 8 6]
[1 2 3 4]*[24 12 8 6]'
```

[2]It is named after Gabriel Daniel Fahrenheit (1686–1736), who invented it in 1714, while working in Amsterdam.

Explain the differences.

Exercise 8.

Let $\boldsymbol{x} = (-2, -1, 3, 4)$. Compute $\sum_{i=1}^{4} x_i^5$.

Hint:
The MATLAB function `sum(y)` sums the components of the vector `y`.

Exercise 9.

Consider the vector $\boldsymbol{x} = \begin{pmatrix} 2 \\ 1 \\ 3 \end{pmatrix}$. Construct two vectors $\boldsymbol{y}$ and $\boldsymbol{z}$ orthogonal to $\boldsymbol{x}$ and to each other. Compute the components of $\boldsymbol{a} = \begin{pmatrix} 3 \\ -1 \\ 2 \end{pmatrix}$ along $\boldsymbol{x}$, $\boldsymbol{y}$ and $\boldsymbol{z}$. Then reflect the vector $\boldsymbol{a}$ into the plane spanned by $\boldsymbol{y}$ and $\boldsymbol{z}$. Let the reflected vector be $\boldsymbol{a}'$. Verify that $\boldsymbol{a} - \boldsymbol{a}'$ is orthogonal to the reflection plane.

Exercise 10.

The vectors

$$\boldsymbol{r}_1 = \begin{pmatrix} 3 \\ 2 \\ 1 \end{pmatrix} \text{ and } \boldsymbol{r}_2 = \begin{pmatrix} 2 \\ -1 \\ -4 \end{pmatrix}$$

are orthogonal. We easily get an orthogonal basis for $\mathbb{R}^3$ by defining $\boldsymbol{r}_3 = \boldsymbol{r}_1 \times \boldsymbol{r}_2$. Calculate the components of

$$\boldsymbol{e}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \text{ and } \boldsymbol{e}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \text{ and } \boldsymbol{e}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

with respect to the basis $\boldsymbol{r}_1,\ \boldsymbol{r}_2,\ \boldsymbol{r}_3$.

Exercise 11.

The O–H bond distance in the water molecule H_2O is 0.91 Å. The H-O-H angle is 104.69°. Compute the distance between the protons.
Hint: Compute the Cartesian coordinates of the vectors $\boldsymbol{x}_1 = \overrightarrow{OH_1}$ and $\boldsymbol{x}_2 = \overrightarrow{OH_2}$ with respect to an orthonormal (= orthogonal with normalized basis vectors) frame centered at O. The distance between H_1 and H_2 is $|\boldsymbol{x}_1 - \boldsymbol{x}_2|$.

2. Matrices

Before introducing matrix multiplication we wish to point out that—as a modern computer package—MATLAB has extensive built-in documentation. The command `helpdesk` gives access to a very elaborate interactive help facility. The command `help cmd` gives help on the specified command `cmd`. The command `more on` causes `help` to pause between screenfuls if the help text runs to several screens. In the online help, keywords are capitalized to make them stand out. *Always type commands in lowercase* since *all* command and function names are actually in lowercase. Recall in this context that MATLAB is case sensitive. Don't be confused by the capitals in the help, practically all MATLAB commands are in lower case only.

2.1 Matrix multiplication

Matrices and their multiplication.
Turning to matrices, we first observe that a column vector of length n is a special case of an $n \times m$ matrix, namely one with $m = 1$. A matrix can be constructed by concatenation. This is the process of joining smaller matrices (or vectors) to make bigger ones. In fact, you made your first matrix by concatenating its individual elements. The pair of square brackets, `[]`, is the concatenation operator. Example:

```
>> a = [1  3 -5]';
>> b = [2  1  7]';
>> c = [-1 6  1]';
>> [a b c]
ans =
     1     2    -1
     3     1     6
    -5     7     1
>> [a b c c b a]
ans =
     1     2    -1    -1     2     1
     3     1     6     6     1     3
    -5     7     1     1     7    -5
```

A matrix may be entered as rows, just like column vectors, which for MATLAB are in fact nothing but non-square matrices. Example of entering a 2×4 matrix (2 rows, 4 columns):

```
>> A=[ 10.1  -9.1 67.3 88.0;
       -11.0  13.1  1.2 14.7]
A =
   10.1000   -9.1000   67.3000   88.0000
  -11.0000   13.1000    1.2000   14.7000
```

Just as we saw for vectors, single elements may be accessed by e.g., `A(2,3)` (returns `1.2000`). Also ranges, e.g., `A(1,2:end)` (returns the row vector `[-9.1000 67.3000 88.0000]`) can be extracted.

During your linear algebra course you learned the matrix-vector multiplication. We briefly recall the rule. Suppose the matrix $\boldsymbol{A}$ consists of m columns $\boldsymbol{a}_i$, $i = 1, \ldots, m$. Each vector $\boldsymbol{a}_i$ is of length n, i.e., $\boldsymbol{A}$ is an $n \times m$ matrix. In order that the matrix-vector multiply $\boldsymbol{A}\,\boldsymbol{c}$ is possible, it is necessary that the column vector $\boldsymbol{c}$ is of length m. Indeed,

$$\boldsymbol{A}\,\boldsymbol{c} \equiv (\boldsymbol{a}_1\ \boldsymbol{a}_2 \cdots \boldsymbol{a}_m) \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_m \end{pmatrix} = c_1\boldsymbol{a}_1 + c_2\boldsymbol{a}_2 + \cdots + c_m\boldsymbol{a}_m,$$

from which the j^{th} $(j = 1, \ldots, n)$ component follows

$$(\boldsymbol{A}\,\boldsymbol{c})_j = (\boldsymbol{a}_1)_j\ c_1 + (\boldsymbol{a}_2)_j\ c_2 + \cdots + (\boldsymbol{a}_m)_j\ c_m = \sum_{i=1}^{m} A_{ji}\ c_i,$$

where the matrix element $A_{ji} \equiv (\boldsymbol{a}_i)_j$ is the j^{th} component of $\boldsymbol{a}_i$. The result of the multiplication $\boldsymbol{A}\,\boldsymbol{c}$ is a column vector of length n.

Back in MATLAB we note that the matrix-vector multiplication is simply given by `*`, *provided the dimensions are correct.* In order to give an example we introduce the MATLAB function `rand`; `rand(n,m)` returns a matrix with n rows and m columns of which the elements are positive random numbers in the range $0 \cdots 1$.

```
>> A=rand(4,3)
A =
    0.1934    0.1509    0.8537
    0.6822    0.6979    0.5936
    0.3028    0.3784    0.4966
    0.5417    0.8600    0.8998
```

```
>> c=rand(3,1)  % A column vector of length 3
c =
    0.8216
    0.6449
    0.8180
>> A*c          % Matrix-vector multiply
ans =           % A column vector of length 4
    0.9545
    1.4961
    0.8989
    1.7357
>> d=rand(4,1)  % A column vector of length 4
d =
    0.6602
    0.3420
    0.2897
    0.3412
>> A*d           % Try a matrix vector multiply
??? Error using ==> *
Inner matrix dimensions must agree.
```

Suppose now that we have a set of k column vectors $\boldsymbol{c}_1, \boldsymbol{c}_2, \ldots, \boldsymbol{c}_k$, all of lenght m. We can apply the matrix-vector multiplication rule to the vector $\boldsymbol{c}_j$ and do this consecutively for $j = 1, \ldots, k$,

$$(\boldsymbol{A}\,\boldsymbol{c}_j)_{j'} = \sum_{i=1}^{m} A_{j'i}\,(\boldsymbol{c}_j)_i\,.$$

If we introduce an $m \times k$ matrix $\boldsymbol{C}$ with general element $C_{ij} \equiv (\boldsymbol{c}_j)_i$ we can write

$$(\boldsymbol{A}\,\boldsymbol{C})_{j'j} = \sum_{i=1}^{m} A_{j'i} C_{ij}$$

with $j' = 1, \ldots, n$ and $j = 1, \ldots, k$. The second (column) index of $\boldsymbol{A}$ must agree with the first (row) index of $\boldsymbol{C}$, otherwise matrix multiplication is not possible. MATLAB refers to these indices as 'inner matrix dimensions'. In this parlance n and k are the 'outer matrix dimensions', they are independent.

2.2 Non-singular and special matrices

Non-singular matrices and determinant. The unit matrix, random matrix and a matrix with ones.

The identity (or unit) matrix $\boldsymbol{I}$ plays an important role in linear algebra. It is a square matrix with off-diagonal elements zero and the number one on the diagonal,

$$(\boldsymbol{I})_{ij} = \delta_{ij},$$

where the Kronecker delta was defined in Eq. (1.1). MATLAB has the phonetic name 'eye' for the function that returns the identity matrix.

```
>> eye(4)
ans =
     1     0     0     0
     0     1     0     0
     0     0     1     0
     0     0     0     1
```

The command `ones(n)` returns an $n \times n$ matrix containing unity in all entries. In Table 2.1 we list a few more of these commands.

Table 2.1: *Elementary matrices*

blkdiag	Construct a block diagonal matrix from input arguments
eye	Identity matrix
linspace	Generate linearly spaced vectors
logspace	Generate logarithmically spaced vectors
ones	Create an array of all ones
rand	Uniformly distributed random numbers and arrays
randn	Normally distributed random numbers and arrays
zeros	Create an array of all zeros

The following facts are proved in linear algebra.

1. An $n \times n$ matrix $\boldsymbol{A}$ is called non-singular if it has an inverse. That is, another $n \times n$ matrix $\boldsymbol{A}^{-1}$ (the inverse of $\boldsymbol{A}$) exists that has the property $\boldsymbol{A}^{-1}\boldsymbol{A} = \boldsymbol{A}\boldsymbol{A}^{-1} = \boldsymbol{I}$.

2. If the n columns of an $n \times n$ matrix are linearly independent then the matrix is non-singular.

3. If the n rows of an $n \times n$ matrix are linearly independent then the matrix is non-singular.

4. If a square matrix is non-singular then its columns are linearly independent and so are its rows.

5. Remember that the determinant $\det(\boldsymbol{A})$ of the real square matrix $\boldsymbol{A}$ is a (fairly complicated) map $\boldsymbol{A} \mapsto \mathbb{R}$, i.e., $\det(\boldsymbol{A})$ is a real number. The square matrix $\boldsymbol{A}$ is non-singular if and only if $\det(\boldsymbol{A}) \neq 0$.

```
>> A=rand(4,4)   % Make a square matrix
A =
    0.5341    0.5681    0.4449    0.9568
    0.7271    0.3704    0.6946    0.5226
    0.3093    0.7027    0.6213    0.8801
    0.8385    0.5466    0.7948    0.1730

>> det(A)        % What is its determinant?
ans =
    0.0617       % Non-zero, the inverse of A exists.

>> Ai=inv(A)     % Calculate the inverse
Ai =
    3.6375    0.3718    0.0517   -3.0577
   -3.2104    0.1104   -0.6997    3.7590
   -1.9243    3.4861    0.0636    1.0540
    0.3974   -2.4293    0.9644    0.0306

>> A*Ai-eye(4)   % Subtract unit matrix
ans =
  1.0e-015 *     % Prefactor for the total matrix
   -0.1110   -0.2220    0.0555   -0.0278
   -0.0139   -0.2220   -0.0069   -0.0278
         0         0   -0.1110   -0.0486
    0.1943   -0.2220    0.1110         0
```

Here we used that matrices of the same dimensions can be subtracted and we see that $\boldsymbol{A}\ \boldsymbol{A}^{-1}$ is equal to the identity matrix within numerical precision (15 to 16 digits). Here MATLAB applies the rule that $c\boldsymbol{A}$ gives a matrix in which each individual matrix element is multiplied by the real number c.

We have seen that the operator ' turns a row vector into a column vector and vice versa. If we replace all rows of a matrix by its columns we transpose the matrix, i.e., if $\boldsymbol{A}$ has the matrix elements $A_{ij},\ i = 1, \ldots, n, j = 1, \ldots, m$ then $\boldsymbol{A}^T$ has the matrix elements $A_{ji},\ i = 1, \ldots, n,\ j = 1, \ldots, m$. Transposition of matrices is performed by ' as well.

```
>> A=rand(4,2)
```

```
A =
    0.4235    0.2259
    0.5155    0.5798
    0.3340    0.7604
    0.4329    0.5298
>> B=A'
B =

    0.4235    0.5155    0.3340    0.4329
    0.2259    0.5798    0.7604    0.5298
```

2.3 Matrix factorizations

QR decomposition of arbitrary matrices and diagonalization of symmetric matrices.

The purpose of this section is to introduce the important MATLAB functions `qr`, `eig`, and `sort`. Before introducing these functions, we recall again some relevant linear algebra.

A real $n \times n$ matrix $\boldsymbol{Q} = (\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{q}_n)$ is called *orthogonal* when its columns are orthonormal (orthogonal *and* normalized). This condition can be expressed in two ways,

$$\boldsymbol{Q}^T\boldsymbol{Q} = \boldsymbol{I} \Longleftrightarrow \boldsymbol{q}_i \cdot \boldsymbol{q}_j = \delta_{ij} \text{ for } i, j = 1, \ldots, n. \tag{2.1}$$

It follows immediately that also the rows of $\boldsymbol{Q}$ are orthonormal, because,

$$\begin{aligned} \boldsymbol{Q}^T\boldsymbol{Q} &= \boldsymbol{I} \Longrightarrow \boldsymbol{Q}^T = \boldsymbol{Q}^{-1} \Longrightarrow \boldsymbol{Q}\boldsymbol{Q}^T = \boldsymbol{I} \\ &\Rightarrow \delta_{ij} = \left(\boldsymbol{Q}\boldsymbol{Q}^T\right)_{ij} = \sum_k \boldsymbol{Q}_{ik}\boldsymbol{Q}^T_{kj} = \sum_k \boldsymbol{Q}_{ik}\boldsymbol{Q}_{jk}. \end{aligned} \tag{2.2}$$

Since the sum is over the column index k, the rightmost expression is nothing but the inner product between row i and row j of $\boldsymbol{Q}$.

An important theorem of linear algebra states that *any* real $n \times m$ matrix $\boldsymbol{A}$ can be factorized as

$$\boldsymbol{A} = \boldsymbol{Q}\boldsymbol{R},$$

where $\boldsymbol{Q}$ is an $n \times n$ orthogonal matrix and $\boldsymbol{R}$ is an $n \times m$ upper triangular matrix. (Remember that an upper triangular matrix $\boldsymbol{R}$ has only vanishing elements below the main diagonal, i.e., $R_{ij} = 0$ for $i > j$). This theorem is known as the "QR decomposition" of $\boldsymbol{A}$. One way of looking upon this

theorem is as a decomposition of the columns $\boldsymbol{a}_j$ of $\boldsymbol{A}$ in an orthonormal basis $\{\boldsymbol{q}_k\}$:

$$\begin{aligned} A_{ij} &= \sum_{k=1}^{n} Q_{ik}R_{kj} = \sum_{k=1}^{j} (\boldsymbol{q}_k)_i R_{kj} \Longleftrightarrow (\boldsymbol{a}_j)_i = \sum_{k=1}^{j} (\boldsymbol{q}_k)_i R_{kj} \\ &\Leftrightarrow \quad \boldsymbol{a}_j = \sum_{k=1}^{j} \boldsymbol{q}_k R_{kj} = \boldsymbol{q}_1 R_{1j} + \boldsymbol{q}_2 R_{2j} + \cdots + \boldsymbol{q}_j R_{jj}. \end{aligned} \tag{2.3}$$

A matrix $\boldsymbol{D}$ is called *diagonal* when all its off-diagonal elements D_{ij}, $i \neq j$, are zero, $D_{ij} = d_i\,\delta_{ij}$. A real $n \times n$ matrix $\boldsymbol{H}$ is called *symmetric* if $\boldsymbol{H} = \boldsymbol{H}^T$, i.e., $H_{ij} = H_{ji}$ for all $i, j = 1, \ldots, n$.

Another important theorem states that an $n \times n$ symmetric matrix $\boldsymbol{H}$ can be brought to diagonal form by the following "orthogonal similarity transformation"

$$\boldsymbol{Q}^T\,\boldsymbol{H}\,\boldsymbol{Q} = \boldsymbol{D} \tag{2.4}$$

Here $\boldsymbol{Q}$ is orthogonal and $\boldsymbol{D}$ is diagonal. If $\boldsymbol{H}$ is real, then also $\boldsymbol{Q}$ and $\boldsymbol{D}$ are real. Because $\boldsymbol{Q}^T = \boldsymbol{Q}^{-1}$, this equation can be rewritten:

$$\boldsymbol{H}\boldsymbol{Q} = \boldsymbol{Q}\boldsymbol{D} \Longrightarrow \boldsymbol{H}\boldsymbol{q}_i = \boldsymbol{q}_i\,d_i, \quad \text{for} \quad i = 1, \ldots, n. \tag{2.5}$$

The equation $\boldsymbol{H}\,\boldsymbol{q} = d\,\boldsymbol{q}$ is known as the *eigenvalue equation* of $\boldsymbol{H}$. The scalar (real number) d is an eigenvalue of $\boldsymbol{H}$ and the vector $\boldsymbol{q}$ is the corresponding eigenvector. Equations (2.4) and (2.5) state in fact that a symmetric matrix has n eigenvectors $\boldsymbol{q}_i$ that are orthonormal. Since orthonormality implies linear independence, the n vectors $\boldsymbol{q}_i$ form an orthonormal basis of $\mathbb{R}^n$.

The collection of eigenvalues $\{d_i\}$ of $\boldsymbol{H}$ is called the *spectrum* of $\boldsymbol{H}$. (This term originates from quantum mechanics, where eigenvalue problems of symmetric matrices explain the existence of spectra of atoms and molecules). The process of finding the diagonal matrix $\boldsymbol{D}$ containing the eigenvalues of $\boldsymbol{H}$ and the corresponding eigenvectors of $\boldsymbol{H}$ (the columns of $\boldsymbol{Q}$) is called *the diagonalization of* $\boldsymbol{H}$.

Remember the rule $(\boldsymbol{A}\boldsymbol{B})^T = \boldsymbol{B}^T\,\boldsymbol{A}^T$, then applying this rule, we find easily that $\left(\boldsymbol{Q}^T\,\boldsymbol{A}\,\boldsymbol{Q}\right)^T = \boldsymbol{Q}^T\,\boldsymbol{A}^T\,\boldsymbol{Q}$. If $\boldsymbol{A}$ is symmetric, $\boldsymbol{A}^T = \boldsymbol{A}$, then the threefold product is also symmetric. Note that this general fact holds for the special case in Eq. (2.4), because a (real) diagonal matrix is obviously symmetric.

Finally, we want to point out that Eq. (2.4), or equivalently Eq. (2.5), determines the eigenvectors up to sign. If $\boldsymbol{q}$ is a normalized eigenvector with eigenvalue d then so is $-\boldsymbol{q}$,

$$\boldsymbol{H}\,\boldsymbol{q} = d\,\boldsymbol{q} \Longrightarrow \boldsymbol{H}(-\boldsymbol{q}) = d(-\boldsymbol{q}) \quad \text{and} \quad \boldsymbol{q}\cdot\boldsymbol{q} = (-\boldsymbol{q})\cdot(-\boldsymbol{q}) = 1. \tag{2.6}$$

2.4 Exercises

Exercise 12.

Consider the following matrices and their dimensions: $\boldsymbol{A}$ (4×5), $\boldsymbol{B}$ (4×10), $\boldsymbol{C}$ (10×4), and $\boldsymbol{D}$ (5×5). Predict the dimensions of $\boldsymbol{ADA}^T$ and $\boldsymbol{BCAD}$. Verify your answer by creating the matrices with the MATLAB function `rand` and by explicit matrix multiplication in MATLAB.

Exercise 13.

1. Enter the statements necessary to create the following matrices:

$$\boldsymbol{A}=\begin{pmatrix}1&4&6\\2&3&5\\1&0&4\end{pmatrix}\quad \boldsymbol{B}=\begin{pmatrix}2&3&5\\1&0&6\\2&3&1\end{pmatrix}$$

$$\boldsymbol{C}=\begin{pmatrix}5&1&9&0\\4&0&6&2\\3&1&2&4\end{pmatrix}\quad \boldsymbol{D}=\begin{pmatrix}3&2&5\\4&1&3\\0&2&1\\2&5&6\end{pmatrix}$$

2. Compute the following using MATLAB, and write down the results. If you receive an error message rather than a numerical result, explain the error.

a.	`A+B`	g.	`C+D`
b.	`A-2.*B`	h.	`C'+D`
c.	`(A-2).*B`	i.	`C.*D`
d.	`A.^2`	j.	`A-2*eye(3)`
e.	`sqrt(A)`	k.	`A-ones(3)`
f.	`C'`	l.	`A^2`

Exercise 14.

Read the help of `eye` and `ones`. Create the following matrices, each with one statement,

$$\begin{pmatrix}1&0&0&0&0\\0&1&0&0&0\\0&0&1&0&0\end{pmatrix}\quad\text{and also}\quad\begin{pmatrix}1&1&1\\1&1&1\\1&1&1\\1&1&1\\1&1&1\end{pmatrix}.$$

Exercise 15.

The position of the center of mass of a rigid molecule consisting of n nuclei is given by the vector

$$\boldsymbol{c} = \frac{1}{M}\sum_{i=1}^{n} m_i \boldsymbol{r}_i = \frac{1}{M}(\boldsymbol{r}_1\ \boldsymbol{r}_2\ \cdots\ \boldsymbol{r}_n)\begin{pmatrix} m_1 \\ m_2 \\ \vdots \\ m_n \end{pmatrix}$$

Here m_i is the mass of nucleus i (mass of electrons is neglected) and $\boldsymbol{r}_i$ is the position of nucleus i, $M = \sum_{i=1}^{n} m_i$ is the total nuclear mass of the molecule.

Consider now the isotope substituted methane CH_2D_2 with $m_C \equiv 12$ u, $m_H \approx 1$ u, $m_D \approx 2$ u, where u is the unified atomic mass unit. Take a frame (system of axes) with C in the origin and use the geometry of methane described in exercise 6 of Sec. 1.3.

- Compute the position coordinates of the protons and the deuterons and put these together with the position vector of carbon into a 3×5 matrix $\boldsymbol{R}$.
- Put the five nuclear masses into a corresponding column vector and compute the total mass (the MATLAB function `sum` returns the sum of the elements of a vector).
- Compute the center of mass $\boldsymbol{c}$ by matrix vector multiplication. Is the center of mass closer to the deuterons than to the protons?

Next we translate the frame so that its origin coincides with the center of mass. Mathematically, this is accomplished as follows

$$\boldsymbol{R}' \equiv \boldsymbol{R} - \underbrace{(\boldsymbol{c}\ \boldsymbol{c}\ \cdots\ \boldsymbol{c})}_{n \text{ times}} \text{ with } \boldsymbol{R} \equiv (\boldsymbol{r}_1\ \boldsymbol{r}_2\ \cdots\ \boldsymbol{r}_n)$$

since

$$\begin{aligned} \boldsymbol{R}'\begin{pmatrix} m_1 \\ m_2 \\ \vdots \\ m_n \end{pmatrix} &\equiv (\boldsymbol{r}'_1\ \boldsymbol{r}'_2\ \cdots\ \boldsymbol{r}'_n)\begin{pmatrix} m_1 \\ m_2 \\ \vdots \\ m_n \end{pmatrix} = \boldsymbol{R}\begin{pmatrix} m_1 \\ m_2 \\ \vdots \\ m_n \end{pmatrix} - (\boldsymbol{c}\ \cdots\ \boldsymbol{c})\begin{pmatrix} m_1 \\ m_2 \\ \vdots \\ m_n \end{pmatrix} \\ &= M\boldsymbol{c} - \boldsymbol{c}\sum_{i=1}^{n} m_i = \boldsymbol{0} \end{aligned}$$

or

$$\boldsymbol{c}' \equiv \frac{1}{M}\sum_{i=1}^{n} m_i \boldsymbol{r}'_i = \boldsymbol{0}.$$

- Compute the coordinates of the nuclei of CH_2D_2 (including the position of carbon) with respect to the translated frame.
  Hint: The translation matrix can be constructed as `[c c c c c]`, more elegant is by `repmat(c,1,5)`, see help repmat.

Exercise 16.

The function reference `qr(A)` gives the QR decomposition of `A`. The function `qr(A)` is an example of a MATLAB function that can optionally return more than one parameter: `[Q R] = qr(A)` returns both the orthogonal matrix `Q` and the upper triangular matrix `R`. Decompose `A=rand(5,i)` for `i=1,3,5,7`. Check in all four cases whether `Q` is orthogonal and inspect `R` to see if it is upper triangular.

Exercise 17.

In this exercise we construct a symmetric matrix with a known spectrum (the set $\{0, 1, 2, 3, 4, 5, 6, 7, 8, 9\}$) and we will diagonalize this matrix to verify that the spectrum is indeed generated.

- Create a 10×10 diagonal matrix `D` with 0,1, ..., 9 on the diagonal. (See help of `diag`).
- Create a 10×10 random orthogonal matrix `Q` from `A=rand(10)` and `qr(A)`.
- Create a 10×10 symmetric matrix `H=Q*D*Q'`. Check whether `H-H'` is the zero matrix, i.e., that `H` is indeed symmetric. The matrix `H` has by construction the spectrum `0,1,...,9`.
- Get the eigenvectors `V` and eigenvalue matrix `D1` of `H`. (See the help of `eig`). Inspect the diagonal matrix `D1`, are the diagonal elements indeed what you expect? Verify that `V` is orthogonal.
- Get the eigenvalues (diagonal elements of `D1`) of `H` into a column vector `D2` (see again the help of `diag`) and sort this vector, with the result in `Ds` (see the help of `sort`). In addition to `Ds`, the function `sort` can also return a permutation that may be applied to the columns of `V`. Apply this permutation to get a sorted 10×10 matrix `Vs`. (Note in this connection that a statement of the type `V(:,[2,3,1]` returns an array with the second, third, and first column of `V`, respectively).
- Make out of the vector `Ds` a 10×10 diagonal matrix `D3` and verify that within numerical precision

```
H*Vs = Vs*D3
```

Do this by performing explicitly the matrix multiplication on the left and right hand side of this equation.

- Compare the columns of `Vs` with those of `Q`. Are they the same?

3. Scripts and plotting

3.1 Scripts

Use of matlab editor for writing scripts.
So far we used MATLAB as a calculator and typed in commands on the fly (although doubtlessly you will have discovered MATLAB's history mechanism). When one has to type in longer sequences of MATLAB commands, it is pleasant to be able to edit and save them. Sequences of commands can be stored in *scripts*. A script is a flat (ASCII, plain) file containing MATLAB commands that are executed one after the other. A script can be prepared by any ASCII editor, such as Microsoft's NOTEPAD (but not by Microsoft's WORDPAD or WORD!). We will use the editor contained in MATLAB. This editor can be started from the MATLAB prompt by the command `edit`. The scripts must be saved under the name `anyname.m`, where `anyname` is for the user to define.
Advice:

- Use meaningful names for your scripts, because experience shows that you will forget very soon what a script is supposed to do.
- Save your scripts on your UNIX disk, this disk is backed up, whereas your MS-WINDOWS disk is cleared after you finish working, (not at home, of course, but in the university computer rooms).
- Mind where you are with your directories and disks. MATLAB shows your current directory in the toolbar. When you are about to save a script, the editor allows you to browse and change directories to your UNIX disk before actually saving. From the MATLAB session you can also browse and change directories by clicking the button to the right of the "current directory" field.
- Let the first few lines be comments explaining the script. These comments can be shown in your MATLAB session by `help name`, where `name` is the name of your script.

Provided your script is in your current directory, you can execute it by simply typing in `anyname`, where `anyname` is the meaningful name you have given to your script. Depending on the semicolons, you will see the commands being executed. If you have too much output on your screen you can toggle

`more on/more off`. Press the "q" key to exit out of displaying the current item.

It is important to notice that a script simply continues your MATLAB session, all variables that you introduced 'by hand' are known to the script. After the script has finished, all variables changed or assigned by the script stay valid in your MATLAB session. Technically this is expressed by the statement: *script variables are global*.

Sometimes statements in a script become unwieldily long. They can be continued over more than one line by the use of three periods `...`, as for example

```
s = 1 - 1/2 + 1/3 - 1/4 + 1/5 - 1/6 + 1/7 ...
      - 1/8 + 1/9 - 1/10 + 1/11 - 1/12 ...
      + 1/13 - 1/14;
```

Blanks around the $=$, $+$, and $-$ signs are optional, but they improve readability.

3.2 Plotting

Grids, 2D plotting.
Scripts are particularly useful for creating plots. MATLAB has extensive facilities for plotting. Very often one plots a function on a discrete grid. The MATLAB command for creating a grid is simple,

```
grid = beg:inc:end
```

Here `beg` gives the first grid value, `inc` the increment (default 1) and `end` the end value. Example:

```
>> g=0:pi/10:pi
g =
  Columns 1 through  5
  0  0.3142  0.6283  0.9425  1.2566  1.5708
  Columns 6 through  10
  1.8850  2.1991  2.5133  2.8274
  Column 11
  3.1416
```

If we now want to plot the sine function on this grid we simply issue the command `plot(g, sin(g))`, since the command `plot(x,y)` plots vector `y` versus vector `x`. After this command a new window opens with the plot.

Suppose we now also want to plot the cosine in the same figure. If we would enter `plot(g, cos(g))`, then the previous plot would be overwritten. We can toggle `hold on/off` to hold the plot. Alternatively, we can create two plots in one statement: `plot(g, sin(g), g, cos(g) )`, i.e,

```
>> plot(x1, y1, x2, y2)
```

plots vector `y1` versus vector `x1` and `y2` versus `x2`. Different colors and line types can be chosen, see help plot for information on this. For example, `plot(g,cos(g), 'r:')` plots the cosine as a red dotted line. Even briefer: `plot(g',[sin(g') cos(g')])` (columns of a matrix plotted against a vector, whta happens if you leave the '''s off).

The `xlabel` and `ylabel` functions add labels to the x and y axis of the current figure. Their parameter is a string (is contained in quotes), thus, e.g., `ylabel('sin(\phi)')` and `xlabel('\phi')`. The `title` function adds a title on top of the plot. Example:

```
phi=[0:pi/100:2*pi];
plot(phi*180/pi,sin(phi))
ylabel('sin(\phi)')
xlabel('\phi (degrees)')
title('Graph of the sine function')
```

For people who know the text editing system LaTeX this part of MATLAB is easy, since it uses quite a few of the LaTeX commands. `\phi` is LaTeX to get the Greek letter ϕ. (The present lecture notes are prepared by the use of LaTeX).

In case we want to plot more than one set of y values for the same grid of x values, MATLAB offers a solution. In the command `plot(x,y)` `x` is a vector, let us say it is a column vector of length n. Then `y` can be an $n \times k$ matrix (by definition consisting of k columns of length n). The plot command gives k curves as function of the grid x.
Example:

```
phi=[0:pi/100:2*pi]';
y(:,1) = cos(phi);
y(:,2) = sin(phi);
plot(phi, y)
title('Graph of the sine and cosine functions')
```

3.3 Exercises

Exercise 18.

Return to exercise 4 where you were asked to find the roots (zeros) of the polynomial

$$x^4 - 11.0x^3 + 42.35x^2 - 66.550x + 35.1384.$$

Write a MATLAB script to plot this function. Define first a grid (set of x points) with $0.6 \leq x \leq 4.9$ and plot the function on this grid (do not forget dots in the dot operations!). Try to find the roots of this polynomial graphically. When you have located the roots approximately refine your grids and try to get the roots with a two digit precision. The command `grid on` is helpful, try it!

Exercise 19.

Write a MATLAB script that plots the functions $\exp(-\alpha R)$ and $R\exp(-\alpha R)$ in one figure. Do not forget the dot (pointwise operation) at the appropriate places! Let the first curve be solid green and the second dashdotted blue. Assume that the grid R and the parameter α are first set by hand in the MATLAB session that calls the script. Once the script is finished, experiment with α and the grid to get a nice figure. Put to the x axis: 'distance R (a_0)', and use as a title 'Radial part of s and p functions'. **Hint:** the subscript 0 is obtained by the underscore: `a_0`.

Exercise 20.

Write a MATLAB script that plots the function

$$y = \frac{1}{(x-0.3)^2 + 0.01} + \frac{1}{(x-0.9)^2 + 0.04} - 6,$$

which has two humps. Compute in the script first the grid `0:0.002:1` and then the array (= vector) y and then call `plot(x,y)`. Start the script with the command `clear all`, which removes all variables from your MATLAB workspace, to avoid possible side effects.

Exercise 21.

Draw a circle with radius 1 and midpoint at $(0, 0)$.
Two possibilities (try both):
1. Make a grid for $-1 \leq x \leq 1$. Use $y = \pm\sqrt{1 - x^2}$, compute $\pm y$.
2. Make a grid of ϕ values $0 \leq \phi \leq 2\pi$, use $x = \cos\phi$, $y = \sin\phi$.

4. Matrices continued, flow control

4.1 Matrix sections

Sections out of matrices.
Thus far we have met twice the colon (`:`) operator: once to get a section out of a matrix and once to generate a grid. In fact, these are the very same uses of this operator. To explain this, we first observe that elements from an array (= matrix) may be extracted by the use of an index array with integer elements.
Example:

```
>> A = rand(5);
>> I = [1 3 5];
>> B = A(I,:);
>> A, B
A =
    0.9501    0.7621    0.6154    0.4057    0.0579
    0.2311    0.4565    0.7919    0.9355    0.3529
    0.6068    0.0185    0.9218    0.9169    0.8132
    0.4860    0.8214    0.7382    0.4103    0.0099
    0.8913    0.4447    0.1763    0.8936    0.1389

B =
    0.9501    0.7621    0.6154    0.4057    0.0579
    0.6068    0.0185    0.9218    0.9169    0.8132
    0.8913    0.4447    0.1763    0.8936    0.1389
```

Explanation:
For illustration purpose we created a 5×5 matrix `A` suppressing its printing. Then we created the integer array `I` and used it to create an array `B` that has the same columns as `A` but only row 1, 3, and 5 of `A`. Parenthetically, note the use of the comma, we can put more than one command on a single line: the commands must be separated by a semicolon (no printing) or a comma (do print).

We get the very same matrix `B` by the command `B=A(1:2:5,:)`, because 'on the fly' an array `[1,3,5]` is prepared and used to index `A`. Recall that

`1:2:5` generates the grid `[1,3,5]`, so that indeed the two uses of the colon are the same.

A similar mechanism can be used to remove rows and/or columns from a matrix. Using the same `A` and `I` as in the previous example,

```
>> C=A;
>> C(I,:)=[]
C =
    0.2311    0.4565    0.7919    0.9355    0.3529
    0.4860    0.8214    0.7382    0.4103    0.0099
```

Rows 1, 3 and 5 of `C` are replaced by empty rows indicated by `[]`. The arrays `B` and `C` are now complementary, together they give `A`. The matrix created by concatenation

```
>> D=[B(1,:); C(1,:); B(2,:); C(2,:); B(3,:)]
```

is identical to `A`.

If `v` has `m` components and `w` has `n` components, then `A(v,w)` is the $m \times n$ matrix formed from the elements of `A` whose subscripts are the elements of `v` and `w`. Example:

```
>> A,v,w  % show A and the index arrays
A =
    0.2028    0.0153    0.4186    0.8381
    0.1987    0.7468    0.8462    0.0196
    0.6038    0.4451    0.5252    0.6813
    0.2722    0.9318    0.2026    0.3795
    0.1988    0.4660    0.6721    0.8318
v =
     1     1     2              % m = 3
w =
     3     4     3     4     2  % n = 5
>> B=A(v,w)                     % 3-by-5 matrix
B =
    0.4186    0.8381    0.4186    0.8381    0.0153
    0.4186    0.8381    0.4186    0.8381    0.0153
    0.8462    0.0196    0.8462    0.0196    0.7468
```

Explanation: The matrix `B` becomes

$$\begin{pmatrix} A_{13} & A_{14} & A_{13} & A_{14} & A_{12} \\ A_{13} & A_{14} & A_{13} & A_{14} & A_{12} \\ A_{23} & A_{24} & A_{23} & A_{24} & A_{22} \end{pmatrix}$$

Rows are labeled by `v` and columns by `w`. Note that elements of `A` can be used more than once. This mechanism allows us, for example, to replicate a vector:

```
x =                    % show x
     1
     2
     3
     4
     5
>> X=x(:,ones(1,3))  % is the same as x([1:5],[1 1 1])
X =
     1     1     1
     2     2     2
     3     3     3
     4     4     4
     5     5     5
```

Alternatively, we may use the MATLAB command `repmat`, which in fact uses the same mechanism. The following command constructs the very same matrix `X`: `repmat(x,1,3)`.

4.2 Flow control

For and while loops, if then else, break.
It often happens that one wants to repeat a calculation for different values of a parameter. To this end MATLAB uses the *for loop*. The general form of a `for` statement is:

```
for var = expr
   statement
    ...
   statement
end
```

Here `expr` can be a rectangular array, although in practice it is usually a row vector of the form `x:y`, in which case its columns are simply scalars. The columns of `expr` are assigned one at a time to `var` and then the following statements, up to `end`, are executed. For loops can be nested:

```
A=zeros(10,5);
for i = 1:10
    for j = 1:5
```

```
        A(i,j) = 1/(i+j-1);
    end
end
```

In a situation as in this example it helps MATLAB a lot if it knows in advance how large a matrix is going to be. It saves much computer time if the loops in the previous example are preceded by the command which initializes `A` to a 10×5 matrix, (which are here taken to be zeros, but `ones(10,5)` would have done as well).

As an example where columns are used as loop variables we flip the columns of `A`

```
A=rand(5,3);
B=zeros(5,3);
i=4;
for a=A       % a runs from column 1 upwards to column 3
  i=i-1;      % i counts down
  B(:,i) = a;
end
```

(This loop is achieved in one statement by the MATLAB function `fliplr` which issues a statement similar to `B=A(:,3:-1:1)`).

The `break` statement can be used to terminate the loop prematurely. To explain this we first need to discuss the `if` expression.

Leaving aside some sophisticated array indexing situations, MATLAB behaves most of the time as if it does not know logical (boolean) variables. MATLAB uses non-zero for true and zero for false. The comparison operator is `==`, i.e., `a==b` yields non-zero (1) if `a` and `b` are equal and 0 otherwise:

```
>> 1==2
ans =
     0
>> 1==1
ans =
     1
```

The function `disp` can be used to display strings and the following statements illustrate the use of `if`

```
>> if pi disp('yes'), end   % pi=3.14.. is non-zero
yes                         % output of disp
>> if 0 disp('yes'), end    % no output
```

The keyword `if` needs a corresponding `end`.

The general syntax of the `if` statement is

```
if expression
  statements
elseif expression
  statements
else
  statements
end
```

The statements are executed if the expression has all non-zero elements. The `else` and `elseif` parts are optional. Zero or more `elseif` parts can be used as well as nested `if`s. The expression is usually of the form

```
expr rop expr
```

where the relational operator `rop` is:

`==`	equal
`<`	less than
`>`	greater than
`<=`	less or equal
`>=`	greater or equal
`~=`	not equal

We return now to the `break` command which terminates execution of a for (and while) loop. In nested loops, `break` exits from the innermost loop only. As an example we suppose that we have an array with a number of positive elements followed by negative elements. We want to take square roots of the positive elements only.

```
V=[rand(5,1); -rand(4,1)]; % a column
i = 0;
for v=V'                   % here we want a row
  if v >= 0, i = i+1; w(i)=sqrt(v);
  else break
  end                      % end of if
end                        % end of for loop
i                          % break jumps to here
```

An alternative solution of the same problem is with the *while loop*:

```
V=[rand(5,1); -rand(4,1)];
i = 1;
v = V(1);
while v >=0    % returns zero(false) or non-zero(true)
  w(i)=sqrt(v);
  i = i+1;
  v = V(i);
end
v              % v is negative here!
```

Explanation:
The command `while` repeats statements up to `end` an indefinite number of times. The general form of a `while` statement is:

```
while expr
    statements
    ....
    statements
end
```

The statements in the body of the while loop are executed as long as the `expr` has only non-zero elements. Usually `expr` is a logical expression that results in 0 or 1. As soon as `expr` becomes 0 the loop is quitted.

4.3 Exercises

Exercise 22.

What is the value of `i` printed as last statement of the following script?

```
V=[rand(2,1); -rand(2,1); rand(2,1); -rand(2,1)]
i = 1;
v = V(i);
while v >= 0
  i = i+1;
  v = V(i);
end
i
```

Exercise 23.

1. Write a script with the MATLAB editor to create a 10×10 matrix `V` in which row i contains the numbers

$$10(i-1)+1,\ 10(i-1)+2,\ \cdots,\ 10(i-1)+10 = 10i.$$

   Use a for loop running from 1 to 10. The body of this loop must contain one statement only.

2. Create a vector `v` containing the numbers $1, 2, \cdots, 100$. Read the help of `reshape` and create the matrix `V` of the previous question out of `v`.

3. Create from `V` a 10×5 matrix containing even numbers ≤ 100 only.

Exercise 24.

Write a script that returns the unique matrix elements of a square matrix `A` in a column vector. Use the following algorithm:

- Make a vector out of `A` by `a=A(:)`. This creates a column vector with the columns of `A` stacked on top of each other.
- Sort the vector `a` by the MATLAB command `sort`, now we are assured that the elements appearing more than once are adjacent.
- Loop over the sorted vector and retain of each element only one unique copy. The length of `a` is obtained by `l=length(a)`.

Apply your script to the matrix:

$$\boldsymbol{A} = \begin{pmatrix} 1 & 2 & 1 \\ 2 & 4 & 2 \\ 3 & 3 & 5 \end{pmatrix}.$$

Exercise 25.

A Vandermonde[1] matrix is generated from the column vector $\boldsymbol{x} = \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix}$ as follows:

$$\begin{pmatrix} 1 & x_1 & x_1^2 & x_1^3 & \cdots & x_1^{n-1} \\ 1 & x_2 & x_2^2 & x_2^3 & \cdots & x_2^{n-1} \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ 1 & x_n & x_n^2 & x_n^3 & \cdots & x_n^{n-1} \end{pmatrix}$$

Write a script that computes the Vandermonde matrix from a column vector `x` of arbitrary length.

[1] Alexandre-Théophile Vandermonde (1735-1796) was the founder of determinant theory.

Hint:
This script does not need more than three statements if we use `cumprod`; see its help.

Exercise 26.

You may have noticed that the description above of the `if elseif else end` construction was very brief. In particular it was not explained what happens if conditions in different `elseif`s are simultaneously true. Look at the following three programs and predict what they put on the screen.

```
a=-3;                 |  a=-3;                 |  a=-3;
if a < -5             |  if a < -5             |  if a < -3
  disp(' < -5 ')      |    disp(' < -5 ')      |    disp(' < -3 ')
elseif a < -2         |  elseif a < -1         |  elseif a < -4
  disp(' < -2 ')      |    disp(' < -1 ')      |    disp(' < -4 ')
elseif a < -1         |  elseif a < -2         |  elseif a < -5
  disp(' < -1 ')      |    disp(' < -2 ')      |    disp(' < -5 ')
else                  |  else                  |  else
  disp('rest')        |    disp('rest')        |    disp('rest')
end                   |  end                   |  end
```

Make a script out of the first program and verify your prediction. Then edit this script to get the second program and verify again, and do this also for the third program.

Exercise 27.

In quantum mechanics the angular momentum operators $l_x,\ l_y,\ l_z$ play an important role. Also $l_+ \equiv l_x + il_y$ and $l_- \equiv l_x - il_y$ are often considered. The latter operators are represented by $(2l+1) \times (2l+1)$ matrices with indices $m = -l, \ldots, l$ and $m' = -l, \ldots, l$. They are defined by

$$(\boldsymbol{L}_\pm)_{mm'} = \delta_{m,m'\pm 1}\sqrt{l(l+1) - m'(m' \pm 1)}$$

That is, $\boldsymbol{L}_+$ is almost completely zero with only non-zero elements on the diagonal above the main diagonal. Likewise, $\boldsymbol{L}_-$ has only elements on the diagonal below the main diagonal.

1. Compute the two vectors $\boldsymbol{s}_\pm = \sqrt{l(l+1) - m(m \pm 1)}$ for $l = 5$ and $m = -5, \ldots 5$. Both vectors are of length $2l + 1$.

2. Read the help of `diag` and construct from the two vectors $\boldsymbol{s}_\pm$ the matrices $\boldsymbol{L}_+$ and $\boldsymbol{L}_-$ by means of `diag`.

Hint: The lower diagonal matrix $\boldsymbol{L}_-$ starts at $(m, m') = (-l+1, -l)$ and ends at $(m, m') = (l, l-1)$, whereas the upper diagonal matrix $\boldsymbol{L}_+$ starts at $(m, m') = (-l, -l+1)$ and ends at $(m, m') = (l-1, l)$. This means that the first and last element, respectively, of the vectors $\boldsymbol{s}_-$ and $\boldsymbol{s}_+$ must not be used in the command `diag`.

3. Compute $\boldsymbol{L}_x = (\boldsymbol{L}_+ + \boldsymbol{L}_-)/2$ and $\boldsymbol{L}_y = (\boldsymbol{L}_+ - \boldsymbol{L}_-)/(2i)$.
   Hint: Compute the imaginary number i by $\sqrt{-1}$.

4. Compute $i\big(\boldsymbol{L}_x\boldsymbol{L}_y - \boldsymbol{L}_y\boldsymbol{L}_x\big)$. Do you recognize the result?

5. Least squares fitting

5.1 Linear equations

Linear equations, backslash operator.
Consider the square system of n linear equations with n unknowns $x_1, \cdots, x_n$,

$$\begin{aligned} A_{11}x_1 + A_{12}x_2 + \cdots A_{1n}x_n &= y_1 \\ A_{21}x_1 + A_{22}x_2 + \cdots A_{2n}x_n &= y_2 \\ \cdots\cdots\cdots & \\ A_{n1}x_1 + A_{n2}x_2 + \cdots A_{nn}x_n &= y_n \end{aligned}$$

or more compactly

$$\boldsymbol{A}\,\boldsymbol{x} = \boldsymbol{y} \quad \text{where } \boldsymbol{A} \text{ is } n \times n, \quad \boldsymbol{x} \text{ and } \boldsymbol{y} \text{ are } n \times 1. \tag{5.1}$$

Here $\boldsymbol{A}$ and $\boldsymbol{y}$ are known and $\boldsymbol{x}$ must be solved. We already met the matrix function `inv`. This function computes the inverse of a non-singular matrix. One solution would be therefore to write simply `x = inv(A)*y`. Since inverting a matrix is in fact equivalent to solving n times a system of n linear equations with the n columns of the identity matrix playing the role of the right hand sides $\boldsymbol{y}$, it is clear that inversion of $\boldsymbol{A}$ is usually too expensive in terms of computer time. MATLAB can solve the system in one statement: `x=A\y`. Here we meet for the first time the backslash operator (`\`). This operator has much similarity with the slash operator (`/`). A quantity hiding under the slash is inverted, thus `1/5=0.200` and

$$\begin{pmatrix} 1 & 1 \end{pmatrix} / \begin{pmatrix} 5 & 0 \\ 0 & 2 \end{pmatrix} \equiv \begin{pmatrix} 1 & 1 \end{pmatrix} \begin{pmatrix} 5 & 0 \\ 0 & 2 \end{pmatrix}^{-1} = \begin{pmatrix} 1/5 & 1/2 \end{pmatrix}.$$

This reads in MATLAB

```
>> [1 1]/[5 0; 0 2]
ans =
    0.2000    0.5000
```

(Remember that the inverse of a diagonal matrix is again a diagonal matrix with the inverses of the diagonal elements on the diagonal). In the very same

way a quantity hiding under the backslash is inverted, thus `5\1=0.200`. The equation

$$\begin{pmatrix} 5 & 0 \\ 0 & 2 \end{pmatrix}^{-1} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1/5 \\ 1/2 \end{pmatrix}$$

reads in MATLAB

```
>> [5 0; 0 2]\ [1; 1]
ans =
    0.2000
    0.5000
```

So, as long as the matrix $\boldsymbol{A}$ in Eq. (5.1) is non-singular, the solution of linear equations is straightforward: if a column vector $\boldsymbol{x}$ must be solved we use the backslash and if a row vector $\boldsymbol{x}$ must be solved we use the ordinary slash,

$$\begin{aligned} \boldsymbol{A}\boldsymbol{x} = \boldsymbol{y} \quad &\Longrightarrow \quad \boldsymbol{x} = \boldsymbol{A}\backslash\boldsymbol{y} \qquad \text{(multiplication with } \boldsymbol{A}^{-1} \text{ on the left)} \\ \boldsymbol{x}^T\boldsymbol{A} = \boldsymbol{y}^T \quad &\Longrightarrow \quad \boldsymbol{x}^T = \boldsymbol{y}^T/\boldsymbol{A} \quad \text{(multiplication with } \boldsymbol{A}^{-1} \text{ on the right)} \end{aligned}$$

5.2 Least squares

Linear least squares, pseudo inverse.

A system of linear equations cannot be solved so straightforwardly when its coefficient matrix is non-square. Most often one meets $m \times n$ coefficient matrices with $m > n$ in *linear fits*. To explain this we first discuss curve fitting (also known as regression).

Suppose we have a measurable quantity y which is a function of x. (For instance, y can be the pressure of a gas and x its temperature. Or y can be the torsion energy associated with rotation of a methyl group around a bond in a molecule; then x is the torsion angle.)

Assume that we have measured m values $y_1, y_2, \ldots, y_m$ for $x_1, x_2, \ldots, x_m$, respectively. Very often one wants to find a curve $f(x)$ that passes as well as possible through the points, i.e, $f(x_i)$ must be as close as possible to y_i, for all $i = 1, \ldots, m$. One then guesses a family of functions $f_{\alpha_1,\alpha_2,\ldots,\alpha_n}(x)$, of which the family members only differ in the *fit parameters* $\alpha_1, \alpha_2, \ldots, \alpha_n$. A simple example of a four parameter family of fit functions is

$$f_{\alpha_1,\alpha_2,\alpha_3,\alpha_4}(x) = \alpha_1 \exp(-\alpha_2 x^2) + \alpha_3 \exp(-\alpha_4 x^2).$$

This function depends linearly on α_1 and α_3, these are the *linear fit parameters*, and exponentially on α_2 and α_4 (non-linear fit parameters). The least

squares fitting problem is the determination of the parameters of a chosen fit function f such that the sum of squares is least, i.e.,

$$\left[\sum_{i=1}^{m}\big(f(x_i)-y_i\big)^2\right]^{1/2} \quad \text{is a minimum.} \tag{5.2}$$

This condition becomes clearer if we introduce the vector

$$\boldsymbol{f} \equiv \big(f(x_1),\ f(x_2),\ldots,f(x_m)\big)$$

and a vector containing the experimental results

$$\boldsymbol{y} \equiv \big(y_1,\ y_2,\ldots,y_m\big).$$

Now condition (5.2) reads that the norm of the difference vector $\boldsymbol{f}-\boldsymbol{y}$ must be as small as possible, or in other words, the vector $\boldsymbol{f}$ must be as close as possible to the vector $\boldsymbol{y}$. Both vectors are in $\mathbb{R}^m$.

The problem of determining non-linear fit parameters is difficult, often one meets different local minima in $|\boldsymbol{f}-\boldsymbol{y}|$ as function of these parameters and the global minimum is not always physically meaningful.

The determination of linear parameters on the other hand is easy and can be performed by one MATLAB statement. So we will concentrate on linear fitting. First one chooses a linear expansion basis $\chi_1(x),\ \ldots,\chi_n(x)$. The choice of this basis depends on the problem at hand. For instance in the case of torsion energy, which is periodic with period 2π, one would choose $\cos k\phi$ and $\sin k'\phi$ as the expansion basis with $k,k'=0,1,2,\ldots$. Gaussian functions are often used $\chi_i(x)=\exp(-\alpha_i x^2)$, provided the exponents α_i are known, otherwise we have a non-linear fitting problem. Most often one uses powers of x, $\chi_i(x)=x^i$, so that the expansion becomes a polynomial [first terms of the Taylor series of $y(x)$]. In any case we write

$$f(x)=c_1\chi_1(x)+c_2\chi_2(x)+\cdots+c_n\chi_n(x)=\sum_{j=1}^{n}c_j\chi_j(x),$$

where the c_j are the linear fit parameters to be determined by minimizing $|\boldsymbol{f}-\boldsymbol{y}|$. Consider f in the point x_i,

$$f(x_i)=\sum_{j=1}^{n}\chi_j(x_i)c_j, \quad i=1,\ldots,m.$$

Introducing the matrix element $A_{ij}\equiv\chi_j(x_i)$ and $f_i\equiv f(x_i)$ we have

$$f_i=\sum_{j=1}^{n}A_{ij}c_j \Longrightarrow \boldsymbol{f}=\boldsymbol{A}\,\boldsymbol{c}.$$

The functions $\chi_i(x)$ are known, we assume that we know the points x_i at which the measurements are performed and hence we can compute the $m \times n$ matrix $\boldsymbol{A}$. Usually we have many more measurements than fit parameters: $m \gg n$. We do not know $\boldsymbol{f}$, but we want it to be as close as possible to the known (measured) vector $\boldsymbol{y}$.

Minimization of $|\boldsymbol{f} - \boldsymbol{y}|$ leads to the n equations

$$\boldsymbol{A}^T \boldsymbol{A}\, \boldsymbol{c} = \boldsymbol{A}^T \boldsymbol{y}. \tag{5.3}$$

These are known as the *normal equations* of the linear least square problem. Before proceeding we prove Eqs. (5.3). We minimize $S \equiv |\boldsymbol{f} - \boldsymbol{y}|^2$ (which obviously has the same minimum as $|\boldsymbol{f} - \boldsymbol{y}|$) with respect to c_i, $i = 1, \ldots, n$, i.e., we put the first derivatives equal to zero. By invoking the chain rule we get:

$$\frac{\partial S}{\partial c_i} = \frac{\partial}{\partial c_i} \sum_{j=1}^{m} (f_j - y_j)^2 = 2 \sum_{j=1}^{m} \frac{\partial f_j}{\partial c_i} (f_j - y_j). \tag{5.4}$$

Now,

$$\frac{\partial f_j}{\partial c_i} = \frac{\partial}{\partial c_i} \sum_{k=1}^{n} A_{jk} c_k = \sum_{k=1}^{n} A_{jk} \delta_{ki} = A_{ji} \equiv A^T_{ij}, \tag{5.5}$$

where we used $\partial c_k / \partial c_i = \delta_{ki}$. Note that δ_{ki}, with k running and i fixed, gives zero always, except for $k = i$, in that case we get $A_{ji} \times 1$. The Kronecker delta 'filters' from the sum over k only the $k = i$ term. Substitute Eq. (5.5) into Eq. (5.4) and put the derivatives equal to zero

$$0 = \frac{\partial S}{\partial c_i} = 2 \sum_{j=1}^{m} A^T_{ij} (f_j - y_j),$$

or, using $\boldsymbol{f} = \boldsymbol{A}\, \boldsymbol{c}$,

$$\boldsymbol{A}^T \boldsymbol{f} = \boldsymbol{A}^T \boldsymbol{y} \Longrightarrow \boldsymbol{A}^T \boldsymbol{A}\, \boldsymbol{c} = \boldsymbol{A}^T \boldsymbol{y}.$$

Strictly speaking, we must consider next the second derivatives to check whether we have a minimum, saddle point or maximum, but we skip this part of the proof[1].

The matrix $\boldsymbol{A}^T$ is $n \times m$ and $\boldsymbol{A}$ is $m \times n$, so their product is square: $n \times n$. The vector $\boldsymbol{A}^T \boldsymbol{y}$ is of dimension n. If the expansion functions $\chi_i(x)$ are linearly independent and the points x_i are well chosen (not too close to each other), then the matrix $\boldsymbol{A}$ is of rank n, i.e., its n columns are linearly independent. The $n \times n$ matrix $\boldsymbol{A}^T \boldsymbol{A}$ is non-singular if and only if $\boldsymbol{A}$ is of

[1] The second derivatives lead to consideration of $\boldsymbol{A}^T \boldsymbol{A}$. This matrix is positive definite (has only positive eigenvalues) and therefore we have a minimum.

rank n. If $\boldsymbol{A}$ is of rank n then $\boldsymbol{c} = (\boldsymbol{A}^T\boldsymbol{A})^{-1}\boldsymbol{A}^T\boldsymbol{y}$ is a unique solution. We conclude that the normal equations have a unique solution, irrespective of the fact whether $\boldsymbol{y}$ depends linearly on the columns of $\boldsymbol{A}$, as long as the columns of $\boldsymbol{A}$ are linearly independent.

The $n \times m$ matrix $\boldsymbol{B} \equiv (\boldsymbol{A}^T\boldsymbol{A})^{-1}\boldsymbol{A}^T$ is the *pseudo inverse* of $\boldsymbol{A}$, because, obviously $\boldsymbol{B}\,\boldsymbol{A} = \boldsymbol{I}_{n\times n}$. Note that $\boldsymbol{A}\,\boldsymbol{B} \neq \boldsymbol{I}_{m\times m}$. The matrix $\boldsymbol{B}$ is also known as the Moore-Penrose inverse of $\boldsymbol{A}$. For the special case that $\boldsymbol{A}$ is non-singular (and hence square), it is easily seen that $\boldsymbol{B} = \boldsymbol{A}^{-1}$.

Returning to MATLAB we first note that the command `pinv(A)` returns the pseudo inverse of `A`. So, the equation $\boldsymbol{A}\boldsymbol{c} = \boldsymbol{y}$ can be solved in the least squares sense by `c = pinv(A)* y`. However, it can be shorter, because the backslash operator performs in fact pseudo inversion, `c = A\y` gives the same result.
Example:
We first generate an arbitrary 3×2 matrix `A` consisting of integers between 0 and 10:

```
>> A = fix(10*rand(3,2))
A =
     9     4
     2     8
     6     7
```

The function `fix` rounds a floating point number down to the nearest integer, e.g., `fix(9.9) = 9`. Recall that `rand` returns random numbers between 0 and 1. Next we compute the pseudo inverse:

```
>> B=pinv(A)
B =
    0.0401   -0.1492    0.1050
    0.0110    0.1657   -0.0055

>> B*A                 % To check for the identity matrix
ans =
    1.0000         0
    0.0000    1.0000

>> A*B                 % No identity?
ans =
    0.2044    0.0663    0.3978
    0.0663    0.9945   -0.0331
    0.3978   -0.0331    0.8011
```

```
>> y = rand(3,1)       % Make a right hand side
y =
    0.4057
    0.9355
    0.9169

>> B*y
ans =
   -0.0270
    0.1545

>> A\y
ans =
   -0.0270
    0.1545
```

An example of fitting a straight line through data that are made somewhat noisy:

```
% Synthesize data:
% Straight line, slope 3/2, 10% noise.
>> x=[1:25]';           % simple x values
>> r=rand(25,1)-0.5;    % -0.5 < random < 0.5
>> y=1+3/2*(x+r.*x/10);

% The actual fit:
>> A=[x.^0 x.^1];       % f(x) = c(1) + c(2)*x
>> c=A\y                % c(1) is intercept, c(2) is  slope
% Plot fit and original:
>> plot(x,y, x, A*c);   % (x,y) original, (x, A*c) fitted
```

5.3 Necessity of least squares

Linear least square equations are overdetermined.
One could be tempted to make the approximation $\boldsymbol{f} \approx \boldsymbol{y}$ in the linear model $\boldsymbol{f} = \boldsymbol{A}\,\boldsymbol{c}$. This leads to a set of linear equations

$$\boldsymbol{y} = \boldsymbol{A}\,\boldsymbol{c}, \tag{5.6}$$

where the $m \times n$ matrix $\boldsymbol{A}$ is rectangular, $m > n$. When we write the columns of $\boldsymbol{A}$ as $\boldsymbol{a}_1, \ldots, \boldsymbol{a}_n$, this set of equations is equivalent to

$$\boldsymbol{y} = c_1\boldsymbol{a}_1 + c_2\boldsymbol{a}_2 + \cdots + c_n\boldsymbol{a}_n \quad \text{(columns of length } m\text{)}.$$

From this we see clearly that the column vector $\boldsymbol{y}$ must depend linearly on the columns of $\boldsymbol{A}$ in order that the approximation $\boldsymbol{f} \approx \boldsymbol{y}$ makes sense. Usually this is not the case, of course, and then these equations do not have a solution; simplification of the equations by elementary row transformations will lead to contradictory equations.

In order to show this, we try to solve the equations (5.6) by the usual techniques for solving linear equations. That is, we consider the augmented matrix `[A, y]` and by elementary row transformations we "sweep" this matrix to its simplest form. MATLAB has the command `rref` to do this. Using $\boldsymbol{A}$ and $\boldsymbol{y}$ of the previous example, we get

```
>> rref([A, y])   % A and y as in the previous example
ans =
 1     0     0
 0     1     0
 0     0     1
 0     0     0
    ...
 0     0     0
```

(the last 22 rows contain only zeros). Hence the first two equations of $\boldsymbol{A}\,\boldsymbol{c} = \boldsymbol{y}$ are equivalent to

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

which have the solution $c_1 = c_2 = 0$. The third equation is equivalent to $0 = 1$. From this contradiction we conclude that, although the linear least square solution $\boldsymbol{c}$ is uniquely determined, the equations $\boldsymbol{A}\,\boldsymbol{c} = \boldsymbol{y}$ have no solution in the ordinary sense. Or in other words, the three vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $\boldsymbol{y}$ are linearly independent. (This is due to the addition of noise, if we had simply put $y = 1 + 3x/2$, $\boldsymbol{y}$ would have been the first column plus a multiple of the second column of $\boldsymbol{A}$, and the three vectors would have been linearly dependent).

Suppose now that $\boldsymbol{y}$ depends linearly on the columns of $\boldsymbol{A}$. This means that there is a vector $\boldsymbol{d} = (d_1, d_2, \ldots, d_n)$ of length n such that

$$\boldsymbol{y} = d_1\boldsymbol{a}_1 + d_2\boldsymbol{a}_2 + \cdots + d_n\boldsymbol{a}_n = \boldsymbol{A}\,\boldsymbol{d},$$

where $\boldsymbol{a}_i$ is the i^{th} column of $\boldsymbol{A}$. These columns are of length m. It is immediately obvious that the least square solution $\boldsymbol{c}$ gives the correct answer, for

$$\boldsymbol{c} = (\boldsymbol{A}^T\boldsymbol{A})^{-1}\boldsymbol{A}^T\,\boldsymbol{y} = (\boldsymbol{A}^T\boldsymbol{A})^{-1}\boldsymbol{A}^T\,\boldsymbol{A}\,\boldsymbol{d} = \boldsymbol{d}.$$

If we had written $y = 1 + 3x/2$ in the example above, without adding noise, we would have found $c(1) = 1$ and $c(2) = 3/2$. The corresponding least squares solution $y = 1 + 3x/2$ gives back exactly what we put in. In that sense the method of least squares is stable.

5.4 Exercises

Exercise 28.

Visit for this exercise

`http:/www.theochem.kun.nl/~pwormer`,

where you find a link to course material. Follow this link and click the link `heatH2O.txt` and an ASCII file containing comments and two columns is opened. The columns are temperatures (°C) and heat capacities C_p of steam at 1 atm [units: Cal/(°C g)]. Save this file in your current directory (most browsers have this option under their `File` button).

MATLAB can read ASCII files that contain columns and skips comments while reading. Issue the command `load heatH2O.txt` in your MATLAB session. You now have an array `heatH2O` containing the two columns. (The command: `load arr.any` creates an array with the name of the string before the dot—in this case `arr`—and discards the arbitrary string after the dot). Create a column vector `T` containing the temperatures and the column vector `Cp` containing the heat capacities.

- Perform a quadratic fit $C_p \approx c_1 + c_2 T + c_3 T^2$ and compute the error (norm of the vector containing the differences between the original and the fitted points). Plot the fitted and the original values as a function of temperature.

- Perform a cubic fit $C_p \approx d_1 + d_2 T + d_3 T^2 + d_4 T^3$ and compute the error (norm of the difference vector). Which of the two fits has the smaller error? Plot also this fit.

- Use both fits to extrapolate the heat capacity to 750 and 1000 °C. Plot the fits in one figure including the extrapolated points. Which of the two fits give extrapolated values closest to the real value, you think?

Exercise 29.

The linear parameters obtained in a least squares fit can be given statistical significance. Write $\nu \equiv m - n$ for the number of degrees of freedom (number

of measurements m minus number of fit parameters n). The measure for the fit error: $s_e^2 \equiv \frac{1}{\nu}|\boldsymbol{f}-\boldsymbol{y}|^2$ appears in the variance-covariance matrix

$$\boldsymbol{V} = s_e^2(\boldsymbol{A}^T\boldsymbol{A})^{-1} \ ,$$

where $A_{ij} = x_i^j$, $i = 1,\ldots,m$, $j = 0,\ldots,n-1$, (x_i^j is x_i to the power j). The vector $\boldsymbol{y}$ contains the measured values and $\boldsymbol{f}$ the fitted ones. The estimated standard deviation s_i of the fit coefficient c_i is given by $\sqrt{V_{ii}}$. The 95% confidence interval for fit parameters $\boldsymbol{c} = (c_1,\ldots,c_n)$ can now be obtained from

$$c_i \pm t_{0.05,\nu}s_i,$$

where $t_{0.05,\nu}$ is an entry in Student's t-table[2]. Recall that the rows and columns of a t-table are given by confidence levels (here 0.05) and number of degrees of freedom (ν). If $c_i - t_{0.05,\nu}s_i \leq 0 \leq c_i + t_{0.05,\nu}s_i$, then the variable c_i is not significantly different from zero.

Confidence intervals for interpolating predictions can be calculated as well. Consider $\boldsymbol{x}_0 = (x_{10}, x_{20},\ldots,x_{m0})^T$, a column vector consisting of m points spanning the same range as the x-values of the measurements. These points interpolate the x-values of the measurements. Consider the $m \times n$ matrix

$$\boldsymbol{X}_0 = \begin{pmatrix} 1 & x_{10} & x_{10}^2 & \cdots & x_{10}^{n-1} \\ \vdots & \vdots & & & \vdots \\ 1 & x_{m0} & x_{m0}^2 & \cdots & x_{m0}^{n-1} \end{pmatrix}.$$

Then the 95% confidence interval at point x_{i0} is

$$f_{i0} \pm t_{0.05,\nu}\sqrt{\left(\boldsymbol{X}_0\,\boldsymbol{V}\,\boldsymbol{X}_0^T\right)_{ii}}, \quad i = 1,\ldots,m,$$

where $\boldsymbol{f}_0 \equiv \boldsymbol{X}_0\boldsymbol{c}$, (a column vector of length m), interpolates the measured values.

Take care not to confuse this interval with a *prediction* interval for a single measurement, which is given by

$$f_{i0} \pm t_{0.05,\nu}\sqrt{s_e^2 + \left(\boldsymbol{X}_0\,\boldsymbol{V}\,\boldsymbol{X}_0^T\right)_{ii}}.$$

Note that prediction intervals are wider than confidence intervals.

After this preamble consider again the data from the previous Exercise (file `heatH2O.txt`).

[2]Discovered by William Sealy Gosset (1876–1937), who was employed by Guinness breweries in Dublin. Guinness encouraged their employees to publish under pseudonyms; Gosset chose 'Student'.

- Perform again the quadratic fit $C_p \approx c_1 + c_2 T + c_3 T^2$. Calculate the standard deviations s_i of the coefficients. Are all coefficients significantly different from zero? Form an equidistant grid of 100 temperature points (see help `linspace`) spanning the same range as the input points. Compute the 95% confidence intervals where you can take $t_{0.05,\nu} = 2$. Plot the fitted values, confidence intervals and original values (dashed) in one figure.

- For the same 100 points, calculate the prediction intervals for a single measurement (i.e., within what values would you expect one single measurement to be the outcome for 95% of the time)? Plot these in the same figure as dotted lines.

Exercise 30.

Visit for this exercise

`http:/www.theochem.kun.nl/~pwormer`.

Follow the link to the course material. When you click `O2.txt` an ASCII file containing comments and two columns is opened. The columns are interatomic distances (bohr) and energies (hartree) for the oxygen molecule O_2. Save this file in your current directory. See previous exercise for more details on how to do this.

- Write a script that loads the oxygen file into your MATLAB session and fits the energies as function of the distance r with the following function: $V \approx D_0 + D_1 \exp(-\beta r) + D_2 \exp(-2\beta r)$. The linear fit parameters D_0, D_1 and D_2 can be obtained by the backslash operator. Use $\beta = 1$. Plot the fit and the original data.

- To determine the nonlinear fit parameter β modify the script. Put a loop with $0.8 \leq \beta \leq 1.8$ with steps of 0.1 around the linear fit. Compute in the body of the loop the norm of the difference vector $\boldsymbol{V} - \boldsymbol{V}_{\text{fit}}$ (original and fitted values) and determine the value of β which has the smallest norm. Plot for this β again the original and fitted values.

6. Functions and function functions

6.1 Functions

Difference between scripts and functions, subfunctions.
Functions resemble scripts: both reside in an ASCII file with extension `.m`. As a matter of fact, many of the MATLAB functions that we used so far are simply `.m` files. One can inspect them by the command `type`, e.g., `type fliplr` will type the content of `fliplr.m`. The difference between scripts and functions is that all variables in scripts are global, whereas *all variables in functions are local*. This means that variables inside functions lead their own life. Say, we have assigned the value -1.5 to the variable `D` in our MATLAB session and we call a function that also assigns a value to a variable called `D`. Upon return from the function the variable `D` still has the value -1.5. Conversely, `D` must be assigned a value inside the function before it can be used. The function does not know that `D` already has a value in our MATLAB session.

If both are stored in an `.m` file, how does MATLAB tell the difference between a script and a function? This is a good question with a simple answer: the very first word of a function is `function`. So, when MATLAB reads an `.m` file from disk, it looks at the first string and decides from this whether it is a function or a script.

If all variables in a function are local, what is the use of a function? One would like to get something useful out of a function, as for instance an array with its columns flipped. In other words, how does a function communicate with its environment? To explain this we give the syntax of the first line of a function:

```
function [out1, out2, ...] = name(in1, in2, ...)
```

The first observation is that a function accepts input arguments between round brackets. Any number (including zero) of variables can be written here. These variables can be of any type: scalars, matrices (and MATLAB objects that we have not yet met). The second observation is that a function returns a number of output parameters in square brackets. The values of `out1`, `out2`, etc. must be assigned within the function. These variables can also be of any type. *The square brackets here have nothing to do with the*

concatenation operators that made larger matrices from smaller ones. The third observation is that the function has a name. It is common to use here the same name as of the `.m` file, but this is not compulsory. The name of an `.m` file begins with an alphabetic character, and has a filename extension of `.m`. The `.m` filename, less its extension, is what MATLAB searches for when you try to use the script or function.

For example, assume the existence of a file on disk called `stat.m` and containing:

```
function [mean,stdev] = stat(x)
   n     = length(x);
   mean  = sum(x)/n;
   stdev = sqrt(sum((x-mean).^2)/n);
```

This defines a function called `stat` that calculates the mean and standard deviation of the components of a vector. We emphasize again that the variables within the body of the function are all local variables. We can call this function in our MATLAB session in three different ways:

```
>> stat(x)      % no explicit assignment
ans =           % default assignment to ans
    0.0159

>> m = stat(x)  % assignment of first output parameter
m =
  0.0159

>> [m, s] = stat(x) % assignment of both output parameters
m =
    0.0159
s =
    1.0023
```

Note that `m` and `s` are *not* concatenated to a 1×2 matrix; the square brackets *do not* act as concatenation operators in this context, i.e., to the left of the assignment sign. Notice that the concatenation operators `[` and `]` only appear on the right hand sides of assignments.

A *subfunction*, visible only to the other functions in the same file, is created by defining a new function with the function keyword after the body of the preceding function or subfunction. For example, `avg` is a subfunction within the file `stat.m`:

```
function [mean,stdev] = stat(x)
   n     = length(x);
   mean  = avg(x,n);
   stdev = sqrt(sum((x-avg(x,n)).^2)/n);
function [mean] = avg(x,n)
   mean  = sum(x)/n;
```

Subfunctions are not visible outside the file where they are defined. Also, subfunctions are not allowed in scripts, only inside other functions. Functions normally return when the end of the function is reached. We may use a `return` statement to force an early return from the function. When MATLAB does not recognize a function by name, it searches for a `.m` file of the same name on disk. If the function is found, MATLAB stores it in parsed form into memory for subsequent use. In general, if you input the name of something to MATLAB, the MATLAB interpreter does the following: It checks to see if the name is a variable. It checks to see if the name is a built-in function (as, for instance, `sqrt` or `sin`). It checks to see if the name is a local subfunction. When you call an `.m` file function from the command line or from within another `.m` file, MATLAB parses the function and stores it in memory. The parsed function remains in memory until cleared with the clear command or you quit MATLAB.

6.2 Function functions

Function functions, function handles.
MATLAB has a number of functions that work through functions. This sounds cryptic, so let us give an example immediately. The built-in function `fminsearch` performs minimization. It finds minima of non-linear functions of one or more variables. It does not apply constraints. That is, the search for minima is on the whole real axis (or complex plane as the case maybe). We invoke this function by

```
X = fminsearch(@fun,X0)
```

The search starts at `X0` and finds a local minimum of `fun` at the point `X`. It is our duty to supply the function `fun`. The function must accept the input `X`, and must return the scalar function value `fun` evaluated at `X`. The input variable `X` can be a scalar, vector or matrix.

Suppose we want to find the local minima of the following function:

```
function [y] = hump(x)
% We use dot operations so that hump may be called
% with a vector, e.g., for plotting.
y = 1 ./ ((x-0.3).^2 + 0.01) + 1 ./ ((x-0.9).^2 + 0.04) - 6;
```

which we have as `hump.m` on disk. The function call

```
x = fminsearch(@hump,0.3)
```

now returns the value of `x` for which the function has a minimum. (Or, in case of more minima, the local minimum closest to 0.3).

The function `fminsearch` belongs to the class of functions called "function functions". Such a "function function" works with (non)linear functions. That is, one function works on another function. The function functions include

- Zero finding
- Optimization
- Quadrature (numerical integration)
- Solution of ordinary differential equations

See table 6.1 for the most important function functions.

Table 6.1: *Function functions*

dblquad	Numerical double integration
fminbnd	Minimize a function of one variable
fminsearch	Minimize a function of several variables
fzero	Zero of a function of one variable
ode45, ode23, ode113, ode15s, ode23s, ode23t, ode23tb	Solve ordinary differential equations
odefile	Define a differential equation problem for ODE solvers
odeget	Extract properties from options structure created with odeset
odeset	Create or alter options structure for input to ODE solvers
quad, quad8	Numerical evaluation of integrals
vectorize	Vectorize expression

Sometimes the function to be processed is so simple that it is hardly worth the effort to create a separate `.m` file for it. For this MATLAB has the function `inline`. The function `fzero` finds zeros of polynomials, i.e., values of x for which a polynomial in x is zero. The function `quad` gives a quadrature (numerical integration). Thus, for example, enter

```
>> fzero(inline('x^3-2*x-5'),1.5)
>> quad(inline('1./(1+x.^2)'),-1000, 1000)
```

to find the real zero closest to 1.5 of the third degree polynomial and to integrate numerically the Lorentz function $1/(1 + x^2)$. (This integral is known from complex function theory to be π).

The symbol `@fun` returns a *function handle* on `fun`. A function handle contains all the information about a function that MATLAB needs to execute that function. As we saw above, a function handle is passed in an argument list to other functions. The receiving functions can then execute the function through the handle that was passed in. You can, for example, execute a subfunction using a function handle, as long as the handle was created within the subfunction's `.m` file. That is, the following construction is allowed, where `model` is a subfunction of `fit`

```
function fit
   ...
   fminsearch{@model,x}   % create function handle
   ...
function model(x)         % subfunction in same m file
   ...
```

The subfunction `model` is visible to `fminsearch`.

The function handle is the first MATLAB data type that we meet which is not a matrix. You can manipulate and operate on function handles in the same manner as on other data types. Function handles enable you to do the following: (i) Pass function access information to other functions. (ii) Allow wider access to subfunctions. (iii) Reduce the number of files that define your functions.

6.3 Coupled first order ordinary differential equations

Coupled differential equations, chemical kinetics

MATLAB has several ordinary differential equation solvers (ODE solvers, see `help ode45`). An ordinary differential equation has only one parameter, which often is the time t. We will restrict ourselves in this section to first order equations, i.e., equations containing only first derivatives with respect to t. Usually differential equations are coupled and have the following general form,

$$\begin{pmatrix} dy_1/dt \\ dy_2/dt \\ \cdots \\ dy_n/dt \end{pmatrix} = \begin{pmatrix} f_1\big(t, \boldsymbol{y}(t)\big) \\ f_2\big(t, \boldsymbol{y}(t)\big) \\ \cdots \\ f_n\big(t, \boldsymbol{y}(t)\big) \end{pmatrix}, \tag{6.1}$$

here $\boldsymbol{y}(t) = \big(y_1(t), y_2(t), \ldots, y_n(t)\big)$ is to be computed by MATLAB from a given initial vector $\boldsymbol{y}(t_0)$. The functions f_1, $f_2, \ldots,$ f_n are known and must be supplied by the user. The ODE solver most often used is `ode45`. It is called as

```
[T Y] = ode45(@Yprime, Tspan, Init)
```

`Yprime` is the name of the `.m`-file that returns $f_1, f_2, \ldots, f_n$ as a column vector. The array `Tspan = [t0 tf]` contains the initial and final time, i.e., the equations are integrated from `t0` to `tf`. The initial y values (for $t = t_0$) are given in the vector `Init`. The $K \times n$ matrix `Y`, returned by `ode45`, contains y-values at K points t_i in time $t_0 \leq t_i \leq t_f$ for which MATLAB computed the vector $\boldsymbol{y}(t_i)$. The corresponding t values are in the $K \times 1$ array `T`. Before calling `ode45` the user does not know K, the number of integration points that MATLAB will generate. The time points, contained in the column vector `T`, are also known only after the call.

As an example of a set of coupled differential equations we consider the chemical reactions,

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \overset{k_3}{\rightarrow} C \tag{6.2}$$

with the kinetic equations

$$\begin{aligned} \frac{d[A]}{dt} &= -k_1[A] + k_2[B] \\ \frac{d[B]}{dt} &= k_1[A] - [B](k_2 + k_3) \\ \frac{d[C]}{dt} &= k_3[B]. \end{aligned} \tag{6.3}$$

The concentrations $[A]$, $[B]$ and $[C]$ as functions of time are obtained by solving these equations. We call `ode45` as follows:

```
[T Y]=ode45(@kinetic, Tspan, Init)
```

The array `Y` will contain the concentrations at the points in time $t_1 \leq t_i \leq t_K$ at which MATLAB computed them. We make the following identifications:

$$Y(i,1) = [A], \quad Y(i,2) = [B], \quad Y(i,3) = [C], \quad i = 1, \ldots, K,$$

which means that the i^{th} row `Y(i,:)` contains the concentrations at $t = t_i$. The vector `T` contains the time points: $T(i) = t_i,\ i = 1, \ldots, K$. Furthermore the name of the `.m`-file supplied by the user is `kinetic`. It must return the right hand sides of the differential equations as a column vector of the same dimension as `Init`. This is the number (n) of coupled equations. In the present example $n = 3$.

First `ode45` assigns the values of `Init` (the initial concentrations) to the first row `[Y(1,1), Y(1,2), Y(1,3)]` of `Y`. During integration `ode45` will repeatedly call `kinetic.m` with the respective rows of `Y` as input parameters. The function `kinetic` returns f_1, f_2 and f_3 for given time t. Besides `Y`, also the time `t` (a scalar) is inputted. Although in reaction kinetics `t` is not used

explicitly, time must be present in the parameter list of the function, since `ode45` expects a parameter in this position.

The function `kinetic` may look as follows

```
function  [f] = kinetic(t, Conc)
%  Conc is a vector with 3 concentrations and
%  k1, k2 and k3 are  rate constants.

k1 = 0.8;
k2 = 0.2;
k3 = 0.1;

f    = zeros(length(Conc),1);
f(1) = -k1*Conc(1) + k2*Conc(2);
f(2) =  k1*Conc(1) - Conc(2)*(k2+k3);
f(3) =  k3*Conc(2);
```

and can for instance be called as

```
[T, Y] = ode45(@kinetic, [0 30], [1 0 0]);
```

where the time span is: $t_1 = 0$ and $t_f = 30$ (in the same units of time as are in the k-values). Initially $[A] = 1$ and $[B] = [C] = 0$. After `ode45` has finished the command `plot(T, Y)` may be used to show the concentrations as function of time and `length(T)` returns the number of time steps K.

To simplify the kinetic equations one often introduces the *"steady state"* approximation. In this approximation it is assumed that the concentrations of intermediate reactants do not change during the reactions. This means that their time derivatives are zero. In the present example we assume $d[B]/dt = 0$. Knowing this, we can eliminate the concentrations of the intermediate reactants and thus reduce the number of coupled equations. In our example we can reduce the number of equations from 3 to 2 by means of the steady state approximation.

$$\begin{aligned} \frac{d[A]}{dt} &= [A]\left(-k_1 + \frac{k_1 k_2}{k_2 + k_3}\right) \\ \frac{d[C]}{dt} &= [A]\frac{k_1 k_3}{k_2 + k_3}. \end{aligned} \tag{6.4}$$

So far, the rate constants got their values within the function `kinetic`. Since we want to be able to vary these k-values, it is more convenient to assign values outside the function. MATLAB offers a possibility to pass more parameters to the function than mentioned above. A more complete call to `ode45` is

```
[T, Y] = ode45(@function, Tspan, Init, options, P1, P2...)
```

The parameters `function`, `Tspan` and `Init` are as before. We skip explanation of `options`, we take it simply to be empty `[]`. After it we find an undetermined number of parameters `P1, P2..` that are passed unchanged to `function`. Supposing that the function referred to `ode45` is called `steady.m`, then its first line may look like this

```
function [f] = steady(t, Conc, k1, k2, k3)
```

where `k1, k2, k3` are the rate constants that must be assigned before calling `ode45`. Further `t` and `Conc` are the times and concentrations passed to `steady` by `ode45`. The function `steady` is called through `ode45` from a MATLAB session as

```
[Ts Ys] = ode45(@steady, [0 30], [1 0], [], k1, k2, k3);
```

The fourth parameter (the third array) can contain options that govern the accuracy of the solution. Because we are satisfied with the default options we leave it empty: `[]`. We reiterate that `k1, k2` and `k3` must have a value before we invoke `ode45`.

6.4 Higher order differential equations

Reduction higher order diffential equations to coupled first order differential equations.
An ordinary n^{th} order differential equation can be reduced to a coupled system of n first order differential equations. To show this we introduce the notation: $y' \equiv dy/dt$, $y'' \equiv d^2y/dt^2$, $y^{(k)} \equiv d^ky/dt^k$. An n^{th} order differential equation can be written as

$$\frac{d^n y}{dt^n} = f(t, y, y', y'', \ldots, y^{(n-1)}),$$

where f indicates that the right hand side is a given function of t and the lower order derivatives. We simply put

$$\begin{aligned} y_1 &\equiv y \\ y_2 &\equiv \frac{dy_1}{dt} = \frac{dy}{dt} \\ y_3 &\equiv \frac{dy_2}{dt} = \frac{d^2y}{dt^2} \\ \ldots &\quad \ldots \\ y_n &\equiv \frac{dy_{n-1}}{dt} = \frac{d^{n-1}y}{dt^{n-1}}, \end{aligned} \tag{6.5}$$

and get the set of n first order coupled equations

$$\begin{aligned}
\frac{dy_1}{dt} &= y_2 \\
\frac{dy_2}{dt} &= y_3 \\
\cdots &\quad \cdots \\
\frac{dy_{n-1}}{dt} &= y_{n-2} \\
\frac{dy_n}{dt} &\equiv \frac{d^n y}{dt^n} = f(t, y, y', y'', \ldots, y^{(n-1)}) \\
&= f(t, y_1, y_2, y_3, \ldots, y_n).
\end{aligned} \tag{6.6}$$

Example

$$\frac{d^2y}{dt^2} = t\frac{dy}{dt} - y^2 \tag{6.7}$$

becomes

$$f_1 \equiv \frac{dy_1}{dt} = y_2 \tag{6.8}$$

$$f_2 \equiv \frac{dy_2}{dt} = ty_2 - y_1^2. \tag{6.9}$$

In MATLAB the corresponding function called by the ode solvers would look like:

```
function [f] = difeq(t, y)
f = zeros(2,1);  % Tell matlab we return a column vector
f(1) = y(2);
f(2) = t*y(2) - y(1)^2;
```

6.5 Exercises

Exercise 31.

A classic test example for multidimensional minimization is the Rosenbrock banana function $f(x, y) = 100(y - x^2)^2 + (1 - x)^2$.

1. Write the MATLAB function `banana` that evaluates f for the vector $\boldsymbol{r} = (x, y)$.

2. Call 'by hand' `fminsearch` from your MATLAB session to minimize the banana function. Use as a start $\boldsymbol{r} = (-1.2, 1)$.

3. Modify function `banana` to $f(x, y) = 100(y - x^2)^2 + (a - x)^2$ and let a be an input parameter. Read the help of `fminsearch` to discover how to pass a to `banana` via `fminsearch`.

Exercise 32.

Compute the integral

$$\int_0^1 \left[\frac{1}{(x-0.3)^2+0.01} + \frac{1}{(x-0.9)^2+0.04} - 6 \right] dx$$

with the command `quad` (see helpfile).

Exercise 33.

Write the function

```
function [r, theta, phi] = cartpol(x)
```

that returns spherical polar coordinates from the 3-dimensional column vector `x` that contains Cartesian coordinates. Remember the equations ($0 \le r < \infty,\ 0 \le \theta \le \pi,\ 0 \le \phi < 2\pi$)

$$\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} r\sin\theta\cos\phi \\ r\sin\theta\sin\phi \\ r\cos\theta \end{pmatrix}$$

Hints:

- Check first if $r = |\boldsymbol{r}| < 10\epsilon$. If this is the case then set all output parameters equal to zero and return (with MATLAB command `return`). The constant `eps` (floating point relative accuracy) is built into MATLAB; it is $2^{-52} \approx 10^{-16}$.
- Then test if $x_1^2 + x_2^2 \le 10\epsilon$. If this is the case the vector is along the third axis and $\phi = 0°$; it can be pointing up ($\theta = 0°$) or pointing down ($\theta = 180°$).
- Finally compute θ from x_3 and ϕ from x_1 and notice that $\phi = \arccos y$ gives results in the interval $0 \le \phi \le \pi$. If $x_2 < 0$ then $\phi = 2\pi - \phi$.

Exercise 34.

In this exercise we will investigate the steady state approximation by looking at the increase of concentration of reactant C, see Eq. (6.2). In a reasonable approximation $[C]$ increases as

$$[C] = 1 - \exp(-k_{\text{eff}} t), \tag{6.10}$$

where k_{eff} is an effective rate constant. By fitting a straight line through $\ln(1-[C])$ as function of time t we can obtain k_{eff}.

1. Write the `.m`-files that can be used for the integration of the exact (6.3) and the steady state equations (6.4).

2. Write a function based on Eq. (6.10) that returns k_{eff}.

3. Write a script that first solves the exact equations [by calling the function you wrote under (1)], then determines k_{eff}, and finally solves the steady state equations and again returns k_{eff}. Repeat this for $k_1 = 0.5$, $\mathrm{k}_2 = 0.5$ and $k_3 = 100k_1, 10k_1, k_1, k_1/10, k_1/100$. Take as initial conditions $[A] = 1$, $[B] = 0$ and $[C] = 0$.

   Hint: Do not integrate too long (take t_f not too large), a reasonable upper limit is

   ```
   tmax= 3/min([k1 k2 k3])
   ```

   You will see that the steady state approximation is good when B vanishes quickly, that is if $k_3 \gg k_1 \approx k_2$.

   In the case that $k_3 \ll k_1 \approx k_2$ the steady state approximation yields a k_{eff} which is twice too large.

Exercise 35.

Solve Eq. (6.7) by `ode45` with initial conditions $y_1(0) = 1$ and $y_2(0) = 0$. Integrate from $t = 0$ to $t = 0.2$. Plot the resulting function $y(t) \equiv y_1(t)$.

Exercise 36.

For this exercise we immerse a one-dimensional spring, with a point mass m attached to it, into a vessel containing a viscous liquid, e.g., syrup. We pull the spring away from equilibrium over a distance $y = 1$. At the point $t = 0$ we let the spring go, so at this point in time the velocity of m is zero: $dy(0)/dt = 0$. The spring will start to vibrate following Newton's equation of motion: $md^2y/dt^2 = F$. The forces acting on the mass are Hooke's law: $-ky$ and the friction force: $-fdy/dt$ (proportional to the velocity). In total, this so-called "damped harmonic oscillator" satisfies the equation of motion[1]

$$m\frac{d^2y}{dt^2} = -ky - f\frac{dy}{dt}$$

or

$$\frac{d^2y}{dt^2} + \omega^2 y + 2b\frac{dy}{dt} = 0, \tag{6.11}$$

where $\omega = \sqrt{k/m}$ and $b = f/2m$.

[1]The reader may wonder why somebody in his right mind would put a spring into a bowl of syrup. However, the damped harmonic oscillator is a useful model in many branches of science: LCR electric circuits, dispersion of light, etc.

1. Write a function for solving Eq. (6.11), which has, besides t and y, also b and ω as parameters.

2. Solve this equation by means of `ode45` with $\omega = 1$ and $b = 0.2$. Integrate over the time span $[0, 20]$. Take as initial conditions $y(0) = 1$ and $dy(0)/dt = 0$.

3. The analytic solution of Eq. (6.11) for $b < \omega$ is, with $\Omega \equiv \omega^2 - b^2$,

$$y = y(0)e^{-bt}\left(\cos\Omega t + \frac{b}{\Omega}\sin\Omega t\right). \tag{6.12}$$

   Write a script that (i) numerically integrates Eq. (6.11), (ii) implements the analytic solution, Eq. (6.12), and (iii) shows both solutions in one plot.

7. More plotting

7.1 3D plots

3D plots and contours

So far we only made two-dimensional plots—values of y against x. We will now turn to displaying 3D data, i.e., $z = f(x, y)$ will be plotted against x and y. Of course, we must discretize the function parameters and value. Let $\boldsymbol{x} = (x_1, \ldots, x_m)$ and $\boldsymbol{y} = (y_1, \ldots, y_n)$ be vectors and let $\boldsymbol{Z}$ be a matrix of function values

$$Z_{ij} = f(x_j, y_i).$$

Note that x carries the column index j of the $n \times m$ matrix $\boldsymbol{Z}$ and y the row index i. The reason is that the x-axis is usually horizontal (corresponds to running within rows of $\boldsymbol{Z}$) and the y-axis is usually vertical (runs within columns of $\boldsymbol{Z}$).

A MATLAB function that is useful in the computation of $\boldsymbol{Z}$ is `meshgrid`. The statement

```
[X,Y] = meshgrid(x,y)
```

transforms vectors (one-dimensional arrays) `x` and `y` into two-dimensional arrays `X` and `Y` that can be used with dot operations to compute `Z`. The rows of the output array `X` are simply copies of the vector `x` and the columns of the output array `Y` are copies of the vector `y`. The number of rows of `x` contained in `X` is the length n of `y` and the number of columns of `Y` is equal to the length m of `x`. Example:

```
>> x=[1 2 3 4];  y=[5 4 3];
>> [X Y] = meshgrid(x,y)
X =
     1     2     3     4
     1     2     3     4
     1     2     3     4
Y =
     5     5     5     5
     4     4     4     4
     3     3     3     3
```

That is, $X_{i,j} = x_j$ (independent of i) and $Y_{i,j} = y_i$ (independent of j). The two matrices `X` and `Y` created by `meshgrid` are of the same shape and can be combined with dot operations, such as `.*` or `./`.

As an example of the use of `meshgrid`, we evaluate the function

$$z = f(x, y) = x \exp(-x^2 - y^2)$$

on an x grid over the range $-2 < x < 2$ and a y grid with $-2 < y < 2$.

```
>> x = -2:0.2:2; y = -2:0.2:2;
>> [X,Y] = meshgrid(x, y);
>> Z = X .* exp(-X.^2 - Y.^2); % Dot operations everywhere
```

Now

$$Z_{i,j} \equiv X_{i,j} \exp(-X_{i,j}^2 - Y_{i,j}^2) = x_j \exp(-x_j^2 - y_i^2) = f(x_j, y_i).$$

The commands `mesh(X,Y,Z)` and `surf(X,Y,Z)` give 3D plots on the screen, while the command `contour(X,Y,Z)` gives the very same information as a contour plot. For presentations the output of `surf` is the most spectacular, but for obtaining quantitative information a contour plot is generally more useful. The difference between `mesh` and `surf` is that the former gives a colored wire frame, while the latter gives a faceted view of the surface.

We just saw that the first three parameters of the 3D plotting commands: `contour`, `mesh`, and `surf` were two-dimensional matrices, all of the same dimension. By use of `meshgrid` we created two such matrices from two vectors. However, this is not necessary, the first two parameters of the 3D plotting commands may as well be vectors. Obviously, *the third parameter* `Z`, containing the function values $Z_{ij} = f(x_j, y_i)$, *must be a* $n \times m$ *matrix* with its column index j corresponding to x values and its row index i corresponding to y values.

When the first two parameters, `x` and `y`, are vectors, their dimensions must agree with those of the third parameter `Z`. That is, if `Z` is an $n \times m$ matrix, then `x` must be of dimension m and `y` must be of dimension n. It is useful that the 3D plotting commands of MATLAB can accept vectors when one wants to plot data generated outside MATLAB (by another program or by measurements as, for instance, 2D NMR). In such a case you usually have at your disposal a vector of x values, a vector of y values and a matrix of function values that correspond to these vectors. There is then no need to blow up the vectors x and y to matrices, which we did by the use of `meshgrid`.

7.2 Handle Graphics

Graphical hierarchy

MATLAB has a system, called Handle Graphics, by which you can directly manipulate graphics elements. This system offers unlimited possibilities to create and modify all types of graphs. The organization of a graph is hierarchical and object oriented. At the top is the Root, which simply is your MATLAB screen. This object is created when you start up MATLAB.

Figure objects are the individual windows on the Root screen, they are referred to as the *children* of the Root. There is no limit on the number of Figures. A Figure object is created automatically by the commands that we introduced earlier, namely `plot`, `mesh`, `contour` and `surf`. As for all graphical objects, there is also a separate low level command that creates the object: `figure` creates a new Figure as a child of Root. If there are multiple Figures within the Root, one Figure is always designated as the "current" figure; all subsequent graphics commands, such as `xlabel` will give output to this figure.

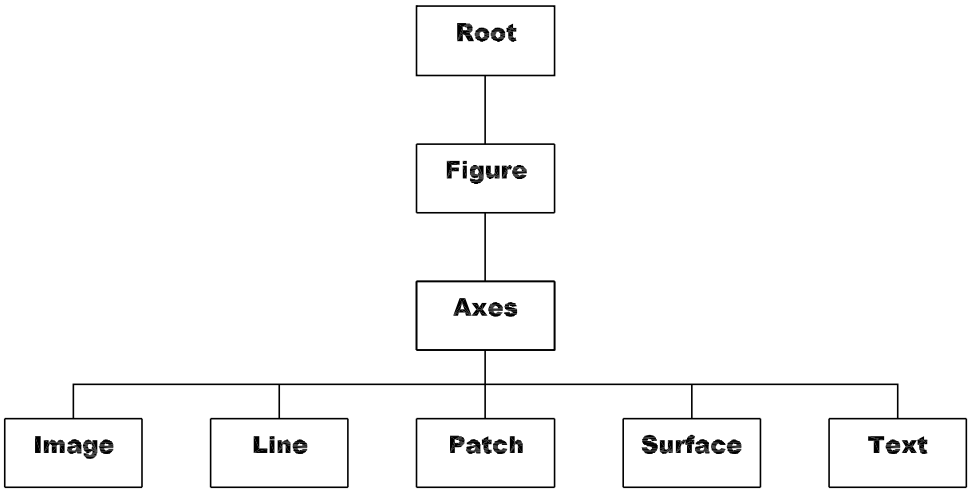


Figure 7.1: *Graphics Hierarchy Tree*

A Figure object has as children the objects Axes, which define regions in a Figure window. All commands such as `plot` automatically create an Axes object if it does not exist. Only one Axes object can be current. The children of Axes are Image, Line, Patch, Surface, and Text. Image consists of pixels; see the MATLAB on-line documentation for more details. The Line object is the basic graphic primitive used for most 2D and 3D plots. High level functions such as `plot` and `contour` create these objects. The coordinate system of the parent Axes positions the Line object in the plot.

Patch objects are filled polygons and are created by high level commands such as `bar`, which creates a bar graph. Surface objects represent 3D data and are created by `mesh` and `surf`.

The final objects are Text, which are also children of Axes. Text objects are character strings and are created by high level commands such as `xlabel`, `ylabel` and `title`, which we met earlier.

7.3 Handles of graphical objects

Handles and a few low level graphical commands.
Every individual graphics object has a unique identifier, called a *handle*, that MATLAB assigns to it when the object is created. By using these handles as variables we can manipulate very easily all objects in a plot. As an example we return to `contour`. Thus far we plotted contours without numbers, which is not particularly useful. However, the MATLAB command `contour` can return values associated with each contour line. Moreover the command returns the *handle* of every contour line. Example:

```
>> x     = linspace(-1,1,20); % 20 equidistant points
>> y     = linspace(-2,2,40);
>> [X Y] = meshgrid(x,y);
>> Z     = Y.^2.*exp(-X.^2-Y.^2);
>> [c h] = contour(X,Y,Z,10);    % 10 levels
>> whos  c h
Name      Size                    Bytes  Class
  c         2x892                   14272  double array
  h        32x1                       256  double array
```

MATLAB interpolates the z values by means of an unspecified algorithm. Furthermore, the length of `c`, containing contour values, is unpredictable, as is the length of `h`. One would perhaps expect the vector of handles `h` to be of length 20 (10 levels are requested of a two-fold symmetric function). However, lines cut by borders become separate graphical objects and therefore `h` is longer than 20 (in the example 32). The important use of the arrays `c` and `h` is in the command `clabel`. This command draws the labels in the contour plot. Continuing the example, the command

```
>> clabel(c,h)
```

draws labels in the current figure (which must be drawn by `contour`). Doing this, one gets a crowded plot, the labels are often too close to each other. The command `clabel(c,h,'manual')` offers the possibility to pick the positions interactively.

As another example of the use of handles, we consider the command `plot`. When we issue `h=plot(x,Y)`, where `Y` is a matrix, then of course the plots appear, but in addition the vector `h` will appear on the screen. Its elements contain unique identification numbers of the curves: the line handles. Each curve in the figure corresponds to an element of the vector `h`. These line handles allow us to make modifications to the individual curves. (Obviously, `h` is only of length > 1 if we plot more than one curve with the same plot statement. If we plot two curves one after the other by issuing the plot command twice and the toggle `hold` in the `on` state, then we get twice a different scalar back as the line handle.)

As an example of the use of a line handle, we first plot two straight lines and then change the color of the second to red, which by default was drawn by MATLAB in faint green.

```
>> h = plot([1:10]', [[1:10]' [2:11]']) % no semicolon
h =
  103.0029   % these are the handles
    3.0063   % usually they are floating point numbers
>> set(h(2), 'color', 'red')  % second line red
```

The low level command `set` acts on the line with line handle `h(2)` and changes the color of this line to red. Note that `set` does not erase the plot and does not start a new one, it acts on the existing (current) plot. High level commands, such as `plot`, `contour`, etc., do start a new plot (unless the hold status is on).

Line handles can also be used to get information about the graphical object.

```
>> set(h(2)) % Inspect possible settings of second curve
        Color
        EraseMode: [ {normal} | background | xor | none ]
        LineStyle: [ {-} | -- | : | -. | none ]
        ....
>> get(h(2)) % Inspect actual settings of second curve
        Color = [1 0 0]
        EraseMode = normal
        LineStyle = -
        ....
```

The command `set(h(2))` returns the possible settings for the second curve, the command `get(h(2))` returns the actual choices. We see that "color" is a property of object Line, and that the actual choice of color is given by the array `[1 0 0]`.

In the "rgb" color scheme used here, this implies that the color chosen is pure red, as is expected because we changed the line color to red. (The array `[1 0 1]` would give an equal mixture of red and blue, which is magenta). We see the possible line styles (see help plot) and the actual choice: solid (the default).

Suppose now we want change the line style of the second curve to dotted. We see that `linestyle` (not case sensitive!) is a property of object with handle `h(2)`. We can change it with `set(h(2), 'linest', ':')`. This turns it into a dotted line. Note that unique abbreviations (`linest` instead of `linestyle`) of the property names of the objects are allowed.

As we said, all objects have a handle, also the Axes objects in a Figure object; by `gca` ("get current axes") we get the handle of the current Axes in the current Figure and by `get(gca)` we get the actual values of the properties of this Axes object. We see that one of the Axes properties is `FontSize`. If we want to increase to 20 points the size of the digits on the axes, we issue `set(gca, 'Fontsize', 20)`.

Fortunately, it is often not necessary to use these low level commands, MATLAB has several high level commands that make life easier. For instance the aspect ratio (ratio between x-axis and y-axis scale) can be set by a command of the type `set(gca,'DataAspectRatio',[1 1 1])`. However, much easier is the use of the high level function `axis`; see its help.

By left clicking with the mouse on an object we turn it into the "current object". Its handle is returned by the command `gco` ("get current object"). So, if we want to change the color of a line on the screen to blue and we forgot to save its handle, then we can click on it and issue the command `set(gco, 'col', 'b')`.

Remove an object by using the function `delete`, passing the object's handle as the argument. For example, delete the current Axes (and all of its children!) by `delete(gca)`.

We can draw lines in the coordinate system of the current Axes object by the low level command

```
line([x1 x2 .. xn], [y1 y2 .. yn])
```

This draws a line from point (x_1, y_1) to point (x_2, y_2), etc., to point (x_n, y_n). But first we want to give the plot a definite size by

```
axis([xmin xmax ymin ymax])
```

which defines an x-axis from `xmin` to `xmax` and a y-axis from `ymin` to `ymax`. For example, the following code draws a rectangular box:

```
>> close all          % close all existing figures
>> axis([0 10 0 20])
>> h = line([2 5 5 2 2], [2 2 4 4 2])
```

We define first an x-axis from 0 to 10 and a y axis from 0 to 20. If we do not do this, the axes are generated by the line command and the boundaries of the box will coincide with the axes, which is usually not what you want. The line command draws lines from the successive points $(2, 2)$ to $(5, 2)$ to $(5, 4)$ to $(2, 4)$ back to $(2, 2)$. This is a rectangular box with width 3 and height 2 with the lower left hand corner at the point $(2, 2)$.

We can place text in the plot by the command `text(x,y,'text')`. For instance in the box that we just drew, beginning at point $(2.5, 3)$:

```
>> t = text(2.5, 3, ' Text ', 'fontsize', 20, ...
   'fontname', 'arial black')
```

Note that the fontsize has a different unit of size than the axes. Arial black is the name of a font; MATLAB can handle different fonts, enter `listfonts` to see which ones are available.

7.4 Polar plots

2D and 3D polar plots

Atomic orbitals pervade all of chemistry. Invariably they are drawn as 3D polar plots and therefore we will show how MATLAB can visualize 3D polar plots. Of course, orbitals may also be drawn as contour diagrams, which is commonly done for molecular orbitals.

Atomic orbitals are products of the form $f(r)\, g(\theta, \phi)$, where we meet again spherical polar coordinates defined by

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} r\sin\theta\cos\phi \\ r\sin\theta\sin\phi \\ r\cos\theta \end{pmatrix}, \quad 0 \le r < \infty,\ 0 \le \theta \le \pi,\ 0 \le \phi < 2\pi. \qquad (7.1)$$

In polar plots one draws only the angular part $g(\theta, \phi)$, taking a fixed radial part $f(r_0)$.

MATLAB is able to make 2D polar plots, but not 3D polar plots, so we must do this ourselves. Let us first explain how to make a 2D polar plot by hand. Say, we want to plot the angular part of the function $f(r)g(\phi)$. Figure 7.2 shows polar graph paper that helps us do this. We choose a fixed value r_0 and mark points for $\phi = 0°, 20°, \cdots, 340°$ with the value of $h(\phi_i) \equiv |f(r_0)g(\phi_i)|$ as the distance from the origin. The equidistant circles help us in measuring this distance. In other words, we mark points

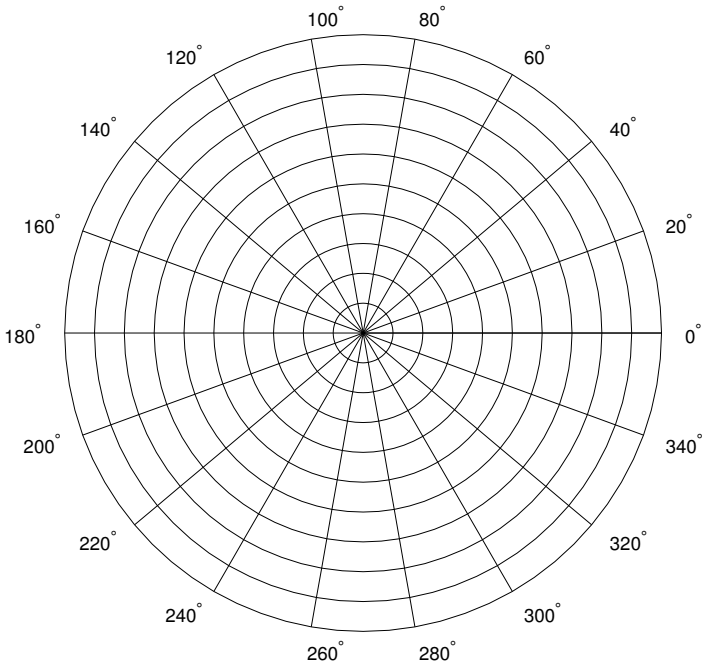


Figure 7.2: Polar plot paper

$(x_i,\, y_i) = (r\cos\phi_i, r\sin\phi_i)$, but substitute for r the positive function values $h(\phi_i)$. After marking the points we draw a line through the points.

As an example, we make a polar plot of $g(\phi) = \cos\phi$ $[f(r_0) = 1]$ and since the computer does the work, we take a much finer grid than we would do by hand.

```
phi = [0:1:360]*pi/180;
x   = cos(phi);
y   = sin(phi);
h   = abs(cos(phi));
plot( h.*x, h.*y)
axis equal
```

The generalization to 3D is clear now. For instance, if we want to plot the $2p_z$ atomic orbital $r\exp(-r)\cos\theta$, we choose a constant value r_0 for r, but since the factor $r_0\exp(-r_0)$ does not affect the shape of the plot, we ignore it. We write $g(\theta,\phi) = \cos\theta$, $h(\theta) = |g(\theta)|$ and plot $z = \cos\theta$ against $x = h(\phi)\sin\theta\cos\phi$ and $y = h(\phi)\sin\theta\sin\phi$. In MATLAB:

```
theta = [0:5:180]*pi/180;
phi   = [0:5:360]*pi/180;
[Theta, Phi] = meshgrid(theta, phi);
```

```
H     = abs(cos(Theta));
X     = H.*sin(Theta).*cos(Phi);
Y     = H.*sin(Theta).*sin(Phi);
Z     = H.*cos(Theta);
surf(X,Y,Z)
axis equal off
```

The same can be achieved in a slightly more efficient manner

```
theta = [0:5:180]*pi/180;
phi   = [0:5:360]*pi/180;
h     = abs(cos(theta));
X     = cos(phi')*sin(theta)*diag(h);
Y     = sin(phi')*sin(theta)*diag(h);
Z     = repmat(cos(theta), length(phi),1)*diag(h);
surf(X,Y,Z)
axis equal off
```

Here `X` and `Y` are obtained from column vector times row vector multiplication (dyadic product).

7.5 Exercises

Exercise 37.

Write a script (or function) that, by using `meshgrid`, draws the "Mexican hat"

$$z = (1 - x^2 - y^2)\exp(-0.5(x^2 + y^2))$$

on the x and y interval $[-3, 3]$. Do not use any `for loops`. Apply one after the other: `mesh`, `surf`, and `contour`. Use matrices for all parameters.

Hint:

Between the plot commands you may enter in your script the MATLAB command `pause`. This allows you to have a look at the plot until you hit the enter key.

Exercise 38.

Return to the previous exercise, change your script (or function) so that the first two parameters of `contour`, `mesh`, and `surf` are the vectors that were used in the `meshgrid` command. Verify that the figures are exactly the same as when the first two parameters were the two matrices created by `meshgrid`.

Exercise 39.

The so-called "sinc" function is defined as follows

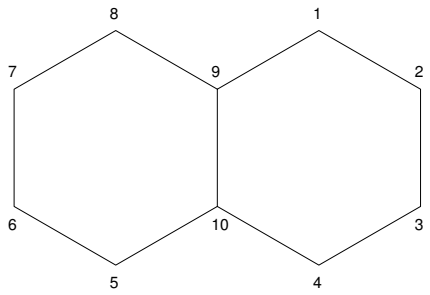
$$\mathrm{sinc}(r) = \begin{cases} \dfrac{\sin(\pi r)}{\pi r} & \text{if } r \neq 0 \\ 1 & \text{if } r = 0. \end{cases}$$

The MATLAB function `sinc` can be called with any matrix as input. Use this function to plot $\mathrm{sinc}(x^2 + y^2)$ on the grid $[-3, 3]$ for both x and y. First look at the result of `surf` and use the rotate button to admire the function from all sides. Then use the `contour` and `clabel` command to put manually values on the contours.

Exercise 40.

Draw the naphthalene molecule as in Fig. 7.3.

Figure 7.3: *Standard numbering of the naphthalene molecule*



Hints: Build a 2×10 matrix $\boldsymbol{R}$ that contains the coordinates of the carbon atoms.

- Choose $(0, 1)$ as coordinates of atom 1 and obtain coordinates of atom 2, 3, 4, 10, and 9 by consecutive rotations over 60°.
- Translate the 6 ring thus obtained to the left: $x_i \mapsto x_i - x_{10}$.
- Get atoms 5, 6, 7, and 8 by reflection, $x_8 = -x_1$ and $y_8 = y_1$, etc.

Then put all x-coordinates of points to be connected in a single array and do the same for the y-coordinates. Determine the size of your plot by `axis` and use `line` to do the actual drawing.

The numbers can be written by `text(x,y,'s')`. This can be done 'by hand', or more elegantly in a loop over the atoms. Use the command `num2str` to convert `n` to a string (quotes must then not be used in the command `text`).

Exercise 41.

A normalized hydrogen $3d_{z^2}$ orbital has the form

$$N\, r^2\, e^{-\zeta r}\, (3z^2 - r^2) \text{ with } r = \sqrt{x^2 + y^2 + z^2} \text{ and } N = \frac{1}{3}\sqrt{\frac{1}{2\pi}}\zeta^{7/2}.$$

Write a script that plots the intersection of this orbital with the yz-plane, that is, for $x = 0$. Choose $\zeta = 3$, and let y and z range from -4 to $+4$.
Hint:
Use for contouring something like

```
[c h]=contour(Y, Z, dorb, [-1:0.05:1]);
clabel(c,h, 'fontsize',6.5)
```

where `dorb` must contain the values of the $3d_{z^2}$ orbital on the y-z grid, the array `[-1:0.05:1]` gives the contour levels and the second statement puts labels on the contours.

Exercise 42.

- Plot the d-orbital of the previous exercise in polar form. Here you may forget about the normalization constant, because only the shape matters, not the values.
- Plot $2p_x^2 = r^2 \exp(-2r) \sin^2\theta \cos^2\phi$ (unnormalized) in polar form. Do not forget the aspect ratio `axis equal`! Do you recognize this plot?

8. Cell arrays and structures

Other data structures than double arrays.
In large MATLAB programs, containing many variables and arrays, it is easy to lose track of the data. MATLAB offers two data structures that make it possible to tidy up such programs: cell arrays and structures. Collecting data in cell arrays or structures may be compared with the tidying up of large collections of disk files by storing them in tar- or zip-files. Related data are brought under a common denominator: the name of the cell array, structure, tar or zip file. Cell arrays and structures are particularly useful if parameter lists in function calls become unwieldily long, because a complete list can be generated by a single reference to a cell array or a named field of a structure.

Since structures and cell arrays are often used to store character data, we also give a short introduction to character handling in MATLAB.

Even if one does not have the intention to write extensive MATLAB programs, it pays to have some knowledge of cell arrays and structures, because MATLAB itself makes heavy use of it. To mention one example: MATLAB can handle variable length input argument lists. This allows any number of arguments to a function. The MATLAB variable `varargin` is a cell array containing the optional arguments to the function. Structures are used in setting parameters for function functions. For instance, the command `odeset` creates or alters the structure `options`, which contains parameters used in solving ordinary differential equations (ODEs). The command `optimset` creates a structure used in, among others, `fzero` and `fminsearch`.

8.1 Cell arrays

Cell arrays in MATLAB are (multidimensional) arrays whose elements are cells. A cell can be looked upon as a container with an array inside. (Remember that a number is also an array, namely a 1×1 array). Usually cell arrays are created by enclosing a miscellaneous collection of arrays in curly braces, {}. For example,

```
>> A = magic(5)      % creates magic square
A =
    17    24     1     8    15
    23     5     7    14    16
```

```
     4     6    13    20    22
    10    12    19    21     3
    11    18    25     2     9
>> C = {A sum(A) prod(prod(A))}    % creates cell array
C =
    [5x5 double]    [1x5 double]    [1.5511e+025]
```

These two commands produce (i) the magic square matrix `A` (all rows and columns sum to 65, elements are $1, 2, \ldots, 25$) and (ii) the 1×3 cell array `C`. The function `prod` takes the products of elements in the columns of `A` and returns a row vector. The second `prod` takes the product of the elements in this row vector. The three cells of cell array `C` contain now the following arrays, which are of different dimension:

- the square matrix `A` in `C(1,1)`,
- the row vector of column sums in `C(1,2)`,
- the product of all its elements in `C(1,3)`.

The contents of the cells in cell array `C` are not fully displayed because the first two cells are too large to print in this limited space, but the third cell contains only a single number, 25!, so there is room to print it.

Here are two important points to remember. First, to retrieve the *cell itself* (container plus content) use round brackets. Since a cell is nothing but a 1×1 cell array, MATLAB command `whos` tells us that e.g. `C(1,2)` retrieves a cell array. Second to retrieve the *content of the cell* use subscripts in curly braces. For example, `C{3}`, or equivalently `C{1,3}`, retrieves 25!, whereas `C(3)` retrieves the third cell. Notice the difference (`C` is the cell array of previous example):

```
>> c=C(1)       % Get cell (1-by-1 cell array)
c =
[5x5 double]

>> whos c
  Name      Size                    Bytes  Class
  c         1x1                       260  cell array

>> d=C{1}      % Get content of cell (5-by-5 magic square)
d =
    17    24     1     8    15
    23     5     7    14    16
```

```
     4     6    13    20    22
    10    12    19    21     3
    11    18    25     2     9

>> whos d
  Name      Size                    Bytes  Class
  d         5x5                       200  double array
```

The MATLAB documentation refers to this as 'cell indexing' (round brackets) and 'content indexing' (curly braces), respectively. *The curly braces peel off the walls of the container and return its contents and the round brackets return the container as a whole.*

Cell arrays contain copies of other arrays, not pointers to those arrays. If you subsequently change the array `A`, nothing happens to `C`.

As we just saw, cell arrays can be used to store a sequence of matrices of different sizes. As another example, we create first an 8×1 cell array with empty matrices and then we store magic squares of different dimensions,

```
% create cell array with a row of empty matrices
>> M = cell(8,1);
>> for n = 1:8
>>   M{n} = magic(n); %content of cell n <--  magic square
>> end
>> M
M =
[ 1]
[ 2x2 double]
[ 3x3 double]
[ 4x4 double]
[ 5x5 double]
[ 6x6 double]
[ 7x7 double]
[ 8x8 double]
```

We see that `M` contains a sequence of magic squares. We retrieve the contents of a cell from this one-dimensional cell array by `M{i}`, for instance,

```
>> prod(prod(M{3}))  % Content of cell M(3) is 3-by-3 array
ans =
      362880

>> prod([1:9])   % 9!
```

```
ans =
      362880
```

Using round brackets, as in `prod(M(3))`, we get an error message because the function `prod` cannot take the product of a cell, only the contents of the cell can be multiplied.

As we saw above, a set of curly brackets around a set of one or more arrays converts the set into a cell array. So, in the example above we could as well have written `M(n)={magic(n)}` instead of `M{n}=magic(n)`. The first form creates on the right hand side a cell containing a magic square and assigns this cell to the n^{th} cell of `M`. The second form adds the magic square to the content of the n^{th} cell of `M`

Only cells may be assigned to cells:

```
>> a    = cell(2);
>> a(1) = [1 2 3]     % Wrong, rhs is not a cell
??? Conversion to cell from double is not possible.

>> a(1) = {[1 2 3]}   % OK, rhs is a cell
a =
    [1x3 double]

>> b      = cell(2,2);
>> b(1,2) = a(1)   % cell a(1) assigned to cell b(1,2)

% Content of cell a(1) to content of cell b(1,2):
>> b{1,2} = a{1}
```

When you use a range of cells in curly brackets, as in `A{i:j}`, the contents of the cells are listed one after the other separated by commas. In a situation where MATLAB expects such a *comma separated list* this is OK. For instance,

```
>> A{1} = [1 2];
>> A{2} = [3 4 5];
>> A{3} = [6 7 8 9 10];
>> % Comma separated list between square brackets
>> [A{1:3}]
>> % identical to:
>> [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]
```

To assign more than one element of a cell array to another, do not use curly brackets on the left hand side, because in general a comma separated list is not allowed on the left hand side of an assignment. Example:

```
>> clear a,  for i=1:20,  a{i}= i^2; end
>> clear A,  for i=1:20,  A{i}=-i^2; end
% To assign part of cell array a to A, use cell indexing
>> a(5:10) = A(5:10); % Assignment of cells
>> a{5:10}            % Display part of cell array:
```

Explanation: the statement `a{5:10}=A{5:10}` is wrong because the left hand side would expand to the comma separated list `25, 36, 49, 64, 81, 100` and such a list on the left hand side of an assignment makes no sense to MATLAB. The next statement (`a{5:10}`) is OK, because it simply is equivalent to:

```
>> 25, 36, 49, 64, 81, 100
ans =
    25
ans =
    36
ans =
    49
ans =
    64
ans =
    81
ans =
   100
```

which asks MATLAB to display the six squared numbers. As we see in the example above, ranges of cell arrays can be assigned to each other by the use of cell indexing (round brackets). We could try the assignment `a(5:10)=A{5:10}`. This gives an error message for the following reason: on the left hand side we have a range of cells and on the right hand side we have numbers (the contents of the cells). We can only assign a cell to a cell, that is, on the right hand side we must also have cells. We can convert the right hand side to a cell array by enclosing it in curly brackets: `a(5:10)={A{5:10}}` is identical to `a(5:10)=A(5:10)`.

Cell arrays are useful in calling functions, where comma separated lists are expected as parameter lists. Example:

```
>> Param    = cell(1,4);     % Create cell array
>> Param(1) = {'linest'};    % Assign first
>> Param(2) = {':'};         %    and second cell
>> Param{3} = 'color';       % Put content into third
```

```
>> Param{4} = 'red';          %     and fourth cell
>> plot(sin(0:pi/10:2*pi), Param{:})
```

Here `Param{:}` expands to a comma separated list, i.e., the four parameters are passed (separated by commas) to `plot`.

In summary, a cell array is a MATLAB array for which the elements are cells, containers that hold other MATLAB arrays. For example, one cell of a cell array might contain a real matrix, another an array of text strings, and another a vector of complex values. You can build cell arrays of any valid size or shape, including multidimensional structure arrays.

8.2 Characters

We can enter text into MATLAB by using single quotes. For example,

```
s = 'Hello'
```

The result is not the same kind of numeric array as we have been dealing with up to now. It is a 1×5 character array, briefly referred to as a string. Internally MATLAB stores a letter as a two byte numeric value, not as a floating point number (8 bytes).

There exists a well-known convention called ASCII (American Standard Code for Information Interchange) to store letters as numbers. In ASCII the uppercase letters A,..., Z have code 65, ...,90 and the lowercase letters a,..., z have code 97,...,122. The function `char` converts an ASCII code to an internal MATLAB code. Conversely, the statement `a = double(s)` converts the character array to a numeric matrix `a` containing the ASCII codes for each character. Example:

```
>> s = 'hello';

>> a = double(s)
a =
   104   101   108   108   111

>> b = char(a)     % array a contains numbers
b =
   hello
```

The result `a = 104 101 108 108 111` is the ASCII representation of `hello`.

Concatenation with square brackets joins text variables together into larger strings. The second statement joins the strings horizontally:

```
>> s = 'Hello';
>> h = [s, ' world']  % a 1-by-11 character array
h =
Hello world
```

The statement `v = [s; 'world']` joins the strings vertically. Note that both words in `v` must have the same length. The resulting array is a 2×5 character array.

To manipulate a body of text containing lines of different lengths, you can construct a character array padded with blanks by the use of `char`. We have just seen that `char` converts an array containing ASCII codes into a MATLAB character array. There are more uses of `char`. If we write `s = char(t1,t2,t3,..)` then a character array `s` is formed containing the text strings `t1,t2,t3,...` as rows. Automatically each string is padded with blanks at the end in order to form a valid matrix. The function `char` accepts any number of lines, adds blanks to each line to make them all the length of the longest line, and forms a character array with each line in a separate row. The reference to `char` in the following example produces a 6×9 character array

```
>> S = char('Raindrops', 'keep', 'falling', 'on', ...
            'my', 'head.')
S =
Raindrops
keep
falling
on
my
head.

>> whos S
  Name      Size          Bytes  Class
  S         6x9             108  char array
```

The function `char` adds enough blanks in each of the last five rows of S to make all the rows the same length, i.e., the length of `Raindrops`.

Alternatively, you can store text in a cell array. As an example we construct a column cell array,

```
>> C ={'Raindrops'; 'keep'; 'falling'; 'on'; 'my'; 'head.'};

>> whos C
```

```
Name      Size          Bytes  Class
C         6x1             610  cell array
```

The contents of the cells are arrays (in this example character arrays), in agreement with our definition of a cell array. You can convert a character array `S` to a cell array of strings with `C = cellstr(S)` and reverse the process with `S = char(C{:})` (comma separated list passed to `char`).

Generally speaking cell arrays are more flexible than character arrays. For instance, transposition of the 6×1 cell array `C` gives

```
>> C'   % cell array from the previous example
 ans =
   'Raindrops'   'keep'   'falling'   'on'   'my'   'head.'
```

which is a 1×6 cell array with the same strings as contents of the cells. Transposition of the 6×9 character array `S` on the other hand gives

```
>> S'   % character array
ans =
    Rkfomh
    aeanye
    iel  a
    npl  d
    d i  .
    r n
    o g
    p
    s
```

which is generally less useful (unless you are a composer of crosswords).

8.3 Structures

Structures are multidimensional MATLAB arrays with elements accessed by designators that are strings. For example, let us build a data base for a certain course. Each entry contains a student name, student number and grade,

```
>> S.name   = 'Hans Jansen';
>> S.number = '005143';
>> S.grade  = 7.5
```

creates a scalar structure with three fields:

```
S =
      name: 'Hans Jansen'
    number: '005143'
     grade: 7.5000
```

Like everything else in MATLAB, structures are arrays, so you can insert additional elements. In this case, each element of the array is a structure with several fields. The fields can be added one at a time,

```
>> S(2).name   = 'Sandy de Vries';
>> S(2).number = '995103';
>> S(2).grade  = 8;
```

The scalar structure `S` has now become a 1×2 array, with `S(1)` referring to student Hans Jansen and `S(2)` to Sandy de Vries.

An entire element can be added with a single statement.

```
>> S(3) = struct('name','Jerry Zwartwater',...
      'number','985099','grade',7)
```

The structure is large enough that only a summary is printed,

```
S =
1x3 struct array with fields:
    name
    number
    grade
```

There are several ways to reassemble the various fields into other MATLAB arrays. They are all based on the notion of a comma separated list. We have already met this notion in the discussion of the cell arrays. Typing

```
>> S.number
```

is the same as typing `S(1).number, S(2).number, S(3).number`. This is a comma separated list. It assigns the three student numbers, one at a time, to the default variable `ans` and displays these numbers. When you enclose the expression in square brackets, `[S.grade]` it is the same as `[S(1).grade, S(2).grade, S(3).grade]` which produces a row vector containing all of the grades. The statement

```
>> mean([S.grade])
ans =
    7.5000
```

gives the average grade of the three students now present in our data base. Just as in the case of comma separated lists obtained from cell arrays, we must be careful that we generate the lists only in contexts where MATLAB expects such lists. This is in six situations:

- Combination of statements on one line plus output, e.g. `>> a,b,c,d`
- inside `[ ]` for horizontal concatenation, e.g. `[a,b,c,d]`
- inside `{ }` to create a cell array, e.g. `{a,b,c,d}`
- inside `( )` for function input arguments, e.g. `test(a,b)`
- inside `( )` for array indexing, e.g. `A(k,l)`
- inside `[ ]` for multiple function output arguments, e.g. `[v,d] = eig(a)`.

Because of this expansion into a comma separated list, structures can be easily converted to cell arrays. Enclosing an expression in curly braces, as for instance `{S.name}`, creates a 1×3 cell array containing the three names.

```
>> {S.name}
ans =
    'Hans Jansen'    'Sandy de Vries'    'Jerry Zwartwater'
```

Since `S.name` expands to a list containing the contents of the name fields, this statement is completely equivalent to

```
ans = {'Hans Jansen', 'Sandy de Vries', 'Jerry Zwartwater'}
```

which, as we saw above, creates a cell array with three cells having the three student names as their contents.

An expansion to a comma separated list is useful as a parameter list in a function call. Above we gave an example where we passed a parameter list to `plot` by expanding the cell array `Param`. As an example of expanding a structure, we call `char`, which, as we saw in subsection 8.2, creates a character array with the entries padded with blanks, so that all rows are of equal length:

```
>> N=char(S.name) % expansion to comma separated list
N =
Hans Jansen
Sandy de Vries
Jerry Zwartwater

>> whos N
Name      Size         Bytes  Class
N         3x16            96  char array
```

In Table 8.1 we list a few MATLAB functions that can handle text, cell arrays, and structures.

Table 8.1: *Some functions useful for cell array, structure and character handling; see help files for details.*

cell	Create cell array.
cell2struct	Convert cell array into structure array.
celldisp	Display cell array contents.
cellfun	Apply a cell function to a cell array.
cellplot	Display graphical depiction of cell array.
char	Create character array (string).
deal	Deal inputs to outputs
deblank	Remove trailing blanks from a string
fieldnames	Get structure field names.
findstr	Find one string within another.
int2str	Convert integer to string.
iscell	True for cell array.
isfield	True if field is in structure array.
isstruct	True for structures.
num2cell	Convert numeric array into cell array.
num2str	Convert number to string.
rmfield	Remove structure field.
strcat	Concatenate strings
strcmp	Compare strings
strmatch	Find possible matches for a string
struct	Create or convert to structure array.
struct2cell	Convert structure array into cell array.

Cell arrays are useful for organizing data that consist of different sizes or kinds of data. Cell arrays are better than structures for applications when you don't have a fixed set of field names. Furthermore, retrieving data from a cell array can be done in one statement, whereas retrieving from different fields of a structure would take more than one statement. As an example of the latter assertion, assume that your data consist of:

- A 3×4 array with measured values (real numbers).
- A 15-character string containing the name of the student who performed the measurements.
- The date of the experiment, a 10-character string as '23-09-2003'.
- A $3 \times 4 \times 5$ array containing a record of measurements taken for the past 5 experiments.

A good data construct for these data could be a structure. But if you usually access only the first three fields, then a cell array might be more convenient for indexing purposes. To access the first three elements of the cell array `TEST` use the command `deal`. The statement

```
[newdata, name, date] = deal(TEST{1:3})
```

retrieves the contents of the first three cells and assigns them to the array `newdata` and the strings `name` and `date`, respectively. The function `deal` is new. It is a general function that deals inputs to outputs:

```
[a,b,c,...] = deal(x,y,z,...)
```

simply matches up the input and output lists. It is the same as `a=x`, `b=y`, `c=z`,.... The only way to assign multiple values to a left hand side is by means of a function call. This is the reason of the existence of the function `deal`. On the other hand, to access different fields of the structure `test`, we need three statements:

```
newdata = test.measure
name    = test.name
date    = test.date
```

8.4 Exercises

Exercise 43.

1. Type in

   ```
   t = 'oranges are grown in the tropics'
   ```

   Read the help of `findstr`. Parse this string into words by the aid of the output of `findstr`. That is, get six strings (character arrays) that contain the respective words. Store these strings in a cell array. Make sure that you do not have beginning or trailing blanks in the words.

2. Write a function `parse` that parses general strings.

   Hints:
   Check the input of the function by `ischar`. Make sure that the input string does not have trailing blanks by the use of `deblank`.

Exercise 44.

Write a script that writes names and sizes of files in the current directory to the screen. Each line must show the filename followed by its size (in bytes). Show the files sorted with respect to size.
Hints:

1. The command `dir` returns a structure with the current filenames and sizes.

2. The command `sort` can return the sorted array together with the permutation that achieves the actual sorting.

3. MATLAB does not echo properly an array of the kind `[char num]`. Apply `int2str` to `num` to get readable output.

Exercise 45.

Predict—without executing the following script—what it will put on your screen:

```
clear all;
a = magic(3);
b = {'a' 'b' 'c'
     'd' 'e' 'f'};
c(1,1).income = 22000;
c(2,4).age = 24;
d = rand(4,7);
e = {a b ...
     c d };

u = size(e);
k = 0;
for i=1:u(1)
for j=1:u(2)
  k = k+1;
  siz(k,:) = [size(e{i,j})];
end
end

siz = [siz; u]
clear u i j k siz

A = whos;
for i=1:length(A)
  siz(i,:) = A(i).size;
end
siz
```

Visit

`http:/www.theochem.kun.nl/~pwormer/matlab/ml.html`.

where you will find this script under the name `size_struct.m`. Download it to your directory and execute it. Was your prediction correct? If not, experiment with the appropriate MATLAB statements until you feel that you understand what is going on in this script (that serves no other purpose than comparing MATLAB data structures and their dimensions).

Exercise 46.

Design a MATLAB data structure for the periodic system of elements. Include the following information:

- The full English name of the element and its standard chemical abbreviation.
- The masses and abundances of the naturally occurring isotopes.
- Electron configuration, i.e., number of electrons in $n = 1, 2, \ldots$. shells.
- Prepare the periodic system for the first 10 elements. A `.txt` file of isotopic masses can be found at the url

  `http:/www.theochem.kun.nl/~pwormer/matlab/ml.html`.

  The same site contains a periodic system as a `.pdf` file. This information originates from the USA government:

  `http://physics.nist.gov/PhysRefData/Compositions/index.html`