PR Advanced Exercises for Theoretical Chemistry and Computational Chemistry

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Instructions

Welcome to the instruction page of the 724651 PR Advanced Exercises for Theoretical Chemistry and Computational Chemistry!

The sidebar contains links to the respective exercise. For the exercise a scientific introduction is provided along with a detailed HowTo and a checklist which results should be included on the poster.

```
import matplotlib.pyplot as plt
import numpy as np
from matplotlib.ticker import (MultipleLocator, AutoMinorLocator)

# 100 linearly spaced numbers
x = np.linspace(-4.9,4.9,100)

# the function, which is y = x^2 here
y = x**2+10

# setting the axes at the centre
fig = plt.figure()
ax = fig.add_subplot(1, 1, 1)
ax.set_ylim([-5, 35])
ax.xaxis.set_minor_locator(MultipleLocator(0.5))
ax.yaxis.set_minor_locator(MultipleLocator(2.5))

# plot the function
plt.plot(x,y, 'r', linewidth = 2.5)
plt.axvline(x = 0, ymin = 0.1, ymax = 0.9, color = 'r', linewidth =
 ↪  2.5)
#plt.axis('off')
plt.grid(True)

# show the plot
plt.show()
```

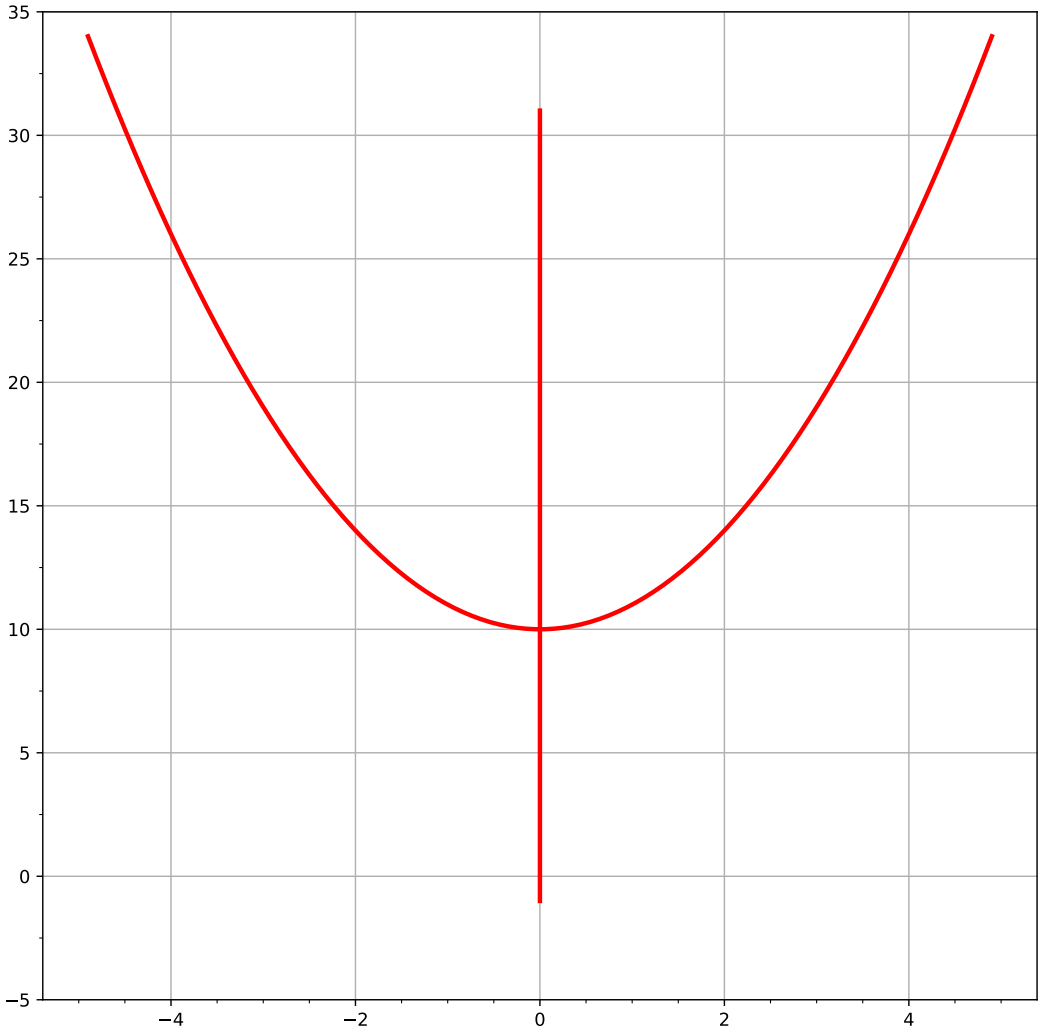


Figure 1: Example code with corresponding plot. Any similarity to the greek letter Ψ is pure coincidence ;)

Exercise: Vibrational Spectroscopy

Background Info

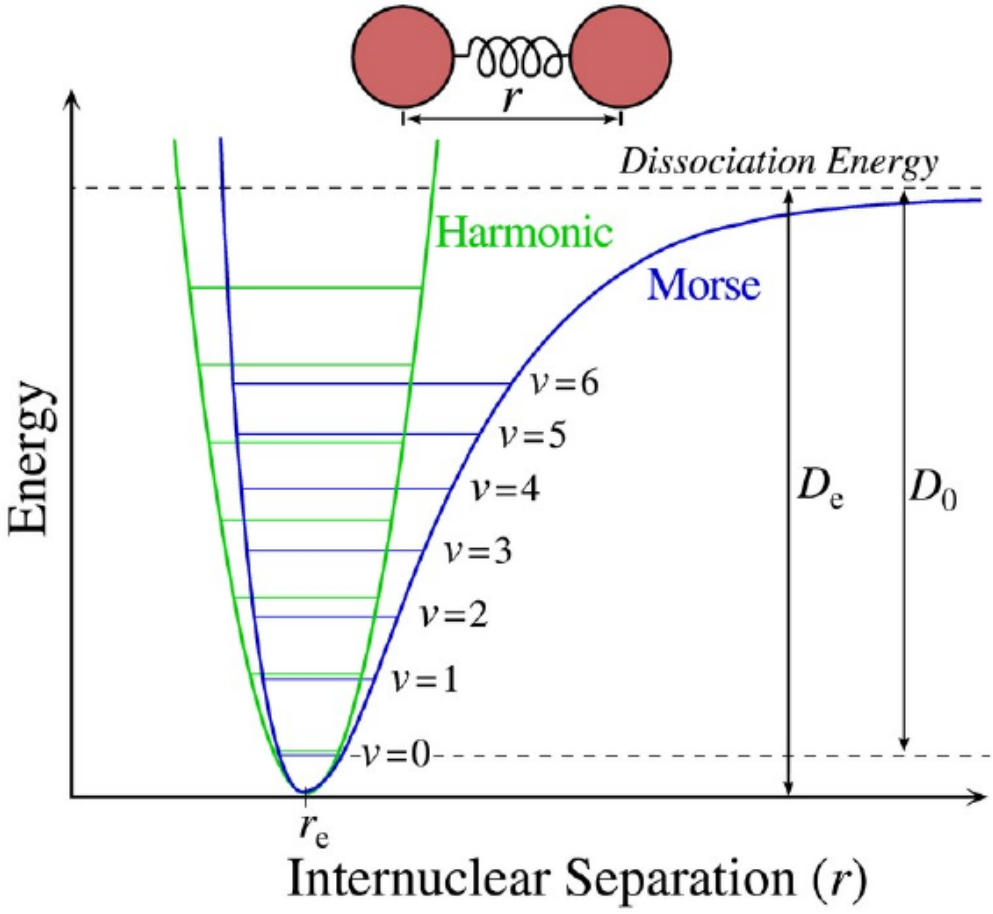
Exercise – Vibrational Spectroscopy using Nuclear Wave Functions

The simplest way to generate vibrational spectra is the **harmonic approximation**: all second derivatives of the energy with respect to the nuclear degrees of freedom are computed at a pre-optimized minimum structure, yielding the Hessian:

$$H_{ij} = \frac{\partial^2 \langle E \rangle}{\partial q_i \partial q_j}$$

After extraction of the force constants k of each vibrational mode from the Hess-matrix (via diagonalisation), the harmonic frequencies ν can be obtained via

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$



with μ being the associated reduced mass. However, a short-coming of this approach is the **neglect of anharmonicity**, **mode coupling** and **nuclear quantum effects**. In some cases these contributions cancel, while for other systems the error in the harmonic frequencies can be up to $300\,\mathrm{cm}^{-1}$.

An elegant alternative is the calculation of vibrational wave functions by numerically solving the nuclear Schrödinger equation. One method to achieve this is a method according to **Boris V. Numerov** requiring the potential curve as input in form of a discretised grid. The latter can be obtained from a potential energy scan executed for instance using the QM program `gaussian`. The difference between the eigenvalue of the ground state ($n = 0$) and the first ($n = 1$) and second ($n = 2$) excited states correspond to the expected vibrational frequency of the fundamental and first overtone, when divided by Planck's constant:

$$\nu_{n0} = \frac{E_n - E_0}{h}$$

From the frequencies ν_{n0} (in s^{-1}) the respective wave numbers $\bar{\nu}_{n0}$ (in cm^{-1}) have to be calculated and reported. Knowledge of the wave function also enables the calculation of the oscillator strengths f_{n0}, providing an accurate estimate of the expected IR absorption intensities.

$$f_{n0} = \frac{4\pi m_\mathrm{e}}{3\mathrm{e}^2\hbar c}|\mu_{n0}|^2\bar{\nu}_{n0} = 4.702 \cdot 10^{-7}\,\frac{\mathrm{cm}}{\mathrm{D}^2}|\mu_{n0}|^2\bar{\nu}_{n0}$$

To calculate the oscillator strength, the wave numbers $\bar{\nu}_{n0}$ and the respective transition dipole moment μ_{n0} is required. The latter is given as:

$$|\mu_{n0}|^2 = |\mu^x_{n0}|^2 + |\mu^y_{n0}|^2 + |\mu^z_{n0}|^2$$

with

$$|\mu^x_{n0}| = \langle\psi_0|\mu^x|\psi_n\rangle = \int_{-\infty}^{\infty} \psi_0 \mu^x \psi_n dx$$

While this integral appears intimidating, it can be easily evaluated in an approximate way using the trapezoidal rule:

$$\int_a^b f(x)dx \approx \frac{\Delta x}{2}(y_1 + 2y_2 + 2y_3 + ... + 2y_{n-1} + y_n)$$

$$\approx \frac{\Delta x}{2}\sum_{i=1}^{n-1}(y_i + y_{i+1})$$

The calculation of the trapezoidal integration is actually very simple and can be easily implemented in a spreadsheet editor such as `libreoffice` or `excel` (or computed using data science software such as `matlab`, `octave`,`python`, `R`, etc.)

Diatomic molecule

In this part the vibration of a diatomic molecule is investigated. After drawing the molecule using `gaussview`, an energy minimisation (= geometry optimisation) and a harmonic frequency calculation has to be carried out. In the next step a potential energy scan has to be performed in the range of approx. -0.5 Å to +1.5 Å using a step length $\Delta r = 0.01$ Å. This yields about 150 individual potential points.

The energy and dipole moment information can be extracted in the terminal using the provided tool:

```
./extract_data.sh  scan-logfile  >  data-file
```

The data file contains the distance information in Å, the QM energy in Hartree, and the components of the dipole moment in x, y and z direction in Debye. Next, the force constant k according to the harmonic approximation has to be determined via finite differences from the energy column of the data-file (second column).

$$k \approx \frac{E_1 - 2E_{\text{min}} + E_{+1}}{\Delta r^2}$$

with E_{min} being the minum energy and $E_{\pm 1}$ corresponding to the energy values of the two neighbouring points. Please report the force constant in kcal $\cdot$ mol^{-1}Å^{-2}:

Because the program gaussian provides a wrong reduced mass μ in case of diatomic systems, this property has to be calculated manually in this part of the exercise.

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Using the reduced mass μ and the force constant k the frequency (in s^{-1}) and corresponding wave number (in cm^{-1}) should be calculated and compared to the result obtained from gaussian.

> **Note**
>
> Extra care is required to apply all factors to obtain the correct unit of the frequency and wavenumber (i.e. just dividing the force constant k in kcal $\cdot$ mol^{-1}Å^{-2} by the reduced mass μ given in g $\cdot$ mol^{-1} will obviously yield a wrong result …)

In the final step the Numerov calculation is carried out, requiring the data file and the reduced mass as input:

```
./numerov    data-file    mass    >  numerov-outfile
```

The output of the Numerov procedure contains the coordinate and potential information (in units Å and kcal $\cdot$ mol^{-1}) as well as the wave-functions for the five lowest states. The energy eigenvalues are given as comment line (also in kcal $\cdot$ mol^{-1}) on top of the Nuermov output file. The respective energy differences have to be transformed into cm^{-1}.

The report for this part should include:

- A screenshot of the equilibrium geometry (white background!).
- The calculation of the force constant k and the reduced mass μ.
- Calculation of the frequency and wave number showing ALL(!) required conversion factors.
- A figure showing the QM energy as a function of distance and the Numerov wave functions plus the energy graph showing the harmonic approximation (all in the same figure).
- A table comparing the wavenumbers obtained via the Numerov procedure with the results obtained from the harmonic approximation for $n = 1$ - 4.
- For all points a short description/interpretation should be included as text.

Note

In this part, the transition dipole moments and oscillator strengths are **NOT(!)** required.

Stretch Vibration in a Polyatomic Molecule

In this example, the X-H stretch motion of a polyatomic molecule (X=O,N) provides a suitable approximation to the actual normal mode. In order to assess the influence of quantum effects, both hydrated and deuterated species (i.e. X-H and X-D) have to be investigated. After the geometry optimisation and frequency computation, the potential energy scan of the X-H distance in the range of approx. 0.5 Å to 2.0 Å has to be carried out, using again a step length of 0.01 Å.

Careful:

Be sure to select the correct bond for the potential energy scan! (This is a **very** frequent error in this excercise.)

As before the energy and dipole moment information can be extracted in the terminal using the provided tool:

```
./extract_data.sh    scan-logfile    >    data-file
```

The resulting data file contains the coordinate, energy and dipole moment information (in units of Å, Hartree and Debye) and can be directly used as input for the Numerov programm:

```
./numerov    data-file    mass    > numerov-outfile
```

In addition to the data file, the reduced mass of the vibrational mode has to be provided as a second input. For polyatomic molecules the reduced mass provided in the gaussian output file is correct! To identify the correct mode, a visual inspection in `gaussview` is required.

Careful:

Be sure to make a separate check in the deuterated case – the order of vibrations is sometimes different (again a **very** common error in this excercise).

As before the output of the Numerov procedure contains the coordinate and potential information (in units Å and kcal $\cdot$ mol^{-1}) as well as the wave-functions for the five lowest states. The energy eigenvalues are given as comment line (also in kcal $\cdot$ mol^{-1}) on top of the file. The respective energy differences have to be transformed into cm^{-1}. Prior to computing the transition dipole moments it should be verified that the wave functions are orthonormal for the states $i, j = 0 - 2$.

$$\langle \psi_i | \psi_j \rangle - \delta_{ij} = 0$$

Next, the oscillator strength f_{n0} (for $n = 1, 2$) should be computed from the transition dipole moments and reported relative to f_{10}. (*i.e.* the oscillator strengths are divided by f_{10}, thus always giving a number of 1.0 for the ground state transition).

The report for this part should include:

- A screenshot of the equilibrium geometries (white background!).
- Two figures comparing the potential energy and the first five wave functions including also the potential energy of the harmonic approximation for both the hydrated and deuterated species.
- A graph showing the components of the dipole moment as a function of the distance.
- Results of the orthonormality check between the states i, $j = 0, 1, 2$ in form of a table.
- A table comparing the frequencies and oscillator strengths of the fundamental and first overtone modes obtained via the Numerov procedure and the harmonic approximation.
- For all points a short description/interpretation should be included as text.

Protocol:

The protocol in this section should be designed as an A0-Poster (similar to those Ph.D. students typically prepare for their presentations in the Atrium of the CCB building), see poster templeates. All data generated along with a discussion of results fit easily on a single page. Please include your name and matriculation number, and provide the protocol as pdf-file including your surname in the name of the file.

HowTo

The required scripts and programs for this exercise are provided in the folder:

```
cd
 ↪ /media/TC_Lehre/03_PR_Fortgeschrittene_Uebungen_zu_TC_und_Comp_Chemie/vibration/
```

Note

This HowTo assumes you remember how to
i) create new directories and
ii) copy/move/rename files.

If you are unsure please look at this Linux quickstart guide.

Vibrational spectroscopy of a diatomic molecule at the example of H_2

Tasks

- Execute an energy minimisation, a frequency calculation and a potential energy scan using `gaussian`
- Extract the potential energy data from the output file
- Execute a Numerov calculation

Results

- Numeric evaluation of the force constant from the potential plot
- Calculation of the harmonic vibrational wave numbers from the force constant (compare this value to the gaussian result for verification – deviation typically about 1-2 cm^{-1})
- Calculation of the anharmonic vibrational wave numbers from the Numerov eigenvalues
- 1 plot V_{QM} vs bond length including the vibrational wave function from the Numerov output and the harmonic approximation to the potential energy
- Table comparing the harmonic and anharmonic wave numbers for the states 01 to 04
- A screenshot of the equilibrium geometry (use a white background color!)

HowTo

1) Draw the structure using `gaussview` (command `gv`) and save the file, *e.g.* as `h2_opt.com`.

```
gv
```

GaussView

draw stuff
File > Save
Be sure to **NOT** save cartesian coordinates, so "Write Cartesian" must be unticked!

2) Open the File in your favourite editor (`code`, `nedit`, `gedit`, `vi`, ...) and change the command line (`#`) to

h2_opt.com

```
# B3LYP/6-311++G(3df,3pd) OPT=TIGHT SCF=VERYTIGHT INT=ULTRAFINE
```

! Important

It is important to include **one (and only one) blank line** after the command line (`#`-line), the title-line as well as the atom list and at least one blank-line after the last input for all `gaussian` input file!

3) Execute the geometry optimisation:

```
g16 h2_opt.com
```

4) Open the log-file (`code`,`nedit`, `gedit`, `vi`, ...) and get the equilibrium bond distance,*e.g.*:

```
nedit h2_opt.log
```

h2_opt.log

[...]
[...]
Final structure in terms of initial Z-matrix:
H
H,1,B1
Variables:
B1= 0.74273528
[...]
[...]

5) Copy the in-file and change the command line to that of a frequency calculation, *e.g.*:

```
cp h2_opt.com h2_freq.com
```

h2_freq.com

```
# B3LYP/6-311++G(3df,3pd) FREQ SCF=VERYTIGHT INT=ULTRAFINE
```

Also set the bond length to the minimum distance, *e.g.*

h2_freq.com

```
[...]
0  1
H
H     1     B1

B1    0.74273528
[...]
```

6) Execute the frequency calculation and get the harmonic frequency from the log-file

```
g16 h2_freq.com
```

```
nedit h2_freq.log
```

h2_freq.log

```
[...]
[...]
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
activities (A**4/AMU), depolarization ratios for plane and unpolarized
incident light, reduced masses (AMU), force constants (mDyne/A),
and normal coordinates:
                     1
                     SGG
Frequencies --        4410.4726
Red. masses --           1.0078
Frc consts --           11.550
IR Inten --              0.0000
[...]
[...]
```

! Be careful

For diatomics the force constant and the reduced mass are not given correctly! (according to the developers that's a feature, not an error ...) This is the reason why in this exercise, the force constant has to be determined from the potential energy scan! Do **NOT** use the force constant from the output file.

7) Copy the in-file and change the command line for the potential energy scan, *e.g.*:

```
cp h2_freq.com h2_scan.com
```

h2_scan.com

```
# B3LYP/6-311++G(3df,3pd) SCAN SCF=VERYTIGHT INT=ULTRAFINE
# GEOM=NOCROWD NOSYMM POP=ALWAYS
```

8) Change the starting value of the bond length by subtracting 0.5 Å, and set up the scan points *e.g.*:

Note

$0.7427352 - 0.5 = 0.2427352$

h2_scan.com

```
[...]
0  1
H
H     1     B1

B1    0.24273528   150   0.01
[...]
```

This will perform a potential energy scan from 0.2427352 Å, increasing the H-H distance 150 times by 0.01 Å, thus the scan will end at a H-H distance of 1.7427352 Å. Don't forget to include a final blank line in the gaussian input.

9) Execute the potential energy scan and grab a coffee:

```
g16 h2_scan.com
```

10) Copy the extraction-script and the Numerov analysis code to your working directory:

```
cp
 ↪ /media/TC_Lehre/03_PR_Fortgeschrittene_Uebungen_zu_TC_und_Comp_Chemie/vibration/extract_data.sh
 ↪ .
cp
 ↪ /media/TC_Lehre/03_PR_Fortgeschrittene_Uebungen_zu_TC_und_Comp_Chemie/vibration/numerov
 ↪ .
```

11) Extract the potential energy and dipole moment information from the log-file and use `>` to redirect the output:

```
./extract_data.sh h2_scan.log > scan_data.dat
```

Warning

Careful – if told, the redirect `>` will overwrite existing files and there is no undo if this happens!

The file `scan_data.dat` contains five data columns:

scan_data.dat

- column 1 : Distance in Å
- column 2 : Energy in Hartree

- columns 3 to 5 : x, y and z-component of the dipole moment

This file can be directly imported into graphic-programs, *e.g.* `office`,`xmgrace`, `gnuplot`, …

The dipole moment data is only required in part A.2 of this practical course.

12) Calculate the reduced mass of the vibration and execute the Numerov analysis:

- In this course always the reduced mass formula for two particles should be used.

> **Warning**
>
> Be sure to use the mass of the correct isotopes, *e.g.* $^{1}H_2$, $^{2}D_2$, ^{12}C, ^{18}O and do **NOT** use the averaged mass given in the periodic table.

- The Numerov-program requires two inputs, being the data-file from step 11 above and the reduced mass, e.g. in case of $^{1}H_2$:

```
./numerov scan_data.dat 0.50391251605 > numerov.dat
```

Again, be careful while redirecting `>` to not overwrite any files.

The file `numerov.dat` contains a headline (`#`) and twelve data columns. Columns 1 to 7 are to generate the required figure, columns 8 to 12 are for data analysis:

numerov.dat

- # headline – energy eigenvalues E of the five lowest wave functions Ψ_0 to Ψ_4 in kcal/mol
- column 1 : Distance in Å

- column 2 : Energy in kcal/mol and shifted to zero at the minimum
- columns 3 to 7 : wave functions Ψ_0 to Ψ_4 shifted by the respective eigenvalue
- columns 8 to 12: wave functions Ψ_0 to Ψ_4 without shift

This file can be directly imported into graphic programs (e.g. office, xmgrace, gnuplot, …) as well as data software (`office`, `matlab`, `octave`, `R`, `bash`, `origin`, …) to perform the analyses required in A.2.2.

> **Note**
>
> Which software you choose for the analysis part (or if you want to write your own code) is entirely up to you. There are different ways to obtain the requested data, *e.g.* the numerical integration can be carried out i) in an `excel`-sheet, ii) using `Python`/`R` datascience routines, iii) on the command line using a (very simple) `awk`-script or iv) even graphically in the program `xmgrace`. You can choose whichever method works best for you.

Stretch Vibration in a Polyatomic Molecule

Tasks

i) Execute an energy minimisation, a frequency calculation and a potential energy scan using gaussian
ii) Extract the potential energy data from the output file
iii) Execute a Numerov calculation
iv) Analyse both a hydrated (^{1}H) and deuterated system (^{2}D)

Results

- Numeric evaluation of the force constant from the potential plot

- Calculation of the harmonic vibrational wave numbers from the force constant for ^{1}H and ^{2}D (compare these values to the gaussian results for verification – deviation typically about $1-2$ cm^{-1})
- Calculation of the anharmonic vibrational wave numbers from the Numerov eigenvalues
- 2 plots V_{QM} vs bond length including the vibrational wave function from the Numerov output and the harmonic approximation to the potential energy
- 1 plot showing the components of the dipole moment and the total dipole moment as a function of the distance.
- Results of the orthonormality check between the states $i, j = 0, 1, 2$ should be provided in a table.
- A table comparing the frequencies and oscillator strengths of the fundamental and 1$^{\mathrm{st}}$ overtone modes obtained via the Numerov procedure and the harmonic approximation should be included.
- A screenshot of the equilibrium geometry (use a white background color!)

Follow steps 1) to 12) of part 2.1 for the polyatomic system. Redo the calculations for the deuterated system, but be smart - not all calculations of the steps i) to iii) above have to be repeated for the deuterated system. Just consider which calculation steps are mass-independent and which one is not.

In order to change the isotope from ^{1}H and ^{2}D in the gaussian calculation, the iso-keyword should be applied, *e.g.* in case of a frequency calculation for D_2:

d2_scan.dat

```
# B3LYP/6-311++G(3df,3pd) FREQ SCF=VERYTIGHT INT=ULTRAFINE

D2 Frequency calculation (at minimum geometry)

0 1
H  (iso=2)
H  (iso=2)    1    B1

B1    0.74273528
```

! Common errors/pitfalls in this exercise

- Be **VERY** careful which bond to scan – in many cases the correct bond is NOT `B1` (a very common error!). Which bond to scan depends on the way the molecule is drawn and the resulting order of atoms.
- If you start to draw the molecule starting with the functional group of interest (*e.g.* start with the OH- group in case of methanol), the y-component of the dipole moment will be zero. This means less work in the analysis of the transition dipole moment and the oscillator strengths.
- Be aware of the units of the different properties and take your time to perform a dimensional analysis. For instance, typical units of the force constants k and the reduced mass μ are kcal $\cdot$ mol^{-1} $\cdot$ Å^{-2} and g/mol, respectively. It is not possible to simple use the associated values to calculate the frequency without first making the units compatible:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Here, the units kcal, Å^{-2} and g need to be converted to obtain the unit of s^{-1} for the frequency.

Checklist

The protocol in this section should be designed as an A0-Poster (similar to those Ph.D. students typically prepare for their presentations in the Atrium of the CCB building). All data generated along with a discussion of results fit easily on a single page. Please include your name and matriculation number, and provide the protocol as pdf-file including your surname in the name of the file.

The report for exercise A.1 should include:

- ☐ A screenshot of the equilibrium geometry (white background!).
- ☐ The calculation of the force constant k and the reduced mass μ.
- ☐ Calculation of the frequency and wave number showing **ALL(!)** required conversion factors.
- ☐ A figure showing the QM energy as a function of distance and the Numerov wave functions plus the energy graph showing the harmonic approximation (all in the same figure).
- ☐ A table comparing the wavenumbers obtained via the Numerov procedure with the results obtained from the harmonic approximation for $n = 01$ - 04.

> **Note**
>
> In this part, the transition dipole moments and oscillator strengths are **NOT(!)** required.

The report for exercise A.2 should include:

- ☐ A screenshot of the equilibrium geometries (white background!).
- ☐ Two figures comparing the potential energy and the first five wave functions including also the potential energy of the harmonic approximation for both the hydrated and deuterated species.
- ☐ A graph showing the components of the dipole moment as a function of the distance.
- ☐ Results of the orthonormality check between the states $i, j = 0, 1, 2$ in form of a table.
- ☐ A table comparing the frequencies and oscillator strengths of the fundamental and first overtone modes obtained via the Numerov procedure and the harmonic approximation.
- ☐ For all points a short description/interpretation should be included as text.

> **Note**
>
> In this part, the transition dipole moments and oscillator strengths **ARE(!)** required for the analysis.

Exercise: NNP-MD

Background Info

Exercise - NNP MD Simulations of CO_2@ZIF-8

Metal-organic frameworks (MOFs) are hybrid crystalline materials assembled from both inorganic and organic residues containing potential voids [1]. The key advantage of MOFs over naturally occurring porous compounds such as zeolites (*i.e.* aluminosilicates) or polymers lies in their crystalline nature, which allows for systematic modification through crystal engineering principles by altering their organic linkers or metal nodes. This capability leads to an almost limitless number of possible framework topologies and properties, making them particularly appealing for technological applications. In 2025, the Nobel Prize in Chemistry

was awarded to Profs. Susumu Kitagawa, Richard Robson and Omar M. Yaghi "for the developement of metal-organic frameworks".

One of the most widely discussed applications is associated to the enormous gas storage capacity of MOF materials. Storage and separation of critical green house gases such as CO_2 and CH_4 are widely discussed [2,3]. In addition, due to their ultrahigh internal surface area, tunable pore dimensions, and rapid kinetics for gas adsorption and desorption, MOFs have emerged as highly promising candidates for capturing and storing carbon dioxide, called direct air capture (DAC) [4].

An increasing number of MOF compounds are discussed as potential host matrices for green house gases [4]. In this exercise, carbon dioxide storage in the comparably simple ZIF-8 (zeolitic imidazolate framework) is investigated via molecular dynamics simulations (MD), to keep the computational effort and memory demand manageable.

The ZIF-8 system Zn(2-methylimidazolate)$_2$ crystallizes in the non-centrosymmetric cubic space group I43m (space group no. 217) with a lattice parameter of approx 1.7 nm. The cubic unit cell contains a total of 12 Zn^{2+} cations that are each tetrahedrally coordinated by four 2-methylimidazolate linkers. The pore structure of ZIF-8 is similar to the topology of a prototypic sodalite zeolite (hence the name zeolitic imidazolate framework). Several studies have investigated ZIF systems with respect to their CO_2 storage capacity [5-8].

In order to achieve fast and accurate MD simulations, the MACE-MP neural network potential (NNP) [9-11] is applied, in particular the MACE-DAC-1 model [12], which is trained not only on solid-state systems but also on interactions with gases for direct air capture (DAC) applications. If trained properly, NNPs provide an efficient and versatile description of chemical systems, combining the accuracy of high level quantum chemical methods with the speed of classical force field approaches.

In this exercise the properties of the pristine host material (lattice parameter and thermal expansion coefficient) and the interaction between the inserted CO_2 molecules and the ZIF-8 host (diffusion coefficient and activation energy of diffusion) will be studied.

[1] Yusuf, V. F.; Malek, N. I.; Kailasa, S. K. "Review on Organic Framework Classification, Synthetic Approaches, and Influencing Factors: Applications in Energy, Drug Delivery, and Wastewater Treatment." ACS Omega 2022, 7, 44507 – 44531, DOI: 10.1021/acsomega.2c05310

[2] Li, B.; Wen, H.-M.; Zhou, W.; Chen, B. "Porous Metal–Organic Frameworks for Gas Storage and Separation: What, How, and Why?" J. Phys. Chem. Lett. 2014, 5, 3468 – 3479 DOI: 10.1021/jz501586e

[3] Li, H.; Li, L.; Lin, R.-B.; Zhou, W.; Zhang, Z.; Xiang, S.; Chen, B. "Porous metal-organic frameworks for gas storage and separation: Status and challenges" EnergyChem 2019, 1, 100006/1 – 100006/39 DOI: 10.1016/j.enchem.2019.100006

[4] Mahajan, S.; Lahtinen Ma. "Recent progress in metal-organic frameworks (MOFs) for CO_2 capture at different pressures" J. Environ. Chem. Eng. 2022, 10, 108930/1 – 108930/35 DOI: 10.1016/j.jece.2022.108930

[5] Abraha, Yuel W.; Tsai, C.-W.; Niemantsverdriet, J. W. H.; Langner E. H. G. "Optimized CO_2 Capture of the Zeolitic Imidazolate Framework ZIF-8 Modified by Solvent-Assisted Ligand Exchange" ACS Omega 2021, 6, 21850 – 21860 DOI: 10.1021/acsomega.1c01130

[6] Jiang, S.; Liu, J.; Guan J.; Du, X.; Chen, S.; Song, Y.; Huan, Y. "Enhancing CO_2 adsorption capacity of ZIF-8 by synergetic effect of high pressure and temperature" Sci. Rep. 2023, 17584/1 – 17584/8 DOI: 10.1038/s41598-023-44960-4

[7] Kalauni, K.; Vedrtnam, A.; Wdowin, M.; Chaturvedi, S. "ZIF for CO_2 Capture: Structure, Mechanism, Optimization, and Modeling" Processes 2022, 10, 2689/1 – 2689/32 DOI: 10.3390/pr10122689

[8] Heinz, K.; Rogge, S. M. J.; Kalytta-Mewes, A.; Volkmer, D.; Bunzen, H. "MOFs for long-term gas storage: exploiting kinetic trapping in ZIF-8 for on-demand and stimuli-controlled gas release" Inorg. Chem. Front. 2023, 10, 4763 – 4772 DOI: 10.1039/D3QI01007D

[9] Batatia, I.; Kovacs, D. P.; Simm, G.; Ortner, C.; Csanyi G. "MACE: Higher Order Equivariant Message Passing Neural Networks for Fast and Accurate Force Fields" arXiv,

2022, DOI: 10.48550/ARXIV.2206.07697

[10] Batatia, I. et al. “A foundation model for atomistic materials chemistry” arXiv, 2024, DOI: 10.48550/ARXIV.2401.00096

[11] ACEsuit/mace-mp https://github.com/ACEsuit/mace-mp (accessed 16. 10. 2024)

[12] Yunsung L., Hyunsoo P., Aron W., Jihan K. “Accelerating CO2 direct air capture screening for metal-organic frameworks with a transferable machine learning force field” Matter 2025, 8, 102203 DOI: 10.1016/j.matt.2025.102203

HowTo

> ⚠ Warning
>
> Links to the **Google Sheets** with the assigned temperatures and carbon dioxide loadings:
> - Thermal Expansion
> - Gas Diffusion

Each student will be assigned two specific temperature values and a specific carbon dioxide loading for the simulations. One temperature will be used for Part B.1 and the other for Part B.2. The carbon dioxide loading will be used for the simulation in Part B.1

> ❗ Important
>
> Before you run any simulations, please make sure you know your assigned **TEMPERATURES** and **CARBON DIOXIDE LOADING**!

Tools and Programs

All tools and programs are provided by the HoferLab™. The simulation engine that will be used is PQ. The analysis tools are written in Python and C, and are partially based on the PQAnalysis library.

The required tools and programs for this exercise are provided by executing the following command:

```
module load pq
```

> ❗ Important
>
> This command needs to be executed only once per terminal session. If you close the terminal, you will need to execute the command again when you open a new terminal.

The simulation engine PQ can be executed by running the following command:

```
PQ <input_file>
```

The analysis tools are written in an intuitive way and have a help function that can be accessed by running the script with the `--help` flag. For example:

```
<analysis_tool> --help
```

Analysis Tools

The following analysis tools are provided for this exercise:

Tool	Description
`average_a`	Averages the lattice parameter a of the provided box files.
`average_V`	Averages the volume of the provided box files.
`extract_co2`	Extracts the carbon dioxide molecules of trajectory/velocity-files and calculates the center of mass coordinates/velocities.
`msd`	Calculates the mean squared displacement of the carbon dioxide molecules from a trajectory. (Note: The carbon dioxide molecules have to be extracted first using `extract_co2`).
`rdf_zif8`	Calculates the radial distribution function of the carbon dioxide molecule from a trajectory.
`vacf`	Calculates the velocity autocorrelation function of the carbon dioxide molecule from a velocity file. (Note: The carbon dioxide molecules have to be extracted first using `extract_co2`).
`linearfit`	Fits a linear function to the mean squared displacement data to calculate the diffusion coefficient according to the Einstein relation.
`integration`	Integrates the velocity autocorrelation function to calculate the diffusion coefficient according to the Green-Kubo relation.

Files

The directories encoded in the `ZIF_DIR` variable contain all necessary files for the simulations. The files are organized in the following way:

File Structure

```
co2
    co2.rst
general_input
    moldescriptor.dat
    run-01.in
    run-02.in
    run-03.in
    run-04.in
preeq
    248
        shake_zif8_248.top
        zif8_preeq_248.rst
    273
        shake_zif8_273.top
        zif8_preeq_273.rst
    298
        shake_zif8_298.top
        zif8_preeq_298.rst
    323
        shake_zif8_323.top
        zif8_preeq_323.rst
    348
        shake_zif8_348.top
        zif8_preeq_348.rst
    373
        shake_zif8_373.top
        zif8_preeq_373.rst
    398
        shake_zif8_398.top
        zif8_preeq_398.rst
```

Folder/File	Description
`co2`	Contains the carbon dioxide restart-file (`co2.rst`)
`general_input`	Contains the input files for the simulations (`moldescriptor.dat` and `run-0?.in`).
`preeq`	Contains the pre-equilibrated restart-files (`zif8_preeq_*.rst`) and associated topology files (`shake_zif8_*.top`).

Part B.1) Gas simulation in ZIF-8

The first part of the exercise is to simulate the diffusion of carbon dioxide molecules in ZIF-8. There are a total of five different temperatures (298.15 K, 323.15 K, 348.15 K, 373.15 K, 398.15 K) and five different CO_2 loadings (6, 8, 10, 12, 14). Each student is carrying out one CO_2@ZIF-8 simulation at the assigned temperature with the assigned loading.

System Setup

The simulation system is set up by running the following command:

1. Copy the necessary files to the working directory

```
cp $ZIF_DIR/zif8_files/co2/* .
cp $ZIF_DIR/zif8_files/preeq/<TEMPERATURE>/* .
cp $ZIF_DIR/zif8_files/general_input/* .
```

2. Add the CO_2 loading to restart files (e.g. 32 carbon dioxide molecules and 298 K)

```
add_molecules zif8_preeq_298.rst co2.rst --rst-mol-desc-file
 ↪  moldescriptor.dat -n 32 > 32xco2-zif8-00.rst
```

Simulation

1. Edit the input files `run-01.in` to `run-04.in` to include your assigned temperature, generated restart file, and topology file.

> **!** Important
>
> Please make sure and double check that all input files `.in` are edited accordingly and no typos are present! Otherwise, PQ won't be able to read in the input files and the simulation will stop prematurely!

```
...
# Temperature algorithm (velocity rescaling), Target T in K and Relaxation time in ps
      thermostat = velocity_rescaling; temp = XXX.XX; t_relaxation = 0.1;
...
# Files
      start_file    = XXX-00.rst;
      topology_file = XXX.top;

      file_prefix   = XXX-01;
```

> **i** Note
>
> Replace `XXX` with the assigned temperature value and the corresponding restart and topology files. The `file_prefix` can be any name you choose. Please make sure to use `-00.rst` as the start file and `-01` as the file prefix in `run-01.in` and increment the numbers by one for each following input file. This will help to keep track of the different simulation steps.

2. Run NVT equilibration

```
PQ run-01.in
```

Start multiple input files one after the other

```
PQ run-01.in && PQ run-02.in && PQ run-03.in && PQ run-04.in
```

> **!** Important
>
> The overall equilibration is split into two stages. The first stage is a 10 ps NVT equilibration (`run-01.in`). The second stage is a 10 ps NPT equilibration (`run-02.in`). After the equilibration, the production run is performed for 1 ns, which is split into 2 runs of 500 ps each (`run-03.in` and `run-04.in`).

Extract Carbon Dioxide Molecules

Extract the carbon dioxide molecules from the trajectory and velocity files using the `extract_co2` tool:

```
extract_co2 <trajectory_files>.xyz
```

and

```
extract_co2 <velocity_files>.vel
```

Einstein Relation

1. Calculate the mean squared displacement (MSD) of the carbon dioxide molecule using the `msd` tool:

```
msd
```

2. Fit a linear function to the MSD data using the `linearfit` tool:

```
linearfit --window 5
```

> **!** Important
>
> For the assigned carbon dioxide loading, please insert the calculated self-diffusion coefficient value into the **Google Sheet**.

Green-Kubo Relation

1. Calculate the velocity autocorrelation function (VACF) of the carbon dioxide molecule using the `vacf` tool:

```
vacf
```

2. Integrate the VACF data using the `integration` tool:

```
integration
```

> **!** Important
>
> For the assigned carbon dioxide loading, insert the calculated self-diffusion coefficient value into the **Google Sheet**.

Radial Distribution Function

1. Calculate the radial distribution function (RDF) of the carbon dioxide molecule using the `rdf_zif8` tool:

```
rdf_zif8 <trajectory_file-03>.xyz <trajectory_file-04>.xyz
```

2. Calculate the RDF for `Zn` and `C` or `O` atoms (gas) using the `rdf_zif8` tool:

```
rdf_zif8 <trajectory_file-03>.xyz <trajectory_file-04>.xyz --center Zn
 ↪  --ligand1 X
```

> **i** Note
>
> The RDF calculation will generate a `output` file named `rdf-C-C.out` and `rdf-Zn-C.out`, accordingly. Plot the 1st column (distance) against the 2nd column (RDF) using your preferred plotting tool.

Visualization

1. Visualize the trajectory files using the `vmd` tool:

```
vmd <trajectory_file>.xyz
```

2. Box files can be made with the `traj2box` tool:

```
traj2box <trajectory_file>.xyz --vmd > <box_file>.xyz
```

> **i** Note
>
> The `traj2box` tool generates a box file that can be visualized in VMD. The box file contains the unit cell information with `X` atoms at the corners of the unit cell. The box file can be used to visualize the unit cell of the simulation.

3. Visualize the box file using the `vmd` tool:

`File > New Molecule > Filename (Browse to the box file) > Load (All at once)`

4. Representations can be changed in the `Graphics > Representations...` window. Good representations are:

- `Licorice` for the framework atoms (and Box atoms)
- `DynamicBonds` for the framework atoms (and Box atoms)
- `VDW` for the carbon dioxide atoms (Selected Atoms `index > 275`)
- `VDW` for the Zn atoms (Selected Atoms `name Zn`)

5. General color and setting recommendations:

- Color box atoms: Change the color of the box atoms to `Coloring Method > ColorID 8` (white) for both `Licorice` and `DynamicBonds` representations.
- Change the background color to white: `Graphics > Colors > Categories (Display) > Names (Background) > Colors (White)`
- Disable depth cueing: `Display > Depth Cueing > Off`

- Render the image: `File > Render > Tachyon`

Part B.2) Thermal Expansion of ZIF-8

The second part of the exercise is to calculate the thermal expansion of the pristine ZIF-8 framework at the assigned temperature value.

System Setup

The simulation system is set up by running the following command:

1. Copy the necessary files to the working directory

```
cp $ZIF_DIR/zif8_files/preeq/<TEMPERATURE>/* .
cp $ZIF_DIR/zif8_files/general_input/* .
```

Simulation

1. Edit the input files `run-01.in` to `run-03.in` to include your assigned temperature, generated restart file, and topology file. `run-04.in` is not needed for this part of the exercise.

> **!** Important
>
> Please make sure and double check that all input files `.in` are edited accordingly and no typos are present! Otherwise, PQ won't be able to read in the input files and the simulation will stop prematurely!

```
...
# Temperature algorithm (velocity rescaling), Target T in K and Relaxation time in ps
      thermostat = velocity_rescaling; temp = XXX.XX; t_relaxation = 0.1;
...
# Files
      start_file    = zif8_preeq_XXX.rst;
      topology_file = shake_zif8_XXX.top;

      file_prefix   = zif8-01;
```

> **i** Note
>
> Replace `XXX` with the assigned temperature value and the corresponding restart and topology files. The `file_prefix` can be any name you choose. Please make sure to use `-00.rst` as the start file and `-01` as the file prefix in `run-01.in` and increment the numbers by one for each following input file. This will help to keep track of the different simulation steps.

2. Run NVT equlibration

```
PQ run-01.in
```

Start multiple input files one after the other

```
PQ run-01.in && PQ run-02.in && PQ run-03.in
```

> **!** Important
>
> The overall equilibration is split into two stages. The first stage is a 10 ps NVT equilibration (`run-01.in`). The second stage is a 10 ps NPT equilibration (`run-02.in`).

After the equilibration, the production run is performed for 500 ps (`run-03.in`). Only the trajectory from the last run `run-03.in` is used for the thermal expansion coefficient calculation.

Analysis

1. Average the lattice parameter `a` of the ZIF-8 framework using the `average_a` tool:

```
average_a zif8-03.box
```

2. Average the volume of the ZIF-8 framework using the `average_V` tool:

```
average_V zif8-03.box
```

> **!** Important
>
> For the assigned temperature, insert the calculated average lattice parameter and average volume into the **Google Sheet**.

3. Calculate the thermal expansion coefficient using the values from your group and the following formula: thermal expansion.

4. Compare the calculated thermal expansion coefficient of ZIF-8 with literature values.

> **i** Note
>
> Include the source of the reference on the poster and which method they used to obtain it. Google Scholar is your friend for this research ;)

Analysis

Preanalysis

Log-file check

Open the `*.log` file with any editor.

Check if the log file ends with this:

- ☐ "PQ ended normally"

You can also grep for this statement to verify the normal termination of the simulation for all files:

```
grep "PQ ended" *.log
```

Visual inspection

Check if the system is behaving as expected.

Open the `*.xyz` file with `VMD`.

It is a good sign if

- ☐ no atom has been shot out of the box
- ☐ the system remains intact (does not collapse or blow up)
- ☐ no unanticipated movements can be observed etc.

Troubleshooting

In the event that the simulation does not produce the anticipated results:

- ☐ Try to understand any error messages that may have occured
- ☐ Check if the simulation was set up correctly by inspecting the `*.log` file and `*.in`
- ☐ Check the starting structure
- ☐ Check the moldescriptor file

etc.

Equilibrium state of simulation

Firstly, in order to obtain meaningful physical properties from a simulation, it is essential to ensure that the system is in an equilibrium state. However, what constitutes an *equilibrium state*?

> **!** An equilibrium state:
>
> can be defined as a state in which macroscopic properties A (*e.g* temperature T, pressure P, energies E, volume V, ...) do **NOT** undergo major changes over time.

Once these properties fluctuate around a constant pattern without any long-term trends, it can be assumed that the system reached an equilibrium state.

Arithmetic Average, Standard Deviation and Standard Error

The aforementioned constant relaxation of the properties can be verified by calculating the arithmetic mean of the properties $\langle A \rangle$

$$\langle A \rangle = \frac{1}{n} \sum_{i=0}^{n} a(t_i)$$

where $a(t_i)$ is the property a at time step t_i and n the total sampling time

as well as the standard deviation A_σ

$$A_\sigma = \sqrt{\frac{1}{n} \sum_{i=0}^{n} (a(t_i) - \langle A \rangle)^2}.$$

and standard error A_ν of the arithmetic average

$$A_\nu = \frac{A_\sigma}{\sqrt{n}}$$

Running Average

Further, the running average $\langle A \rangle_\tau$ at time τ with a window size of ω and a gap size g

$$\langle A \rangle_\tau = \frac{1}{\omega} \sum_{i=\tau-(\omega-1)g}^{\tau} a(t_i)$$

e.g. $\tau = 5$, $\omega = 5$, $g = 2$

$$\langle A \rangle_5 = \frac{1}{3}(a(t_1) + a(t_3) + a(t_5))$$

can help to estimate the fluctuation of the properties over time.

Cumulative Average

And the cumulative average is a running average that is added at each step.

$$\langle A \rangle_n = \frac{(n-1)\langle A \rangle_{n-1} + \langle A \rangle_n}{n}$$

Linear Regression Fit

A linear regression fit can help to estimate the trend of your simulation.

For further detail: statistics

Plot of temperature over simulation time

The temperature during the simulation can be found in the associated energy file `*.en`, which can be readily used for plotting. The `*.info` file contains information about the individual columns in the `*.en` file. An example code to plot the temperature vs simulation time is shown below.

```
import numpy as np
import pandas as pd
import matplotlib.pyplot as plt
from scipy.stats import linregress
import matplotlib as mpl

mpl.rcParams["font.size"] = 15
mpl.rcParams["axes.labelsize"] = 20


physical_properties = ["SIMULATION-TIME", "TEMPERATURE", "PRESSURE",
 ↪  "E(TOT)", "E(QM)", "N(QM-ATOMS)", "E(KIN)",
 ↪  "E(INTRA)","VOLUME","DENSITY","MOMENTUM","LOOPTIME"]
physical_units = ["fs", "K","bar", "kcal/mol", "kcal/mol",
 ↪  "-","kcal/mol","kcal/mol","A^3", "g/cm^3", "amuA/fs", "s"]
data = pd.read_csv("../data/physical_properties.en",sep='\t+',names=
 ↪  physical_properties)
print(data.head())
print("Shape of data: ", data.shape)
time = data["SIMULATION-TIME"]/1e6 # ns
temperature_avg = np.mean(data["TEMPERATURE"])
temperature_std = np.std(data["TEMPERATURE"])
window = 50
gap = 2
running_average = data["TEMPERATURE"].rolling(window=window).mean()
 ↪  #window=window,min_periods=1,center=True,step=gap

def linear_function(x,a,b):
  return a*x+b



plt.figure(figsize=(8,4))
plt.plot(time,data["TEMPERATURE"],color="black",
 ↪  alpha=0.5,label=r"simulation")
plt.plot(time,running_average,label=r"$T_{\mathrm{run.avg}}$")
plt.hlines(temperature_avg,xmin=np.min(time),xmax=np.max
 ↪  (time),linestyles="solid",color="black",label=r"$T_{\mathrm{avg}}
 ↪  $")
```

```
plt.hlines(temperature_avg+temperature_std,xmin=np.min(time),xmax=np.max(time),linestyles="dashed",color="black",label=r"$T_{\mathrm{athrm{std}}}$")
plt.hlines(temperature_avg-temperature_std,xmin=np.min(time),xmax=np.max(time),linestyles="dashed",color="black")

plt.xlabel(r"$t$ / ns")
plt.ylabel(r"$T$ / K")
plt.legend(fontsize=12)
plt.show()
```

```
   SIMULATION-TIME  TEMPERATURE      PRESSURE         E(TOT)          E(QM)  \
0          1656002   265.867307  -9219.140442 -39593.157062 -39779.394319
1          1656004   232.575082 -10168.957588 -39594.249861 -39757.166264
2          1656006   326.845099  -6236.688599 -39600.546646 -39829.498207
3          1656008   398.202185   2882.459019 -39597.914972 -39876.851422
4          1656010   382.115074   9870.653269 -39596.205739 -39863.873337

   N(QM-ATOMS)      E(KIN)  E(INTRA)       VOLUME   DENSITY  MOMENTUM  \
0        276.0  186.237257       0.0  4946.281581  0.916867  0.000011
1        276.0  162.916403       0.0  4944.425576  0.917211  0.000011
2        276.0  228.951560       0.0  4943.049144  0.917466  0.000011
3        276.0  278.936450       0.0  4943.121195  0.917453  0.000011
4        276.0  267.667598       0.0  4944.683355  0.917163  0.000011

   LOOPTIME
0   5.08360
1   1.58753
2   3.05997
3   0.18536
4   0.17990
Shape of data:  (50000, 12)
```

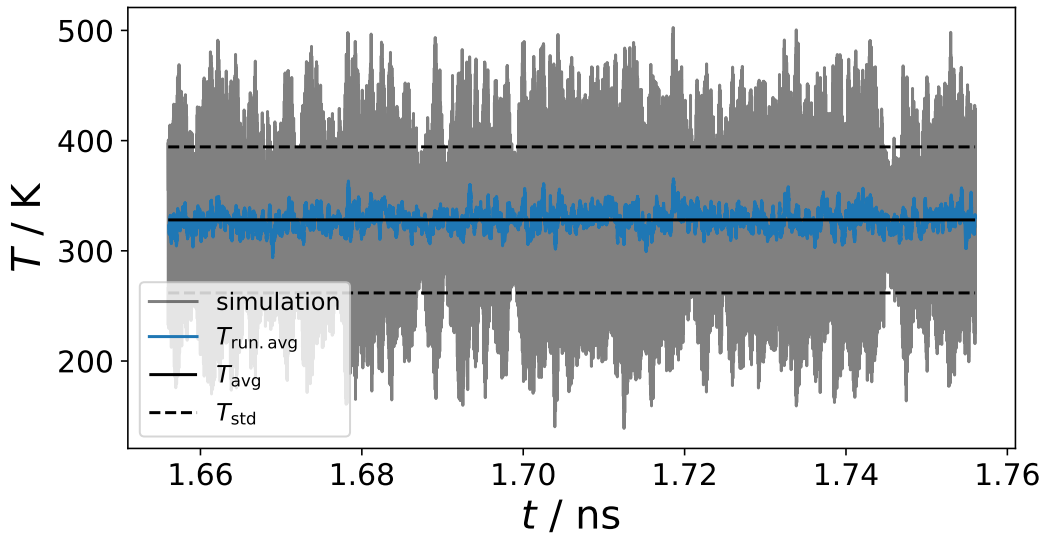


Figure 2: Temperature vs Time plot

Linear / Volumetric Thermal Expansion Coefficient

The thermal expansion coefficient is a quantity that describes the extent to which a solid substance undergoes a change in size in response to variations in temperature.

Therefore the system is computed in the NPT ensemble at different temperatures T_i at 1 bar.

In our case we consider a temperature range from 248 to 348 K in 25 K steps.

- **Linear thermal expansion coefficient**

The linear thermal expansion coefficient at 298 K is calculated from the temperature gradient of the respective average lattice parameter $\langle a \rangle$, $\langle b \rangle$ or $\langle c \rangle$ at constant pressure P (NPT ensemble).

$$\alpha_x^{T_{298\,\mathrm{K}}} = \frac{1}{x}\left(\frac{\partial x}{\partial T}\right)_P, x = a, b, c$$

The slope can be estimated numerically in different ways. A simple way is to employ a finite difference method. There are three fundamental types of finite differentiation: *forward*, *backward* and *central* finite differentiation.

We will use the central finite difference method with a **five-point stencil**. In general it is formulated in 1D as:

$$f'(x) = \frac{-f(x+2h) + 8f(x+h) - 8f(x-h) + f(x-2h)}{12h} + \frac{h^4}{30} f^{(5)(c)}, c \in [x-2h, x+2h]$$

where h is the change of x.

If you use more than five points, a higher order stencil can be used.

In our case the differentiation can be written as:

$$\frac{\partial x}{\partial T} \approx \frac{\langle x^{T_{248\,\mathrm{K}}} \rangle - 8 \langle x^{T_{273\,\mathrm{K}}} \rangle + 8 \langle x^{T_{323\,\mathrm{K}}} \rangle - \langle x^{T_{348\,\mathrm{K}}} \rangle}{12\Delta T}$$

- **Volumetric thermal expansion coefficient** It is the same formulation as for the linear thermal expansion coefficient, except that the volume V is used instead of the individual lattice parameters:

$$\alpha_V^{T_{298\,\mathrm{K}}} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

The volume of a orthorhombic system can be calculated as:

$$V = a \cdot b \cdot c$$

In general, the volume of a non-orthorhombic crystal systems is calculated as:

$$V = abc\sqrt{1 - \cos^2(\alpha) - \cos^2(\beta) - \cos^2(\gamma) + 2(\cos(\alpha)\cos(\beta)\cos(\gamma))}$$

Plot Lattice Parameter vs. Temperature

```
import numpy as np
import matplotlib.pyplot as plt

import matplotlib as mpl

mpl.rcParams["font.size"] = 15
mpl.rcParams["axes.labelsize"] = 20

temperature = np.array([248.15,273.15,298.15,323.15,348.15])
a = np.array([25.8, 25.77, 25.73, 25.70, 25.66])
a_err = np.array([0.2,0.1,0.15,0.2,0.23])

plt.figure(figsize=(8,4))
plt.errorbar(temperature,a,a_err,fmt='ok',label=r"$\left < a \right
 ↪  >$")
plt.xlabel(r"$T$ in K")
```

```
plt.ylabel(r"$\left < a \right > $ in $\mathrm{\AA}$")
plt.xlim(223,373)
plt.xticks(temperature)
# plt.legend(fontsize=12)
plt.show()
```

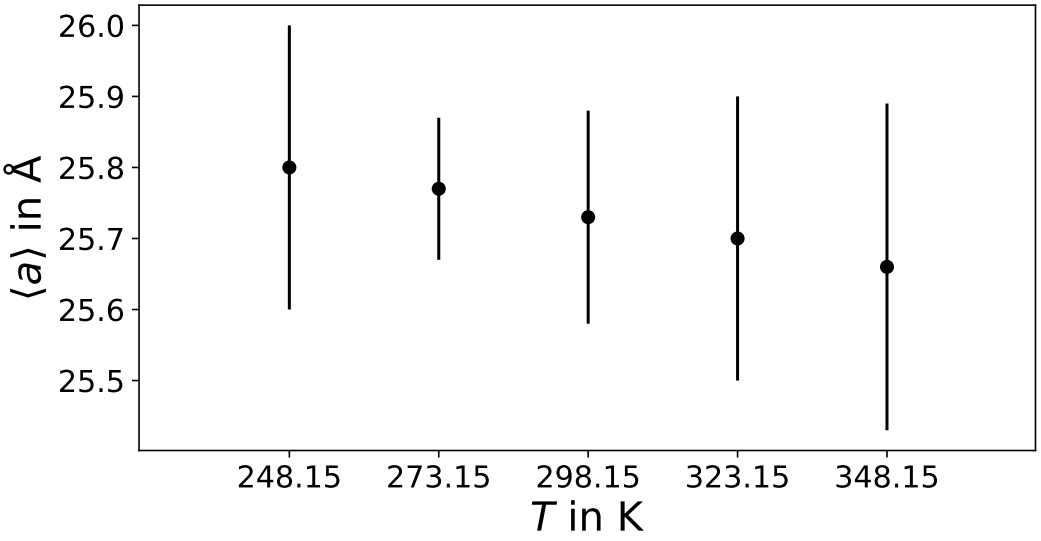


Figure 3: T vs a plot

Experimental Measurement Data is available from:

X-ray Diffraction (XRD)
Powder X-ray Diffraction (PXRD)
Neutron Powder Diffraction (NPD)

Radial Distribution Functions (RDFs)

The radial distribution function (RDF) is a simple measurement to get structural information of the system.

It describes the probability $P_{ab}(r)$ to find a target particle type b at distance r away from a reference particle type a; *e.g.* the probability to find CO_2 from Zn^{2+} clusters at distance r:

$$P_{ab}(r) = \int_0^{r'} 4\pi r'^2 g_{ab}(r')dr'$$

where $g_{ab}(r)$ is the RDF. The RDF formulates the average local density $\langle\rho_{ab}(r)\rangle$ normalized by $\rho = (N_a N_b)$

$$g(r) = \frac{\langle\rho_{ab}(r)\rangle}{\rho}.$$

The two-particle density correlation function is defined as:

$$\rho_{ab}(r) = \sum_{i=1}^{N_a}\sum_{j=1}^{N_b}\left\langle\delta(|\vec{r}_i - \vec{r}_j| - r)\right\rangle.$$

The average number of particles b that can be found in the shell of distance r can be determined by multiplying the density ρ with the probability $G(r)$

$$N_{ab}(r) = \rho G_{ab}(r)$$

Dirac-Delta Function

$$\delta(x - x_0) = \begin{cases} 0 & x \neq x_0 \\ \infty & x = x_0 \end{cases}$$

$$\int_L \delta(x - x_0)dx = 1, x_0 \in L$$

Self-Diffusion Coefficient

In order to describe the dynamic of guests in host systems, it is necessary to calculate transport properties. A transport property would be for example the *diffusion*, *viscosity*, *electrical or thermal conductivity*.

In general, transport properties can be described as a property coefficient γ which depends on microscopic variable A (*e.g.* positions $\Delta\vec{r}$ or the velocities $\vec{v}$) that is written as an infinite time integration of a non-normalized time correlation function $\left\langle \dot{A}(t)\dot{A}(t_0)\right\rangle$:

$$\gamma = \int_0^\infty dt \left\langle \dot{A}(t)\dot{A}(t_0)\right\rangle .$$

This is also known as **Green-Kubo** relation [@Kubo1957] which can also written as the equivalent **Einstein** expression

$$\gamma = \lim_{t\to\infty} \frac{\left\langle (A(t) - A(t_0))^2\right\rangle}{2t} = \frac{1}{2}\lim_{t\to\infty}\frac{d}{dt}\left\langle (A(t) - A(t_0))^2\right\rangle$$

In case of self-diffusion coefficient D_s the variable A is the molecular position $\vec{r}_\mathrm{cm}$ which in general is the center of mass position of the particles:

$$\vec{r}_\mathrm{cm} = \frac{\sum_{i=1}^N m_i\vec{r}_i}{\sum_{i=1}^N m_i}$$

where m_i is the atomic mass, $\vec{r}_i$ is the atomic positions and N the number of atoms in the particle.

As well as $\dot{A}$ is the molecular velocity which should be also considered as center of mass.

Einstein-Relation

The Einstein Relation can be therefore written as slope of the mean-squared-displacement ($MSD(\tau)$) over time origins τ

$$D_\mathrm{s} = \frac{1}{2\cdot d}\lim_{t\to\infty}\frac{d}{dt}MSD(\tau)$$

where $d = 1, 2, 3$ is the dimensionality.

Mean-Squared Displacement

The mean-squared displacement describes the temporal displacement of the particle from a time origin t_0 averaged over the time interval τ

$$MSD(\tau) = \left\langle \frac{1}{N}\sum_{i=1}^N |\vec{r}_i(t) - \vec{r}_i(t_0)|^2 \right\rangle_\tau$$

where N is the number of the particle, $\vec{r}_i$ is the center-of-mass position vector of the particle i.

Looking at Figure Figure 4 (a), we see that the beginning of the MSD is not linear. Only at higher correlation times the expected diffusion (see Figure Figure 4 (b)) behaviour can be observed.

Question:

- How do you get the self-diffusion coefficient out of the MSD regarding the Einstein-relation?
- How do you get the gradient/slope of the MSD?
- What does the limes in that formula mean?

Answer:

The self-diffusion coefficient is the slope of the MSD divided by $2 \cdot d$.
But this is only true if the correlation time is long enough. We can say that in the linear regime we fulfill this limes due to the constant slope, which represents the diffusion coefficient.
Therefore, in order to apply the Einstein relation, it is important to be in the linear regime of the MSD plot.
You get the slope by fitting a linear regression to the linear part of the dataset.

```
import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import curve_fit
import matplotlib as mpl

mpl.rcParams["font.size"] = 15
mpl.rcParams["axes.labelsize"] = 20

data = np.genfromtxt("../data/diff.out")
steps = data[:,0]
time = steps*0.002
MSD_x = data[:,1]
MSD_y = data[:,2]
MSD_z = data[:,3]
MSD_xyz = MSD_x + MSD_y + MSD_z

def ballistic_regime(x,a):
  return a*x**2

def superdiffusion(x,a):
  return a*x**1.5

def subdiffusion(x,a):
  return a*x**0.5

def normaldiffusion(x,a):
  return a*x

def confined_diffusion(x,a,b):
  return a*(1-np.exp(-b*x))

def linear_regression(x,a,b):
  return a*x + b

popt, pcov = curve_fit(linear_regression,time[-500:],MSD_xyz[-500:])

d_einstein = popt[0]/6
time_regime= np.linspace(0,10,1000)

fig, axs = plt.subplots(2,1,figsize=(4,8),gridspec_kw={'hspace': 0.4})
axs[0].plot(time,MSD_x,label=r"$MSD_x$",color="C0")
axs[0].plot(time,MSD_y,label=r"$MSD_y$",color="purple")
```

```
axs[0].plot(time,MSD_z,label=r"$MSD_z$",color="grey")
axs[0].plot(time,MSD_xyz,label=r"$MSD_{x+y+z}$",color="k")
axs[0].vlines(time[-500],0,500,color="k",linestyle="dotted",label=
 ↪  r"fitting regime")
axs[0].plot(time[-500:],linear_regression(time[-500:],*popt),color=
 ↪  "red",linestyle="dashed",label=r"linear fit $y=a\cdot x + b$: $a=
 ↪  {:.2f}$, $b= {:.2f}$ ".format(popt[0],popt[1]))
axs[0].text(-0.5, 1.05, '(a)', transform=axs[0].transAxes,
 ↪  fontsize=14, verticalalignment='top')
axs[0].text(1.0,400, r"$D_s=%2.2f\,\mathrm{\AA^2 ps^{-1}}$"
 ↪  %(d_einstein),fontsize=14)
axs[0].legend(fontsize=12,loc='upper left', bbox_to_anchor=(1.05,
 ↪  1.05))


axs[1].plot(time_regime,ballistic_regime(time_regime,100),label=
 ↪  r"ballistic regime $\propto \tau^2$", color="gold",
 ↪  linestyle="dashed")
axs[1].plot(time_regime,superdiffusion(time_regime,100),label=
 ↪  r"superdiffusion regime $\propto \tau^{\alpha}, \alpha>1$",
 ↪  color="darkred", linestyle="dashed")
axs[1].plot(time_regime,normaldiffusion(time_regime,100),label=
 ↪  r"normal diffusion regime $\propto \tau$", color="red",
 ↪  linestyle="dashed")
axs[1].plot(time_regime,subdiffusion(time_regime,100),label=
 ↪  r"subdiffusion regime $\propto \tau^{\alpha}, \alpha<1$",
 ↪  color="salmon", linestyle="dashed")

axs[1].plot(time_regime,confined_diffusion(time_regime,50,2),label=
 ↪  r"confined diffusion regime $\propto$ const.", color="hotpink",
 ↪  linestyle="dashed")


axs[0].set_xlabel(r"correlation time $\tau$ in ps")
axs[0].set_ylabel(r"$MSD(t)$ in $\mathrm{\AA^2}$")

axs[0].set_ylim(0,500)


axs[1].set_xlabel(r"correlation time $\tau$ in ps")
axs[1].set_ylabel(r"$MSD(t)$ in $\mathrm{\AA^2}$")
axs[1].set_xlim(0,5)
axs[1].set_ylim(0,500)
axs[1].text(-0.5, 1.05, '(b)', transform=axs[1].transAxes,
 ↪  fontsize=14, verticalalignment='top')

axs[1].legend(fontsize=12,loc='upper left', bbox_to_anchor=(1.05,
 ↪  1.05))
plt.show()
```

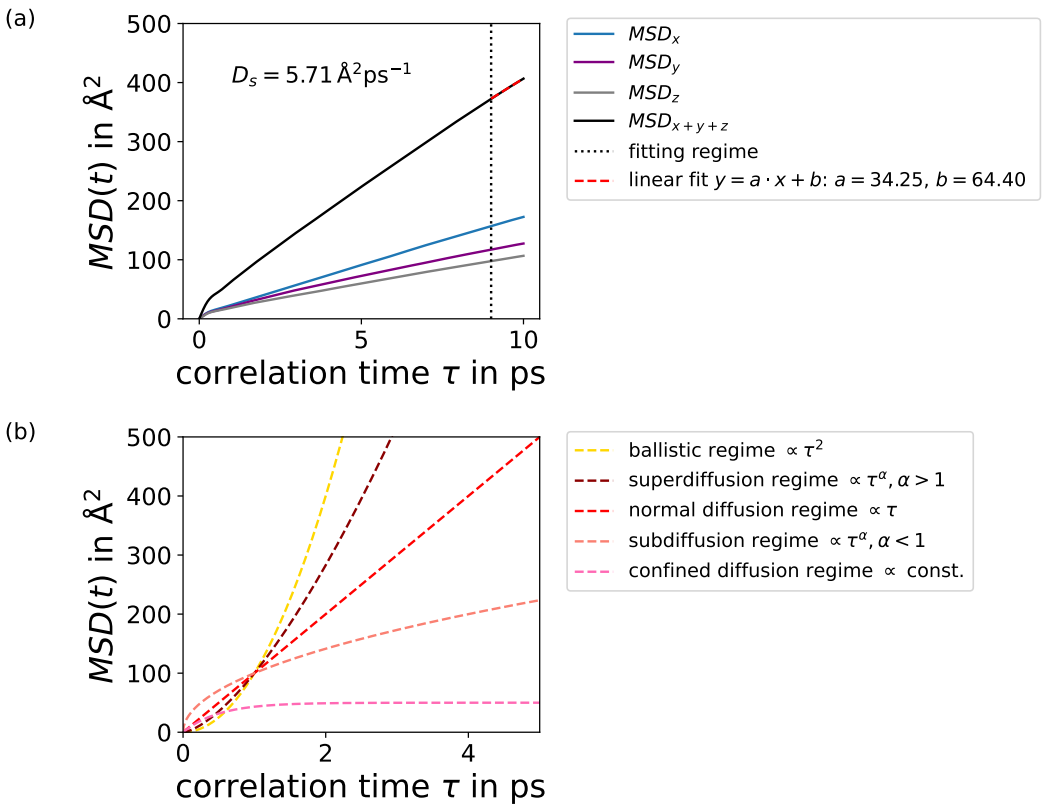


Figure 4: (a) MSD(t) plot, (b) diffusion regimes

Green-Kubo Relation

The Green-Kubo formalism needs a numerical integration of the velocity-autocorrelation function $VACF(t)$ to get the self-diffusion coefficent D_s

$$D_\mathrm{s} = \frac{1}{d}\int_0^\infty VACF(t)dt$$

where $d = 1, 2, 3$ is the dimension.

Velocity-Autocorrelation Function

The velocity-autocorrelation function $VACF(\tau)$ is averaged over a time interval τ

$$VACF(\tau) = \left\langle \frac{1}{N}\sum_{i=1}^{N} |\vec{v}_i(t)\vec{v}_i(t_0)|^2 \right\rangle_\tau$$

where $\vec{v}_i$ is the velocity of the particle i and t_0 labels the time origin.

```
import numpy as np
import matplotlib.pyplot as plt
from scipy.integrate import simpson
from scipy.integrate import cumulative_trapezoid
import matplotlib as mpl

mpl.rcParams["font.size"] = 15
mpl.rcParams["axes.labelsize"] = 20

data = np.genfromtxt("../data/green_kubo.out")
time = data[:,0]
VACF_x = data[:,1]
VACF_y = data[:,2]
```

```
VACF_z = data[:,3]
VACF_xyz = data[:,4]


integral_VACF_xyz = simpson(VACF_xyz, x=time)
cumulative_integral = cumulative_trapezoid(VACF_xyz, time, initial=0)
d_green_kubo = integral_VACF_xyz / 3

fig, axs = plt.subplots(1,figsize=(4,4))
axs.plot(time,VACF_x,label=r"$VACF_x$",color="C0")
axs.plot(time,VACF_y,label=r"$VACF_y$",color="purple")
axs.plot(time,VACF_z,label=r"$VACF_z$",color="grey")
axs.plot(time,VACF_xyz,label=r"$VACF_{x+y+z}$",color="k")
axs.plot(time, cumulative_integral, label=r'Cumulative Integral of
 ↪  $VACF_{x+y+z}$',color="red")

axs.text(0.05, 0.95, r"$D_s = %.2f \, \mathrm{\AA^2 ps^{-1}}$"
 ↪  %(d_green_kubo), transform=axs.transAxes, fontsize=14,
 ↪  verticalalignment='top')


axs.set_xlabel(r"correlation time $\tau$ in ps")
axs.set_ylabel(r"$VACF(t)$ in $\mathrm{(\AA ps^{-1})^{2}}$")
axs.legend(fontsize=12,loc='upper left', bbox_to_anchor=(1.05, 1.05))
plt.show()
```

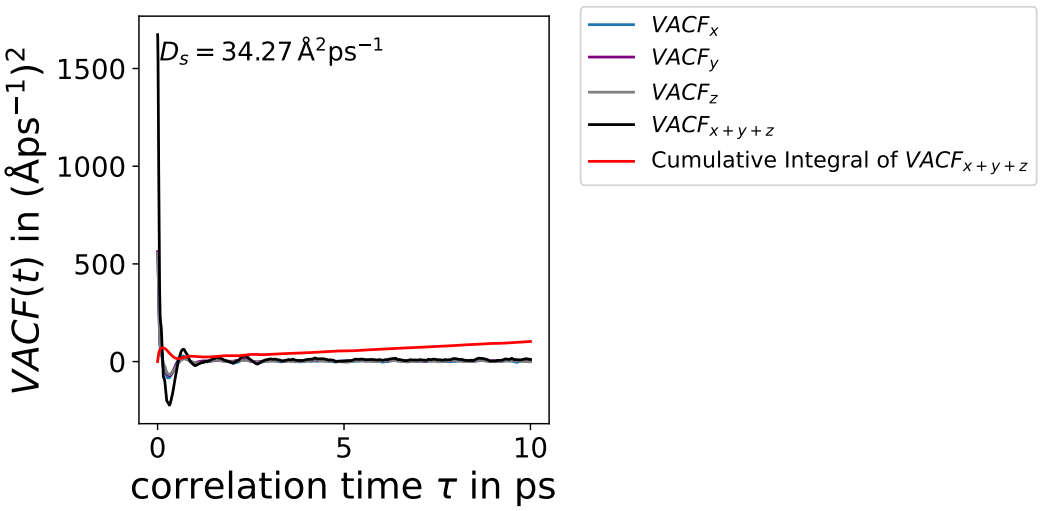


Figure 5: VACF(t) plot

Activation Energy

The diffusion coefficient is directly depending on the activation energy E_a by an exponential decay

$$D_\mathrm{s} = D_0 e^{-\frac{E_\mathrm{a}}{RT}}$$

where D_0 is factor of the exponential function, $R = 8.3145\,\mathrm{JK^{-1}mol^{-1}}$ is the ideal gas constant and T is the temperature.

With this formalism we can apply an Arrhenius equation to fit a linear function to get the activation energy E_a.

$$\ln(D_\mathrm{s}) = -\frac{E_\mathrm{a}}{RT} + \ln D_0$$

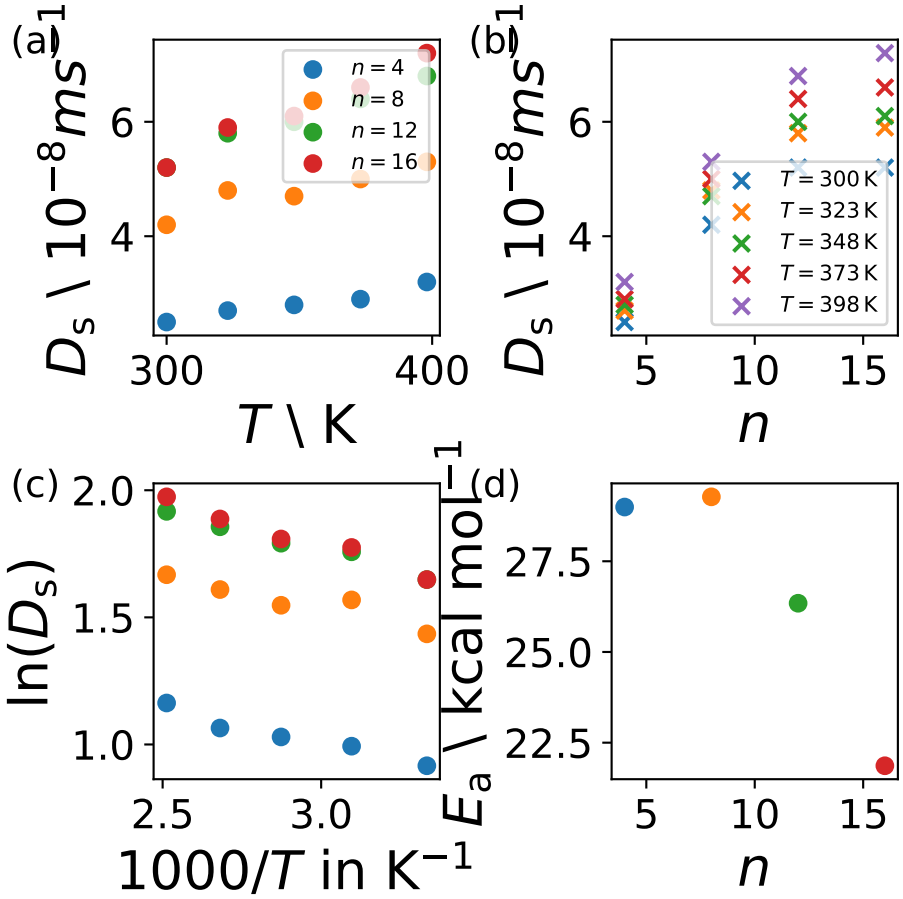


Figure 6: (a) D(T), (b) D(n), (c) ln(D(1000/T) and (d) Ea(n))

Checklist

All data generated along with a discussion of results fit easily on a single page. The images and graphs to be plotted are grouped into three subsections, which should also be grouped together on the poster.

Subsection 1 - System Setup and Equilibration:

- ☐ A screenshot of the CO2@ZIF-8 hybrid system including the simulatin box
- ☐ A graph showing the lattice parameter of the pristine (= empty) ZIF-8 against the simulation time a(t)

Subsection 2 - Gas Diffusion:

- ☐ A graph showing the mean-square-displacement (MSD) of the CO2 molecules vs time including a fit
- ☐ A graph showing the Green-Kubo correlation function vs time and the associated integral

Subsection 3 - Group Work:

- ☐ A graph showing the lattice parameter of the pristine (= empty) ZIF-8 at the five different temperatures (248.15 K - 348.15 K) and the resulting linear thermal expansion coefficient
- ☐ A comparison of the calculated linear thermal expansion coefficient of ZIF-8 with reported literature data (include the source and mention the method they have used!)
- ☐ A graph showing the Arrhenius plot of the Einstein diffusion coefficient for the assigned loading at the five different temperatures (298.15 K - 398.15 K) including a fit
- ☐ A graph showing the Arrhenius plot of the Green-Kubo diffusion coefficient for the assigned loading at the five different temperatures (298.15 K - 398.15 K) including a fit

Templates

Matplotlib

How to read data into python:

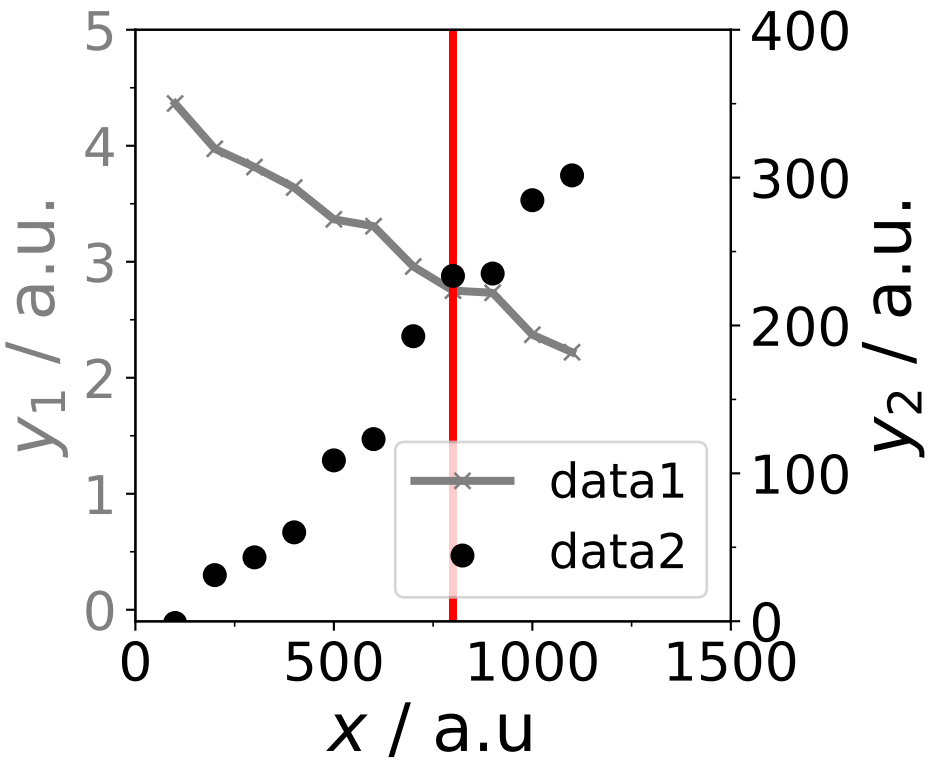
```
import numpy as np

data = np.genfromtxt("../data/data.dat",delimiter="    ",
 ↪  skip_header=2)
print(data)
```

```
[[ 100.          4.36417563   -1.19      ]
 [ 200.          3.97386645   31.19      ]
 [ 300.          3.81670518   43.19      ]
 [ 400.          3.63958609   60.1       ]
 [ 500.          3.36586221  108.77      ]
 [ 600.          3.30685375  123.16      ]
 [ 700.          2.95904139  192.74      ]
 [ 800.          2.7512791   233.53      ]
 [ 900.          2.73239376  235.13      ]
 [1000.          2.37106786  284.71      ]
 [1100.          2.22010809  301.51      ]]
```

Two axis plot

```
import matplotlib.pyplot as plt
from matplotlib.ticker import AutoMinorLocator,FixedLocator


# global matplotlib settings
plt.rcParams.update({
    'legend.fontsize': 18,
    'figure.figsize': (4, 4),
    'axes.labelsize': 25,
    'xtick.labelsize': 20,
    'ytick.labelsize': 20}
)

# create a figure with a subfigure to create 2 different y-axes
fig, ax1 = plt.subplots()
# create second subfigure with with sharing the x-axis of ax1
 ↪  subfigure
ax2 = ax1.twinx()
# plot the first data as line plot as ax1 subfigure
# set color, linewidth, marker symbol and label
ax1.plot(data[:,0], data[:,1], color="grey", linewidth=3,
 ↪  marker="x",label="data1")
# define the color of the y-axis
ax1.tick_params(axis='y', labelcolor="grey")

# plot the second data as the ax2 subfigure by using scatter plot
ax2.scatter(data[:,0], data[:,2],color="black",
 ↪  linewidths=3,label="data2")
ax2.tick_params(axis='y', labelcolor="black")

# add all labels in one
lines1, labels1 = ax1.get_legend_handles_labels() # get labels of ax1
 ↪  subfigure
lines2, labels2 = ax2.get_legend_handles_labels() # get labels of ax2
 ↪  subfigures
ax2.legend(lines1 + lines2, labels1+ labels2, loc=4) # location of
 ↪  legend

# set x- and y-limits of the axes
ax1.set_xlim(0,1500)
ax1.set_ylim(-0.1,5)
ax2.set_ylim(-0.1,400)

# set the x- and y-labels of the axes
ax1.set_xlabel(r"$x$ / a.u")
ax1.set_ylabel(r"$y_1$ / a.u.",color="grey") # define also the color
 ↪  of the labels
ax2.set_ylabel(r"$y_2$ / a.u.",color="black")

# create a vertical line at 800 starting from 0 until 5
ax1.axvline(800,0,5,color="red",linewidth=3)

# define manjor and minor axes ticks
ax1.xaxis.set_major_locator(FixedLocator(np.arange(0, 2000, 500)))
ax1.xaxis.set_minor_locator(AutoMinorLocator(2))
ax1.yaxis.set_major_locator(FixedLocator(np.arange(-1, 6, 1)))
ax1.yaxis.set_minor_locator(AutoMinorLocator(2))
ax2.yaxis.set_major_locator(FixedLocator(np.arange(-100, 500, 100)))
```

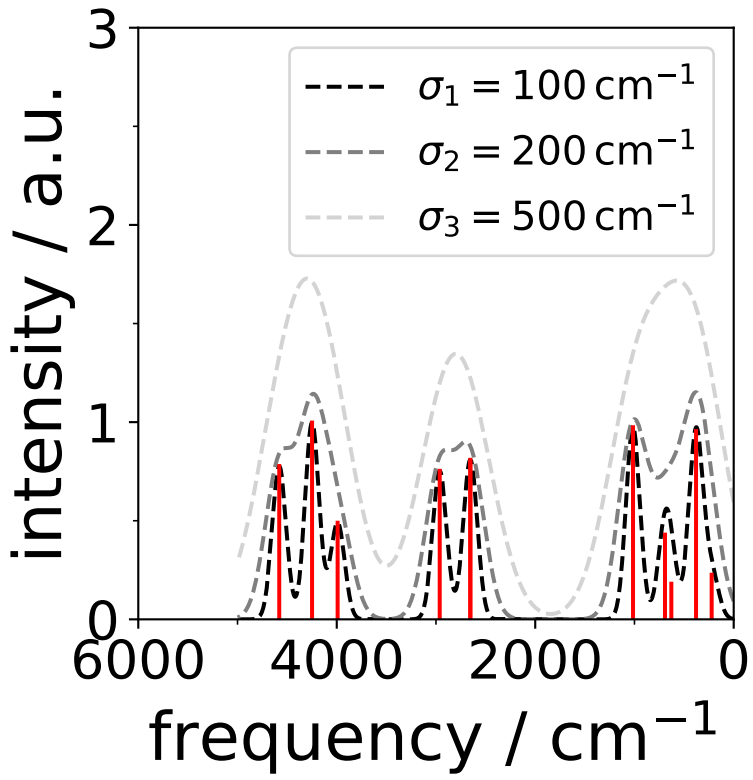
```
ax2.yaxis.set_minor_locator(AutoMinorLocator(2))

# save the figure as png
# plt.savefig("figure.png", dpi=300)
# show the picture
plt.show()
```



Line spectra with Gaussian broadening

```
import numpy as np
import matplotlib.pyplot as plt

# create random frequencies between 20 and 5000 cm-1
vib = np.random.rand(10)*(5000-20)
# with random intensity
intensity = np.random.rand(10)

# define gaussian broadening
def spectrum(vib,intensity,sigma,v):
    gvib=[]
    for vibi in v:
        tot=0
        for vibj,I in zip(vib,intensity):
            tot = tot + I*np.exp(-((((vibj-vibi)/sigma)**2)))
        gvib.append(tot)
    return gvib

# create the broaded function with smooth frequency values
v=np.linspace(0,5000, num=10000, endpoint=True)
# use different sigma
sigma1=100
sigma2=200
```

```
sigma3=400

gvib1=spectrum(vib,intensity,sigma1,v)
gvib2=spectrum(vib,intensity,sigma2,v)
gvib3=spectrum(vib,intensity,sigma3,v)

fig,ax=plt.subplots(figsize=(4,4))

# plot the gaussian broadenings
ax.plot(v,gvib1,"--k", label=r"$\sigma_1=100\,\mathrm{cm^{-1}}$")
ax.plot(v,gvib2,linestyle="--", color="grey",
 ↪  label=r"$\sigma_2=200\,\mathrm{cm^{-1}}$")
ax.plot(v,gvib3, linestyle="dashed", color="lightgrey",
 ↪  label=r"$\sigma_3=500\,\mathrm{cm^{-1}}$")

# plot the line spectra
for v,I in zip(vib,intensity):
    ax.plot((v,v),(0,I),c="red")

# or use vlines
ax.vlines(v,0,I,color="red")

# set x- and y-axis limits
ax.set_xlim(0,6000)
ax.set_ylim(0,3)

# set minor ticks
ax.xaxis.set_minor_locator(AutoMinorLocator(2))
ax.yaxis.set_minor_locator(AutoMinorLocator(2))

# invert the x-axis
plt.gca().invert_xaxis()

# set the axes labels
plt.xlabel('frequency / cm$^{-1}$')
plt.ylabel('intensity / a.u.')

# plot the legend
plt.legend(fontsize=15)
# save the figure
# # plt.savefig('random_line_spectra.png')

plt.show()
```



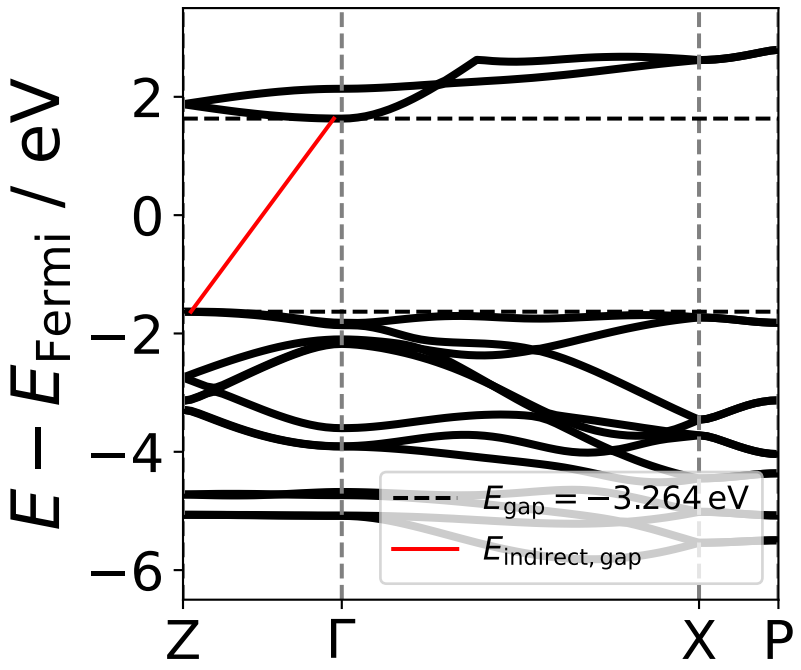
Band Plot

```
import numpy as np
import matplotlib.pyplot as plt

# define the kpoints and the kpoint_labels
kpoints = np.array([1,21,66,76])
kpoint_labels = ["Z",r"$\Gamma$","X","P"]

# an example of random band data
bands = np.genfromtxt("../data/band_tot.dat")
```

```
EFermi = -0.5681 #eV taken from detailed.out
# size of the band data
shape = bands.shape

# put all data in one array to calculate the band gap
y = np.array([])
for i in range(1,shape[1]):
    y = np.append(y,bands[:,i])

x = np.array([])
for i in range(1,shape[1]):
    x = np.append(x,bands[:,0])
# use the convention of E-EFermi
yF = y - EFermi

# the maximum energy of the valence band
max_valence = np.max(yF[yF<0])
# the minimum energy of the conduction band
min_conduction = np.min(yF[yF>0])
```

```
k_max_valence = x[np.argmin(yF[yF>0])]
k_min_conduction = x[np.argmax(yF[yF<0])]

# band gap
E_gap = max_valence - min_conduction
```

```
plt.figure()
# plot the bands
for i in range(1,19):
    plt.plot(bands[:,0], bands[:,i]-EFermi, color="black",
 ↪  linewidth=3)
# plot the vertical lines for the k-points of the Brillouin zone
for j in kpoints:
    plt.axvline(j, color="grey", linestyle="dashed")

# set some axes limits
plt.xlim(1,76)
plt.ylim(-6.5,3.5)

# plot Egap
plt.axhline(max_valence, color="black", linestyle="dashed")
plt.axhline(min_conduction, color="black",
 ↪  linestyle="dashed",label=r"$E_{\mathrm{gap}}=%2.3f\,\mathrm{eV}$"
 ↪  %E_gap)


]
 ↪  plt.plot([k_min_conduction,k_max_valence],[max_valence,min_conduction],
 ↪  color="red",label=r"$E_{\mathrm{indirect,gap}}$")

plt.xticks(kpoints,kpoint_labels)
plt.ylabel(r"$E-E_{\mathrm{Fermi}}$ / eV")
plt.legend(fontsize=12,loc=4)
plt.show()
```



```
import numpy as np
import matplotlib.pyplot as plt
# it is used for constants
from scipy import constants
# it is used for showing the latex equations
from IPython.display import display, Latex

# define constants
eV = constants.eV
hbar = constants.hbar
mol = constants.Avogadro
cal = constants.calorie
kB = constants.k
u = constants.u
A = constants.angstrom

print("eV = ",eV, "J")
print("hbar = ",hbar, "J s")
print("mol = ",mol, "mol")
print("cal = ",cal, "J")
print("kB = ",kB, "J K-1")
print("u = ",u, "kg")
print("A = ",A, "m")

display(Latex( r"$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ in cm
 ↪  $^{-1}$"))

display(Latex(r"$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$ in g $\cdot$
 ↪  mol $^{-1}$"))
```

```
eV =  1.602176634e-19 J
hbar =  1.0545718176461565e-34 J s
mol =  6.02214076e+23 mol
cal =  4.184 J
kB =  1.380649e-23 J K-1
u =  1.66053906892e-27 kg
A =  1e-10 m
```

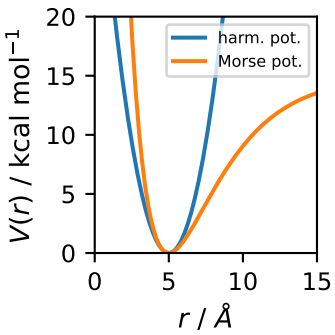
$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ in cm $^{-1}$

$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$ in g $\cdot$ mol $^{-1}$

Plot functions

```
# plt.switch_backend("TkAgg")
# it is used for plotting the figures in the jupyter notebook as
 ↪  interactive figures
# %matplotlib widget
plt.rcParams.update({
    'legend.fontsize': 9,
    'figure.figsize': (2,2),
    'axes.labelsize': 10,
    'xtick.labelsize': 9,
    'ytick.labelsize': 9}
)

# array of r values from 0 to 10 with 100 points
r = np.linspace(0, 15, 1000)
# force constant is extracted
```

```
k = 3 # check the units of k it should be in kcal mol-1 A-2

# translation of the units



# harmonic potential
def harmonic_potential(r, k, r0):
    return 0.5 * k * (r-r0)**2

def morse_potential(r, D, a, r0):
    return D * (1 - np.exp(-a*(r-r0)))**2




fig  = plt.figure(dpi=300)
plt.plot(r, harmonic_potential(r, k, 5), label=r"harm. pot.")
plt.plot(r, morse_potential(r, 15,0.3, 5), label=r"Morse pot.")

plt.xlabel(r"$r$ / $\AA$")
plt.ylabel(r"$V(r)$ / kcal mol$^{-1}$")
plt.xlim(0, 15)
plt.ylim(0, 20)
plt.legend(fontsize=6)
plt.tight_layout()
plt.show()
```

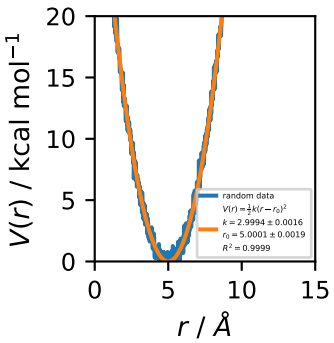


Fit a function to data

```
from scipy.optimize import curve_fit
from sklearn.metrics import r2_score
import numpy as np
import matplotlib.pyplot as plt
# global matplotlib settings
plt.rcParams.update({
    'legend.fontsize': 9,
    'figure.figsize': (2,2),
    'axes.labelsize': 10,
    'xtick.labelsize': 9,
    'ytick.labelsize': 9}
)
# define the function to fit
def harmonic_potential(r, k, r0):
    return 0.5 * k * (r-r0)**2
```

```
# generate some data
r = np.linspace(0, 15, 1000)
k = 3
r0 = 5
data = harmonic_potential(r, k, r0) + np.random.normal(0, 0.5, r.size)

# fit the data
popt, pcov = curve_fit(harmonic_potential, r, data)
# calculate the R2 score
r2 = r2_score(data, harmonic_potential(r, *popt))

# print the fit parameters
print("k = ", popt[0], " +/- ", np.sqrt(pcov[0,0]))
print("r0 = ", popt[1], " +/- ", np.sqrt(pcov[1,1]))
print("R2 = ", r2)



plt.figure(dpi=300)
# plot the data and the fit
plt.plot(r, data, label="random data")
plt.plot(r, harmonic_potential(r, *popt), label=r"$V(r) = \frac{1}{2}
 ↪  k (r-r_0)^2$" + "\n" + r"$k = %2.4f \pm %2.4f$" %(popt[0],
 ↪  np.sqrt(pcov[0,0])) + "\n" + r"$r_0 = %2.4f \pm %2.4f$" %(popt[1],
 ↪  np.sqrt(pcov[1,1])) + "\n" + r"$R^2 = %2.4f$" %r2)
plt.xlabel(r"$r$ / $\AA$")
plt.ylabel(r"$V(r)$ / kcal mol$^{-1}$")
plt.tight_layout()
plt.legend(fontsize=3)
plt.xlim(0, 15)
plt.ylim(0, 20)
plt.show()
```

```
k =  2.9993819580135725  +/-  0.001559127126482928
r0 =  5.00009084352949  +/-  0.0019288218314949725
R2 =  0.999856492346134
```



Poster Templates

Here are some poster templates:

- UIBK Poster template
- Overleaf Templates

Think about how to create the poster. Figures and tables should be informative and readable. Choose a suitable font size and style. Divide the poster in reasonable sections.

Guides

Statistical Excursion

Linear Regression

Regression analsis helps to understand the relationship between independent and dependent variables.

The regression describes a model e.g. linear regression is using a linear function $f(x_i, \alpha)$

$$f = \alpha_0 + \alpha_1 x_i$$

which should describe your relationship between your dependent y_i and the independent x_i variables

$$y_i = f(x_i, \alpha) + \epsilon_i$$

within small error terms ϵ_i.

To estimate the parameter of your model α_i so that the error terms ϵ_i are small as possible the most time an ordinary least squares fit is performed:

$$(\alpha_0, \alpha_1) = \text{argmin}(g(\alpha_0, \alpha_1))$$

where

$$g(\alpha) = \sum_i \epsilon_i^2 = \sum_i (y_i - \alpha_0 + \alpha_1 x_i)^2$$

so that α_0 and α_1 can computed as

$$\alpha_0 = \bar{y} - \alpha_1 \bar{x}$$

$$\alpha_1 = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sum_i (x_i - \bar{x}^2)} = \frac{\sum_i \Delta x_i \Delta y_i}{\sum_i \Delta x_i^2}$$

where $\bar{x}$ and $\bar{y}$ are the respective averages and Δx_i Δy_i are the respective deviations.

Linux Quickstart Guide

Introduction

This guide is for people new to Linux. The aim of this documents is to help with everyday challenges when working with Linux systems. Generally, manual pages (*e.g.* `man sed` gives the terminal manual of sed) are almost everytime helpful and also `-h` (or `--help`) flags after commands quickly display helpful information. Obviously, the internet often helps as well and most of the time new things are learned doing. A good overview of the command line interface on linux is on the following github repository (there is also a german version, but reading the english one is recommended):

https://github.com/jlevy/the-art-of-command-line

command [options]	description

Probably most used linux commands:

command [options]	description
cd /path/to/directory	Change to directory
mkdir [options] directory	Create a new directory
touch filename	Create an empty file with the specified name
cp [options] source destination	Copy files and directories
mv [options] source destination	Rename or move file(s) or directories
ls [options]	List directory contents
pwd	Display the pathname for the current directory
rm [options] directory	Remove (delete) file(s) and/or directories
rm -r [options] directory	Delete directories
cat [filename]	Display file's contents to the standard output device
less [options] [filename]	View the contents of a file one page at a time
tail [options] [filename]	Display the last n lines of a file (the default is 10)
head [options] [filename]	Display the first n lines of a file (the default is 10)
grep [options] pattern [filesname]	Search files or output for a particular pattern
chmod [options] mode filename	Change a file's permissions (u+x to make executable)
find [pathname] [expression]	Search for files matching a provided pattern.
sort [options] file	sort the file via [option]
ps [options]	Display a snapshot of the currently running processes
top	Displays the resources being used on your system. Press q to exit
kill [options] pid	Stop a process. If the process refuses to stop, use kill -9 pid

More commands are:

Table 1: Basic Linux Commands (modified version of source: here)

command [options]	description
man [command]	Display the help information for the specified command
echo [options]	Print string, variable, etc.
tar [options] filename	Store and extract files from a tarfile (.tar) or tarball (.tar.gz or .tgz)
bc	basic calculator (e.g. echo "3+2"| bc gives 5 for floats use flag -l)
chown [options] filename	Change who owns a file
clear	Clear a command line screen/window for a fresh start
date [options]	Display or set the system date and time
df [options]	Display used and available disk space
du [options]	Show how much space each file takes up

command [options]	description
ln [options] source [destination]	Create a shortcut.
locate filename	Search a copy of your filesystem for the specified filename.
passwd [name [password]]	Change the password
ssh [options] user@machine	Remotely log in to another Linux machine, over the network
who [options]	Display who is logged on
> [oufile]	Write stdout (text written to terminal) to outfile (e.g. dftb+ > dftb.out)

You can use `Tab` for autocompletion of commands.

Commands can usually be combined with the pipe: `|`. To write a pipe press `Alt Gr + <|>`-key (usually located on the left of Y on German keyboards) in between. For example:

```
grep "Done" dftb.out | cat -n
```

To send your job to the background, stop it with `CTRL+Z` and then enter `bg`. Afterwards, you can logout with `CTRL+D` and the process will still be running (can be observed with `top` when relogging in) after you closed the terminal.
On the desktop computers in the office you can search the history with `PageUp` and `PageDown` keys. The prefix you entered will then be autocompleted by searching in the history for matching commands you entered before.

> **i** Note
>
> If you want quick access to files or directories in your home folder, the ~-symbol is an alias for your home directory `/home/user` (= `\$HOME`).

How to: edit files

For editing files you can use any editor that you like *e.g.*:

- `VSCode` (code)
- `nedit`
- `gedit`
- `Emacs` (emacs)

For quick changes in files `vim` is a good option as it runs in the terminal (no `-X` in `ssh` required). To learn the basic commands the vimtutor (just type "vimtutor" in your terminal) is highly recommended. **To exit vim, just type :q and Enter.**

Vim cheat sheet

How to: gawk

Basic usage of `gawk`:

```
gawk '{ [commands] }' file
```

Example: print the first and third column of the file `example.dat`. Be sure to add some spaces in between the columns using " ":

```
gawk '{print $1"   "$3}' example.dat
```

Example: print the first column and $500 * x^2$ of the first column column of the file `x.dat` to calculate a harmonic potential and output then data to the file `potential.dat`:

```
gawk '{print $1"   " 500*$1*$1}' x.dat > potential.dat
```

For more advanced usage, also `printf` and `if/else` statements can be used similar in the language `C`. And `sed` (see below) can be used to substitute characters with white spaces which then generate new columns that can be printed with `gawk`.

How to: sed

Basic usage of `sed`:

```
sed -flags '[commands]' file
```

Example: every occurrence (g for global at the end) of "apple" in `fruit.dat` will be substituted (`s` at the beginning) by "banana":

```
sed 's/apple/banana/g' fruit.dat
```

To extract lines between two strings (print every line between "pear" and "kiwi"), use:

```
sed '/pear/,/kiwi/p' fruit.dat
```

> **Note**
>
> Note that symbols, numbers, words, strings can be replaced with a white space (" ") to separate columns which can be printed with `gawk`. The combination of sed and gawk is very powerful!

How to: for-loops in bash

A simple for loop looks like:

```
for i in [list]
    do
    [commands]
    done
```

For every item in [list] the commands between the lines `do` and `done` will be executed. For example to print all the items in the fruit list:

```
for i in pear banana apple
    do
    echo $i
    done
```

or print a sequence of numbers (here 1-10):

```
for i in $(seq 1 1 10)
    do
    echo $i
```

```
    done
```

or iterate over output files (here grep for the Total Energy of a QM calculation):

```
for i in $(ls *.out)
    do
    grep "Total Energy" $i
    done
```

How to: ssh & scp

Note the ~ symbol is an alias for `/home/\$USER` where `\$USER` is your username. To connect with a remote pc via `ssh` (no colon!)

```
ssh username@remote_host
```

To enable streaming of windows (*e.g.* `nedit`) to your computer add `-X` (when accessing from home, `-CY` might be faster and more stable):

```
ssh -X username@remote_host
```

Copy file from a remote host to local host (your computer):

```
scp   username@from_host:one_file.txt   some/folder/
```

Copy file from local host (your computer) to a remote host:

```
scp   one_file.txt   username@to_host:/some/folder/
```

Copy directory from a remote host to local host:

```
scp -r   username@from_host:/some/folder/    other/folder/
```

Copy directory from local host to a remote host:

```
scp -r   some/folder/   username@to_host:/other/folder/
```

The use of rsync is recommended. See:
https://www.tecmint.com/rsync-local-remote-file-synchronization-commands/

To login into remote computers without password authentication run *ssh-keygen* (just press *Enter* a few times) and *ssh-copyid* $USER@$HOST and enter the password. This is especially convenient for accessing the clusters.

Appendix: Vim Cheat Sheet

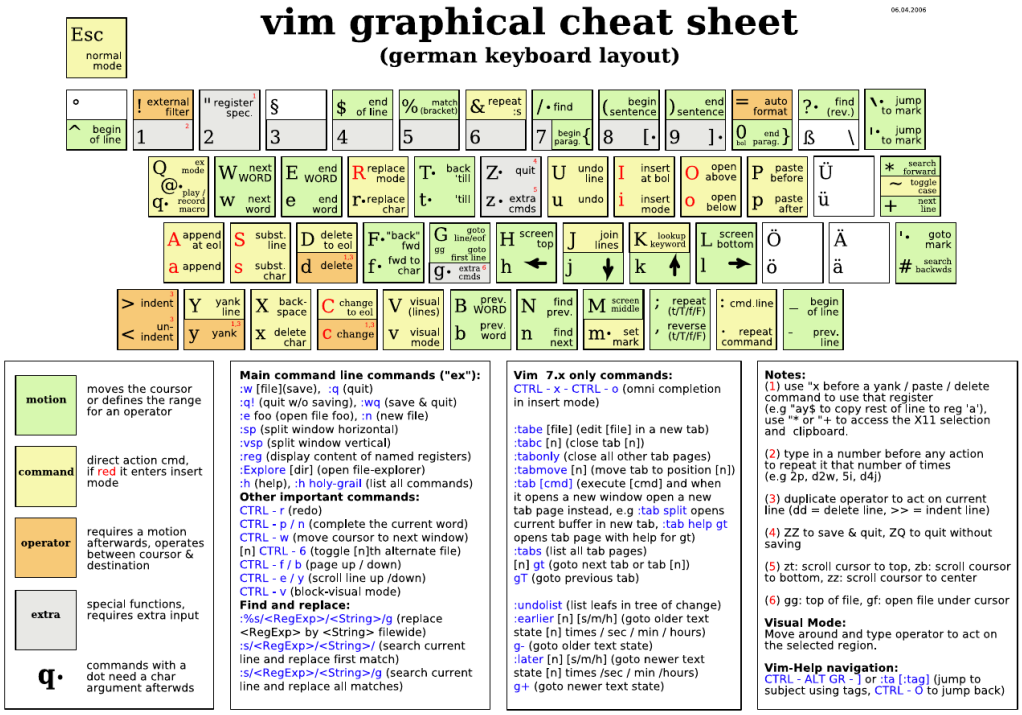


Figure 7: Vim Cheat Sheet

Visual. Quickstart Guide

How to: scientific plots

xmgrace

A tutorial can be found here:
https://universe.bits-pilani.ac.in/uploads/Pilani/navin/ReadPDFDOC/xmgrace.pdf

gnuplot

A lot of example plots can be seen here (an example plot is also shown in the appendix):
http://gnuplot.sourceforge.net/demo/

Gnuplot template for pdf plots (resulting example plot shown below):

```
#!/usr/bin/gnuplot
reset
# plot a pdf
set terminal pdfcairo enhanced font "Times New Roman,12.0" rounded
set output 'confinement_plot.pdf'
set border linewidth 1.0
set size ratio 0.55
# set plot line styles
set style line 1 linecolor rgb 'black'   linetype 1 linewidth 1
set style line 2 linecolor rgb '#FFB85F' linetype 1 linewidth 1
 ↪  #yellow
# set legend position
set key left top
```

```
# set axis properties
set ylabel 'V(r)'
set xlabel 'r / Bohr'
set xtics nomirror
set ytics nomirror
set xr[0:10]
set yr[0:9]
#variables
w = 8.5
r0 = 4.0
a = 2.0
r1=2.5
#functions
f (x) = w / ( 1 + exp (a * (r0 - x)))
g (x) = (x/r1)**2
# plot funcitons
plot  f(x)  title 'Wood-Saxon Confinement' w lines linestyle 1, \
          g(x)  title 'Power Confinement'      w lines linestyle 2

### for plotting data files:
# plot "name_of_datafile.dat" w lines
```

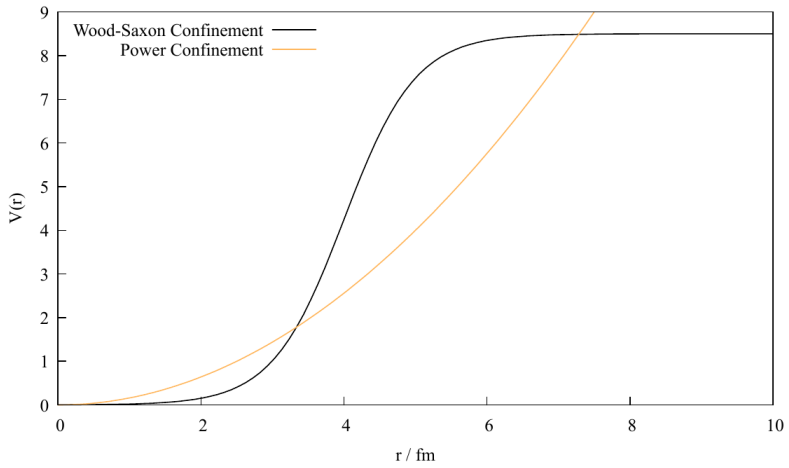


Figure 8: gnuplot example plot

matplotlib

Quickstart guide:
https://matplotlib.org/stable/users/getting_started/index.html

julia

Found on the net (not testet yet, but seems useful):
https://nextjournal.com/leandromartinez98/tips-to-create-beautiful-publication-quality-plots-in-julia

How to: vmd eye candy

- Set background color to white (a good .vmdrc file is shown in the appendix)
- Adjust camera to a nice perspective of the molecule and set the resolution of atoms and bonds in graphical representations to 25
- File -> Render ...

- Select ”Tachyon”
- add to the the command before the -o flag ”-res 3000 3000” so that i looks like ”... TARGA -res 3000 3000 -o ...”
- autocrop and scale the image to a smaller size it with gimp, done!

Good default `VMD` settings (stolen from Bernhard, copy content end save it in `.vmdrc` in your home directory):

```
color Display Background white
color Axes Labels black
color Labels Bonds black
color Labels Angles black
display depthcue off
## position and turn on menus
menu main move 5 225
menu display move 395 30
menu graphics move 395 500
menu main on
menu graphics on
mol delrep 0 top
mol representation Licorice 0.100000 12.000000 1.000000
mol addrep top
mol representation DynamicBonds 1.600000 0.100000 12.000000
mol addrep top
```

Latex Quickstart Guide

How to: LaTeX

- A Short Introduction to LATEX
- The Not So Short Introduction to LATEX 2_ϵ
- Overleaf Documentation A list of LaTeX editors:

- TeXStudio
- Kile
- Any texteditor with a LaTeX plugin (*e.g.* VScode, (neo)vim, Kile, …)
- Overleaf (online tool) - it is not recommended if you want to compile a very large project like a thesis because it is getting very slow.

Python Quickstart Guide

How to learn programming

- A good free option to learn python is `python` for Everybody
- Excersim offers programming challenges (various languages) Udemy courses have a good reputation as well.

Python Tutorial

Welcome to the `python` tutorial! In this tutorial, we will cover the basics of the `python` programming language, including variables, data types, loops, and functions.

Variables

In python, a variable is a container that holds a value. To create a variable, you simply assign a value to it using the assignment operator (=). For example:

```
x = 5
```

This creates a variable called x and assigns it the value 5. You can then use the variable x in your code to refer to the value 5.

Data Types

python has several built-in data types, including:

- Integers: whole numbers, like 5
- Floats: decimal numbers, like 3.14
- Strings: sequences of characters, like "hello"
- Booleans: values that can be either True or False

You can use the type() function to check the data type of a variable. For example:

```
x = 5
print(type(x)) # Output: <class 'int'>
```

Loops

Loops are used to repeat a block of code multiple times. In python, there are two types of loops: for loops and while loops.

For loops are used to iterate over a sequence of values, such as a list or a string. For example:

```
fruits = ["apple", "banana", "cherry"]
for fruit in fruits:
  print(fruit)
```

This will output each fruit in the list, one at a time.

While loops are used to repeat a block of code while a certain condition is true. For example:

```
x = 0
while x < 5:
  print(x)
  x += 1
```

This will output the numbers 0 through 4, one at a time.

Functions

Functions are reusable blocks of code that perform a specific task. To define a function in python, you use the def keyword followed by the name of the function and a colon. For example:

```
def greet(name):
  print("Hello, " + name + "!")
```

This defines a function called greet that takes a single argument called name. You can then call the function using the name of the function followed by parentheses containing any arguments. For example:

```
greet("Alice") # Output: Hello, Alice!
```

This will call the `greet` function with the argument `"Alice"`, which will print the message "Hello, Alice!".

Conclusion

That's it for the `python` tutorial!

Data Visualization

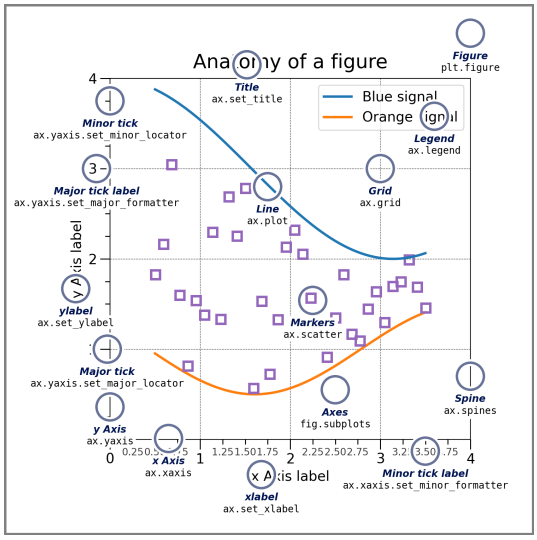
Matplotlib

Matplotlib is the main plotting library in Python. It is a very powerful tool for creating high-quality plots and figures.

More informations can be found under https://matplotlib.org/

```
from matplotlib import pyplot as plt
# change style to default
plt.style.use('default')
```

Components of Matplotlib Figure:



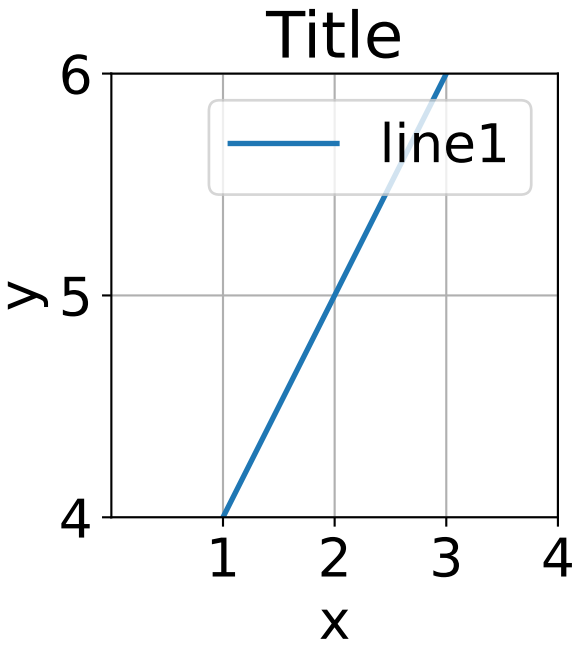
Global settings

```
import matplotlib as mpl
mpl.rcParams['font.size'] = 20
mpl.rcParams['lines.linewidth'] = 2
mpl.rcParams['lines.linestyle'] = '-'
mpl.rcParams['figure.figsize'] = (3,3)
```

Figure

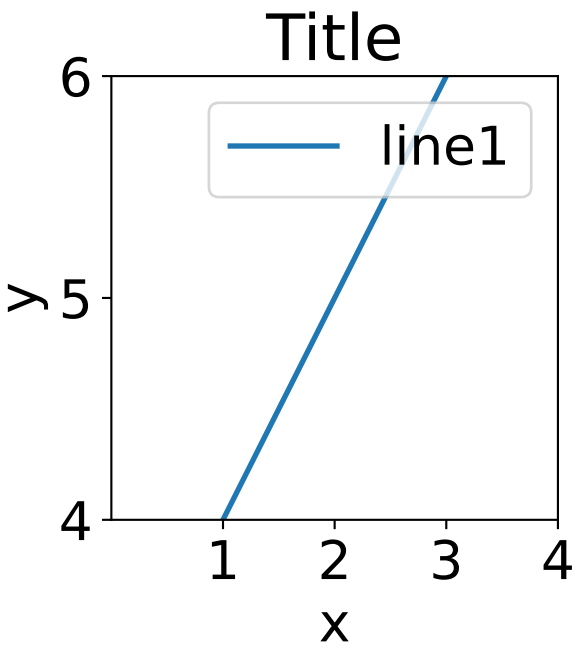
```
fig = plt.figure()
plt.xlabel('x') # x label
plt.ylabel('y') # y label
plt.title('Title') # title
# plot line with x and y data , label for legend
```

```
plt.plot([1, 2, 3], [4, 5, 6], label='line1')
plt.xlim(0, 4) # x axis limits
plt.ylim(4, 6) # y axis limits
plt.xticks([1, 2, 3, 4]) # x axis ticks
plt.yticks([ 4, 5, 6]) # y axis ticks
plt.grid(True) # show grid
plt.legend() # show legend
plt.show()
```



Axes

```
fig, ax = plt.subplots()
ax.set_xlabel('x')
ax.set_ylabel('y')
ax.set_title('Title')
ax.plot([1, 2, 3], [4, 5, 6], label='line1')
ax.set_xlim(0, 4)
ax.set_ylim(4, 6)
ax.set_xticks([1, 2, 3, 4])
ax.set_yticks([ 4, 5, 6])
ax.legend()
plt.show()
```

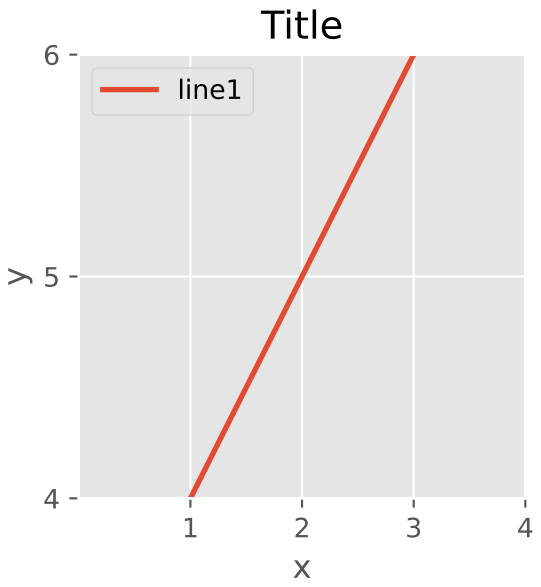


Use different styles

You can use different styles for your plots. The following code shows how to use the `ggplot` style.

```
plt.style.use('ggplot')
```

```
fig = plt.figure()
plt.xlabel('x')
plt.ylabel('y')
plt.title('Title')
plt.plot([1, 2, 3], [4, 5, 6], label='line1')
plt.xlim(0, 4)
plt.ylim(4, 6)
plt.xticks([1, 2, 3, 4])
plt.yticks([ 4, 5, 6])
plt.grid(True)
plt.legend()
plt.show()
```



Other style can be found under https://matplotlib.org/stable/gallery/style_sheets/style_sheets_reference.html

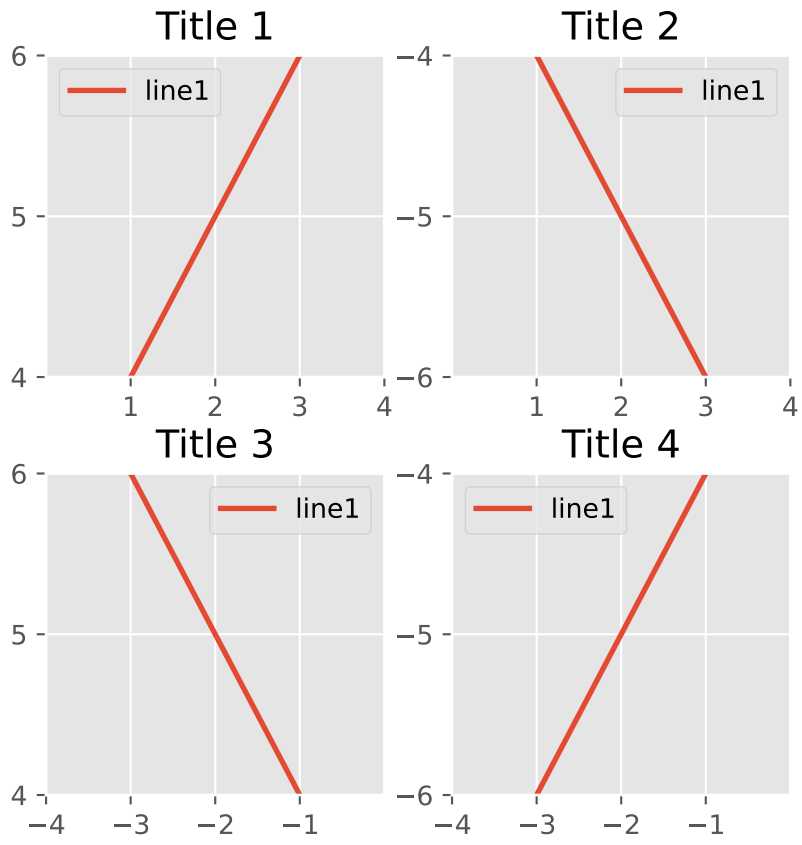
Subplots

You can create subplots in a figure. The following code shows how to create a figure with 2x2 subplots.

```
plt.style.use('default')
```

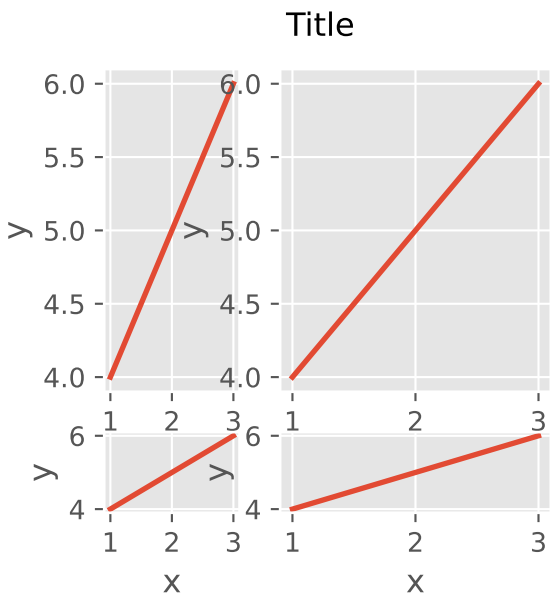
```
fig, axes = plt.subplots(2, 2, sharex=False, sharey=False, figsize=(5,
 ↪  5),gridspec_kw={'hspace': 0.3, 'wspace': 0.2})
axes[0, 0].set_title('Title 1')
axes[0, 0].plot([1, 2, 3], [4, 5, 6], label='line1')
axes[0, 0].set_xlim(0, 4)
axes[0, 0].set_ylim(4, 6)
axes[0, 0].set_xticks([1, 2, 3, 4])
axes[0, 0].set_yticks([ 4, 5, 6])
axes[0, 0].legend()
axes[0, 1].set_title('Title 2')
axes[0, 1].plot([1, 2, 3], [-4, -5, -6], label='line1')
axes[0, 1].set_xlim(0, 4)
axes[0, 1].set_ylim(-6,-4)
axes[0, 1].set_xticks([1, 2, 3, 4])
axes[0, 1].set_yticks([ -4, -5, -6])
axes[0, 1].legend()
axes[1, 0].set_title('Title 3')
axes[1, 0].plot([-1, -2, -3], [4, 5, 6], label='line1')
axes[1, 0].set_xlim(-4,0)
axes[1, 0].set_ylim(4, 6)
axes[1, 0].set_xticks([-1, -2, -3, -4])
axes[1, 0].set_yticks([ 4, 5, 6])
axes[1, 0].legend()
axes[1, 1].set_title('Title 4')
axes[1, 1].plot([-1, -2, -3], [-4, -5, -6], label='line1')
axes[1, 1].set_xlim(-4,0)
axes[1, 1].set_ylim( -6,-4)
axes[1, 1].set_xticks([-1, -2, -3, -4])
axes[1, 1].set_yticks([ -4,- 5, -6])
axes[1, 1].legend()
```

```
plt.show()
```



You can also use `gridspec` to create subplots.

```
from matplotlib.gridspec import GridSpec
fig = plt.figure()
gs =  GridSpec(2,2 ,width_ratios=[1, 2], height_ratios=[4, 1])
ax1 = fig.add_subplot(gs[0, 0])
ax2 = fig.add_subplot(gs[0, 1])
ax3 = fig.add_subplot(gs[1, 0])
ax4 = fig.add_subplot(gs[1, 1])
fig.suptitle('Title') # title for the entire figure
for i,ax in enumerate(fig.get_axes()):
    ax.set(xlabel='x', ylabel='y')
    ax.plot([1, 2, 3], [4, 5, 6],label = "ax%d" %i)

plt.show()
```

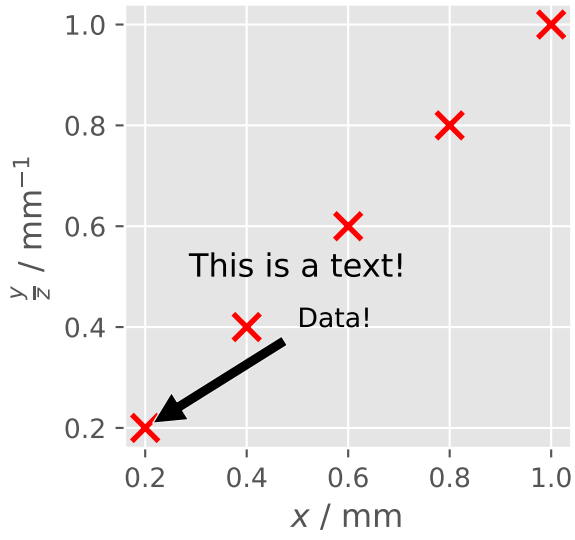


Colors and Color maps

Matplotlib provides a large number of color maps. Here your can find a list of all available color maps: https://matplotlib.org/stable/tutorials/colors/colormaps.html and colors: https://matplotlib.org/stable/tutorials/colors/colors.html and https://matplotlib.org/stable/gallery/color/named_colors.html.

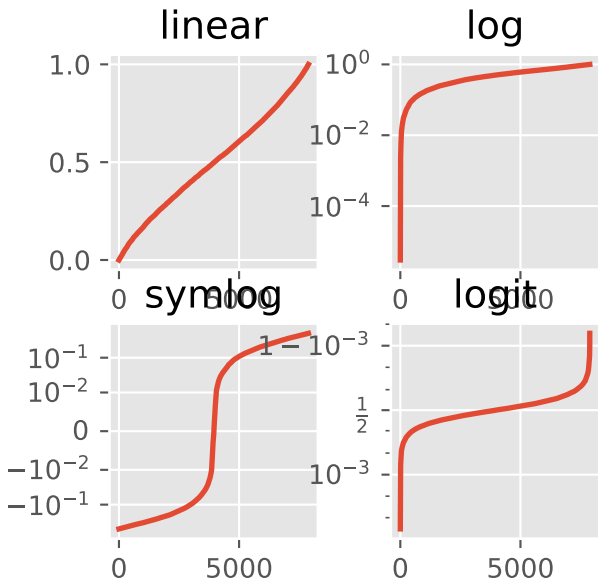
Texts and Annotations

```
import numpy as np
x = [0.2,0.4,0.6,0.8,1.0]
y = [0.2,0.4,0.6,0.8,1.0]
plt.text(0.5, 0.5, 'This is a text!', fontsize=12, ha='center')
plt.annotate('Data!', xy=(0.2, 0.2), xytext=(0.5,
 ↪  0.4),arrowprops=dict(facecolor='black', shrink=0.05))
plt.scatter(x,y, color='red',marker='x',s=100)
plt.xlabel(r'$x$ / mm') # using LaTeX syntax
plt.ylabel(r'$\frac{y}{z}$ / mm$^{-1}$') # using LaTeX syntax
plt.show()
```



Logarithmic scale

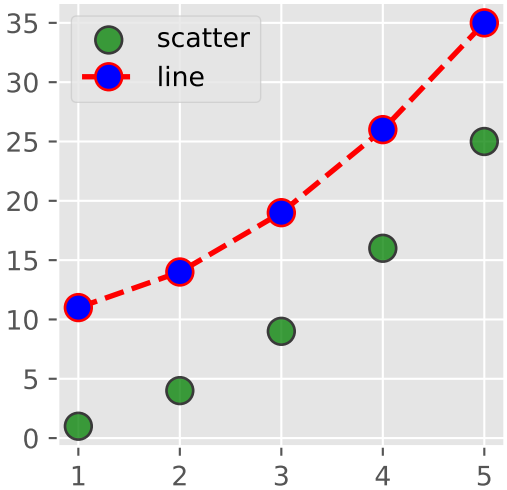
```
y = np.random.normal(loc=0.5,scale=0.4,size=10000)
y = y[(y > 0) & (y < 1)]
y.sort()
x = np.arange(len(y))
plt.figure()

# linear
plt.subplot(221)
plt.plot(x, y)
plt.yscale('linear')
plt.title('linear')
plt.grid(True)

# log
plt.subplot(222)
plt.plot(x, y)
plt.yscale('log')
plt.title('log')
plt.grid(True)

# symmetric log
plt.subplot(223)
plt.plot(x, y - y.mean())
plt.yscale('symlog', linthresh=0.01)
plt.title('symlog')
plt.grid(True)

# logit
plt.subplot(224)
plt.plot(x, y)
plt.yscale('logit')
plt.title('logit')
plt.grid(True)
# Adjust the subplot layout, because the logit one may take more space
# than usual, due to y-tick labels like "1 - 10^{-3}"
plt.subplots_adjust(top=0.92, bottom=0.08, left=0.10, right=0.95,
 ↪  hspace=0.25,
                    wspace=0.35)

plt.show()
```



Scatter / Line plot

```
import numpy as np
x = np.array([1, 2, 3, 4, 5])
y = np.array([1, 4, 9, 16, 25])
y2 = y + 10
```

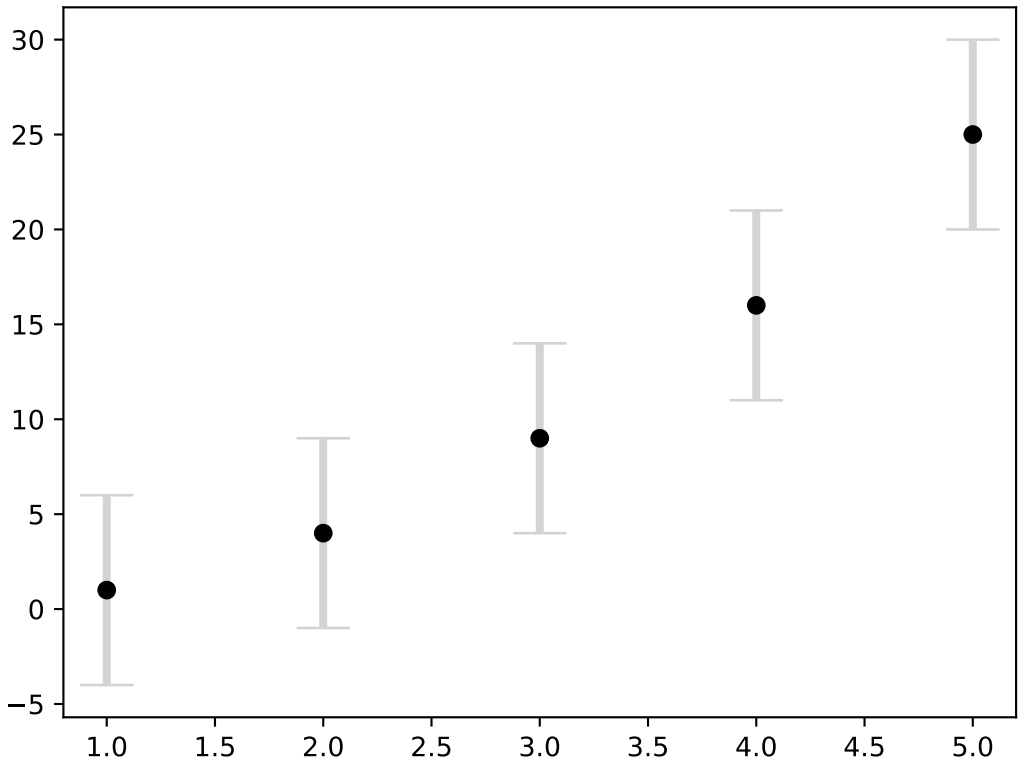
```
plt.scatter(x, y, s=100, c='green', edgecolor='black', linewidth=1,
 ↪  alpha=0.75, marker='o', label='scatter')
plt.plot(x, y2, color='red', marker='o', markersize=10,
 ↪  markerfacecolor='blue', linestyle='--', linewidth=2,label='line')
plt.legend()
plt.show()
```



Error bars

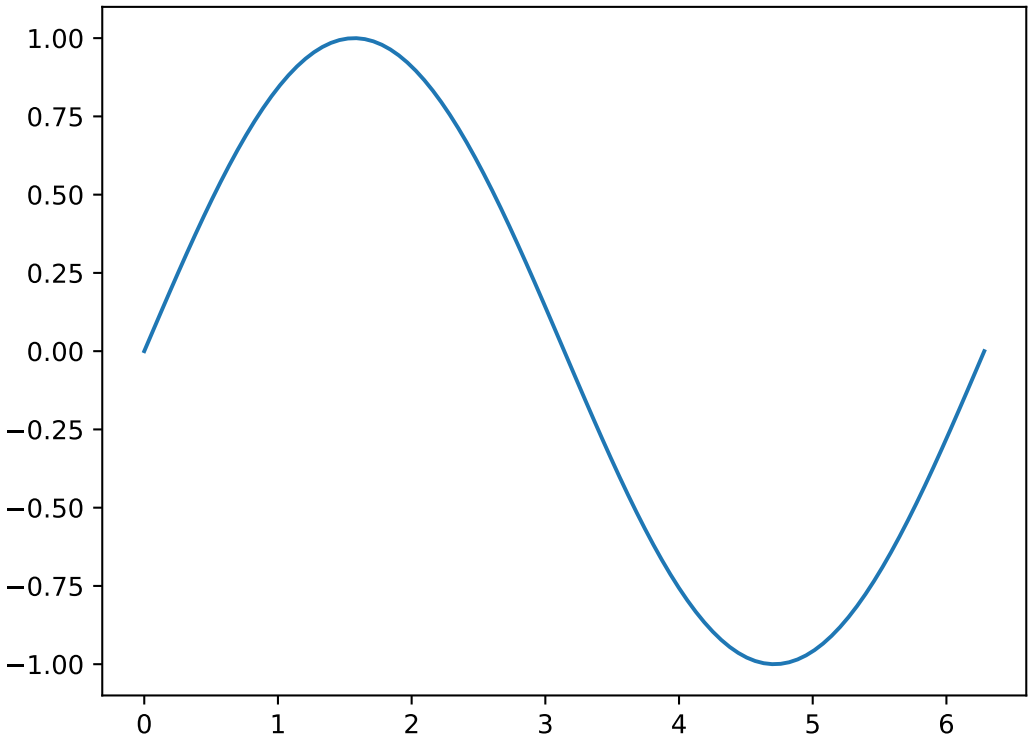
```
plt.style.use('default')
plt.errorbar(x, y, yerr=5, fmt='o', color='black', ecolor='lightgray',
 ↪  elinewidth=3, capsize=10)
```

```
# fmt is the format of the marker, ecolor is the color of the error
 ↪  bar, elinewidth is the width of the error bar line, capsize is the
 ↪  size of the error bar cap
plt.show()
```



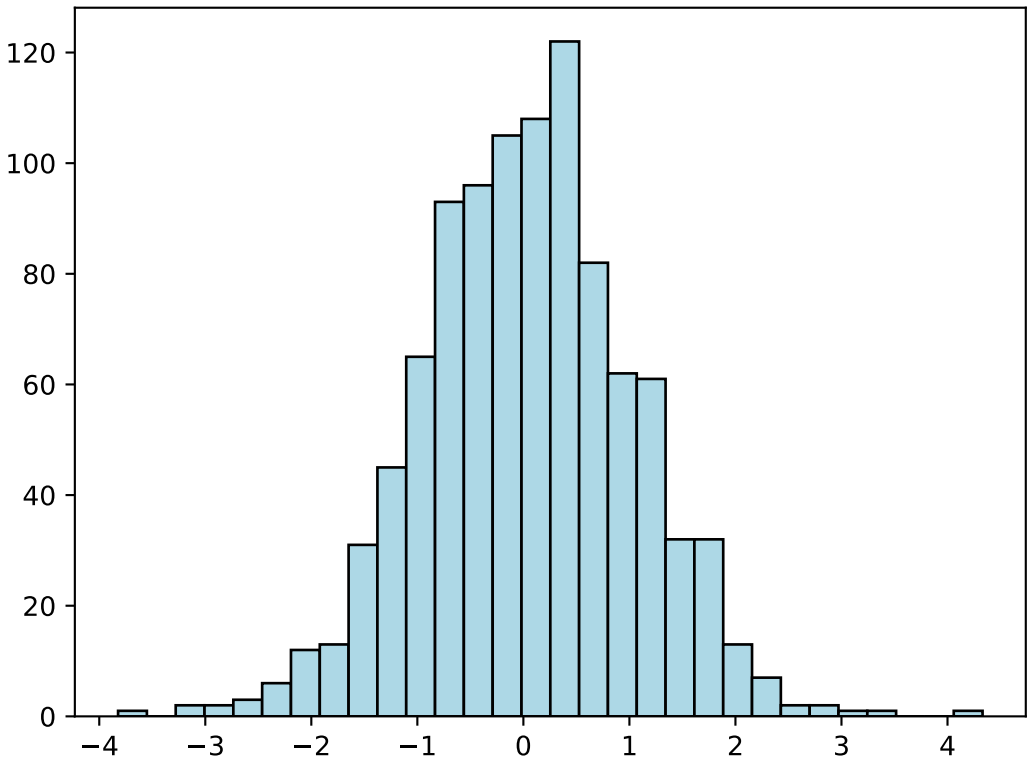
Save figure

```
x = np.linspace(0, 2 * np.pi, 100)
y = np.sin(x)
fig, ax = plt.subplots()
ax.plot(x, y, label='line1')
# bbox_inches is the bounding box in inches.
# If 'tight', it will fit the figure to the plot area.
plt.savefig('../data/test.png', dpi=300, bbox_inches='tight')
plt.show()
```

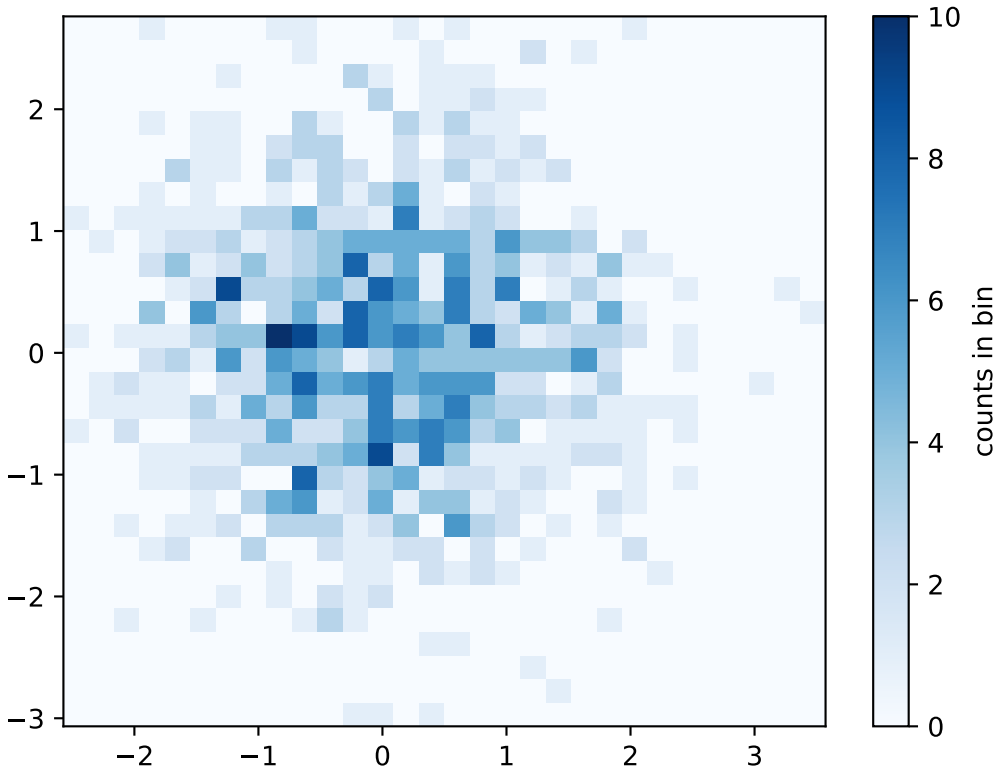


Histogram

```
x = np.linspace(0, 200,1000)
y = np.random.normal(0,1,1000)
fig, ax = plt.subplots()
ax.hist(y, bins=30, color='lightblue', edgecolor='black')
plt.show()
```



```
# 2D histogram
x = np.random.normal(0,1,1000)
y = np.random.normal(0,1,1000)

plt.hist2d(x, y, bins=30, cmap='Blues')
colorbar = plt.colorbar()
colorbar.set_label('counts in bin')
plt.show()
```

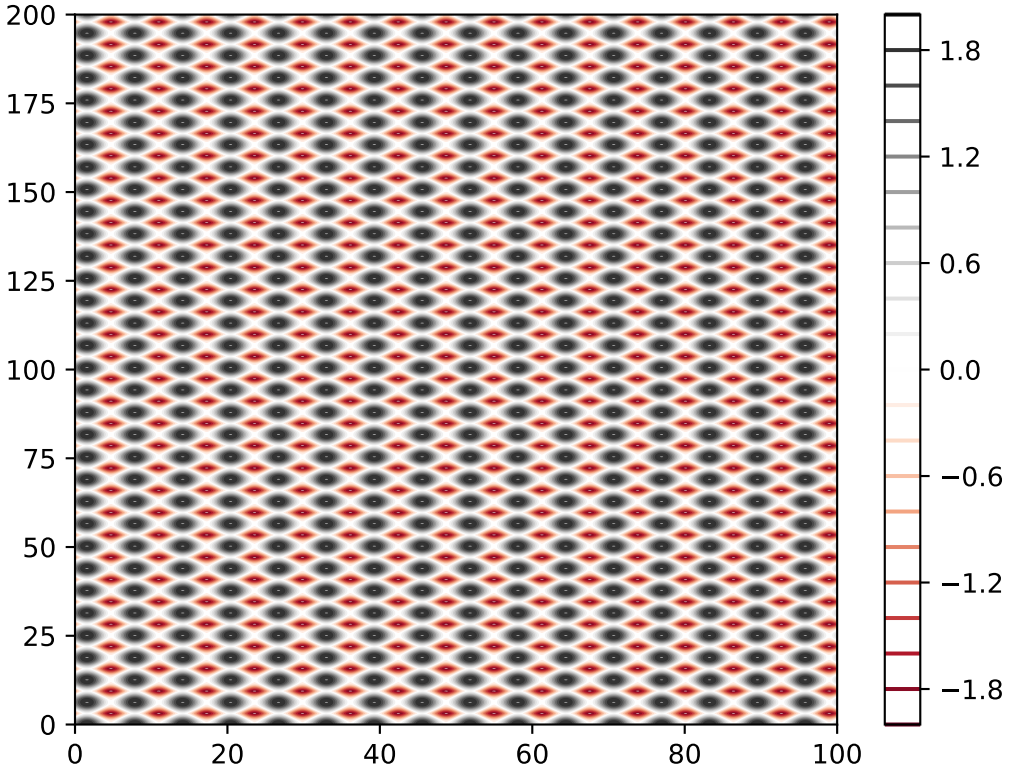


Density plot

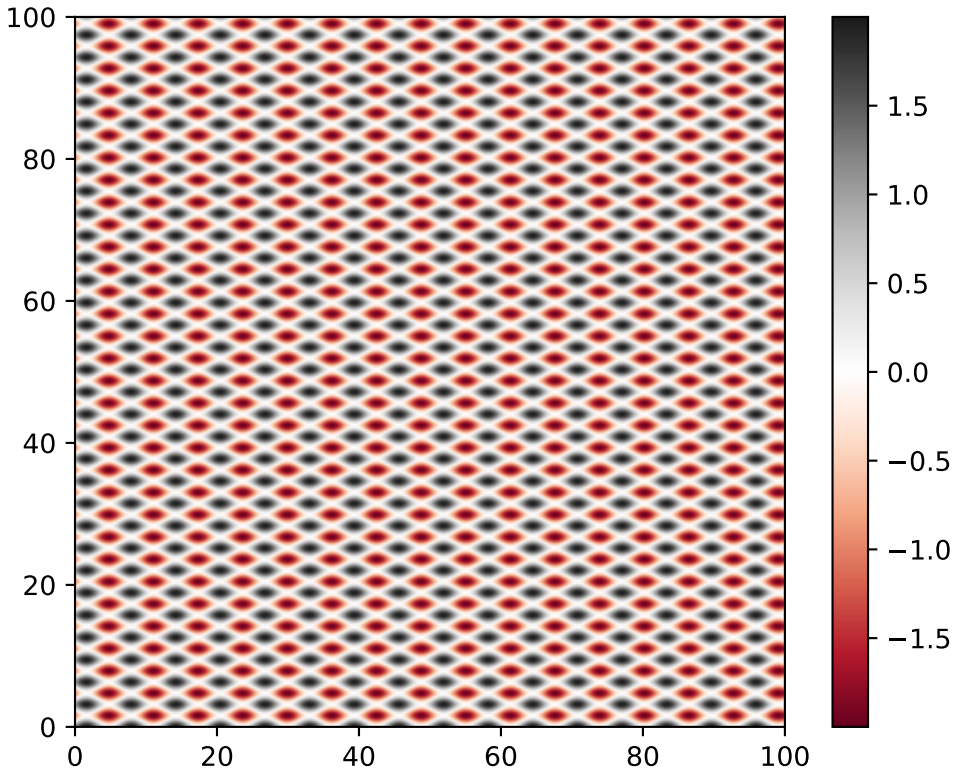
```
x = np.linspace(0, 100, 1000)
y = np.linspace(0, 100, 1000)*2
# Create a 2D array of shape (1000,1000)
X, Y = np.meshgrid(x, y)
# Z is a 2D array of shape (1000,1000)
Z = np.sin(X) + np.cos(Y)
print("Shape of X:", X.shape)
print("Shape of Y:", Y.shape)
print("Shape of Z:", Z.shape)
```

```
Shape of X: (1000, 1000)
Shape of Y: (1000, 1000)
Shape of Z: (1000, 1000)
```

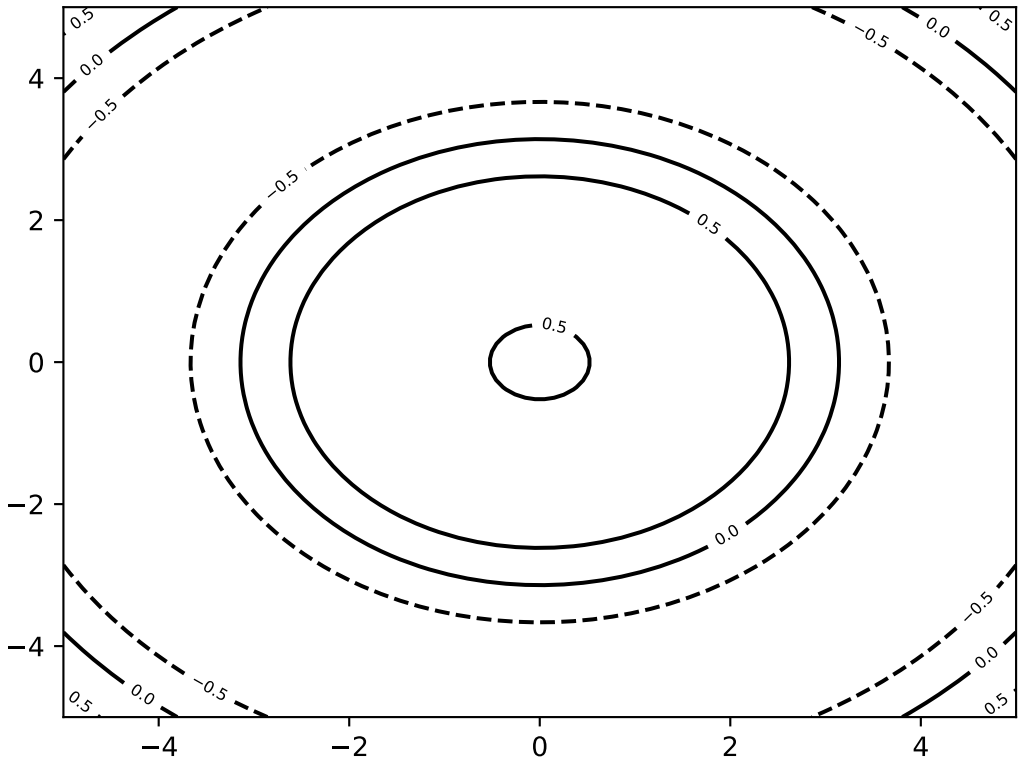
```
fig, ax = plt.subplots()
# Create a contour plot
plt.contour(X, Y, Z, 20, cmap='RdGy')
plt.colorbar()
plt.show()
```




```
# 2D grid is interpreted as an image with imshow
plt.imshow(Z, extent=[0, 100, 0, 100], origin='lower', cmap='RdGy')
plt.colorbar()
plt.show()
```



```
# contour plot with labels
X = np.linspace(-5, 5, 100)
Y = np.linspace(-5, 5, 100)
X, Y = np.meshgrid(X, Y)
Z = np.sin(np.sqrt(X**2 + Y**2))

contours = plt.contour(X,Y,Z,3, colors='black') #
 ↪  plt.contour([X,Y],Z,[levels])
plt.clabel(contours, inline=True, fontsize=6)
```



Seaborn

`Searborn` is based on `Matplotlib`and is made for statistical graphics. It is comparable with `R`'s `ggplot2` library.

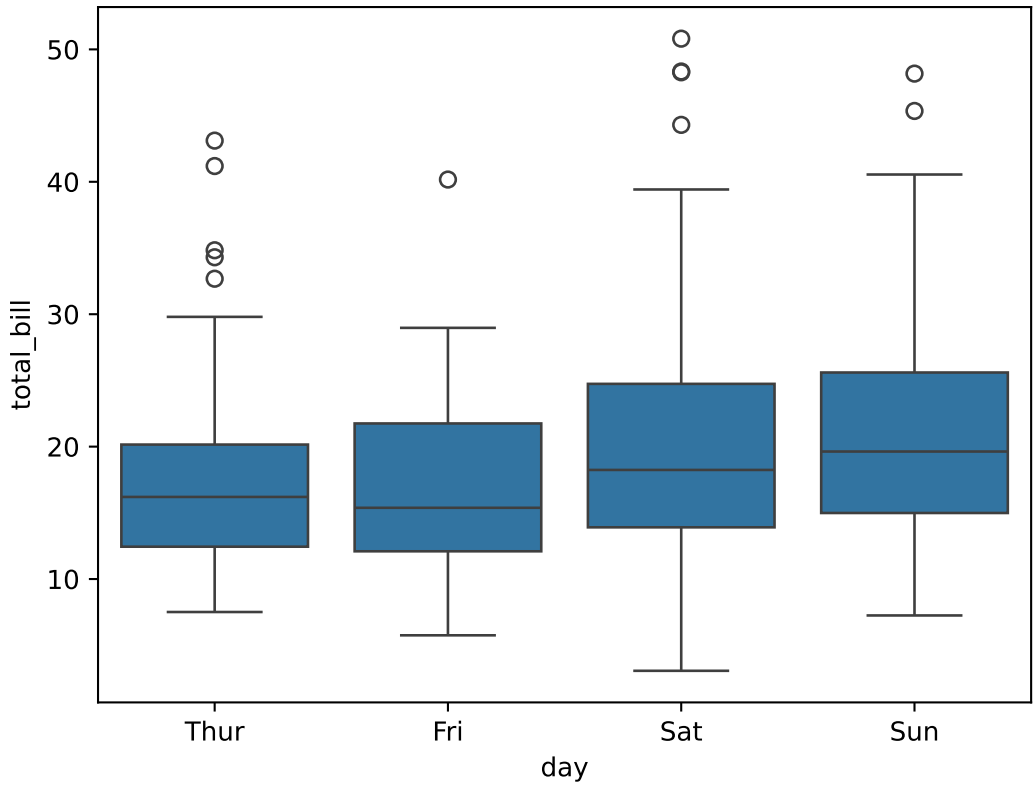
It works best with `Pandas` DataFrames. You can easly create complex plots with only a few lines of code by grouping and aggregating data.

More informations can be found under https://seaborn.pydata.org/

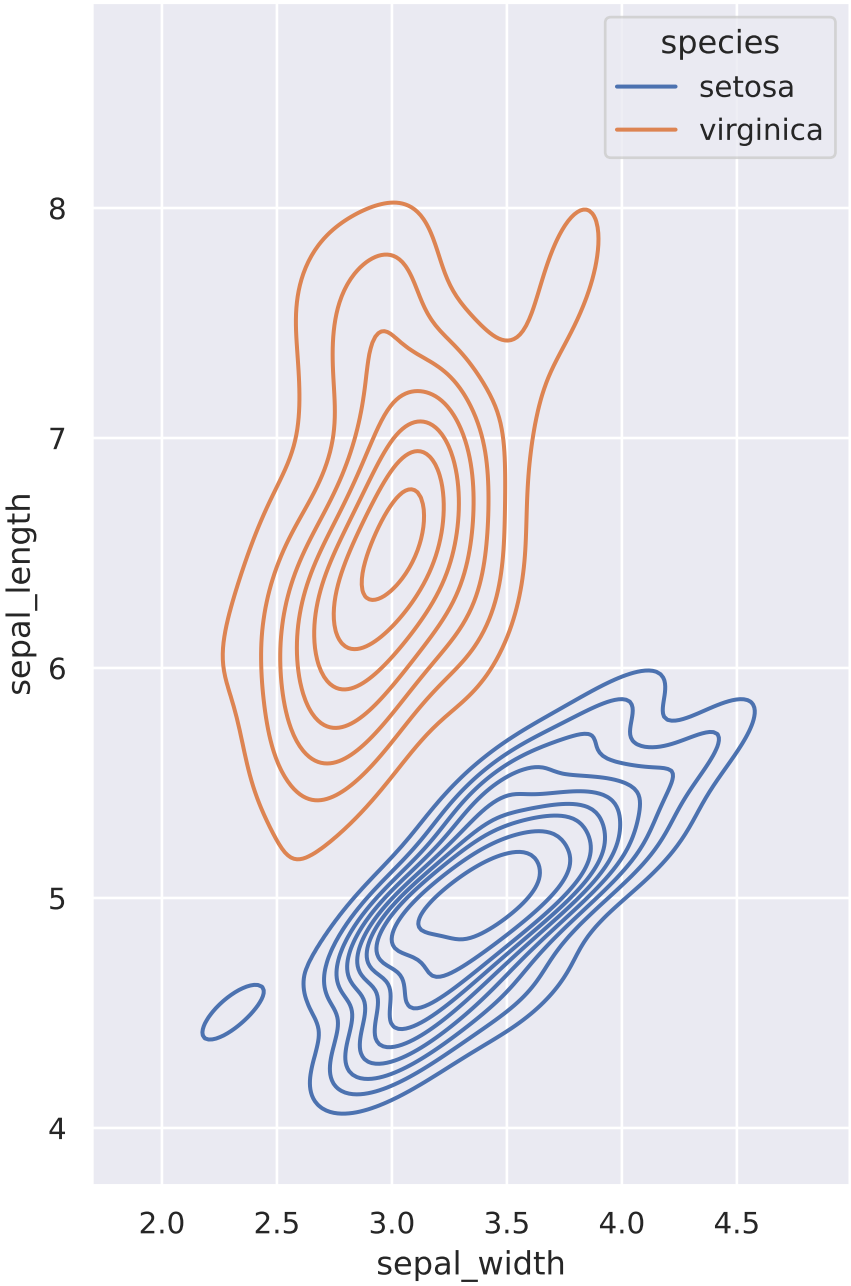
```
import seaborn as sns
```

Example

```
# Use the default data set from seaborn
tips = sns.load_dataset('tips')
# Create a boxplot
sns.boxplot(x='day', y='total_bill', data=tips)
```




```
import matplotlib.pyplot as plt
import seaborn as sns


sns.set_theme(style="darkgrid")
iris = sns.load_dataset("iris")

# Set up the figure
f, ax = plt.subplots(figsize=(8, 8))
ax.set_aspect("equal")

# Draw a contour plot to represent each bivariate density
sns.kdeplot(
    data=iris.query("species != 'versicolor'"),
    x="sepal_width",
    y="sepal_length",
    hue="species",
    thresh=.1,
)
```

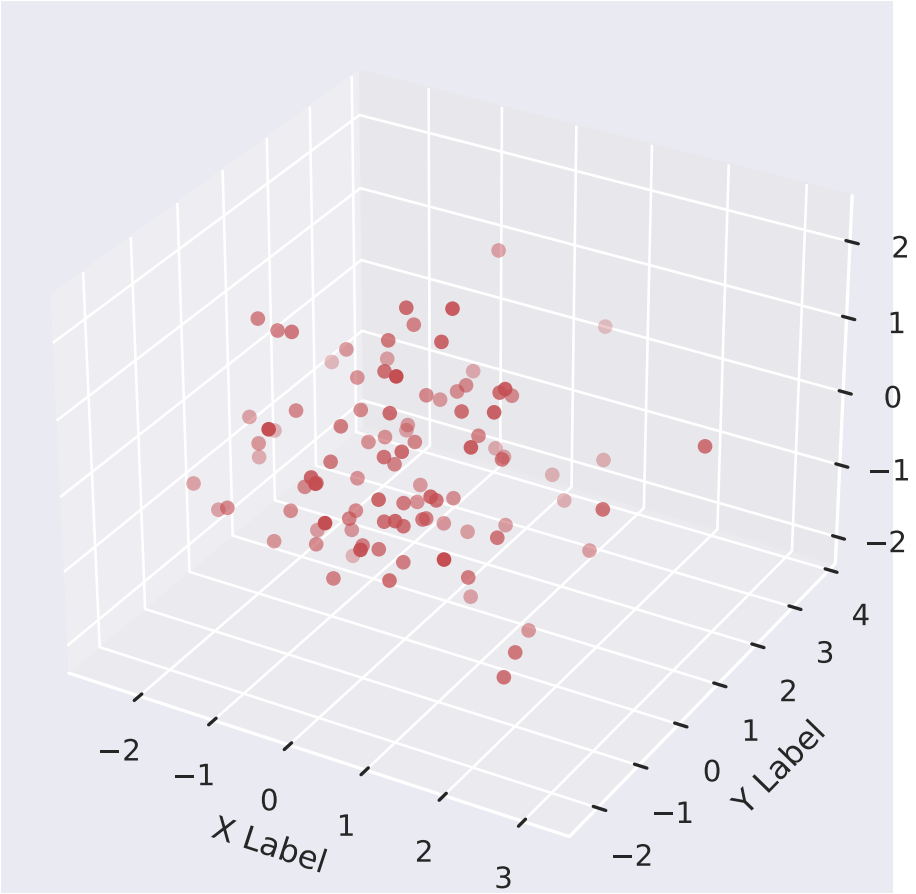


3D plots

Matplotlib can also be used to create 3D plots but it is not the best tool for this.

```
from mpl_toolkits.mplot3d import Axes3D
import matplotlib.pyplot as plt
import numpy as np

fig = plt.figure(figsize=(5, 5))
ax = fig.add_subplot(111, projection='3d')
x = np.random.standard_normal(100)
y = np.random.standard_normal(100)
z = np.random.standard_normal(100)
ax.scatter(x, y, z, c='r', marker='o')
ax.set_xlabel('X Label')
ax.set_ylabel('Y Label')
ax.set_zlabel('Z Label')
```

```
plt.tight_layout() # adjust the plot to the figure
plt.show()
```



Better tools for 3D plots are `Mayavi` and `Plotly`.

Other plotting libraries

- Plotly
- Mayavi
- Bokeh
- Altair
- ggplot
- pygal
- pandas