FHI-aims Cheat Sheet: Anharmonic Vibrations

FHI-aims team

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In the framework of Linear Response Theory, one can rewrite the Fermi's Golden Rule by means of the Fourier transform of the dipole moment time correlation function:

$$I(\omega) \propto \omega^2 \int_{-\infty}^{\infty} dt\, \mathrm{e}^{i\omega t} \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle_t = \int_{-\infty}^{\infty} dt\, \mathrm{e}^{i\omega t} \langle \dot{\mathbf{M}}(t) \cdot \dot{\mathbf{M}}(0) \rangle_t \tag{1}$$

In this formula, $I(\omega)$ is the intensity of the vibrations, $\mathbf{M}$ is the dipole moment of the system, and $\dot{\mathbf{M}}$ its time derivative. The angular brackets mean a statistical time average of the auto-correlation of the dipole moment of the molecule. Formula 1 will give all frequencies that are active in the IR range. Therefore, within one MD run, the whole IR spectrum of the molecule can be calculated, since one can choose various t=0 to average the dipole auto-correlation over.

A similar relation can be found for the time average of the velocity auto correlation function:

$$\mathrm{VDOS}(\omega) = \sum_{i=1,N} \int_{-\infty}^{\infty} dt\, \mathrm{e}^{i\omega t} \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle_t \tag{2}$$

In this case, N is the number of atoms in the molecule and the quantities that are computed are all possible frequencies of vibration of the molecule, not only the ones active in the IR range (due to selection rules). The advantage is that with this function, one can assign the frequencies to individual atom's displacements.

How to begin?

1) Setup and run a thermalization molecular dynamics (MD) run with the temperature you wish to simulate your system at, and let it run for at the very least a few ps. An example of settings for this "thermalization" part (in the `control.in`) would be:

`MD_run 10.0 NVT_andersen` <*temperature*> `200`
`MD_time_step 0.001`
`MD_MB_init` *temperature*

2) Start the microcanonical production run(s) from the thermalized MD snapshots (cartesian coordinates and velocities). Disregard the first few (at least 5) ps of the thermalization run, and after that, consider geometry and velocities starting points from the output. You can simply copy/paste a block with the atomic positions and velocities into a new `geometry.in` file. You can choose several geometries that are at least 1 ps apart and start several microcanonical runs from them. For a "first-shot", one microcanonical simulation will suffice. An example of settings for the NVE runs (in the `control.in`) would be:

```
MD_run 20.0 NVE
MD_time_step 0.001
```

Attention: Remember to also add the flag `output dipole` in your `control.in` file. From these microcanonical simulations you can extract the autocorrelation functions.

3) Calculate the spectra by using the python script that can be found in `aimsfiles/utilities/auto_correlation/auto-correlate-AVG.py`. It requires a fortran code that performs fourier transforms, that can be found in the same folder.
Compile the fortran code (e.g. `ifort -O3 home_made_ft.f90 -x home_made_ft.x`) and copy the executable to the folder where you will run the python script. All necessary help for the usage of the python script can be found by typing:

```
python auto-correlate-AVG.py -h
```

What do we get?

The most important files to look at are:

`autocorr.dat` - File containing in the first column the time of simulation in ps, in the second column the autocorrelation function, and in the third column the autocorrelation function multiplied by the windowing function.

`raw_fourier_transform.dat` - File containing the frequencies in cm^{-1} in the first column and the intensities in arbitrary units in the second column.

You can check the convergence of your spectrum by analyzing the behavior of the autocorrelation function and of the peaks of your spectrum with longer and longer simulation times (or more simulations). For very harmonic systems, a lot of sampling is required.

Attention!

These cheat sheets are not intended to substitute for reading the manuals of the programs involved and the original literature cited therein!

Have fun!