Analysis II: visualization of dynamics and vibrational modes

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Vibrational Modes of Benzene Molecule

Vibration modes and phonons

In this set of exercises we will use the method of finite-differences implemented in Siesta to compute force constants in real space. We will explore the cases of a crystal and a molecule. In the former case we will focus on the need of a supercell to represent the real-space force constants, while in the second we will understand how to visualize the vibrational modes.

Have you set up the local environment?

If not, do that now before proceeding.

Note

Phonon calculations can be very sensitive to numerical artifacts such as those derived from the eggbox effect. Be sure to have the rest of your simulation parameters already converged as best as you can before running the actual force constant matrix calculations.

- Phonon dispersion of bulk Si
- Modes of vibration of the 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

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

```
%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
```

Vibrational Modes of Benzene Molecule

- Step 2: Compute the Interatomic Force Constants

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.

```
LatticeConstant      1.0 Bohr
%block LatticeVectors
 21.938124322      0.000000000      0.000000000
  0.000000000     20.556799916      0.000000000
  0.000000000      0.000000000     11.910755412
%endblock LatticeVectors

AtomicCoordinatesFormat NotScaledCartesianBohr
%block AtomicCoordinatesAndAtomicSpecies
   4.732644349   9.448630623   0.000000000  2   12.01070
   6.054339080  11.737873050   0.000000000  2   12.01070
   8.697728543  11.737873050   0.000000000  2   12.01070
  10.019423274   9.448630623   0.000000000  2   12.01070
   8.697728543   7.159388196   0.000000000  2   12.01070
   6.054339080   7.159388196   0.000000000  2   12.01070
   2.637688094   9.448630623   0.000000000  1    1.00794
   5.006860953  13.552158387   0.000000000  1    1.00794
   9.745206671  13.552158387   0.000000000  1    1.00794
  12.114379529   9.448630623   0.000000000  1    1.00794
   9.745206671   5.345102860   0.000000000  1    1.00794
   5.006860953   5.345102806   0.000000000  1    1.00794
%endblock AtomicCoordinatesAndAtomicSpecies
```

Vibrational Modes of Benzene Molecule

- Step 2: Compute the Interatomic Force Constants

  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.

```
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
```

Vibrational Modes of Benzene Molecule

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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: Visualization of the normal modes

Needed files:

benzene.XV
benzene.vectors

You need to specify:

1) units of lattice vectors (Angstroms or Bohr)
2) the zero of the coordinates
3) the unit cell lattice vectors
4) modes to visualize (the first and the last)
5) the amplitude
6) the steps of the animation

Vibrational Modes of Benzene Molecule

- Step 4: Visualization of the normal modes

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```
vib2xsf < vib2xsf.dat
```

Vibrational Modes of Benzene Molecule

- Step 4: Visualization of the normal modes

Needed files:

benzene.XV
benzene.vectors

You need to specify:

1) units of lattice vectors (Angstroms or Bohr)
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```
vib2xsf < vib2xsf.dat
```

Vibrational Modes of Benzene Molecule

- Step 4: Visualization of the normal modes

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.

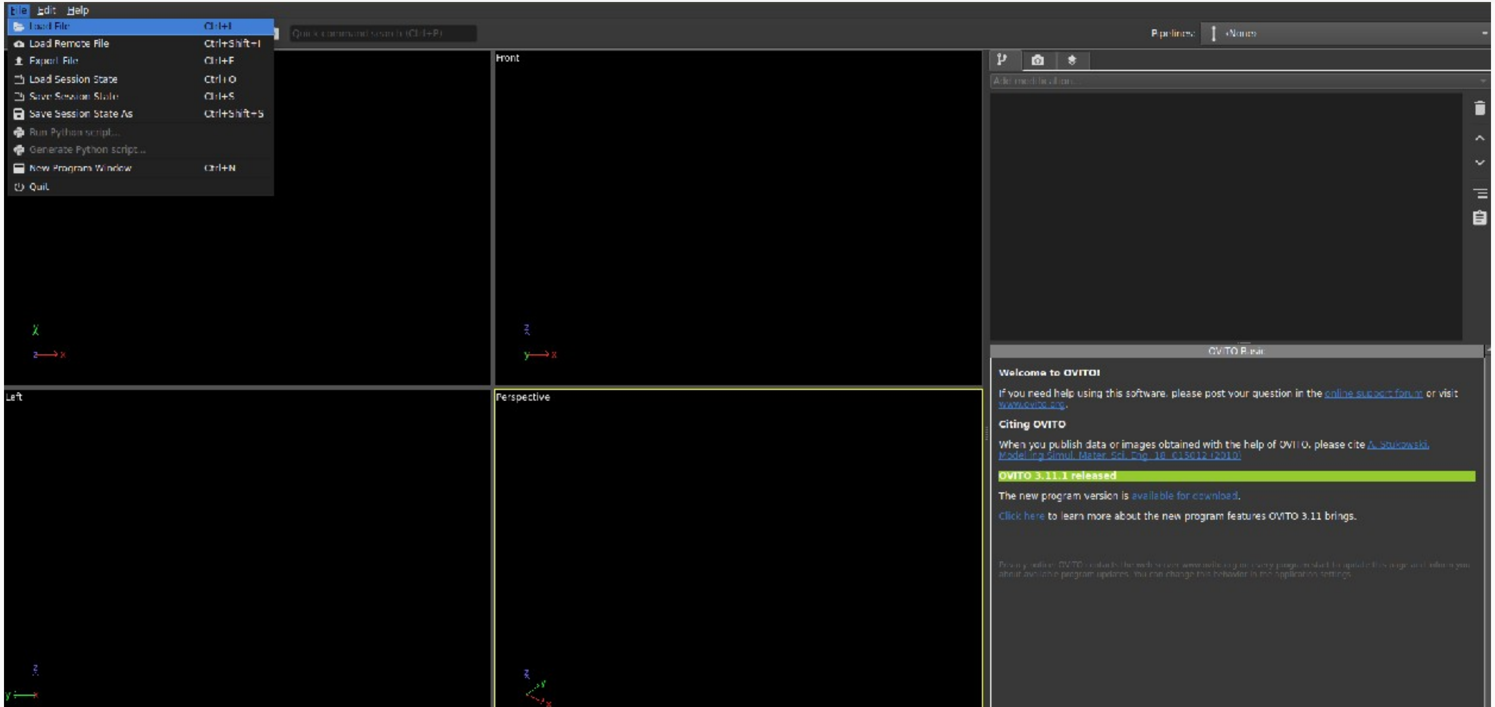
Vibrational Modes of Benzene Molecule

- Step 4: Visualization of the normal modes

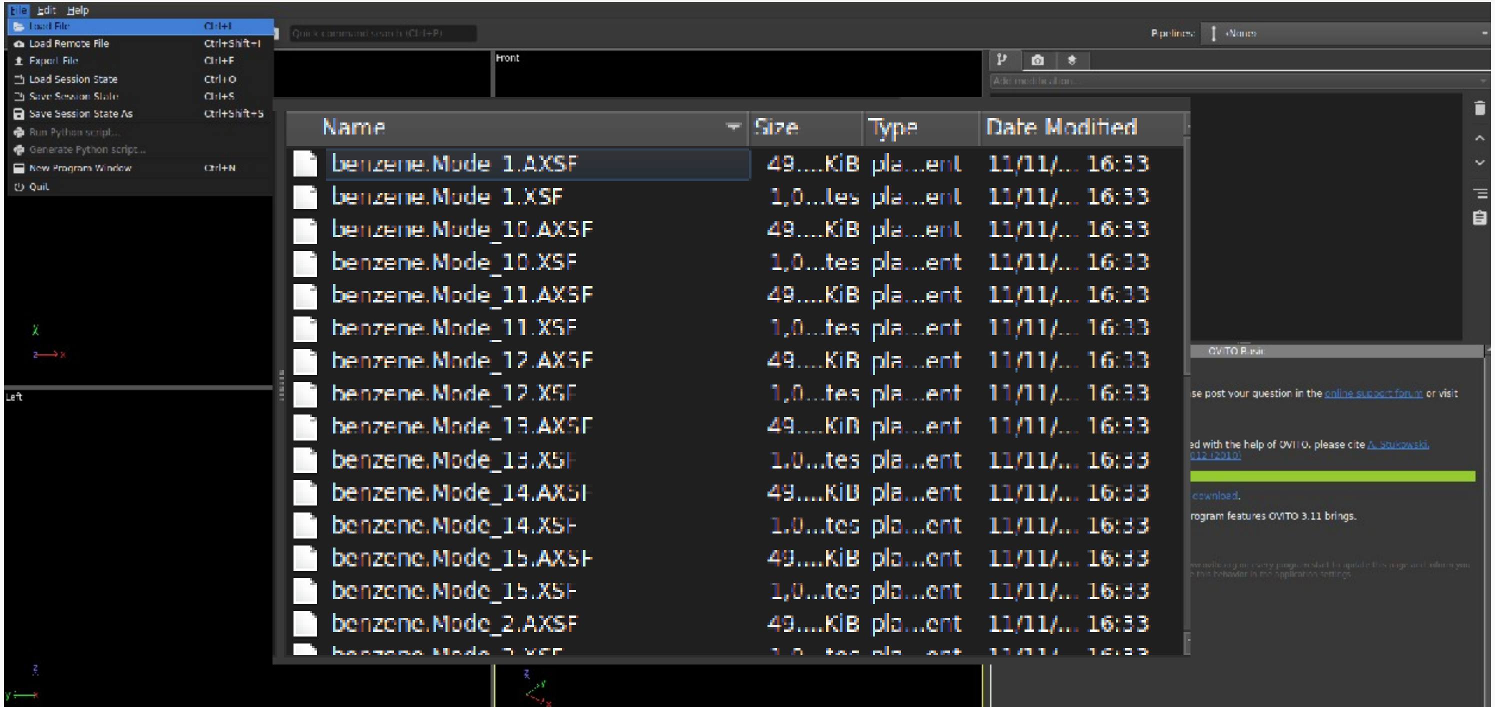
Ovito:

```
$ ovito
File > Load File
Load benzen.Mode_*.AXSF
```

Vibrational Modes of Benzene Molecule

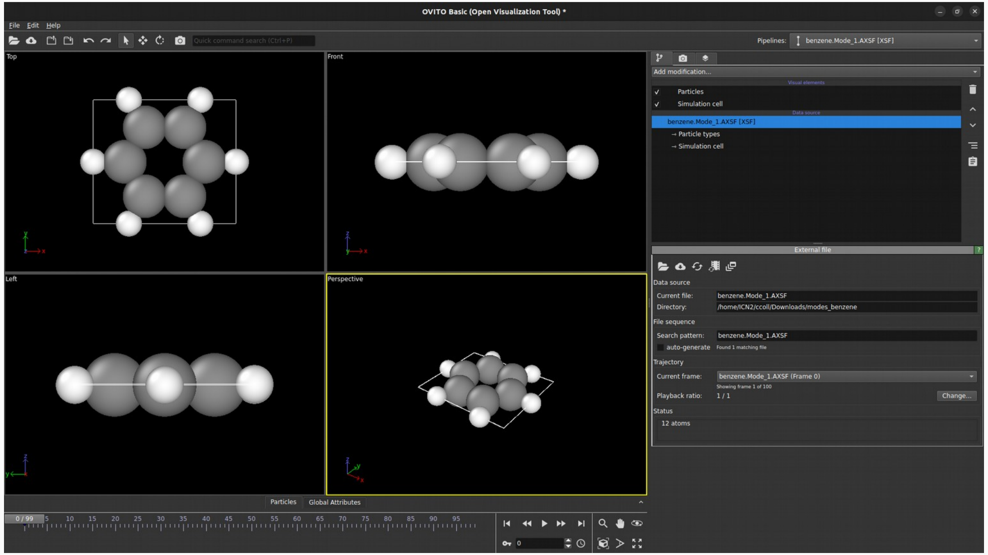


Vibrational Modes of Benzene Molecule



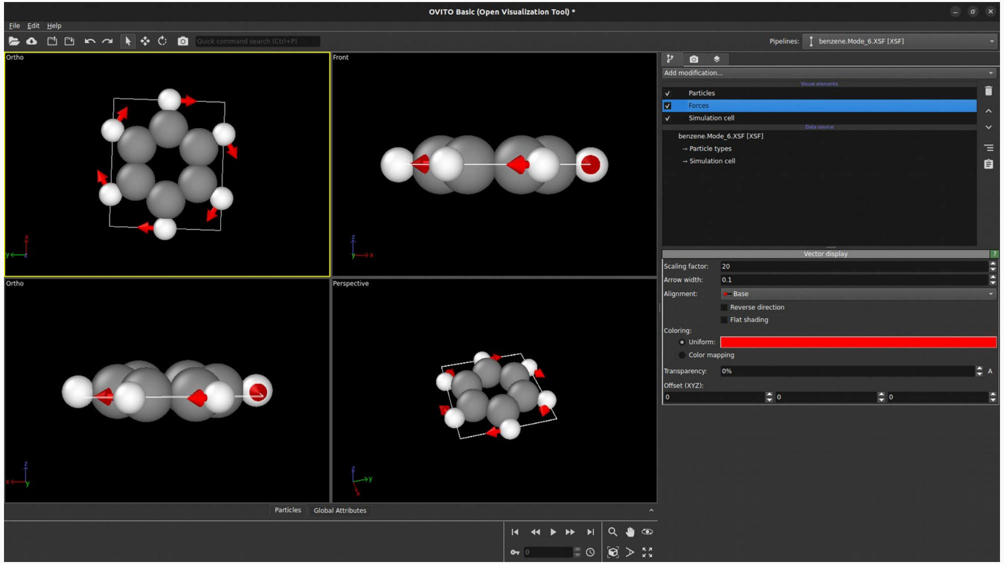
Vibrational Modes of Benzene Molecule

- Step 4: Visualization of the normal modes: ***.AXSF file**



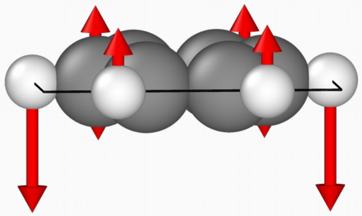
Vibrational Modes of Benzene Molecule

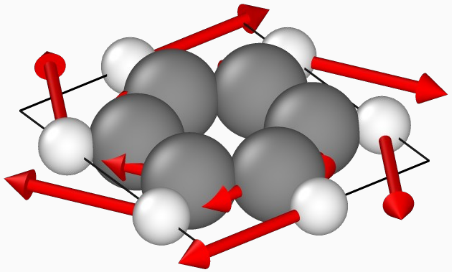
- Step 4: Visualization of the normal modes: ***.XSF file**



Vibrational Modes of Benzene Molecule

- Step 4: Visualization of the normal modes





Questions?