Computing IR / Raman / VCD / ROA Spectra with CP2k and TRAVIS

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0. Introduction

In this exercise, we will compute the full set of vibrational spectra (IR, Raman, VCD, ROA) from a CP2k AIMD simulation of one (*R*)-propylene oxide molecule in vacuum. Normally, this takes several days/weeks of computer time on one full node. Here, we have only 3 hours and 4 CPU cores per user. Some severe simplications had to be introduced to the computational setup, so that the calculations will finish in time. This is only to get a hand on the workflow; the spectra computed here will be of no scientific use (sorry). If you want „real“ spectra, feel free to redo all steps with adequate parameters (as I have shown in my talk). You find some nicely predicted bulk phase spectra in some of our articles in the literature (see chapter 6 in this document).

Apart from CP2k, we will use the TRAVIS program package. It is freely available in the internet on

```
http://www.travis-analyzer.de/
```

Everything except the compression of CUBE trajectories to BQB format (chapter 3 in this exercise) is already included in the public version. The BQB format will be included to the public version in some weeks, after the BQB article has been accepted by the journal :-)

An updated version of the tutorial on how to compute spectra with CP2k and TRAVIS (the stuff which we do today in the exercise) will be uploaded to the TRAVIS and CP2k homepages in some weeks. Please stay tuned.

As TRAVIS is a serial code and not parallelized by MPI, we can’t start it via mpirun. Today, we will directly log in to the node that has been assigned to each user, and will directly run all our calculations there. To do so, first find out which node you were assigned to:

```
cat hosts
```

You will see something like „node**-***“ on the screen, where every star corresponds to a digit. Then, please enter

```
ssh node**-***
```

where, of course, all stars are replaced by the digits of your node. Now you are working directly on your node. Make sure to do this every time you open a new SSH session (e.g., after you have been kicked out by the WLAN).

1. Computing the Trajectory

First, we need to copy all the files for today's exercise. In your user directory, please execute

```
cp -r ../ 00_workshop_files/day03 .
cd day03
```

You find several sub-directories (traj, nofield, exp, eyp, ezp, spectra) inside of this directory. We will start by computing the trajectory.

```
cd traj
```

Have a look at the CP2k input file there (propox.inp) and convince yourself that it runs a standard AIMD simulation (with very sloppy computational parameters; though). Then, run the calculation:

```
mpirun -np 4 -x LIBRARY_PATH -x PATH cp2k.popt propox.inp | tee log.out
```

It will run for around 10 Minutes. Then, you will find a file „propox-pos-1.xyz", which contains the trajectory of the system.

2. Computing the Electron Densities

With the trajectory which we just computed, we now produce the electron density CUBE trajectories. We need to do this without external electric field, and with external field applied along the X, Y, and Z axes. This leads to four calculations in total. We will run them all simultaneously, each on one CPU core.

```
cd ..
cd nofield
mpirun -np 1 -x LIBRARY_PATH -x PATH cp2k.popt propox.inp > log.out &
cd ..
cd exp
mpirun -np 1 -x LIBRARY_PATH -x PATH cp2k.popt propox.inp > log.out &
cd ..
cd eyp
mpirun -np 1 -x LIBRARY_PATH -x PATH cp2k.popt propox.inp > log.out &
cd ..
cd ezp
mpirun -np 1 -x LIBRARY_PATH -x PATH cp2k.popt propox.inp > log.out &
cd ..
```

These calculations should run for around 30 minutes. While they run, you can have a look to the „.ener" files to see the progress. The calculations are finished when the .ener file has 1024 lines (we run 1024 simulation steps). We obtained one .cube file per trajectory, which contains the electron density on a grid in every simulation step.

Just for completeness, I added the writing out of Wannier centers to the four input files. I recommended in my talk to not perform Wannier localization. However, for such a small gas phase system, this is really quick, so it does not hurt.

3. Compressing the CUBE Trajectories

This optional step can help to drastically reduce the size of the electron density data. As mentioned above, these methods are not yet included in the official TRAVIS version on the homepage, but will be published in some weeks.

```
cd nofield
travis compress cube result.cube result.bqb > log.out &
cd ..
cd exp
travis compress cube result.cube result.bqb > log.out &
cd ..
cd eyp
travis compress cube result.cube result.bqb > log.out &
cd ..
cd ezp
travis compress cube result.cube result.bqb > log.out &
cd ..
```

This will run for around 15 minutes. We obtained .bqb files, which are much smaller than the .cube files (reduced from 2.8 GiB to 88 MiB in our case!), but still contain the same amount of information.

4. Performing Voronoi Integration and Solving Current PDE

Now, we need to obtain the atomic and molecular electromagnetic moments, which are required for the spectra. We use TRAVIS to solve the classical current PDE and to perform the Voronoi integration of the electron density. Normally, TRAVIS is an interactive program, which asks questions to the user; but in this case, I prepared some TRAVIS input files („integrate.txt“) to speed up the process.

```
cd nofield
travis -p result.bqb -i integrate.txt > log.out &
cd ..
cd exp
travis -p result.bqb -i integrate.txt > log.out &
cd ..
cd eyp
travis -p result.bqb -i integrate.txt > log.out &
cd ..
cd ezp
travis -p result.bqb -i integrate.txt > log.out &
cd ..
```

This will run for around 20 minutes. For each trajectory, we will obtain an electromagnetic property file (*.emp), which contains the electric dipole vector, quadrupole tensor, and magnetic dipole vector (among other properties) per atom.

Apart from the properties.emp file, you also obtained a properties.csv text file, where you can have a look at all the electric and magnetic moments per atom :-)

5. Compute the Spectra

Now, we finally have all the data to compute the spectra. We need to supply the four .emp files from the last chapter. We start TRAVIS with the field-free property file:

```
cd spectra
travis ../nofield/properties.emp
```

As mentioned above, TRAVIS is an interactive program and asks questions. Please give the following answers in that order (and read the questions before). The lines starting with exclamation marks are just comments which indicate the question that was asked. If the answer line is empty, simply press RETURN; this will choose the default answer to that question, which is indicated in square brackets.

```
! Use the advanced mode until the analysis selection menu (y/n)? [no]

! Use these values (y) or enter different values (n)? [yes]

! Update cell geometry in every time step (y) or use fixed cell (n)? [yes]

! Create images of the structural formulas (y/n)? [no]

! Accept these molecules (y) or change something (n)? [yes]

! Which functions to compute (comma separated)?
spec
! Use the advanced mode for the main part (y/n)? [no]

! Use two-pass mode (y/n)? [yes]

! Is this a gathering run (y) or the analyzing run (n)? [no]

! Enter the length of one trajectory time step in fs: [0.5]

! In which time step to start processing the trajectory? [1]

! How many time steps to use (from this position on)? [all]

! Use every n-th time step from the trajectory? [1]

! Spectra to compute for this observation (comma separated):
ir,raman,vcd,roa
! Observe molecules of type C3H6O for this spectrum (y/n)? [yes]

! Which molecules of type C3H6O to observe (e.g. 1,5-7)? [all]

! Enter the resolution of the correlation functions: [511]
512
! Calculate spectrum up to which wave number (cm^-1)? [5000.00 cm^-1]

! Calculate scattering for which wave number (cm^-1)? [20000.0]

! Calculate scattering cross section for which temperature (K)? [350.0]

! Correct spectrum for a certain simulation temperature (y/n)? [yes]

! Enter the simulation temperature (K): [350.0]

! Add another observation (y/n)? [no]

! Use central finite differences (y) or one-sided differences (n)? [no]

! Enter electric field strength for field trajectories (in a.u.): [5.0E-3]

! Enter core charge for atom type C: [4.0]

! Enter core charge for atom type H: [1.0]

! Enter core charge for atom type O: [6.0]

! Enter data file name for field X:
../exp/properties.emp
! Enter data file name for field Y:
../eyp/properties.emp
! Enter data file name for field Z:
../ezp/properties.emp
```

After you answered all questions, TRAVIS will run a few seconds, and then you will have all spectra as .csv text files. You can plot these spectra with any plotting program of your choice (gnuplot, xmgrace, ...). The first column always contains the wave number in cm^{-1}, the second column contains the spectral intensity.

Have a look at the following five spectra:

```
power_spectrum.csv
spectrum_ir_C3H6O.csv
spectrum_raman_ortho_ct_C3H6O.csv
spectrum_vcd_ct_C3H6O.csv
spectrum_roa_90deg_ortho_ct_C3H6O.csv
```

6. Literature

"TRAVIS - A Free Analyzer and Visualizer for Monte Carlo and Molecular Dynamics Trajectories", M. Brehm, B. Kirchner; *J. Chem. Inf. Model.* **2011**, *51 (8)*, pp 2007-2023.

"An Efficient Lossless Compression Algorithm for Trajectories of Atom Positions and Volumetric Data", M. Brehm, M. Thomas; *J. Chem. Inf. Model.* **2018**, *submitted*.

"Computing vibrational spectra from ab initio molecular dynamics", M. Thomas, M. Brehm, R. Fligg, P. Voehringer, B. Kirchner; *Phys. Chem. Chem. Phys.* **2013**, *15*, pp 6608-6622.

"Simulating the vibrational spectra of ionic liquid systems: 1-Ethyl-3-methylimidazolium acetate and its mixtures", M. Thomas, M. Brehm, O. Holloczki, Z. Kelemen, L. Nyulaszi, T. Pasinszki, B. Kirchner; *J. Chem. Phys.* **2014**, *141*, 024510.

"Voronoi dipole moments for the simulation of bulk phase vibrational spectra", M. Thomas, M. Brehm, B. Kirchner; *Phys. Chem. Chem. Phys.* **2015**, *17*, pp 3207-3213.

"Classical Magnetic Dipole Moments for the Simulation of Vibrational Circular Dichroism by Ab Initio Molecular Dynamics", M. Thomas, B. Kirchner; *J. Phys. Chem. Lett.* **2016**, *7*, pp 509-513.

"Computing Bulk Phase Raman Optical Activity Spectra from ab initio Molecular Dynamics Simulations", M. Brehm, M. Thomas; *J. Phys. Chem. Lett.* **2017**, *8 (14)*, pp 3409-3414.