Harmonic Vibrational Analysis

The purpose of this project is to extend your fundamental python language programming techniques through a normal coordinate/harmonic vibrational frequency calculation. The theoretical background and a concise set of instructions for this project may be found below

Step 1: Read the Coordinate Data

The input to the program is the set of Cartesian coordinates of the atoms (in bohr) and their associated atomic numbers. A sample molecule (acetaldehyde) to use as input to the program is:

```
7
6  0.000000000000    0.000000000000    0.000000000000
6  0.000000000000    0.000000000000    2.845112131228
8  1.899115961744    0.000000000000    4.139062527233
1 -1.894048308506    0.000000000000    3.747688672216
1  1.942500819960    0.000000000000   -0.701145981971
1 -1.007295466862   -1.669971842687   -0.705916966833
1 -1.007295466862    1.669971842687   -0.705916966833
```

The first line above is the number of atoms (an integer), while the remaining lines contain the z-values and x-, y-, and z-coordinates of each atom (one integer followed by three double-precision floating-point numbers). This input file (.dat extension) for the test cases in the input directory.

Step 2: Read the Cartesian Hessian Data

The primary input data for the harmonic vibrational calculation is the Hessian matrix, which consists of second derivatives of the energy with respect to atomic positions.

$$F_{ij} = \frac{\partial^2 V}{\partial q_i \partial q_j}$$

The Hessian matrix (in units of E_h/a_0^2) can be found in the input directory . The first integer in the file is the number of atoms (which you should compare to the corresponding value from the geometry file as a test of consistency), while the remaining values have the following format:

$$\begin{matrix} F_{x_1,x_1} & F_{x_1,y_1} & F_{x_1,z_1} \\ F_{x_1,x_2} & F_{x_1,y_2} & F_{x_1,z_2} \\ \vdots & \vdots & \vdots \\ F_{x_2,x_1} & F_{x_2,y_1} & F_{x_2,z_1} \\ \vdots & \vdots & \vdots \end{matrix}$$

Step 3: Mass-Weight the Hessian Matrix

Divide each element of the Hessian matrix by the product of square-roots of the masses of the atoms associated with the given coordinates:

$$F_{ij}^{M} = \frac{F_{ij}}{\sqrt{m_i m_j}}$$

where m_i represents the mass of the atom corresponding to atom *i*. Use atomic mass units (amu) for the masses, An excellent source for atomic masses and other physical constants is the National Institute of Standard and Technology (NIST) website.

Step 4: Diagonalize the Mass-Weighted Hessian Matrix

Compute the eigenvalues of the mass-weighted Hessian:

$$F^{M}\mathbf{L} = \mathbf{L}\Lambda$$

Step 5: Compute the Harmonic Vibrational Frequencies

The vibrational frequencies are proportional to the square root of the eigenvalues of the mass-weighted Hessian:

$$\omega_i = \text{constant} \times \sqrt{\lambda_i}$$

The most common units to use for vibrational frequencies is cm^{-1}.

Reference

E.B. Willson, J.C. Decius, and P.C. Cross, Molecular Vibrations, McGraw-Hill, 1955.

(The above content is adapted from the programing tutorial of Crawford Group)