Assessment of Trajectory Surface Hopping Methods in Long-Time Nonadiabatic Dynamics

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VISTA Seminar 107

University at Buffalo The State University of New York

Motivation

AI-Generated

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- Comparative analyses and assessments are conducted periodically on subsets of methods and models
  - Long-time internal conversion dynamics
  - Molecular photodynamics
  - Multidimensional spin-boson models

Mukherjee, S.; Pinheiro, M., Jr; Demoulin, B.; Barbatti, M. Simulations of molecular photodynamics in long timescales. Philos. Trans. A Math. Phys. Eng. Sci. 2022, 380, 20200382

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Botticelli, S., Accomasso, D., Granucci, G. Assessing surface hopping methods for long-time internal conversion dynamics: The case of lutein, 2026

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    - Molecular photodynamics
    - **Multidimensional spin-boson models (1 year of calculations for exact MCTDH results)**
- Expensive exact calculations prohibit systematic evaluation

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Model and Calculations Setup

Model

Spin-Boson Hamiltonian

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

$$H_S = \epsilon_0\sigma_z - \Delta_0\sigma_x = \begin{pmatrix} \epsilon_0 & -\Delta_0 \\ -\Delta_0 & -\epsilon_0 \end{pmatrix}$$

$$H_B = \sum_{i=0}^{N-1} \hbar\omega_i b_i^+ b_i = \begin{pmatrix} \frac{1}{2}\sum_{i=0}^{N-1} m_i\omega_i^2 R_i^2 & 0 \\ 0 & \frac{1}{2}\sum_{i=0}^{N-1} m_i\omega_i^2 R_i^2 \end{pmatrix}$$

$$H_{SB} = \sigma_z \sum_{i=0}^{N-1} g_i(b_i^+ + b_i) = \begin{pmatrix} \sum_{i=0}^{N-1} g_i R_i & 0 \\ 0 & -\sum_{i=0}^{N-1} g_i R_i \end{pmatrix}$$

$$\Delta_0 = 0.001 \qquad J(\omega_i) = \frac{E_r}{2}\frac{\omega_i\omega_c}{\omega_i^2 + \omega_c^2}$$

$$E_r = 0.0125 \text{ a.u.} \approx 0.34 \text{ eV}$$

$$\omega_c = 1000 \text{ cm}^{-1}$$

Mode	Frequency, ω_i (cm^{-1})	Coupling, g_i $\left(\frac{\text{Hartree}}{\text{bohr}}\right)$
ν_1	129.74	$0.563 \cdot 10^{-3}$
ν_2	263.64	$1.143 \cdot 10^{-3}$
ν_3	406.41	$1.1762 \cdot 10^{-3}$
ν_4	564.00	$2.446 \cdot 10^{-3}$
ν_5	744.78	$3.230 \cdot 10^{-3}$
ν_6	961.55	$4.170 \cdot 10^{-3}$
ν_7	1235.66	$5.358 \cdot 10^{-3}$
ν_8	1606.62	$6.966 \cdot 10^{-3}$
ν_9	2157.56	$9.356 \cdot 10^{-3}$
ν_{10}	3100.00	$13.444 \cdot 10^{-3}$

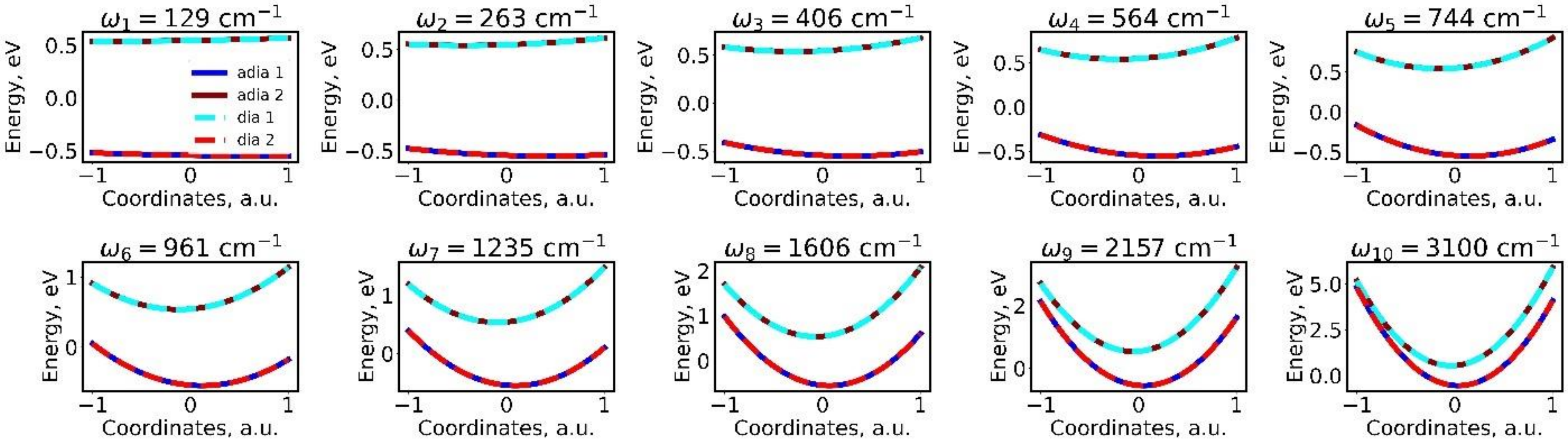
$$E_{ZPE} = \frac{1}{2}\sum_{i=1}^{10} \hbar\omega_i \approx 0.051 \text{ a.u.}$$

S. Mukherjee *et al.* J. Chem. Theory Comput. 21, 29–37 (2025).

Model and Calculations Setup

Model

Spin-Boson Hamiltonian



Model and Calculations Setup

Model

Initialization

Spin-Boson Hamiltonian

1- Wigner, 0 K limit 2- Boltzmann, 300 K

$$P(\{\boldsymbol{R}\},\{\boldsymbol{p}\}) = \Pi_i P(R_i, p_i)$$

$$P(R_i, p_i) = \exp\left(-\frac{1}{2\sigma_{R_i}^2}\left(R_i - R_{i,0}\right)^2 - \frac{1}{2\sigma_{p_i}^2}p_i^2\right)$$

- Wigner 0 K limit: $\sigma_{R_i} = \sqrt{\frac{\hbar}{m_i\omega_i}}, \quad \sigma_{p_i} = \sqrt{\hbar m_i \omega_i}$
- Boltzmann: $\sigma_{R_i} = \frac{1}{\sqrt{m_i\beta\omega_i}}, \quad \sigma_{p_i} = \sqrt{\frac{m_i}{\beta}}$

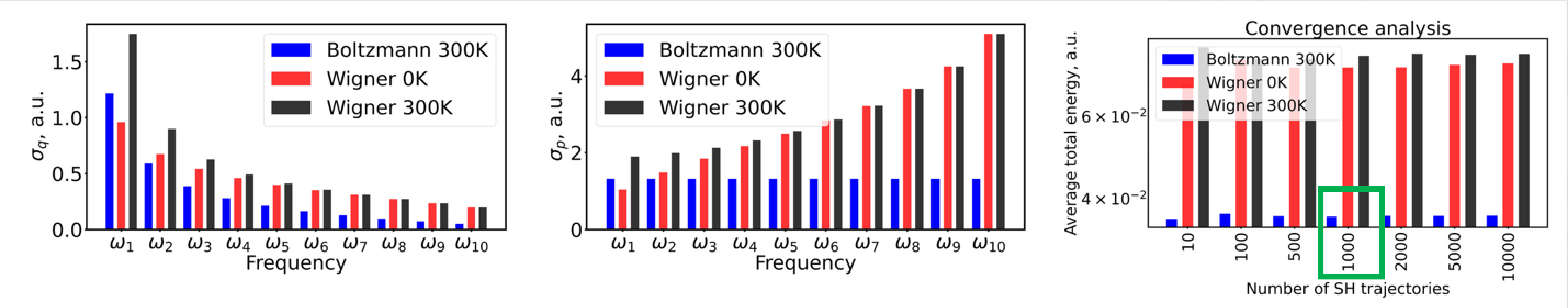
Model and Calculations Setup

Model

Initialization

Spin-Boson Hamiltonian

1- Wigner, 0 K limit 2- Boltzmann, 300 K



- For both sampling methods, the average total energies of the SH trajectories are $\sim E_{ZPE} \pm 0.02$ a.u.
- The Boltzmann distribution is valid when $k_B T \gg \hbar\omega_i$, this condition is satisfied only for the ω_1

Shakiba *et al. J. Chem. Phys.* 164, 104110 (2026)

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization

Granucci et al. J. Chem. Phys. 114, 10608-10615 (2001)
Plasser et al. J. Chem. Phys. 137, 22A514 (2012)
Shakiba *et al. Theoretical Chem. Acc.* 142, 68 (2023)

Model and Calculations Setup

Model — Spin-Boson Hamiltonian

Initialization — 1- Wigner, 0 K limit 2- Boltzmann, 300 K

Electronic Propagation — Local Diabatization

Hop Proposal — 1- FSSH 2- FSSH-2 3- GFSH

$$g_{i\to j}^{FSSH}(t, t+\Delta t) = \max\left(0, \frac{2Re\left(c_i^*(t)c_j(t)d_{ij}(t)\right)}{|c_i(t)|^2}\Delta t\right)$$

$$g_{i\to j}^{FSSH-2}(t, t+\Delta t) = \min\left(\sigma\left(-\frac{\rho_{ii}(t+\Delta t)-\rho_{ii}(t)}{\rho_{ii}(t)}\right), \sigma\left(\frac{\rho_{jj}(t+\Delta t)-\rho_{jj}(t)}{\rho_{ii}(t)}\right)\right)$$

$$g_{i\to j}^{GFSH}(t, t+\Delta t) = \frac{\rho_{ii}(t+\Delta t)-\rho_{ii}(t)}{\sum_{k\in A}\left(\rho_{kk}(t+\Delta t)-\rho_{kk}(t)\right)} \times \frac{\rho_{jj}(t+\Delta t)-\rho_{jj}(t)}{\rho_{ii}(t)}, i\in A, j\in B$$

Tully *J. Phys. Chem. 93, 1061-1071* (1990)
Araujo et al. J. Chem. Theory and Comput. 20, 3413-3419, (2024)
Wang et al. J. Chem. Theory and Comput. 10, 3598-3605 (2014)

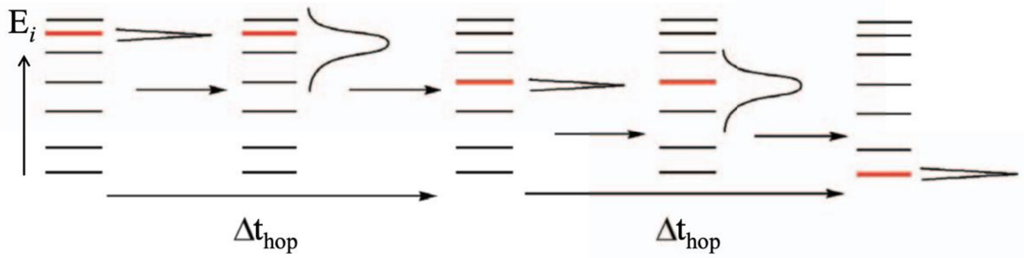
Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH 2- FSSH-2 3- GFSH
Decoherence Correction	1- Instantaneous Decoherence at Attempted Hops (ID-A)

- Instantaneous collapse of the wave function at every attempted hop

$\tilde{c}_i = 0, \forall i \neq a$

$\tilde{c}_a = \frac{c_a}{|c_a|}$



Nelson et al. J. Chem. Phys. 138, 224111 (2013)

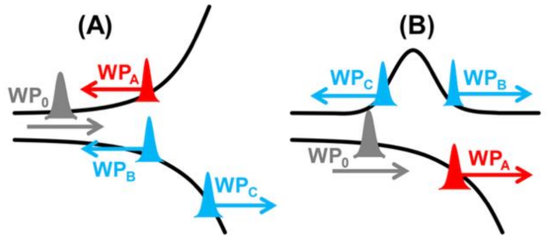
Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH 2- FSSH-2 3- GFSH
Decoherence Correction	1- ID-A 2- Branching Corrected Surface Hopping (BCSH)

- Collapse onto the active surface if wave packet reflection detected on that surface:

$$\tilde{c}_a = \frac{c_a}{|c_a|}$$

- Project out the nonactive surface if wave packet reflection is detected on that state and renormalize other states



Xu and Wang, J. Chem. Phys. 150, 164101 (2019)

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH 2- FSSH-2 3- GFSH
Decoherence Correction	1- ID-A 2- BCSH 3- Simplified Decay of Mixing (SDM)

- Gradual damping of the nonactive states amplitudes
- Renormalization of the active state amplitude

$$\tilde{c_i} = c_i \exp\left(-\frac{\Delta t}{\tau_{ij}}\right), \forall i \neq a$$

$$\tilde{c_a} = c_a \sqrt{\frac{1-\sum_{i\neq a}|\tilde{c_i}|^2}{|c_a|^2}}$$

Granucci & Persico, J. Chem. Phys. 126, 134114 (2007)

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH 2- FSSH-2 3- GFSH
Decoherence Correction	1- ID-A 2- BCSH 3- SDM 4- Decoherence Induced Surface Hopping (DISH)

- Coherence time for each state:

$$\tau_i^{-1} = \sum_{k \neq i} \rho_{kk}(t)\, \tau_{ik}^{-1}$$

- Counts the time since the last decoherence event for that state
- DISH checks which states have evolved coherently more than the coherence time
- Collapses on that state with the probability of $|c_i|^2$, projecting it out with the probability of $1 - |c_i|^2$

Jaeger et al. J. Chem. Phys. 137, 22A545 (2012)
Akimov J. Chem. Phys. 155, 134106 (2021)

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH 2- FSSH-2 3- GFSH
Decoherence Correction	1- ID-A 2- BCSH 3- SDM 4- DISH 5- Surface Hopping with Exact Factorization (SHXF)

$$(H_{XF})_{ab} = \sum_{\nu} \rho_{ab} \frac{\mathcal{P}_\nu}{M_\nu} (\phi_{\nu,a} - \phi_{\nu,b})$$

$$\boldsymbol{\mathcal{P}}(\boldsymbol{R}, t) = -i\hbar \frac{\nabla_{\boldsymbol{R}} |\chi(\boldsymbol{R},t)|^2}{2|\chi(\boldsymbol{R},t)|^2} \approx \frac{i\hbar}{2} \boldsymbol{\sigma}^{-2} \sum_i \rho_{ii} (\boldsymbol{R}_a - \boldsymbol{R}_i)$$

$$\phi_{\nu,i}(t + \Delta t) = \phi_{\nu,i}(t) + P_{\nu,i}(t + \Delta t) - P_{\nu,i}(t)$$

Filatov et al. J. Chem. Theory and Comput. 14, 4499-4512 (2018)
Vindel-Zandbergen et al. J. Chem. Theory and Comput. 17, 3852-3862 (2021)
Han & Akimov J. Chem. Theory and Comput. 20, 5022-5042 (2024)

When trajectories are in a coherent superposition, determined by a numerical threshold for the electronic amplitude, auxiliary trajectories are spawned on nonactive-state potential energy surfaces to mimic wave packet branching.

The width parameter $\boldsymbol{\sigma}$ is usually obtained from the initial distribution of the nuclear trajectories.

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH 2- FSSH-2 3- GFSH
Decoherence Correction	1- ID-A 2- BCSH 3- SDM 4- DISH 5- Surface Hopping with Exact Factorization (SHXF)

- The width of the auxiliary wave packet is used as a meta-parameter controlling decoherence times
  - Larger values: longer decoherence time
  - Smaller values: shorter decoherence time

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH 2- FSSH-2 3- GFSH
Decoherence Correction	1- ID-A 2- BCSH 3- SDM 4- DISH 5- SHXF
Decoherence Time	1- Energy-based Decoherence (EDC)

$$\tau_{ij}^{-1} = \frac{|H_{ii} - H_{jj}|}{\hbar} \times \left(\frac{E_{kin}}{E_{kin} + \epsilon} \right)$$

ϵ: an empirical parameter (default: 0.1 Ha)

- ϵ value is used as a meta-parameter:
- Higher kinetic energy: faster decoherence
- Smaller ϵ value: faster decoherence
- Larger ϵ value: slower decoherence

Zhu et al. J. Chem. Phys. 120, 5543-5557 (2004)

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit · 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH · 2- FSSH-2 · 3- GFSH
Decoherence Correction	1- ID-A · 2- BCSH · 3- SDM · 4- DISH · 5- SHXF
Decoherence Time	1- EDC · 2- Schwartz 1 · 3- Schwartz 2

$$\tau_i^{-2} = \sum_k \frac{\left(F_k - F_{k,i}\right)^2}{4\hbar^2 A_k}$$

$$\tau_{ij}^{-2}(t) = \sum_k \frac{\left(F_{k,i} - F_{k,j}\right)^2}{4\hbar^2 A_k}$$

- In limit of large A_k: never lose their overlap and remain persistently coherent
- In limit of small A_k : fast decoherence

Bittner & Rossky J. Chem. Phys. 103, 8130-8143 (1995)
Esch & Levine J. Chem. Phys. 152, 234105 (2020)

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit; 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH; 2- FSSH-2; 3- GFSH
Decoherence Correction	1- ID-A; 2- BCSH; 3- SDM; 4- DISH; 5- SHXF
Decoherence Time	1- EDC; 2- Schwartz 1; 3- Schwartz 2; 4- Gu-Franco

$$\tau_{ij} = |c_i|^{-1}|c_j|^{-1}\frac{\hbar}{\sqrt{4E_r k_B T}}$$

- Current SB model E_r, gives a minimum of 7 fs decoherence time: fluctuates over time
- Longer decoherence time at the beginning and end of the dynamics
- Shorter decoherence time with higher E_r

Gu & Franco J. Phys. Chem. Lett. 8, 4289-4294 (2017)

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH 2- FSSH-2 3- GFSH
Decoherence Correction	1- ID-A 2- BCSH 3- SDM 4- DISH 5- SHXF
Decoherence Time	1- EDC 2- Schwartz 1 3- Schwartz 2 4- Gu-Franco
Phase Correction	Shenvi-Subotnik-Yang (SSY) phase correction

$$H_{aj}(t) = \begin{pmatrix} -p_a^T(t)M^{-1}p_a(t) & -i\hbar p_a^T(t)M^{-1}d_{aj}(t) \\ i\hbar p_a(t)M^{-1}d_{aj}(t) & -p_a^T(t)M^{-1}p_j(t) \end{pmatrix}$$

- Accounts for the relative phase differences by replacing the original electronic Hamiltonian by an effective Hamiltonian
- The collinearity assumption of the active and auxiliary momentum
- The wave packets evolve independently with time

Shenvi, Subotnik, Yang J. Chem. Phys. 135, 024101 (2011)

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit; 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH; 2- FSSH-2; 3- GFSH
Decoherence Correction	1- ID-A; 2- BCSH; 3- SDM; 4- DISH; 5- SHXF
Decoherence Time	1- EDC; 2- Schwartz 1; 3- Schwartz 2; 4- Gu-Franco
Phase Correction	SSY correction

Libra Code

Wigner
Boltzmann
✖
FSSH
FSSH-2
GFSH
✖
No decoherence correction,
BCSH, SHXF, IDA, SDM-Schw2,
SDM-EDC, SDM-GF, DISH-Schw1,
DISH-Schw2, DISH-EDC, DISH-GF
✖
No SSY
With SSY
=
132 Recipes

Akimov J. Comput. Chem. 37, 1626-1649 (2016)
Shakiba et al. Software Impacts 14, 100445 (2022)

Model and Calculations Setup

Model	Spin-Boson Hamiltonian
Initialization	1- Wigner, 0 K limit; 2- Boltzmann, 300 K
Electronic Propagation	Local Diabatization
Hop Proposal	1- FSSH; 2- FSSH-2; 3- GFSH
Decoherence Correction	1- ID-A; 2- BCSH; 3- SDM; 4- DISH; 5- SHXF
Decoherence Time	1- EDC; 2- Schwartz 1; 3- Schwartz 2; 4- Gu-Franco
Phase Correction	SSY correction

Libra Code

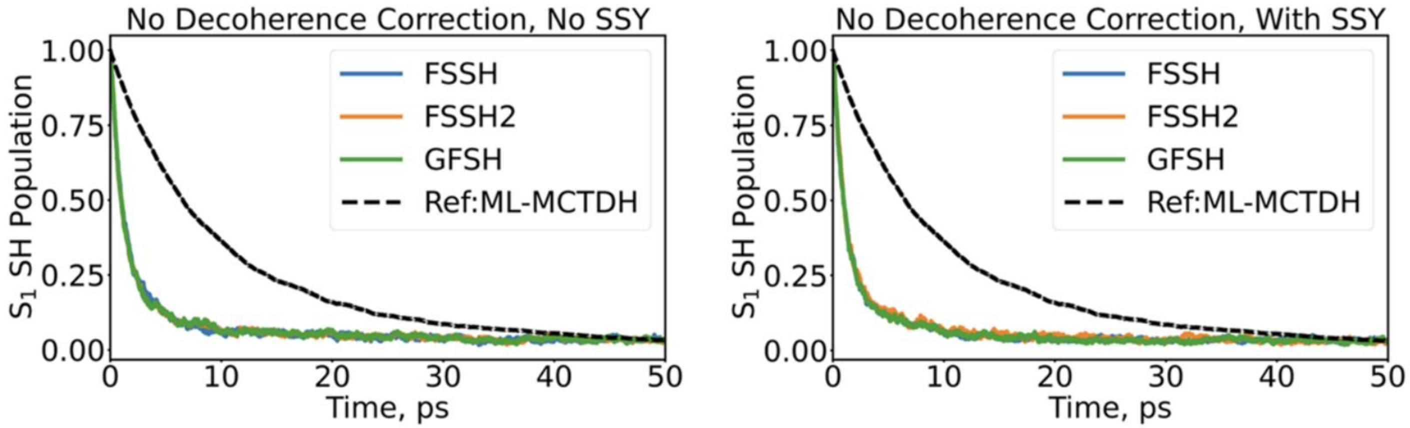
Accuracy is defined with a population-based error metric:

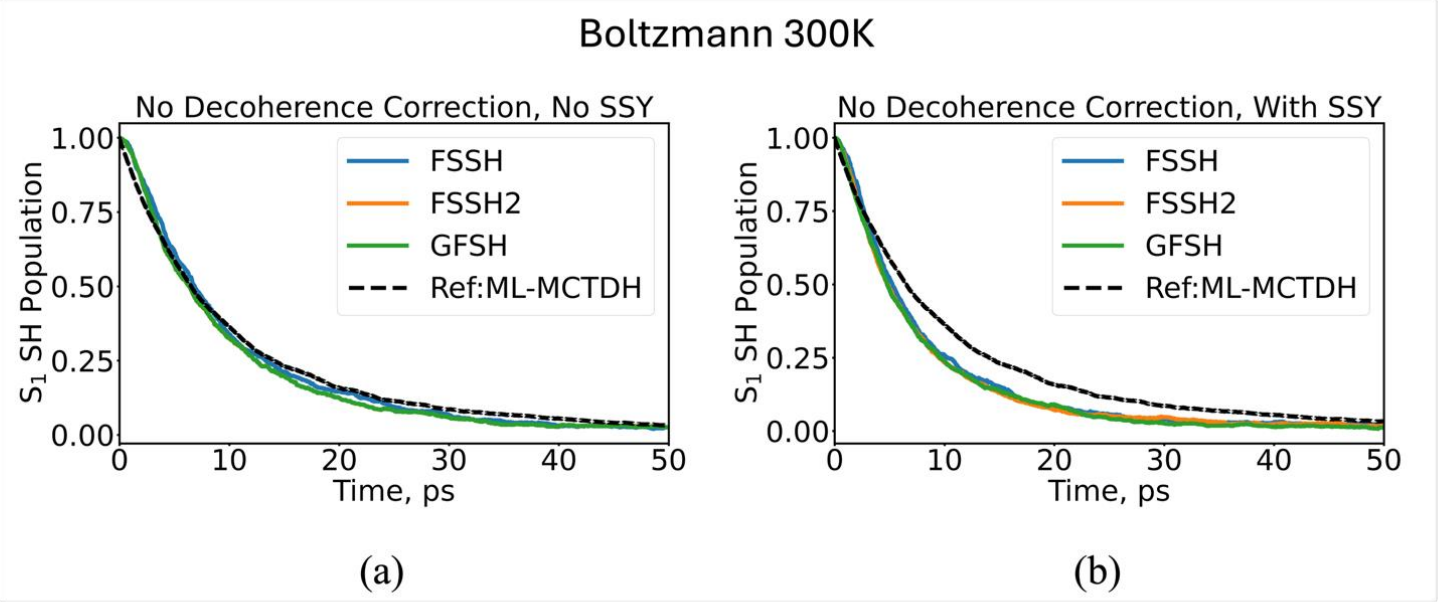
$$\epsilon_{\text{pop}} = \sqrt{\frac{1}{N\times N_{step}} \sum_{i=0}^{N-1} \sum_{n=0}^{N_{steps}-1} \left(P_{TSH}(t_n) - P_{Exact}(t_n)\right)^2}$$

Akimov J. Comput. Chem. 37, 1626-1649 (2016)
Shakiba et al. Software Impacts 14, 100445 (2022)

Hop Proposal and Initial Conditions

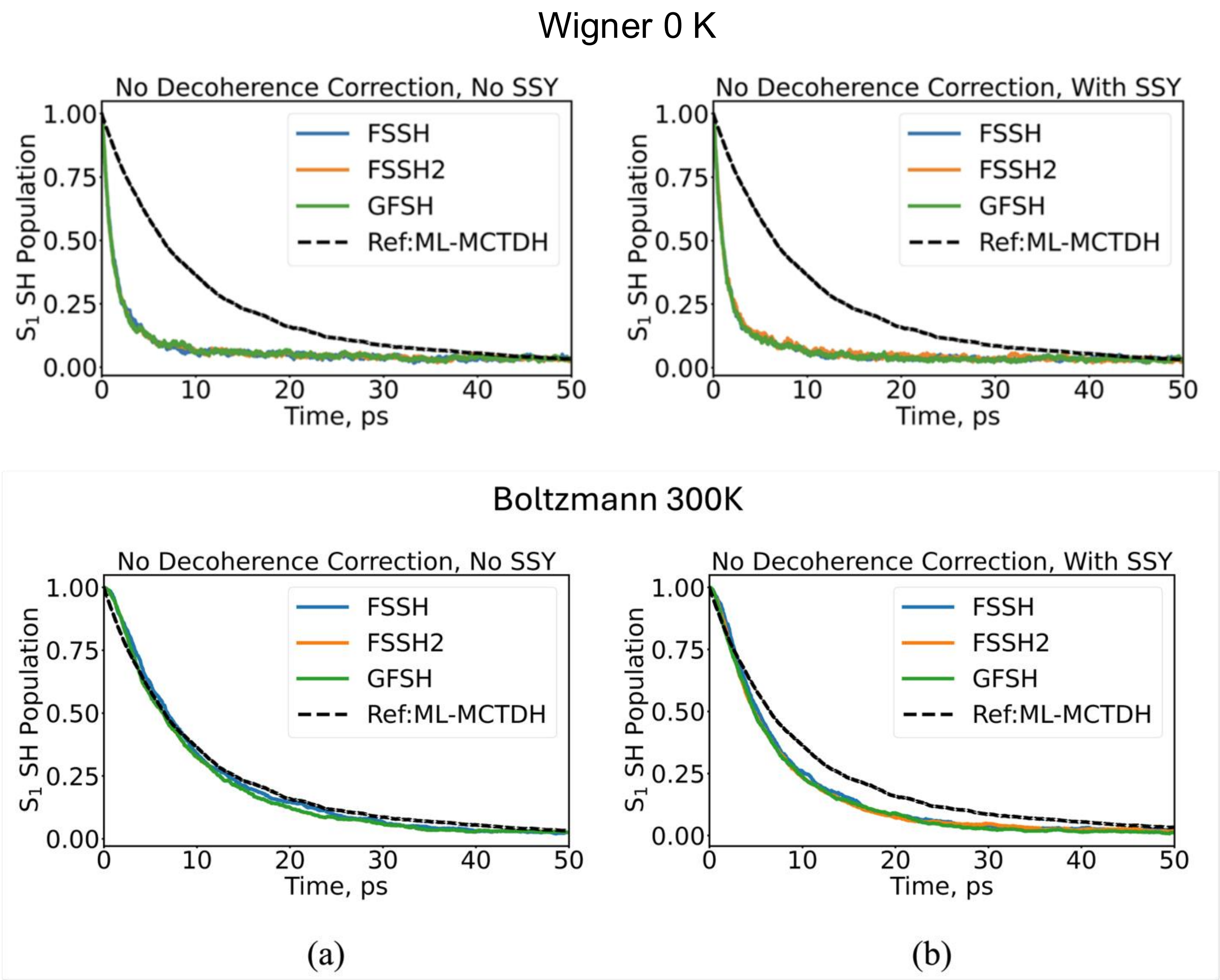
Wigner 0 K





- Base TSH methods yield almost similar dynamics: expected in two-state model

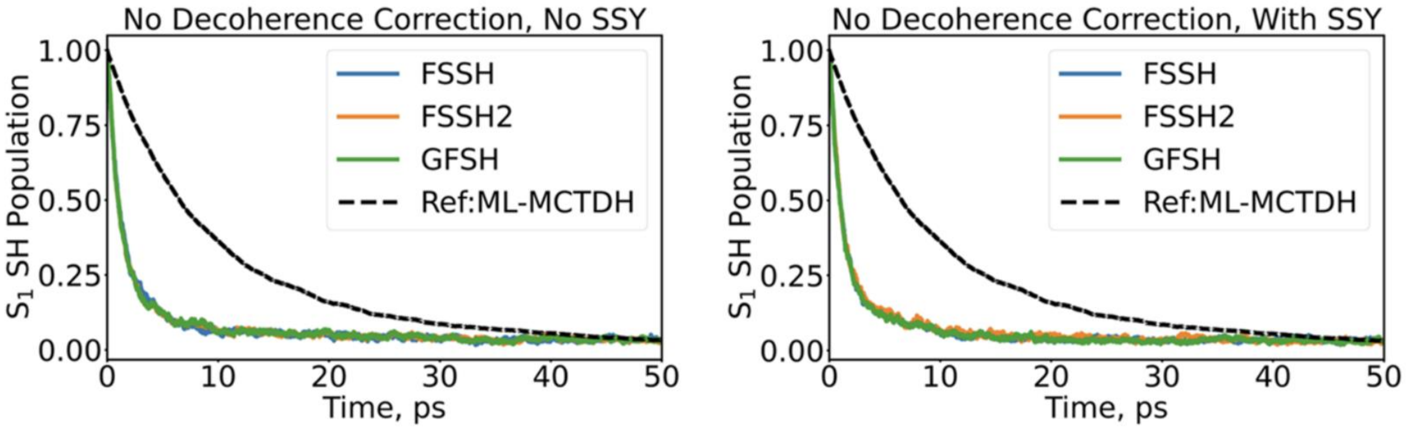
Hop Proposal and Initial Conditions



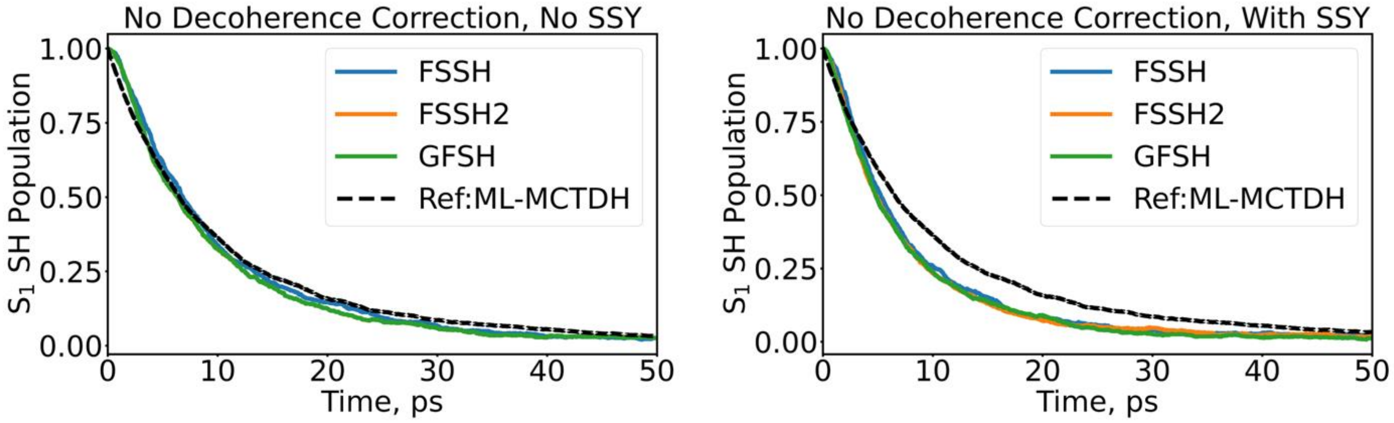
- Base TSH methods yield almost similar dynamics: expected in two-state model
- Wigner sampling gives faster dynamics because of higher energy
- Wigner trajectories explore larger configurational regions
- Boltzmann trajectories less often reach strong nonadiabatic-coupling regions, so dynamics is slower
- Boltzmann without decoherence matches exact results likely by error cancellation

SSY Phase Correction

Wigner 0 K



Boltzmann 300K

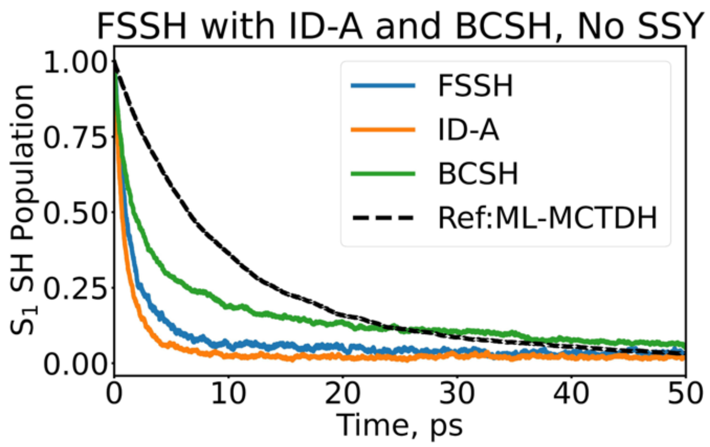


(a) (b)

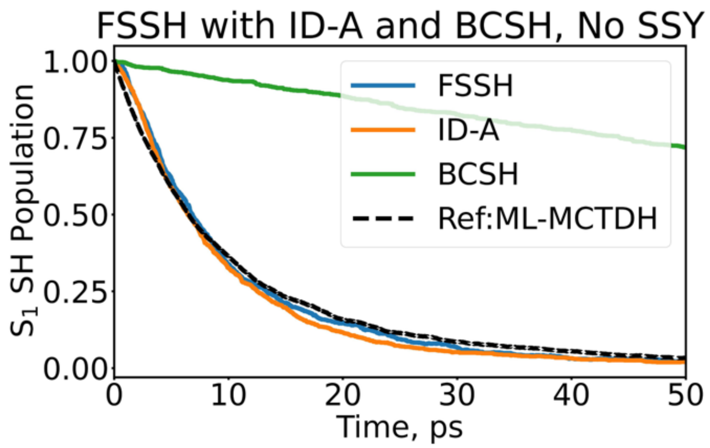
- SSY makes the dynamics faster
- Momentum collinearity assumption in multidimensional systems breaks down
- More apparent in the Boltzmann sampling case

Nonparametric Decoherence Correction

Wigner 0 K



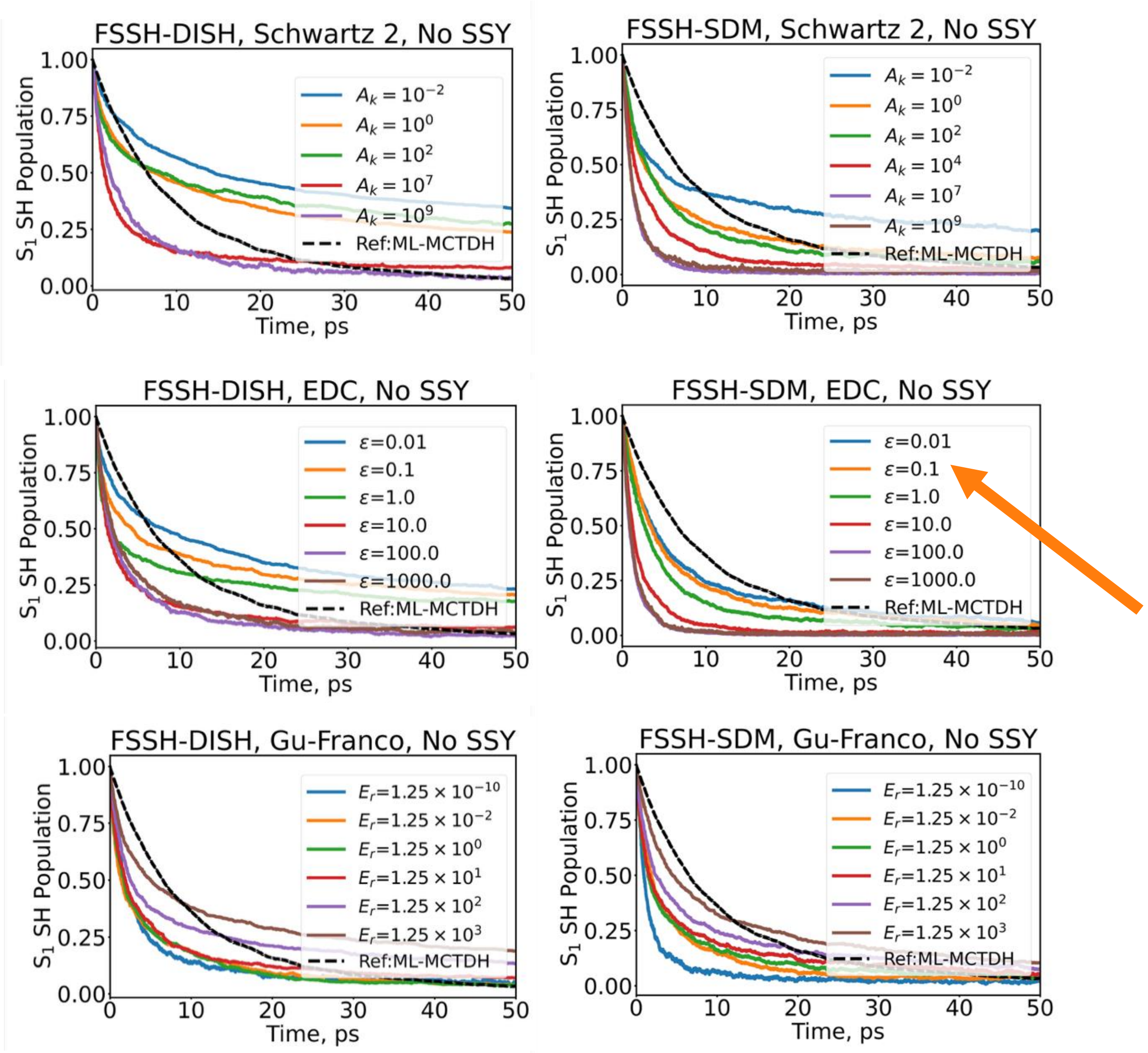
Boltzmann 300 K



- ID-A:
  - Similar to FSSH
  - Starts in higher energy state
  - Almost all attempted hops are accepted
  - ID collapses coincide with state transitions and amplitude updates
- BCSH:
  - Slows the dynamics via frequent active-state collapse at turning points
  - Reflections can be triggered by nuclear DOFs not coupled to the transition
  - This can cause unnecessarily frequent wavefunction collapses

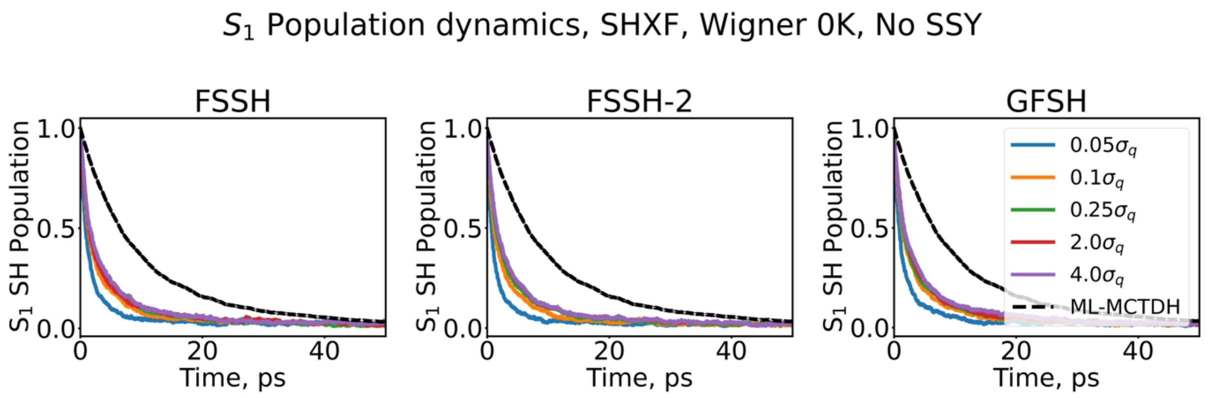
SDM vs DISH

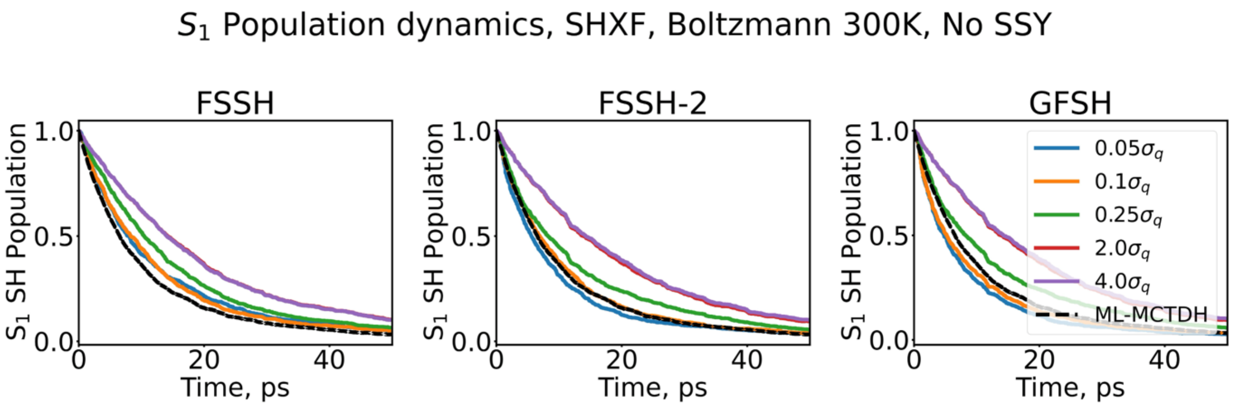
Wigner 0 K



- Large decoherence times recover the base TSH results
- Ultrashort decoherence times slow the dynamics: quantum Zeno effect
- DISH gives slower dynamics because decoherence happens only after the coherence interval
- In SDM, amplitudes are gradually damped over time
- EDC + SDM is qualitatively closer to reference than EDC + DISH with the default value of $\epsilon = 0.1$ Ha

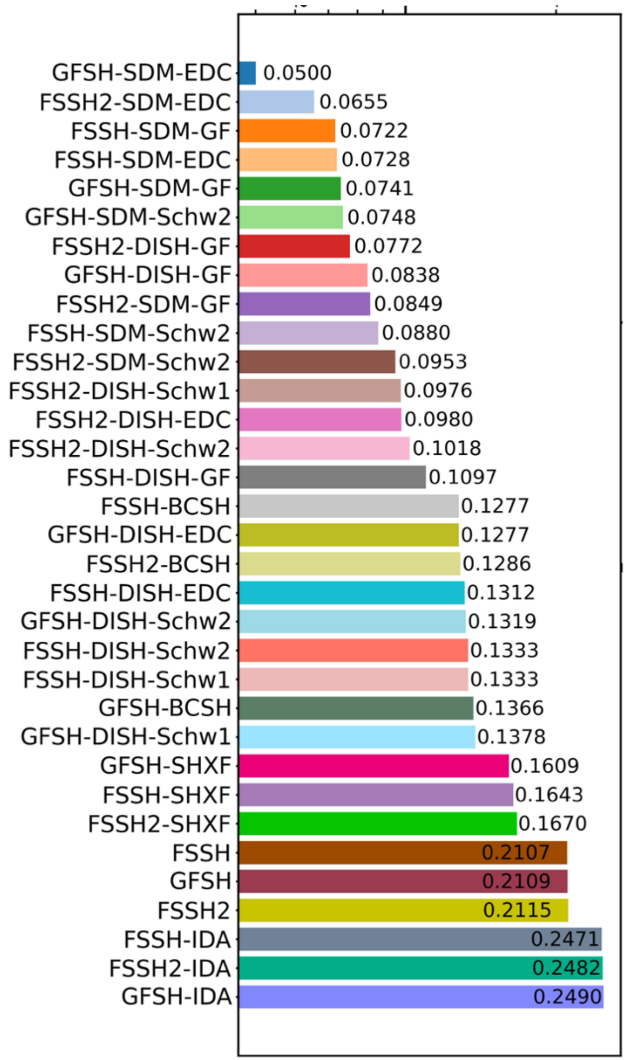
SHXF

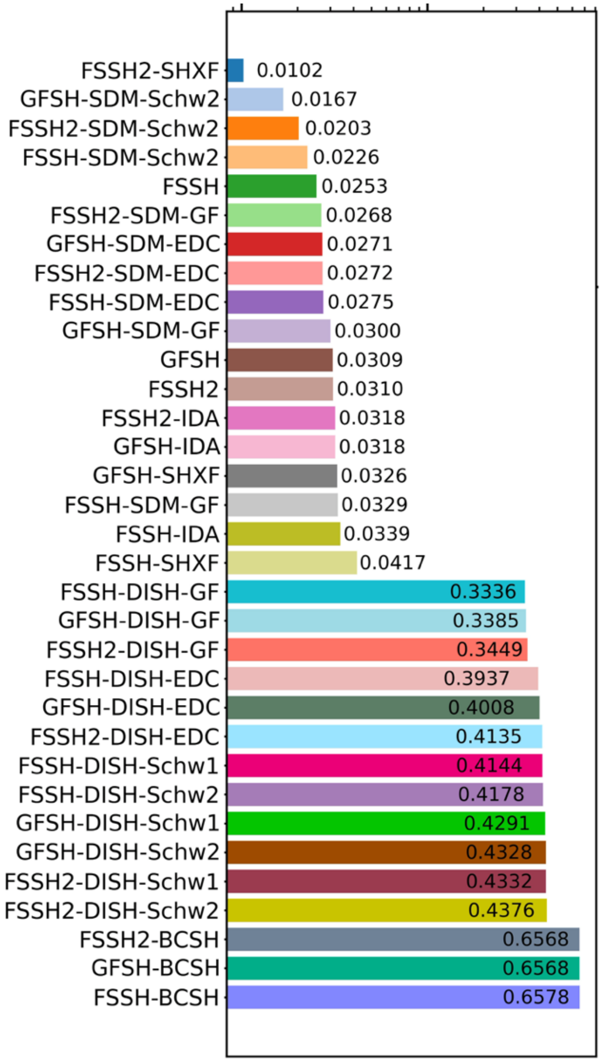




- Contrary to expectation, decreasing σ accelerates population relaxation
- This is consistent with a quantum anti-Zeno effect: faster decoherence can enhance population transfer by promoting quantum chaotic behavior and state delocalization
- The effect may stem from the nonlinear dependence of H_{XF} on the reduced density matrix ρ
- The effect is more pronounced with Boltzmann sampling

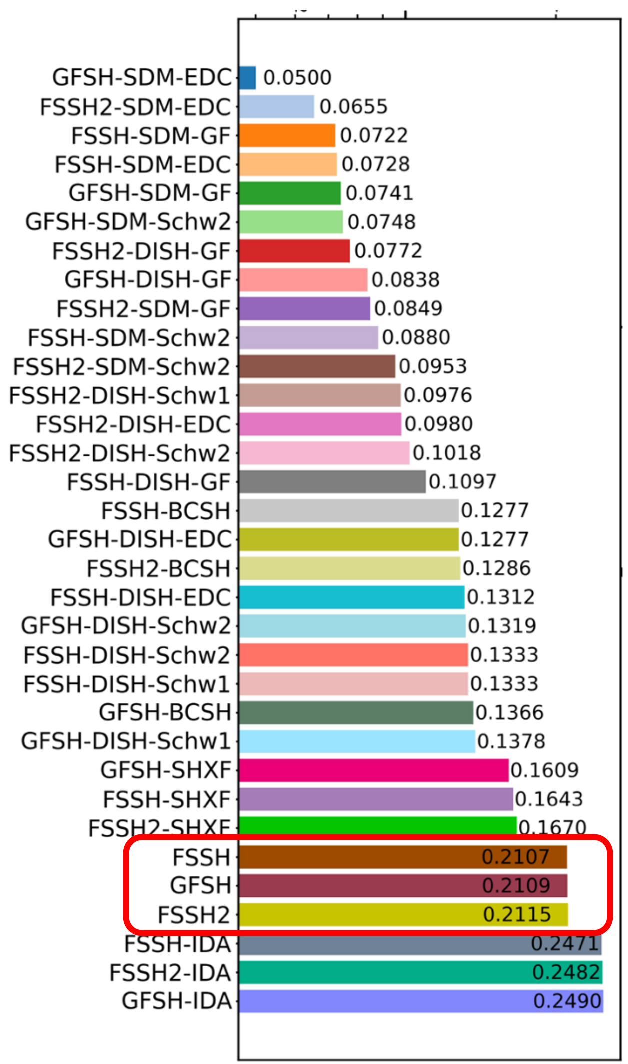
Comparison of MQC methods



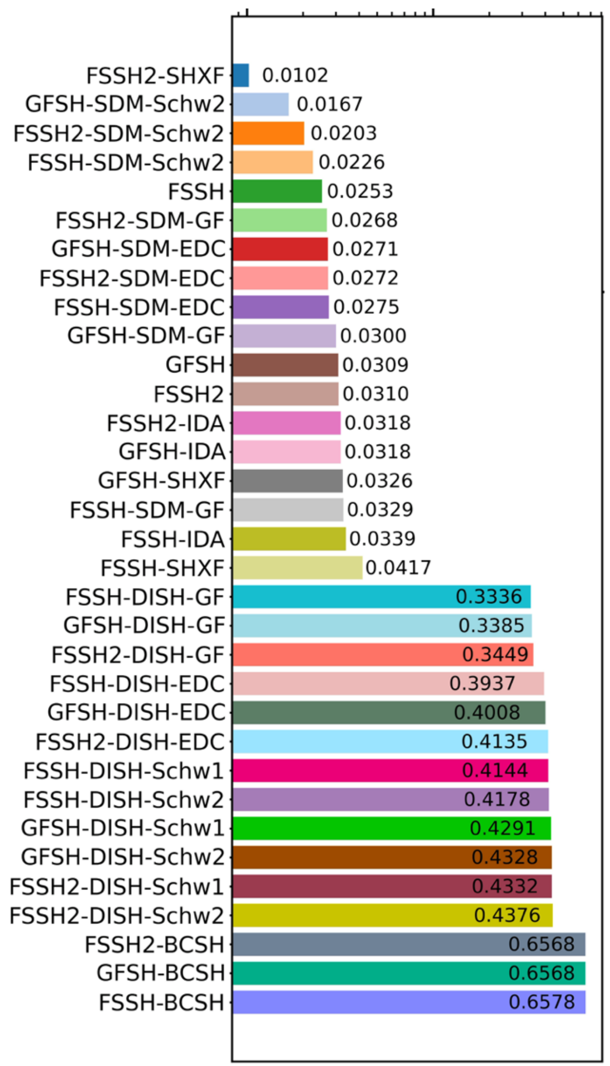


Comparison of MQC methods (Wigner)

Wigner 0 K



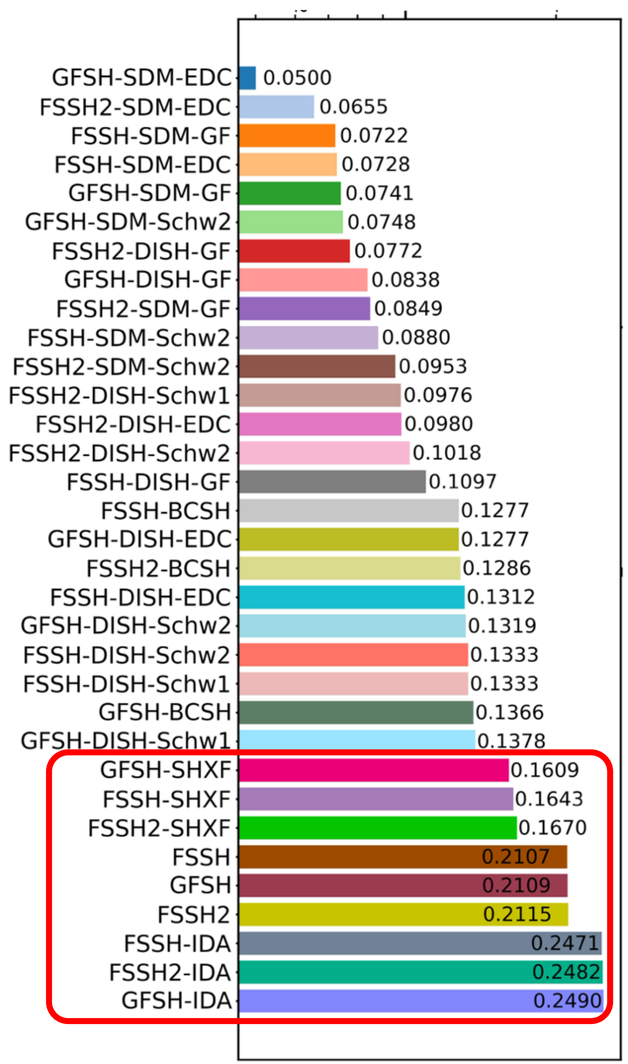
Boltzmann 300 K



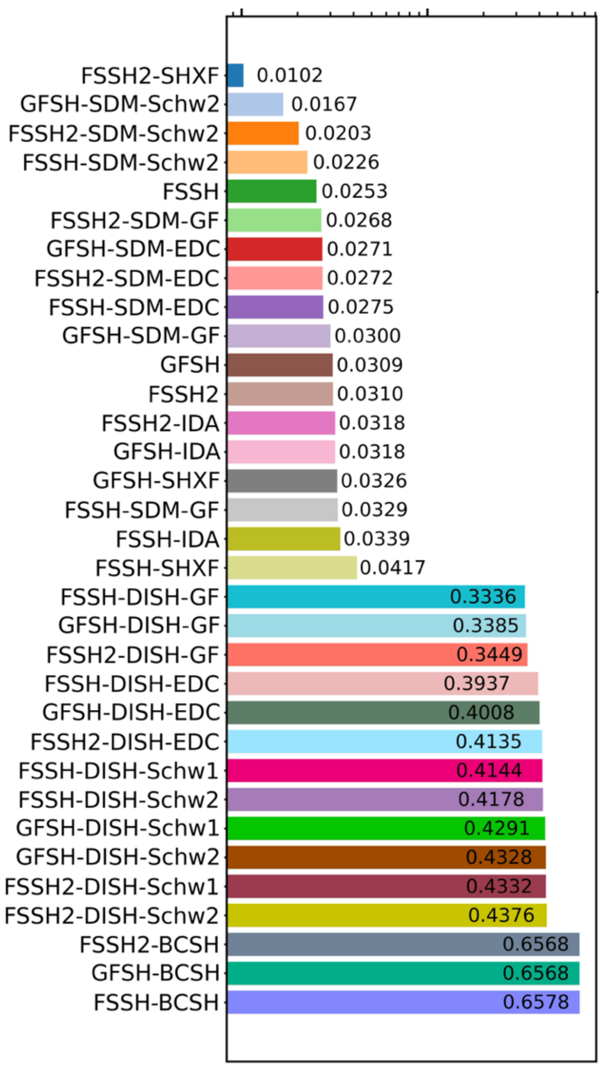
- Bare TSH schemes (FSSH, FSSH2, GFSH) show similarly high error metrics
- Errors are on the order of 0.21
- This is due to overly rapid population relaxation

Comparison of MQC methods (Wigner)

Wigner 0 K



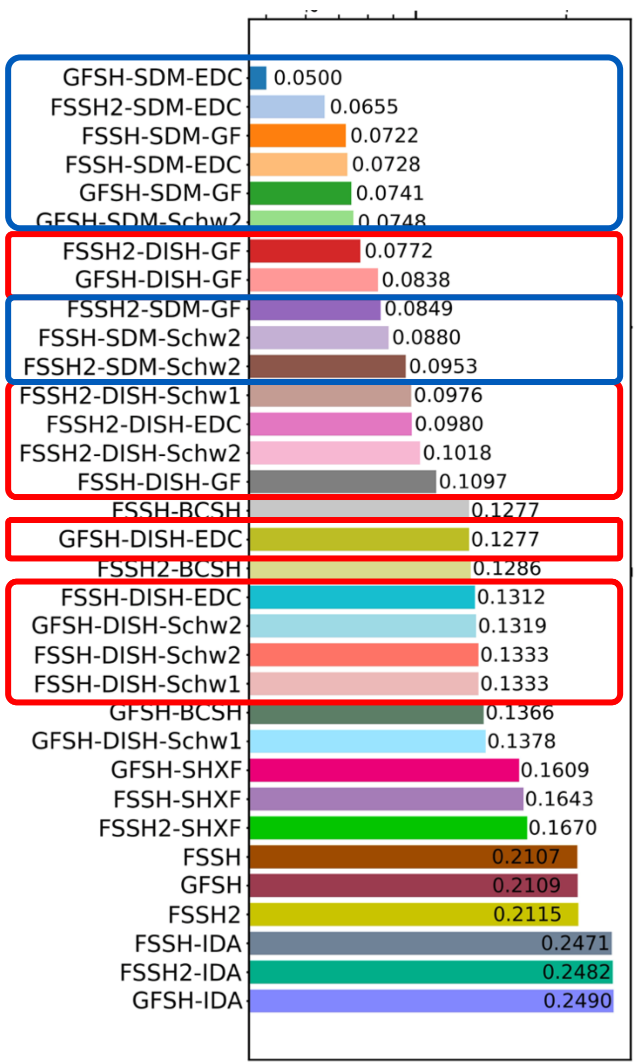
Boltzmann 300 K



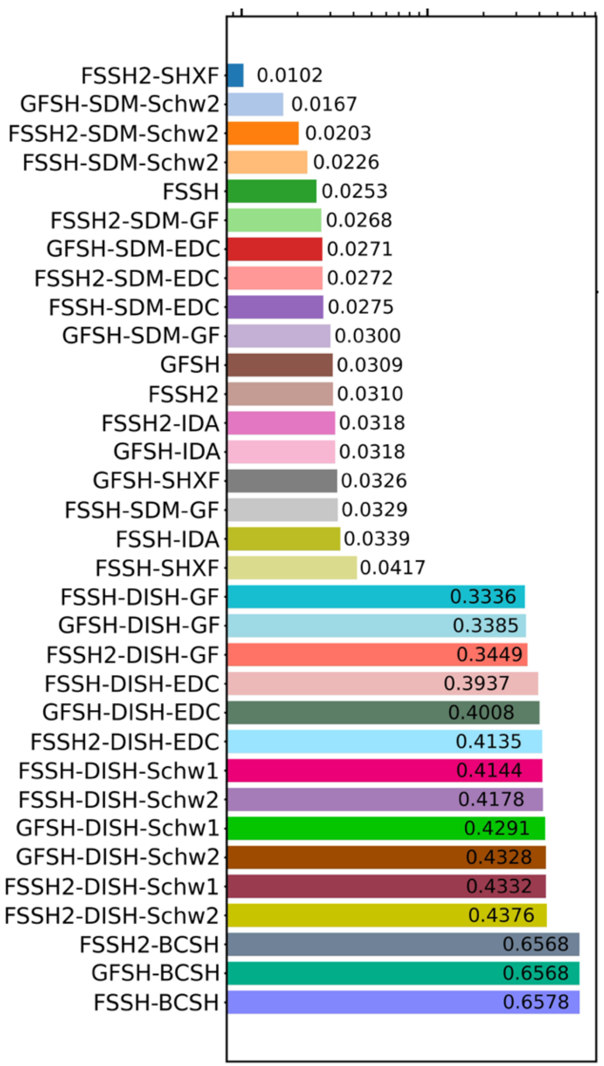
- Bare TSH schemes (FSSH, FSSH2, GFSH) show similarly high error metrics
- Errors are on the order of 0.21
- This is due to overly rapid population relaxation
- ID-A slightly worsens the results to about 0.25
- SHXF reduces the error to about 0.16–0.17

Comparison of MQC methods (Wigner)

Wigner 0 K



Boltzmann 300 K



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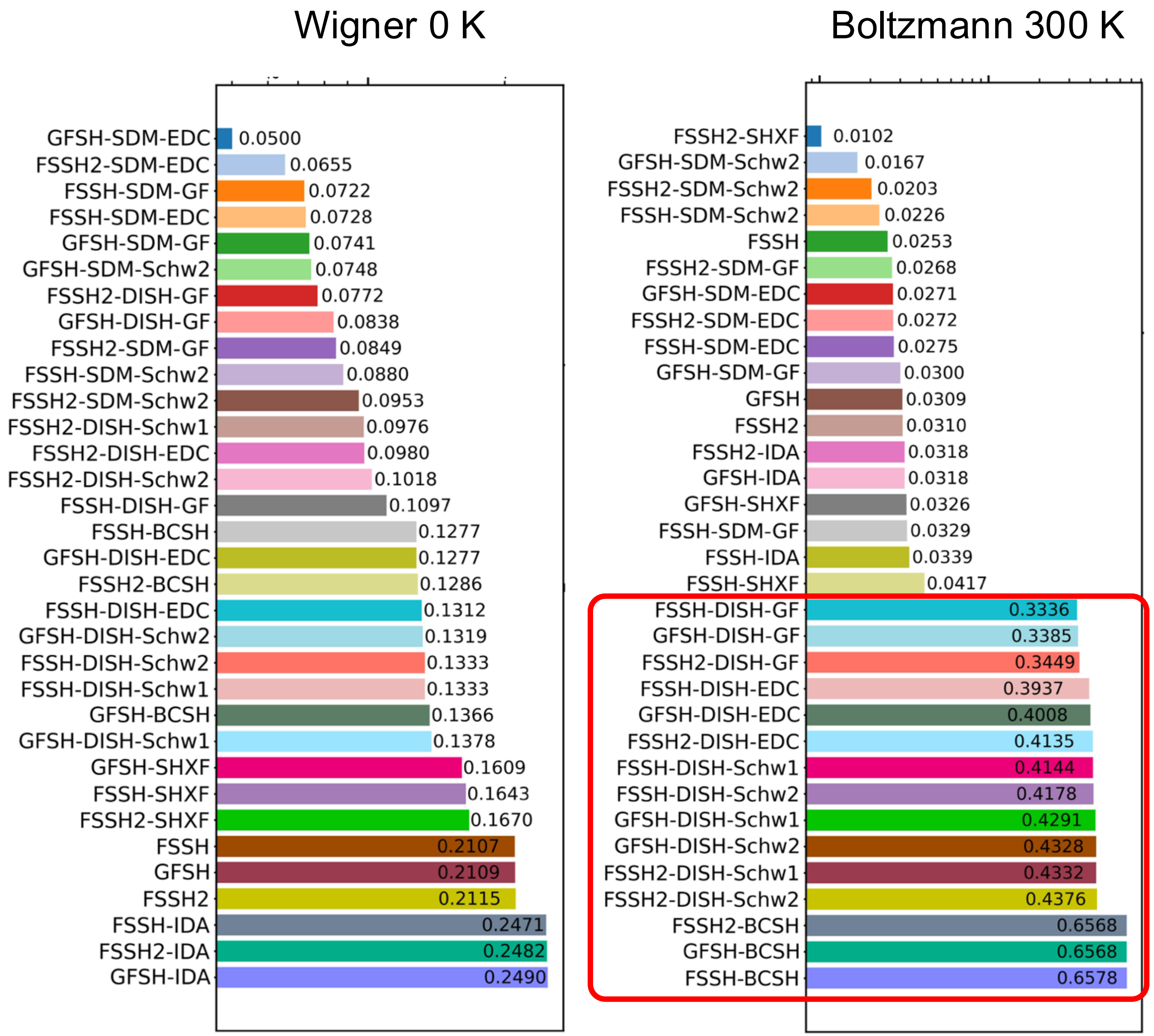
- Errors are on the order of 0.21
- This is due to overly rapid population relaxation
- ID-A slightly worsens the results to about 0.25
- SHXF reduces the error to about 0.16–0.17
- SDM and DISH both improve the dynamics
- The error varies smoothly across methods, roughly from 0.05 to 0.14

Comparison of MQC methods (Boltzmann)



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Comparison of MQC methods (Boltzmann)

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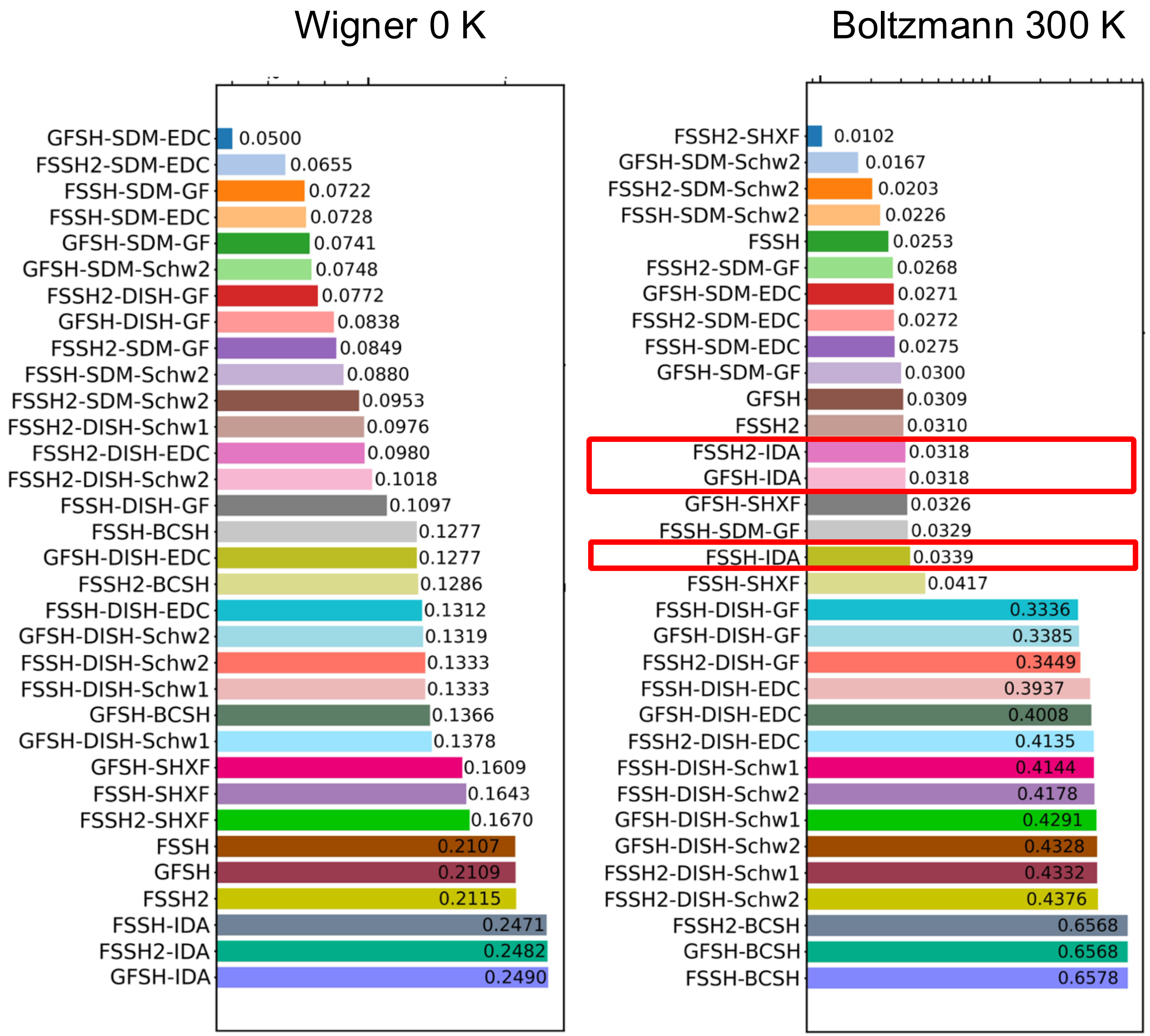
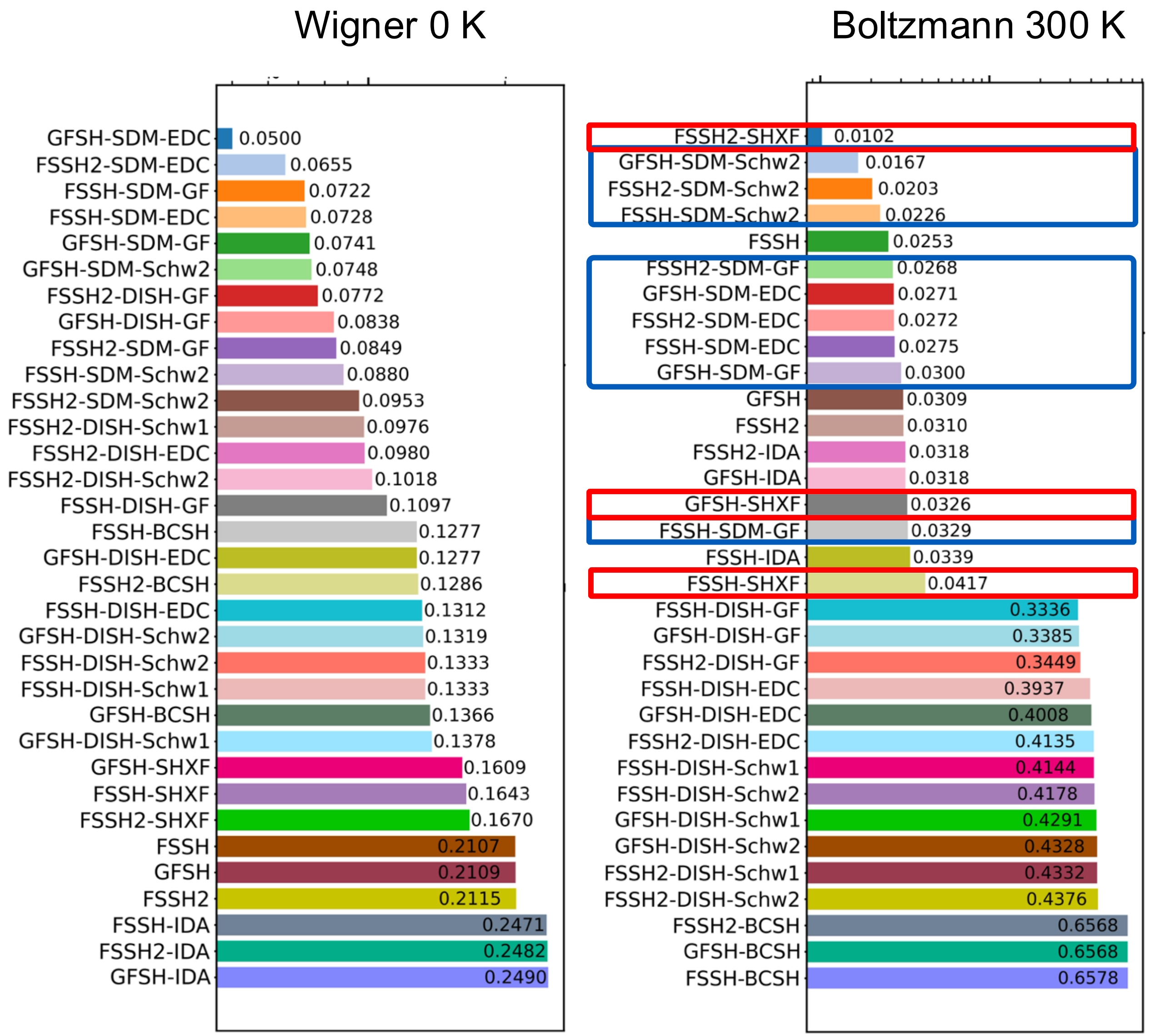


- DISH and BCSH yield the slowest relaxation dynamics and the highest errors
- All other methods show nearly an order-of-magnitude smaller errors, outperforming all methods with Wigner sampling
- The base TSH methods lie in the middle, with error scores around 0.025-0.031
- ID-A gives slightly worse results in both Wigner and Boltzmann sampling

Comparison of MQC methods (Boltzmann)



- SDM overall performs better than other decoherence-corrected methods
- Its best performance often appears in asymptotic regimes, where very large or very small meta-parameters give long decoherence times

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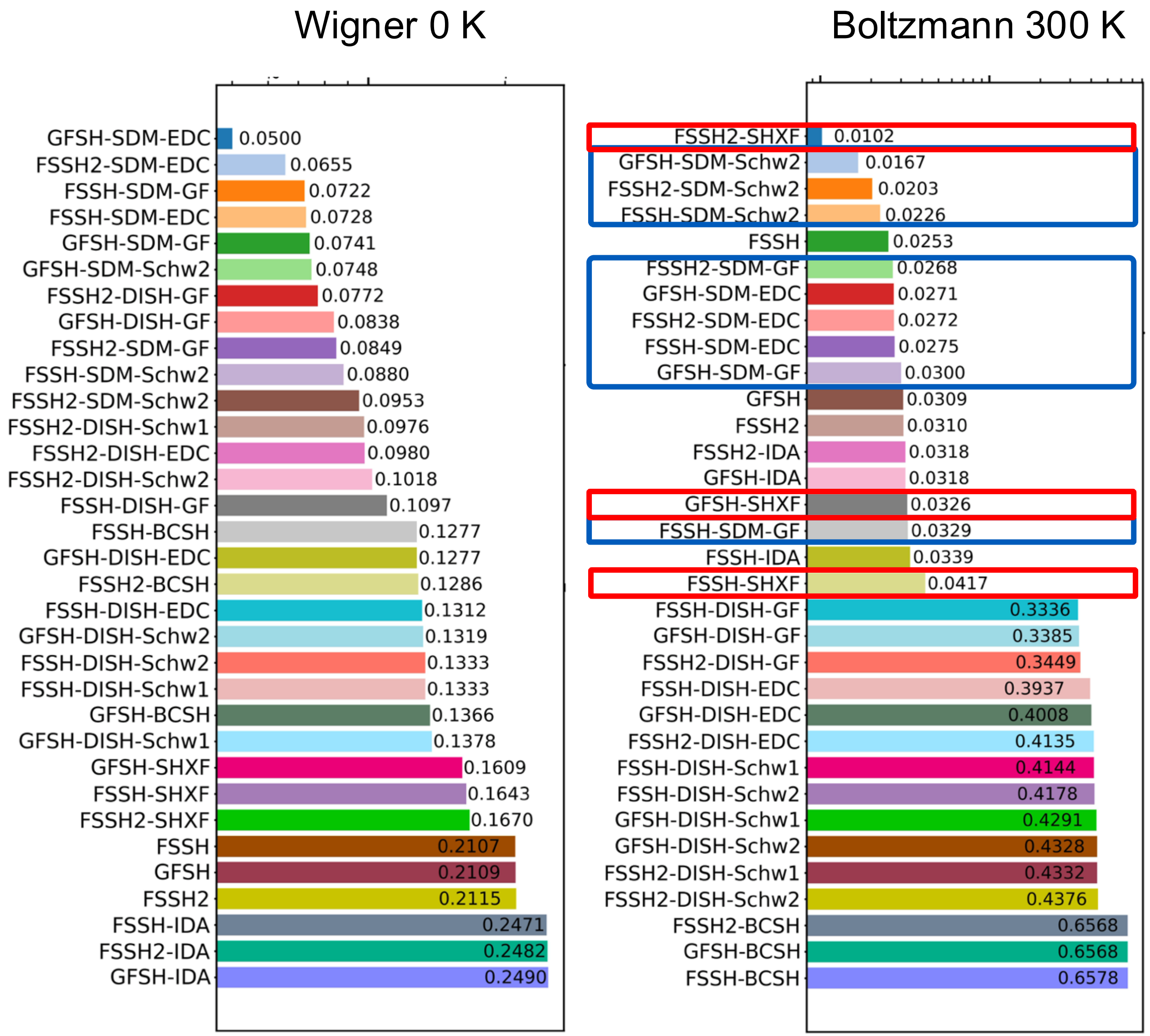

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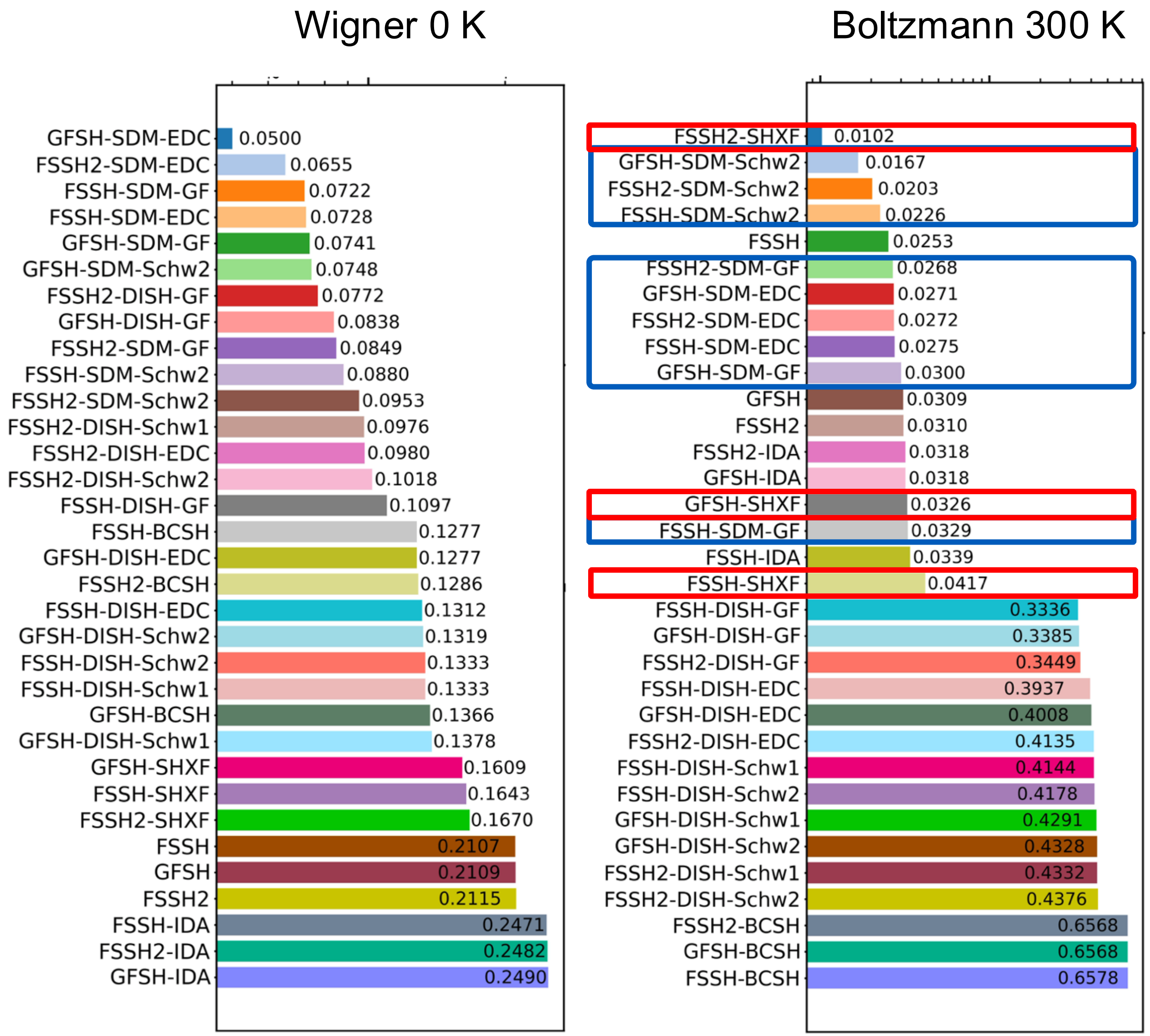

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- Its best performance often appears in asymptotic regimes, where very large or very small meta-parameters give long decoherence times
- In that limit, SDM effectively coincides with bare TSH, so the agreement is likely due to error cancellation
- For SHXF, better performance can arise at shorter decoherence times, consistent with an anti-Zeno effect

Comparison of MQC methods

Table S1. Selected meta-parameter values yielding the smallest error for each MQC method using Wigner sampling at 0K.
For SHXF, the auxiliary wave packet width is shown as the multiple of the σ_q, the width of the position distribution, in a.u.
A_k: Gaussian wave packet width parameter in Schwartz decoherence time methods, a.u.
E_r: Reorganization energy parameter for Gu-Franco decoherence time, a.u.
ϵ: The empirical energy parameter for EDC decoherence time, a.u.

MQC method	No SSY	With SSY
FSSH-DISH-Schw1	$A_k = 10^9$	$A_k = 10^9$
FSSH2-DISH-Schw1	$A_k = 1.0$	$A_k = 10.0$
GFSH-DISH-Schw1	$A_k = 10^9$	$A_k = 10^9$
FSSH-DISH-Schw2	$A_k = 10^9$	$A_k = 10^9$
FSSH2-DISH-Schw2	$A_k = 1.0$	$A_k = 1.0$
GFSH-DISH-Schw2	$A_k = 10^9$	$A_k = 10^9$
FSSH-SDM-Schw2	$A_k = 10.0$	$A = 10.0$
FSSH2-SDM-Schw2	$A_k = 10.0$	$A_k = 10.0$
GFSH-SDM-Schw2	$A_k = 100.0$	$A_k = 100.0$
FSSH-DISH-EDC	$\epsilon = 1000.0$	$\epsilon = 1000.0$
FSSH2-DISH-EDC	$\epsilon = 0.01$	$\epsilon = 0.01$
GFSH-DISH-EDC	$\epsilon = 1000.0$	$\epsilon = 1000.0$
FSSH-SDM-EDC	$\epsilon = 0.01$	$\epsilon = 0.01$
FSSH2-SDM-EDC	$\epsilon = 0.2$	$\epsilon = 0.05$
GFSH-SDM-EDC	$\epsilon = 0.2$	$\epsilon = 0.1$
FSSH-DISH-GF	$E_r = 125.0$	$E_r = 125.0$
FSSH2-DISH-GF	$E_r = 125.0$	$E_r = 125.0$
GFSH-DISH-GF	$E_r = 1250.0$	$E_r = 1250.0$
FSSH-SDM-GF	$E_r = 1250.0$	$E_r = 1250.0$
FSSH2-SDM-GF	$E_r = 1.25$	$E_r = 12.5$
GFSH-SDM-GF	$E_r = 12.5$	$E_r = 12.5$
FSSH-SHXF	$4.0\sigma_q$	$4.0\sigma_q$
FSSH2-SHXF	$4.0\sigma_q$	$4.0\sigma_q$
GFSH-SHXF	$4.0\sigma_q$	$4.0\sigma_q$

- In some recipes, reasonable or default parameter values already give good performance, as in EDC + SDM
- In others, the best results appear only in asymptotic limits, requiring very large or very small meta-parameters
- With Wigner sampling, the optimal meta-parameters are generally more reasonable than with Boltzmann sampling, though some are still large and may seem unphysical

Comparison of MQC methods

Table S1. Selected meta-parameter values yielding the smallest error for each MQC method using Wigner sampling at 0K.
For SHXF, the auxiliary wave packet width is shown as the multiple of the σ_q, the width of the position distribution, in a.u.
A_k: Gaussian wave packet width parameter in Schwartz decoherence time methods, a.u.
E_r: Reorganization energy parameter for Gu-Franco decoherence time, a.u.
ϵ: The empirical energy parameter for EDC decoherence time, a.u.

MQC method	No SSY	With SSY
FSSH-DISH-Schw1	$A_k = 10^9$	$A_k = 10^9$
FSSH2-DISH-Schw1	$A_k = 1.0$	$A_k = 10.0$
GFSH-DISH-Schw1	$A_k = 10^9$	$A_k = 10^9$
FSSH-DISH-Schw2	$A_k = 10^9$	$A_k = 10^9$
FSSH2-DISH-Schw2	$A_k = 1.0$	$A_k = 1.0$
GFSH-DISH-Schw2	$A_k = 10^9$	$A_k = 10^9$
FSSH-SDM-Schw2	$A_k = 10.0$	$A = 10.0$
FSSH2-SDM-Schw2	$A_k = 10.0$	$A_k = 10.0$
GFSH-SDM-Schw2	$A_k = 100.0$	$A_k = 100.0$
FSSH-DISH-EDC	$\epsilon = 1000.0$	$\epsilon = 1000.0$
FSSH2-DISH-EDC	$\epsilon = 0.01$	$\epsilon = 0.01$
GFSH-DISH-EDC	$\epsilon = 1000.0$	$\epsilon = 1000.0$
FSSH-SDM-EDC	$\epsilon = 0.01$	$\epsilon = 0.01$
FSSH2-SDM-EDC	$\epsilon = 0.2$	$\epsilon = 0.05$
GFSH-SDM-EDC	$\epsilon = 0.2$	$\epsilon = 0.1$
FSSH-DISH-GF	$E_r = 125.0$	$E_r = 125.0$
FSSH2-DISH-GF	$E_r = 125.0$	$E_r = 125.0$
GFSH-DISH-GF	$E_r = 1250.0$	$E_r = 1250.0$
FSSH-SDM-GF	$E_r = 1250.0$	$E_r = 1250.0$
FSSH2-SDM-GF	$E_r = 1.25$	$E_r = 12.5$
GFSH-SDM-GF	$E_r = 12.5$	$E_r = 12.5$
FSSH-SHXF	$4.0\sigma_q$	$4.0\sigma_q$
FSSH2-SHXF	$4.0\sigma_q$	$4.0\sigma_q$
GFSH-SHXF	$4.0\sigma_q$	$4.0\sigma_q$

Table S2. Selected meta-parameter values yielding the smallest error for each MQC method using Boltzmann sampling at 300K.
For SHXF, the auxiliary wave packet width is shown as the multiple of the σ_q, the width of the position distribution, in a.u.
A_k: Gaussian wave packet width parameter in Schwartz decoherence time methods, a.u.
E_r: Reorganization energy parameter for Gu-Franco decoherence time, a.u.
ϵ: The empirical energy parameter for EDC decoherence time, a.u.

MQC method	No SSY	With SSY
FSSH-DISH-Schw1	$A_k = 10^9$	$A_k = 10^9$
FSSH2-DISH-Schw1	$A_k = 10^9$	$A_k = 10^9$
GFSH-DISH-Schw1	$A_k = 10^9$	$A_k = 10^9$
FSSH-DISH-Schw2	$A_k = 10^9$	$A_k = 10^9$
FSSH2-DISH-Schw2	$A_k = 10^9$	$A_k = 10^9$
GFSH-DISH-Schw2	$A_k = 10^9$	$A_k = 10^9$
FSSH-SDM-Schw2	$A_k = 10^8$	$A = 10^7$
FSSH2-SDM-Schw2	$A_k = 10^8$	$A_k = 10^7$
GFSH-SDM-Schw2	$A_k = 10^9$	$A_k = 10^7$
FSSH-DISH-EDC	$\epsilon = 1000.0$	$\epsilon = 1000.0$
FSSH2-DISH-EDC	$\epsilon = 1000.0$	$\epsilon = 1000.0$
GFSH-DISH-EDC	$\epsilon = 1000.0$	$\epsilon = 1000.0$
FSSH-SDM-EDC	$\epsilon = 500.0$	$\epsilon = 50.0$
FSSH2-SDM-EDC	$\epsilon = 500.0$	$\epsilon = 50.0$
GFSH-SDM-EDC	$\epsilon = 500.0$	$\epsilon = 50.0$
FSSH-DISH-GF	$E_r = 1.25 \times 10^{-10}$	$E_r = 1.25 \times 10^{-10}$
FSSH2-DISH-GF	$E_r = 1.25 \times 10^{-10}$	$E_r = 1.25 \times 10^{-10}$
GFSH-DISH-GF	$E_r = 1.25 \times 10^{-10}$	$E_r = 1.25 \times 10^{-10}$
FSSH-SDM-GF	$E_r = 1.25 \times 10^{-10}$	$E_r = 1.25 \times 10^{-10}$
FSSH2-SDM-GF	$E_r = 1.25 \times 10^{-10}$	$E_r = 1.25 \times 10^{-5}$
GFSH-SDM-GF	$E_r = 1.25 \times 10^{-10}$	$E_r = 1.25 \times 10^{-10}$
FSSH-SHXF	$0.1\sigma_q$	$0.1\sigma_q$
FSSH2-SHXF	$0.1\sigma_q$	$0.25\sigma_q$
GFSH-SHXF	$0.1\sigma_q$	$0.25\sigma_q$

Conclusion

- 132 TSH recipes benchmarked against exact ML-MCTDH for a two-level SB model
- Initial-condition sampling is crucial: Wigner gives higher energy and faster transfer than Boltzmann
- With Wigner, SDM/DISH decoherence corrections improve agreement with physical meta-parameters
- With Boltzmann, bare TSH agrees well, likely by error cancellation; decoherence corrections often worsen accuracy except in asymptotic limits
- SSY generally over-accelerates transfer in this model
- These conclusions are model-specific and method/parameter tuning remains essential

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- ❖ Alexey V. Akimov (University at Buffalo)
- ❖ Daeho Han (University at Buffalo)
- ❖ Saikat Mukherjee (Nicolaus Copernicus University in Torun, Poland)
- ❖ VISTA Talks Organizers

Thank You!

Questions?

Supporting Information

Convergence Analysis