Session 5

Molecular Dynamics

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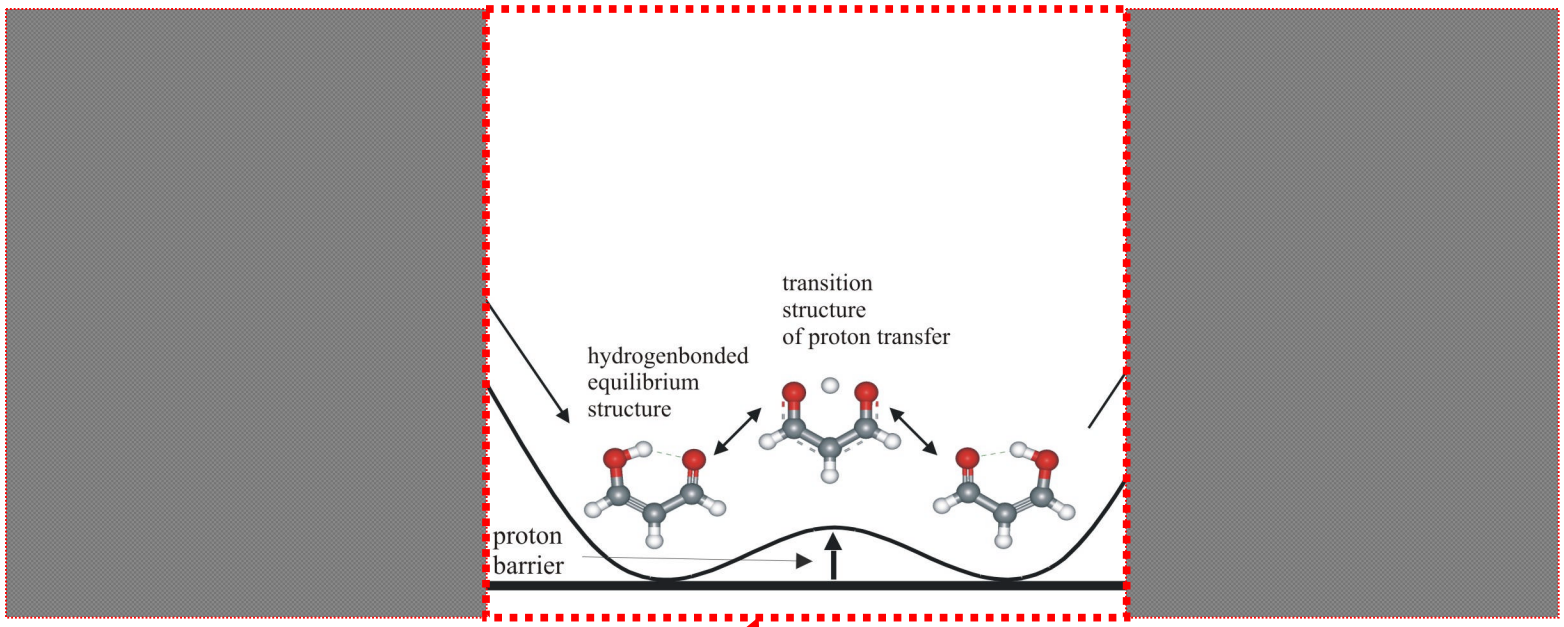
System: Malonaldehyde

Intra-molecular hydrogen bonding and proton transfer
in the malonaldehyde molecule



Focus of the excercise: proton transfer (rather than hydrogen bonding)

Output files and tools

New output files in this session:

“relaxHist.dat”

output and control file of the structure optimization
contains the evolution of structure, forces, total energy etc.

“moldynHist.dat”

output and control file of the molecular dynamics run
contains trajectory, velocities, forces, total energy etc.

“modes.molf”

output file of the frozen phonon calculation
contains harmonic eigenfrequencies and eigenvelocities.

New add-ons in this session:

“sxhist2corr”

calculates the generalized frequency spectrum out of the file “moldynHist.dat”

“sxhist2molf”

converts the file “moldynHist.dat” respectively “relaxHist.dat” to MOLDEN-format (readable by ‘molekel’ for visualisation)

Session: Overview

Preparation: Setting up supercell, electronic basis and DFT-Functional

Excercise 01: Structure optimization of the hydrogen bonded equilibrium structure

Excercise 02: Structure optimization of the transition structure of proton transfer

Excercise 03: Harmonic vibrational analysis of equilibrium and transition state

Excercise 04: Molecular dynamics simulation of a induced proton transfer process

Directory tree

Preparation	⇨	„E5/preparation“
Excercise 01	⇨	„E5/01-relax-Equ-Struc“
Excercise 02	⇨	„E5/02-relax-Tr-Struc“
Excercise 03	⇨	„E5/03-vibrations“
Excercise 04	⇨	„E5/04-MD“
Session-handout	⇨	„E5/doc/session.ps“

Preparation: Setting up supercell, electronic basis and DFT-Functional

- supercell, electronic basis and XC-Functional are setted up once in the file "preparation/header.sx" and then linked in by each excercise

Preparation

Set up
- basisset size,
- supercell size
- XC-Functional

in the file:
„~E5/preparation/header.sx"

This file is included in the input-file of each exercise:
include „../preparation/header.sx";

Exercise 01
Optimization of hydrogen bonded equilibrium structure

Exercise 02
Optimization of transition structure of proton transfer

Exercise 03
Harmonic vibrational analysis

Exercise 04
Molecular Dynamics

These quantitys are related to the accuracy in describing the Born-Oppenheimer surface

The excercises deal with methods that explore the Born-Oppenheimer surface

Preparation: Setting up supercell, electronic basis and DFT-Functional

File: „preparation/header.sx“

```
format sfhingx;
include <parameters.sx>;

//--- Malonaldehyde contains
//    3 Carbon, 2 Oxygen and 4 Hydrogen ion cores
species_1 = <species/o-pbe-tm.sx>;
species_2 = <species/c-pbe-tm.sx>;
species_3 = <species/h-coulomb.sx>;

//--- Setup the orthorombic supercell here
xExt = xxxx;
yExt = xxxx;
zExt = xxxx;

structure  {
  include "tau_equ_init.sx";
   cell = [ [xExt,     0,     0],
            [   0,  yExt,     0],
            [   0,     0,  zExt] ];
  symmetry {
     operator {S = [[1,0,0],[0,1,0],[0,0,1]]; }
  }
}
```

```
basis  {
   //--- Setup the cutoff energy here to define
   //    the size of the electronic basisset
   eCut = xxxx;
   //--- k-Point setting to optimize convergence
   //    behaviour with respect to supercell size
   kUnits = [ 1, 1, 1];
   kPoint { coords = [0.25, 0.25, 0.];
            weight = 1; relative; }
   folding = [ 1, 1, 1];
}

Hamiltonian  {
   // --- fully isolating (artificial) crystal
   //     of molecules: electronic temperature is 0
   ekt        = 0;
   // --- setup XC-Functional here
   xc = xxxx;
}

// --- LCAO-initialisation for electronic loop
initialGuess  {
   waves { lcao { maxSteps = 1; rhoMixing = 0.05; } }
   rho { atomicOrbitals; }
}
```

Preparation:

⇨ Setup size of basisset, supercell size and XC-Functional in this file

Preparation: Setting up supercell, electronic basis and DFT-Functional

Recommended supercell size for this session:	**12x4x12 Bohr**
Recommended plane wave cutoff:	**43 Rd**
Recommended XC-Functional:	**PBE**

Results are not fully converged with respect to these parameters

Aim of this session:

qualitative analysis

first step in a convergence process

At home (if interested):

check convergence with respect to supercell and basisset

try other XC-functional (PBE-LDA)

Exercise 01: Structure optimization of hydrogen bonded equilibrium structure

Quasi-Newton structure optimization loop

Update of gradient

Structure optimization calls **electronic loop** to get electronic groundstate and forces acting on atomic geometry

$$\vec{g}^{\,n} = -\vec{F}(\vec{X}^{\,n})$$

Update of atomic geometry

$$\vec{X}^{\,n+1} = \vec{X}^{\,n} - (\underline{\underline{H}}^{\,n})^{-1}\,\vec{g}^{\,n}$$

Update of hessian matrix (BFGS)

$$\underline{\underline{H}}^{\,n+1} = \underline{\underline{H}}^{\,n} + \frac{\Delta\vec{g}^{\,n}(\Delta\vec{g}^{\,n})^{tr}}{(\Delta\vec{X}^{\,n})^{tr}\,\Delta\vec{g}^{\,n}} - \frac{\underline{\underline{H}}^{\,n}\Delta\vec{X}^{\,n}(\Delta\vec{X}^{\,n})^{tr}\,\underline{\underline{H}}^{\,n}}{(\Delta\vec{X}^{\,n})^{tr}\,\underline{\underline{H}}^{\,n}\Delta\vec{X}^{\,n}}$$

harmonic decoupling of movement correct preconditioning (contained in eigenvalues)

the information about the energy-surface gained during optimization steps is stored in the guess for the hessian

Problem:
Hessian matrix not known from the beginning

Solution

Exercise 01: Structure optimization of hydrogen bonded equilibrium structure

Tasks:

- a structure optimization always needs an initial guess
  - ⇨ setup an initial guess for the hydrogen bonded equilibrium structure

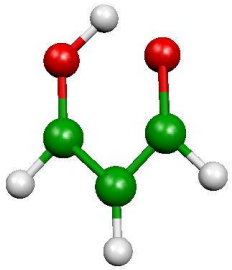
- to improve the performance, the structure optimization is performed in a 2-stage scheme
  - ⇨ define the intersection between the two stages

- after the structure optimization:
  - ⇨ check performance
  - ⇨ analyse outcoming structure and total energy

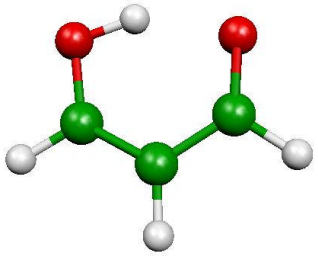
Exercise 01: Structure optimization of hydrogen bonded equilibrium structure

(Task: set up an initial guess for the hydrogen bonded equilibrium structure)

Initial guess based on simple geometric considerations provided in „E5/01-relax-Equ-Struc/tau_equ_init.sx“



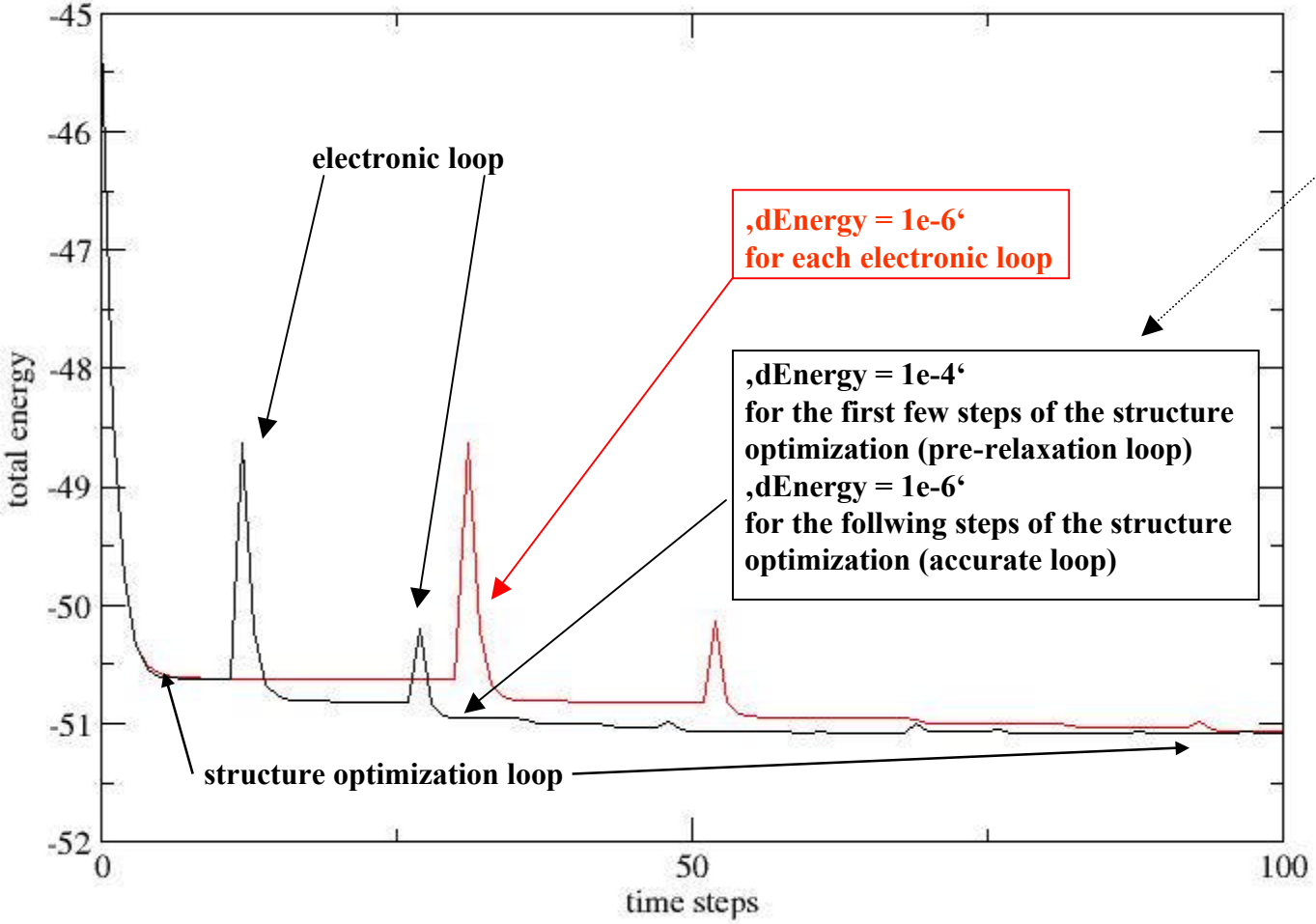
The optimized structure looks like this



- initial guess is allready provided in the file “tau_equ_init.sx”, if you want to improve the provided initial guess modify this file
- keep planarity! (all y – coords must stay 0)

Note: the movemement is constrained to the molecules plain for the structure optimization and the MD run

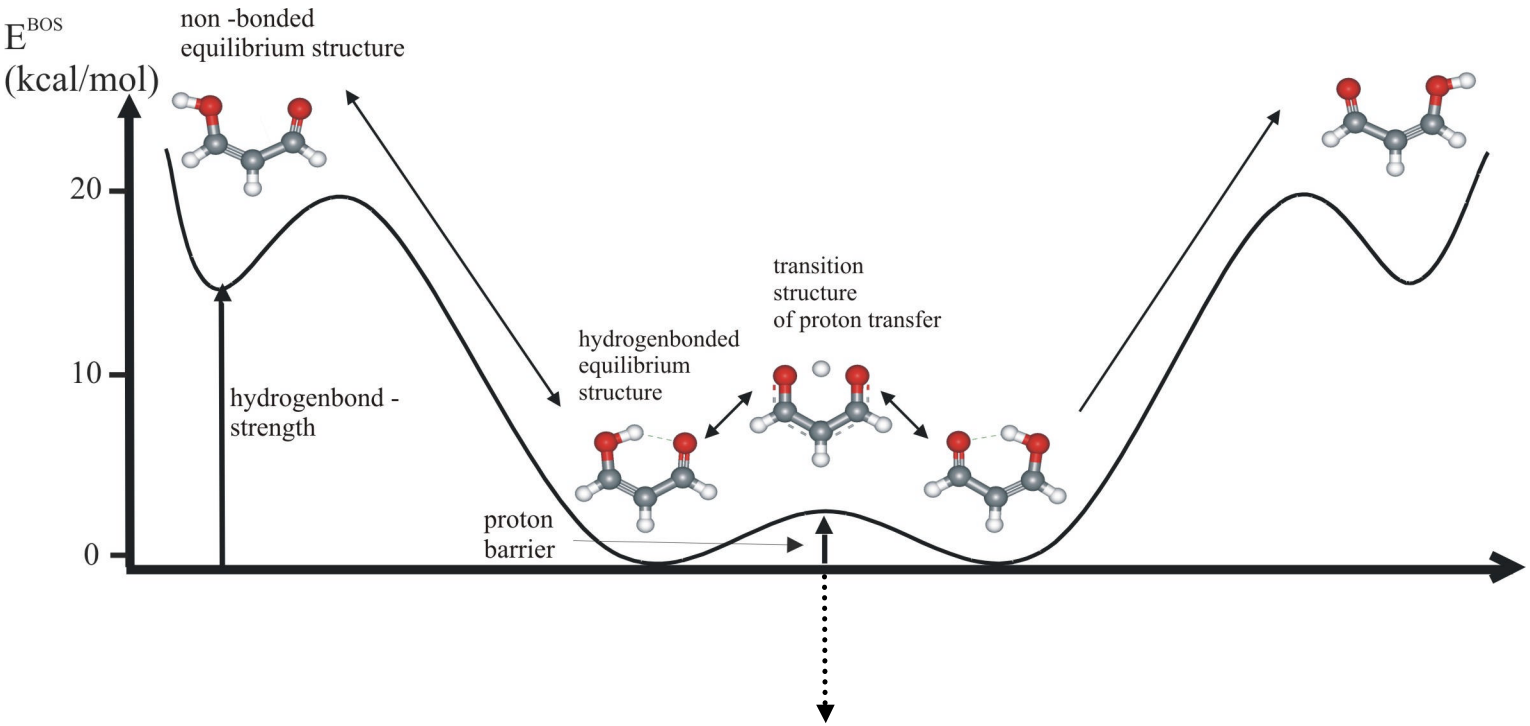
Exercise 01: Structure optimization of hydrogen bonded equilibrium structure



Defining a pre-relaxation increases performance!

Tasks:
- ⇨ set up the electronic accuracy for the pre-relaxation loop
- ⇨ define intersection of the two structure optimization loops

Exercise 02: Structure optimization of transition structure of proton transfer



Which symmetry operation ?

Tasks:
- ⇨ symmetrize the relaxed equilibrium structure or take the provided file
- ⇨ load in the symmetrized structure as initial guess for the structure optimization
- ⇨ analyse converged structure and total energy, calculate proton barrier

Exercise 03: Harmonic vibrational analysis

Born-Oppenheimer surface in harmonic approximation

$$H^{ion} \approx \sum_{I=1}^{N^{ions}} \frac{1}{2M_I} \frac{\partial^2}{\partial \mathbf{X}_I{}^2} + \frac{1}{2} \Delta \mathbf{X}^{tr} \underline{\underline{\mathbf{H}}} \Delta \mathbf{X}; \quad \mathbf{X} = \{\mathbf{X}_I\}; \quad H_{ij} = \left. \frac{\partial^2 E^{\mathrm{BOS}}}{\partial \mathrm{X_i} \partial \mathrm{X_j}} \right|_{\mathbf{X}_0}$$

⇨ **describes movement of 3N coupled oscillators**

Unitary transformation on eigenbasis of dynamical matrix $D_{ij} = \frac{1}{\sqrt{M_i M_j}} H_{ij}$

$$H^{ion} = \sum_{k=1}^{3N} H_k^{vib}$$

$$H_k^{vib} = \frac{1}{2} p_k^2 + \frac{1}{2} \mathrm{w}_k^2 q_k^2$$

⇨ **movement is decoupled**

⇨ **decomposes into 3N independent oscillators with vibration with frequencies**

⇨ Full description of the systems dynamics in harmonic approximation

⇨ partition function is fully determined by vibrational frequencies

Exercise 03: Harmonic vibrational analysis

Harmonic vibrational analysis in SFHIngX

Calculation of force constant matrix via the finite differences "frozen phonon"-method

$$H_{ij} = \frac{\partial^2 E}{\partial X_i \partial X_j} = \frac{\partial F_i}{\partial X_j} = \lim_{\Delta X_j \to 0} \frac{\Delta F_i}{\Delta X_j} \approx \frac{\Delta F_i}{\Delta X_j}$$

(time consuming part)

↓

Diagonalisation of dynamical matrix in a post-processing step

↓

Output of eigenfrequencies and eigenvelocities in the file „modes_equ.molf"

Finite differences should be as small as possible to avoid anharmonic contributions and to increase performance !

On the other hand they must be large enough to avoid influence of numerical noise on the forces!

Gauss: $\Delta X_j \geq \frac{\Delta F_j}{\Delta H_{ij}}$

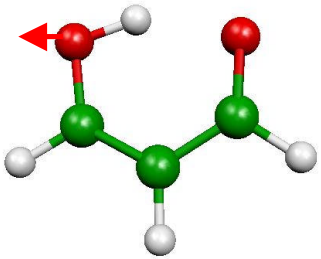
Tasks :
- ⇨ Set up finite differences and range of degrees of freedom
- ⇨ Analyse outcoming eigenfrequencies and eigenvelocities

Exercise 04: Molecular Dynamics

glance beyond the harmonic approximation by analysing an induced proton transfer process

Tasks:

⇨ displace proton-donor oxygen out of its equilibrium position by a distance that corresponds to a potential energy of 10-13 times the proton barrier



⇨ visualize the outcoming trajectory and observe the system‘s behaviour

⇨ calculate the generalized frequency spectrum (sxhist2corr)
identify harmonic and anharmonic contributions to the spectrum
determine red-shift in the proton-donor stretching frequency
find peaks in the spectrum which indicate proton-jump process

Exercise 04: Molecular Dynamics

Velocity-velocitiy auto-correlation function

$$G(\mathrm{t}) = \frac{1}{N^{ion}} \sum_{I=1}^{N^{ion}} \sum_{t=0}^{t^{\max}} \left\langle \dot{\mathbf{X}}_I(t) \middle| \dot{\mathbf{X}}_I(t+\mathrm{t}) \right\rangle$$

Generalized frequency spectrum

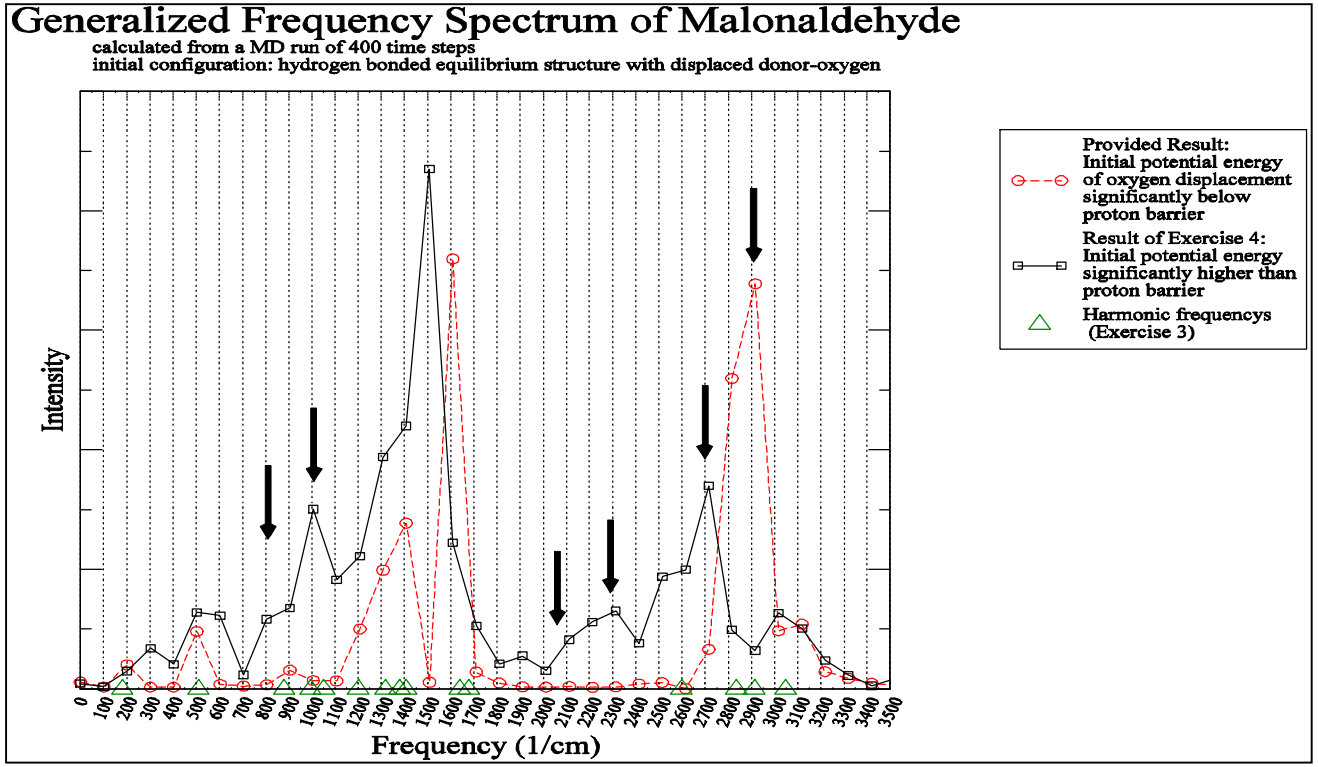
$$I(\mathrm{w}) \propto \int \exp(-i\mathrm{w}\mathrm{t})G(\mathrm{t})d\mathrm{t}$$

MD-run $\xrightarrow{\text{sfhingx}}$ particle velocities $\dot{\mathbf{X}}_I(t)$ $\xrightarrow{\text{sxhist2corr}}$ frequency spectrum $I(\mathrm{w})$

Task: ⇨ determine resolution in frequency space for given simulation time

Exercise 04: Molecular Dynamics

Comparison of the frequency spectra for a MD run without proton jump (red dotted line) an a MD run with proton jumps (black straight line)

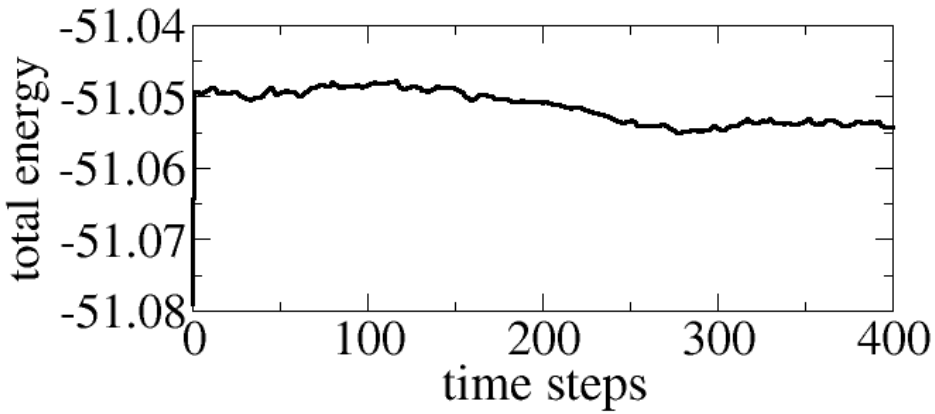


Task:

- ⇨ determine red-shift for proton-donor stretching frequency compared to the harmonic frequency
- ⇨ identify peaks which indicate the proton-jump process
- ⇨ watch the animation of the trajectory

Exercise 04: Molecular Dynamics

Drift in total energy due to rather large time step



Drift for the simulation time of the exercise ≈ 5-15%

Ok for the session, problematic for longer simulation times

At home (if interested):

for longer simulation times and initial displacements of the proton-donor outside the recommended range use smaller time step (0.5 fs) !