Basic Concepts on Surface Hopping (as in implemented in Newton-X)

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The Light and Molecules Group

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Methods

Mixed quantum-classical dyn

Software

Newton-X

Ulamdyn

PySOC

Applications

Photoprocesses in

- Fundamental PhysChem
- Molecular biology
- Organic devices
- Environment

The Light and Molecules Group

www.barbatti.org

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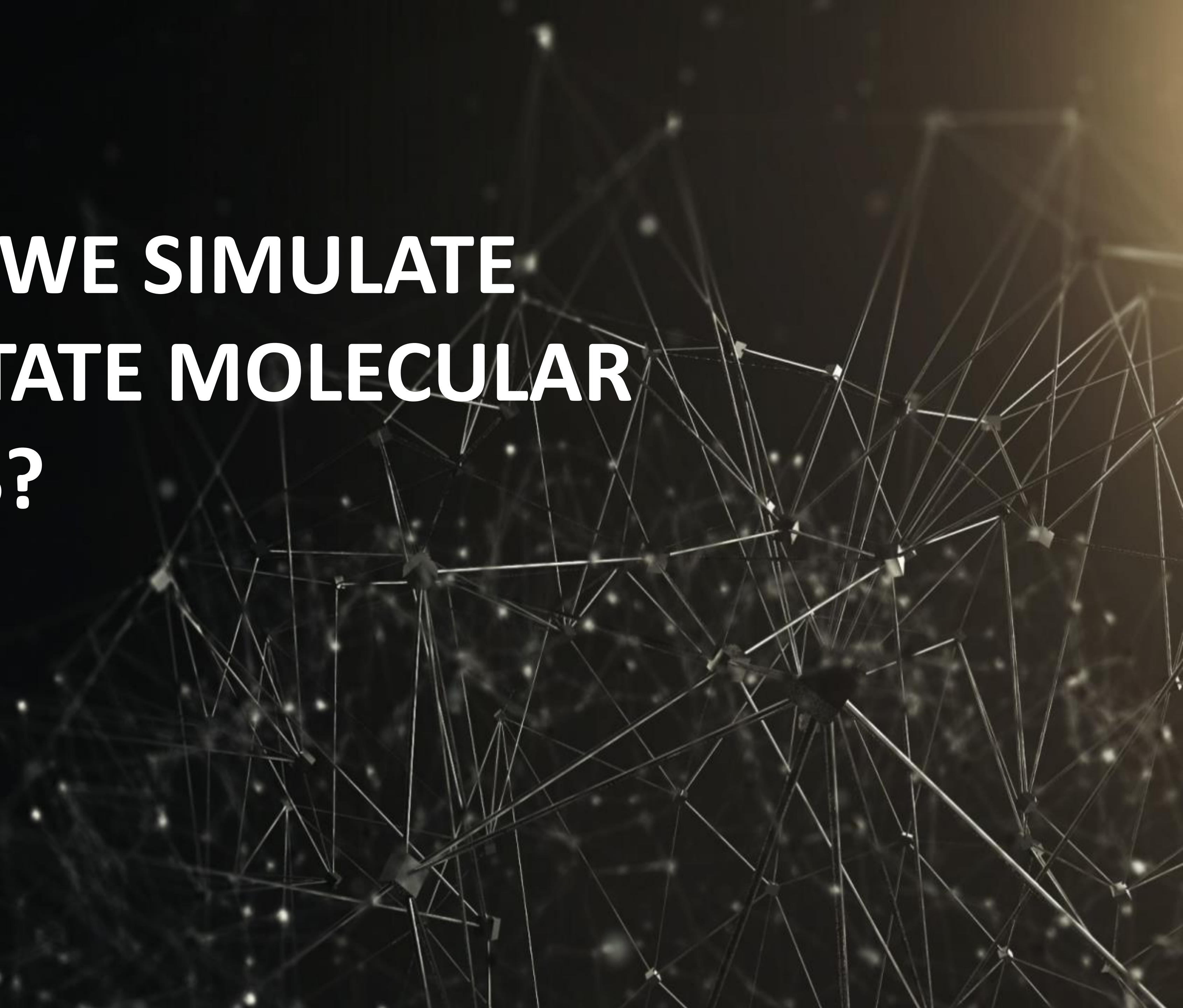
Mithun M (internship)

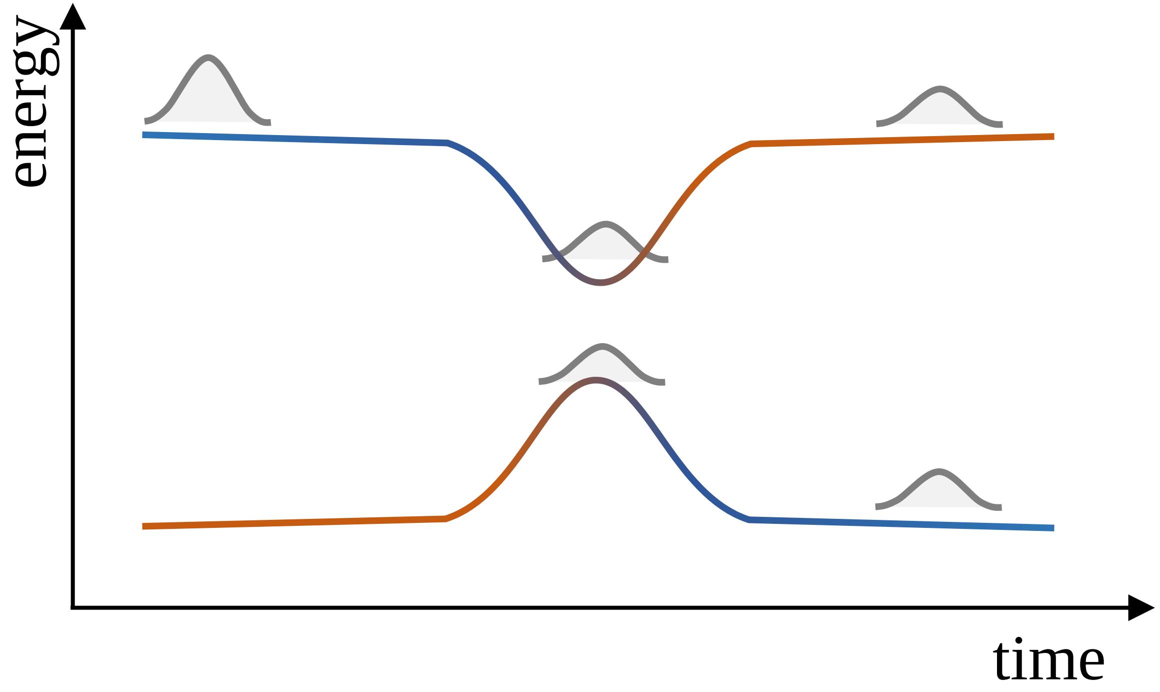
Special thanks to

LIGHT AND MOLECULES

HOW CAN WE SIMULATE EXCITED-STATE MOLECULAR DYNAMICS?



Photochemical and photophysical phenomena in molecules involve the
time evolution of the nuclear wavepacket through a manifold of electronic states

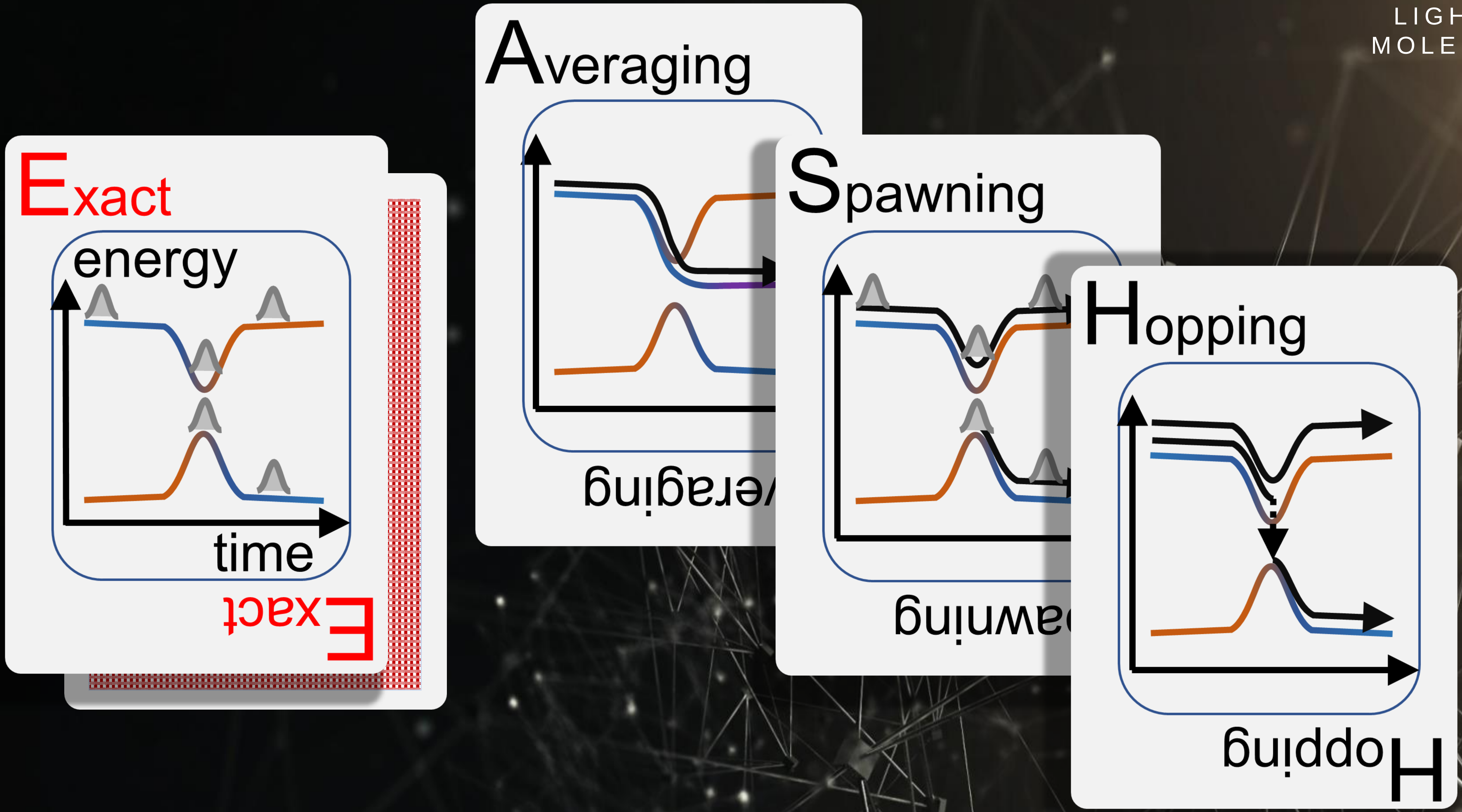


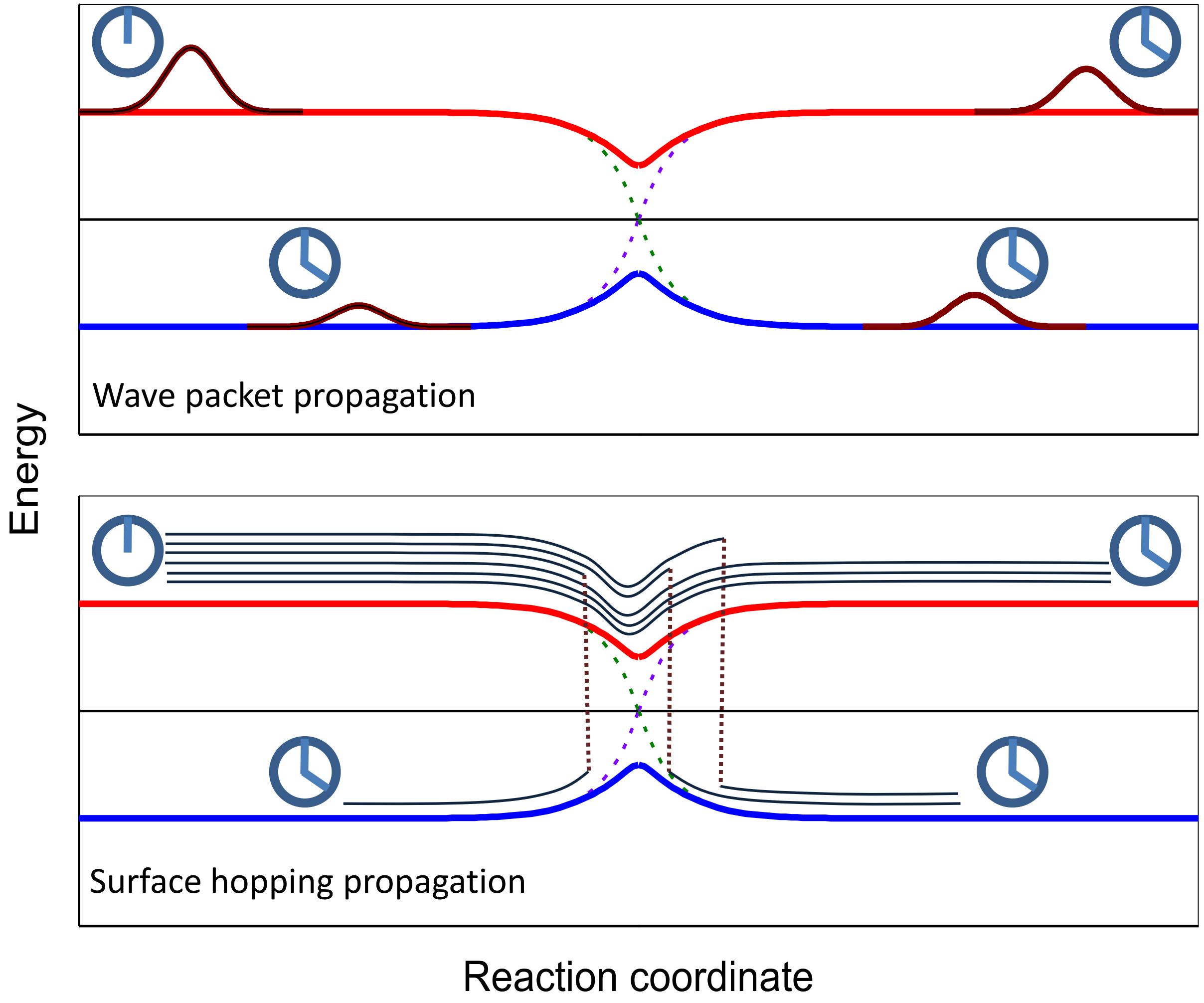
Modeling these processes requires considering
the coupling between the nuclear and electronic motions (**nonadiabatic** regime)

Nonadiabatic Mixed Quantum-Classical dynamics (NA-MQCD)

1. Nuclei are treated via *classical trajectories*
2. Electrons are treated *quantum mechanically*
3. A nonadiabatic algorithm ensures introduces *post Born-Oppenheimer effects*

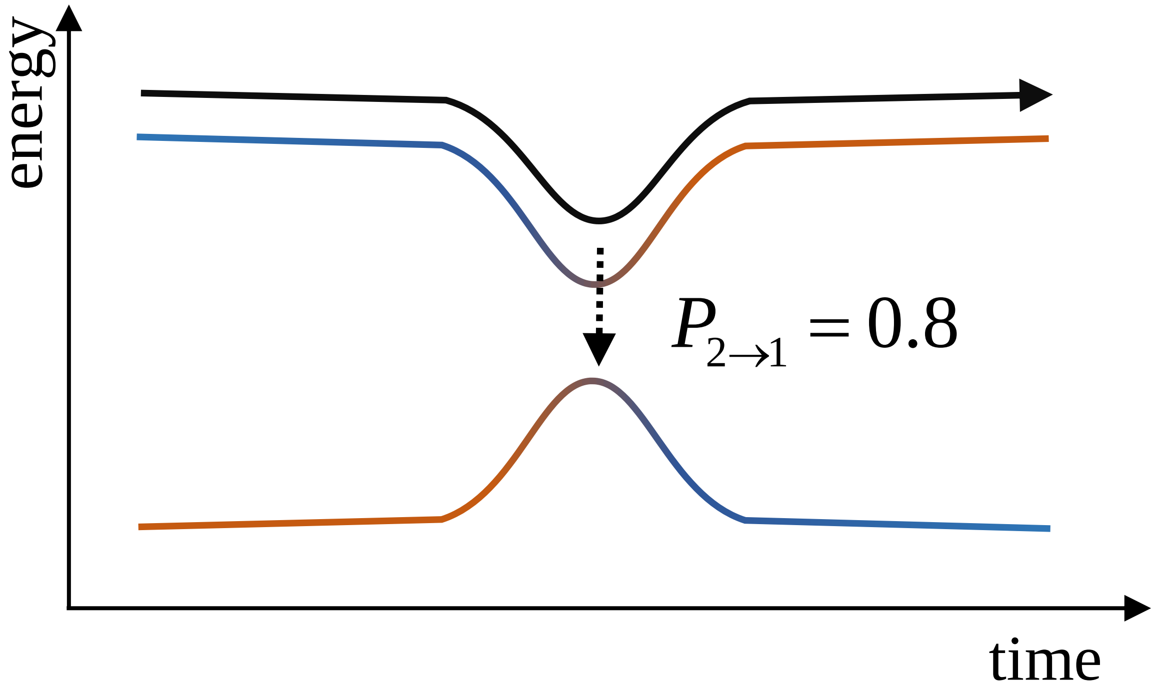
- Tully. *J Chem Phys* **1990,** *93*, 1061.
- *Review*: Crespo-Otero; Barbatti. *Chem Rev* **2018,** *118*, 7026


Exact
energy
time
Exact
Averaging
Averaging
Spawning
Spawning
Hopping
Hopping

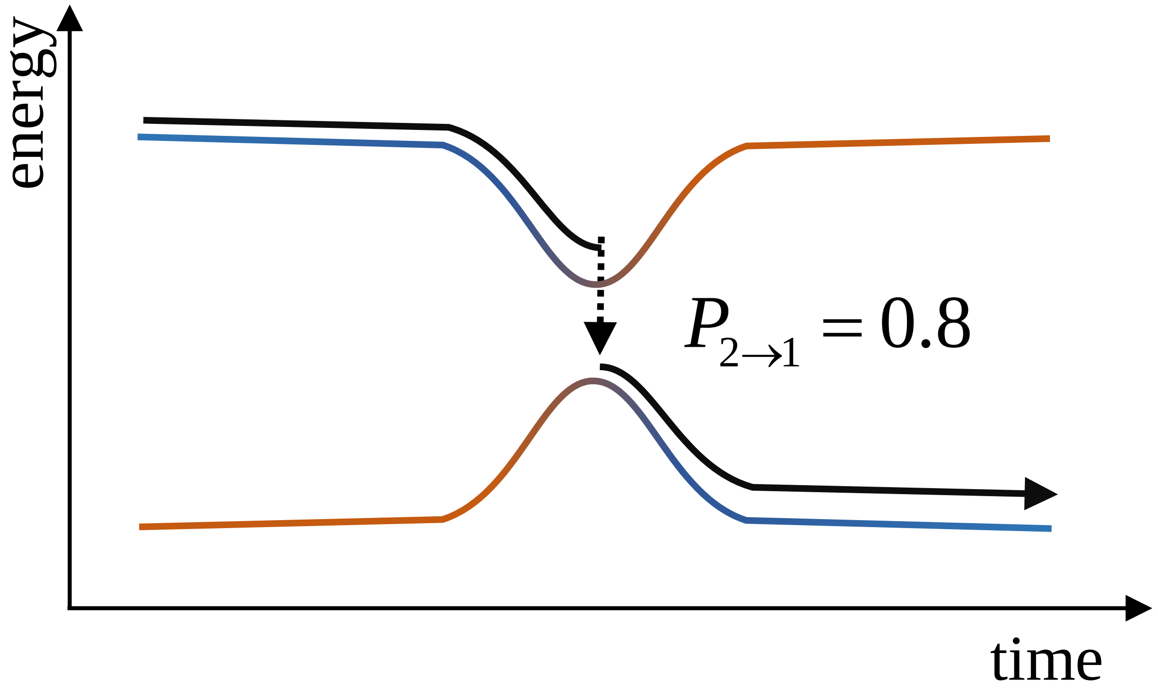


- Tully. *J Chem Phys* **1990,** *93*, 1061.
- *Review*: Crespo-Otero; Barbatti. *Chem Rev* **2018,** *118*, 7026

$r = 0.85$



$r = 0.75$



THE NEWTON-X PLATFORM

The NEWTON-X platform

- Surface hopping & Nuclear ensemble spectrum simulations
- Freeware
- Open source

- Barbatti; Ruckenbauer; Plasser; Pittner; Granucci; Persico; Lischka. *WIREs* **2014,** *4*, 26
- Barbatti; Granucci; Persico; Ruckenbauer; Vazdar; Eckert-Maksić; Lischka. *J Photochem Photobiol A* **2007**, 190, 228

Newtonian Dynamics Close to the X-Seam

Electronic structure	Program
MRCI, MCSCF (+MM)	COLUMBUS
XMS-CASPT2, CASSCF (+MM)	BAGEL
MCSCF	GAMESS
MCSCF	GAUSSIAN
(LR, RI) CC2, (SOS) ADC(2) (+MM)	TURBOMOLE
(LR) (TDA), TD(U)DFT, (U)CIS	GAUSSIAN
(LR) TDDFT	TURBOMOLE
(LR) LC-TD-DFTB	DFTB+
Machine learning	MLATOM
Spin Boson Hamiltonian 2D Conical intersection 1D models collection	Built-in models

Newtonian Dynamics Close to the X-Seam

newtonx.org

Core developers

M Barbatti (FR)
R Crespo-Otero (UK)
J Pittner (CZ)
M Ruckenbauer (AT), F Plasser (UK)
H Lischka (US)
G Granucci, M Persico (IT)

Development team in Marseille

S Mukherjee	*Vibronic effects, ZPE leak*
M Pinheiro Jr	*Machine learning*
B Demoulin	*Newton-X NS*
M Bondanza	*Polarizable FF*

Contributors

JW Park, T Shiozaki (US):	*CASPT2 dynamics*
J Nagesh, A Izmaylov (CA):	*OD couplings*
A West, T Windus (US):	*GAMESS interface*
X Gao (US):	*SOC matrix*
P Dral (CN):	*Machine learning*

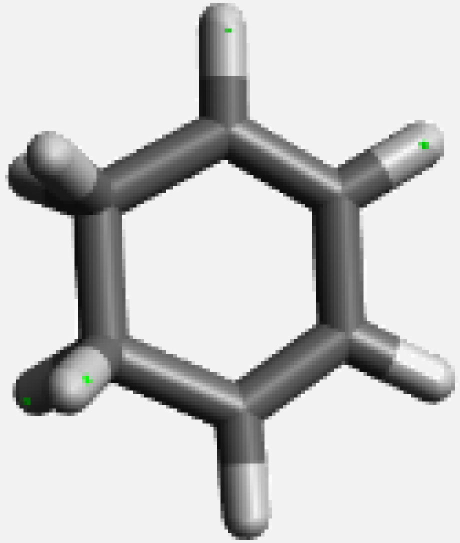
External developers

M Pederzoli (CZ):	*ISC dynamics*
L Stojanović (UK):	*TD-DFTB dynamics*
W Arbelo-González (US):	*Photoelectron spectrum*
F Kossoski (FR):	*CS-FSSH, import sampling*
P Goel (DE):	*Zero-model interface*

NX newtonx.org Newtonian Dynamics Close to the X-Seam

XMS-CASPT2

Cyclohexadiene



- 14 atoms
- 3 electronic states
- 150 trajectories
- 0.4 ps/trajectory
- 0.5 fs time step

Polyak; Hutton; Crespo-Otero; Barbatti; Knowles.
JCTC **2019**, *15*, 3929

Cycloparaphenylene

Stojanović; Aziz; Hilal; Plasser; Niehaus; Barbatti.
JCTC **2017**, *13*, 5845

TD-LC-DFTB

- 100 atoms
- 7 electronic states
- 50 trajectories
- 3 ps/trajectory
- 0.5 fs time step

- **MQC-PE: Dynamics induced by thermal light**
  Barbatti. *J Chem Theory Comput* **2020,** *16*, 4849

- **NAE-ML: Nuclear ensemble spectra with machine learning**
  Xue; Barbatti; Dral. *J Phys Chem A* **2020,** *124*, 7199

- **CS-FSSH: Nonadiabatic dynamics on complex-valued PES**
  Kossoski; Barbatti. *Chem Sci* **2020,** *11*, 9827

- **TD-BA: Nonadiabatic couplings evaluation without wave functions**
  T. do Casal; Toldo; Pinheiro Jr; Barbatti. *Open Res Europe* **2021,** *1*, 49

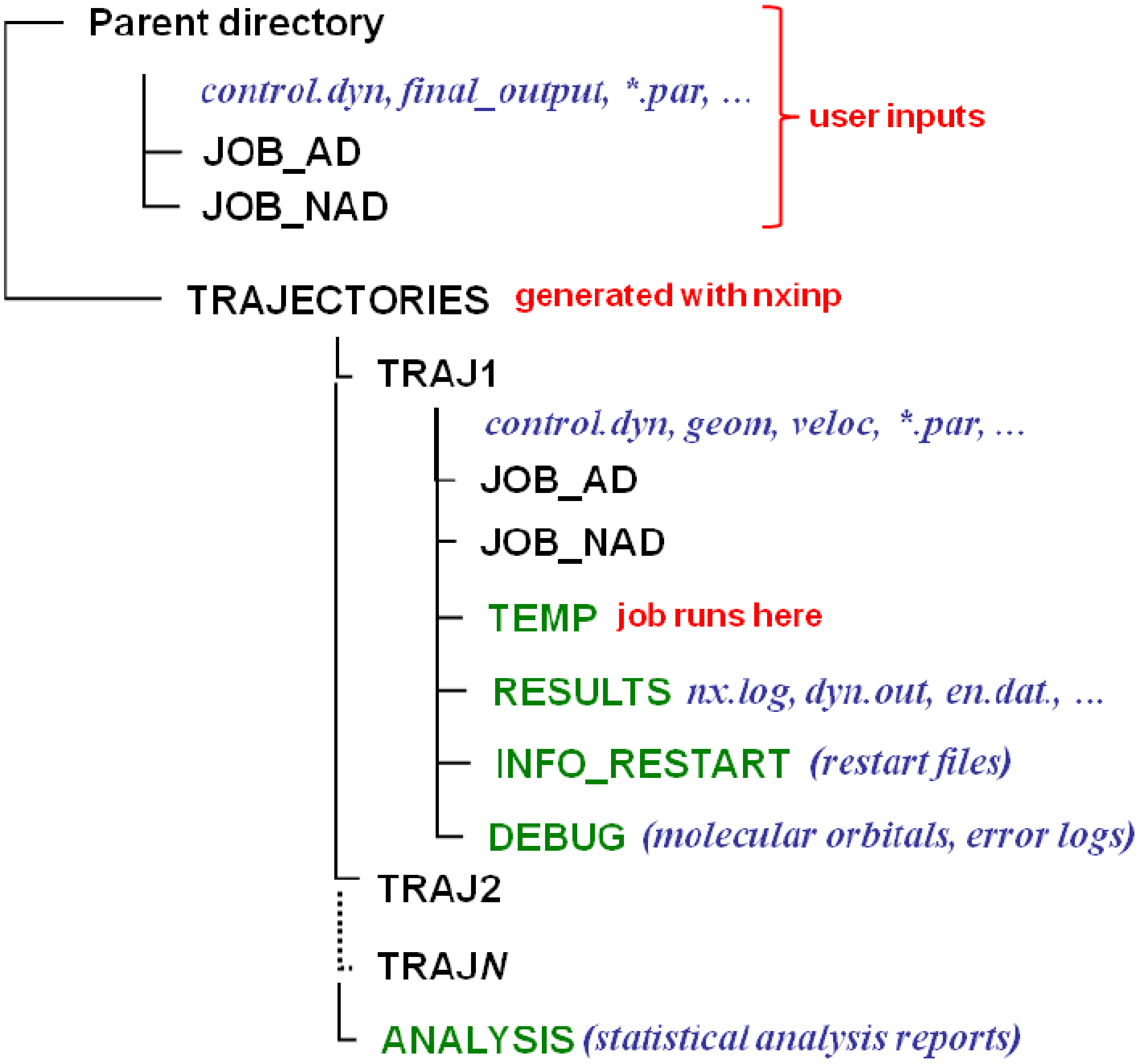
- **Simulation of time-resolved UV pump−IR probe spectra**
  Fingerhut; Dorfman; Mukamel. *J Phys Chem Lett* **2013,** *4*, 1933

- **Nonadiabatic dynamics with ONIOM**
  Fingerhut; Oesterling; Haiser; Heil; Glas; Schreier; Zinth; Carell; de Vivie-Riedle. *J Chem Phys* **2012,** *136*, 204307

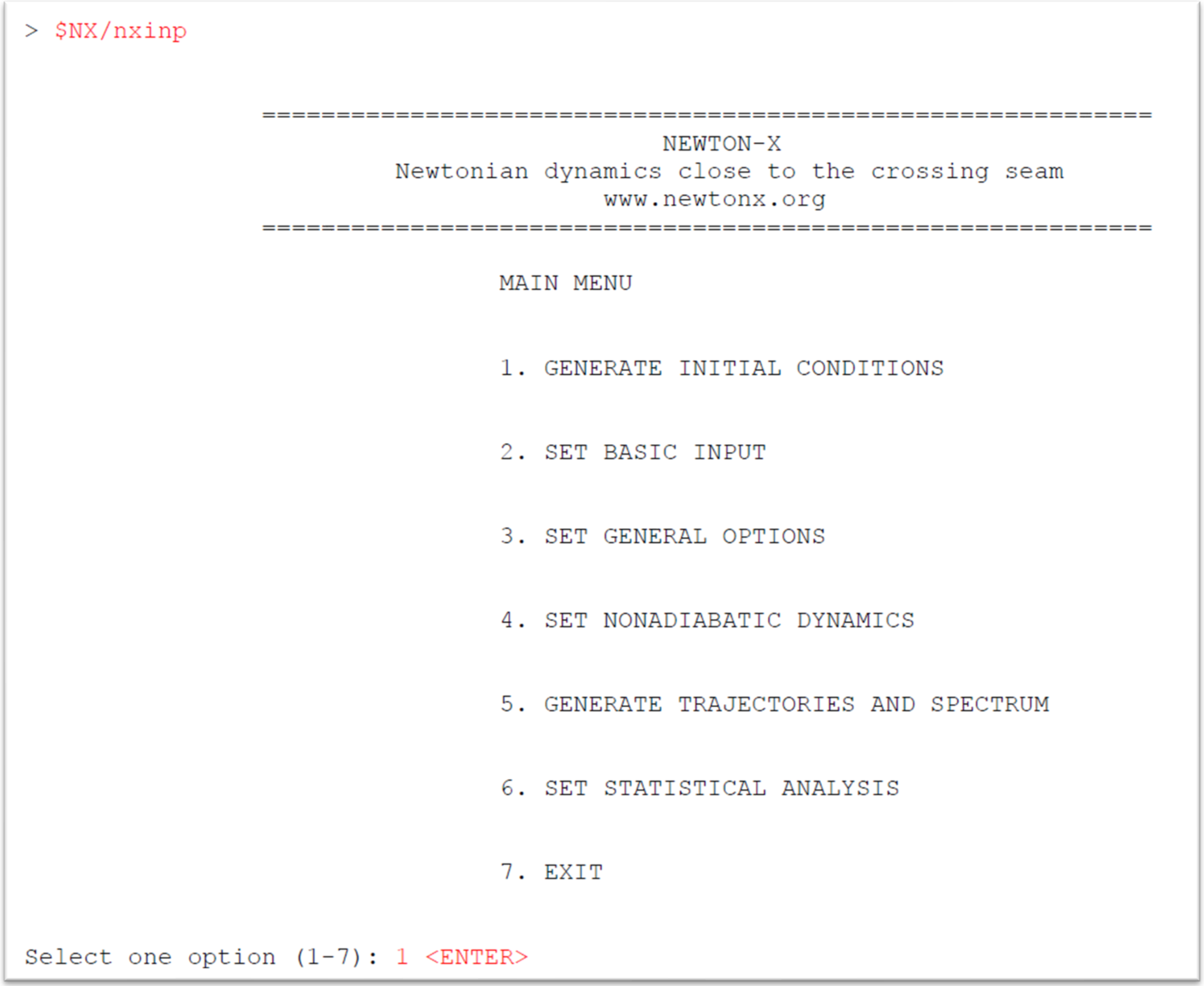
- **Fast evaluation of time-derivative nonadiabatic couplings**
  Ryabinkin; Nagesh; Izmaylov. *J Phys Chem Lett* **2015,** *6*, 4200

- **On-the-fly Dynamics with CASPT2 analytical gradients**
  Park; Shiozaki. *JCTC* **2017,** *13*, 3676

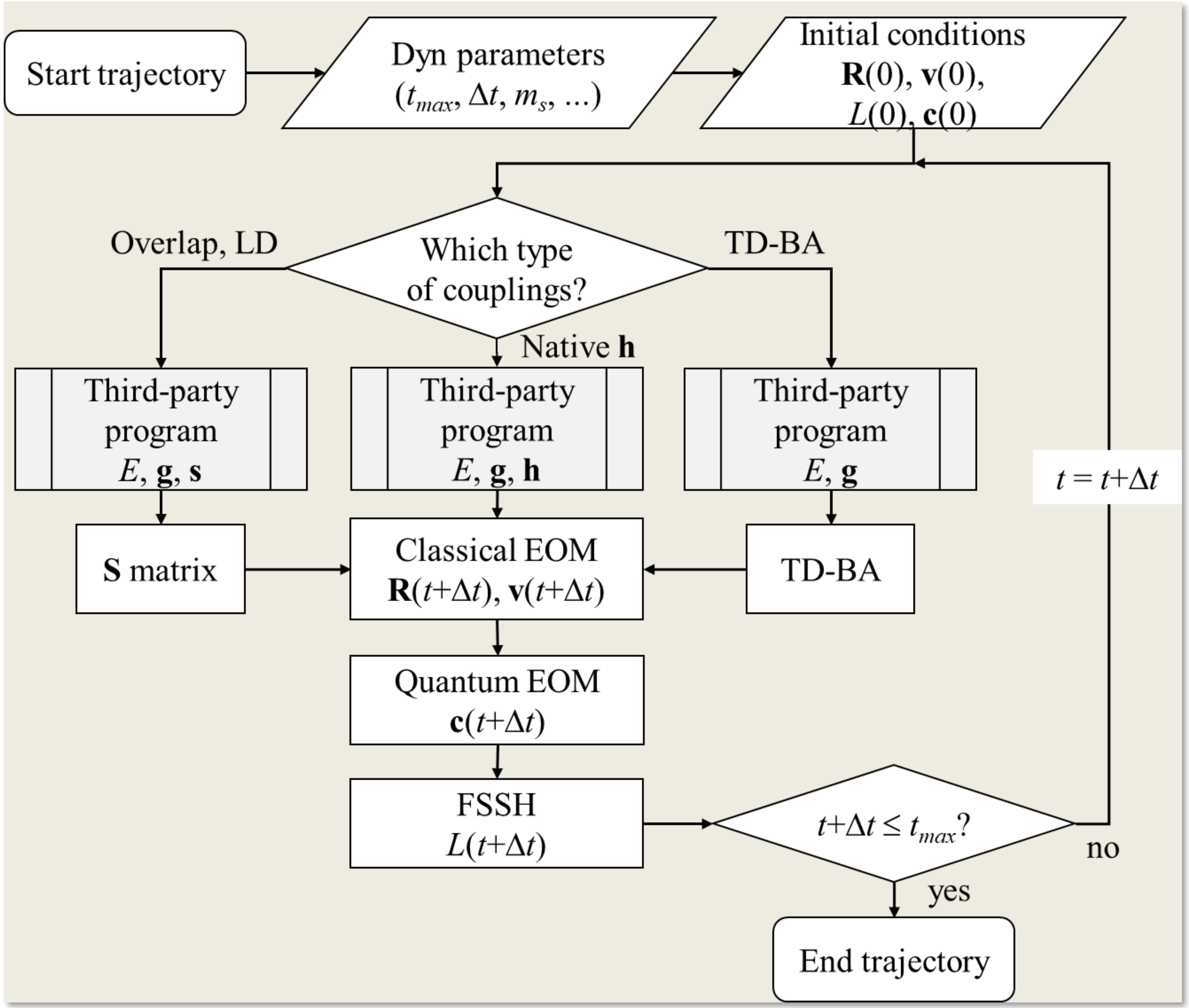
DYNAMICS WITH DC-FSSH



- Parent directory
  - *control.dyn, final_output, *.par, …*
  - JOB_AD
  - JOB_NAD
  - user inputs
- TRAJECTORIES generated with nxinp
  - TRAJ1
    - *control.dyn, geom, veloc, *.par, …*
    - JOB_AD
    - JOB_NAD
    - TEMP job runs here
    - RESULTS *nx.log, dyn.out, en.dat., …*
    - INFO_RESTART *(restart files)*
    - DEBUG *(molecular orbitals, error logs)*
  - TRAJ2
  - TRAJ*N*
  - ANALYSIS *(statistical analysis reports)*



```
> $NX/nxinp


                 ================================================================
                                          NEWTON-X
                          Newtonian dynamics close to the crossing seam
                                      www.newtonx.org
                 ================================================================

                                  MAIN MENU


                                  1. GENERATE INITIAL CONDITIONS

                                  2. SET BASIC INPUT

                                  3. SET GENERAL OPTIONS

                                  4. SET NONADIABATIC DYNAMICS

                                  5. GENERATE TRAJECTORIES AND SPECTRUM

                                  6. SET STATISTICAL ANALYSIS

                                  7. EXIT

Select one option (1-7): 1 <ENTER>
```


Start trajectory
Dyn parameters (t_{max}, Δt, m_s, …)
Initial conditions $\mathbf{R}(0)$, $\mathbf{v}(0)$, $L(0)$, $\mathbf{c}(0)$
Which type of couplings?
Overlap, LD
Native **h**
TD-BA
Third-party program E, $\mathbf{g}$, $\mathbf{s}$
Third-party program E, $\mathbf{g}$, $\mathbf{h}$
Third-party program E, $\mathbf{g}$
S matrix
Classical EOM $\mathbf{R}(t+\Delta t)$, $\mathbf{v}(t+\Delta t)$
TD-BA
Quantum EOM $\mathbf{c}(t+\Delta t)$
FSSH $L(t+\Delta t)$
$t+\Delta t \leq t_{max}$?
no
$t = t+\Delta t$
yes
End trajectory

1. Treat Nuclei classically on a single BO surface

$$\frac{d^2\bar{\mathbf{R}}}{dt^2} = \frac{1}{M_\alpha}\mathbf{F}\left(\bar{\mathbf{R}}\right) \qquad \mathbf{F}\left(\bar{\mathbf{R}}\right) = -\nabla_\alpha E_L$$

Velocity Verlet:

$$\bar{\mathbf{R}}_\alpha(t+\Delta t) = \bar{\mathbf{R}}_\alpha(t) + \bar{\mathbf{v}}_\alpha(t)\Delta t + \frac{1}{2}\bar{\mathbf{a}}_\alpha(t)\Delta t^2$$

$$\mathbf{v}_m^c\left(t+\frac{\Delta t}{2}\right) = \bar{\mathbf{v}}_\alpha(t) + \frac{1}{2}\mathbf{a}_m^c(t)\Delta t$$

$$\bar{\mathbf{a}}_\alpha(t) = -\frac{1}{M_\alpha}\nabla_R E\left[\bar{\mathbf{R}}_\alpha(t+\Delta t)\right]$$

$$\bar{\mathbf{v}}_\alpha(t+\Delta t) = \bar{\mathbf{v}}_\alpha\left(t+\frac{\Delta t}{2}\right) + \frac{1}{2}\bar{\mathbf{a}}_\alpha(t+\Delta t)\Delta t$$

control.dyn:

DT = time step

PROG = QM program for **a**

- Swope; Andersen; Berens; Wilson. *J Chem Phys* **1982,** *76*, 637

Time-step

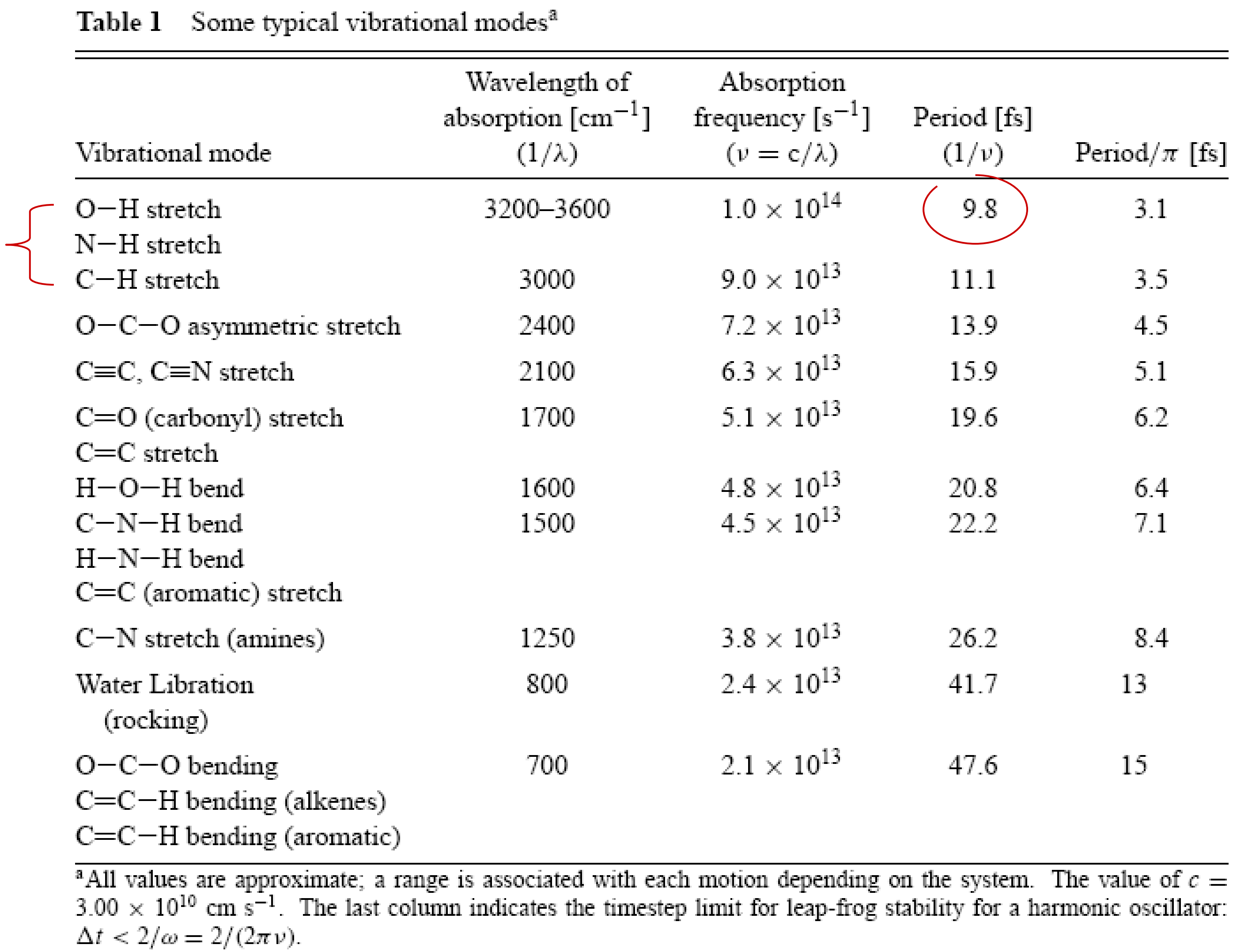


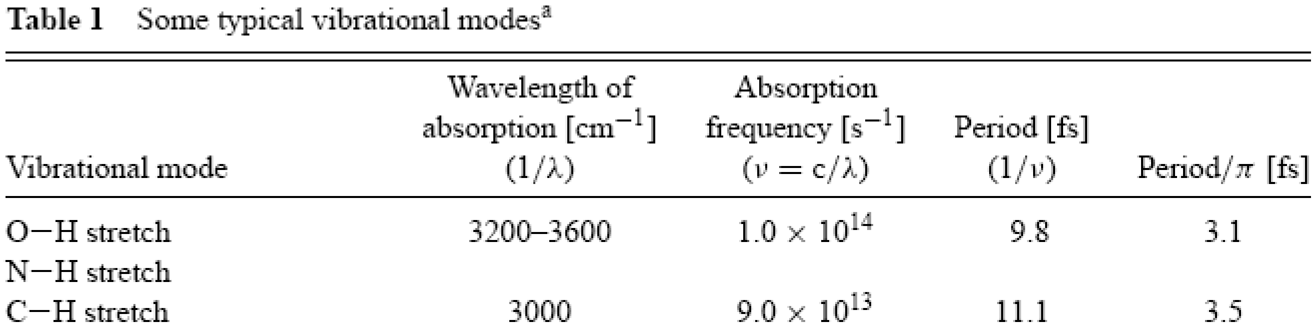
Table 1 Some typical vibrational modes[a]

Vibrational mode	Wavelength of absorption [cm^{-1}] (1/λ)	Absorption frequency [s^{-1}] ($\nu = c/\lambda$)	Period [fs] ($1/\nu$)	Period/π [fs]
O−H stretch N−H stretch	3200–3600	1.0×10^{14}	9.8	3.1
C−H stretch	3000	9.0×10^{13}	11.1	3.5
O−C−O asymmetric stretch	2400	7.2×10^{13}	13.9	4.5
C≡C, C≡N stretch	2100	6.3×10^{13}	15.9	5.1
C=O (carbonyl) stretch C=C stretch	1700	5.1×10^{13}	19.6	6.2
H−O−H bend	1600	4.8×10^{13}	20.8	6.4
C−N−H bend H−N−H bend C=C (aromatic) stretch	1500	4.5×10^{13}	22.2	7.1
C−N stretch (amines)	1250	3.8×10^{13}	26.2	8.4
Water Libration (rocking)	800	2.4×10^{13}	41.7	13
O−C−O bending C=C−H bending (alkenes) C=C−H bending (aromatic)	700	2.1×10^{13}	47.6	15

[a] All values are approximate; a range is associated with each motion depending on the system. The value of $c = 3.00 \times 10^{10}$ cm s^{-1}. The last column indicates the timestep limit for leap-frog stability for a harmonic oscillator: $\Delta t < 2/\omega = 2/(2\pi\nu)$.

- Schlick; Barth; Mandziuk. Annu Rev Biophys Struct **1997**, *26*, 181

Time-step



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O−H stretch	3200–3600	1.0×10^{14}	9.8	3.1
N−H stretch				
C−H stretch	3000	9.0×10^{13}	11.1	3.5

Time step should smaller than 1 fs (1/10*v*)

Δt = 0.5 fs assures a good level of conservation of energy

Exceptions:

- Dynamics close to the conical intersection may require 0.25 fs
- Dissociation processes may require even smaller time steps

2. Solve the locally-approximated TDSE

$$\frac{dc_J}{dt} = -\sum_K \left(\frac{i}{\hbar} E_L + \sigma_{JK} \right) c_K$$

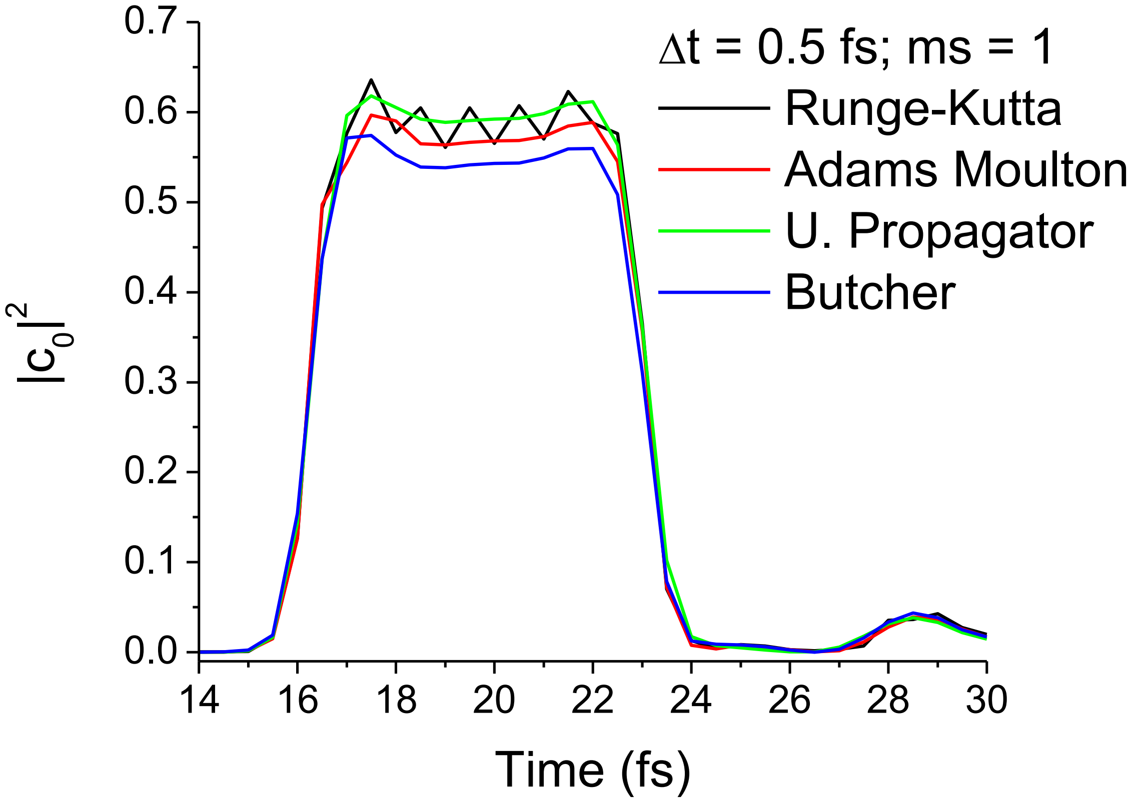
- Tully. *J Chem Phys* **1990,** *93*, 1061

$$\frac{dc_J}{dt} = -\sum_{K \neq J} c_K e^{i\gamma_{JK}} \sigma_{JK}$$

$$\gamma_{JK} = \frac{1}{\hbar} \int_0^t \left(E_J\left(\mathbf{R}\left(t'\right)\right) - E_K\left(\mathbf{R}\left(t'\right)\right) \right) dt'$$

- Ferretti; Granucci; Lami; Persico; Villani. *J Chem Phys* **1996,** *104*, 5517

The TDSE is solved with standard methods (Unitary Propagator, Adams Moulton 6th-order, Butcher 5th-oder)

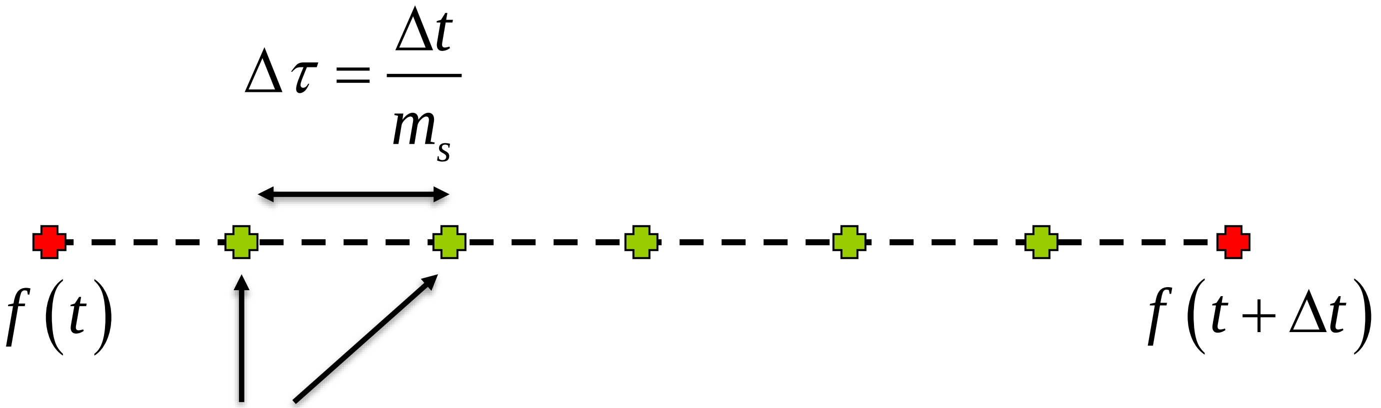


sh.inp:
INTEGRATOR = integration algorithm

Time step for TDSE

sh.inp:

MS = number of substeps



$$\Delta\tau = \frac{\Delta t}{m_s}$$

$$f\left(t+\Delta t\left(1-\frac{n}{m_s}\right)\right) = f(t)+\frac{n}{m_s}\big(f(t+\Delta t)-f(t)\big) \quad (n=1\cdots m_s-1)$$

3. Introduce nonadiabatic events via surface hoppings

$$P_{L\to J} = \frac{\text{Population increment in } J \text{ due to flux from } L \text{ during } \Delta\tau}{\text{Population of } L}$$

$$\rho_{LJ} = c_L c_J^*$$

$$P_{L\to J}\left(t\right) = \max\left[0, \frac{-2\Delta t}{\left|c_L\left(t\right)\right|^2}\sigma_{LJ}\left(t\right)\mathrm{Re}\left(c_J\left(t\right)c_L^*\left(t\right)\right)\right]$$

sh.inp:
TULLY = 0

$$\sum_{K=1}^{J-1} P_{L\to K} < r_t \le \sum_{K=1}^{J} P_{L\to K}$$

- Tully. *J Chem Phys* **1990,** *93*, 1061

4. Correct momentum to conserve energy

$$\mathbf{v}_{\alpha}^{(J)} = \mathbf{v}_{\alpha}^{(L)} + \gamma_{LJ} \frac{\mathbf{u}_{\alpha}}{M_{\alpha}}$$

$$\gamma_{LJ} = \begin{cases} \dfrac{-b+\sqrt{\Delta}}{2a} & \text{if } \left|-b+\sqrt{\Delta}\right| < \left|-b-\sqrt{\Delta}\right| \\ \dfrac{-b-\sqrt{\Delta}}{2a} & \text{if } \left|-b+\sqrt{\Delta}\right| \geq \left|-b-\sqrt{\Delta}\right| \end{cases}$$

$$a \equiv \frac{1}{2}\sum_{\alpha} \frac{\mathbf{u}_{\alpha} \cdot \mathbf{u}_{\alpha}}{M_{\alpha}}$$

$$b \equiv \sum_{\alpha} \left(\mathbf{v}_{\alpha}^{(L)} \cdot \mathbf{u}_{\alpha} \right)$$

$$\Delta \equiv b^2 - 4a\Delta E_{LJ}$$

sh.inp:
ADJMON = **u** direction

If $\Delta < 0$, hopping is not allowed

- Barbatti. *JCTC* **2021,** *17*, 3010.

5. Correct for decoherence

Decoherence correction with SDM (simplified decay of mixing):

$$c_K^{new} = c_K e^{-\Delta\tau/\tau_{KL}}, \quad \forall K \neq L,$$

$$c_L^{new} = \frac{c_L}{|c_L|}\left[1 - \sum_{K\neq L} \left|c_K^{new}\right|^2\right]^{1/2}$$

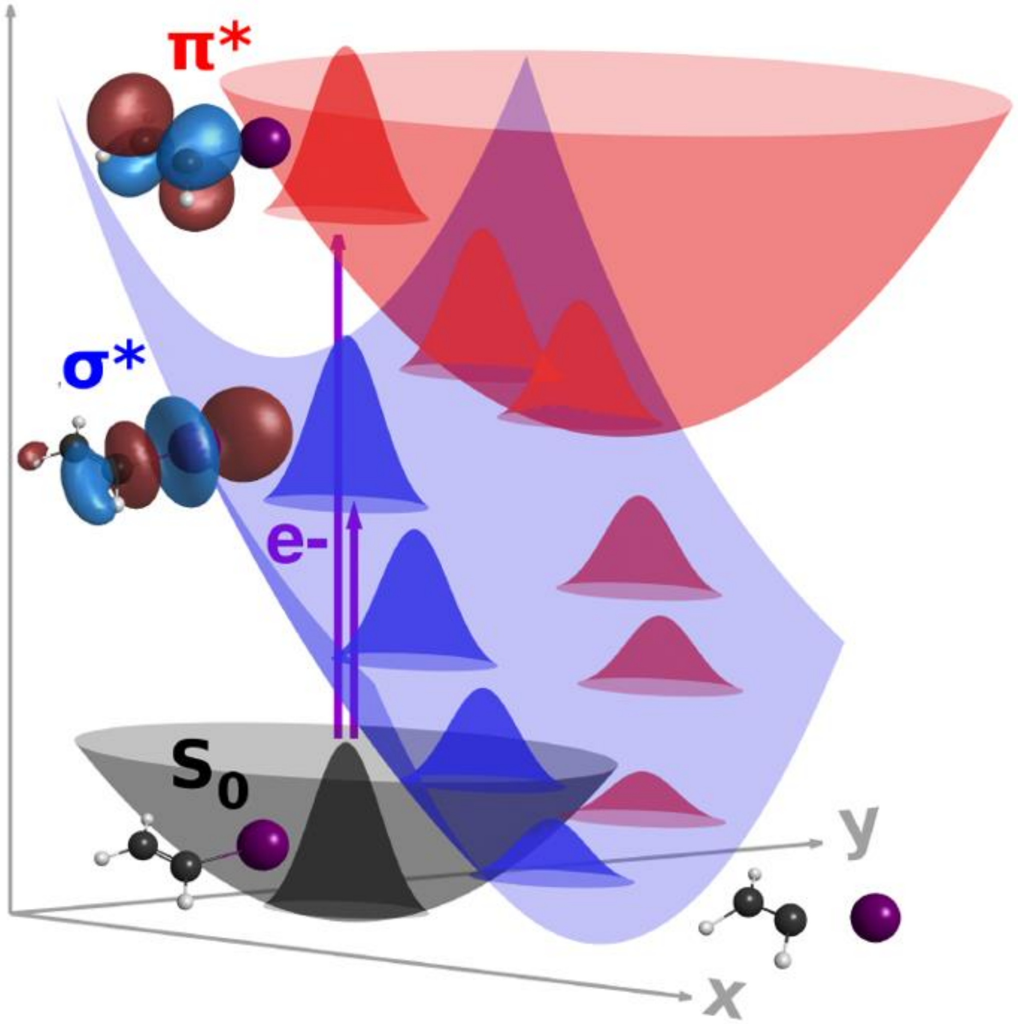
$$\frac{1}{\tau_{KL}^{SDM}} = \frac{|E_K - E_L|}{\hbar}\left(C + \frac{\varepsilon}{\bar{K}_n}\right)^{-1}$$

sh.inp
DECAY = ε value

- Granucci; Persico. *J Chem Phys* **2007,** *126*, 134114

Fewest Switches Surface Hopping on Complex-Valued Surfaces (CS-FSSH)

Kossoski; Barbatti. *Chem Sci* **2020,** *11*, 9827



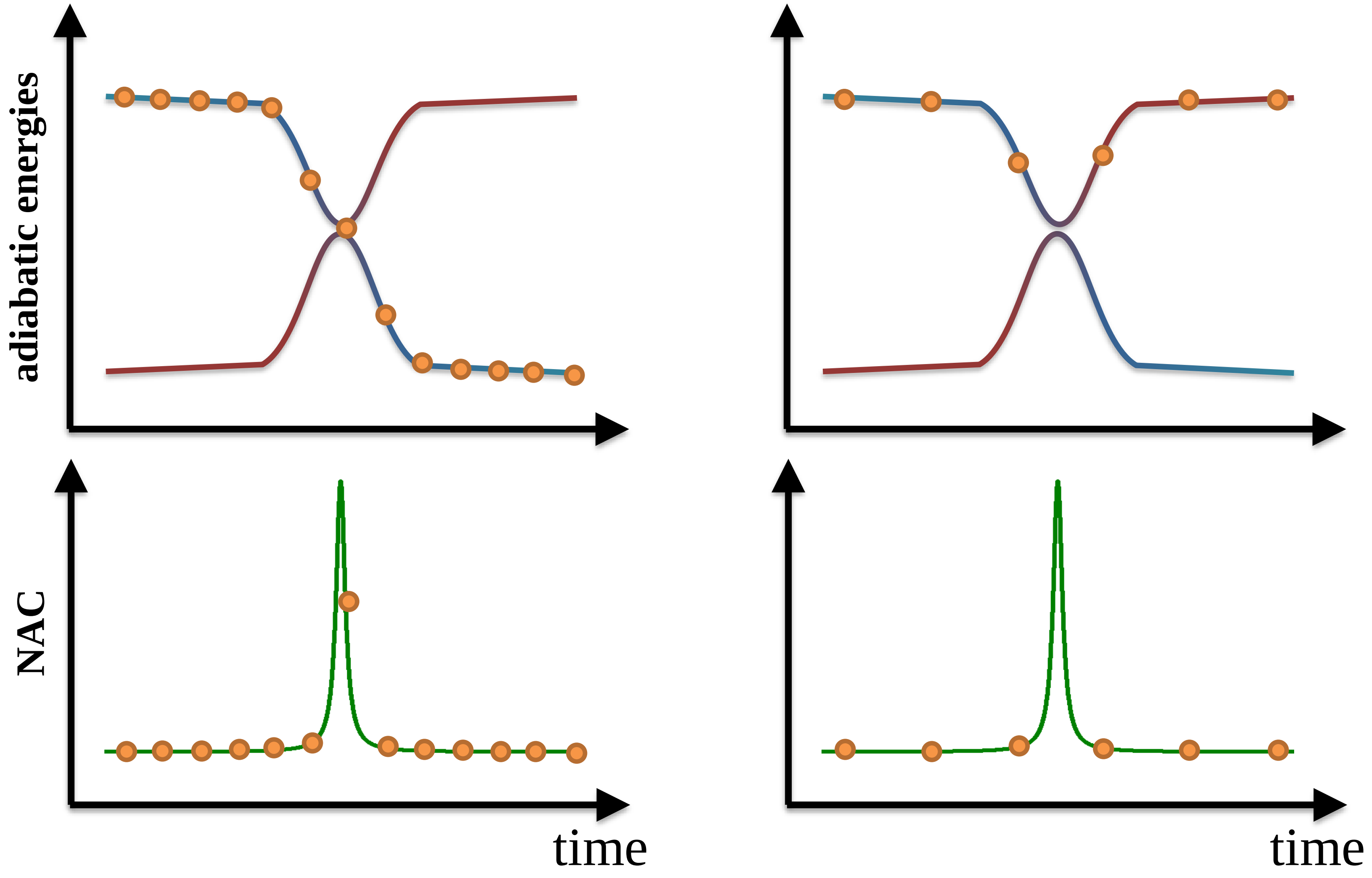
Problems with **h**

Problems with **h**

I. h is a narrow function, which diverges at small gaps:

$$\mathbf{h}_{JL} = \left\langle \psi_J \middle| \nabla \psi_L \right\rangle = \frac{\left\langle \psi_J \middle| \nabla H \middle| \psi_L \right\rangle}{E_L - E_J}$$

Dynamics near intersections



FSSH with local diabatization

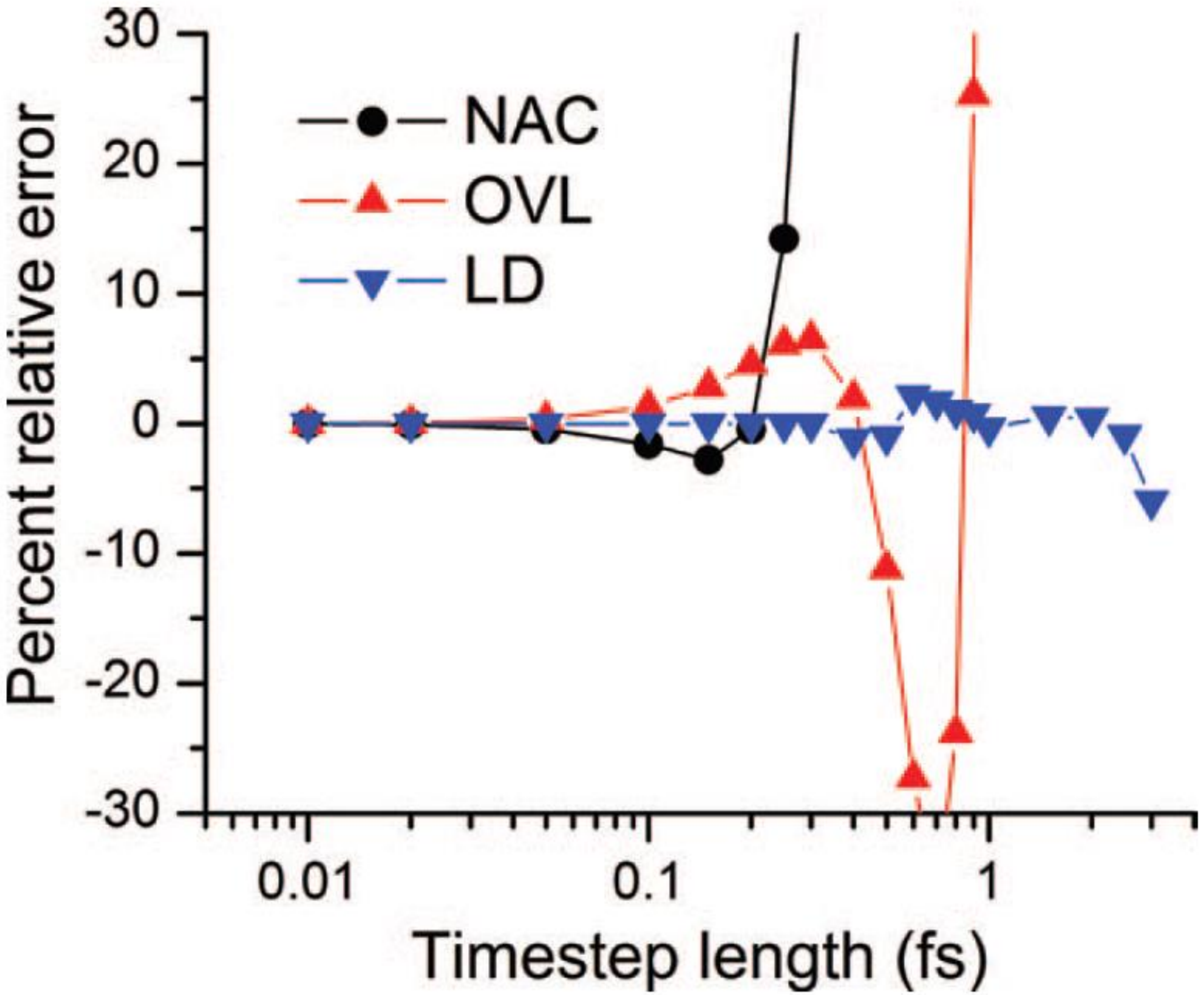
$$\boxed{P_{L\to J}=\max\left[0,\left(1-\frac{\left|c_L\left(t+\Delta t\right)\right|^2}{\left|c_L\left(t\right)\right|^2}\right)\frac{\mathrm{Re}\left(c_J\left(t+\Delta t\right)\Pi_{JL}^{*}c_L^{*}\left(t\right)\right)}{\left|c_L\left(t\right)\right|^2-\mathrm{Re}\left(c_L\left(t+\Delta t\right)\Pi_{LL}^{*}c_L^{*}\left(t\right)\right)}\right]}$$

$$\mathbf{c}\left(t+\Delta t\right)=\mathbf{U}\left(t\right)\mathbf{c}\left(t\right)$$

$\mathbf{U}$ and $\mathbf{\Pi}$ are functions of the overlaps $\left\langle\psi_I\left(t\right)\middle|\psi_J\left(t+\Delta t\right)\right\rangle$

- Granucci; Persico; Toniolo. *J Chem Phys* **2001,** *114*, 10608

sh.inp: VDOTH = -1



- Plasser; Granucci; Pittner; Barbatti; Persico; Lischka. *J Chem Phys* **2012,** *137*, 22A514

Problems with **h**

II. h has an arbitrary phase

Two calculations for the same geometry may give +**h** or –**h**.

Phase correction

$$\cos\left(\theta_{n_c}\right)=\frac{\mathbf{h}_{n_c}\left(t\right)}{\left|\mathbf{h}_{n_c}\left(t\right)\right|}\cdot\frac{\mathbf{h}_{n_c}\left(t-\Delta t\right)}{\left|\mathbf{h}_{n_c}\left(t-\Delta t\right)\right|}\quad\left(n_c=1,\cdots,n_{coup}\right)$$

$$n_{phase,n_c}=\begin{cases}1 & \text{if } \cos\left(\theta_{n_c}\right)\geq 0\\ -1 & \text{if } \cos\left(\theta_{n_c}\right)<0\end{cases}$$

$$\mathbf{h}_{n_c}^{(corrected)}\left(t\right)=n_{phase,n_c}\mathbf{h}_{n_c}\left(t\right)$$

Problems with **h**

III. h is not always available

Hammes-Schiffer-Tully (HST) approach

$$\sigma_{JK}^{NAC}\left(t+\frac{\Delta t}{2}\right)\approx\frac{1}{2\Delta t}\left[S_{JK}\left(t+\Delta t\right)-S_{KJ}\left(t+\Delta t\right)\right]$$

$$S_{JK}\left(t\right)=\left\langle\psi_J\left(t-\Delta t\right)\middle|\psi_K\left(t\right)\right\rangle$$

- Hammes-Schiffer; Tully. *J Chem Phys* **1994,** *101*, 4657

$$\sigma_{JK}^{NAC}\left(t\right)\approx\frac{1}{4\Delta t}\left[3S_{JK}\left(t\right)-3S_{KJ}\left(t\right)-S_{JK}\left(t-\Delta t\right)+S_{KJ}\left(t-\Delta t\right)\right],$$

- Pittner; Lischka; Barbatti. *Chem Phys* **2009,** *356*, 147

HST for linear-response methods

$$\left|\psi_K\right\rangle = \sum_{ia} C_{ia}^{K} \left|\Theta_i^a\right\rangle$$

$$C_{ia}^{K} = \begin{cases} R_{ia}^{K}, L_{ia}^{K} & for \quad \text{CC2} \\ M_{ia}^{K} & for \quad \text{ADC(2)} \\ \left(X+Y\right)_{ia}^{K} & for \quad \text{TDDFT;TD-DFTB} \end{cases}$$

- Plasser; Crespo-Otero; Pederzoli; Pittner; Lischka; Barbatti. *JCTC* **2014,** *10*, 1395

Determinant derivative (DD)

General determinants with multiple excitations but slow

- Pittner; Lischka; Barbatti. *Chem Phys* **2009,** *356*, 147

jiri.inp: CPROG = 1

Orbital derivative (OD)

Fast but singly-excited determinants only

- Ryabinkin; Nagesh; Izmaylov. J Phys Chem Lett **2015,** *6*, 4200

jiri.inp: CPROG = 2

Time-dependent Baeck-An (TD-BA)

$$\sigma_{JL} \approx \begin{cases} \dfrac{\operatorname{sgn}\left(\Delta E_{JL}\right)}{2}\sqrt{\dfrac{1}{\Delta E_{JL}}\dfrac{d^2\Delta E_{JL}}{dt^2}} & \text{if } \dfrac{1}{\Delta E_{JL}}\dfrac{d^2\Delta E_{JL}}{dt^2} > 0 \\ 0 & \text{if } \dfrac{1}{\Delta E_{JL}}\dfrac{d^2\Delta E_{JL}}{dt^2} \leq 0 \end{cases}$$

Available in Newton-X 2.2 b15 and above

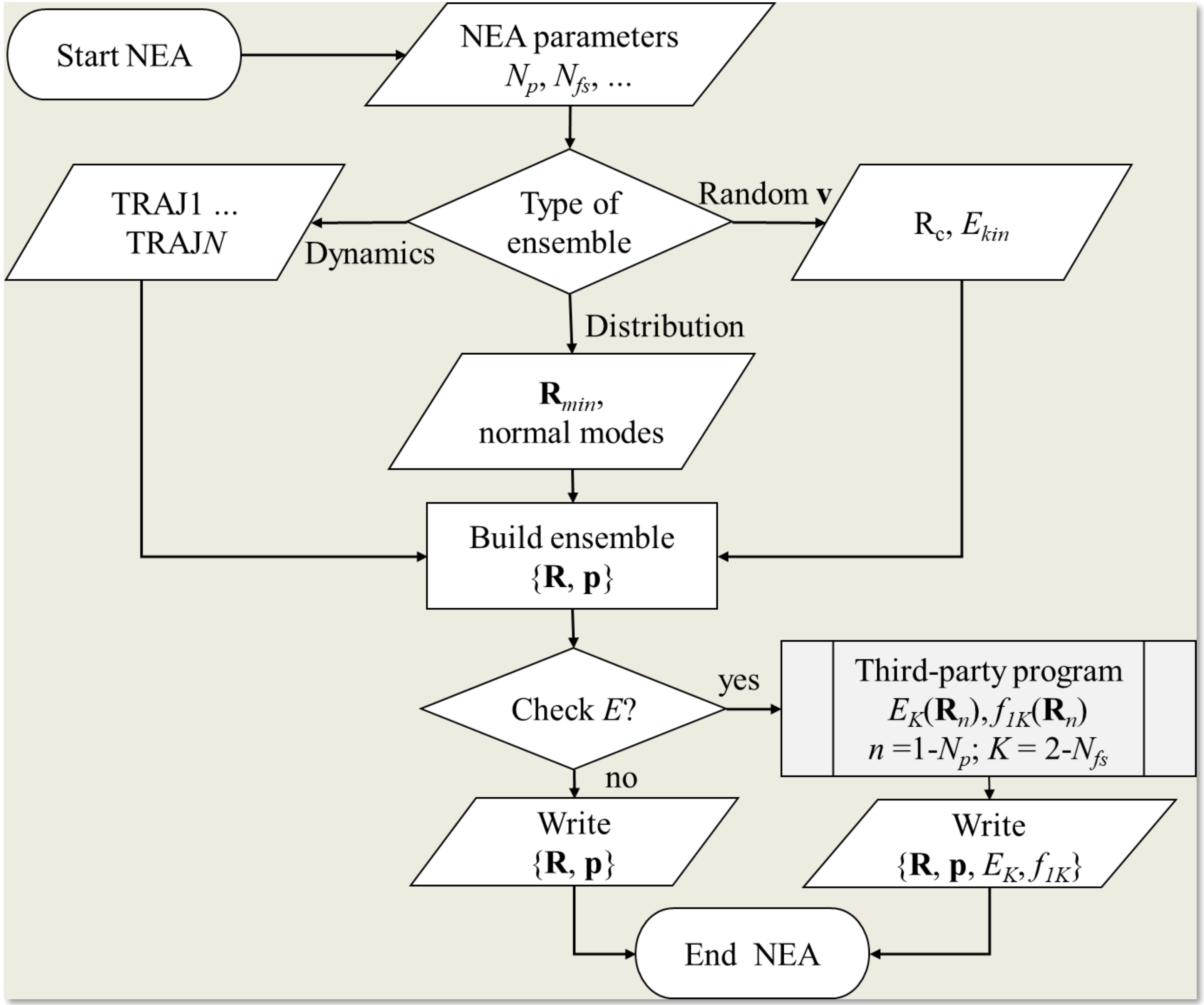
- T. do Casal; Toldo; Pinheiro Jr; Barbatti. *Open Res Europe* **2021,** *1*, 49

sh.inp: VDOTH = 2

INITIAL CONDITIONS AND SPECTRUM

To initiate the simulation of a trajectory we need initial conditions:

• Initial geometry	geom file
• Initial velocity	veloc file
• Initial electronic state	control.dyn: NSTATDYN
• Initial TDSE coefficients	wf.inp (optional)



Start NEA

NEA parameters
N_p, N_{fs}, …

Type of ensemble

Dynamics

TRAJ1 …
TRAJN

Random $\mathbf{v}$

R_c, E_{kin}

Distribution

$\mathbf{R}_{min}$,
normal modes

Build ensemble
$\{\mathbf{R}, \mathbf{p}\}$

Check E?

yes

Third-party program
$E_K(\mathbf{R}_n), f_{1K}(\mathbf{R}_n)$
$n = 1\text{-}N_p$; $K = 2\text{-}N_{fs}$

no

Write
$\{\mathbf{R}, \mathbf{p}\}$

Write
$\{\mathbf{R}, \mathbf{p}, E_K, f_{1K}\}$

End NEA

To get them, we build an ensemble of {**R**,**P**} nuclear points.

Nuclear ensembles

Method 1: Probability distribution functions

For a molecule represented as $3N_{at}$–6 quantum harmonic oscillators in the vibrational ground state, P_W is:

$$P_W\left(\mathbf{q},\mathbf{p}\right)=\prod_{i=1}^{N_F}\frac{\alpha_i}{\pi\hbar}\exp\left(-\frac{2\alpha_i}{\hbar\omega_i}\left(\frac{\mu_i\omega_i^2q_i^2}{2}+\frac{p_i^2}{2\mu_i}\right)\right)$$

$$\alpha_i=\tanh\left(\frac{\hbar\omega_i}{2k_BT}\right)$$

- Schinke, Photodissociation Dynamics, Cambridge, 1993.

$$P_W(\mathbf{q},\mathbf{p}) = \prod_{i=1}^{N_F} \frac{\alpha_i}{\pi\hbar} \exp\left(-\frac{2\alpha_i}{\hbar\omega_i} \left(\frac{\mu_i \omega_i^2 q_i^2}{2} + \frac{p_i^2}{2\mu_i} \right) \right)$$

First way of using this equation:

Uncorrelated sampling. Sample q_i and p_i randomly

initqp_input: NACT = 2

Advantage: it's a true Wigner distribution
Disadvantage: broad total energy distribution

$$\langle E_{tot} \rangle \pm \sigma = \sum_{i=1}^{3N_{at}-6} \frac{\hbar\omega_i}{2\alpha_i} \pm \sqrt{\sum_{i=1}^{3N_{at}-6} \left(\frac{\hbar\omega_i}{2\alpha_i} \right)^2}$$

$$P_W(\mathbf{q},\mathbf{p}) = \prod_{i=1}^{N_F} \frac{\alpha_i}{\pi\hbar} \exp\left(-\frac{2\alpha_i}{\hbar\omega_i} \left(\frac{\mu_i \omega_i^2 q_i^2}{2} + \frac{p_i^2}{2\mu_i} \right) \right)$$

Second way of using this equation:

Correlated sampling. Sample q_i randomly and get p_i as

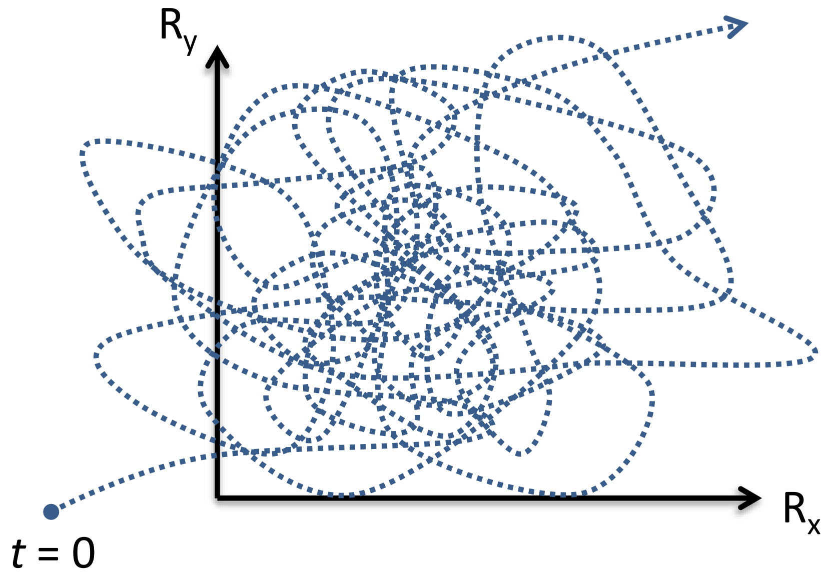
$$p_i = r\sqrt{\mu_i \left(\frac{\hbar\omega_i}{\alpha_i} - \mu_i \omega_i^2 q_i^2 \right)}$$

initqp_input: NACT = 3

Advantage: narrow total energy distribution.
Disadvantage: it’s not a true Wigner distribution

Method 2: Trajectories

Run trajectories in the ground state



initqp_input: NACT = 4

After a long time (~1 ns), the distribution of points will reflect the probability of finding the molecule with each (**R**,**P**)

Pick up ~500 points from the trajectories

Method 3: Random velocities

For a fixed geometry, create random velocities satisfying:

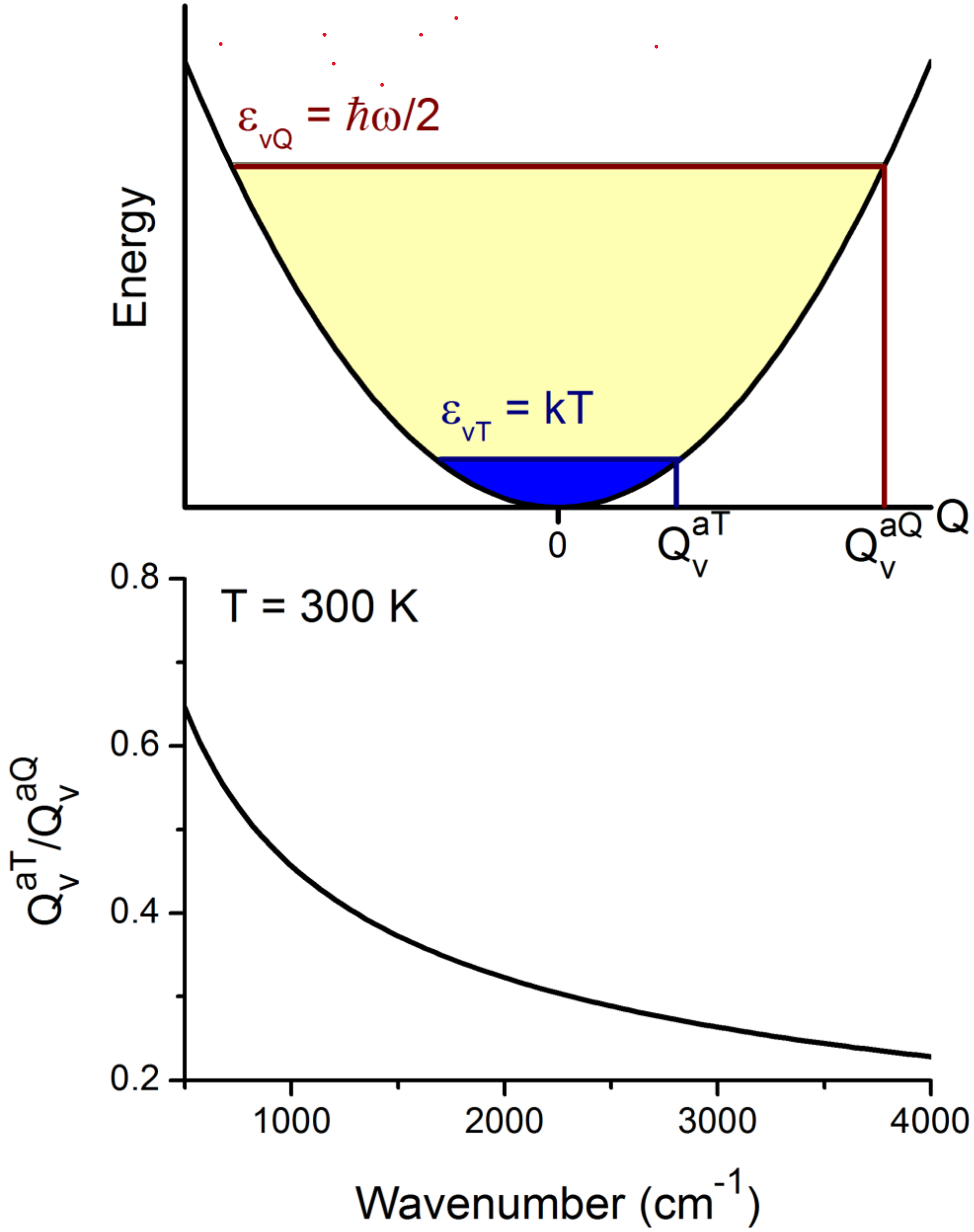
$$\mathbf{v}_0 = \sqrt{\frac{2T_0}{\sum_{\alpha} M_{\alpha} v_{\alpha}^2}}\mathbf{v}_r$$

initqp_input: NACT = 5

T_0 – initial kinetic energy
$\mathbf{v}_r$ – random velocity (without translational and rotational components)

- Sellner; Barbatti; Lischka. *J Chem Phys* **2009,** *131*, 024312

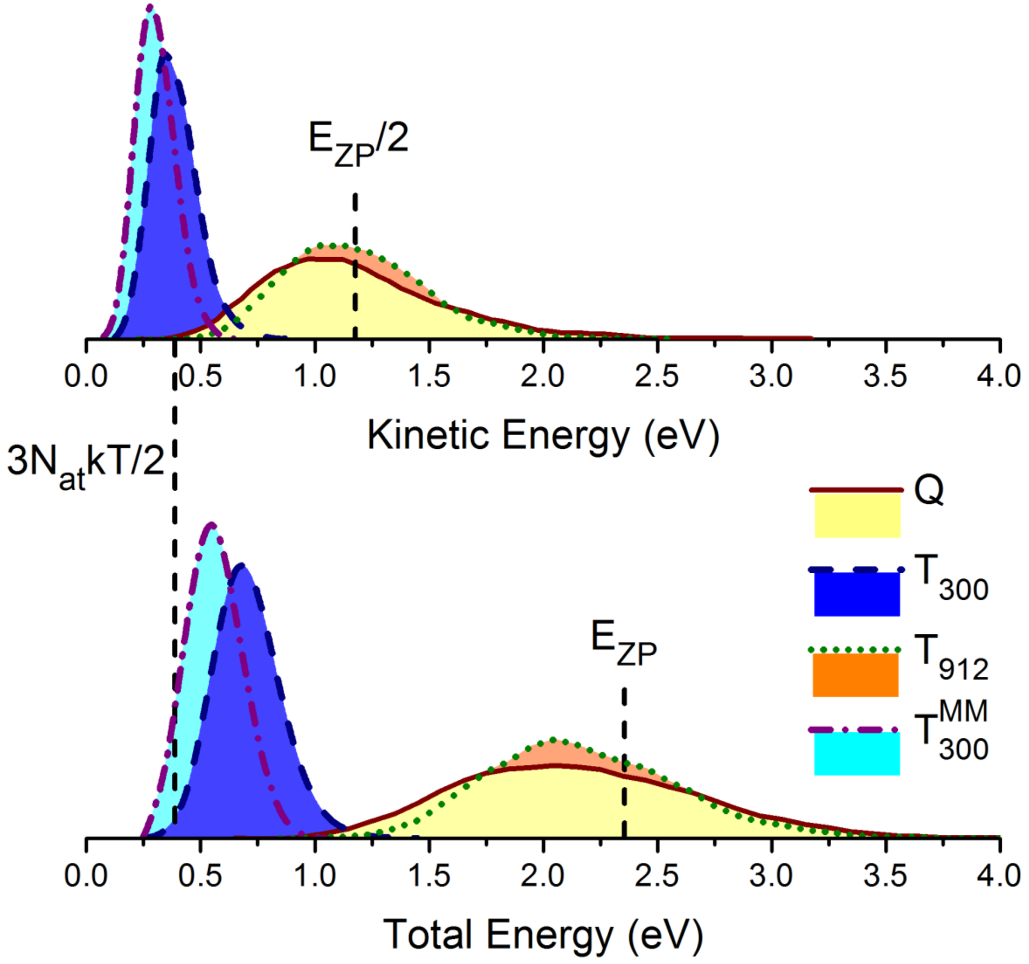
Trajectory x distribution samplings



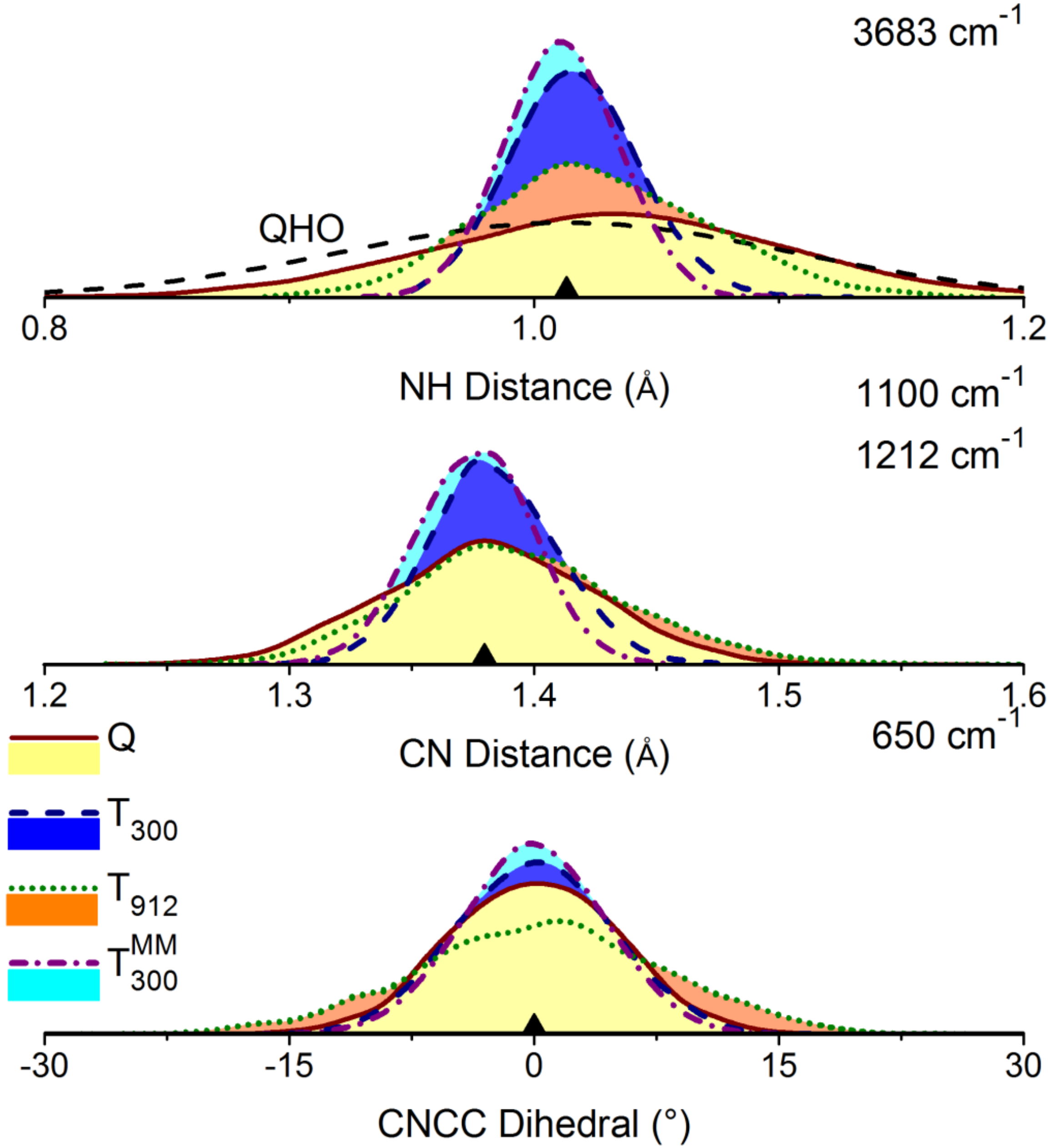
Thermal amplitudes at 300 K are much smaller than quantum amplitudes with ZPE.

This difference is especially important for large wavenumbers.

- Barbatti; Sen. *Int J Quantum Chem* **2016,** *116*, 762.



The ground state energy distribution in a *Q* ensemble and in a *T* ensemble are completely different.

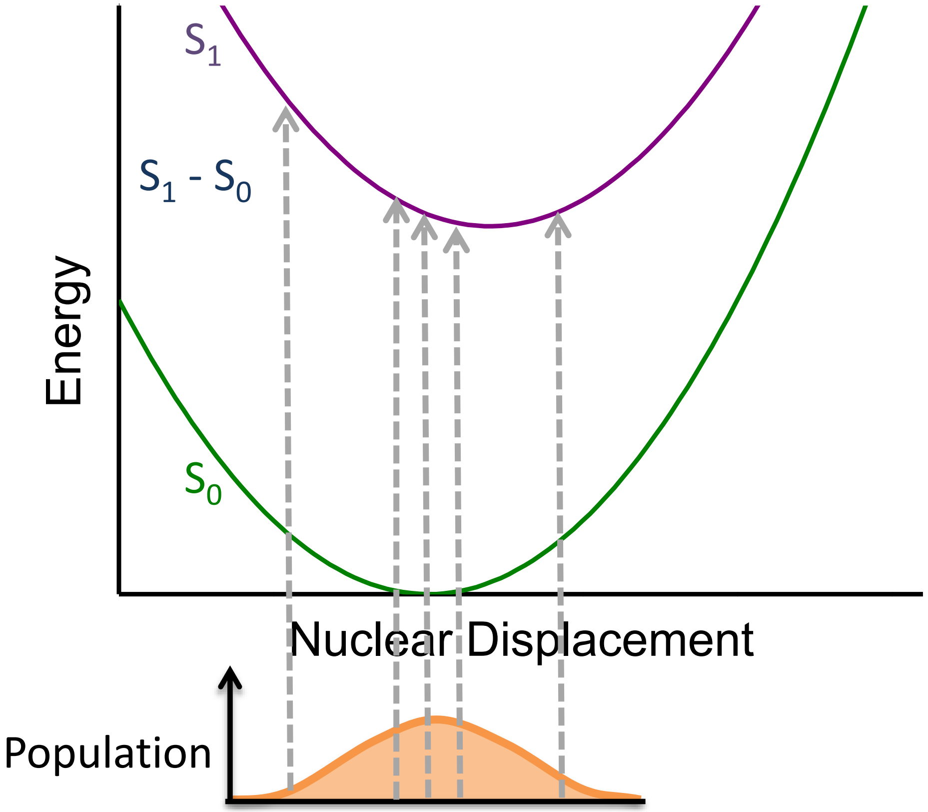


The *Q* distribution of geometries is much broader than the *T*.

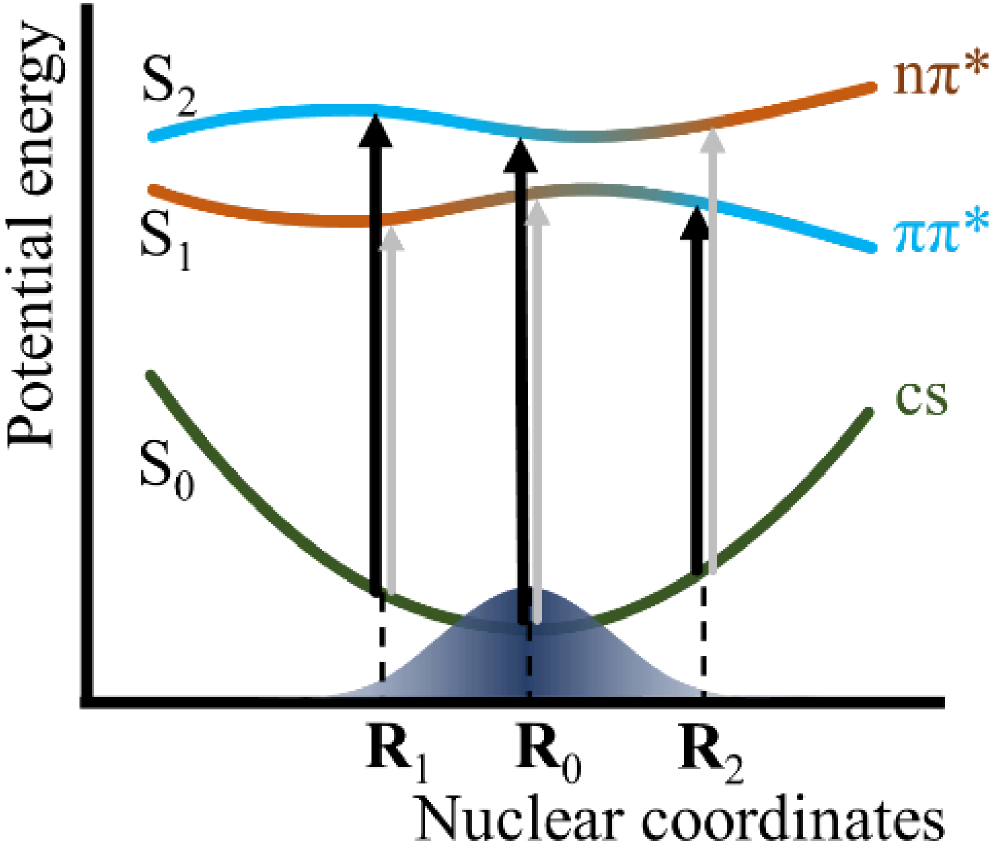
The effect is larger for bigger wavenumbers.

Initial state

Simulations of excited-state trajectories have a very clear starting point:
The photo excitation, which is taken as instantaneous and defining *t* = 0.



To define the initial state, we should take care of state crossings.
In this example, geometry R_1 should start in S_2, while R_2 should start in S_1.

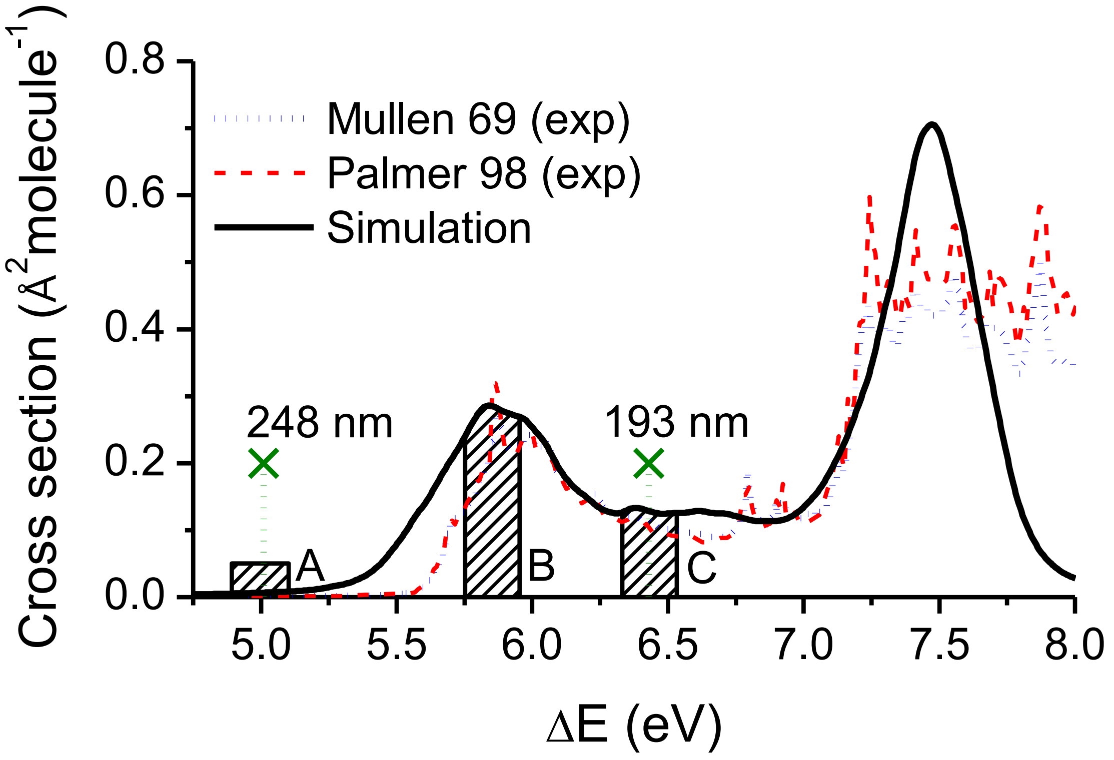


Accept initial condition if:

1. $\left|\Delta E_{1N}\left(\mathbf{R}_i\right)-\varepsilon\right| \leq \delta\varepsilon$
2. $r \leq \dfrac{f_{1N}\left(\mathbf{R}_i\right)}{f_{0N}^{\max}} \qquad r = random\left(0,1\right)$

nxinp:
Select initial conditions for multiple excited states

Example: Pyrrole



State	Window A 4.90-5.10 eV	Window B 5.75-5.95 eV	Window C 6.33-6.53 eV
S_1	15	0	0
S_2	0	5	0
S_3	0	6	0
S_4	0	31	0
S_5	0	13	2
S_6	0	0	8
S_7	0	0	8
S_8	0	0	15
S_9	0	0	12
S_{10}	0	0	1
Total	15	55	46

- Barbatti; Pittner; Pederzoli; Werner; Mitrić; Bonačić-Koutecký; Lischka. *Chem Phys* **2010,** *375*, 26

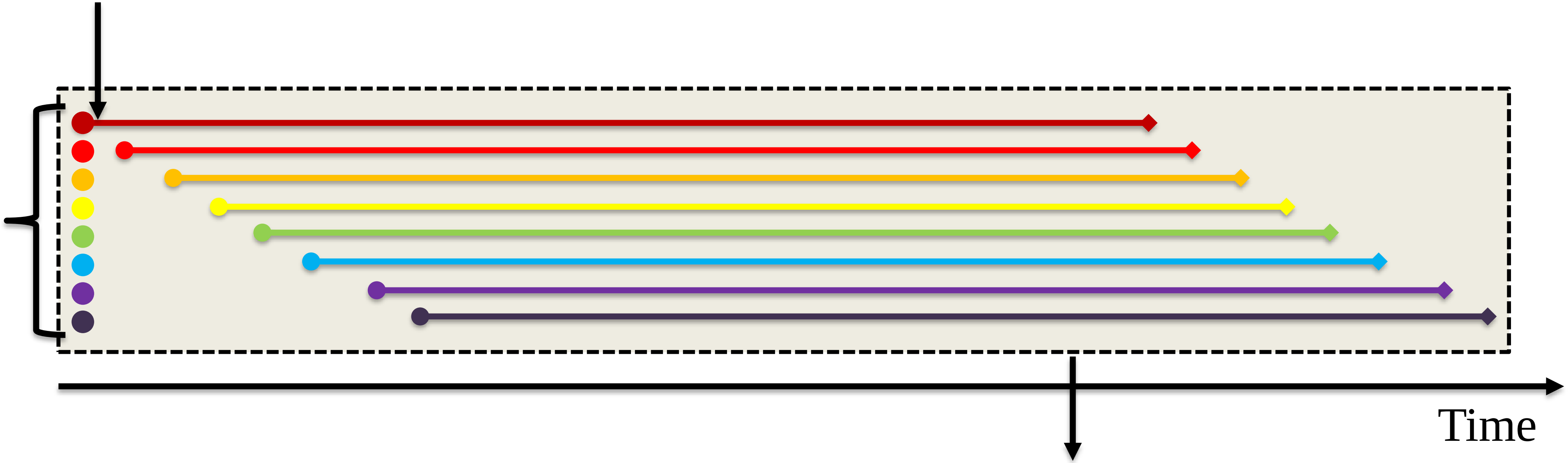
Mixed Quantum-Classical Dynamics with Pulse Ensemble (MQC-PE)

Cis-Trans Isomerization of Retinal

Type	Light source	τ
Coherent	fs-Laser pulse	200 fs
Incoherent	Extra-terrestrial	42 μs
	Earth surface	56 μs
	Scotopic vision	96 days

Barbatti. *JCTC* **2020,** *16*, 4849

Dynamics with thermal light: MQC-PE



Run MQC dynamics with displaced starting points

Sample initial conditions from a blackbody

Average trajectories weighted by Chenu-Brumer densities

- Barbatti. *JCTC* **2020,** *16*, 4849

Spectrum

The sum over the excitations in the ensemble gives an approximation for the absorption spectrum

$$\sigma^{pa}(E) = \frac{\pi e^2 \hbar}{2 m_e c \varepsilon_0 E} \sum_{L}^{N_{fs}} \frac{1}{N_p} \sum_{n}^{N_p} \Delta E_{1L}(\mathbf{R}_n) f_{1L}(\mathbf{R}_n) w_s\left(E - \Delta E_{1L}(\mathbf{R}_n), \delta\right)$$

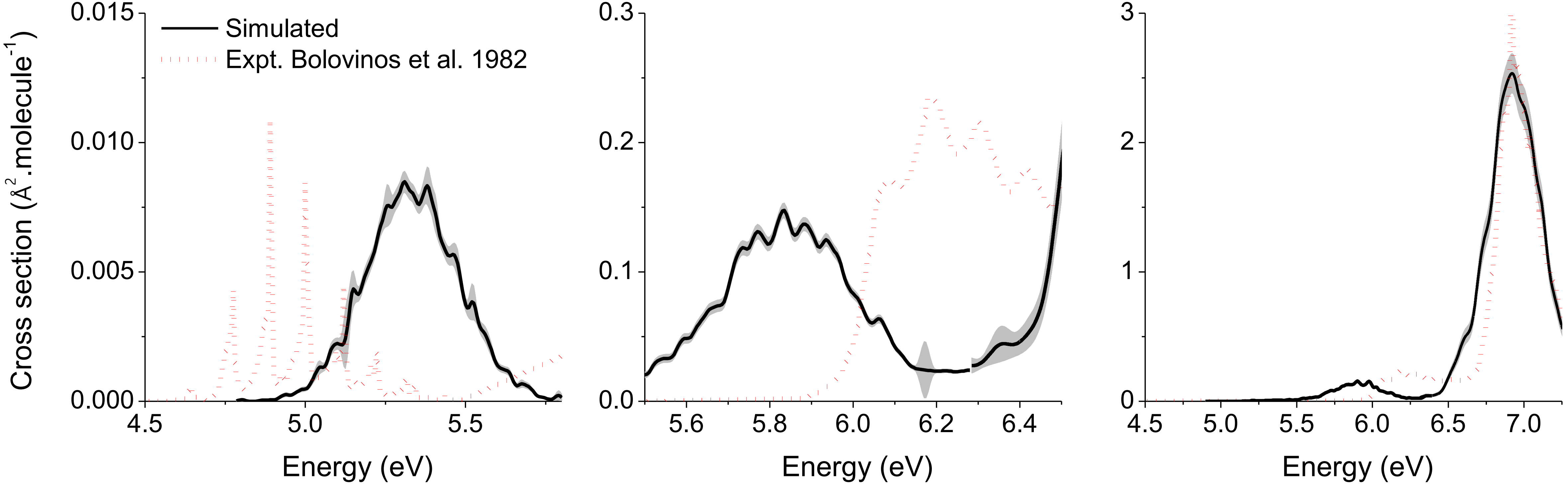
mkd.inp: PROB_KIND = F

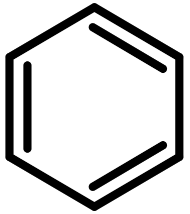
If the sampling is done in the minimum of S_1, the sum is an approximation for the fluorescence spectrum:

$$\Gamma_{fl}\left(E\right)=\frac{e^2}{2\pi\hbar m_e c^3\varepsilon_0}\frac{1}{N_p}\sum_{n}^{N_p}\Delta E_{21}\left(\mathbf{R}_n\right)^2\left|f_{21}\left(\mathbf{R}_n\right)\right|w_s\left(E-\Delta E_{21}\left(\mathbf{R}_n\right),\delta\right)$$

mkd.inp: PROB_KIND = E

Example: benzene

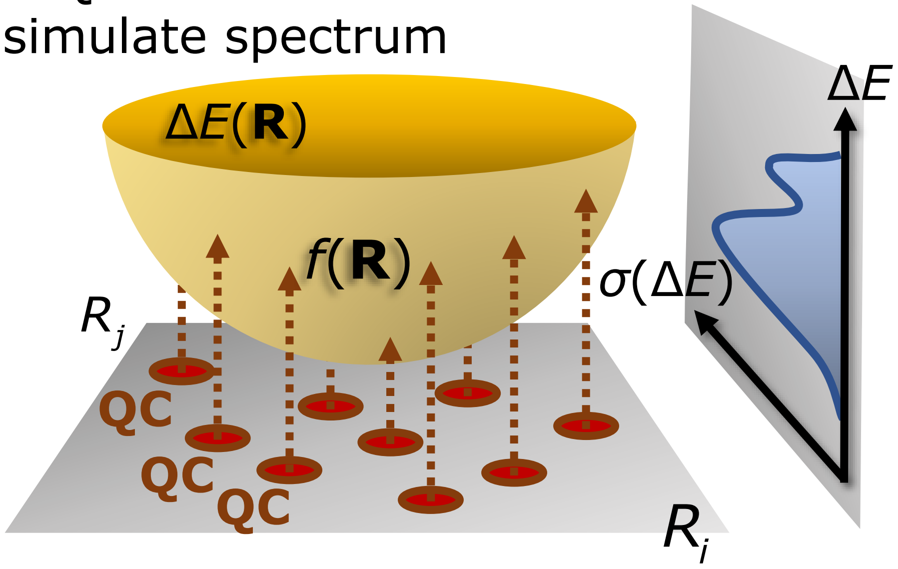




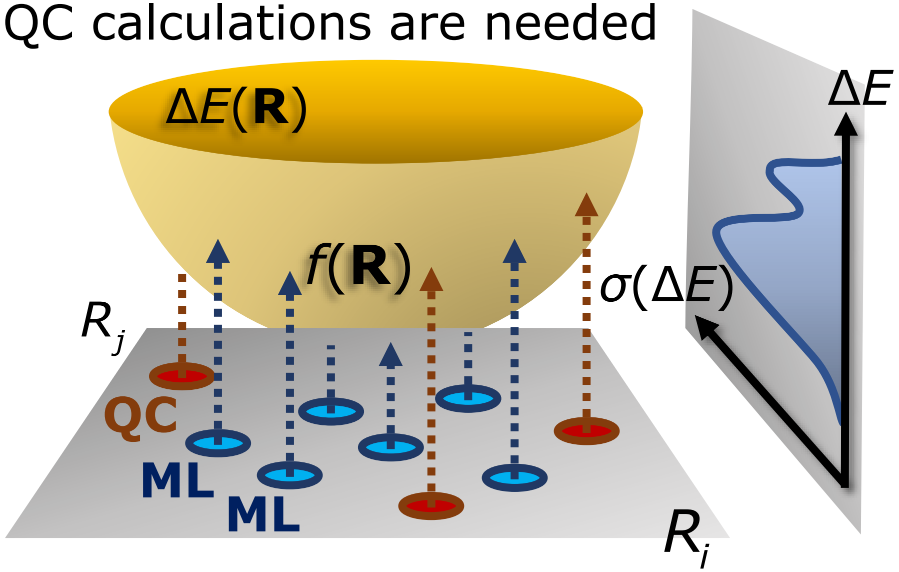
- Crespo-Otero, Barbatti, Theor Chem Acc **131**, 1237 (2012)

Nuclear Ensemble Approach Based on Machine Learning (ML-NEA)

N QC calculations are need to simulate spectrum



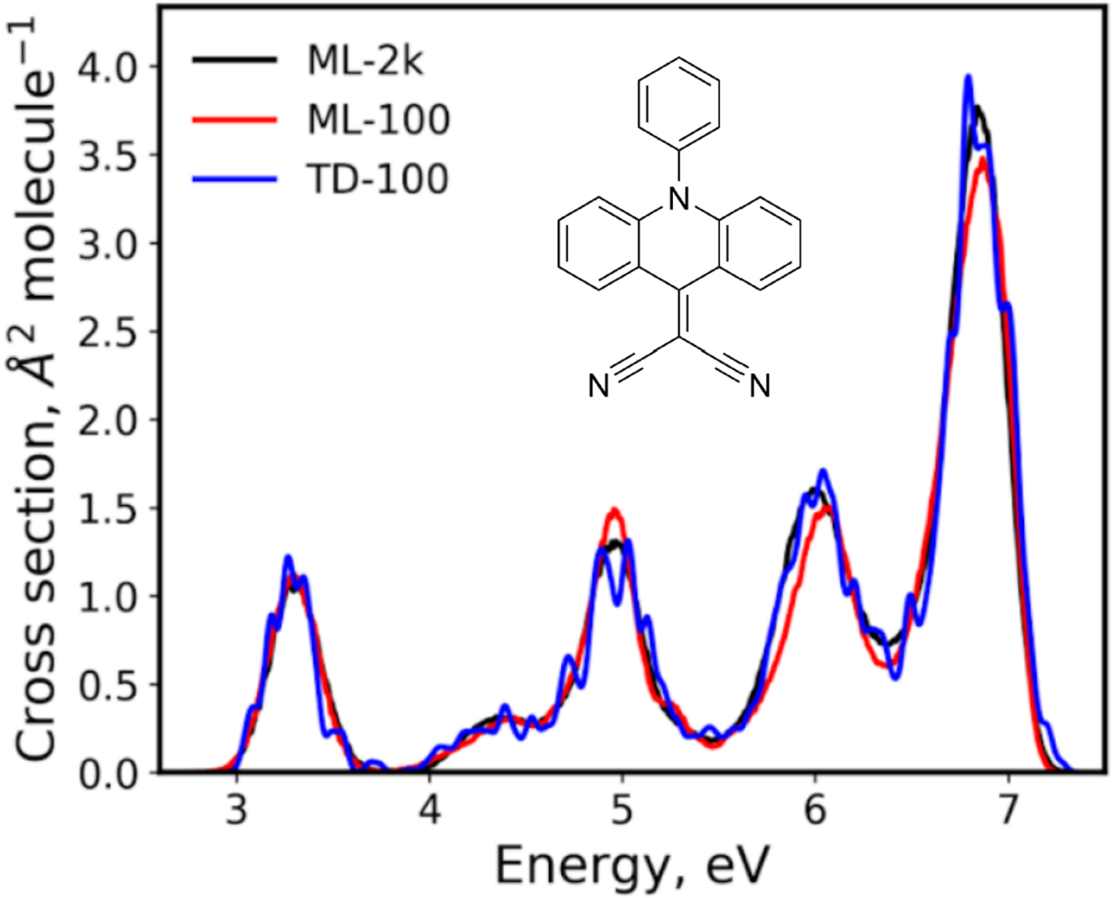
With ML, only $M \ll N$
QC calculations are needed



- Xue; Barbatti; Dral. *J Phys Chem A* **2020,** *124*, 7199

ML-NEA

- Automatic determination of optimal training set size
- Few hundred points for statistically converged results
- ML-training and predictions are extremely fast (minutes)



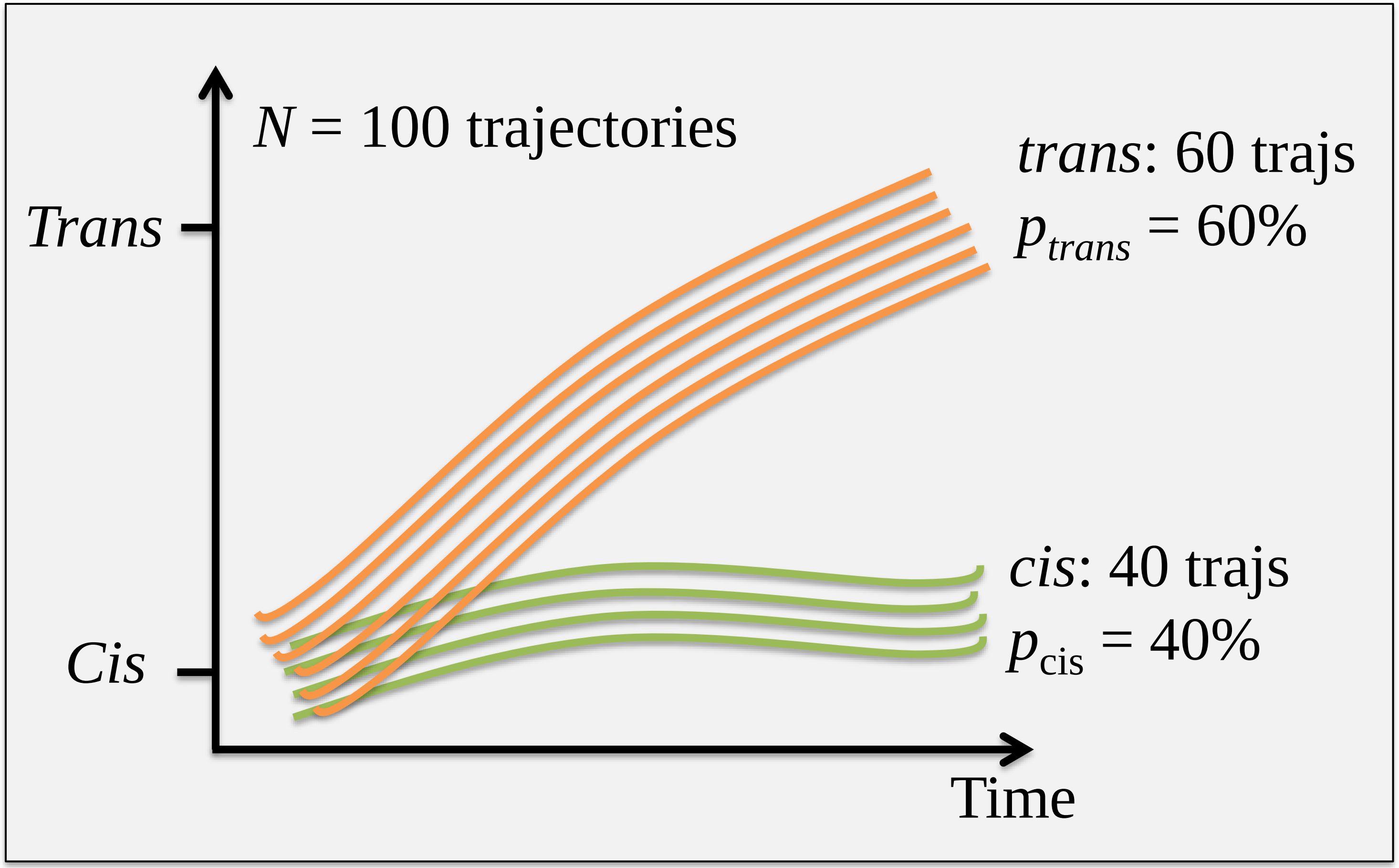
- Tutorial available at mlatom.com/tutorial/tutorial-mlnea/

ELEMENTS OF STATISTICAL ANALYSIS

Margin of error for a sample proportion

$$\boxed{\varepsilon = 1.96\sqrt{\frac{p(1-p)}{N}}}$$

$$N \times p > 5$$



$$\varepsilon_{cis} = 1.96\sqrt{\frac{0.4(1-0.4)}{100}} = 0.096$$

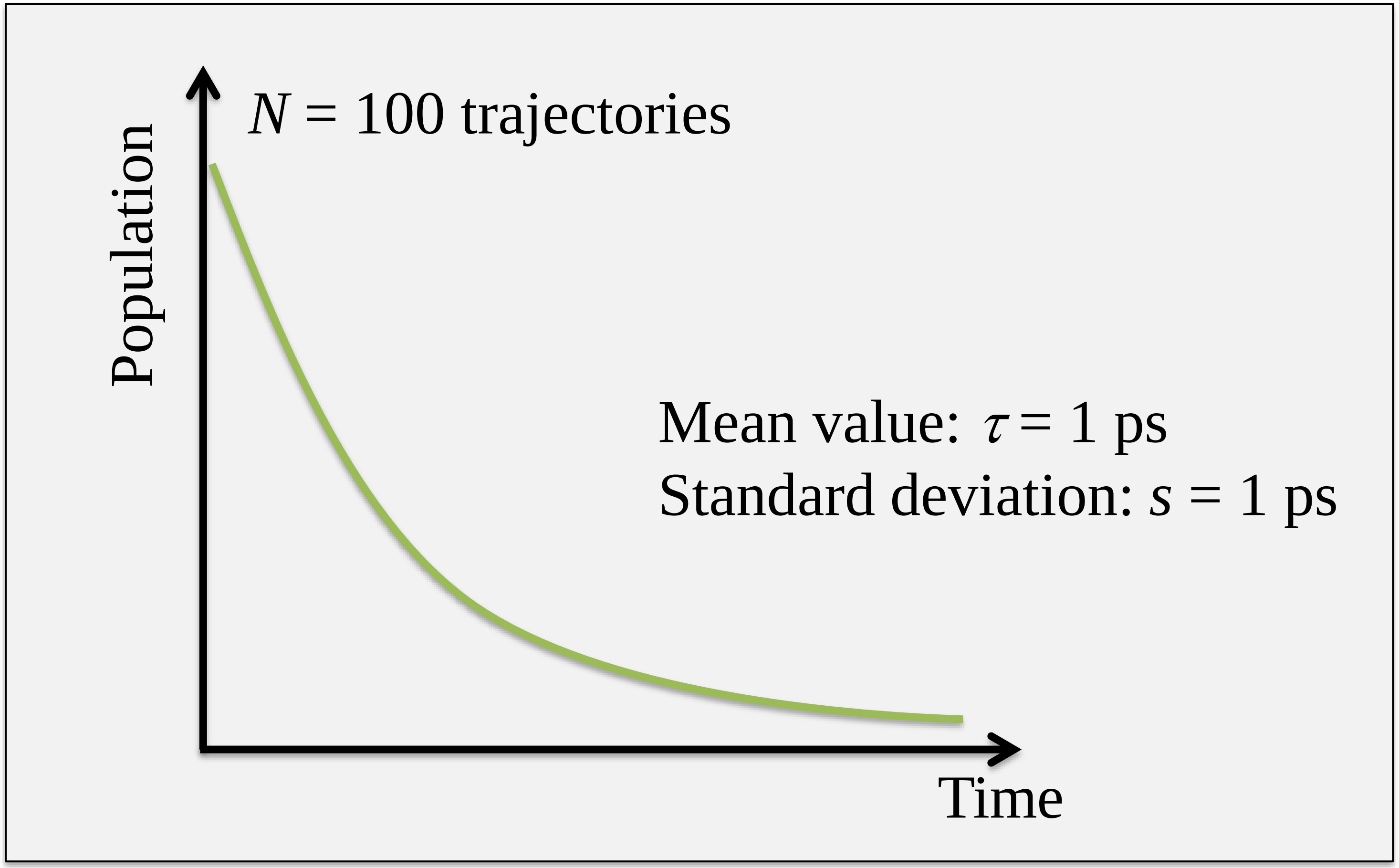
$$\varepsilon_{trans} = 1.96\sqrt{\frac{0.6(1-0.6)}{100}} = 0.096$$

$$p_{cis} = 0.4 \pm 0.1$$
$$p_{trans} = 0.6 \pm 0.1$$

Margin of error for a sample average

$$\boxed{\varepsilon = 1.96\frac{s}{\sqrt{N}}}$$

$N > 30$



N = 100 trajectories

Mean value: τ = 1 ps
Standard deviation: s = 1 ps

$$\varepsilon = 1.96\frac{1}{\sqrt{100}} = 0.196 \text{ ps}$$

$$\boxed{\tau = 1.0 \pm 0.2 \text{ ps}}$$

We know that

$$N > 30$$

$$N \times p > 5$$

How many trajectories do we need?

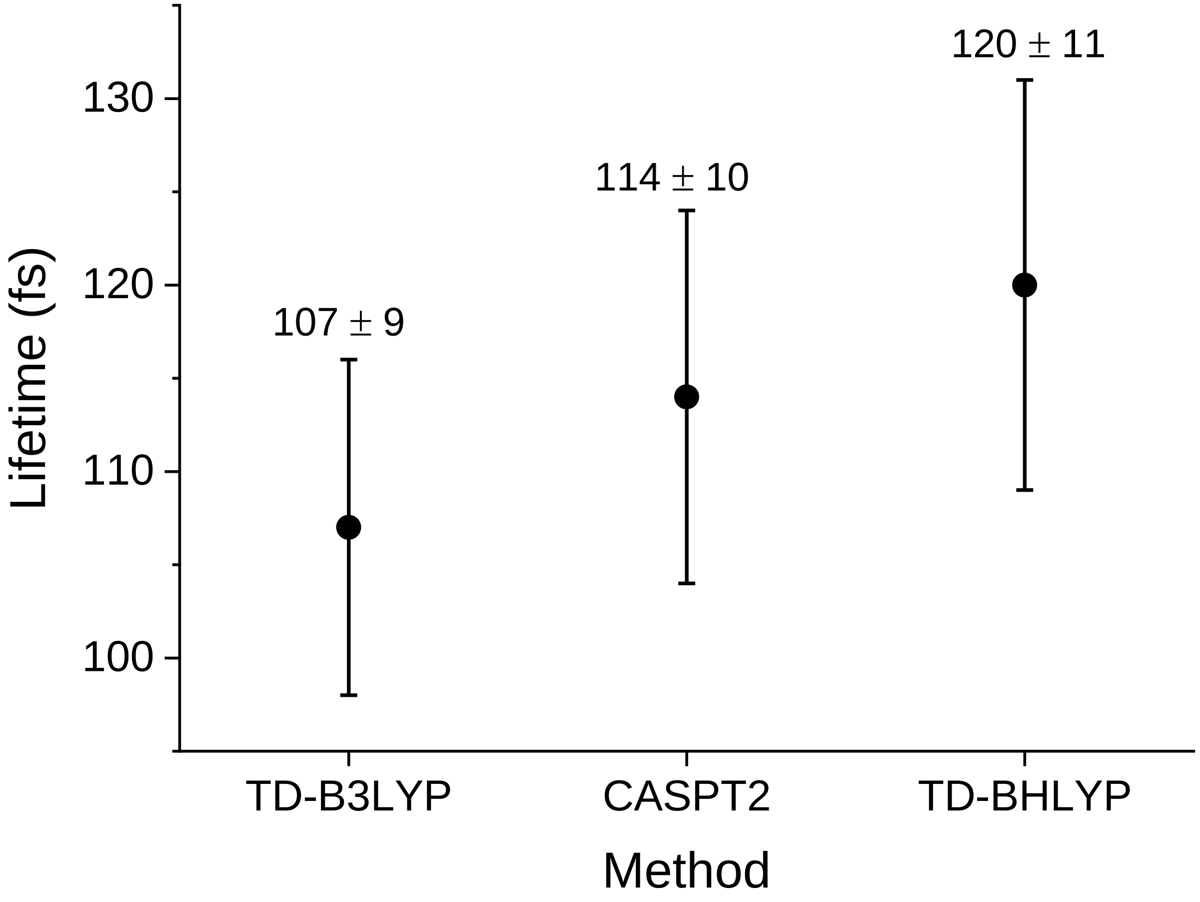
If we want to analyse $p > 10\%$

$$\boxed{N > 50}$$

Λ *analysis*

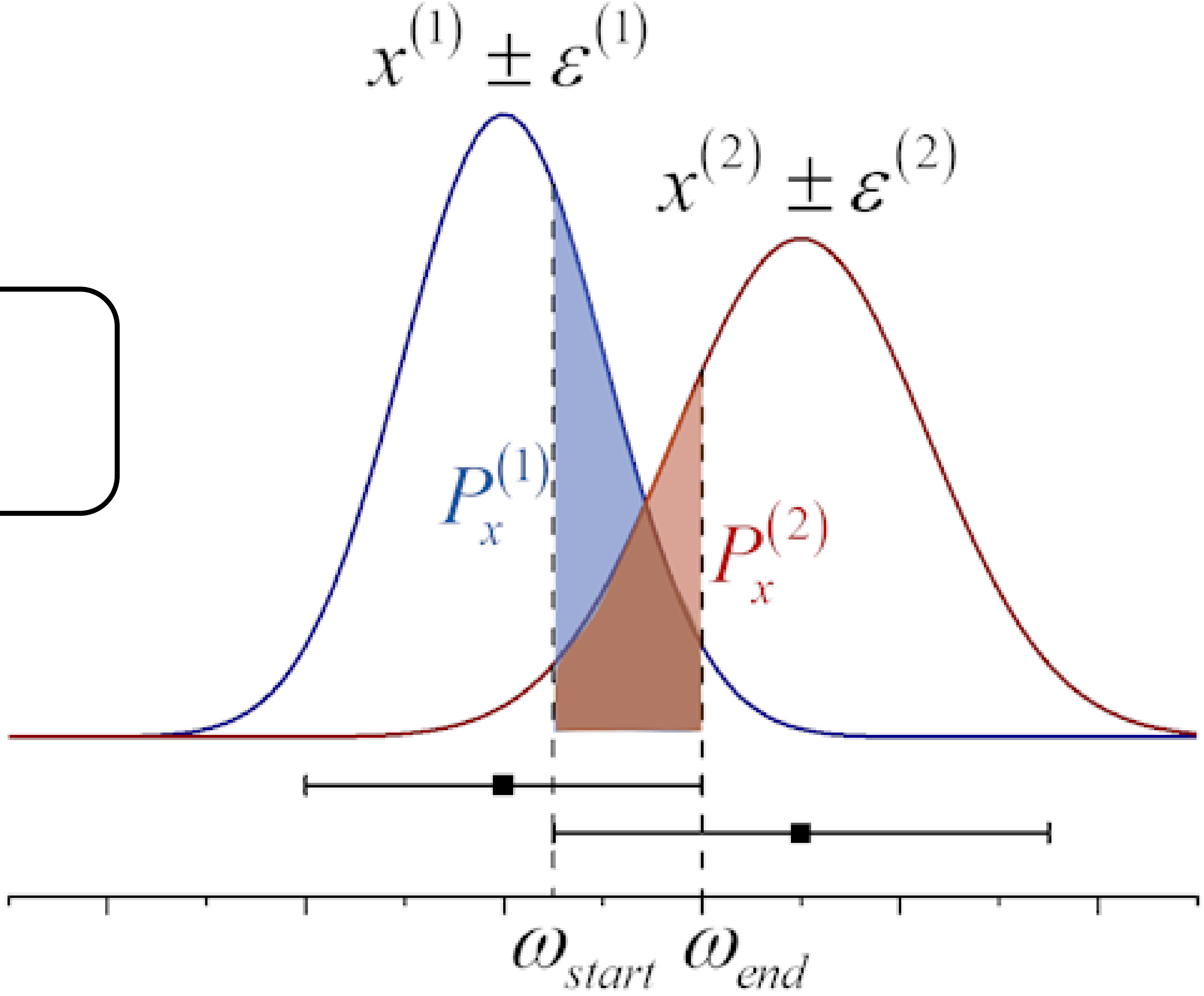
Comparing error bars

Compared to CASPT2, which functional does make the best prediction?



λ analysis

$$\boxed{\lambda_x^{(1,2)} = \frac{P_x^{(1)} P_x^{(2)}}{P_{\max}^{(1)} P_{\max}^{(2)}}}$$



- Barbatti. *JCTC* **2021,** *17*, 3010

$$\boxed{\begin{aligned}\lambda_x^{(1,2)} = \frac{1}{3.61}&\left[erf\left(\frac{1.96\sqrt{2}\left(-\omega_{start}+x^{(1)}\right)}{2\varepsilon^{(1)}}\right)-erf\left(\frac{1.96\sqrt{2}\left(-\omega_{end}+x^{(1)}\right)}{2\varepsilon^{(1)}}\right)\right]\\ \times&\left[erf\left(\frac{1.96\sqrt{2}\left(-\omega_{start}+x^{(2)}\right)}{2\varepsilon^{(2)}}\right)-erf\left(\frac{1.96\sqrt{2}\left(-\omega_{end}+x^{(2)}\right)}{2\varepsilon^{(2)}}\right)\right]\end{aligned}}$$

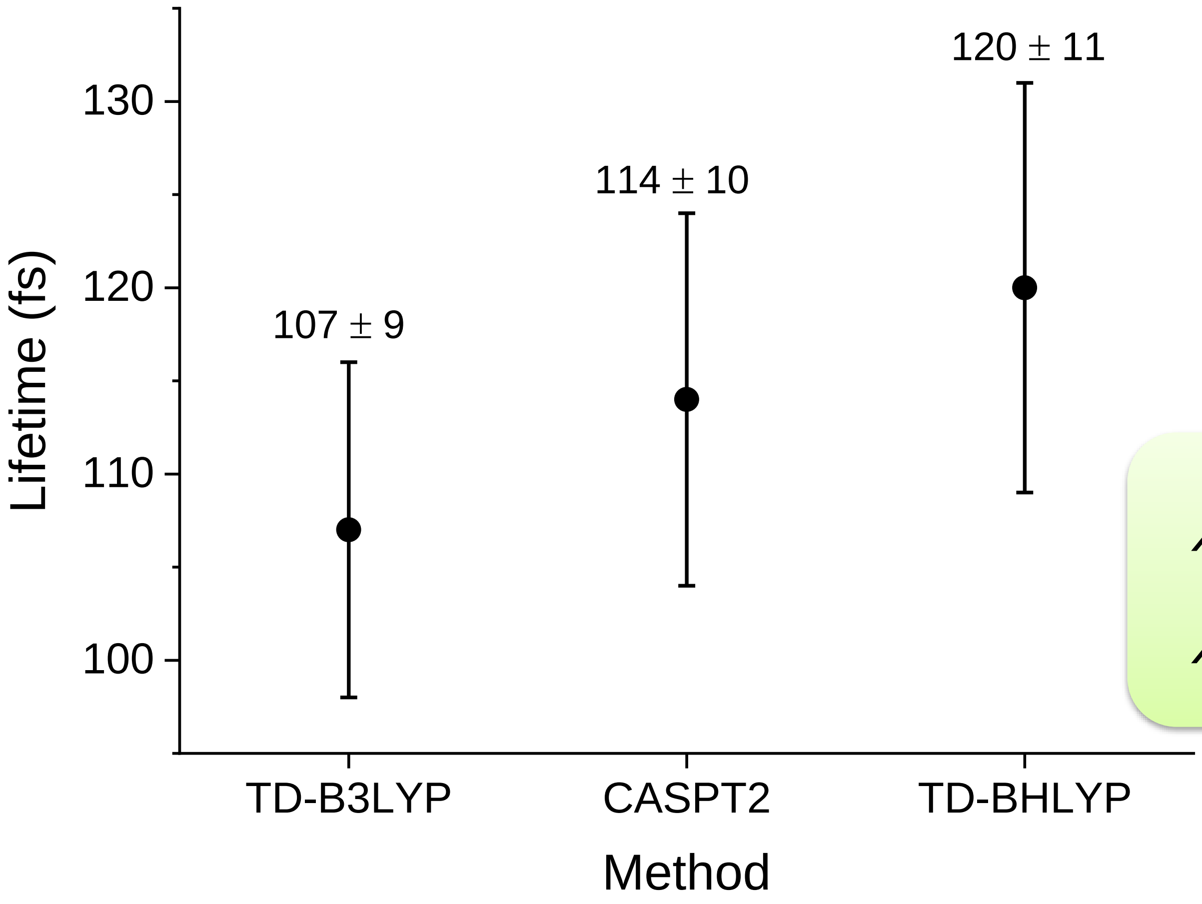
$$\lambda_x^{(1,2)} = 1: \quad \text{perfect agreement}$$

$$\lambda_x^{(1,2)} = 0: \quad \text{no agreement at all}$$

- Barbatti. *JCTC* **2021,** *17*, 3010

Comparing error bars

Compared to CASPT2, which functional does make the best prediction?



$$\lambda_{\tau}^{(PT2,B3LYP)} = 0.49$$

$$\lambda_{\tau}^{(PT2,BHLYP)} = 0.66$$

Λ analysis for many observables

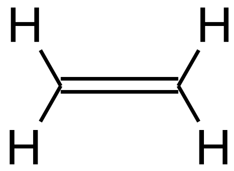
$$\boxed{\Lambda^{(1,2)} = \frac{1}{N_o} \sum_x \lambda_x^{(1,2)}}$$

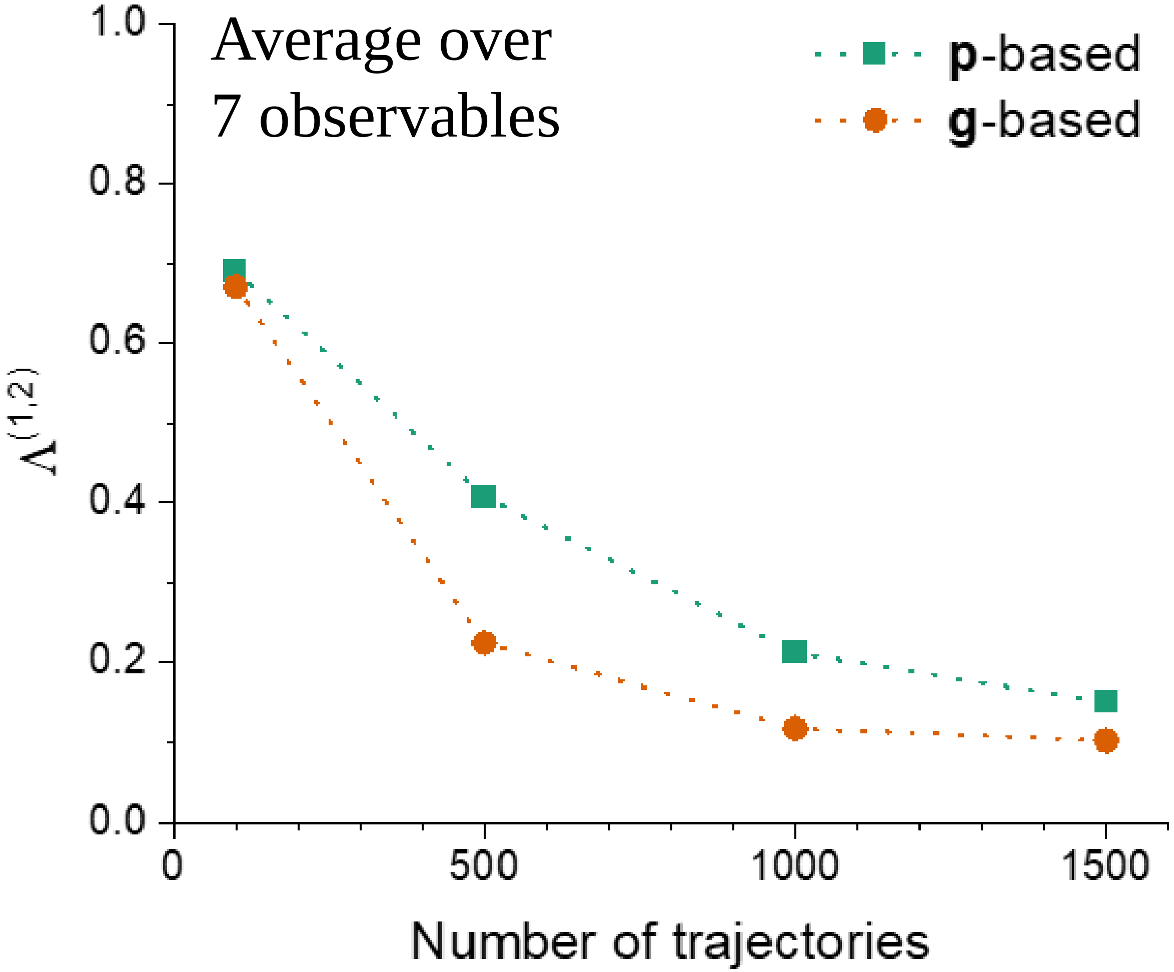
$\Lambda^{(1,2)} = 1$: perfect agreement

$\Lambda^{(1,2)} = 0$: total disagreement

- Barbatti. *JCTC* **2021,** *17*, 3010

FSSH dependence on velocity adjustment direction





- Barbatti. *JCTC* **2021,** *17*, 3010

HOW MUCH DOES SURFACE HOPPING COST?

Basic cost estimate

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

$N_{\text{Trajectories}}$ = 100 trajectories
$T_{\text{Single Point}}$ = 0.5 CPU.h
$\tau_{\text{chem process}}$ = 1 ps
$\Delta\tau$ = 0.5 fs
T_{total} = 100,000 CPU.h

- Price 1 CPU.h = 0.02 €
- Price 100,000 CPU.h = 2,000 €

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

How to cope with computational costs

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

Two strategies have been followed to cope with computational costs:

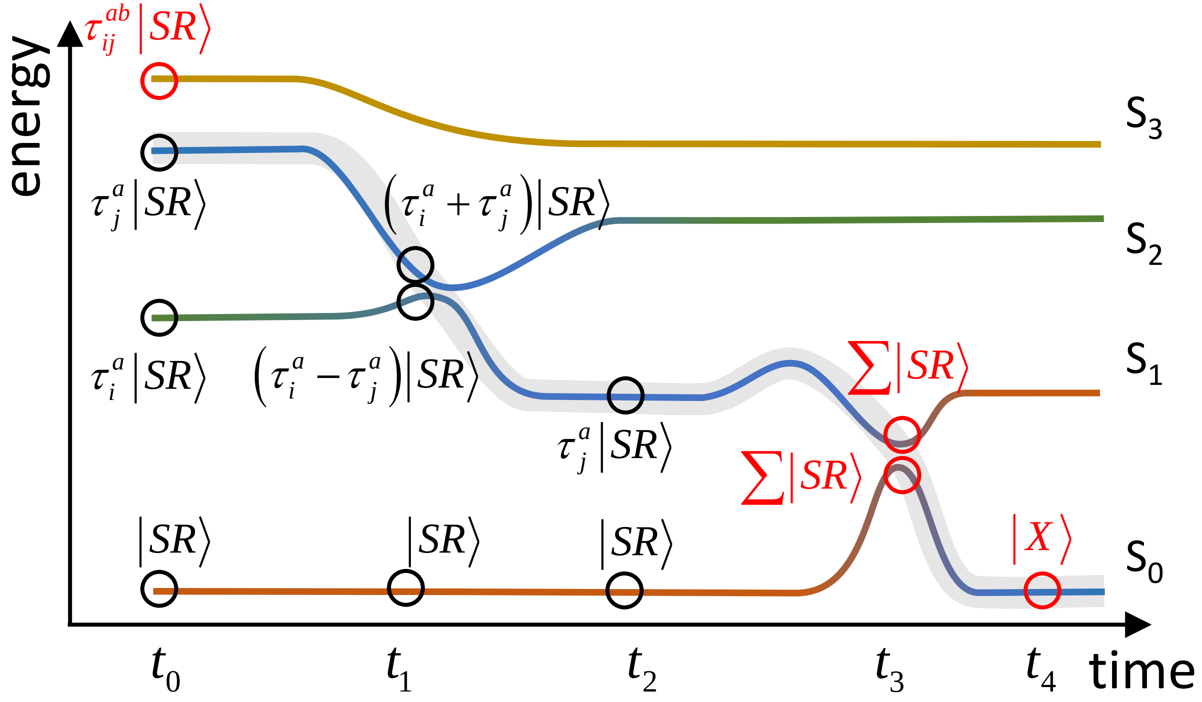
- Statistical ensembles are reduced,
  which affects the precision of the calculations
  - ✓ Reduce $N_{\text{trajectories}}$
  - ✓ Reduce $\tau_{\text{chem process}}$
  - ✓ Increase $\Delta\tau$
- Electronic structure methods are downgraded,
  which affects the accuracy of the simulations
  - ✓ Reduce $T_{\text{Single Point}}$

ELECTRONIC STRUCTURE

Electronic structure	Program
MRCI, MCSCF (+MM)	Columbus
XMS-CASPT2, CASSCF (+MM)	Bagel
MCSCF	Gamess
MCSCF	Gaussian
(LR, RI) CC2, (SOS) ADC(2) (+MM)	Turbomole
(LR) (TDA), TD(U)DFT, (U)CIS	Gaussian
(LR) TDDFT	Turbomole
(LR) LC-TD-DFTB	Dftb+
Machine learning	MLatom
Spin Boson Hamiltonian 2D Conical intersection 1D models collection	Built-in models

control.dyn:
PROG

TSH with single-reference: does it make sense?

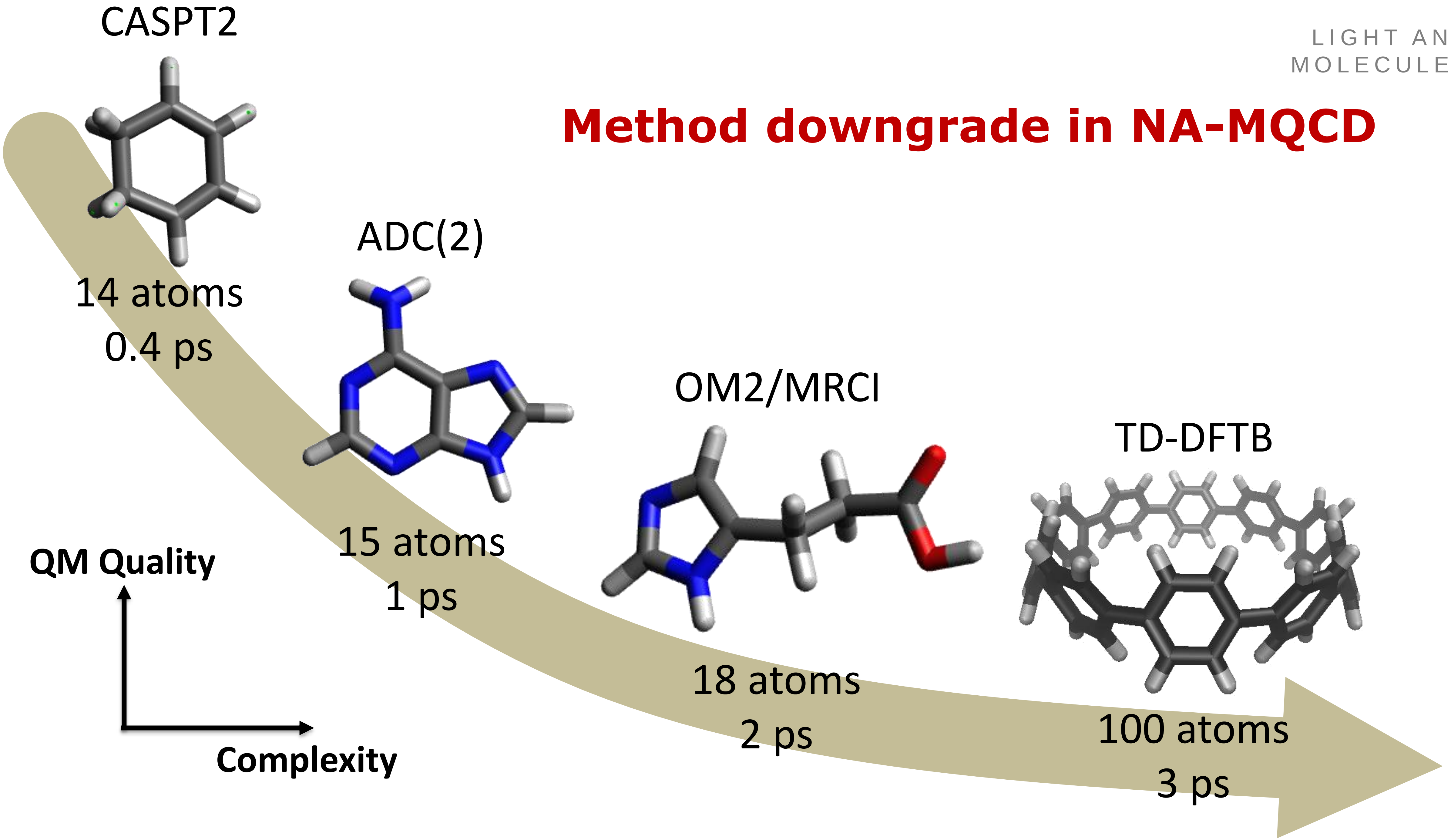


While dynamics doesn't reach $\sum|SR\rangle$ or $\tau_{ij}^{ab}|SR\rangle$ regions,

SR methods may be a reliable option for NA-MQCD

- Plasser; Crespo-Otero; Pederzoli; Pittner; Lischka; Barbatti. *JCTC* **2014,** *10*, 1395

Method downgrade in NA-MQCD



CASPT2

14 atoms
0.4 ps

ADC(2)

15 atoms
1 ps

OM2/MRCI

18 atoms
2 ps

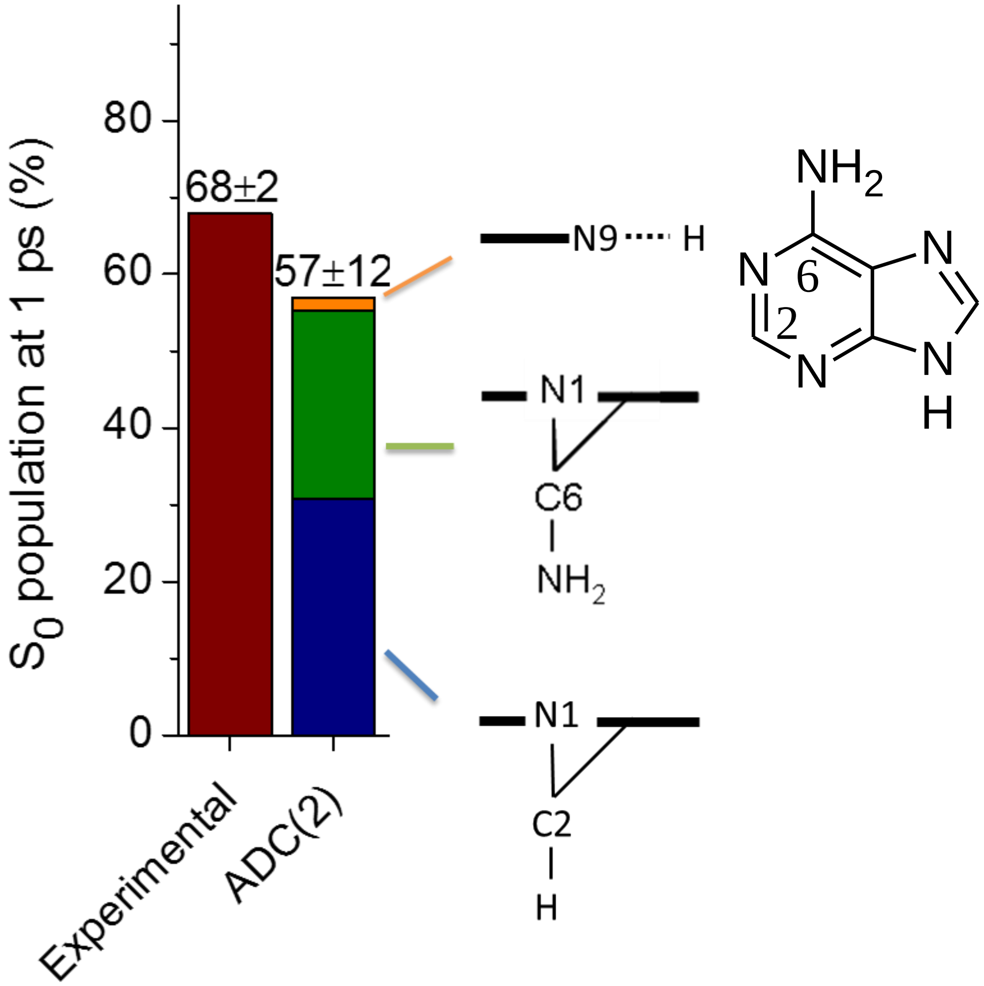
TD-DFTB

100 atoms
3 ps

QM Quality

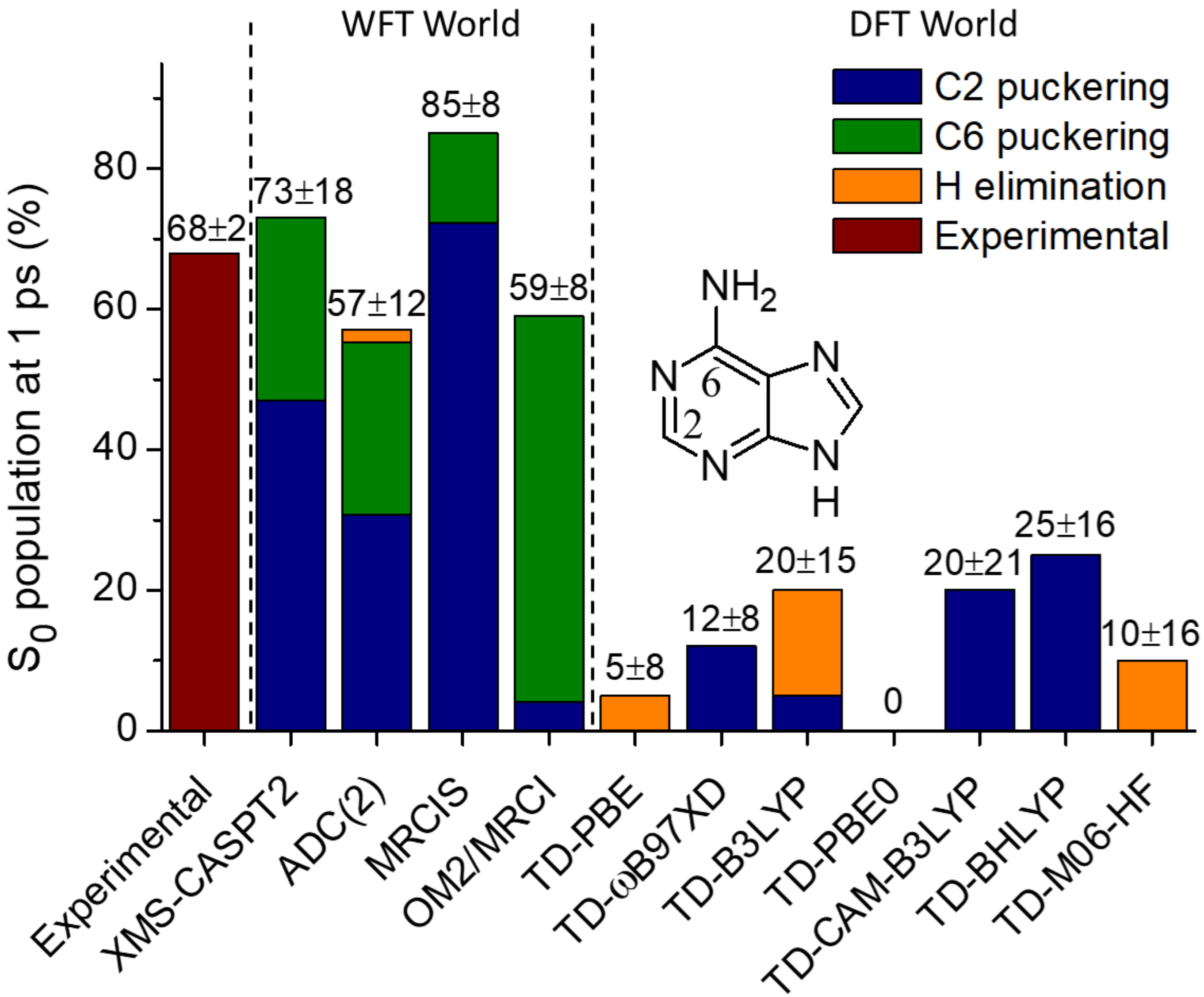
Complexity

Ground-state population at 1 ps



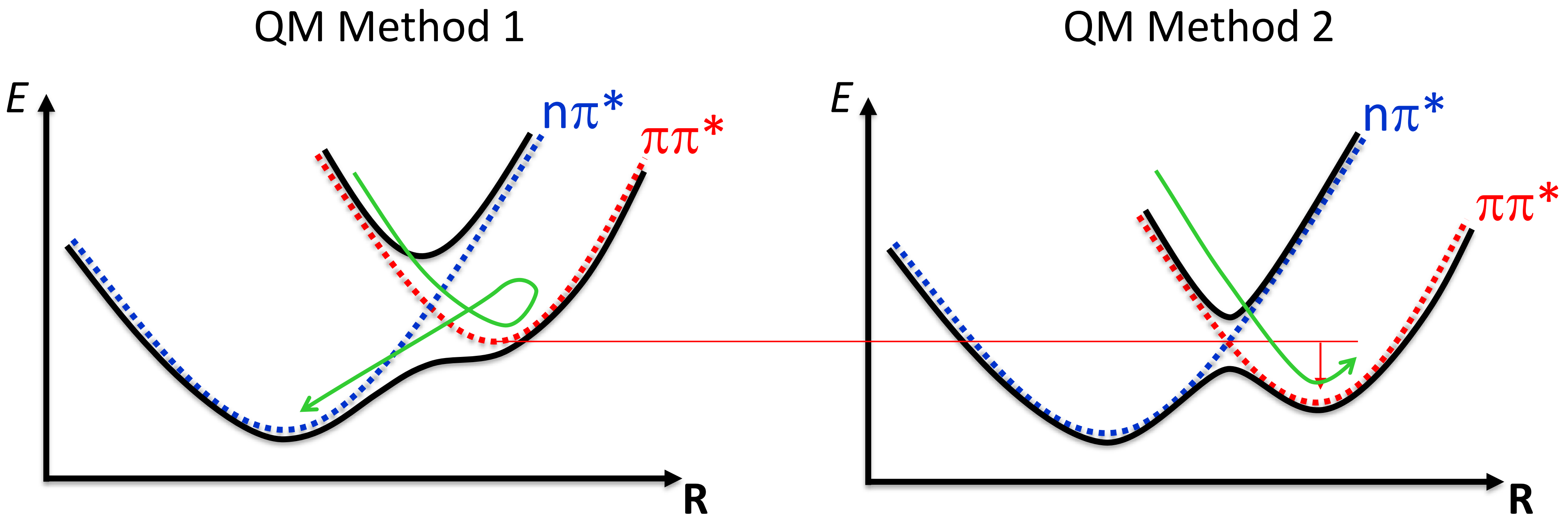
- Plasser; Crespo-Otero; Pederzoli; Pittner; Lischka; Barbatti. *JCTC* **2014**, *10*, 1395

The worst of the worlds: extreme method dependence



- Plasser; Crespo-Otero; Pederzoli; Pittner; Lischka; Barbatti. *JCTC* **2014**, *10*, 1395
- PT2: Park; Shiozaki. *JCTC* **2017**, *13*, 3676

The root of all evil



- No affordable method can describe **all characters at the same level**
- Excited-state spectral region has **high density of states**
- Small variation in geometry leads to a change of electronic character

Problem	Methods affected	Solution / workaround
Overshoot of ionic states	MCSCF, CASSCF	Use fully correlated methods. Scaled CASSCF
Orbital exchange between subspaces	MCSCF, CASSCF	Enlarge active space
Intruder states	CASPT2	Enlarge active space. Use level shifts
Unphysical responses when the difference between the excitation energies of two states matches the excitation of a third state	Any LR method	Avoid systems showing crossings with the ground state
Numerical instabilities near crossings between excited states	LR coupled cluster	Use a Hermitian method like ADC
Numerical instabilities near crossings with the ground state	Single reference methods	Avoid systems showing crossing with S_0. Stop trajectory at the crossing. D_1 and D_2 diagnostics for MP and CC may help to detect MR character of S_0. Increase DFT grid.
Wrong dimensionality of intersections with the ground state	CIS-type, LR, SS-CASPT2	Avoid systems showing crossing with the ground state. Stop trajectories at the crossing. Use SF
Negative excitations	Methods giving only excitation energies, like in LR	Stop trajectories at the crossing with the ground state
Wrong dissociation	Single reference methods	TDA may help in TDDFT. D_1 and D_2 diagnostics for MP and CC may help to detect the problem in ADC and CC
Underestimated charge transfer states	LR TDDFT	Use range-separated functionals
Missing double and higher excitations	LR ADC(2), LR ALDA TDDFT	Use another method to monitor higher excitations. Use SF
Underestimation of high-energy states	LR TDDFT	Use LC-corrected functionals
Undesired C=O dissociation	ADC(2)	Try TDDFT
Lack of ring puckering	TDDFT	Try ADC(2)

NEWTON-X NS

NX
newtonx.org

**Newtonian Dynamics
Close to the X-Seam**

Since 2005, Newton-X has been used in over 200 studies of nonadiabatic dynamics and spectra of photoexcited molecules.

```
PERL:
for $t = 0$ until $t = t_{max}$

    $E_K, \nabla E_K, |\psi_K\rangle$ = PERL: call EXTERNAL PROGRAM ( $\mathbf{R}$ )

    $\mathbf{R}, \mathbf{v}$ = call FORTRAN: VELOCITY VERLET ( $\mathbf{R}, \mathbf{v}, \nabla E_L$ )

    $\sigma_{LK}$ = call C++: COUPLING ( $|\psi_L\rangle, |\psi_K\rangle$ )

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

    $t = t + \Delta t$
```

- I/O Excess
- Convoluted code
- Nonoptimized routines
- Nonoptimized data format
- Unclear development protocol

NEWTON-X NS: tackling the challenges

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

Running-Time Test

Surface Hopping Dynamics of Spin-Boson Hamiltonian

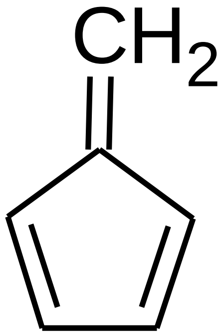
- Dimensions = 10
- t_{max} = 1000 fs
- Δt = 0.1 fs
- N_{cores} = 1

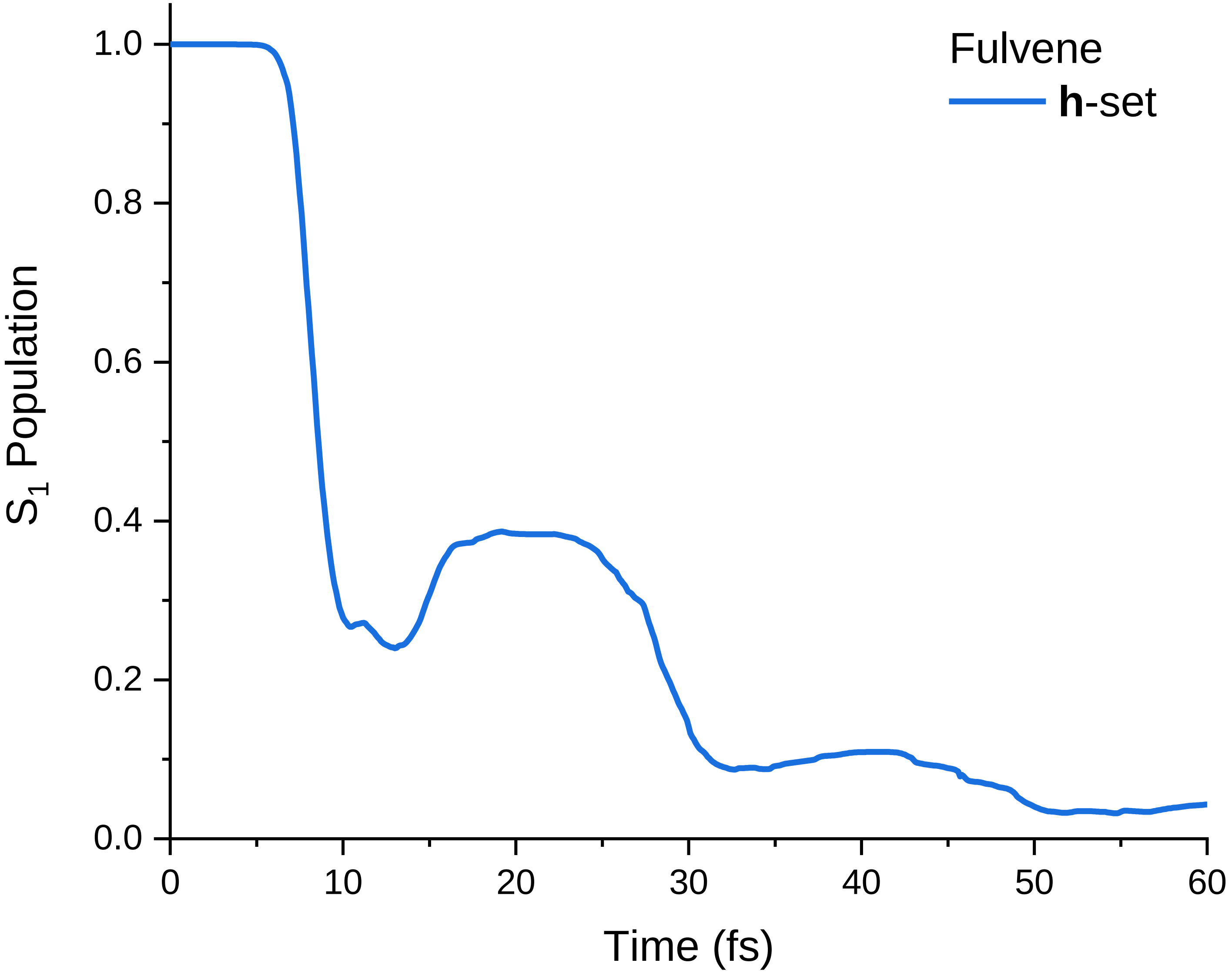
NEWTON-X CS	NEWTON-X NS
03:58:50	00:10:00

NEWTON-X NS

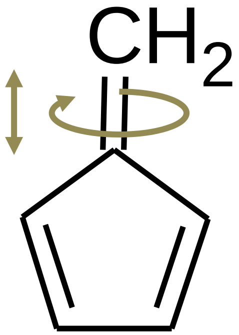
Release in the fall 2021

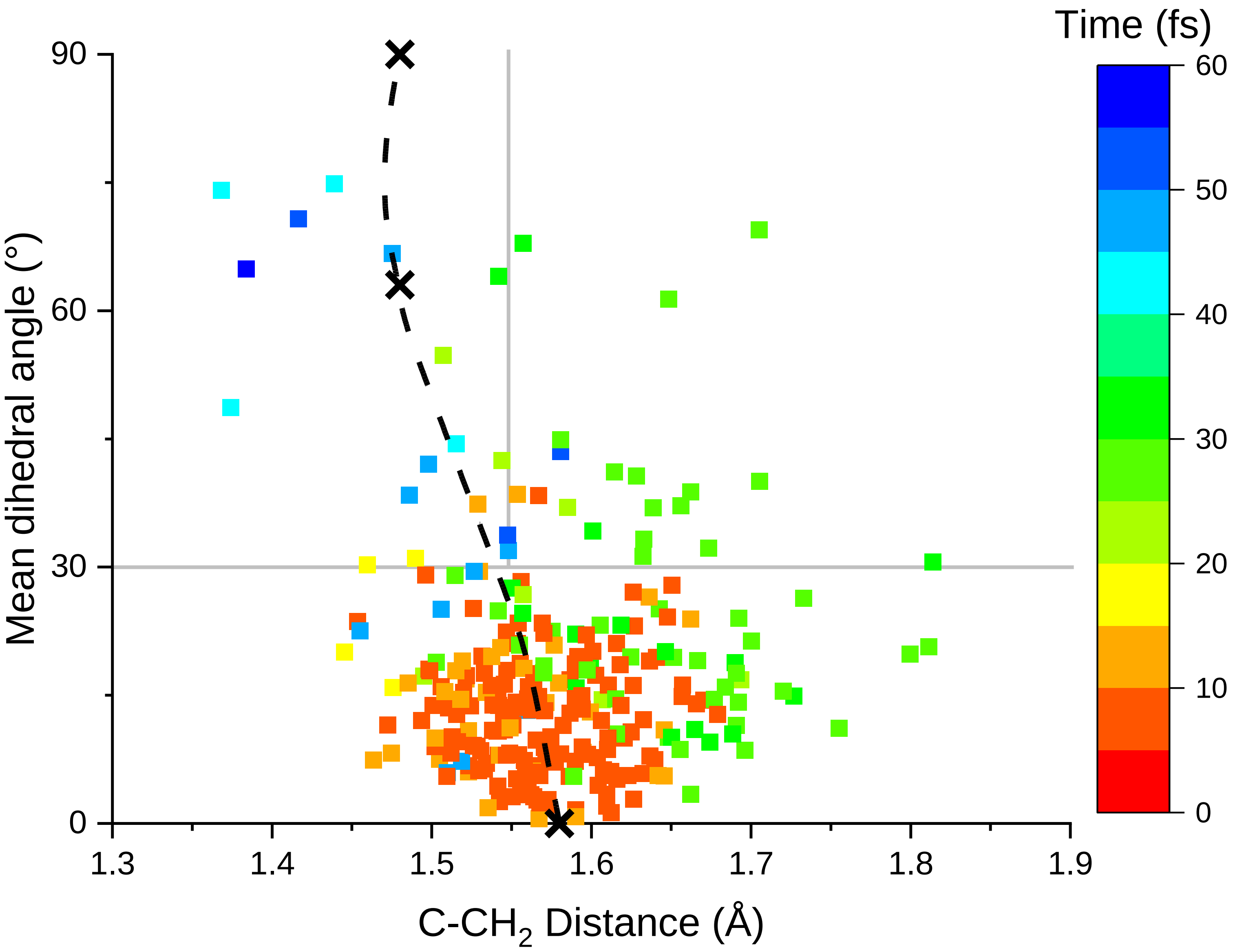
TUTORIAL: FULVENE DYNAMICS





- T. do Casal; Toldo; Pinheiro Jr; Barbatti. *Open Res Europe* **2021,** *1*, 49





- T. do Casal; Toldo; Pinheiro Jr; Barbatti. *Open Res Europe* **2021,** *1*, 49

Method / programs

- DC-FSSH with Newton-X / Columbus

Electronic structure

- SA2-CAS(6,6)/6-31G*

Initial conditions

- Uncorrelated Wigner sampling
- Excitation window: 4.00 ± 0.34 eV

Surface hopping

- Number of states: 2
- Initial state: S_1
- Classical timestep: 0.1 fs
- TDSE timestep: 0.2/20 fs
- Trajectory duration: 60 fs
- Columbus interface
- Nonadiabatic couplings vectors
- Decoherence: SDM 0.1 au

Tasks:

1. Prepare Columbus input for initial conditions
2. Compute initial conditions
3. Compute spectrum
4. Select initial conditions
5. Prepare Columbus input for trajectories
6. Prepare and run trajectories
7. Analyse

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6. Prepare and run trajectories
7. Analyse

Dalton int. C_1 point group. 6-31G*. No SCF. No gradient. SA2-CAS(6,6). Single point. MCSCF. Transition moment for MCSCF.

Dalton int. C_1 point group. 6-31G*. No SCF. Gradient for MCSCF. SA2-CAS(6,6). Single point. MCSCF. Nonadiabatic coupling. Transition moment for MCSCF. Full coupling. No slope analysis.

System: Fulvene Point Group: C1

N. Electrons: 42 Multiplicity: 1

Level: SA2-CAS(6,6)/6-31G*

		IRREP							
		A							
SCF	DOCC	21							
	OPSH	-							
MCSCF	DOCC	18							
	RAS	0							
	CAS	6							
	AUX	0							

State	Multiplicity	N. electrons	Symmetry
1	1	42	A
2	1	42	A

Number of distinct rows (DRTs): 1

LIGHT AND MOLECULES

SUBNANO

erc

FET OPEN

BOOST CROP

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