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Trajectory-based nonadiabatic dynamics with a surface-hopping motif: Recent progress in Libra

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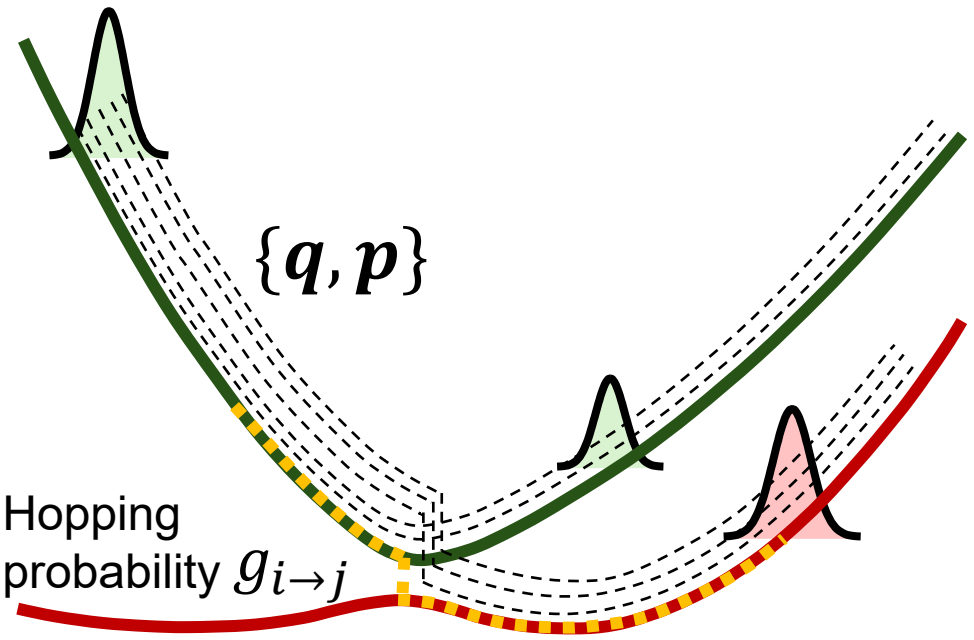
Outline

New trajectory-based nonadiabatic dynamics methods with a surface hopping (SH) motif!

- SH based on exact factorization (SHXF)
- Quantum-trajectory SH (QTSH)
- Fully-integrated SH (FISH)

The TSH protocol

Effective potential in TSH



The force is stochastically set to one of adiabatic forces.

electrons

$$i\hbar\dot{\psi}(\boldsymbol{r}, t; \boldsymbol{q}) = \hat{H}_{BO}(\boldsymbol{q})\psi(\boldsymbol{r}, t; \boldsymbol{q})$$

Tully, J. C. *JCP.* **1990**, *93* (2), 1061–1071.

Hopping

$$g_{i\to j} = \max\left[0, \frac{2\Re[\rho_{ij} d_{ij}]}{\rho_{ii}}\Delta t\right]$$

TSH

Velocity adjustment

$$\dot{\boldsymbol{q}} := \dot{\boldsymbol{q}} + \frac{1}{2}\gamma_{i\to j} M^{-1}\boldsymbol{u}$$

Barbatti, M. *JCTC.* **2021**, *17* (5), 3010–3018.

$$\dot{\boldsymbol{p}} = -\boldsymbol{\nabla} E_a$$

nuclei

SH based on exact factorization (SHXF)

Overcoherence in TSH

electrons

$$i\hbar\dot{\psi}(\boldsymbol{r},t;\boldsymbol{q}) = \hat{H}_{BO}(\boldsymbol{q})\psi(\boldsymbol{r},t;\boldsymbol{q})$$

Hopping

$$g_{i\to j} = \max\left[0, \frac{2\Re[\rho_{ij}d_{ij}]}{\rho_{ii}}\Delta t\right]$$

TSH

Velocity adjustment

$$\dot{\boldsymbol{q}} := \dot{\boldsymbol{q}} + \frac{1}{2}\gamma_{i\to j}M^{-1}\boldsymbol{u}$$

$$\dot{\boldsymbol{p}} = -\boldsymbol{\nabla}E_a$$

nuclei

Off-diagonal elements in the density matrix remain constant, after the dynamics leaves away the nonadiabatic coupling region.

BH expansion for an electron-nuclear state

$$|\Psi(\boldsymbol{q},t)\rangle = \sum_i F_i(\boldsymbol{q},t)|\Phi_i(t;\boldsymbol{q})\rangle$$

$$= \sum_i c_i\chi_i(\boldsymbol{q},t)|\Phi_i(t;\boldsymbol{q})\rangle \quad \forall i, \sum_i |c_i|^2 = 1$$

Coherence

$$\rho_{ij}^{QD}(t) = \int c_i c_j^* \chi_i \chi_j^*(\boldsymbol{q},t)\, d\boldsymbol{q}$$

$$\rho_{ij}^{MQC}(t) \approx \frac{1}{N_{tr}}\sum_k^{N_{tr}} c_{i,k}c_{j,k}^*$$

Xu, J.; Shi, Z.; Wang, L. *JCTC.* **2024**, *20* (6), 2349–2361.

Electronic propagation in the conventional TSH

$$\dot{c}_i = -\frac{i}{\hbar}E_i c_i - \sum_j d_{ij}c_j$$

Zero away from the NAC region

SHXF tackles overcoherence

electrons

$$i\hbar\dot{\psi}(\boldsymbol{r},t;\boldsymbol{q}) = \left[\hat{H}_{BO} + \hat{H}_{XF}\right]\psi(\boldsymbol{r},t;\boldsymbol{q})$$

Auxiliary trajectories $\{\boldsymbol{q}_i, \boldsymbol{p}_i\}$ & XF quantities

SHXF

Hopping

$$g_{i\to j} = \max\left[0, \frac{2\Re[\rho_{ij}d_{ij}]}{\rho_{ii}}\Delta t\right]$$

Velocity adjustment

$$\dot{\boldsymbol{q}} := \dot{\boldsymbol{q}} + \frac{1}{2}\gamma_{i\to j}M^{-1}\boldsymbol{u}$$

$$\dot{\boldsymbol{p}} = -\boldsymbol{\nabla}E_a$$

nuclei

Ha, J.-K.; Lee, I. S.; Min, S. K. *JPCL.* **2018**, *9* (5), 1097–1104.

Exact factorization (XF) ansatz

$$|\Psi(\boldsymbol{q},t)\rangle = \chi(\boldsymbol{q},t)|\psi(t;\boldsymbol{q})\rangle$$

under $\forall\boldsymbol{q}\forall t, \langle\psi(t;\boldsymbol{q})|\psi(t;\boldsymbol{q})\rangle = 1$

Abedi, A.; Maitra, N. T.; Gross, E. K. U. *PRL.* **2010**, *105* (12), 123002.

Agostini, F.; Min, S. K.; Abedi, A.; Gross, E. K. U. *JCTC.* **2016**, *12* (5), 2127–2143.

Electronic propagation in SHXF

$$\dot{c}_i = -\frac{i}{\hbar}E_i c_i - \sum_j d_{ij}c_j + \sum_\nu \frac{i\mathcal{P}_\nu}{\hbar M_\nu}\cdot\left(\sum_j |c_j|^2\phi_{j\nu} - \phi_{i\nu}\right)c_i$$

Auxiliary trajectory propagation $\{\boldsymbol{q}_i, \boldsymbol{p}_i\}$ & XF quantities

Quantum momentum

$$\mathcal{P}_\nu = -i\hbar\frac{\nabla_\nu|\chi|}{|\chi|} \approx \frac{i\hbar}{2\sigma_\nu^2}(q_\nu - \langle q_\nu\rangle)$$

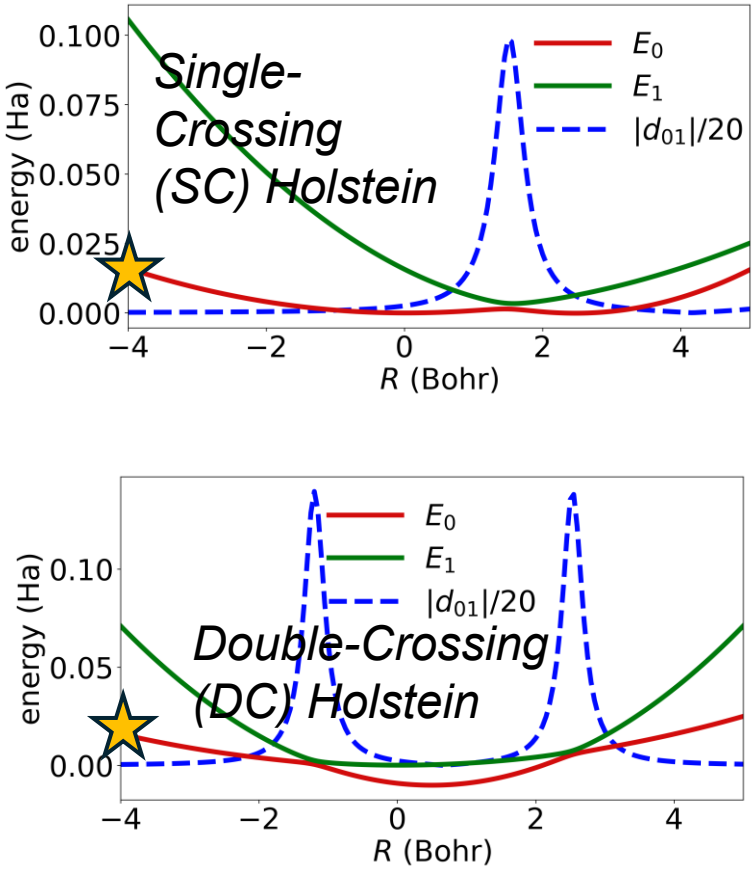
Phase gradient

$$\phi_{i,\nu}(t) = \nabla_\nu \arg c_i \approx p_i(t) - p_i(t_i)$$

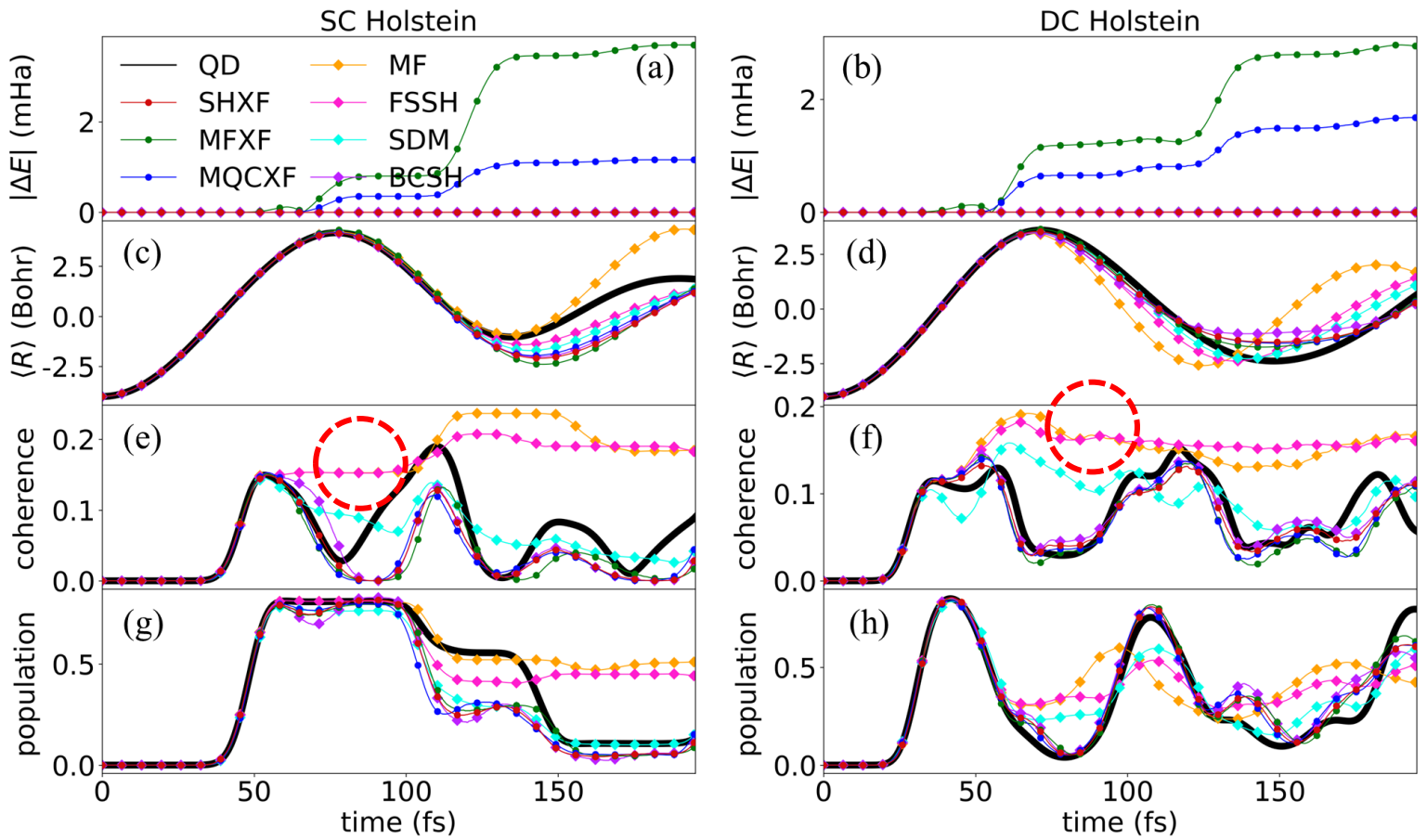
Han, D.; Akimov, A. V. *JCTC.* **2024**, *20* (12), 5022–5042.

SHXF tackles overcoherence

PES



Population & coherence in Holstein models

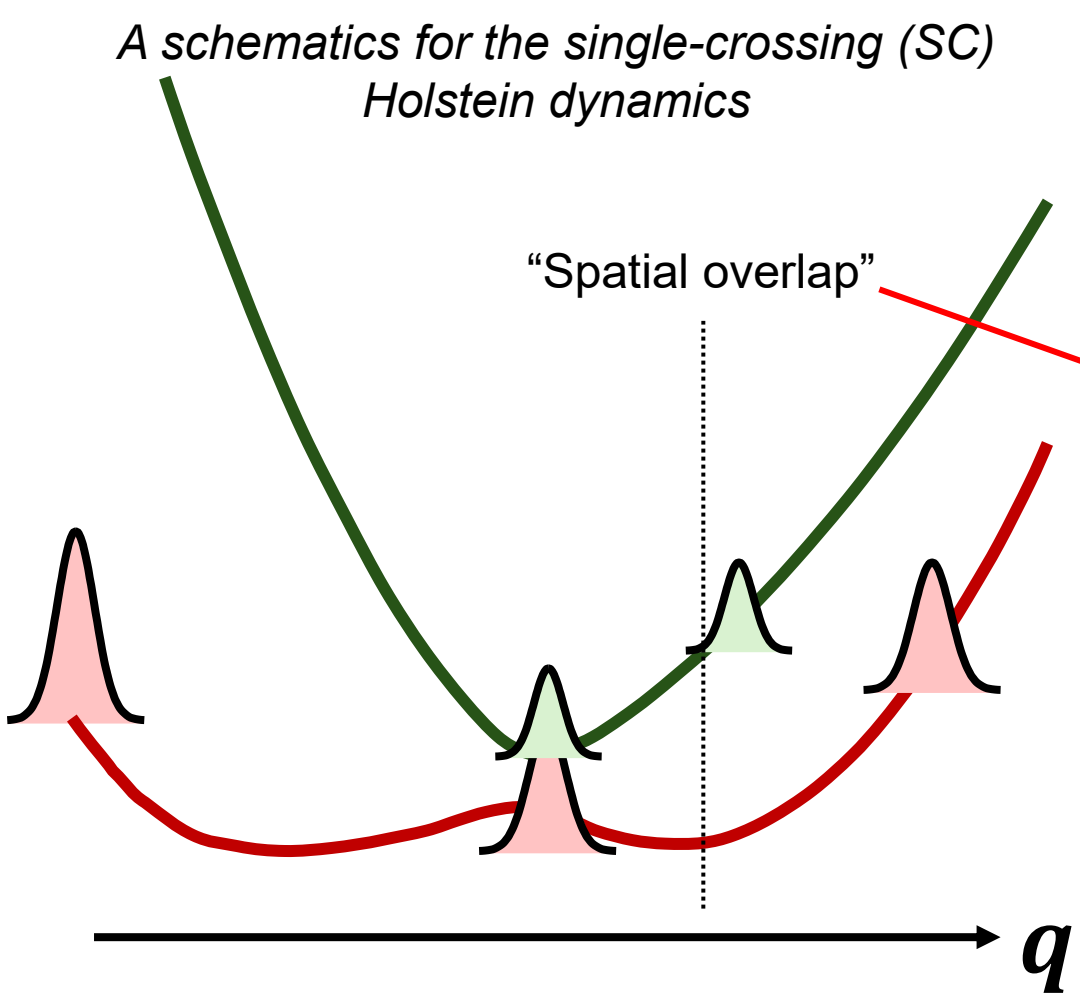


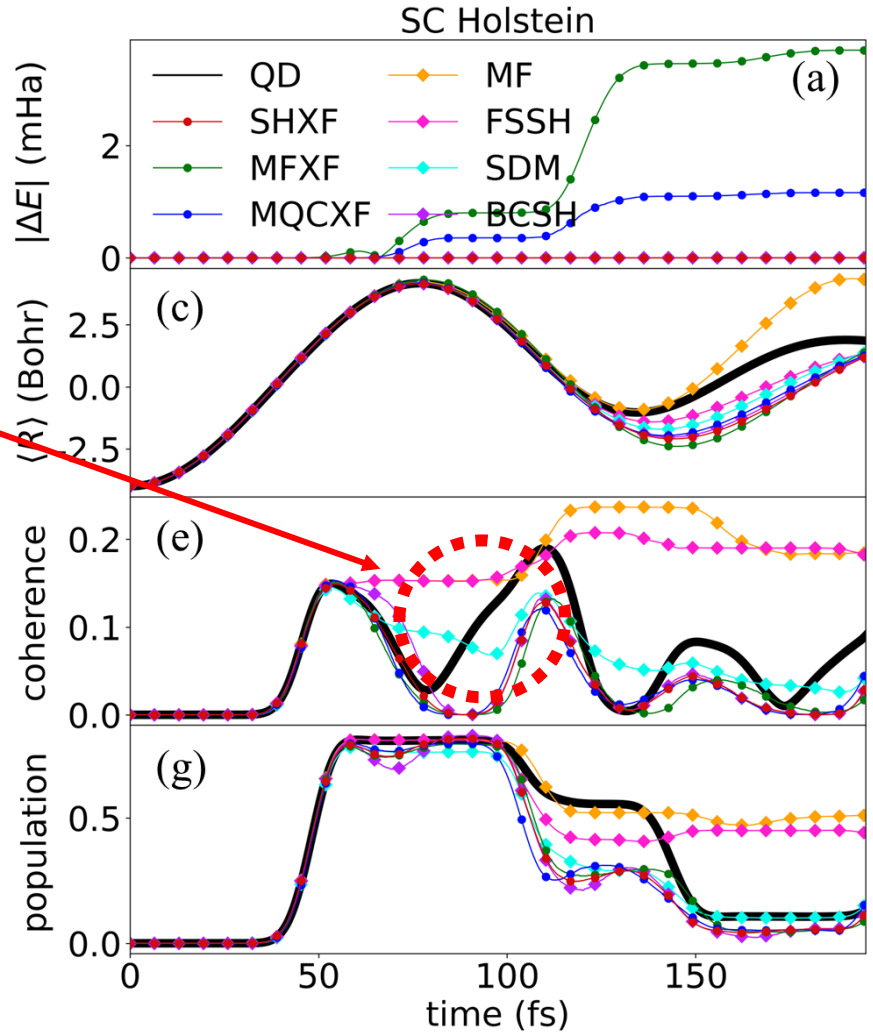
While FSSH suffers from the overcoherence, SHXF and other decoherence-corrected methods such as BCSH and SDM shows a clear damping in coherence.

Han, D.; Akimov, A. V. *JCTC.* **2024**, *20* (12), 5022–5042.

SHXF tackles overcoherence

A schematics for the single-crossing (SC) Holstein dynamics





There is missing coherence due to spatial overlap in the off-coupling region after the first crossing.

Quantum-Trajectory SH (QTSH)

Too “strict” energy conservation in TSH

electrons

$$i\hbar\dot{\psi}(\boldsymbol{r},t;\boldsymbol{q}) = \hat{H}_{BO}(\boldsymbol{q})\psi(\boldsymbol{r},t;\boldsymbol{q})$$

TSH

Hopping

$$g_{i\to j} = \max\left[0, \frac{2\Re[\rho_{ij}d_{ij}]}{\rho_{ii}}\Delta t\right]$$

Velocity adjustment

$$\dot{\boldsymbol{q}} := \dot{\boldsymbol{q}} + \frac{1}{2}\gamma_{i\to j}M^{-1}\boldsymbol{u}$$

$$\dot{\boldsymbol{p}} = -\boldsymbol{\nabla}E_a$$

nuclei

In TSH, the velocity adjustment procedure enforces energy conservation at the level of individual trajectories.

What TSH does

$$\forall\, k, \dot{E}_{tot,k} = 0$$

$\Rightarrow$ ~~$\Leftarrow$~~

What is supposed to be done

$$\frac{1}{N_{tr}}\sum_{K}^{N_{tr}}\dot{E}_{tot,k} = 0$$

Han, D.; Martens, C. C.; Akimov, A. V. *JCTC.* **2025**, *21* (6), 2839–2853.

QTSH achieves ensemble-level energy conservation

electrons

An optional decoherence correction can be added.

$$i\hbar\dot{\psi}(\boldsymbol{r},t;\boldsymbol{q}) = \hat{H}_{BO}(\boldsymbol{q})\psi(\boldsymbol{r},t;\boldsymbol{q})$$

Hopping

$$g_{i\to j} = \max\left[0, \frac{2\Re[\rho_{ij}d_{ij}]}{\rho_{ii}}\Delta t\right]$$

QTSH

~~Velocity adjustment~~

~~$\dot{\boldsymbol{q}} := \dot{\boldsymbol{q}} + \frac{1}{2}\gamma_{i\to j}M^{-1}\boldsymbol{u}$~~

$$\dot{\boldsymbol{P}} = -\nabla E_a + \boldsymbol{F}_{quant}$$

Nuclear propagation is governed by kinematic momentum and quantum force

nuclei

Martens, C. C. *JPCA* **2019**, *123* (5), 1110–1128.

Huang, D. M.; Green, A. T.; Martens, C. C. *JCP.* **2023**, *159* (21), 214108.

Dupuy, L.; Rikus, A.; Maitra, N. T. *JPCL.* **2024**, 2643–2649.

Quantum-Classical Liouville Equation

$$i\hbar\frac{\partial\rho_{ij}(\boldsymbol{z},t)}{\partial t} = \sum_k (H_{ik}(\boldsymbol{z})\rho_{kj}(\boldsymbol{z},t) - \rho_{ik}(\boldsymbol{z},t)H_{kj}(\boldsymbol{z}))$$

$$+\frac{i\hbar}{2}\sum_k \left(\{H_{ik}(\boldsymbol{z}),\rho_{kj}(\boldsymbol{z},t)\} - \{\rho_{ik}(\boldsymbol{z},t),H_{kj}(\boldsymbol{z})\}\right)$$

With the electronic basis $\{|i\rangle\}$ and phase-space variables, $\boldsymbol{z} = (\boldsymbol{q},\boldsymbol{p})$

Equations of motion & kinematic momentum

$\rho_{ij}(\boldsymbol{z},t) := \tilde{\rho}_{ij}(t)g(\boldsymbol{z})$ Phase-space density ~ proxy density matrix × Gaussian basis

$$\begin{cases} i\hbar\frac{d\tilde{\rho}_{ij}}{dt} = \sum_k \left(H_{ik}\tilde{\rho}_{jk} - \tilde{\rho}_{ik}H_{kj}\right) - i\hbar\frac{\dot{z}\nabla_z g}{g}\tilde{\rho}_{ij} \\ \dot{\boldsymbol{q}} = \boldsymbol{M}^{-1}\boldsymbol{p} - 2\hbar\sum_{i<j}\boldsymbol{M}^{-1}\boldsymbol{h}_{ij}\Im\rho_{ij} \\ \dot{\boldsymbol{p}} = -\sum_i \nabla E_i\tilde{\rho}_{ii} + 2\hbar\sum_{i<j}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\nabla_{\boldsymbol{q}}\boldsymbol{h}_{ij}\right)\Im\rho_{ij} \end{cases}$$

decoherence

Inconvenient!

$$\boldsymbol{h}_{ij} = \langle i|\nabla j\rangle \qquad d_{ij} = \boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{h}_{ij}$$

$$\dot{\boldsymbol{q}} = \boldsymbol{M}^{-1}\boldsymbol{P}$$

Kinematic momentum $\boldsymbol{P} = \boldsymbol{p} - 2\hbar\sum_{i<j}\boldsymbol{h}_{ij}\Im\rho_{ij}$

$$\dot{\boldsymbol{P}} = -\nabla_{\boldsymbol{q}}E_a + 2\sum_{i<j}\left(E_i - E_j\right)\Re\rho_{ij}\boldsymbol{h}_{ij}$$

$$-2\hbar\sum_{i<j}\sum_k\left(\Im\rho_{ik}d_{kj} - d_{ik}\Im\rho_{kj}\right)\boldsymbol{h}_{ij} + 2\hbar\sum_{i<j}\Im\rho_{ij}\frac{\dot{z}\nabla_z g}{g}\boldsymbol{h}_{ij}$$

Cotton, S. J.; Liang, R.; Miller, W. H. *JCP.* **2017**, *147* (6), 064112.

Han, D.; Martens, C. C.; Akimov, A. V. *JCTC.* **2025**, *21* (6), 2839–2853.

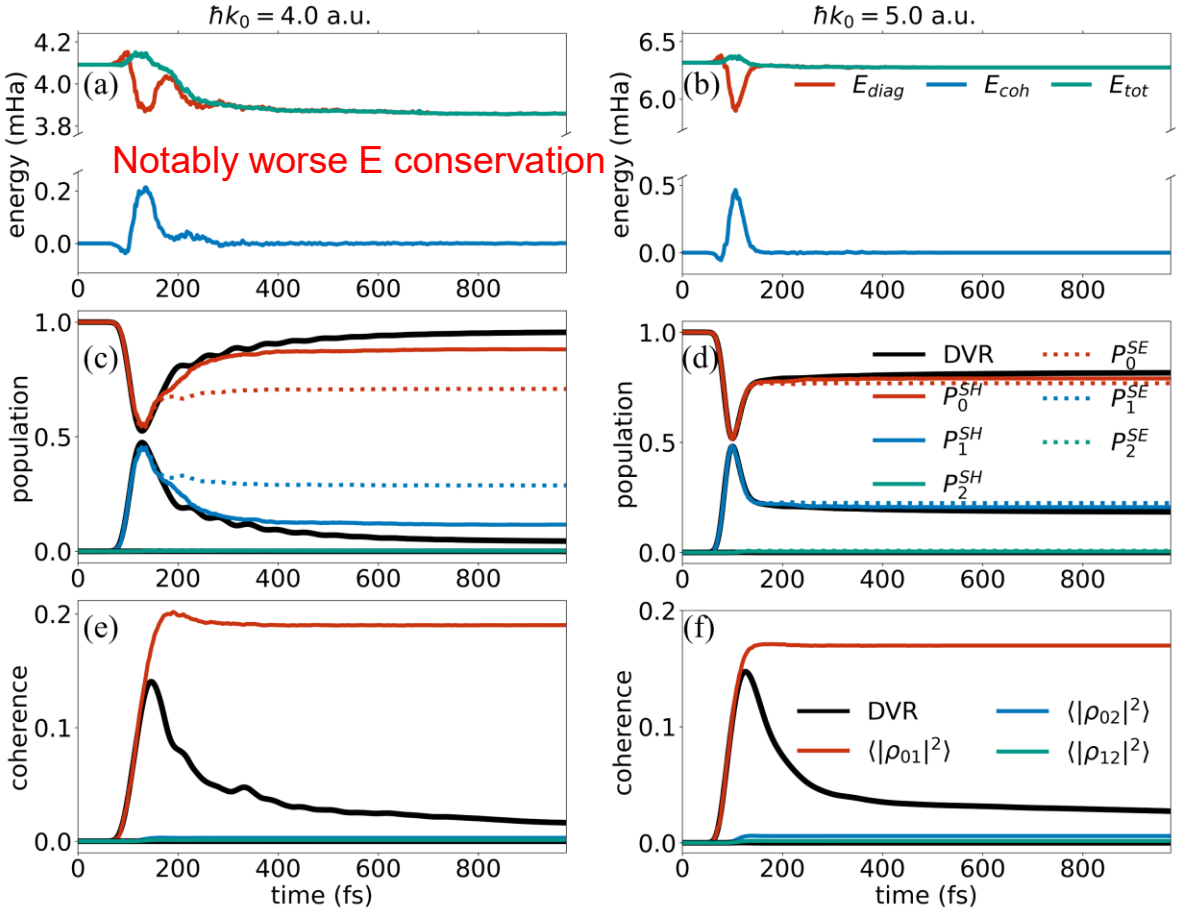
QTSH achieves ensemble-level energy conservation

Energy conservation & internal consistency

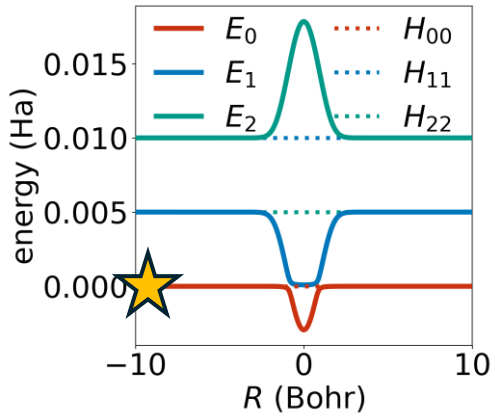
$$E_{tot} = \frac{1}{N_{tr}}\sum_{k}^{N_{tr}}\left(\underbrace{\frac{1}{2}\boldsymbol{p}_k^T\boldsymbol{M}^{-1}\boldsymbol{p}_k + E_{a_k a_k}}_{E_{diag}} \underbrace{-\frac{2\hbar}{N_{tr}}\sum_{i<j}^{N}\Im\rho_{ij,k}d_{ij,k}}_{E_{coh}}\right) = \frac{1}{N_{tr}}\sum_{k}^{N_{tr}}\left(\frac{1}{2}\boldsymbol{P}_k^T\boldsymbol{M}^{-1}\boldsymbol{P}_k + E_{a_k a_k}\right) \approx 0 \Leftarrow \dot{\delta}_{i,a_k} \approx \dot{\rho}_{ii,k}, \forall k$$

$a_k(t)$ = the active-state index of kth trajectory at t

QTSH on the superexchange model



Superexchange model



$$H_{00} = 0; H_{11} = 0.005; H_{22} = 0.01$$

$$V_{01} = V_{10} = 0$$

$$V_{02} = V_{20} = 0.001\exp(-R^2/2)$$

$$V_{12} = V_{21} = 0.01\exp(-R^2/2)$$

$$P_i^{SE} = \frac{1}{N_{tr}}\sum_{k}^{N_{tr}}\left|c_{i,k}(t)\right|^2$$

Population from the density matrix

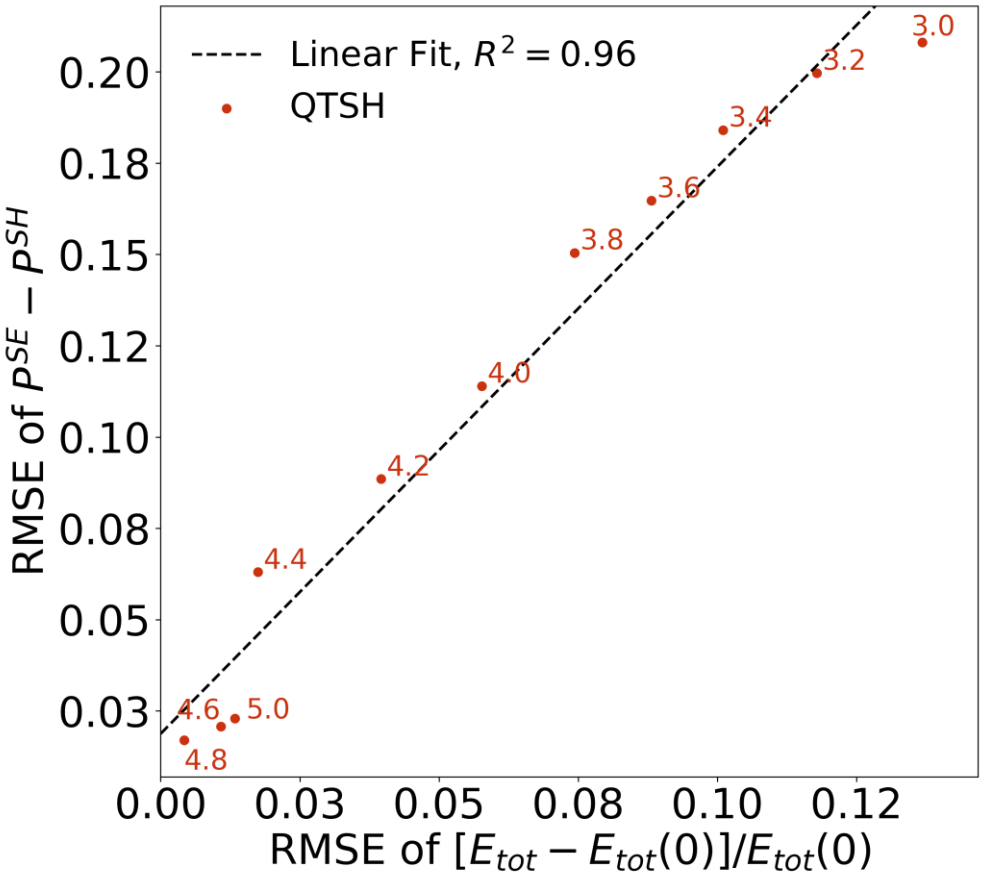
$$P_i^{SH} = \frac{1}{N_{tr}}\sum_{k}^{N_{tr}}\delta_{i,a_k}(t)$$

Population from the active-state occurrence

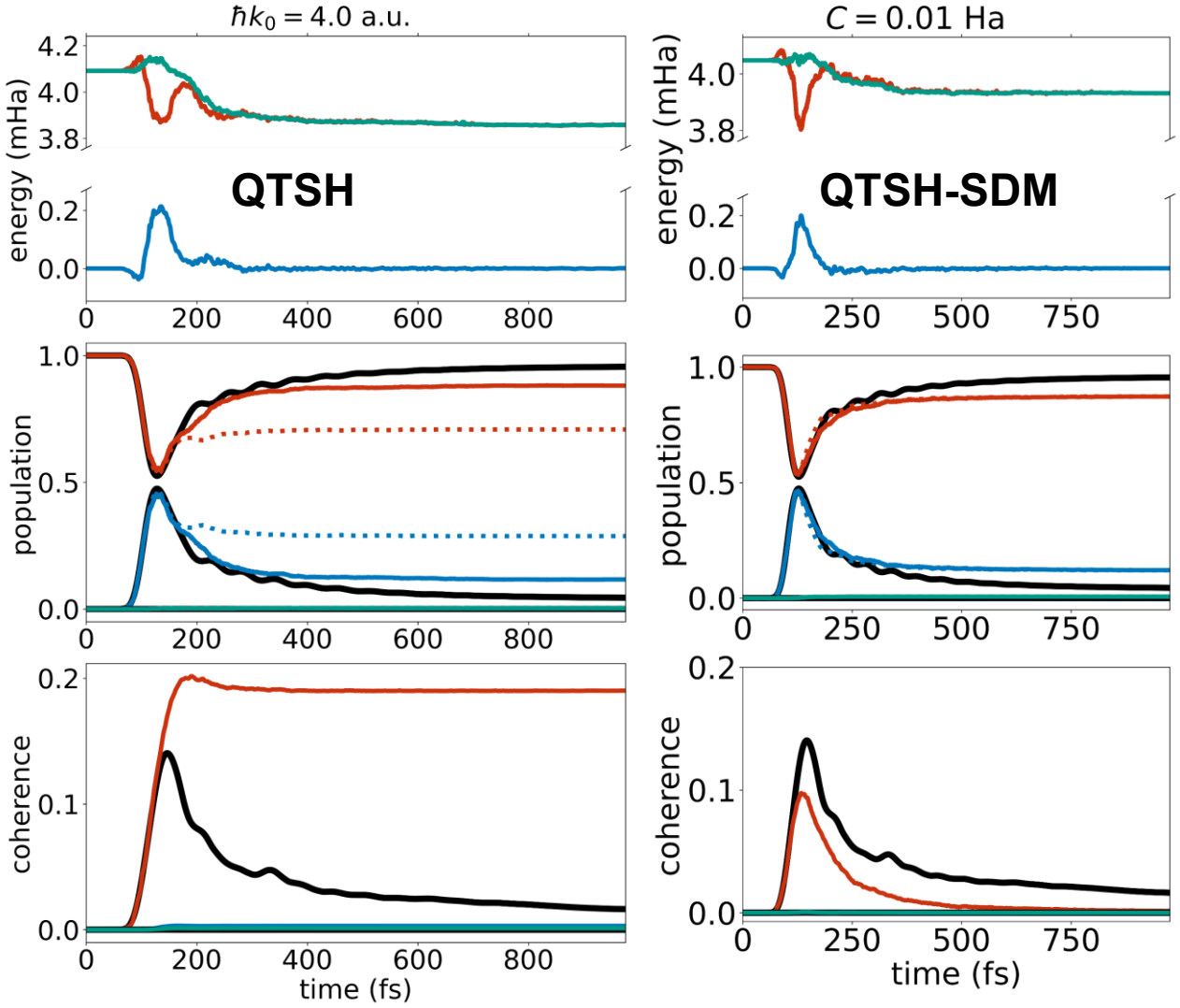
Han, D.; Martens, C. C.; Akimov, A. V. *JCTC.* **2025**, *21* (6), 2839–2853.

QTSH achieves ensemble-level energy conservation

Energy conservation & internal consistency



Improved energy conservation by combining QTSH with decoherence



Fully-Integrated SH (FISH)

Conventional NBRA-TSH

electrons

NBRA = Neglect of Back-Reaction Approximation

$$i\hbar\dot{\psi}(\boldsymbol{r},t;\boldsymbol{q}) = \hat{H}_{BO}(\boldsymbol{q})\psi(\boldsymbol{r},t;\boldsymbol{q})$$

Hopping

$$g_{i\to j} = \max\left[0, \frac{2\Re[\rho_{ij}d_{ij}]}{\rho_{ii}}\Delta t\right]$$

NBRA-TSH

Velocity adjustment

$$\dot{\boldsymbol{q}} := \dot{\boldsymbol{q}} + \frac{1}{2}\gamma_{i\to j}M^{-1}\boldsymbol{u}$$

No electroni backreactio to nuclei

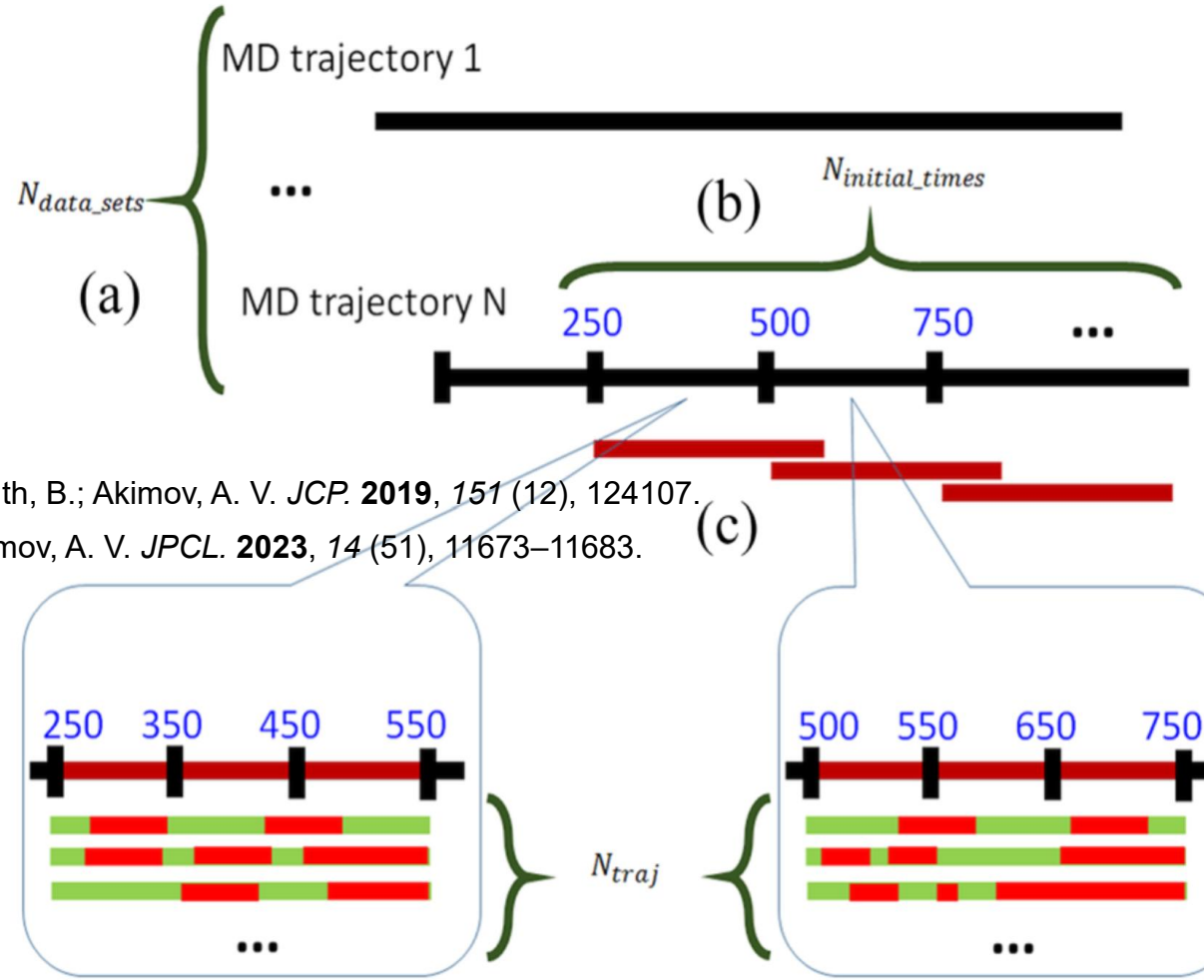
$$\dot{\boldsymbol{p}} = -\boldsymbol{\nabla}E_a$$

a = Usually just set to the ground state

nuclei

No on-the-fly electronic computation and propagation!

Obtain a "guiding" trajectory first and run multiple stochastic SH calculations to achieve statistical convergence.



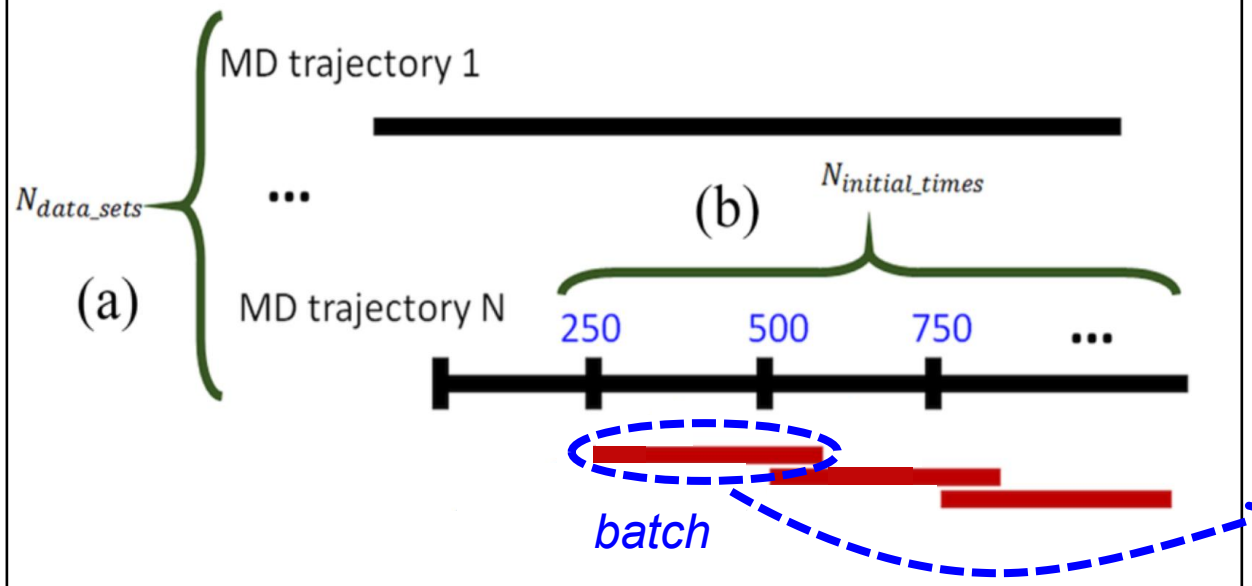
Smith, B.; Akimov, A. V. *JCP.* **2019**, *151* (12), 124107.

Akimov, A. V. *JPCL.* **2023**, *14* (51), 11673–11683.

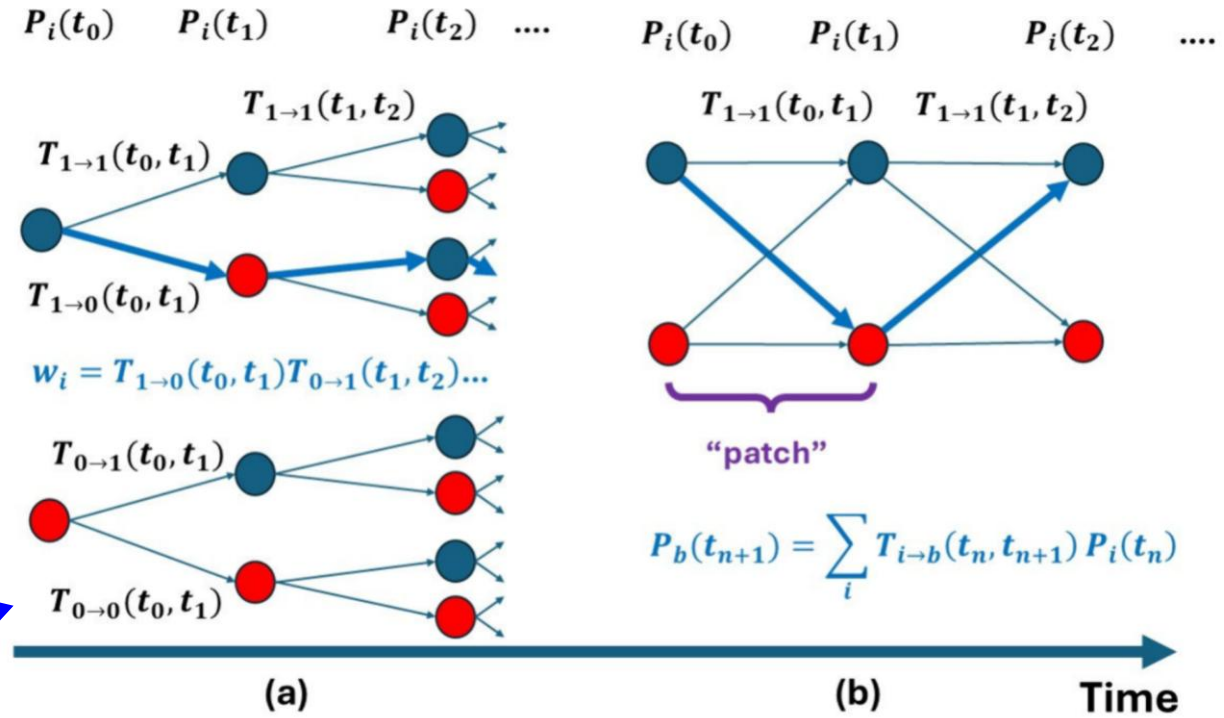
Han, D.; Shakiba, M.; Akimov, A. V. *JPCL.* **2025**, *16* (28), 7168–7176.

FISH cuts out multiple SH calculations in NBRA-TSH

Following the NBRA-based approach, we prepare a guiding trajectory and multiple batches as in NBRA-TSH.



Each batch is divided into coherent histories called ***"patches."***



Population is propagated recursively up to the transition probability $T_{i\to b}$. The transition probability $T_{i\to b}$ from a branching point, shown as a node, is determined by a coherent evolution with the corresponding initial state i.

$$P_b(t) = \sum_i T_{i\to b}(t_n,t)P_i(t_n) \qquad t \in [t_n,t_{n+1}]$$

$$T_{i\to b}(t_n,t) := |c_b(t)|^2 \text{ with } |c_i(t_n)|^2 = 1 \qquad \dot{c}_i = -\frac{i}{\hbar}E_i c_i - \sum_j d_{ij}c_j$$

Coherence from the previous patch is not considered. → The time duration for each patch can be considered as a characteristic decoherence time.

Han, D.; Shakiba, M.; Akimov, A. V. *JPCL.* **2025**, *16* (28), 7168–7176.

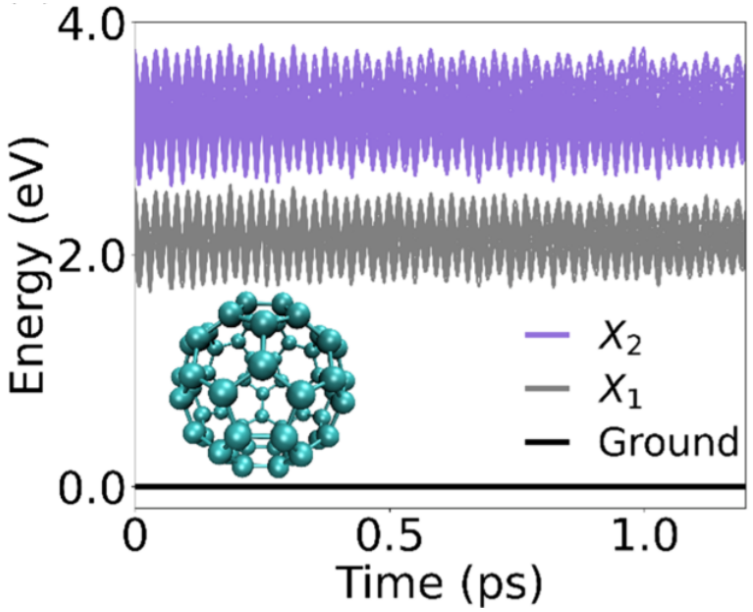
FISH cuts out multiple SH calculations in NBRA-TSH

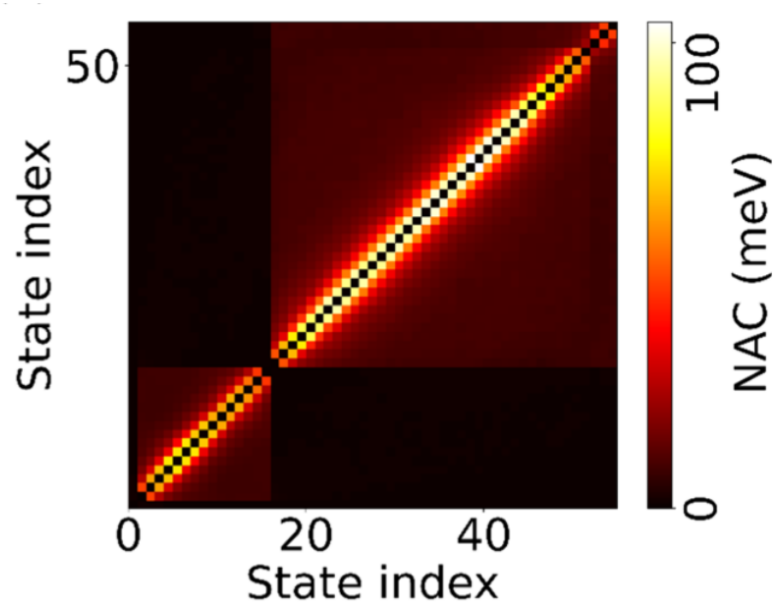
Total number of electronic integrations

NBRA-TSH = $N_{initial\_times} \times N_{traj} \times N_{step}$ FISH = $N_{initial\_times} \times \frac{N_{step}}{N_{patches}} \times N_{patches} \times N_{states}$

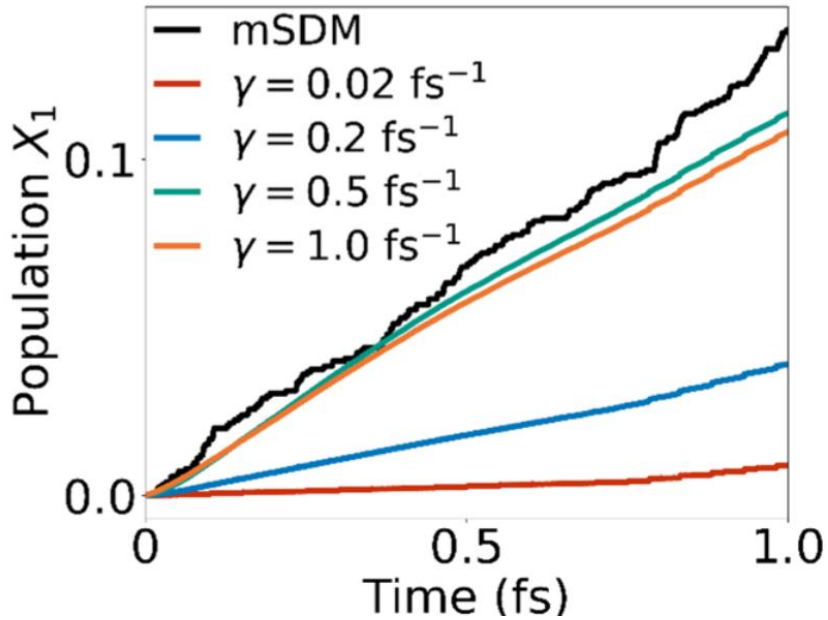
FISH is beneficial when $N_{state} \ll N_{traj}$.

Fullerene NBRA simulations





Decoherence frequency γ *is given by the reciprocal of patch time duration.*



For the fullerene system, FISH can agree with the conventional NBRA-mSDM.

Conclusion

- **SHXF (SH based on eXact Factorization)** tackles with the overcoherence problem with a decoherence term beyond the BO Hamiltonian, emerging from the electronic equation from XF.

- **QTSH (Quantum-Trajectory Surface Hopping)** eliminates the need for the velocity adjustment with the quantum force from the quantum-classical Liouville formalism and achives the ensemble-level energy conservation.

- **FISH (Fully-Integrated Surface Hopping)** serves as a further reduction of the conventional NBRA-TSH, considering all possible branching that would be usually expressed as multiple SH trajectories in the recursive summation of coherent histories.

Current Group Members

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Dr. Lee, In Seong

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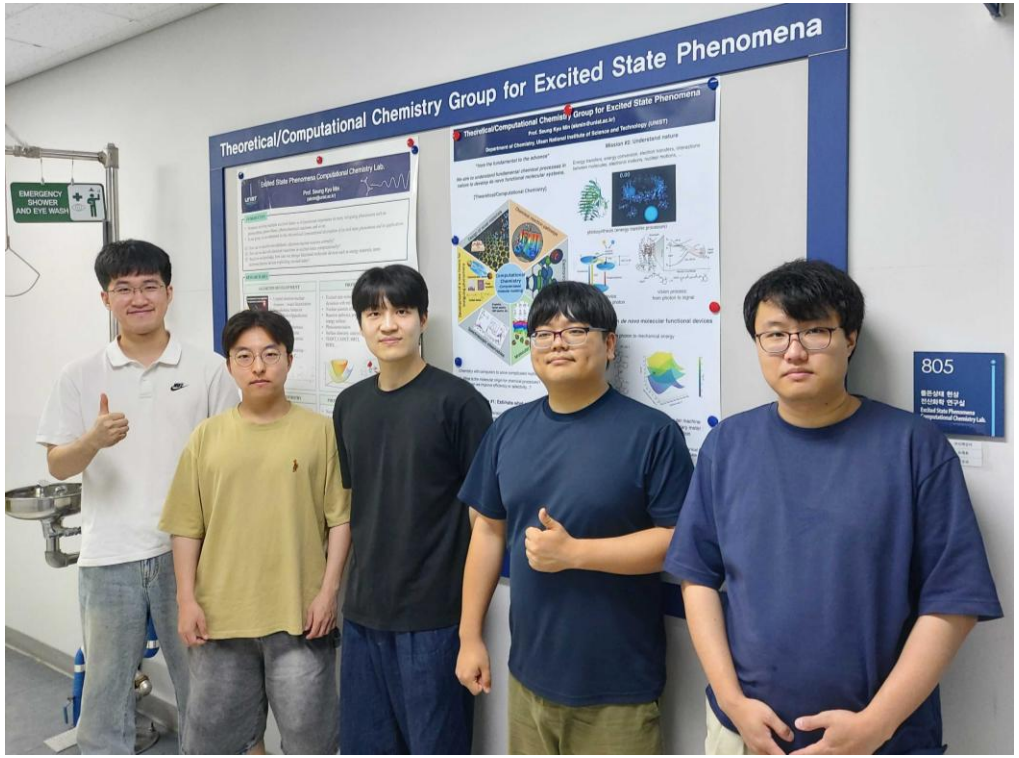


Graduate students (from left to right):

Mr. Lee, Jae Hyeok
Mr. Kim, Seong Ho
Mr. Lee, Jonghwan
Mr. Kim, Dokyun
Mr. Kim, Seok Jin

Suppl. Exact coherence

For an abstract electron-nuclear state $|\Psi(t)\rangle$, the density matrix operator is given as $\hat{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)|$.

From the Born-Huang expansion,

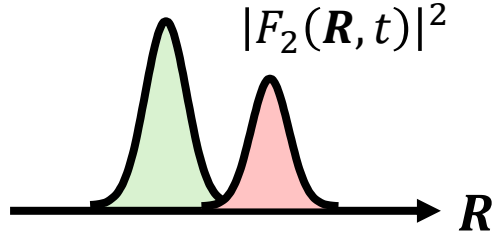
$$|\Psi(t)\rangle = \langle \boldsymbol{R}|\Psi(t)\rangle = \sum_i F_i(\boldsymbol{R},t)|i(t;\boldsymbol{R})\rangle = \sum_i c_i(\boldsymbol{R},t)\chi_i(\boldsymbol{R},t)|i(t;\boldsymbol{R})\rangle \qquad \sum_i |c_i|^2 = 1$$

where $\hat{H}_{BO}(\boldsymbol{R})|i(t;\boldsymbol{R})\rangle = E_i(\boldsymbol{R})|i(t;\boldsymbol{R})\rangle$. Then

$$\hat{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)| = \int d\boldsymbol{R}\,|\boldsymbol{R}\rangle\langle\boldsymbol{R}|\psi(t)\rangle\langle\psi(t)|\int d\boldsymbol{R}'|\boldsymbol{R}'\rangle\langle\boldsymbol{R}'|$$

$$= \iint |\boldsymbol{R}\rangle \sum_{ij} F_i(\boldsymbol{R},t)F_j^*(\boldsymbol{R}',t)|i(t;\boldsymbol{R})\rangle\langle j(t;\boldsymbol{R}')|\langle\boldsymbol{R}'|d\boldsymbol{R}d\boldsymbol{R}'$$

$\langle\Psi|\Psi\rangle_e = |F_1(\boldsymbol{R},t)|^2 + |F_2(\boldsymbol{R},t)|^2$



Thus, the reduced electron density matrix elements are

$$\hat{\rho}_e(t) = Tr_{\{|\boldsymbol{R}''\rangle\}}\hat{\rho}(t) = \int d\boldsymbol{R}''\langle\boldsymbol{R}''|\hat{\rho}(t)|\boldsymbol{R}''\rangle d\boldsymbol{R}'' = \sum_{ij}\int d\boldsymbol{R}\,|i(t;\boldsymbol{R})\rangle F_i(\boldsymbol{R},t)F_j^*(\boldsymbol{R},t)\langle j(t;\boldsymbol{R})|$$

$$\rho_{ij}(\boldsymbol{R},t) = F_i(\boldsymbol{R},t)F_j^*(\boldsymbol{R},t),$$

$$\langle\rho_{ij}(t)\rangle = \int d\boldsymbol{R}\,F_i(\boldsymbol{R},t)F_j^*(\boldsymbol{R},t)$$

Suppl. Towards the MQC equations from XF

- Molecular wave function is factored into the nuclear and electronic wave functions (WFCs).

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) = \chi(\boldsymbol{R},t)\Phi_{\boldsymbol{R}}(\boldsymbol{r},t) \qquad \forall \boldsymbol{R} \int |\Phi_{\boldsymbol{R}}(\boldsymbol{r},t)|^2 \, d\boldsymbol{r} = 1$$

Partial Normalization Condition

$$\Rightarrow \quad |\Psi(\boldsymbol{r},\boldsymbol{R},t)|^2 d\boldsymbol{r}d\boldsymbol{R} = |\chi(\boldsymbol{R},t)|^2 d\boldsymbol{R} \times |\Phi_{\boldsymbol{R}}(\boldsymbol{r},t)|^2 d\boldsymbol{r}$$

Total probability — Marginal probability for $\boldsymbol{R}$ — Conditional probability for $\boldsymbol{r}$ under $\boldsymbol{R}$

- The probability amplitude $|\chi|^2$ stands for the exact time-dependent nuclear density.

$$|\chi(\boldsymbol{R},t)|^2 = \sum_i^{\infty} |\chi_i(\boldsymbol{R},t)|^2$$

cf. Born-Huang expansion

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) = \sum_i^{\infty} \chi_i(\boldsymbol{R},t)\Phi_i(\boldsymbol{r};\boldsymbol{R}(t))$$

Abedi, A.; Maitra, N. T.; Gross, E. K. U. *PRL* **2010**, *105* (12), 123002.
Abedi, A.; Maitra, N. T.; Gross, E. K. U. *JCP* **2012**, *137* (22), 22A530.

Suppl. Towards the MQC equations from XF

- Coupled XF equations

$$\begin{cases} i\hbar\partial_t \chi(\boldsymbol{R},t) = \left(\sum_\nu \dfrac{[-i\hbar\nabla_\nu + A_\nu(\boldsymbol{R},t)]^2}{2M_\nu} + \epsilon(\boldsymbol{R},t)\right)\chi(\boldsymbol{R},t) \\ i\hbar\partial_t \Phi_{\boldsymbol{R}}(\boldsymbol{r},t) = \left(H_{BO}(r,\boldsymbol{R}) + U_{en}^{coup}[\Phi_{\boldsymbol{R}},\chi] - \epsilon(\boldsymbol{R},t)\right)\Phi_{\boldsymbol{R}}(\boldsymbol{R},t) \end{cases}$$

Time-dependent (TD) PES

$$\epsilon(\boldsymbol{R},t) = \left\langle \Phi_{\boldsymbol{R}}(t)\middle| H_{BO} + U_{en}^{coup} - i\hbar\partial_t \middle|\Phi_{\boldsymbol{R}}(t)\right\rangle_{\boldsymbol{r}}$$

TD vector potential

$$A_\nu(\boldsymbol{R},t) = \langle \Phi_{\boldsymbol{R}}(t)| - i\hbar\nabla_\nu \Phi_{\boldsymbol{R}}(t)\rangle_{\boldsymbol{r}}$$

Electron-nuclear correlation operator

$$U_{en}^{coup}[\Phi_{\boldsymbol{R}},\chi] = \sum_\nu \frac{1}{M_\nu}\left[\frac{[-i\hbar\nabla_\nu - A_\nu(\boldsymbol{R},t)]^2}{2} + \left(\frac{-i\hbar\nabla_\nu\chi}{\chi} + A_\nu(\boldsymbol{R},t)\right)\cdot(-i\hbar\nabla_\nu - A_\nu(\boldsymbol{R},t))\right]$$

Leading to Diagonal BO correction

Major electron-nuclear correlation

Abedi, A.; Maitra, N. T.; Gross, E. K. U. *PRL.* **2010**, *105* (12), 123002.
Abedi, A.; Maitra, N. T.; Gross, E. K. U. *JCP.* **2012**, *137* (22), 22A530.

Suppl. Towards the MQC equations from XF

- Inserting the polar form of nuclear WFC, $\chi(\boldsymbol{R},t) = |\chi(\boldsymbol{R},t)| \exp\left(\frac{i}{\hbar} S(\boldsymbol{R},t)\right)$, into the nuclear TDSE:

Real part

$$\partial_t S(\boldsymbol{R},t) = -\sum_\nu \frac{[\nabla_\nu S(\boldsymbol{R},t) + A_\nu(\boldsymbol{R},t)]^2}{2M_\nu} - \epsilon(\boldsymbol{R},t) + \hbar^2 \sum_\nu \frac{1}{2M_\nu} \frac{\nabla_\nu^2 |\chi(\boldsymbol{R},t)|}{|\chi(\boldsymbol{R},t)|}$$

Quantum Hamilton-Jacobi equation

Imaginary part

$$\partial_t |\chi(\boldsymbol{R},t)|^2 = \sum_\nu -\frac{1}{M_\nu} \nabla_\nu \cdot \left[\left(\nabla_\nu S(\boldsymbol{R},t) + \boldsymbol{A}_\nu(\boldsymbol{R},t)\right)|\chi(\boldsymbol{R},t)|^2\right]$$

Continuity equation → Throw away
(Within MQC, we assume its solution, i.e., a delta function).

cf. Hamilton-Jacobi equation

$$\partial_t S + H(\boldsymbol{R}, \boldsymbol{\nabla}_{\boldsymbol{R}} S, t) = 0$$

Min, S. K.; Agostini, F.; Gross, E. K. U. *PRL.* **2015**, *115* (7), 073001.
Agostini, F.; Min, S. K.; Abedi, A.; Gross, E. K. U. *JCTC.* **2016**, *12* (5), 2127–2143.

Suppl. Towards the MQC equations from XF

- Identifying the classical momentum: $P_\nu = \nabla_\nu S + A_\nu$ by neglecting the quantum potential.

$$\partial_t S(\boldsymbol{R},t) \approx -\sum_\nu \frac{[\nabla_\nu S(\boldsymbol{R},t) + A_\nu(\boldsymbol{R},t)]^2}{2M_\nu} - \epsilon(\boldsymbol{R},t)$$

$$\Rightarrow \quad \dot{S}(\boldsymbol{R},t) = -\sum_\nu \left[\frac{[\nabla_\nu S(\boldsymbol{R},t) + A_\nu(\boldsymbol{R},t)]^2}{2M_\nu} - \frac{P_\nu}{M_\nu}\cdot\nabla_\nu S(\boldsymbol{R},t)\right] - \epsilon(\boldsymbol{R},t) \qquad \text{In the Lagrangian frame}$$

$$= -\sum_\nu \left[\frac{P_\nu^2}{2M_\nu} - \frac{P_\nu}{M_\nu}\cdot(P_\nu - A_\nu)\right] - \epsilon(\boldsymbol{R},t) = -\left(\epsilon(\boldsymbol{R},t) + \sum_\nu A_\nu \cdot \frac{P_\nu}{M_\nu}\right)$$

Applying ∇_μ

$$\Rightarrow \quad \dot{P}_\mu - \dot{A}_\mu = -\nabla_\mu\left(\epsilon(\boldsymbol{R},t) + \textstyle\sum_\nu A_\nu \cdot \frac{P_\nu}{M_\nu}\right) \coloneqq 0 \text{ (by setting the Gauge condition)}$$

$$\therefore \dot{P}_\mu = \dot{A}_\mu \qquad \text{under } \epsilon(\boldsymbol{R},t) + \textstyle\sum_\nu A_\nu \cdot \frac{P_\nu}{M_\nu} = 0$$

Min, S. K.; Agostini, F.; Gross, E. K. U. *PRL* **2015**, *115* (7), 073001.

Agostini, F.; Min, S. K.; Abedi, A.; Gross, E. K. U. *JCTC* **2016**, *12* (5), 2127–2143.

Suppl. Towards the MQC equations from XF

- Approximation to the electronic TDSE

$$i\hbar\partial_t \Phi_{\boldsymbol{R}}(\boldsymbol{r},t) = \left(H_{BO}(r,\boldsymbol{R}) + U_{en}^{coup}[\Phi_{\boldsymbol{R}},\chi] - \epsilon(\boldsymbol{R},t)\right)\chi(\boldsymbol{R},t)$$

Neglecting the 2nd order terms generating the DBOC contribution

$$U_{en}^{coup}[\Phi_{\boldsymbol{R}},\chi] \approx \sum_{\nu}\frac{1}{M_\nu}\left(\frac{-i\hbar\nabla_\nu\chi}{\chi} + A_\nu(\boldsymbol{R},t)\right)\cdot\left(-i\hbar\nabla_\nu - A_\nu(\boldsymbol{R},t)\right)$$

$$i\hbar\dot{\Phi}_{\boldsymbol{R}}(\boldsymbol{r},t) - i\hbar\sum_{\nu}\frac{P_\nu}{M_\nu}\cdot\nabla_\nu\Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$

$$= \left(H_{BO}(r,\boldsymbol{R}) + \sum_{\nu}\frac{1}{M_\nu}\left(\frac{-i\hbar\nabla_\nu\chi}{\chi} + A_\nu(\boldsymbol{R},t)\right)\cdot\left(-i\hbar\nabla_\nu - A_\nu(\boldsymbol{R},t)\right) - \epsilon(\boldsymbol{R},t)\right)\Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$

Min, S. K.; Agostini, F.; Gross, E. K. U. *PRL* **2015**, *115* (7), 073001.

Agostini, F.; Min, S. K.; Abedi, A.; Gross, E. K. U. *JCTC* **2016**, *12* (5), 2127–2143.

Suppl. Towards the MQC equations from XF

- Approximation to the electronic TDSE

$$i\hbar\dot{\Phi}_{\boldsymbol{R}}(\boldsymbol{r},t) = \left(H_{BO}(r,\boldsymbol{R}) + \sum_{\nu} \frac{1}{M_\nu} \left(\frac{-i\hbar\nabla_\nu \chi}{\chi} + A_\nu(\boldsymbol{R},t) - P_\nu \right) \cdot (-i\hbar\nabla_\nu) \right) \Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$
$$- \left[\sum_{\nu} \frac{1}{M_\nu} \left(\frac{-i\hbar\nabla_\nu \chi}{\chi} + A_\nu(\boldsymbol{R},t) \right) \cdot A_\nu(\boldsymbol{R},t) + \epsilon(\boldsymbol{R},t) \right] \Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$

Utilizing the polar form

$$\frac{-i\hbar\nabla_\nu \chi}{\chi} + A_\nu(\boldsymbol{R},t) = \nabla_\nu S + A_\nu(\boldsymbol{R},t) - i\hbar \frac{\nabla_\nu |\chi(\boldsymbol{R},t)|}{|\chi(\boldsymbol{R},t)|} = P_\nu + \mathcal{P}_\nu$$

Quantum momentum

$$\mathcal{P}_\nu = -i\hbar \frac{\nabla_\nu |\chi(\boldsymbol{R},t)|}{|\chi(\boldsymbol{R},t)|}$$

$$\Rightarrow \quad i\hbar\dot{\Phi}_{\boldsymbol{R}}(\boldsymbol{r},t) = \left(H_{BO}(r,\boldsymbol{R}) + \sum_{\nu} \frac{\mathcal{P}_\nu}{M_\nu} \cdot (-i\hbar\nabla_\nu) \right) \Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$
$$- \left[\sum_{\nu} \frac{\mathcal{P}_\nu}{M_\nu} \cdot A_\nu(\boldsymbol{R},t) + \underbrace{\left(\sum_{\nu} \frac{P_\nu}{M_\nu} \cdot A_\nu(\boldsymbol{R},t) + \epsilon(\boldsymbol{R},t) \right)}_{\equiv 0 \text{ (The Gauge condition)}} \right] \Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$

$$\Rightarrow \quad i\hbar\dot{\Phi}_{\boldsymbol{R}}(\boldsymbol{r},t) = \left(H_{BO}(r,\boldsymbol{R}) - \sum_{\nu} \frac{\mathcal{P}_\nu}{M_\nu} \cdot (A_\nu(\boldsymbol{R},t) + i\hbar\nabla_\nu) \right) \Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$

Min, S. K.; Agostini, F.; Gross, E. K. U. *PRL* **2015**, *115* (7), 073001.

Agostini, F.; Min, S. K.; Abedi, A.; Gross, E. K. U. *JCTC* **2016**, *12* (5), 2127–2143.

Suppl. Towards the MQC equations from XF

- The XFMQC equations

$$i\hbar\dot{\Phi}_{\boldsymbol{R}}(\boldsymbol{r},t) = \left(H_{BO}(r,\boldsymbol{R}) - \sum_{\nu} \frac{\mathcal{P}_\nu}{M_\nu} \cdot \left(A_\nu(\boldsymbol{R},t) + i\hbar\nabla_\nu\right) \right) \Phi_{\boldsymbol{R}}(\boldsymbol{r},t)$$

$$\boldsymbol{F}_\nu = -\langle \Phi_{\boldsymbol{R}}(t) | \nabla_\nu H_{BO} | \Phi_{\boldsymbol{R}}(t) \rangle_{\boldsymbol{r}} + \sum_{\mu} \frac{2i\mathcal{P}_\mu}{\hbar M_\mu} \cdot \left(A_\mu(\boldsymbol{R},t) A_\nu(\boldsymbol{R},t) - \hbar^2 \left\langle \nabla_\mu \Phi_{\boldsymbol{R}}(t) \middle| \nabla_\nu \Phi_{\boldsymbol{R}}(t) \right\rangle_{\boldsymbol{r}} \right)$$

Beyond the conventional Ehrenfest terms, the resulting coupled TDSEs explicitly contain the electron-nuclear correlation terms arising from the XF formalism, without adding any ad hoc decoherence correction.

Min, S. K.; Agostini, F.; Gross, E. K. U. *PRL* **2015**, *115* (7), 073001.

Agostini, F.; Min, S. K.; Abedi, A.; Gross, E. K. U. *JCTC* **2016**, *12* (5), 2127–2143.

Suppl. Auxiliary-trajectory Propagation in SHXF

- Auxiliary trajectory propagation
  - When the coherence criterion, that is, $\epsilon < |C_i|^2 < 1 - \epsilon$, are satisfied for a state, the auxiliary trajectory is spawned for that state.
  - The initial aux. position $\boldsymbol{R}_i$ is set to the real position at the spawning time t_i.

$$\boldsymbol{R}_i(t_i) = \boldsymbol{R}(t_i)$$

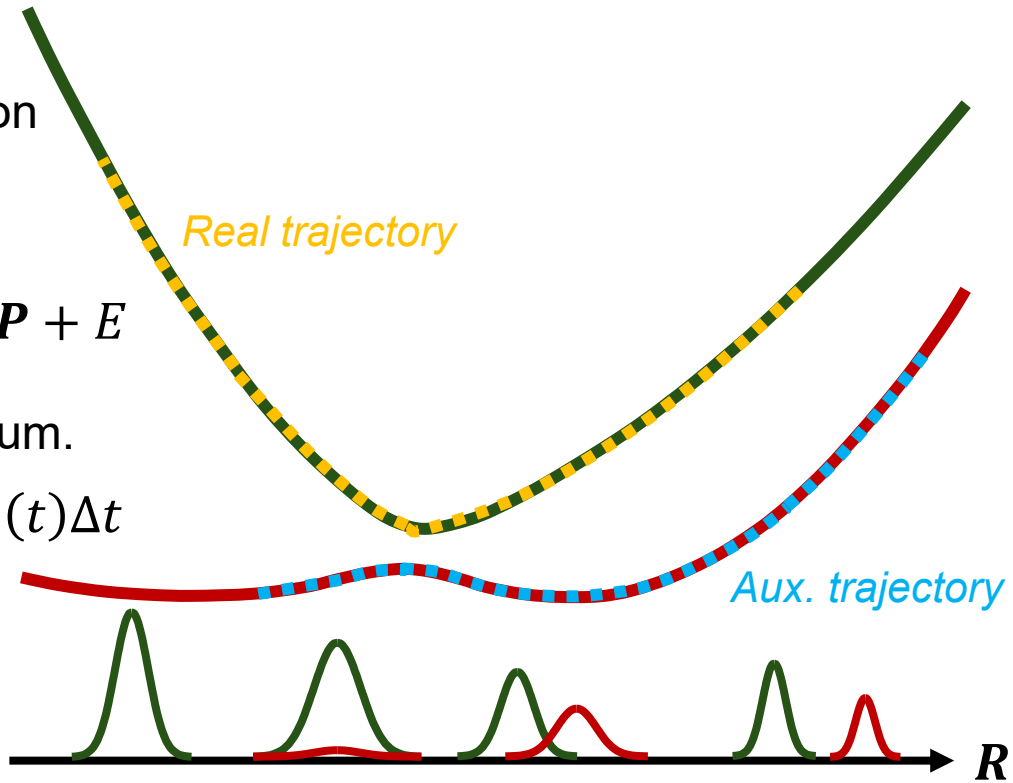
  - The aux. momentum $\boldsymbol{P}_i$ is set by rescaling $\boldsymbol{P}_i = \alpha_i \boldsymbol{P}$ based on the energy conservation.

$$\frac{1}{2}\boldsymbol{P}_i^T \boldsymbol{M}^{-1} \boldsymbol{P}_i + E_i = \frac{1}{2}\boldsymbol{P}^T \boldsymbol{M}^{-1} \boldsymbol{P} + E$$

  - The aux. position is propagated by the current aux. momentum.

$$\boldsymbol{R}_i(t + \Delta t) = \boldsymbol{R}_i(t) + \boldsymbol{M}^{-1} \boldsymbol{P}_i(t) \Delta t$$

  - When the coherence criterion is no longer satisfied, or a hop occurs, aux. trajectories are initialized.



Ha, J.-K.; Lee, I. S.; Min, S. K. *JPCL.* **2018**, *9* (5), 1097–1104.

Suppl. Auxiliary-trajectory Propagation in SHXF

- Quantum momentum

The nuclear density is assumed to be combination of Gaussian functions having each aux. position as its center.

$$|\chi|^2 = \sum_i |\chi_i|^2 = \sum_i N_i \prod_\nu \exp\left(-\frac{\left(R_\nu - R_{i,\nu}\right)^2}{2\sigma_{i,\nu}^2} \right)$$

$$\mathcal{P}_\nu \approx \frac{i\hbar}{2\sigma_\nu^2}\left(R - \langle R_\nu \rangle\right) \approx \frac{i\hbar}{2\sigma_\nu^2}\left(R_{a,\nu} - \sum_i \rho_{ii} R_{i,\nu} \right)$$

Eventually, the sign of quantum momentum is determined by the displacement between the real position and average position. By this procedure, each trajectory possesses its own quantum momentum constructed by its auxiliary trajectories.

Ha, J.-K.; Lee, I. S.; Min, S. K. *JPCL.* **2018**, *9* (5), 1097–1104.

Suppl. Auxiliary-trajectory Propagation in SHXF

- Phase gradient

The phase gradient is computed by the momentum difference during the coherence.

$$\phi_{i,\nu} = -\int_{t_i}^{t} dt' \, \nabla_\nu E_i = \int_{t_i}^{t} dt' \, F_i = \int_{t_i}^{t} dP_i$$

$$\phi_{i,\nu}(t) = P_i(t) - P_i(t_i)$$

Thus, quantum momentum and phase gradient become physical quantities in terms of the relative position and momentum.

Ha, J.-K.; Lee, I. S.; Min, S. K. *JPCL.* **2018**, *9* (5), 1097–1104.

Suppl. Auxiliary-trajectory Propagation in SHXF

- Decoherence correction through the electron-nuclear correlation term

The newly deduced electron-nuclear correlation contribution to the density is the following.

$$\dot{\rho}_{ii}^{XF} = \sum_{\nu} \frac{2i\mathcal{P}_{\nu}}{M_{\nu}} \cdot \sum_{j} \left(\phi_{j,\nu} - \phi_{i,\nu}\right) \rho_{jj}\rho_{ii}$$

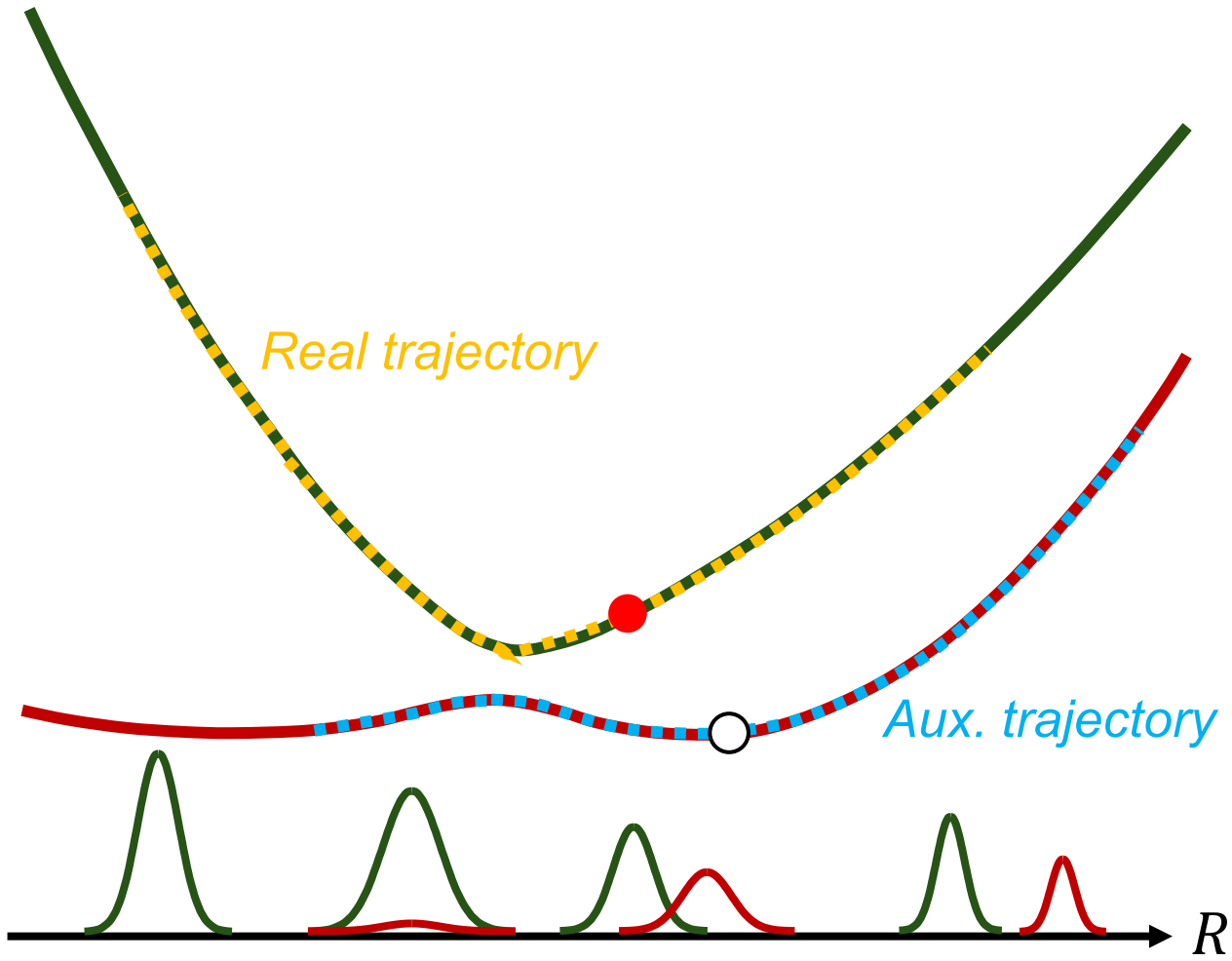
$$\dot{\rho}_{ii}^{XF} = -\sum_{\nu} \frac{\hbar}{M_{\nu}\sigma_{\nu}} \left(R_{\nu} - \langle R_{\nu} \rangle\right) \cdot \sum_{j} \left(\phi_{j,\nu} - \phi_{i,\nu}\right) \rho_{jj}\rho_{ii}$$

The direction of the decoherence is determined by the interplay between the relative position and momentum.

Ha, J.-K.; Lee, I. S.; Min, S. K. *JPCL.* **2018**, *9* (5), 1097–1104.

Suppl. Auxiliary-trajectory Propagation in SHXF

- Auxiliary trajectory propagation & decoherence correction



$$\dot{\rho}_{00}^{XF} = -\frac{\hbar}{M\sigma}(R - \langle R \rangle) \cdot (\phi_1 - \phi_0)\rho_{11}\rho_{00}$$

$$\dot{\rho}_{11}^{XF} = -\frac{\hbar}{M\sigma}(R - \langle R \rangle) \cdot (\phi_0 - \phi_1)\rho_{00}\rho_{11}$$

< 0 $(\phi_1 - \phi_0)$

< 0 $(R - \langle R \rangle)$

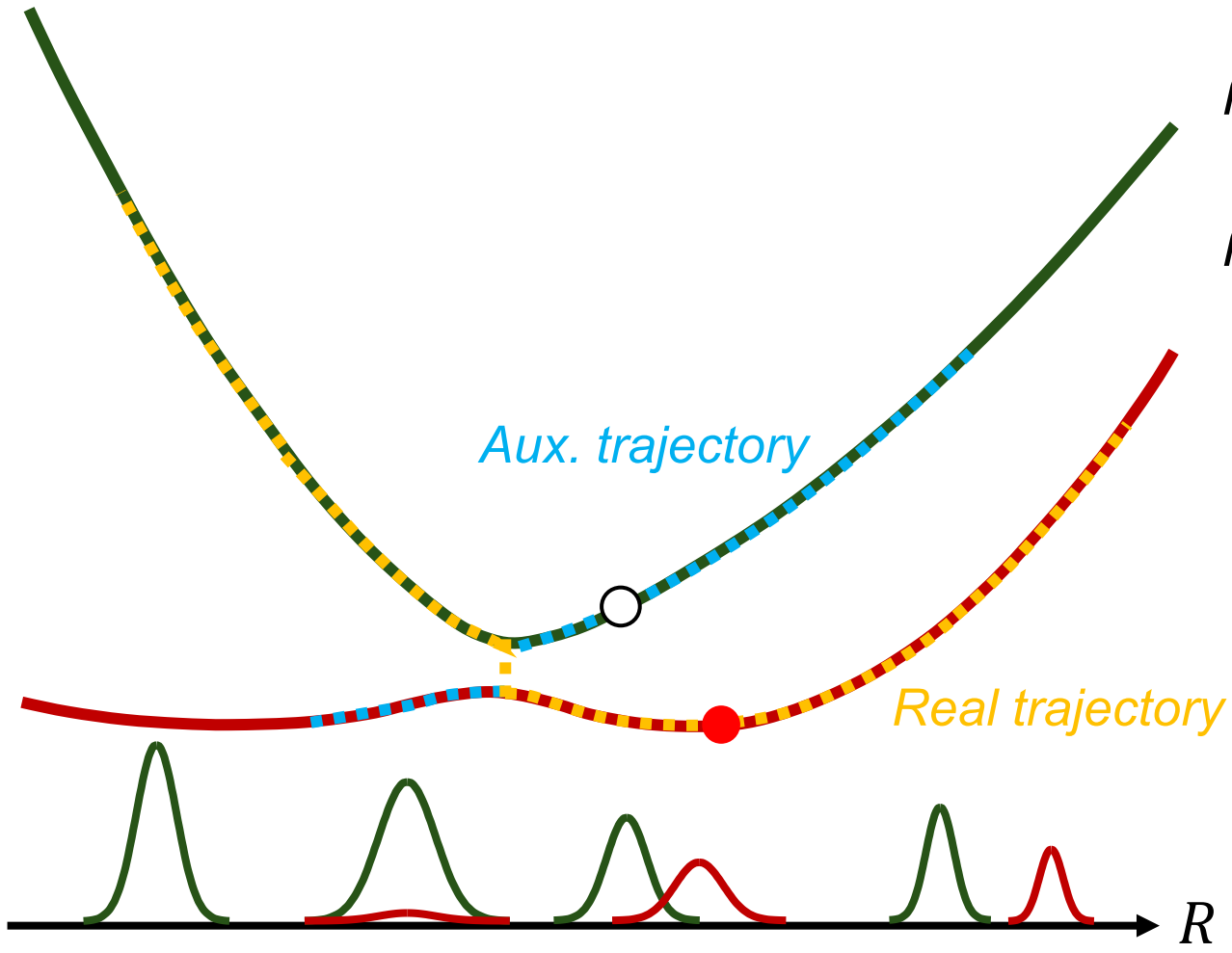
> 0 $(\phi_0 - \phi_1)$

The electron-nuclear correlation acts as the decoherence correction, increasing ρ_{11} and decreasing ρ_{00}.

Ha, J.-K.; Lee, I. S.; Min, S. K. *JPCL.* **2018**, *9* (5), 1097–1104.

Suppl. Auxiliary-trajectory Propagation in SHXF

- Auxiliary trajectory propagation & decoherence correction



$$\dot{\rho}_{00}^{XF} = -\frac{\hbar}{M\sigma}(R - \langle R \rangle) \cdot (\phi_1 - \phi_0)\rho_{11}\rho_{00}$$

$$\dot{\rho}_{11}^{XF} = -\frac{\hbar}{M\sigma}(R - \langle R \rangle) \cdot (\phi_0 - \phi_1)\rho_{00}\rho_{11}$$

< 0

> 0 $\quad$ > 0

The electron-nuclear correlation acts as the decoherence correction, increasing ρ_{00} and decreasing ρ_{11}.

Decoherence facilitates the population transfer to the active state → The active state serves as the pointer state!

Ha, J.-K.; Lee, I. S.; Min, S. K. *JPCL.* **2018**, *9* (5), 1097–1104.

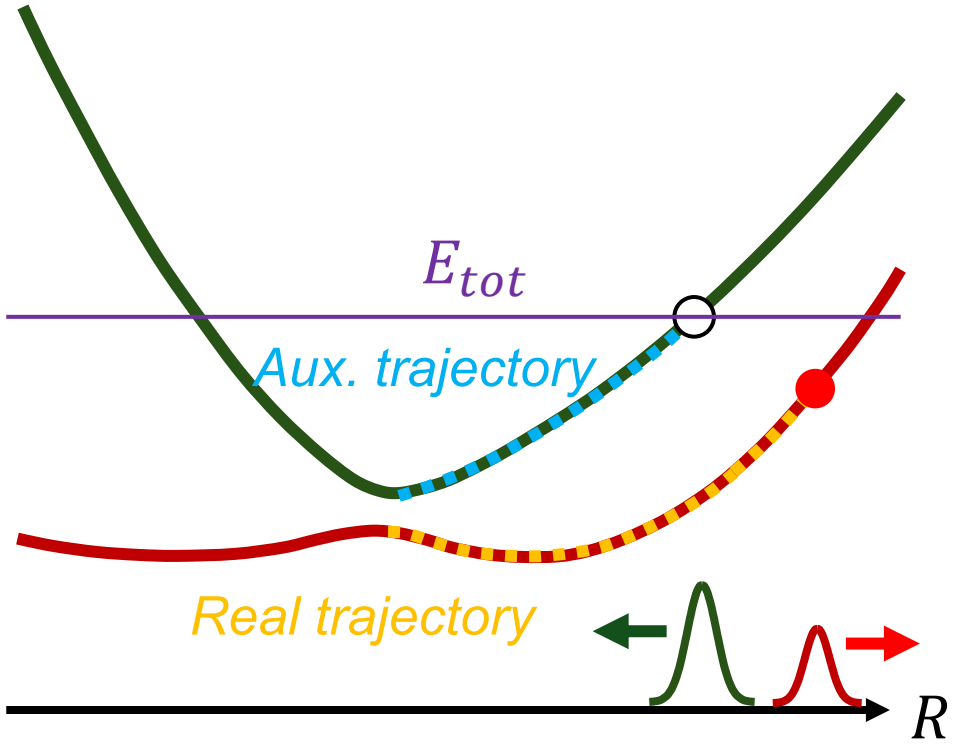
Shu, Y.; Truhlar, D. G. *JCTC.* **2023**, *19* (2), 380–395.

Suppl. Auxiliary-trajectory Propagation in SHXF

- Branching correction on the auxiliary trajectory propagation

When the dynamics encounters the classical turning point, there are some difficulties for defining the auxiliary momenta

Case I. An auxiliary trajectory encounters the turning point.



In this case, the auxiliary trajectory needs to reflect. However, the aux. momentum is computed by the positive scaling of the real momentum. Thus, a special treatment is necessary.

$$\boldsymbol{P}_i = \alpha_i(>0)\boldsymbol{P}$$

Inspired by the BCSH method, one can the density of the auxiliary state and initialize the auxiliary project out trajectory.

Arribas, E. V.; Vindel-Zandbergen, P.; Roy, S.; Maitra, N. T. *PCCP.* **2023**, *25* (38), 26380–26395.

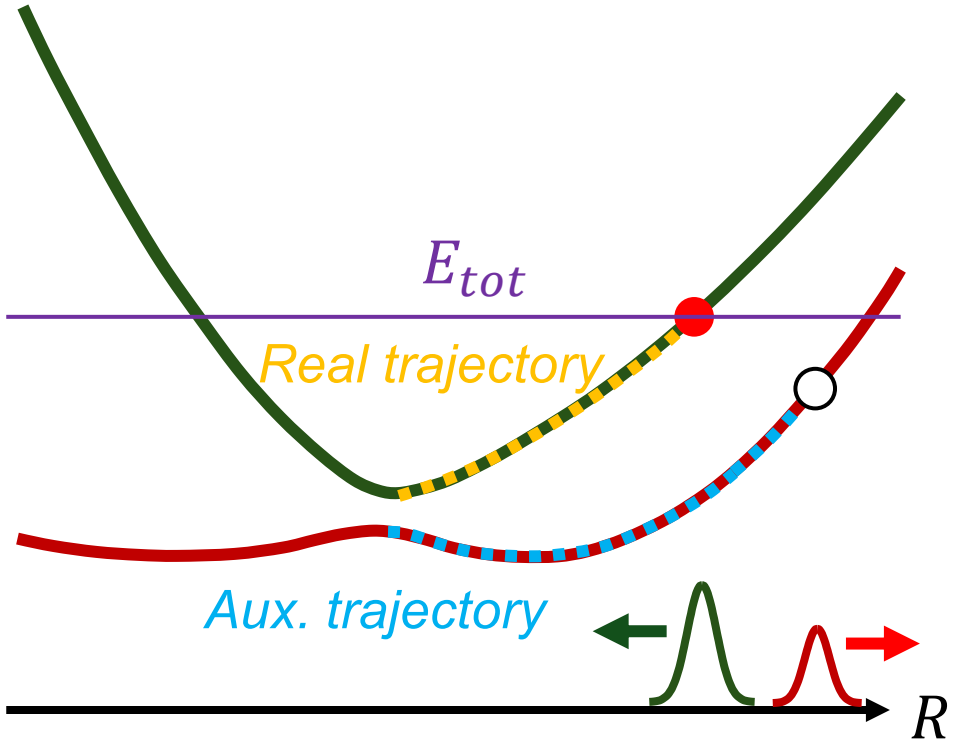
Xu, J.; Wang, L. *JCP.* **2019**, *150* (16), 164101.

Suppl. Auxiliary-trajectory Propagation in SHXF

- Branching correction on the auxiliary trajectory propagation

When the dynamics encounters the classical turning point, there are some difficulties for defining the auxiliary momenta

Case II. The real trajectory encounters the turning point.



In this case, the auxiliary trajectory would experience abrupt momentum reversal, which could cause a wrong decoherence correction.

Here, one can collapse the state to the active state. The criterion for the turning point is based on the BCSH turning point descriptor.

$$\boldsymbol{F}^T(t+\Delta t)\boldsymbol{P}_i(t+\Delta t)\cdot\boldsymbol{F}^T(t+\Delta t)\boldsymbol{P}_i(t)<0 \;\Rightarrow\; \textit{turning point}$$

Ha, J.-K.; Min, S. K. *JCP.* **2022**, *156* (17), 174109.

Xu, J.; Wang, L. *JCP.* **2019**, *150* (16), 164101.

Suppl. The Wigner-Moyal approach to quantum Liouville

For the full system's Hamiltonian $\hat{H} = \hat{T} + \hat{V}$, the quantum Liouville equation is

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}].$$

With a complete orthonormal electronic basis, $\{|i\rangle\}$, applying the resolution of identity, $\hat{I} = \sum_i |i\rangle\langle i|$,

$$i\hbar \frac{d\hat{\rho}_{ij}}{dt} = \sum_k \left(\hat{H}_{ik}\hat{\rho}_{kj} - \hat{\rho}_{ik}\hat{H}_{kj}\right)$$

In the Wigner-Moyal representation, the nuclear operators becomes functions of the nuclear phase space coordinates, $\boldsymbol{z} = (\boldsymbol{q}, \boldsymbol{p})$. Products of operators are represented by the star (or Moyal) product:

$$\hat{A}\hat{B} \rightarrow A(\boldsymbol{q},\boldsymbol{p}) \bigstar B(\boldsymbol{q},\boldsymbol{p}) = A(\boldsymbol{q},\boldsymbol{p}) e^{\frac{i\hbar}{2}\overleftrightarrow{\boldsymbol{\Lambda}}} B(\boldsymbol{q},\boldsymbol{p})$$

where $\overleftrightarrow{\boldsymbol{\Lambda}} = \overleftarrow{\boldsymbol{\nabla}}_{\boldsymbol{q}} \overrightarrow{\boldsymbol{\nabla}}_{\boldsymbol{p}} - \overleftarrow{\boldsymbol{\nabla}}_{\boldsymbol{q}} \overrightarrow{\boldsymbol{\nabla}}_{\boldsymbol{p}}$ and the arrows indicate the direction that differential operators act.

Suppl. The Wigner-Moyal approach to quantum Liouville

The quantum-classical Liouville equation (QCLE) is then obtained if one keeps only the lowest order nonclassical term in the expansion of the Moyal product:

$$\hat{A}\hat{B} \to AB + \frac{i\hbar}{2}\{\hat{A}, \hat{B}\}$$

where $\{A, B\} = \nabla_{\boldsymbol{q}} A \nabla_{\boldsymbol{p}} B - \nabla_{\boldsymbol{p}} A \nabla_{\boldsymbol{q}} B$ is the Poisson bracket of the phase-space functions. Applying the Wigner-Moyal transformation to the quantum Liouville equation yields

$$i\hbar \frac{\partial \rho_{ij}(\boldsymbol{z}, t)}{\partial t} = \sum_k \left(H_{ik}(\boldsymbol{z})\rho_{kj}(\boldsymbol{z}, t) - \rho_{ik}(\boldsymbol{z}, t)H_{kj}(\boldsymbol{z})\right)$$
$$+ \frac{i\hbar}{2}\sum_k \left(\{H_{ik}(\boldsymbol{z}), \rho_{kj}(\boldsymbol{z}, t)\} - \{\rho_{ik}(\boldsymbol{z}, t), H_{kj}(\boldsymbol{z})\}\right).$$

Suppl. Derivation of QTSH equations

Starting from the QCLE equation,

$$i\hbar\frac{\partial\rho_{ij}}{\partial t}=\sum_{k=0}^{N-1}\left(H_{ik}\rho_{kj}-\rho_{ik}H_{kj}\right)+\frac{i\hbar}{2}\sum_{k=0}^{N-1}\left(\{H_{ik},\rho_{kj}\}-\{\rho_{ik},H_{kj}\}\right),$$

We have

$$i\hbar\left[\frac{d\rho_{ij}}{dt}(\boldsymbol{z},t)-\boldsymbol{\nabla_q}\rho_{ij}(\boldsymbol{z},t)\dot{\boldsymbol{q}}-\boldsymbol{\nabla_p}\rho_{ij}(\boldsymbol{z},t)\dot{\boldsymbol{p}}\right]=\sum_{k=0}^{N-1}\left(H_{ik}(\boldsymbol{z})\rho_{kj}(\boldsymbol{z},t)-\rho_{ik}(\boldsymbol{z},t)H_{kj}\right)$$
$$+\frac{i\hbar}{2}\sum_{k=0}^{N-1}\left(\boldsymbol{\nabla_q}H_{ik}\boldsymbol{\nabla_p}\rho_{kj}-\boldsymbol{\nabla_p}H_{ik}\boldsymbol{\nabla_q}\rho_{kj}-\boldsymbol{\nabla_q}\rho_{ik}\boldsymbol{\nabla_p}H_{kj}+\boldsymbol{\nabla_p}\rho_{ik}\boldsymbol{\nabla_q}H_{kj}\right).$$

We classify terms in equations according to phase-space derivatives. First, consider the equation involving only the density matrix functions themselves (black equations):

$$i\hbar\frac{d\rho_{ij}(\boldsymbol{z},t)}{dt}=\sum_{k=0}^{N-1}\left(H_{ik}(\boldsymbol{z})\rho_{kj}(\boldsymbol{z},t)-\rho_{ik}(\boldsymbol{z},t)H_{kj}\right)$$

Suppl. Derivation of QTSH equations

Applying our phase-density ansatz, $\rho_{ij}(\boldsymbol{z},t) = \tilde{\rho}_{ij}(t)g(\boldsymbol{z})$, yields

$$i\hbar\frac{\partial\tilde{\rho}_{ij}(t)}{\partial t}g(\boldsymbol{z}) + i\hbar\tilde{\rho}_{ij}(t)\dot{\boldsymbol{z}}\nabla_{\boldsymbol{z}}g = \sum_{k=0}^{N-1}\Big(H_{ik}(\boldsymbol{z})\tilde{\rho}_{kj}(t) - \tilde{\rho}_{ik}(t)H_{kj}(\boldsymbol{z})\Big)g(\boldsymbol{z}),$$

or

$$i\hbar\frac{\partial\tilde{\rho}_{ij}(t)}{\partial t} = \sum_{k=0}^{N-1}\Big(H_{ik}(\boldsymbol{z})\tilde{\rho}_{kj}(t) - \tilde{\rho}_{ik}(t)H_{kj}(\boldsymbol{z})\Big) - i\hbar\frac{\dot{\boldsymbol{z}}\nabla_{\boldsymbol{z}}g}{g(\boldsymbol{z})}\tilde{\rho}_{ij}(t).$$

We work out blue and red equations as well, with the full Hamiltonian matrix definition,

$$H_{ij} \approx \left(\frac{1}{2}\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{p} + V_{ii}\right)\delta_{ij} - i\hbar\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{h}_{ij}.$$

Suppl. Derivation of QTSH equations

The blue and red equations:

$$-i\hbar\boldsymbol{\nabla}_{\boldsymbol{q}}\rho_{ij}(\boldsymbol{z},t)\dot{\boldsymbol{q}} = \frac{i\hbar}{2}\sum_{k=0}^{N-1}\left(-\boldsymbol{\nabla}_{\boldsymbol{p}}H_{ik}\boldsymbol{\nabla}_{\boldsymbol{q}}\rho_{kj} - \boldsymbol{\nabla}_{\boldsymbol{q}}\rho_{ik}\boldsymbol{\nabla}_{\boldsymbol{p}}H_{kj}\right)$$

$$\dot{\boldsymbol{q}}\boldsymbol{\nabla}_{\boldsymbol{q}}\rho_{ij}(\boldsymbol{z},t) = \dot{\boldsymbol{q}}\tilde{\rho}_{ij} = -i\hbar\boldsymbol{M}^{-1}\boldsymbol{p}\boldsymbol{\nabla}_{\boldsymbol{q}}\rho_{ij} + (i\hbar)\frac{i\hbar}{2}\boldsymbol{M}^{-1}\sum_{k=0}^{N-1}\left(\boldsymbol{h}_{ik}\boldsymbol{\nabla}_{\boldsymbol{q}}\rho_{kj} + \boldsymbol{\nabla}_{\boldsymbol{q}}\rho_{ik}\boldsymbol{h}_{kj}\right)$$

$$-i\hbar\boldsymbol{\nabla}_{\boldsymbol{p}}\rho_{ij}(\boldsymbol{z},t)\dot{\boldsymbol{p}} = \frac{i\hbar}{2}\sum_{k=0}^{N-1}\left(\boldsymbol{\nabla}_{\boldsymbol{q}}H_{ik}\boldsymbol{\nabla}_{\boldsymbol{p}}\rho_{kj} + \boldsymbol{\nabla}_{\boldsymbol{p}}\rho_{ik}\boldsymbol{\nabla}_{\boldsymbol{q}}H_{kj}\right)$$

$$\boldsymbol{\nabla}_{\boldsymbol{p}}\rho_{ij}(\boldsymbol{z},t)\dot{\boldsymbol{p}} = \frac{1}{2}\left(\boldsymbol{F}_i + \boldsymbol{F}_j\right)\boldsymbol{\nabla}_{\boldsymbol{p}}\rho_{ij} + \frac{i\hbar}{2}\sum_{k=0}^{N-1}\left(\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{h}_{ik}\right)\boldsymbol{\nabla}_{\boldsymbol{p}}\rho_{kj} + \boldsymbol{\nabla}_{\boldsymbol{p}}\rho_{ik}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{h}_{kj}\right)\right)$$

Suppl. Derivation of QTSH equations

Applying $\rho_{ij}(\boldsymbol{z},t) = \tilde{\rho}_{ij}(t)g(\boldsymbol{z})$ to both equations and normalization conditions, $\sum_i \tilde{\rho}_{ii} = 1$,

$$\dot{\boldsymbol{q}}\tilde{\rho}_{ij} = \boldsymbol{M}^{-1}\boldsymbol{p}\tilde{\rho}_{ij} - \frac{i\hbar}{2}\boldsymbol{M}^{-1}\sum_{k=0}^{N-1}\left(\boldsymbol{h}_{ik}\tilde{\rho}_{kj} + \tilde{\rho}_{ik}\boldsymbol{h}_{kj}\right) \Rightarrow \dot{\boldsymbol{q}} = \boldsymbol{M}^{-1}\boldsymbol{p} - \frac{i\hbar}{2}\boldsymbol{M}^{-1}\sum_{k,i}(\boldsymbol{h}_{ik}\tilde{\rho}_{ki} + \tilde{\rho}_{ik}\boldsymbol{h}_{ki}).$$

$$\tilde{\rho}_{ij}\dot{\boldsymbol{p}} = \frac{1}{2}\left(\boldsymbol{F}_i + \boldsymbol{F}_j\right)\tilde{\rho}_{ij} + \frac{i\hbar}{2}\sum_{k=0}^{N-1}\left(\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{h}_{ik}\right)\tilde{\rho}_{kj} + \tilde{\rho}_{ik}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{h}_{kj}\right)\right)$$

$$\Rightarrow \dot{\boldsymbol{p}} = \sum_{i=0}^{N-1}\boldsymbol{F}_i\tilde{\rho}_{ii} + \frac{i\hbar}{2}\sum_{k,i}\left(\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{h}_{ik}\right)\tilde{\rho}_{ki} + \tilde{\rho}_{ik}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{h}_{ki}\right)\right)$$

Thus,

$$\dot{\boldsymbol{q}} = \boldsymbol{M}^{-1}\boldsymbol{p} - \frac{i\hbar}{2}\boldsymbol{M}^{-1}\sum_{k,i}(\boldsymbol{h}_{ik}\tilde{\rho}_{ki} + \tilde{\rho}_{ik}\boldsymbol{h}_{ki}),$$

$$\dot{\boldsymbol{p}} = \sum_{i=0}^{N-1}\boldsymbol{F}_i\tilde{\rho}_{ii} + \frac{i\hbar}{2}\sum_{k,i}\left(\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{h}_{ik}\right)\tilde{\rho}_{ki} + \tilde{\rho}_{ik}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{h}_{ki}\right)\right).$$

Suppl. Derivation of QTSH equations

The differential equation for $\boldsymbol{q}$ is simplified by

$$-\frac{i\hbar}{2}\boldsymbol{M}^{-1}\sum_{k,i}(\boldsymbol{h}_{ik}\tilde{\rho}_{ki}+\tilde{\rho}_{ik}\boldsymbol{h}_{ki})=-\frac{i\hbar}{2}\boldsymbol{M}^{-1}\sum_{k,i}(\boldsymbol{h}_{ik}(\alpha_{ki}+i\beta_{ki})+(\alpha_{ik}+i\beta_{ik})\boldsymbol{h}_{ki})$$

$$=-\frac{i\hbar}{2}\boldsymbol{M}^{-1}\sum_{k,i}\boldsymbol{h}_{ik}\big((\alpha_{ki}+i\beta_{ki})-(\alpha_{ki}-i\beta_{ki})\big)=-\frac{i\hbar}{2}\boldsymbol{M}^{-1}\sum_{k,i}2i\beta_{ki}\boldsymbol{h}_{ik}=\hbar\boldsymbol{M}^{-1}\sum_{k,i}\beta_{ki}\boldsymbol{h}_{ik}$$

$$=-\hbar\boldsymbol{M}^{-1}\sum_{k,i}\beta_{ik}\boldsymbol{h}_{ik}=-2\hbar\sum_{i,k:i<k}\beta_{ik}\boldsymbol{h}_{ik}\,.$$

Thus,

$$\dot{\boldsymbol{q}}=\boldsymbol{M}^{-1}\boldsymbol{p}-2\hbar\sum_{i,k:i<k}\beta_{ik}\boldsymbol{h}_{ik}\,.$$

Suppl. Derivation of QTSH equations

The differential equation for $\boldsymbol{p}$ is simplified by

$$\frac{i\hbar}{2}\sum_{k,i}\left(\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ik}\right)\tilde{\rho}_{ki}+\tilde{\rho}_{ik}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ki}\right)\right)$$

$$=\frac{i\hbar}{2}\sum_{k,i}\left(\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ik}\right)(\alpha_{ki}+i\beta_{ki})+(\alpha_{ik}+i\beta_{ik})\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ki}\right)\right)$$

$$=\frac{i\hbar}{2}\sum_{k,i}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ik}\right)\left((\alpha_{ki}+i\beta_{ki})-(\alpha_{ki}-i\beta_{ki})\right)=\frac{i\hbar}{2}\sum_{k,i}2i\beta_{ki}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ik}\right)$$

$$=-\hbar\sum_{k,i}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ik}\right)\beta_{ki}=\hbar\sum_{k,i}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ik}\right)\beta_{ik}=2\hbar\sum_{k,i:i<k}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ik}\right)\beta_{ik}\,.$$

Thus,

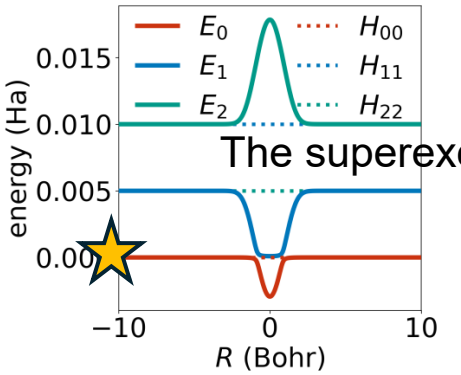
$$\dot{\boldsymbol{p}}=\sum_{i=0}^{N-1}\boldsymbol{F}_i\tilde{\rho}_{ii}+2\hbar\sum_{i,k:i<k}\left(\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{\nabla_q}\boldsymbol{h}_{ik}\right)\beta_{ik}\,.$$

Suppl. The superexchange model dynamics in QTSH

Energy conservation & internal consistency

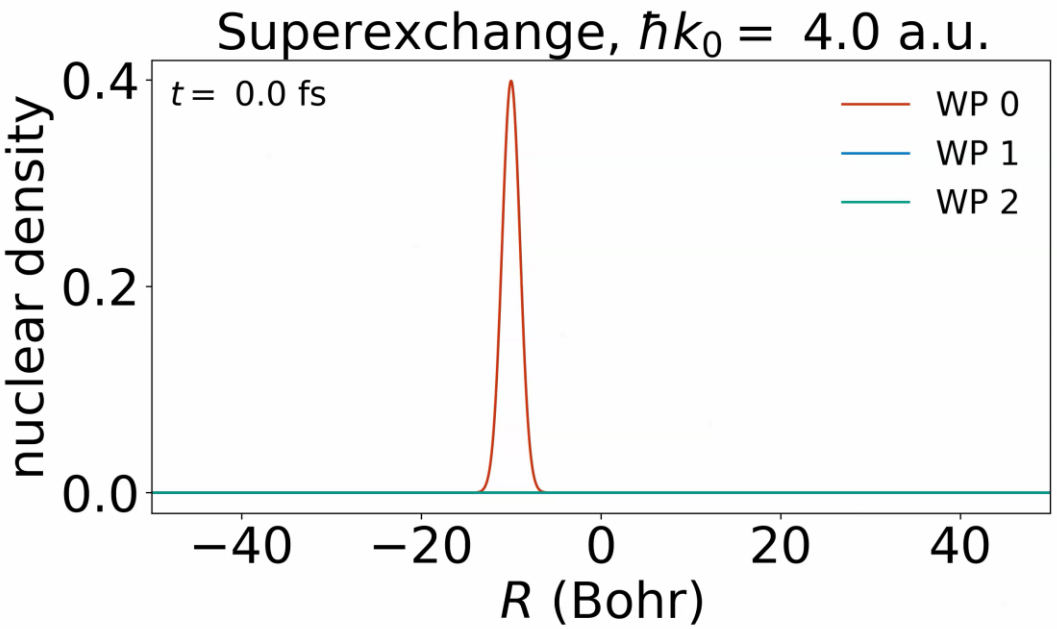
$$E_{tot} = \frac{1}{N_{tr}} \sum_{k}^{N_{tr}} \left(\underbrace{\frac{1}{2} \boldsymbol{p}_k^T \boldsymbol{M}^{-1} \boldsymbol{p}_k + E_{a_k a_k}}_{E_{diag}} \underbrace{- \frac{2\hbar}{N_{tr}} \sum_{i<j}^{N} \Im \rho_{ij,k} d_{ij,k}}_{E_{coh}} \right)$$

$a_k(t)$ = the active-state index of kth trajectory at t

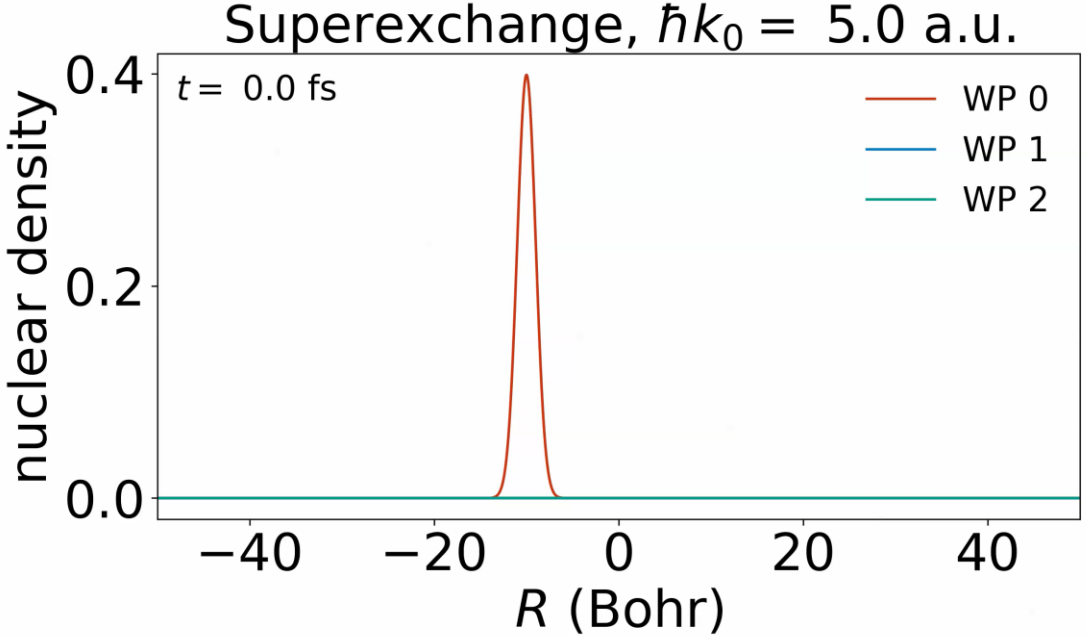


The superexchange model

QTSH on the superexchange model



The low-momentum case, multiple crossing due to a temporary trap on the 1st excited state.



After passing the coupling region once, transmission goes on, i.e., just the adiabatic dynamics on the ground-state PES.

Suppl. Individual-state population in NBRA-TSH and FISH