Visualization of phonons:

The case of benzene (C_6H_6)

Javier Junquera

Andrei Postnikov

First step: relaxation of the internal coordinates of the benzene molecule

See the tutorial on how to set up the coordinates of a molecule using the Z-matrix

```
ZM.UnitsLength  Ang
ZM.UnitsAngle   deg

%block Zmatrix
molecule
      2 0 0 0  xm1 ym1  zm1    0 0 0
      2 1 0 0  CC  90.0 60.0   0 0 0
      2 2 1 0  CC  CCC  90.0   0 0 0
      2 3 2 1  CC  CCC  0.0    0 0 0
      2 4 3 2  CC  CCC  0.0    0 0 0
      2 5 4 3  CC  CCC  0.0    0 0 0
      1 1 2 3  CH  CCH  180.0  0 0 0
      1 2 1 7  CH  CCH  0.0    0 0 0
      1 3 2 8  CH  CCH  0.0    0 0 0
      1 4 3 9  CH  CCH  0.0    0 0 0
      1 5 4 10 CH  CCH  0.0    0 0 0
      1 6 5 11 CH  CCH  0.0    0 0 0
constants
        ym1 5.00
        zm1 0.00
        CCC 120.0
        CCH 120.0
variables
        CC 1.390
        CH 1.090
constraints
        xm1 CC -1.0 3.903229
%endblock Zmatrix

ZM.ForceTolLength   0.01   eV/Ang
ZM.ForceTolAngle    0.0001 eV/deg
ZM.MaxDisplLength   0.1    Ang
ZM.MaxDisplAngle   20.0    deg
```

The structure has been prepared in a file called bezene.relax.fdf

We are imposing a constant angle between C-C-C and C-C-H of 120°

Experimental distances as initial guess

The Z-matrix provides a description of each atom in a molecule in terms of the internal coordinates

Internal coordinates:

- Species of each atom
- Distances
- Angles
- Torsion (dihedral) angles

This is particularly useful when working with molecular systems or restricted optimizations (control optimization variables)

The name arises because the Z-matrix assigns the second atom along the Z-axis from the first atom, which is at the origin.

First step: relaxation of the internal coordinates of the benzene molecule

$ siesta < benzene.relax.fdf > benzene.relax.out

```
    Max    0.006916    constrained

Stress-tensor-Voigt (kbar):        0.03       -0.07       -0.06       -0.00        0.00        0.00
(Free)E + p*V (eV/cell)    -1023.1886
Target enthalpy (eV/cell)    -1023.2025

outcoor: Relaxed atomic coordinates (Ang):
     2.50762421    5.00000000    0.00000000   2       1  C
     3.20542660    6.20862920   -0.00000000   2       2  C
     4.60103140    6.20862920   -0.00000000   2       3  C
     5.29883379    5.00000000   -0.00000000   2       4  C
     4.60103140    3.79137080   -0.00000000   2       5  C
     3.20542660    3.79137080   -0.00000000   2       6  C
     1.40124960    5.00000000   -0.00000000   1       7  H
     2.65223930    7.16677772   -0.00000000   1       8  H
     5.15421870    7.16677772   -0.00000000   1       9  H
     6.40520840    5.00000000   -0.00000000   1      10  H
     5.15421870    2.83322228   -0.00000000   1      11  H
     2.65223930    2.83322228   -0.00000000   1      12  H

zmatrix: Z-matrix coordinates: (Ang ; deg )
zmatrix: (Fractional coordinates have been converted to cartesian)
molecule    1 (    12 atoms)
       2.50762421      5.00000000      0.00000000
       1.39560479     90.00000000     60.00000000
       1.39560479    120.00000000     90.00000000
       1.39560479    120.00000000      0.00000000
       1.39560479    120.00000000      0.00000000
       1.39560479    120.00000000      0.00000000
       1.10637461    120.00000000    180.00000000
       1.10637461    120.00000000      0.00000000
       1.10637461    120.00000000      0.00000000
       1.10637461    120.00000000      0.00000000
       1.10637461    120.00000000      0.00000000
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```

The relaxed coordinates are also written in cartesian in Bohrs in benzene.XV

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```

The relaxed coordinates are also written in cartesian in Bohrs in benzene.XV

Second step: compute the interatomic force constant matrix for the benzene molecule

Copy the relaxed coordinates in cartesian coordinates and the lattice vectors in a new input file.

We have done this for you in the file benzene.ifc.fdf

```
# Input file for the benzene molecule using the Z-matrix
# An atomic relaxation will be performed,
# starting from the experimental coordinates
# (distance C-C = 1.39 Ang, distance C-H = 1.09 Ang, angles = 120 degrees),
# with the constraint of the angles between C-C-C and C-C-H = 120 degrees.

SystemName      benzene
SystemLabel     benzene

NumberOfSpecies 2
NumberOfAtoms   12

%block ChemicalSpeciesLabel
1    1 H
2    6 C
%endblock ChemicalSpeciesLabel

%block PS.lmax
  C   3
  H   3
%endblock PS.lmax
LatticeConstant     1.0 Bohr
%block LatticeVectors
   20.932528150       0.000000000       0.000000000
    0.000000000      19.551203193       0.000000000
    0.000000000       0.000000000      10.714661844
%endblock LatticeVectors

AtomicCoordinatesFormat NotScaledCartesianBohr
%block AtomicCoordinatesAndAtomicSpecies
    4.738724869       9.448634389       0.000000000     2    12.0107
    6.057380810      11.732613477      -0.000000000     2    12.0107
    8.694692693      11.732613477      -0.000000000     2    12.0107
   10.013348634       9.448634389      -0.000000000     2    12.0107
    8.694692693       7.164655301      -0.000000000     2    12.0107
    6.057380810       7.164655301      -0.000000000     2    12.0107
    2.647979028       9.448634389      -0.000000000     1     1.00794
    5.012007889      13.543252488      -0.000000000     1     1.00794
    9.740065613      13.543252488      -0.000000000     1     1.00794
   12.104094475       9.448634389      -0.000000000     1     1.00794
    9.740065613       5.354016289      -0.000000000     1     1.00794
    5.012007889       5.354016289      -0.000000000     1     1.00794
%endblock AtomicCoordinatesAndAtomicSpecies
MeshCutoff     200 Ry
DM.NumberPulay  5
DM.MixingWeight 0.3

MD.TypeOfRun    FC            # Compute the interatomic force constants matrix
MD.FCfirst      1             # Index of first atom to displace
MD.FClast       12            # Index of the last atom to displace
MD.FCdispl      0.040  Bohr   # Displacement to use for the computation
                              #   of the interatomic force constant matrix
                              #   (Remember that the second derivative of the
                              #   energy with respect the displacement of two
```

Relaxed coordinates and lattice vectors. Do not forget to introduce the mass of the atoms in the block AtomicCoordinatesAndAtomicSpecies

Instructions to compute the interatomic force constant matrix

Second step: compute the interatomic force constant matrix for the benzene molecule

```
$ siesta < benzene.ifc.fdf > benzene.ifc.out
```

A successful run will produce a file called benzene.FC

The content of the file is explained in the previous talk on phonons on Si

Third step: compute the dynamical matrix and diagonalize to obtain the vibrational frequencies

```
Eigenvectors =    True
Computing Eigenvalues and Eigenvectors
  eigenvalue # 1   omega= -25.000904892341158
  eigenvalue # 2   omega= -0.11272612521253839
  eigenvalue # 3   omega= -0.07793464396621091
  eigenvalue # 4   omega= 0.16999416229687175
  eigenvalue # 5   omega= 33.03214598439611
  eigenvalue # 6   omega= 41.4898100258537
  eigenvalue # 7   omega= 385.87282808656636
  eigenvalue # 8   omega= 387.4841842160962
  eigenvalue # 9   omega= 591.842760052141
  eigenvalue # 10   omega= 592.8066499661824
  eigenvalue # 11   omega= 658.052514694998
  eigenvalue # 12   omega= 694.5957444212764
  eigenvalue # 13   omega= 820.9901377846342
  eigenvalue # 14   omega= 823.7209255418799
  eigenvalue # 15   omega= 937.1454098480077
  eigenvalue # 16   omega= 938.6562720997748
  eigenvalue # 17   omega= 964.5314970572412
  eigenvalue # 18   omega= 973.8917716198797
  eigenvalue # 19   omega= 1045.3437880443003
  eigenvalue # 20   omega= 1046.75165858855
  eigenvalue # 21   omega= 1049.2774594155042
  eigenvalue # 22   omega= 1110.1192495636428
  eigenvalue # 23   omega= 1139.4794851279562
  eigenvalue # 24   omega= 1140.8476781350053
  eigenvalue # 25   omega= 1287.655823490828
  eigenvalue # 26   omega= 1471.7354884987683
  eigenvalue # 27   omega= 1480.3455207094541
  eigenvalue # 28   omega= 1481.67973882388
  eigenvalue # 29   omega= 1678.1406528562138
  eigenvalue # 30   omega= 1678.4743901339168
  eigenvalue # 31   omega= 3108.168157261722
  eigenvalue # 32   omega= 3117.114403552922
  eigenvalue # 33   omega= 3119.183273347605
  eigenvalue # 34   omega= 3130.8803864157967
  eigenvalue # 35   omega= 3131.3634086695674
  eigenvalue # 36   omega= 3140.219946851562

 Writing eigenvalues and eigenvectors
 to output file benzene.vectors

 Zero point energy =              2.678149 eV
```

$ vibrator < benzene.ifc.fdf > vibrator.out

$ more vibrator.out

There should be six frequencies equal to zero:

- **Three rigid translational modes**
- **Three rigid rotations**

To get them, we should converge more the grid to avoid the “egg-box” effect

File with the eigenvalues and eigenvectors

Fourth step: visualization of phonons

We need:

- The benzene.vectos file produced by vibrator
- The benzene.XV file produced by Siesta
- The vib2xsf program implemented by Andrei Postnikov (you can find it in the Util/Contrib/Apostnikov directory

Vib2xsf will ask some questions on the fly, regarding:

- the name of the files where the .vectors are stored,
- the units to be used to introduce the lattice vectors (Bohrs or Angstroms),
- the zero of coordinates,
- the unit cell lattice vectors,
- the first mode to visualize,
- the last mode to visualize,
- the amplitude of the modes to be visualized, and
- the number of steps in the movie.

We have prepared the answers for you in this example, in the file vib2xsf.dat

```
$ vib2xsf < vib2xsf.dat
```

Fourth step: visualization of phonons

$ vib2xsf < vib2xsf.dat

This produces two files per mode:

- .XSF file: contains a static structures (as in .XV), with arrors added to each atom to indicate displacement pattern.

- .AXSF file: contains the animation of a phonon, for a (user-chosen) amplitude and number of steps.

$ xcrysden

Select

- Open file
- Open structure
- Open AXSF (or XSF depending on your choice)