Hessian Calculations and Simulation of IR Spectra

Keywords: Hessian, normal mode, stretching & bending vibration, IR frequency, IR spectrum.

In this chapter we will talk about calculations of hessians, molecular vibrations and vibrational Infrared (IR) Spectra of a molecular system. We will describe a little on back ground theoretical method of calculation for molecular vibration and take a few examples for calculations of vibrational frequency.

Theoretical Method

Mathematically, hessian is second-order partial derivatives of a function of many variables and it describes local curvature of a function. In case of geometry optimization, it is mandatory to calculate the second derivative of energy or hessian to check if the optimization has reached to a local minimum or a local maximum of the energy function of coordinate variables, x_i. If hessian is positive definite at x, then the function attains a local minimum at x and if the hessian is negative definite at x, then the function attains a local maximum at x (saddle point). On doing hessian calculations, one can easily calculate vibrational frequency.

To a first approximation, a molecular vibration may be described in terms of a harmonic oscillator. This can be derived simply by expanding the energy of the molecule as a function of the nuclear coordinates in a Taylor series around the equilibrium geometry. In case of a diatomic molecule, this expansion may be carried out in terms of inter nuclear distance, R.

$$E(R) = E(R_0) + dE/dR\ (R-R_0) + 1/2\ d^2E/dR^2\ (R-R_0)^2 + 1/6\ d^3E/dR^3\ (R-R_0)^3 + \dots\dots\dots$$

or, $$E(\Delta R) = dE/dR\ (\Delta R) + 1/2\ d^2E/dR^2\ (\Delta R)^2 + 1/6\ d^3E/dR^3\ (\Delta R)^3 + \dots\dots\dots$$

where R_0 is equilibrium inter nuclear distance and $\Delta R = R - R_0$. The first term in the second equation is zero as this expansion is around the equilibrium geometry and at the equilibrium geometry the gradient is zero. This leads to the harmonic approximation in terms of force constant, k when only the square term is considered.

$$E(\Delta R) = 1/2\ d^2E/dR^2\ (\Delta R)^2 = 1/2\ k\ (\Delta R)^2$$

Based on the relation, $\nu = 1/2\pi\ (k/\mu)^{1/2}$ vibration frequency (ν) can be calculated from force constant (k) and reduced mass (μ) of the molecular system. Anharmonic corrections to the vibration may be calculated by considering the higher order terms of the expansion.

Calculation of vibration frequency

The following INPUT is prepared for a hessian calculation. The input is essentially the same as in case of geometry optimization except that the input geometrical parameters have to be the final optimized one at the same level of theory. It is the requirement of theory as explained in the previous section that at the equilibrium geometry only the gradient is zero. In the present case, we consider the final optimized structure of H_2O molecule calculated at B3LYP/6-31++G(d,p) for hessian calculation. The input consider for this calculation is as follows.

```
********************

$SYSTEM TIMLIM=6000.0 MWORDS=11 MEMDDI=90 $END
$CONTRL SCFTYP=RHF MPLEVL=0 MAXIT=100 ICHARG=0 MULT=1
COORD=ZMT RUNTYP=HESSIAN TDDFT=NONE $END
$DFT DFTTYP=B3LYP METHOD=GRID $END
$SCF DIRSCF=.F. DAMP=.T. SHIFT=.T. $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=1 DIFFSP=.T. DIFFS=.T. $END
$DATA
water: hessian//B3LYP/6-31++G(d,p)
CN 1

O
H   1   roh
H   1   roh   2   ahoh

roh=0.9655191
ahoh=105.7086105
$END
********************
```

These geometrical parameters are taken from optimized structure of H_2O molecule calculated at B3LYP/6-31++G(d,p) level

Selected portion of GAMESS 'OUTPUT' based on the 'INPUT' for hessian calculation is as follows.

```
     -------------------------------------------------------
     NORMAL COORDINATE ANALYSIS IN THE HARMONIC APPROXIMATION
     -------------------------------------------------------

     ATOMIC WEIGHTS (AMU)

   1     O              15.99491
   2     H               1.00782
   3     H               1.00782

 MODES 1 TO 6 ARE TAKEN AS ROTATIONS AND TRANSLATIONS.

 FREQUENCIES IN CM**-1, IR INTENSITIES IN DEBYE**2/AMU-ANGSTROM**2,
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```
REDUCED MASSES IN AMU.

                         1          2          3          4          5
FREQUENCY:            27.71       0.01       0.12       1.16      13.75
REDUCED MASS:        1.04648    6.00360    5.94876    5.84117    1.00784
IR INTENSITY:        2.65180    0.00000    0.00005    0.00048    0.00095

 1  O            X  0.04964805  0.00001669  0.23541428  0.00000000  0.00000000
                 Y -0.00000012  0.23563345 -0.00001669  0.00000000  0.00000000
                 Z  0.00000000  0.00000000  0.00000000  0.23497161 -0.00093952

 2  H            X -0.38459053  0.00001856  0.23734907  0.00000000  0.00000000
                 Y  0.57327840  0.23563079 -0.00257252  0.00000000  0.00000000
                 Z  0.00000000  0.00000000  0.00000000  0.24082260  0.71157581

 3  H            X -0.38459025  0.00001476  0.23734910  0.00000000  0.00000000
                 Y -0.57327820  0.23563070  0.00253916  0.00000000  0.00000000
                 Z  0.00000000  0.00000000  0.00000000  0.24081402 -0.69705209

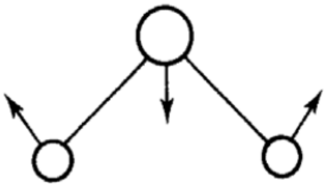

                        6          7          8          9
FREQUENCY:           14.63    1599.82    3803.50     3926.0
REDUCED MASS:      1.13177    1.08378    1.04414    1.08306
IR INTENSITY:      7.85816    2.06083    0.11787    1.26377

 1  O             X  0.00000000 -0.00000003  0.00000000 -0.06808141
                  Y  0.00000000 -0.06838202 -0.04817326  0.00000002
                 Z  -0.08548304  0.00000000  0.00000000  0.00000000

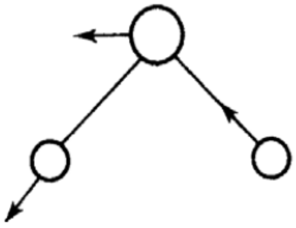
 2  H            X  0.00000000 -0.40564392  0.57582181  0.54025323
                 Y  0.00000000  0.54264539  0.38227202  0.40922272
                 Z  0.65414073  0.00000000  0.00000000  0.00000000

 3  H            X  0.00000000  0.40564438 -0.57582172  0.54025317
                 Y  0.00000000  0.54264564  0.38227196 -0.40922297
                 Z  0.66959895  0.00000000  0.00000000  0.00000000
```

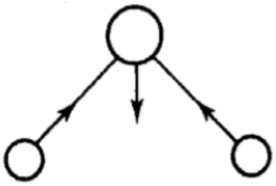
For H_2O molecule 9 normal modes (3 atoms and each has 3 modes) and frequency for corresponding modes are calculated. Out of these 9 modes, first 6 modes are for translational and rotational motions and last 3 frequencies are for vibrational motions, namely bending and stretching (symmetric and asymmetric) of this tri atomic system. One can easily visualize these motions by using visualization software MOLDEN and identify different normal modes. In the present



Bending



Asymmetric Stretching



Symmetric stretching

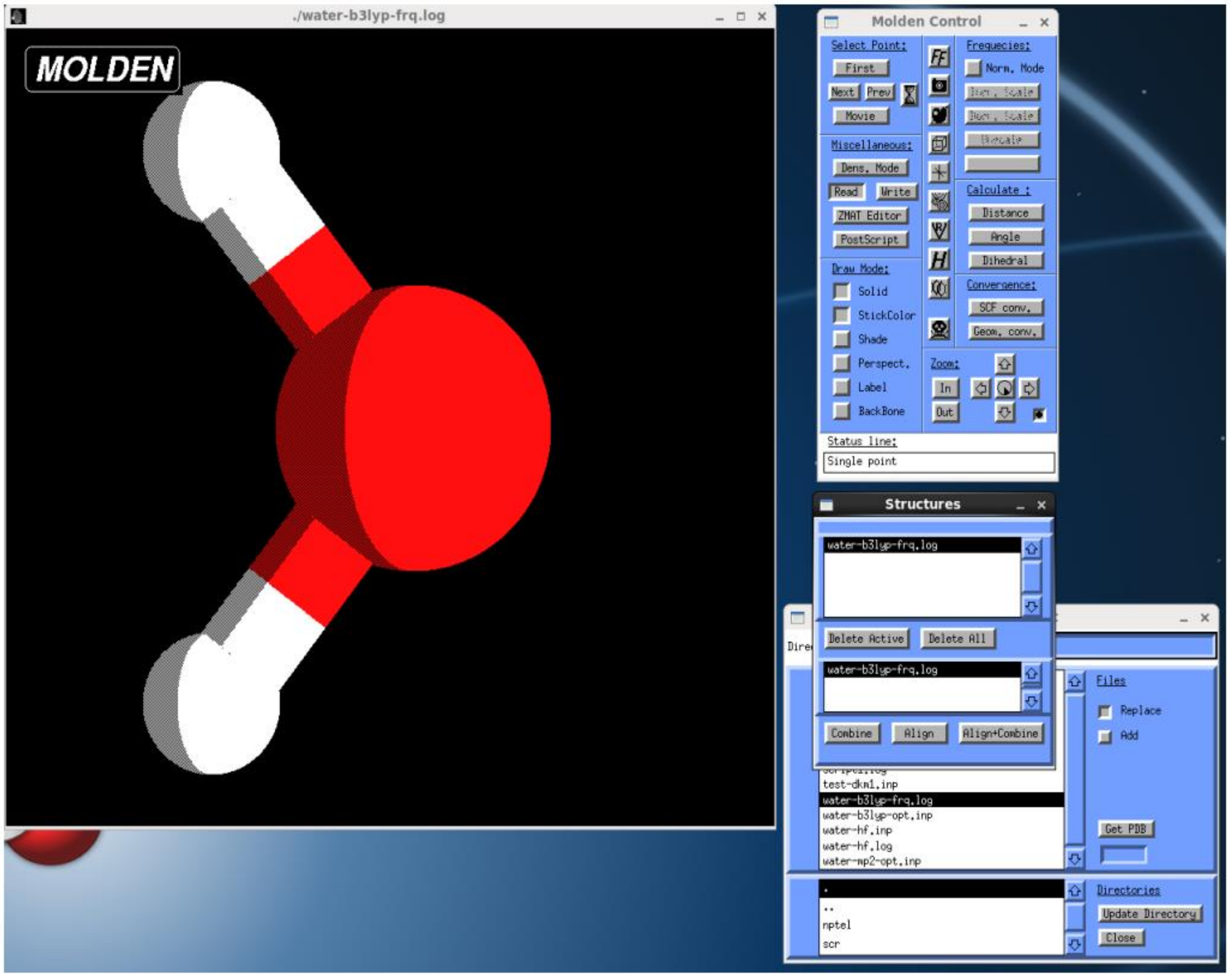
case, the calculated frequency of 1600 cm^{-1} corresponds to bending motion in H_2O. Frequencies 3803 and 3926 cm^{-1} are for symmetric and asymmetric stretching of O-H bonds of H_2O molecule. It is to be noted that gas phase experimental frequency for the different normal modes in H_2O molecule are 1595, 3657 and 3756 cm^{-1} for bending, symmetric and asymmetric stretching of O-H bonds respectively. It is clearly observed that error in calculated frequency of bending mode is very small compared to that of stretching modes. The major source of error in stretching modes is due to harmonic approximation of normal modes. Error in calculated frequency may reduce substantially by incorporating anharmonic treatment in the hessian calculation at the cost of huge computational time. Error in calculated harmonic frequency may also be close to experimental value by applying a more accurate theoretical method and larger set of atomic basis functions. The following Table displays the calculated frequency of H_2O molecule in cm^{-1} at different levels of theory and two different basis sets.

Normal mode of vibration	Expt	HF		B3LYP		MP2	
		6-31++G(d,p)	aug-cc-pVDZ	6-31++G(d,p)	aug-cc-pVDZ	6-31++G(d,p)	aug-cc-pVDZ
Bending	1595	1728	1744	1600	1617	1619	1622
Symmetric Stretching	3657	4147	4130	3803	3792	3863	3804
Asymmetric Stretching	3756	4269	4238	3926	3902	4010	3938

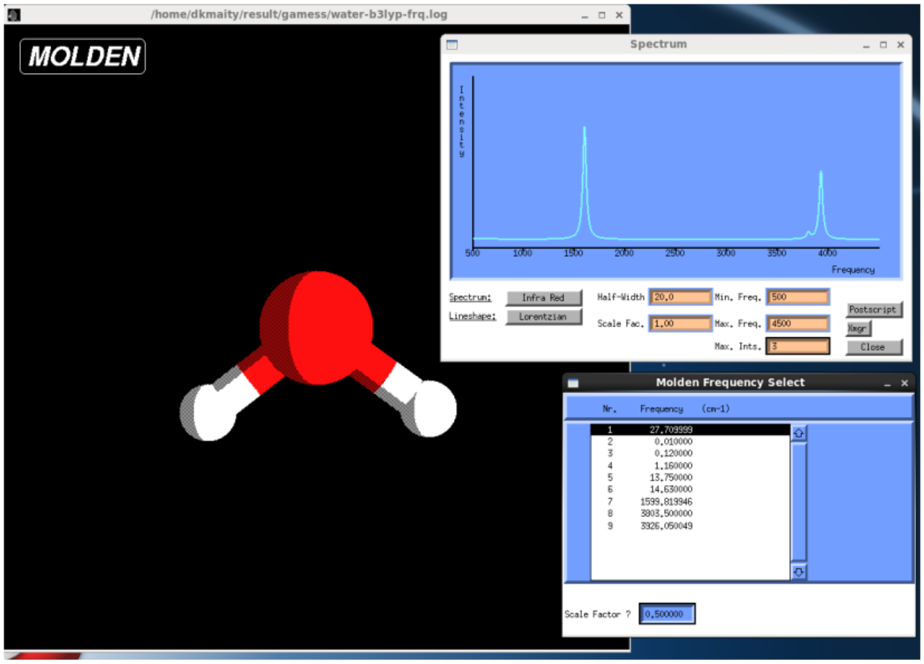
Table indicates that error in calculated frequency is minimum in case of B3LYP with aug-cc-pVDZ basis set. Large error with the results calculated at HF level of theory does justify the importance of electron correlation for vibrational IR frequency. Note that hessian calculation has to be performed. Note that hessian calculation should be carried out at the same level of theory at which geometry optimization has been carried out. Only in that case harmonic approximation could be applied.

Simulation of IR spectrum

Hessian calculation gives intensity of different IR modes along with frequency of different vibration modes. Thus, one may easily simulate the whole IR spectrum of H_2O molecule from these calculated data considering Gaussian or Lorentzian line shape of any suitable band width. We have already discussed about the visualization program MOLDEN which can be used to view molecular structure and normal modes of vibration in H_2O molecule from the result of hessian calculation. When one reads the output file of hessian calculation through molden, button 'Norm. Mode' at the right side of 'Molden Control' becomes active as shown in the following snapshot.



On clicking the button ‘Norm. Mode’ in the control panel, IR spectrum of the molecule with the default setting will be simulated and displayed. The default parameters set for simulating IR spectrum will also be displayed on the screen and one may modify the parameters as per requirement with respect to range of spectrum, line shape and band width. The calculated frequency number and corresponding values will also be displayed in a tabular form as depicted in the next screen shot. On click of a particular frequency in the table, normal mode of vibration can be visualized as bending, symmetric stretch, asymmetric stretch etc. In case of H_2O molecule, nine frequency values are displayed in which first six are for translational and rotational modes. Frequency for bending, symmetric stretching and asymmetric stretching modes are listed as 7th, 8th and 9th normal modes in the following figure.



Spectrum: Infra Red
Lineshape: Lorentzian
Half-Width 20.0
Scale Fac. 1.00
Min. Freq. 500
Max. Freq. 4500
Max. Ints. 3

Nr.	Frequency (cm-1)
1	27.709999
2	0.010000
3	0.120000
4	1.160000
5	13.750000
6	14.630000
7	1599.819946
8	3803.500000
9	3926.050049

Scale Factor ? 0.500000

It is important to note that all the calculated frequency values are positive in this case suggesting that a true equilibrium structure of H_2O is obtained in optimization. In case of transition state search for any reaction, one and only one frequency should be negative corresponding to the normal mode connecting reactant and product. Equilibrium geometry having negative frequency does not refer to true equilibrium geometry. So, one has to repeat the optimization procedure with a different set of geometry.

Apart from frequency data of a molecular system, hessian calculation does write macroscopic data related to thermo-chemistry at any T and P applying basic relations of statistical mechanics within certain approximations. Selected portion related to thermo-chemistry of GAMESS 'OUTPUT' based on the 'INPUT' for hessian calculation is as follows.

```
   --------------------------------
   THERMOCHEMISTRY AT T=  298.15 K
   --------------------------------

 USING IDEAL GAS, RIGID ROTOR, HARMONIC NORMAL MODE APPROXIMATIONS.

 P=  1.01325E+05 PASCAL.

 ALL FREQUENCIES ARE SCALED BY   1.00000

 THE MOMENTS OF INERTIA ARE (IN AMU*BOHR**2)
    2.17289     4.26347     6.43636

 THE ROTATIONAL CONSTANTS ARE (IN GHZ)
   829.80971   422.91588   280.14092

 THE HARMONIC ZERO POINT ENERGY IS (SCALED BY   1.000)
```

```
   0.021254 HARTREE/MOLECULE    4664.682547 CM**-1/MOLECULE
  13.337010 KCAL/MOL            55.802050 KJ/MOL

               Q              LN Q
ELEC.          1.00000E+00    0.000000
TRANS.         3.00431E+06   14.915558
ROT.           8.74102E+01    4.470613
VIB.           1.00044E+00    0.000444
TOT.           2.62724E+08   19.386614
```

{Q refers to partition function}

Thermodynamic parameters of different motions (electronic, translational, rotational and vibration) are calculated.....

```
               E          H          G          CV         CP         S
               KJ/MOL     KJ/MOL     KJ/MOL     J/MOL-K    J/MOL-K    J/MOL-K

ELEC.          0.000      0.000      0.000      0.000      0.000      0.000
TRANS.         3.718      6.197      -36.975    12.472     20.786     144.800
ROT.           3.718      3.718      -11.082    12.472     12.472     49.642
VIB.           55.811     55.811     55.801     0.220      0.220      0.032
TOTAL          63.247     65.726     7.744      25.163     33.478     194.474

VIBRATIONAL THERMAL CORRECTION E(T) - E(0) = H(T) - H(0) =    8.497 J/MOL

               E          H          G          CV         CP         S
               KCAL/MOL   KCAL/MOL   KCAL/MOL   CAL/MOL-K  CAL/MOL-K  CAL/MOL-K

ELEC.          0.000      0.000      0.000      0.000      0.000      0.000
TRANS.         0.889      1.481      -8.837     2.981      4.968      34.608
ROT.           0.889      0.889      -2.649     2.981      2.981      11.865
VIB.           13.339     13.339     13.337     0.053      0.053      0.008
TOTAL          15.116     15.709     1.851      6.014      8.001      46.480

VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) =    2.031 CAL/MOL

......END OF NORMAL COORDINATE ANALYSIS......
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One can calculate these thermochemical data at different temperature and pressure also by supplying appropriate P and T parameters.

Conclusions: This chapter deals with hessian calculation and simulation of IR spectrum. Calculated frequency data are compared from the results of different levels of theory. Calculated data on thermochemistry of H_2O molecule at 1 atm pressure and 298.15 K temperature are also presented.