Nonadiabatic dynamics in the long timescale

The next challenge in computational photochemistry

Mario Barbatti

Aix Marseille University, Institut de Chimie Radicalaire

Institut Universitaire de France

www.barbatti.org

The Light and Molecules Group

www.barbatti.org

Methods

Mixed quantum-classical dynamics

Software

NEWTON-X

ULAMDYN

PYSOC

Applications

Photoprocesses in

- Fundamental PhysChem
- Molecular biology
- Organic devices
- Environment

LIGHT AND MOLECULES

The Light and Molecules Group

www.barbatti.org

Mario Barbatti (PI)

Baptiste Demoulin (IT researcher)

Josene Toldo (postdoc)
Max Pinheiro Jr (postdoc)
Saikat Mukherjee (postdoc)
Moumita Kar (postdoc)

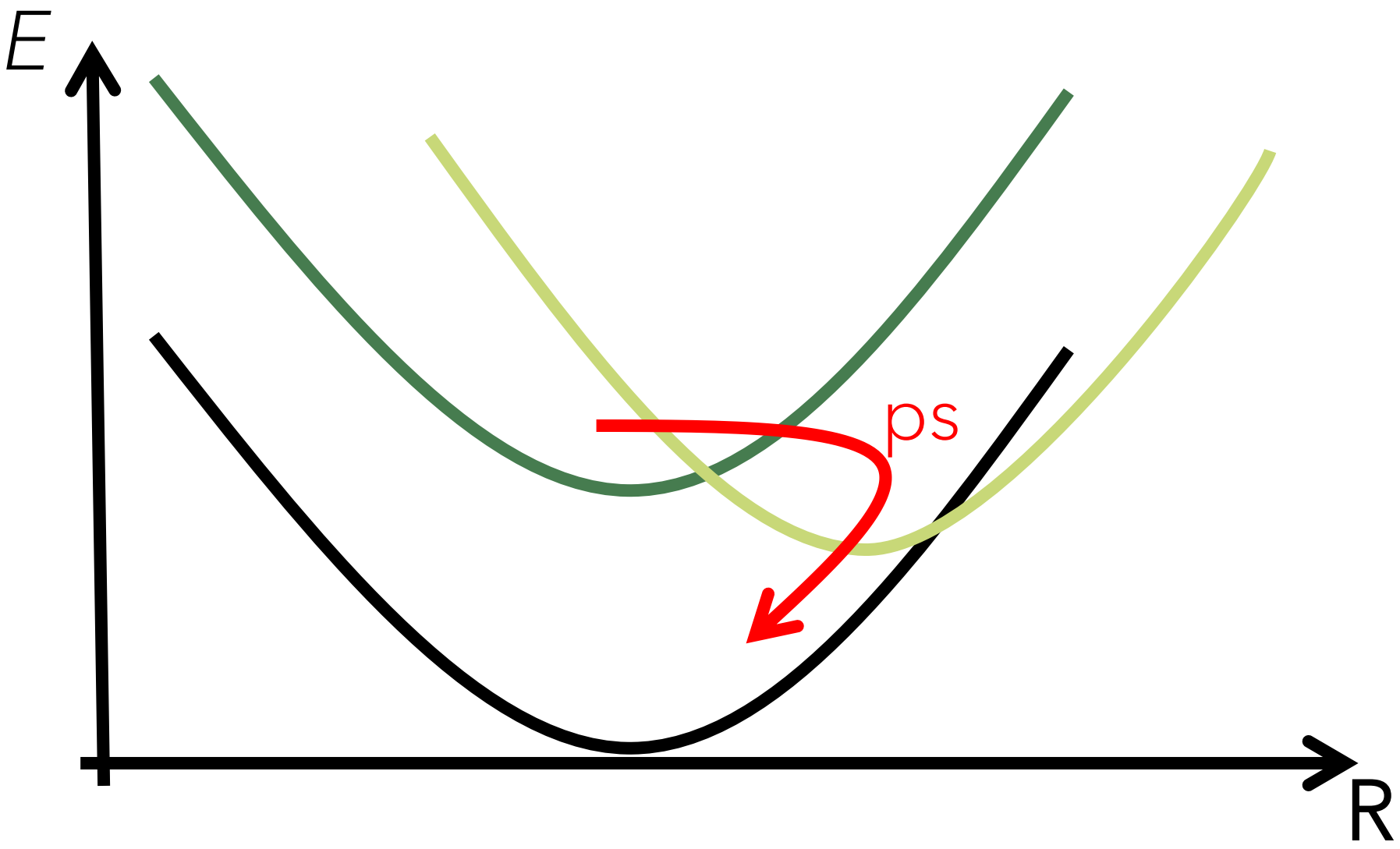
Mariana Casal (PhD candidate)
Ritam Mansour (PhD candidate)
Rafael Mattos (PhD candidate)

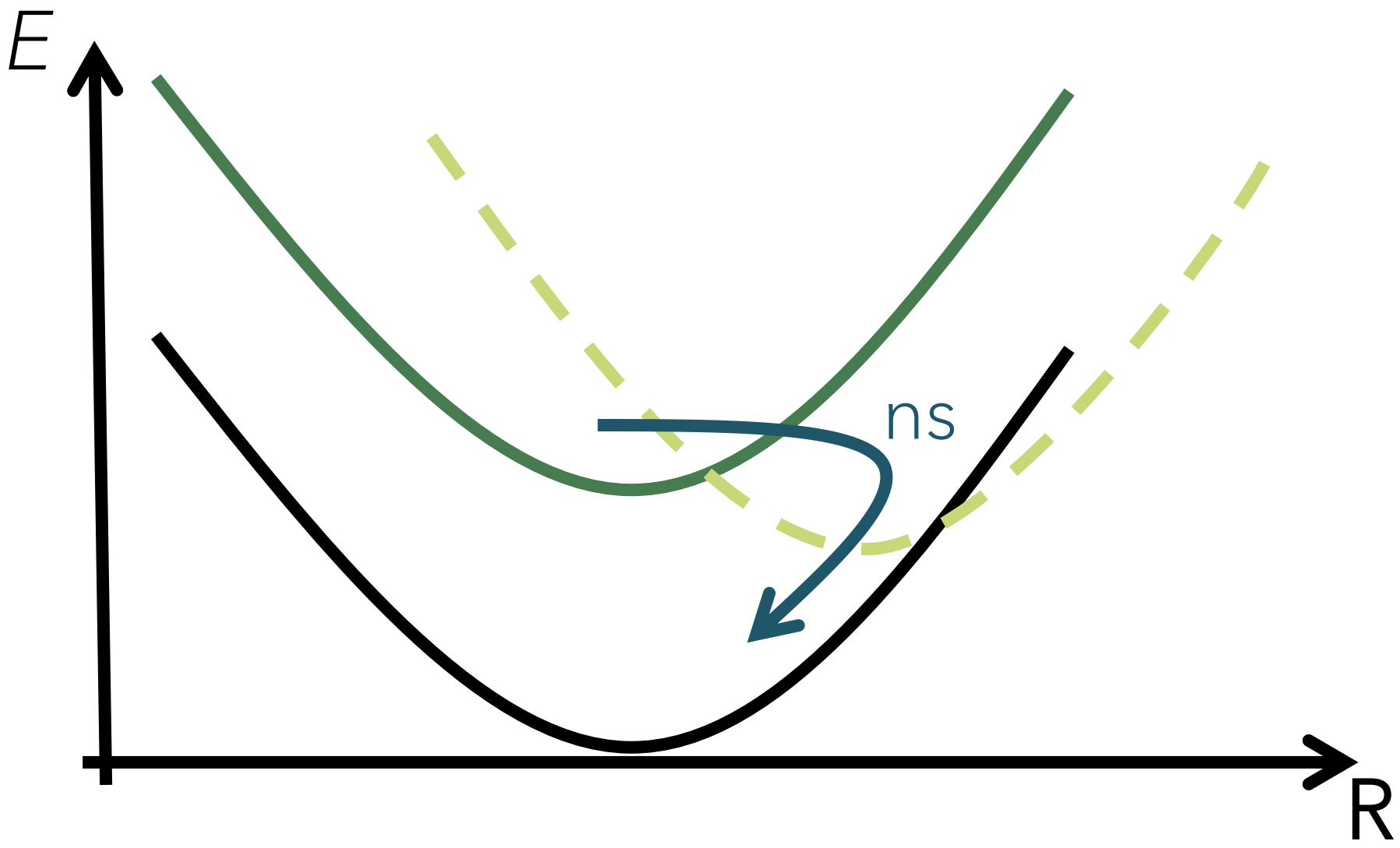
Elizete Ventura (visiting res, Joao Pessoa)
Silmar Monte (visiting res, Joao Pessoa)

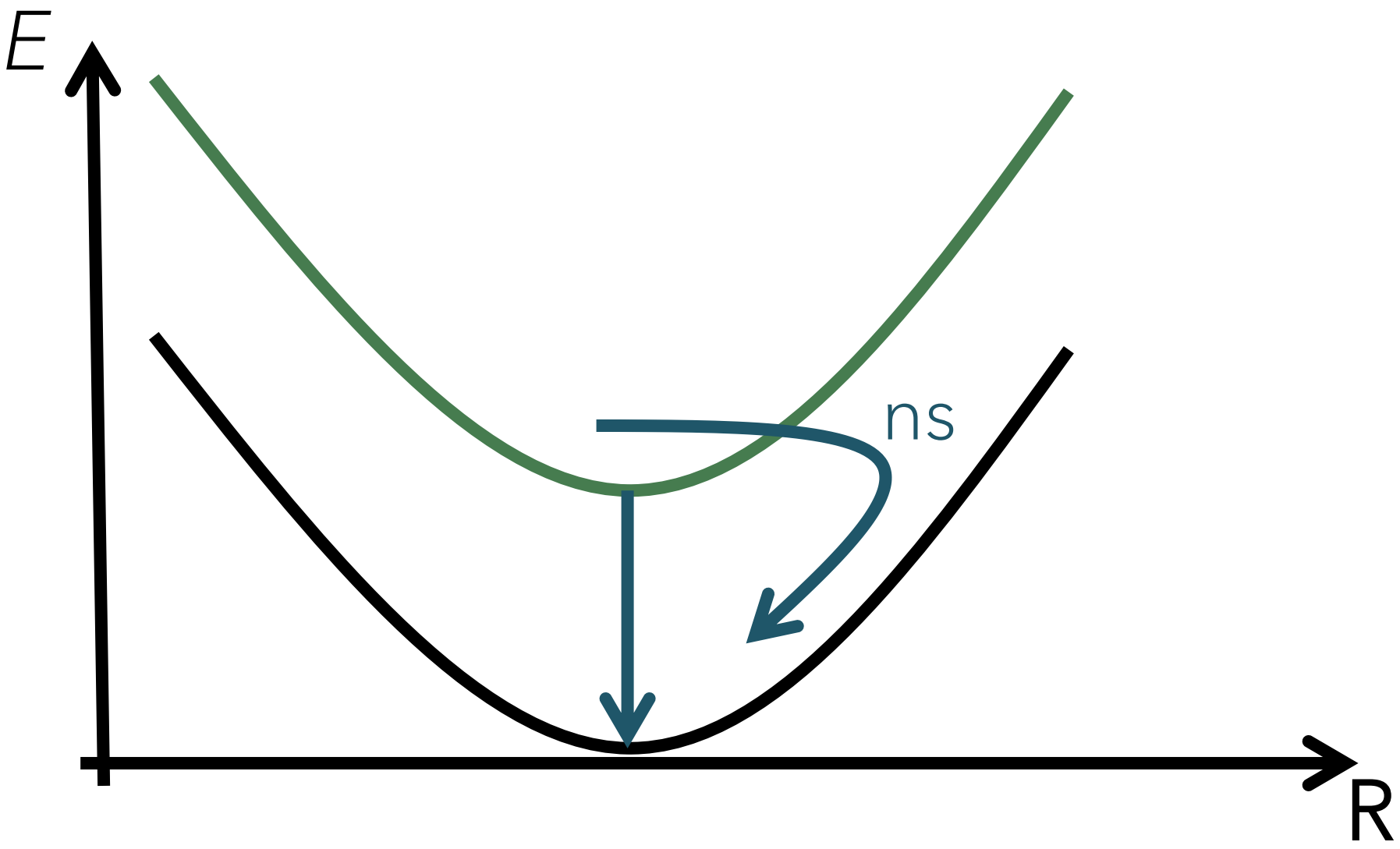
Mattia Bondanza (PhD internship, Pisa)
Eduarda Gil (PhD insternship, Pisa)
Mansi Bhati (PhD internship, Bohpal)
Mithun M (PhD internship, Bathinda)

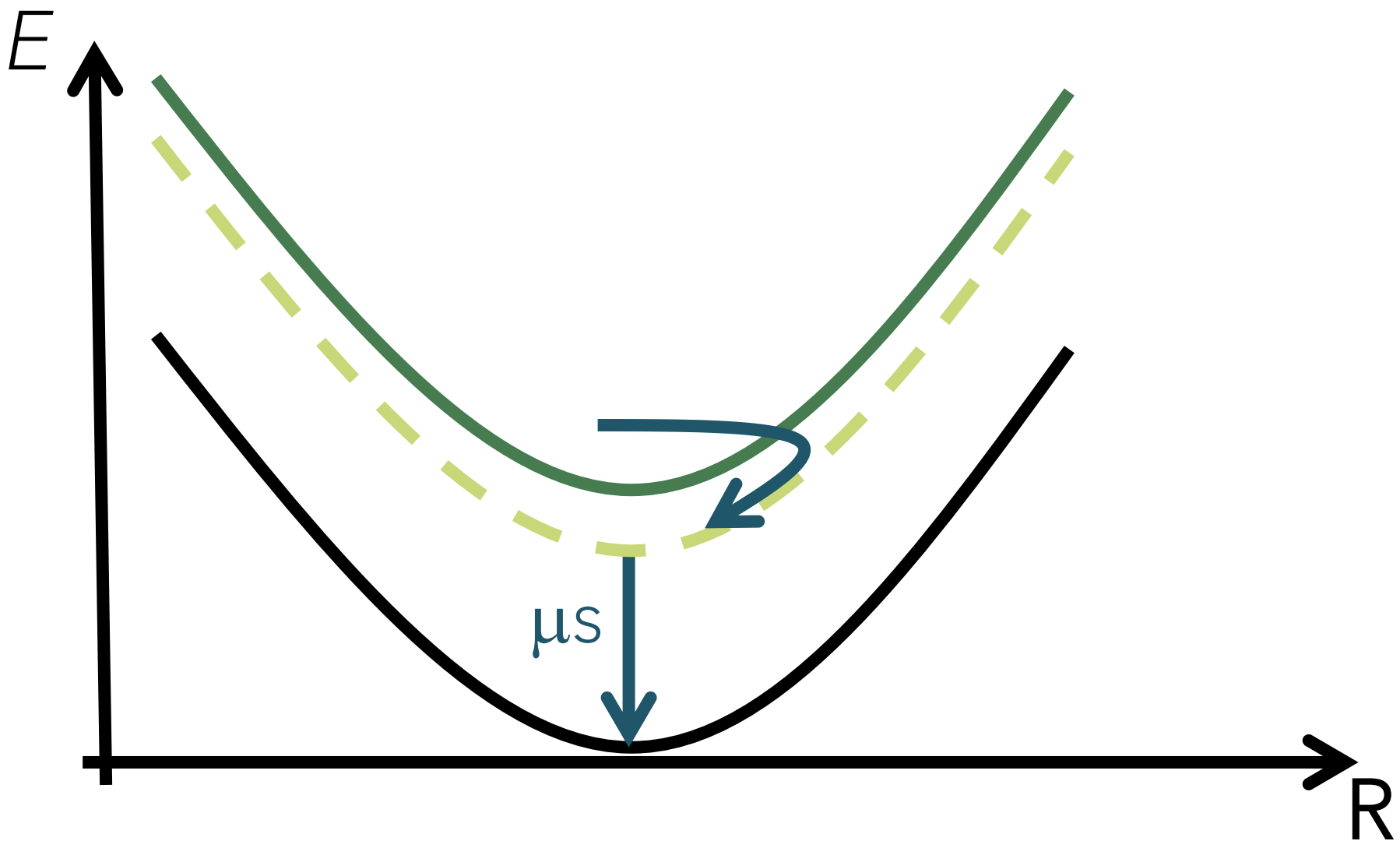
Soumaya Moussa (MSc internship, Marseille)
Nesrine Haddaji (MSc internship, Tunis)

LIGHT AND MOLECULES


E
ps
R


E
ns
R


E
ns
R


E
μs
R

- Akimov. *J Phys Chem Lett* **2017,** *8*, 5190
- Westermayr et al. *Chem Sci* **2019,** *10*, 8100
- Barbatti. *JCTC* **2020,** *16*, 4849
- Li et al. *Chem Sci* **2021,** *12*, 5302
- Mukherjee et al. *Philos Trans R Soc A* **2022**, DOI: 10.1098/rsta-2020-0382

What do we want from a long timescale method?

What do we want from a long timescale method?

- [x] It should consider all nuclear degrees of freedom
- [ ] It can be applied to any type of molecule
- [ ] It should not require much more computational resources than we use today

The primary advantage of dynamics is
to reveal non-trivial reaction pathways,
beyond our chemical intuition.

It loses this edge in reduced dimensionality.

Mixed quantum-classical methods are
the best options for nonadiabatic,
full dimensional dynamics.

Crespo-Otero; Barbatti. *Chem Rev* **2018,** *118*, 7026

What do we want from a long timescale method?

- ☑ It should consider all nuclear degrees of freedom
- ☑ It can be applied to any type of molecule
- ☑ It should not require much more computational resources than we use today

Dynamics is expensive

$$T_{total} \approx N_{\text{Trajectories}} \times N_{\frac{\tau_{\text{chem process}}}{\Delta\tau}}^{\text{Single Points}} \times T_{\text{Single Point}}$$

$N_{\text{Trajectories}}$ = 100 trajectories
$T_{\text{Single Point}}$ = 0.1 CPU.h
$\tau_{\text{chem process}}$ = 0.5 ns
$\Delta\tau$ = 0.5 fs

$T_{total} \approx 10$ MCPU.h

Price 1 CPU.h = 0.02 €

Price 10 MCPU.h = 200 k€

How much does dynamics cost? **tinyurl.com/dyncost**
How many trajectories should we run? **tinyurl.com/trajs**

Dynamics leaves a huge carbon footprint

1 CPU.h = 4×10^{-5} tCO_2e

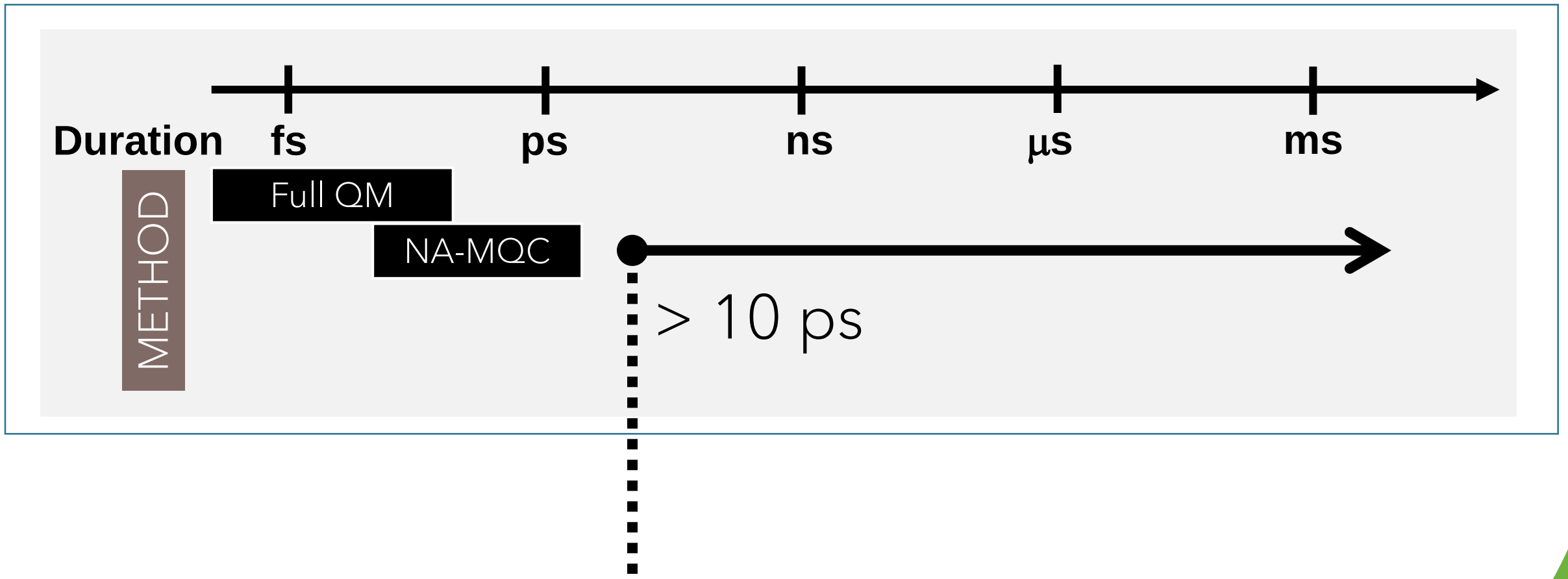
10 MCPU.h = 400 tCO_2e

11.5 tCO_2e/year

35 French people

Stevens et al. *Nat Astron* **2020,** *4*, 843

What is a *long timescale* anyway?



> 10 ps/0.1 fs = 100,000 time steps

Characteristic timestep

$$\Delta\tau = \frac{1}{10}\min\left[\sqrt{\frac{|\Delta R_{ij}|}{|\Delta a_{ij}|}}\right]$$

Boekholt; Zwart. *Comput Astrophys Cosmol* **2015,** *2*, 2

Characteristic timestep

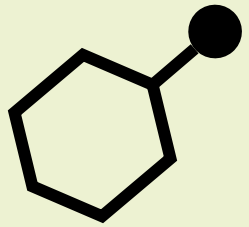
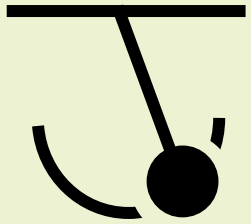
$$\Delta\tau = \frac{1}{10}\min\left[\sqrt{\frac{|\Delta R_{ij}|}{|\Delta a_{ij}|}}\right]$$

Hamonic oscillator

$$\Delta\tau = \frac{1}{20\pi f}$$

Gravitational motion

$$\Delta\tau = \frac{1}{10}\min\left[\sqrt{\frac{\Delta R^3}{GM}}\right]$$

	$\Delta\tau = \frac{1}{20\pi f}$	$f = 3000\ \mathrm{cm}^{-1}$	$\Delta\tau \approx 0.1\ \mathrm{fs}$ $\tau > 10\ \mathrm{ps}$
	$\Delta\tau = \frac{1}{20\pi f}$	$f = 1\ \mathrm{Hz}$	$\Delta\tau \approx 0.01\ \mathrm{s}$ $\tau > 16\ \mathrm{min}$
	$\Delta\tau = \frac{1}{10}\min\left[\sqrt{\frac{\Delta R^3}{GM}}\right]$	*Earth orbital motion*	$\Delta\tau \approx 100\ \mathrm{h}$ $\tau > 1100\ \mathrm{years}$

How to get there?

Challenges we must face

- Extreme cost reduction
- Stability of integration
- Accuracy of MQC methods
- Software optimization

Challenges we must face

- Extreme cost reduction
- Stability of integration
- Accuracy of MQC methods
- Software optimization

Challenges we must face

- Extreme cost reduction
  - ☑ Parameterized quantum chemistry
  - ❑ Model Hamiltonians
  - ❑ Machine learning potentials

Excited-state parameterized methods:

- FOMO-CI (Persico, Granucci)
- OM2-MRCI (Thiel)
- TD-SCF (Tretiak et al.)
- TD-DFTB (Niehaus, Mitrić)
- TD-KS (Akimov, Prezhdo)

They are fast, general, and full dimensional.

However, accuracy and parameterization pose serious issues.

Challenges we must face

- Extreme cost reduction
  - ☑ Parameterized quantum chemistry
  - ☑ Model Hamiltonians
  - ❑ Machine learning potentials

Example: Adiabatic Spin-Boson Hamiltonian (SBH)

Energies

$$V_i = \frac{1}{2}\sum_{j=1}^{N} M_j \omega_j^2 R_j^2 + (-1)^i \left[\eta^2 + v_0^2\right]^{1/2} \quad (i = 1, 2)$$

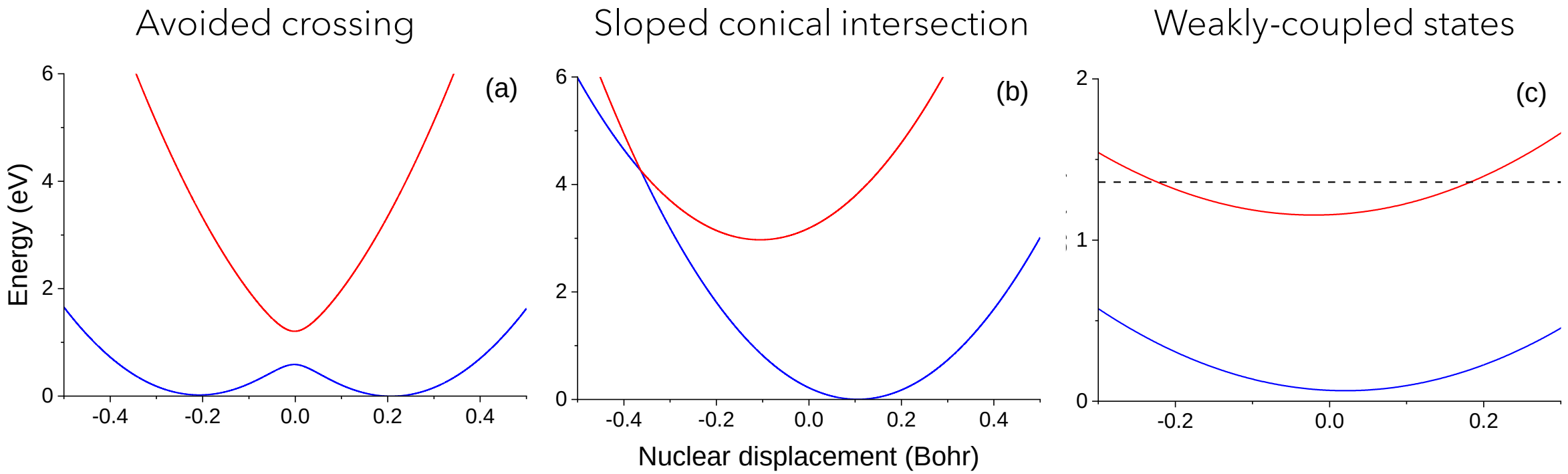
Energy gradients

$$\frac{\partial V_i}{\partial R_k} = M_k \omega_k^2 R_k + (-1)^i g_k \left[\frac{\eta}{\left[\eta^2 + v_0^2\right]^{1/2}}\right] \quad (k = 1 \cdots N)$$

Nonadiabatic couplings

$$h_{12}^k = -h_{21}^k = -\frac{1}{2} g_k \left[\frac{v_0}{\eta^2 + v_0^2}\right]$$

1D cut of different SBH models



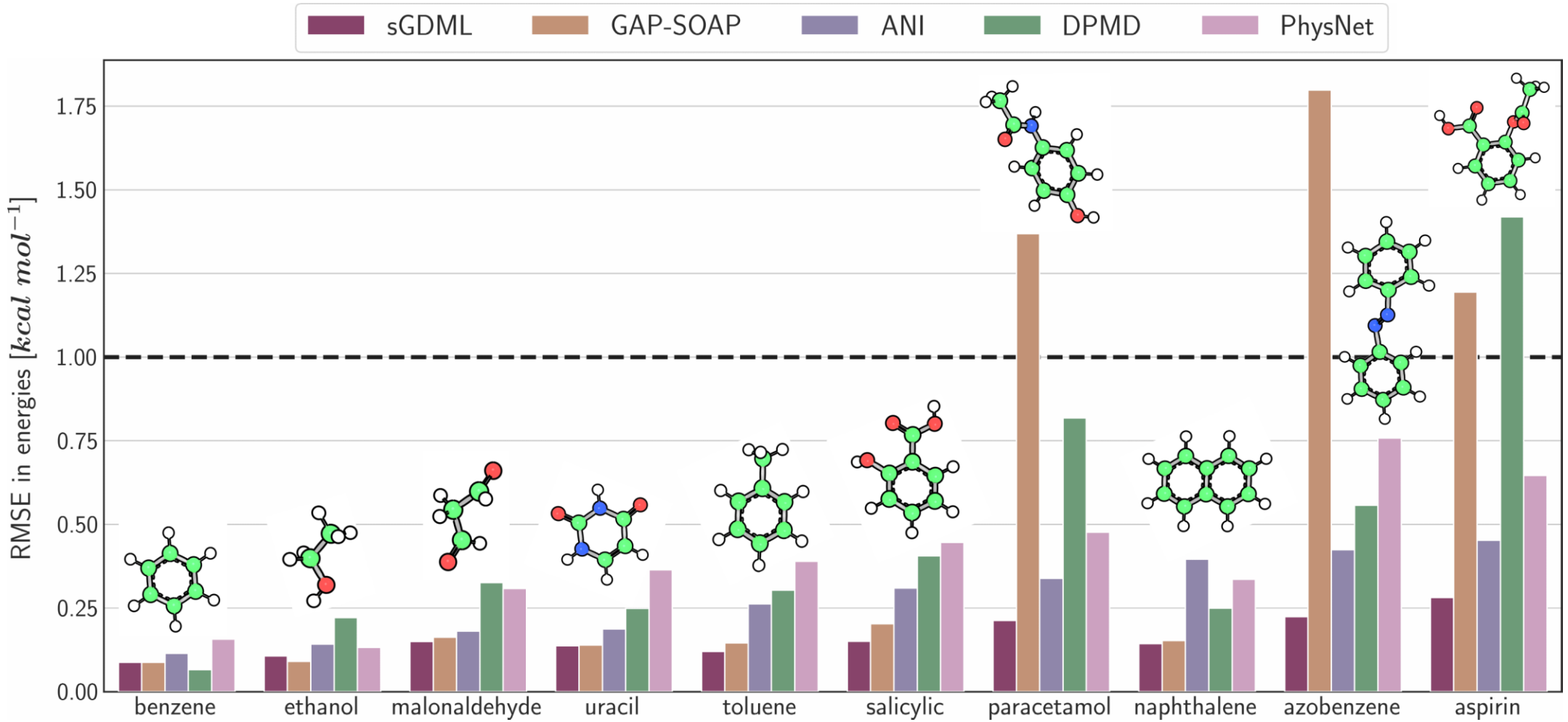
Full dimensional H-models [$(3N_a\text{-}6)$D]

H Model	# states	# parameters	Pros	Cons
SBH	2	$2(3N_a\text{-}5)$	Analyt. adiabatic rep.	Low flexibility
LVC	N_s	$(3N_a\text{-}6)N_s(N_s+1)/2$	Number of states	Parameterization
. . .				

SBH: Leggett et al. *Rev Mod Phys* **1987,** *59*, 1
LVC: Koppel; Domcke; Cederbaum. *Adv Chem Phys* **1984,** *57*, 59

Challenges we must face

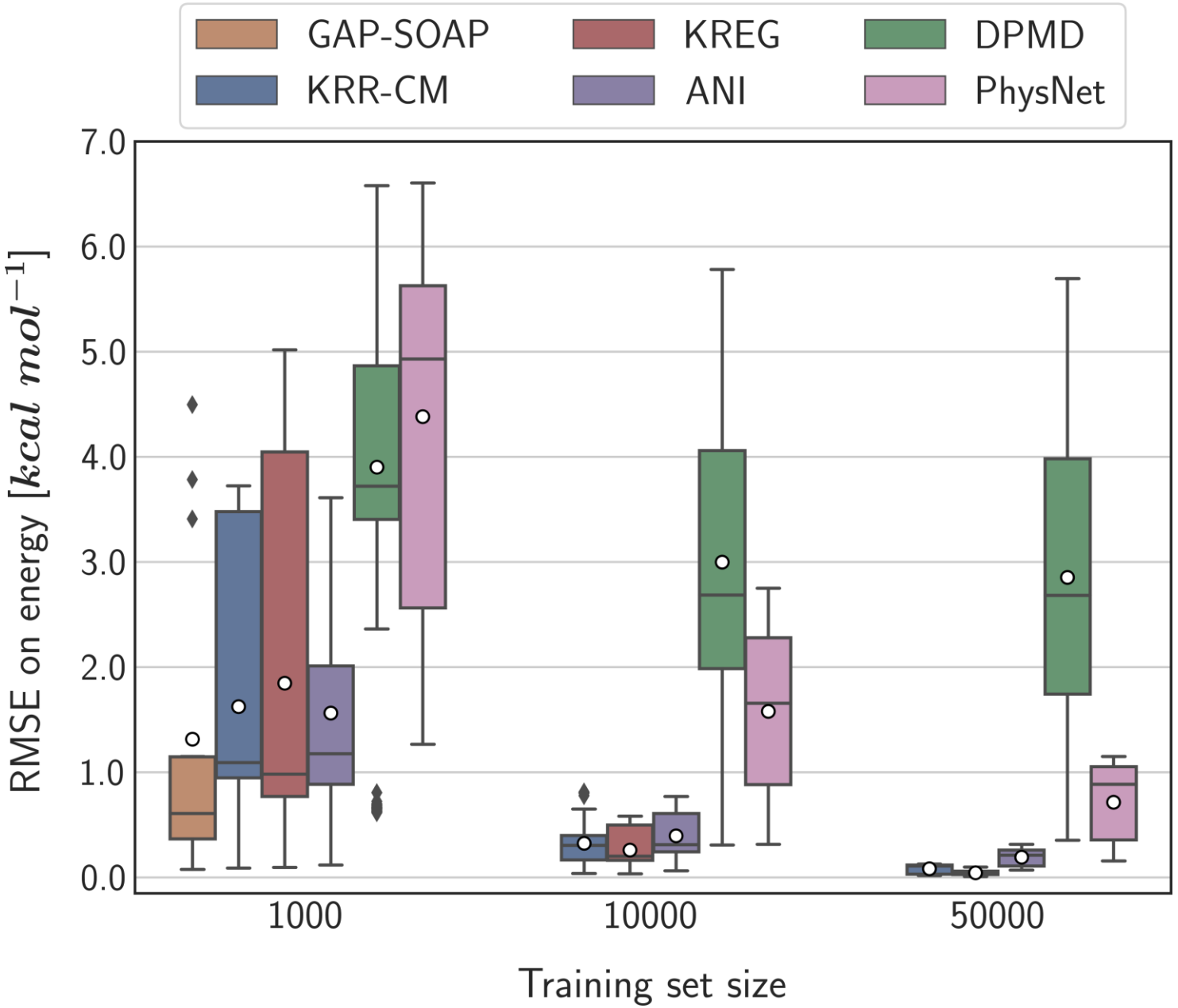
- Extreme cost reduction
  - ☑ Parameterized quantum chemistry
  - ☑ Model Hamiltonians
  - ☑ Machine learning potentials



- MD17 Database
- Energy + Force
- N_{train} = 1k; N_{model} = 20; N_{test} = 20k

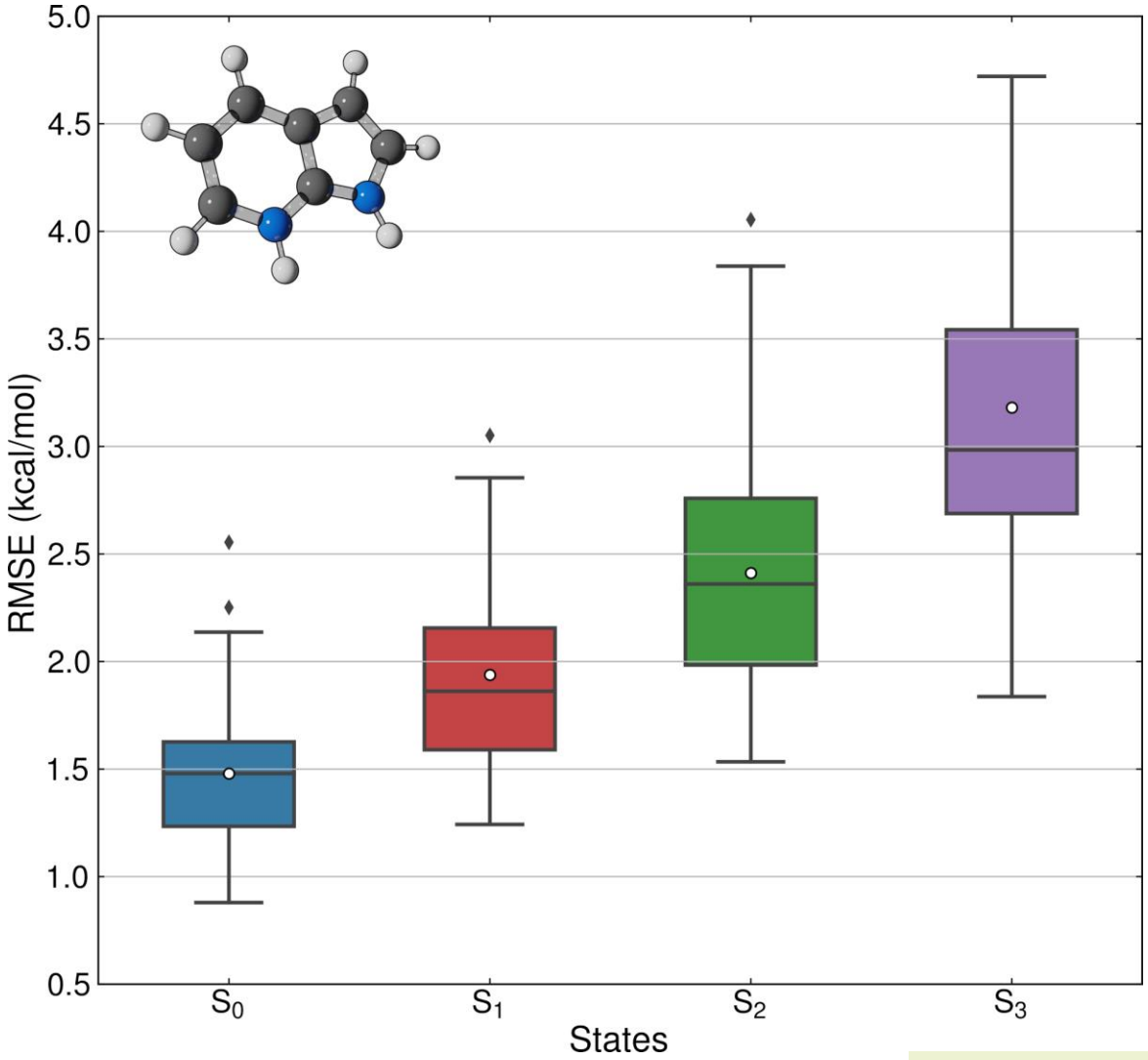
Pinheiro Jr et al. *Chem Sci* **2021**, DOI: 10.1039/D1SC03564A

LIGHT AND MOLECULES



- MD17 Database
- Energy only
- N_{test} = 20k

Pinheiro Jr et al. *Chem Sci* **2021**, DOI: 10.1039/D1SC03564A



- RI-ADC(2)/cc-pVDZ
- DC-FSSH: 50 trajs; 0.5 fs; 300 ps

Mukherjee et al. *Philos Trans R Soc A* **2022**, DOI: 10.1098/rsta-2020-0382

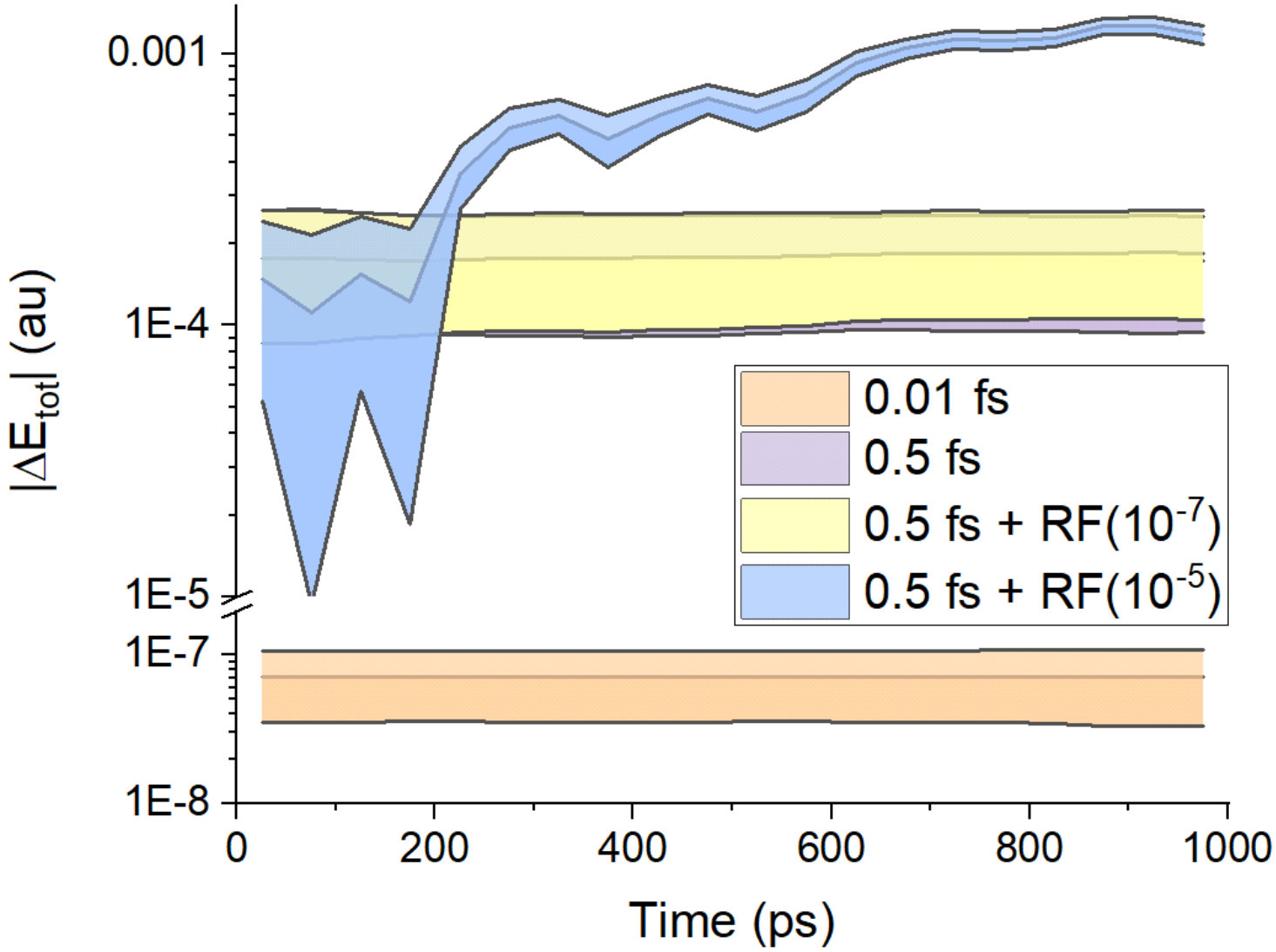
Challenges we must face

- Extreme cost reduction
- Stability of integration
- Accuracy of MQC methods
- Software optimization

Challenges we must face

- Stability of integration
  - ☑ Performance of integration algorithms
  - ❑ ZPE spilling

Velocity Verlet

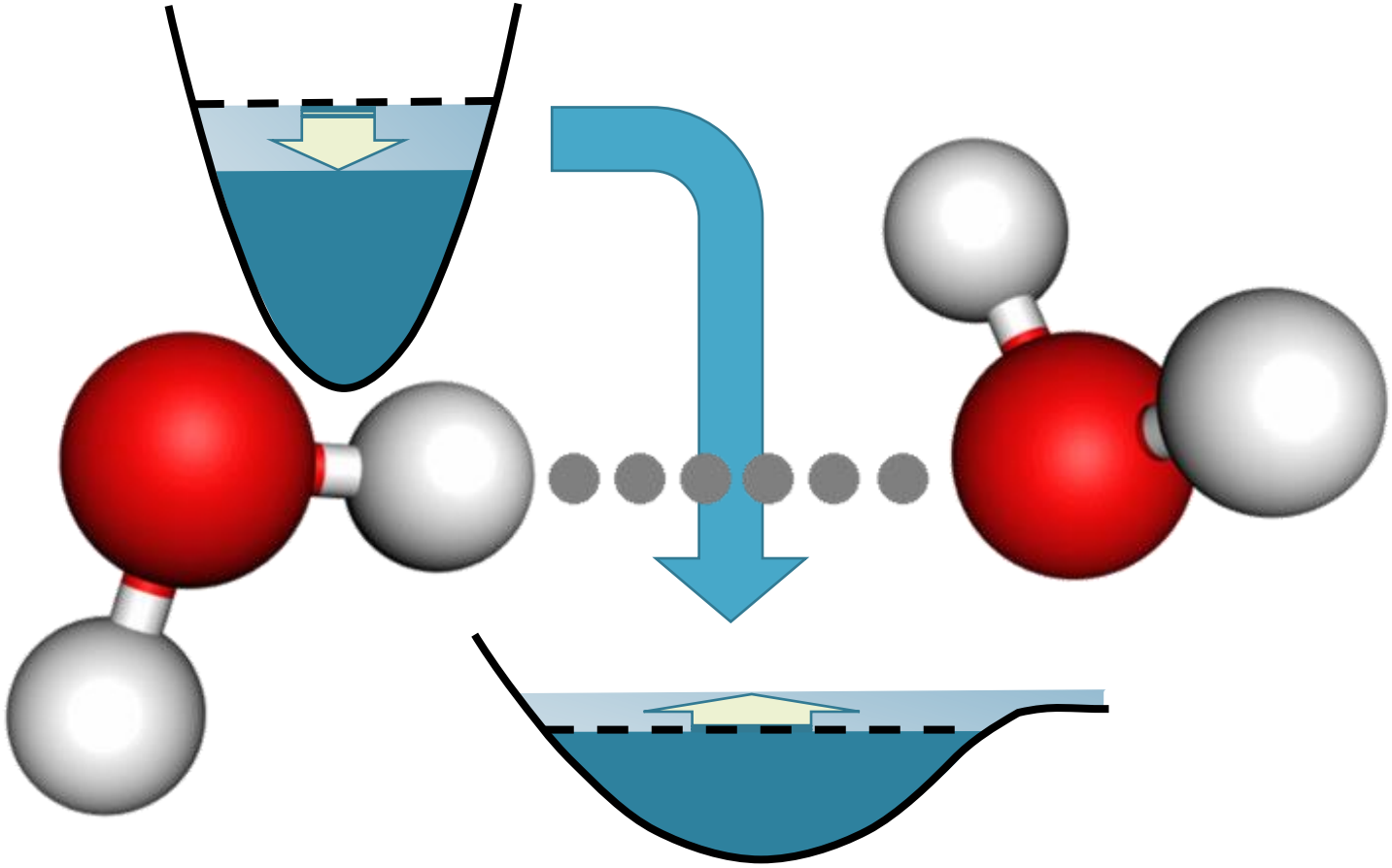


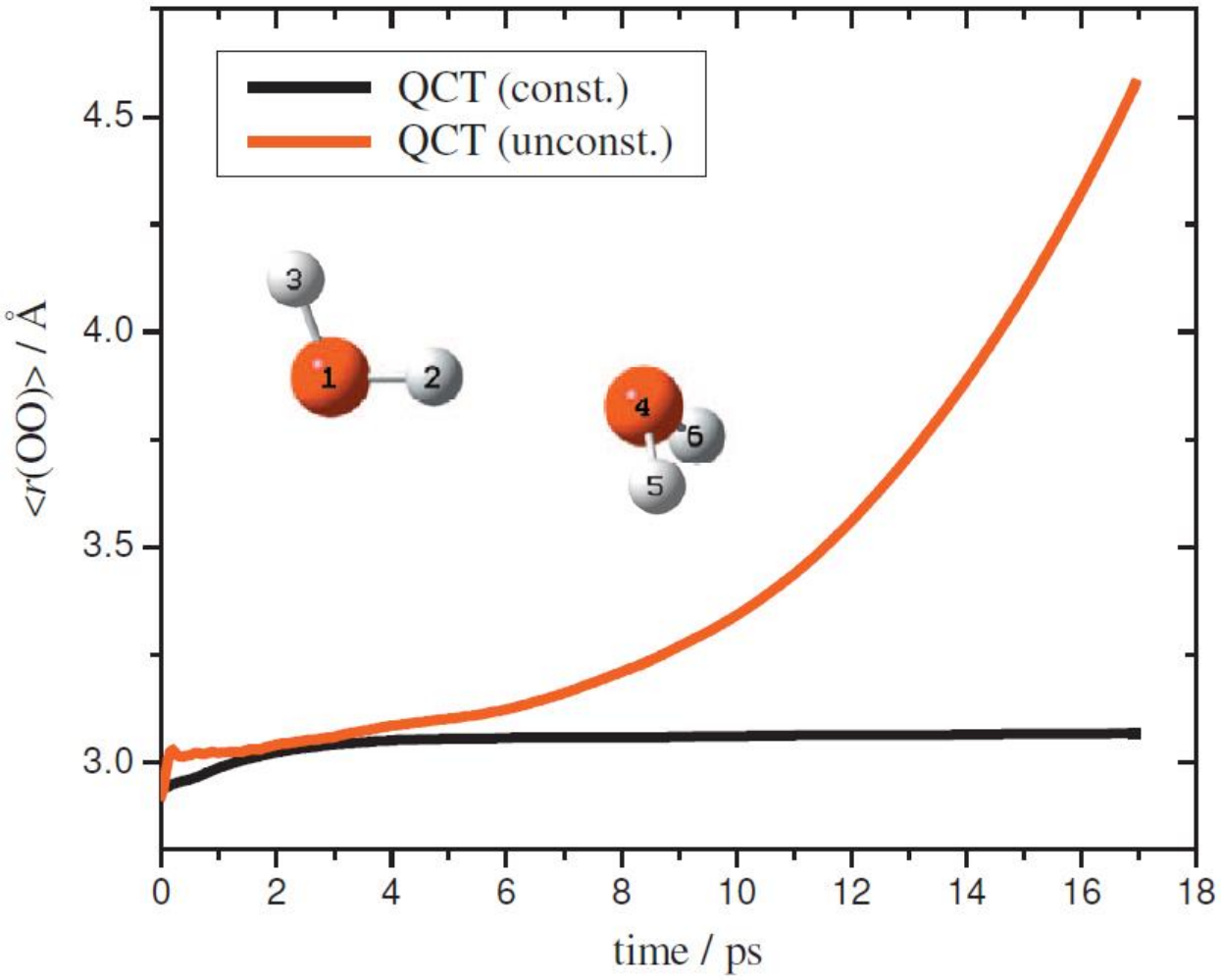
- A-SBH 33D
- dynamics on V_2

Mukherjee et al. *Philos Trans R Soc A* **2022**, DOI: 10.1098/rsta-2020-0382

Challenges we must face

- Stability of integration
  - ☑ Performance of integration algorithms
  - ☑ ZPE spilling





Czakó; Kaledin; Bowman. *J Chem Phys* **2010,** *132*, 164103

There are many ZPE-corrections proposed.

But they either require Hessians
or introduce statistical biases.

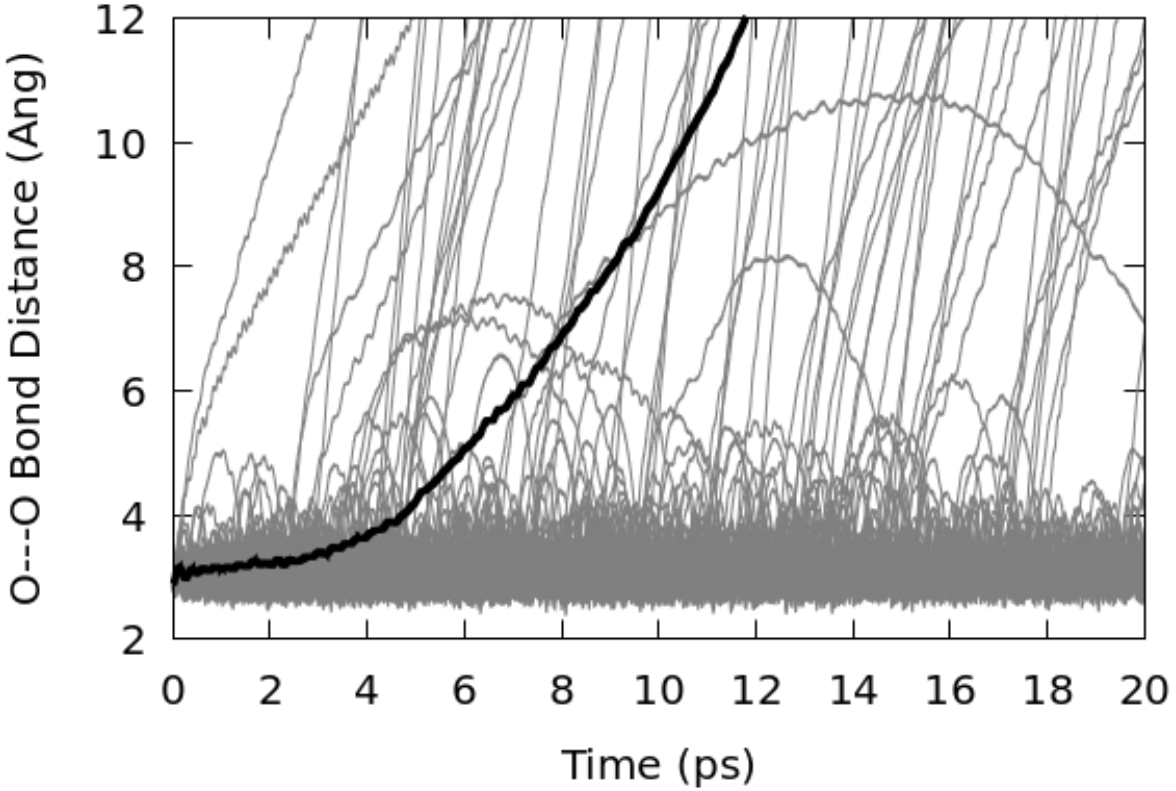
Miller; Hase; Darling. *J Chem Phys* **1989,** *91*, 2863
Bowman; Gazdy; Sun. *J Chem Phys* **1989,** *91*, 2859
Varandas; Marques. *J Chem Phys* **1994,** *100*, 1908
Guo; Thompson; Sewell. *J Chem Phys* **1996,** *104*, 576
....
Czakó; Kaledin; Bowman. *J Chem Phys* **2010,** *132*, 164103

Recently, Saikat Mukherjee and I developed a **Hessian-free ZPE correction**.

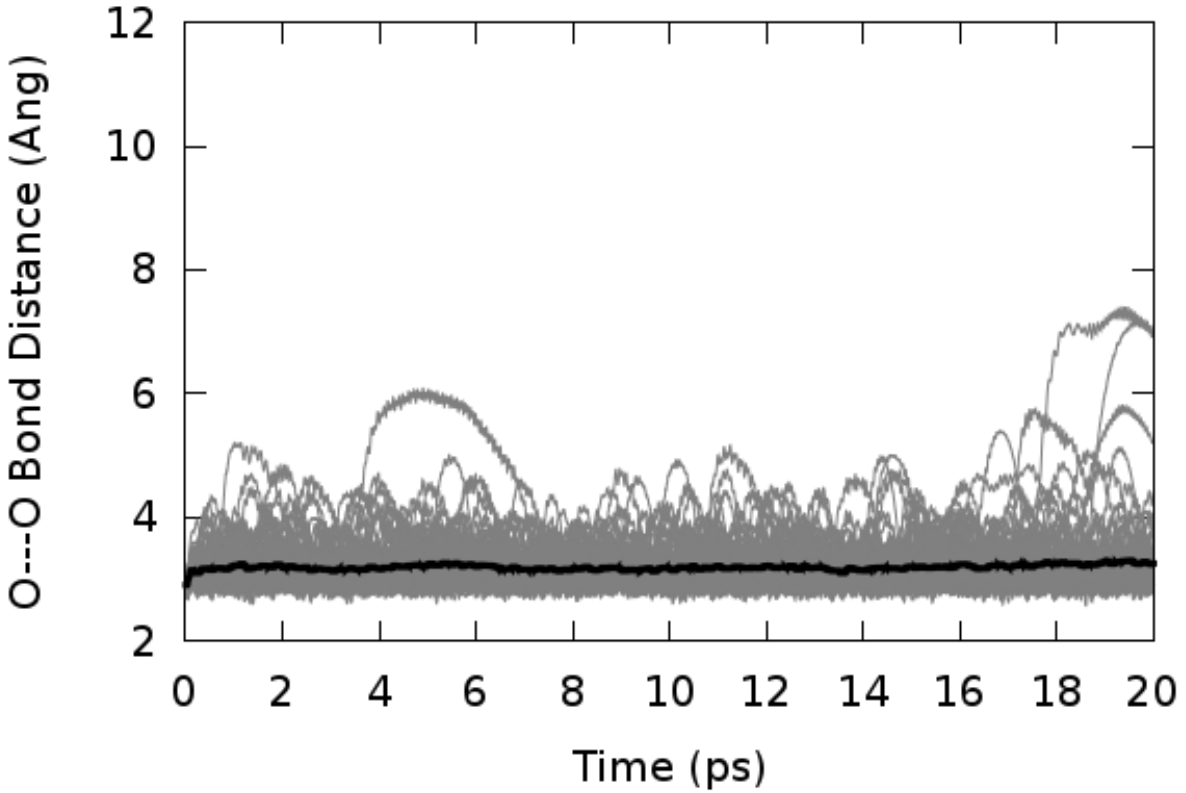
It works like a thermostat, transferring kinetic energy from the slow vibrations into fast vibrations, whenever a ZPE drop is detected.

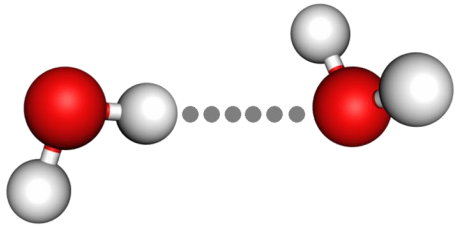
The correction conserves energy, momentum, and CM angular momentum.

No ZPE Correction



Hessian-free ZPE Correction





- S_0 MP2/aug-cc-pVDZ
- 100 trajs; 20 ps; Δt = 0.5 fs
- ZPE correction every 10 fs

Mukherjee; Barbatti. **2021**, coming soon

Challenges we must face

- Extreme cost reduction
- Stability of integration
- Accuracy of MQC methods
- Software optimization

Terms mediating nonadiabatic transitions

Full TDSE

$$H_{IJ} \propto \sum_{\alpha=1}^{3N_a} \frac{\hbar^2}{M_\alpha} \left\langle \chi_k^{(J)} \middle| \left\langle \Phi_J \middle| \frac{\partial}{\partial R_\alpha} \middle| \Phi_I \right\rangle_{\mathbf{r}} \frac{\partial}{\partial R_\alpha} \middle| \chi_i^{(I)} \right\rangle_{\mathbf{R}} + \sum_{\alpha=1}^{3N_a} \frac{\hbar^2}{2M_\alpha} \left\langle \chi_k^{(J)} \middle| \left\langle \Phi_J \middle| \frac{\partial^2}{\partial R_\alpha^2} \middle| \Phi_I \right\rangle_{\mathbf{r}} \middle| \chi_i^{(I)} \right\rangle_{\mathbf{R}}$$

AIMS

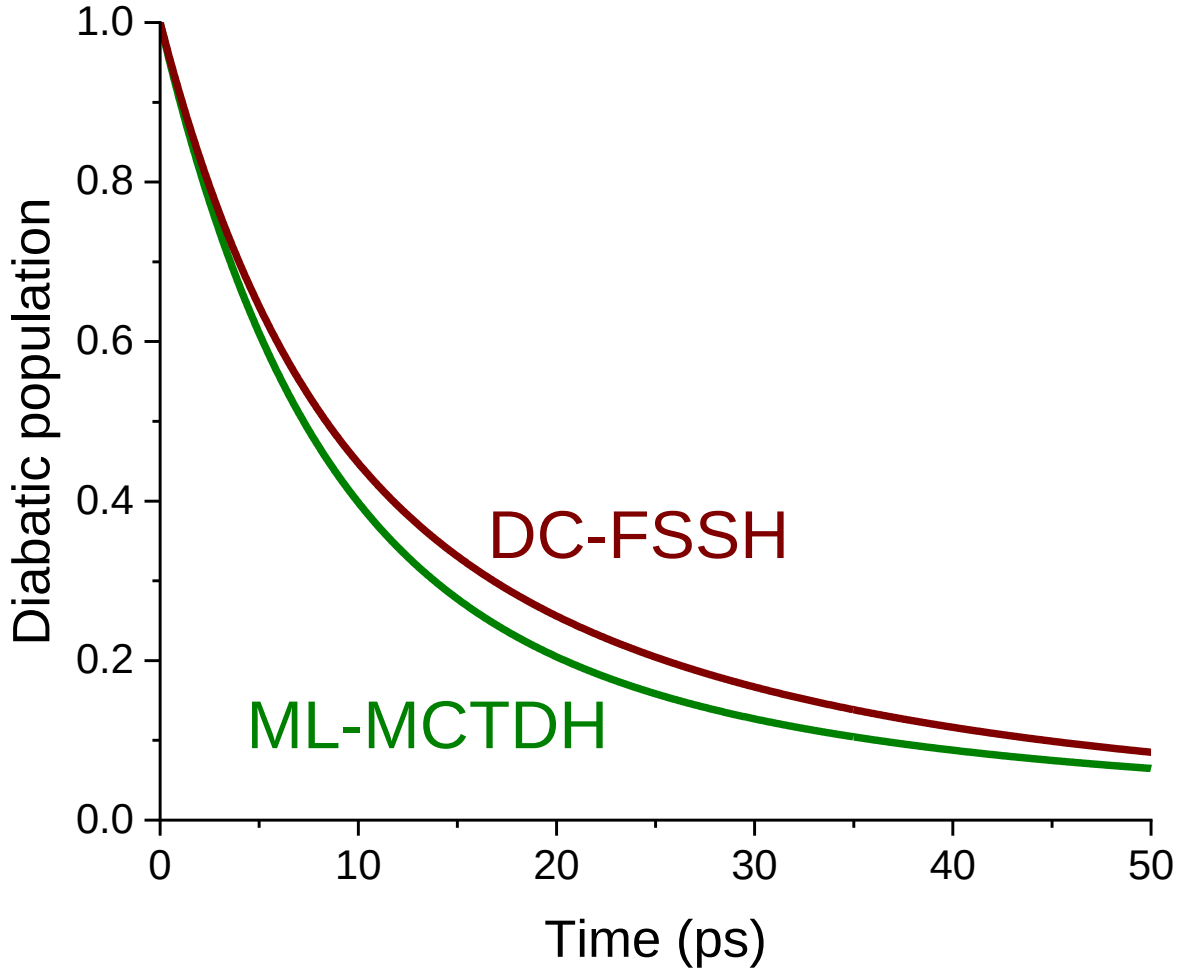
$$H_{IJ} \propto \sum_{\alpha=1}^{3N_a} \frac{\hbar^2}{M_\alpha} \left\langle \chi_k^{(J)} \middle| \frac{\partial}{\partial R_\alpha} \middle| \chi_i^{(I)} \right\rangle_{\mathbf{R}} \left\langle \Phi_J \middle| \frac{\partial}{\partial R_\alpha} \middle| \Phi_I \right\rangle_{\mathbf{r}} \Big|_{\bar{\mathbf{R}}}$$

FSSH

$$H_{IJ} \propto \sum_{\alpha=1}^{3N_a} \frac{\hbar}{M_\alpha} \bar{p}_\alpha \left\langle \Phi_J \middle| \frac{\partial}{\partial R_\alpha} \middle| \Phi_I \right\rangle_{\mathbf{r}} \Big|_{\bar{\mathbf{R}}}$$

Curchod; Martínez. *Chem Rev* **2018,** *118*, 3305

A-SBH 10D (weak coupling)



- DC-FSSH: 2000 trajs; 0.1 fs; 100 ps
- ML-MCTDH: SPFs = 16; Grid size = 64

Mukherjee et al. *Philos Trans R Soc A* **2022**, DOI: 10.1098/rsta-2020-0382

Challenges we must face

- Extreme cost reduction
- Stability of integration
- Accuracy of MQC methods
- Software optimization

Challenges we must face

- Software optimization
  - ☑ Fast processing
  - ☑ Handling big data
  - ☑ Comply with open-data requirements

Newtonian Dynamics Close to the X-Seam

The NEWTON-X platform

- Surface hopping & Nuclear ensemble spectrum simulations
- Freeware
- Open source
- Simulations with MRCI, MCSCF, CASPT2, ADC(2), TDDFT, TD-DFTB, Analytical models, Machine learning potentials

Barbatti et al. *WIREs* **2014,** *4*, 26

Newton-X
new series

Speed-up execution

- Rewriting core loop
- Minimize I/O

Optimize development environment

- Restructuring variable management
- GitLab UI
- Clear development protocol

Comply with new open data standard

- HDF5 data standard (H5MD)

Keep established functionalities

- Deep-level cleaning & debugging

Newton-X
new series

Rewriting the core loop

NEWTON-X CS

PERL:

for t = 0 until $t = t_{max}$

E_K, ∇E_K, $|\psi_K\rangle$ = **PERL**: call EXTERNAL PROG (**R**)

R, **v** = call **FORTRAN:** VELOCITY VERLET (**R**, **v**, ∇E_L)

σ_{LK} = call [**PERL**:**C++**]: COUPLING ($|\psi_L\rangle$,$|\psi_K\rangle$)

L = call **FORTRAN**: SURFACE HOPPING(E_K, σ_{LK}, $\mathbf{v}_L$)

$t = t + \Delta t$

NEWTON-X NS

FORTRAN:

for t = 0 until $t = t_{max}$

E_K, ∇E_K, $|\psi_K\rangle$ = call **PERL:** EXTERNAL PROG (**R**)

R, **v** = call **FORTRAN:** VELOCITY VERLET (**R**, **v**, ∇E_L)

σ_{LK} = call [**FORTRAN**:**C++**]: COUPLING ($|\psi_L\rangle$,$|\psi_K\rangle$)

L = call **FORTRAN**: SURFACE HOPPING(E_K, σ_{LK}, $\mathbf{v}_L$)

$t = t + \Delta t$

LIGHT AND
MOLECULES

Newton-X new series

NEWTON-X CS	NEWTON-X NS
05:40:00	00:11:00

- A-SBH 10D
- DC-FSSH: 1 traj, 0.1 fs; 1 ps
- 1 core

LIGHT AND MOLECULES

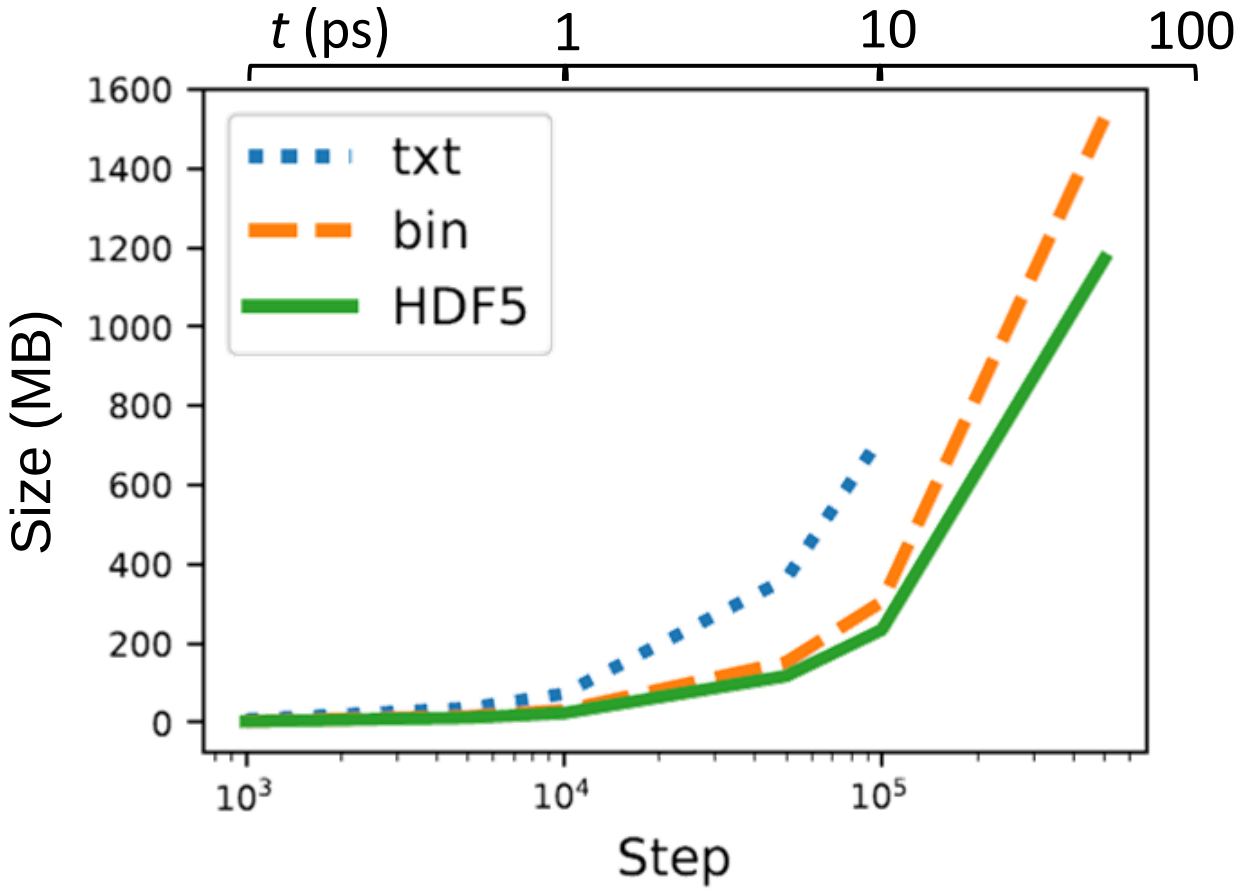
Newton-X
new series

New data format
H5MD: MD-oriented HDF5

- ✓ Data structured
- ✓ Data compressed
- ✓ Fast and parallel I/O
- ✓ Portable
- ✓ Self-contained

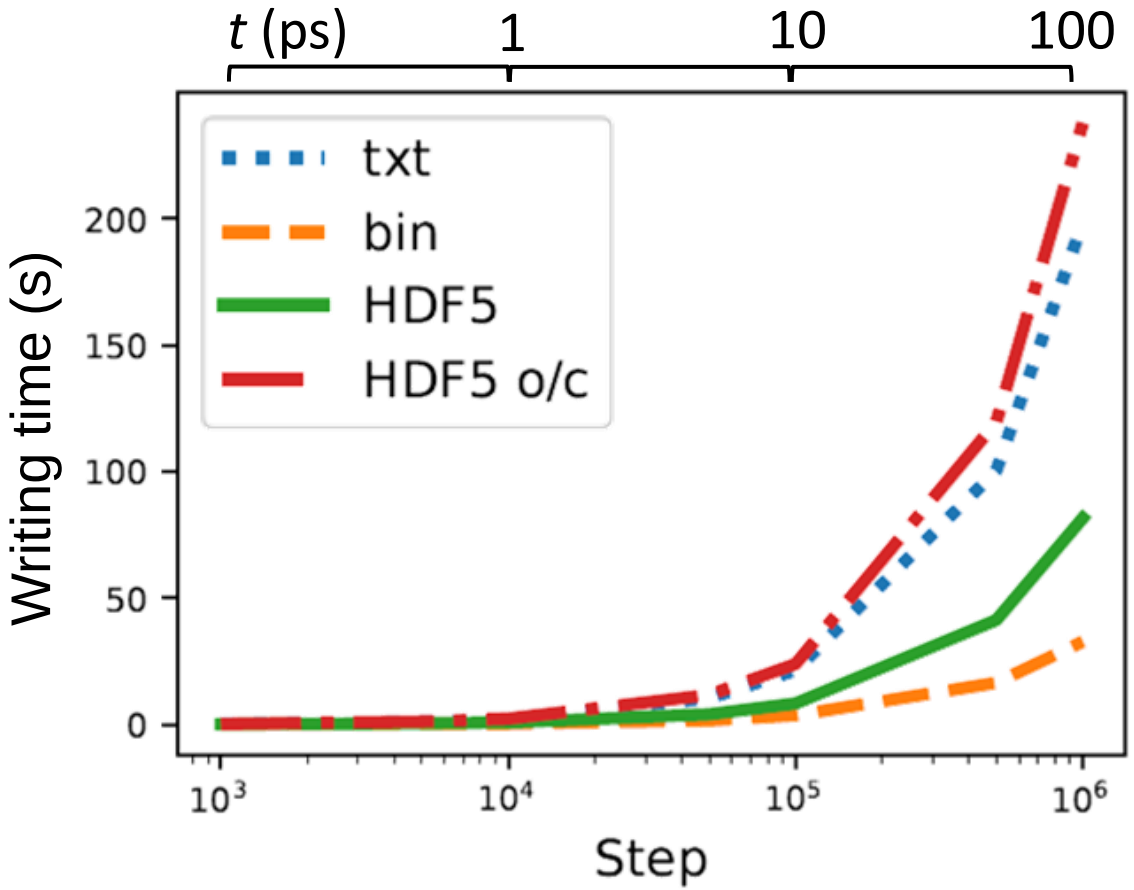
de Buyl; Colberg; Höfling. *Comput Phys Commun* **2014,** *185*, 1546

Newton-X
new series



LIGHT AND
MOLECULES

Newton-X
new series



LIGHT AND
MOLECULES

Newton-X
new series

Open-data compliance

We are developing protocols to guarantee that our simulation results are:

- Searchable (standard format, public repositories)
- Auditable (full dataset available)
- Reproducible (source codes and inputs available)

What's coming next?

Many nonadiabatic phenomena happen in the long timescale. They are inaccessible for current dynamics methods.

Machine learning should be the main driving force for a new generation of methods.

We may expect a publication rush in the field.

We are computing benchmarks, developing methods, proposing protocols, and rewriting Newton-X to face this demand.

NEWTON-X NS

Release in Spring 2022

LIGHT AND MOLECULES

LIGHT AND MOLECULES

Machine learning and Integration stability:
Max Pinheiro Jr

ZPE corrections and MQCD accuracy:
Saikat Mukherjee

Newton-X NS:
Baptiste Demoulin

LIGHT AND
MOLECULES

Marseille-Xiamen
Machine Learning Consortium

Mario Barbatti
Max Pinheiro Jr
Baptiste Demoulin
Mithun M

Pavlo Dral
Baoxin Xu
Fuchun Ge
Lina Zhang
Yanchi Ou
Yifan Hou

Dral; Barbatti. *Nat Rev Chem* **2021,** *5*, 388

SUBNANO

erc

FET OPEN

BOOST CROP

Aix*Marseille université

Initiative d'excellence

institut universitaire de France

LIGHT AND MOLECULES

SciPost: SciPost Chemistry

scipost.org/SciPostChem

Bookmarks | dyna | Orthorhombic | Google Translate | MediaCom Worldwi... | How to Install and... | Proposals - Researc... | Other bookmarks | Reading list

SciPost

Search

Journals | Submissions | More | About SciPost | Login or register

Journals / Chemistry Journals / SciPost Chemistry / Home

SciPost Chemistry

Home | Authoring | Refereeing | Submit a manuscript | About

Latest publications | Accepted Submissions | Most cited | Issues

Relativistic density-functional theory based on effective quantum electrodynamics

Julien Toulouse

SciPost Chem. 1, 002 (2021) · published 18 May 2021 | Toggle abstract · pdf

The seniority quantum number in Tensor Network States

Klaas Gunst, Dimitri Van Neck, Peter Andreas Limacher, Stijn De Baerdemacker

SciPost Chem. 1, 001 (2021) · published 15 January 2021 | Toggle abstract · pdf

Open review

Open finances

Diamond Open Access

www.barbatti.org

mario.barbatti@univ-amu.fr

@MarioBarbatti