

Assignment 3: Normal Modes

December 2020

1 Introduction

One of the most common approaches in quantum chemistry is to change the representation, we describe our system in, to simplify the equations we have to solve. A common example is to use polar coordinates instead of cartesian ones, e.g. for computation of the colombic equations in electrostatics. In this assignment, we introduce normal modes, a representation in which the complicated Hamiltonian can be simplified as a sum of independent harmonic oscillators (exact up to second order). This can be achieved by switching to so-called mass weighted displacement coordinates, instead of the usual cartesian coordinates. Besides the great feature that the Hamiltonian simplifies, normal modes can be used to understand the characteristic motion of a molecule by decomposing it into the motion of independent normal modes. This is typically used to understand IR or Raman-Spectra. Where the resonant frequencies of the normal modes corresponds to the frequencies one obtains in an IR/Raman-Spectra.

In the assignment, you will write your own code to transform from cartesian coordinates to normal mode coordinates and compute the IR frequencies of the system. Therefore, you have to read in an 'hessian.dat' file, which contains the hessian of the given molecular system in the format:

$F_{x1,x1}$	$F_{x1,y1}$	$F_{x1,z1}$
$F_{x1,x2}$	$F_{x1,y2}$	$F_{x1,z2}$
...		
$F_{x2,x1}$	$F_{x2,y1}$	$F_{x2,z1}$
...		

Afterwards, the hessian is massweighted:

$$F_{IJ}^M = \frac{F_{IJ}}{\sqrt{m_i * m_j}} \quad (1)$$

Diagonalize the mass weighted hessian and compute the harmonic frequencies as a function of its eigenvalues λ_i .

$$\omega_i = \sqrt{C * \lambda_i} \quad (2)$$

$$C = \frac{1}{4\pi^2 c^2} \quad (3)$$

$$(4)$$

1.1 References:

1. <https://gaussian.com/vib/>
2. E.B. Willson, J.C. Decius, and P.C. Cross, Molecular Vibrations, McGraw-Hill, 1955.