MultiSpec reference guide

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Contents

1   Installation

MultiSpec can be downloaded and installed using cmake:

```
$ git clone https://github.com/kananenka-group/MultiSpec.git
$ cd ./MultiSpec/src
$ mkdir build
$ cmake -S . -B build
$ cmake --build build
```

Note that MultiSpec uses Boost and Blas, both are needed to be installed before attempting to install MultiSpec.

2 Exciton module

Exciton module is the main module that computes spectra. Currently only linear IR and Raman spectra are implemented.

2.1 Input parameters

-- **dt**: (`double`) time step between frames in ps.

-- **tc**: (`double`) correlation time for 1D time-correlation functions.

-- **H**: (`string`) name of the file containing Hamiltonian trajectory.

-- **D**: (`string`) name of the file containing transition dipole trajectory.

-- **P**: (`string`) name of the file containing transition polarizability trajectory.

-- **IR**: (`bool`) calculate linear IR spectra, options: {1,0}.

-- **Raman**: (`bool`) calculate Raman spectra, options: {1,0}. This will calculate VV, VH, isotropic, and unpolarized Raman spectra.

-- **SFG**: (`bool`) calculate sum-frequency generation (SFG) spectra, options: {1,0}. This will calculate SFG in *ssp* polarization.

-- **nframes**: (`int`) how many frames are stored in trajectory files.

-- **T1**: (`double`) T_1 time, life-time of the first exited state.

-- **navg**: (`int`) the number of segments the input trajectories will be divided into and used for statistical averaging.

-- **tstart**: (`double`) Starting time for calculating spectra (ps). Rewind the trajectory to this time and start calculating spectra.

-- **tsep**: (`double`) time separation in ps between segments.

-- **w_avg**: (`double`) (optional parameter) average frequency in cm^{-1}. It helps mitigate numerical instabilities.

-- **inh**: (`bool`) calculate spectra in the inhomogeneous broadening limit. This also requests calculation of distribution of excitonic frequencies.

3 Water module

Water module generates an input for the exciton module. The input consists of excitonic hamiltonian trajectory as well as transition dipole and transition polarizability trajectories for IR, Raman, and SFG calculations.

3.1 Input parameters

-- **xtc**: (`string`) path to gromacs *.xtc file.

-- **gro_file**: (`string`) path to gromacs *.gro file.

-- **start**: (`int`) starting frame to read from the trajectory (xtc file).

-- **IR**: (`bool`) calculate transition dipole derivative moments for IR spectra, options: {1,0}.

-- **Raman**: (`bool`) calculate transition polarizability trajectories for Raman spectra, options: {1,0}.

-- **SFG**: (`bool`) calculate transition polarizability and transition dipole trajectories for SFG spectra, options: {1,0}.

-- **nframes**: (`int`) how many frames read from *.xtc file and process.

-- **atoms_file**: (`string`) path to the file containing charges and masses of all atoms. This is a simple three-column file containing atom names matching atoms in *.gro file, corresponding charges and masses. Comment lines must start with #. An example of such file can be found in Sec. A.

-- **water_model**: (`string`) water model. Supported water models: `SPC`, `SPCE`, `TIP4P`, `TIP4P/2005`, `E3B2`, `E3B3`. Note that in each case `atoms_file` is required and must have charges and masses of all atoms of the model making it possible to use any of these models with any desired charges.

-- **stretch_map**: (`string`) spectroscopic map for OH and OD stretch. The following maps have been implemented so far: `li_2010_tip4p`, `gruenbaum_2013_tip4p`, and `auer_2008_spce`. See Sec. 3.2 for more details.

-- **bend_map**: (`string`) spectroscopic map for HOH and DOD bend. The following maps have been implemented so far:

  – `ni_2015_tip4p` from Y. Ni and J. L. Skinner, J. Chem. Phys. 143, 014502 (2015)

  – `ni_2015_kananenka_2019_tip4p` from Y. Ni and J. L. Skinner , J. Chem. Phys. 143, 014502 (2015) updated with HOD and D_2O bending frequencies used in Kananenka *et al.*, J. Phys. Chem. B 123, 5139-5146 (2019).

-- **spec_type**: (`string`) type of calculation that will be performed. Supported types:

  – OH stretch, keyword: `wsOH`

  – OD stretch, keyword: `wsOD`

  – hydroxyl stretch in water isotope mixtures, keyword: `wsiso`

- OH-stretch fundamental-HOH bend overtone, keyword: `wswbH2O`
- OD-stretch fundamental-DOD bend overtone, keyword: `wswbD2O`
- hydroxyl stretch fundamental-bend overtone in water isotope mixtures, keyword: `wswbiso`.
- uncoupled OH-stretch fundamental, keyword: `wuOH`
- uncoupled OD-stretch fundamental, keyword: `wuOD`

-- **D2O**: (`int`) the number of D_2O molecules mixed with H_2O. This is only required for `--spec_type=wsiso` and `--spec_type=wswbiso`.

-- **Fc**: (`float`) OH-stretch fundamental-HOH bend overtone Fermi coupling. This is required only for `--spec_type=wswbH2O`, `--spec_type=wswbD2O`, and `--spec_type=wswbiso`.

-- **DOD_overtone**: (`bool`) use this option to turn on/off DOD bend overtone in water hydroxyl stretch fundamental/bend overtone calculations of isotope mixtures. This option only works with `--spec_type=wswbiso`.

-- **trdipSFG**: (`float`) distance in Å between O atom and the OH-stretch transition dipole along the O-H(D) bond. This only works with `--SFG=1`.

-- **intrac**: (`bool`) turns on and off OH stretch intramolecular couplings, options: {1,0}. Default value is 1.

-- **intercOH**: (`bool`) turns on and off OH stretch intermolecular couplings, options: {1,0}. Default value is 1.

-- **exc_ham**: (`bool`) if set to 1 will print diagonal frequencies, intermolecular, and intramolecular couplings to separate files. Options: {1,0}. Default value is 0.

3.2 Water Spectroscopic maps

3.2.1 gruenbaum_2013_tip4p

These maps were developed by Gruenbaum et al. in J. Chem. Theory Comput. 9, 3109 (2013) based on clusters of water molecules from a liquid-state simulation of TIP4P water. Note that some of the maps shown below have been developed before this paper. OH stretching maps:

$$
\begin{aligned}
\omega_{10} &= 3760.2 - 3541.7E - 152677E^2 \\
\omega_{21} &= 3606.0 - 3498.6E - 198715E^2 \\
x_{10} &= 0.19285 - 1.7261 \cdot 10^{-5}\omega_{10} \\
x_{21} &= 0.26836 - 2.3788 \cdot 10^{-5}\omega_{21} \\
p_{10} &= 1.6466 + 5.7692 \cdot 10^{-4}\omega_{10} \\
p_{21} &= 2.0160 + 8.7684 \cdot 10^{-4}\omega_{21}
\end{aligned}
$$

OD stretching maps:

$$
\begin{aligned}
\omega_{10} &= 2767.8 - 2630.3E - 102601E^2 \\
\omega_{21} &= 2673.0 - 1763.5E - 138534E^2 \\
x_{10} &= 0.16593 - 2.0632 \cdot 10^{-5}\omega_{10} \\
x_{21} &= 0.23167 - 2.8596 \cdot 10^{-5}\omega_{21} \\
p_{10} &= 2.0475 + 8.9108 \cdot 10^{-4}\omega_{10} \\
p_{21} &= 2.6233 + 13.1443 \cdot 10^{-4}\omega_{21}
\end{aligned}
$$

Dipole derivative and intramolecular coupling maps:

$$
\begin{aligned}
\mu' &= 0.1646 + 11.39E + 63.41E^2 \\
\omega_{jk}^{\mathrm{intra}} &= [-1361 + 27165(E_j + E_k)]x_j x_k - 1.887p_j p_k
\end{aligned}
$$

OH/OD stretch transition dipole is located 0.67 Å away from the water oxygen atom along the OH/OD bond.

3.2.2 li_2010_tip4p

These maps were developed by Li and Skinner in J. Chem. Phys. 132, 244504 (2010) based on clusters of water molecules from a liquid-state simulation of TIP4P water. OH stretching maps:

$$
\begin{aligned}
\omega_{10} &= 3732.9 - 3519.8E - 1.5353 \cdot 10^5 E^2 \\
x_{10} &= 0.19318 - 1.7248 \cdot 10^{-5}\omega_{10} \\
p_{10} &= 1.6120 + 5.8697 \cdot 10^{-4}\omega_{10}
\end{aligned}
\tag{1}
$$

OD stretching maps:

$$
\begin{aligned}
\omega_{10} &= 2748.2 - 2572.2E - 1.0298 \cdot 10^5 E^2 \\
x_{10} &= 0.16598 - 2.0752 \cdot 10^{-5}\omega_{10} \\
p_{10} &= 1.9813 + 9.1419 \cdot 10^{-4}\omega_{10}
\end{aligned}
\tag{2}
$$

Dipole derivative and intramolecular coupling maps:

$$
\begin{aligned}
\mu' &= 0.1622 + 10.381E + 137.6E^2 \\
\omega_{jk}^{\mathrm{intra}} &= [-1361 + 27165(E_j + E_k)]x_j x_k - 1.887p_j p_k
\end{aligned}
$$

OH/OD stretch transition dipole is located 0.67 Å away from the water oxygen atom along the OH/OD bond.

3.2.3 auer_2008_spce

These maps were developed by Auer et al. in J. Chem. Phys. 128, 224511 (2008) and J. Chem. Phys. 132, 174505 (2010) (OD ω_{21} and x_{21} maps) and PNAS 104, 14215-4220 (OH ω_{21} and x_{21} maps) based on clusters of water molecules from a liquid-state simulation of SPC/E water. OH stretching maps:

$$
\begin{aligned}
\omega_{10} &= 3761.6 - 5060.4E - 86225E^2 \\
x_{10} &= 0.1934 - 1.75 \cdot 10^{-5}\omega_{10} \\
p_{10} &= 1.611 + 5.893 \cdot 10^{-4}\omega_{10} \\
\omega_{21} &= 3614.1 - 5493.7E - 115670E^2 \\
x_{21} &= 0.1428 - 1.29 \cdot 10^{-5}\omega_{21}
\end{aligned}
$$

OD stretching maps:

$$
\begin{aligned}
\omega_{10} &= 2762.6 - 3640.8E - 56641E^2 \\
x_{10} &= 0.16627 - 2.0884 \cdot 10^{-5}\omega_{10} \\
p_{10} &= 1.9844 + 9.1907 \cdot 10^{-4}\omega_{10} \\
\omega_{21} &= 2695.8 - 3785.1E - 73074E^2 \\
x_{21} &= 0.1229 - 1.525 \cdot 10^{-5}\omega_{21}
\end{aligned}
$$

Dipole derivative and intramolecular couplings:

$$
\begin{aligned}
\mu' &= 0.1333 + 14.17E \\
\omega_{jk}^{\text{intra}} &= [-1789 + 23852(E_j + E_k)]x_j x_k - 1.966 p_j p_k
\end{aligned}
$$

OH/OD stretch transition dipole is located 0.58 Å away from the water oxygen atom along the OH/OD bond.

4 AmideI module

4.1 Input parameters

-- **xtc**: (`string`) path to gromacs *.xtc file.

-- **gro_file**: (`string`) path to gromacs *.gro file.

-- **top_file**: (`string`) path to gromacs *.top file.

-- **itp_files**: (`vector<string>`) path to GROMACS topology files (*.itp) containing residue information and charges and masses of all atoms. Provide a list of files if more than one file contains the topology info about the whole system.

-- **nframes**: (`int`) how many frames read from *.xtc file and process.

-- **spec_type**: (`string`) type of calculation that will be performed. Supported types:

- – Amide I spectroscopy with all amide I groups included (no isotope labels), keyword: `full`
- – Isotope labels placed at selected residues, keyword: `iso`

-- **isotope_labels**: (`vector<string>`) provide a list of residues whose C=O groups are isotope labeled. Example: "22SER 23ALA...".

-- **nn_map**: (`string`) Nearest-neighbor map diagonal frequency map. Currently implemented: `Jansen_2006` map.

-- **isotope_shift**: (`float`) isotope frequency shift. The default value is -66 cm^{-1} corresponding to ^{13}C^{18}O isotope shift taken from JACS 134, 19118-19128 (2012).

5   Examples

A   atoms_file

Below is an example of a file that can be used with the **atoms_file** command line. This is a pure water TIP4P simulation:

```
# this is a comment line; atom   charge   mass
OW      0.0      16.000
HW1     0.52     1.008
HW2     0.52     1.008
MW      -1.04    0.000
```