

ABC of DFT: Hands-on session 4

Molecular vibrations

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Wo? KIT Campus Süd, Flachbau Physik, Geb. 30.22, Computerpool, Raum FE-6

- Reminder: normal modes of vibration
- Introductory example
 - **water H₂O**
- Try advanced examples yourself !
 - **benzene (C₆H₆)**
 - **C60 buckyball**

Preparing for the hands-on session 4 ...

- Log into **intact** cluster (have a look at a separate sheet of paper with instructions)
- Switch to a working directory:

```
cd ~/ABC_of_DFT/hands-on-sessions/
```
- Copy a script `session2` from **dft20** account:

```
cp ~/../dft20/ABC_of_DFT/session4 .
```
- Type from a command line:

```
./session4
```
- Examples (with this tutorial) will be imported to a directory

```
~/ABC_of_DFT/hands-on-sessions/session4
```

Reminder: molecular vibrations

- Consider energy of the system in harmonic approximation

$$H_{\text{ion}} = \frac{1}{2} \sum_k M_k \dot{Q}_k^2 + \frac{1}{2} \sum_{ij} B_{ij} Q_i Q_j$$

were $\mathbf{Q} = \{\delta x_1, \delta y_1, \delta z_1, \delta x_2, \delta y_2, \delta z_2, \dots\}$: 3N component vector
of atom displacements

B : Hessian matrix

- We are seeking for such a unitary transformation of H_{ion} ,

$$H_{\text{ion}} \rightarrow \frac{1}{2} \sum_{\alpha} (\dot{q}_{\alpha}^2 + \omega_{\alpha}^2 q_{\alpha}^2)$$

that Hamiltonian becomes a sum of *independent oscillators*

Reminder: molecular vibrations

- Step 1: introduce mass-weighted coordinates: $Q_k \sqrt{M_k} = \alpha_k$

$$H_{\text{ion}} = \frac{1}{2} \sum_k \dot{\alpha}_k^2 + \frac{1}{2} \sum_{ij} D_{ij} \alpha_i \alpha_j = \frac{1}{2} \dot{\alpha}^T \dot{\alpha} + \frac{1}{2} \alpha^T D \alpha$$

were
$$D_{ij} = \frac{B_{ij}}{\sqrt{M_i M_j}}$$

- Step 2: decompose individual displacement into *normal modes*

$$\alpha_k = \sum_{\mu} A_{k\mu} q_{\mu}$$

where columns of matrix A are eigenvectors of D :

$$D A^{(\mu)} = \omega_{\mu}^2 A^{(\mu)}, \quad \text{or} \quad D A = A \Omega, \quad \Omega = \text{diag}\{\omega_{\mu}^2\}$$

Reminder: molecular vibrations

- Then:
$$\frac{1}{2} \alpha^T D \alpha \quad \rightarrow \quad \frac{1}{2} q^T A^T D A q = \frac{1}{2} q^T \Omega q = \frac{1}{2} \sum_{\alpha} \omega_{\alpha}^2 q_{\alpha}^2$$
$$\frac{1}{2} \dot{\alpha}^T \dot{\alpha} \quad \rightarrow \quad \frac{1}{2} \dot{q}^T A^T A \dot{q} = \frac{1}{2} \dot{q}^T \dot{q} = \frac{1}{2} \sum_{\alpha} \dot{q}_{\alpha}^2$$

So, Hamiltonian takes a form:
$$H_{\text{ion}} = \frac{1}{2} \sum_{\alpha} (\dot{q}_{\alpha}^2 + \omega_{\alpha}^2 q_{\alpha}^2)$$

- Now, if only $q_{\nu} \neq 0$ and all other $q_{\mu} = 0$ then atomic displacements oscillate with frequency ω_{ν}

$$Q_k = \frac{1}{\sqrt{M_k}} A_{k\nu} \cos(\omega_{\nu} t + \varphi_{\nu})$$

Example 1: Molecular vibrations - H₂O

- With help of TURBOMOLE module `aoforce`, one can compute second derivatives of the energy with respect to atomic positions, and predict vibrational frequencies and normal modes.

- Let us illustrate that, by taking as example H₂O molecule

- Switch to a directory:

```
cd ~/ABC_of_DFT/hands-on-sessions/session.4/  
example.1.vibrations.h2o
```

- Make your subdirectory, copy a structure of a molecule:

```
cp -r structure.h2o my.h2o  
cd my.h2o
```

Example 1: Molecular vibrations - H₂O

- Set-up calculation for H₂O with `define` module: choose C_{2v} symmetry, def-SVP basis, and DFT with default b-p functional
- Perform electronic structure calculation & subsequent geometry optimization, check your results:

```
ridft | tee ridft.out  
jobex -grad  
eiger > molecular.levels.dat  
cat molecular.levels.dat
```


Example 1: Molecular vibrations - H₂O

- Proceed with computation of vibrational normal modes:
- Type: `vib <Enter>`
(this script adds required keywords to a `control` file),
followed by:
`aoforce | tee aoforce.out <Enter>`
- When done, you'll see files `vib_norm_modes` and `vib_spectrum` which contain information about normal modes and frequencies, respectively.

Example 2: Molecular vibrations - H₂O

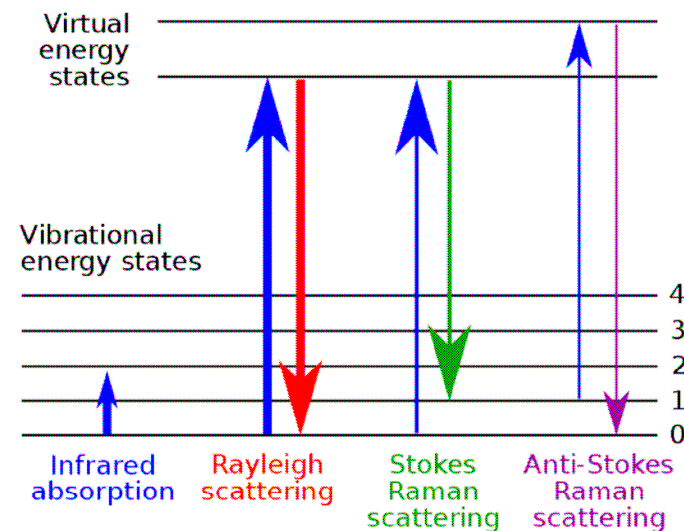
■ Type: `cat vib_spectrum`

```
$vibrational spectrum
```

```
# mode      symmetry      wave number      IR intensity      selection rules
#           cm** (-1)      km/mol           IR      RAMAN
  1           0.00           0.00000         -      -
  2           0.00           0.00000         -      -
  3           0.00           0.00000         -      -
  4           0.00           0.00000         -      -
  5           0.00           0.00000         -      -
  6           0.00           0.00000         -      -
  7           a1           1607.73         48.23574        YES      YES
  8           a1           3684.68          2.63684        YES      YES
  9           b1           3783.78         20.86162        YES      YES
$end
```

- Zero frequency normal modes refer to the **rotation** and **displacement** of the molecule as a whole. Each mode is indicated as infrared (IR) and/or Raman active.

- **IR spectroscopy:** exploits the fact that molecules absorb light (in the infrared region of electromagnetic spectrum) at resonant frequencies of normal modes that are characteristic of a molecular structure and determined by the shape of the potential energy surface. **Vibrational mode is "IR active"** if it is associated with changes in the permanent dipole.
- **Raman spectroscopy:** based on **Raman scattering** of light on a molecule by an excitation, with the scattered photons having a frequency different from the incident photons.

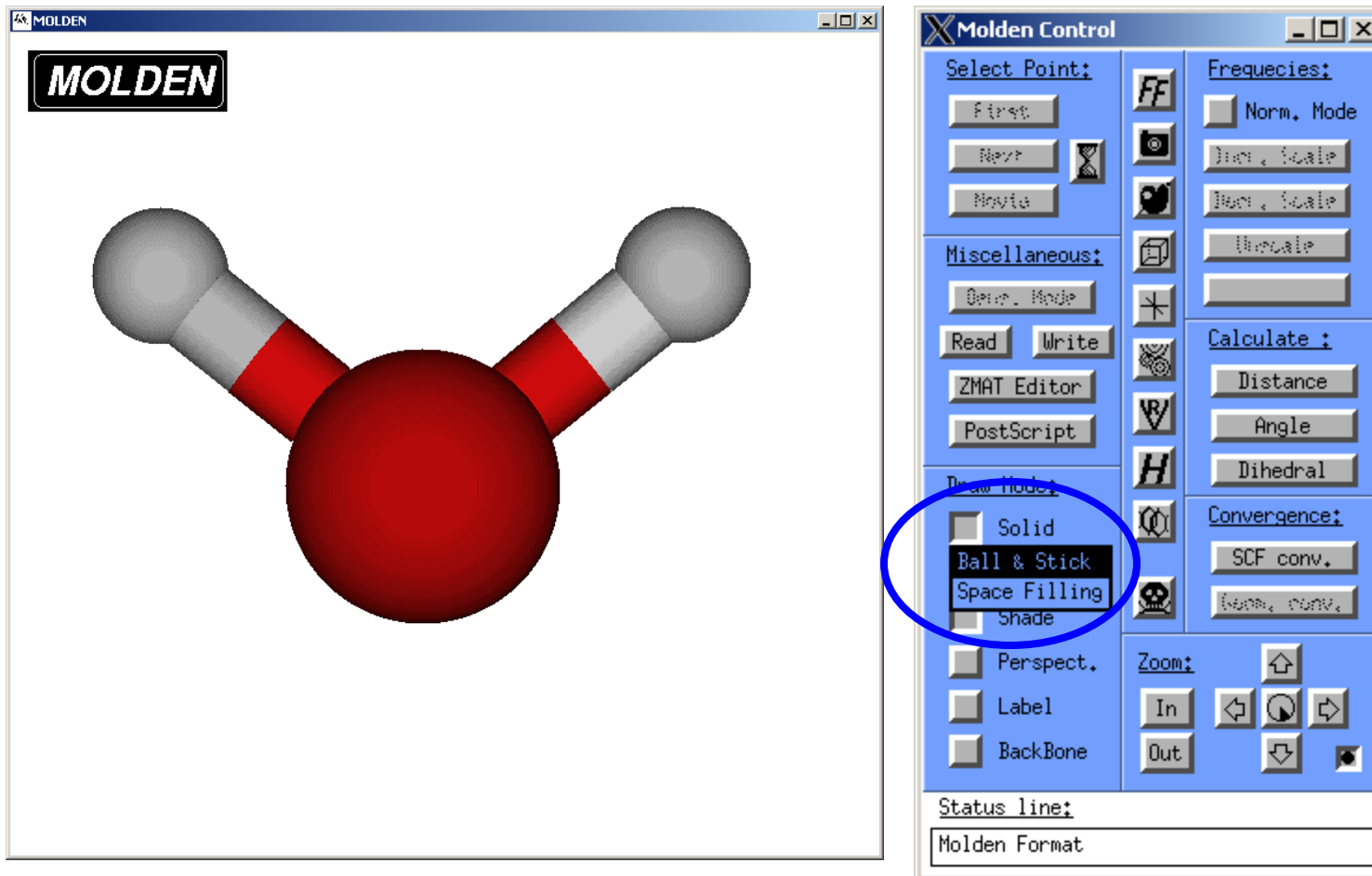


Example 1 (continued): Molecular vibrations, H₂O

- Vibrational normal modes can be visualized using a package MOLDEN (documentation can be found at [~/ABC_of_DFT/documentation/molden.manual.pdf](#))
- To convert TURBOMOLE output to the MOLDEN format, type from a command line: `t2molden <Enter>`
- A file `molecule.molf` will be created
- Run MOLDEN typing from a command line `molden -s 2.0 molecule.molf &`
(a short info on input flags can be obtained via `molden -h`)

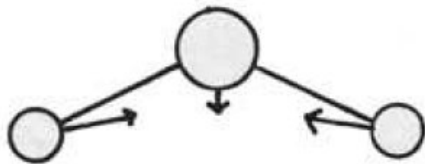
Example 1 (continued): Molecular vibrations, H₂O

- Two windows will show up: in a control window a drawing mode can be switched to **Ball & Stick**

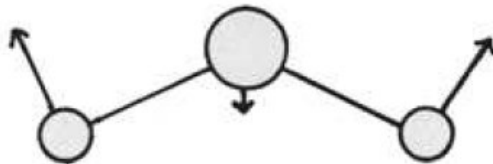


Example 1 (continued): Molecular vibrations, H₂O

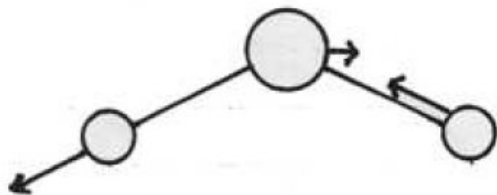
- Convince yourself that three vibrational normal modes of a water molecule look like that :



$\nu_1 = 3685 \text{ cm}^{-1}$
symmetric stretch



$\nu_2 = 1608 \text{ cm}^{-1}$
mostly bending mode (scissoring)



$\nu_3 = 3784 \text{ cm}^{-1}$
asymmetric stretch

Exercise 1: benzene

- Compute vibrational modes of benzene, molecular structure is found in

```
~/ABC_of_DFT/hands-on-sessions/session.2/  
example.2.benzene
```
- Run `define` module, set-up calculation for a benzene. Choose D_{6h} symmetry, def-SVP basis, DFT b-p functional, RI approximation
- Perform electronic structure calculation & geometry relaxation, check your results

Exercise 1: benzene (continued)

- Compute vibrational frequencies and normal modes
- Visualize molecular vibrations with MOLDEN
- Convince yourself that few IR active modes can be characterized as

671 cm⁻¹ : CH bending (out of plane)

1033 cm⁻¹ : in plane CH bending + ring deformation

1464 cm⁻¹ : ring (C=C) stretching + deformation

3117 cm⁻¹ : CH stretching (in plane)

Exercise 2*: C60 buckyball

- Compute & visualize vibrational modes of C60 fullurene ; structure is found at
[~/ABC_of_DFT/hands-on-sessions/session.2/example.3.c60](#)
- Perform calculations assuming the high icosahedral symmetry (I_h) of the molecule
- Try to find a correlation between your results and those found at the web-page
www.public.asu.edu/~cosmen/C60_vibrations/mode_assignments.htm
At the above web-page, by clicking on the mode one can view animation of the mode's displacement pattern (very similar to what you are able to do with MOLDEN)