XACS
Xiamen Atomistic Computing Suite
XACScloud.com

MLatom.com

Towards more accessible excited-state simulations with AI

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MLatom@XACS, Xiamen University

Virtual International Seminar on Theory Advancement" (VISTA)
20 March 2024

dr-dral.com

Group & Acknowledgements

Hiring post-docs, PhD & MSc students!

Funding

PCOSS

国家自然科学基金委员会
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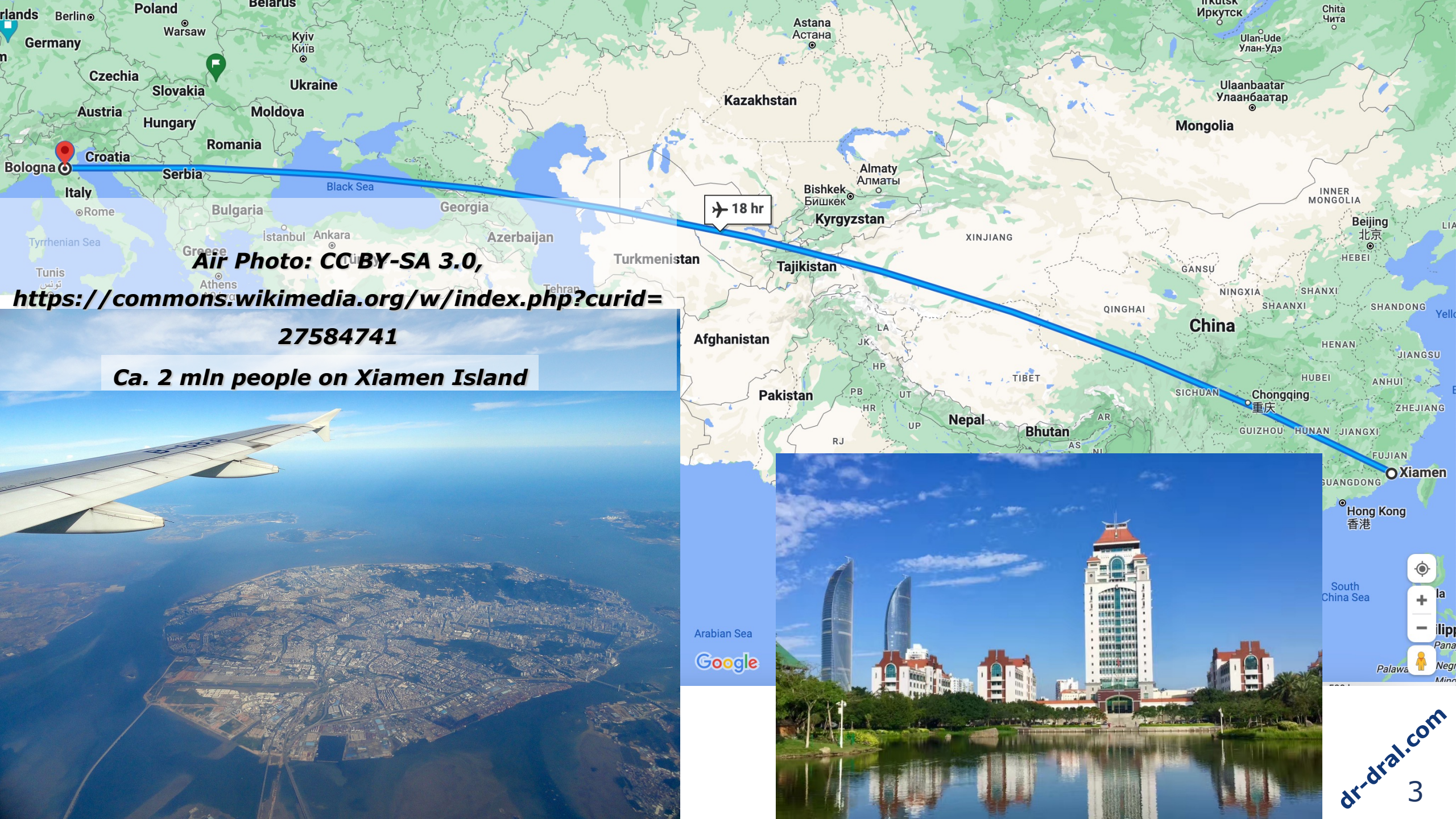
嘉庚创新实验室
TAN KAH KEE INNOVATION LABORATORY



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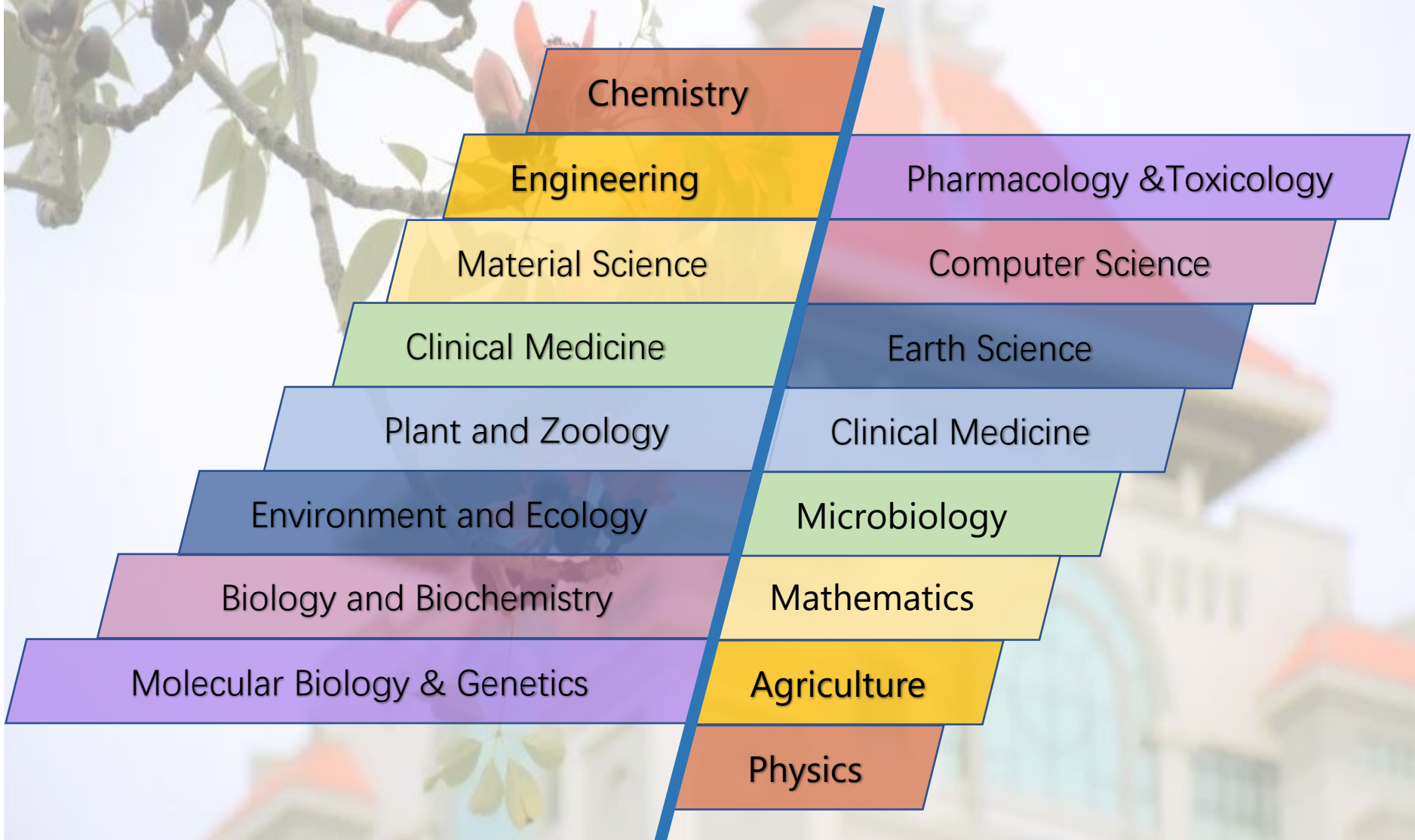
Ca. 2 mln people on Xiamen Island

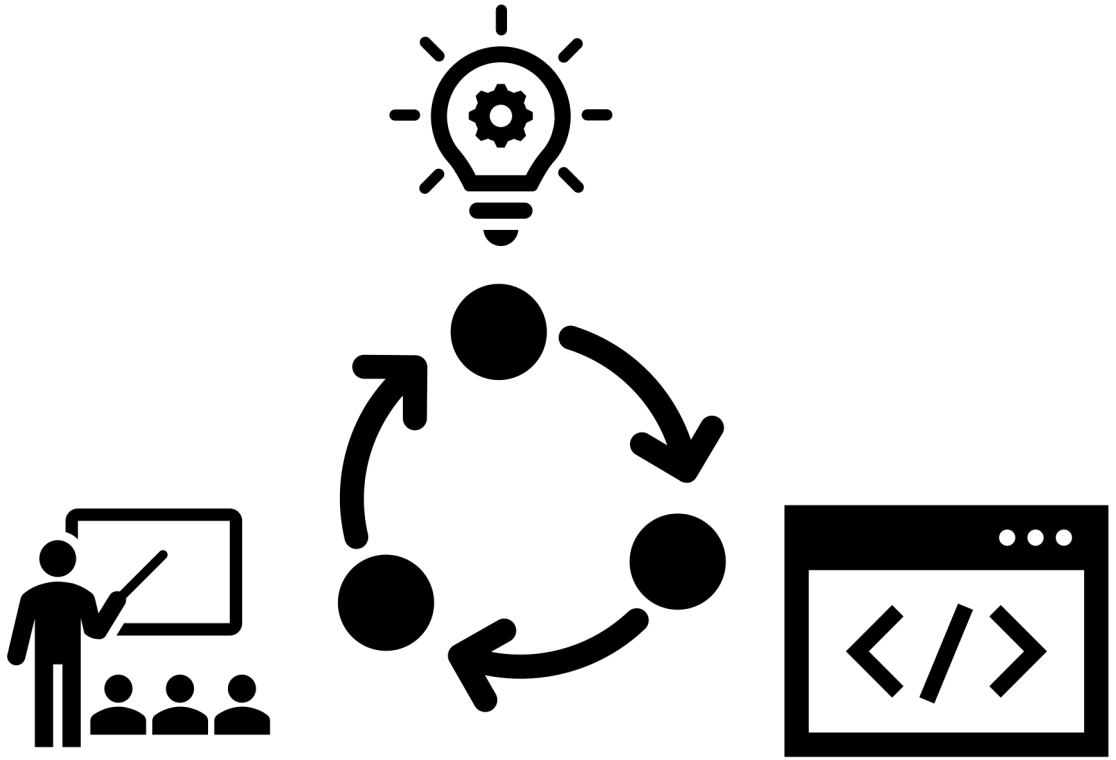
16 subjects rank top 1% globally. 11th in Mainland China.

Chemistry ranks top 1‰ globally (*ESI as of March 2019*).



Develop AI methods and concepts to break the limitations of traditional quantum chemistry

Educate and promote



Provide tools

XACS
Xiamen Atomistic Computing Suite
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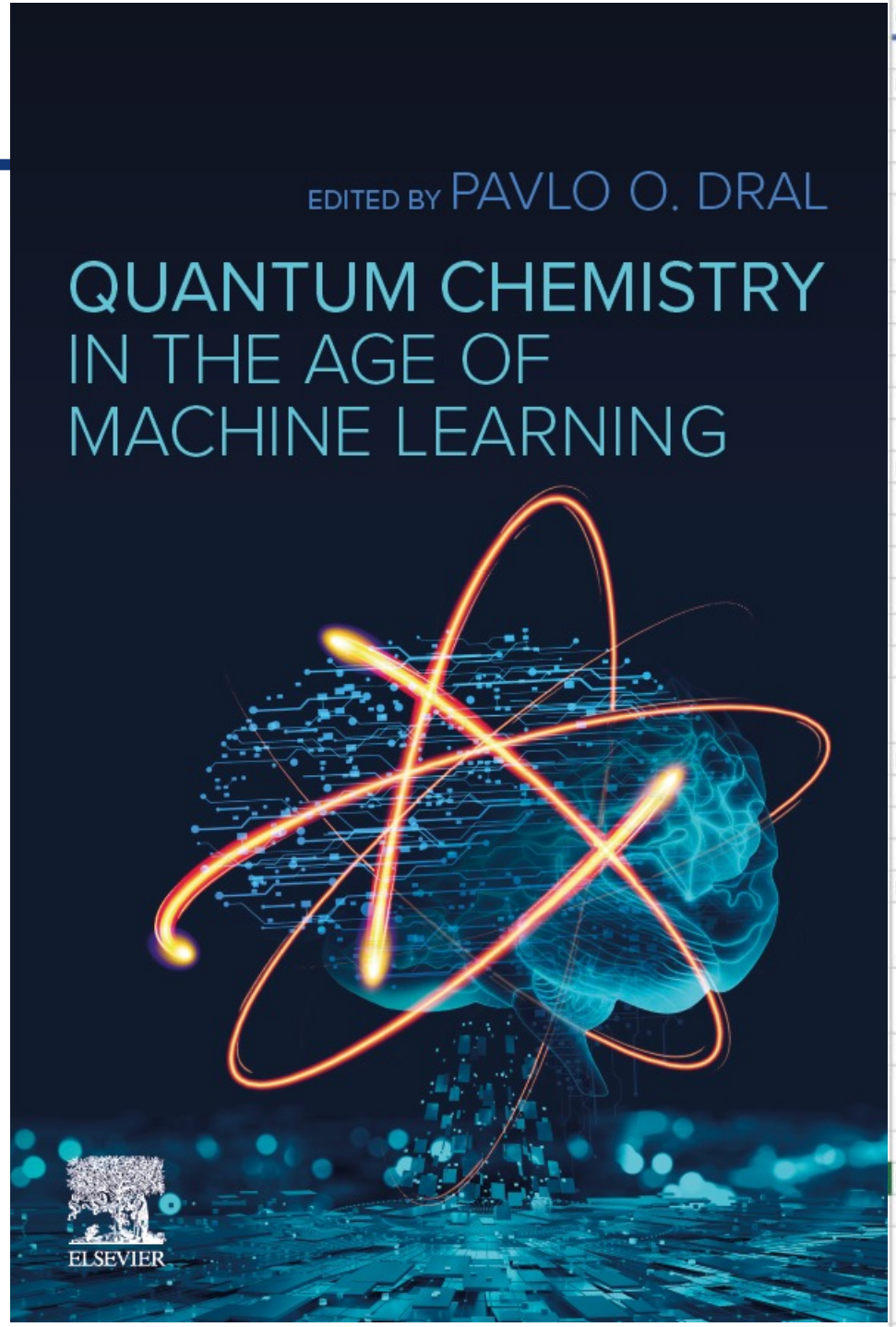


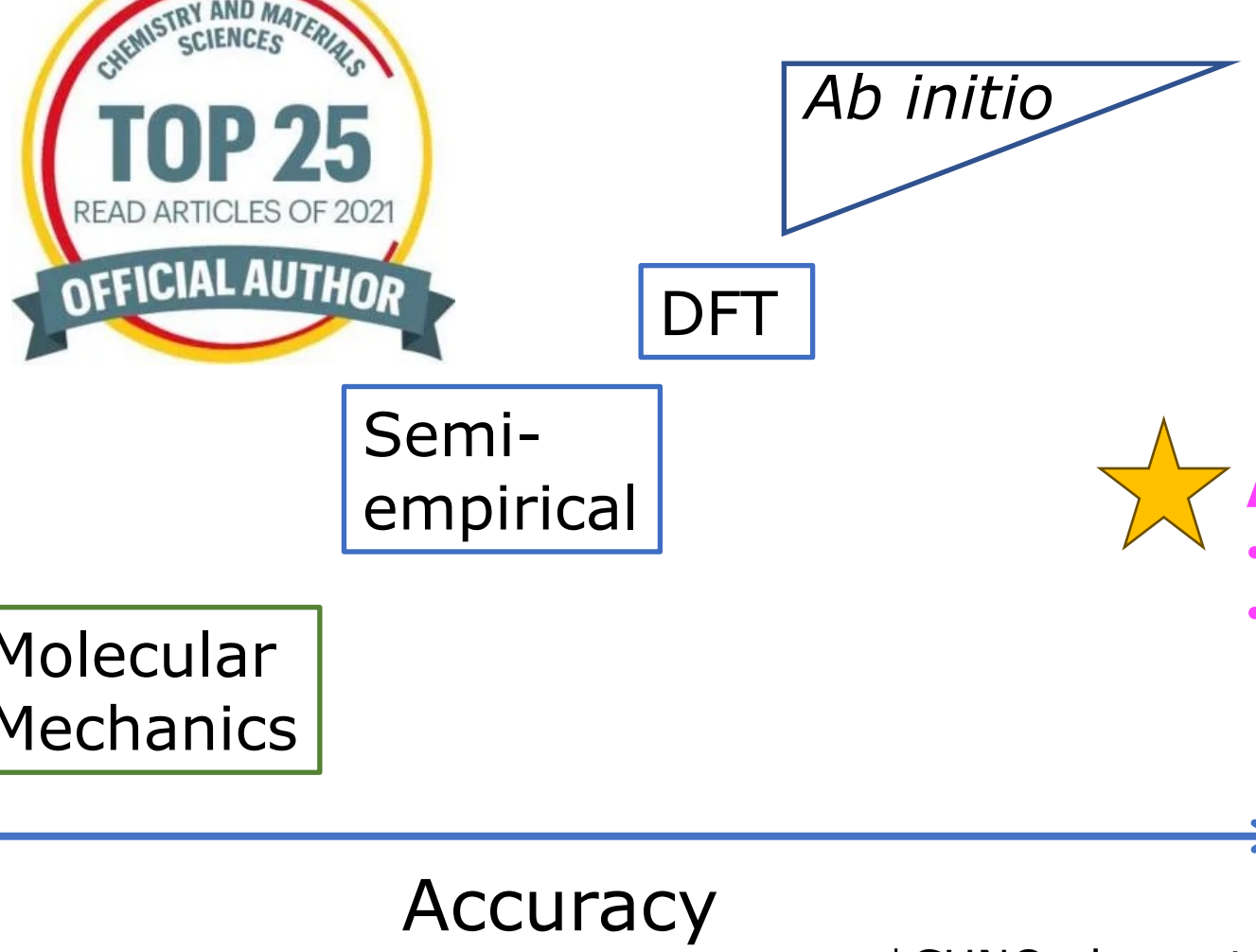
Chapter	Title
	Preface
Part 1	**Introduction**
1	Very brief introduction to quantum chemistry
2	Density functional theory
3	Semiempirical quantum mechanical methods
4	From small molecules to solid-state materials: A brief discourse on an example of carbon compounds
5	Basics of dynamics
6	Machine learning: An overview
7	Unsupervised learning
8	Neural networks
9	Kernel methods
10	Bayesian inference
Part 2	**Machine learning potentials**
11	Potentials based on linear models
12	Neural network potentials
13	Kernel method potentials
14	Constructing machine learning potentials with active learning
15	Excited-state dynamics with machine learning
16	Machine learning for vibrational spectroscopy
17	Molecular structure optimizations with Gaussian process regression
Part 3	**Machine learning of quantum chemical properties**
18	Learning electron densities
19	Learning dipole moments and polarizabilities
20	Learning excited-state properties
Part 4	**Machine learning-improved quantum chemical methods**
21	Learning from multiple quantum chemical methods: Δ-learning, transfer learning, co-kriging, and beyond
22	Data-driven acceleration of coupled-cluster and perturbation theory methods
23	Redesigning density functional theory with machine learning
24	Improving semiempirical quantum mechanical methods with machine learning
25	Machine learning wavefunction
Part 5	**Analysis of Big Data**
26	Analysis of nonadiabatic molecular dynamics trajectories
27	Design of organic materials with tailored optical properties: Predicting quantum-chemical polarizabilities and derived quantities

Published in September 2022

65 authors!

Exercises on GitHub

Quantum chemistry approximations



AIQM1*

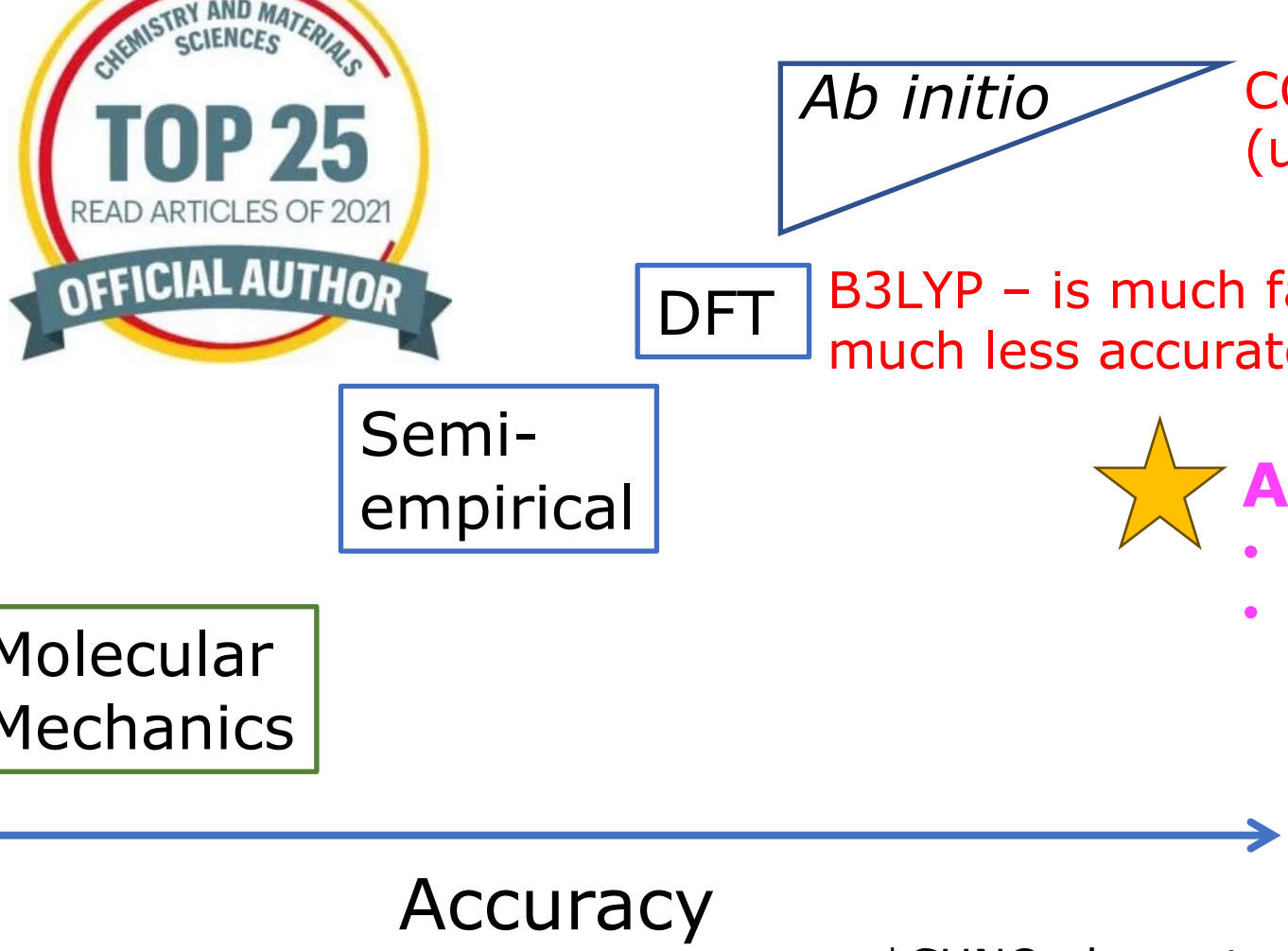
- **Accuracy of CCSD(T)**
- **Orders of magnitude faster than B3LYP**

AIQM1: P. Zheng, R. Zubatyuk, W. Wu, O. Isayev, P. O. Dral, *Nat. Commun.* **2021**, *12*, 7022

*CHNO elements only – extensions on the way

P. O. Dral, *J. Phys. Chem. Lett.* **2020**, *11*, 2336

Quantum chemistry approximations



CCSD(T) – gold standard, very slow (use it if you can!)

B3LYP – is much faster than the CCSD(T) but is much less accurate

Do not use B3LYP if you can use AIQM1!

AIQM1*

- **Accuracy of CCSD(T)**
- **Orders of magnitude faster than B3LYP**

AIQM1: P. Zheng, R. Zubatyuk, W. Wu, O. Isayev, P. O. Dral, *Nat. Commun.* **2021**, *12*, 7022

*CHNO elements only – extensions on the way

P. O. Dral, *J. Phys. Chem. Lett.* **2020**, *11*, 2336

Quantum chemistry approximations

Not so simple for excited states!

much less accurate

Semi-empirical

Molecular Mechanics

Timing

Accuracy

Do not use B3LYP if you can use AIQM1!

AIQM1*

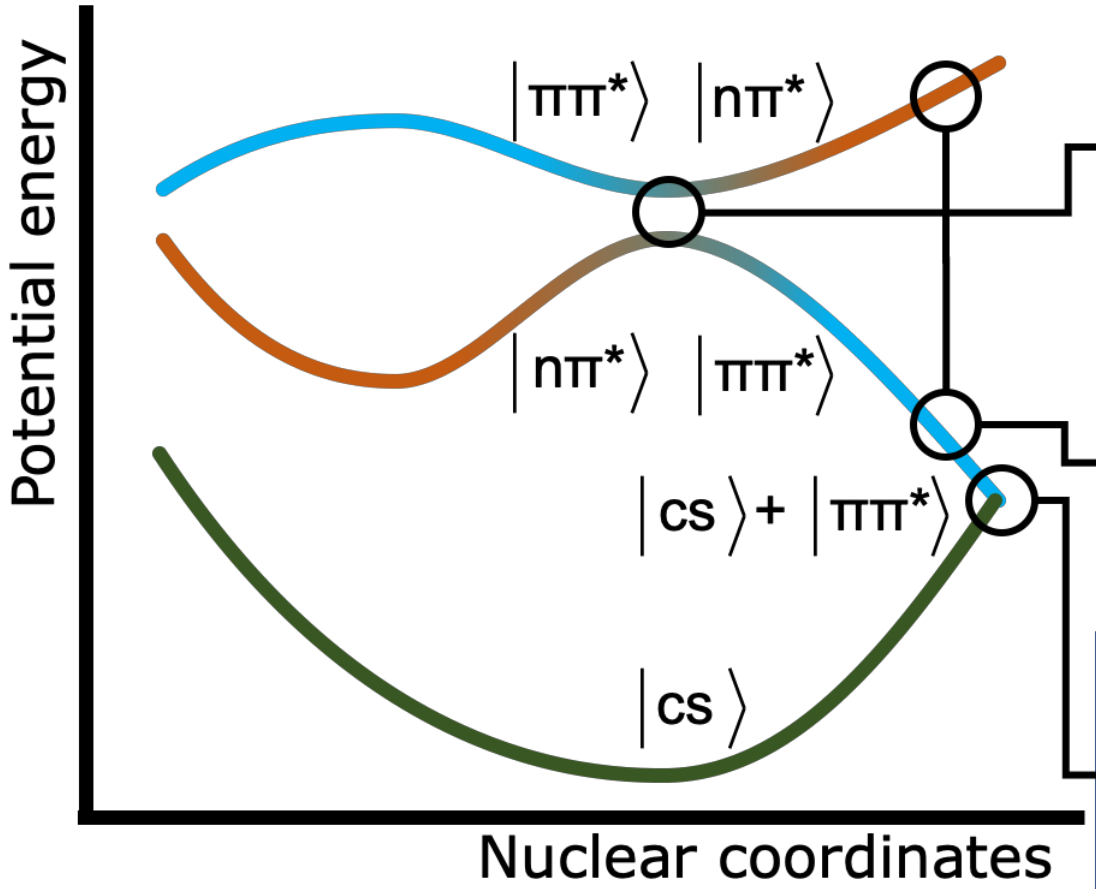
- **Accuracy of CCSD(T)**
- **Orders of magnitude faster than B3LYP**

AIQM1: P. Zheng, R. Zubatyuk, W. Wu, O. Isayev, P. O. Dral, *Nat. Commun.* **2021**, *12*, 7022

*CHNO elements only – extensions on the way

P. O. Dral, *J. Phys. Chem. Lett.* **2020**, *11*, 2336

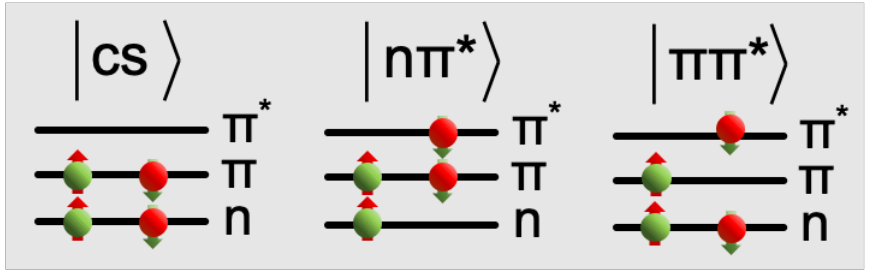
Why excited states are challenging



Small nuclear displacements change the wavefunction

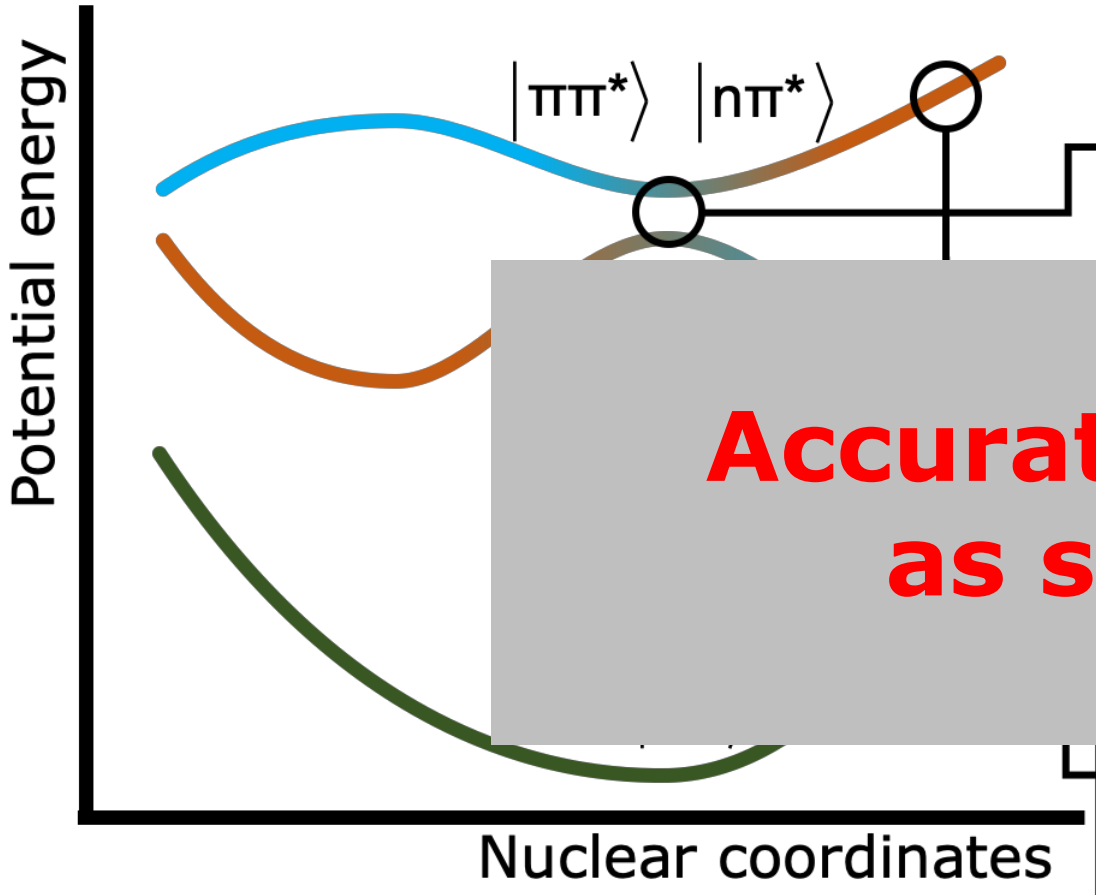
QM methods have different accuracy for different characters

Geometries with strong multireference character are challenging



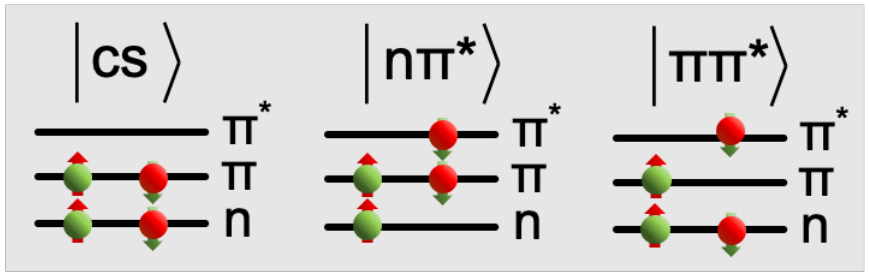
P. O. Dral, M. Barbatti, *Nat. Rev. Chem.* **2021,** *5*, 388

Why excited states are challenging



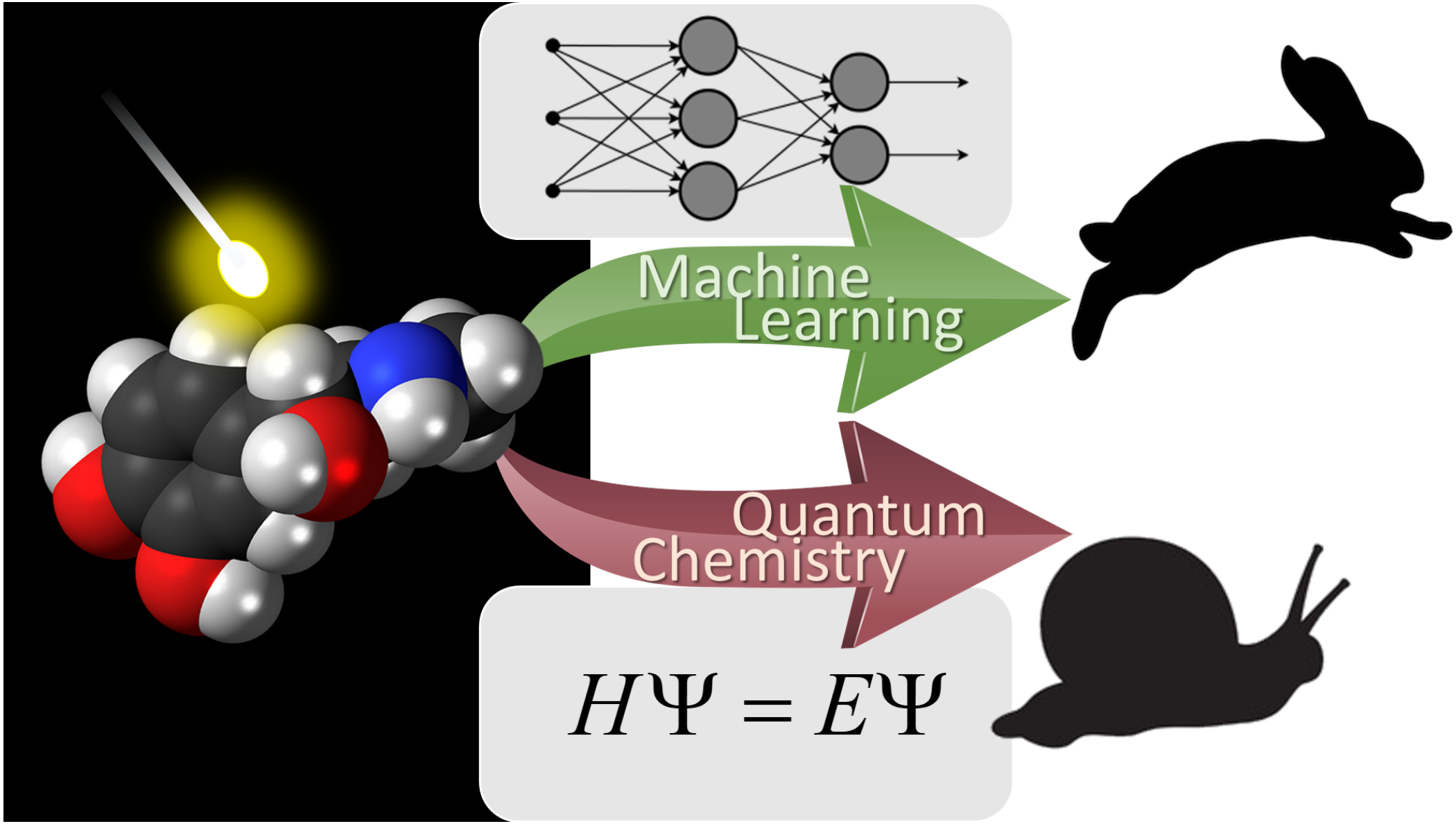
Small nuclear displacements change the wavefunction

Accurate simulations are as slow as a snail!



P. O. Dral, M. Barbatti, *Nat. Rev. Chem.* **2021,** *5*, 388

Why excited states are challenging



P. O. Dral, M. Barbatti, *Nat. Rev. Chem.* **2021,** *5*, 388

Quantum chemistry vs Machine learning

Conventional programming in quantum chemistry:

→ Code for molecular orbitals

→ Code for excitation energies

→ Code for oscillator strengths

→ …

Machine learning (in principle – adaptations required!):

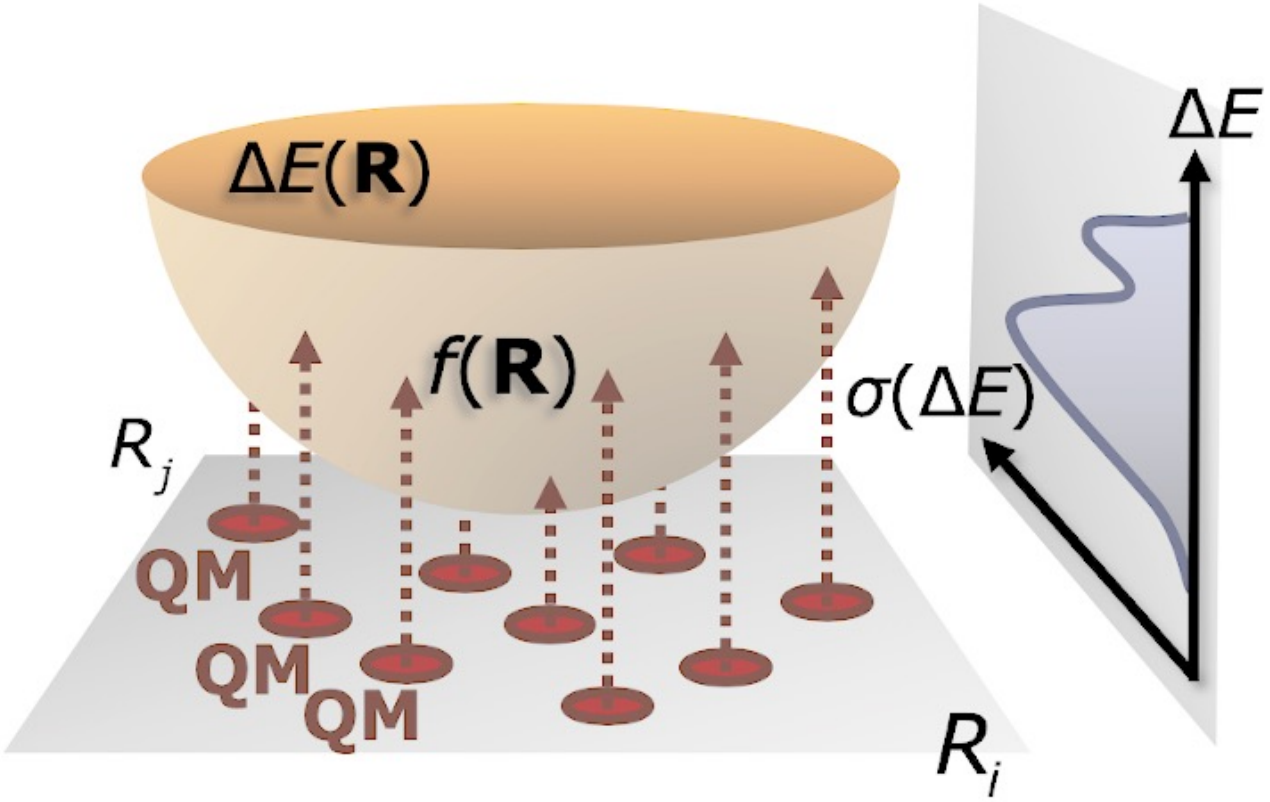
→ The same code for all above

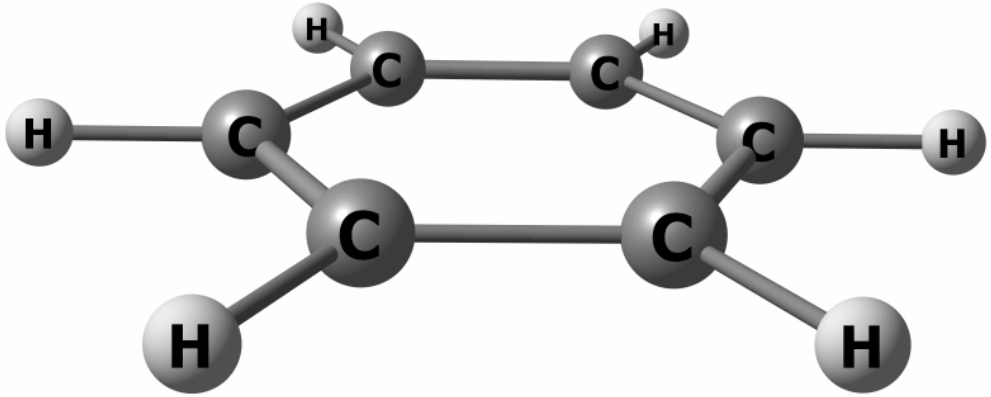
↑ MOs ↑ excitation energies ↑ Oscillator strength

Training data

ML-nuclear ensemble approach (ML-NEA)

N QM calculations are needed to simulate spectrum





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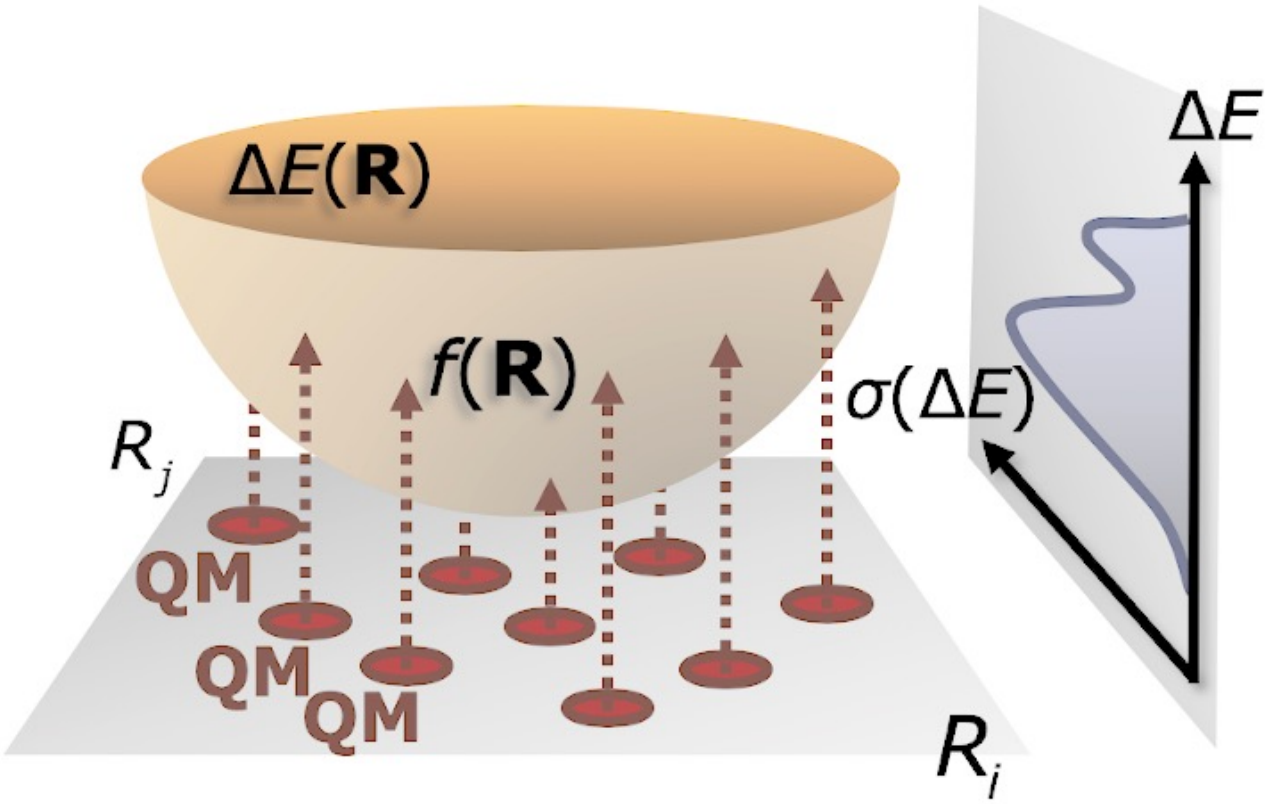
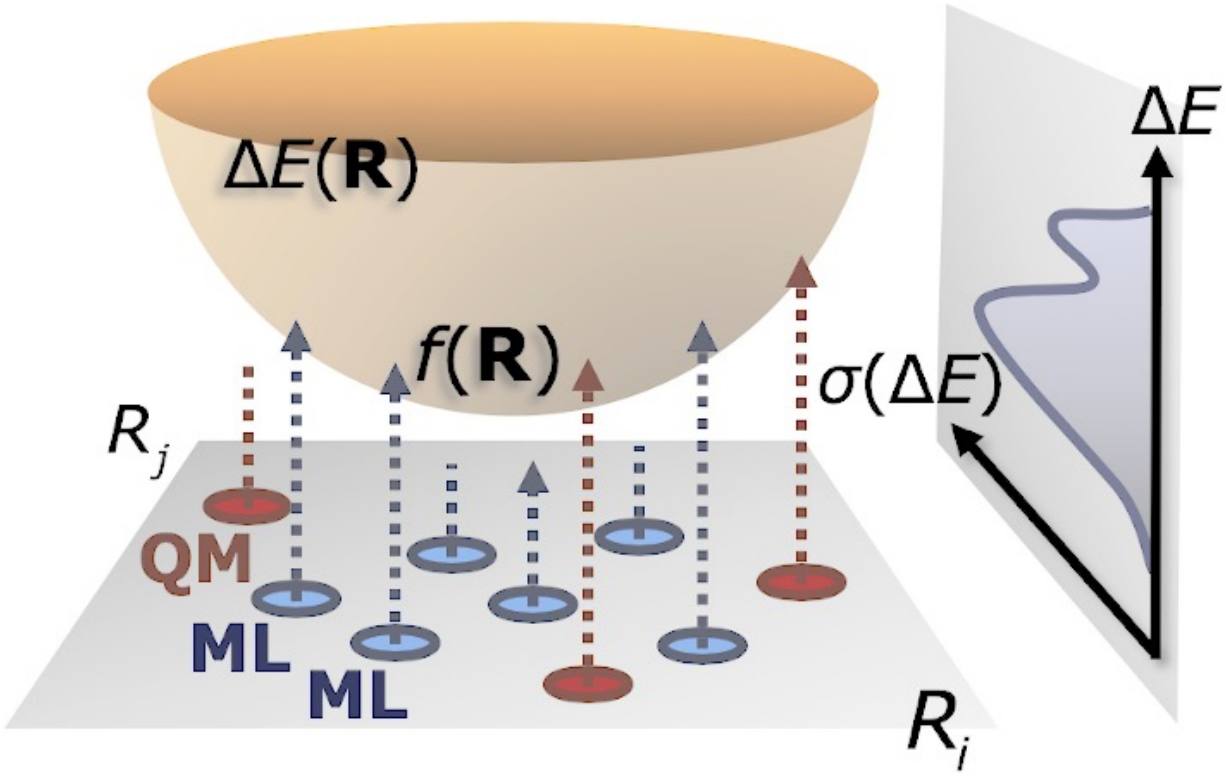
ML-nuclear ensemble approach (ML-NEA)

N QM calculations are needed to simulate spectrum



With ML, only *M* << *N* QM calculations are needed



P. O. Dral, M. Barbatti, *Nat. Rev. Chem.* **2021,** *5*, 388

ML-nuclear ensemble approach (ML-NEA)

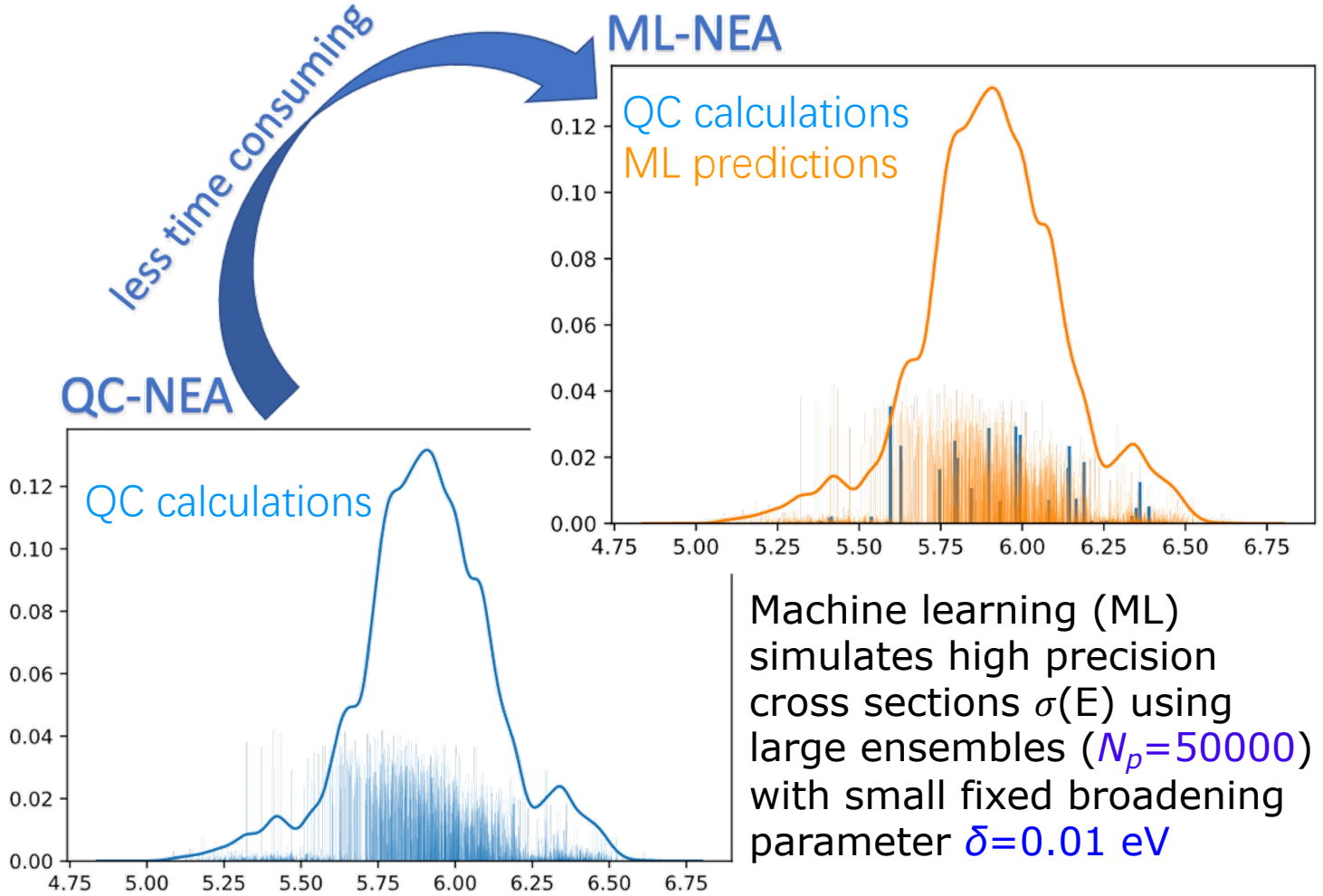
Learned properties:

- excitation energies

$$\Delta E_{0n}(\mathbf{x}_i)$$

- Oscillator strengths

$$f_{0n}(\mathbf{x}_i)$$



Machine learning (ML) simulates high precision cross sections σ(E) using large ensembles (N_p=50000) with small fixed broadening parameter δ=0.01 eV

$$\sigma(E) = \frac{\pi e^2 h}{2mc\varepsilon_0 E} \sum_n^{N_{fs}} \frac{1}{N_p} \sum_i^{N_p} \Delta E_{0n}(\mathbf{x}_i) f_{0n}(\mathbf{x}_i) \frac{1}{\sqrt{2\pi(\delta/2)^2}} \exp\left(-\frac{(E-\Delta E_{0n})^2}{2(\delta/2)^2}\right)$$

B.-X. Xue, P. O. Dral, M. Barbatti, *J. Phys. Chem. A* **2020**, *124*, 7199–7210

The KREG model

$$f(\mathbf{x}_i) = \sum_{j=1}^{N_{\text{tr}}} \alpha_j k(\mathbf{x}_i, \mathbf{x}_j)$$

$$k(\mathbf{x}_i, \mathbf{x}_j) = \exp\left(-\frac{1}{2\sigma^2}\sum_{s}^{N_x}(x_{i,s} - x_{j,s})^2\right)$$

the Gaussian kernel function
(σ is the kernel width)

$$x = \begin{pmatrix} \dots & \frac{R^{eq}}{R} & \dots \end{pmatrix}^T$$

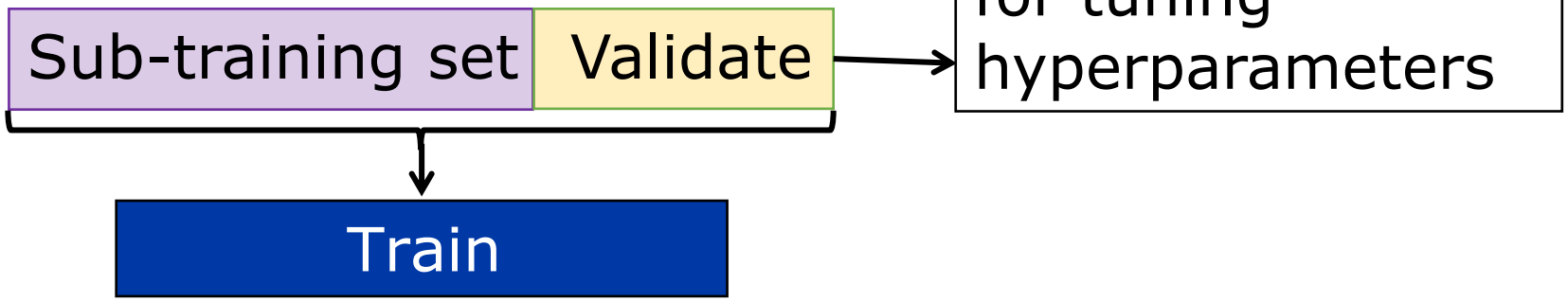
RE descriptor

Analytical solution for the regression coefficients α given N_{tr} training points

$$\begin{pmatrix} k(\mathbf{x}_1, \mathbf{x}_1) + \lambda & \cdots & k\left(\mathbf{x}_1, \mathbf{x}_{N_{\text{tr}}}\right) \\ \vdots & \ddots & \vdots \\ k\left(\mathbf{x}_{N_{\text{tr}}}, \mathbf{x}_1\right) & \cdots & k\left(\mathbf{x}_{N_{\text{tr}}}, \mathbf{x}_{N_{\text{tr}}}\right) + \lambda \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_{N_{\text{tr}}} \end{pmatrix} = \begin{pmatrix} y_1 \\ \vdots \\ y_{N_{\text{tr}}} \end{pmatrix}$$

λ is the regularization parameter ensuring transferability

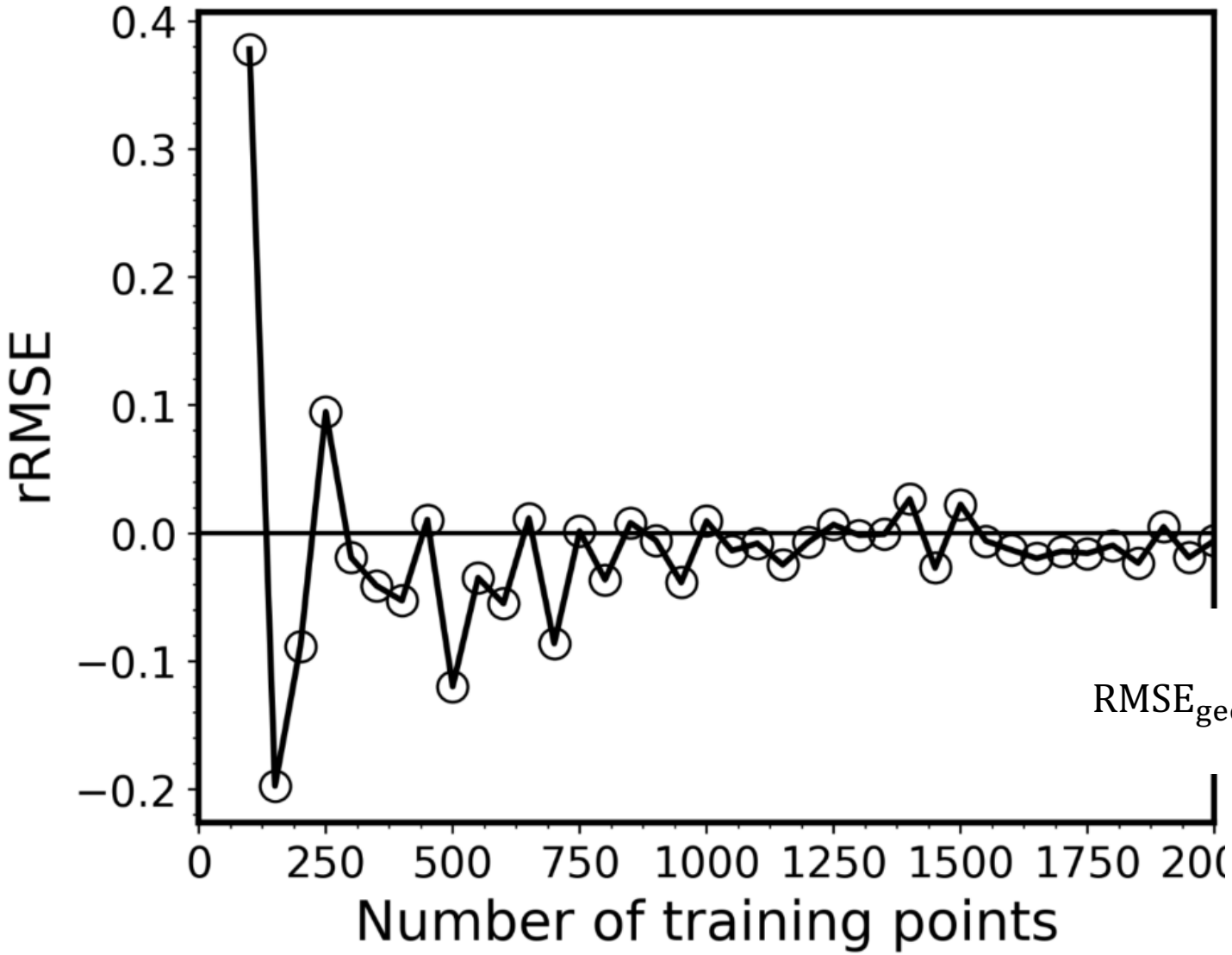
$$(\mathbf{K} + \lambda\mathbf{I})\boldsymbol{\alpha} = \mathbf{y}$$



The **KREG** model (**K**ernel ridge regression [KRR] with **RE** descriptor and the **G**aussian kernel function; RE descriptor stands for Internuclear distances **R**elative to **E**quilibrium) to complete all the ML tasks.

P. O. Dral, A. Owens, S. Yurchenko, W. Thiel, *J. Chem. Phys.* **2017**, *146*, 244108

Automatic selection of training points



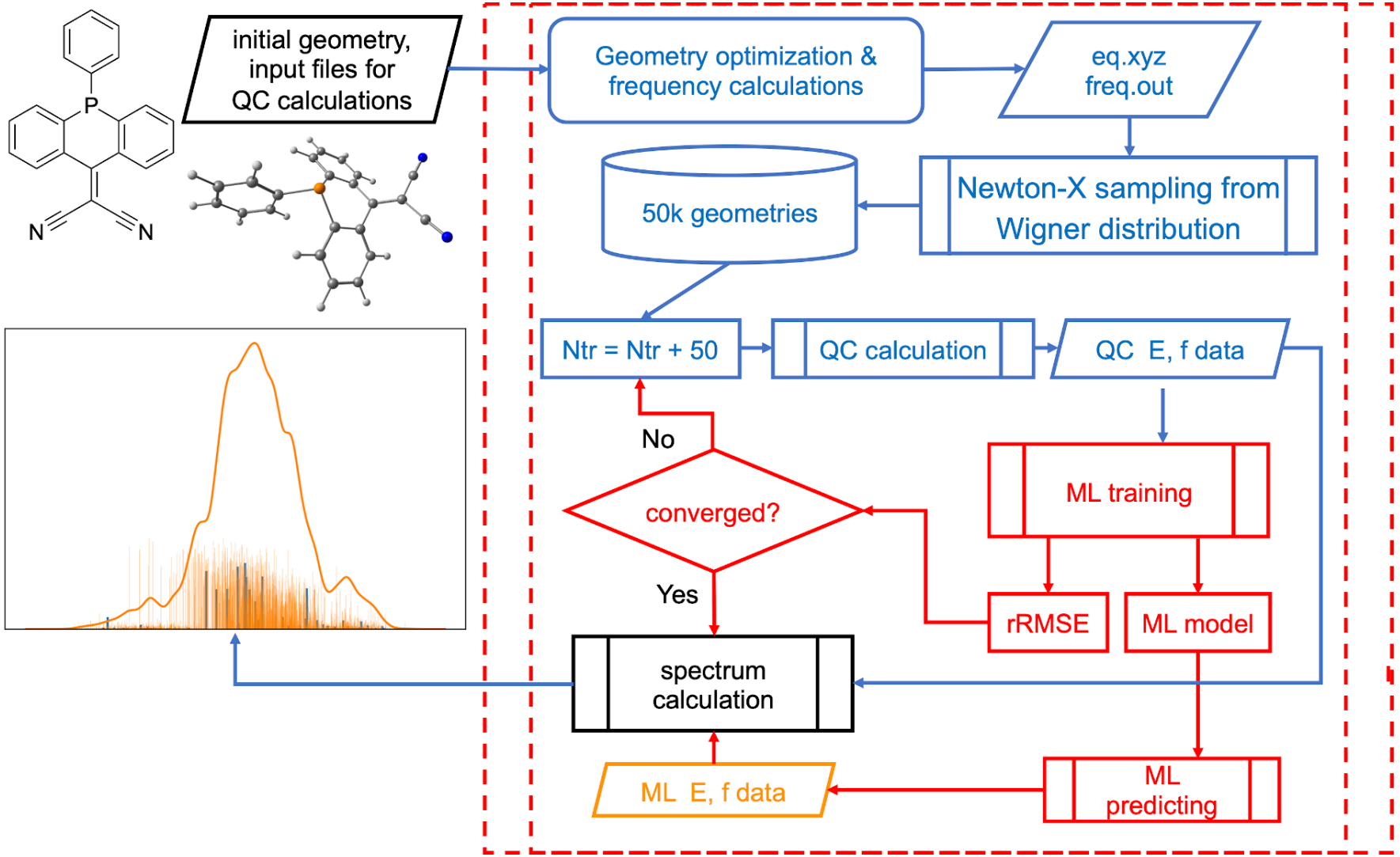
Optimal number of training points can be determined automatically using iterative procedure that stops after the relative change in ML validation errors drops below the threshold (typically rRMSE < 0.1).

$$\mathrm{rRMSE} = \frac{RMSE_{geom}(N_{tr}) - RMSE_{geom}(N_{tr} - N_{step})}{RMSE_{geom}(N_{tr})}$$

$$\mathrm{RMSE}_{\mathrm{geom}}(N_{tr}) = \sqrt[2N_s]{\prod_{i=1}^{N_s} \mathrm{RMSE}_{\Delta E_{0n}}(N_{tr}) \cdot \mathrm{RMSE}_{f_{0n}}(N_{tr})}$$

B.-X. Xue, P. O. Dral, M. Barbatti, *J. Phys. Chem. A* **2020**, *124*, 7199–7210

Machine learning single-photon absorption spectra

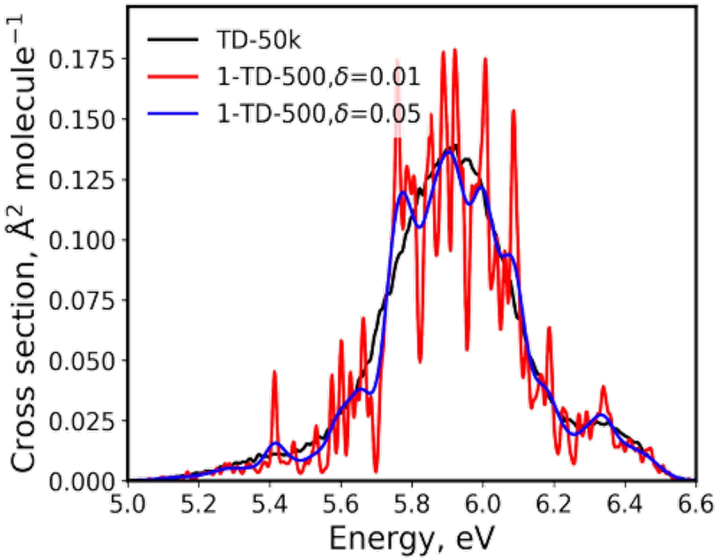


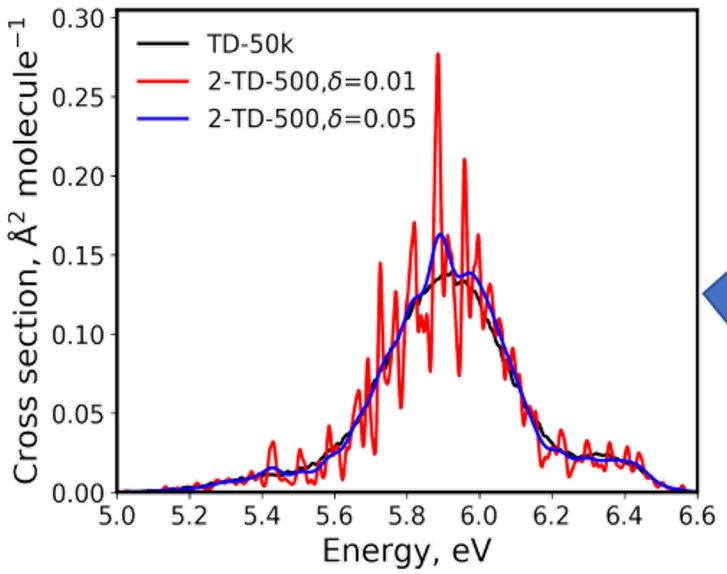
Mario Barbatti

Bao-Xin Xue

ML-NEA method: B.-X. Xue, P. O. Dral, M. Barbatti, *J. Phys. Chem. A* **2020**, *124*, 7199–7210
Implementation in MLatom: P. O. Dral, F. Ge, B.-X. Xue, Y.-F. Hou, M. Pinheiro Jr, J. Huang, M. Barbatti, *Top. Curr. Chem.*, ***2021***, *379*, 27

High-precision spectra of benzene

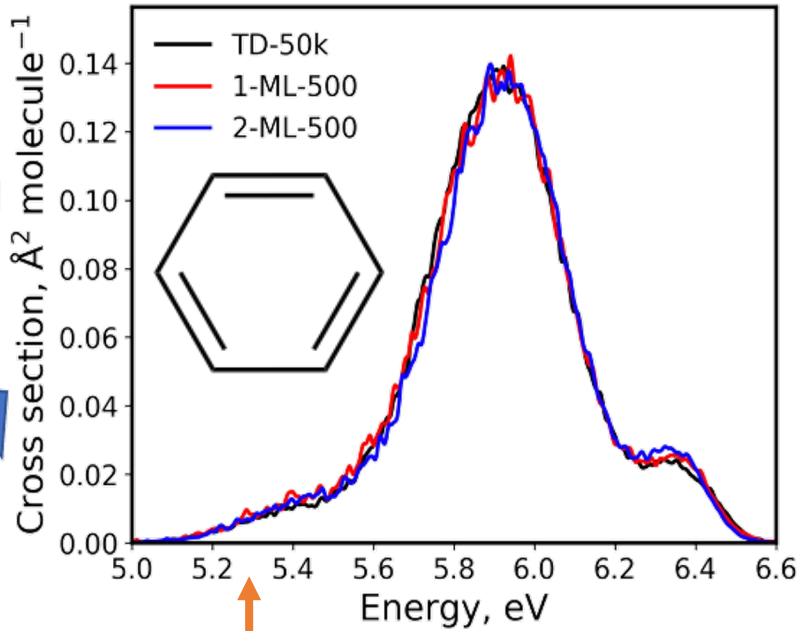




Two different mesium-sized ensembles of the same size (500 points) sampled from a Wigner distribution give very different spectra at QC level

train & predict

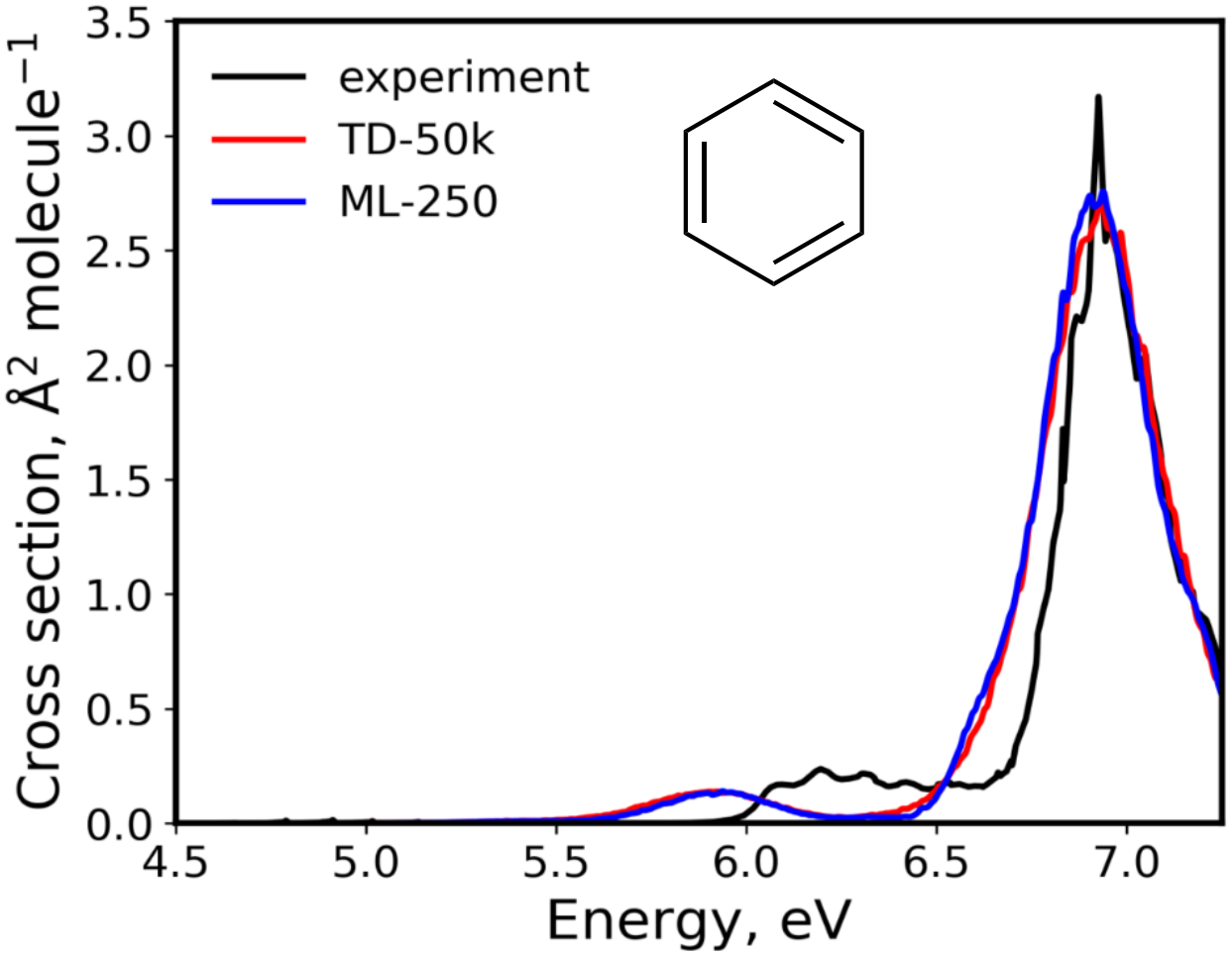
train & predict

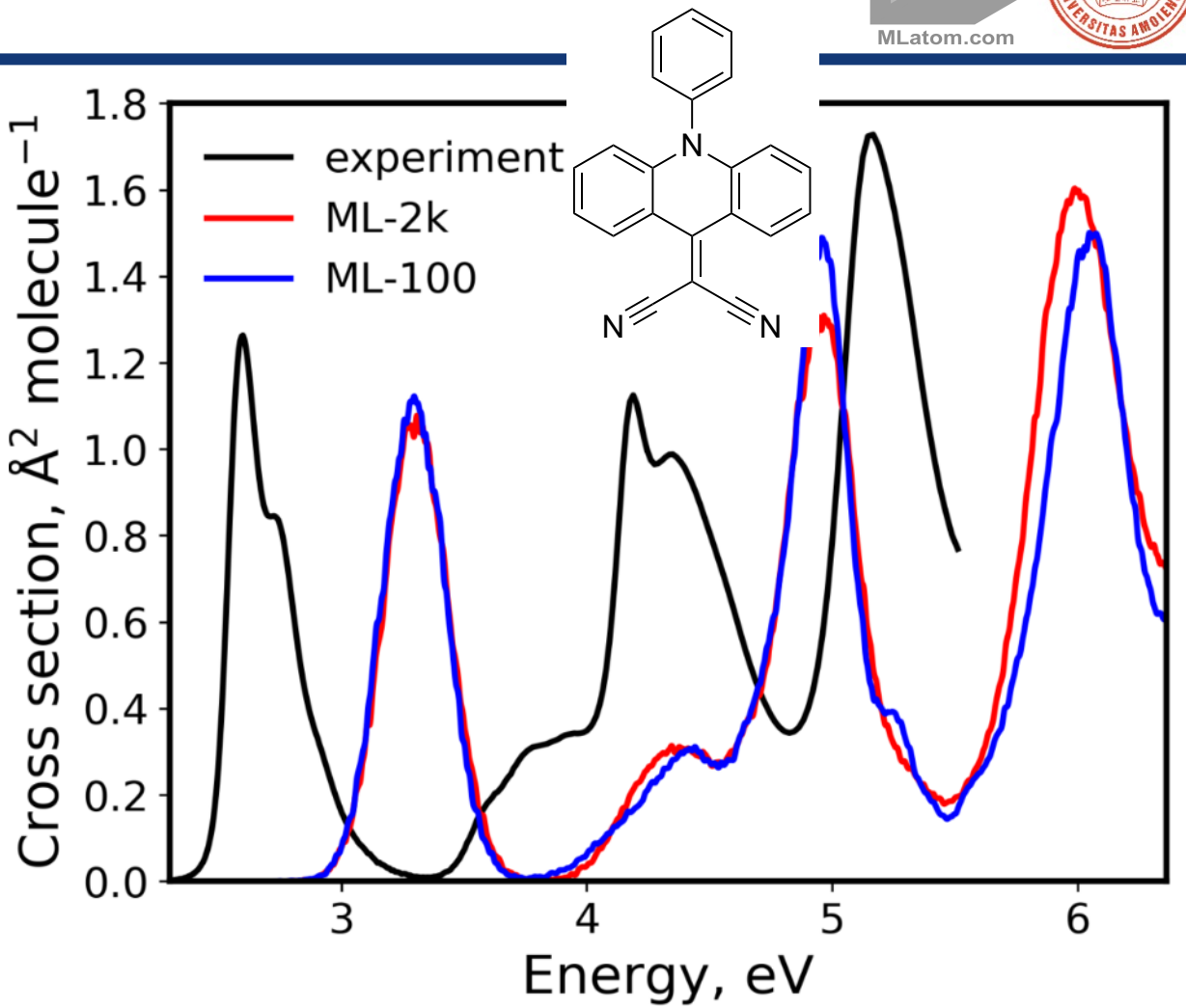


ML trained on both QC ensembles considerably improves precision of spectra that are very similar to each other

B.-X. Xue, P. O. Dral, M. Barbatti, *J. Phys. Chem. A* **2020**, *124*, 7199–7210

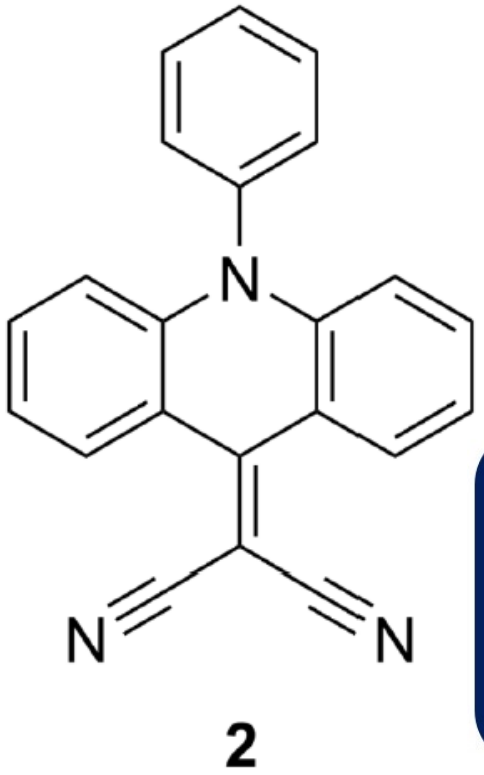
The error of ML vs reference QM is smaller than the error of QM vs experiment





B.-X. Xue, P. O. Dral, M. Barbatti, *J. Phys. Chem. A* **2020**, *124*, 7199–7210

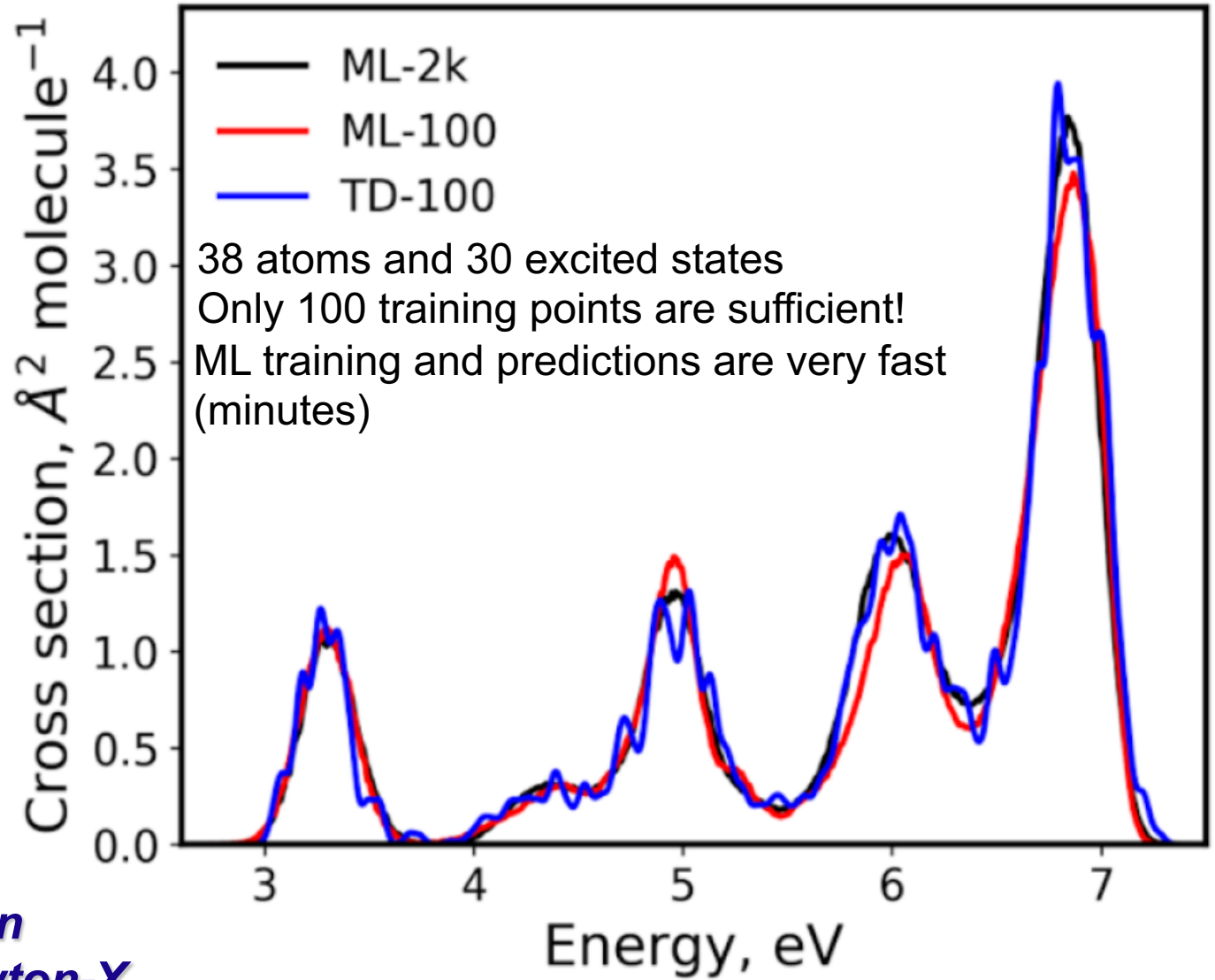
Black-box implementation into MLatom



2

MLatom.com

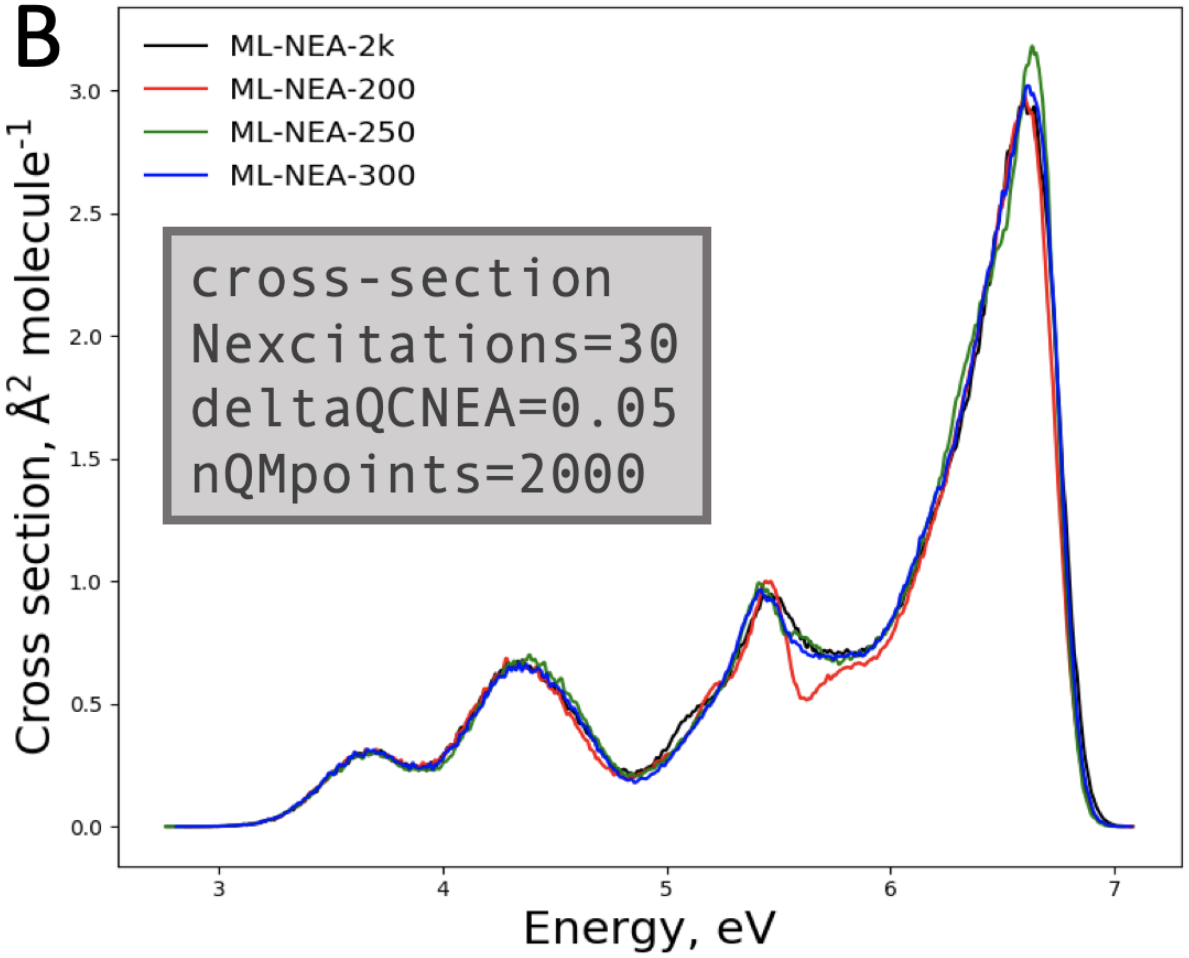
NX
newtonx.org

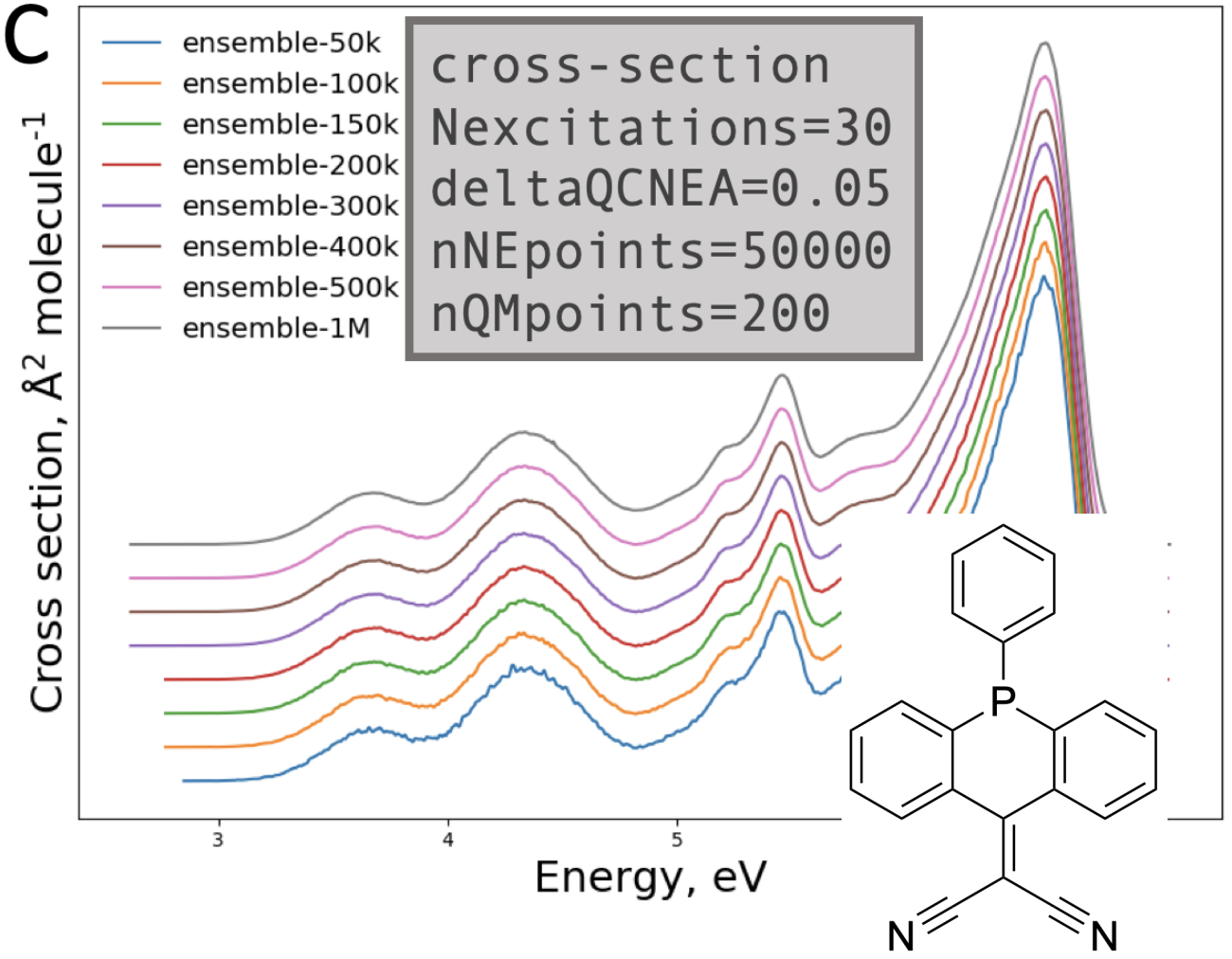


ML-NEA is available in MLatom interfaced to Newton-X

B.-X. Xue, P. O. Dral, M. Barbatti, *J. Phys. Chem. A* **2020**, *124*, 7199–7210

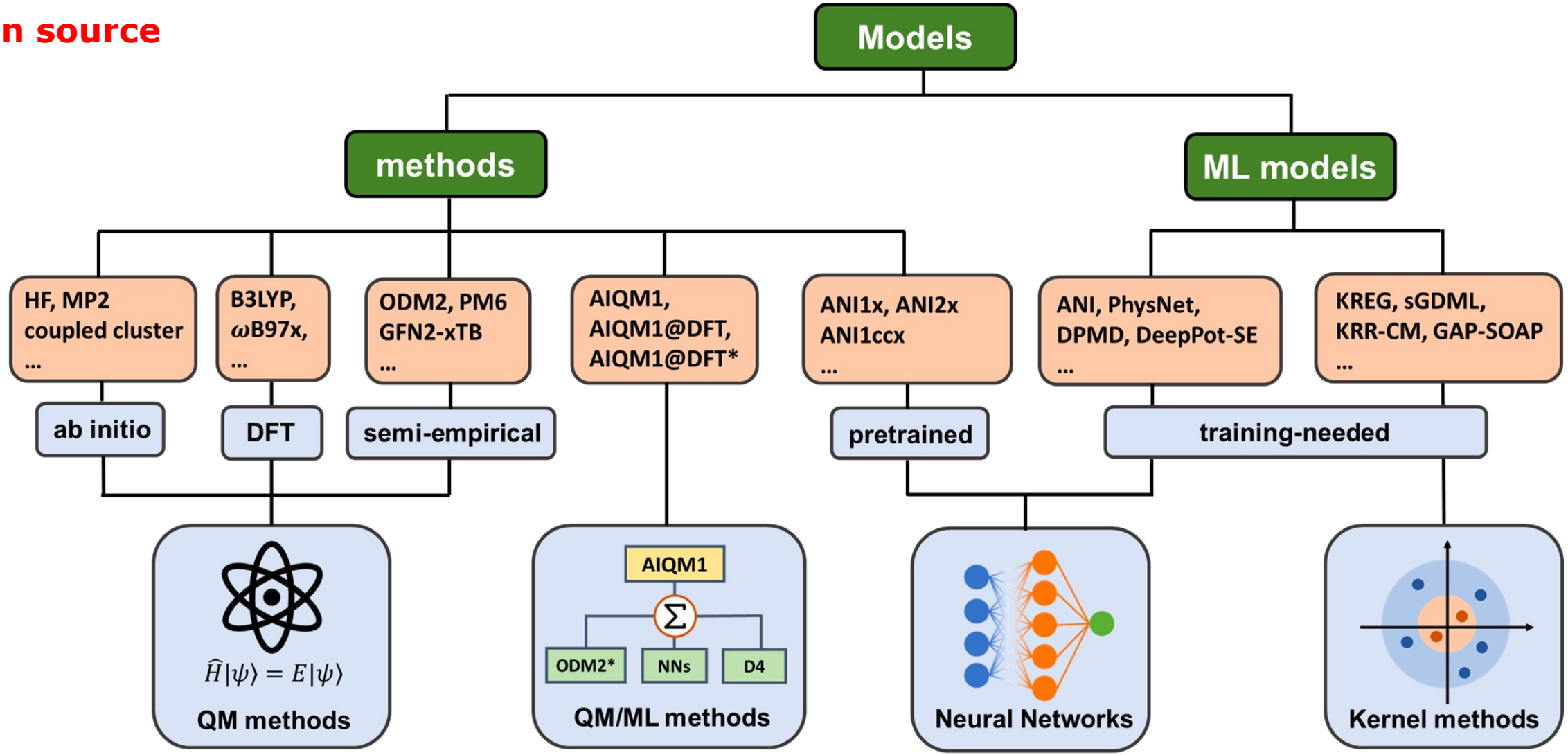
Black-box implementation into MLatom





MLatom: Program for AI-enhanced computational chemistry

Open source

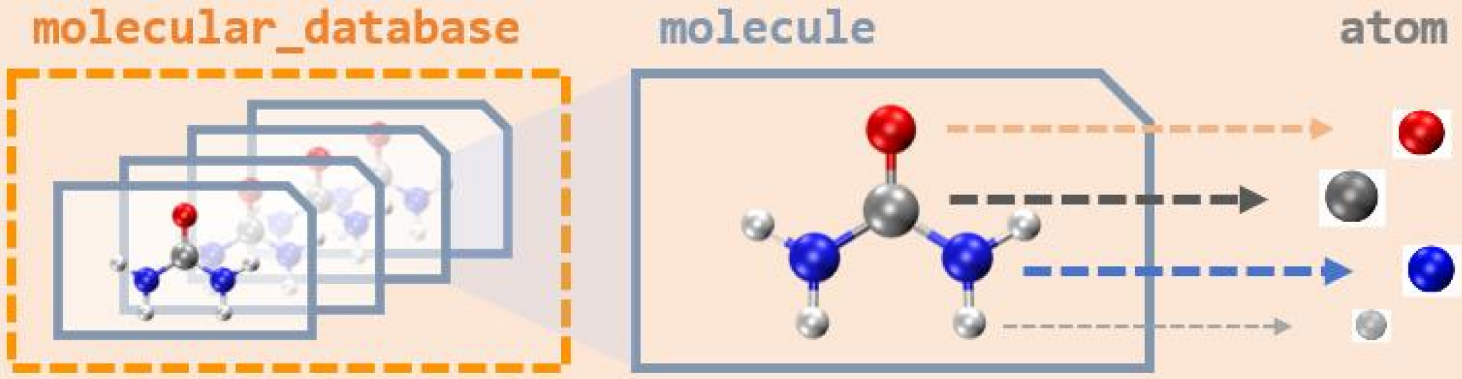


P. O. Dral, F. Ge, Y.-F. Hou, P. Zheng, Y. Chen, M. Barbatti, O. Isayev, C. Wang, B.-X. Xue, M. Pinheiro Jr, Y. Su, Y. Dai, Y. Chen, S. Zhang, L. Zhang, A. Ullah, Q. Zhang, Y. Ou. *J. Chem. Theory Comput.* **2024,** *20*, 1193

Open source

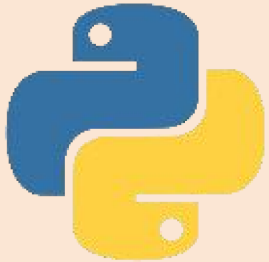
Implementation and use

- Data in different formats and types **V3**



- Python API **V3**

```
import mlatom as ml
```



- Input file

```
ANI-1ccx
geomopt
xyzfile=init.xyz
optxyz=opt.xyz
```

- Command line

```
> $mlatom ANI-1ccx geomopt xyzfile=init.xyz optxyz=opt.xyz
```

* 'V3' marks implementations released in MLatom 3

Extras!

MLQD

A Package for Quantum Dissipative Dynamics with Machine Learning
by Arif Ullah, Anhui University

[MLQD: A. Ullah, P. O. Dral. *Comput. Phys. Commun*. **2024**, *294*, 108940]

Quantum chemical programs:

Gaussian
GAMESS
ORCA
PySCF

Interfaces

Semi-empirical quantum chemical programs:

xTB
SPARROW
MNDO

Machine learning programs:

PhysNet
GAP
TORCHANI
SCANML
hyperopt

Dynamics and other atomistic simulation:

ASE
NX newtonx.org

XACS

Xiamen Atomistic Computing Suite

XMVB **XEDA** **MLatom**

Cloud computing (free!)

XACScloud.com

- *Ab initio* valence bond calculations (**VBSCF**, **VBCI**, **BOVB**, …)
- Generalized Kohn–Sham energy decomposition analysis (**GKS-EDA**)
- Artificial intelligence-enhanced quantum mechanical method 1 (**AIQM1**, faster and more accurate than B3LYP)
- Fast geometry optimization, MD, thermochemistry
- … and much more

Principal investigators (Xiamen University)

- Wei Wu
- Peifeng Su
- Pavlo O. Dral

Partners

- Mario Barbatti, Aix Marseille University
- Benoît Braïda, Sorbonne Université
- Philippe Hiberty, University of Paris-Saclay
- Olexandr Isayev, Carnegie Mellon University
- Yirong Mo, UNC Greensboro
- Sason Shaik, Hebrew University
- Avital Shurki, Hebrew University
- Cheng Wang, Xiamen University

Interfaces

TORCHANI SPARROW

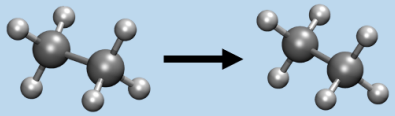
ASE hyperopt

MLatom: Program for AI-enhanced computational chemistry

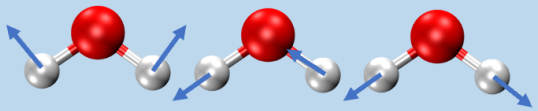
Open source

Single point calculations — Energies, forces, Hessian matrix...

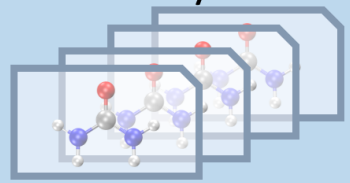
Geometry optimizations



Frequency calculations



Molecular dynamics

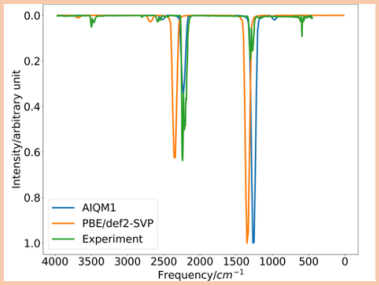


Thermochemistry calculations

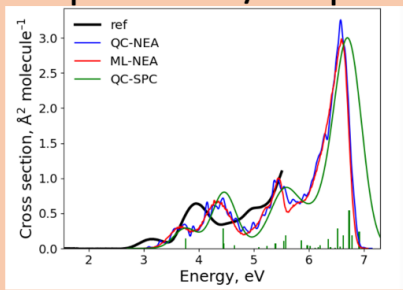
Heat of formation:

$$\Delta H_{\mathrm{at},T} = \left[\sum_A H_T(A)\right] - H_T$$

(Ro)vibrational spectra



One-photon UV/vis spectra



Simulations

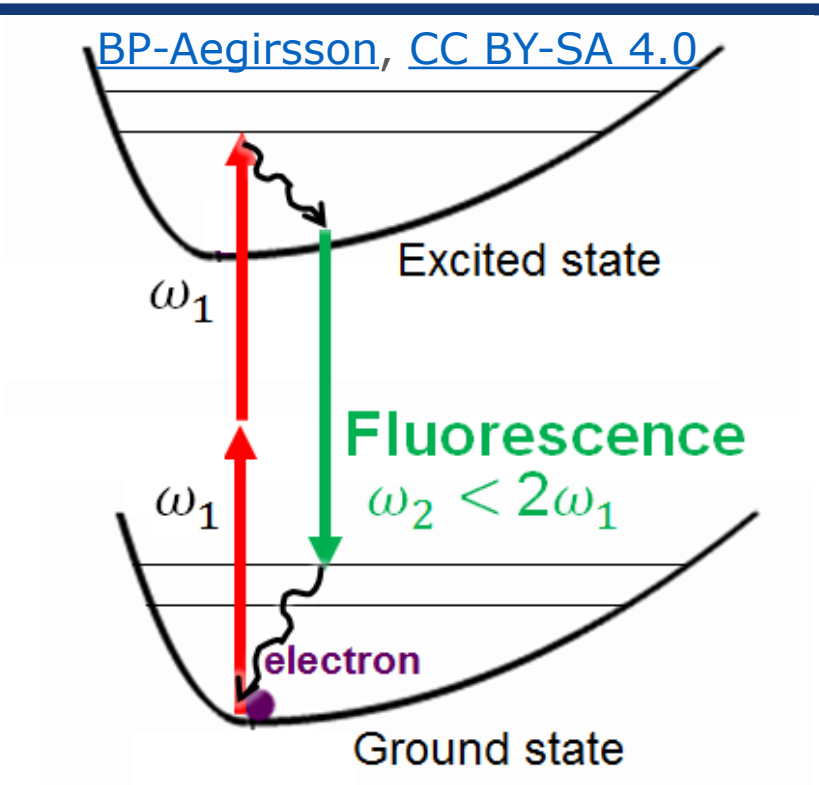
Properties & spectra

Quantum dissipative dynamics

Two-photon absorption spectra

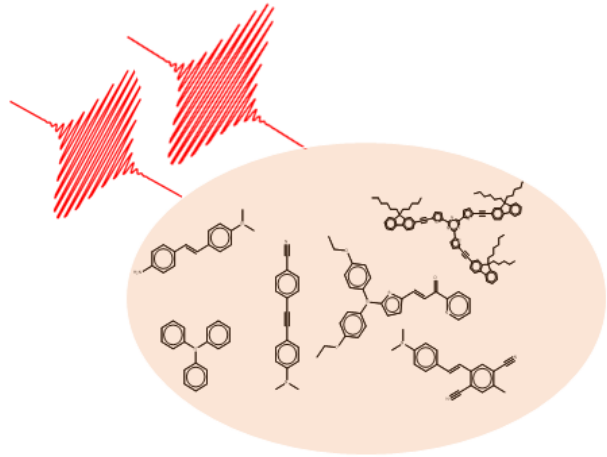
P. O. Dral, F. Ge, Y.-F. Hou, P. Zheng, Y. Chen, M. Barbatti, O. Isayev, C. Wang, B.-X. Xue, M. Pinheiro Jr, Y. Su, Y. Dai, Y. Chen, S. Zhang, L. Zhang, A. Ullah, Q. Zhang, Y. Ou. *J. Chem. Theory Comput.* **2024,** *20*, 1193

ML two-photon absorption



Here we show how to calculate TPA cross section for RHODAMINE 6G and RHODAMINE 123 molecules with MLatom input file `mltpa.inp`:

```
MLTPA
SMILESfile=Smiles.csv
auxfile=_aux.txt
```



This input requires `Smiles.csv` file with SMILES of molecules:

```
CCNC1=CC2=C(C=C1C)C(=C3C=C(C(=[NH+]CC)C=C302)C)C4=CC=CC=C4C(=O)OCC.[Cl-]
COC(=O)C1=CC=CC=C1C2=C3C=CC(=N)C=C30C4=C2C=CC(=C4)N.Cl
```

Two-photon absorption applications:

- two-photon lithography
- Photodynamic therapy
- Bioimaging
- 3D printing
- Upconverted laser

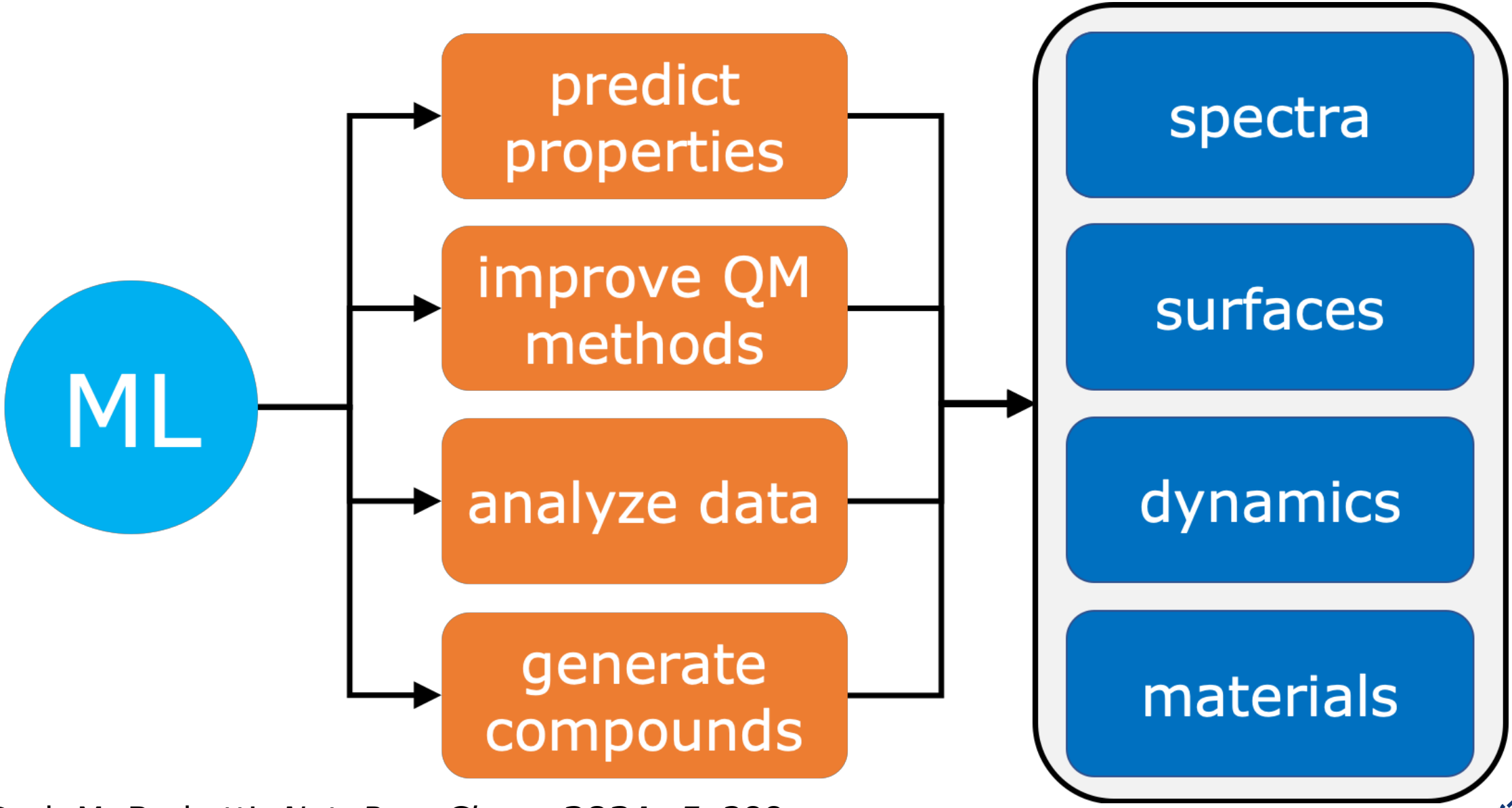
Yuming Su

Zhou Da

Cheng Wang

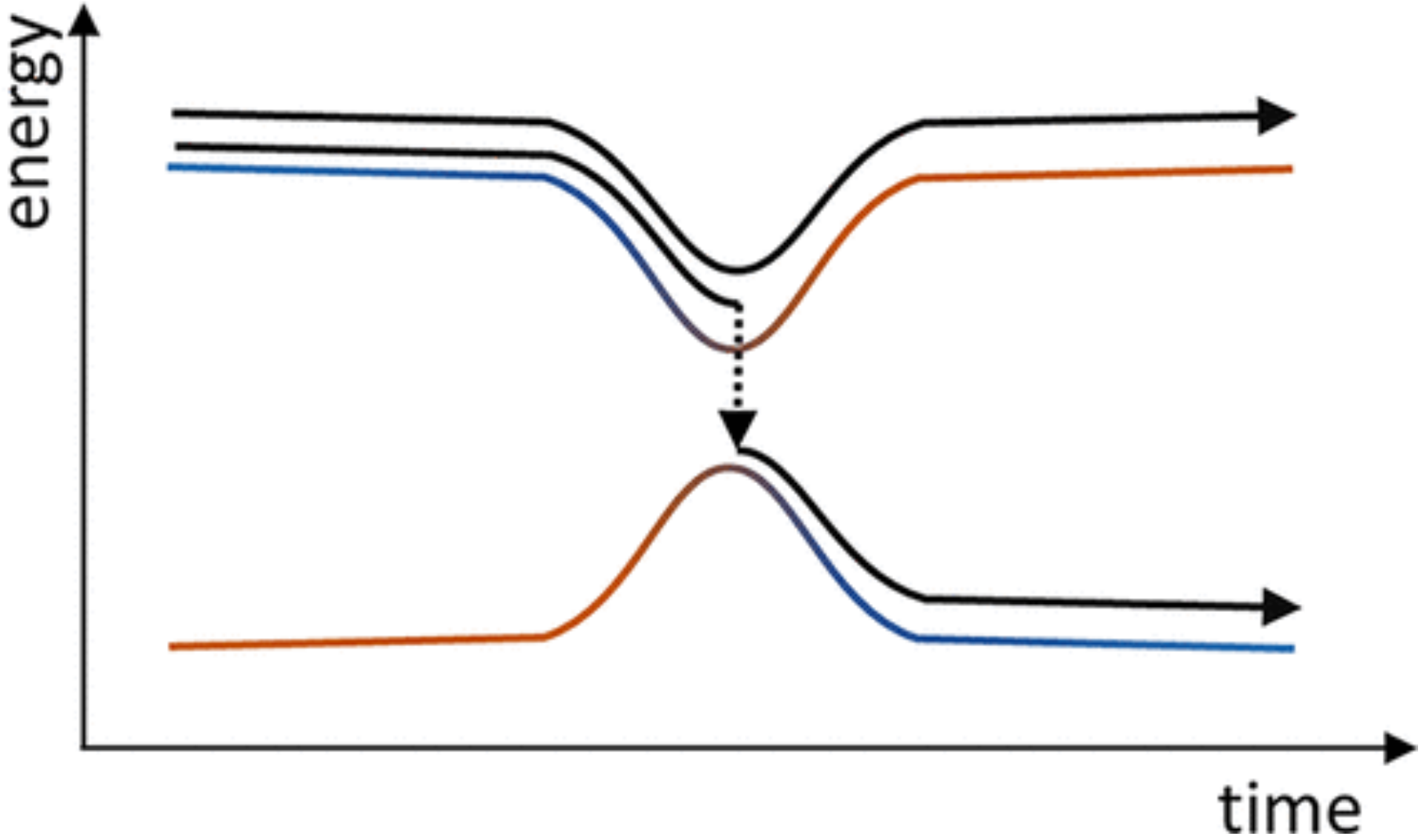
Y. Su, Y. Dai, Y. Zeng, …, P. Zheng, D. Zhou, P. O. Dral, C. Wang. *Adv. Sci.* **2023**, 2204902

Machine learning in chemistry



P. O. Dral, M. Barbatti, *Nat. Rev. Chem.* **2021,** *5*, 388

Surface Hopping



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

Cost of Dynamics

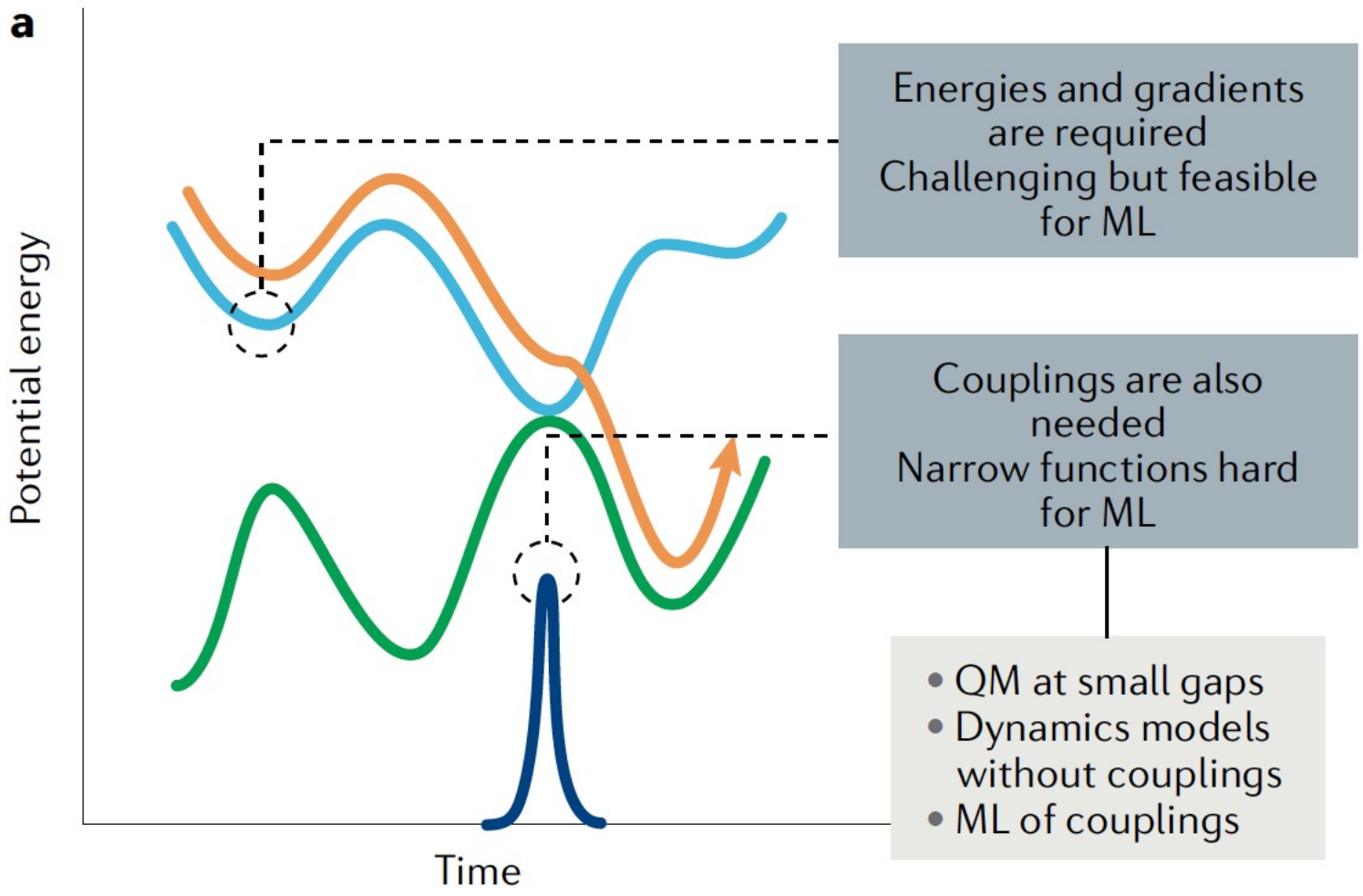
Typical nonadiabatic excited-state simulations:

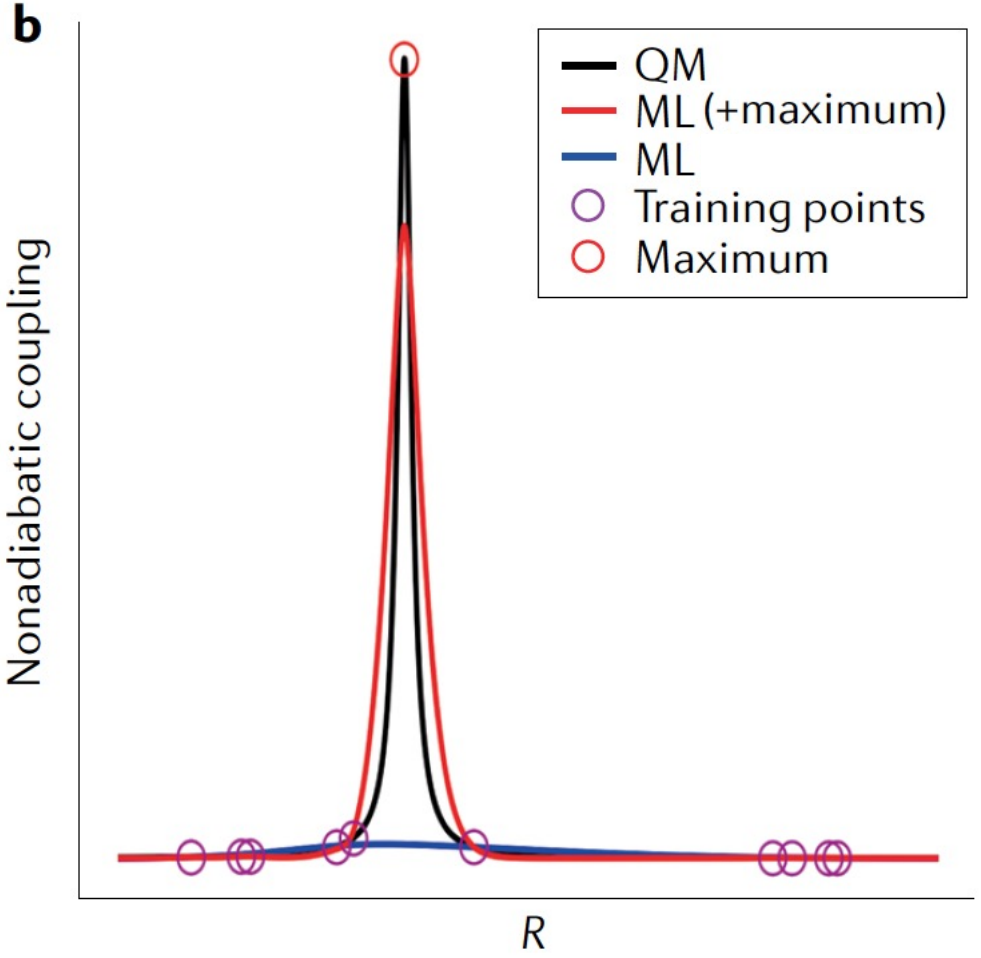
- 100 trajectories
- for 1 ps = 1000 fs
- 0.5 fs time step

Number of QM calculations:

- 2000 per trajectory
- 200 000 in total

Why ML-TSH is challenging





+ phase problem

P. O. Dral, M. Barbatti, *Nat. Rev. Chem.* **2021,** *5*, 388

Adiabatic Spin-Boson Hamiltonian

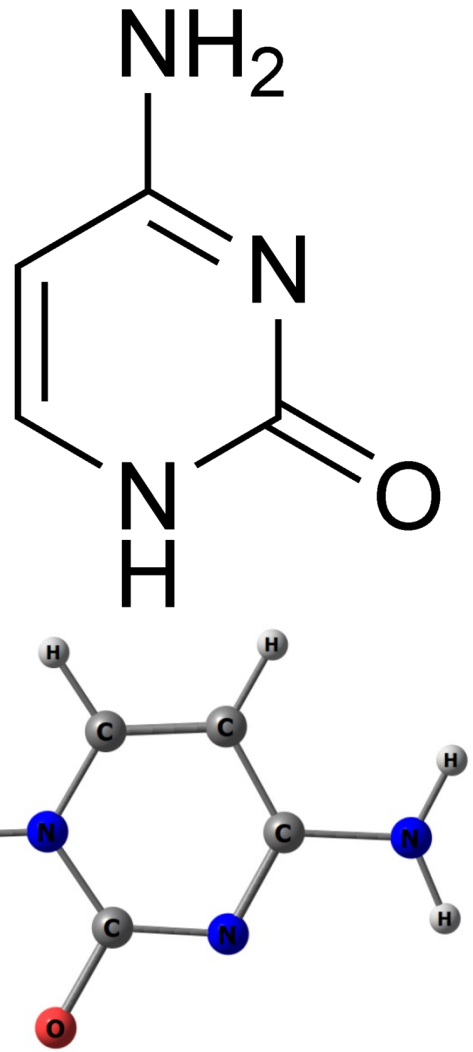
33-D A-SBH inspired by cytosine

$$H = H_s + H_b + H_{sb}$$

$$V_J = \frac{1}{2}\sum_{k=1}^{N} M_k \omega_k^2 R_k^2 + (-1)^J \left[\eta^2 + v_0^2\right]^{1/2}, \quad (J = 1, 2)$$

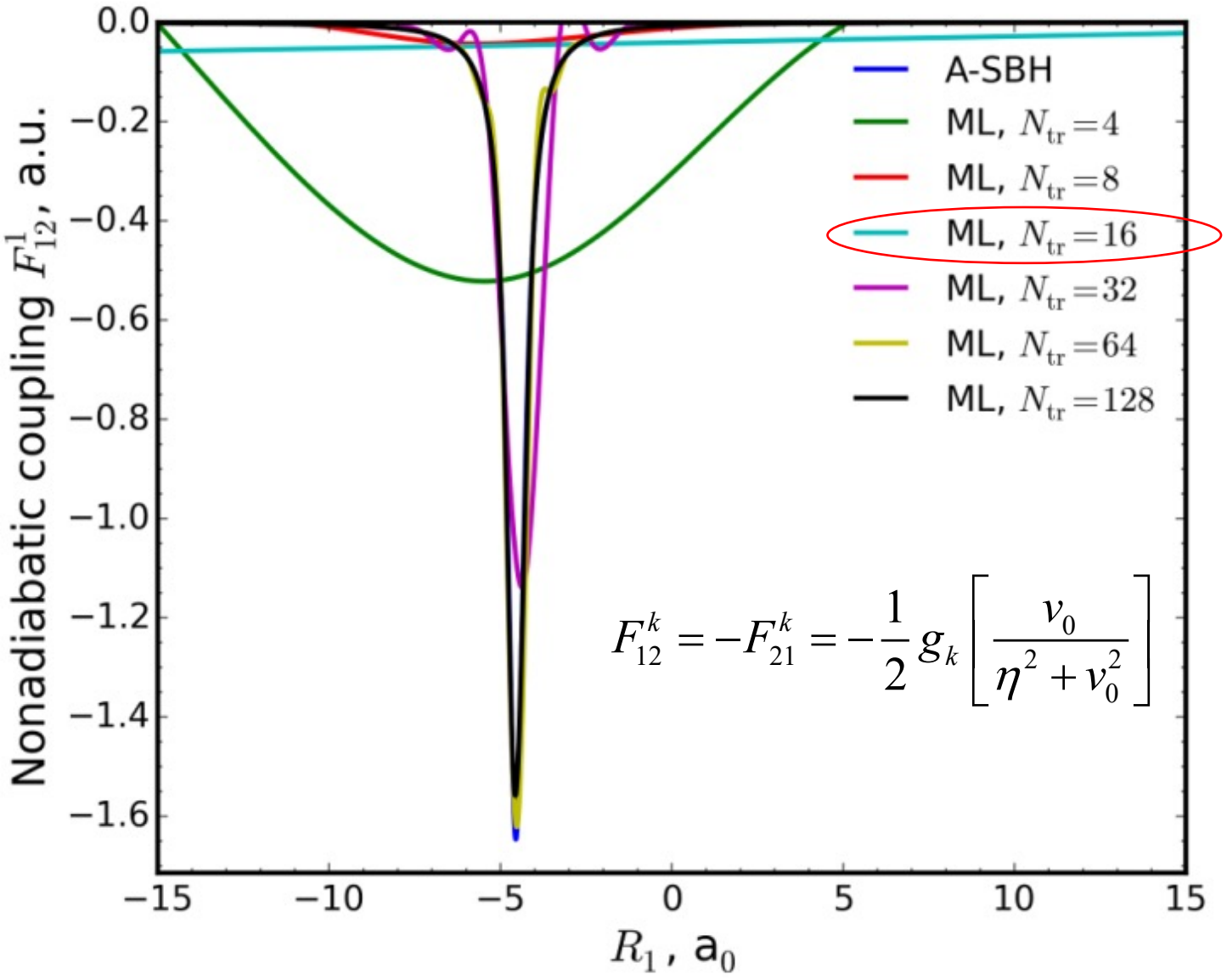
$$\frac{\partial V_J}{\partial R_k} = M_k \omega_k^2 R_k + (-1)^J g_k \left[\frac{\eta}{\left[\eta^2 + v_0^2\right]^{1/2}}\right]$$

$$\eta = \left(\sum_{k=1}^{N} g_k R_k + \varepsilon_0\right)$$



P. O. Dral, M. Barbatti, W. Thiel, *J. Phys. Chem. Lett.* **2018**, *9*, 5660

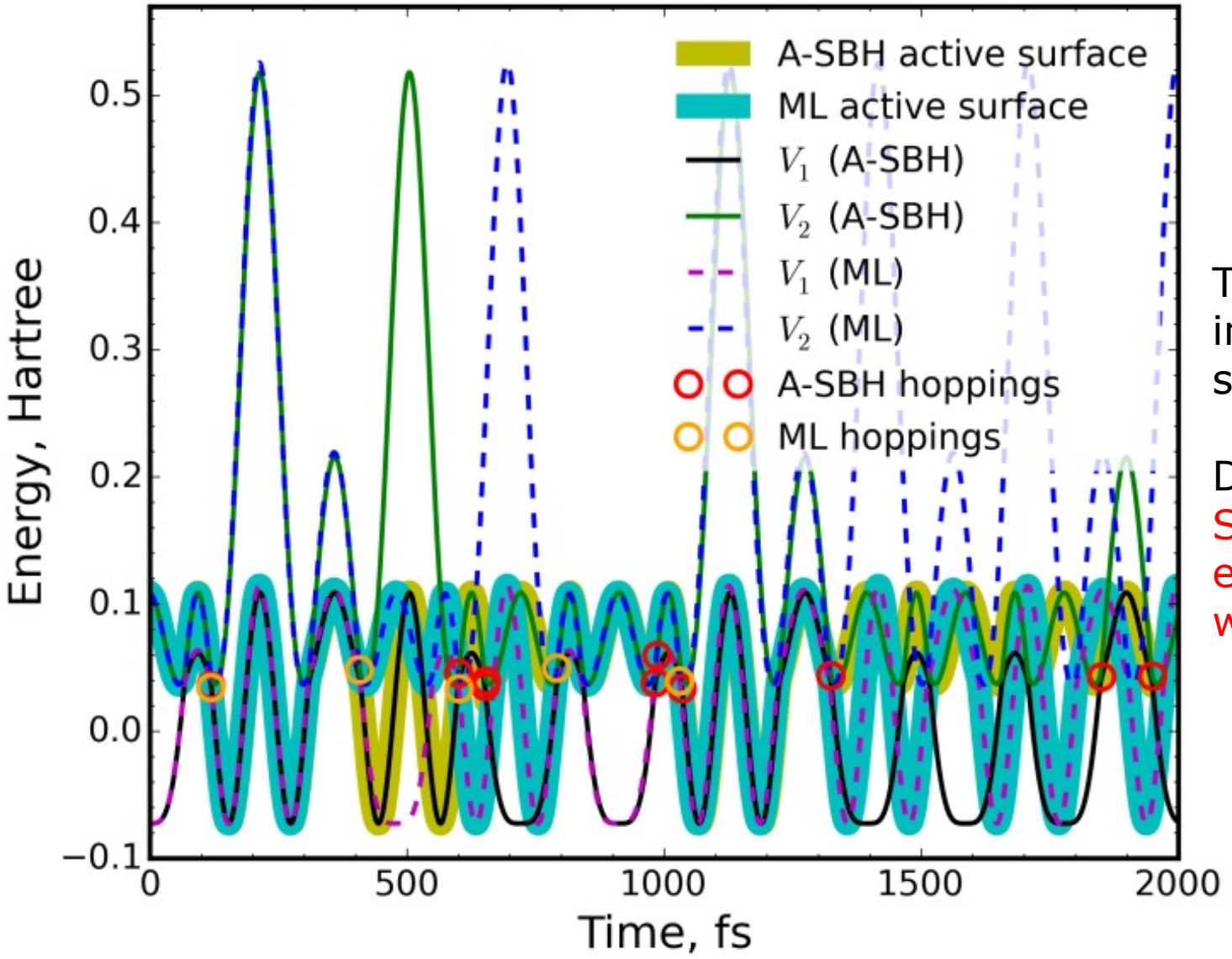
ML for nonadiabatic dynamics



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

P. O. Dral, M. Barbatti, W. Thiel, *J. Phys. Chem. Lett.* **2018**, *9*, 5660

ML for nonadiabatic dynamics



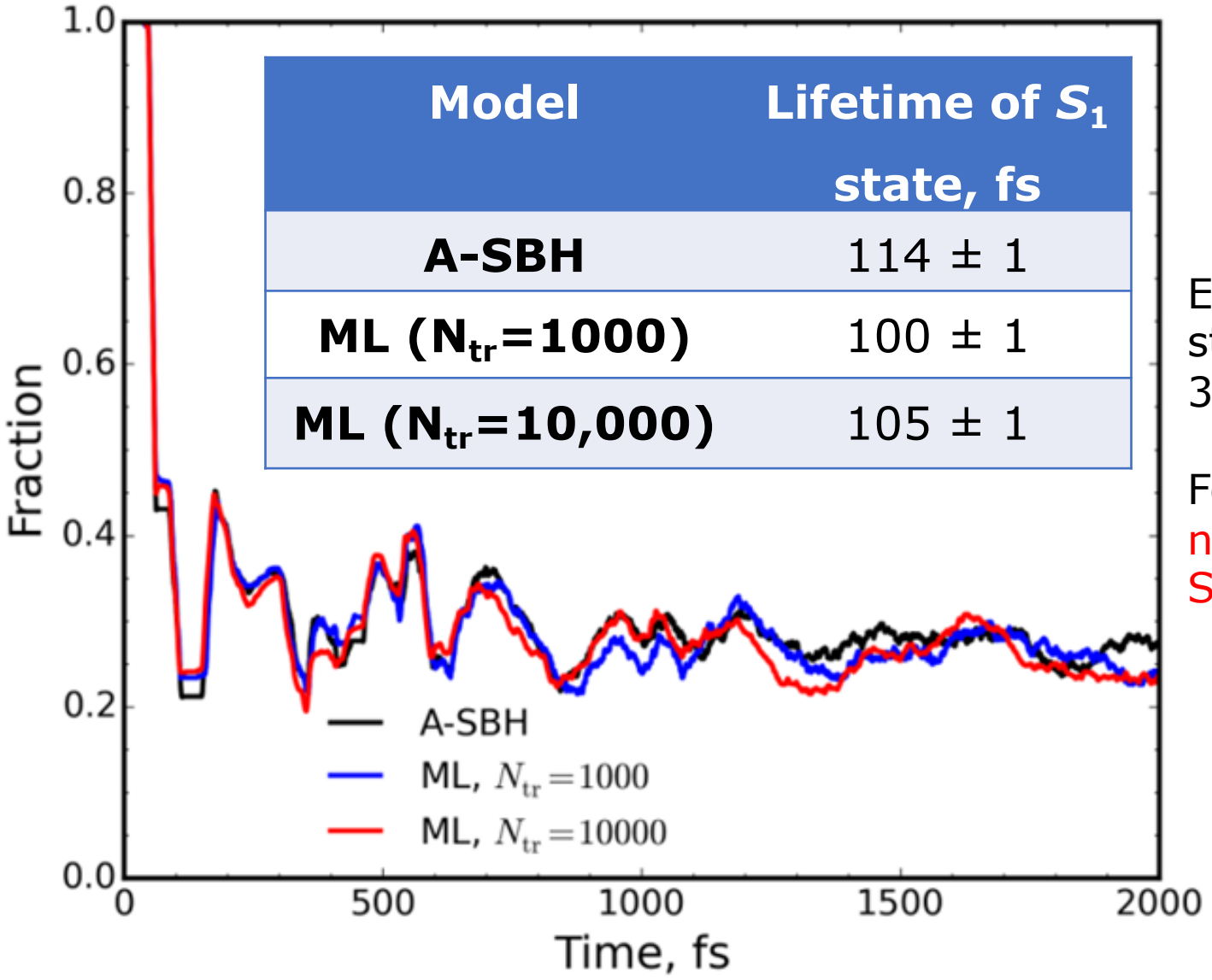
The simulations started from the same initial conditions and were run with the same random seed

During the ML trajectory propagation, A-SBH calculations were performed when the estimated energy gap between S_1 and S_0 was below 0.03 Hartree

P. O. Dral, M. Barbatti, W. Thiel, *J. Phys. Chem. Lett.* **2018**, *9*, 5660

ML for nonadiabatic dynamics

Model	Lifetime of S_1 state, fs
A-SBH	114 ± 1
ML (N_{tr}=1000)	100 ± 1
ML (N_{tr}=10,000)	105 ± 1

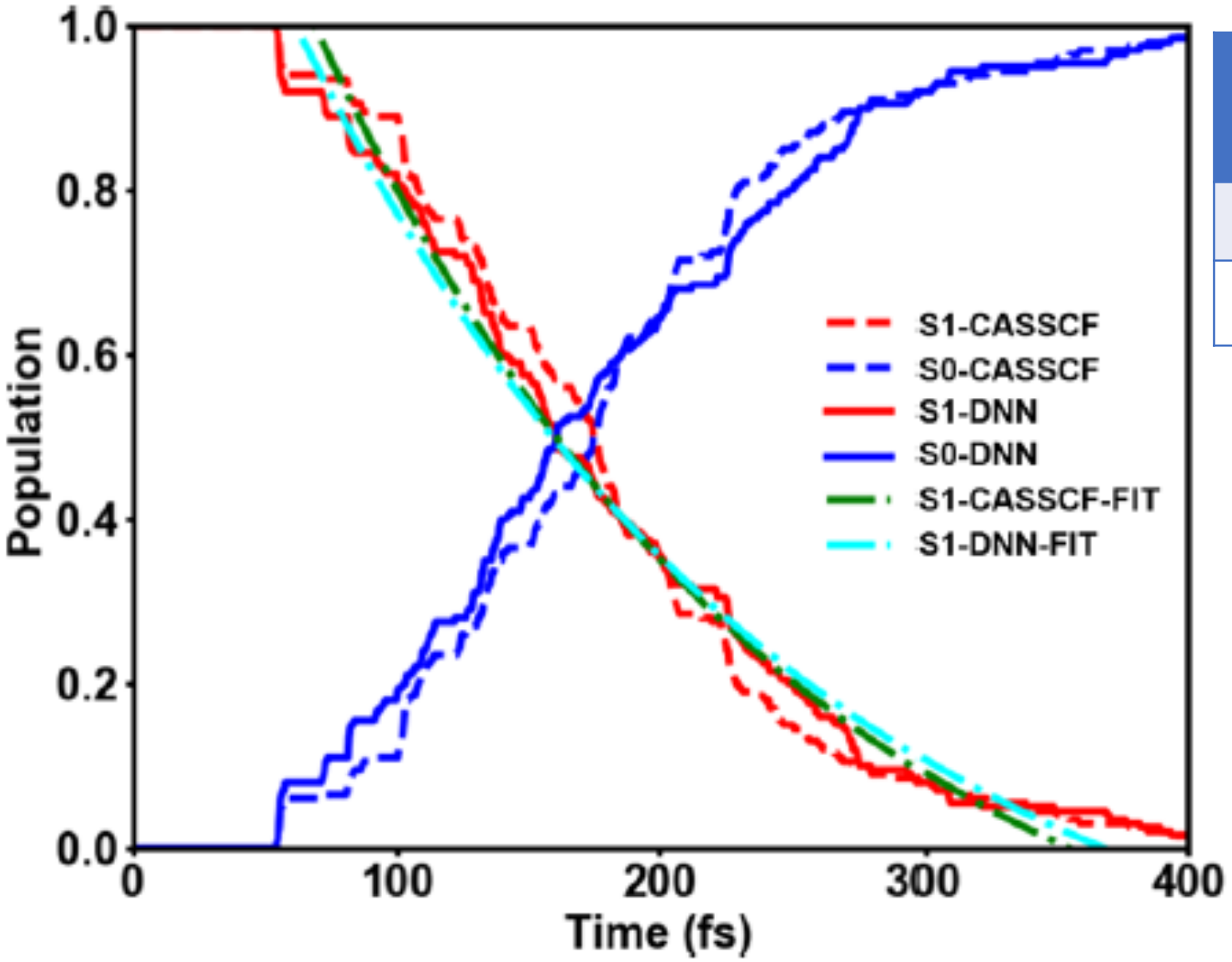


Evolution of the fraction of trajectories on state S_1 for the 33-D model averaged for 1,000 trajectories

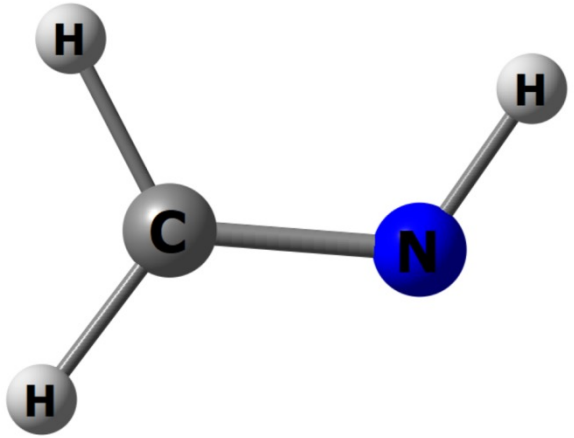
For small band gaps (<0.03 Hartree) nonadiabatic couplings were calculated with A-SBH

P. O. Dral, M. Barbatti, W. Thiel, *J. Phys. Chem. Lett.* **2018**, *9*, 5660

ML for nonadiabatic dynamics



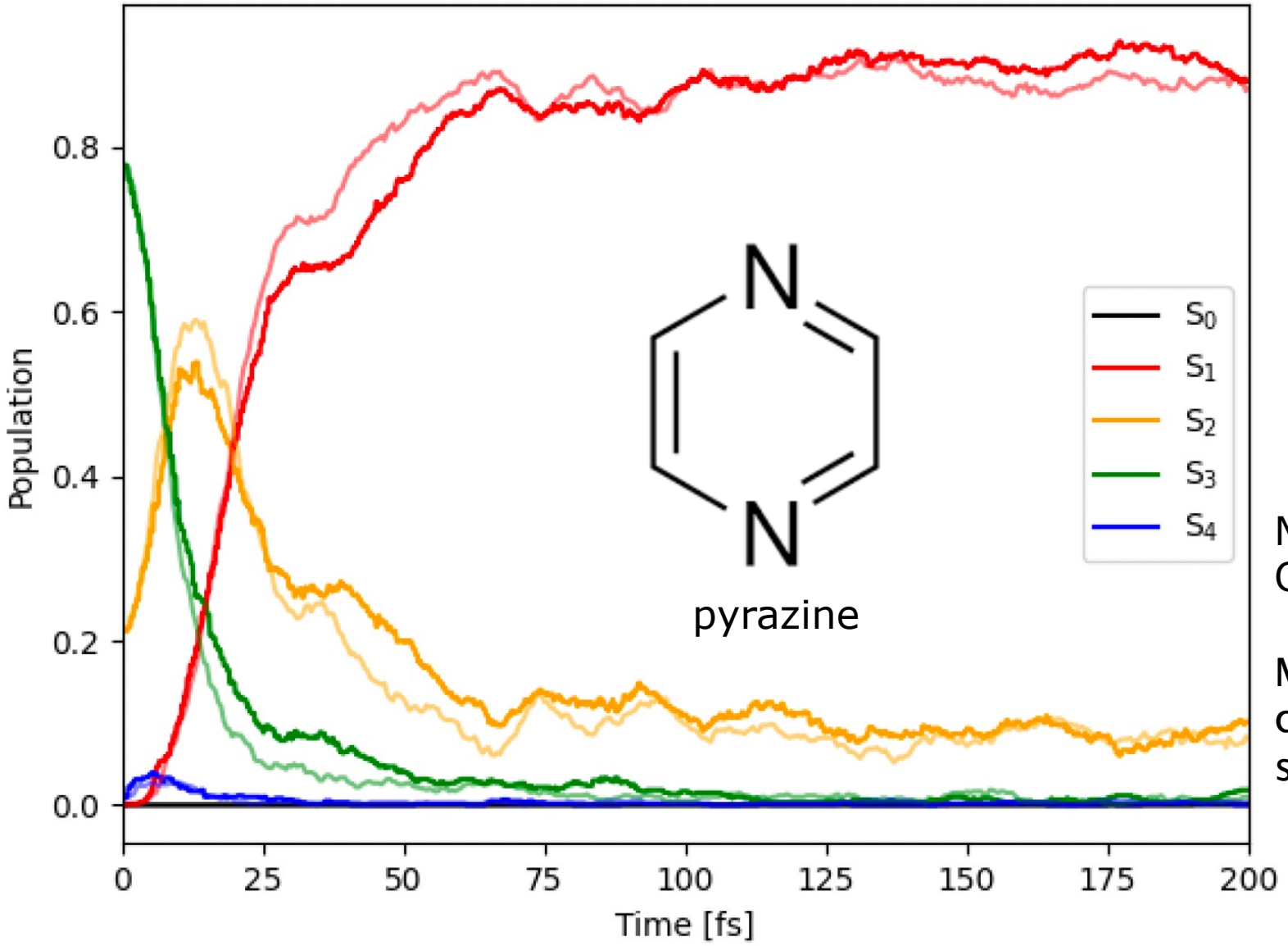
Model	Lifetime of S_1 state, fs
CASSCF	182
Deep NNs	191



Zhu–Nakamura method for dynamics

W.-K. Chen, X.-Y. Liu, W. Fang, P. O. Dral, G. Cui, *J. Phys. Chem. Lett.* **2018**, *9*, 670

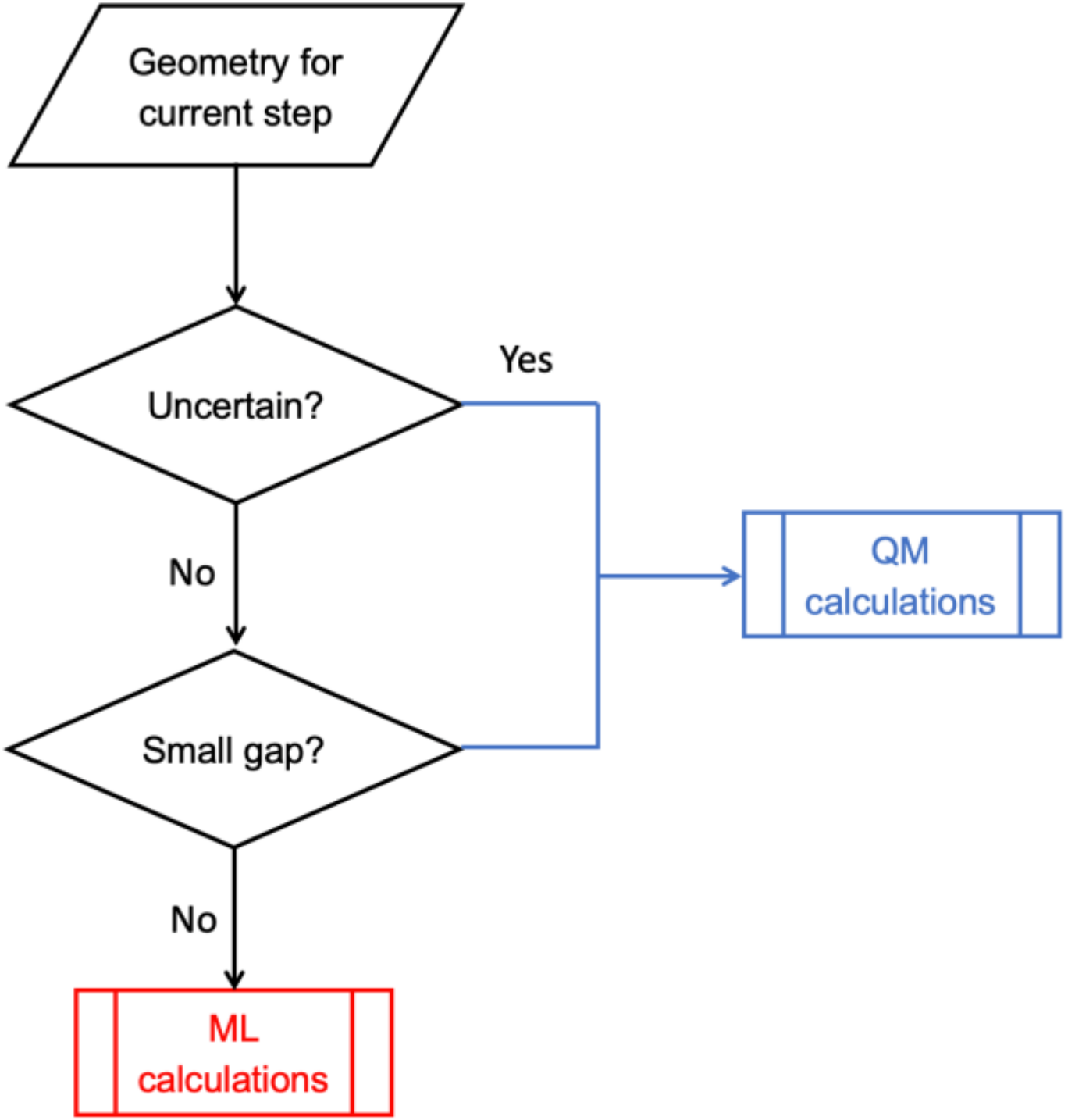
Landau–Zener NAMD accelerated by ML



ML (ANI-type MLPs) – full colors
QM reference – pale

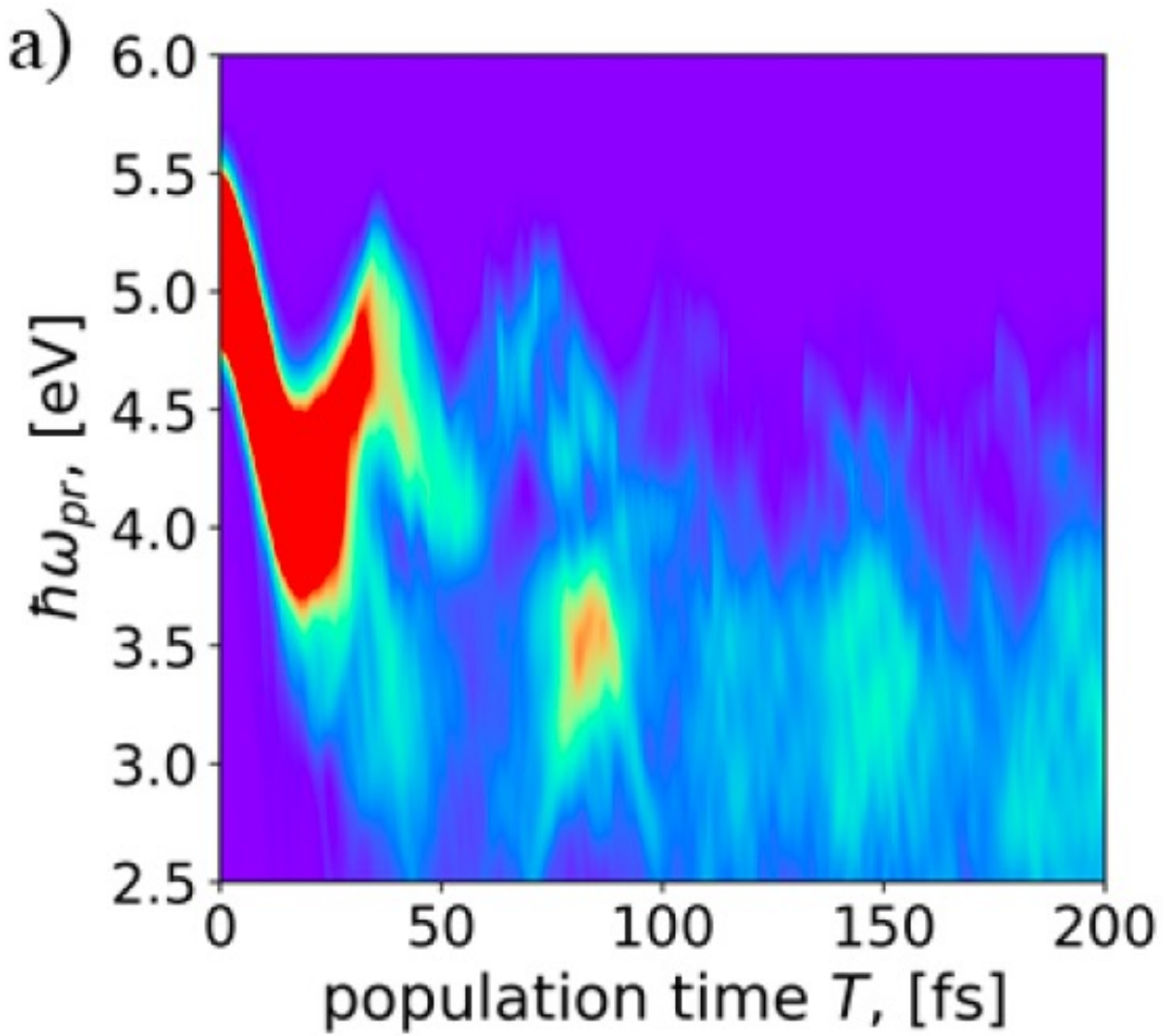
ML cut the cost by at least 95% compared to pure first-principles simulations

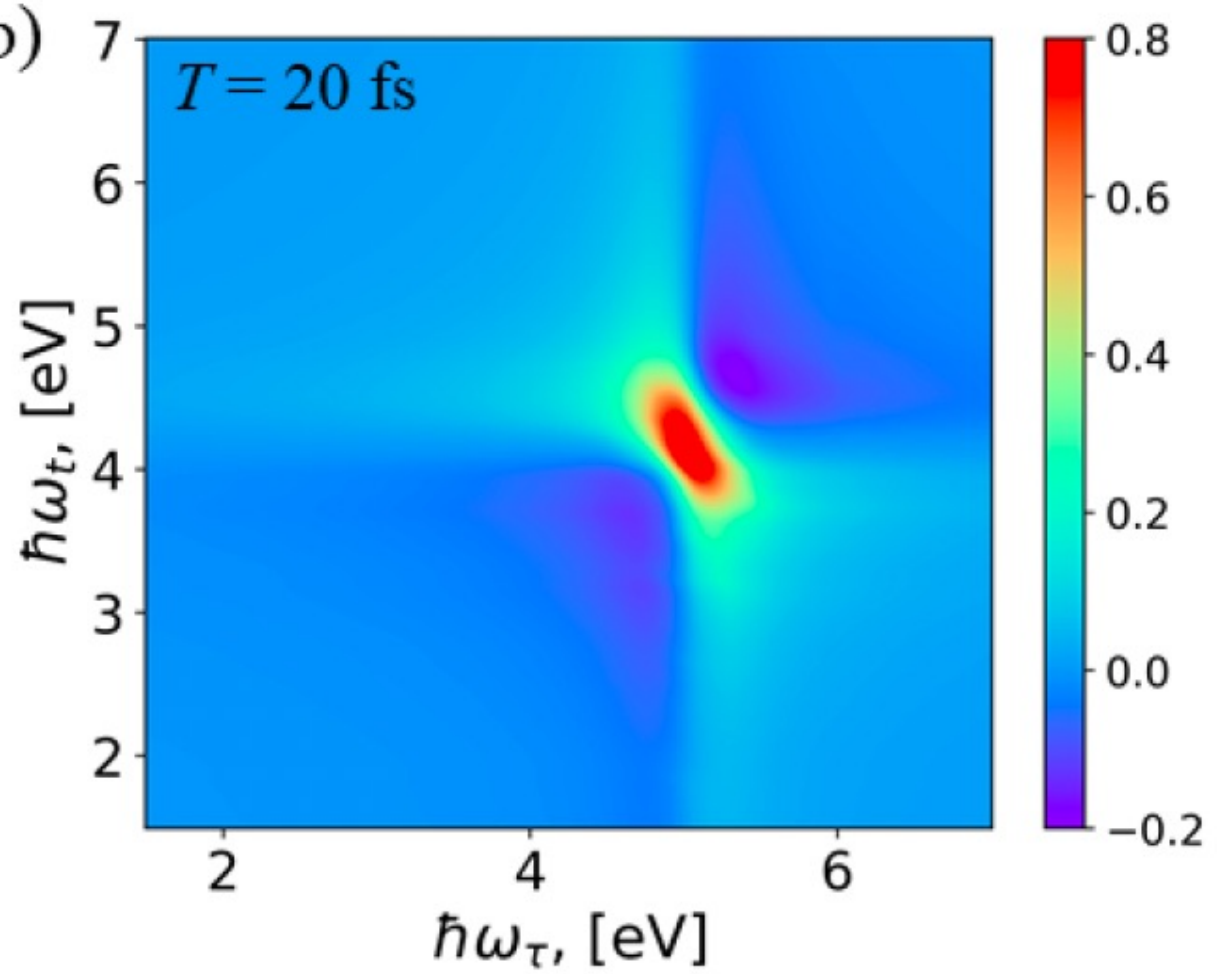
S. V. Pios, M. F. Gelin, A. Ullah, P. O. Dral*, L. Chen*, *J. Phys. Chem. Lett.* **2024**, *15*, 2325



S. V. Pios, M. F. Gelin, A. Ullah, P. O. Dral*, L. Chen*, *J. Phys. Chem. Lett.* **2024**, *15*, 2325

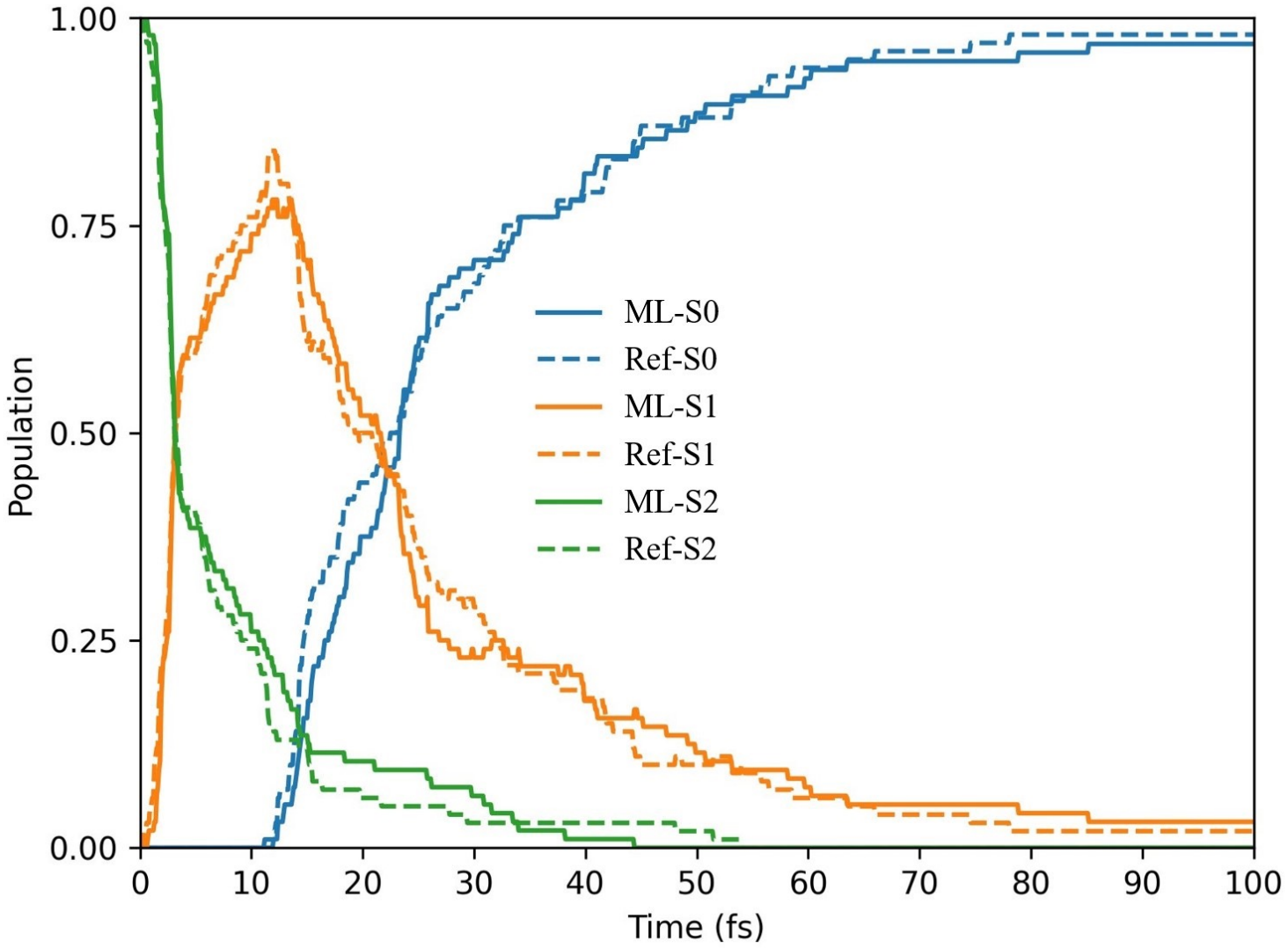
2D spectra – AI-accelerated simulations





S. V. Pios, M. F. Gelin, A. Ullah, P. O. Dral*, L. Chen*, *J. Phys. Chem. Lett.* **2024**, *15*, 2325

Active learning for nonadiabatic dynamics



Molecule: CNH_4^+

Reference:
SA-3-CASSCF(12,8)/
6-31G(d)

ML: ANI-type, trained on ca. 2500 points.

(back-hoppings prevented)

Zhang Lina, P. O. Dral, M. Barbatti, et al., *unpublished*

XACS
Xiamen Atomistic Computing Suite
XACScloud.com

Zoo of machine learning potentials

MLatom.com

Categories of machine learning potentials

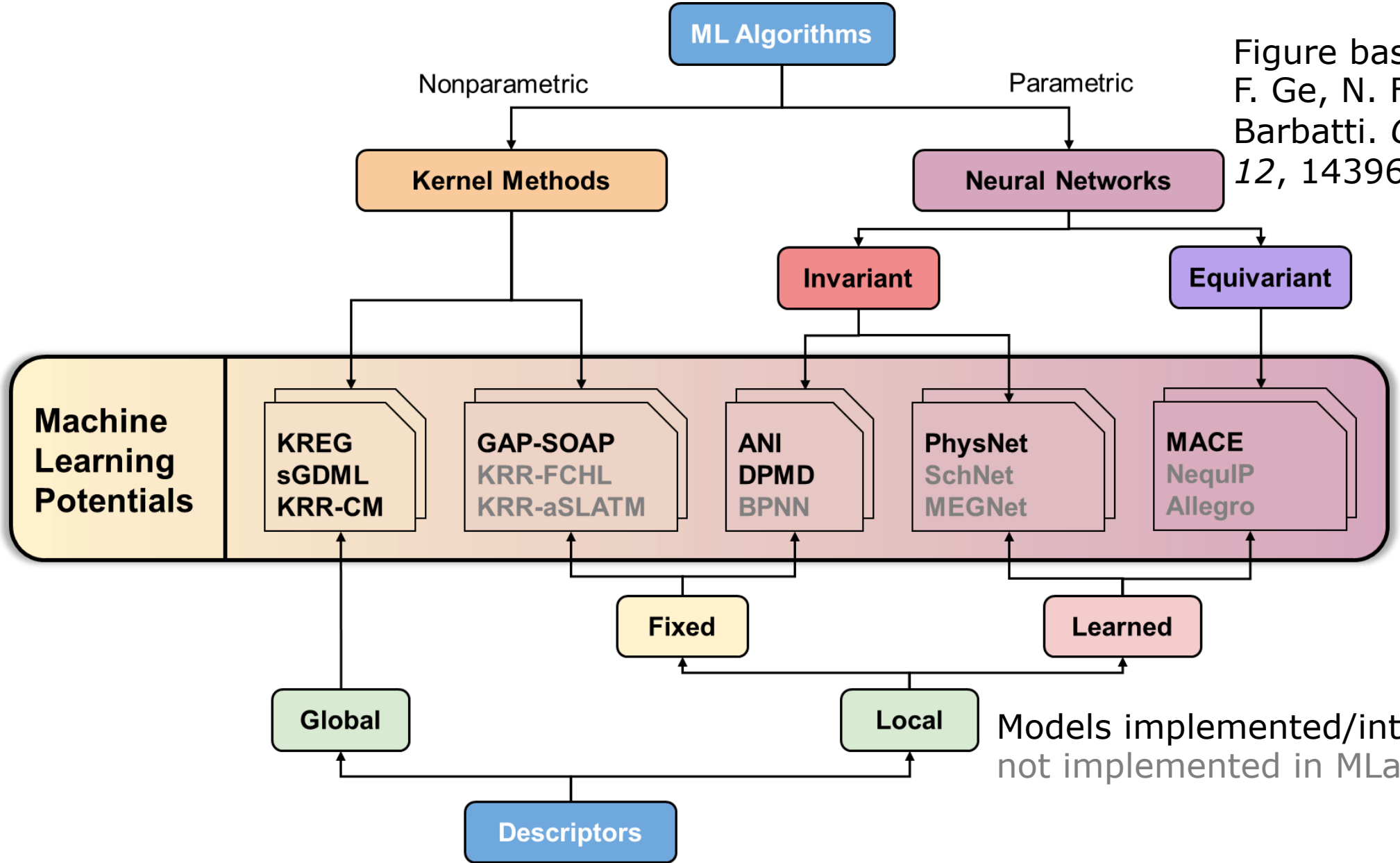


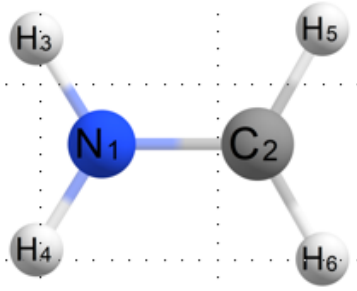
Figure based on M. Pinheiro Jr, F. Ge, N. Ferré, P. O. Dral, M. Barbatti. *Chem. Sci.* **2021**, *12*, 14396–14413

Models implemented/interfaced in MLatom

not implemented in MLatom

Current Work – AIQM1 Landau-Zener Surface Hopping

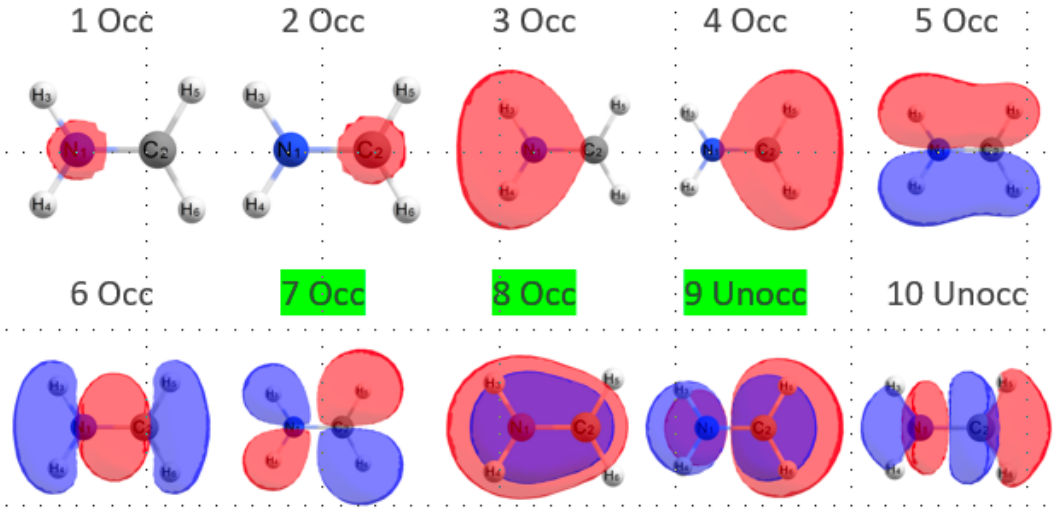
Research System: $CH_2NH_2^+$
Number of Electrons: 16
TSH Package: MLatom
QC Calculation Package: Columbus
Reference Method: SA-3-CASSCF(12,8)/6-31G(d)+LZ
Prediction Method: AIQM1(GUGA-CI)+LZ
AIQM1 GUGA-CI Active Space: Orb7-Orb9 (4,3)

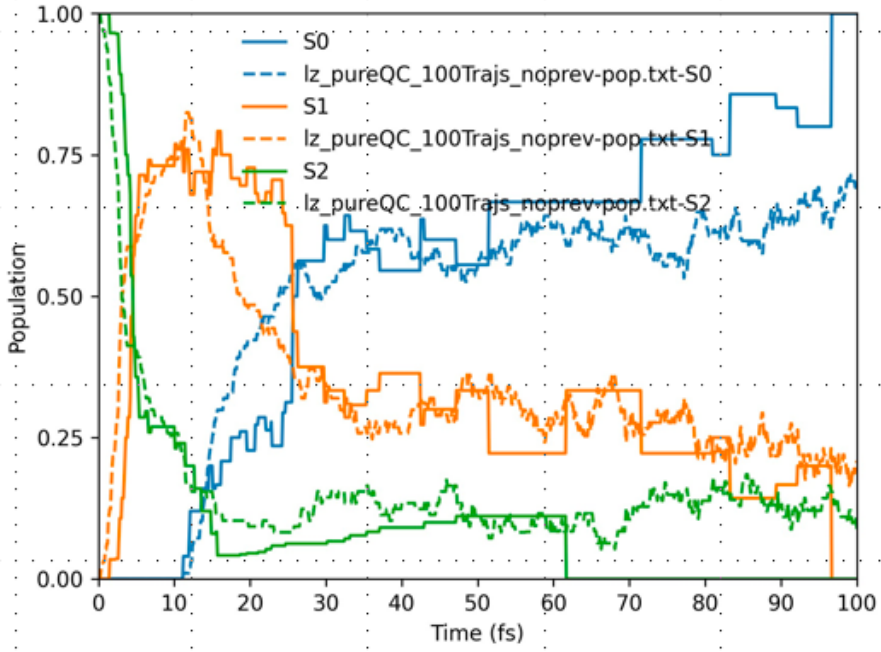


(small, ultrafast dynamics, classical photochemistry model system)

Lina Zhang

Lina Zhang, Pavlo O. Dral, *et al.*, *unpublished*





data set	ODM2	B3LYP/ 6-31G*	ωB97X/ 6-31G*	ωB97X-D/ 6-31G*	ωB97X/ def2-TZVPP	ωB97X-D4/ def2-TZVPP	ANI-1ccx	AIQM1 @DFT*	AIQM1 @DFT	AIQM1	CCSD(T)* /CBS
	energies, kcal/mol										
CHNO	2.64	6.71	4.10	3.84	3.21	2.76	—	2.49	2.12	0.87	—
G3/99	3.04	8.53	3.46	3.22	4.18	3.20	—	2.83	2.06	0.88	—
ISOMERS44 (ΔH_f)	1.16	8.08	3.57	3.53	4.52	3.78	—	3.00	2.27	0.42	—
ISOMERS44 (ΔH_r)	0.70	2.29	1.45	1.31	1.19	1.10	1.68	0.95	0.89	0.50	—
IsoL6/11	1.48	5.26	3.83	3.36	1.75	1.64	1.46	1.65	1.55	0.62	0.47
HC7/11	5.37	6.44	16.90	13.98	6.83	7.10	2.53	8.89	9.16	1.43	1.57
Torsion	0.74	0.55	0.30	0.29	0.20	0.19	0.23	0.23	0.23	0.19	0.05
	bond lengths, Å										
CHNO	0.015	0.006	0.008	0.007	0.010	0.010	0.011	0.010	0.010	0.007	—
MGHBL9	0.023	0.007	0.006	0.005	0.002	0.002	0.047	0.011	0.011	0.004	—
MGNHBL11	0.026	0.006	0.003	0.002	0.008	0.008	0.004	0.008	0.008	0.002	—
	bond angles, °										
CHNO	2.04	0.70	0.68	0.64	0.68	0.68	1.00	0.77	0.77	0.70	—
	dihedral angles, °										
CHNO	4.07	5.20	4.68	6.10	7.12	7.11	5.86	2.14	2.14	2.31	—

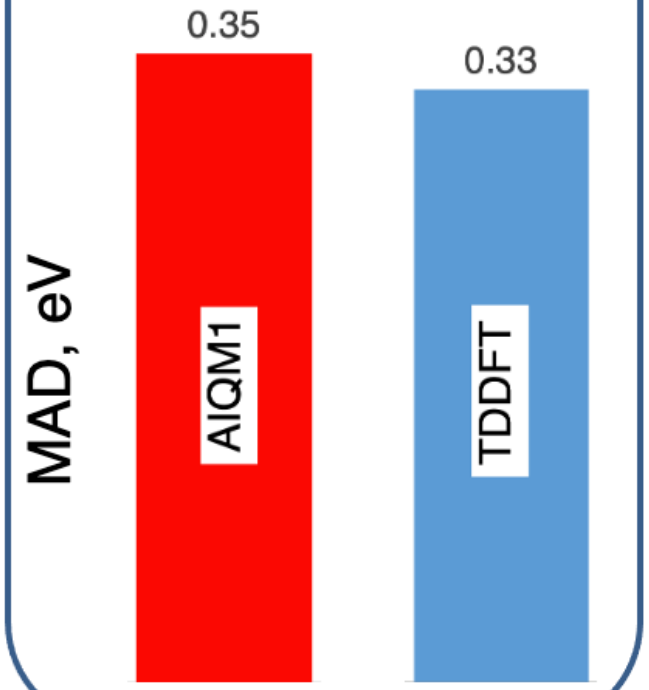
Ground-state properties of neutral, closed-shell compounds
(heats of formation, reaction enthalpies, and ZPVE-exclusive reaction energies)

P. Zheng, R. Zubatyuk, W. Wu, O. Isayev, P. O. Dral, *Nat. Commun.* **2021**, *12*, 7022

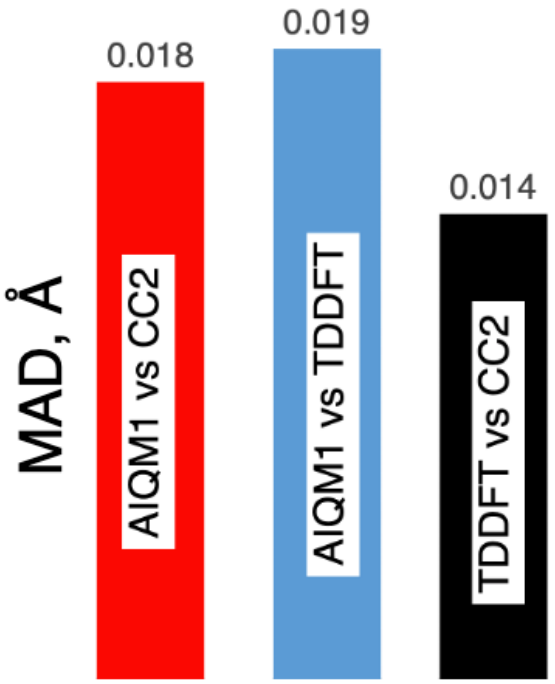
Excited states with AIQM1/MRCI

data set	ODM2	B3LYP/ 6-31G*	ωB97X/ 6-31G*	ωB97X-D/ 6-31G*	ωB97X/ def2-TZVPP	ωB97X-D4/ def2-TZVPP	ANI-1ccx	AIQM1 @DFT*	AIQM1 @DFT	AIQM1	CCSD(T)* /CBS
	excitation energies, eV										
Thiel's set	0.35	0.32	0.45	0.36	0.36	0.36	—	0.35	0.35	0.35	—

a Thiel's set benchmark

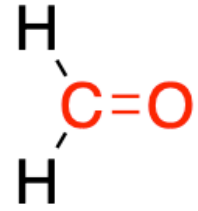


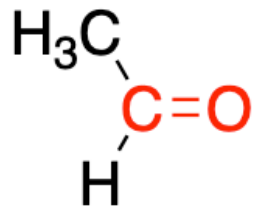
b ExGeom benchmark



TDDFT:
Linear-response TD B3LYP/TZVP

c bond length Å





	1nπ*	3nπ*	3ππ*	1nπ*
exp.	1.323	1.307	1.423	1.320
AIQM1	1.339	1.304	1.608	1.342
TDDFT	1.296	1.298	–	1.304
CC2	1.361	1.343	1.469	1.387

P. Zheng, R. Zubatyuk, W. Wu, O. Isayev, P. O. Dral, *Nat. Commun.* **2021**, *12*, 7022

AIQM1 investigation of cycloparaphenylenes

AIQM1 also predicts fluorescence quenching

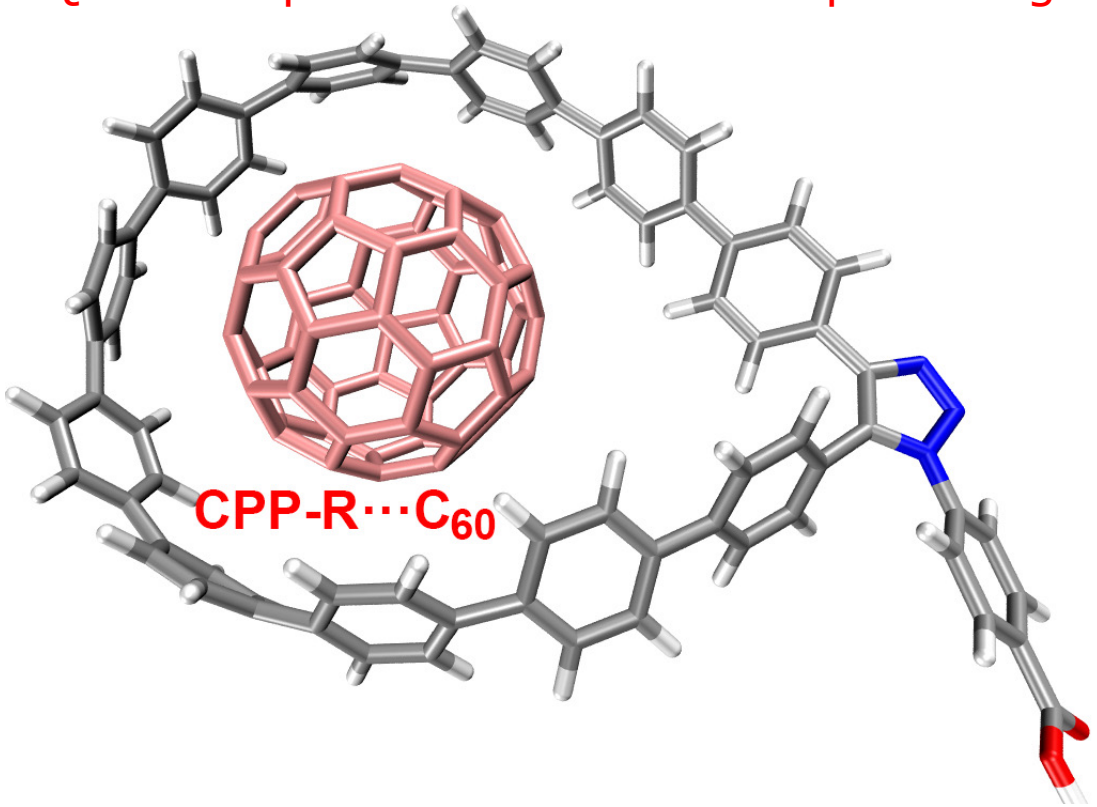


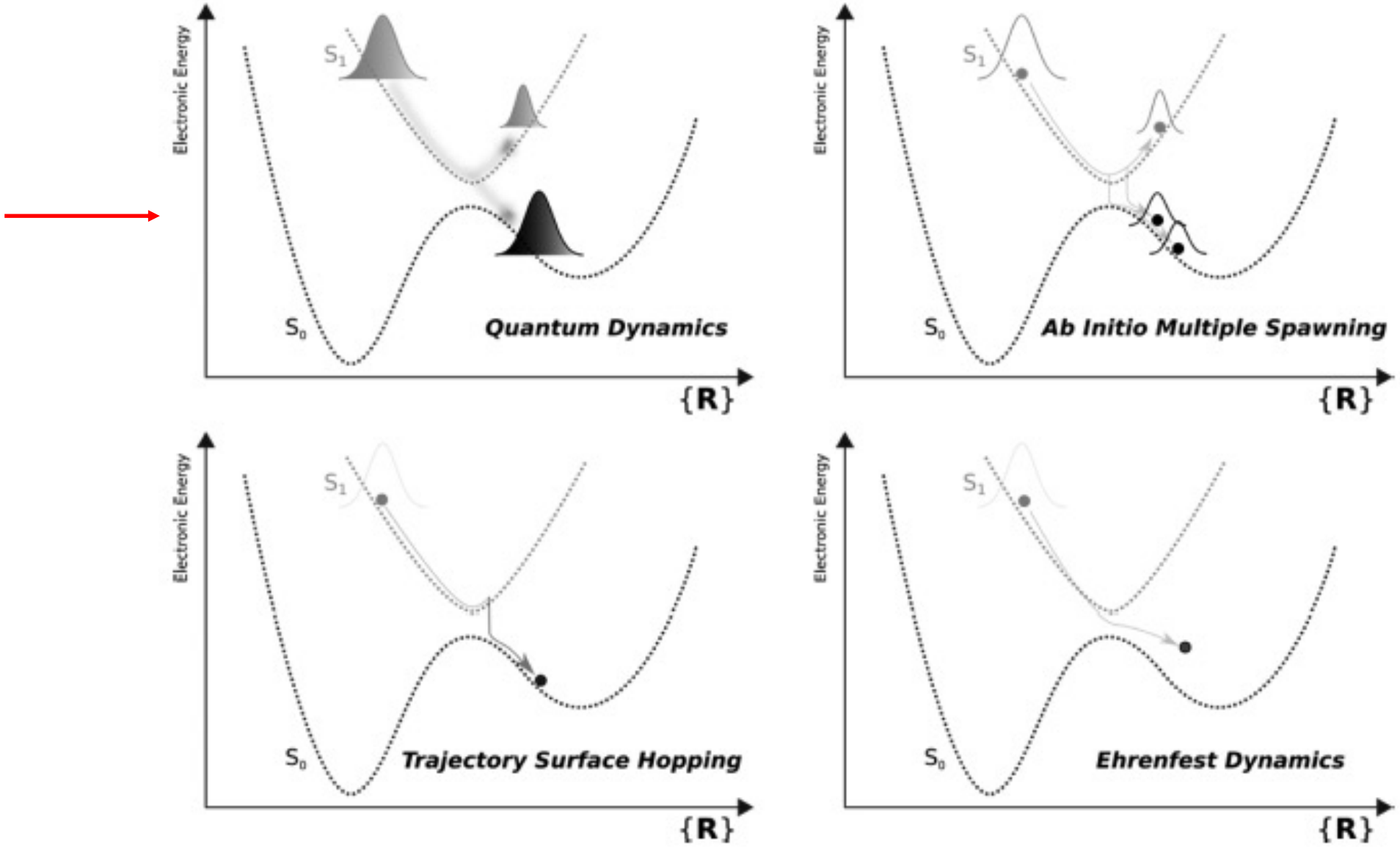
Table S9. Emission energy and oscillator strengths *f* of free molecules and their complexes with C_{60} and C_{70} at AIQM1/CIS in vacuum (S_1 to S_0 transition).

Species	*f*	Energy (eV)
3	0.750	3.11
4	0.751	3.12
5	0.750	3.12
6	0.750	3.12
7	0.748	3.12
3 ⊃ C_{60}	0.000	2.58
4 ⊃ C_{60}	0.000	2.58
5 ⊃ C_{60}	0.000	2.58
6 ⊃ C_{60}	0.000	2.58
7 ⊃ C_{60}	0.000	2.59
M-**3**⊃ C_{70}	0.000	2.10
M-**4** ⊃ C_{70}	0.000	2.09
M-**5** ⊃ C_{70}	0.000	2.10
M-**6** ⊃ C_{70}	0.000	2.10
M-**7** ⊃ C_{70}	0.000	2.10

AIQM1 can be useful for aggregation-induced emission, photocatalysis

T. A. Schaub, A. Zieleniewska, R. Kaur, M. Minameyer, W. Yang, C. M. Schüßlbauer, L. Zhang, M. Freiberger, L. N. Zakharov, T. Drewello, P. O. Dral, D. Guldi, R. Jasti. Tunable Macrocyclic Polyparaphenylene Nanolassos via Copper-Free Click Chemistry. *Chem. Eur. J.* **2023**, *29*, e202300668

Many flavors for quantum dynamics (QD)



B. F. E. Curchod, T. J. Martínez, *Chem. Rev.* **2018,** *118*, 3305

Wish list for quantum dynamics (QD)

- Treat both nuclei and electrons quantum mechanically
- Treat the system and environment
- Computationally fast enough for real systems

Quantum dynamics of open systems

$$\hat{H} = \hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{env}} + \hat{H}_{\mathrm{S-env}}[+\hat{H}_{\mathrm{reorg}}]$$

- $\hat{H}_{\mathrm{S}}$ Hamiltonian of the system
- $\hat{H}_{\mathrm{env}}$ Hamiltonian of environment (bath)
- $\hat{H}_{\mathrm{S-env}}$ Hamiltonian of system-environment (system-bath) interaction
- $\hat{H}_{\mathrm{reorg}}$ the reorganization terms

Different ways to propagate QD

$$\frac{d}{dt}\boldsymbol{\rho}(t) = \frac{i}{\hbar}\left[\hat{H}, \boldsymbol{\rho}(t)\right]$$

Different integrators of Liouville–von Neumann equation, $\boldsymbol{\rho}$ – the density matrix

- hierarchical equations of motion (HEOM)
- the local thermalising Linblad master equation (LTLME)
- …

Machine learning to speed up dynamics

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

dynamics

dynamics propagation is

- computationally expensive

Machine learning to speed up dynamics

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

dynamics propagation is

- ~~computationally expensive~~

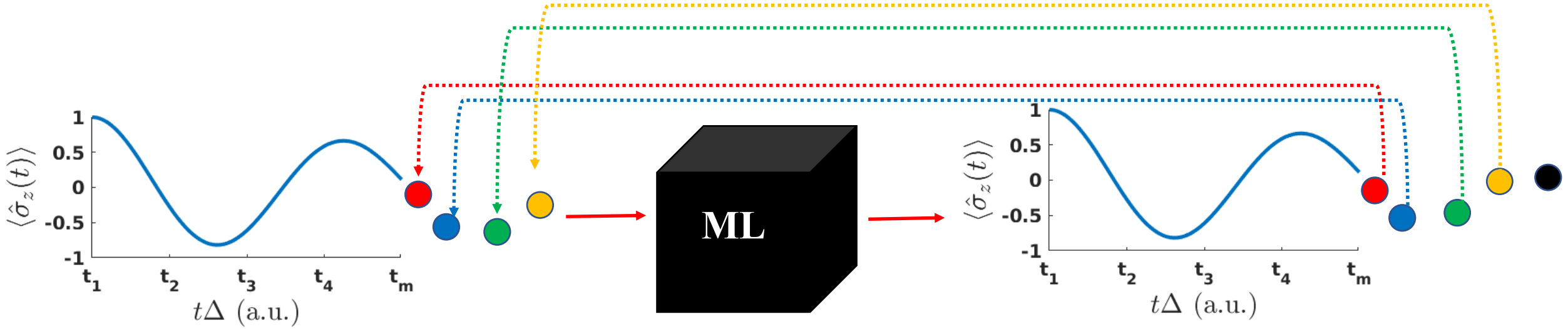
dynamics

ML dynamics

$$\boldsymbol{\rho}(t) = f^{\mathrm{ML}}[\rho(t - \Delta t)]$$

Inspired by: L. E. Herrera Rodriguez, A. A. Kananenka. Convolutional Neural Networks for Long Time Dissipative Quantum Dynamics. *J. Phys. Chem. Lett.* **2021,** *12*, 2476−2483

Machine learning to speed up dynamics



$$\boldsymbol{\rho}(t) = f^{\mathrm{ML}}[\rho(t - \Delta t)]$$

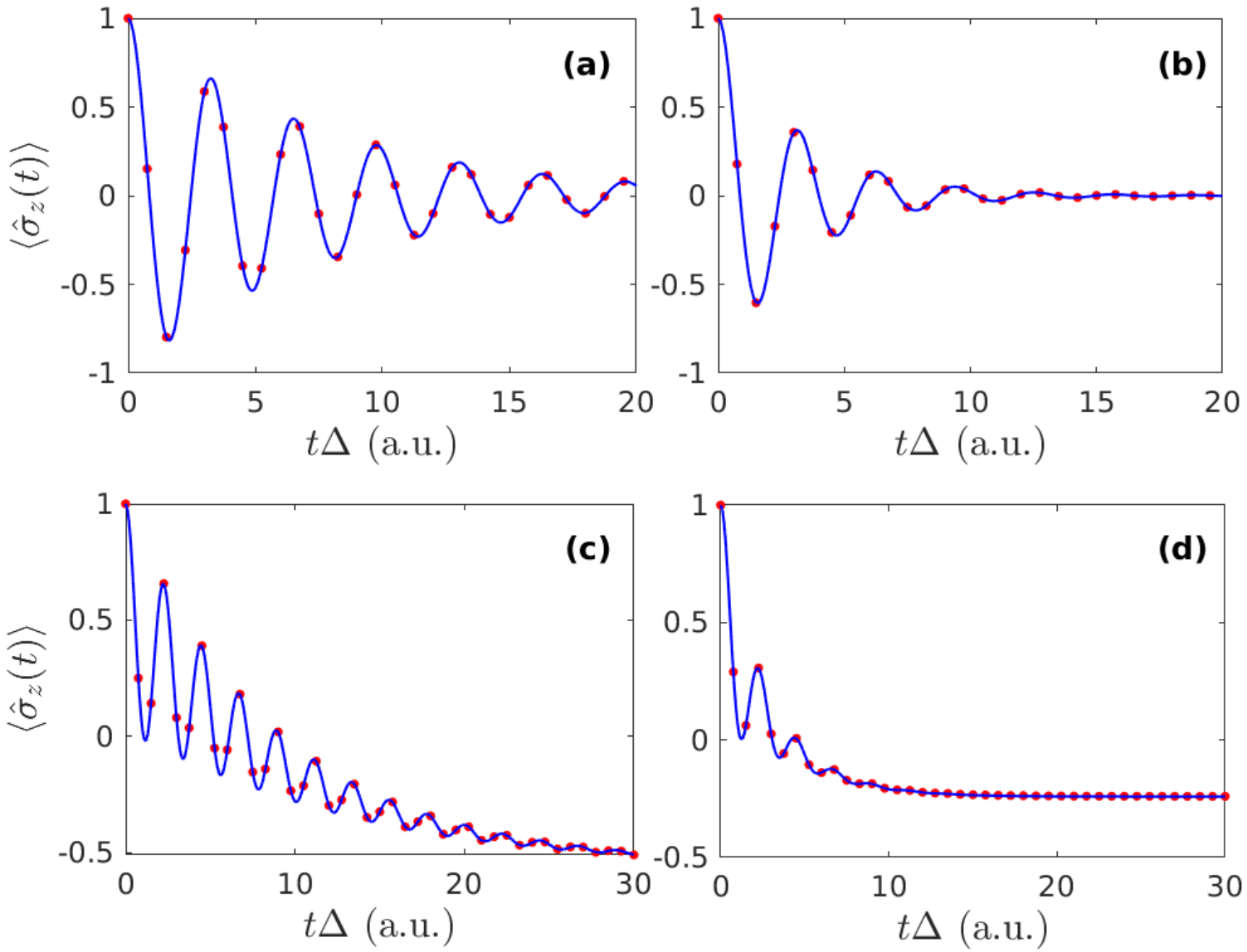
Arif Ullah

Spin-boson Hamiltonian:

$$\hat{H} = \frac{1}{2}\varepsilon\hat{\sigma}_z + \frac{1}{2}\Delta\hat{\sigma}_x + \sum_k \omega_k \hat{b}_k^\dagger \hat{b}_k + \hat{\sigma}_z \sum_k c_k\left(\hat{b}_k^\dagger + \hat{b}_k\right)$$

A. Ullah, P. O. Dral. Speeding up quantum dissipative dynamics of open systems with kernel methods. *New J. Phys.* **2021,** *23*, 113019

Machine learning to speed up dynamics



Test (unseen) trajectories for parameters not used in training trajectories

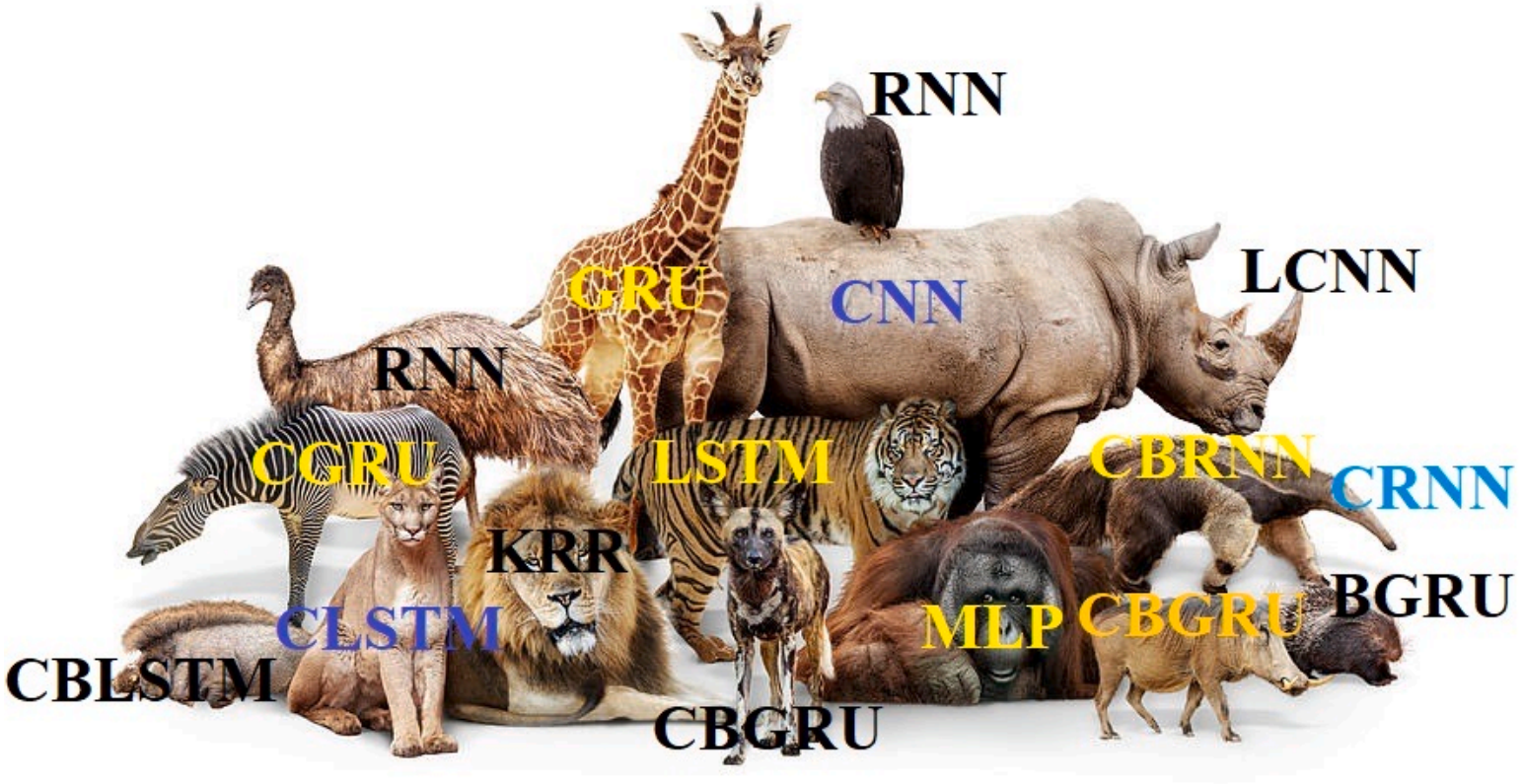
A. Ullah, P. O. Dral. *New J. Phys.* **2021,** *23*, 113019

Machine learning to speed up dynamics

$$\boldsymbol{\rho}(t) = f^{\mathrm{ML}}[\rho(t - \Delta t)]$$

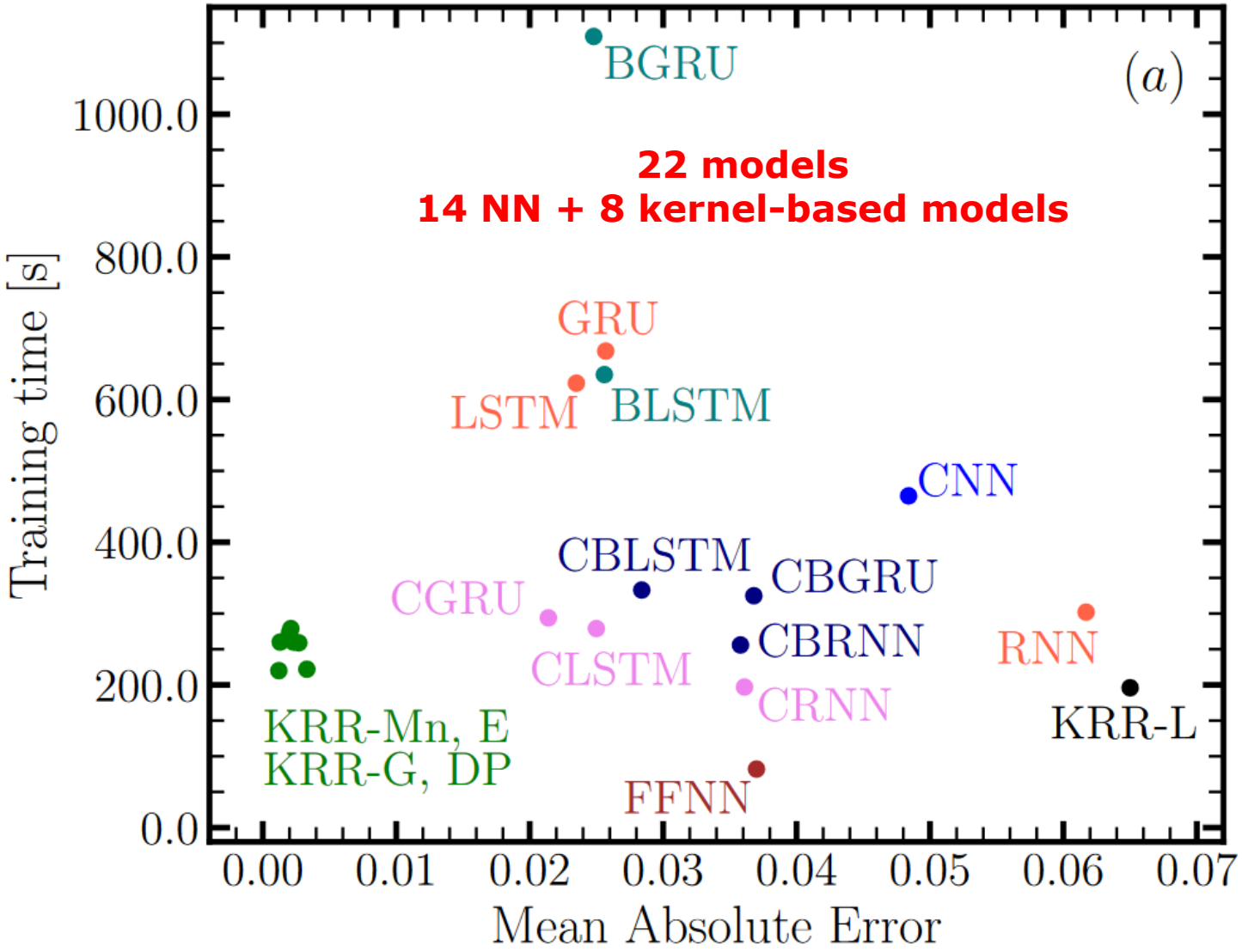
Many ways to do it:

- different algorithms
- different properties to learn ($\boldsymbol{\rho}$ or population)
- different systems, data sets…



- L. E. Herrera Rodriguez, A. A. Kananenka. **Convolutional Neural Networks** for Long Time Dissipative Quantum Dynamics. *J. Phys. Chem. Lett.* **2021,** *12*, 2476−2483
- K. Lin, J. Peng, F. L. Gu, Z. Lan. Simulation of Open Quantum Dynamics with Bootstrap-Based **Long Short-Term Memory Recurrent Neural Network**. *J. Phys. Chem. Lett.* **2021,** *12*, 10225–10234
- A. Ullah, P. O. Dral. Speeding up quantum dissipative dynamics of open systems with **kernel methods**. *New J. Phys.* **2021,** *23*, 113019

Good ML method for quantum dynamics?



Alexei Kananenka

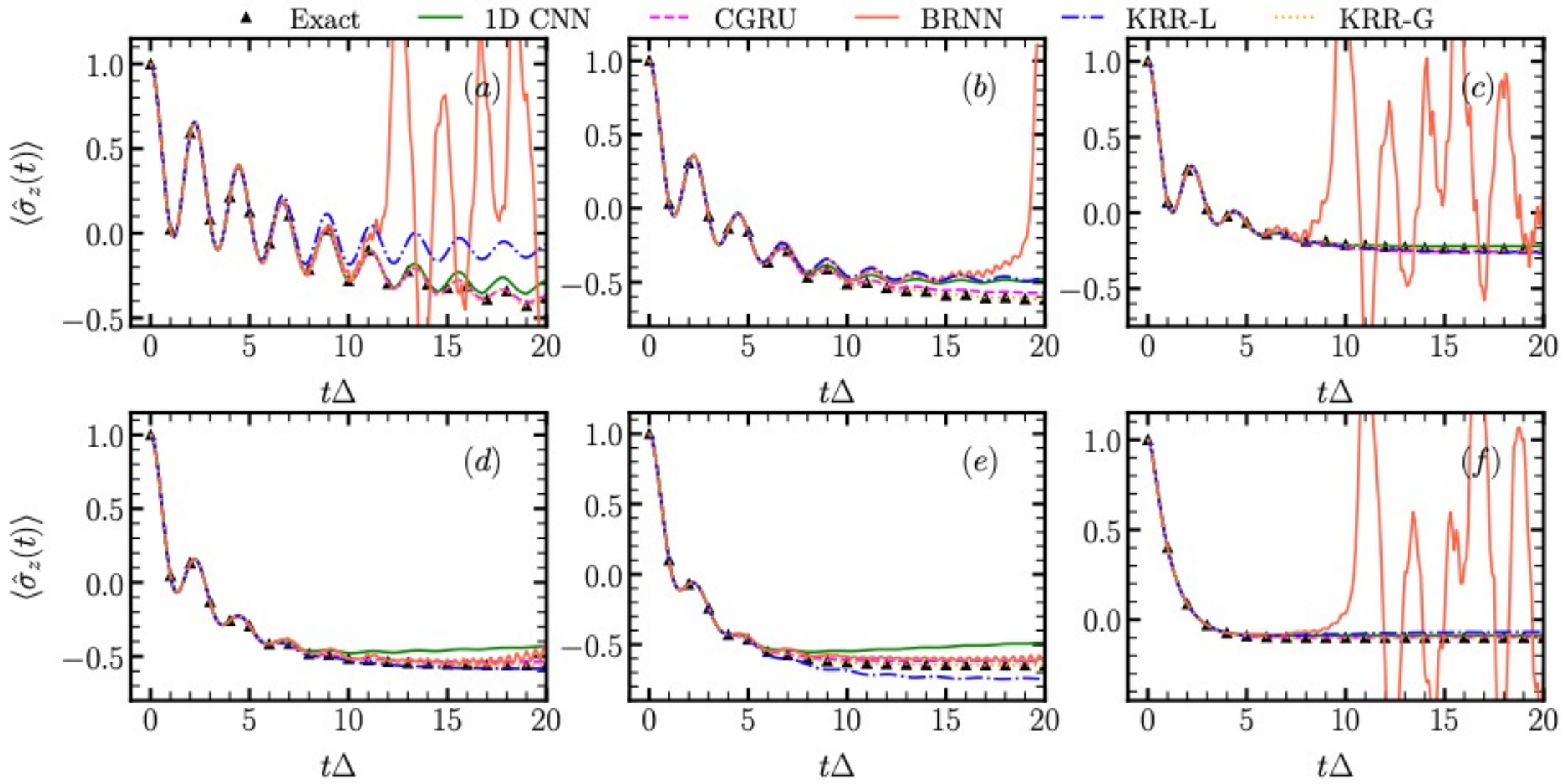
Arif Ullah

Luis Eduardo Herrera Rodríguez

Kennet Julian R. Espinosa

L. E. H. Rodrıguez, A. Ullah, K. J. R. Espinosa, P. O. Dral, A. A. Kananenka. *Mach. Learn. Sci. Technol.* **2022,** *3*, 045016

Good ML method for quantum dynamics?



L. E. H. Rodrıguez, A. Ullah, K. J. R. Espinosa, P. O. Dral, A. A. Kananenka. *Mach. Learn. Sci. Technol.* **2022,** *3*, 045016

Machine learning to speed up dynamics

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

dynamics propagation is

- ~~computationally expensive~~

dynamics

ML dynamics

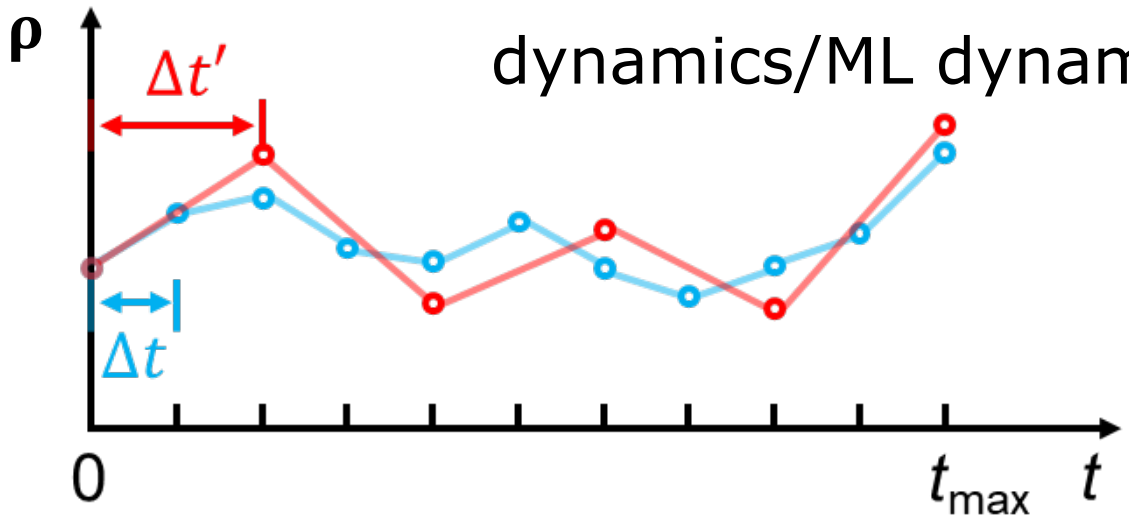
$$\boldsymbol{\rho}(t) = f^{\mathrm{ML}}[\rho(t - \Delta t)]$$

Can we do better?

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

dynamics propagation is

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



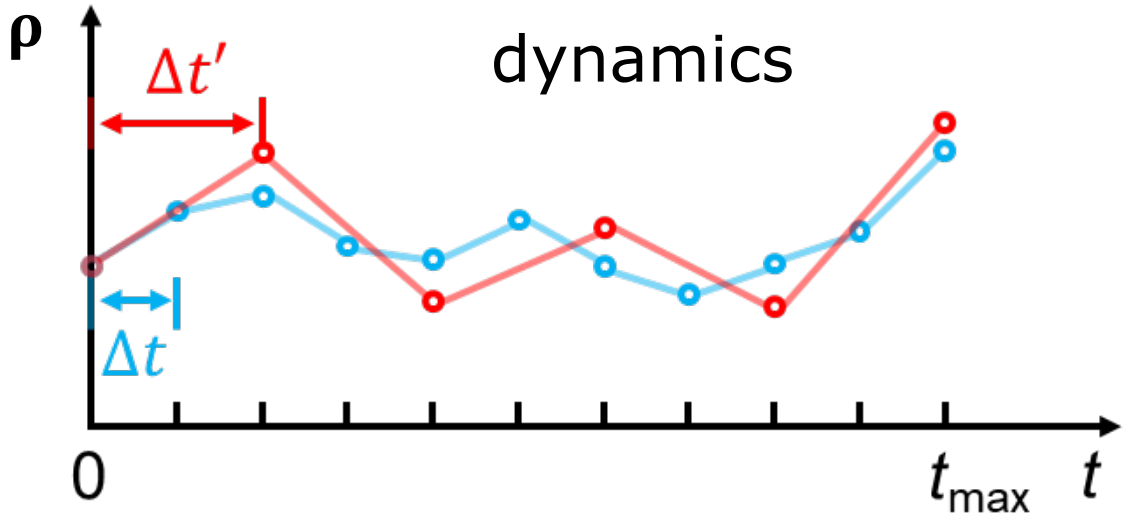
Can we do better?

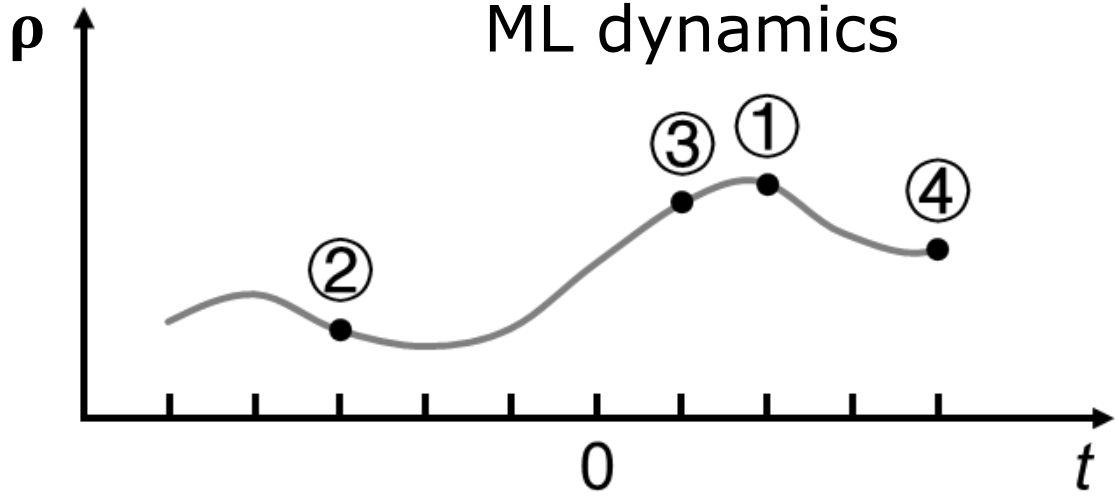
~~$\boldsymbol{\rho}(t) = f[\boldsymbol{\rho}(t - \Delta t)]$~~

dynamics propagation is

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

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



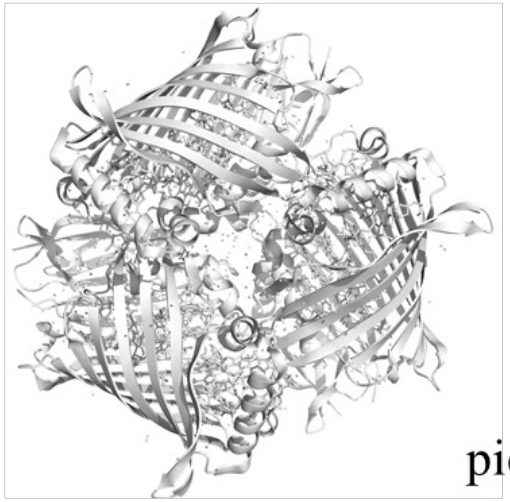


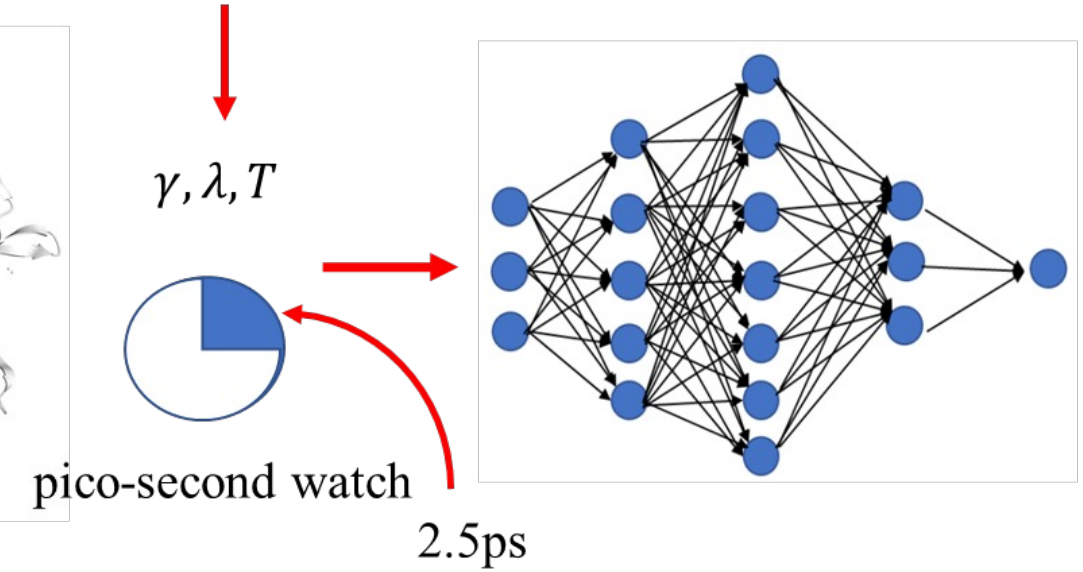
AI-QD (artificial intelligence-based quantum dynamics)

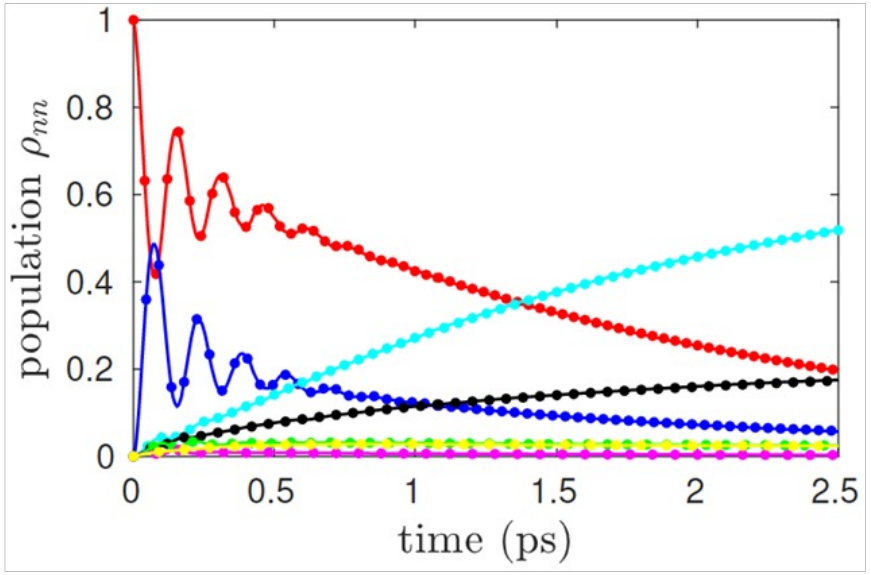
γ = characteristic frequency
λ = reorganization energy
T = temperature

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

PDB code: 3ENI





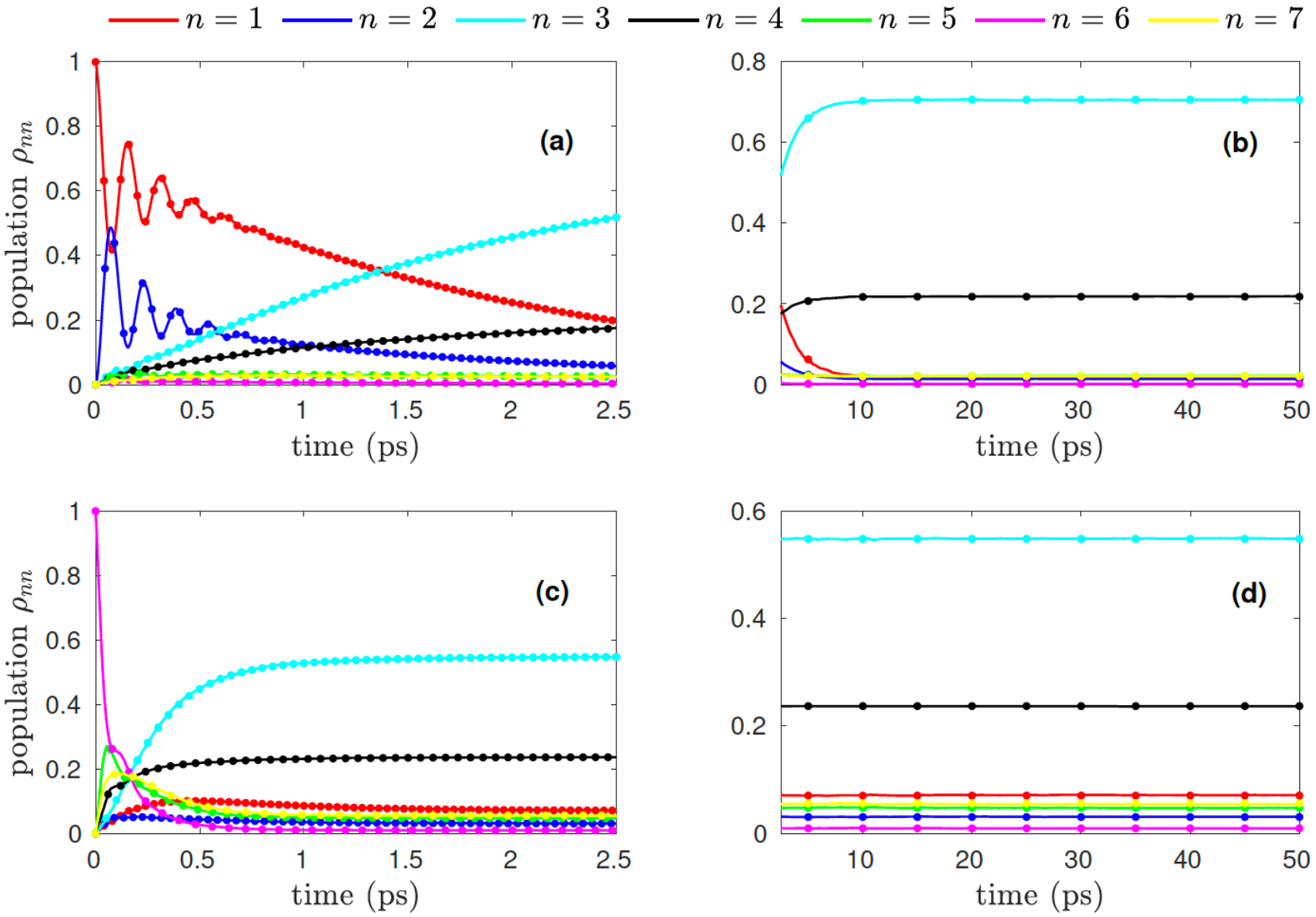


Dots: Reference
Line: AI-QD

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

AI-QD vs reference trajectories



Test (unseen) trajectories for parameters not used in training trajectories

Predictions of 0.57M trajectories up to 1 ns

A. Ullah, P. O. Dral. *Nat. Commun.* **2022**, *13*, 1930

Can we do even better?

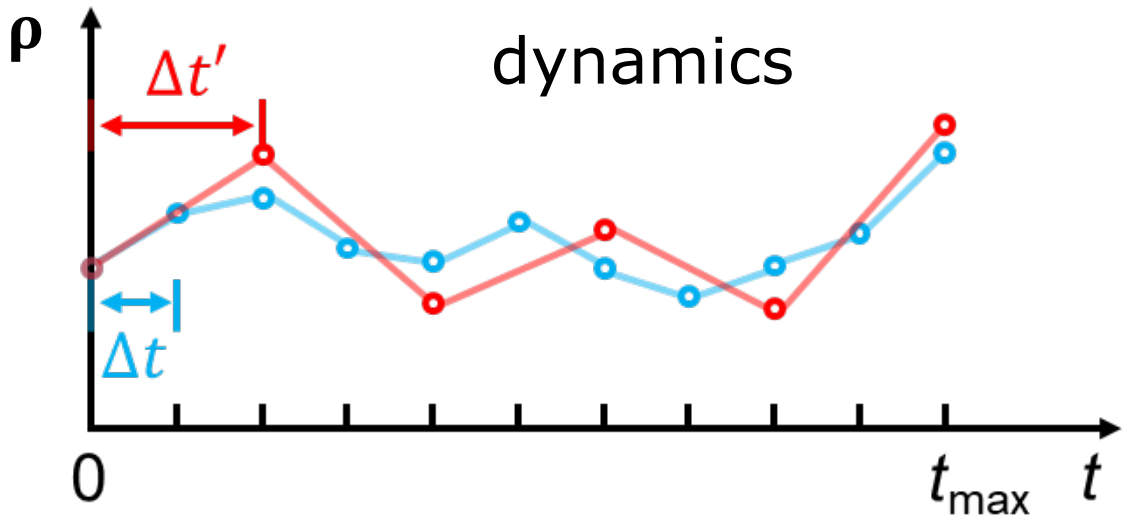
$$\boldsymbol{\rho}(t) = f[\boldsymbol{\rho}(t - \Delta t)]$$

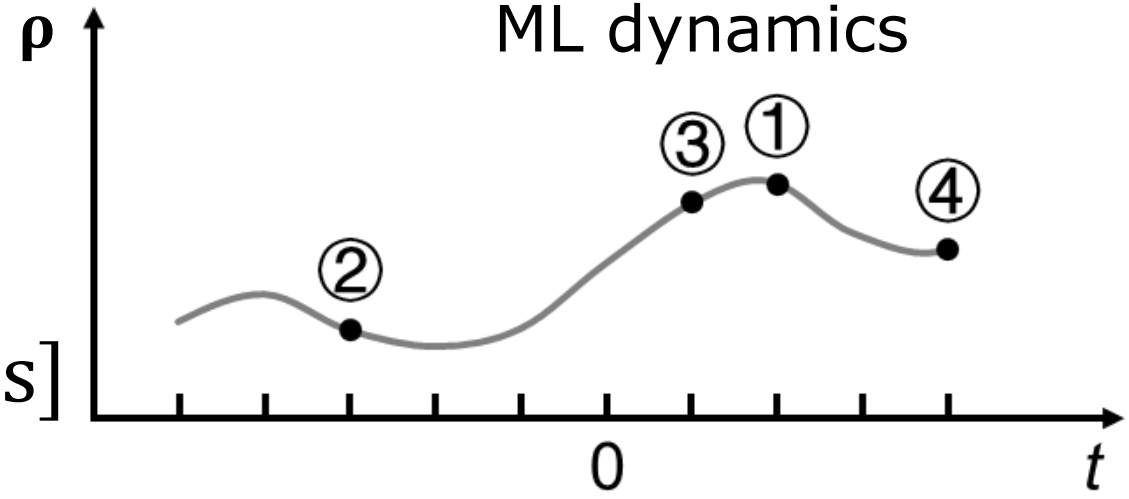
dynamics propagation is

- computationally expensive
- recursive (iterative)

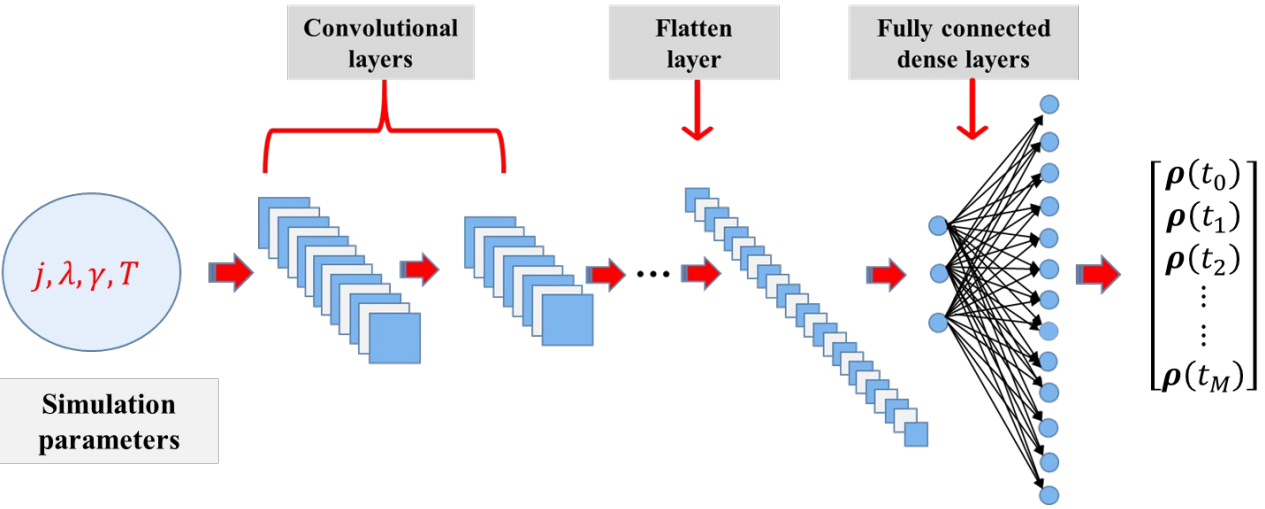
$$\boldsymbol{\rho}(t) = f[t; \text{other parameters}]$$

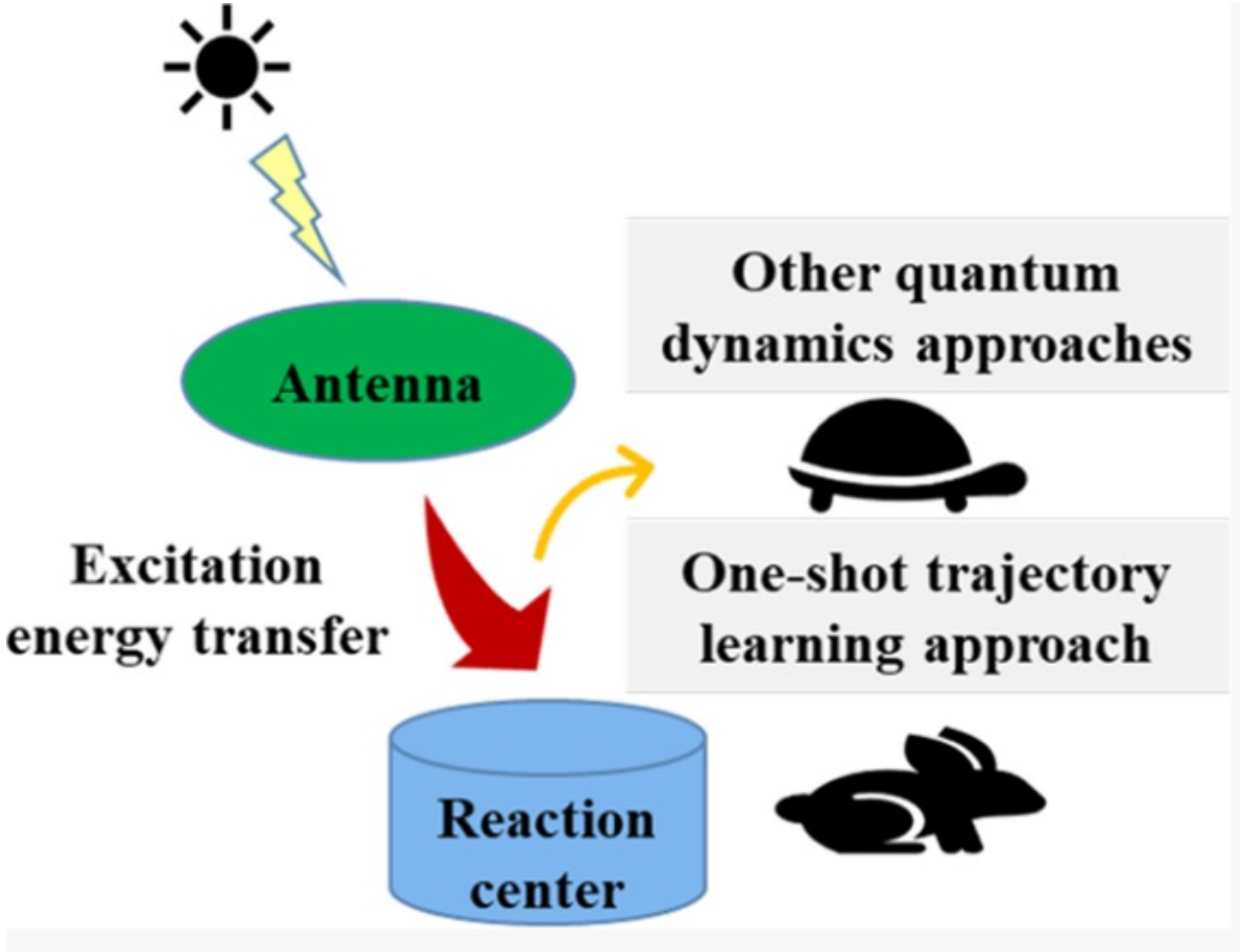
$$\{\boldsymbol{\rho}(t_k)\}_{k=0}^{M} = f[\text{other parameters}]$$





One-Shot Trajectory Learning (OSTL)



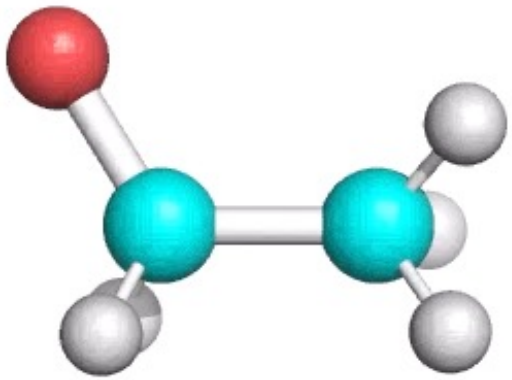


$$\{\boldsymbol{\rho}(t_k)\}_{k=0}^{M} = f[\text{other parameters}]$$

- **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

3D MD

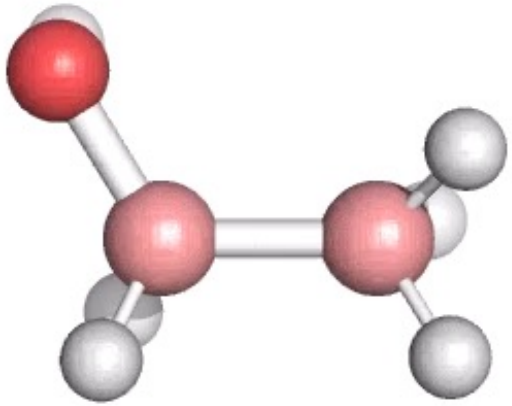


Very slow

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

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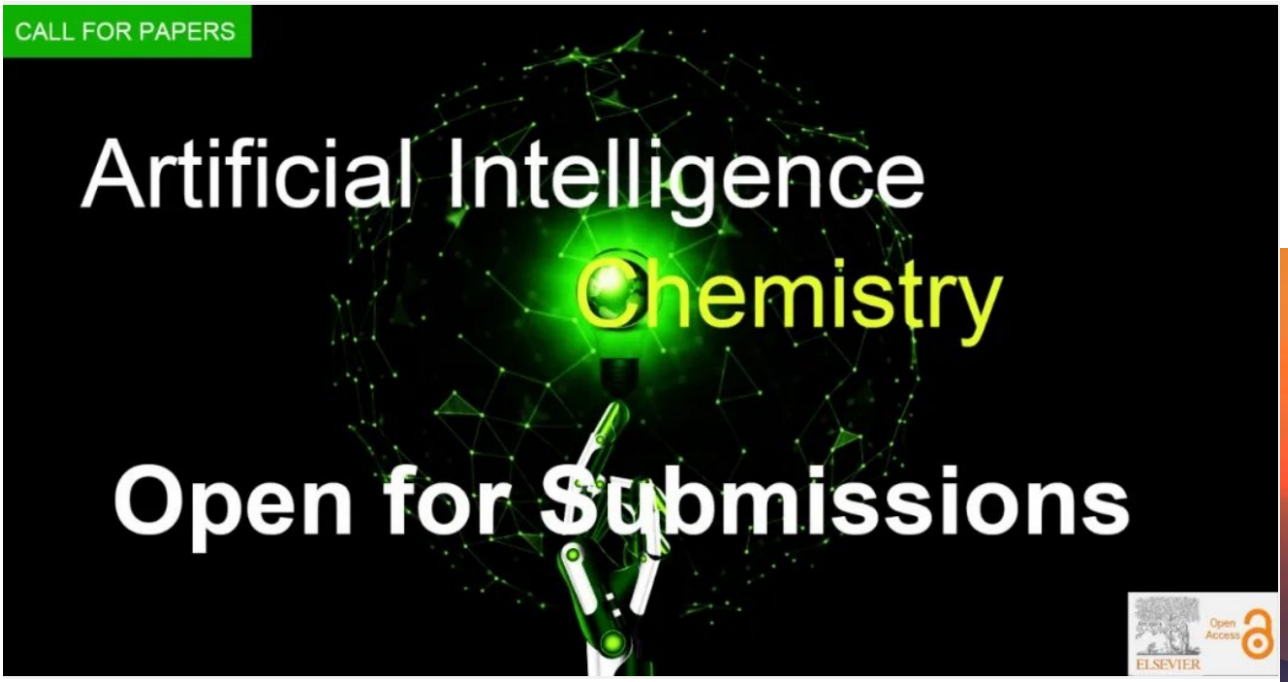

Organizer: Konstantinos Vogiatzis,
University of Tennessee, US