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

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13.07.2017

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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:

$$iL = \sum_{j=1}^{f} \left[\dot{x}_j \frac{\partial}{\partial x_j} + F_j^1 \frac{\partial}{\partial p_j} + F_j^2 \frac{\partial}{\partial p_j} \right]$$

RESPA

The **multistep** propagator:

$$e^{iL\Delta t} =$$

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

δt is not equal to Δt!

$$F^1 = F^{cheap}$$

$$F^2 = F^{expensive} - F^{cheap}$$

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
    ENSEMBLE NVE
    STEPS  1000
    TIMESTEP 1.5
&END MD
```

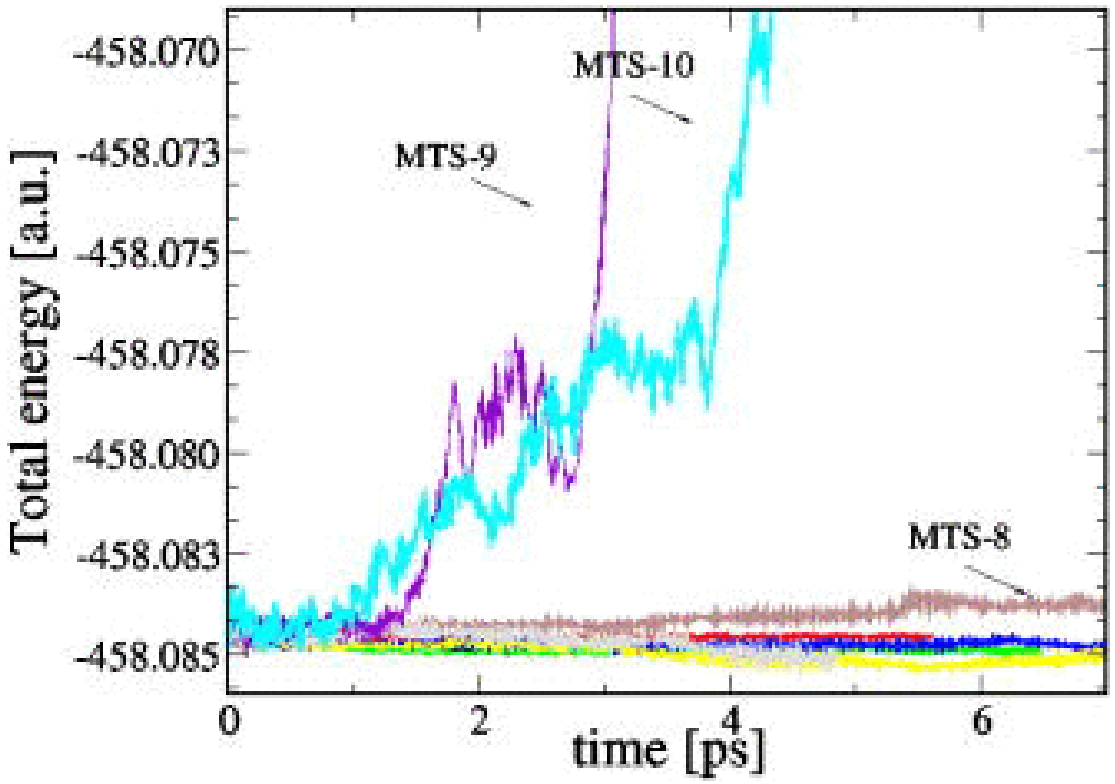
Core section:

```
&MULTIPLE_FORCE_EVALS
! 1 is the cheap one
! 2 is the expensive
   FORCE_EVAL_ORDER 2 1
   MULTIPLE_SUBSYS
&END
```

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

Multiple times-step integration stability

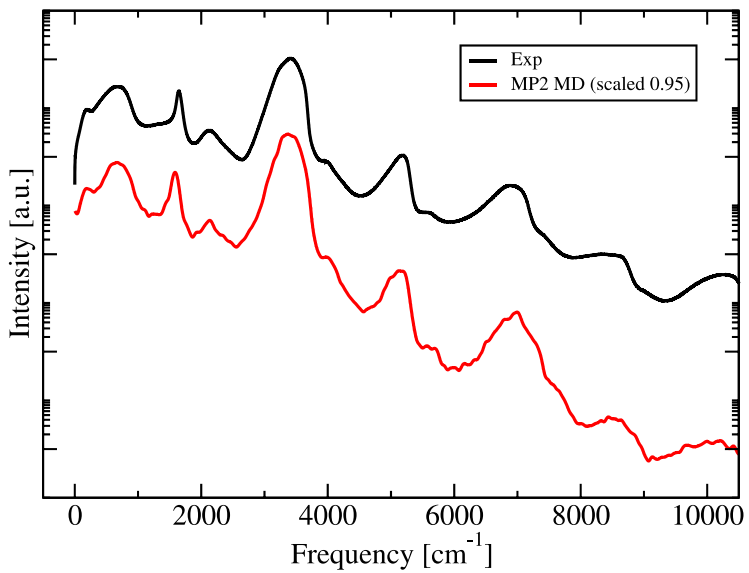
$(H_2O)_6$ cluster with PBE (cheap) and HSE06 (expensive)



$\delta t = 0.5$ fs, $\Delta t = n * \delta t$: 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_2O cell
- $\delta t = 0.25$ fs, $\Delta t = 6 * \delta t = 1.5$ 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

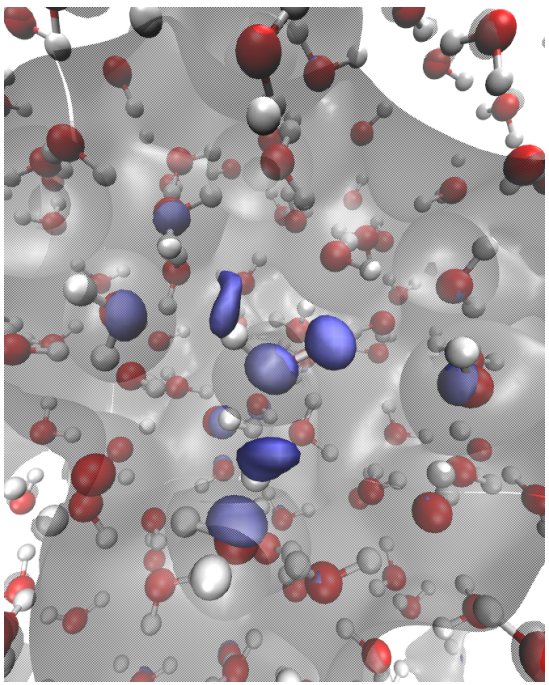


Figure: **0 ps**: delocalized

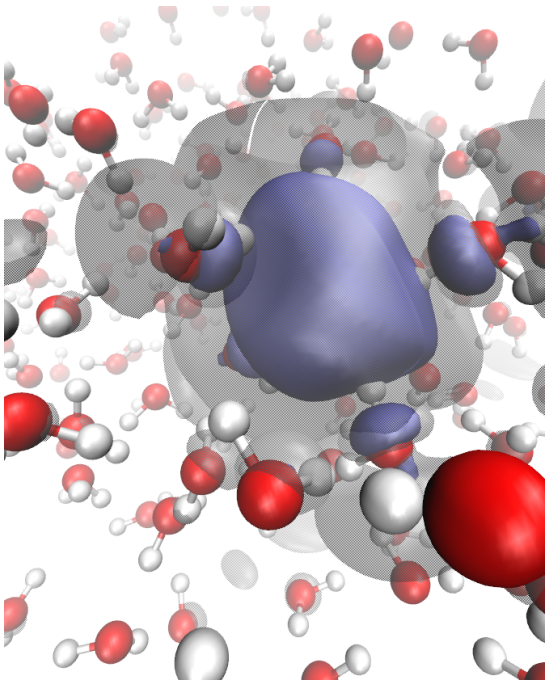


Figure: **0.5 ps**: irregular cavity

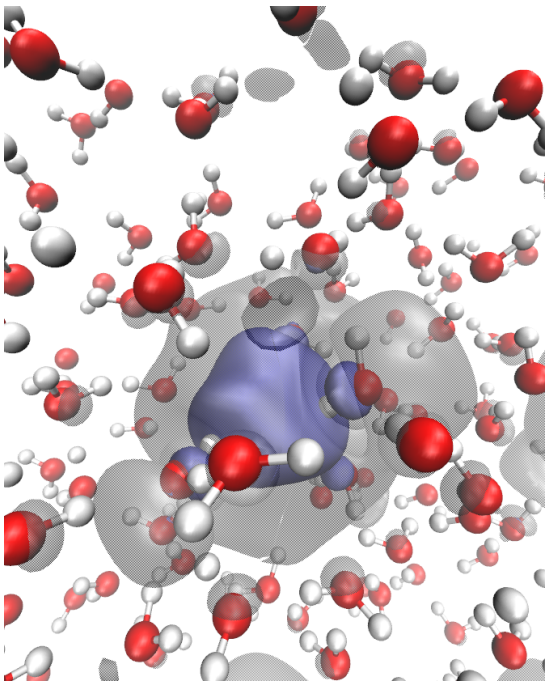


Figure: **1 ps**: regular cavity

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
- **RESPA in CP2K**: M. Guidon, F. Schiffmann, J. Hutter, and J. VandeVondele, JCP **128**, 214104 (2008).
- **Liquid water**: M. Del Ben, J. Hutter, and J. VandeVondele, JCP **143**, 054506 (2015).