Ehrenfest Dynamics for Weakly-Bound Complexes in FHI-aims

FHI-aims Developers' and Users' Meeting 2026

MPI for the Structure and Dynamics of Matter, Hamburg

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mpsd

SABIA Simulations from Ab Initio Approaches Structure and Dynamics from Quantum Mechanics

TIMES

Energy redistribution at interfaces

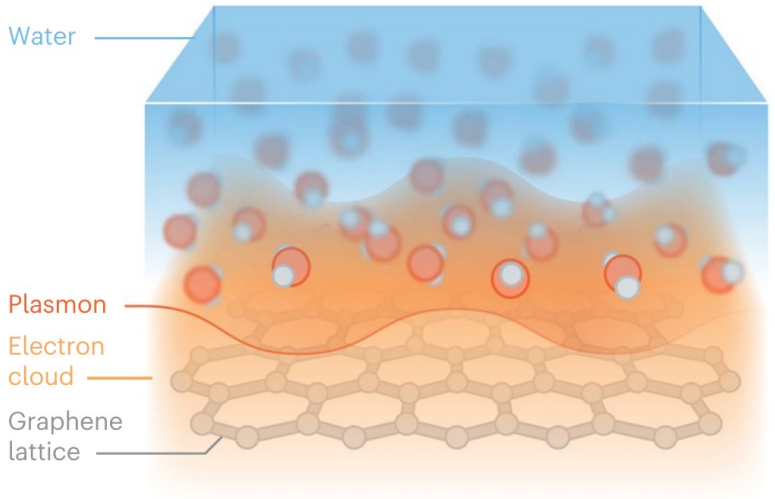
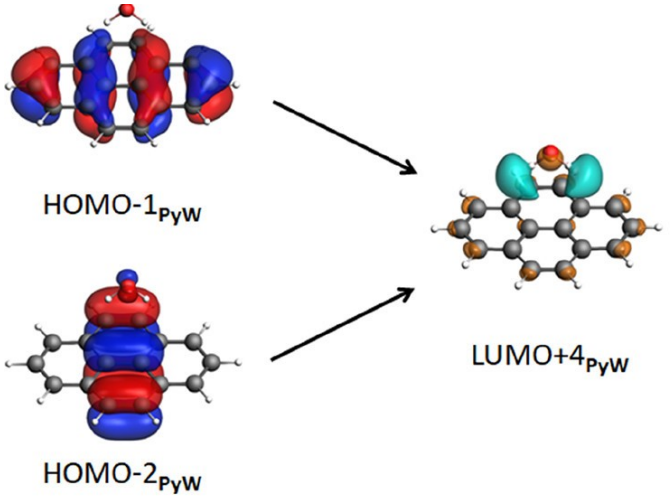


Fig. 1 | Heat transfer and friction at the solid–liquid interface

Yu, X. et al. Nat. Nanotechnol. 18, 898-904 (2023).

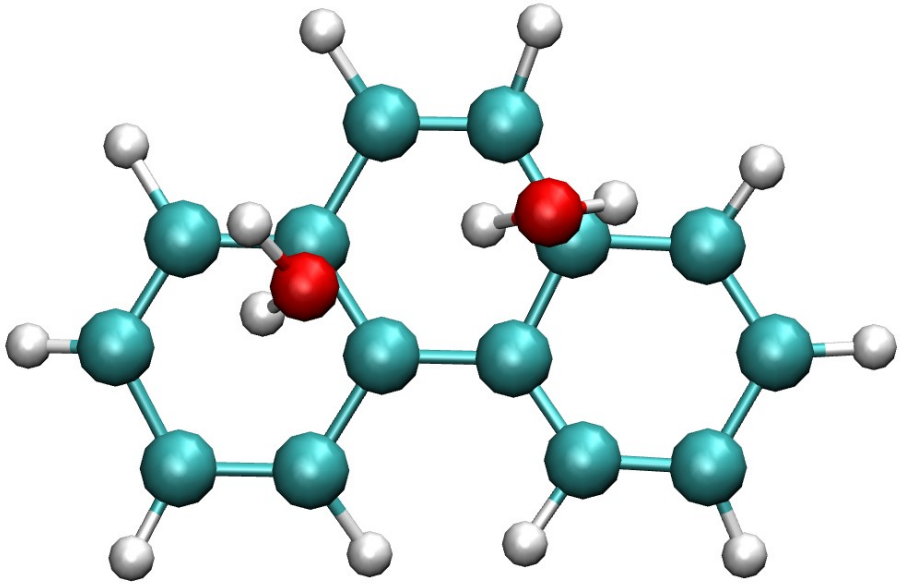


ten Brinck, S. et al. ACS Earth and Space Chem. 6 (3), 766-774 (2022).

- Simulate excitation dynamics in real-time
- Take into account nuclear dynamics

An interface prototype: $(H_2O)_2$ on phenanthrene

- Excite electronic charge transfer from phenanthrene to water dimer
  → application of electric field
- Water dimer weakly-bound to phenanthrene → disperision forces
- Many local minima for adsorption of water dimer



RT-TDDFT and Ehrenfest dynamics in FHI-aims

Real-time time-dependent density functional theory (RT-TDDFT)[1]:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi_n(\boldsymbol{r},t) = \left\{-\frac{1}{2}\nabla^2 + V_{\mathrm{en}}[\boldsymbol{r},\{\boldsymbol{R}\}(t)] + V_{\mathrm{H}}[\rho] + V_{\mathrm{xc}}[\rho] + V_{\mathrm{ext}}[\boldsymbol{r},t]\right\}\psi_n(\boldsymbol{r},t) \qquad V_{\mathrm{ext}}[\boldsymbol{r},t] = \boldsymbol{r}\cdot\boldsymbol{E}(t)$$

$$\rho(\boldsymbol{r},t) = \sum_{n=1}^{N_{occ}} |\psi_n(\boldsymbol{r},t)|^2$$

- Propagate electronic density in real-time
- Include interaction with external time-dependent field

Ehrenfest dynamics[2]:

$$M_I\frac{d^2}{dt^2}\boldsymbol{R}_I(t) = -\nabla_{\boldsymbol{R}_I}\left[V_{\mathrm{nn}}(\{\boldsymbol{R}\}) + \int V_{\mathrm{en}}(\boldsymbol{r},\{\boldsymbol{R}\})\rho(\boldsymbol{r},t)\; d^3r + V_{\mathrm{ext}}(\{\boldsymbol{R}\},t)\right]$$

- Classical nuclear dynamics
- Mean-field nonadiabatic

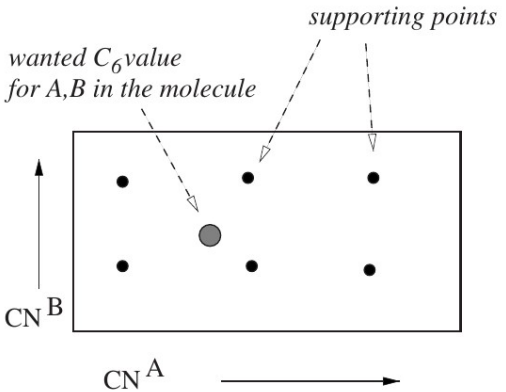
[1]Hekele, J. et al. J. Chem. Phys. 155, 154801 (2021)
[2]Xu, J. et al. J. Chem. Phys. 161, 194109 (2024)

Dispersion interactions

$$E_{\text{disp}}^{(2)} = -\frac{1}{2}\sum_{AB} f_{\text{damp}}(R_{AB}, R_A^0, R_B^0) C_{6AB} R_{AB}^{-6}$$

Grimme D3[1]:

- Based on geometric coordination number (CN)



- Atom-pairwise dispersion coefficients
  → depends on chemical environment

Tkatchenko-Scheffler[2]:

$$C_{6AA} \approx \left(\frac{V_A^{\text{eff}}}{V_A^{\text{free}}}\right)^2 C_{6AA}^{\text{free}}$$

- Effective volume of an atom in a molecule
- Hirshfeld partitioning of the electronic density

- Practical approximation in excited states

[1]Grimme, S. et al. J. Chem. Phys. 132, 154104 (2010)
[2]Tkatchenko, A. and Scheffler, M. Phys. Rev. Lett. 102, 073005 (2009)

Dispersion interactions for Ehrenfest dynamics in FHI-aims

in `control.in`:

`d3`

`vdw_correction_hirshfeld`

in `subroutine collect_time_dependent_forces`:

`call calc_dftd3(en_vdw, vdw_forces)`

- Uses instantaneous Ehrenfest geometry

- Make sure density calculated for all grid points

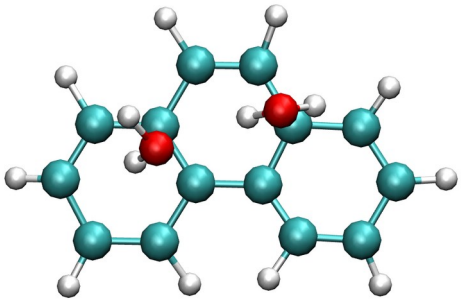
`call calc_vdw_hirshfeld(en_vdw, vdw_forces)`

- Uses instantaneous Ehrenfest geometry
- and density

output `en_vdw`
add `vdw_forces` to total forces

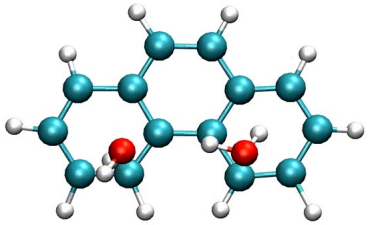
Modelling electronic charge transfer dynamics

Sampling of initial conditions



Modelling electronic charge transfer dynamics

Sampling of initial conditions

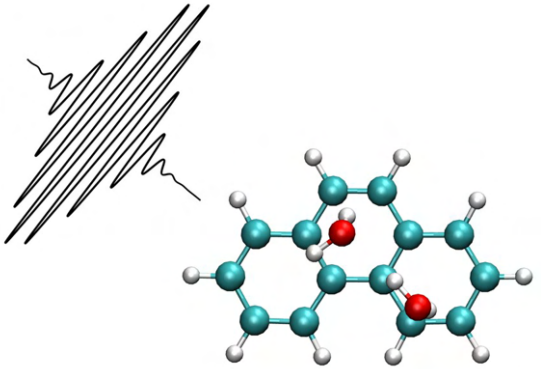


i-PI

- Electronic ground state:
  Machine learned (MACE[1]) potential trained on DFT data
- Nuclear fluctuations at 120 K:
  approximated with quantum thermostat

[1]Batatia, I. et al. Advances in Neural Information Processing Systems (2022)

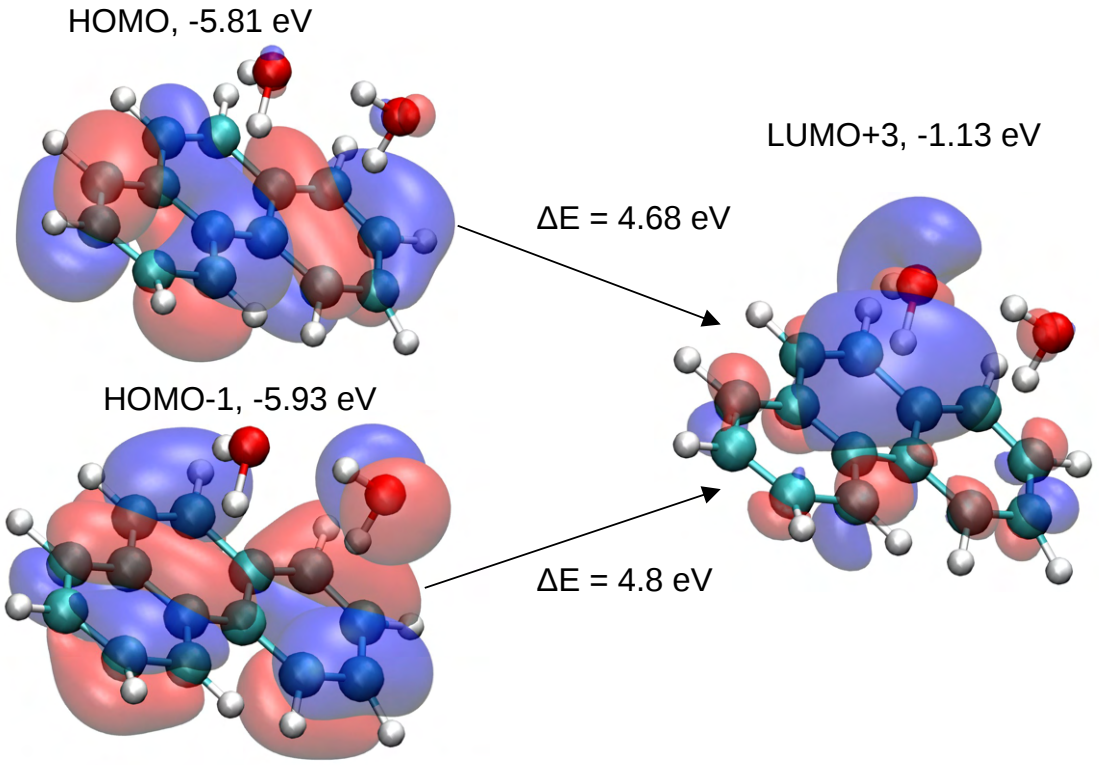
Excitation and propagation



FHI-aims
The ab initio materials simulation package

- Excited electronic states:
  RT-TDDFT
- Nuclear motion
  - Clamped nuclei
  - Ehrenfest dynamics

How to excite a charge transfer?



- Transition from orbitals on phenanthrene to water
- Electronic density transfers to water
- Excite transitions with a 5 eV electric field

Inputs for Ehrenfest dynamics

control.in:

```
xc                                 rpbe
relativistic                       none
d3
RT_TDDFT_input_units               atomic
RT_TDDFT_propagation               3600 0.15 0.6
RT_TDDFT_propagator                crank_nicolson
RT_TDDFT_ehrenfest                 default 0.15
RT_TDDFT_td_field                  0 0 3 0.0292 0 320 211.9 0 0 0.02
RT_TDDFT_td_field_gauge            length
RT_TDDFT_output_energies           T T
RT_TDDFT_output_dipole             T T
RT_TDDFT_ehrenfest_output_trajectory T T
RT_TDDFT_output_mulliken           T
RT_TDDFT_output_hirshfeld          T
RT_TDDFT_restart_write_period      600

# tight basis set information
```

geometry.in:

```
atom -0.774999 -0.325632 -0.026087 C
RT_TDDFT_initial_velocity 4.260427 4.751924 0.948047
...
```

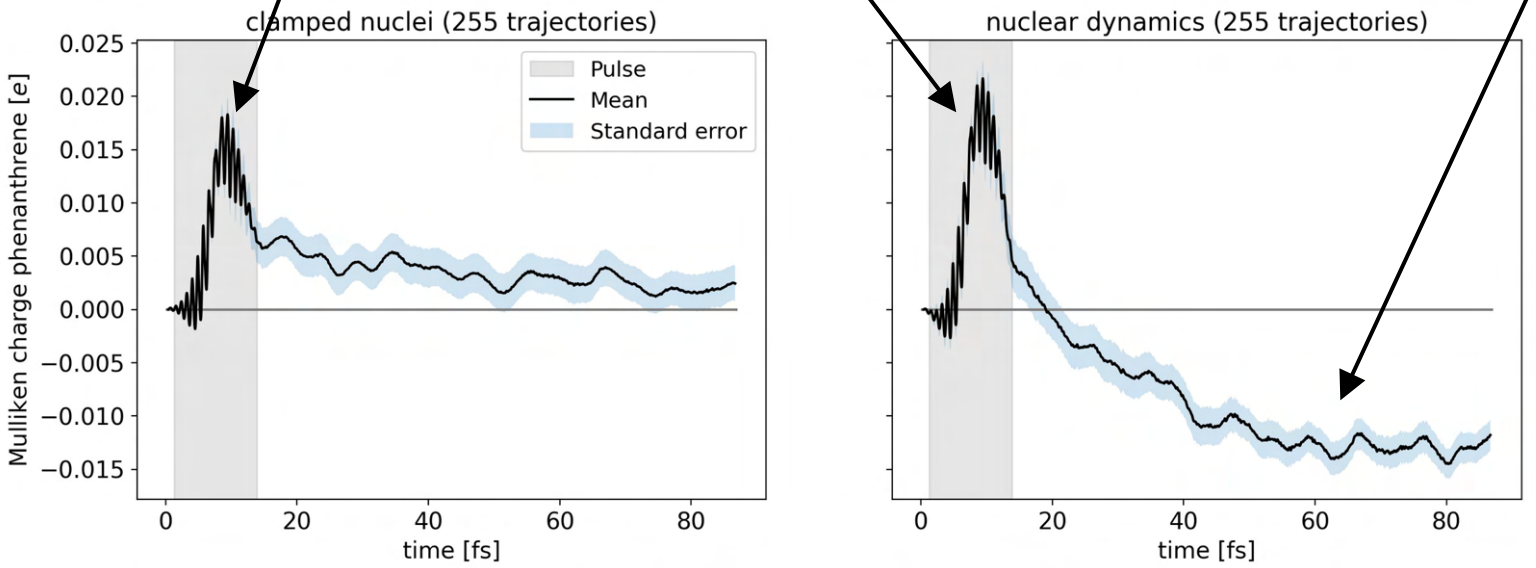
- Grimme D3 dispersion interactions
- Same timestep for electronic and nuclear propagation
- 5 eV electric field
- Output of atomic mulliken and hirshfeld charges

Multitrajectory results

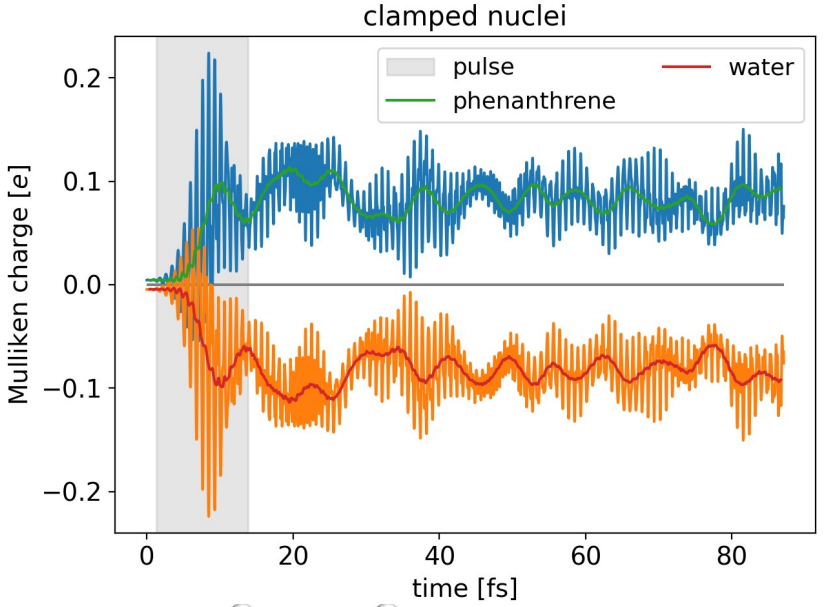
- Average over many trajectories
- Nuclear positions (and momenta) initialized from quantum thermostat sampling

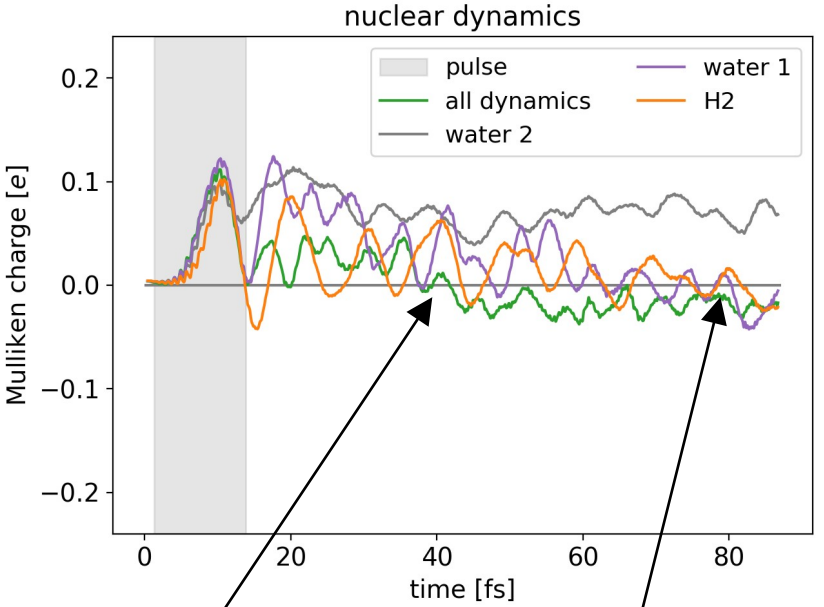
Transfer of electron density from phenanthrene to $(H_2O)_2$

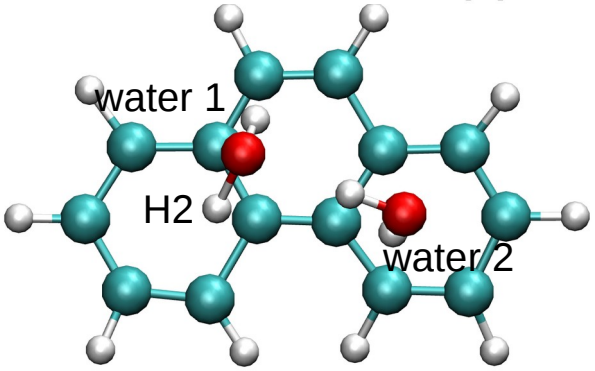
Back-transfer of electron density to phenanthrene



The impact of nuclear motion on charge redistribution







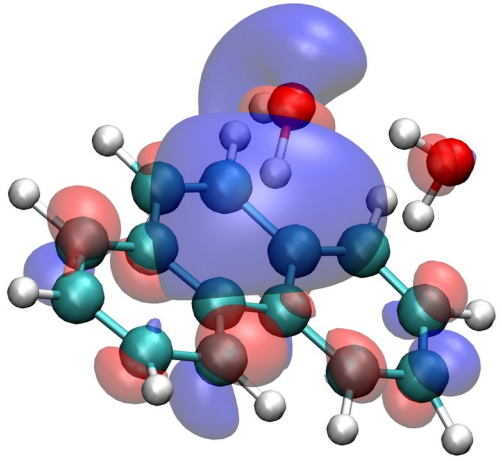
Reversal of the charge transfer

Effect reproduced by only moving water 1

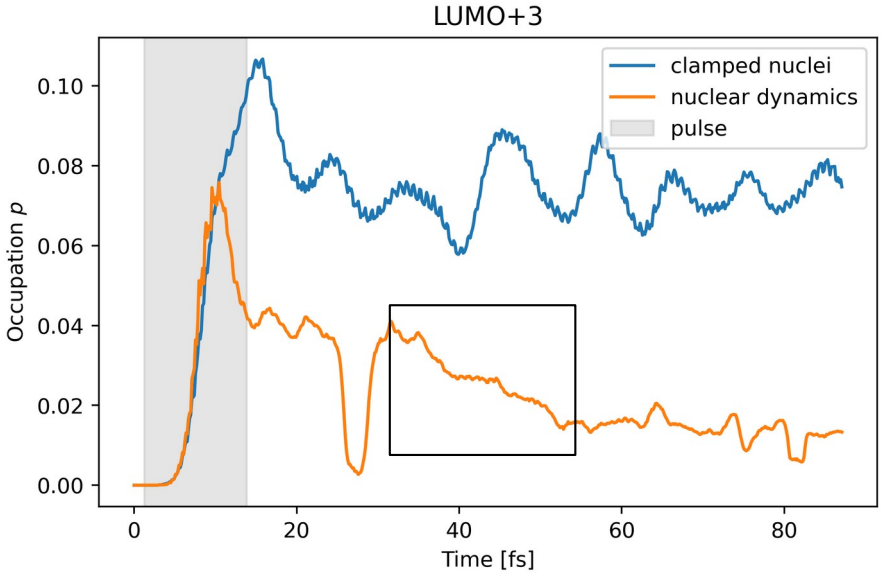
Occupation of ground state orbitals

LUMO+3:

$$c_{i\alpha}(t) = \left\langle \phi_i^{\mathrm{gs}}(\{\boldsymbol{R}(t)\}) \middle| \psi_\alpha^{\mathrm{td}}(t) \right\rangle, \quad p_i(t) = \sum_{\alpha=1}^{N_{\mathrm{occ}}} |c_{i\alpha}(t)|^2$$



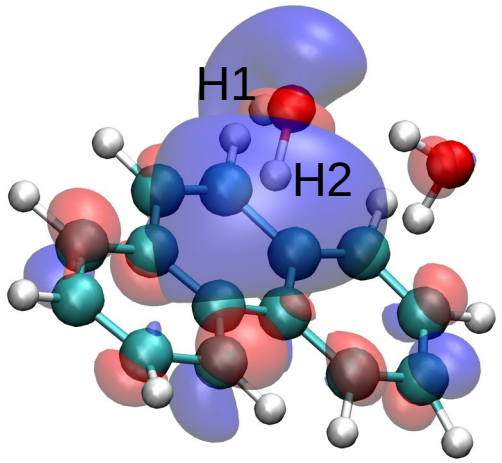
Lowest unoccupied ground state orbital on water



Nuclear dynamics: loss of the occupation of LUMO+3, i.e. decay of the charge on water dimer

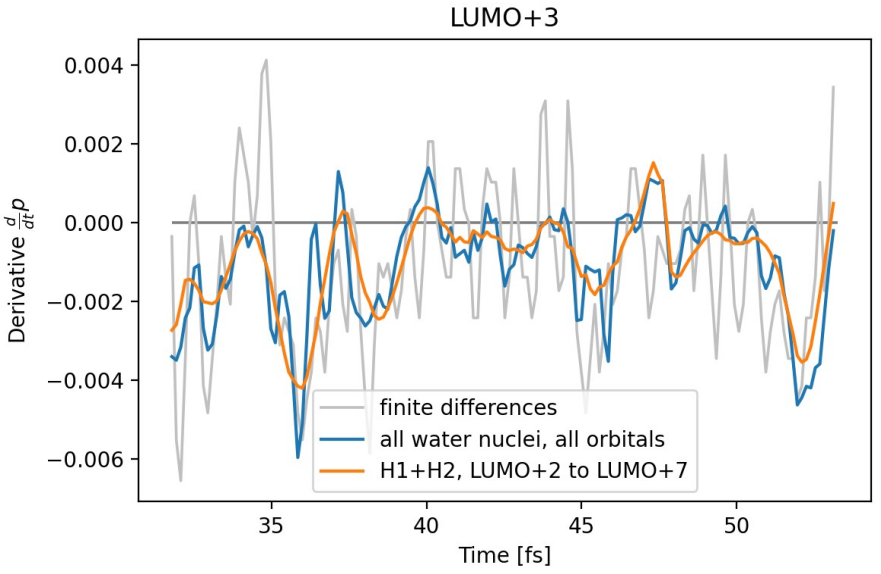
Role of nonadiabatic couplings

LUMO+3:



$$d_{ij}^{x} = \langle \phi_i^{\mathrm{gs}} | \frac{\partial}{\partial R_x} | \phi_j^{\mathrm{gs}} \rangle = \frac{1}{\varepsilon_j - \varepsilon_i} \langle \phi_i^{\mathrm{gs}} | \frac{\partial V}{\partial R_x} | \phi_j^{\mathrm{gs}} \rangle$$

Electronic friction code in FHI-aims
Box, C. L. et al. Electron. Struct. 5 035005 (2023)

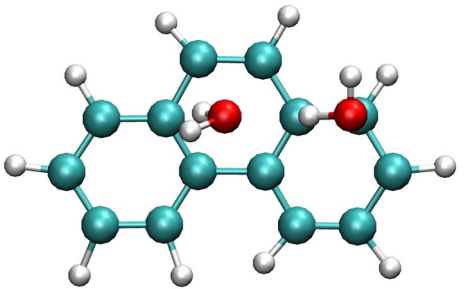


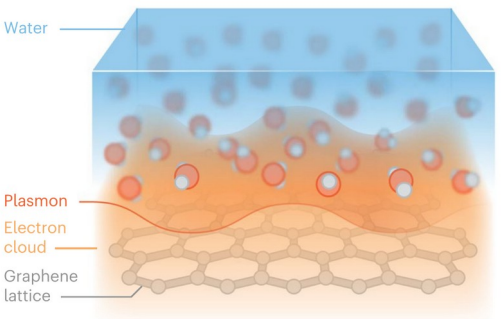
Decay of occupation LUMO+3 is driven by
- motion of two water hydrogen nuclei (H1 + H2)
- coupling to close by orbitals (LUMO+2 to LUMO+7)

Conclusion and outlook

- Practical implementation of dispersion corrections for Ehrenfest dynamics
- Application of RT-TDDFT and Ehrenfest dynamics using FHI-aims
- Modelling of charge transfer from phenanthrene to $(H_2O)_2$
  - Nuclear motion influence charge redistribution
  - i.e. nonadiabatic couplings from water dynamics
- Automated workflow for multitrajectory Ehrenfest dynamics
- Investigate energy transfer at liquid 2D interfaces

FHI-aims
The ab initio materials simulation package

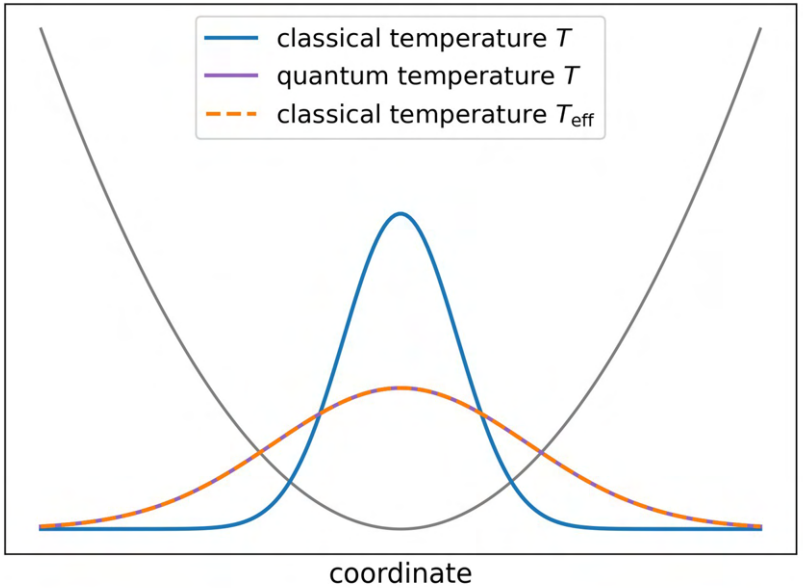




Appendix: Quantum thermostat

- Molecular dynamics (MD) with exact anharmonic forces
- Thermostat supplies correct zero-point energy in harmonic limit

$$T_{\text{eff}}(\omega) = \frac{\hbar\omega}{2k_B} \coth\left(\frac{\hbar\omega}{2k_B T}\right)$$

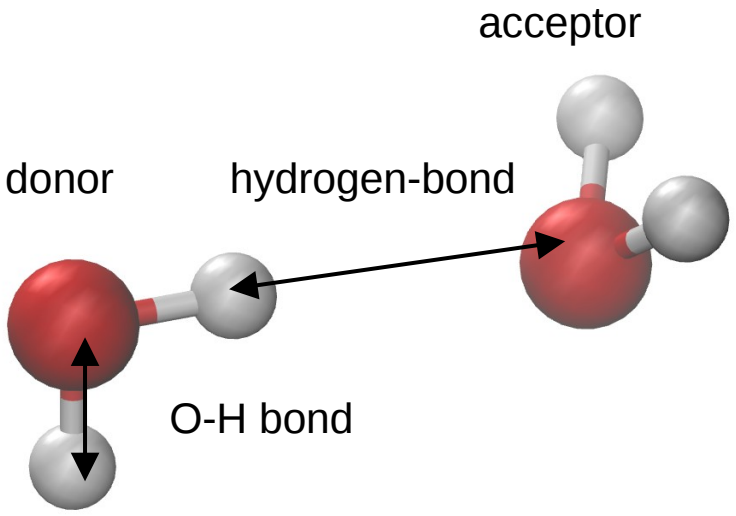


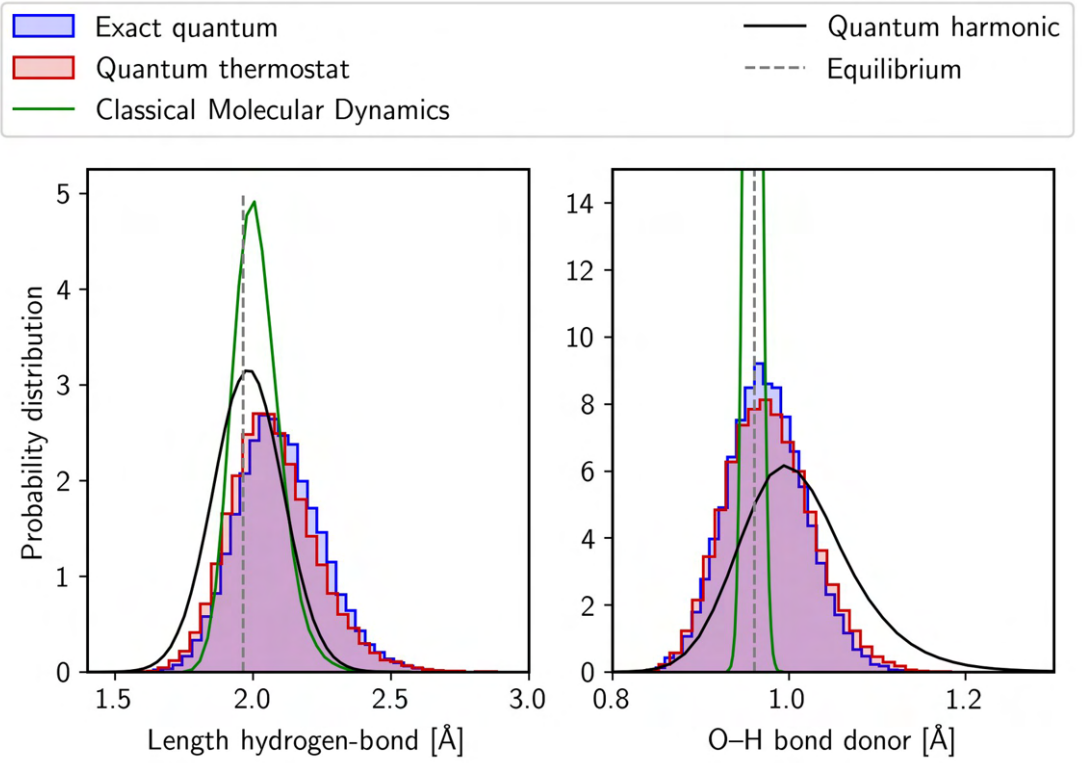
- Cost of quantum thermostat MD comparable to classical MD
- Approximate quantum anharmonic position and momenta sampling

Ceriotti, M. et al. Phys. Rev. Lett. 103, 030603 (2009)
Ceriotti, M. et al. J. Chem. Theory Comput. 6, 1170-1180 (2010)

Appendix: Sampling the nuclear degrees of freedom

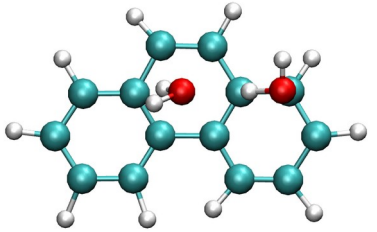
- Benchmark of sampling methods on water dimer at 60 K

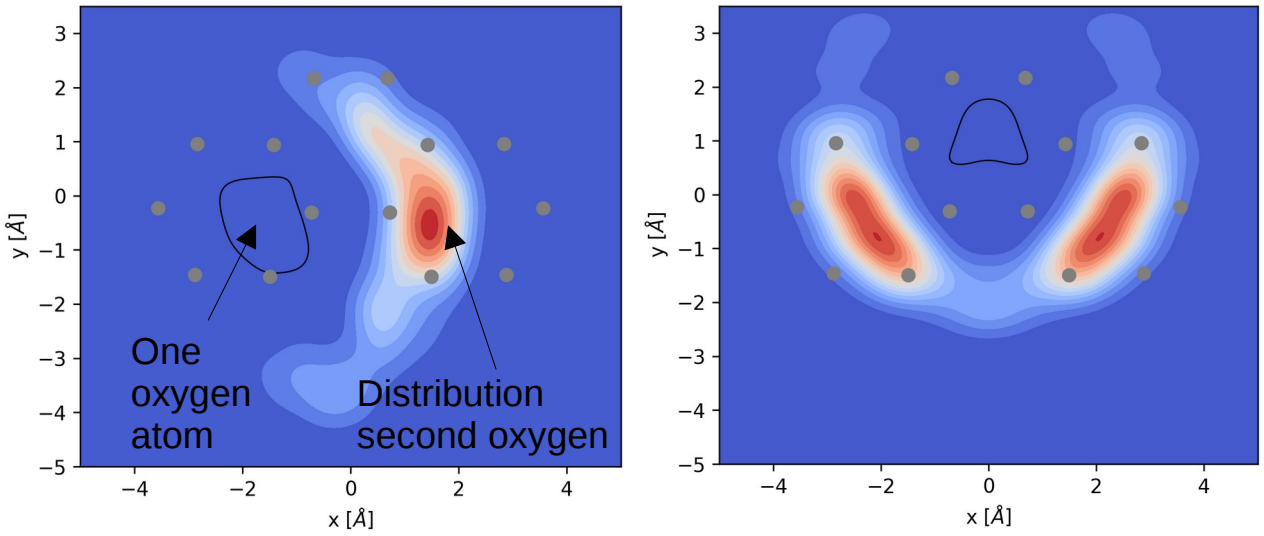


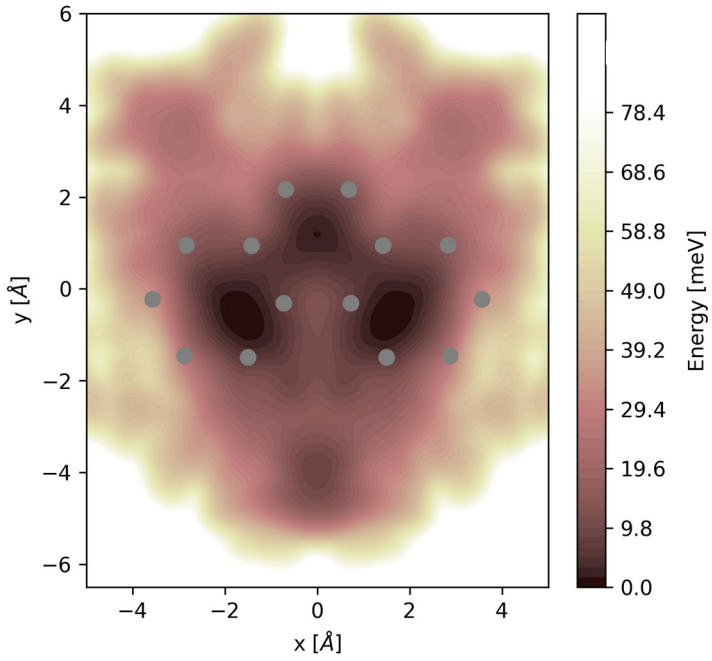


Appendix: Sampling $(H_2O)_2$ on phenanthrene

- Machine learned potential (MACE[1]) trained from DFT data
- 4 ns of sampling at 120 K with quantum thermostat
- Free energy of oxygen position: $k_B T \ \ln(P(x,y))$

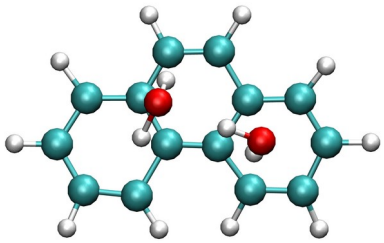




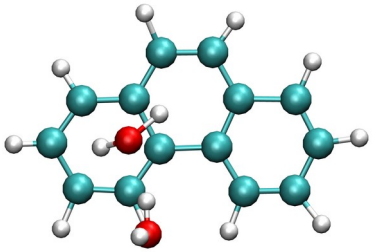


[1]Batatia, I. et al. Advances in Neural Information Processing Systems (2022)

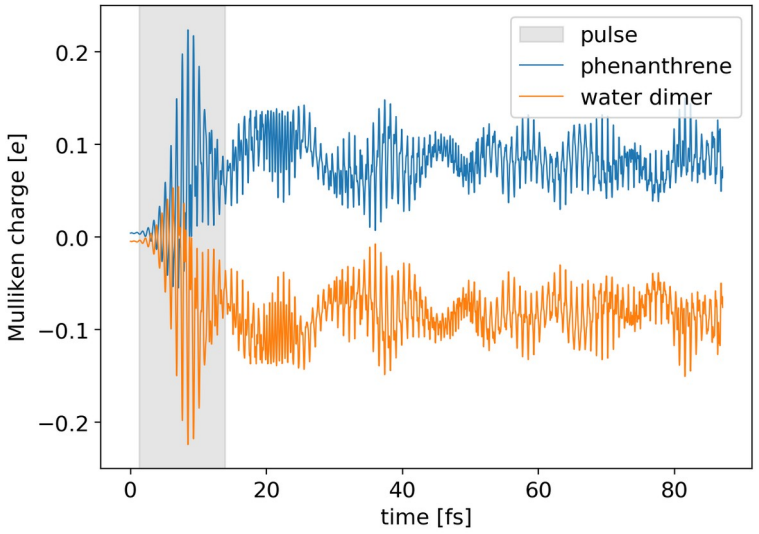
Appendix: Charge transfer: initial nuclear conditions matter

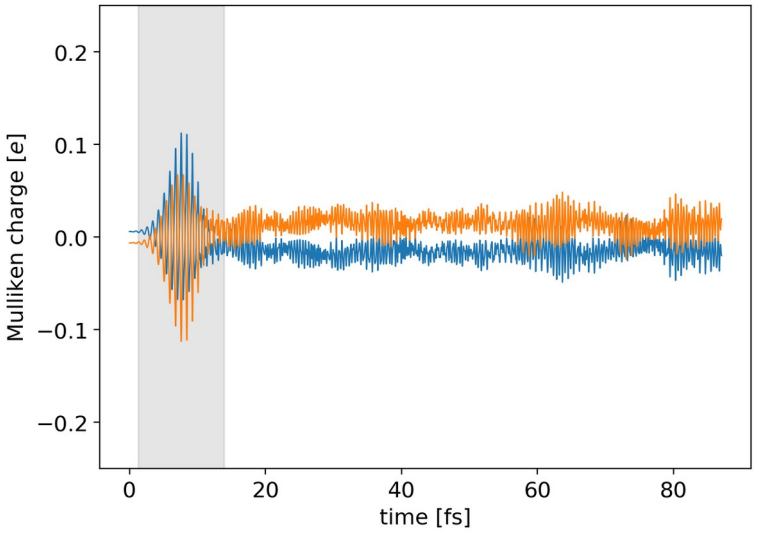


Electron density transfer
phenanthrene → $(H_2O)_2$



Electron density transfer
$(H_2O)_2$ → phenanthrene





Appendix: Occupation dynamics with nonadiabatic couplings

$$c_{i\alpha}(t) = \left\langle \phi_i^{\mathrm{gs}}(\{\boldsymbol{R}(t)\}) \middle| \psi_\alpha^{\mathrm{td}}(t) \right\rangle, \quad p_i(t) = \sum_{\alpha=1}^{N_{\mathrm{occ}}} |c_{i\alpha}(t)|^2$$

Occupations p change because of:

- Nuclear dynamics
- External field
- Intrinsic coupling between ground state orbitals in rt-tddft

Assuming only nuclear dynamics matters one can derive the change of occupations:

$$\frac{d}{dt} c_{j\alpha} = -\frac{i}{\hbar} \varepsilon_j c_{j\alpha} - \sum_x v_x \sum_i d_{ji}^x c_{i\alpha}$$

$$\frac{d}{dt} p_i = 2\ \mathrm{Re}\left[-\sum_\alpha \sum_x \frac{\partial R_x}{\partial t} \sum_j d_{ij}^x c_{j\alpha} c_{i\alpha}^* \right], \quad d_{ij}^x = \langle \phi_i | \frac{\partial}{\partial R_x} | \phi_j \rangle$$