Introduction to Advanced Sampling in CP2K: multiple time-step MD

Vladimir Rybkin

University of Zurich, Department of Chemistry

13.07.2017
Reference system propagator algorithm, RESPA

Liouville operator representation of Hamiltonian mechanics:

\[
iL = \sum_{j=1}^{f} \left[ \frac{\partial H}{\partial p_j} \frac{\partial}{\partial x_j} + \frac{\partial H}{\partial x_j} \frac{\partial}{\partial p_j} \right]
\]

Classical propagator:

\[
U(t) = e^{iLt}
\]

Decomposition into several forces:

\[
iL = \sum_{j=1}^{f} \left[ \dot{x}_j \frac{\partial}{\partial x_j} + F^1_j \frac{\partial}{\partial p_j} + F^2_j \frac{\partial}{\partial p_j} \right]
\]
The **multistep** propagator:

\[
e^{iL\Delta t} =
\]

\[
e^{(\Delta t/2)F^2(\frac{\partial}{\partial p})} \left[ e^{(\delta t/2)F^1(\frac{\partial}{\partial p})} e^{\delta t \dot{x}_j} e^{(\delta t/2)F^1(\frac{\partial}{\partial p})} \right]^n e^{(\Delta t/2)F^2(\frac{\partial}{\partial p})}
\]

\( \delta t \) is not equal to \( \Delta t \)!

\[
F^1 = F^{\text{cheap}}
\]

\[
F^2 = F^{\text{expensive}} - F^{\text{cheap}}
\]

Possible methods:

- Cheap: GGA DFT, small basis sets etc.
- Expensive: hybrid DFT, MP2, large basis sets etc.
Input: RESPA

Motion section:

```
&MD
  &RESPA
    FREQUENCY 6
  &END RESPA
END MD
ENSEMBLE NVE
STEPS 1000
TIMESTEP 1.5
```

- Cheap forces every 1.5 fs
- Expensive forces every 0.25 fs - 6 substeps inbetween

Core section:

```
&MULTIPLE_FORCE_EVALS
  ! 1 is the cheap one
  ! 2 is the expensive
  FORCE_EVAL_ORDER 2 1
  MULTIPLE_SUBSYS
&END
```
Multiple times-step integration stability

\((\text{H}_2\text{O})_6\) cluster with PBE (cheap) and HSE06 (expensive)

\[ \delta t = 0.5 \text{ fs}, \quad \Delta t = n \times \delta t: \text{ stable until 4 fs between expensive forces evaluation!} \]
IR spectrum of liquid water from MP2 MD

- Dynamic property: requires dipole moment time-autocorrelation function (need for MD)
- Bulk water with 64 H$_2$O cell
- $\delta t = 0.25$ fs, $\Delta t = 6 \times \delta t = 1.5$ fs; PBE and MP2
- Total of 10 ps: ca. 3 times cheaper than pure MP2 (with 0.5 fs step)
Cavity formation in the bulk hydrated electron

Figure: 0 ps: delocalized

Figure: 0.5 ps: irregular cavity

Figure: 1 ps: regular cavity
Conclusions

- Multiple time-step MD (RESPA in CP2K) significantly accelerates integration with expensive methods (hybrid DFT, MP2)
- Available for NVE ensembles
- Can be extended to accelerated path-integral MD (lectures tomorrow!)

Literature:

- **General**: D. Frenkel and B. Smit, Understanding Molecular Simulation
- **Liquid water**: M. Del Ben, J. Hutter, and J. VandeVondele, JCP 143, 054506 (2015).