ABC of DFT: Hands-on session 5
Simulation of infrared spectra of molecules

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

Overview

- Infrared absorption intensity: short introduction

- Examples
  - **Benzene (C6H6)**
  - **Pyridine (C5H5N)**

- Convergence of computed data (frequencies & intensities) vs basis set
  - **Example: CH4**

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 `session5` from **dft20** account:

  `cp ~/../dft20/ABC_of_DFT/session5 .`

- Type from a command line:

  `./session5`

- Examples (with this tutorial) will be imported to a directory

  `~/ABC_of_DFT/hands-on-sessions/session5`
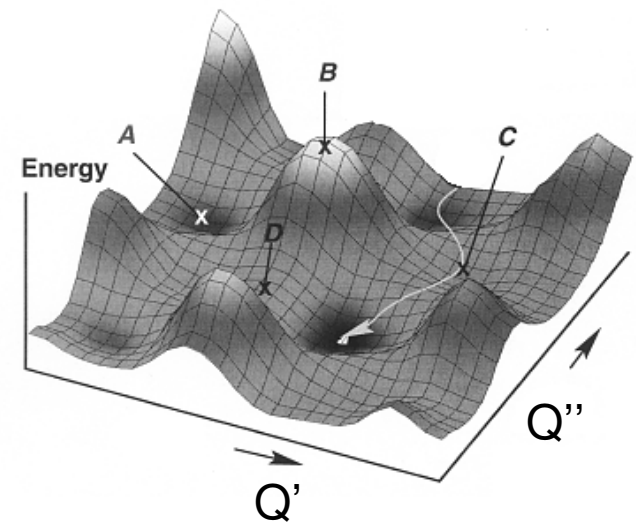
IR absorption: short introduction

- We consider molecular vibrations
  in harmonic approximation

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

were : $\mathbf{Q} = \{\delta x_1, \delta y_1, \delta z_1, \delta x_2, \delta y_2, \delta z_2, \ldots\}$

3N component vector of atom displacements

$$B_{ij} = \frac{\partial^2 E}{\partial Q_i \partial Q_j} \qquad : \text{Hessian matrix}$$

Example of potential
energy surface

IR absorption: short introduction

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

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

  that Hamiltonian becomes a sum of *independent oscillators*

- Solution: decompose individual displacement into *normal modes*

$$Q_k = \sum_{\mu} \frac{1}{\sqrt{M_k}} A_{k\mu} q_\mu$$

  where columns of matrix *A* are eigenvectors of $\quad D_{ij} = \dfrac{B_{ij}}{\sqrt{M_i M_j}}$

$$D A^{(\mu)} = \omega_\mu^2 A^{(\mu)}, \quad \text{or} \quad DA = A\Omega, \quad \Omega = \text{diag}\{\omega_\mu^2\}$$
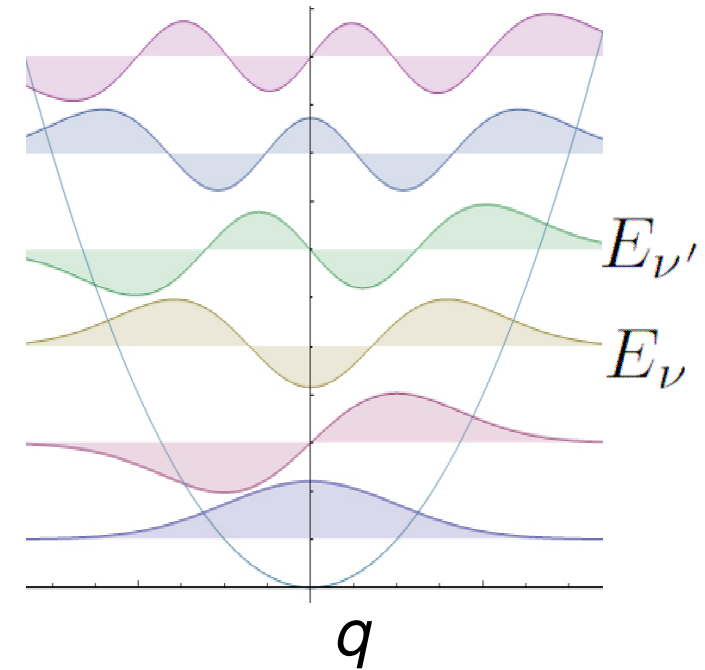
IR absorption: short introduction

- Consider a perturbation (electromagnetic field in the infrared region)

$$H' = -\boldsymbol{\mu}\boldsymbol{\varepsilon_0}e^{-i\omega t}$$

- Transition probability is given by the Fermi golden rule

$$P_{\nu' \leftarrow \nu} \quad \propto \quad |\langle \nu' | \boldsymbol{\mu}\boldsymbol{\varepsilon_0} | \nu \rangle|^2$$
$$\times \; \delta\left(E_{\nu'} - E_\nu - \hbar\omega\right)$$

$$|\nu\rangle \; = \; |\Psi_\alpha(\mathbf{x}, q)\rangle \; \otimes \; |\varphi_n(q)\rangle \qquad E_\nu = \varepsilon_\alpha + n\hbar\omega$$

$$|\nu'\rangle \; = \; |\Psi_\alpha(\mathbf{x}, q)\rangle \; \otimes \; |\varphi_{n'}(q)\rangle \qquad E_{\nu'} = \varepsilon_\alpha + n'\hbar\omega$$
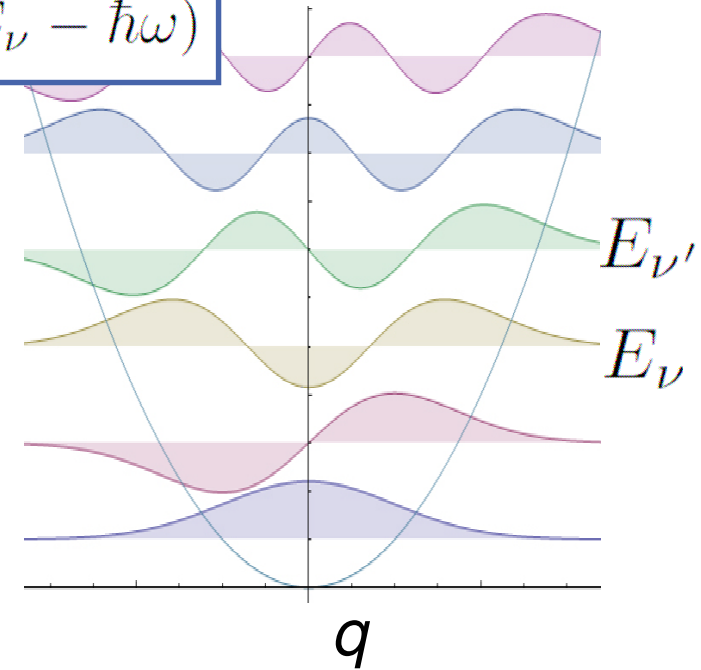
$E_{\nu'}$

E_ν

q

Born-Oppenheimer: Electronic part & Nuclear part

IR absorption: short introduction

- Transition probability

$$P_{\nu' \leftarrow \nu} \propto \left| \langle \nu' \left| \boldsymbol{\mu}(q) \boldsymbol{\varepsilon_0} \right| \nu \rangle \right|^2 \cdot \delta \left(E_{\nu'} - E_\nu - \hbar\omega \right)$$

- … can be evaluated through the dipole moment $\boldsymbol{\mu}(q)$ considered as function of displacement along the normal mode q

$$
\begin{aligned}
\boldsymbol{\mu}(q) &= \langle \Psi_\alpha(\mathbf{x}, q) | \boldsymbol{\mu} | \Psi_\alpha(\mathbf{x}, q) \rangle \\
&= \sum_i \int d^3\mathbf{x}_i \, \psi^*_{\alpha_i}(\mathbf{x}_i, q) e \mathbf{x}_i \psi_{\alpha_i}(\mathbf{x}_i, q) \\
&= \boldsymbol{\mu}_0 + \left. \frac{\partial \boldsymbol{\mu}}{\partial q} \right|_{q=0} q + \dots
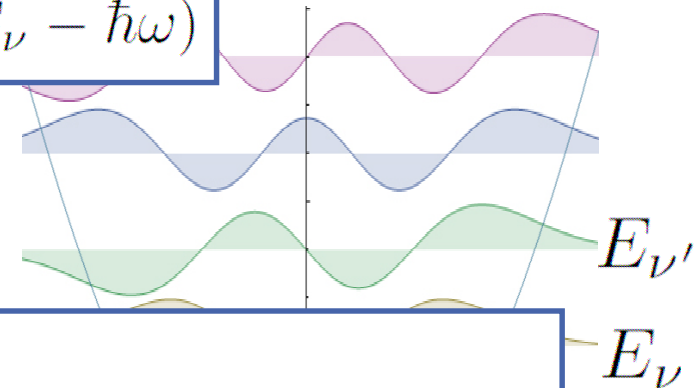\end{aligned}
$$

$E_{\nu'}$

E_ν

q

- … with selection rules for IR intensity of k mode

$$I_k \propto \left| \langle n_k \left| q_k \right| n'_k \rangle \right|^2 \cdot \left(\frac{\partial \boldsymbol{\mu}}{\partial q} \right)^2$$

$$q_k \propto (a_k^\dagger + a_k) \qquad \Delta n_k = \pm 1 \qquad \left| \frac{\partial \boldsymbol{\mu}}{\partial q_k} \right| \neq 0$$

IR absorption: short introduction

- Transition probability

$$P_{\nu' \leftarrow \nu} \propto |\langle \nu' | \boldsymbol{\mu}(q)\boldsymbol{\varepsilon_0} | \nu \rangle|^2 \cdot \delta\left(E_{\nu'} - E_{\nu} - \hbar\omega\right)$$

- … can be evaluated through the dipole moment $\boldsymbol{\mu}(q)$ considered as function of displacement along the normal mode q

$E_{\nu'}$

E_{ν}

Message to take home: vibrational mode is "IR active" if it is associated with changes in the permanent dipole.

- … with selection rules for IR intensity of k mode $\quad I_k \propto |\langle n_k | q_k | n_k' \rangle|^2 \cdot \left(\dfrac{\partial \boldsymbol{\mu}}{\partial q}\right)^2$

$$q_k \propto (a_k^\dagger + a_k) \qquad \Delta n_k = \pm 1 \qquad \left|\frac{\partial \boldsymbol{\mu}}{\partial q_k}\right| \neq 0$$

Exercise 1: IR spectrum - benzene

- A script **ir** simulates IR spectrum (transmittance or absorption) based on the vibrational frequencies and IR intensities evaluated by the aoforce module (exercise of session 4!):

    ~…/hands-on-sessions/session.5/example.1.benzene/output.aoforce

- Type **ir <Enter>** : a short description will show up

```
 # ABC of DFT: hands-on-session 2
#
# simulate IR spectrum of a molecule
# using output of TURBOMOLE 'aoforce' module
#
# usage : ir <gamma> [trans]
#         where <gamma> is level broadening in 1/cm
#
#         if the second flag is specified as 'trans' ,
#         IR transmittance is evaluated
#
#         otherwise, IR molar absorption coefficient is computed
#
# ir -h | -help | --help : prints out help message
```

Exercise 1: IR spectrum - benzene

- Molar absorption coefficient $\varepsilon(\nu)$ is related to intensities of transmitted, $I(\nu)$, and incident, $I_0(\nu)$, light as:
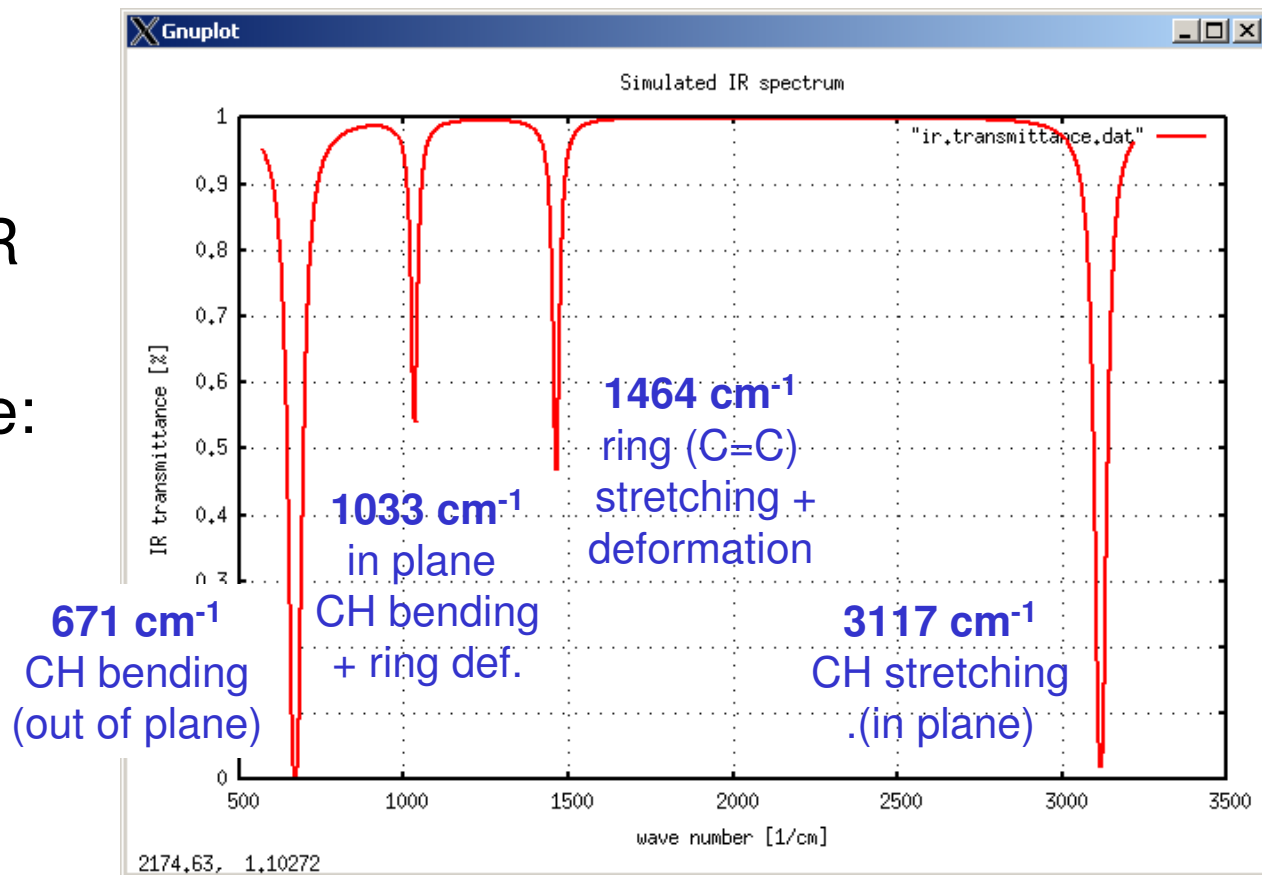
$$\varepsilon(\nu) \sim \log_{10}[I_0(\nu)/I(\nu)]$$

- To compute absorption spectrum, type, e.g.:

  `ir 10 <Enter>`

  A window will show up:

- To quit, press `<Enter>`

- Your plot will be exported to a directory `./ir.data` as `ir_absorption.ps &` `ir_absorption.pdf`
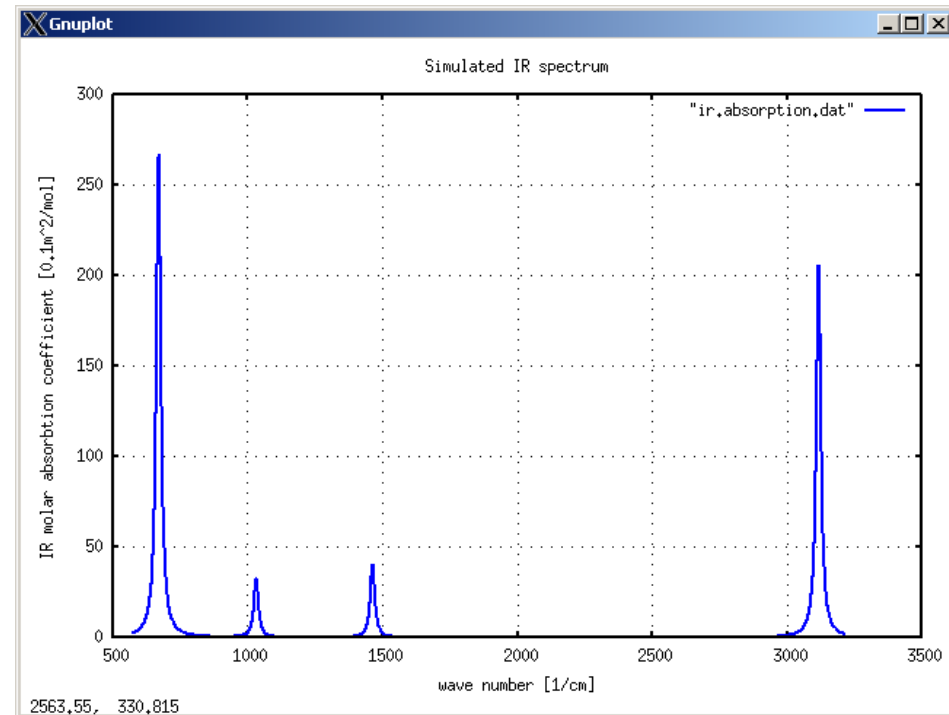
Exercise 1: IR spectrum - benzene

- To compute IR transmittance spectrum, type:
  `ir 10 trans`

- Visualize vibrational modes: prove above assignment. Compare your results with experimental data at NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Exercise 2: IR spectrum - pyridine (exercise)

- Consider a pyridine molecule, C_5H_5N, which is structurally related to benzene, with one CH group replaced by N atom. Look at

    `~/ABC_of_DFT/hands-on-sessions`

    `/session.5/example.2.pyridine`

- Optimize geometry of pyridine (C_{2v} symmetry), compute & visualize its vibraitonal modes

- Convince yourself that due to _reduced symmetry_, IR spectrum is much richer compared to benzene
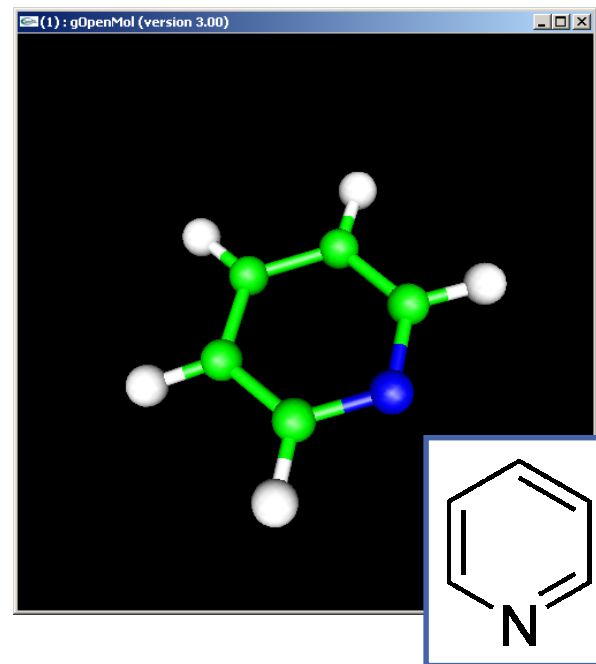
Exercise 3: Methan (CH4)

- Using example of a simple methan molecule
  `~/ABC_of_DFT/hands-on-sessions/session.5/example.3.ch4`
  perform computation of vibrational frequencies
  with def-SVP, def-TZVP and def-QZVP basis
  sets (caution: please, use module **dscf** not **ridft**!)

- Questions:
  (i) Do you observe that values converge when
     larger basis set is used?
  (ii) Confront your findings for two IR active modes
     with experimental data* (1357 cm^{-1} & 3158 cm^{-1})
     What could be said about accuracy (in %) of DFT
     regarding frequencies of vibrational modes?
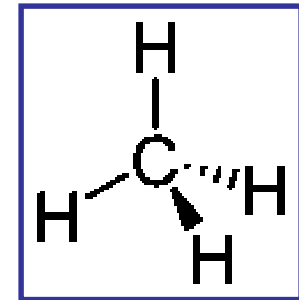
  *Johnson, Gill & Pople, J Chem Phys **98**, 5612 (1992)