VISTA

Virtual International Seminar on Theoretical Advancements
Seminar 112

Detailed Complementary Consistency for Mixed Quantum-Classical Nonadiabatic Dynamics

Linjun Wang
Zhejiang University, China

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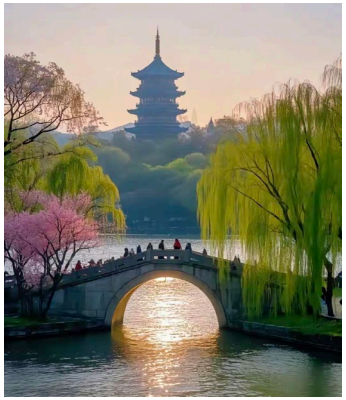
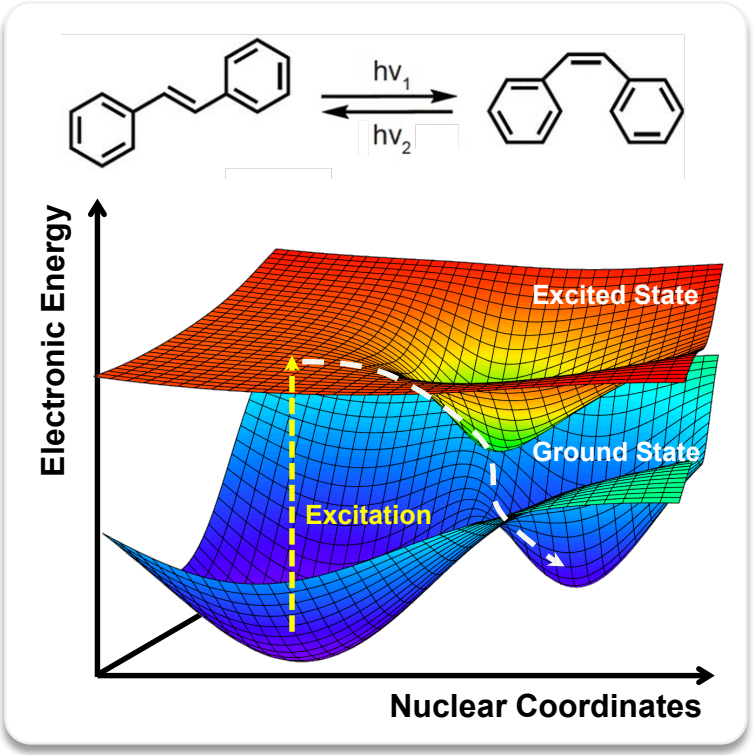
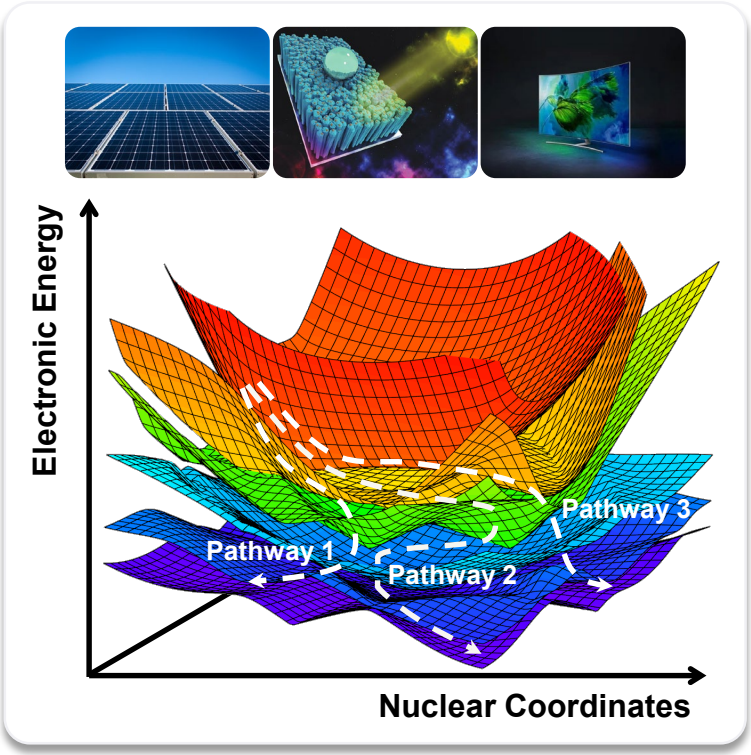


Nonadiabatic Dynamics





- **Nonadiabatic dynamics methods (not a complete list):** $\frac{\partial \psi(\{\vec{R}_\alpha\},\{\vec{r}_i\},t)}{\partial t} = \frac{1}{i\hbar}\hat{H}\psi(\{\vec{R}_\alpha\},\{\vec{r}_i\},t)$

DVR, MCTDH, DMRG, HEOM, DEOM, SSE, AIMS, MQCL, QTMF, CTMQC, EMF, TSH, SCDM, MM, NAF, MASH, DCC …

Quantum dynamics has intrinsic "curse of dimensionality"

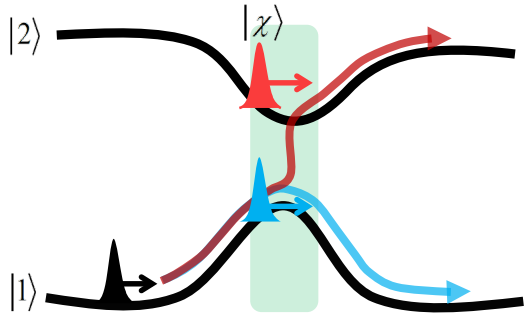
Different methods have different advantages and limitations

Quantum Description of Nonadiabatic Dynamics

Direct product state $|\Psi\rangle = |\chi\rangle|\psi\rangle = |\chi\rangle\left(w_1|1\rangle + w_2|2\rangle\right)$

$$i\hbar\frac{\partial|\Psi\rangle}{\partial t} = (\hat{T}_n + \hat{H}_{el})|\Psi\rangle \xrightarrow{\text{Classical limit}} i\hbar\frac{\partial|\psi\rangle}{\partial t} = \hat{H}_{el}|\psi\rangle$$

Time-dependent propagation $\dot{\sigma} = \frac{1}{i\hbar}\left[\hat{H} - i\hbar\sum_\alpha \mathbf{v}_\alpha \cdot \mathbf{d}^\alpha, \sigma\right]$

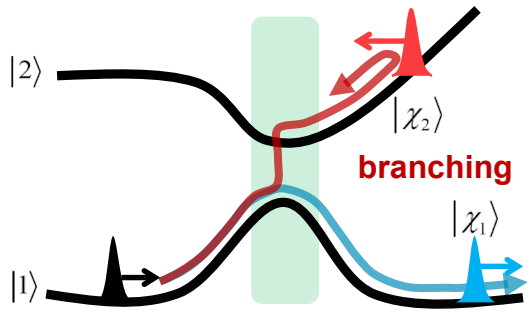


Entangled state $|\Psi\rangle = |\chi_1\rangle|1\rangle + |\chi_2\rangle|2\rangle$

decay with time

$$\rho = |\Psi\rangle\langle\Psi| \longrightarrow \boldsymbol{\sigma} = \mathrm{Tr}_n[\rho] = \begin{pmatrix} \langle\chi_1|\chi_1\rangle & \langle\chi_2|\chi_1\rangle \\ \langle\chi_1|\chi_2\rangle & \langle\chi_2|\chi_2\rangle \end{pmatrix}$$

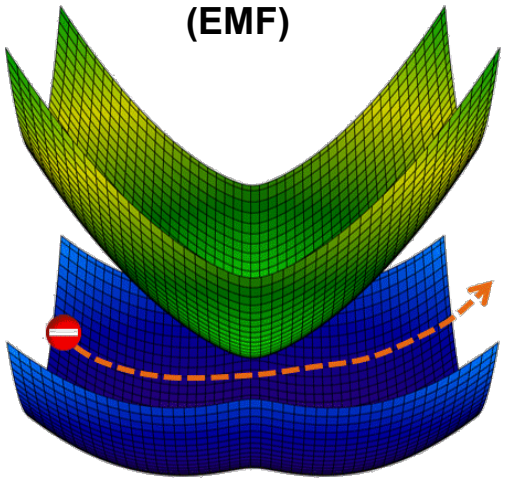
Quantum decoherence $\dot{\sigma} = \frac{1}{i\hbar}\left[\hat{H} - i\hbar\sum_\alpha \mathbf{v}_\alpha \cdot \mathbf{d}^\alpha, \sigma\right] - \mathcal{R}[\sigma]$



Branching and decoherence are essential for nonadiabatic dynamics

Mixed Quantum-Classical Dynamics (MQCD)

Ehrenfest Mean Field (EMF)



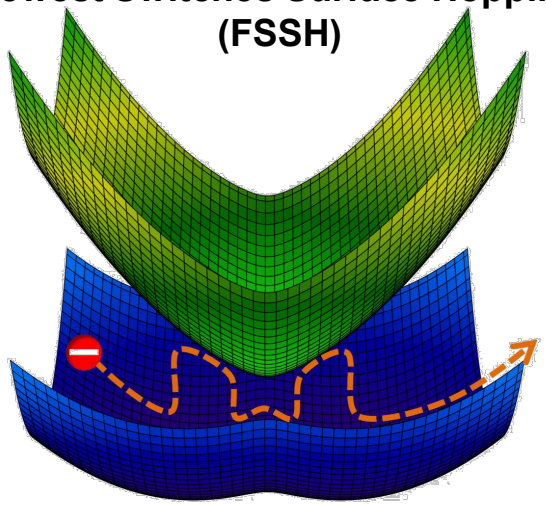
Electron evolution $i\hbar\partial_t|\psi\rangle = \hat{H}_e|\psi\rangle$

Nuclear dynamics $m_\alpha \ddot{\boldsymbol{x}}_\alpha = -\nabla_\alpha \langle\psi|\hat{H}_e|\psi\rangle$

Average surface $E_{eff} = \sum_i |w_i|^2 E_i$

Ehrenfest, ***Z. Physik*** 45, 455 **(1927)**

Fewest Switches Surface Hopping (FSSH)



Electron evolution $i\hbar\partial_t|\psi\rangle = \hat{H}_e|\psi\rangle$

Nuclear dynamics $m_\alpha \ddot{\boldsymbol{x}}_\alpha = -\nabla_\alpha \langle\phi_\lambda|\hat{H}_e|\phi_\lambda\rangle$

Hopping probabilities $g_{\lambda i} = \max(0, -b_{\lambda i}\Delta t / \sigma_{\lambda\lambda})$

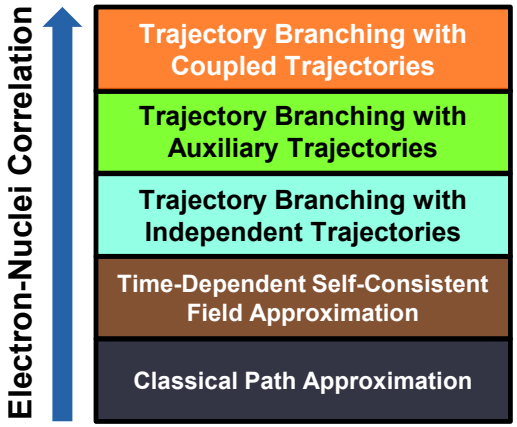
Tully, ***J. Chem. Phys.*** 93, 1061 **(1990)**

EMF trajectory is deterministic, while FSSH ensemble has branching

More robust theoretical framework for MQCD is still needed

Main Research Interests

Consistent Theory



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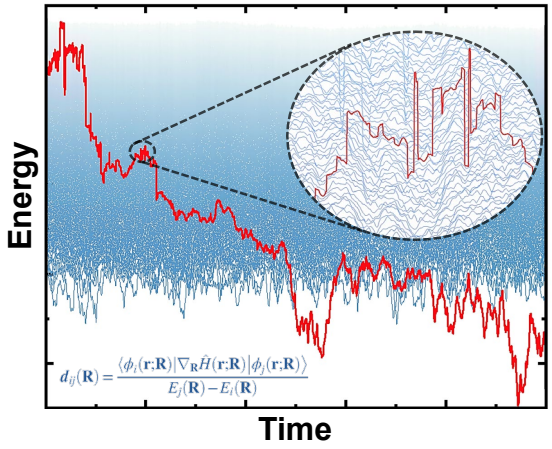
Large-Scale Methods



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Dynamics Mechanisms

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Detailed Complementary Consistency for MQCD

Outline

- **Statistical Interpretation of MQCD**
- Detailed Complementary Consistency
- Some Related Method Developments

Quantum Dynamics

Statistical interpretation of quantum mechanics

The quantity $|\Psi|^2$ has an important physical interpretation:
It is related to the probability that a system can be found in a particular region of space

	Quantum dynamics		MQCD
State description	$\|\psi\rangle$	$\hat{\rho} = \|\psi\rangle\langle\psi\|$	?
Statistical interpretation	$P_i = \|\langle i\|\psi\rangle\|^2$	$P_i = \rho_{ii}$	?
Expectation value of an observable	$\langle\hat{O}\rangle = \langle\psi\|\hat{O}\|\psi\rangle$	$\langle\hat{O}\rangle = Tr(\hat{\rho}\hat{O})$	?
Equation of motion	$\frac{\partial\|\psi\rangle}{\partial t} = \frac{1}{i\hbar}\hat{H}\|\psi\rangle$	$\frac{\partial\hat{\rho}}{\partial t} = \frac{1}{i\hbar}[\hat{H},\hat{\rho}]$	?

Born, ***Science*** 122, 675 **(1955)**; ***Physics in My Generation***, *Springer* **(1969)**

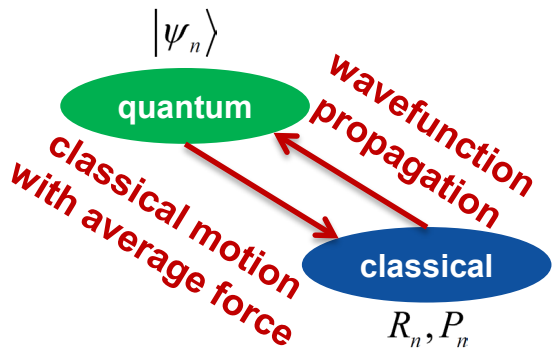
Mixed Quantum-Classical Liouville (MQCL)

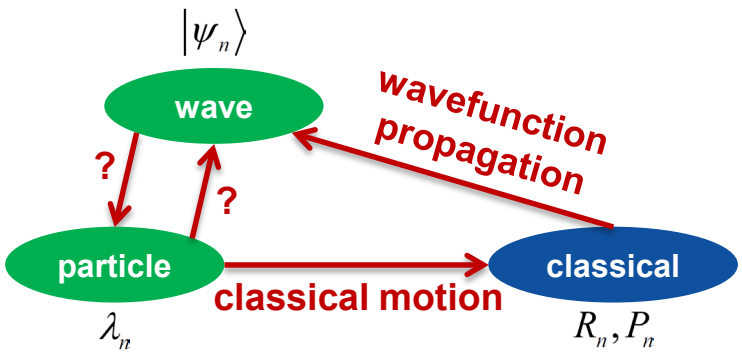
	MQCL
State description	$\hat{\rho}^W(R,P)$
Statistical interpretation	$P_i = \int\int \hat{\rho}^W_{ii}(R,P)dRdP$
Expectation value of an observable	$\left\langle \hat{O} \right\rangle = Tr\left(\int\int \hat{\rho}^W \hat{O}^W dRdP \right)$
Equation of motion	$\frac{\partial \hat{\rho}^W(R,P)}{\partial t} = \frac{1}{i\hbar}\left[\hat{H}^W, \hat{\rho}^W\right] + \frac{1}{2}\left(\left\{\hat{H}^W, \hat{\rho}^W\right\} - \left\{\hat{\rho}^W, \hat{H}^W\right\}\right)$ $\frac{\partial \rho^W_{ij}(R,P)}{\partial t} = \frac{1}{i\hbar}\left(E_i(R) - E_j(R)\right)\rho^W_{ij} - \frac{P}{M}\cdot\nabla_R \rho^W_{ij}$ $-\frac{1}{2}\sum_k \left(F^W_{ik}\cdot\nabla_P \rho^W_{kj} + \nabla_P \rho^W_{ik}\cdot F^W_{kj}\right) + \sum_k \frac{P}{M}\cdot\left(\rho^W_{ik} d_{kj} - d_{ik}\rho^W_{kj}\right)$

It is still challenging to solve the MQCL equation efficiently

Kapral and **Ciccotti**, ***J. Chem. Phys.*** 110, 8919 **(1999)**
Subotnik, **Ouyang**, and **Landry**, ***J. Chem. Phys.*** 139, 214107 **(2013)**

Statistical Interpretation of MQCD

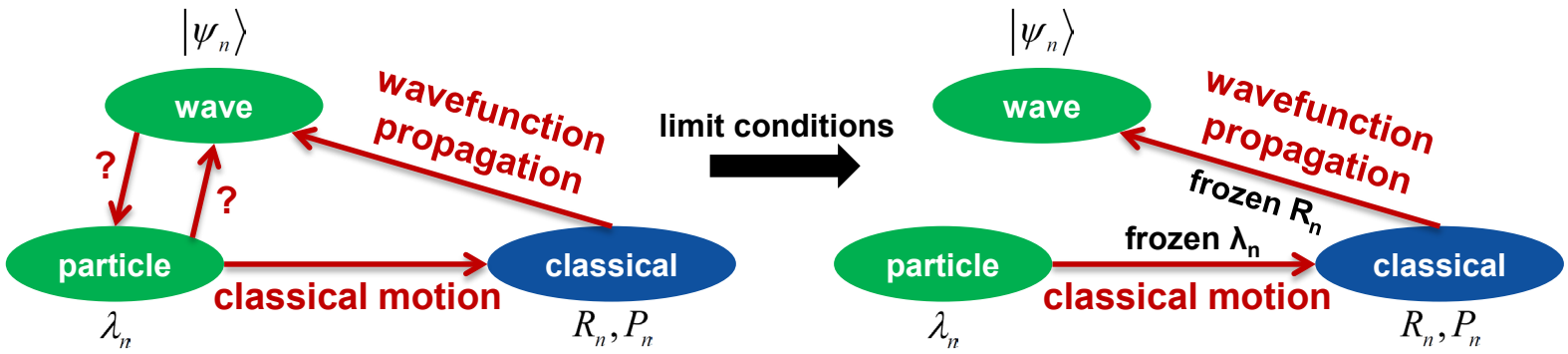




	MQCD
State description	$\{\|\psi_n\rangle, R_n, P_n, \lambda_n\}$
Statistical Interpretation	$\rho_{ii}^{\mathrm{wf}}(R,t) = \frac{1}{N_{\mathrm{traj}}}\sum_{n=1}^{N_{\mathrm{traj}}} \left\|\langle i\|\psi_n(t)\rangle\right\|^2 \delta(R - R_n(t))$ $\rho_{ij}^{\mathrm{wf}}(R,t) = \frac{1}{N_{\mathrm{traj}}}\sum_{n=1}^{N_{\mathrm{traj}}} \langle i\|\psi_n(t)\rangle\langle\psi_n(t)\|j\rangle \delta(R - R_n(t))$ $\rho_{ii}^{\mathrm{as}}(R,t) = \frac{1}{N_{\mathrm{traj}}}\sum_{n=1}^{N_{\mathrm{traj}}} \delta_{i,\lambda_n(t)} \delta(R - R_n(t))$

L. Wang* et al., ***J. Phys. Chem. Lett.*** 15, 6771 **(2024)**

Statistical Interpretation of MQCD



	MQCD
Expectation value of an observable	$\langle \hat{O} \rangle = Tr\left(\int \hat{\rho}^{\mathrm{wf}} \hat{O} dR\right)$ $\quad \langle \hat{O} \rangle = \sum_i \int \rho_{ii}^{\mathrm{as}} O_{ii} dR$ $\langle \hat{O} \rangle^{\mathrm{wf}} = \frac{1}{N_{\mathrm{traj}}} \sum_n^{N_{\mathrm{traj}}} Tr\left(\hat{\rho}_n^{\mathrm{wf}} \hat{O}(R_n)\right)$ $\quad \langle \hat{O} \rangle^{\mathrm{as}} = \frac{1}{N_{\mathrm{traj}}} \sum_n^{N_{\mathrm{traj}}} O_{\lambda_n \lambda_n}(R_n)$
Equation of motion	$\frac{\partial |\psi_n\rangle}{\partial t} = \frac{1}{i\hbar} \hat{H}_e(R_n) |\psi\rangle + \mathcal{X}$ $\quad \lambda_n(t) \xrightarrow{z} \lambda_n(t+dt)$ $\frac{dP_n}{dt} = -\nabla_R E_\lambda(R_n) + \mathcal{Y}$ $\quad \frac{dR_n}{dt} = \frac{1}{M} P_n$

L. Wang* et al., ***J. Phys. Chem. Lett.*** 15, 6771 **(2024)**

Principle of Detailed Internal Consistency

Basic requirement of consistency at the ensemble level: $\rho_{ii}^{\mathrm{wf}}(R,t) = \rho_{ii}^{\mathrm{as}}(R,t)$

	MQCD
State description	$\left\{\left\|\psi_n\right\rangle, R_n, P_n, \lambda_n\right\}$
Statistical interpretation	$\rho_{ij}(R,t) = \frac{1}{N_{\mathrm{traj}}}\sum_{n=1}^{N_{\mathrm{traj}}}\left\langle i\middle\|\psi_n(t)\right\rangle\left\langle\psi_n(t)\middle\| j\right\rangle\delta(R-R_n(t))$
Expectation value of an observable	$\left\langle\hat{O}\right\rangle = \frac{1}{N_{\mathrm{traj}}}\sum_{n}^{N_{\mathrm{traj}}} Tr\left(\left\|\psi_n\right\rangle\left\langle\psi_n\middle|\hat{O}(R_n)\right.\right)$
Equation of motion	$\frac{\partial\left\|\psi_n\right\rangle}{\partial t} = \frac{1}{i\hbar}\hat{H}_e(R_n)\left\|\psi\right\rangle + \mathcal{X}$ $\quad\quad \lambda_n(t) \xrightarrow{z} \lambda_n(t+dt)$ $\frac{dP_n}{dt} = -\nabla_R E_\lambda(R_n) + \mathcal{Y}$ $\quad\quad \frac{dR_n}{dt} = \frac{1}{M}P_n$

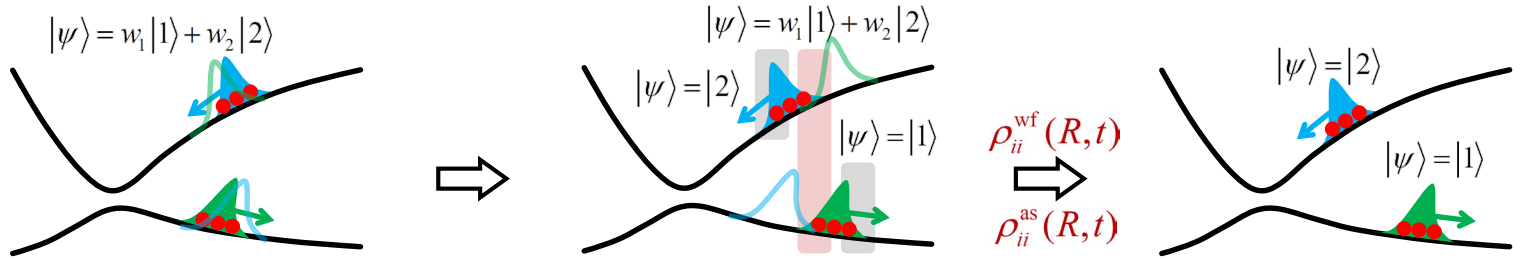
The wave and particle descriptions should yield identical results at any place and any time

L. Wang* et al., ***J. Phys. Chem. Lett.*** 15, 6771 **(2024)**

Outline

- Statistical Interpretation of MQCD
- **Detailed Complementary Consistency**
- Some Related Method Developments

Detailed Complementary Consistency (DCC) Method



The population distributions are difficult to calculate; There are many possible solutions

1. Local trajectory density calculation:

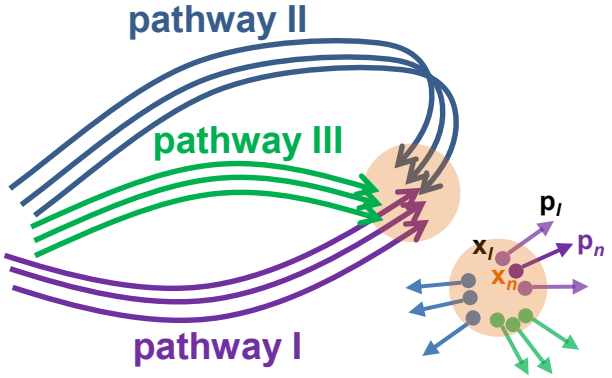
$$N_i^n = \sum_{l=1}^{N} \Theta\left(\varepsilon^2 - \| \mathbf{x}_n - \mathbf{x}_l \|^2\right) \Theta\left(\frac{\mathbf{p}_n \cdot \mathbf{p}_l}{\| \mathbf{p}_n \| \cdot \| \mathbf{p}_l \|} - \cos(\theta)\right) \delta_{i,a_l}$$

$$\Theta(x) = \begin{cases} 1, & x \geq 0 \\ 0, & x < 0 \end{cases} \qquad \rho_{ii}^{n,\mathrm{as}} = \frac{N_i^n}{\sum_j N_j^n} \qquad z_n = \frac{\left|\rho_{11}^{n,\mathrm{as}} - \rho_{11}^{n,\mathrm{wf}}\right|}{\sqrt{\rho_{11}^{n,\mathrm{wf}}(1-\rho_{11}^{n,\mathrm{wf}})} / \sqrt{\sum_l N_l^n}}$$

2. Hypothesis testing: z-test, χ^2-test

3. Consistent correction: $\rho'_{ii} = \rho_{ii}^{\mathrm{as}} \qquad \rho'_{ij} = \frac{\sqrt{\rho'_{ii}\rho'_{jj}}}{|\rho_{ij}|}\rho_{ij}$

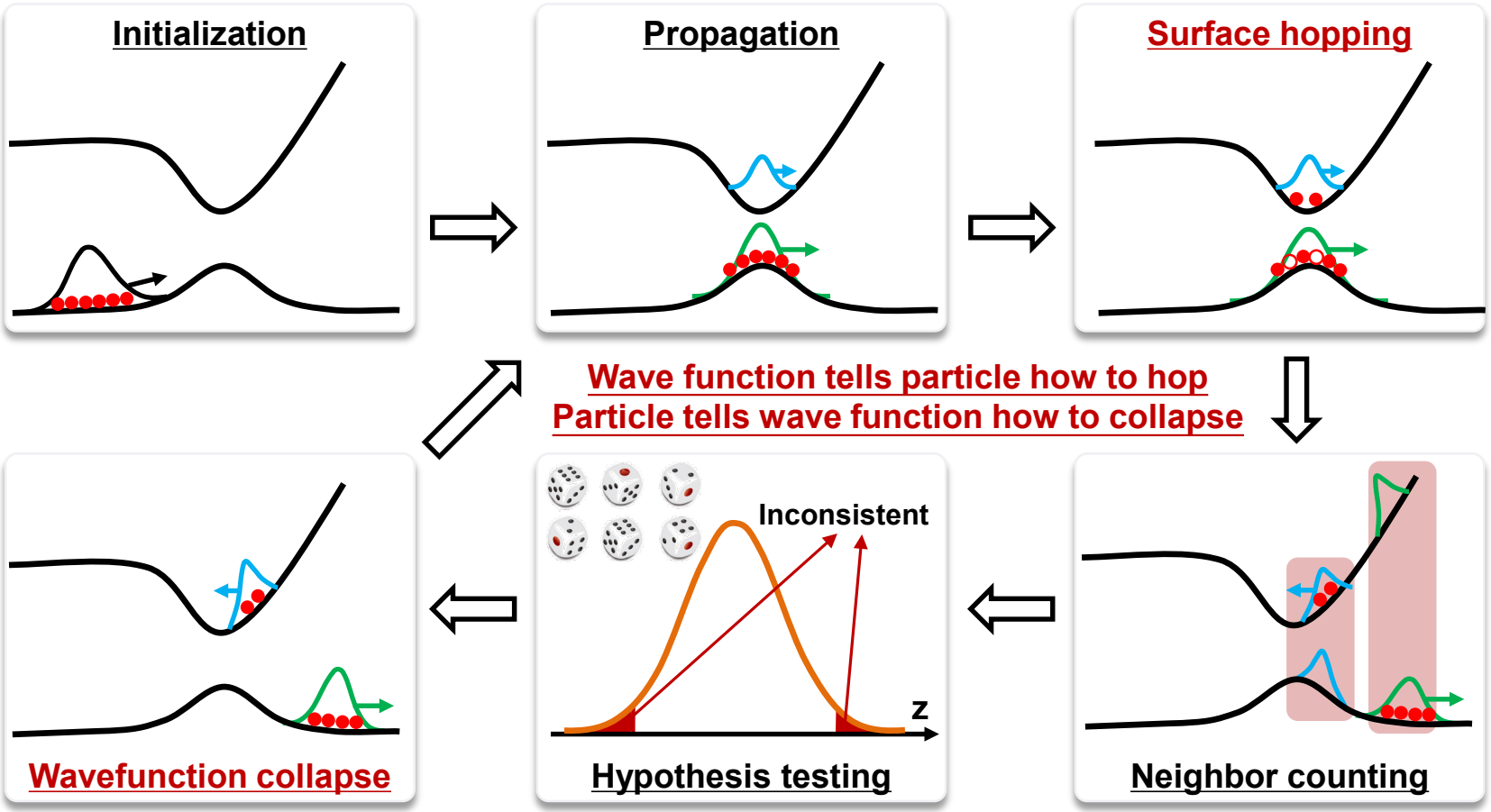
consistency is associated with pathway



If each trajectory is consistent, the trajectory ensemble becomes consistent

L. Wang* et al., ***J. Phys. Chem. Lett.*** 15, 6771 **(2024)**

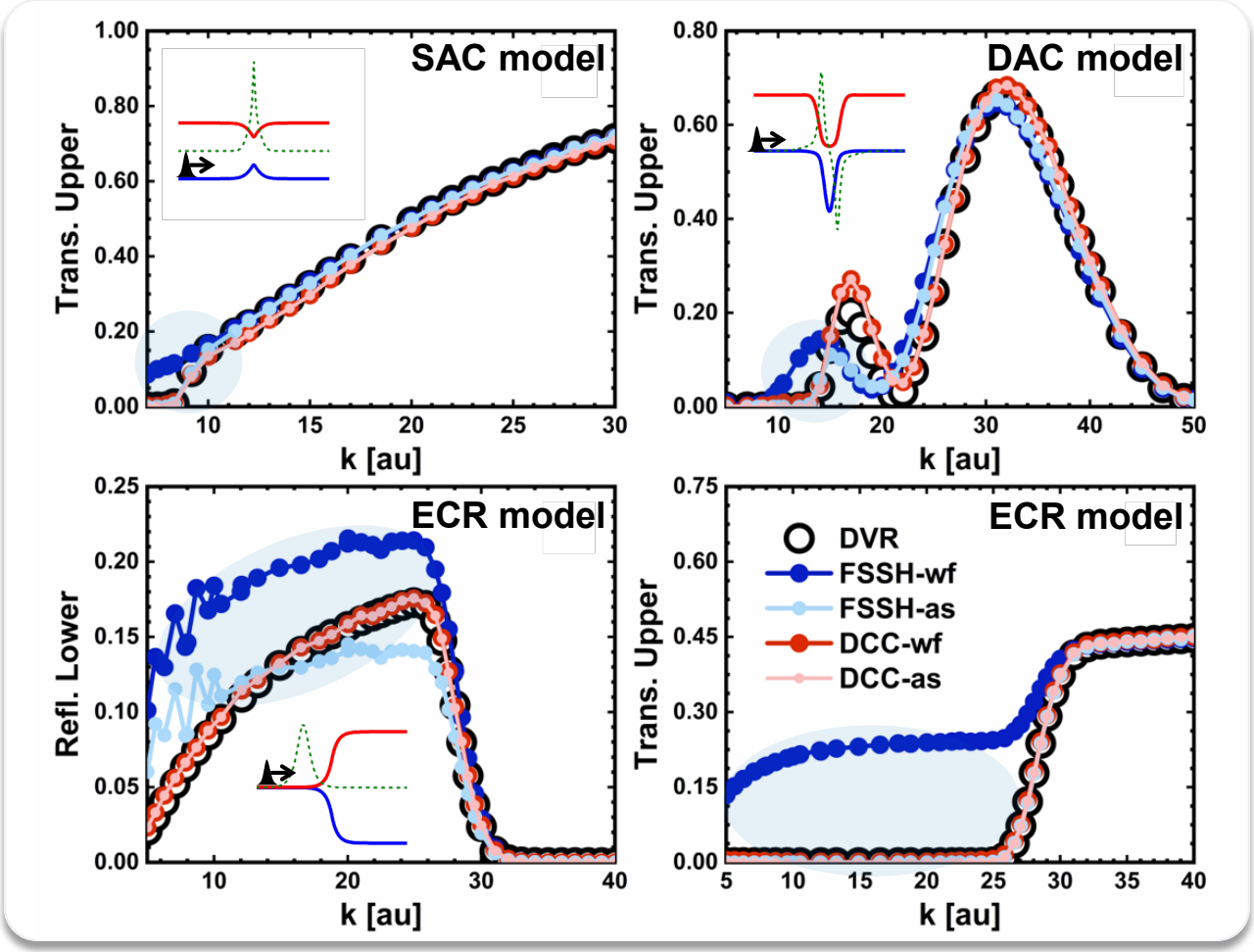
Step-by-Step Algorithms of DCC



DCC naturally gives surface hopping and trajectory branching
DCC also properly describes coherence and decoherence

L. Wang* et al., ***J. Phys. Chem. Lett.*** 15, 6771 **(2024)**

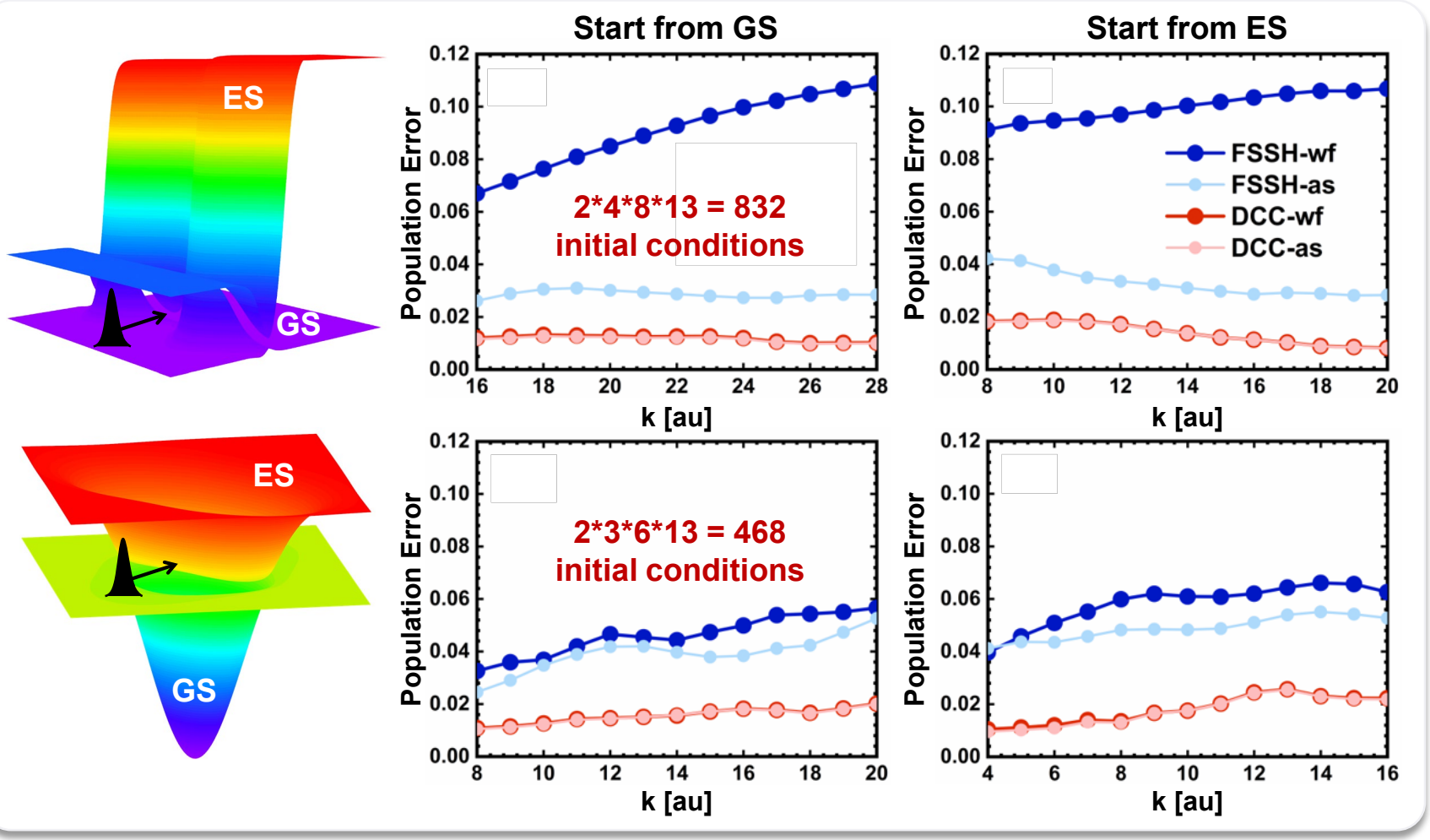
One-Dimensional Tully Scattering Models



Active states and wave functions give identical and accurate results

Tully, ***J. Chem. Phys.*** 93, 1061 **(1990)**

Two-Dimensional Representative Scattering Models

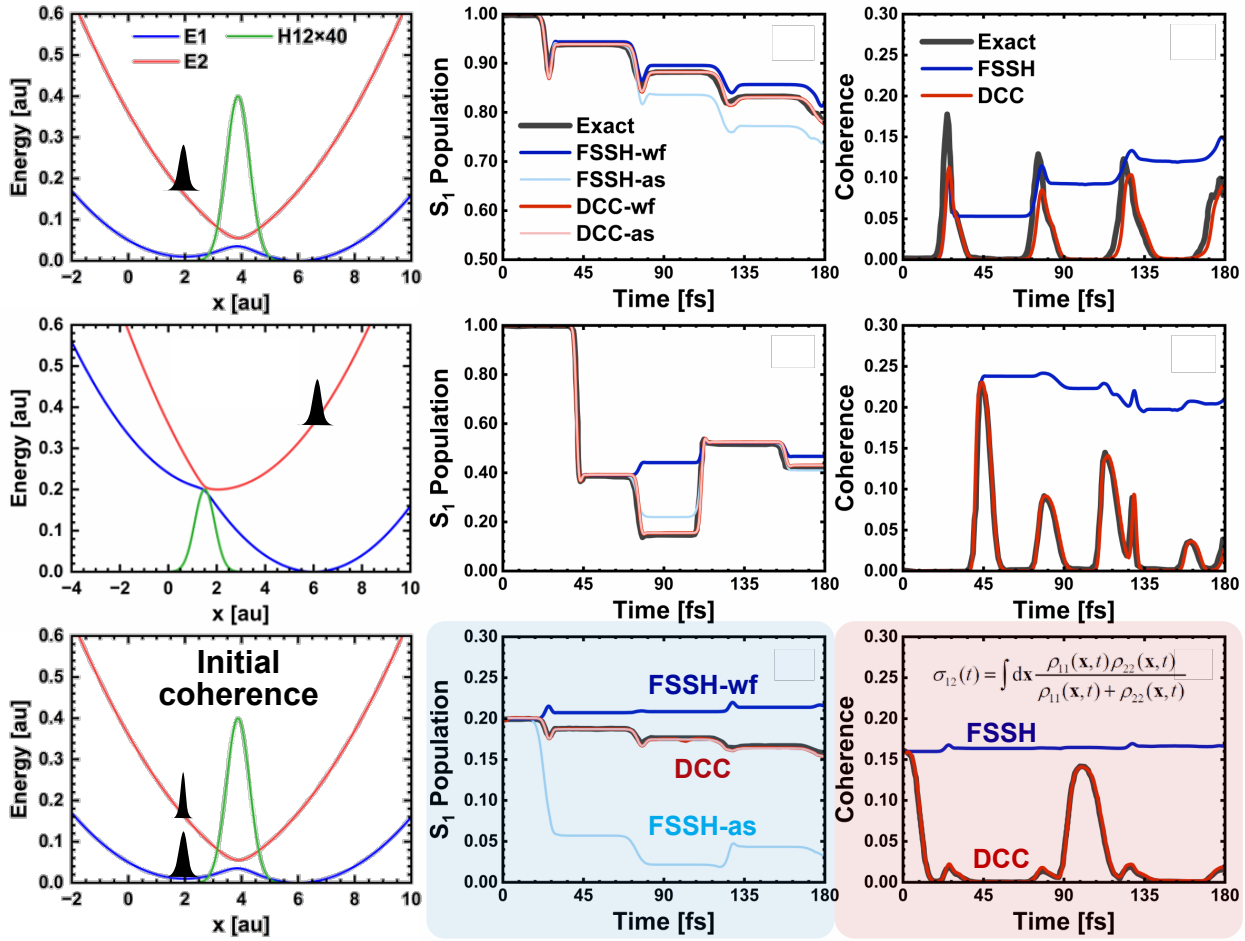


Active states and wave functions give identical and accurate results

Shenvi, **Subotnik** et al., ***J. Chem. Phys.*** 135, 024101 **(2011)**; ***J. Phys. Chem. A*** 115, 12083 **(2011)**

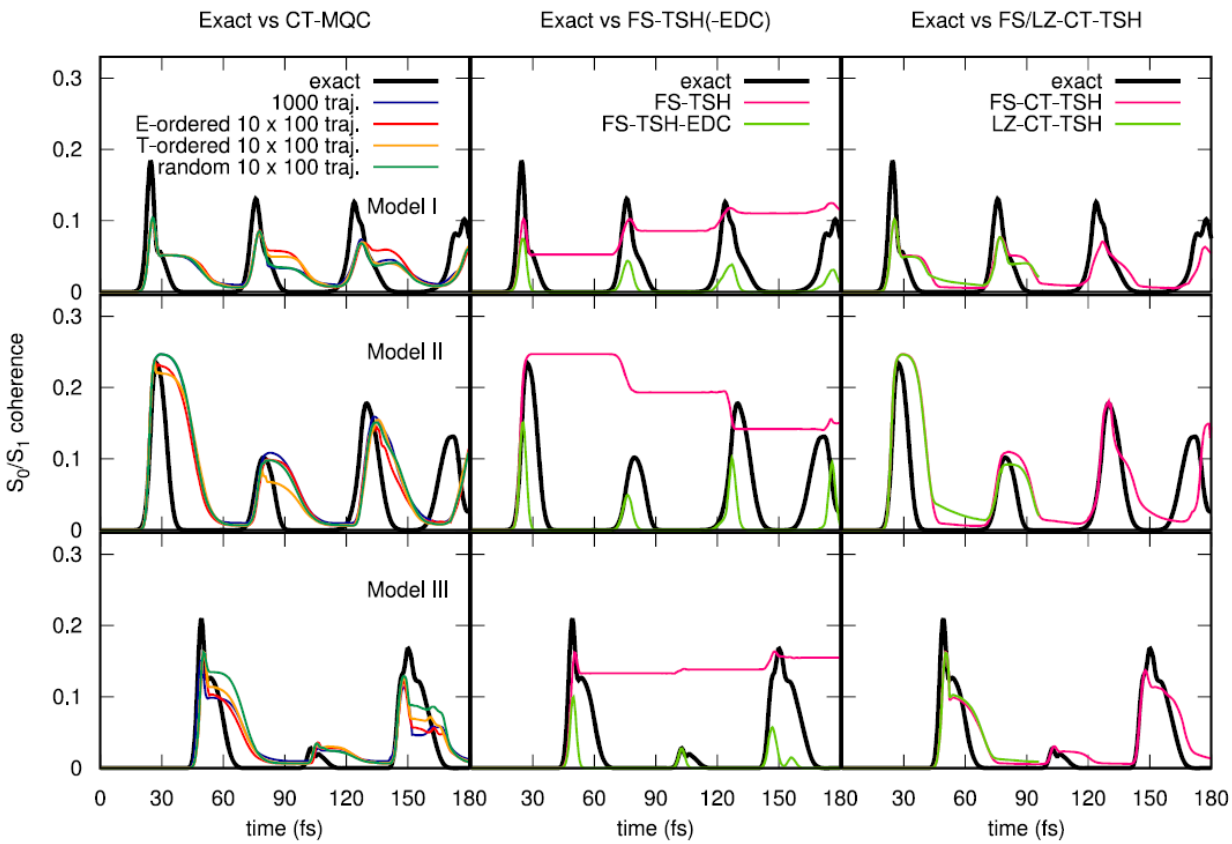
One-Dimensional Bound-State Models

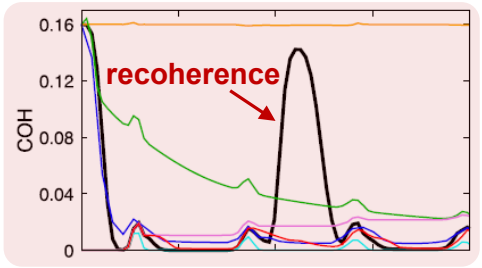
Hamiltonian $H_{11}(x)=\frac{1}{2}k(R-R_1)^2 \qquad H_{22}(x)=\frac{1}{2}k(R-R_2)^2+\Delta \qquad H_{12}(x)=H_{21}(x)=be^{-a(R-R_3)^2}$

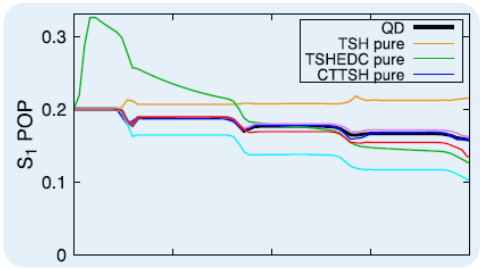


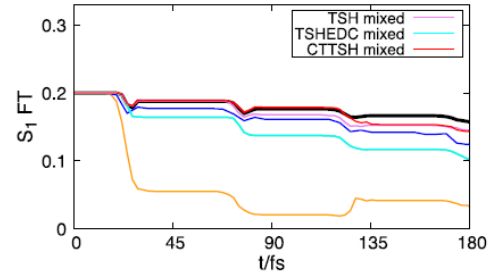
Agostini et al., ***J. Chem. Theory Comput.*** 17, 5969 **(2021)**; ***J. Chem. Phys.*** 160, 054102 **(2024)**

One-Dimensional Bound-State Models









Coherence and recoherence are much more difficult to describe
DCC outperforms all other investigated methods in these models

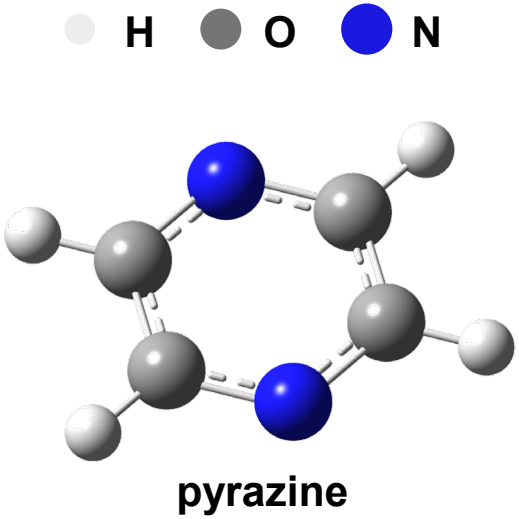
Agostini et al., ***J. Chem. Theory Comput.*** 17, 5969 **(2021)**; ***J. Chem. Phys.*** 160, 054102 **(2024)**

Three-Mode Pyrazine Model

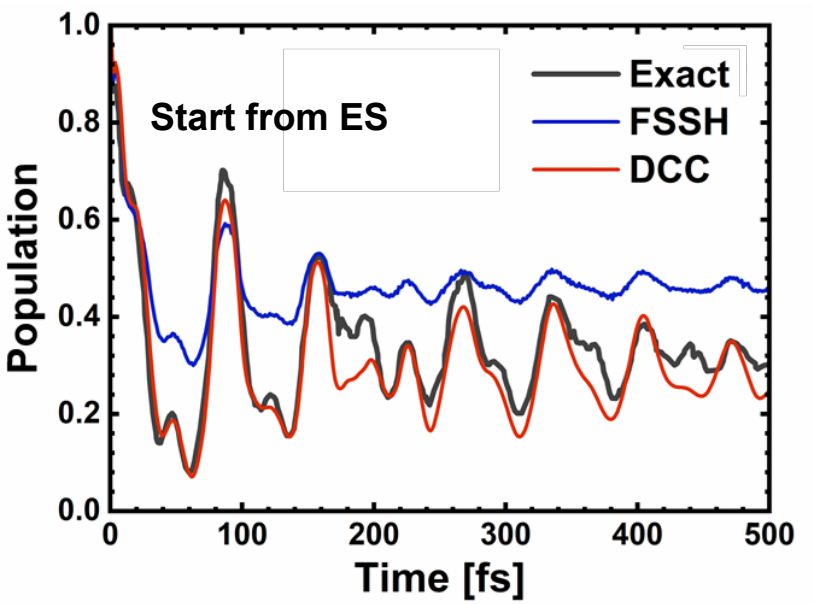
Hamiltonian

$$\hat{H} = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} + \sum_{i=10a,6a,1} \frac{\omega_i}{2}\left(\hat{P}_i^2 + \hat{R}_i^2\right)\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} 0 & \lambda \\ \lambda & 0 \end{bmatrix}\hat{R}_{10a} + \begin{bmatrix} \kappa_{6a}^{(1)} & 0 \\ 0 & \kappa_{6a}^{(2)} \end{bmatrix}\hat{R}_{6a} + \begin{bmatrix} \kappa_1^{(1)} & 0 \\ 0 & \kappa_1^{(2)} \end{bmatrix}\hat{R}_1$$

nonlocal e-ph coupling — local e-ph couplings



pyrazine



DCC gives correct long-time dynamics and equilibrium populations

Schneider and **Domcke**, ***Chem. Phys. Lett.*** 150, 235 **(1988)**

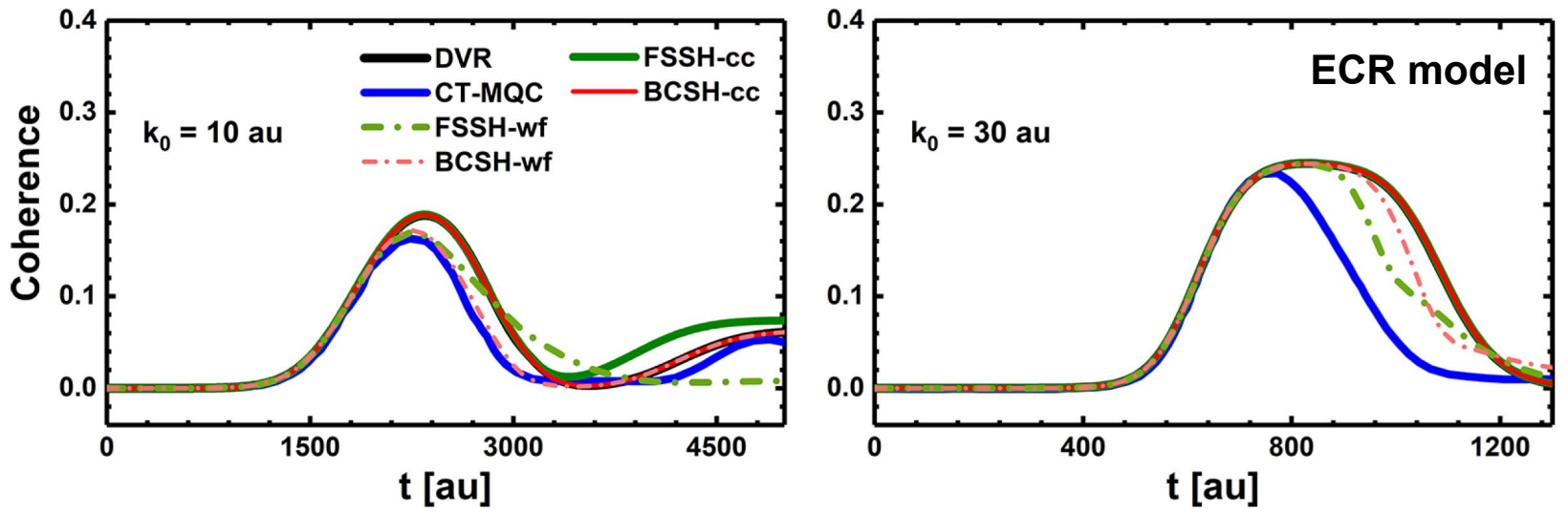
Outline

- Statistical Interpretation of MQCD
- Detailed Complementary Consistency
- **Some Related Method Developments**

1. Consistent Analysis of Independent Trajectories

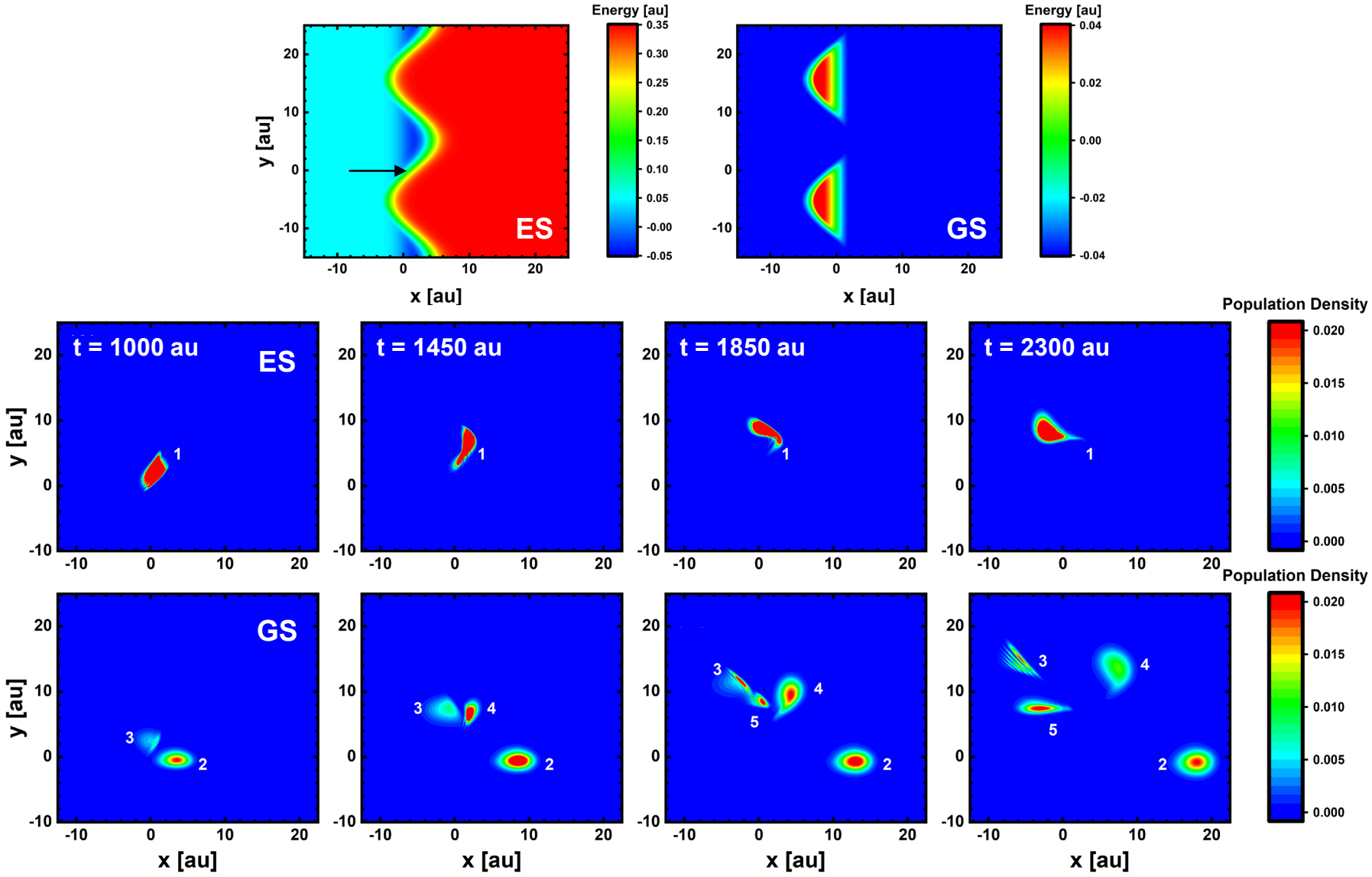
Density matrix: $\rho_{ij}^{\mathrm{cc}}(R,t) = \left|\rho_{ij}^{\mathrm{cc}}(R,t)\right| \exp\left(i\theta_{ij}^{\mathrm{cc}}(R,t)\right) = \left(\rho_{ii}^{\mathrm{as}}(R,t)\rho_{jj}^{\mathrm{as}}(R,t)\right)^{1/2} \dfrac{\rho_{ij}^{\mathrm{wf}}(R,t)}{\left|\rho_{ij}^{\mathrm{wf}}(R,t)\right|}$

Reduced density matrix: $\sigma_{ij}^{\mathrm{cc}}(t) = \int \rho_{ij}^{\mathrm{cc}}(R,t)dR$



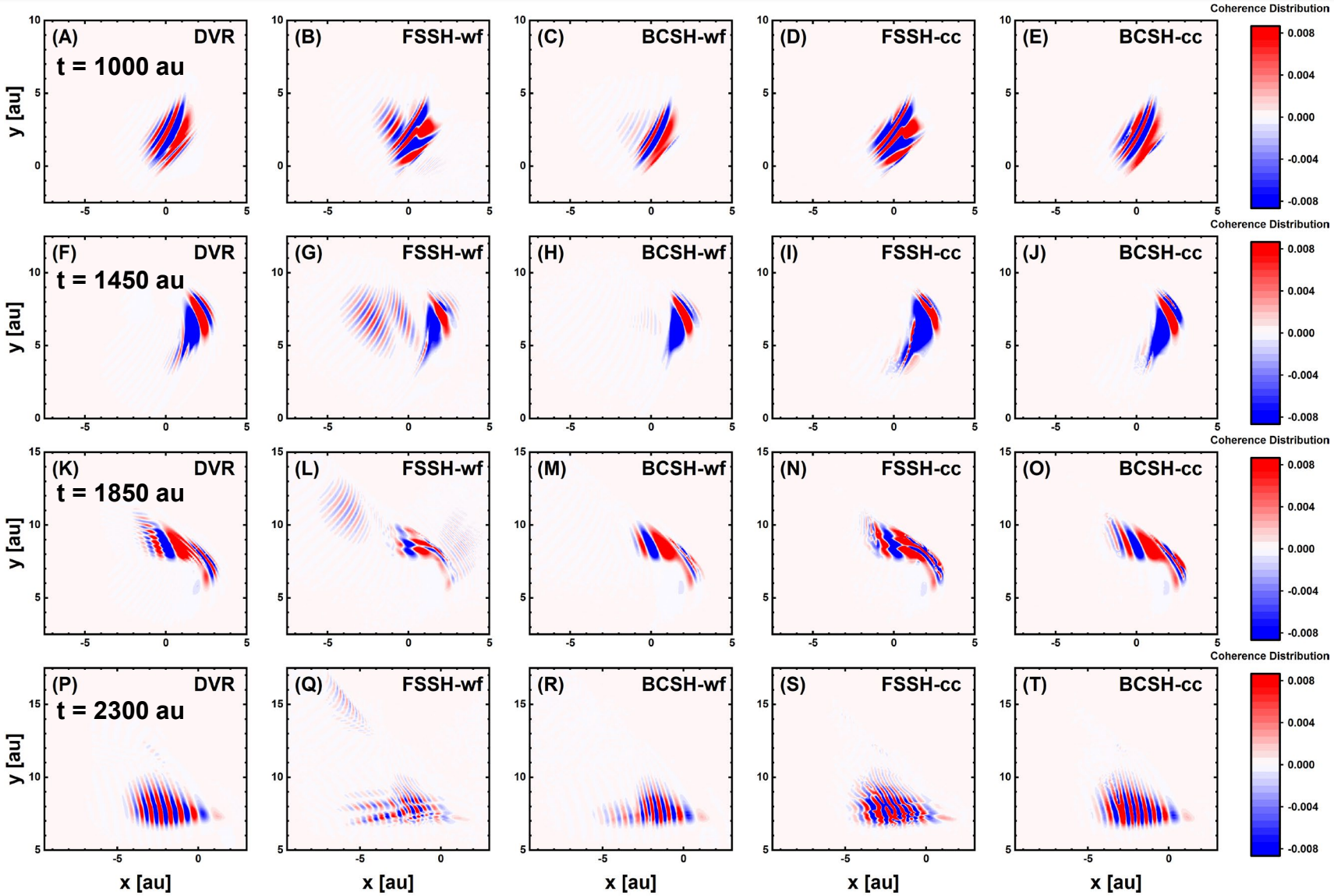
Landry, **Falk**, and **Subotnik**, ***J. Chem. Phys.*** 139, 211101 **(2024)**
Agostini, **Min**, **Abedi**, and **Gross**, ***J. Chem. Theory Comput.*** 12, 2127 **(2016)**
L. Wang* et al., ***J. Chem. Theory Comput.*** 20, 2349 **(2024)**
L. Wang* et al., ***J. Chem. Phys.*** 150, 164101 **(2019)**

Time Dependence and Spatial Distribution of Density Matrix



Subotnik, ***J. Phys. Chem. A*** 115, 12083 **(2011)**

Time Dependence and Spatial Distribution of Density Matrix



L. Wang* et al., ***J. Chem. Theory Comput.*** 20, 2349 **(2024)**

3. Sign-Consistent Coupled-Trajectory SH (SC-CTSH)

$\Psi(\underline{\underline{\mathbf{R}}},\underline{\underline{\mathbf{r}}},t)=\chi(\underline{\underline{\mathbf{R}}},t)\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$ **Exact factorization**

$$i\hbar\frac{\partial}{\partial t}\chi\left(\underline{\underline{\mathbf{R}}},t\right)=\left[\sum_{\nu}\frac{\left(-i\hbar\nabla_{\nu}+\mathbf{A}_{\nu}\left(\underline{\underline{\mathbf{R}}},t\right)\right)^{2}}{2M_{\nu}}+\epsilon\left(\underline{\underline{\mathbf{R}}},t\right)\right]\chi\left(\underline{\underline{\mathbf{R}}},t\right)$$

$$i\hbar\frac{\partial}{\partial t}\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)=\left[\hat{H}_{BO}(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}})+\hat{U}_{en}-\epsilon\left(\underline{\underline{\mathbf{R}}},t\right)\right]\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$$

$$\mathbf{A}_{\nu}\left(\underline{\underline{\mathbf{R}}},t\right)=\langle\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}},t\right)|-i\hbar\nabla_{\nu}\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}},t\right)\rangle_{\underline{\underline{\mathbf{r}}}}$$

$$\epsilon\left(\underline{\underline{\mathbf{R}}},t\right)=\langle\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}},t\right)|\,\hat{H}_{BO}(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}})+\hat{U}_{en}-i\hbar\partial_{t}\,|\,\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}},t\right)\rangle_{\underline{\underline{\mathbf{r}}}}$$

$$\hat{U}_{en}=\sum_{\nu}\frac{1}{M_{\nu}}\left[\frac{(-i\hbar\nabla_{\nu}-\mathbf{A}_{\nu}(\underline{\underline{\mathbf{R}}},t))^{2}}{2}+\left(\frac{-i\hbar\nabla_{\nu}\chi\left(\underline{\underline{\mathbf{R}}},t\right)}{\chi\left(\underline{\underline{\mathbf{R}}},t\right)}+\mathbf{A}_{\nu}(\underline{\underline{\mathbf{R}}},t)\right)\left(-i\hbar\nabla_{\nu}-\mathbf{A}_{\nu}(\underline{\underline{\mathbf{R}}},t)\right)\right]$$

$\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)=\sum_{I}C_{I}(\underline{\underline{\mathbf{R}}},t)\varphi^{I}_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$ **CT-MQC**

$$\dot{C}_{I}^{(I)}\left(t\right)=\dot{C}_{I,\mathrm{Eh}}^{(I)}\left(t\right)+\dot{C}_{I,\mathrm{XF}}^{(I)}\left(t\right)\qquad\dot{\mathbf{P}}_{\nu}^{(I)}\left(t\right)=\dot{\mathbf{P}}_{\nu,\mathrm{Eh}}^{(I)}\left(t\right)+\dot{\mathbf{P}}_{\nu,\mathrm{XF}}^{(I)}\left(t\right)$$

$$\dot{C}_{I,\mathrm{Eh}}^{(I)}\left(t\right)=-\frac{i}{\hbar}\varepsilon_{I}^{(I)}C_{I}^{(I)}-\sum_{k}\sum_{\nu=1}^{N_{\mathrm{n}}}\frac{\mathbf{P}_{\nu}^{(I)}\left(t\right)}{M_{\nu}}\cdot\mathbf{d}_{\nu,Ik}^{(I)}C_{k}^{(I)}$$

$$\dot{\mathbf{P}}_{\nu,\mathrm{Eh}}^{(I)}\left(t\right)=-\sum_{l}\rho_{ll}^{(I)}\left(t\right)\nabla_{\nu}\varepsilon_{l}^{(I)}-\sum_{lk}\rho_{lk}^{(I)}\left(t\right)\left(\varepsilon_{k}^{(I)}-\varepsilon_{l}^{(I)}\right)\mathbf{d}_{\nu,lk}^{(I)}$$

$$\dot{C}_{I,\mathrm{XF}}^{(I)}\left(t\right)=-\sum_{m}\rho_{mm}^{(I)}\left[\sum_{\nu}\frac{\mathbf{Q}_{\nu}^{(I)}\left(t\right)}{\hbar M_{\nu}}\cdot\left(\mathbf{f}_{\nu,m}^{(I)}\left(t\right)-\mathbf{f}_{\nu,I}^{(I)}\left(t\right)\right)\right]C_{I}^{(I)}$$

$$\dot{\mathbf{P}}_{\nu,\mathrm{XF}}^{(I)}\left(t\right)=-\sum_{l,m}\rho_{ll}^{(I)}\rho_{mm}^{(I)}\left[\sum_{\nu}\frac{2\mathbf{Q}_{\nu}^{(I)}\left(t\right)}{\hbar M_{\nu}}\cdot\left(\mathbf{f}_{\nu,m}^{(I)}\left(t\right)-\mathbf{f}_{\nu,I}^{(I)}\left(t\right)\right)\right]\mathbf{f}_{\nu,I}^{(I)}\left(t\right)$$

Quantum momentum

$$\mathbf{Q}_{\nu}^{(I)}\left(t\right)=-\hbar\left(\nabla_{\nu}\left|\chi^{(I)}\left(t\right)\right|^{2}\right)\Big/\left(2\left|\chi^{(I)}\left(t\right)\right|^{2}\right)$$

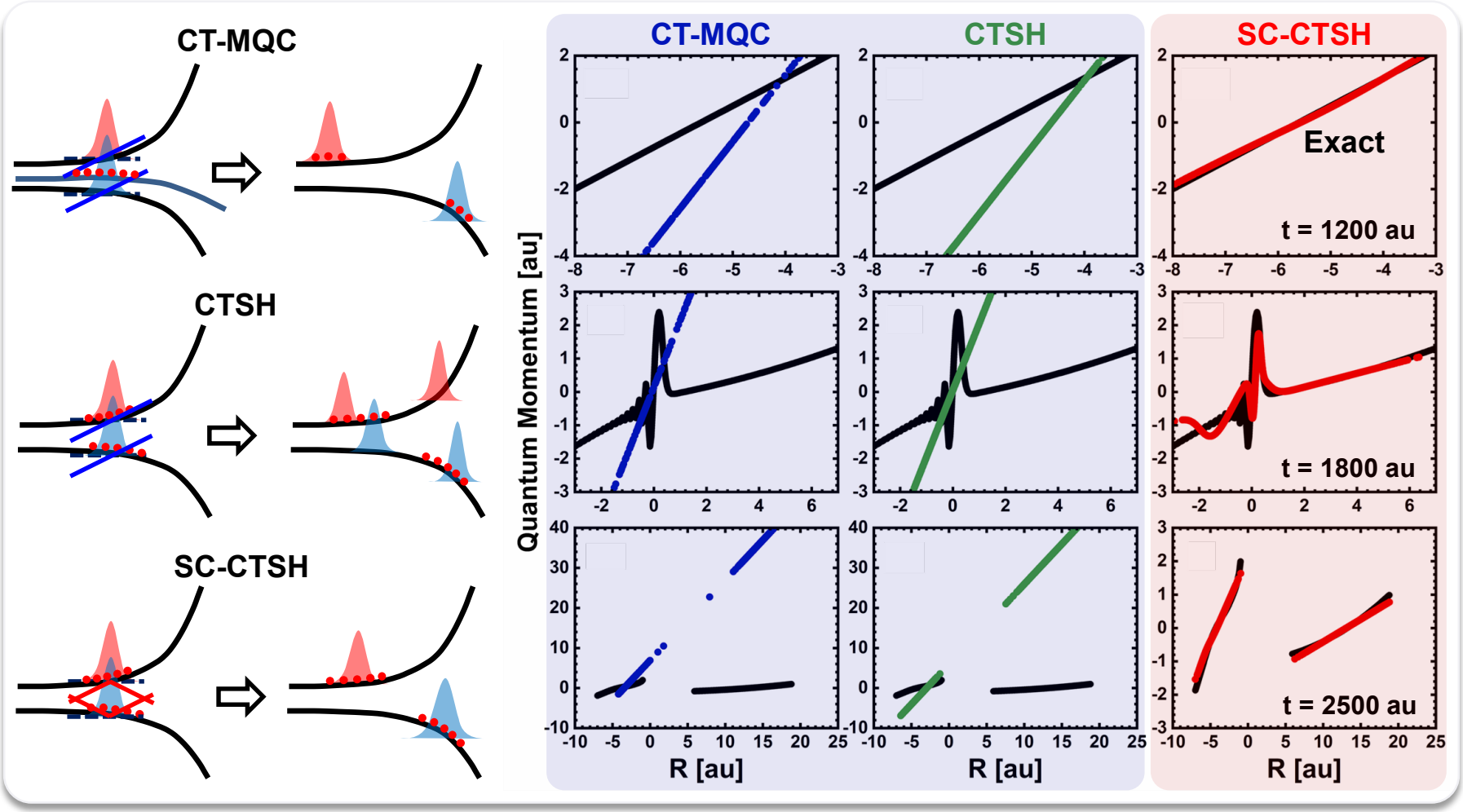
Sign consistency

CTSH: $\dot{\mathbf{P}}_{\nu}^{(I)}\left(t\right)=-\nabla_{\nu}\varepsilon_{a}^{(I)}$

SC-CTSH: $\dot{C}_{I,\mathrm{XF,SC}}^{(I)}\left(t\right)=-\sum_{m}\rho_{mm}^{(I)}\left[\sum_{\nu}\frac{\mathbf{Q}_{\nu}^{(I)}\left(t\right)}{\hbar M_{\nu}}\cdot\left(\mathbf{f}_{\nu,m}^{(I)}\left(t\right)-\mathbf{f}_{\nu,I}^{(I)}\left(t\right)\right)\right]C_{I}^{(I)}\cdot\lambda^{(I)}\left(t\right)$

CT-MQC: Min, **Agostini**, and **Gross**, ***Phys. Rev. Lett.*** 115, 073001 **(2015)**
CTSH: Pieroni and **Agostini**, ***J. Chem. Theory Comput.*** 17, 5969 **(2021)**
SC-CTSH: L. Wang* et al., ***J. Chem. Phys.*** 162, 164103 **(2025)**

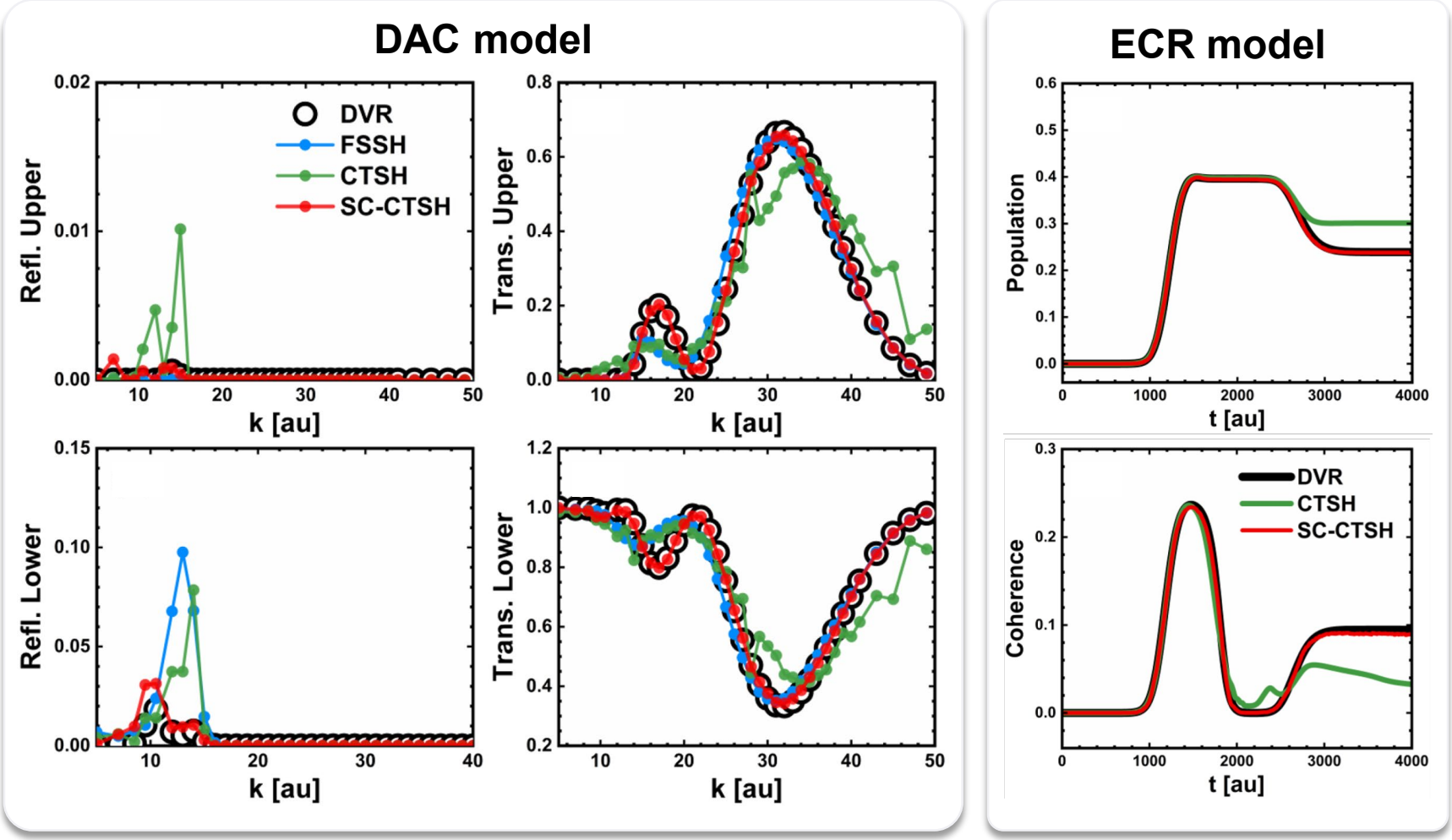
Quantum Momentum by SC-CTSH



SC-CTSH gives the correct quantum momentum and decoherence

<u>**L. Wang**</u>* et al., ***J. Chem. Phys.*** 162, 164103 **(2025)**

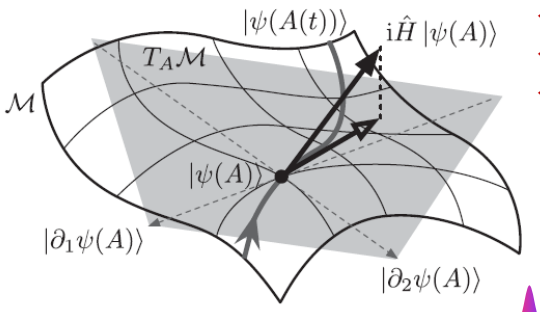
Performance of SC-CTSH



SC-CTSH gives correct channel populations and coherence

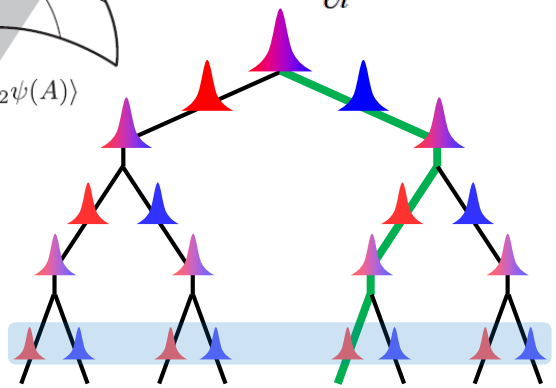
L. Wang* et al., ***J. Chem. Phys.*** 162, 164103 **(2025)**

4. Time-Dependent Variation with Trajectory Basis



- ✓ Nuclear tunneling
- ✓ Zero-point energy
- ✓ Quantum interference

$$\langle \delta\Psi | H - i\hbar\frac{\partial}{\partial t} | \Psi \rangle = 0$$



Configuration:

$$|\psi(t)\rangle = |\phi_{\text{system}}(t)\rangle |\mathbf{z}_{\text{bath}}(t)\rangle$$

$$|\mathbf{z}_{bath}(t)\rangle = \prod_{m=1}^{M} |z^m(t)\rangle$$

$$\langle x|z^m\rangle = \left(\frac{\gamma}{\pi}\right)^{1/4} \exp\left[-\frac{\gamma}{2}(x-q^m)^2 + i\frac{p^m(x-q^m)}{\hbar} + \frac{ip^m q^m}{2\hbar}\right]$$

Initial condition:

$$\hat{\rho}_{tot}(0) = \hat{\rho}_b^{eq} \otimes \hat{\rho}_s(0)$$

$$\hat{\rho}_b^{eq} = \int \frac{d^2\mathbf{z}_{\text{init}}}{\pi^M} |\mathbf{z}_{\text{init}}\rangle \rho_b(\mathbf{z}_{\text{init}}) \langle \mathbf{z}_{\text{init}}|$$

$$= \prod_{m=1}^{M} \int d^2 z^m_{init} \, |z^m_{\text{init}}\rangle \rho_b(z^m_{\text{init}}) \langle z^m_{\text{init}}|$$

$$\rho_b(z^m_{\text{init}}) = \frac{e^{\beta\omega^m} - 1}{\pi} e^{-\left[(\text{Re}(z^m_{\text{init}})+\zeta_x)^2 + (\text{Im}(z^m_{\text{init}})+\zeta_y)^2\right](e^{\beta\omega^m}-1)}$$

$$|\Psi_0(0)\rangle = |\mathbf{z}_{\text{init}}\rangle (1|1\rangle + 0|2\rangle)$$

$$\Downarrow$$

$$|\Psi(t=0)\rangle = \sum_{j=1}^{N} |\mathbf{z}_j\rangle \left(a_j^{(1)}|1\rangle + a_j^{(2)}|2\rangle\right)$$

MCEv1:

$$|\Psi(t)\rangle = \sum_{j=1}^{N} |\psi_j(t)\rangle = \sum_{j=1}^{N}\sum_{s} a_j^{(s)}(t) |\mathbf{z}_j(t)\rangle |s\rangle \Rightarrow \sum_{j=1}^{N} i\hbar \langle \mathbf{z}_l | \mathbf{z}_j \rangle \dot{a}_j^{(s)} = \sum_{j=1}^{N}\sum_{s'} \langle \mathbf{z}_l | \hat{H}_{ss'} | \mathbf{z}_j \rangle a_j^{(s')} - \sum_{j=1}^{N} i\hbar \langle \mathbf{z}_l | \dot{\mathbf{z}}_j \rangle a_j^{(s)}$$

A proper trajectory basis is important for time-dependent variation

Martínez, **Ben-Nun**, and **Levine**, ***J. Phys. Chem.*** 100, 7884 **(1996)**
Shalashilin, ***J. Chem. Phys.*** 130, 244101 **(2009)**

Multiconfigurational Surface Hopping (MCSH)

$$|\Psi(t)\rangle = \sum_{j=1}^{N} |\psi_j(t)\rangle = \sum_{j=1}^{N}\sum_{s} a_j^{(s)}(t)\,|\mathbf{z}_j(t)\rangle|s\rangle$$

$$\langle \delta\Psi | H - i\hbar\frac{\partial}{\partial t} | \Psi\rangle = 0 \Longrightarrow$$

$$\sum_{j=1}^{N} i\hbar\langle \mathbf{z}_l|\mathbf{z}_j\rangle \dot{a}_j^{(s)} = \sum_{j=1}^{N}\sum_{s'}\langle \mathbf{z}_l|\hat{H}_{ss'}|\mathbf{z}_j\rangle a_j^{(s')} - \sum_{j=1}^{N} i\hbar\langle \mathbf{z}_l|\dot{\mathbf{z}}_j\rangle a_j^{(s)}$$

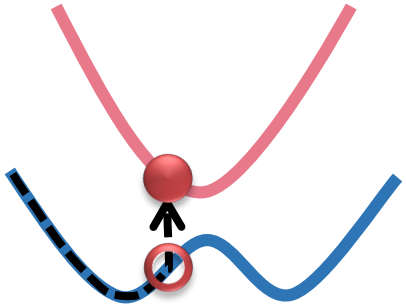
$$\dot{\boldsymbol{p}}_{SH,j} = -\nabla_{\boldsymbol{q}_{SH,j}} E_a \qquad \dot{\boldsymbol{q}}_{SH,j} = \boldsymbol{p}_{SH,j}$$

MQCD trajectories ⟹

$$\mathbf{z}_j = \left(\frac{\gamma}{2}\right)^{\frac{1}{2}} \boldsymbol{q}_{SH,j} + \frac{i}{\hbar}\left(\frac{1}{2\gamma}\right)^{\frac{1}{2}} \boldsymbol{p}_{SH,j}$$

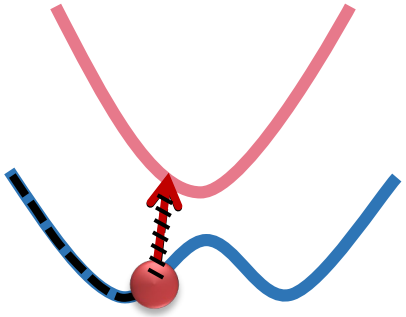
$$\dot{\mathbf{z}}_j = \left(\frac{\gamma}{2}\right)^{\frac{1}{2}} \dot{\boldsymbol{q}}_{SH,j} + \frac{i}{\hbar}\left(\frac{1}{2\gamma}\right)^{\frac{1}{2}} \dot{\boldsymbol{p}}_{SH,j}$$

Surface hopping trajectories cannot be directly used because momenta are discontinuous



Surface hop at time t

⟹ Return to time $t - dt$



Linear interpolation during $[t - dt, t]$

$$\dot{\boldsymbol{p}}_{interpolation} = \frac{\boldsymbol{p}(t) - \boldsymbol{p}(t - dt)}{dt}$$

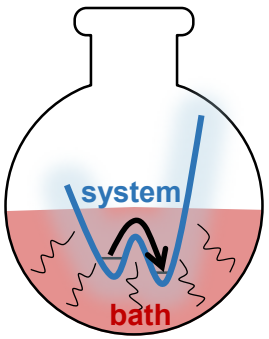
$$\dot{\boldsymbol{q}}_{interpolation} = \frac{\boldsymbol{q}(t) - \boldsymbol{q}(t - dt)}{dt}$$

Linear interpolation generates continuous trajectories and can be used for time variation

Time-dependent variation with momentum-jump trajectories

L. Wang* et al., ***J. Chem. Theory Comput.*** 20, 7755 **(2024)**

Spin-Boson Models at Low Temperatures



Hamiltonian

$$\hat{H}_s = \varepsilon\hat{\sigma}_z + \Delta\hat{\sigma}_x \qquad \hat{H}_b = \sum_m^M \omega^m(\hat{b}^{m\dagger}\hat{b}^m + \frac{1}{2})$$

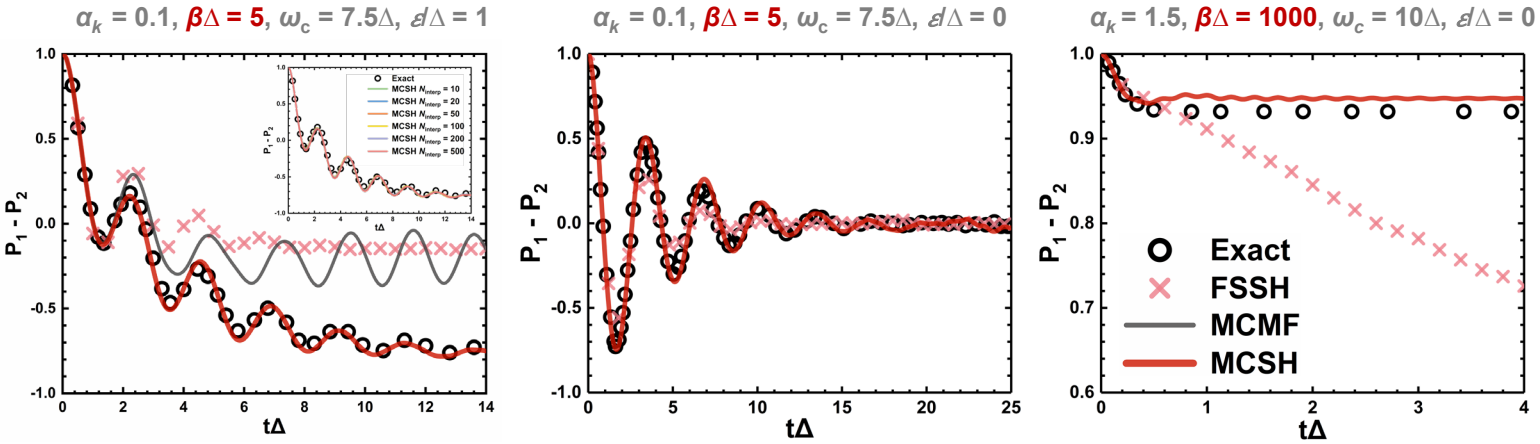
$$\hat{H}_{sb} = \hat{\sigma}_z \sum_m^M \frac{c^m}{\sqrt{2\omega^m}}(\hat{b}^{m\dagger} + \hat{b}^m)$$

Ohmic spectral density

$$J(\omega) = \frac{\pi}{2}\alpha_k \omega e^{-\omega/\omega_c}$$

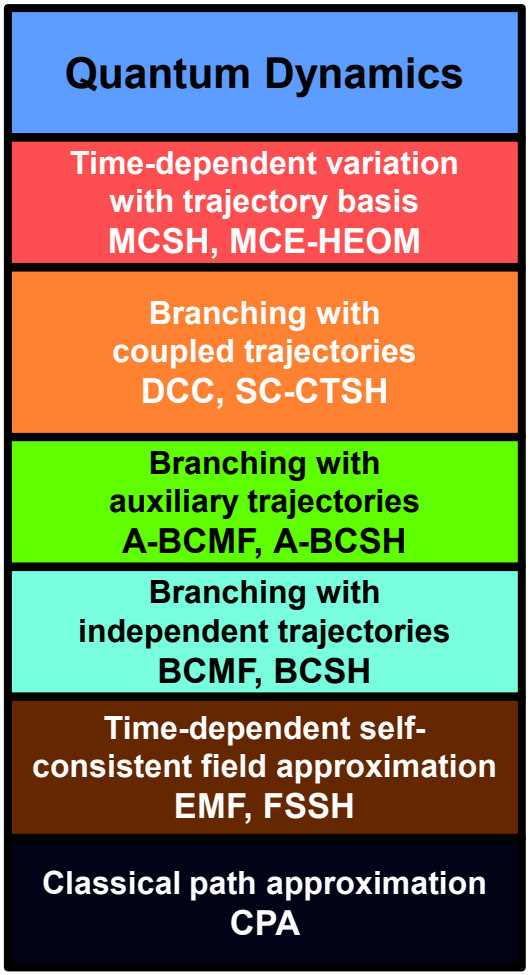
Initial density matrix

$$\hat{\rho}_{tot}(0) = |1\rangle\langle 1| \otimes \hat{\rho}_b^{eq}$$



MCSH consistently shows high performance and makes significant improvements compared with FSSH

Summary



- The **principle of detailed internal consistency** has been proposed as the fundamental principle (or basic relation) for mixed quantum-classical dynamics, which is purely due to **logical consistency** $\rho_{ii}^{\mathrm{wf}}(R,t) = \rho_{ii}^{\mathrm{as}}(R,t)$

- **A series of methods** have been proposed based on the detailed internal consistency, ranging from independent-trajectory, auxiliary-trajectory and coupled-trajectory frameworks

- **MCSH** can efficiently realize multiconfigurational variational dynamics based on different kinds of surface hopping-like trajectories

- **DCC** achieves accurate population, coherence and detailed balance, and is promising to be combined with MCSH to study complex systems

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Guijie Li
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Wang Theoretical Chemistry Group

www.linjun-wang-group.com

Email: ljwang@zju.edu.cn

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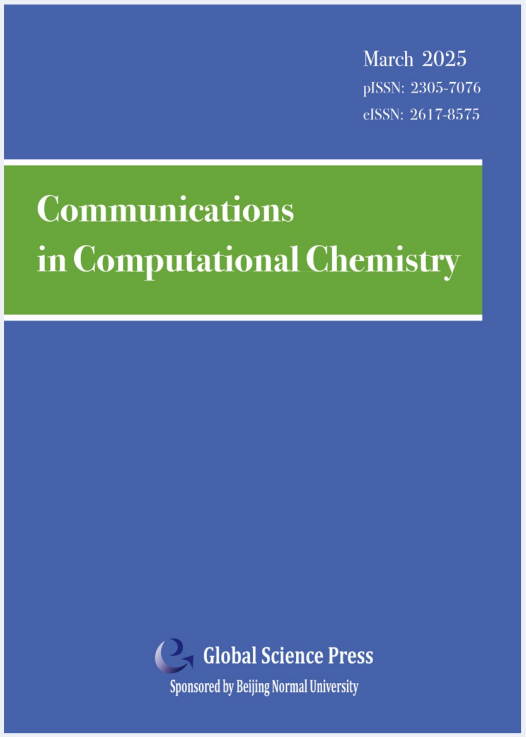

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