XACS
Xiamen Atomistic Computing Suite
XACScloud.com

MLatom.com

(Quasi-classical) molecular dynamics

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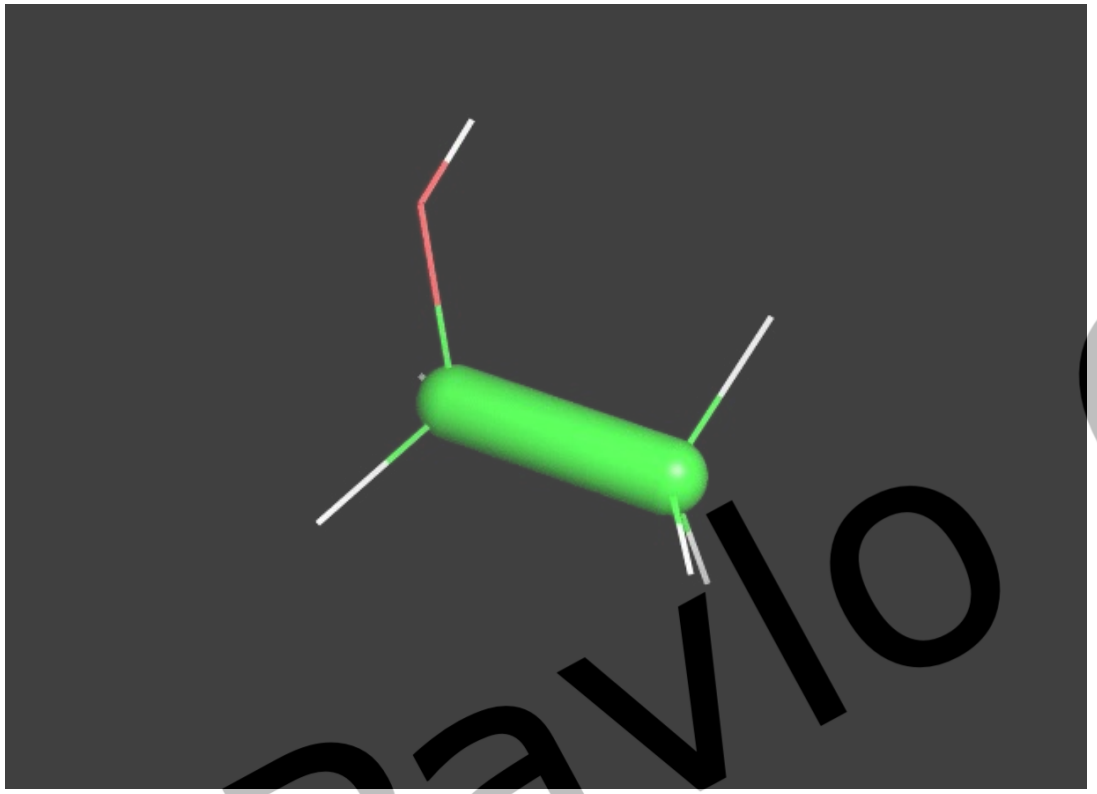
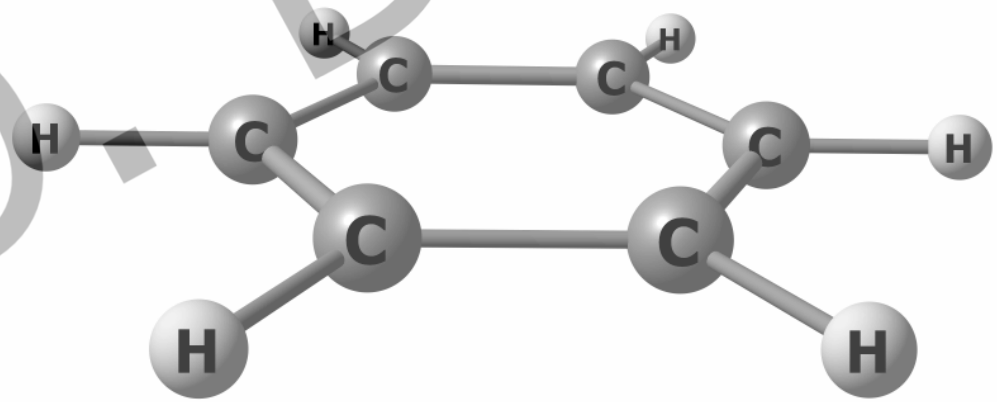
Molecules are always in motion





To propagate molecular dynamics:

- We just need forces
- And solve iteratively Newton's equations of motion

$$F_{A,d} = M_A a_{A,d}$$

$$a_{A,d} = F_{A,d} \frac{1}{M_A}$$

$$\frac{\partial^2 x_{A,d}}{\partial^2 t} = F_{A,d} \frac{1}{M_A}$$

$$\mathbf{F} = -\nabla E(\mathbf{R}) \qquad F_{A,d} = -\frac{\partial E}{\partial x_{A,d}}$$

Velocity Verlet algorithm:

$$\mathbf{x}(t + \Delta t) = \mathbf{x}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\boldsymbol{a}(t)\Delta t^2$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2}[\boldsymbol{a}(t) + \boldsymbol{a}(t + \Delta t)]\Delta t,$$

where $\mathbf{x}$ is the coordinate, $\mathbf{v}$ – the velocity, $\boldsymbol{a}$ – the acceleration, t – the time and

Simplified schematic of the molecular dynamics algorithm

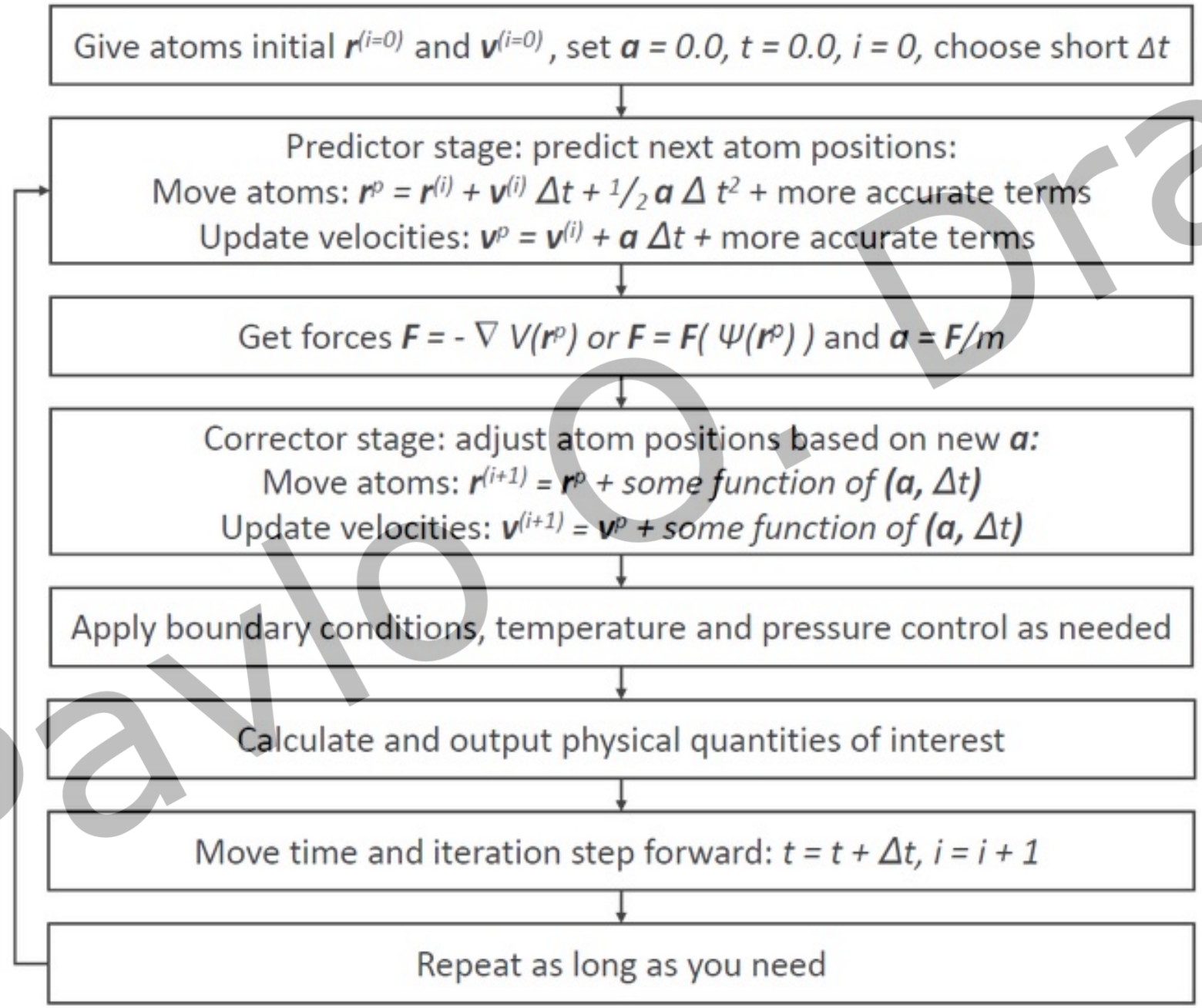


Figure credit: Knordlun, CC BY-SA 3.0, via Wikimedia Commons

Example MD-1.

Propagate an MD trajectory of H_2 molecule with B3LYP/6-31G*.

1. Visualize the trajectory. What is the range the bond length changes (min, max)?
2. How much time did it take to complete the calculations?

The MLatom@XACS input file:

```
MD
B3LYP/6-31G*
dt=0.5 # fs - time step
trun=500 # fs - propagation duration
initConditions=random
initXYZ='2

H 0 0 0
H 0 0 0.8'
```

How can we accelerate MD with ML?

To propagate molecular dynamics:

- We just need forces →
  can be obtained efficiently from machine learning potentials

$$F_{A,d} = M_A a_{A,d}$$

$$a_{A,d} = F_{A,d} \frac{1}{M_A}$$

$$\frac{\partial^2 x_{A,d}}{\partial^2 t} = F_{A,d} \frac{1}{M_A}$$

Velocity Verlet algorithm:

$$\mathbf{x}(t + \Delta t) = \mathbf{x}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\boldsymbol{a}(t)\Delta t^2$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2}[\boldsymbol{a}(t) + \boldsymbol{a}(t + \Delta t)]\Delta t,$$

where $\mathbf{x}$ is the coordinate, $\mathbf{v}$ – the velocity, $\boldsymbol{a}$ – the acceleration, t – the time and

$$\mathbf{F} = -\nabla E(\mathbf{R}) \qquad F_{A,d} = -\frac{\partial E}{\partial x_{A,d}} = -\frac{\partial E^{\text{machine learning potential}}(\mathbf{x})}{\partial x_{A,d}}$$

Example MD-2.

Propagate an MD trajectory of H_2 molecule with ANI-1ccx.

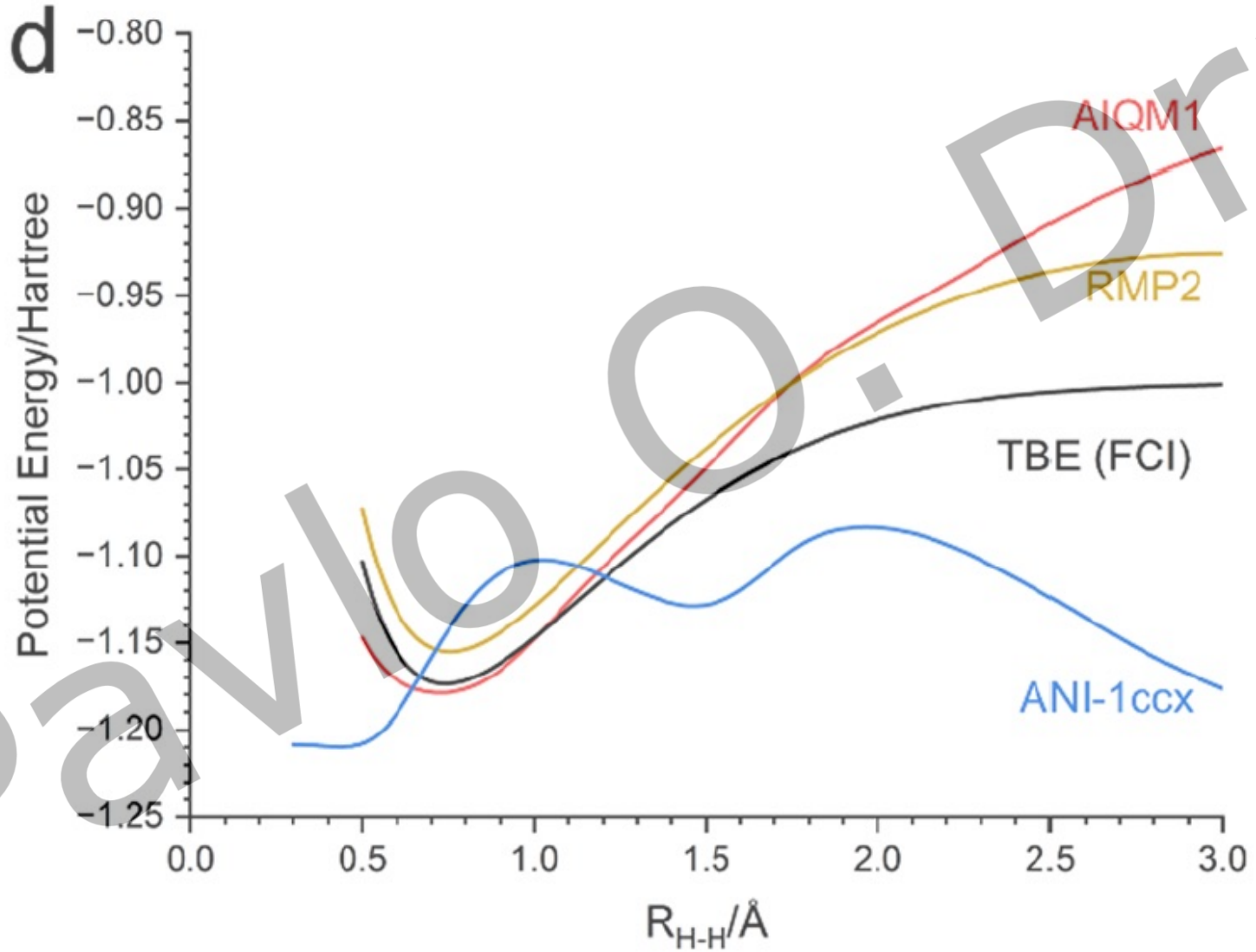
1. Visualize the trajectory. What is the range the bond length changes (min, max)?
2. How much time did it take to complete the calculations?
3. Compare time to DFT calculations.
4. Does ANI-1ccx produce physically-meaningful trajectory?

```
MD
ANI-1ccx
dt=0.5 # fs - time step
trun=500 # fs - propagation duration
initConditions=random
initXYZ='2

H 0 0 0
H 0 0 0.8'
```

Note the speed up for the hydrogen molecule is not so dramatic, but try something larger!

Dissociation curves



L. Zhang & Y. Hou, F. Ge, P. O. Dral, *Phys. Chem. Chem. Phys.* **2023**, *25*, 23467

Task 5.4

Propagate an MD trajectory of H_2 molecule with your own ANI model trained on FCI data.

1. Visualize the trajectory. What is the range the bond length changes (min, max)?
2. How much time did it take to complete the calculations?
3. Does this ANI model produce physically-meaningful trajectory?

Modify the input file from previous task as needed.

Simulations in NVT are more complicated

MLatom implements Nosé–Hoover chain, where the velocities of particles are controlled by a chain of additional degrees of freedom to guarantee the canonical sampling of the original system. The equations of motion are shown below:

$$\mathbf{v}_i = \frac{\mathbf{p}_i}{m_i},$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \frac{p_{\xi_1}}{Q_1},$$

$$\xi_i = \frac{p_{\xi_i}}{Q_i},$$

$$\dot{p}_{\xi_1} = \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - N_f kT \right) - p_{\xi_1} \frac{p_{\xi_2}}{Q_2},$$

$$\dot{p}_{\xi_k} = \left(\frac{p_{\xi_{k-1}}^2}{Q_{k-1}} - kT \right) - p_{\xi_k} \frac{p_{\xi_{k+1}}}{Q_{k+1}},$$

$$\dot{p}_{\xi_M} = \left(\frac{p_{\xi_{M-1}}^2}{Q_{M-1}} - kT \right).$$

Frenkel, D.; Smit, B.; Tobochnik, J.; Mckay, S. R.; Christian, W., *Understanding Molecular Simulation*. Elsevier: Bodmin, Cornwall, 1997.

Example MD-4.

Propagate an MD trajectory of H_2 molecule with your own ANI model trained on FCI data at 300 K using the NVT ensemble.

1. Plot how the total energy changes compared to the simulation in the NVE ensemble. What is the major difference?
2. Plot how the temperature changes too.
3. Is it expected?

You would need to add the following lines to your input file from previous task:

```
temperature=300
ensemble=NVT
thermostat=Nose-Hoover
```

Note

You can find total energy in the files `traj.etot` and temperature in the files `traj.temp`.

Missing zero-point vibrational energy

Example MD-5.

Start MD of H_2 molecule with your own ANI model trained on FCI data from the optimized geometry (with the same model, you can take it f your previous exercise) using the **NVE ensemble**, and using the initial temperature of 0 K.

What happens to MD?

Quasi-classical MD recovers ZPVE

Normal mode sampling from the Wigner distribution

The picture can't be displayed.

MD17 – MD at 500 K
WS22 – Wigner sampling

$$P_w(\boldsymbol{Q},\boldsymbol{P}) = \prod_{i=1}^{N_F} \frac{1}{\pi\hbar} \exp\left(-\frac{1}{\hbar\omega_i}\left(\omega_i^2 Q_i^2 + P_i^2\right)\right)$$

$$Q_i = \mu_i^{1/2} q_i, P_i = \mu_i^{-1/2} p_i$$

Figures: M. Pinheiro Jr, S. Zhang, P. O. Dral, M. Barbatti. Sci. Data 2023, 10, 95.

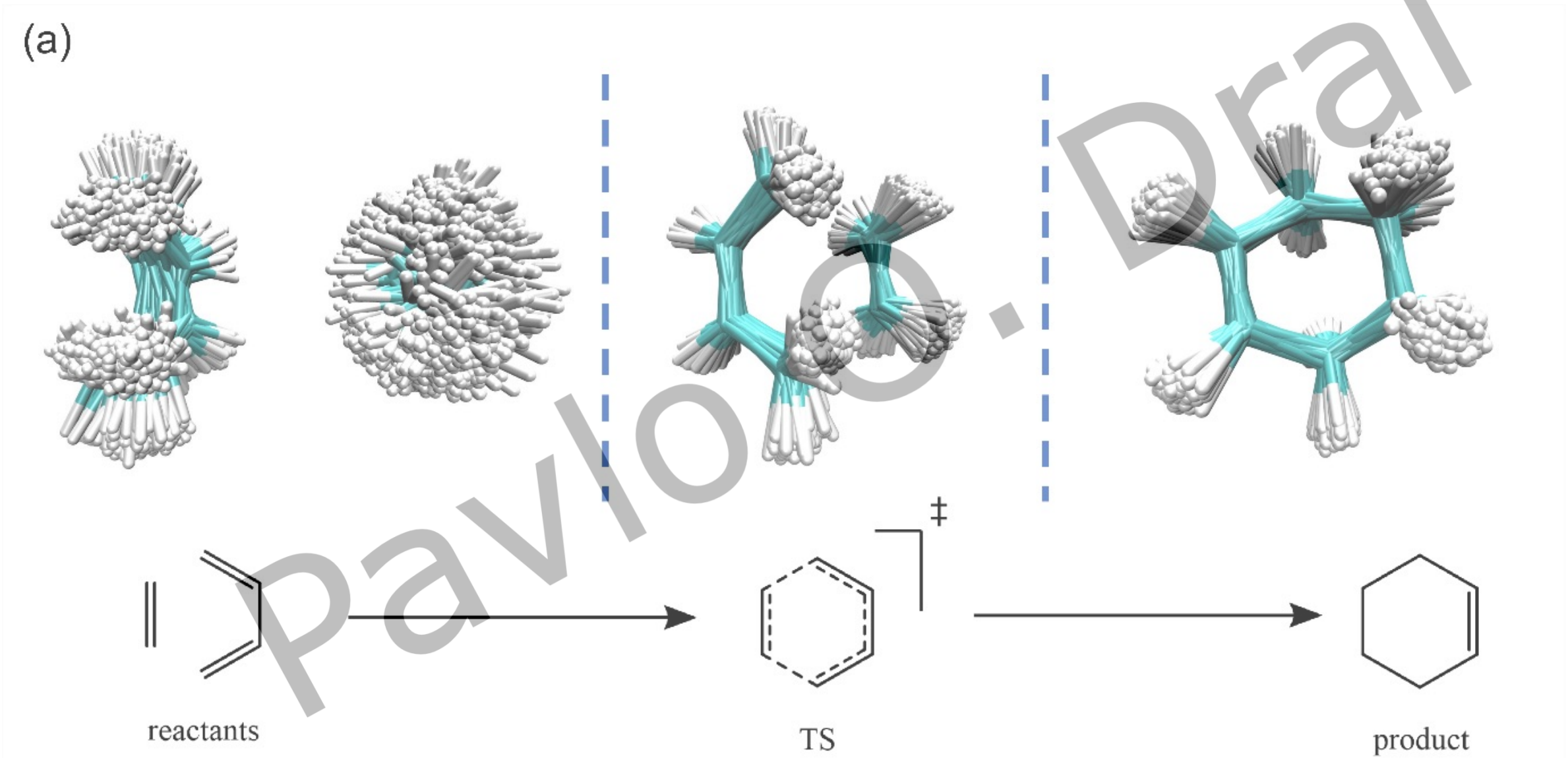
Example MD-6.

Run quasi-classical trajectory MD of H_2 molecule with your own ANI model trained on FCI data from the optimized geometry (with the same model, you can take it from your previous exercise).

For this, you first need to do freq calculations on the optimized geometry. These calculations will produce the `freq1.json` file which you can use in the following input file:

```
MD
MLmodelIn=energies_ani.pt
MLmodelType=ANI
dt=0.5 # fs - time step
trun=100 # fs - propagation duration
initTemperature=0
initConditions=Wigner
normalModeFile=freq1.json
```

How is this MD different to the previous one? What happens to MD?



Y.-F. Hou, L. Zhang, Q. Zhang, F. Ge, P. O. Dral. *Submitted*.

Nuclear quantum effects are not taken into account in MD!

Methods like PIMD are required

Molecular Dynamics with Constrained Nuclear Electronic Orbital Density Functional Theory: Accurate Vibrational Spectra from Efficient Incorporation of Nuclear Quantum Effects

Xi Xu, Zehua Chen, and Yang Yang*

Cite This: *J. Am. Chem. Soc.* 2022, 144, 4039–4046

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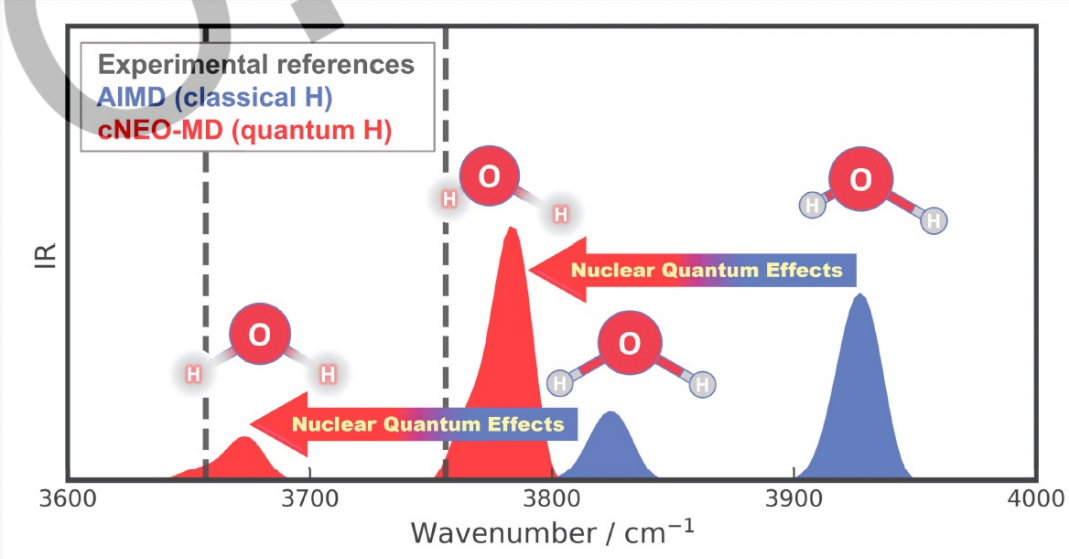
ABSTRACT: Nuclear quantum effects play a crucial role in many chemical and biological systems involving hydrogen atoms yet are difficult to include in practical molecular simulations. In this paper, we combine our recently developed methods of constrained nuclear−electronic orbital density functional theory (cNEO-DFT) and constrained minimized energy surface molecular dynamics (CMES-MD) to create a new method for accurately and efficiently describing nuclear quantum effects in molecular simulations. By use of this new method, dubbed cNEO-MD, the vibrational spectra of a set of small molecules are calculated and compared with those from conventional *ab initio* molecular dynamics (AIMD) as well as from experiments. With the same formal scaling, cNEO-MD greatly outperforms AIMD in describing the vibrational modes with significant hydrogen motion characters, demonstrating the promise of cNEO-MD for simulating chemical and biological systems with significant nuclear quantum effects.



Transitions between electronic states also often have to be taken into account, particularly, when simulating photophysical and photochemical processes

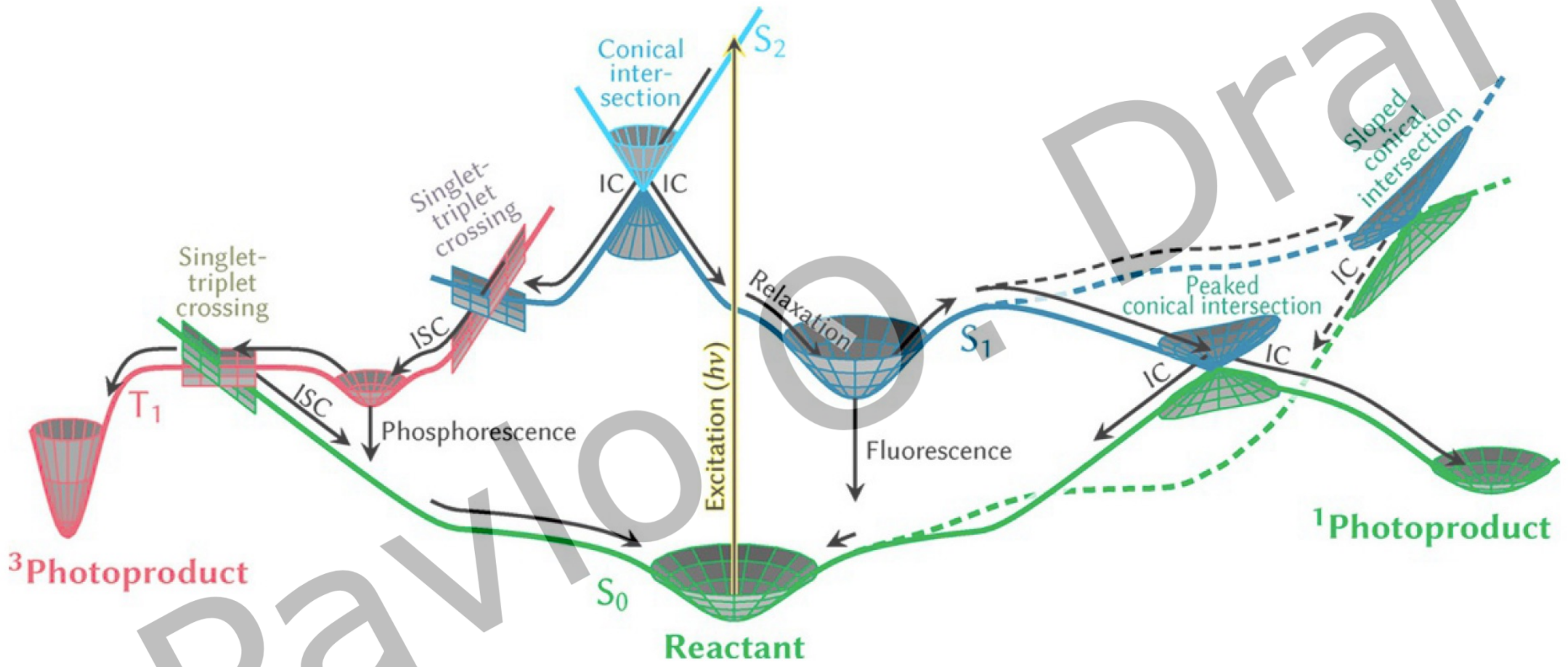
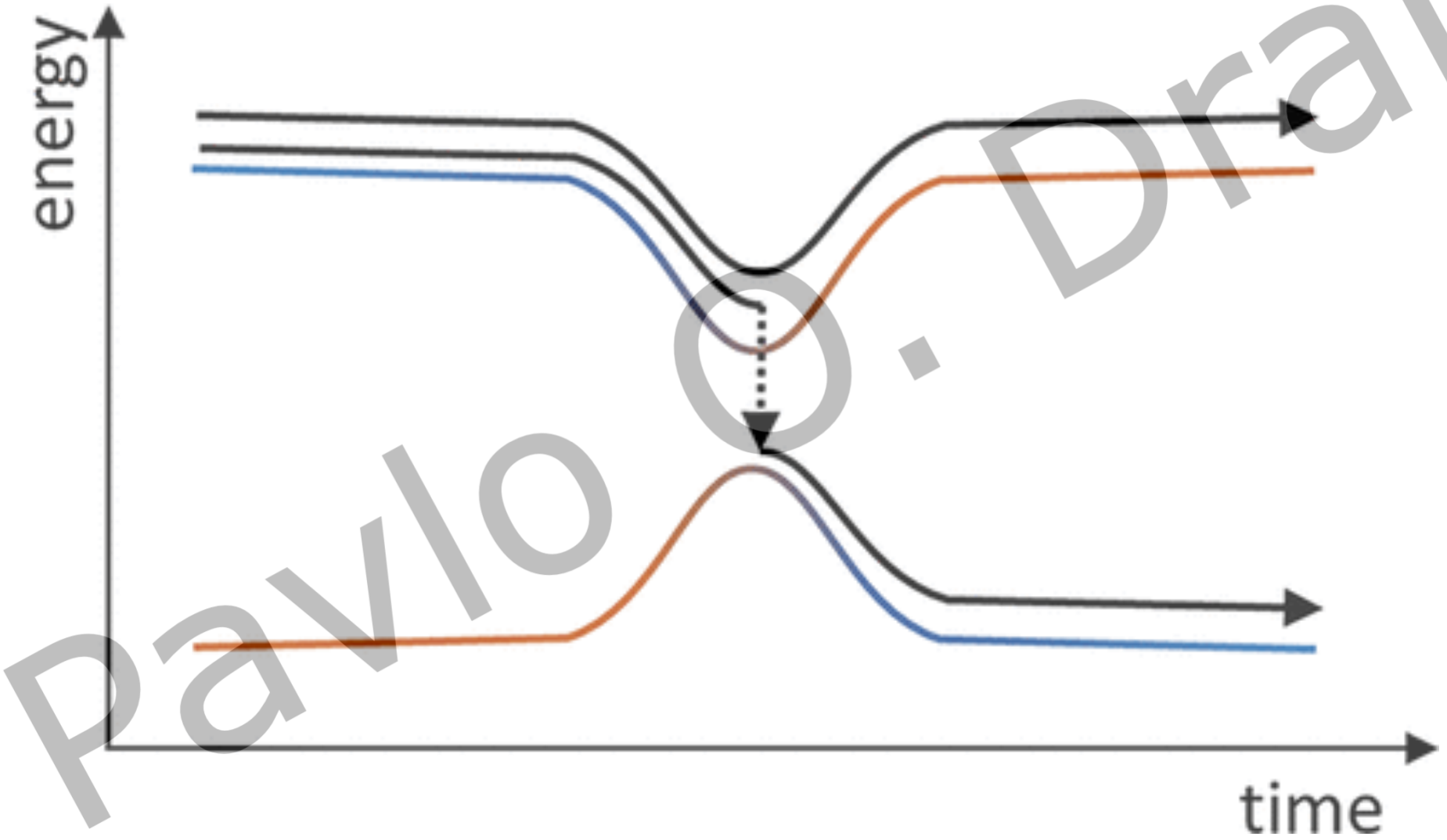


FIG. 3 A typical potential energy surface in NAMD. *Reproduced from S. Mai, L. González, Angew. Chem. Int. Ed. 59 (2020) 16832–16846, under CC BY 4.0.*

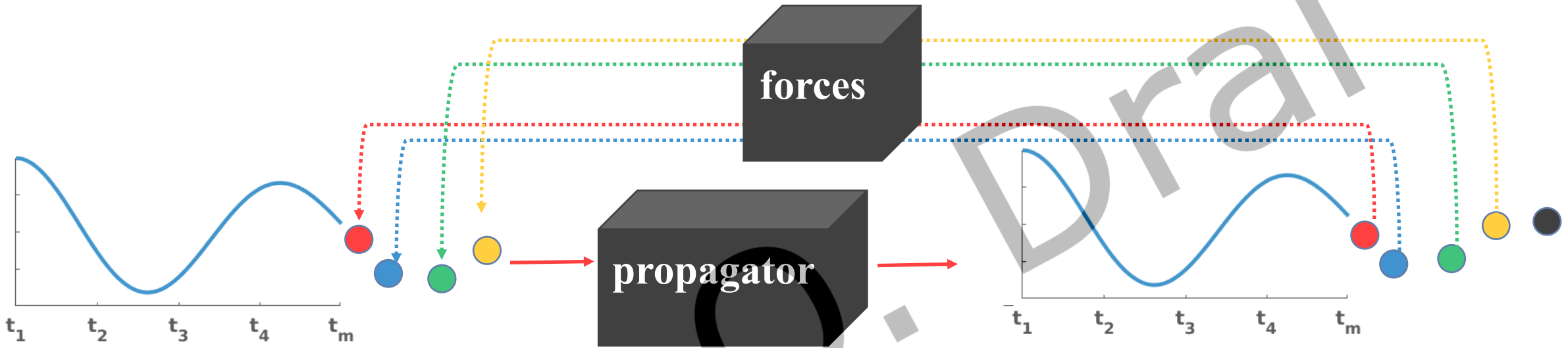
Surface Hopping



J. C. Tully, *J. Chem. Phys.* **1990**, *93*, 1061
R. Crespo-Otero and M. Barbatti, *Chem. Rev.* **2018**, *118*, 7026

How can we accelerate MD with ML?

MD



$$F_{A,d} = -\frac{\partial E}{\partial x_{A,d}} = -\frac{\partial E^{\text{machine learning potential}}(\mathbf{x})}{\partial x_{A,d}}$$

Adapted from animation by Arif Ullah

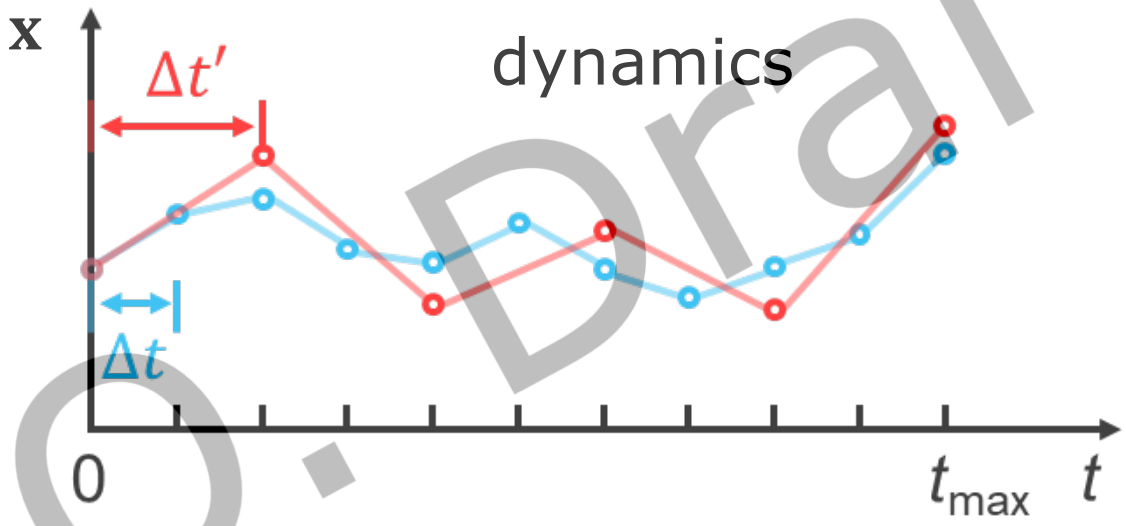
Can we do better?

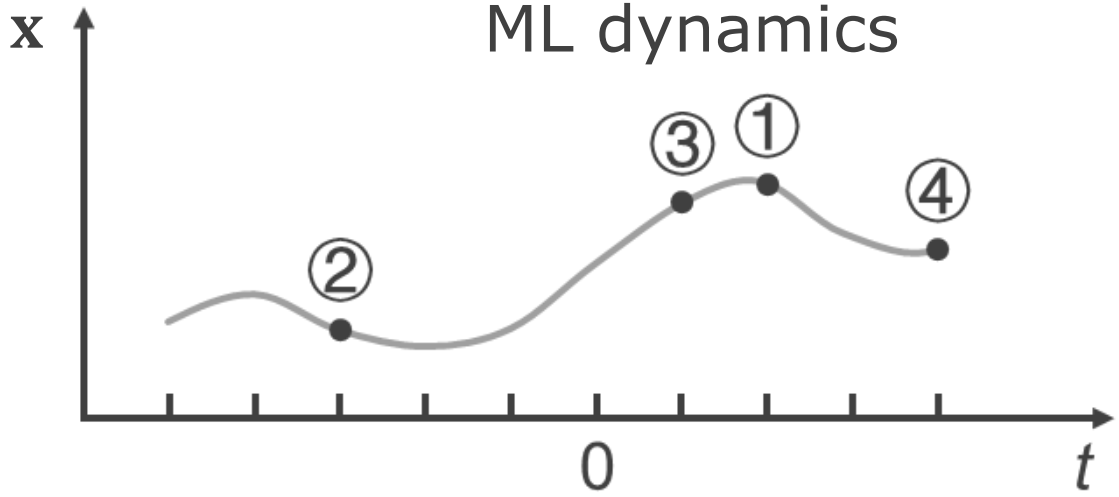
~~dynamics propagation is~~

- ~~Iterative (non-parallelizable)~~
- ~~Depends on time step~~
- ~~Discrete~~

Directly learning dynamics

$$\mathbf{x}_t = f(\mathbf{x}_0, \mathbf{v}_0, t)$$



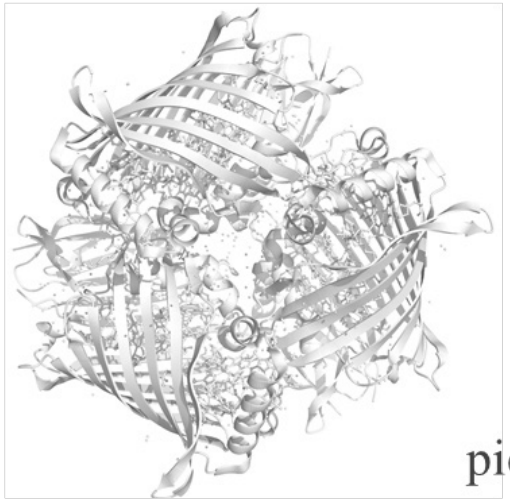


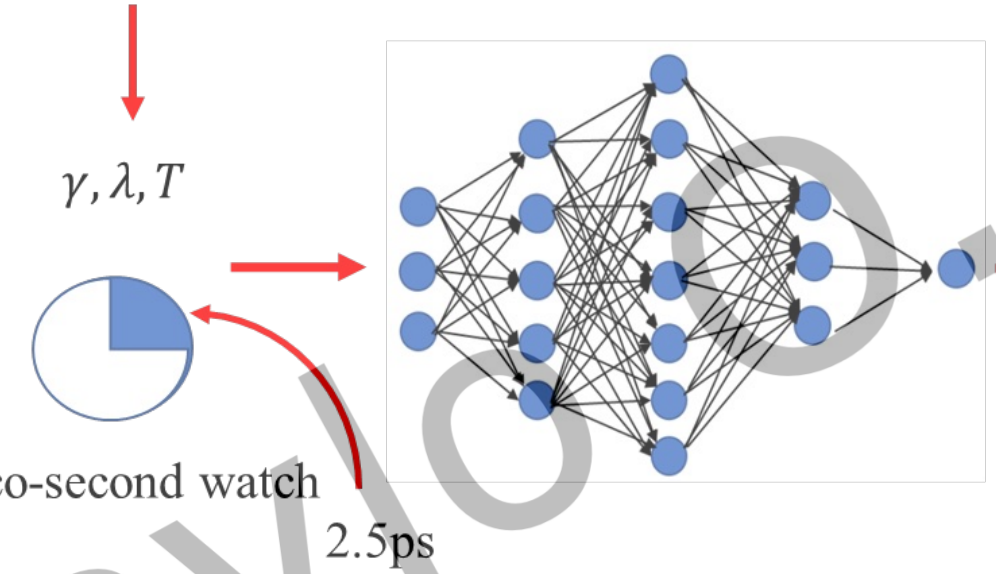
AI-QD (artificial intelligence-based quantum dynamics)

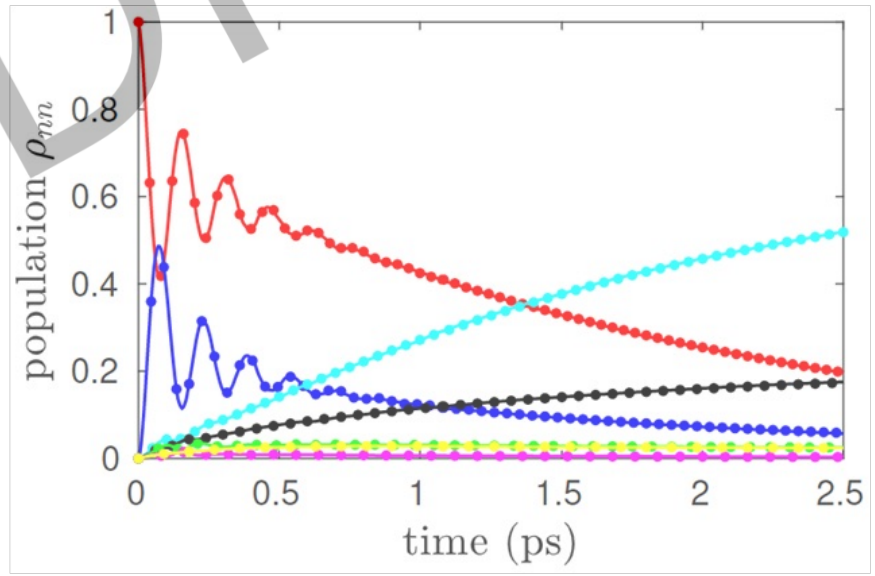
γ = characteristic frequency
λ = reorganization energy
T = temperature

$$\boldsymbol{\rho}(\text{time}) = f[\text{time}; \text{simulation parameters}]$$

PDB code: 3ENI



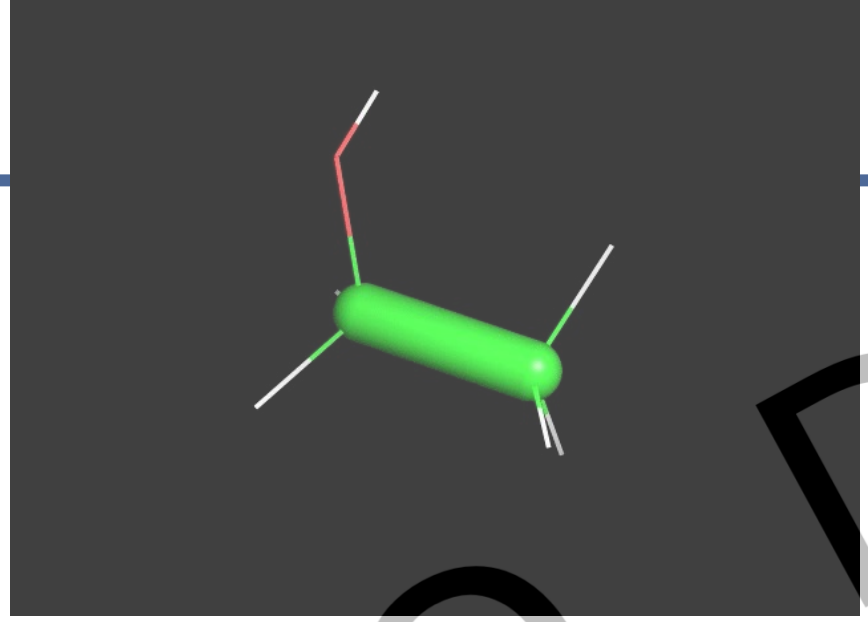




Dots: Reference
Line: AI-QD

7-sites Fenna–Matthews–Olson (FMO) complex

A. Ullah, P. O. Dral. Predicting the future of excitation energy transfer in light-harvesting complex with artificial intelligence-based quantum dynamics. *Nat. Commun.* **2022**, *13*, 1930



MLatom.com

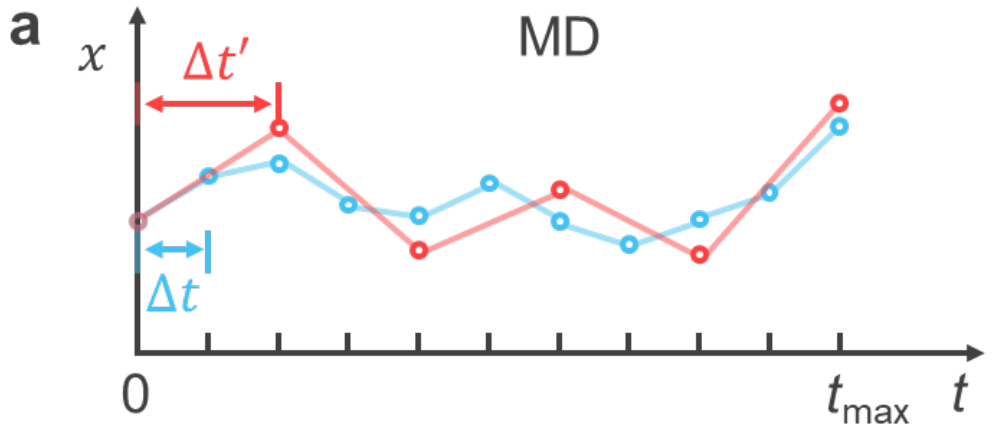
Direct learning of molecular dynamics

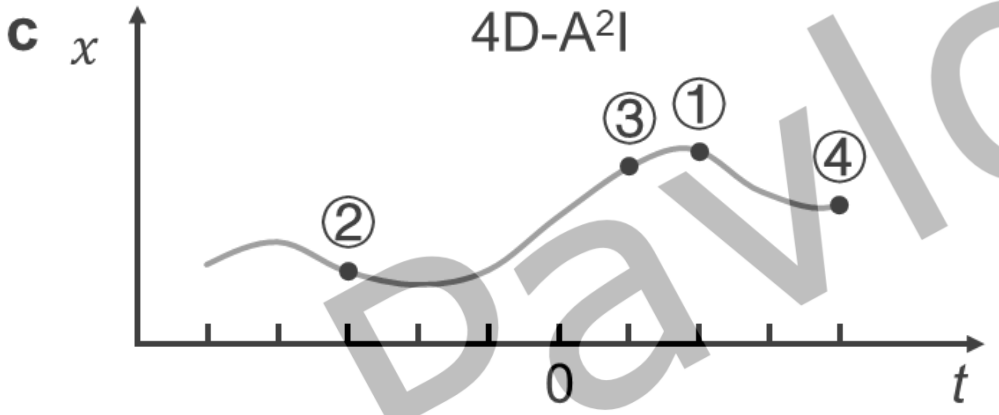
or

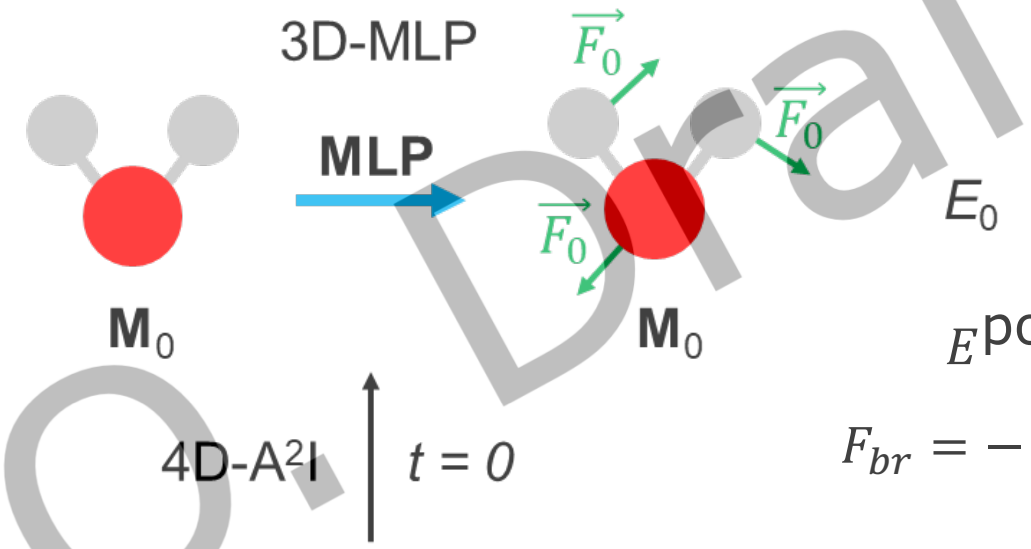
Meet 4D spacetime atomistic artificial intelligence (4D-A²I) models

F. Ge, L. Zhang, Y.-F. Hou, Y. Chen, A. Ullah, P. O. Dral. *J. Phys. Chem. Lett.* **2023**, *14*, 7732

3D vs 4D

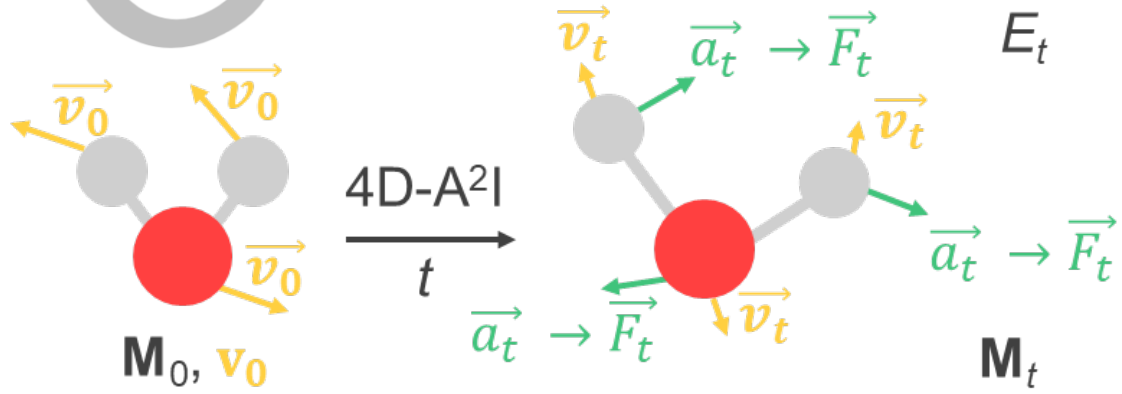






$$E^{\text{pot}} = f(\mathbf{M})$$

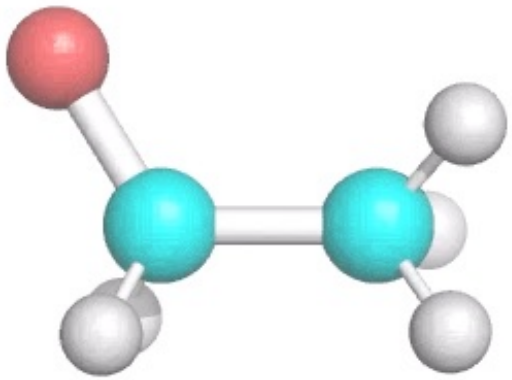
$$F_{br} = -\partial E^{\text{pot}}/\partial x_{br}$$



$$\mathbf{x}_t = f(\mathbf{x}_0, \mathbf{v}_0, t) \longrightarrow v_{br,t} = \frac{dx_{br,t}}{dt} \longrightarrow a_{br,t} = \frac{dv_{br,t}}{dt} \longrightarrow F_{br,t} = m_b a_{br,t}$$

F. Ge, L. Zhang, Y.-F. Hou, Y. Chen, A. Ullah, P. O. Dral. *J. Phys. Chem. Lett.* **2023**, *14*, 7732

3D MD

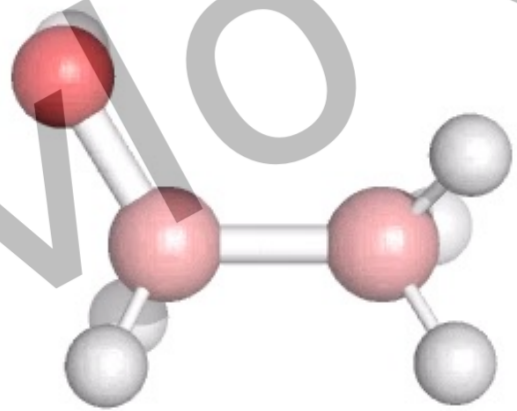


Very slow

The direct learning of molecular dynamics with 4D-spacetime GICnet models

Fuchun Ge

4D–A^2I

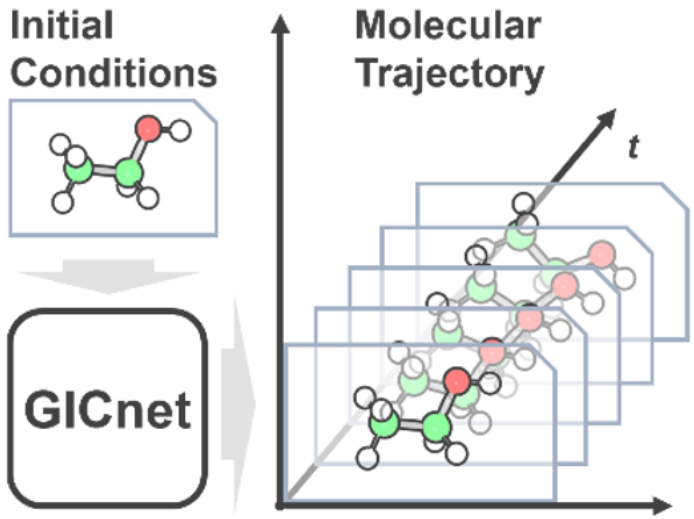


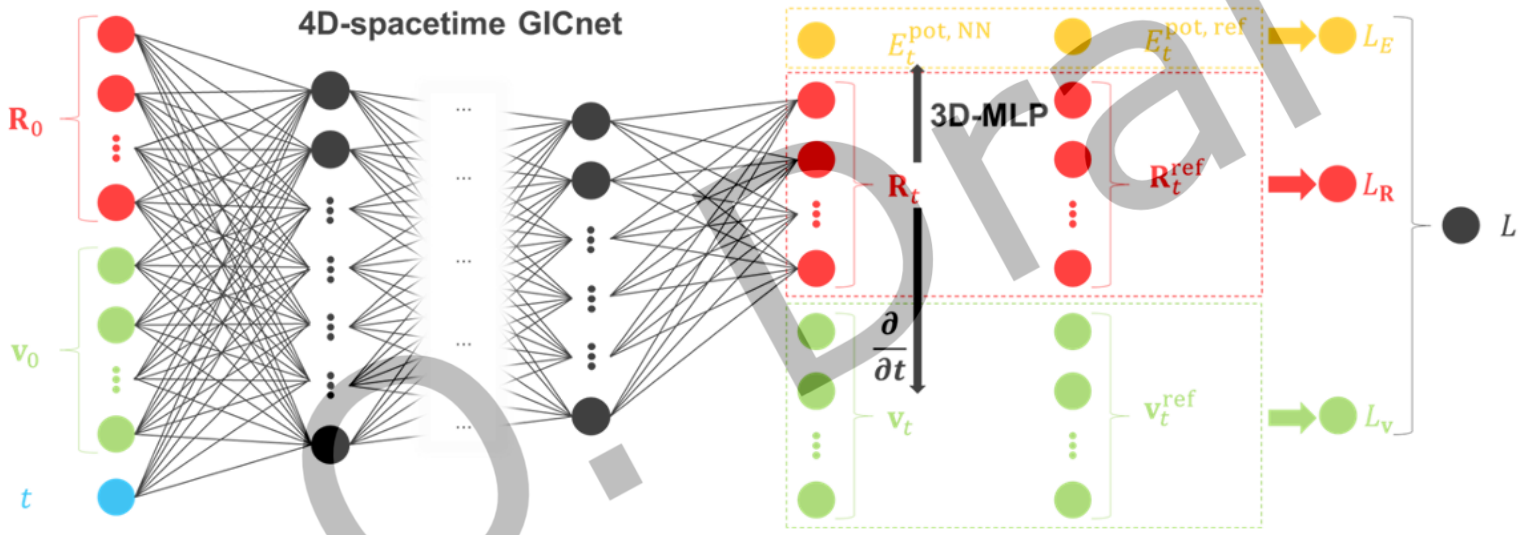
0.05 fs

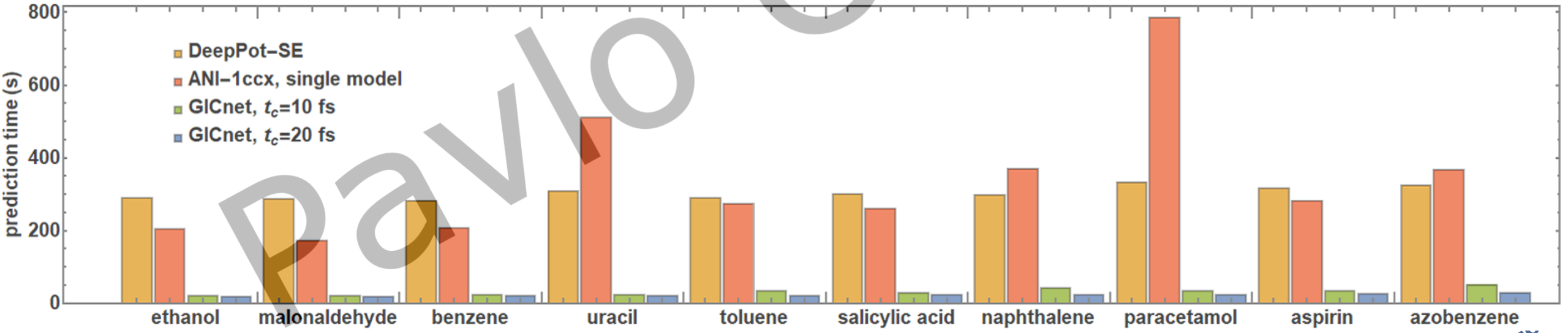
Very fast, e.g., 1 ps trajectory (time step 0.05 fs) within 1 minute

F. Ge, L. Zhang, Y.-F. Hou, Y. Chen, A. Ullah, P. O. Dral. *J. Phys. Chem. Lett.* **2023**, *14*, 7732

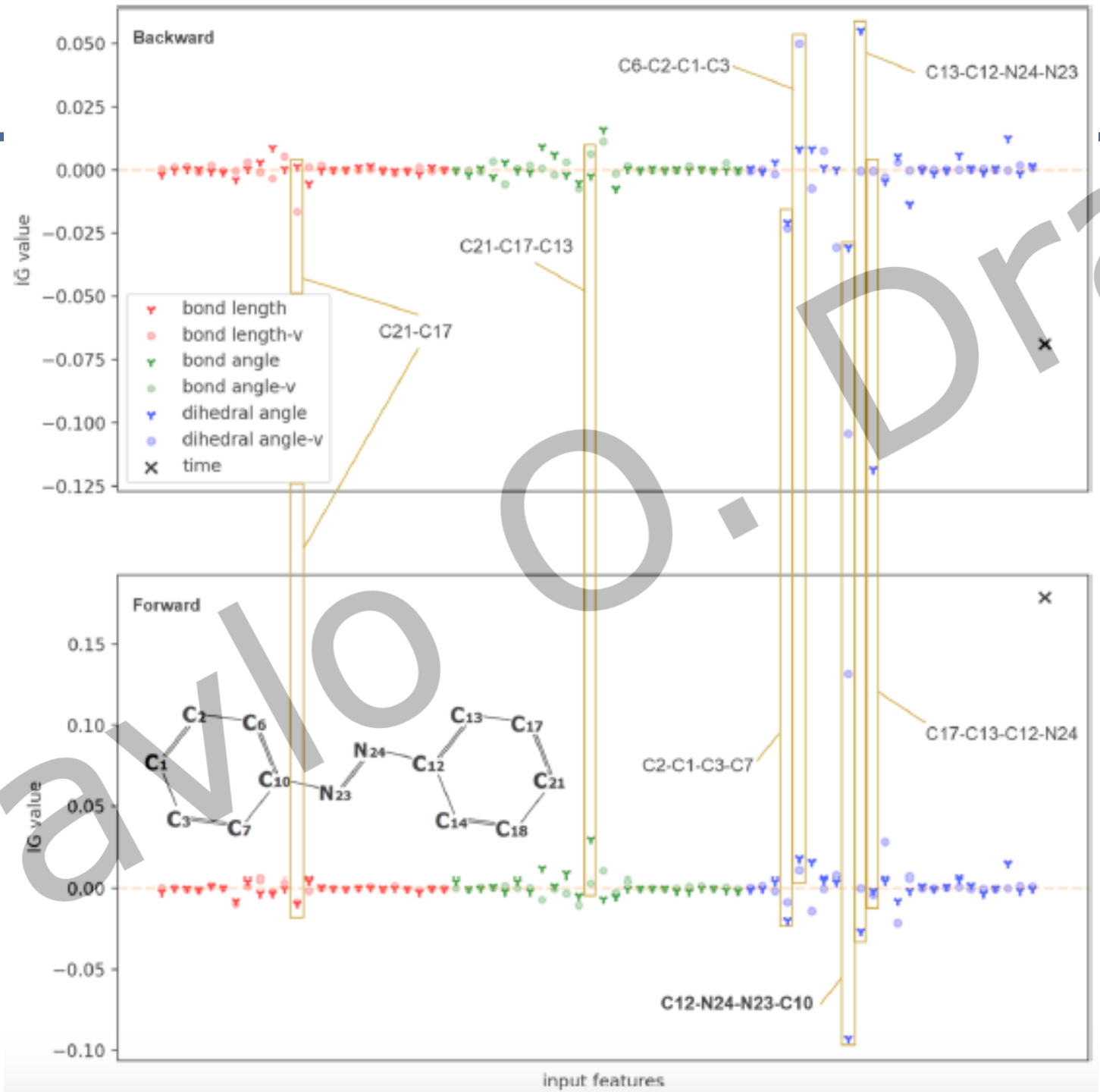
Direct learning of molecular dynamics







F. Ge, L. Zhang, Y.-F. Hou, Y. Chen, A. Ullah, P. O. Dral. *J. Phys. Chem. Lett.* **2023**, *14*, 7732


Backward
IG value
0.050
0.025
0.000
−0.025
−0.050
−0.075
−0.100
−0.125
C6-C2-C1-C3
C13-C12-N24-N23
C21-C17-C13
C21-C17
bond length
bond length-v
bond angle
bond angle-v
dihedral angle
dihedral angle-v
time
Forward
IG value
0.15
0.10
0.05
0.00
−0.05
−0.10
C2-C1-C3-C7
C17-C13-C12-N24
C12-N24-N23-C10
C1
C2
C3
C6
C7
C10
N23
N24
C12
C13
C14
C17
C18
C21
input features

Can we do even better?

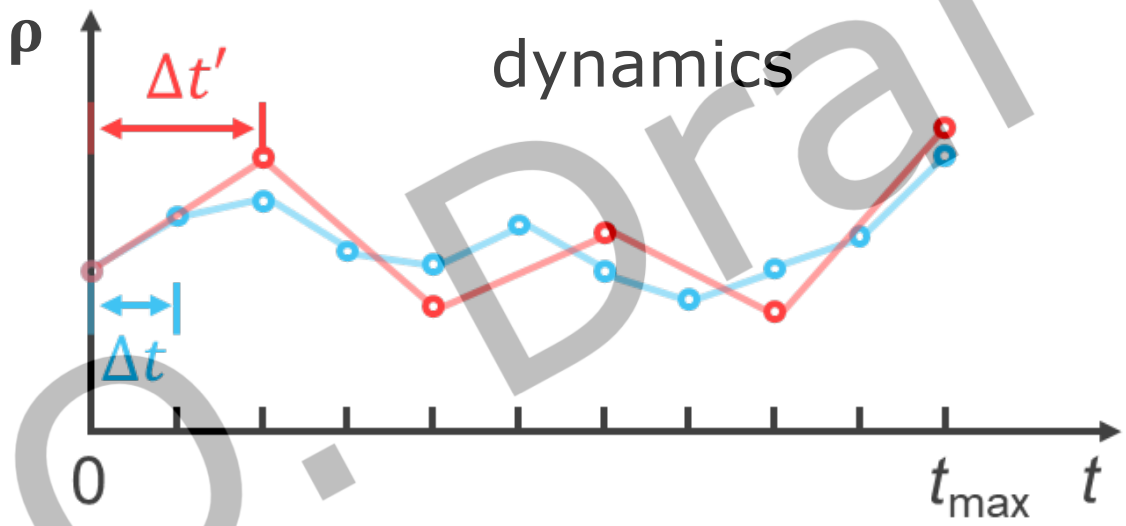
~~$\boldsymbol{\rho}(t) = f[\boldsymbol{\rho}(t - \Delta t)]$~~

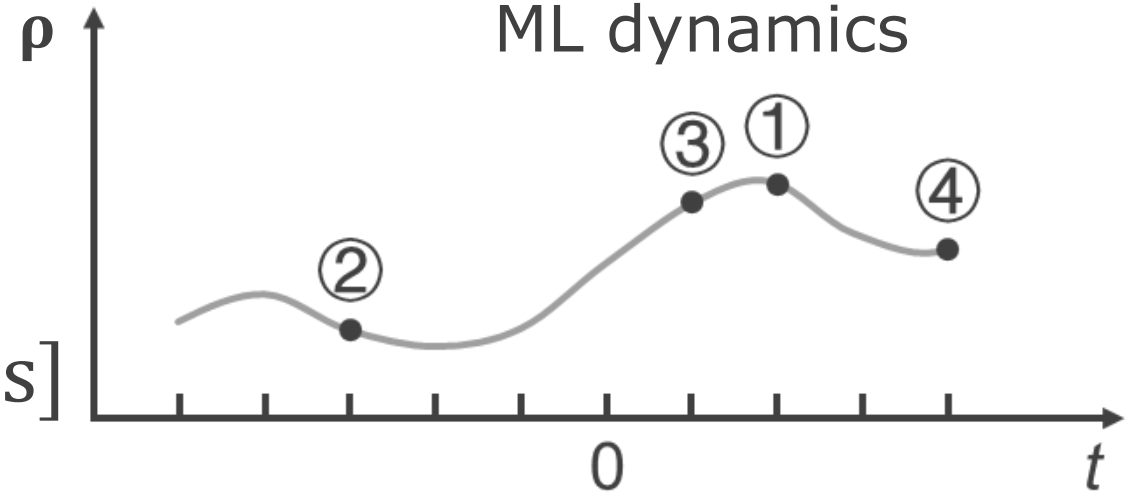
dynamics propagation is

- ~~computationally expensive~~
- ~~recursive (iterative)~~

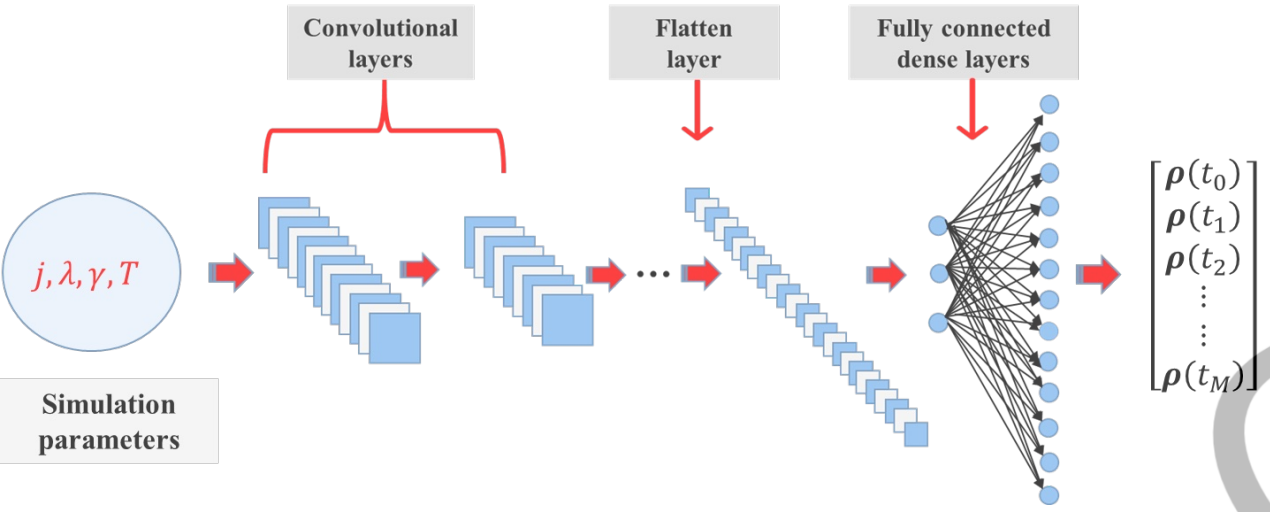
~~$\boldsymbol{\rho}(t) = f[t; \text{other parameters}]$~~

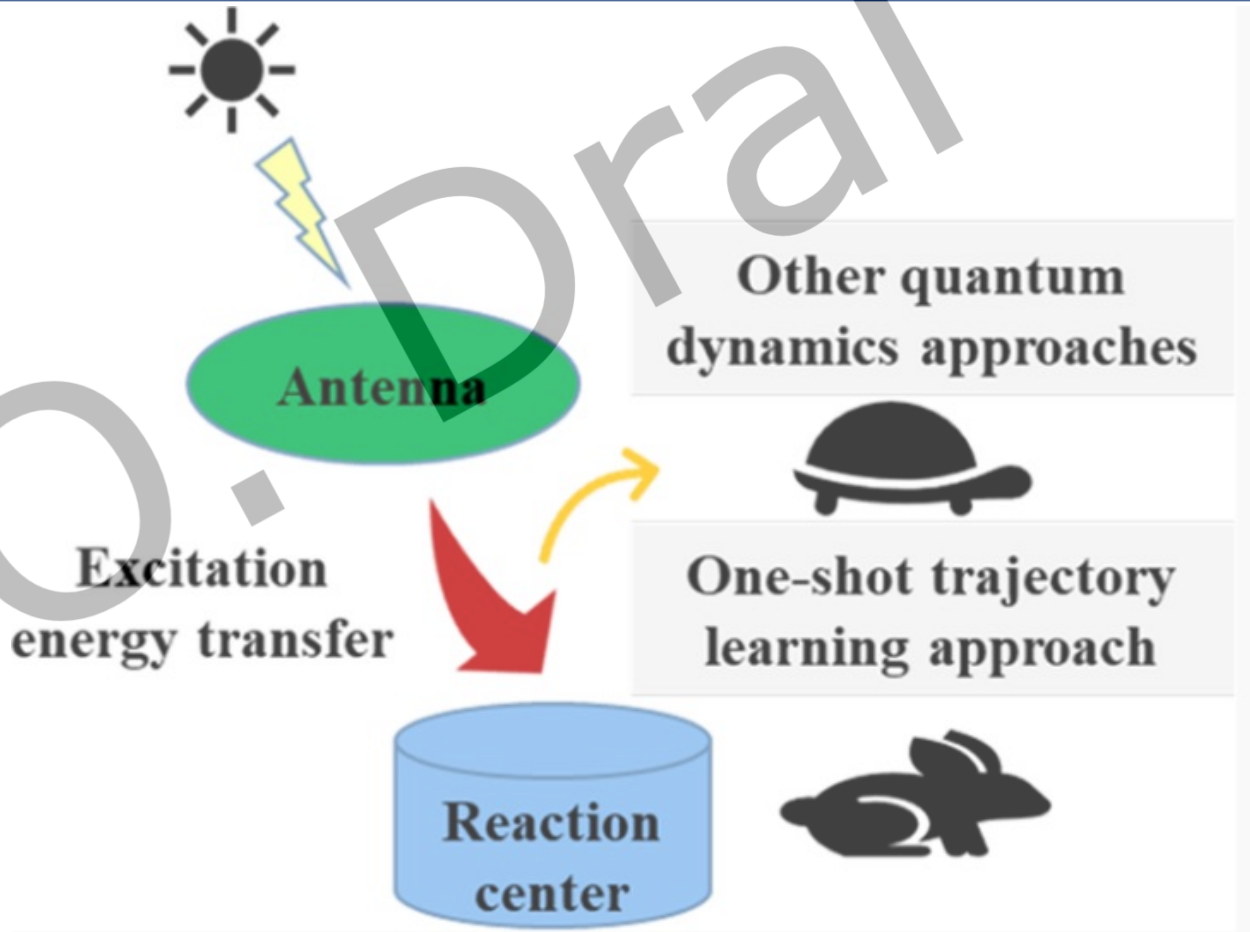
$\{\boldsymbol{\rho}(t_k)\}_{k=0}^{M} = f[\text{other parameters}]$





One-Shot Trajectory Learning (OSTL)





$$\{\boldsymbol{\rho}(t_k)\}_{k=0}^{M} = f[\text{other parameters}]$$

- **10 ps long dynamics in just 70 ms**
- good for massive simulation in parameter space

A. Ullah, P. O. Dral. *J. Phys. Chem. Lett.* **2022**, 6037