VISTA Seminar, 2024

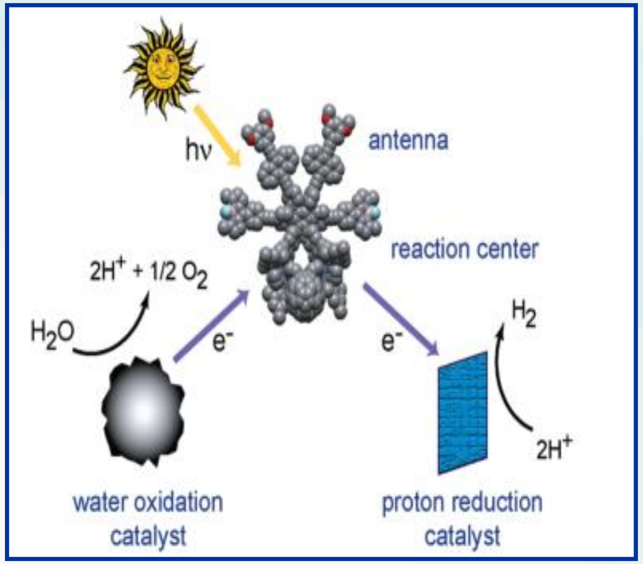
Nonadiabatic Dynamics and Machine Learning

Zhenggang Lan

2024.02

South China Normal University

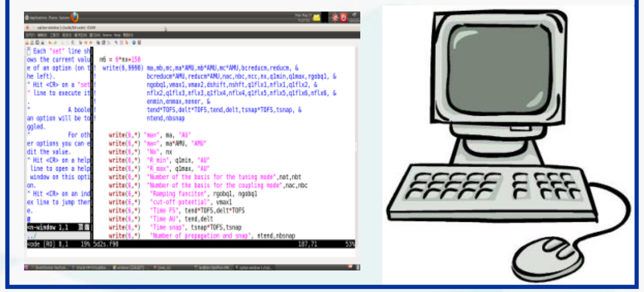
Introduction

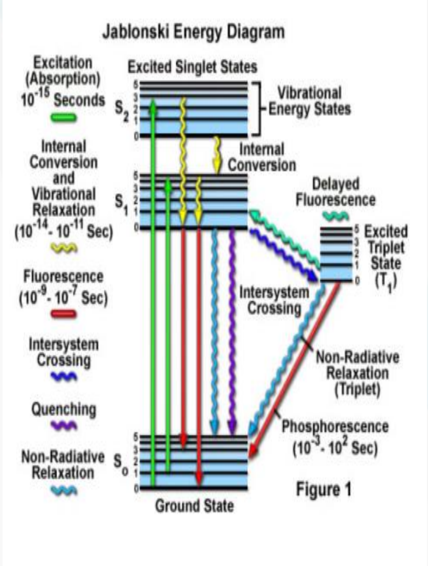


?

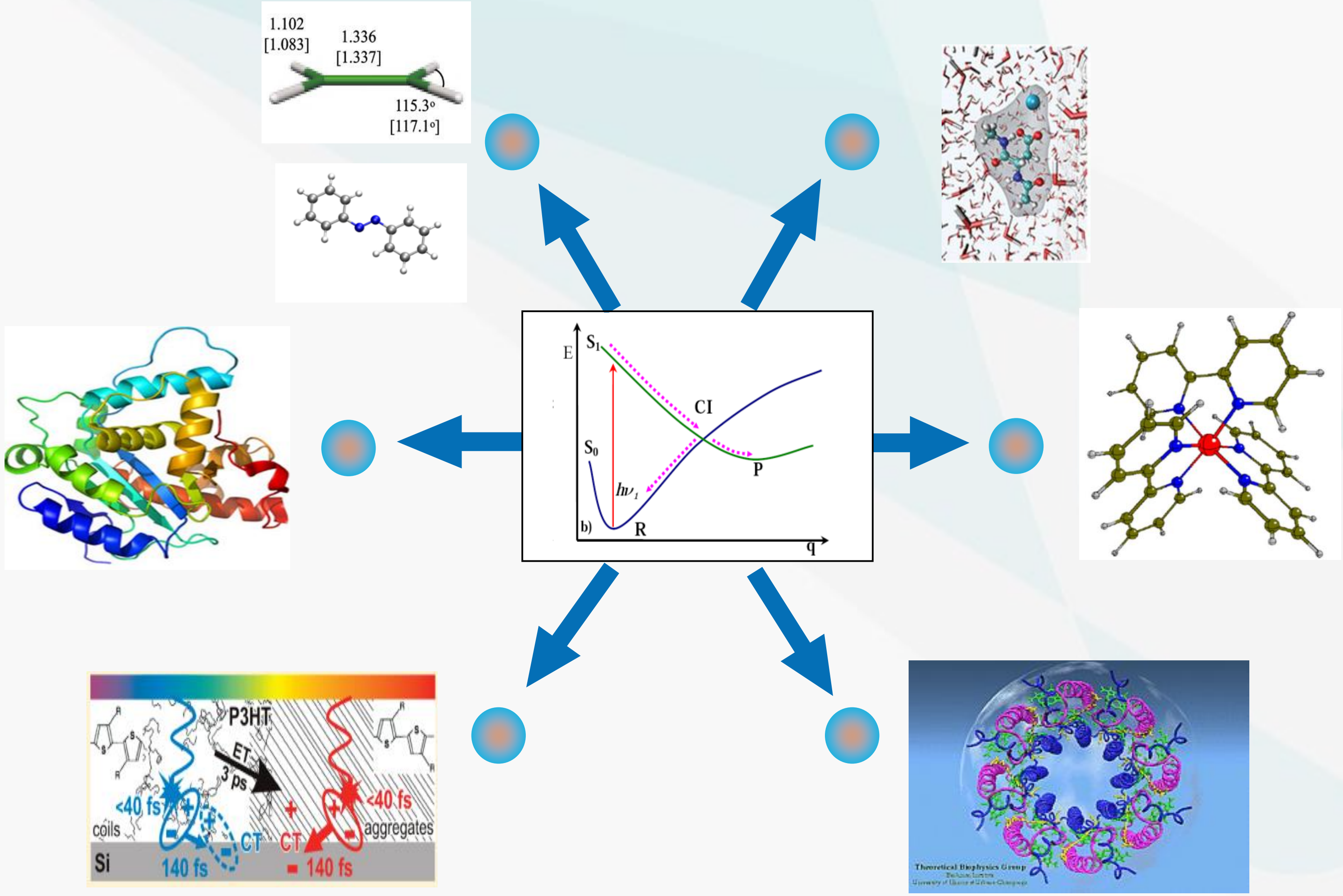
$$H\psi = E\psi, \qquad i\hbar\frac{\partial \psi}{\partial t} = H\psi$$

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}, \qquad \frac{dq_i}{dt} = +\frac{\partial H}{\partial p_i}$$





Nonadiabatic dynamics



- Failure of Born-Oppenheimer approximation
- Complex excited-state electronic wavefunctions
- Complexity in realistic polyatomic systems
- Interpretations of experimental observations

Research highlights

Potential Energy Surfaces

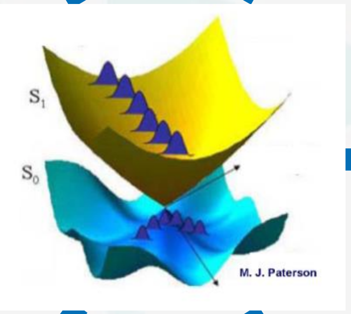
Diabatization

Quantum Wavepacket and Dissipative Dynamics

Time-resolved spectroscopy

Machine Learning

Mixed quantum classical
Quasi-classical
Semiclassical
Dynamics



Nonadiabatic Dynamics Methods

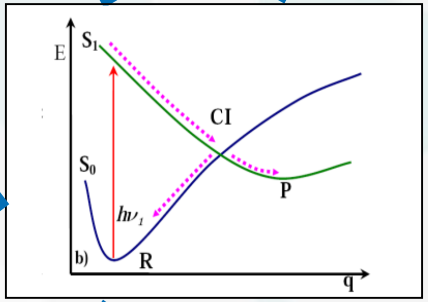
Quantum Dynamics
Quantum Wavepacket
MCTDH, ML-MCTDH
TD-DMRG, Tensor Network

?

Surface Hopping
Tully Fewest Switches
Landau-Zener and Zhu-Nakamura TSH
Exact Factorization
Pechukas' force
Others.

Quantum Dissipative Dynamics
Redfiled
HEOM
Stochastic Wavefunctions

Ehrenfest
Coherent Switching with Decay of Mixing



Bohmian Dynamics

Phase-space Path Branching ...

Gaussian Wavepacket
Multiply Spawning
Multiconfiguational Ehrenfest

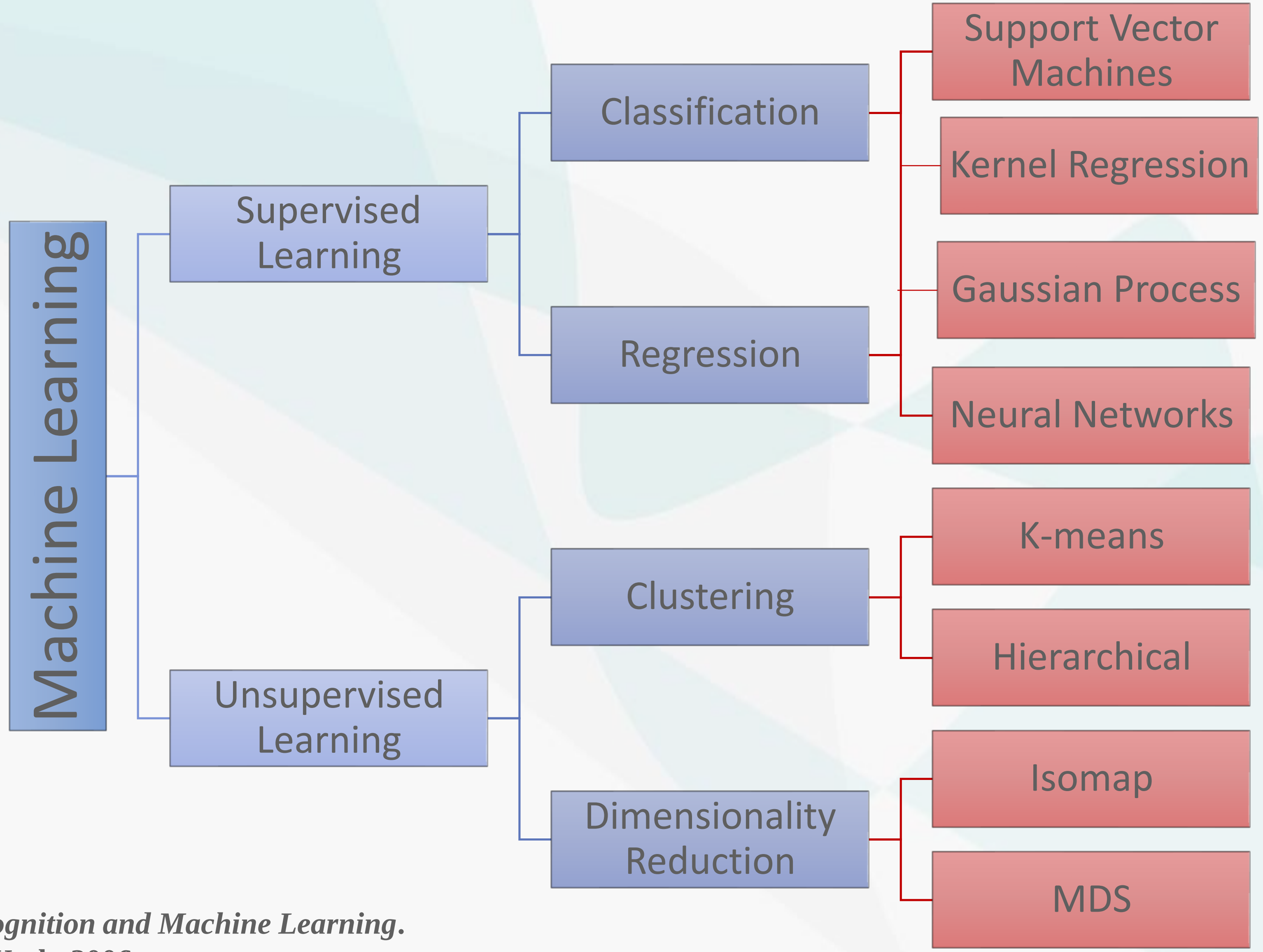
Semiclassical Monte-Carlo

Mapping Hamiltonian
Semiclassical IVR
Quasiclassical Dynamics
Symmetrical Quasi-classical Dynamics

Real time Path Integral

Quantum Classical Liouville Equation

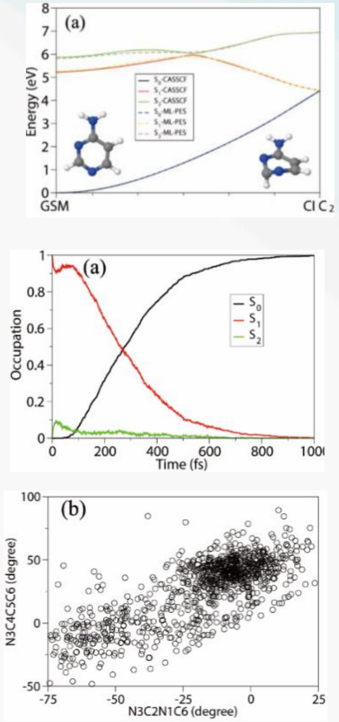
Machine Learning



Bishop, C. *Pattern Recognition and Machine Learning*. Springer-Verlag: New York, 2006.

Nonadiabatic Dynamics and Machine Learning

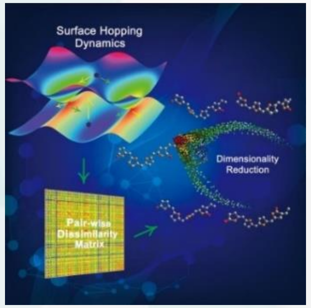
PES Fitting



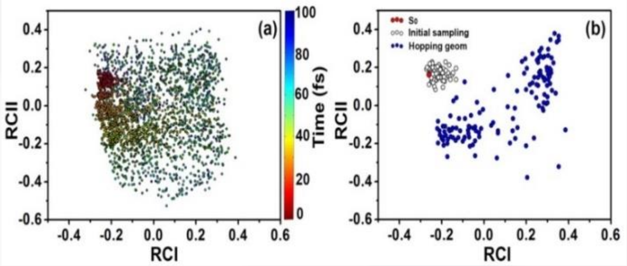
Fast Dynamics

[D. Hu, Z. Lan* et al., ***J. Phys. Chem. Lett.***, 2018, 9, 2725]

Result Analyses



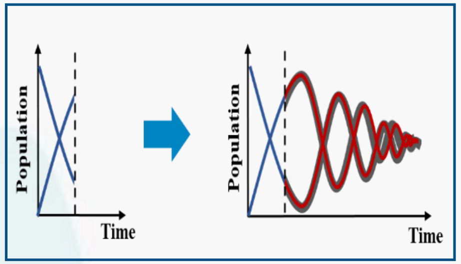
Dimensionality Reduction

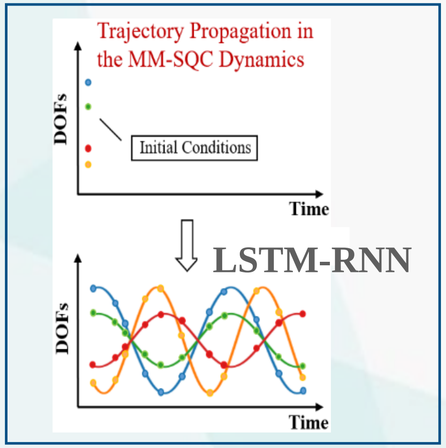


Key Coordinates

[X. Li, Z. Lan* et al., ***J. Chem. Theory Comput.***, 2017, 13, 4611;
X. Li, Z. Lan* et al., ***J. Chem. Phys.***, 2018, 149, 244104;
J. Peng, Z. Lan* et al., ***J. Chem. Phys.***, 2021, 159, 094122;
Y. Zhu, Z. Lan* et al., ***Phys. Chem. Chem. Phys.***, 2022, 24, 24362]

Dynamics Evolution





Direct Solutions

[K. Lin, F.G. Gu*, Z. Lan* et al., ***J. Phys. Chem. Lett.***, 2021, 12, 10225;
K. Lin, F.G. Gu*, Z. Lan* et al., ***J. Phys. Chem. Lett.***, 2022, 13, 11678;
K. Lin, F.G. Gu*, Z. Lan* et al., ***J. Chem. Theory Comput.***, 2022, 18, 5837]

Open Quantum Systems

Open Quantum System $H = H_S + H_B + H_{SB}$

Environment

Hamiltonian H_B

System state ρ_B

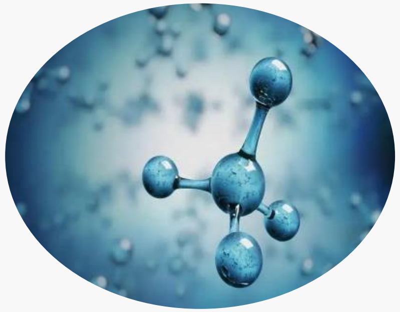
Interaction

H_{SB}

Open System

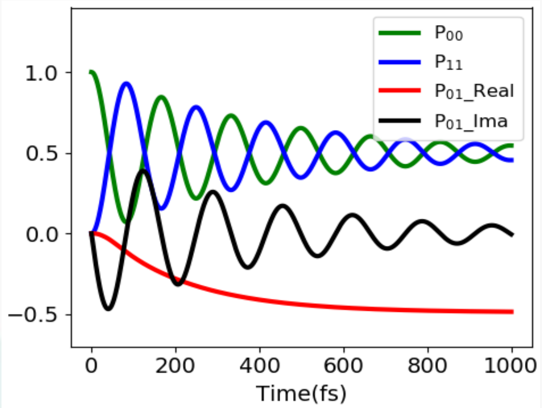
Hamiltonian H_S

System state ρ_S



[***Science*****,** 344, 1001-1005 (2014)] [***Phys. Rep.*****,** 567, 1-78 (2015)]

System-plus-Bath Hamiltonian



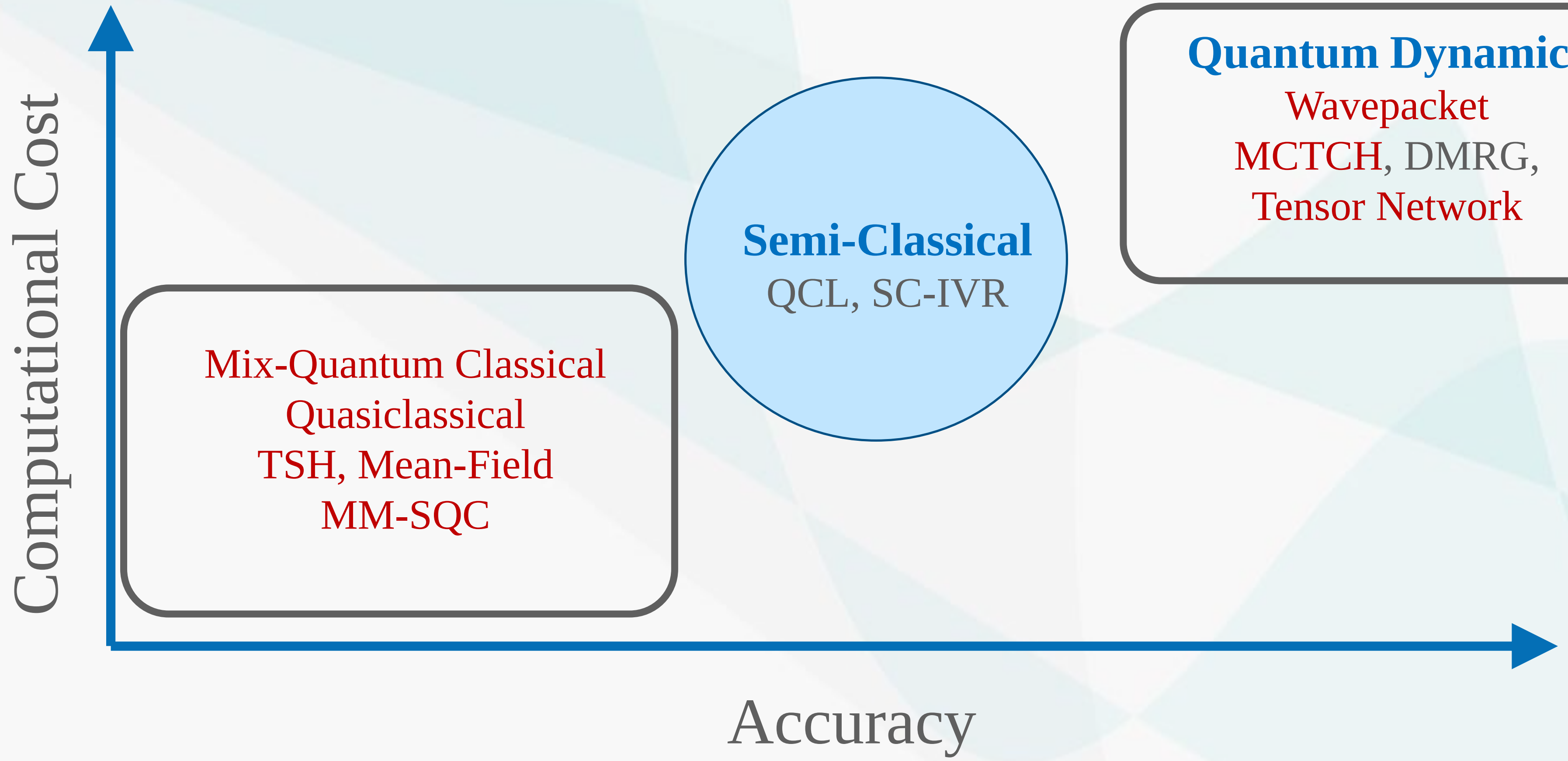
$$H = H_S + H_B + H_{SB}$$

$$H_S = \sum_{k=1}^{2} |\varphi_k\rangle V_{kk} \langle\varphi_k| + \sum_{k\neq l} |\varphi_k\rangle V_{kl} \langle\varphi_k|,$$

$$H_B = \sum_{k=1}^{2} \sum_{j}^{N_b} \frac{1}{2} \omega_{kj} (Q_{kj}^2 + P_{kj}^2),$$

$$H_{SB} = \sum_{k=1}^{2} |\varphi_k\rangle (\sum_{j}^{N_b} \kappa_{kj} Q_{kj}) \langle\varphi_k|.$$

Excited-State Dynamics



ML-MCTDH and Tensor Network

Standard propagation method (f_{max}~ 10)

$$\Psi(Q_1,\cdots,Q_f,t)=\sum_{j_1=1}^{N_1}\cdots\sum_{j_f=1}^{N_f}C_{j_1\cdots j_f}(t)\prod_{\kappa=1}^{f}\chi_{j_\kappa}^{(\kappa)}(Q_\kappa)$$

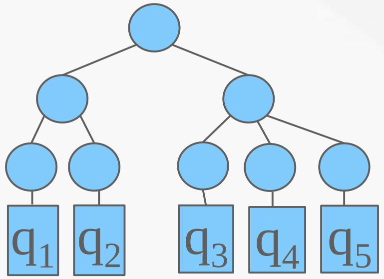
$$i\frac{\partial}{\partial t}C_J=\sum_L H_{JL}C_L$$

ML-MCTDH (f_{max}~ 1500)

$$\varphi_m^{z-1}(Q_{\kappa_{l-1}}^{z-1},t)=\sum_{j_1=1}^{n_1}\cdots\sum_{j_{p_{\kappa_l}}=1}^{n_{\kappa_l}}A^z_{j_1\cdots j_{p_{\kappa_l}}}(t)\prod_{\kappa_l=1}^{p_{\kappa_l}}\varphi_{j_{\kappa_l}}^{z,\kappa_l}(Q^z_{\kappa_l},t)$$

$$i\dot{A}_J^l=\sum_L\langle\Phi_J^l|H|\Phi_L^l\rangle A_L^l$$

$$i\dot{\varphi}_n^{z,\kappa_l}=\left(1-\hat{P}^z_{\kappa_l}\right)\sum\left(\rho^{z,\kappa_l}\right)^{-1}_{nj}\langle H\rangle^{z,\kappa_l}_{jm}\varphi_m^{z,\kappa_l}$$



Tensor-Train

$$i\hbar\frac{d}{dt}|\Psi(t)\rangle=\hat{P}_T\hat{H}|\Psi(t)\rangle \longrightarrow i\hbar\frac{d}{dt}|\Psi(t)\rangle=-\sum_{i=1}^{m-1}\hat{P}_i^L\otimes\hat{P}_{i+1}^R\hat{H}|\Psi(t)\rangle$$

$$|\Psi\rangle=\sum_{\{s_i\}}\mathbf{L}^{s_1}\cdots\mathbf{L}^{s_i}\cdots\mathbf{L}^{s_m}|s_1\cdots s_i\cdots s_m\rangle=\sum_{\{s_i\}}\mathbf{R}^{s_1}\cdots\mathbf{R}^{s_i}\cdots\mathbf{R}^{s_m}|s_1\cdots s_i\cdots s_m\rangle$$

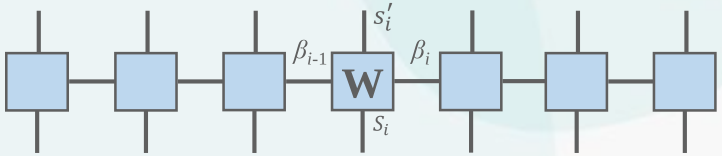
$$=\sum_{\{s_i\}}\mathbf{L}^{s_1}\cdots\mathbf{L}^{s_{i-1}}\mathbf{M}^{s_i}\mathbf{R}^{s_{m-1}}\cdots\mathbf{R}^{s_m}|s_1\cdots s_i\cdots s_m\rangle$$

$$=\sum_{\{\alpha_{i-1},s_i,\alpha_i\}}\left[\mathbf{M}^{s_i}\right]_{\alpha_{i-1},\alpha_i}|\Psi^{[1:i-1]}_{L,\alpha_{i-1}}\rangle|s_i\rangle|\Psi^{[i+1:m]}_{R,\alpha_i}\rangle$$

$$\hat{O}=\sum_{\{s_i\},\{s_i'\},\{\beta_i\}}\mathbf{W}^{s_1,s_1'}_{\beta_0,\beta_1}\cdots\mathbf{W}^{s_i,s_i'}_{\beta_{i-1},\beta_i}\cdots\mathbf{W}^{s_m,s_m'}_{\beta_{m-1},\beta_m}|s_1\cdots s_i\cdots s_m\rangle\langle s_1'\cdots s_i'\cdots s_m'|$$

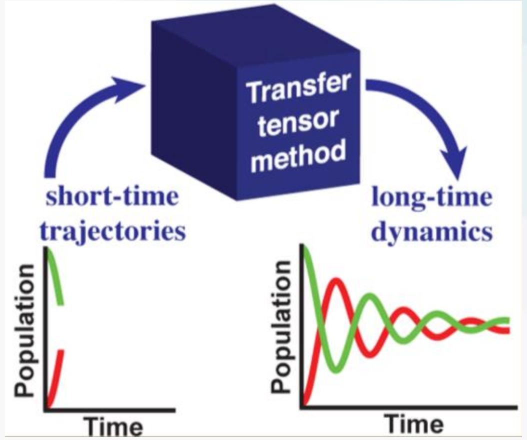
$$\hat{P}_T=\sum_{i=1}^{m}\hat{P}_{i-1}^L\otimes\hat{I}_i\otimes\hat{P}_{i+1}^R-\sum_{i=1}^{m-1}\hat{P}_i^L\otimes\hat{P}_{i+1}^R \qquad \hat{P}_i^L=\sum_{\alpha_i}|\Psi^{[1:i]}_{L,\alpha_i}\rangle\langle\Psi^{[1:i]}_{L,\alpha_i}|$$

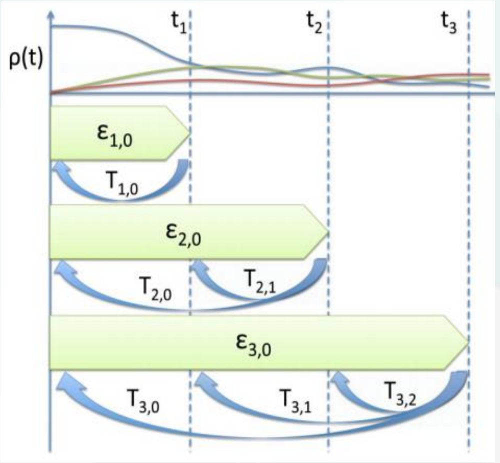
$$\hat{P}_i^R=\sum_{\alpha_i}|\Psi^{[i:m]}_{R,\alpha_{i-1}}\rangle\langle\Psi^{[i:m]}_{R,\alpha_{i-1}}|$$



[*J. Chem. Phys.*, 128:164116 (2008)]
[*J. Chem. Phys.*, 119:1289 (2003)]
[*Phys. Rep.*, 324:100-105 (2000)]
[*J. Phys. Chem. A*, 119:7951-7965 (2015)]
[*Ann. Phys.* 326:96 (2011)]
[*Phys. Rev. B* 94:165116 (2016)]

Transfer-Tensor Method

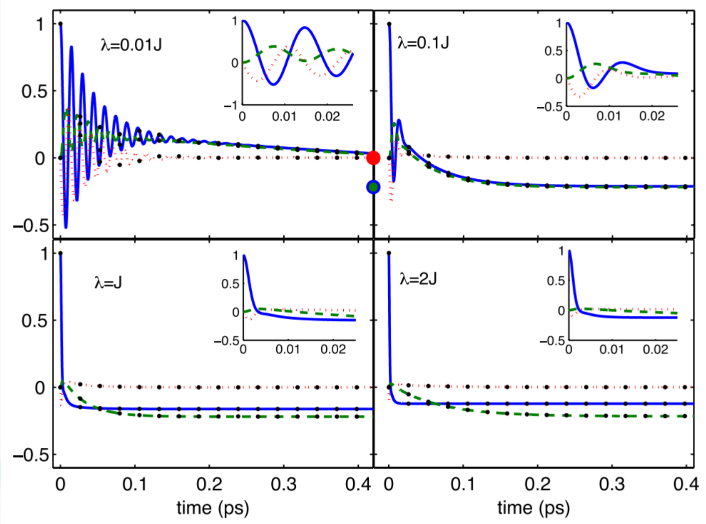


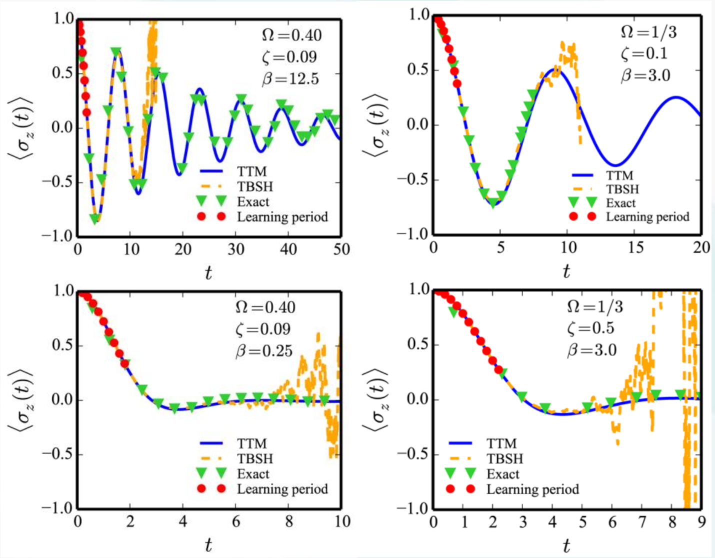


$$T_{n,0} = \mathcal{E}_n - \sum_{m=1}^{n-1} T_{n,m}\mathcal{E}_m,$$

$$\rho(t_n) = \sum_{k=0}^{n-1} T_{n,k}\rho(t_k)$$

$$\rho(t_m) = (\,T_1 T_2 \ldots T_K\,)\begin{pmatrix}\rho(t_{m-1})\\ \rho(t_{m-2})\\ \vdots \\ \rho(t_{m-K})\end{pmatrix}$$



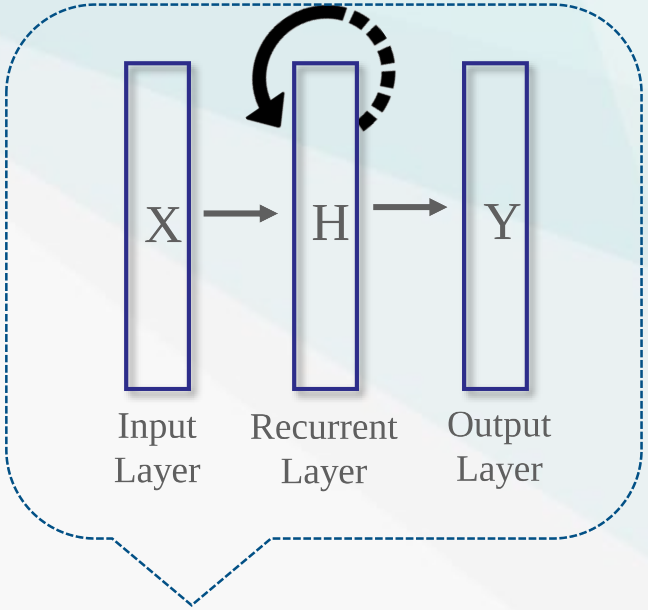


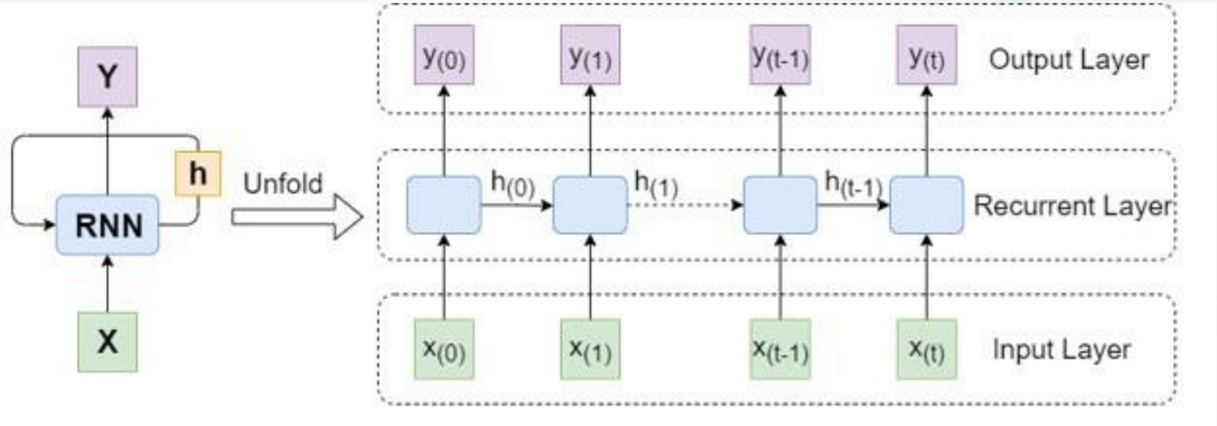
[Kananenka, A. A.; Hsieh, C.-Y.; Cao, J.; Geva, E. ***J. Phys. Chem. Lett.***, 7, 4809-4814 (2016)]

[Cerrillo, J.; Cao, J. ***Phy. Rev. Lett.***, 112, 110401 (2014)]

Long Short-Term Memory RNN

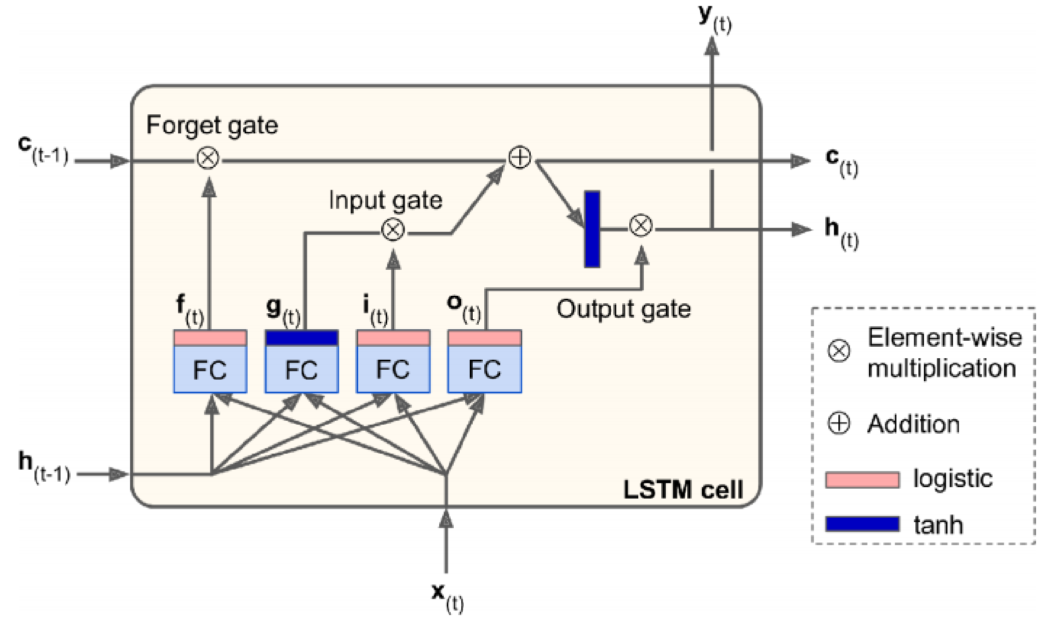
- **The Simple RNN**





[Goodfellow, I.; Bengio, Y.; Courville, A. *Deep Learning*. MIT press: **2016**.]

- **The LSTM Cell**



$$i_{(t)} = \sigma\left(W_{xi}^T x_{(t)} + W_{hi}^T h_{(t-1)} + b_i\right),$$

$$f_{(t)} = \sigma\left(W_{xf}^T x_{(t)} + W_{hf}^T h_{(t-1)} + b_f\right),$$

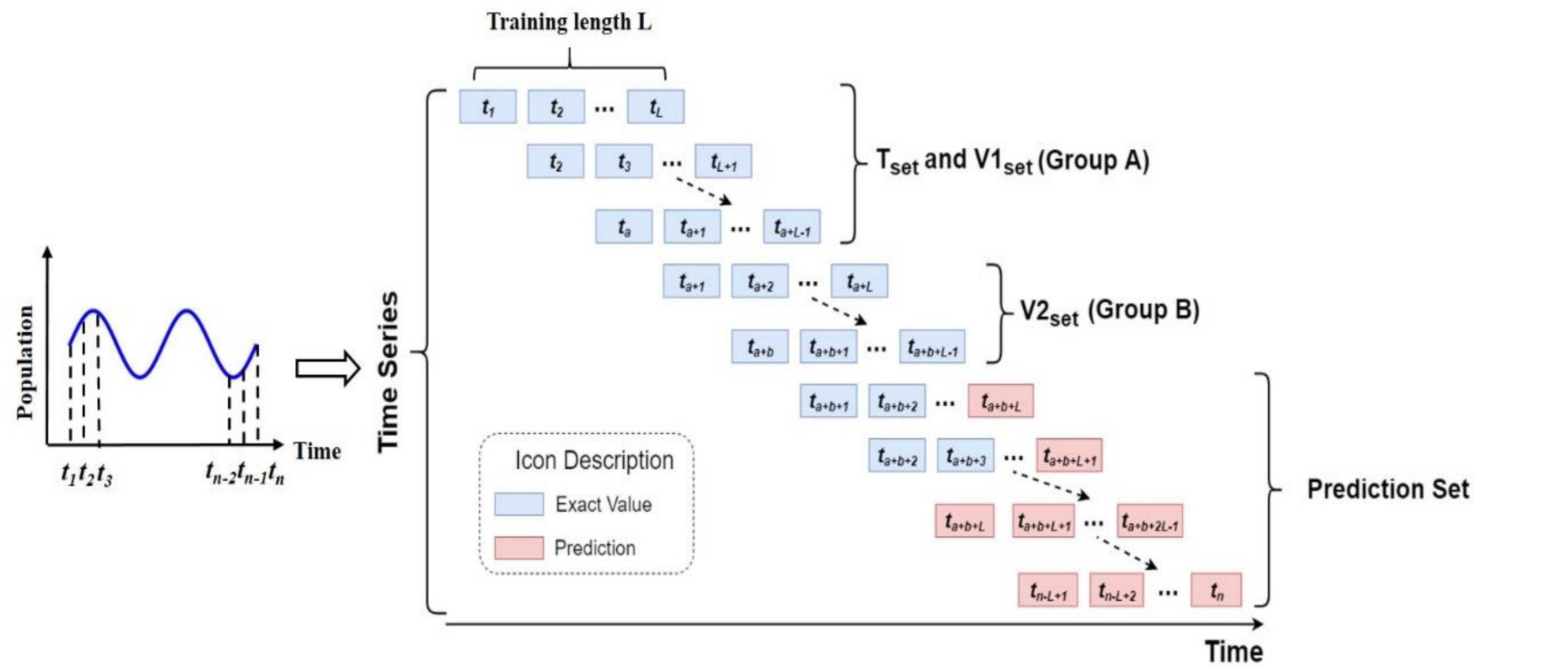
$$o_{(t)} = \sigma\left(W_{xo}^T x_{(t)} + W_{ho}^T h_{(t-1)} + b_o\right),$$

$$g_{(t)} = tanh\left(W_{xg}^T x_{(t)} + W_{hg}^T h_{(t-1)} + b_g\right),$$

$$c_{(t)} = f_{(t)} \cdot c_{(t-1)} + i_{(t)} \cdot g_{(t)},$$

$$y_{(t)} = h_{(t)} = o_{(t)} \cdot tanh\left(c_{(t)}\right).$$

Data Processing



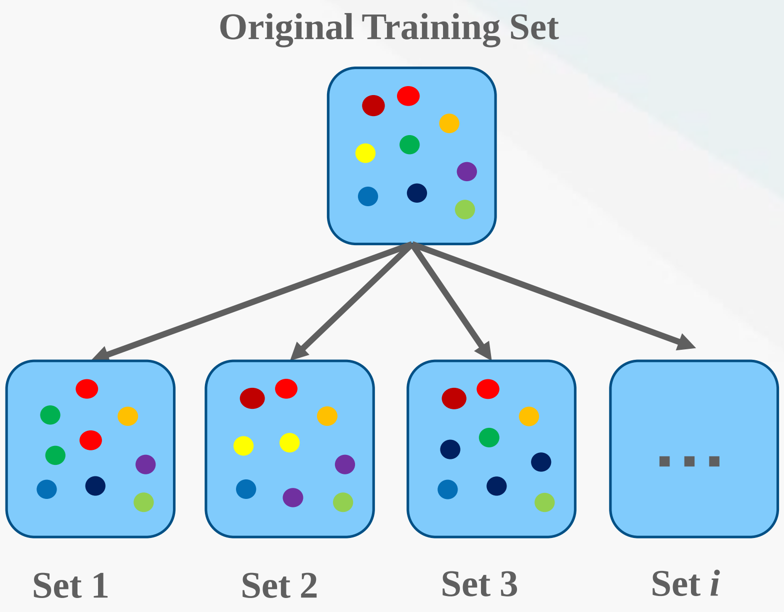
Uncertainty Analysis Methods

The estimation of the uncertainty is un-avoidable in all ML models

Two Uncertainties: ***Model Misspecification***

Model Uncertainty

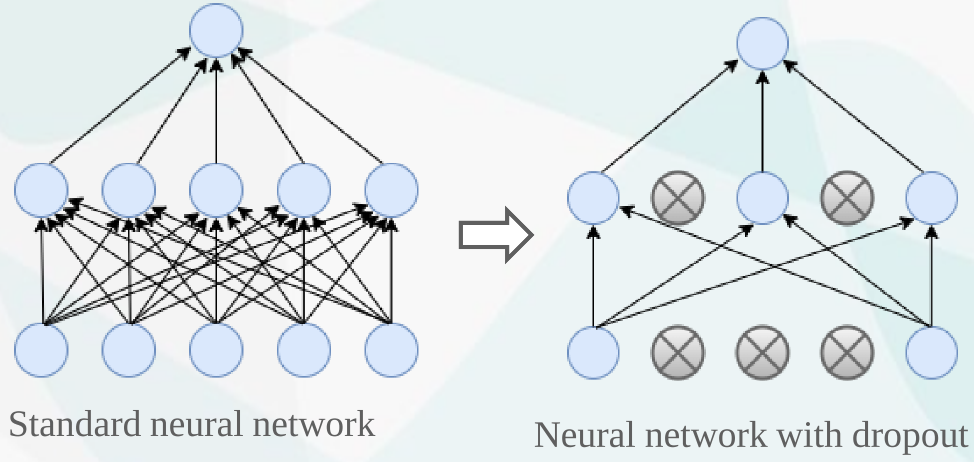
- **Bootstrap Resampling Method**



[Zhu, L.; Laptev, N. **IEEE:** 103-110(2017)]

[Bühlmann, P. ***Stat. Sci.*** 17, 52-72(2002)]

- **Monte-Carlo Dropout Method**



[Gal, Y.; Ghahramani, Z. **PMLR:** 48, 1050-1059(2016)]

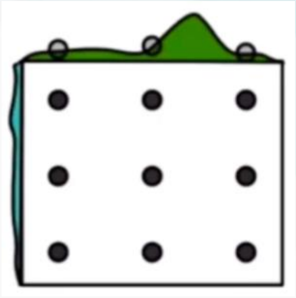
[Gal, Y.; Ghahramani, Z. *Advances in neural information processing systems*, 29(2016)]

Hyperparameter Optimization

- **Random Search**

Grid Layout

Random Layout



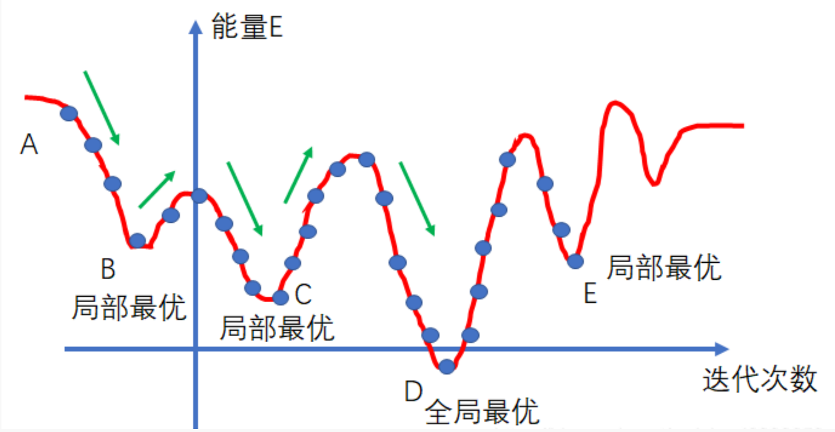
Unimportant Parameter

Important Parameter

Unimportant Parameter

Important Parameter

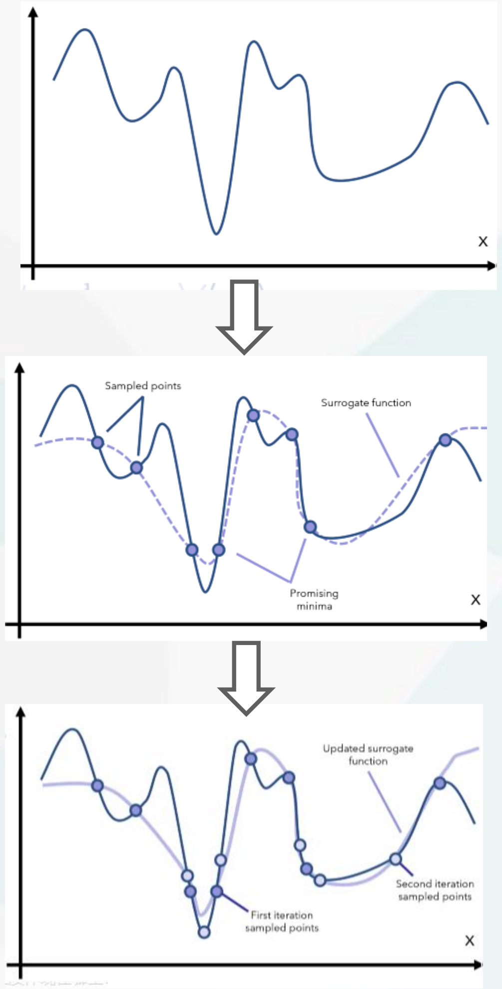
- **Simulated Annealing**



$$p = \begin{cases} \exp\left(-\dfrac{f(x_{t+1}) - f(x_t)}{T}\right) & if\ \ f(x_{t+1}) - f(x_t) \geq 0 \\ 1 & if\ \ f(x_{t+1}) - f(x_t) < 0 \end{cases},$$

[Yang, L.; Shami, A. ***Neurocomputing,*** 415, 295-316(2020)]

- **Bayesian Optimization with TPE**



Hyperparameters

$\{x_i, y_i\}$

Loss function

Parzen window

$$p(x \mid y) = \begin{cases} l(x), & if\ \ y < y^* \\ g(x), & if\ \ y \geq y^* \end{cases},$$

Maximizing *EI*

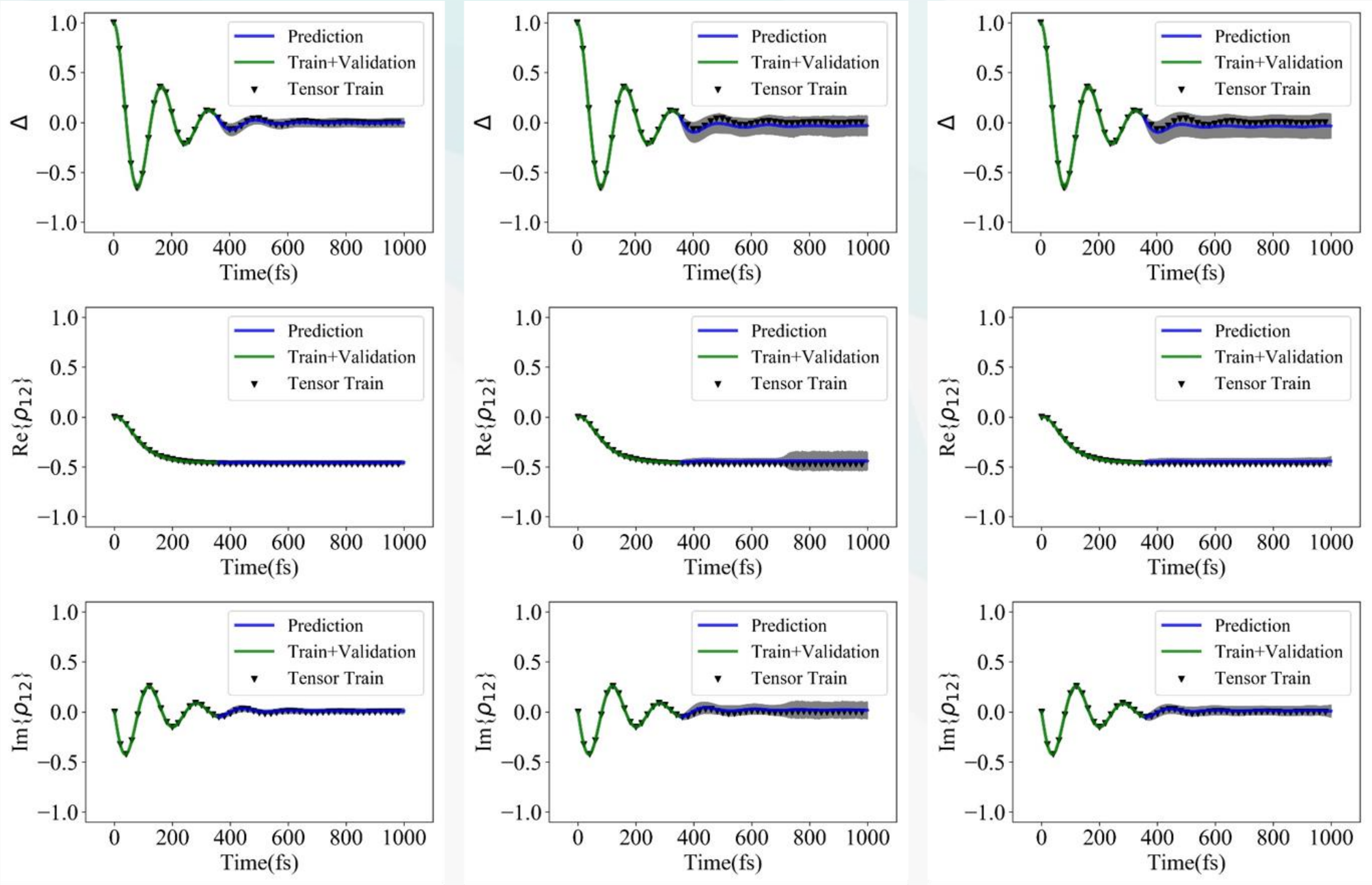
$$EI_{y^*}(x) \propto \left(\gamma + \frac{g(x)}{l(x)}(1-\gamma)\right)^{-1},$$

$$\gamma = p(y < y^*)$$

$$p(x) = \gamma l(x) + (1-\gamma) g(x).$$

[Kirkpatrick, S.; Gelatt Jr, C. D.; Vecchi, M. P. ***Science,*** 220, 671-680(1983)]

Simulation of Open Quantum Dynamics with Uncertainty Analysis



(a) Simulated Annealing + Bootstrap + MC dropout

(b) Bayesian Optimization + Bootstrap + MC dropout

(c) Random Search + Bootstrap + MC dropout

Model I (symmetric)

V_{12} = 0.0124 eV

ω_c = 200cm^{-1}

λ = 64 cm^{-1}

Recommended Choice

⇩

Simulated Annealing

+

Bootstrap

+

MC dropout

[Lin, K.; Peng, J.; Gu, F. L.; Lan, Z. ***J. Phys. Chem. Lett.***, 12(41), 10225-10234 (2021)]

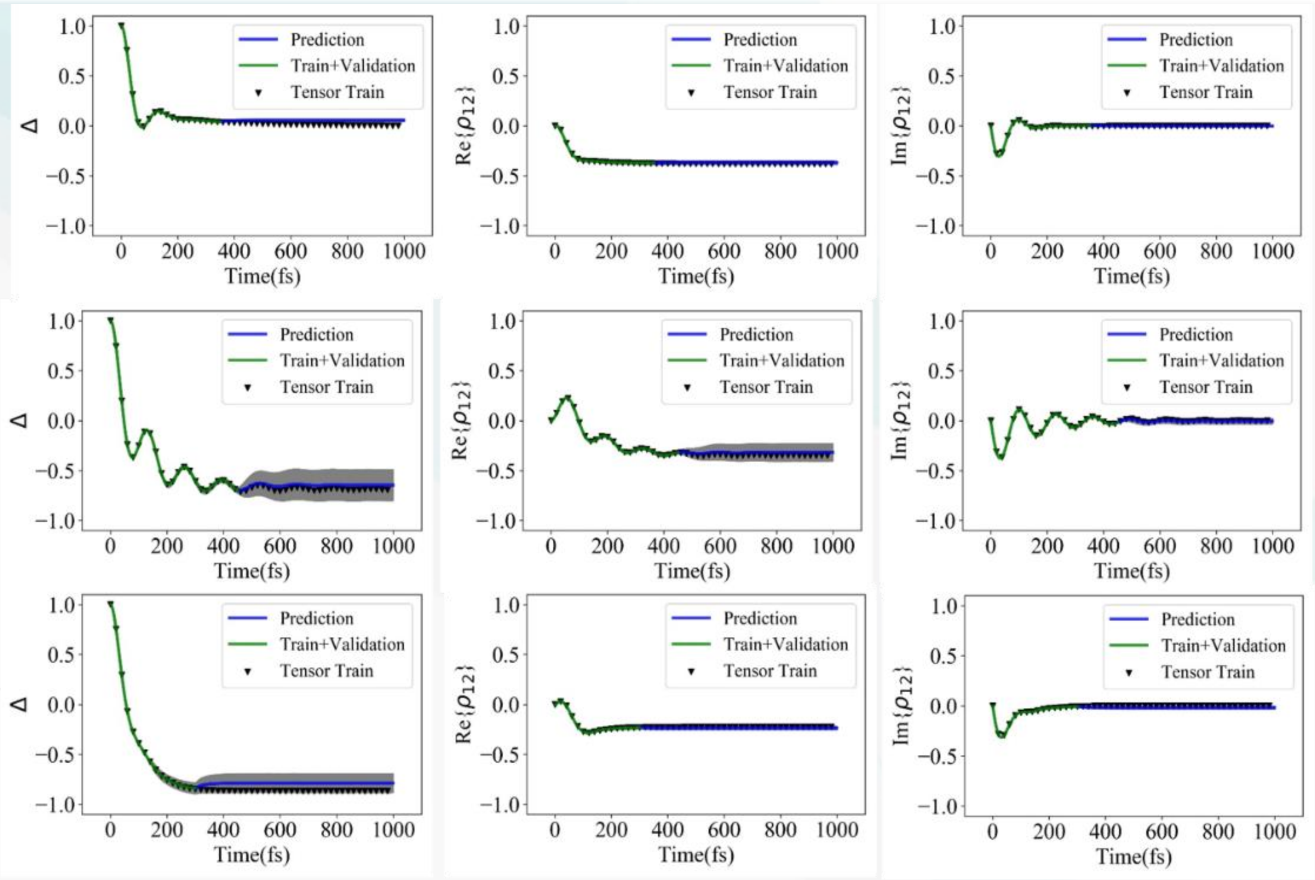
[Lin, K.; Peng, J.; Xu, C.; Gu, F. L.; Lan, Z. ***J. Chem. Theory Comput.,*** 18(10), 5837–5855 (2022)]

Simulation of Open Quantum Dynamics with Uncertainty Analysis

(a) Model II
(asymmetric)

(b) Model III
(asymmetric)

(c) Model IV
(asymmetric)

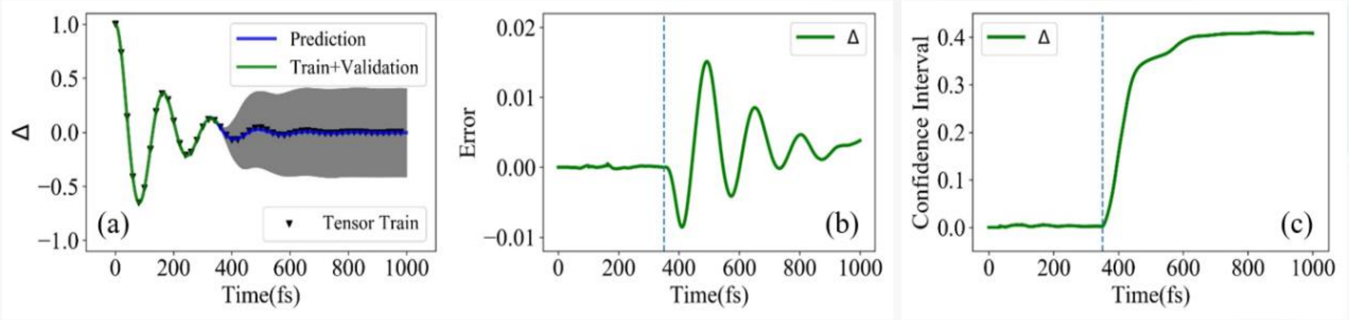


The excellent prediction results of symmetric and asymmetric site-exciton models.

[Lin, K.; Peng, J.; Gu, F. L.; Lan, Z.
J. Phys. Chem. Lett., 12(41), 10225-10234 (2021)]

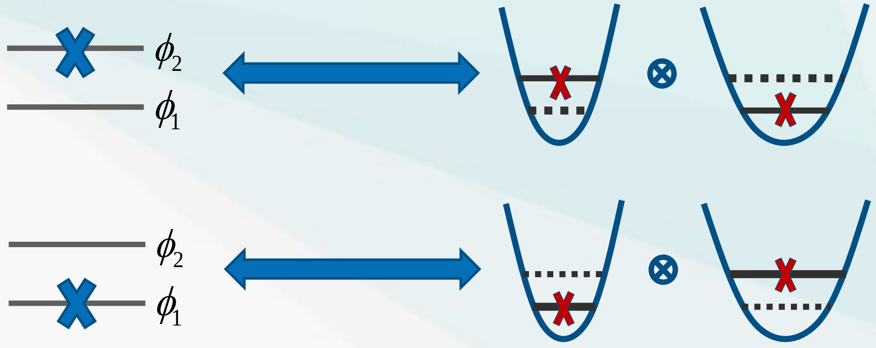
[Lin, K.; Peng, J.; Xu, C.; Gu, F. L.; Lan, Z.
J. Chem. Theory Comput., 18(10), 5837–5855 (2022)]

Model I
(symmetric)
Only Electronic Populations



The off-diagonal elements of the density matrix play a very important role.

Mapping Hamiltonian



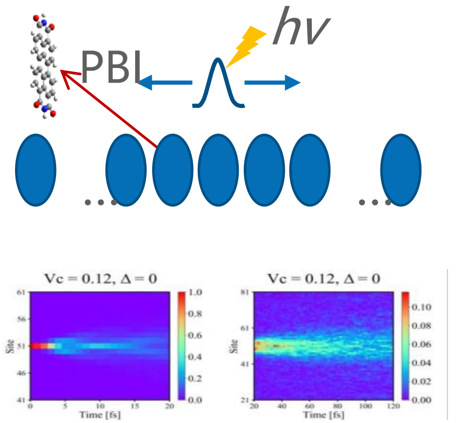
[*J. Chem. Phys.*, 70: 3214-3223 (1979)]
[*Phys. Rev. Lett.*, 78: 578-581 (1997)]

$$|\phi_n\rangle\langle\phi_m| \mapsto a_n^+ a_m,$$
$$|\phi_n\rangle \mapsto |0_1 \cdots 1_n \cdots 0_N\rangle.$$

$$\hat{H} = \sum_{n,m} \hat{h}_{nm} |\phi_n\rangle\langle\phi_m| \quad \longleftrightarrow \quad \hat{H} = \sum_n \frac{1}{2}\left(\hat{x}_n^{\,2} + \hat{p}_n^{\,2} - 1\right)\hat{h}_{nn} + \frac{1}{2}\sum_{n\neq m}\left(\hat{x}_n\hat{x}_m + \hat{p}_n\hat{p}_m\right)\hat{h}_{nm}$$

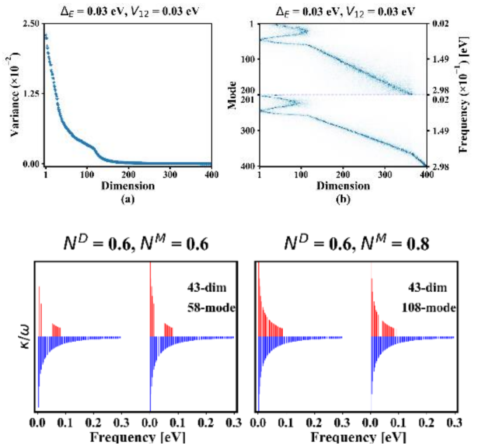
$$\hat{x}_n = \left(\hat{a}_n^+ + \hat{a}_n\right)/\sqrt{2}$$
$$\hat{p}_n = i\left(\hat{a}_n^+ - \hat{a}_n\right)/\sqrt{2}$$

Exciton Dynamics



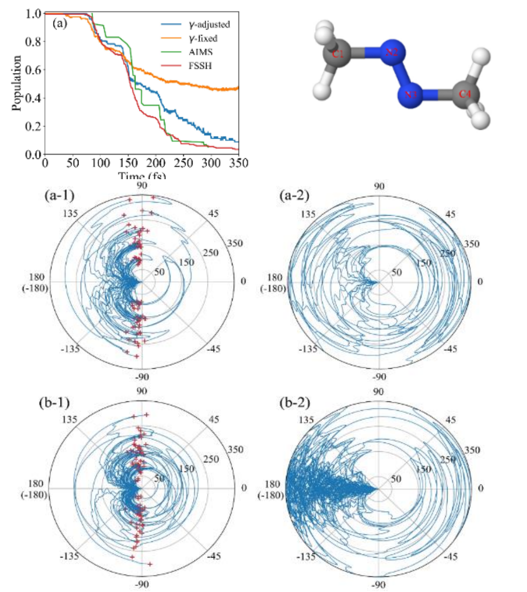
101 Sites, 808 Modes

Analysis Dynamics



Which Modes are important?

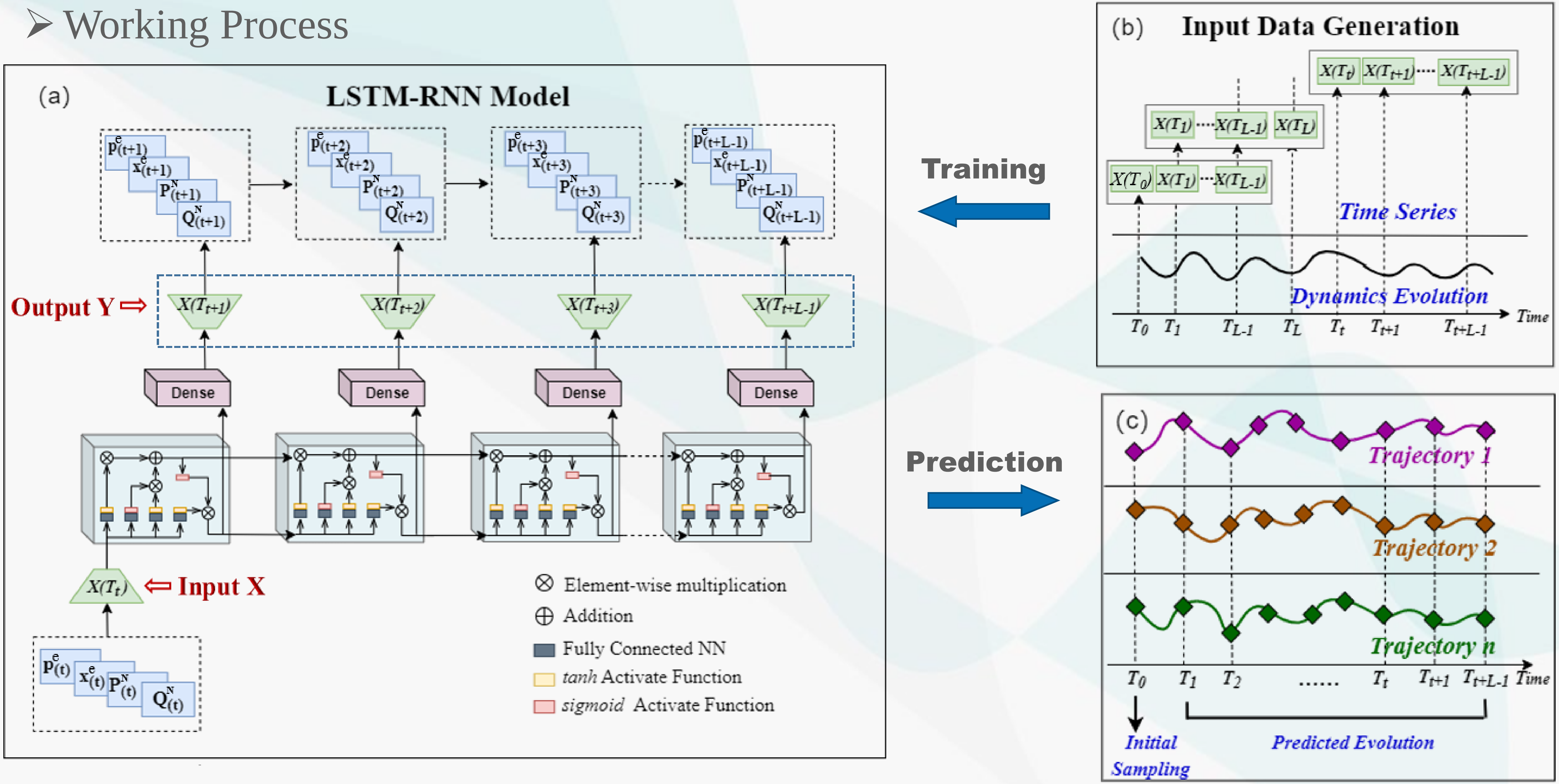
On-the-fly Dynamics



- ***JCP***, 2016, 2018; ***PCCP*** 2019, 2020; ***JCTC*** 2021

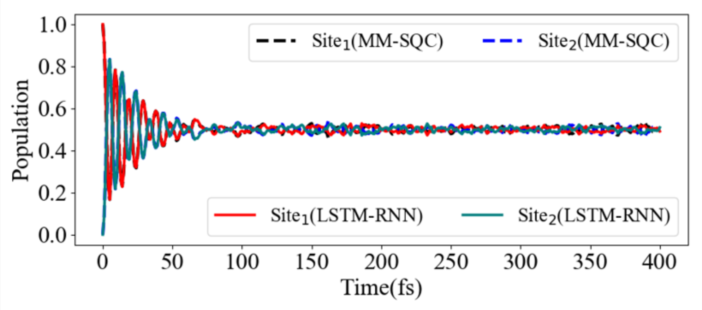
The Prediction of Trajectory-Based MM-SQC Dynamics

➢ Working Process

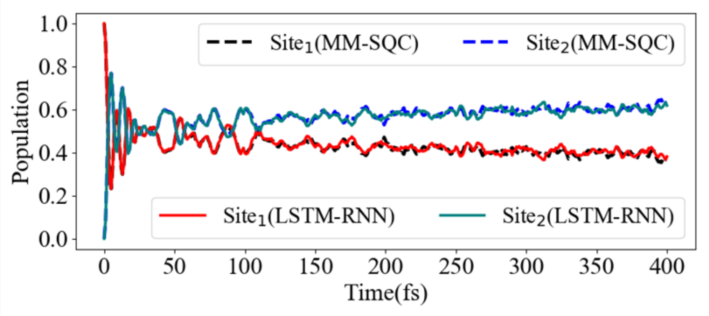


The Prediction of Trajectory-Based MM-SQC Dynamics

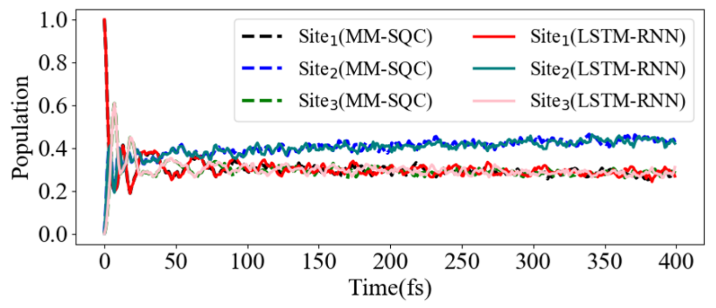
➢ Site-exciton models



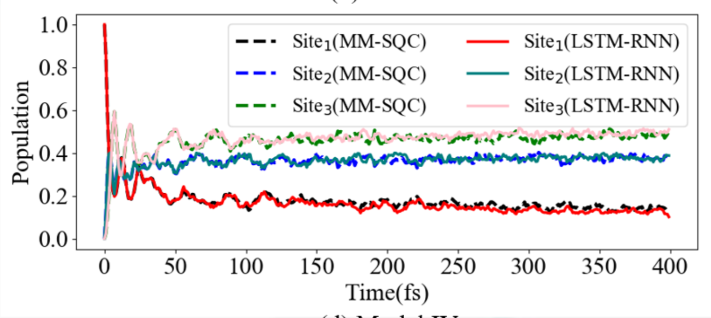
(a) Model I



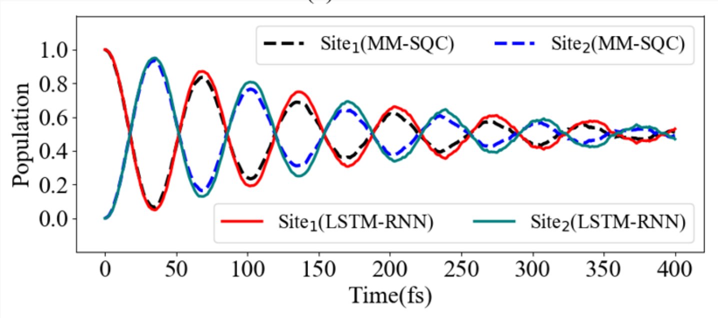
(b) Model II



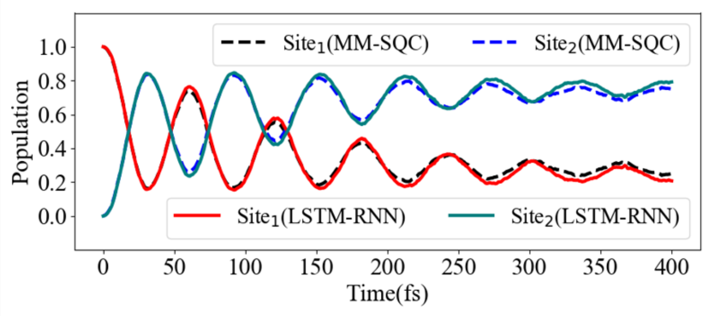
(c) Model III



(d) Model IV

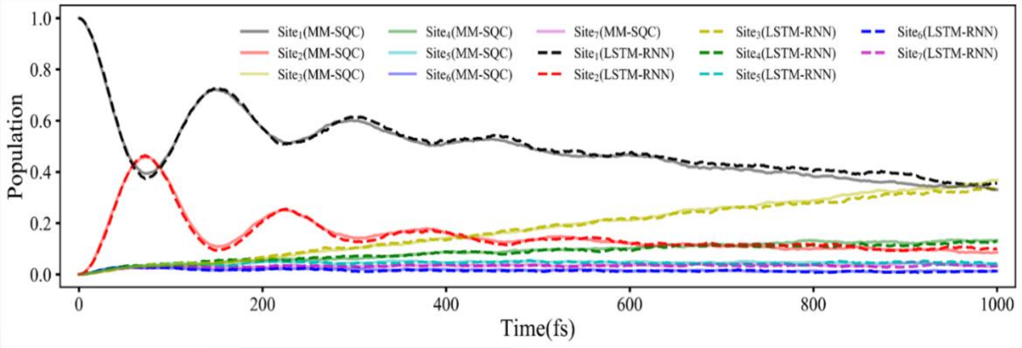


(e) Model V



(f) Model VI

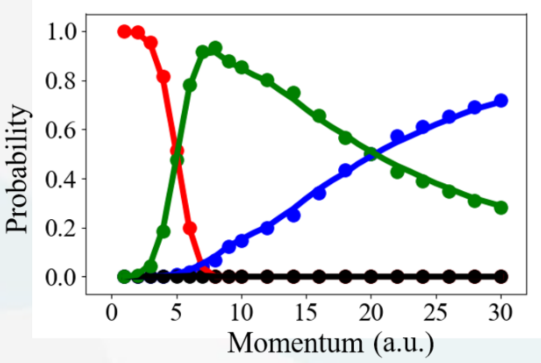
➢ FMO System



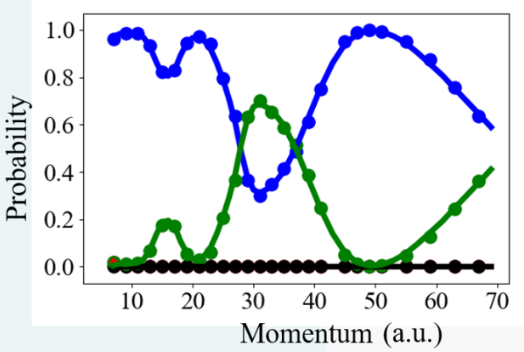
(g) FMO Model

714 Dimensions

➢ Tully's scattering models



(a) Model VIII (Tully's SAC model)



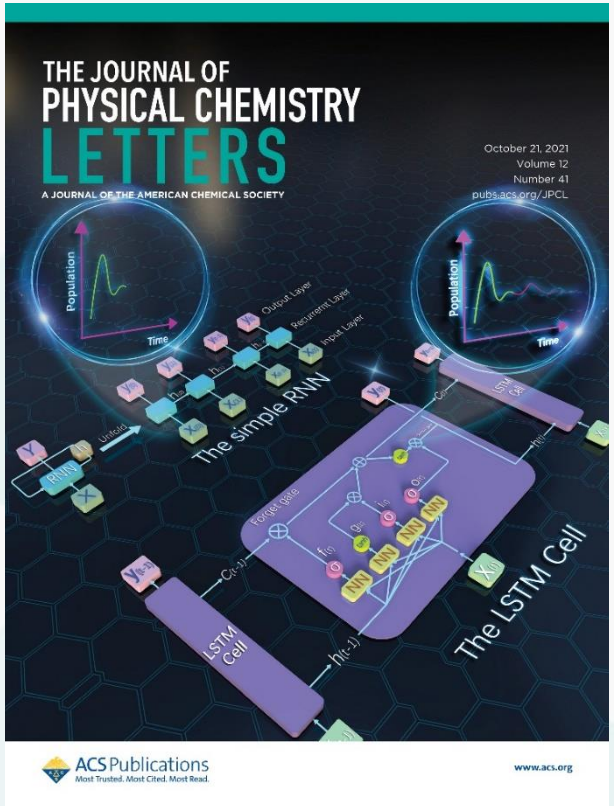
(b) Model IX (Tully's DAC model)

[Lin, K.; Peng, J.; Xu, C.; Gu, F. L.; Lan, Z. ***J. Phys. Chem. Lett.,*** 13, 11678−11688 (2022)]

Time-Series ML Methods

Time-Series Machine Learning Methods may be Used to Simulate the Nonadiabatic Dynamics

Promising **?** **Problems**

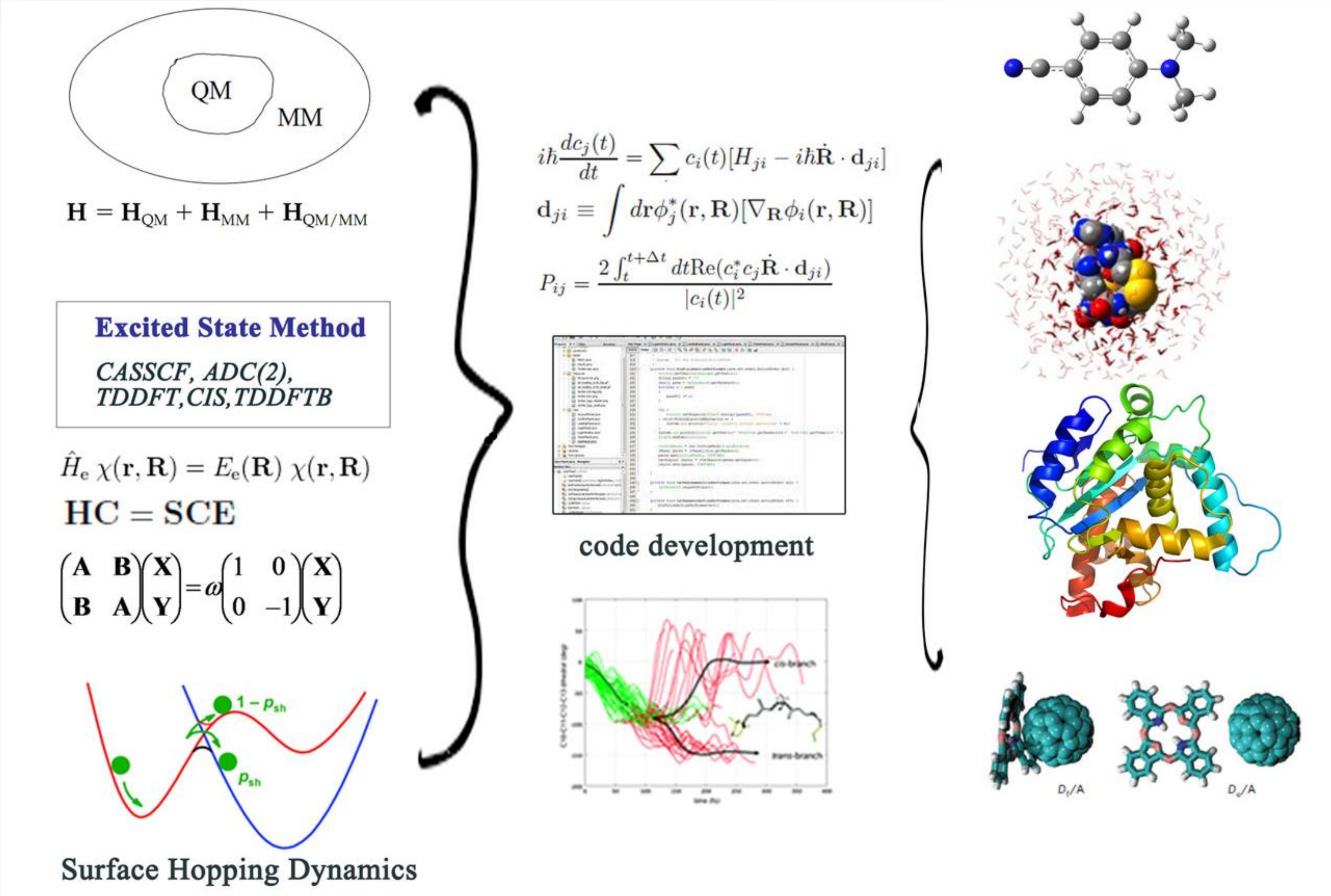


[Lin, K.; Peng, J.; Gu, F. L.; Lan, Z. ***J. Phys. Chem. Lett.***, 12, 10225-10234 (2021)]

[Lin, K.; Peng, J.; Xu, C.; Gu, F. L.; Lan, Z. ***J. Chem. Theory Comput.,*** 18(10), 5837–5855 (2022)]

[Lin, K.; Peng, J.; Xu, C.; Gu, F. L.; Lan, Z. ***J. Phys. Chem. Lett.,*** 13, 11678−11688 (2022)]

On-the-fly Nonadiabatic Dynamics



- On-the-fly Nonadiabatic Dynamics
- All Degrees of Freedom
- Black-Box Simulation Tool

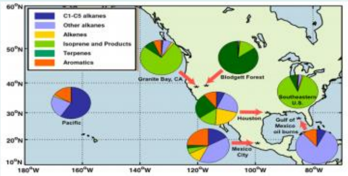
Method and Code Developments:

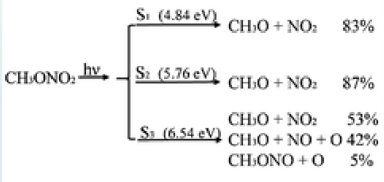
- Initial sampling
  - Wigner, Action-angle Sampling
- Dynamics Module:
  - Surface-hopping dynamics (Tully, Zhu-Nakamura)
  - Quasiclassical Dynamics with Mapping Hamiltonian
- Electronic Strucutre Module:
  - TDDFT, CIS, ADC(2), CASSCF, OM2/MRCI, XMS-CASPT2
  - Turbomole, Gaussian, GAMESS, Molpro, MNDO, BAGEL
- Analytical and Numerical NAC
- Hybrid QM/MM Methods

- L. Du, Z. Lan*, ***J. Chem. Theory Comput.***, 2015, 11, 1360;
- D. Hu, Z. Lan* et al., ***Phys. Chem. Chem. Phys.***, 2017, 19, 19168
- D. Hu, Z. Lan* et al., ***J. Chem. Theory Comput.***, 2021, 17, 3279

Photochemistry and Photophysics

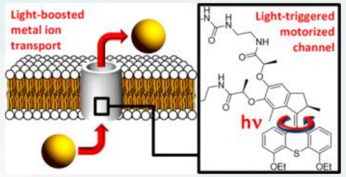
Environmental Photochemistry

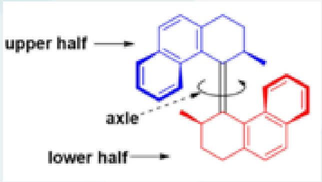




- J. Zhang, Z. Lan* et al., ***Phys. Chem. Chem. Phys.***, 2021, 23, 25597
- S. Lin, F.G. Gu*, Z. Lan* et al., ***J. Chem. Phys.***, 2021, 155, 214105
- K. Lin, F.G. Gu*, Z. Lan* et al., ***Chemosphere.***, 2021, 281, 130831
- X. Kang, Z. Lan* et al., ***Chin. J. Chem. Phys.***, 2023

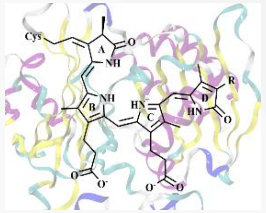
Photoisomerization

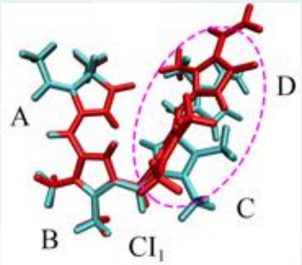




- J. Ma, C. Jiang*, Z. Lan* et al., ***Int. J. Mol. Sci.***, 2022, 23, 9694
- J. Ma, C. Jiang*, Z. Lan* et al., ***Int. J. Mol. Sci.***, 2022, 23, 3908
- C. Xu, Z. Lan* et al., ***J. Phys. Chem. Lett.***, 2022, 13, 661
- D. Hu, Z. Lan* et al., ***J. Chem. Theory Comput.***, 2021, 17, 3267

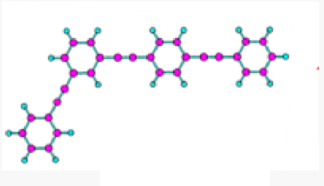
Photobiology

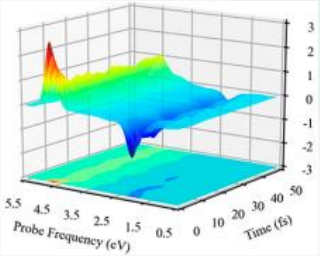




- Y. Fang, F.G. Gu*, Z. Lan* et al., ***Phys. Chem. Chem. Phys.***, 2022, 24, 26190
- H. Huang, C. Xu*, Z. Lan* et al., ***Chin. Chem. Lett.***, 2022, 107850
- Y. Zhu, Z. Lan* et al., ***Phys. Chem. Chem. Phys.***, 2022, 24, 24362
- D. Hu, Z. Lan* et al., ***Phys. Chem. Chem. Phys.***, 2017, 19, 19168

Photovoltaics



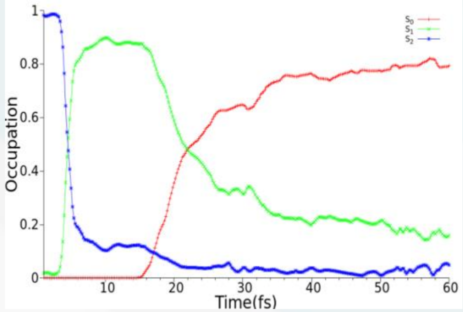


- D. Hu, Z. Lan* et al., ***J. Phys. Chem. Lett.***, 2021, 12, 9710
- J. Zheng, Y. Xie*, Z. Lan* et al., ***Phys. Chem. Chem. Phys.***, 2020, 22, 18192
- Y. Xie, H. Ren*, Z. Lan* et al., ***J. Mater. Chem. A***, 2019, 7, 27484
- S. Jiang, Y. Xie*, Z. Lan* et al., ***Chem. Phys.***, 2018, 515, 603
- Y. Xie, Z. Lan* et al., ***J. Chem. Phys.***, 2018, 149, 174105

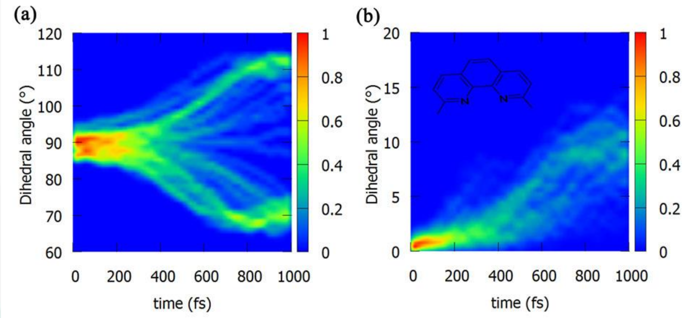
What do we know from nonadiabatic molecular simulation

Population dynamics

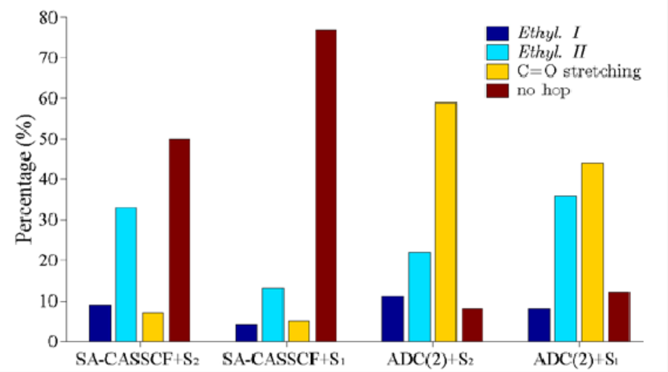
Lifetime



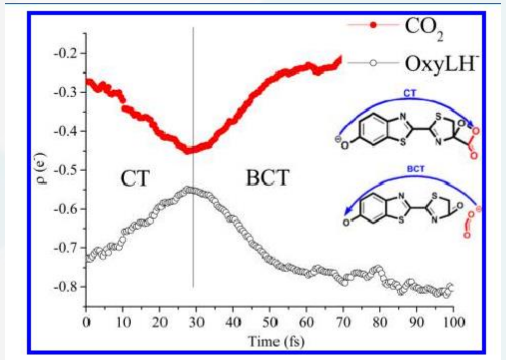
Geometry evolution



Reaction channels

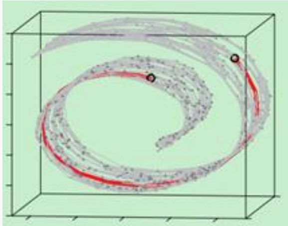


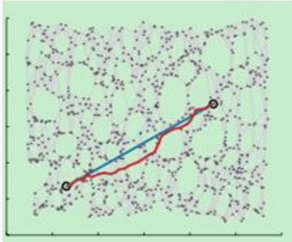
Physical quantities

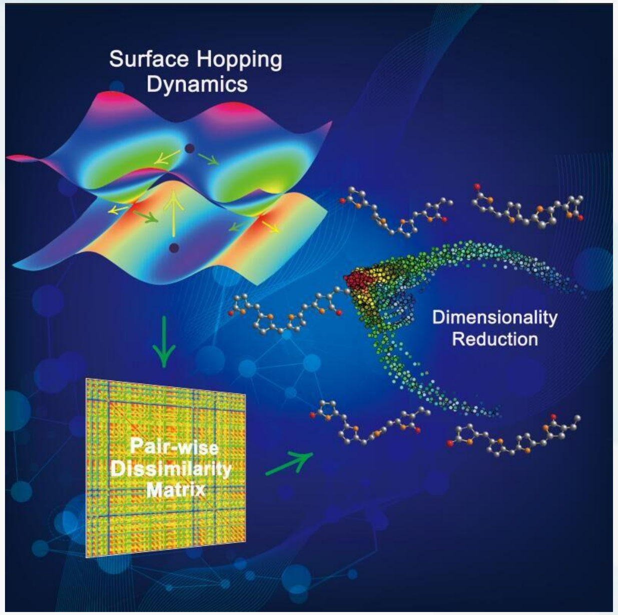


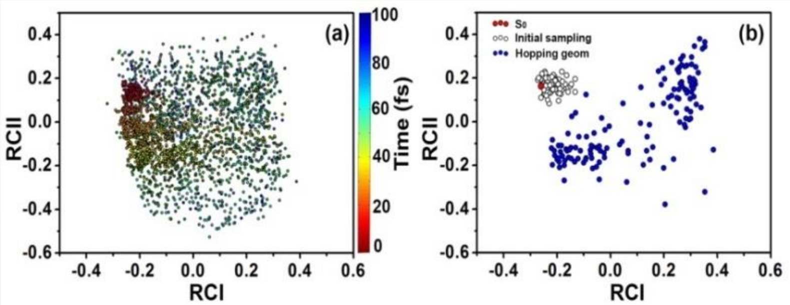
Analysis of trajectory evolution I： geometrical evolution

- Dimensionality reduction approaches to analyze the surface-hopping dynamics simulation results
- Extract the major molecular motion



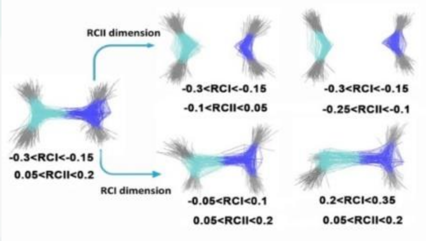


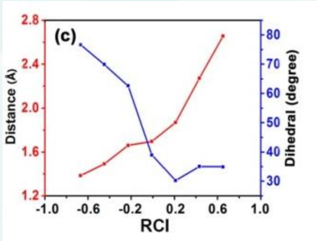




Dimensionality reduction

$\{R_N\} \rightarrow \{r\}$





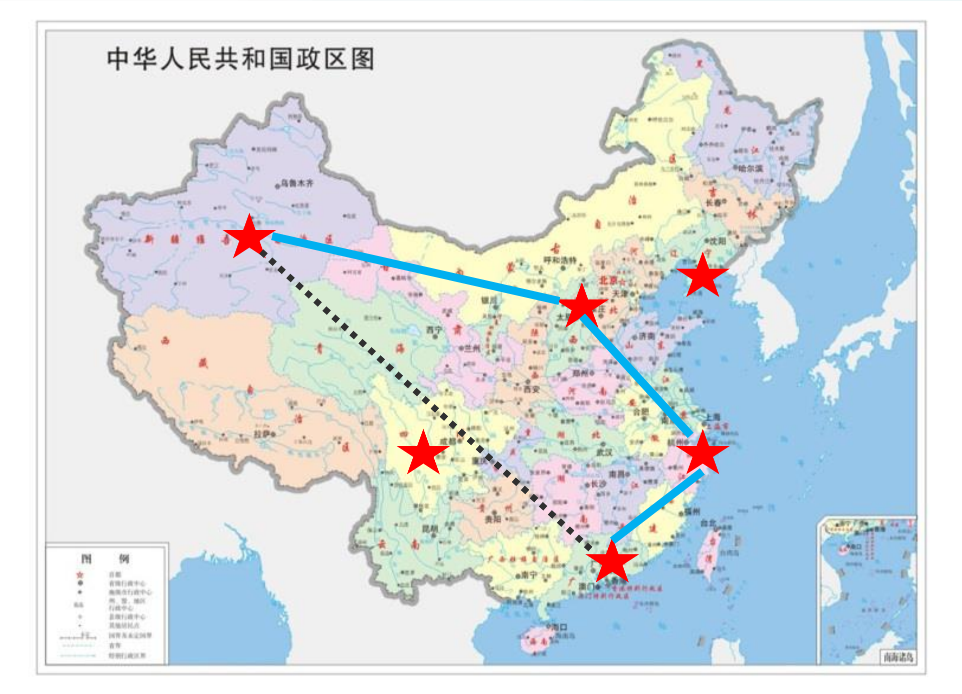
- **A large number of trajectories**
- **Polyatomic molecules**
- **Many degrees of freedom**

- **Multidimensional scaling**
- **Isometric feature mapping**

Virshup, A. M.; Chen, J. H.; **Martinez, T. J.** *J. Chem. Phys.* 2012, 137, 22A519.
Rohrdanz, M. A.; Zheng, W. W.; **Clementi, C.** *Annu. Rev. Phys. Chem.* **2013**, 64, 295-316.

MDS & ISOMAP

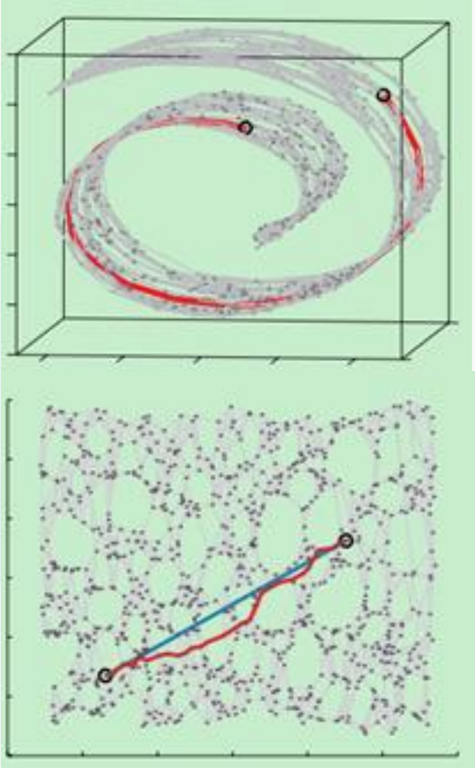
How to draw a map from the inter-city distances?



MDS (Multidimensional Scaling)

	A	B	C	D	E	F
A						
B			Inter-city Distance Matrix （I, J）			
C						
D						
E						
F						

ISOMAP (Isometric Mapping)

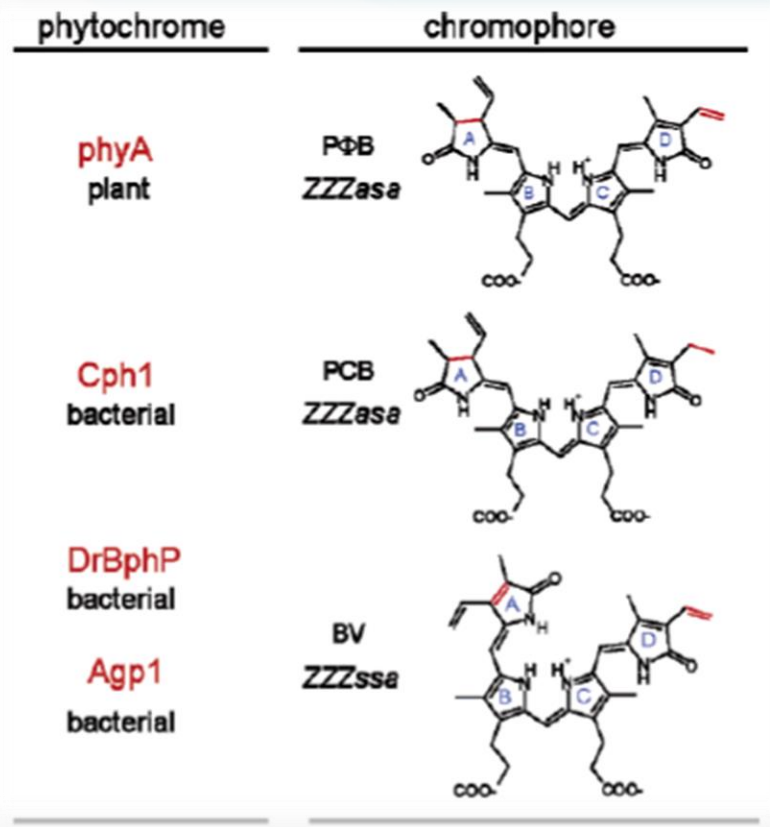


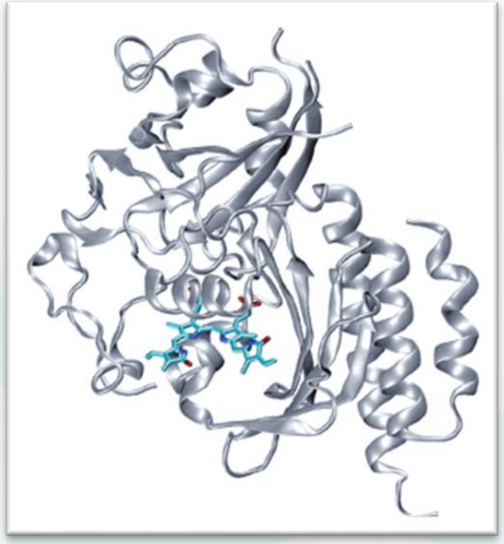
- Euclidean distance → Geodesic distance
- K-points or Epsilon-ball
- Dijkstra or Floyd–Warshall algorithm

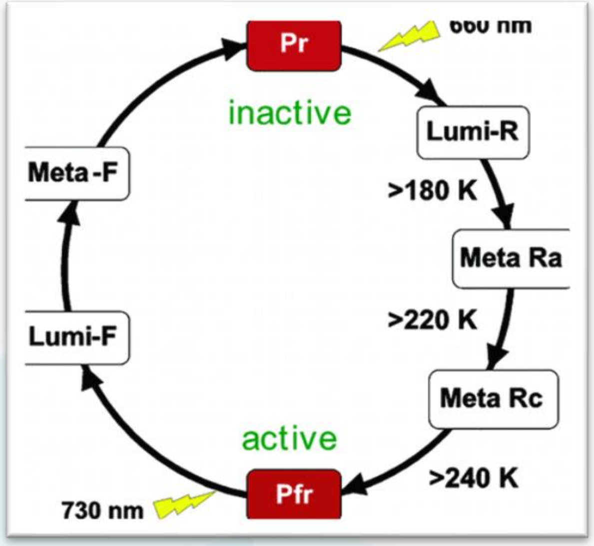
[1] Hardle, W.; Simar, L. *Springer*: Berlin, **2007**.
[2] Borg, I.; Groenen, P. J. F. *Springer Science & Business Media*: America, **2005**.
[3] De Silva, V.; Tenenbaum, J. B.; *Technical report*: Stanford University, **2004**.
[4] Balasubramanian, M.; Schwartz, E. L. *Science* **2002**, 295.
[5] Tenenbaum, J. B.; de Silva, V.; Langford, J. C. *Science* **2000**, 290, 2319-2323.

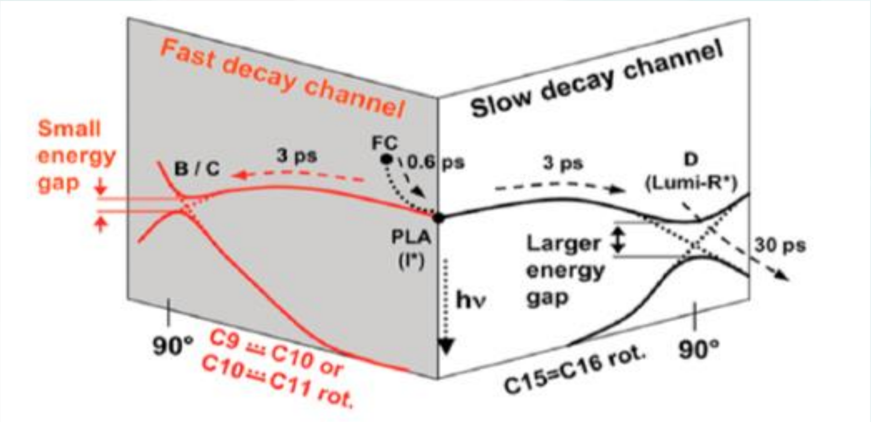
Example: ZaZsZa isomer of PΦB model

The PΦB model





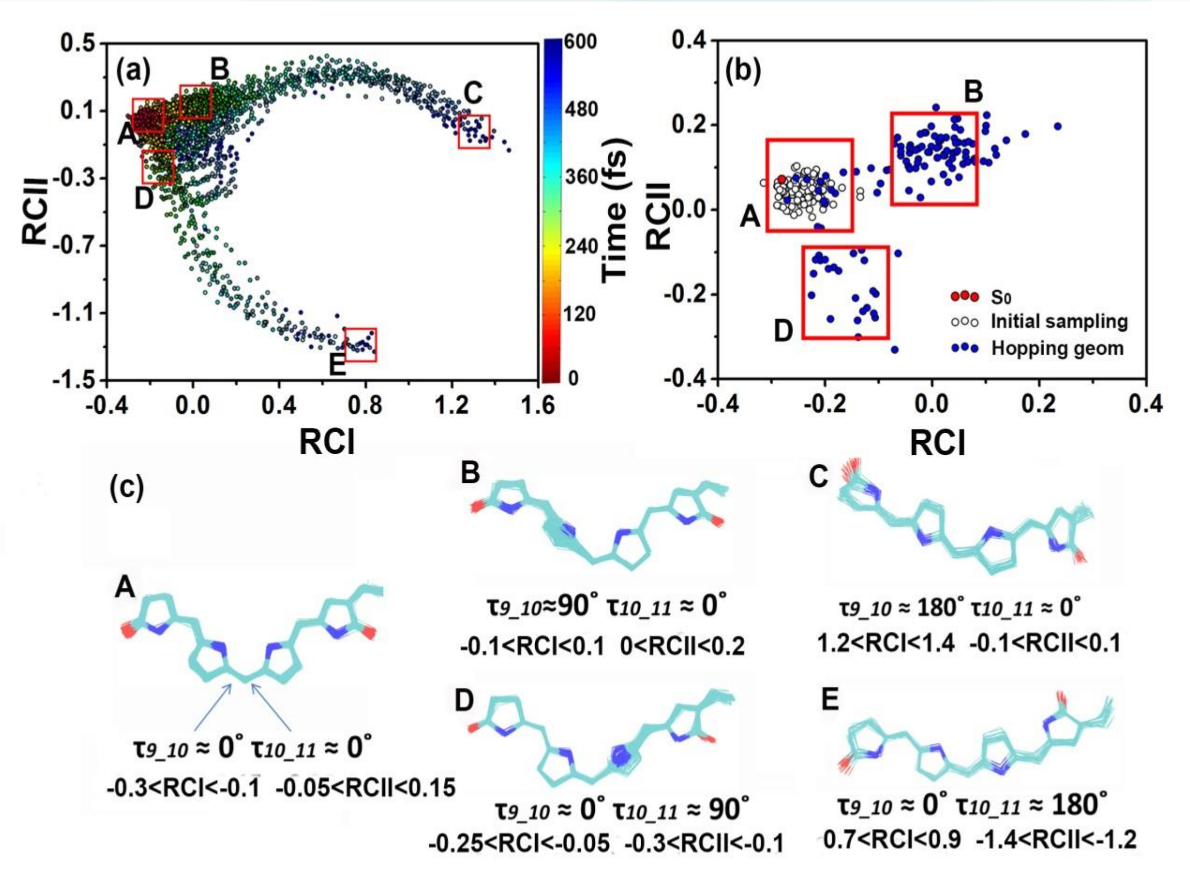




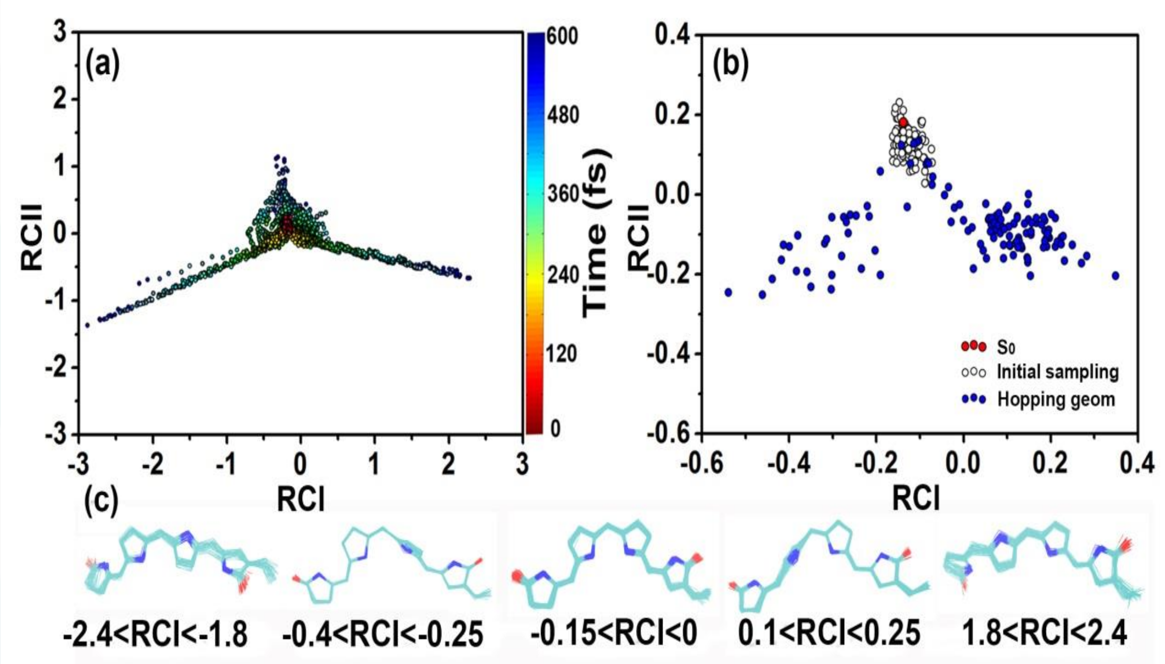
1. *Maria A. M., Daniel H. M., Peter H. Acc. Chem. Res.*, **2007**, *40* (4), pp 258–266
2. Samer G., Hoi L. L., Igor S., Olivucci M. *Chem. Rev.* ***2017*** *DOI: 10.1021/acs.chemrev.7b00177*

Example: ZaZsZa isomer of PΦB model

MDS



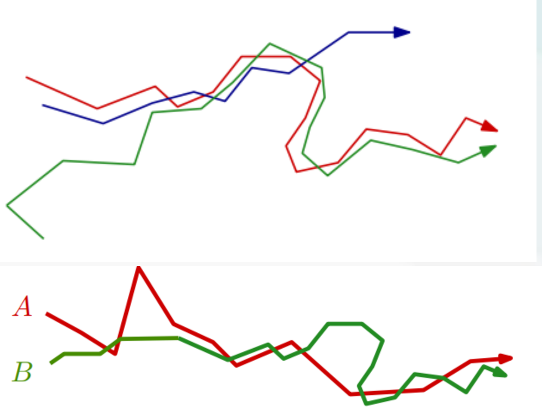
ISOMAP

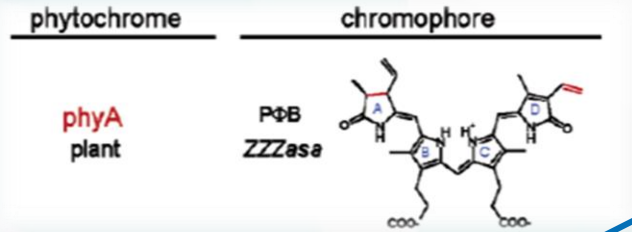


Li; Xie; Hu; **Lan** *J. Chem. Theory Comput.* **2017**, 13, 4611-4623

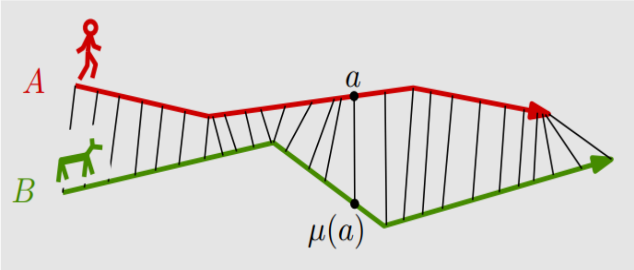
Analysis of trajectory evolution II: trajectory similarity

- An **“automatic”** approach to analyze the trajectory similarity and the configuration similarity in the on-the-fly trajectory surface hopping dynamics.

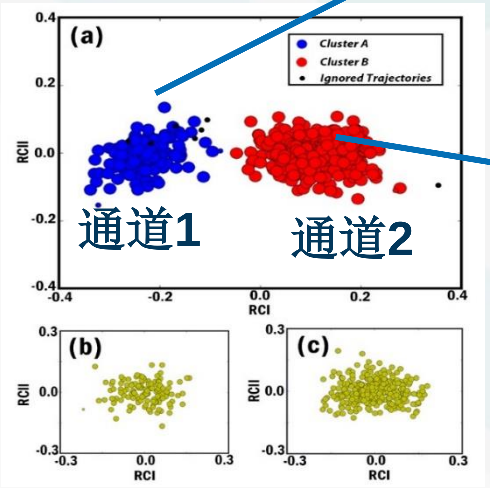


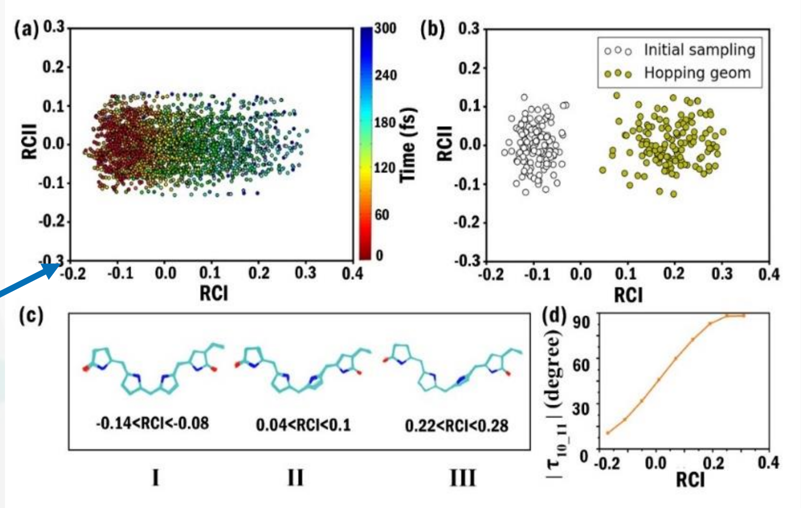


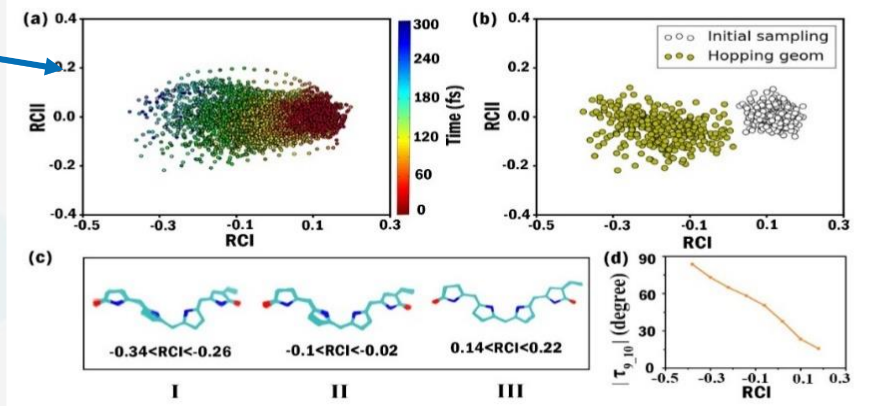
Fréchet Distance



$$\text{Fréchet-dist}(A,B) = \min_{\mu} \max_{a \in A} d(a, \mu(a)),$$





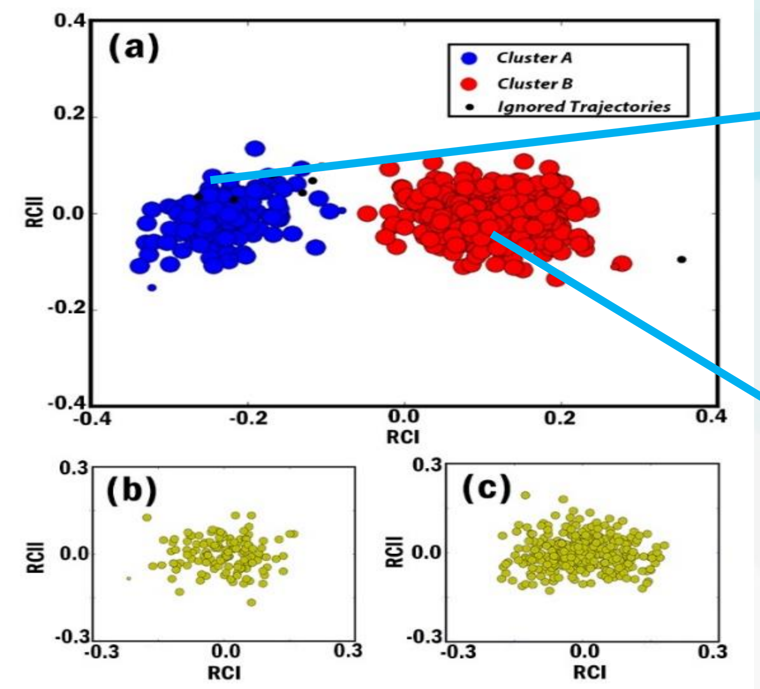


de Berg, Mark, "Analyzing Trajectories of Moving Objects“, Computational Geometry, Two Selected Topics, pp. 11–75

JCP 149, 244104 (2018)

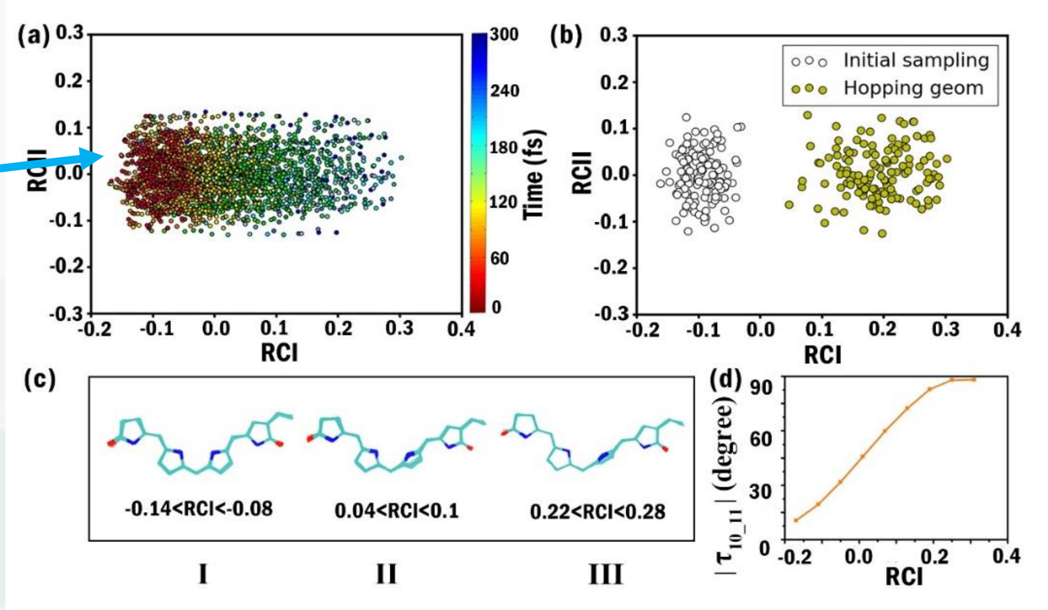
Application In Nonadiabatic Dynamics

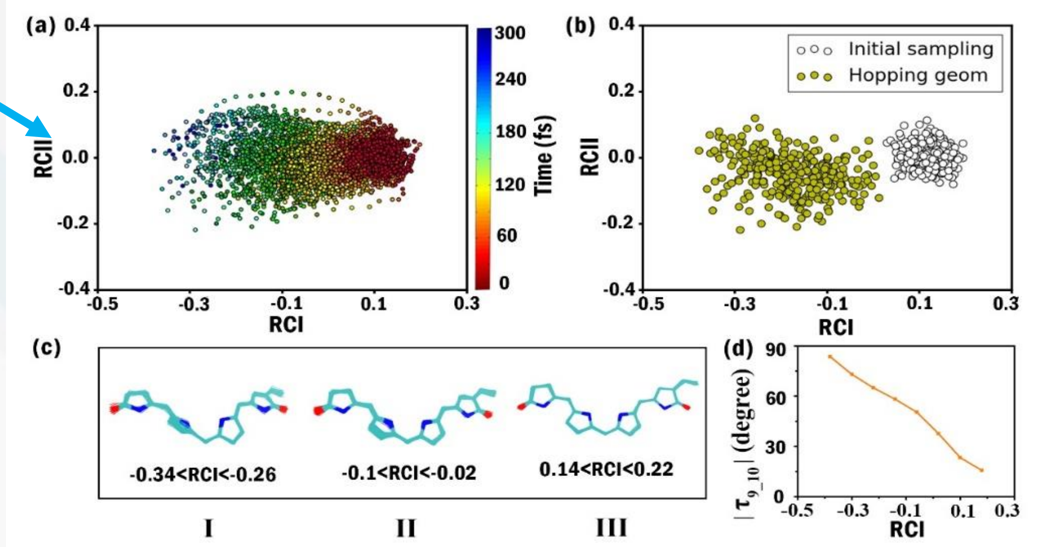
Clustering Analysis of Trajectory Similarity before S_1-S_0 Hops



Cluster A

Cluster B



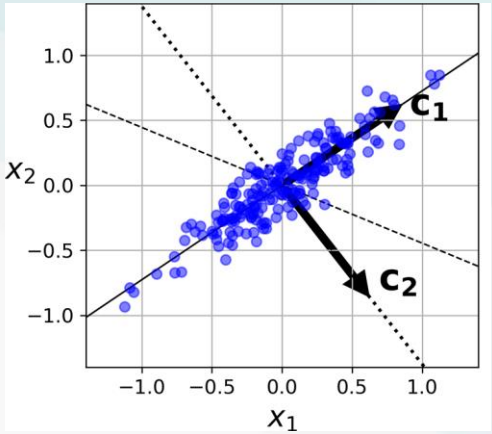


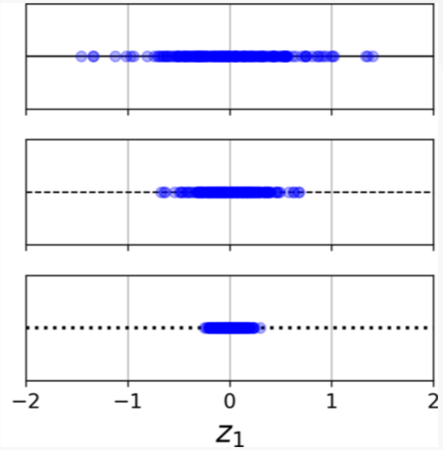
I. Get dynamics results
II. Select geometries
III. Calculate trajectory distance
IV. Clustering
V. Dimensionality reduction analysis

- X. Li, D. Hu, Y. Xie, Y. **Lan*,** JCP, 149, 244104, **2018**

Analysis of Trajectory Evolution III: Bath Motion

Principal Component Analysis





➢ *Geometry Data Collections*

The MM-SQC Dynamics

$$H_{MM}(x,p,Q,P)=\sum_k\left[\frac{1}{2}\left(x_k^2+p_k^2\right)-\gamma\right]H_{kk}(Q,P)+\frac{1}{2}\sum_{k\neq l}\left(x_k x_l+p_k p_l\right)H_{kl}(Q,P)$$

➢ *Descriptor Construction*

- The Action Variable of the Bath Mode: $N_j=\frac{1}{2}Q_j^2+\frac{1}{2}P_j^2$
- The Coordinate of the Bath Mode: Q_j

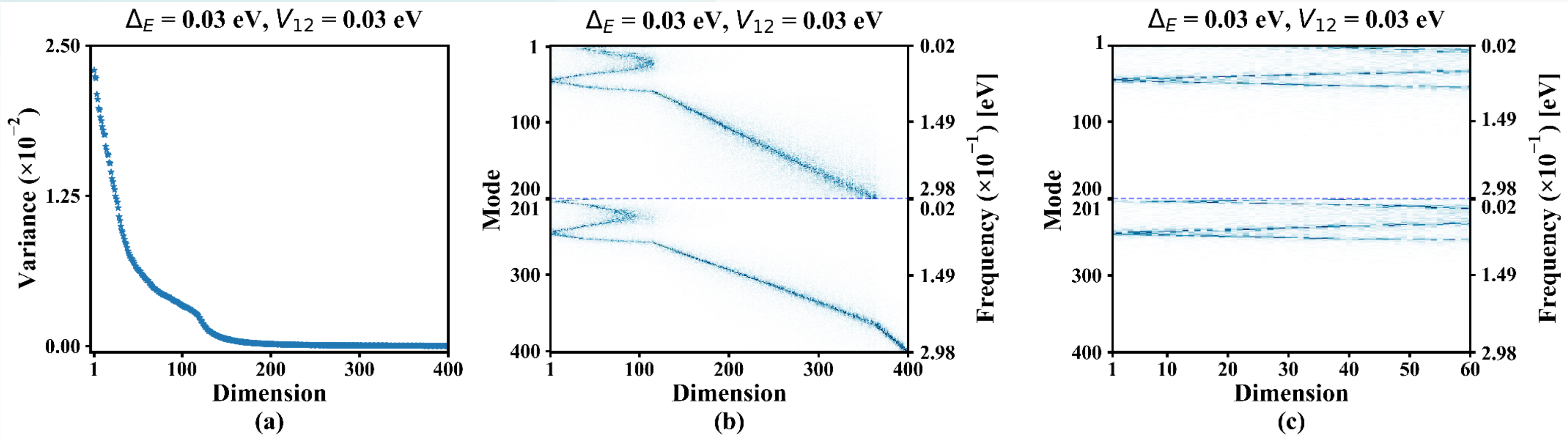
➢ *Dimensionality Reduction*

$$\mathbf{M}_{co}=(\mathbf{X}-\langle\mathbf{X}\rangle)^T(\mathbf{X}-\langle\mathbf{X}\rangle)=\mathbf{U}^T\mathbf{E}\mathbf{U}$$

Peng, J.; Xie, Y.; Hu, D.; Lan, Z. *J. Chem. Phys.* **2021,** *154*, 094122.

Analysis of Trajectory Evolution III: Bath Motion

The Action Variable of the Bath Mode



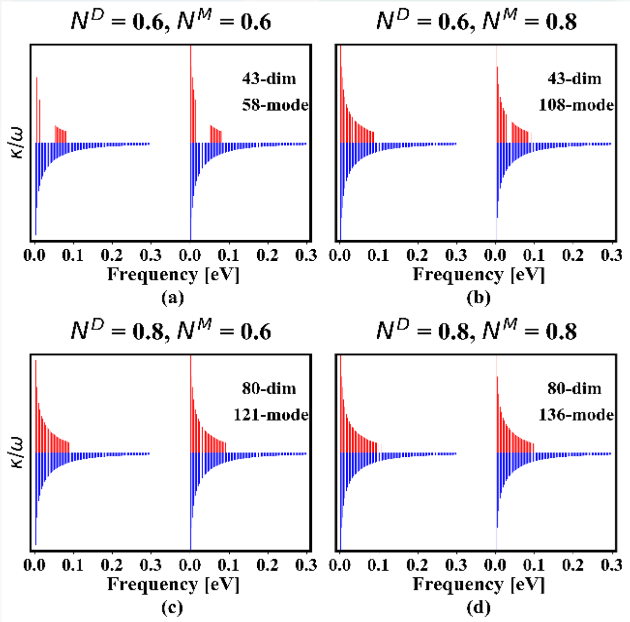
Reduced Model Construction

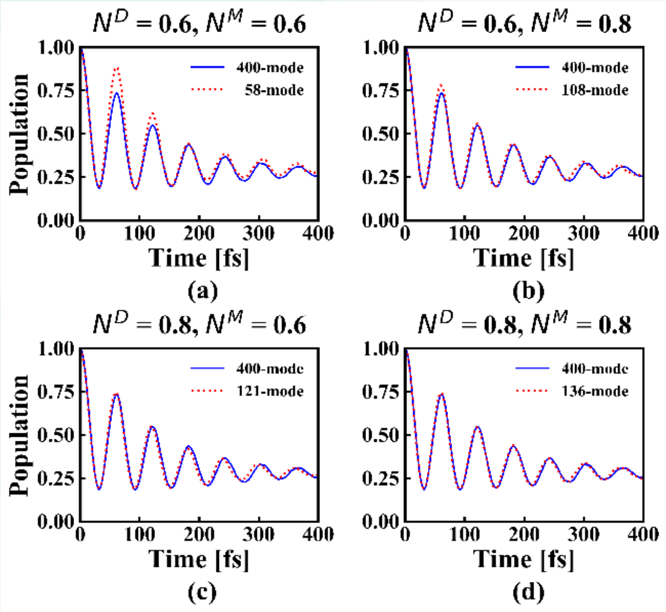
- Select Dimension

$$N^D \sim \sum_i E_i$$

- Select Modes

$$N_i^M \sim \sum_j |U_{ij}|^2$$



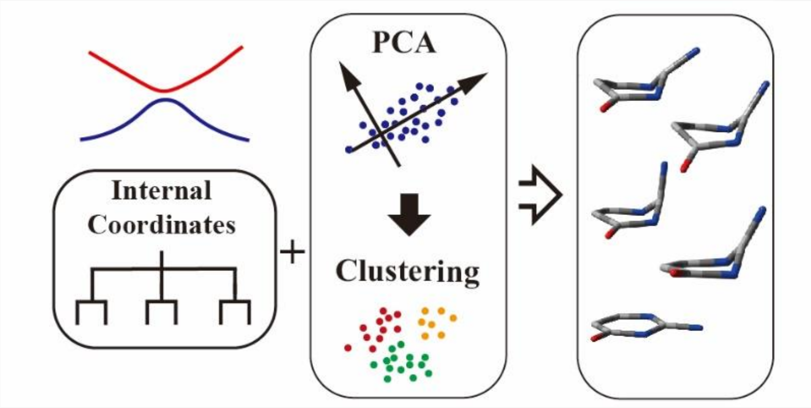


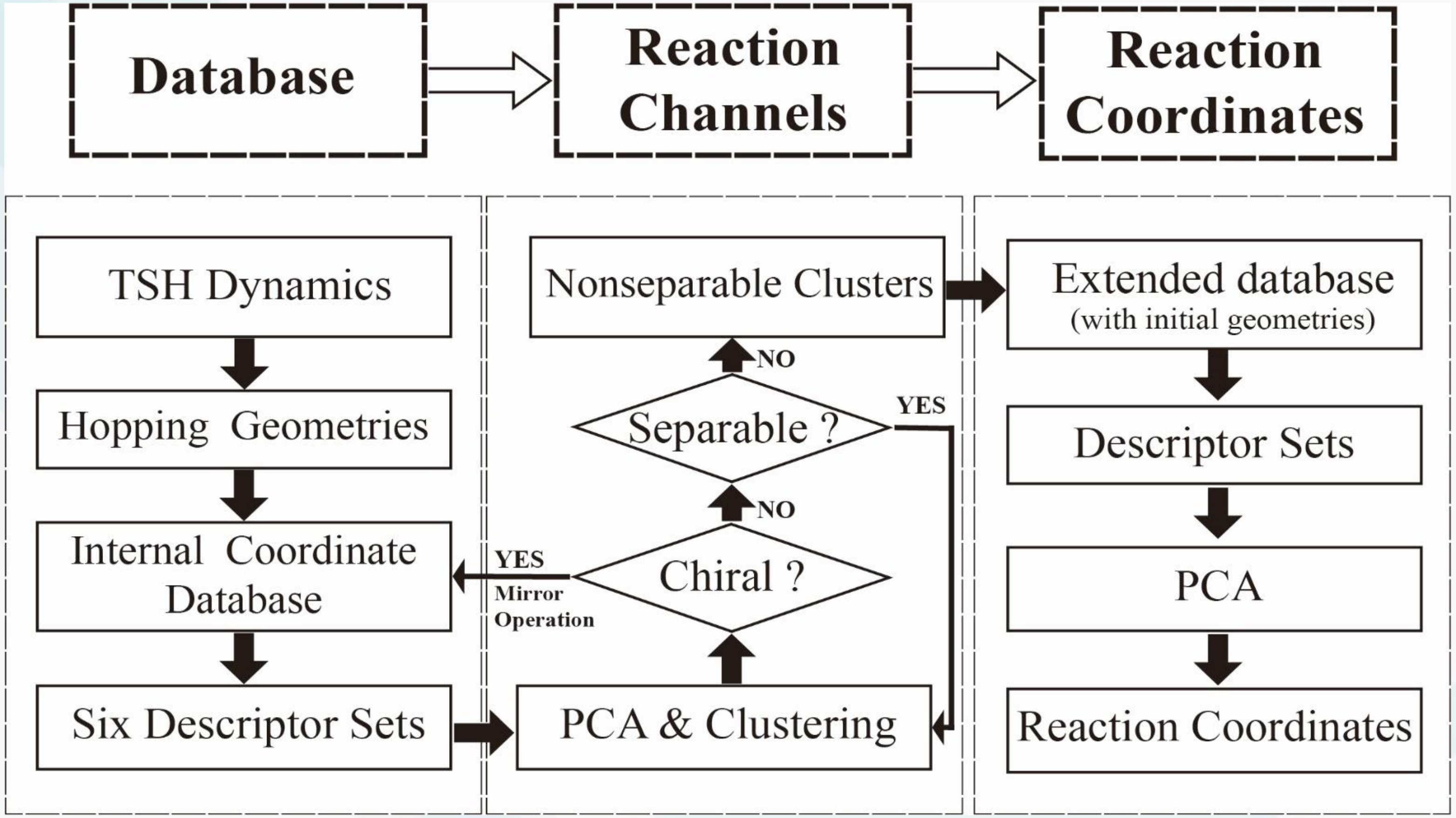
J Peng, Y Xie, D Hu, and Z Lan J. Chem. Phys. 154, 094122 (2021)

Analysis of Trajectory Evolution IV: Ring Motion

An hierarchical protocol based on the PCA and clustering methods for the automatic analysis of the **ring deformation** in the nonadiabatic dynamics

- *Dimensionality reduction : PCA*
- *Clustering : DBSCAN & Agglomerative clustering*





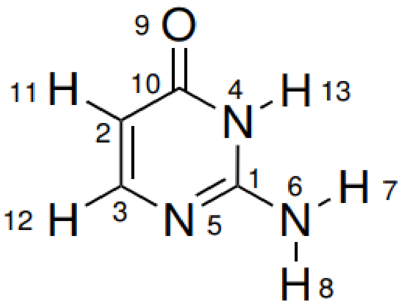
Y Zhu, J Peng, X Kang, C Xu, **Z Lan***, Phys. Chem. Chem. Phys., 2022,24, 24362-24382

Analysis of Trajectory Evolution IV: Ring Motion

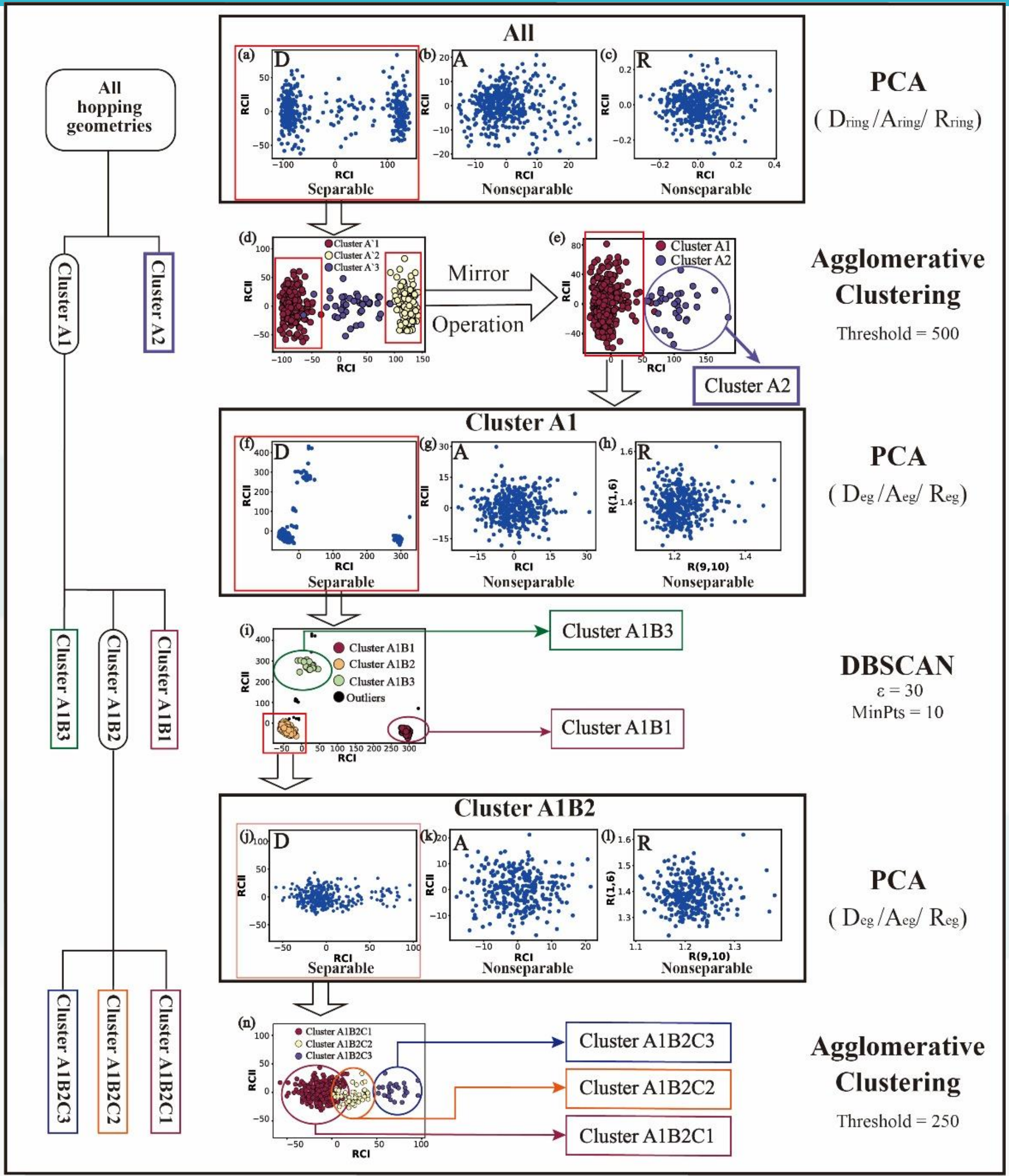
Division scheme and analysis process

Keto-isocytosine

Molecular Structure and Atomic Labels



Descriptor Sets				
D_{ring}	D(4,1,5,3)	D(5,1,4,10)	D(10,2,3,5)	D(3,2,10,4)
	D(4,1,5,3)	D(5,1,4,10)		
A_{ring}	A(4,1,5)	A(3,2,10)	A(2,3,5)	A(1,4,10)
	A(1,5,3)	A(2,10,4)		
R_{ring}	R(1,4)	R(1,5)	R(2,3)	R(4,10)
	R(3,5)	R(2,10)		
D_{eg}	D(6,1,5,3)	D(6,1,4,10)	D(1,4,10,9)	D(3,2,10,9)
A_{eg}	A(4,1,6)	A(2,10,9)	A(5,1,6)	A(4,10,9)
R_{eg}	R(1,6)	R(9,10)		

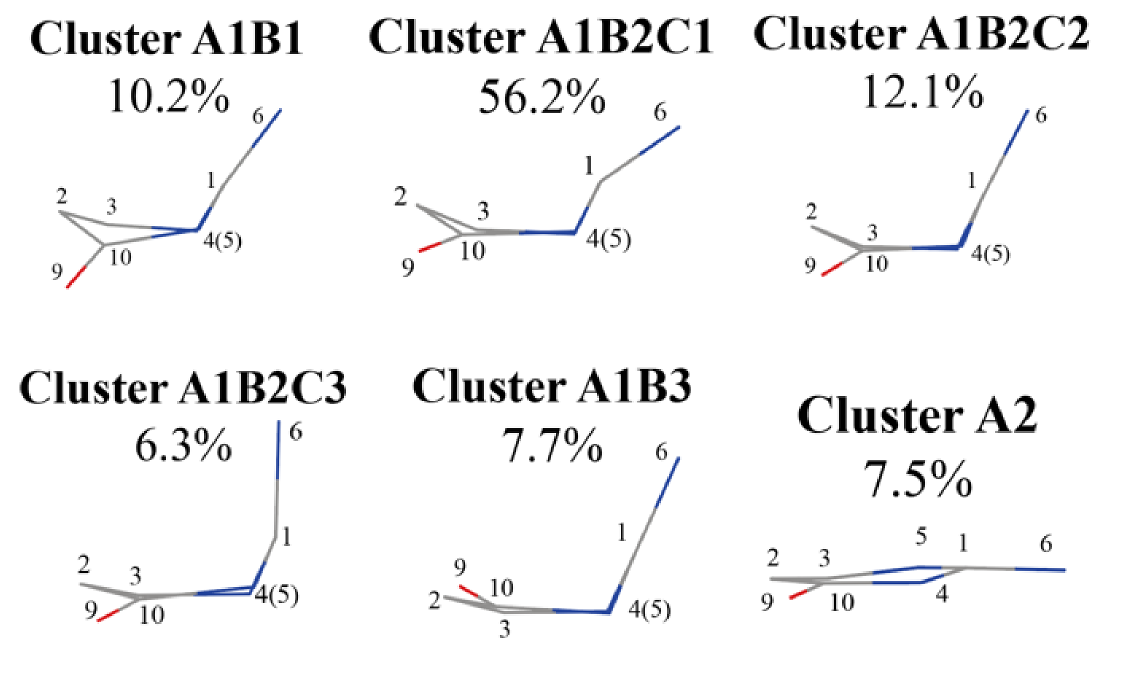


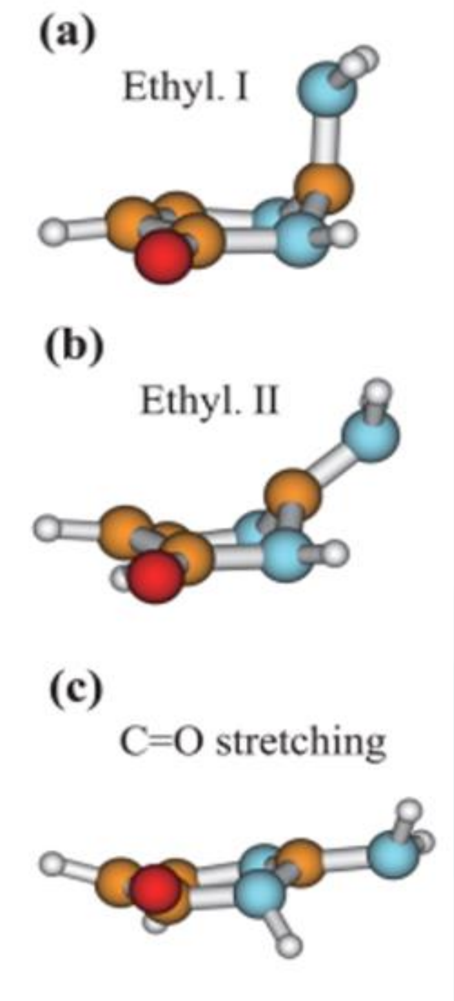
Y Zhu, J Peng, X Kang, C Xu, **Z Lan***, Phys. Chem. Chem. Phys., 2022,24, 24362-24382

Analysis of Trajectory Evolution IV: Ring Motion

Identify reaction coordinates

- Key active coordinates (major and minor)
- Other related information (ratios etc.)
- Further physical insights





Y Zhu, J Peng, X Kang, C Xu, **Z Lan***, Phys. Chem. Chem. Phys., 2022,24, 24362-24382

Short message

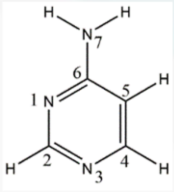
Un-supervised

Machine Learning Methods
may Bring Considerable Impact on
Nonadiabatic Dynamics Simulation

Promising **?** **Problems**

Machine-Learning PES in nonadiabatic dynamics

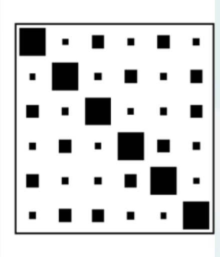
- **The kernel ridge regression is used to build the excited-state PESs**
- **Nonadiabatic dynamics based on ML-PESs**



6-aminopyrimidine (6AP)

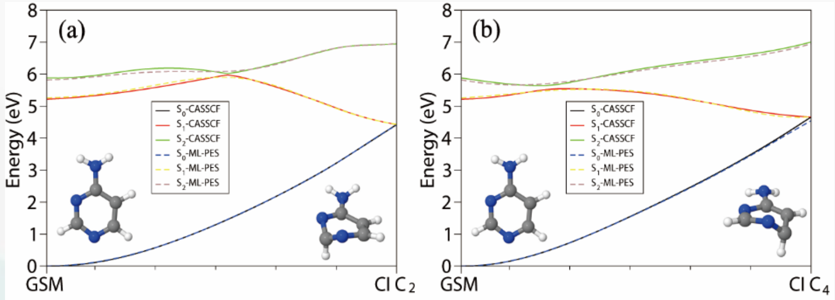
Coulomb Matrix

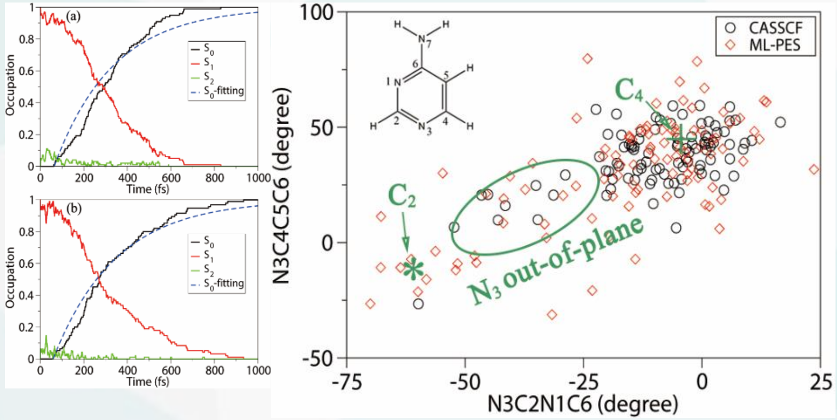
$$M_{kl} = \begin{cases} 0.5Z_k^{2.4} & k = l \\ \dfrac{Z_k Z_l}{\|\boldsymbol{R}_k - \boldsymbol{R}_l\|} & k \neq l \end{cases}$$



$$f(\boldsymbol{m}_i) = \sum_{j=1}^{N_t} c_j \mathrm{K}(\boldsymbol{m}_i, \boldsymbol{m}_j)$$

$$\mathrm{K}(\boldsymbol{m}_i, \boldsymbol{m}_j) = \exp\left(-\frac{\|\boldsymbol{m}_i - \boldsymbol{m}_j\|^2}{2\sigma^2}\right)$$





- **Achieve the efficient massive dynamics simulations with a large number of trajectories.**

JPCL 9, 2725-2732 (2018)

Transient-Absorption Pump-Probe Signals

Hamiltonian

$$\hat{H}(t)=\hat{H}_M+\hat{H}_F(t)$$

$$\hat{H}_F(t)=-\hat{\boldsymbol{\mu}}\cdot\boldsymbol{E}(t)$$

Third-order polarization

$$\boldsymbol{P}^{(3)}(t)=(i)^3\int_0^\infty dt_3\int_0^\infty dt_2\int_0^\infty dt_1\boldsymbol{E}(t-t_3)\boldsymbol{E}(t-t_3-t_2)\boldsymbol{E}(t-t_3-t_2-t_1)S(t_3,t_2,t_1)$$

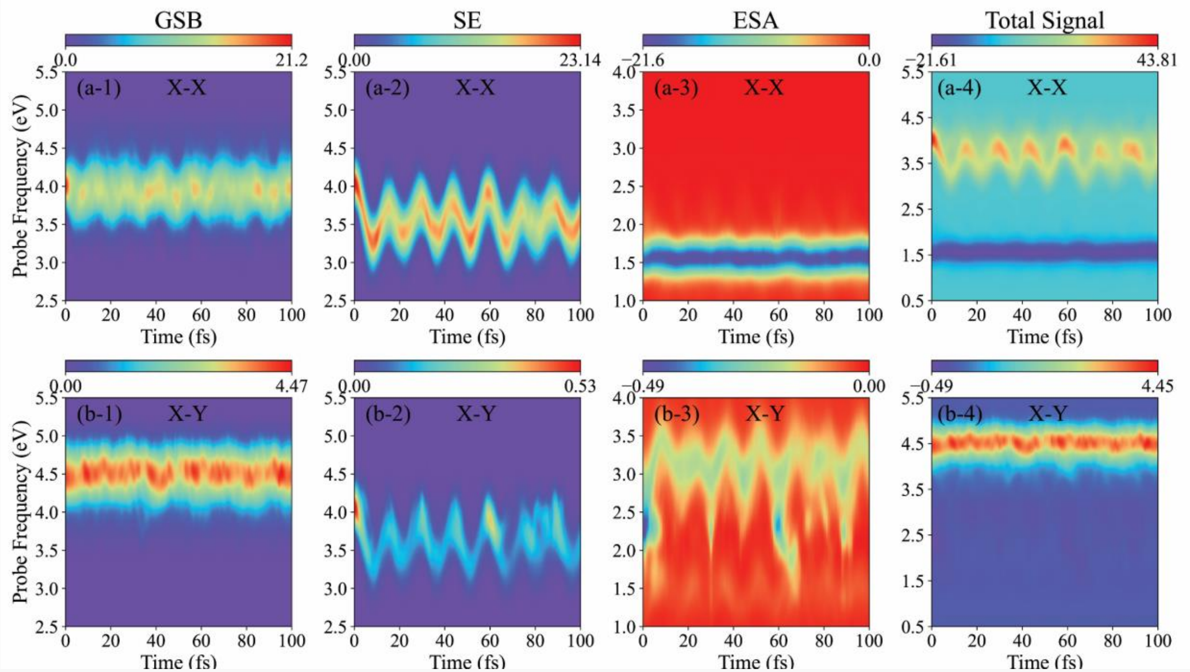
$$S(t_3,t_2,t_1)=Tr\{\hat{\boldsymbol{\mu}}^I(t_1+t_2+t_3)[\hat{\boldsymbol{\mu}}^I(t_1+t_2),[\hat{\boldsymbol{\mu}}^I(t_1),[\hat{\boldsymbol{\mu}}^I(0),\hat{\rho}(-\infty)]]]\}$$

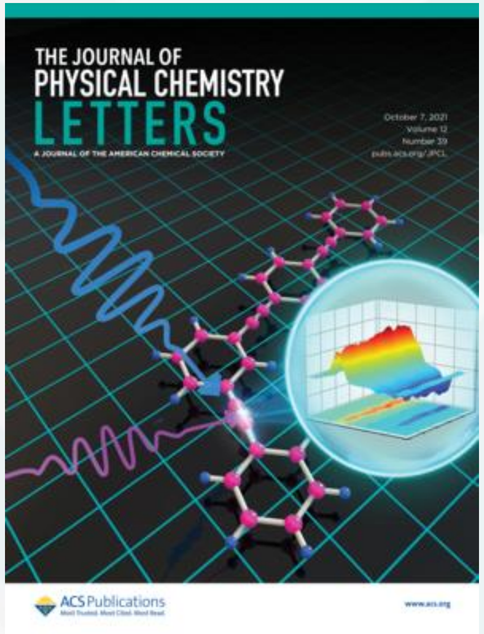
$$\hat{\boldsymbol{\mu}}^I(t)=e^{i\hat{H}_M(t-t_0)}\hat{\boldsymbol{\mu}}e^{-i\hat{H}_M(t-t_0)}$$

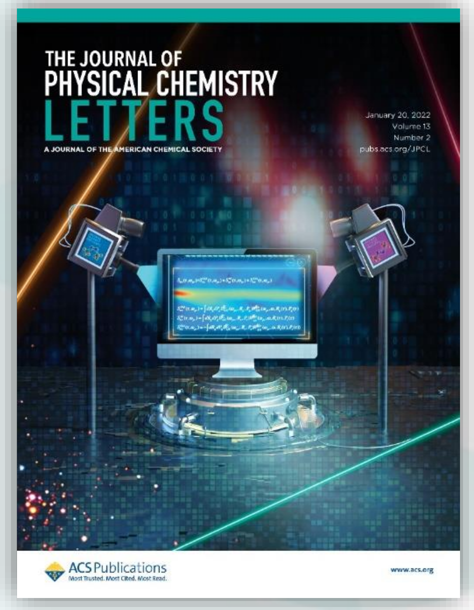
Pump-probe signal

$$I_{\text{int}}(\tau,\omega_{pr})=\omega_{pr}\,\text{Im}\left\{\int_{-\infty}^{\infty}dtE_{pr}(t)e^{i\omega_{pr}t}P^{(3)}_{\boldsymbol{k}_{pr}}(\tau,t)\right\}$$

$$I_{dis}(\tau,\omega)=\omega_{pr}\,\text{Im}\left\{\varepsilon_{pr}(\omega)P^{(3)}_{\boldsymbol{k}_{pr}}(\tau,\omega)\right\}$$







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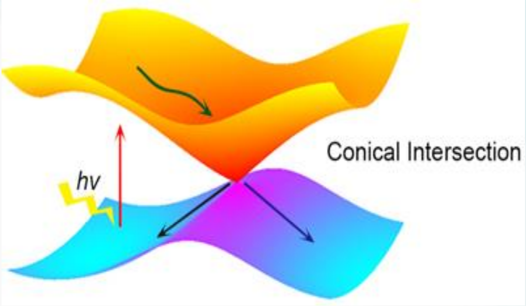
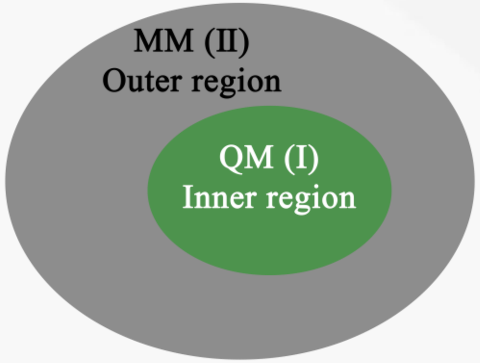
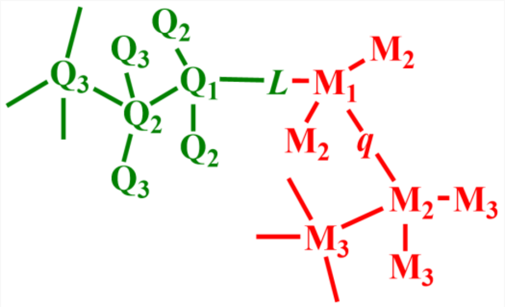
Nonadiabatic Dynamics in Solutions and Biological Environments

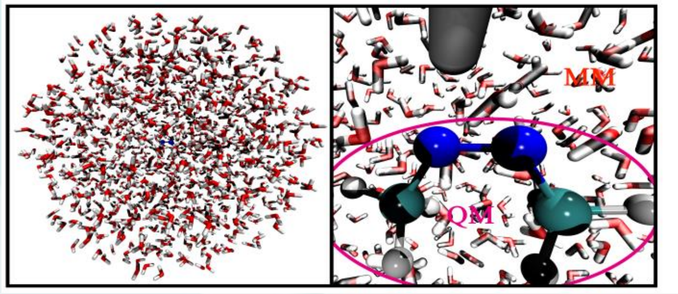
QM/MM Surface Hopping

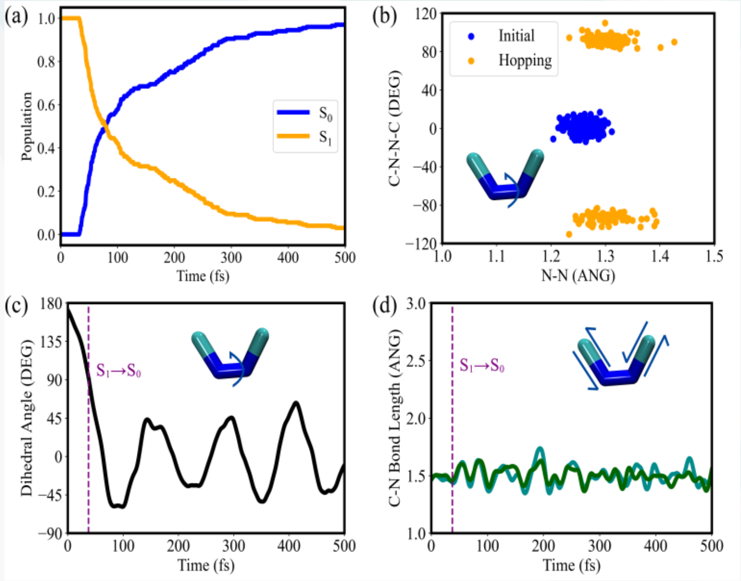




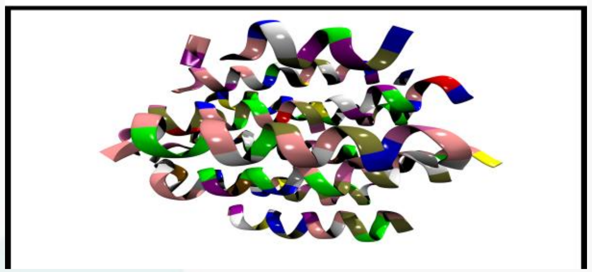


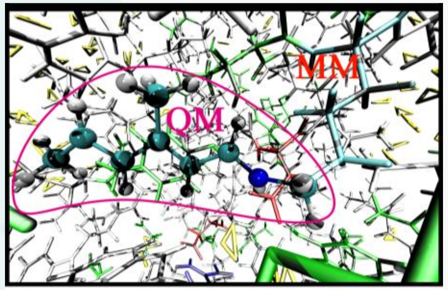
Nonadiabatic Dynamics in Solutions

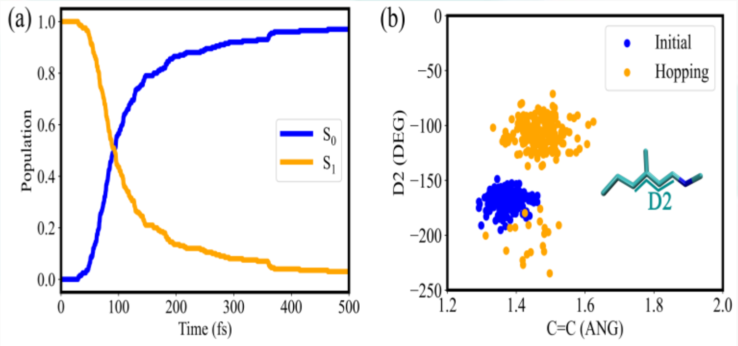




Nonadiabatic Dynamics in Proteins







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New Postdoc and Research Assistant Positions are open !!!

Thank you！

Zhenggang Lan
2024.02