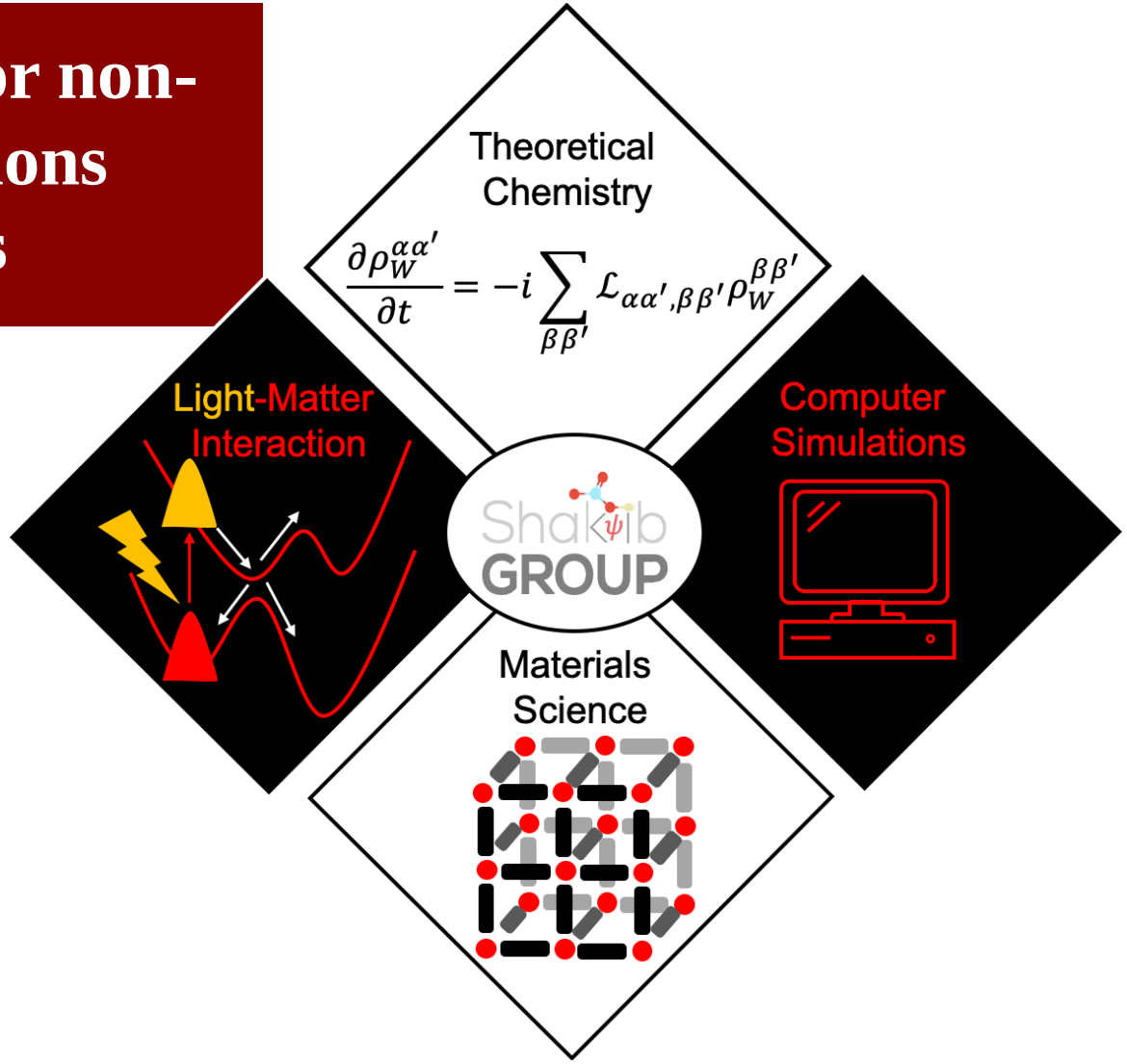
New Jersey Institute of Technology

Development of methods and software for non-adiabatic quantum dynamics simulations subject to nuclear quantum effects



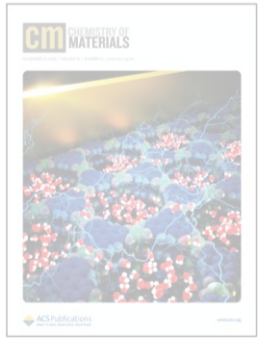
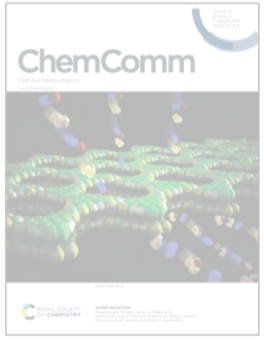
Farnaz A. Shakib

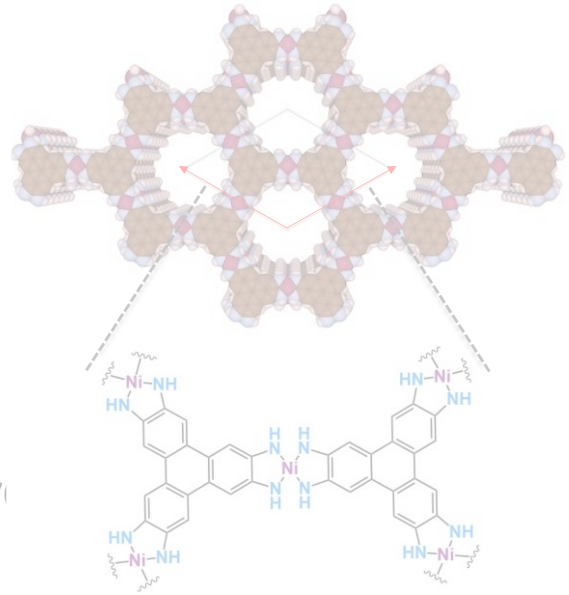
Method Development and Materials Simulations Lab

VISTA seminar series

March 12, 2025

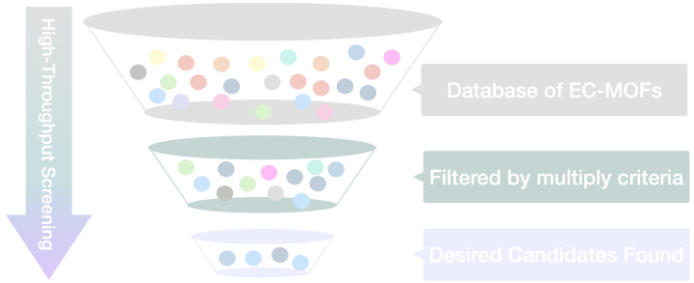
Multifunctional materials: Structure-Function

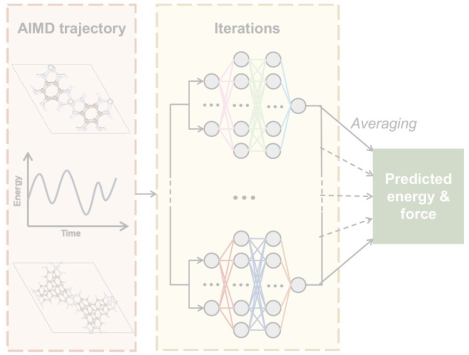





J. Chem. Info. Model. **2023**, *63*, 7097
Chem. Mater. **2022**, *34*, 7730.
J. Chem. Phys. **2022**, *156*, 044109.
ACS Appl. Mater. Interfaces, **2021**, *13*, 2527
APL Matter., **2021**, *9*, 051109.
Chem. Commun., **2021**, *57*, 315

Multifunctional materials: Design & discovery



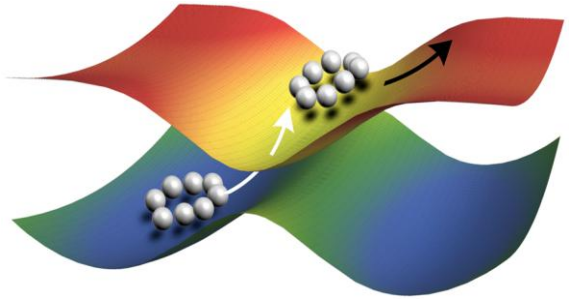


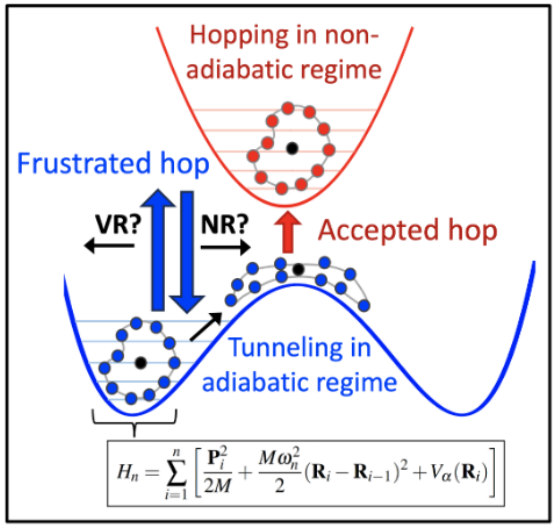
EC-MOFs Database

ACS Appl. Mater. Interfaces, **2025**, *Revisions Requested.*
(Preprint: doi:10.26434/chemrxiv-2024-0mkw8).
J. Phys. Chem. C **2025**, *129*, 2222.
ACS Appl. Mater. Interfaces **2023**, *15*, 9494.

Non-adiabatic quantum dynamics

Ring Polymer Surface Hopping





J. Phys. Chem. Lett. **2023**, *14*, 8658.
Phys. Chem. Chem. Phys., **2021**, *23*, 3135.
J. Phys. Chem. Lett. **2017**, *8*, 3073.

Software development

DLPOLY QUANTUM

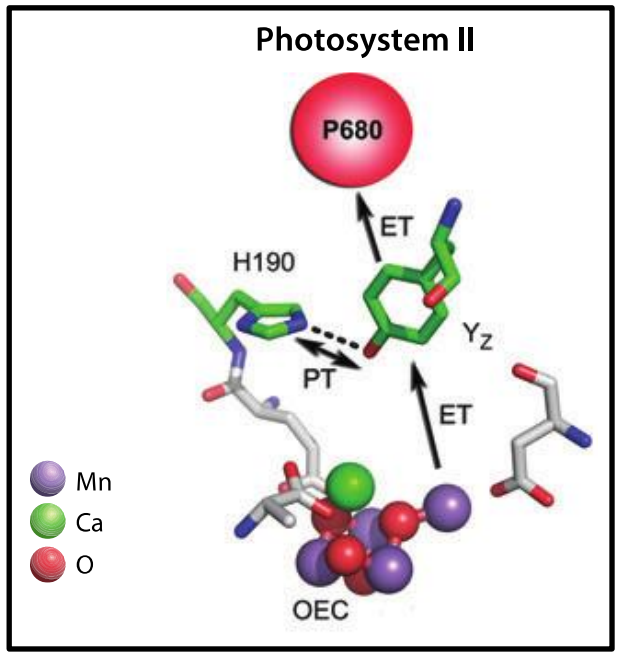
Large-scale molecular dynamics simulations subject to nuclear quantum effects

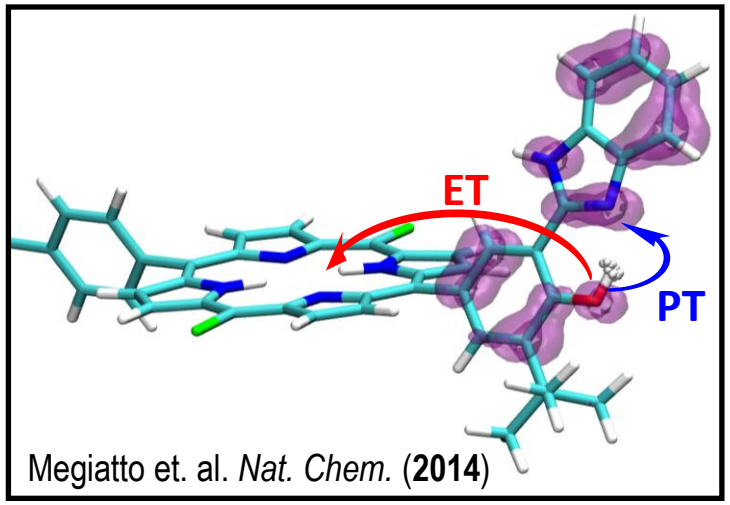
SH|a⟩RP

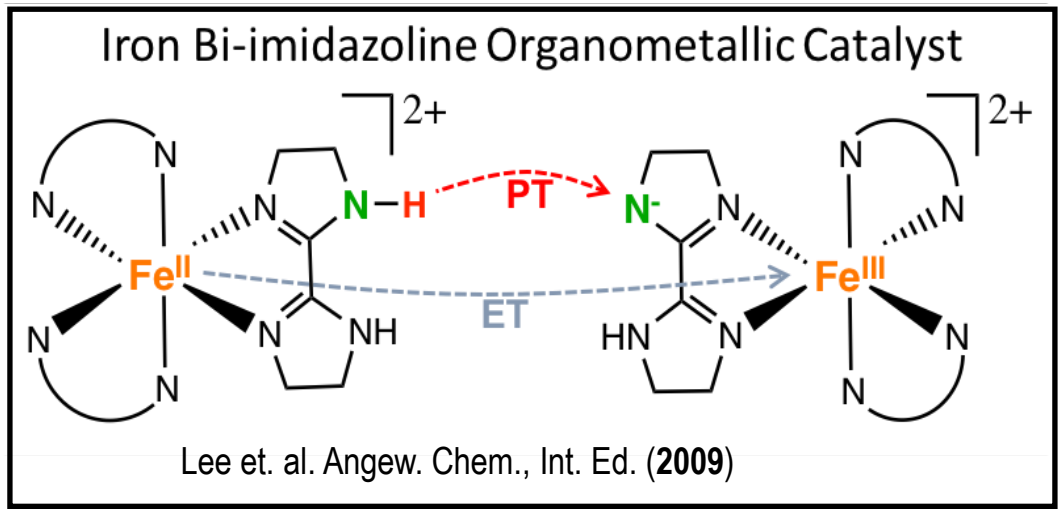
Non-adiabatic quantum dynamics simulations subject to electronic and nuclear quantum effects

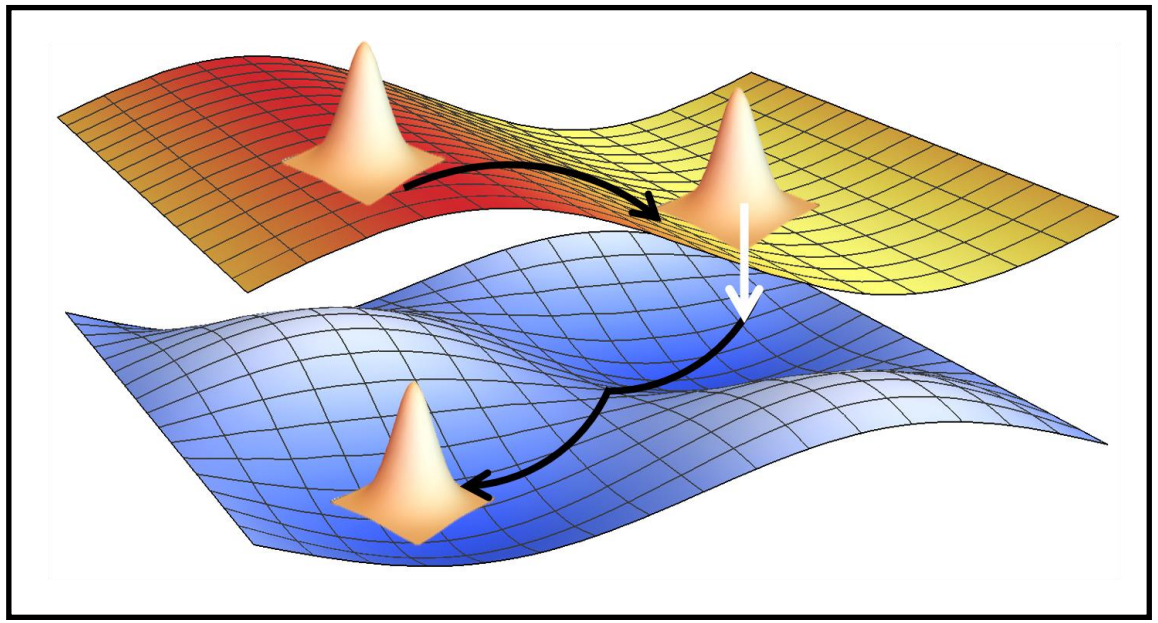
J. Phys. Chem. A **2025**, *Invited Software Paper*.
J. Chem. Phys. **2024**, *160*, 132501.
Software Impacts **2024**, *19*, 100604.

Incorporating NQEs into non-adiabatic quantum dynamics









Path Integral Molecular Dynamics

Path integral formalism: $Z = \mathrm{Tr}\, e^{-\beta \hat{H}} \approx \lim_{n\to\infty} \int dr_1 dr_2 \ldots dr_n \exp[-\beta V_{\mathrm{eff}}(r_1, r_2, \ldots, r_n)]$

$$V_{\mathrm{eff}} = \sum_{i=1}^{n} \left[\frac{nm}{2\beta^2\hbar^2} (r_{i+1} - r_i)^2 + \frac{1}{n} V(r_i) \right]$$

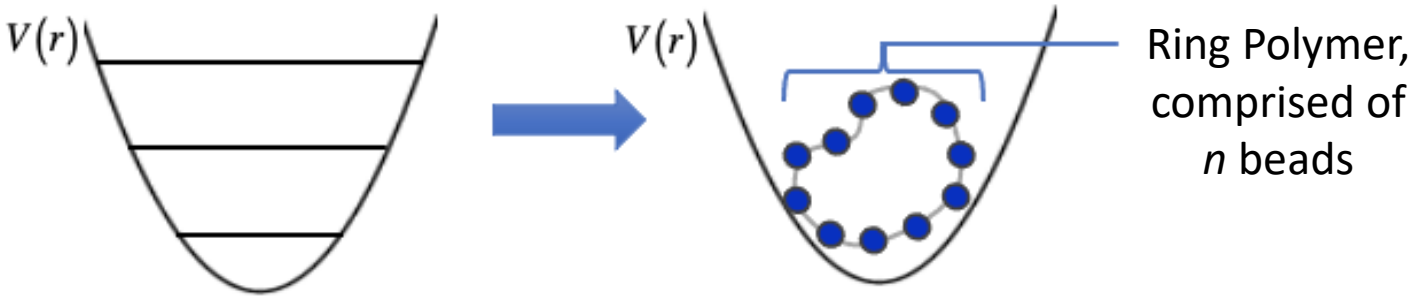
A finite value of n

$$\omega = \frac{\sqrt{n}}{\beta\hbar}$$

$$V_{\mathrm{eff}} = \sum_{i=1}^{n} \left[\frac{1}{2} m\omega^2 (r_{i+1} - r_i)^2 + \frac{1}{n} V(r_i) \right]$$

Remnants of kinetic energy operator

Quantum – Classical Isomorphism



Ring Polymer, comprised of *n* beads

Quantum Mechanics

Classical Mechanics

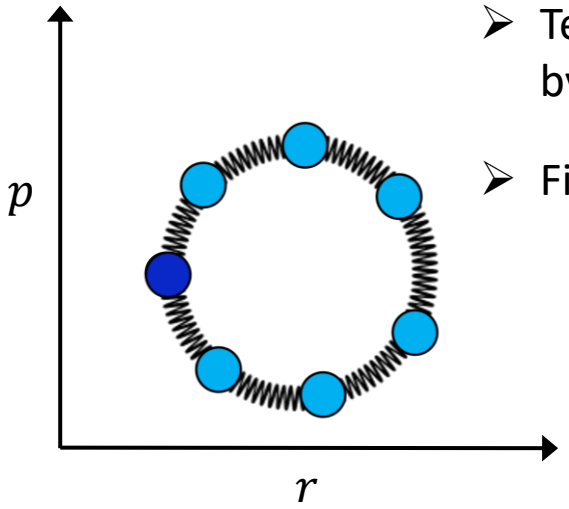
Insertion of a fictitious kinetic energy

$$H_n(r,p) = \sum_{i=1}^{n} \left[\frac{p_i^2}{2m'} + \frac{1}{2} m\omega^2 (r_{i+1} - r_i)^2 + \frac{1}{n} V(r_i) \right]$$

M. Parrinello, A. Rahman, *J. Chem. Phys.*, **1984**, *80*, 860.

Ring Polymer Molecular Dynamics

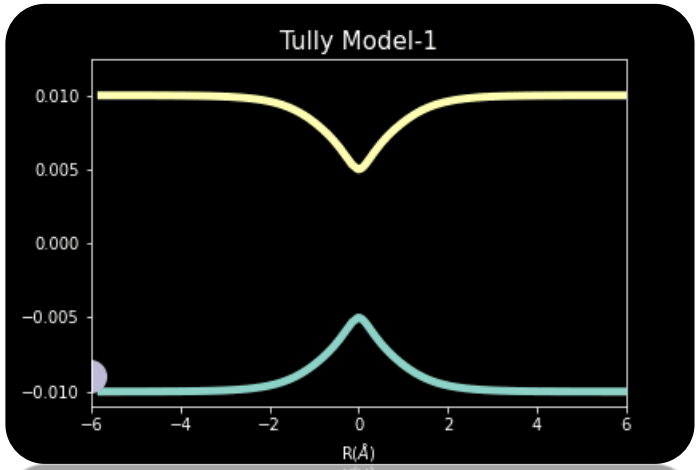
PIMD[1]

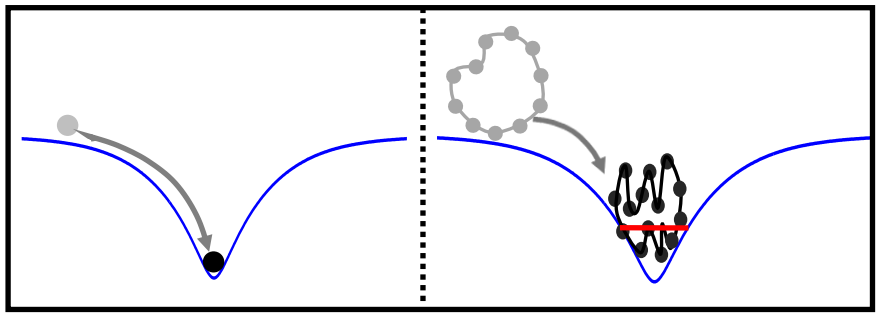


- Temperature controlled by a thermostat (N,V,T)
- Fictitious mass

RPMD[2]

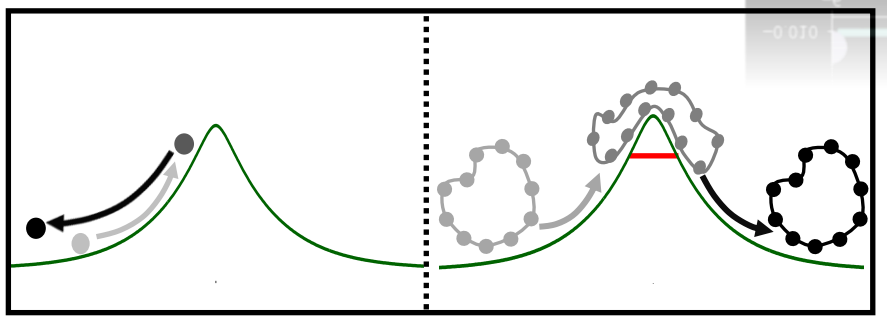
- No thermostat (N,V,E)
- Real mass





Zero-point energy

$$\overline{V} = \frac{1}{n}\sum_{i=0}^{n} V_i$$

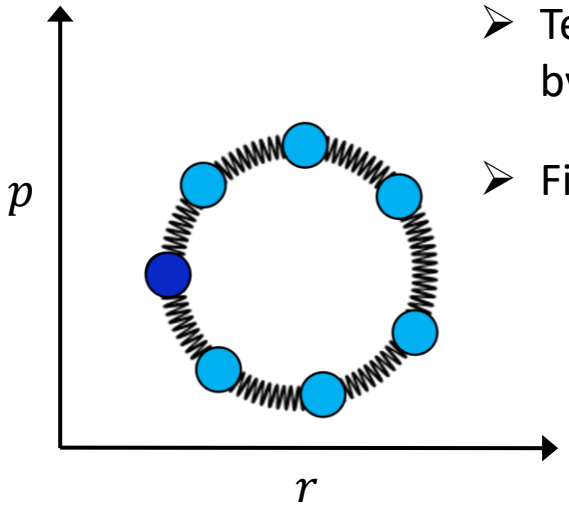


Quantum tunneling

[1]M. Parrinello, A. Rahman, *J. Chem. Phys.*, **1984**, *80*, 860. [2]I.R. Craig, D.E. Manolopoulos, *J. Chem. Phys.*, **2004**, *121*, 3368.

Ring Polymer Molecular Dynamics

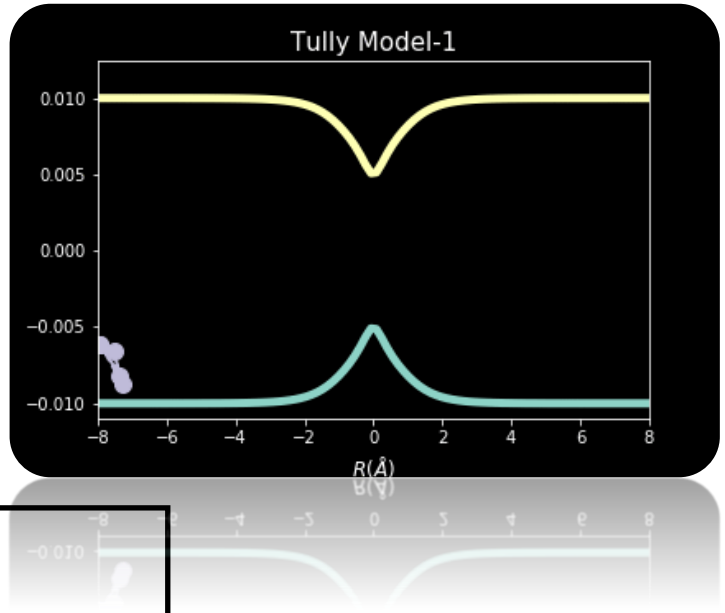
PIMD[1]

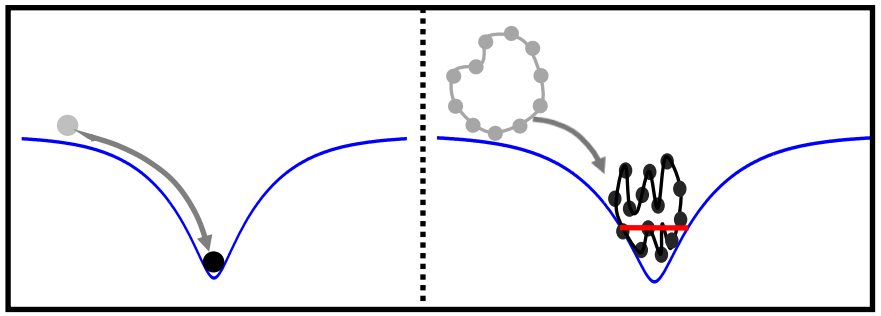


- Temperature controlled by a thermostat (N,V,T)
- Fictitious mass

RPMD[2]

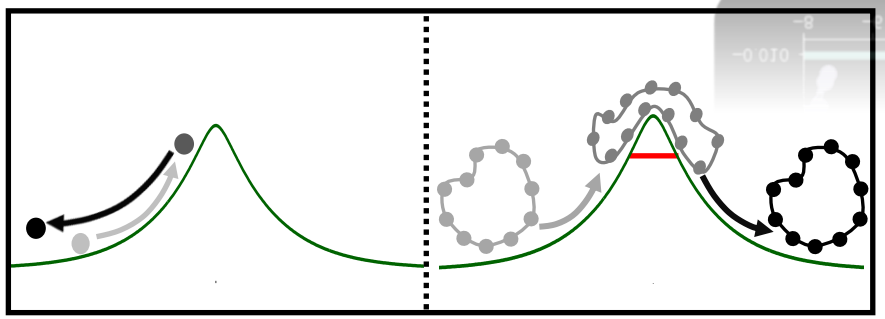
- No thermostat (N,V,E)
- Real mass





Zero-point energy

$$\overline{V} = \frac{1}{n}\sum_{i=0}^{n} V_i$$



Quantum tunneling

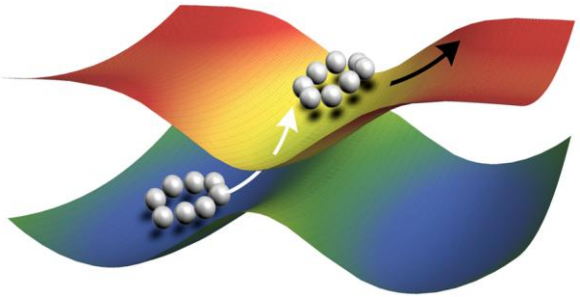
[1]M. Parrinello, A. Rahman, *J. Chem. Phys.*, **1984**, *80*, 860. [2]I.R. Craig, D.E. Manolopoulos, *J. Chem. Phys.*, **2004**, *121*, 3368.

Trajectory-based nonadiabatic dynamics

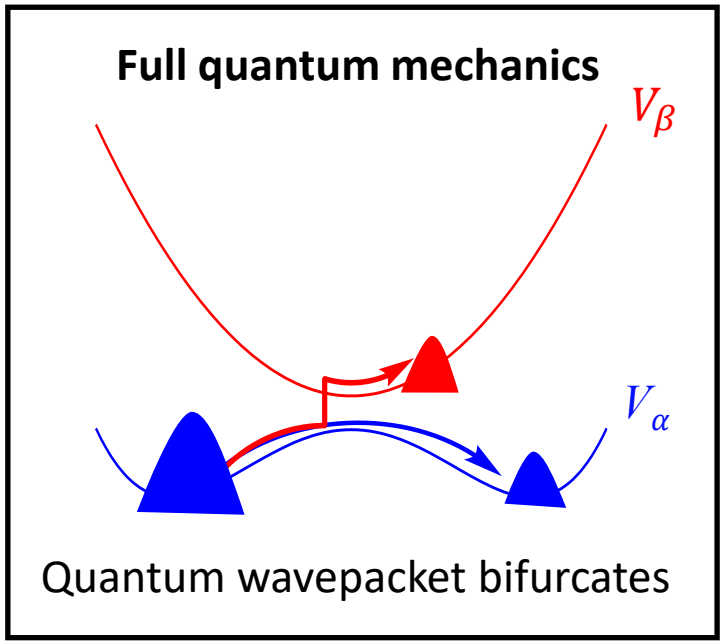
John Tully

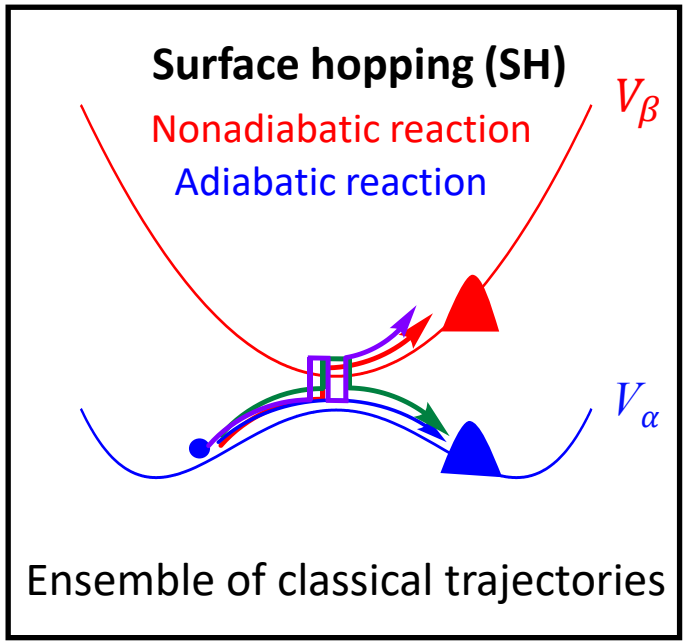
1990: Fewest-Switches Surface Hopping (FSSH)

2012: Ring polymer surface hopping (RPSH)



Adiabatic potential energy surface





$$i\hbar\dot{c}_\alpha(t) = V_\alpha(\mathbf{R})c_\alpha(t) - i\hbar\sum_\beta \dot{\mathbf{R}}\cdot\mathbf{d}_{\alpha\beta}(\mathbf{R})c_\beta(t)$$

Nonadiabatic coupling vector

Probability of non-adiabatic transition

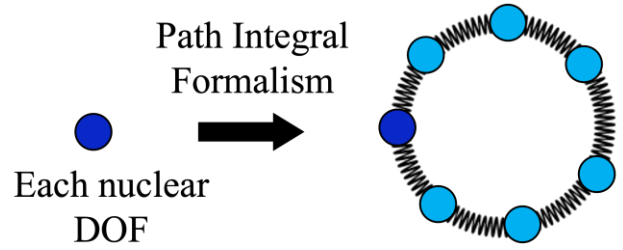
$$g_{\alpha\beta} = \frac{-2\mathrm{Re}(\rho^*_{\beta\alpha}\dot{\mathbf{R}}\cdot\mathbf{d}_{\beta\alpha}(\mathbf{R}))\,\Delta t}{\rho_{\alpha\alpha}} > \xi$$

- ✓ Stochastic, phenomenological methodology
- ✓ Ease of implementation, good convergence
- ✓ Good results in many applications

- ❖ Overcoherence problem
- ❖ Neglect of Nuclear Quantum Effects (NQEs)

Mainstream non-adiabatic dynamics methodology

Ring Polymer Surface Hopping (RPSH) dynamics



$$H_n = \sum_{i=1}^{n}\left[\frac{\mathbf{P}_i^2}{2M} + \frac{M\omega_n^2}{2}(\mathbf{R}_i - \mathbf{R}_{i-1})^2 + V_\alpha(\mathbf{R}_i)\right]$$

Propagation

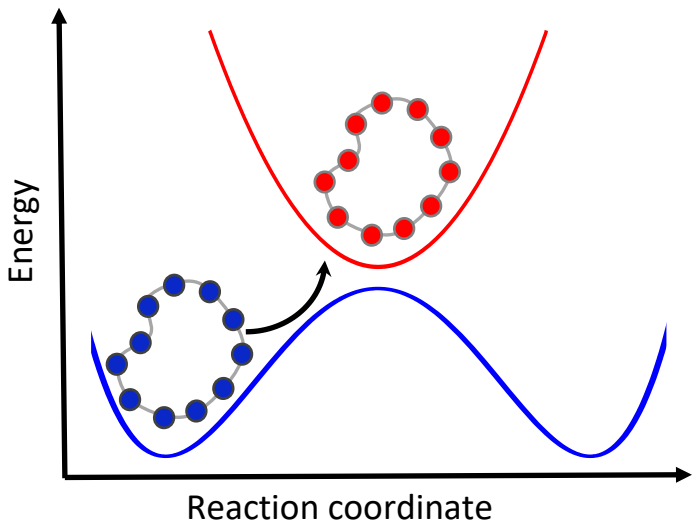
$$\bar{\mathbf{R}} = \frac{1}{n}\sum_{i=1}^{n}\mathbf{R}_i \qquad \bar{\mathbf{P}} = \frac{1}{n}\sum_{i=1}^{n}\mathbf{P}_i$$

Solving TDSE

$$i\hbar\dot{c}_\alpha(t) = V_\alpha(\bar{\mathbf{R}})c_\alpha(t) - i\hbar\sum_\beta \dot{\bar{\mathbf{R}}}\cdot\mathbf{d}_{\alpha\beta}(\bar{\mathbf{R}})c_\beta(t)$$

Non-adiabatic transitions

$$g_{\alpha\beta} = \frac{-2\mathrm{Re}(\rho^*_{\beta\alpha}\dot{\bar{\mathbf{R}}}\cdot\mathbf{d}_{\beta\alpha}(\bar{\mathbf{R}}))\Delta t}{\rho_{\alpha\alpha}} > \xi$$



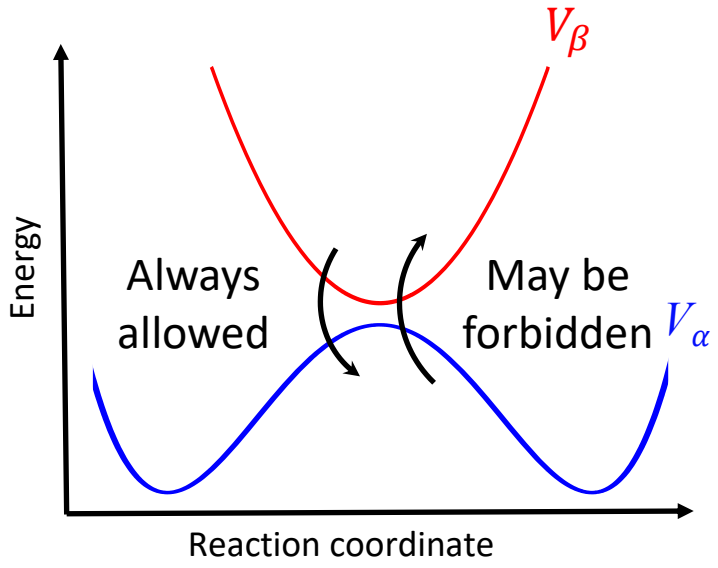
RPSH conserves quantum plus classical energy

Velocity of each bead is re-scaled along the direction of the centroid non-adiabatic coupling vector:

$$\dot{\mathbf{R}}_i' = \dot{\mathbf{R}}_i - \lambda_{\alpha\beta}\mathbf{d}_{\alpha\beta}(\bar{\mathbf{R}})/M$$

FAS; Huo, P. *J. Phys. Chem. Lett.* **2017**, *8*, 3073.
Shushkov, P.; Li, R.; Tully, J.C. *J. Chem. Phys.* **2012**, *137*, 22A549.

Frustrated hops in RPSH



$$V_{new} + K_{new} = V_{old} + K_{old}$$

Frustrated hops

How should be treated?

1. Reverse the velocity.[1]

2. Not reverse the velocity.[2]

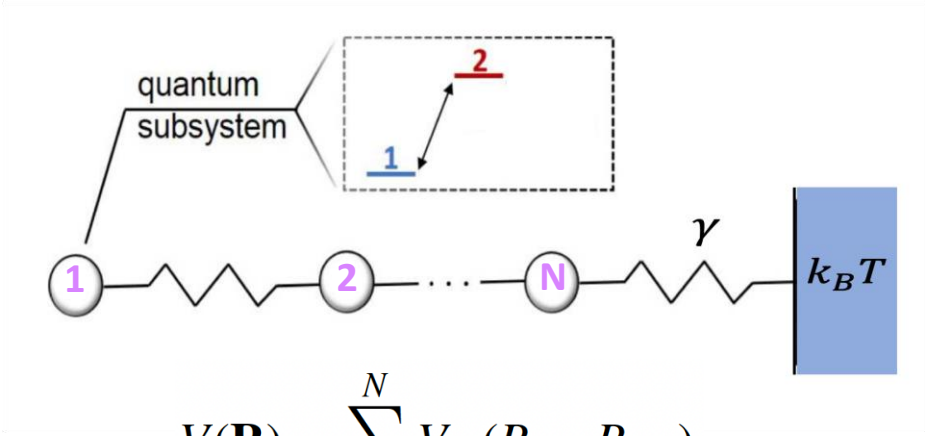
3. Make a decision on reversing or not reversing based on the force that the classical particle feels from the final states.[3,4]

Dr. Dil Limbu

Effect of proper treatment of frustrated hops in reproducing correct quantum Boltzmann populations in RPSH

[1]Tully, J.C. *J. Chem. Phys*. **1990**, *93*, 1061. [2]Müller, U.; Stock, G. *J. Chem. Phys.* **1997**, *107*, 6230. [3]Jasper, A.W.; Truhlar, D.G. *Chem. Phys. Lett.* **2003,** *369*, 60. [4]Jain, A.; Subotnik, J.E. *J. Chem. Phys.* **2015**,143, 134107.

Quantum Boltzmann distribution

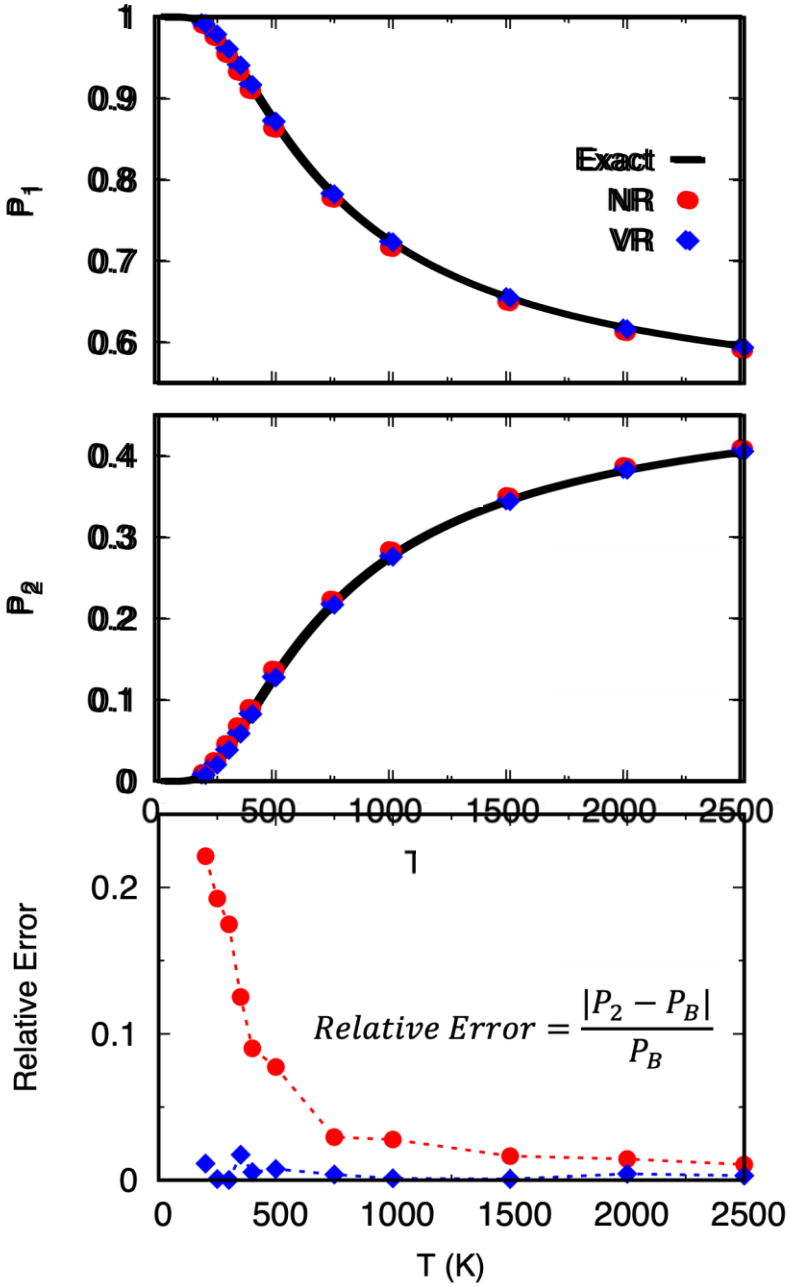


$$V(\mathbf{R}) = \sum_{i=1}^{N} V_M(R_i - R_{i+1})$$

$$V_M(R) = V_0(a^2R^2 - a^3R^3 + 0.58a^4R^4)$$

Followed the recipe for Thermostatted RPMD[2]:

$$\dot{P}_N^{(k)} = -\frac{\partial V}{\partial R_N^{(k)}} - \gamma^{(k)} P_N^{(k)} + \sqrt{\frac{2M\gamma^{(k)}}{\beta_n}}\xi^{(k)}(t)$$



[1]Limbu, D.K.; **FAS** *J. Phys. Chem. Lett.* **2023**, *14*, 8658.
[2]Rossi, M.; Ceriotti, M.; Manolopoulos, D.E. *J. Chem. Phys.* **2014,** *140*, 234116.

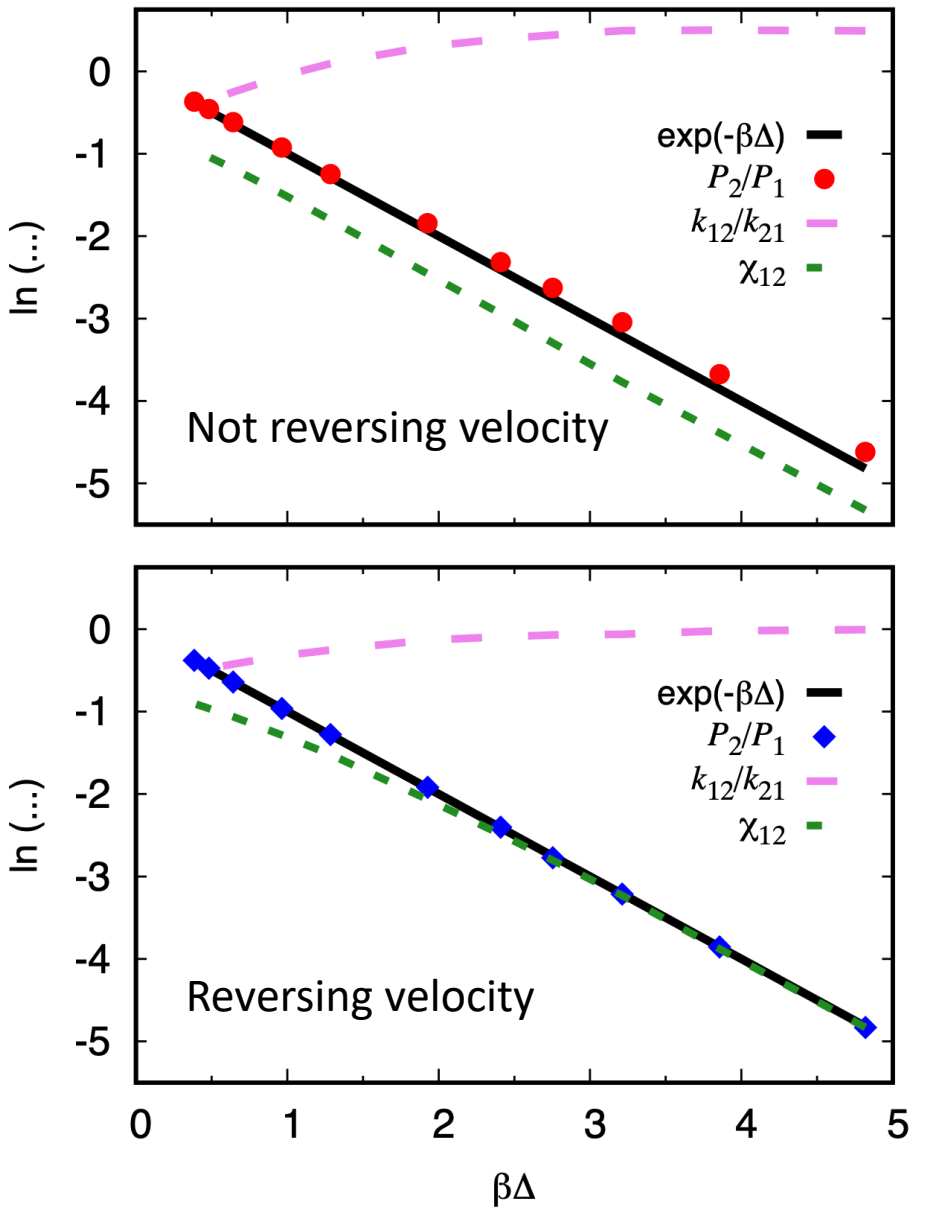
Quantum Boltzmann distribution

Quantum Boltzmann populations are preserved if:

(1) Ratio of attempted upward and downward transitions ($k_{\alpha\beta}/k_{\beta\alpha}$) is to unity.

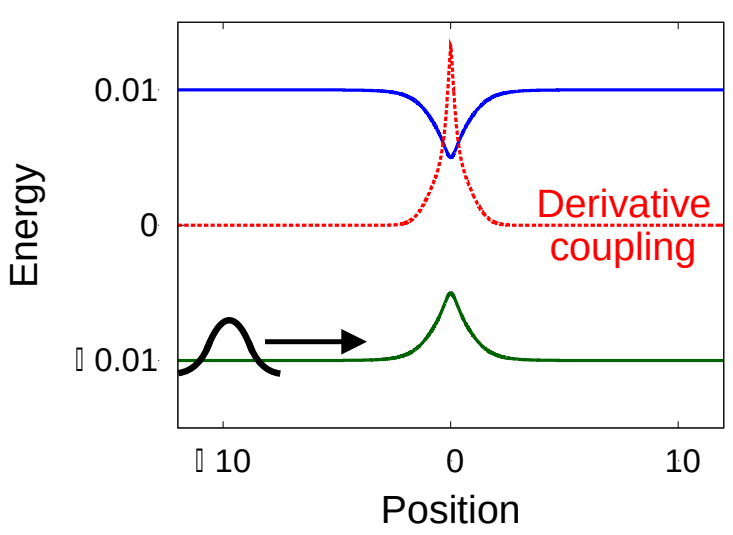
(2) Fraction of accepted upward hops ($\chi_{\alpha\beta}$) is equal to Boltzmann factor $\exp(-\beta\Delta)$.

Q: Does it have an adverse effect on the dynamics?



Frustrated hops in RPSH dynamics

Tully model I: Single avoided crossing

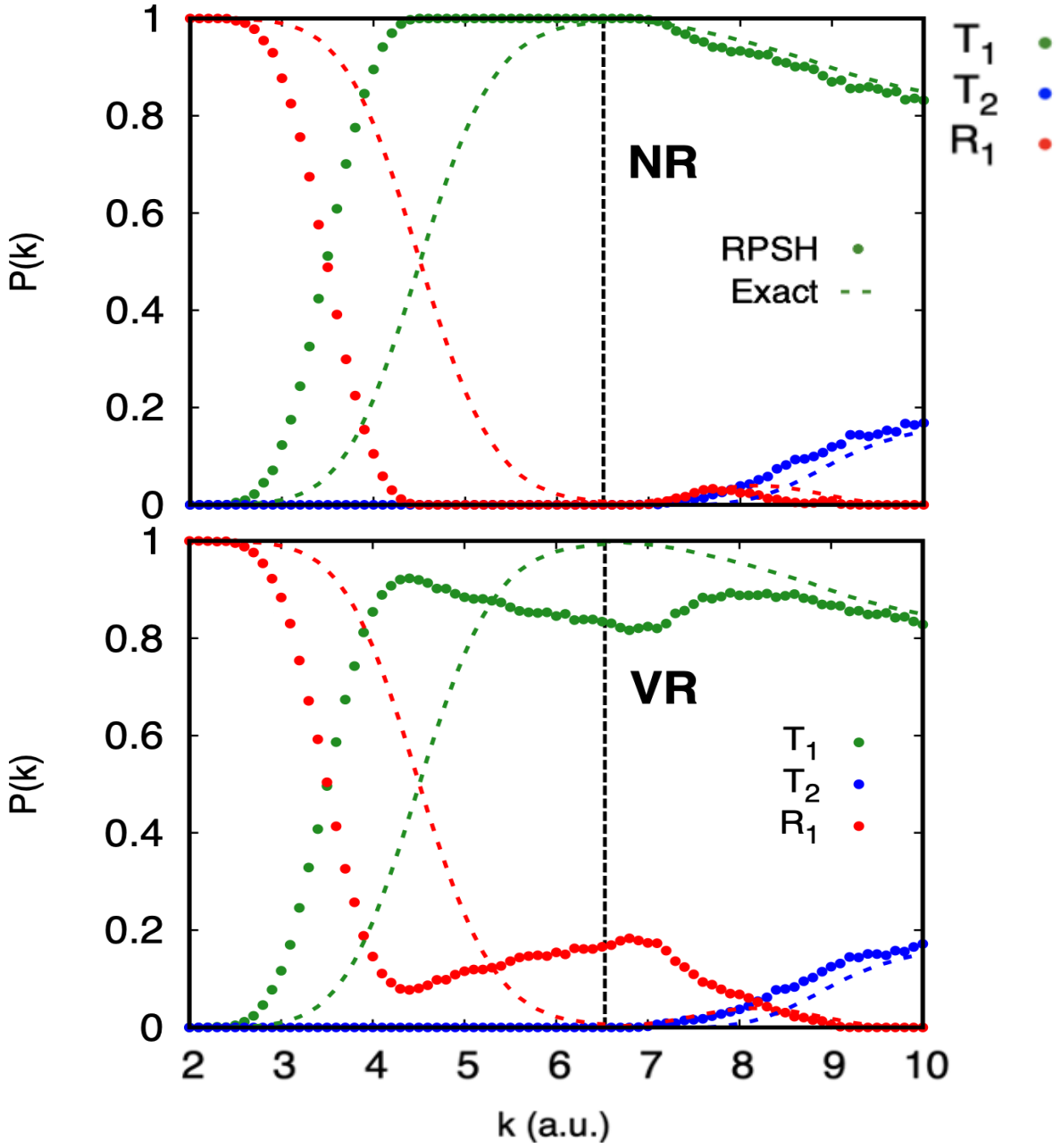


Deterministic momentum

Branching probabilities as a function of initial nuclear momentum

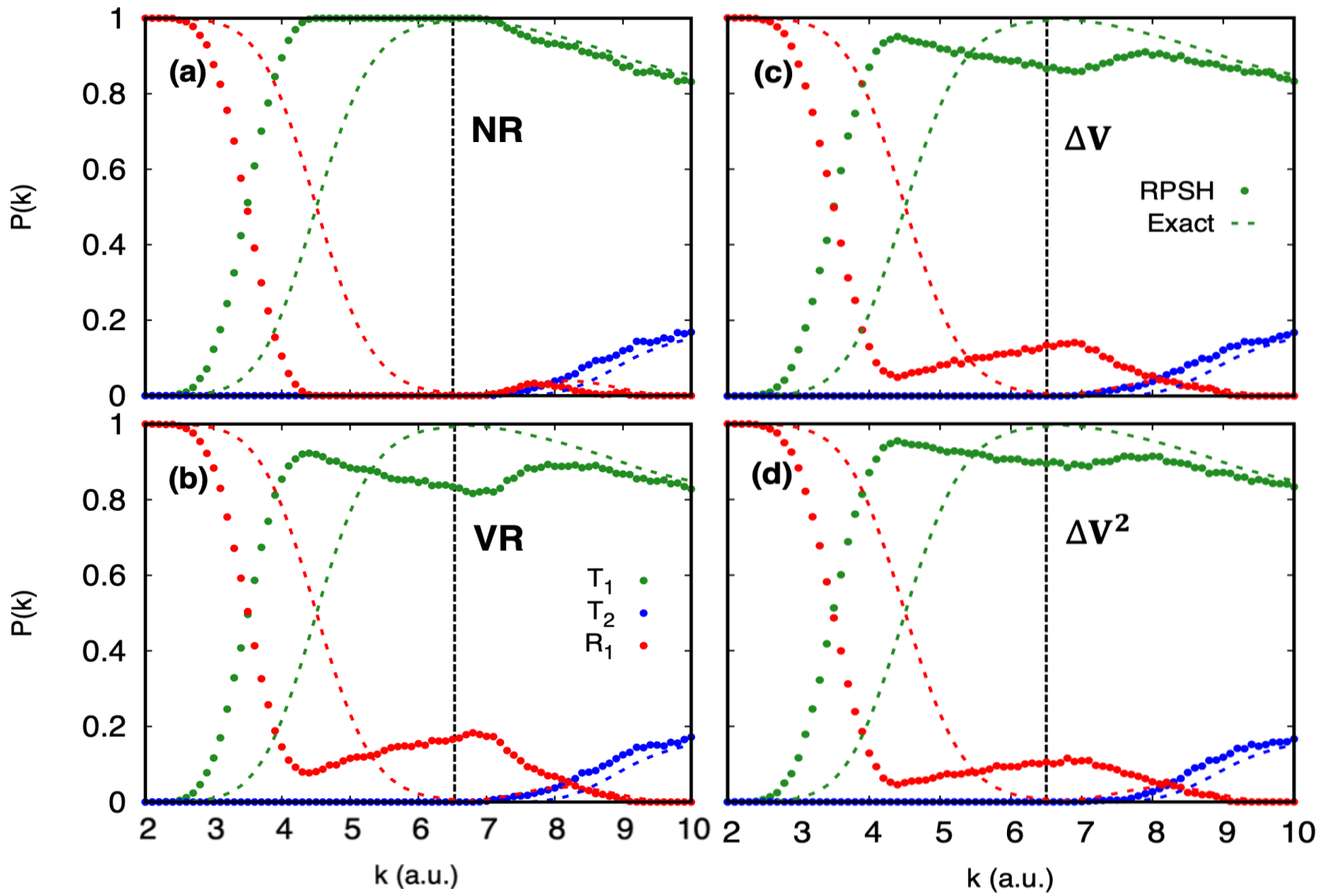
T1/R1: transmission/reflection on state 1

T2/R2: transmission/reflection on state 2



FAS; Huo, P. *J. Phys. Chem. Lett.* **2017**, *8*, 3073.
Limbu, D.K.; **FAS** *J. Phys. Chem. Lett.* **2023**, *14*, 8658.

Frustrated hops in RPSH dynamics



Limbu, D.K.; **FAS** *J. Phys. Chem. Lett.* **2023**, *14*, 8658.
Jasper, A.W.; Truhlar, D.G. *Chem. Phys. Lett.* **2003,** *369*, 60. Jain, A.; Subotnik, J.E. *J. Chem. Phys.* **2015**,143, 134107.

SHARP pack software package

SH|a⟩RP

- RPSH is available to public in the context of a **modular software package**, SHARP pack

  https://github.com/SoftwareImpacts/SIMPAC-2023-481

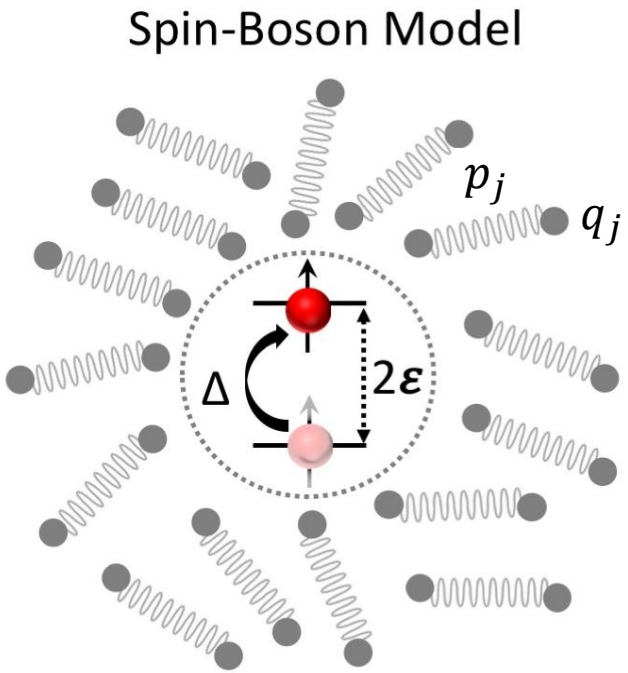
- Developed in Fortran 90.
- A flexible and user-friendly input/output handling system
- Comes with a variety of built-in models for method benchmarking.
- The modular architecture enhances the software's flexibility and adaptability, enabling integration of new methodologies or models.

```
################################
#SHARP PACK INPUT PARAMETERS
################################
model           tully1
nParticle       1
nbeads          4
nsteps          3000
ntraj           10000
ncpu            1
timestep        1.0
kinitial        30.0
beadpos         'gaussian'
vinitial        'fixed'
vreverse        'never'
vrescale        'centroid'
usrkval         'No'
acckval         'No'
rundtail        'No'
iprint          10
finish
################################
```

Limbu, D.K.; **FAS** *Software Impacts.* **2024**, *19*, 100604.

Fleshing out the method: Condensed-phase non-adiabatic dynamics

Spin-boson model is a widely used system to benchmark simulation methods for non-adiabatic dynamics in the condensed phases.



Total Hamiltonian: $H = H_s + H_b + H_{sb}$

$$H_s = \epsilon\sigma_z + \Delta\sigma_x = \begin{pmatrix} \epsilon & \Delta \\ \Delta & -\epsilon \end{pmatrix}$$

$$H_b = \sum_j \frac{1}{2}\left(p_j^2 + \omega_j^2 q_j^2\right)$$

$$H_{sb} = \sigma_z \sum_j c_j q_j = \begin{pmatrix} \sum_j c_j q_j & 0 \\ 0 & -\sum_j c_j q_j \end{pmatrix}$$

The influence of the bath on the dynamics of the system can be captured in the compact form of a spectral density.

Reorganization energy

Deby spectral density: $J(\omega) = \frac{E_r}{2}\frac{\omega\omega_c}{\omega^2 + \omega_c^2}$

Sandip Bhusal

Diana Bagatella

Bhusal, S.; Limbu, D.K.; Castaneda-Bagatella, D.; **FAS** *In preparation* **2025**.

Spin-boson model: Benchmarking RPSH at low temperature limit

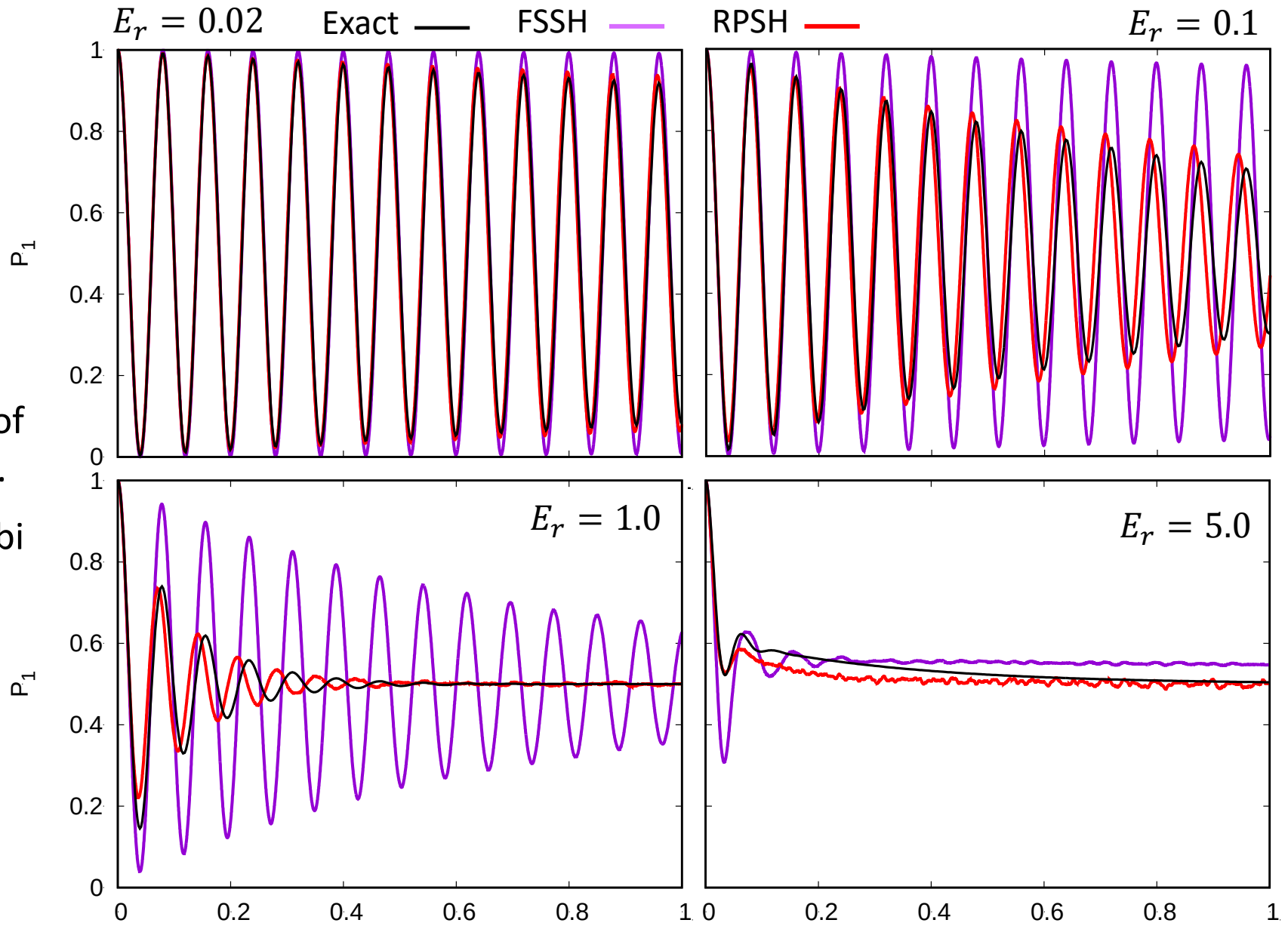
- High diabatic coupling, $\Delta = 1.0$ (in reference unit of 208.5 cm^{-1})
- No energy bias between electronic donor and acceptor, $\epsilon = 0.0$

Increasing number of beads:

(1) Correcting the underestimation of population transfer seen in FSSH.

(2) Deviating from correct Rabi oscillations.

Developing Thermostatted RPSH



Bhusal, S.; Limbu, D.K.; Castaneda-Bagatella, D.; **FAS** *In preparation* **2025**.

Zhu-Nakamura theory of nonadiabatic dynamics

79th VISTA seminar, Nov 13, 2024

- Zhu-Nakamura (ZN) theory of nonadiabatic transitions.
- Probability of nonadiabatic transitions are expressed in simple analytical formula based the shape of PES.
- Applicable to diabatic and adiabatic surfaces.
- It also provides analytical formula for classically forbidden transitions.

Global switching trajectory surface hopping molecular dynamics simulation on on-the-fly TDDFT potential energy surfaces

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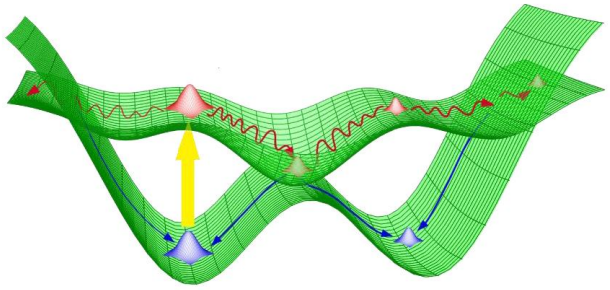
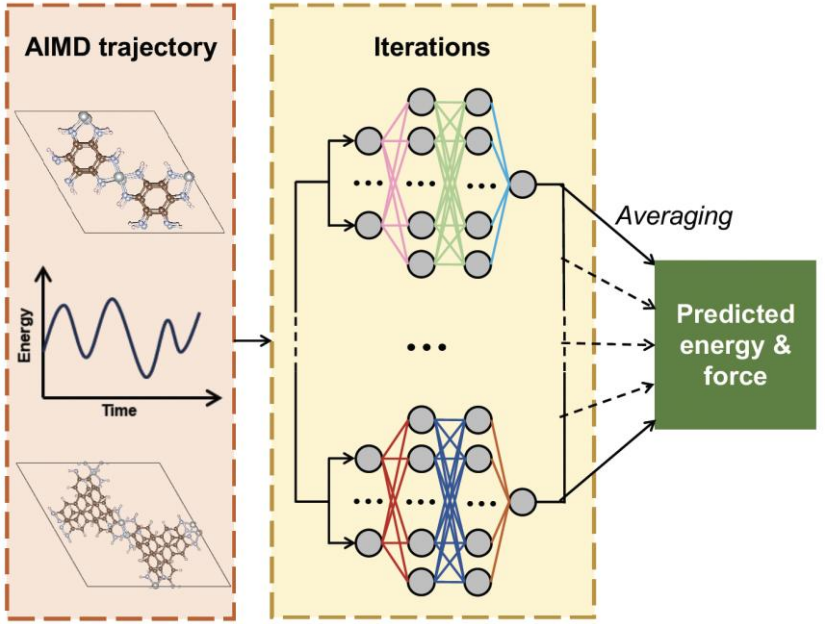


- We expect to see a drastic time-efficiency.
- It will be compatible with the use of machine learning potentials (MLPs) for condensed-phase simulations.
- We have recently developed the first MLP for 2D electrically conductive metal-organic frameworks.



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