Vibrational Modes

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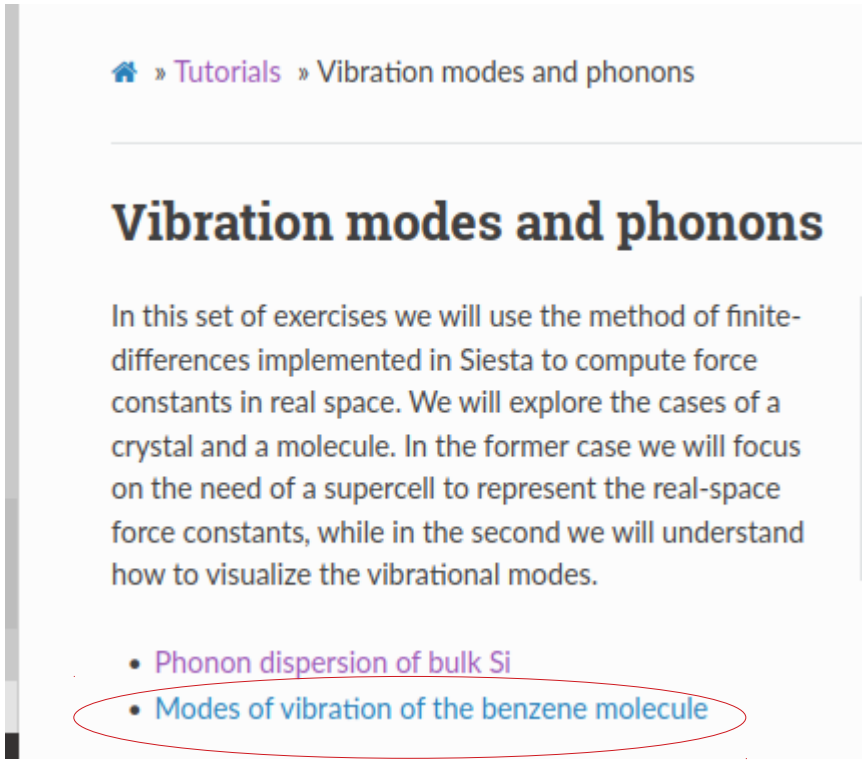
Wednesday 4th October 2023

First steps with SIESTA: from zero to hero

Vibrational Modes of Benzene Molecule



Vibrational Modes of Benzene Molecule

Step 1: Relax the structure.

The input file has been prepared for you in the file benzene.relax.fdf

```
%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
```

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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
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  CC 1.390
  CH 1.090
constraints
  xm1 CC -1.0 3.903229
%endblock Zmatrix
```

```
siesta  benzene.relax.fdf > benzene.relax.out
```

Vibrational Modes of Benzene Molecule

Step 2: Compute the IFCs

There is already a prepared input file with the relaxed structure.
In principle, you should copy the relaxed coordinates and unit cell from the benzene.XV obtained in the previous step.

benzene.ifc.fdf

```
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
```

Vibrational Modes of Benzene Molecule

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benzene.ifc.fdf

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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
4.738724[illegible]  [illegible]  [illegible]  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
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2.647979028       9.448634389      -0.000000000     1     1.00794
5.012007889      13.543252488      -0.000000000     1     1.00794
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9.740065613       5.354016289      -0.000000000     1     1.00794
5.012007889       5.354016289      -0.000000000     1     1.00794
%endblock AtomicCoordinatesAndAtomicSpecies
```

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

Vibrational Modes of Benzene Molecule

Step 3: Compute the dynamical matrix at Gamma

In the case of a molecule, only the Gamma point is relevant. It is specified in the same way as to compute the electronic band structure, in the same file benzene.ifc.fdf

```
Eigenvectors    .true.        # Compute both phonon eigenvalues and eigenvectors
BandLinesScale  pi/a
%block BandLines
1   0.0   0.0   0.0   \Gamma  # Only the Gamma point (enough for a molecule)
%endblock BandLines
```

```
vibra < benzene.ifc.fdf > vibra.out
```

Vibrational Modes of Benzene Molecule

Step 4: Visualize the normal modes:

Needed files:

- benzene.XV
- benzene.vectors

You need to specify:

- units of lattice vectors(Angstroms or Bohr)
- the zero of the coordinates
- the unit cell lattice vectors
- modes to visualize (the first and the last)
- the amplitude
- the steps of the animation

It is already done in vib2xsf.dat for you. Run: **vib2xsf < vib2xsf.dat**

*By Andrei Postnikov

Vibrational Modes of Benzene Molecule

Step 5: XCrysden

Output files:

- Benzene.Mode_*.XSF: contains a static structures (as in .XV), with arrors added to each atom to indicate displacement pattern.
- Benzene.Mode_*.AXSF: contains the animation of a phonon, for a defined amplitude and number of steps.

Vibrational Modes of Benzene Molecule

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Vibrational Modes of Benzene Molecule

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Output files:

- Benzene.Mode_*.XSF: contains a static structures (as in .XV), with arrors added to each atom to indicate displacement pattern.
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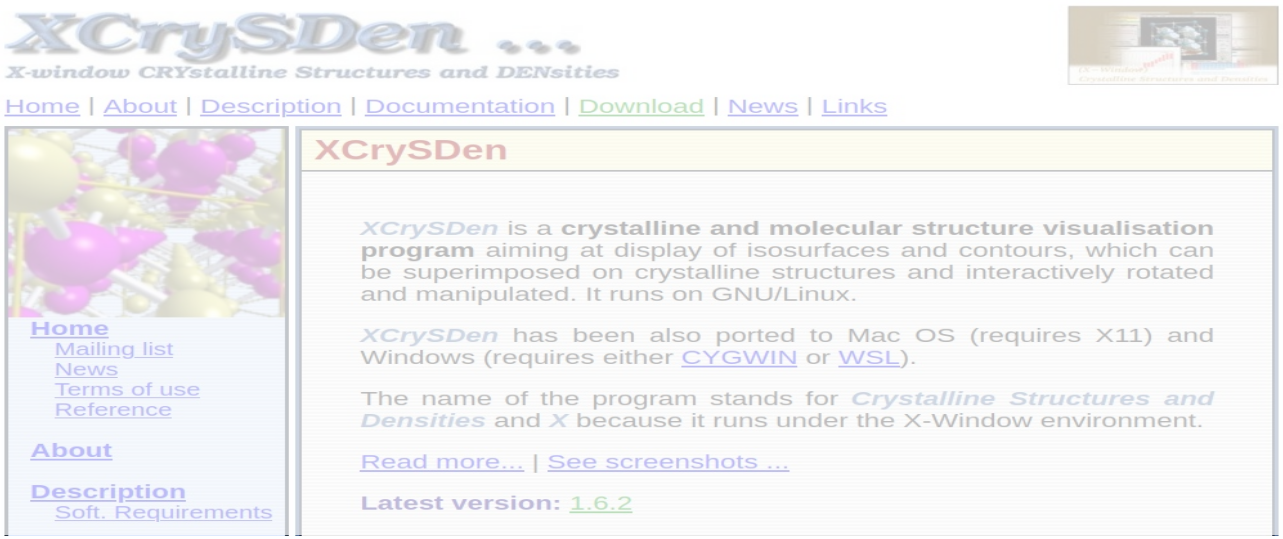
...And have fun!



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Results: examples of two modes….