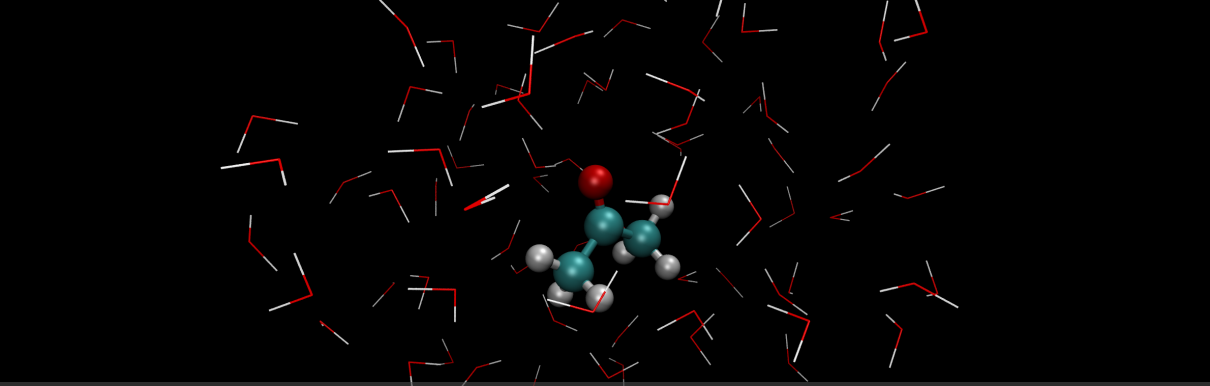


Solvatochromic Shifts in the Spectroscopy of Acetone
with LAMMPS and VOTCA

August 13, 2021

BAUMEIER RESEARCH GROUP

Overview

- How to follow along
- The QM/MM Approach
- Doing QM/MM with LAMMPS AND VOTCA

How to follow along

You can follow along with this tutorial on you own pc, assuming you can run docker. To set it up on a Ubuntu machine, install docker,

```
sudo apt install docker.io
```

and pull the votca image.

```
docker pull votca/votca
```

Next we start docker and load the environment variables of VOTCA

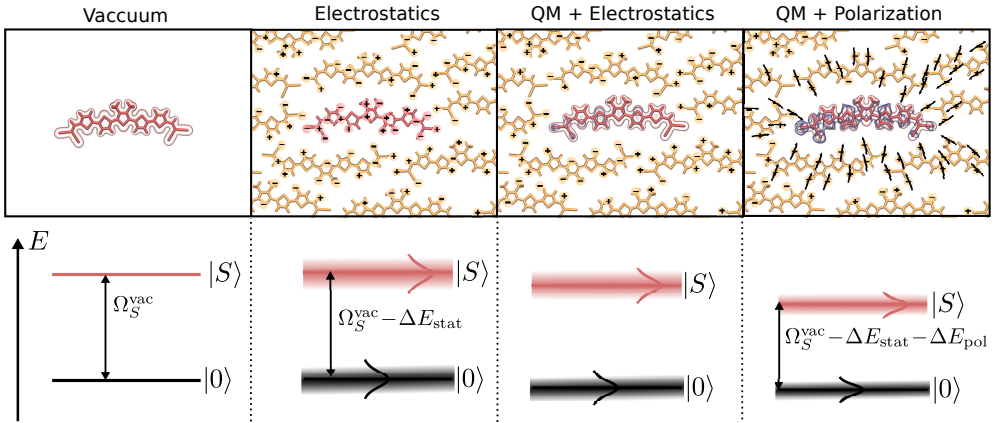
```
docker run -it votca/votca /bin/bash
source VOTCARC.bash
```

To find all the necessary input files

```
git clone https://github.com/rubengerritsen/lammps
cd lammps
```

Now you are all set to follow along.

The QM/MM Approach



The QM/MM Approach: A combination of 4 models

- Molecular Dynamics:
  - Used to obtain a snap shot of the topology of the molecular system
  - **Tool:** LAMMPS (or GROMACS)
  - **Representation:** Geometry + Forcefield
- Quantum Mechanical:
  - Used to compute the excited states of a molecule and generate input files.
  - **Tool:** VOTCA (excited states) + ORCA (input files)
  - **Representation:** Optimized geometry
- Electrostatics:
  - The electrostatics are computed based on a multipole expansion (in this tutorial just partial charges).
  - **Tool:** VOTCA (and ORCA)
  - **Representation:** Distributed multipoles
- Polarization:
  - We use the applequist model with Thole damping, i.e. polarizable dipoles.
  - **Tool:** VOTCA (and ORCA)
  - **Representation:** Distributed polarizabilities

To do a QM/MM calculation we need to setup the representations for each model and generate all the necessary input files.

Performing QM/MM with VOTCA and LAMMPS

The process of performing a QM/MM calculation consists of three general steps.

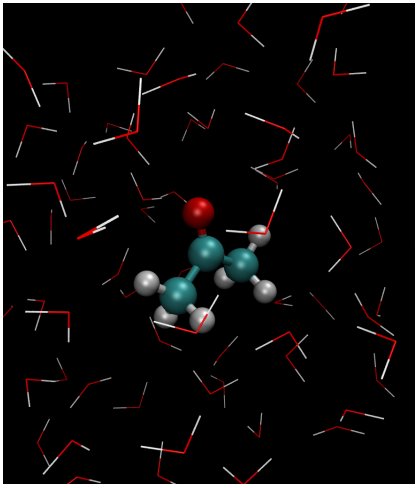
1. Create representations and input files
2. The mapping procedure (combining the representations from the 4 models)
3. Running the QM/MM calculation

The System and Generating Input Files

The MD trajectory of Acetone in Water
The MD trajectory can be obtained by running a normal LAMMPS simulation of your system. For this tutorial we have already performed the MD simulation for you. The relevant data can be found in the `system.data` and `traj1.dump` files.

Optimized geometries
Optimized geometries can be obtained from many QM packages including VOTCA. For this tutorial we have already computed them with ORCA. The ORCA results and the input files that generated them can be found in the `DFT_ORCA` folder.

Multipoles and Polarization
The multipoles and polarization can also be computed with ORCA and that is what we did for this tutorial.The ORCA output files, however, need to be converted to a VOTCA readable format called mps files.



Generating the Multipole and Polarizability files

For the multipoles and polarization VOTCA uses mps files. There is a special tool in VOTCA that converts ORCA log files with CHELPG charges to an mps file.

```
xtp_tools -e log2mps -o OPTIONS/log2mps_water.xml
```

We see here the typical way of calling a VOTCA program

```
xtp_<executableType> -e <calculationType> -o <optionsFile>.xml
```

The option file

```
<options>
    <log2mps>
        <dftpackage>orca</dftpackage>
        <input>DFT_ORCA/water/chelpg.log</input>
        <output>MP_FILES/water_n.mps</output>
    </log2mps>
</options>
```

How to find out which options are available?

1. Look at the description of a program with the describe flag `-d`

```
xtp_tools -d log2mps
```

2. Print (`-p`) an example options file with **all** available options to an output file (`-o`)

```
xtp_tools -p log2mps -o optionsLog2mps.xml
```

The result of *log2mps*

The generated MPS file.

```
! GENERATED BY VOTCA::XTP::::LOG2MPS
! N=3 Q[e]=+0.0000000
Units angstrom
  O +0.0000000 +0.0000000 -0.0043320 Rank 0
    -0.7585550
    P +0.8370000
  H +0.7614610 +0.0000000 +0.5795250 Rank 0
    +0.3787500
    P +0.4960000
  H -0.7614610 +0.0000000 +0.5795250 Rank 0
    +0.3798050
    P +0.4960000
```

But the polarizations are still wrong!

Fitting Polarizabilities

To obtain the atomic polarizabilities we fit them such that they represent the molecular polarizabillity as close as possible. The molecular polarizabilities are calculated with ORCA for this tutorial. VOTCA has a tool specifically for this fitting procedure.

```
xtp_tools -e molpol -o OPTIONS/molpol_water.xml
```

The options file

```
<options>
  <molpol>
    <input>MP_FILES/water_n.mps</input>
    <output>MP_FILES/water_n_pol.mps</output>
    <mode>qmpackage</mode>
    <qmpackage>orca</qmpackage>
    <logfile>DFT_ORCA/water/chelpg.log</logfile>
  </molpol>
</options>
```

Check the output file.

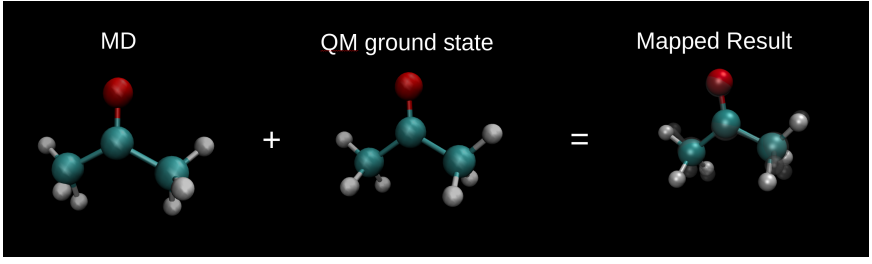
Repeat for the Acetone molecule

To generate the mps file for acetone

```
xtp_tools -e log2mps -o OPTIONS/log2mps_acetone.xml
xtp_tools -e molpol -o OPTIONS/molpol_acetone.xml
```

The Mapping Procedure: An Example

```
<mdatoms>1:O223:0 1:C222:1 1:C80:2 1:C80:3 1:H85:4 1:H85:5 1:H85:6 1:H85:7 1:H85:8 1:H85:9</mdatoms>
<qmatoms>0:O       1:C      2:C     3:C     4:H     5:H     6:H     7:H     8:H     9:H</qmatoms>
<mpoles>0:O       1:C      2:C     3:C     4:H     5:H     6:H     7:H     8:H     9:H</mpoles>
<localframe>0 1 3</localframe>
```



This procedure needs to be done for every

- geometry (i.e. optimized QM geometry or multipole geometry)
- and for every molecule

The Mapping Procedure: The Mapping File

```
<molecule>
  <mdname>C3H6O1</mdname>
  <segments>
    <segment>
      <name>ACETONE</name>
      <qmcoords_n>DFT_ORCA/acetone/acetoneOpt.xyz</qmcoords_n>
      <qmcoords_e>DFT_ORCA/acetone/acetoneOpt.xyz</qmcoords_e>
      <qmcoords_h>DFT_ORCA/acetone/acetoneOpt.xyz</qmcoords_h>
      <multipoles_n>MP_FILES/acetone_n_pol.mps</multipoles_n>
      <map2md>0</map2md>
      <fragments>
        <fragment>
          <name>acetone</name>
          <mdatoms>1:O223:0 1:C222:1 1:C80:2 1:C80:3 1:H85:4 1:H85:5 1:H85:6 1:H85:7 1:H85:8
          ↪  1:H85:9</mdatoms>
          <qmatoms>0:O 1:C 2:C 3:C 4:H 5:H 6:H 7:H 8:H 9:H</qmatoms>
          <mpoles>0:O 1:C 2:C 3:C 4:H 5:H 6:H 7:H 8:H 9:H</mpoles>
          <weights>16 12 12 12 1 1 1 1 1 1</weights>
          <localframe>0 1 3</localframe>
        </fragment>
      </fragments>
    </segment>
  </segments>
</molecule>
```

The Mapping Procedure: Performing and Checking the Mapping

Once the mapping file is setup, performing the mapping is easy.

```
xtp_map -t LAMMPS/system.data -c LAMMPS/traj1.dump -s OPTIONS/mapping.xml -f state.hdf5
```

To check what the mapping did we can print pdb files with the original coordinates and the multipole or qm coordinates to visually check (e.g. in VMD) if the mapping procedure was successful. To run the map checker

```
xtp_run -e mapchecker -o OPTIONS/mapchecker.xml -f state.hdf5
```

In the option file you can specify exactly which states and configurations you would like to check.

Setup the QM/MM jobfile and run the calculation

To perform the QM/MM calculation we need a jobfile that describes for which molecule(s) and which state(s) the calculation is performed.

```
<io_jobfile>
  <states>n s1</states>
  <segments>0 1</segments>
  <use_gs_for_ex>true</use_gs_for_ex>
</io_jobfile>
```

To create the jobfile

```
xtp_parallel -e qmmm -o OPTIONS/qmmm.xml -f state.hdf5 -j "write"
```

Running is easy

```
xtp_parallel -e qmmm -o OPTIONS/qmmm.xml -f state.hdf5 -j "run"
```

Read the results from the output file and store them in `state.hdf5`.

```
xtp_parallel -e qmmm -o OPTIONS/qmmm.xml -f state.hdf5 -j "read"
```

Basic results

The results of the QM/MM calculation can be found in the `qmmm_jobs.xml` file.
Every job has a new `<output>` section where the computed energies can be found.

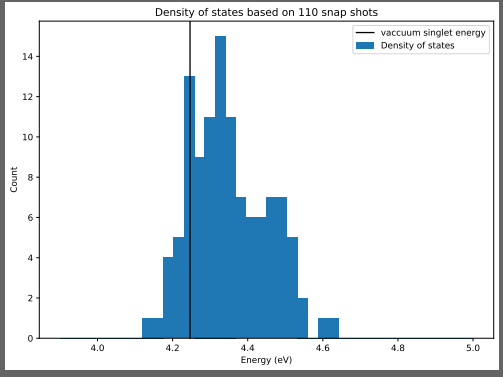
```
<output>
  <regions>
    <region Tot_charge="-3.200000e+01" id="0" size="1" type="qmregion">
      <E_total>-5252.342575</E_total>
    </region>
    <region Tot_charge="0.000000e+00" id="1" size="101" type="polarregion">
      <E_static>-30.978427</E_static>
      <E_polar>-9.246523</E_polar>
      <E_total>-40.224950</E_total>
    </region>
  </regions>
  <E_tot>-5292.567526</E_tot>
  <Compute_Time>24</Compute_Time>
  <Total_Charge>-32.000000</Total_Charge>
  <Iterations>4</Iterations>
</output>
```

NB. Only energy differences make sense here, hence to get the energy of the first singlet level we compute the difference between the total energy of the singlet job with the total energy of the groundstate, i.e. $\Omega_S = E_S - E_n$.

More advanced results: the density of states

To determine the density of states we can perform a QM/MM calculation for many configurations.

The picture on the right shows the density of states for the lowest energy singlet of acetone, computed for 110 configurations, and the vaccuum level as a reference.



The End