

Outline

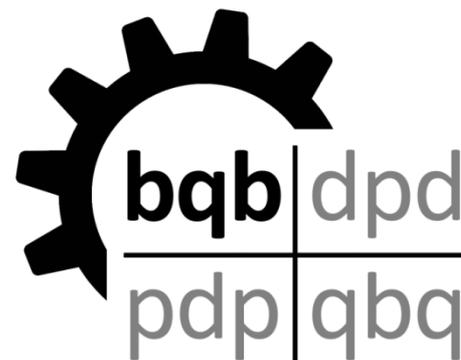
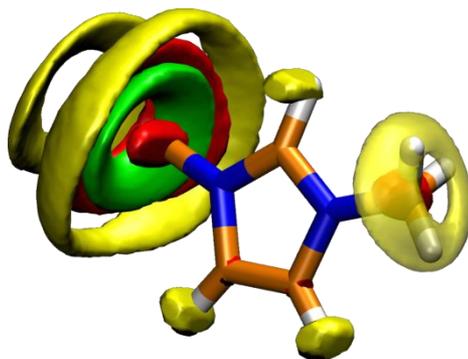
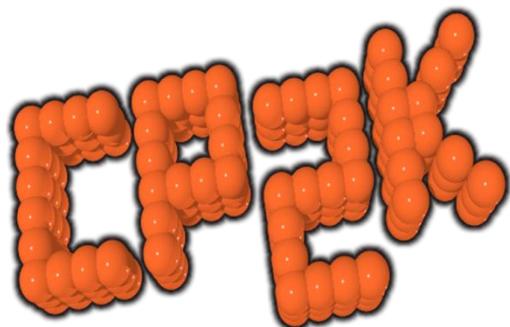
- 1.) Walkthrough of CP2k inputs
- 2.) Voronoi integration in CP2k
- 3.) bqb Compression in CP2k

Tutorial Available

A detailed **step-by-step tutorial** on how to compute IR / Raman / VCD / ROA spectra with CP2k and TRAVIS is available online:

<https://brehm-research.de/spectroscopy>

The tutorial also contains input files for TRAVIS and CP2k.



Tutorial for resonance Raman is still not online, sorry :-(
Will follow soon.

General Workflow

0. Preparation

→ *Starting configuration* **10 kiB**

1. Simulate trajectory

→ *XYZ file* **1 GiB**

2. Obtain electron density trajectories w/ ext. field

→ *CUBE files* **3 TiB**

3. Compress volumetric trajectories (optional)

→ *BQB files* **100 GiB**

4. Solve current PDE, perform Voronoi Integration

→ *EMP files* **1 GiB**

5. Compute spectra from EMP property files

→ *Spectra (text files)* **10 kiB**

General Workflow

0. Preparation

→ *Starting configuration* **10 kiB**

1. Simulate trajectory

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→ *CUBE files* **3 TiB**

3. Compress volumetric trajectories (optional)

→ *BQB files* **100 GiB**

4. Solve current PDE, perform Voronoi Integration

→ *EMP files* **1 GiB**

5. Compute spectra from EMP property files

→ *Spectra (text files)* **10 kiB**

CP2k

bqbttool

TRAVIS

0.) Preparation

- Decide on the system composition ☺
- Prepare bulk phase cell, e.g. with PackMol
- **Run force-field MD for equilibration (e.g. with OPLS-AA)**
- Extract the last snapshot as starting configuration for AIMD

```
&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    POTENTIAL_FILE_NAME POTENTIAL

  &MGRID
    CUTOFF 350
    NGRIDS 5
    REL_CUTOFF 40
  &END MGRID

  &QS
    EPS_DEFAULT 1.0E-12
    EXTRAPOLATION_ORDER 3
  &END QS

  &SCF
    SCF_GUESS ATOMIC
    MAX_SCF 15
    &OT
      PRECONDITIONER FULL_KINETIC
      MINIMIZER DIIS
    &END
    &OUTER_SCF
      MAX_SCF 20
      EPS_SCF 1.0E-6
    &END
    EPS_SCF 1.0E-6
    &PRINT
      &RESTART
      &EACH
        MD 0
      &END EACH
    &END
  &END
&END SCF
```

1.) Trajectory

a) Massive Equilibration (1/4)

```

&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    POTENTIAL_FILE_NAME POTENTIAL
    &MGRID
      CUTOFF 350
      NGRIDS 5
      REL_CUTOFF 40
    &END MGRID
  &QS
    EPS_DEFAULT 1.0E-12
    EXTRAPOLATION_ORDER 3
  &END QS
  &SCF
    SCF_GUESS ATOMIC
    MAX_SCF 15
    &OT
      PRECONDITIONER FULL_KINETIC
      MINIMIZER DIIS
    &END
    &OUTER_SCF
      MAX_SCF 20
      EPS_SCF 1.0E-6
    &END
    EPS_SCF 1.0E-6
    &PRINT
      &RESTART
      &EACH
        MD 0
      &END EACH
    &END
  &END
&END SCF

```

1.) Trajectory

a) Massive Equilibration (1/4)

- „Officially“, you would need to converge your PW cutoff...
- A PW cutoff of 350 Ry is typically Ok for organic liquids
- NGRIDS 5 is a good setting for MOLOPT basis sets
- REL_CUTOFF 40 is default, 50 is more accurate

```

&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    POTENTIAL_FILE_NAME POTENTIAL

    &MGRID
      CUTOFF 350
      NGRIDS 5
      REL_CUTOFF 40
    &END MGRID

    &QS
      EPS_DEFAULT 1.0E-12
      EXTRAPOLATION_ORDER 3
    &END QS

    &SCF
      SCF_GUESS ATOMIC
      MAX_SCF 15
      &OT
        PRECONDITIONER FULL_KINETIC
        MINIMIZER DIIS
      &END
      &OUTER_SCF
        MAX_SCF 20
        EPS_SCF 1.0E-6
      &END
      EPS_SCF 1.0E-6
      &PRINT
        &RESTART
          &EACH
            MD 0
          &END EACH
        &END
      &END
    &END SCF

```

1.) Trajectory

a) Massive Equilibration (1/4)

- EPS_DEFAULT of 10^{-12} is often a good compromise
- EXTRAPOLATION_ORDER can significantly influence the SCF convergence → optimize for long trajectories (typ. 2 ... 5)

```
&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    POTENTIAL_FILE_NAME POTENTIAL

  &MGRID
    CUTOFF 350
    NGRIDS 5
    REL_CUTOFF 40
  &END MGRID

  &QS
    EPS_DEFAULT 1.0E-12
    EXTRAPOLATION_ORDER 3
  &END QS

  &SCF
    SCF_GUESS ATOMIC
    MAX_SCF 15
    &OT
      PRECONDITIONER FULL_KINETIC
      MINIMIZER DIIS
    &END
    &OUTER_SCF
      MAX_SCF 20
      EPS_SCF 1.0E-6
    &END
    EPS_SCF 1.0E-6
  &PRINT
    &RESTART
    &EACH
      MD 0
    &END EACH
  &END
&END
&END SCF
```

1.) Trajectory

a) Massive Equilibration (1/4)

EPS_SCF should always be
square root of EPS_DEFAULT

→ EPS_DEFAULT 1.0E-12 means
EPS_SCF 1.0E-6

This is a good compromise for
SCF convergence.

```

&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    POTENTIAL_FILE_NAME POTENTIAL

  &MGRID
    CUTOFF 350
    NGRIDS 5
    REL_CUTOFF 40
  &END MGRID

  &QS
    EPS_DEFAULT 1.0E-12
    EXTRAPOLATION_ORDER 3
  &END QS

  &SCF
    SCF_GUESS ATOMIC
    MAX_SCF 15
    &OT
      PRECONDITIONER FULL_KINETIC
      MINIMIZER DIIS
    &END
    &OUTER_SCF
      MAX_SCF 20
      EPS_SCF 1.0E-6
    &END
    EPS_SCF 1.0E-6
    &PRINT
      &RESTART
      &EACH
        MD 0
      &END EACH
    &END
  &END
&END SCF

```

1.) Trajectory

a) Massive Equilibration (1/4)

- OT („Orbital Transformation“) is very fast and efficient for molecular liquids
- Choice of preconditioner is crucial for efficiency
- FULL_KINETIC is a fast choice for well-behaved MD runs
- If there are problems with SCF convergence, use FULL_SINGLE_INVERSE, or even FULL_ALL together with ENERGY_GAP 0.001

```

&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    POTENTIAL_FILE_NAME POTENTIAL

  &MGRID
    CUTOFF 350
    NGRIDS 5
    REL_CUTOFF 40
  &END MGRID

  &QS
    EPS_DEFAULT 1.0E-12
    EXTRAPOLATION_ORDER 3
  &END QS

  &SCF
    SCF_GUESS ATOMIC
    MAX_SCF 15
    &OT
      PRECONDITIONER FULL_KINETIC
      MINIMIZER DIIS
    &END
    &OUTER_SCF
      MAX_SCF 20
      EPS_SCF 1.0E-6
    &END
    EPS_SCF 1.0E-6
  &PRINT
    &RESTART
    &EACH
      MD 0
    &END EACH
  &END
&END
&END SCF

```

1.) Trajectory

a) Massive Equilibration (1/4)

- OUTER_SCF is important to cope with convergence problems, especially in the first steps
- Make sure to use the same EPS_SCF value at both positions!

```
&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    POTENTIAL_FILE_NAME POTENTIAL

  &MGRID
    CUTOFF 350
    NGRIDS 5
    REL_CUTOFF 40
  &END MGRID

  &QS
    EPS_DEFAULT 1.0E-12
    EXTRAPOLATION_ORDER 3
  &END QS

  &SCF
    SCF_GUESS ATOMIC
    MAX_SCF 15
    &OT
      PRECONDITIONER FULL_KINETIC
      MINIMIZER DIIS
    &END
    &OUTER_SCF
      MAX_SCF 20
      EPS_SCF 1.0E-6
    &END
    EPS_SCF 1.0E-6

  &PRINT
    &RESTART
      &EACH
        MD 0
      &END EACH
    &END
  &END
&END SCF
```

1.) Trajectory

a) Massive Equilibration (1/4)

- Stop printing WFN file in every MD step (*can be large → slows down the simulation*)

```
&XC
  &XC_FUNCTIONAL BLYP
  &END XC_FUNCTIONAL

  &XC_GRID
  XC_DERIV NN10_SMOOTH
  XC_SMOOTH_RHO NN10
  &END XC_GRID

  &vdW_POTENTIAL
  DISPERSION_FUNCTIONAL PAIR_POTENTIAL
  &PAIR_POTENTIAL
  TYPE DFTD3
  PARAMETER_FILE_NAME dftd3.dat
  REFERENCE_FUNCTIONAL BLYP
  &END PAIR_POTENTIAL
  &END vdW_POTENTIAL
&END XC
&END DFT

&SUBSYS
  &CELL
  ABC 19.8302 19.8302 19.8302
  &END CELL

  &COORD
  C 6.54092440 5.69704107 9.82218709
  H 6.10696440 5.01165107 10.56792709
  ...
  &END COORD
```

1.) Trajectory

a) Massive Equilibration (2/4)

&XC

```
&XC_FUNCTIONAL BLYP
&END XC_FUNCTIONAL
```

```
&XC_GRID
XC_DERIV NN10_SMOOTH
XC_SMOOTH_RHO NN10
&END XC_GRID
```

```
&vdW_POTENTIAL
DISPERSION_FUNCTIONAL PAIR_POTENTIAL
&PAIR_POTENTIAL
TYPE DFTD3
PARAMETER_FILE_NAME dftd3.dat
REFERENCE_FUNCTIONAL BLYP
&END PAIR_POTENTIAL
&END vdW_POTENTIAL
```

&END XC

&END DFT

&SUBSYS

```
&CELL
ABC 19.8302 19.8302 19.8302
&END CELL
```

&COORD

```
C 6.54092440 5.69704107 9.82218709
H 6.10696440 5.01165107 10.56792709
```

...

&END COORD

1.) Trajectory

a) Massive Equilibration (2/4)

- Take functional of your choice 😊
- For organic liquids, often BLYP and PBE are reasonable choices.

```

&XC
  &XC_FUNCTIONAL BLYP
  &END XC_FUNCTIONAL

  &XC_GRID
  XC_DERIV NN10_SMOOTH
  XC_SMOOTH_RHO NN10
  &END XC_GRID

  &vdW_POTENTIAL
  DISPERSION_FUNCTIONAL PAIR_POTENTIAL
  &PAIR_POTENTIAL
  TYPE DFTD3
  PARAMETER_FILE_NAME dftd3.dat
  REFERENCE_FUNCTIONAL BLYP
  &END PAIR_POTENTIAL
  &END vdW_POTENTIAL
&END XC
&END DFT

&SUBSYS
  &CELL
  ABC 19.8302 19.8302 19.8302
  &END CELL

  &COORD
  C 6.54092440 5.69704107 9.82218709
  H 6.10696440 5.01165107 10.56792709
  ...
  &END COORD

```

1.) Trajectory

a) Massive Equilibration (2/4)

- Smoothing mitigates the break of translational invariance due to the plane waves
- For cutoffs < 600 Ry (as we all use), this is **absolutely mandatory**

1.) Trajectory

a) Massive Equilibration (2/4)

- For organic liquids, you always want to use a dispersion correction
- Grimme's D3 is often a very good choice

```
&XC
  &XC_FUNCTIONAL BLYP
  &END XC_FUNCTIONAL

  &XC_GRID
    XC_DERIV NN10_SMOOTH
    XC_SMOOTH_RHO NN10
  &END XC_GRID

  &vdW_POTENTIAL
    DISPERSION_FUNCTIONAL PAIR_POTENTIAL
    &PAIR_POTENTIAL
      TYPE DFTD3
      PARAMETER_FILE_NAME dftd3.dat
      REFERENCE_FUNCTIONAL BLYP
    &END PAIR_POTENTIAL
  &END vdW_POTENTIAL
&END XC
&END DFT

&SUBSYS
  &CELL
    ABC 19.8302 19.8302 19.8302
  &END CELL

  &COORD
    C 6.54092440 5.69704107 9.82218709
    H 6.10696440 5.01165107 10.56792709
    ...
  &END COORD
```

1.) Trajectory

a) Massive Equilibration (3/4)

```
&KIND C
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-BLYP-q4
&END KIND
```

```
&KIND H
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-BLYP-q1
&END KIND
```

```
&KIND N
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-BLYP-q5
&END KIND
```

```
&END SUBSYS
&END FORCE_EVAL
```

```
&GLOBAL
  PROJECT SomeSystem
  RUN_TYPE MD
  PRINT_LEVEL LOW
  FFTW_PLAN_TYPE EXHAUSTIVE
  FFTW_WISDOM_FILE_NAME wisdom.dat
&END GLOBAL
```

1.) Trajectory

a) Massive Equilibration (3/4)

- Basis sets of the type DZVP-MOLOPT-SR-GTH are a **very good compromise** for computing spectra
- For non-homogeneous systems (gas phase, interfaces), you may want to leave out the „-SR-“
- For high accuracy, you can also go to TZVP or even TZVPP.

```
&KIND C
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-BLYP-q4
&END KIND
```

```
&KIND H
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-BLYP-q1
&END KIND
```

```
&KIND N
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-BLYP-q5
&END KIND
```

```
&END SUBSYS
&END FORCE_EVAL
```

```
&GLOBAL
  PROJECT SomeSystem
  RUN_TYPE MD
  PRINT_LEVEL LOW
  FFTW_PLAN_TYPE EXHAUSTIVE
  FFTW_WISDOM_FILE_NAME wisdom.dat
&END GLOBAL
```

1.) Trajectory

a) Massive Equilibration (3/4)

- This takes 1-2 minutes in the start of the run, but can make each MD step faster by $\approx 15\%$
- I recommend this for runs of 12 hours or longer
- The wisdom.dat file is written at the end, and makes FFT planning faster in following runs

```
&KIND C
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-BLYP-q4
&END KIND

&KIND H
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-BLYP-q1
&END KIND

&KIND N
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-BLYP-q5
&END KIND

&END SUBSYS
&END FORCE_EVAL

&GLOBAL
  PROJECT SomeSystem
  RUN_TYPE MD
  PRINT_LEVEL LOW
  FFTW_PLAN_TYPE EXHAUSTIVE
  FFTW_WISDOM_FILE_NAME wisdom.dat
&END GLOBAL
```

&MOTION

&MD

ENSEMBLE NVT

STEPS 2000

TIMESTEP 0.5

&THERMOSTAT

TYPE NOSE

REGION MASSIVE

&NOSE

TIMECON 10.00

&END NOSE

&END THERMOSTAT

TEMPERATURE 350

&END MD

&PRINT

&RESTART

BACKUP_COPIES 0

&EACH

MD 1

&END EACH

&END RESTART

&RESTART_HISTORY

&EACH

MD 0

&END EACH

&END RESTART_HISTORY

&END PRINT

&END MOTION

1.) Trajectory

a) Massive Equilibration (4/4)

```
&MOTION
```

```
&MD
```

```
ENSEMBLE NVT
```

```
STEPS 2000
```

```
TIMESTEP 0.5
```

```
&THERMOSTAT
```

```
TYPE NOSE
```

```
REGION MASSIVE
```

```
&NOSE
```

```
TIMECON 10.00
```

```
&END NOSE
```

```
&END THERMOSTAT
```

```
TEMPERATURE 350
```

```
&END MD
```

```
&PRINT
```

```
&RESTART
```

```
BACKUP_COPIES 0
```

```
&EACH
```

```
MD 1
```

```
&END EACH
```

```
&END RESTART
```

```
&RESTART_HISTORY
```

```
&EACH
```

```
MD 0
```

```
&END EACH
```

```
&END RESTART_HISTORY
```

```
&END PRINT
```

```
&END MOTION
```

1.) Trajectory

a) Massive Equilibration (4/4)

- If you have hydrogen atoms, always use $\Delta t = 0.5$ fs
- **Don't** feel tempted to 1.0 fs (as in force field MD); every MD step will take more SCF cycles, such that you save almost nothing
- Solving the current PDE (for VCD and ROA) requires 0.5 fs even if no hydrogen atoms are present.

&MOTION

&MD

ENSEMBLE NVT

STEPS 2000

TIMESTEP 0.5

&THERMOSTAT

TYPE NOSE

REGION MASSIVE

&NOSE

TIMECON 10.00

&END NOSE

&END THERMOSTAT

TEMPERATURE 350

&END MD

&PRINT

&RESTART

BACKUP_COPIES 0

&EACH

MD 1

&END EACH

&END RESTART

&RESTART_HISTORY

&EACH

MD 0

&END EACH

&END RESTART_HISTORY

&END PRINT

&END MOTION

1.) Trajectory

a) Massive Equilibration (4/4)

- Massive thermostating and rather strong coupling (time constant of 10 fs) in the start

&MOTION

&MD

ENSEMBLE NVT

STEPS 2000

TIMESTEP 0.5

&THERMOSTAT

TYPE NOSE

REGION MASSIVE

&NOSE

TIMECON 10.00

&END NOSE

~~&END THERMOSTAT~~

TEMPERATURE 350

&END MD

&PRINT

&RESTART

BACKUP_COPIES 0

&EACH

MD 1

&END EACH

&END RESTART

&RESTART_HISTORY

&EACH

MD 0

&END EACH

&END RESTART_HISTORY

&END PRINT

&END MOTION

1.) Trajectory

a) Massive Equilibration (4/4)

- Use temperature of your choice
- As AIMD runs are quite short (picoseconds), higher temperature helps to improve sampling
- As „room temperature“, we typically use 350K

&MOTION

&MD

ENSEMBLE NVT

STEPS 2000

TIMESTEP 0.5

&THERMOSTAT

TYPE NOSE

REGION MASSIVE

&NOSE

TIMECON 10.00

&END NOSE

&END THERMOSTAT

TEMPERATURE 350

&END MD

&PRINT

&RESTART

BACKUP_COPIES 0

&EACH

MD 1

&END EACH

&END RESTART

&RESTART_HISTORY

&EACH

MD 0

&END EACH

&END RESTART_HISTORY

&END PRINT

&END MOTION

1.) Trajectory

a) Massive Equilibration (4/4)

- Stop spamming all kinds of restart backup / history files
- Only one single restart file, which is written in every MD step

1.) Trajectory

a) Massive Equilibration

Run for ≈ 2000 time steps (1.0 ps)

```
&FORCE_EVAL
  &DFT
    &SCF
      SCF_GUESS RESTART
    &END SCF
  &END DFT
&END FORCE_EVAL

&MOTION
  &MD
    &THERMOSTAT
      REGION MASSIVE
      &NOSE
        TIMECON 100.00
      &END NOSE
    &END THERMOSTAT
  &END MD
&END MOTION

&EXT_RESTART
  EXTERNAL_FILE SomeSystem-1.restart
  RESTART_THERMOSTAT .FALSE.
&END
```

1.) Trajectory

b) Non-massive Equilibration

```
&FORCE_EVAL
  &DFT
    &SCF
      SCF_GUESS RESTART
    &END SCF
  &END DFT
&END FORCE_EVAL
```

```
&MOTION
  &MD
    &THERMOSTAT
      REGION MASSIVE
      &NOSE
        TIMECON 100.00
      &END NOSE
    &END THERMOSTAT
  &END MD
&END MOTION
```

```
&EXT_RESTART
  EXTERNAL_FILE SomeSystem-1.restart
  RESTART_THERMOSTAT .FALSE.
&END
```

1.) Trajectory

b) Non-massive Equilibration

- Restart from last WFN instead of initial guess

```
&FORCE_EVAL
  &DFT
    &SCF
      SCF_GUESS RESTART
    &END SCF
  &END DFT
&END FORCE_EVAL

&MOTION
  &MD
    &THERMOSTAT
      REGION MASSIVE
    &NOSE
      TIMECON 100.00
    &END NOSE
  &END THERMOSTAT
&END MD
&END MOTION

&EXT_RESTART
  EXTERNAL_FILE SomeSystem-1.restart
  RESTART_THERMOSTAT .FALSE.
&END
```

1.) Trajectory

b) Non-massive Equilibration

- Remove the „MASSIVE“ after the first equilibration phase

```
&FORCE_EVAL
  &DFT
    &SCF
      SCF_GUESS RESTART
    &END SCF
  &END DFT
&END FORCE_EVAL

&MOTION
  &MD
    &THERMOSTAT
      REGION MASSIVE
      &NOSE
        TIMECON 100.00
      &END NOSE
    &END THERMOSTAT
  &END MD
&END MOTION

&EXT_RESTART
  EXTERNAL_FILE SomeSystem-1.restart
  RESTART_THERMOSTAT .FALSE.
&END
```

1.) Trajectory

b) Non-massive Equilibration

- Weaker thermostat coupling (time constant 100 fs) for second equilibration and production run
- Strong thermostat coupling might distort the dynamics and spectra...

```
&FORCE_EVAL
  &DFT
    &SCF
      SCF_GUESS RESTART
    &END SCF
  &END DFT
&END FORCE_EVAL
```

```
&MOTION
  &MD
    &THERMOSTAT
      REGION MASSIVE
      &NOSE
        TIMECON 100.00
      &END NOSE
    &END THERMOSTAT
  &END MD
&END MOTION
```

```
&EXT_RESTART
  EXTERNAL_FILE SomeSystem-1.restart
  RESTART_THERMOSTAT .FALSE.
&END
```

1.) Trajectory

b) Non-massive Equilibration

- You need the EXT_RESTART block now
- Make sure the name of the restart file matches
- After turning off MASSIVE, you want RESTART_THERMOSTATE .FALSE.

1.) Trajectory

b) Non-massive Equilibration

Run for $\approx 20\,000$ time steps (10.0 ps)

```
&EXT_RESTART  
  EXTERNAL_FILE SomeSystem-1.restart  
  RESTART_THERMOSTAT.FALSE.  
&END
```

1.) Trajectory

c) Production Run

```
&EXT_RESTART
EXTERNAL_FILE SomeSystem-1_restart
RESTART_THERMOSTAT .FALSE.
&END
```

1.) Trajectory

c) Production Run

- Don't forget to remove
RESTART_THERMOSTATE .FALSE.
before starting production run

1.) Trajectory

c) Production Run

Run for $\approx 60\,000$ time steps (30.0 ps) to obtain high-quality spectra.

Now we have a 30 ps production trajectory which contains all motions for the spectra.

2.) Electron Density

- We traverse the trajectory again, and store volumetric electron density in every n -th frame
- For IR and VCD: Only one field-free calculation required
- For Raman and ROA: Field-free + 3 (or 6) field directions \rightarrow 4 runs
- Central finite differences (6 field runs, +/-) give more reliable results, but increase the computer time.
- For IR and Raman: Sufficient to consider every 8th frame (\rightarrow every 4.0 fs)
- For VCD and ROA: Need every frame (every 0.5 fs) to solve the PDE for the current

2.) Electron Density (1/2)

```
&FORCE_EVAL
  &DFT
    &PERIODIC_EFIELD
      INTENSITY 5.0E-3
      POLARISATION 1.0 0.0 0.0
    &END PERIODIC_EFIELD

    &PRINT
      &E_DENSITY_CUBE
        STRIDE 1 1 1
        FILENAME =result.cube
        APPEND
      &END
    &END PRINT

  &LOCALIZE
    METHOD CRAZY
    JACOBI_FALLBACK
    MAX_ITER 500
    &PRINT
      &WANNIER_CENTERS
        IONS+CENTERS
        FILENAME =wannier.xyz
      &EACH
        MD 1
      &END EACH
    &END
  &END PRINT
&END LOCALIZE

&END DFT
&END FORCE_EVAL
```

```
&FORCE_EVAL
```

```
&DFT
```

```
&PERIODIC_EFIELD
```

```
  INTENSITY 5.0E-3
```

```
  POLARISATION 1.0 0.0 0.0
```

```
&END PERIODIC_EFIELD
```

```
&PRINT
```

```
&E_DENSITY_CUBE
```

```
  STRIDE 1 1 1
```

```
  FILENAME =result.cube
```

```
  APPEND
```

```
&END
```

```
&END PRINT
```

```
&LOCALIZE
```

```
  METHOD CRAZY
```

```
  JACOBI_FALLBACK
```

```
  MAX_ITER 500
```

```
&PRINT
```

```
&WANNIER_CENTERS
```

```
  IONS+CENTERS
```

```
  FILENAME =wannier.xyz
```

```
&EACH
```

```
  MD 1
```

```
&END EACH
```

```
&END
```

```
&END PRINT
```

```
&END LOCALIZE
```

```
&END DFT
```

```
&END FORCE_EVAL
```

2.) Electron Density (1/2)

- We need an external electric field which works with periodic systems.
- An external field strength of $5.0E-3$ a.u. is a good compromise between noise and linearity (corresponds to $2.5 * 10^9$ V/m !)
- POLARIZATION gives the field vector (here: positive X direction)

2.) Electron Density (1/2)

```
&FORCE_EVAL
  &DFT
    &PERIODIC_EFIELD
      INTENSITY 5.0E-3
      POLARISATION 1.0 0.0 0.0
    &END PERIODIC_EFIELD

    &PRINT
      &E_DENSITY_CUBE
        STRIDE 1 1 1
        FILENAME =result.cube
        APPEND
      &END
    &END PRINT

  &LOCALIZE
    METHOD CRAZY
    JACOBI_FALLBACK
    MAX_ITER 500
    &PRINT
      &WANNIER_CENTERS
        IONS+CENTERS
        FILENAME =wannier.xyz
      &EACH
        MD 1
      &END EACH
    &END
  &END PRINT
&END LOCALIZE

&END DFT
&END FORCE_EVAL
```

- Write the electron density in each MD step to a CUBE trajectory
- STRIDE 1 1 1 is vital for Voronoi integration

2.) Electron Density (1/2)

```
&FORCE_EVAL
  &DFT
    &PERIODIC_EFIELD
      INTENSITY 5.0E-3
      POLARISATION 1.0 0.0 0.0
    &END PERIODIC_EFIELD

    &PRINT
      &E_DENSITY_CUBE
        STRIDE 1 1 1
        FILENAME =result.cube
        APPEND
      &END
    &END PRINT

    &LOCALIZE
      METHOD CRAZY
      JACOBI_FALLBACK
      MAX_ITER 500
      &PRINT
        &WANNIER_CENTERS
          IONS+CENTERS
          FILENAME =wannier.xyz
          &EACH
            MD 1
          &END EACH
        &END
      &END PRINT
    &END LOCALIZE

  &END DFT
&END FORCE_EVAL
```

- Don't compute Wannier centers if you don't have to (can waste a lot of time if CRAZY does not converge)
- If you really need it, insert this section
- Higher numbers for MAX_ITER typically are of no use (if it did not converge after 500 iterations, it will often never converge)

2.) Electron Density (2/2)

```
&MOTION
  &MD
    ENSEMBLE REFTRAJ
    STEPS 1024
    &REFTRAJ
      EVAL_ENERGY_FORCES
      FIRST_SNAPSHOT 1
      TRAJ_FILE_NAME SomeSystem-pos-1.xyz
    &END REFTRAJ
  &END MD
&PRINT
  &RESTART
    &EACH
      MD 0
    &END EACH
  &END RESTART
  &RESTART_HISTORY
    &EACH
      MD 0
    &END EACH
  &END RESTART_HISTORY
&END PRINT
&END MOTION
```

```
&EXT_RESTART
  EXTERNAL_FILE SomeSystem-1.restart
&END
```

&MOTION

```
&MD
  ENSEMBLE REFTRAJ
  STEPS 1024
  &REFTRAJ
    EVAL_ENERGY_FORCES
    FIRST_SNAPSHOT 1
    TRAJ_FILE_NAME SomeSystem-pos-1.xyz
  &END REFTRAJ
&END MD
```

```
&PRINT
  &RESTART
    &EACH
      MD 0
    &END EACH
  &END RESTART
  &RESTART_HISTORY
    &EACH
      MD 0
    &END EACH
  &END RESTART_HISTORY
&END PRINT
&END MOTION
```

```
&EXT_RESTART
  —EXTERNAL_FILE SomeSystem-1.restart
&END
```

2.) Electron Density (2/2)

- Follow the pre-computed reference trajectory instead of doing a „true“ MD
- Make sure to specify the correct reference trajectory file name
- Enter the FIRST_SNAPSHOT and STEPS according to your needs
- EVAL_ENERGY_FORCES is important to re-compute the electron structure

2.) Electron Density (2/2)

```
&MOTION
  &MD
    ENSEMBLE REFTRAJ
    STEPS 1024
    &REFTRAJ
      EVAL_ENERGY_FORCES
      FIRST_SNAPSHOT 1
      TRAJ_FILE_NAME SomeSystem-pos-1.xyz
    &END REFTRAJ
  &END MD
  &PRINT
    &RESTART
      &EACH
        MD 0
      &END EACH
    &END RESTART
    &RESTART_HISTORY
      &EACH
        MD 0
      &END EACH
    &END RESTART_HISTORY
  &END PRINT
&END MOTION
```

```
&EXT_RESTART
  EXTERNAL_FILE SomeSystem-1.restart
&END
```

- This time: No restart files at all, because we just follow the reference trajectory

&MOTION

&MD

ENSEMBLE REFTRAJ

STEPS 1024

&REFTRAJ

EVAL_ENERGY_FORCES

FIRST_SNAPSHOT 1

TRAJ_FILE_NAME SomeSystem-pos-1.xyz

&END REFTRAJ

&END MD

&PRINT

&RESTART

&EACH

MD 0

&END EACH

&END RESTART

&RESTART_HISTORY

&EACH

MD 0

&END EACH

&END RESTART_HISTORY

&END PRINT

&END MOTION

~~&EXT_RESTART~~

~~—EXTERNAL_FILE SomeSystem-1.restart~~

~~&END~~

2.) Electron Density (2/2)

- EXT_RESTART section not required for ENSEMBLE REFTRAJ.

3.) Compress Volumetric Trajectories (Optional)

- Using the `bqbtool`, we can compress the CUBE trajectories
- Typical saving of space is factor 30 – 40 (for $\Delta t = 0.5$ fs)

→ Gigabytes instead of Terabytes

Takes ≈ 5 seconds per frame on 1 CPU core

- If you don't want to keep the electron density data, you can leave out this step

Command:

```
bqbtool compress voltraj result.cube result.bqb
```

or

```
travis compress voltraj result.cube result.bqb
```

4.) Solve current PDE, perform Voronoi Integration

For every atom in each trajectory frame, we want to compute the electromagnetic properties („EMP“). These include:

- Electric dipole vector *(for IR, Raman, VCD, ROA)*
- Electric quadrupole tensor *(for ROA)*
- Electric current vector *(for VCD, ROA)*
- Magnetic dipole vector *(for VCD, ROA)*

This gives one EMP file per trajectory.

Takes around 1 second per frame *(only electric moments)*
or around 15 seconds per frame *(magnetic moments required)*.

If we have trajectories with external electric field,
we can compute the polarizabilities by finite differences.

Details: See tutorial on my homepage!

5.) Compute spectra from EMP property files

Supply the single field-free EMP file (*for IR, VCD*)
or the set of four (*or seven*) EMP files (*for Raman, ROA*) to TRAVIS.

Computation of spectra from EMP files
takes $\approx 1 - 2$ minutes in total 😊

All computationally demanding parts
have already been performed before.

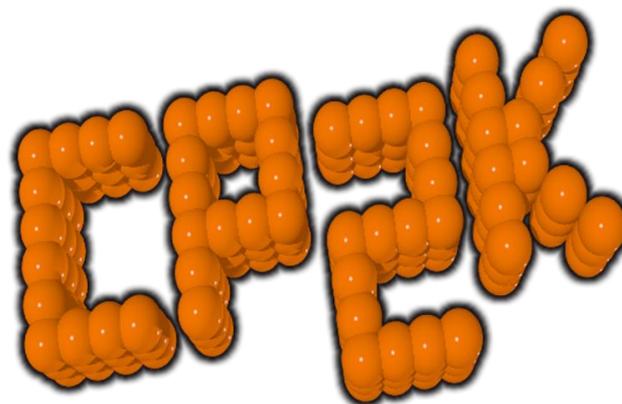
Details: See tutorial on my homepage!

`https://brehm-research.de/spectroscopy`

Voronoi Integration in CP2k

Since 2021, the Voronoi integration is available directly inside of CP2k (*from v8.1*) via „libvori“!

```
&DFT  
  &PRINT  
    &VORONOI  
      ...  
    &END VORONOI  
  &END PRINT  
&END DFT
```



→ see CP2k manual

Literature:

M. Thomas, M. Brehm, B. Kirchner, *Phys. Chem. Chem. Phys.* **2015**, *17*, 3207–3213.

M. Brehm, M. Thomas, *Molecules* **2021**, *26* (7), 1875.

Voronoi Integration in CP2k

→ You can directly write a „properties.emp“ file during the AIMD production run.

No need to store intermediary .cube files.

Can also be combined with ENSEMBLE REFTRAJ to obtain the polarizabilities for Raman spectra.

Classical PDE for the currents not yet implemented in CP2k...
For VCD and ROA, still need to write volumetric electron density.

Literature:

M. Thomas, M. Brehm, B. Kirchner, *Phys. Chem. Chem. Phys.* **2015**, *17*, 3207–3213.

M. Brehm, M. Thomas, *Molecules* **2021**, *26* (7), 1875.

Voronoi Integration in CP2k

Example input:

```
&DFT
  &PRINT
    &VORONOI
      OUTPUT_TEXT .FALSE.
      OUTPUT_EMP
      SKIP_FIRST
      VORONOI_RADII VDW
      SANITY_CHECK
    &END VORONOI
  &END PRINT
&END DFT
```

Literature:

M. Thomas, M. Brehm, B. Kirchner, *Phys. Chem. Chem. Phys.* **2015**, *17*, 3207–3213.

M. Brehm, M. Thomas, *Molecules* **2021**, *26* (7), 1875.

Voronoi Integration in CP2k

Example input:

```
&DFT
  &PRINT
    &VORONOI
      OUTPUT_TEXT .FALSE.
      OUTPUT_EMP
      SKIP_FIRST
      VORONOI_RADII VDW
      SANITY_CHECK
    &END VORONOI
  &END PRINT
&END DFT
```

Disables the text output
of Voronoi results
(*unnecessary and large*)

Literature:

M. Thomas, M. Brehm, B. Kirchner, *Phys. Chem. Chem. Phys.* **2015**, *17*, 3207–3213.

M. Brehm, M. Thomas, *Molecules* **2021**, *26* (7), 1875.

Voronoi Integration in CP2k

Example input:

```
&DFT
  &PRINT
    &VORONOI
      OUTPUT_TEXT .FALSE.
      OUTPUT_EMP
      SKIP_FIRST
      VORONOI_RADII VDW
      SANITY_CHECK
    &END VORONOI
  &END PRINT
&END DFT
```

Writes a „properties.emp“
binary file which TRAVIS
can read later.

(appended by default)

Literature:

M. Thomas, M. Brehm, B. Kirchner, *Phys. Chem. Chem. Phys.* **2015**, *17*, 3207–3213.

M. Brehm, M. Thomas, *Molecules* **2021**, *26* (7), 1875.

Voronoi Integration in CP2k

Example input:

```
&DFT
  &PRINT
    &VORONOI
      OUTPUT_TEXT .FALSE.
      OUTPUT_EMP
      SKIP_FIRST
      VORONOI_RADII VDW
      SANITY_CHECK
    &END VORONOI
  &END PRINT
&END DFT
```

Skips the Voronoi integration for the first frame of a CP2k run.

(required for restarts to not have duplicate frames in „properties.emp“ file)

Literature:

M. Thomas, M. Brehm, B. Kirchner, *Phys. Chem. Chem. Phys.* **2015**, 17, 3207–3213.

M. Brehm, M. Thomas, *Molecules* **2021**, 26 (7), 1875.

Voronoi Integration in CP2k

Example input:

```
&DFT
  &PRINT
    &VORONOI
      OUTPUT_TEXT .FALSE.
      OUTPUT_EMP
      SKIP_FIRST
      VORONOI_RADII VDW
      SANITY_CHECK
    &END VORONOI
  &END PRINT
&END DFT
```

Which radii to use for the radical Voronoi tessellation.

VdW radii are a very good choice for computing spectra.

Literature:

M. Thomas, M. Brehm, B. Kirchner, *Phys. Chem. Chem. Phys.* **2015**, *17*, 3207–3213.

M. Brehm, M. Thomas, *Molecules* **2021**, *26* (7), 1875.

Voronoi Integration in CP2k

Example input:

```
&DFT
  &PRINT
    &VORONOI
      OUTPUT_TEXT .FALSE.
      OUTPUT_EMP
      SKIP_FIRST
      VORONOI_RADII VDW
      SANITY_CHECK
    &END VORONOI
  &END PRINT
&END DFT
```

Performs a sanity check for the Voronoi integration of each frame.

Makes sure that everything is correct, but takes extra time.

→ Not for production run.

Literature:

M. Thomas, M. Brehm, B. Kirchner, *Phys. Chem. Chem. Phys.* **2015**, *17*, 3207–3213.

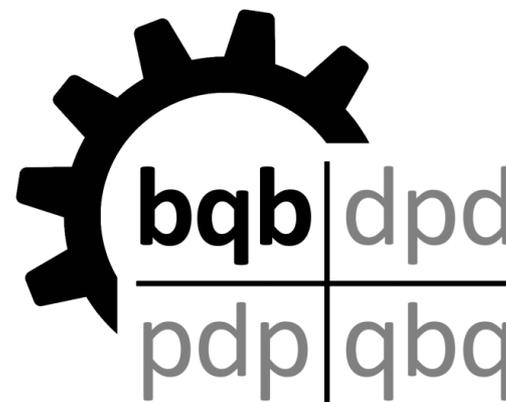
M. Brehm, M. Thomas, *Molecules* **2021**, *26* (7), 1875.

bqb Compression in CP2k

Since 2021, the bqb compression of total electron density is available directly inside of CP2k (*from v8.1*)!

```
&DFT
  &PRINT
    &E_DENSITY_BQB
    ...
  &END E_DENSITY_BQB
&END PRINT
&END DFT
```

→ see CP2k manual



Literature:

M. Brehm, M. Thomas, *J. Chem. Inf. Model.* **2018**, *58* (10), 2092–2107.

bqb Compression in CP2k

Example input:

```
&DFT
  &PRINT
    &E_DENSITY_BQB
      &EACH
        MD 4
      &END EACH
    FILENAME result.bqb
    CHECK
    HISTORY 10
    OPTIMIZE QUICK
    SKIP_FIRST
  &END E_DENSITY_BQB
&END PRINT
&END DFT
```

Literature:

M. Brehm, M. Thomas, *J. Chem. Inf. Model.* **2018**, *58* (10), 2092–2107.

bqb Compression in CP2k

Example input:

```
&DFT
  &PRINT
    &E_DENSITY_BQB
      &EACH
        MD 4
      &END EACH
    FILENAME result.bqb
    CHECK
    HISTORY 10
    OPTIMIZE QUICK
    SKIP_FIRST
  &END E_DENSITY_BQB
&END PRINT
&END DFT
```

Write electron density
every 4th frame only.

Literature:

M. Brehm, M. Thomas, *J. Chem. Inf. Model.* **2018**, 58 (10), 2092–2107.

bqb Compression in CP2k

Example input:

```
&DFT
  &PRINT
    &E_DENSITY_BQB
      &EACH
        MD 4
      &END EACH
    FILENAME result.bqb
    CHECK
    HISTORY 10
    OPTIMIZE QUICK
    SKIP_FIRST
  &END E_DENSITY_BQB
&END PRINT
&END DFT
```

bqb output file name
(appended by default)

Literature:

M. Brehm, M. Thomas, *J. Chem. Inf. Model.* **2018**, 58 (10), 2092–2107.

bqb Compression in CP2k

Example input:

```
&DFT
  &PRINT
    &E_DENSITY_BQB
      &EACH
        MD 4
      &END EACH
    FILENAME result.bqb
    CHECK
    HISTORY 10
    OPTIMIZE QUICK
    SKIP_FIRST
  &END E_DENSITY_BQB
&END PRINT
&END DFT
```

Checks if the compression was correct and lossless by decompressing and comparing the frame.

Takes time, don't activate during production run.

Literature:

M. Brehm, M. Thomas, *J. Chem. Inf. Model.* **2018**, 58 (10), 2092–2107.

bqb Compression in CP2k

Example input:

```
&DFT
  &PRINT
    &E_DENSITY_BQB
      &EACH
        MD 4
      &END EACH
    FILENAME result.bqb
    CHECK
    HISTORY 10
    OPTIMIZE QUICK
    SKIP_FIRST
  &END E_DENSITY_BQB
&END PRINT
&END DFT
```

How many previous volumetric frames to use for the extrapolation.

Controls efficiency, default is 10.

Literature:

M. Brehm, M. Thomas, *J. Chem. Inf. Model.* **2018**, 58 (10), 2092–2107.

bqb Compression in CP2k

Example input:

```
&DFT
  &PRINT
    &E_DENSITY_BQB
      &EACH
        MD 4
      &END EACH
    FILENAME result.bqb
    CHECK
    HISTORY 10
    OPTIMIZE QUICK
    SKIP_FIRST
  &END E_DENSITY_BQB
&END PRINT
&END DFT
```

Optimizes the compression parameters on-the-fly from the first few frames.

Takes some time (*depending on the level*), but significantly improves compression ratio!

Literature:

M. Brehm, M. Thomas, *J. Chem. Inf. Model.* **2018**, 58 (10), 2092–2107.

bqb Compression in CP2k

Example input:

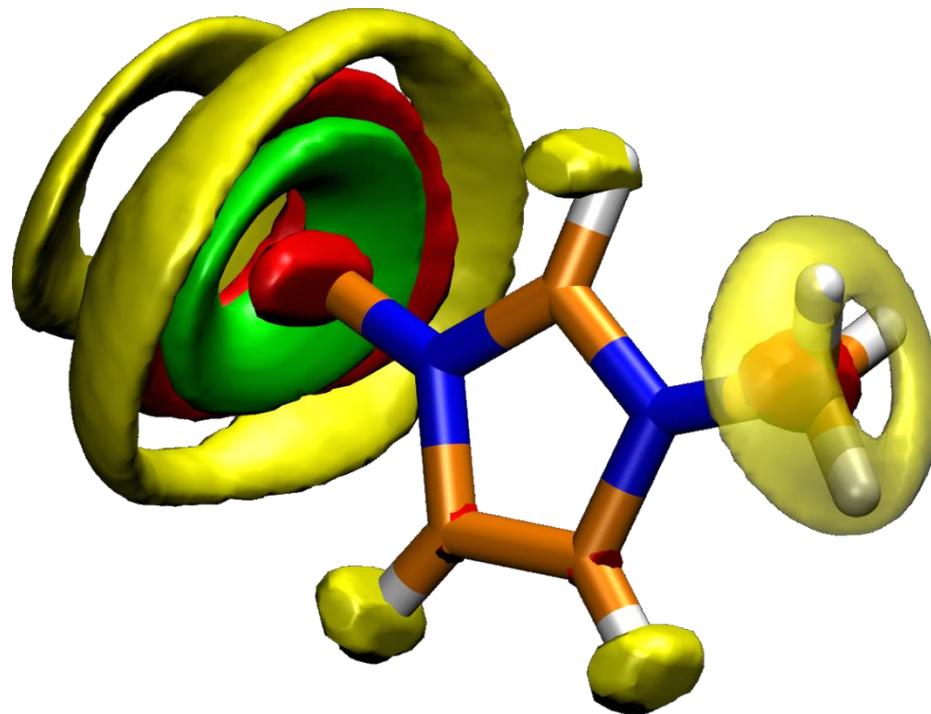
```
&DFT
  &PRINT
    &E_DENSITY_BQB
      &EACH
        MD 4
      &END EACH
    FILENAME result.bqb
    CHECK
    HISTORY 10
    OPTIMIZE QUICK
    SKIP_FIRST
  &END E_DENSITY_BQB
&END PRINT
&END DFT
```

Skips the bqb compression for the first frame of a CP2k run.

(required for restarts to not have duplicate frames in „properties.emp“ file)

Literature:

M. Brehm, M. Thomas, *J. Chem. Inf. Model.* **2018**, 58 (10), 2092–2107.



Thank you for your attention!