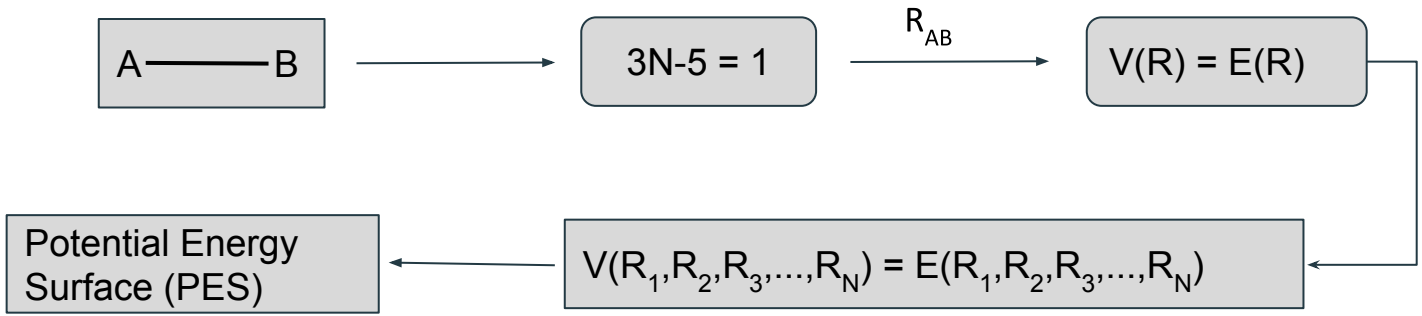
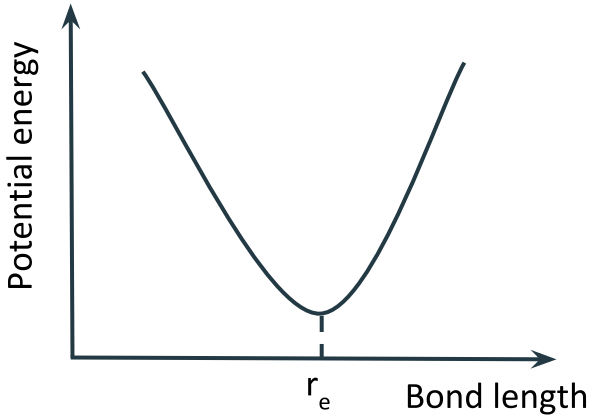
Geometry Optimization, Frequency and IR Calculation

Esmaeil Farajpour Bonab, Oct 22, 2019.

Geometry Optimization

- In order to find a minimum energy structure of a molecule
- A diatomic model:





In local minima:

$\partial F/\partial R = -\partial^2 V(R)/\partial R^2 > 0$

In equilibrium all the force acting on N atoms will vanish: $F_1 = F_2 = F_3 = \ldots = 0$

$F = -\partial V(R)/\partial R$
In eq: $F=0$

$\longrightarrow$ $F_A = F_B = 0$ $\longrightarrow$ Multiatomic system

- In the case of more than two atoms, the minimum condition turns out to be more complex.
- In this case, it needs the Hessian matrix to be calculated.
- $3N \times 3N$ matrix
- Defined as: $H = (\partial^2 V(R_1, R_2, R_3, \ldots, R_1 / \partial R_I \, \partial R_J)$
- It should be calculated and diagonalized (for nonlinear 6 and linear molecules 5 eigenvalues should be zero).
- If all remaining values are positive, the molecule is in a minimum of its PES.
- If one or more eigenvalues are negative, the molecule is in the transition state.

IR spectroscopy

- Infra red (IR) spectroscopy deals with the interaction between a molecule and the IR region of electromagnetic spectrum.
- IR radiation causes the excitation of the vibrations of covalent bonds within a molecules.
- In IR spectrum energy is reported in the scale of wavenumber (1/cm).
- Typical range of experiment for IR region: (400-4000 1/cm)

Wavenumber

Wavenumber: $\tilde{\nu} = 1/\lambda$ (1/cm)

Wavenumber shows how many waves of the radiation is in one centimeter.

$E = h\nu = hc/\lambda$

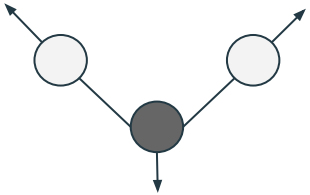
$\tilde{\nu} = 1/\lambda$

$\tilde{\nu} = E/hc$

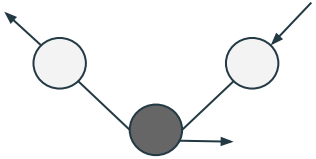
Therefore, the higher wavenumber equals to higher energy radiation.

Normal modes of vibrations

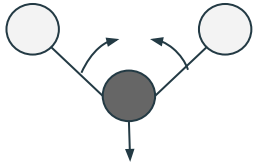
- IR radiation causes the excitation of the vibrations of a covalent bond
- Two type of vibration modes:
  - Stretching
  - Bending
- Molecule with N atoms:
  - 3N-5 degree of freedom (linear molecule)
  - 3N-6 degree of freedom (non-linear molecule)
- Water:



Symmetrical stretching



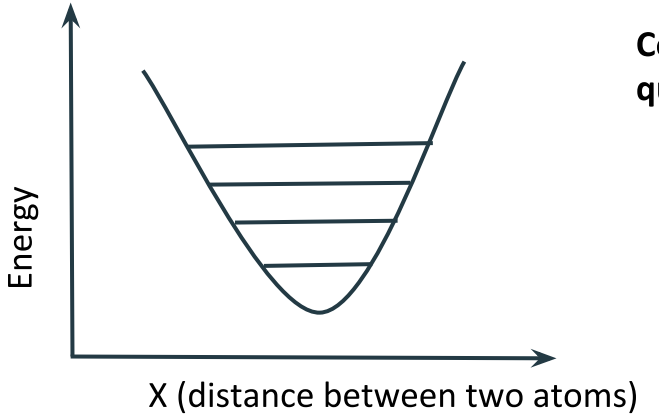
asymmetrical stretching



scissoring (bending)

Model for describing vibrations between atoms

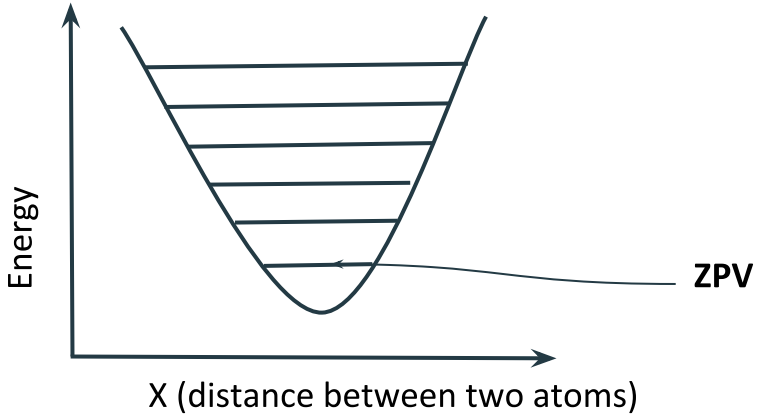
- Simple approximation: atoms are connected with springs
- Hook's law: frequency of vibration is given by mass and force constant
  - $E = 1/2\ kx^2$
  - $\tilde{V} = 1/2\pi c\ (k/m)^{1/2}$



Consideration: The energy is not quantized.

Quantum harmonic oscillator

- Energy is quantized and given by:
  - $E = (n + 1/2)\, h\nu$
  - $n = 0, 1, 2, \ldots.$
  - ν = vibration state ($\nu_0, \nu_1, \nu_2, \ldots$)

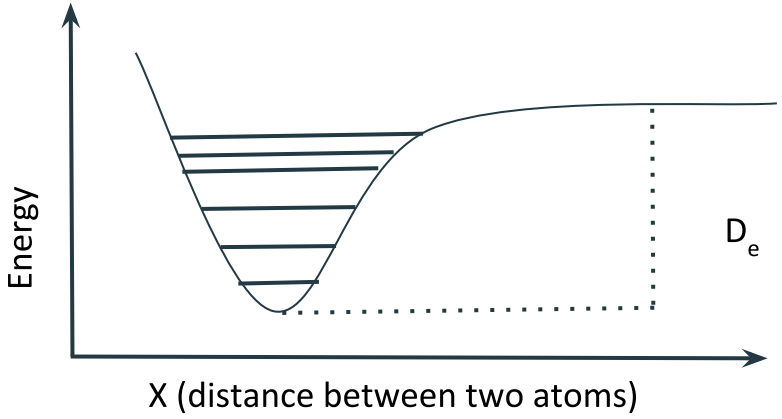


Selection rules:
$\Delta\nu = \pm 1$
For example: $\nu_0 \rightarrow \nu_1, \nu_1 \rightarrow \nu_2, \ldots$

Anharmonic oscillator

- Bonds behave like anharmonic oscillator.
- Morse potential: $V(r) = D_e (1 - e^{-a(r-r_0)})^2$
- Higher energy levels become closer.

- Selection rules: $\Delta v = \pm 1, \pm 2, \ldots$
- Fundamental vibration: $v_0 \rightarrow v_1$
- Overtons:
  - First: $v_0 \rightarrow v_2$
  - Second: $v_0 \rightarrow v_3, \ldots$
- Hot bands:
  - $v_1 \rightarrow v_2$
  - $v_1 \rightarrow v_3, \ldots$



Diatomic oscillator

- Bonded atoms behave as anharmonic oscillators
- For diatomic oscillator:
  - $\tilde{v} = 1/2\pi c \sqrt{f/\mu}$
  - f is the force constant of the bond.
  - $\mu = m_1 m_2/m_1 + m_2$ reduced mass
- Force constants :
  - Single bond : 5×10^{5} dyn. Cm^{-1}
  - Double bond: 10×10^{5} dyn. Cm^{-1}
  - Triple bond: 15 × 10 5 dyn. Cm^{-1}
  - 1dyn = $1g.cm/s^2$

Task (I)

Calculate the absorption energy (in wavenumbers)for following groups:

- C−H, C═O, C≡N
- Compare the results with the experimental values:
  - C−H : 2850- 3000 cm^{-1}
  - C═O: 1670-1820 cm^{-1}
  - C≡N: 2000-2300 cm^{-1}

Task (II)

Perform optimization and frequency calculations for H_2O and CO2 molecules using the following method using B3LYP functional and 6-31G(d) basis set.

- Scaling factor for various levels of theory:
  - https://cccbdb.nist.gov/vibscalejust.asp

Merrick, J.P. et al. J. Phys. Chem. A, 2007, 111, 11683.

Task (III)

Perform opt and frequency calculation for $^{10}BF_3$ and $^{11}BF_3$ using following method:

- **B3LYP functional**
- **6-31G(d,p) basis set extracted from https://www.basissetexchange.org/**
- **Use gen keyboard to employ the external basis sets**

Homework

Perform optimization and anharmonic frequency calculations for CH3F using B3LYP functional and def2-TZVPD basis set (costum basis set extracted from Basis Set Exchange(BSE)) and compare the obtained results with experimental values and calculate the RMSD for this set of calculations.