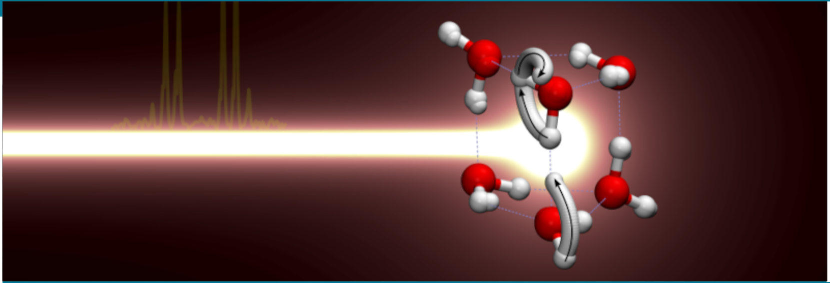
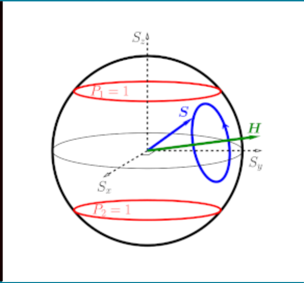
ETH zürich



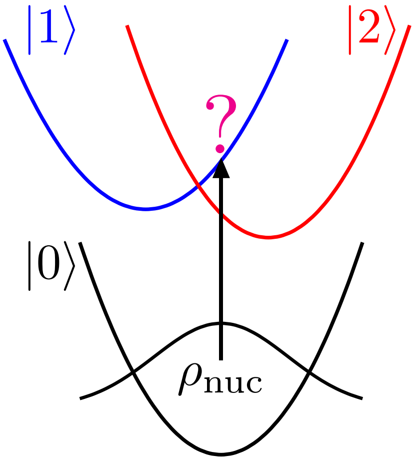


Mapping Approach to Surface Hopping (MASH)

Jeremy O. Richardson, Jonathan Mannouch, Johan Runeson, Joseph Lawrence...

Laboratory of Physical Chemistry, ETH Zurich

Nonadiabatic dynamics



When the Born-Oppenheimer approximation breaks down, we have a Hamiltonian like

$$\hat{\mathcal{H}} = \frac{p^2}{2m} + \begin{pmatrix} V_1(x) & \Delta(x) \\ \Delta(x) & V_2(x) \end{pmatrix}$$
$$= \frac{p^2}{2m} + V_1 |1\rangle\langle 1| + V_2 |2\rangle\langle 2| + \Delta\big(|1\rangle\langle 2| + |2\rangle\langle 1| \big)$$

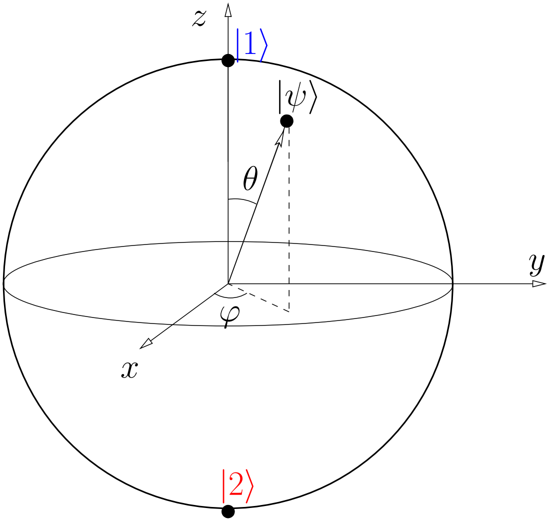
This is a two-level electronic system coupled to many nuclear degrees of freedom

- Describe nuclear dynamics classically with molecular dynamics
- and electronic-state dynamics quantum mechanically
- in a consistent way

Nonadiabatic dynamics methods

- Ground-state classical-path approximation (no back-reaction)
  - Mott 1931
  - QM/MM simulations (Kleinekathöfer. . .)
- Ehrenfest mean-field dynamics
  - Ehrenfest 1927, McLachlan 1964, Micha 1983, Tully 1998
- Quasiclassical mapping methods
  - MMST mapping (Meyer & Miller 1979, Stock & Thoss 1999) and SQC (Cotton & Miller)
  - Spin mapping (Runeson & Richardson 2019)
- Surface Hopping
  - Fewest-switches surface hopping (Tully 1990)
  - Many variants to decoherence corrections, momentum reversals etc. (Subotnik, Truhlar, Martens. . .)
- Others. . .

Superposition (Bloch sphere) $|1\rangle \Leftrightarrow |\uparrow\rangle \quad |2\rangle \Leftrightarrow |\downarrow\rangle$

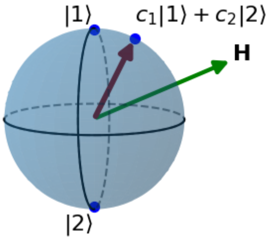


$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle$$
$$c_1 = \cos\frac{\theta}{2}\,\mathrm{e}^{-\mathrm{i}\varphi/2}$$
$$c_2 = \sin\frac{\theta}{2}\,\mathrm{e}^{+\mathrm{i}\varphi/2}$$

$$S_x = \langle\psi|\hat{S}_x|\psi\rangle = \frac{1}{2}\sin\theta\cos\varphi$$
$$S_y = \langle\psi|\hat{S}_y|\psi\rangle = \frac{1}{2}\sin\theta\sin\varphi$$
$$S_z = \langle\psi|\hat{S}_z|\psi\rangle = \frac{1}{2}\cos\theta$$

Coherence (Bloch sphere) $|1\rangle \Leftrightarrow |\uparrow\rangle \quad |2\rangle \Leftrightarrow |\downarrow\rangle$

$$\hat{H}(x) = \begin{pmatrix} V_1 & \Delta \\ \Delta & V_2 \end{pmatrix} = \underbrace{\tfrac{1}{2}(V_1 + V_2)}_{H_0} + \underbrace{2\Delta}_{H_x} \underbrace{\frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{\hat{S}_x} + \underbrace{(V_1 - V_2)}_{H_z} \underbrace{\frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}_{\hat{S}_z} = H_0 + \boldsymbol{H} \cdot \hat{\boldsymbol{S}}$$



which is Hamiltonian for a spin in a magnetic field

Schrödinger equation: $$|\dot{\psi}\rangle = \frac{1}{i\hbar}\hat{H}|\psi\rangle$$

Dynamics: $$\dot{c}_1 = \frac{1}{i\hbar}[V_1 c_1 + \Delta c_2]$$

$$\dot{c}_2 = \frac{1}{i\hbar}[\Delta c_1 + V_2 c_2]$$

or equivalently: $$\frac{\partial}{\partial t}\hat{\boldsymbol{S}} = \frac{1}{i\hbar}[\hat{\boldsymbol{H}}, \hat{\boldsymbol{S}}]$$

Equations of motion

$$\dot{\boldsymbol{S}} = \boldsymbol{H} \times \boldsymbol{S} \qquad \dot{x} = p/m \qquad \dot{p} = -\nabla V_0 + \mathcal{F}$$

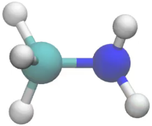
Ground-state classical path approximation: $\mathcal{F} = 0$

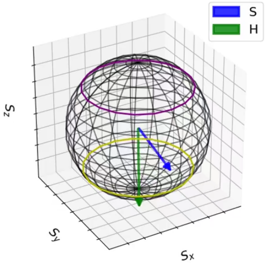
Ehrenfest mean-field: $\mathcal{F} = -\langle \psi | \nabla \hat{H} | \psi \rangle$

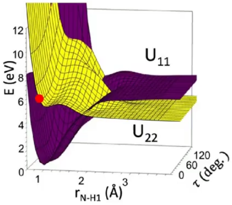
Spin mapping: $\mathcal{F} = -\sqrt{3}[\nabla H_x S_x + \nabla H_y S_y + \nabla H_z S_z]$

Surface hopping: $\mathcal{F} = -\nabla V_n$ stochastic hop of n

Example: N–H photodissociation of methylamine







$$\mathcal{H} = \frac{p^2}{2m} + H_0 + \sqrt{3}\boldsymbol{H}\cdot\boldsymbol{S}$$

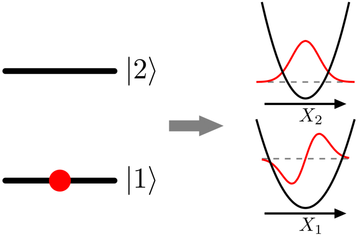
$$\dot{\boldsymbol{S}} = \boldsymbol{H} \times \boldsymbol{S}$$

$$\dot{x} = p/m$$

$$\dot{p} = -\frac{\partial H_0}{\partial x} - \sqrt{3}\frac{\partial \boldsymbol{H}}{\partial x}\cdot\boldsymbol{S}$$

fitted PES from Parker & Truhlar, JCP 152, 244309 (2020)

MMST mapping



$$c_1 \mapsto \frac{1}{\sqrt{2}}(X_1 + \mathrm{i}P_1) \qquad c_2 \mapsto \frac{1}{\sqrt{2}}(X_2 + \mathrm{i}P_2)$$

$$\mathrm{Tr}[\hat{A}\hat{B}] = \frac{1}{(2\pi)^2} \iint A_\mathrm{W}(X,P) B_\mathrm{W}(X,P) \mathrm{d}X \mathrm{d}P$$

where

$$\sigma_x(X,P) = 16(X_1X_2 + P_1P_2)\,\mathrm{e}^{-X^2-P^2}$$

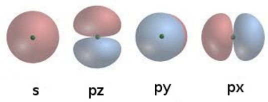
$$\sigma_y(X,P) = 16(X_1P_2 - P_1X_2)\,\mathrm{e}^{-X^2-P^2}$$

$$\sigma_z(X,P) = 8(X_1^2 + P_1^2 - X_2^2 - P_2^2)\,\mathrm{e}^{-X^2-P^2}$$

$$\mathcal{I}(X,P) = 8(X_1^2 + P_1^2 - X_2^2 - P_2^2 - 1)\,\mathrm{e}^{-X^2-P^2}$$

Meyer, Miller, Stock, Thoss. . . Wigner

Spin mapping [Johan Runeson]



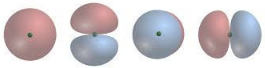
- Want phase-space representation such that

$$\mathrm{Tr}[\hat{\mathcal{I}}^2] = \mathrm{Tr}\left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right] = \frac{1}{2\pi}\iint \underbrace{1}_{\mathcal{I}}\,\underbrace{1}_{\mathcal{I}} \sin\theta \,\mathrm{d}\theta\,\mathrm{d}\varphi$$

$$\mathrm{Tr}[\hat{S}_z^2] = \frac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right] = \frac{1}{2\pi}\iint \underbrace{\frac{\sqrt{3}}{2}\cos\theta}_{S_z}\,\underbrace{\frac{\sqrt{3}}{2}\cos\theta}_{S_z} \sin\theta \,\mathrm{d}\theta\,\mathrm{d}\varphi$$

$$\mathrm{Tr}[\hat{S}_x^2] = \frac{1}{4}\mathrm{Tr}\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right] = \frac{1}{2\pi}\iint \underbrace{\frac{\sqrt{3}}{2}\sin\theta\cos\varphi}_{S_x}\,\underbrace{\frac{\sqrt{3}}{2}\sin\theta\cos\varphi}_{S_x} \sin\theta \,\mathrm{d}\theta\,\mathrm{d}\varphi$$

Spin mapping [Johan Runeson]



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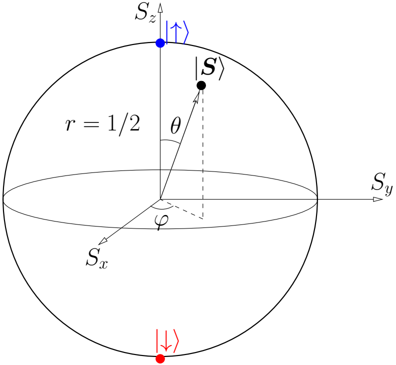
$$\mathrm{Tr}[\hat{S}_z^2] = \frac{1}{4}\mathrm{Tr}\left[\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right] = \frac{1}{2\pi}\iint \underbrace{\frac{\sqrt{3}}{2}\cos\theta}_{S_z}\,\underbrace{\frac{\sqrt{3}}{2}\cos\theta}_{S_z}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

$$\mathrm{Tr}[\hat{S}_x^2] = \frac{1}{4}\mathrm{Tr}\left[\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\right] = \frac{1}{2\pi}\iint \underbrace{\frac{\sqrt{3}}{2}\sin\theta\cos\varphi}_{S_x}\,\underbrace{\frac{\sqrt{3}}{2}\sin\theta\cos\varphi}_{S_x}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$$

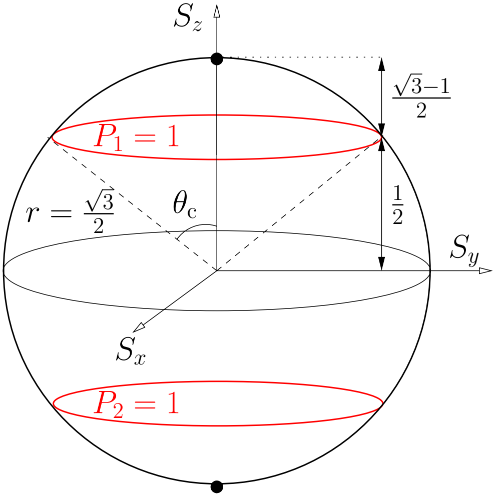
- N.B. $\langle\hat{S}^2\rangle = S(S+1) = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4} = \left(\frac{\sqrt{3}}{2}\right)^2$

Spin Spheres [Johan Runeson]

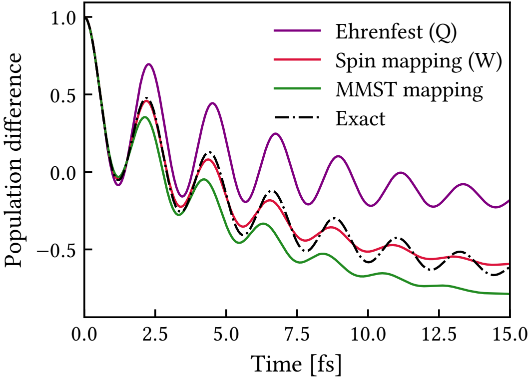
Ehrenfest



Spin mapping

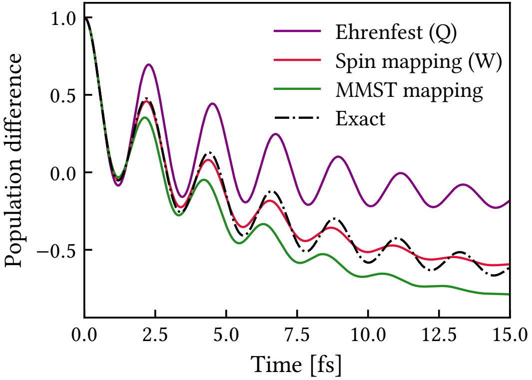


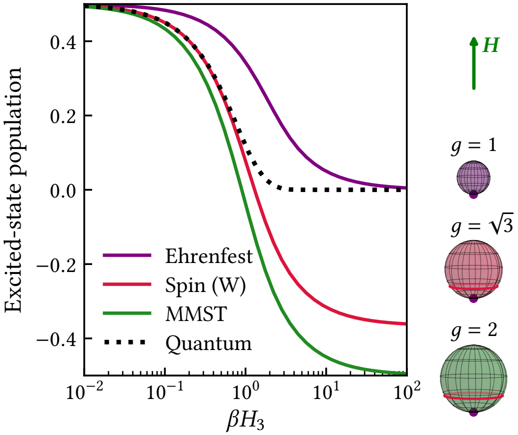
Mapping methods and thermalization [Graziano Amati]



- Runeson, Mannouch, Amati, Fiechter & J.O.R. "Spin-mapping methods for simulating ultrafast nonadiabatic dynamics." *Chimia* **76**, 582 (2022).

Mapping methods and thermalization [Graziano Amati]





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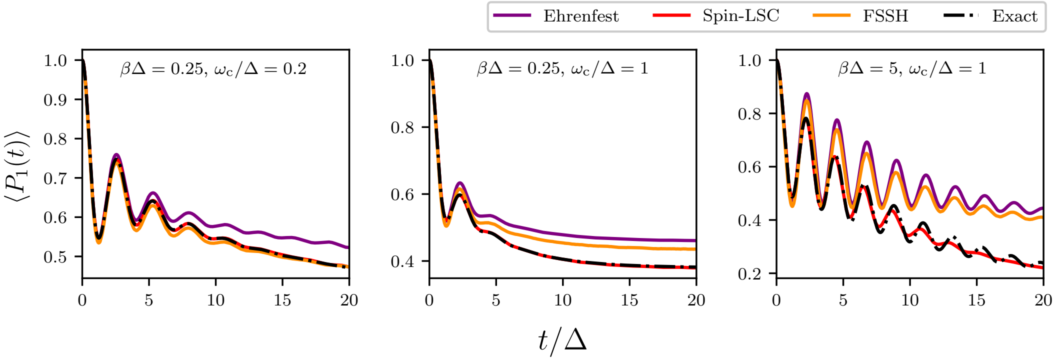
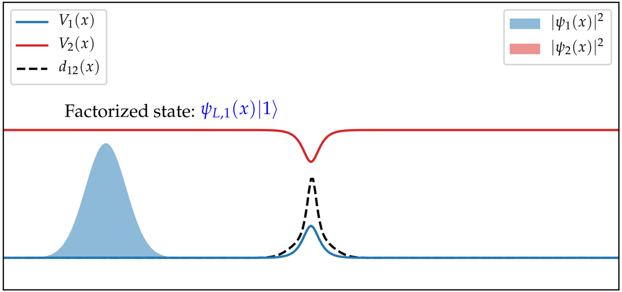
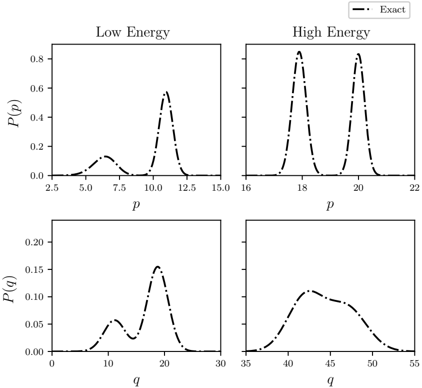
More spin-boson models



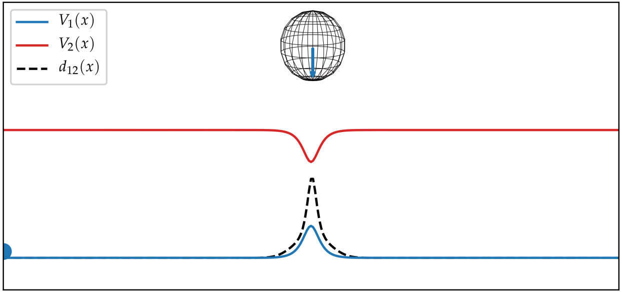
- Mannouch & J.O.R. "A mapping approach to surface hopping." *J. Chem. Phys.* **158**, 104111 (2023).

Wavepacket Branching





Ehrenfest mean-field theory



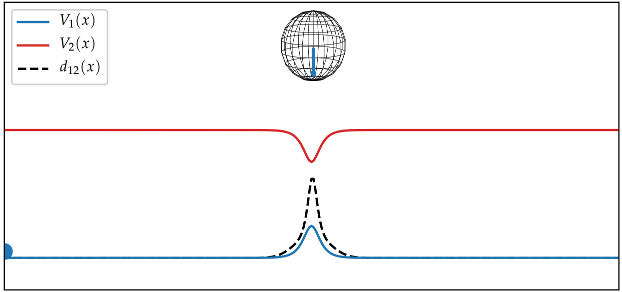
$$E = \frac{p^2}{2m} + V_1|c_1|^2 + V_2|c_2|^2$$

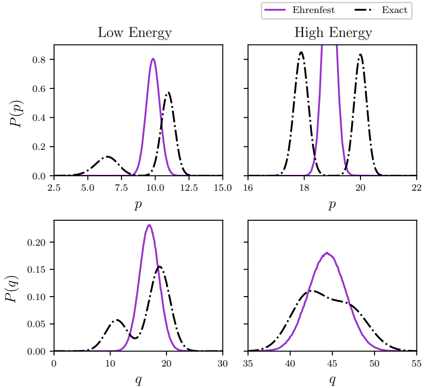
$$\dot{\boldsymbol{S}} = \boldsymbol{H} \times \boldsymbol{S}$$

$$\dot{x} = p/m$$

$$\dot{p} = -\frac{\partial V_1}{\partial x}|c_1|^2 - \frac{\partial V_2}{\partial x}|c_2|^2$$

Ehrenfest mean-field theory





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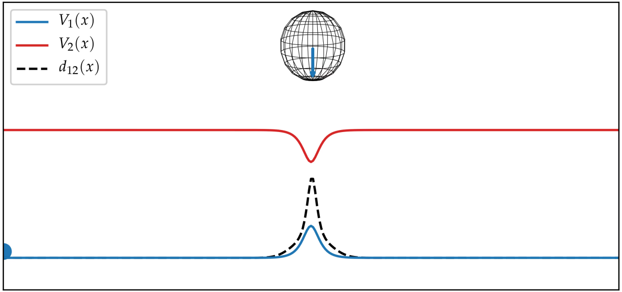
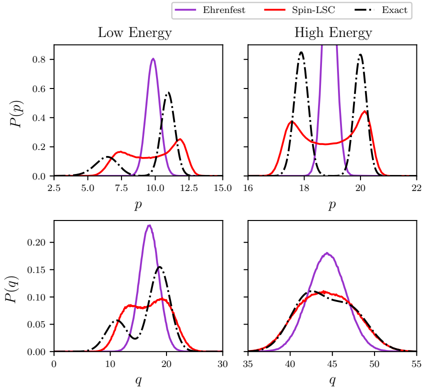
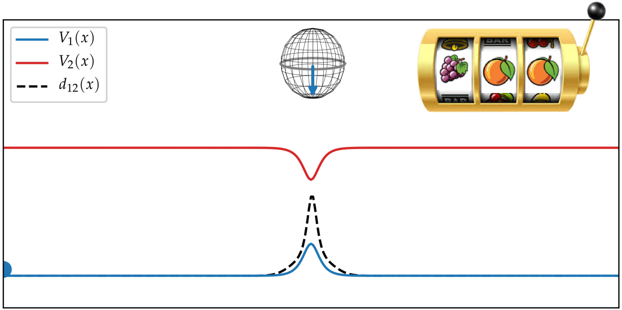




Surface hopping



$$E = \frac{p^2}{2m} + V_1\delta_{n1} + V_2\delta_{n2}$$

$$\dot{\boldsymbol{S}} = \boldsymbol{H} \times \boldsymbol{S}$$

$$\dot{x} = p/m$$

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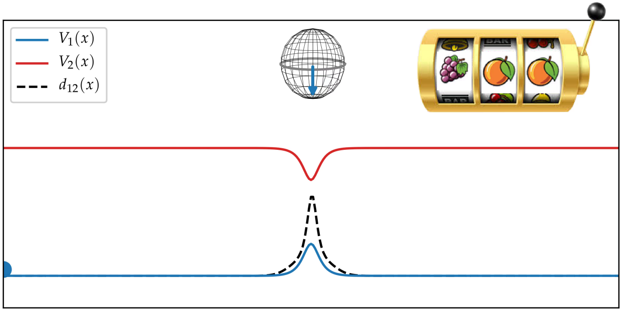
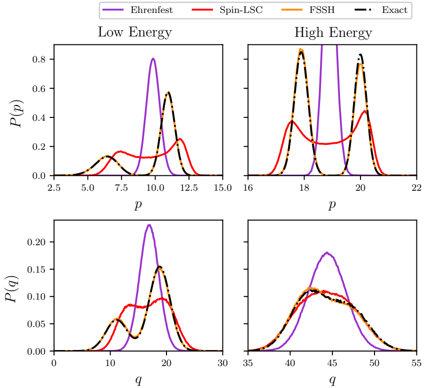
stochastic hop of state, n

+ momentum rescaling

- Tully. "Molecular dynamics with electronic transitions." *J. Chem. Phys.* **93**, 1061 (1990).

Surface hopping





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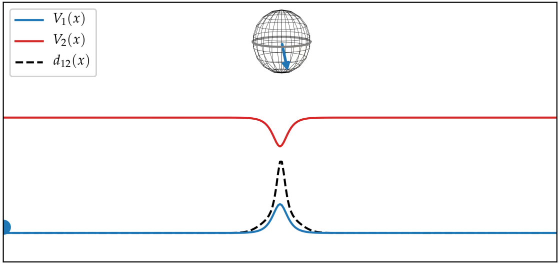
MASH [Jonathan Mannouch]



$$E = \frac{p^2}{2m} + V_1 h(-S_z) + V_2 h(S_z)$$

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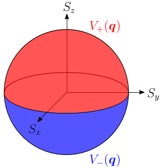

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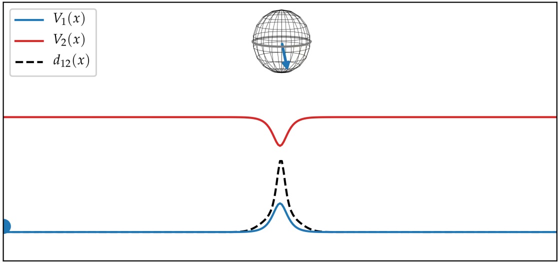

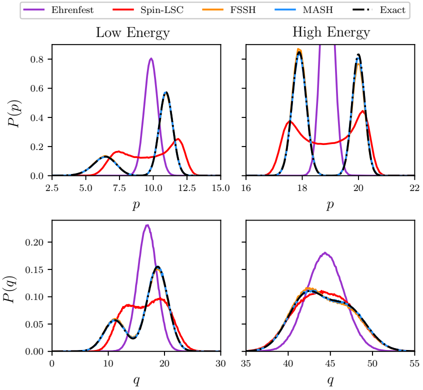

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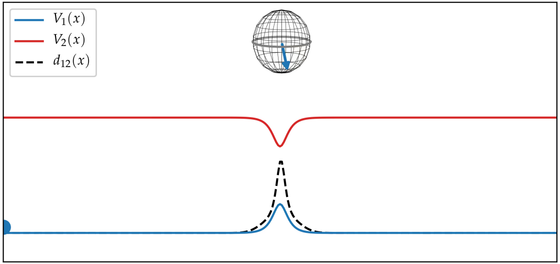

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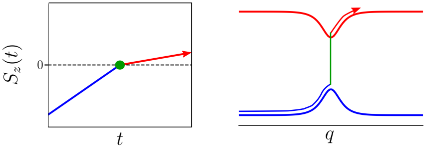

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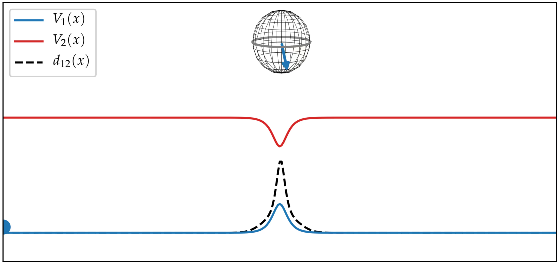

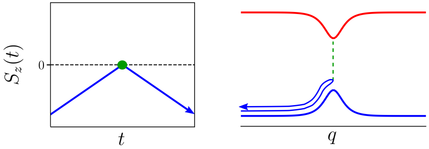

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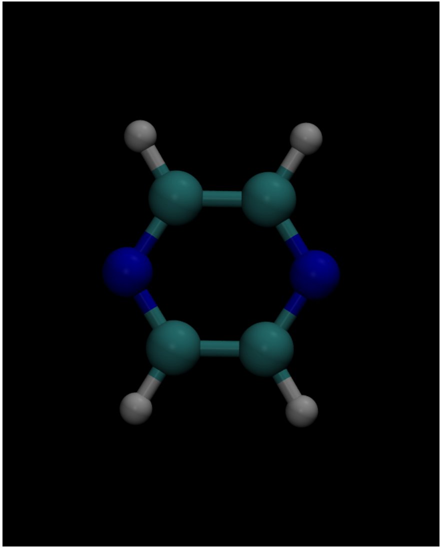
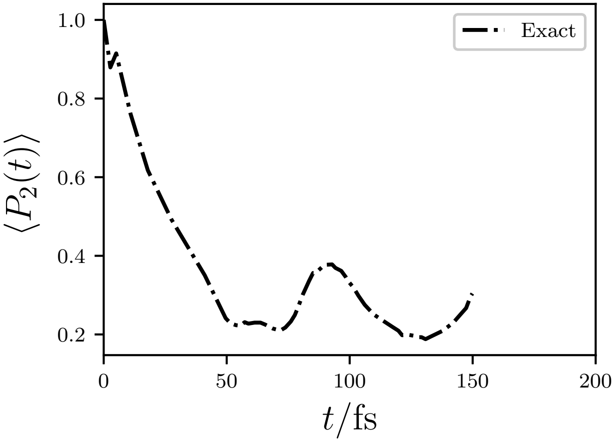
Results for Pyrazine (24D with bilinear couplings)





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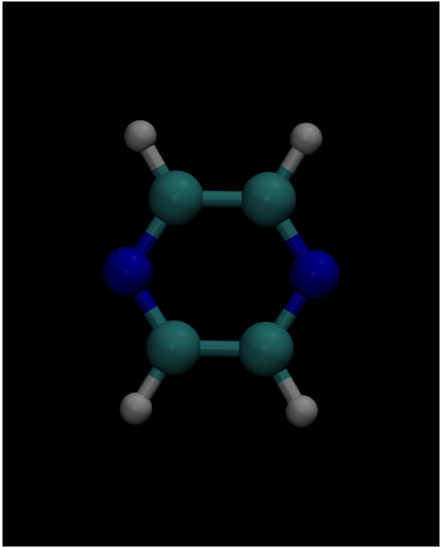

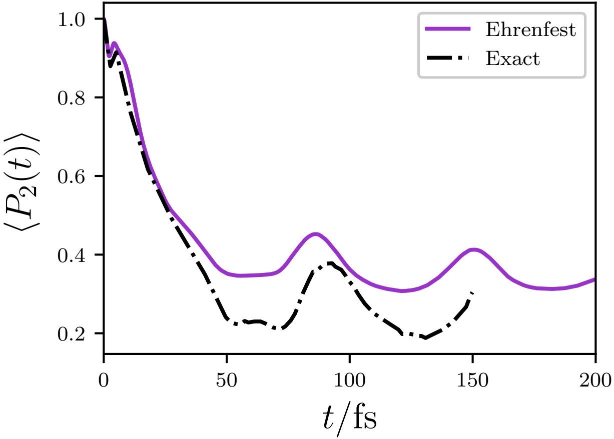

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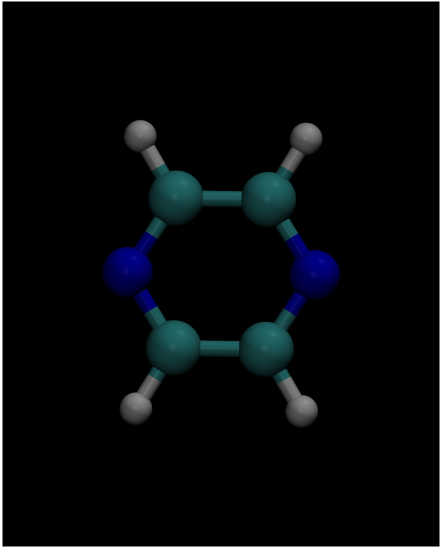

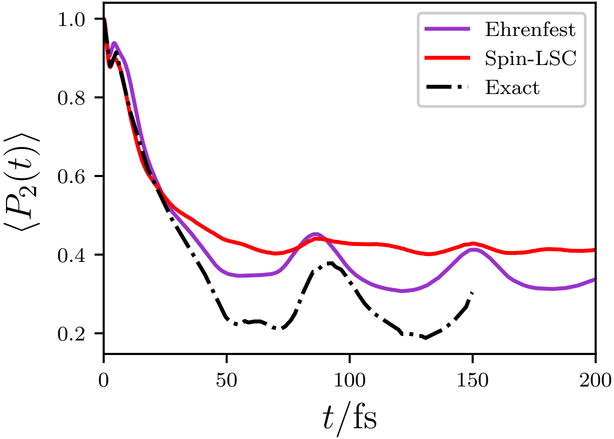

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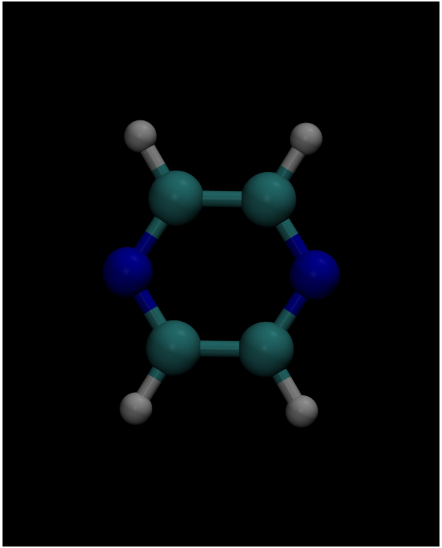
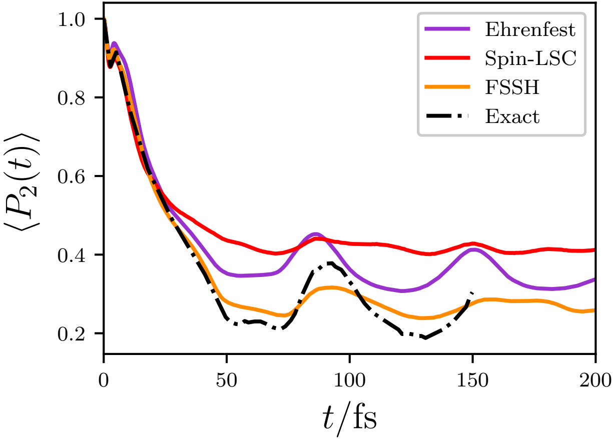
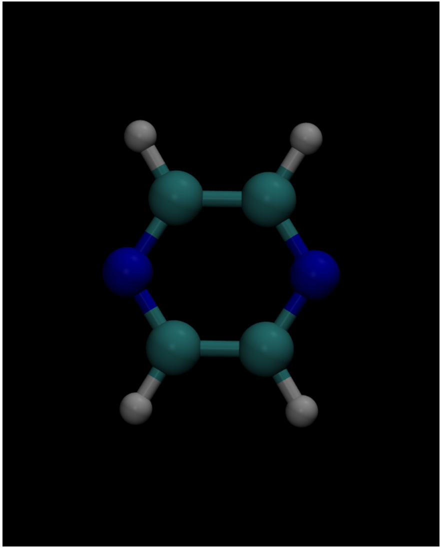
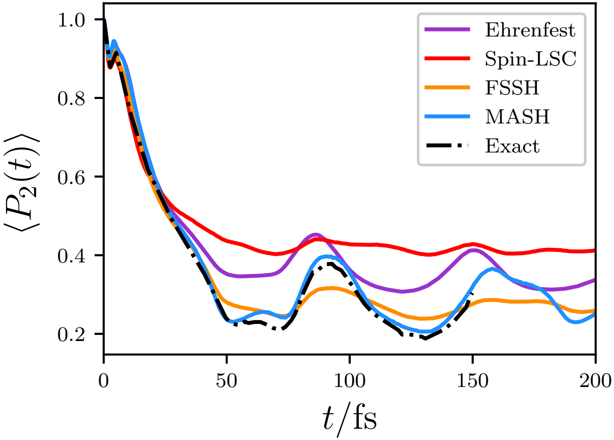


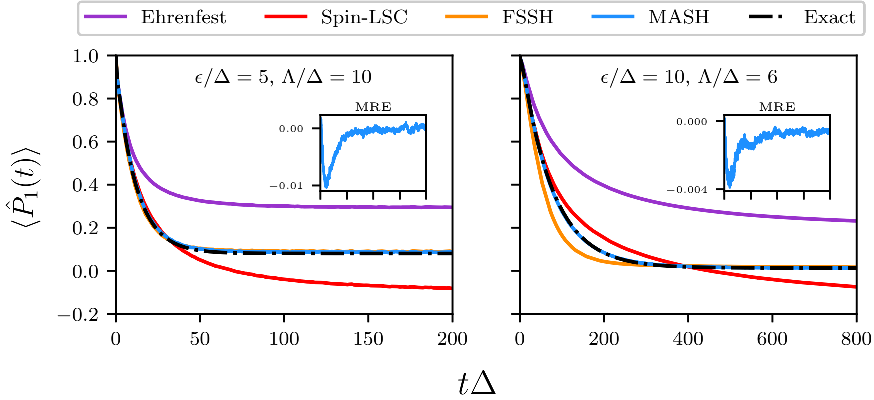


Results for Pyrazine (24D with bilinear couplings)



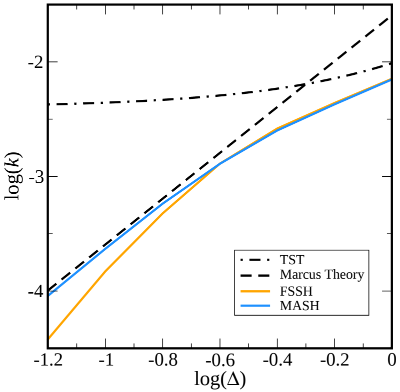


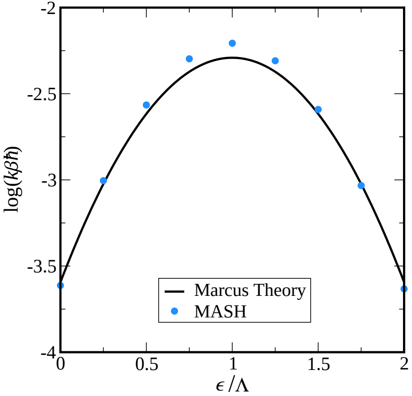
Even more spin-boson models



- Mannouch & J.O.R. "A mapping approach to surface hopping." *J. Chem. Phys.* **158**, 104111 (2023).

Rate theory [Joseph Lawrence]



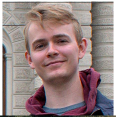


- Lawrence, Mannouch & J.O.R. "Accurate surface hopping rates without decoherence corrections? Use MASH." *in preparation*.

Summary and Outlook

- Spin mapping is similar in spirit but often more accurate than Ehrenfest
- Sometimes surface hopping is better than spin mapping and sometimes not
- Surface hopping suffers from (at least) two different errors
- The mapping approach to surface hopping (MASH) combines the advantages of spin mapping and surface hopping and thus fixes one of the two errors
- MASH is deterministic
- MASH ensures internal consistency between spin vector and active state
- MASH uniquely defines momentum rescaling/reversals and frustrated hops
- MASH almost obeys detailed balance and provides a measure for the error
- MASH recovers Marcus theory without requiring extra decoherence corrections
- MASH is rigorously derived from and systematically improvable to QCLE using rigorous decoherence corrections (required for Tully 2&3)
- caveat: MASH is currently limited to 2 states but we are working on it!

Acknowledgements

Current group members:

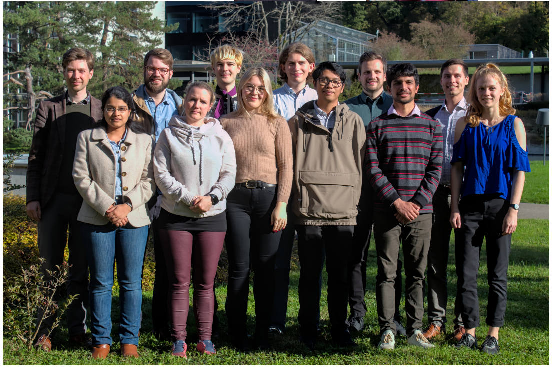
- Eric Heller
- Gabriel Laude
- Rhiannon Zarotiadis
- Dr. George Trenins
- Dr. Joseph Lawrence
- Imaad Ansari
- Marit Fiechter
- Dr. Meghna Manae
- Dr. Yaling Ke
- Kasra Asnaashari

Former members:

- Dr. Jonathan Mannouch
- Dr. Johan Runeson
- Dr. Graziano Amati
- Dr. Maximilian Saller

Collaborators:

- Dr. Aaron Kelly (MPSD Hamburg)

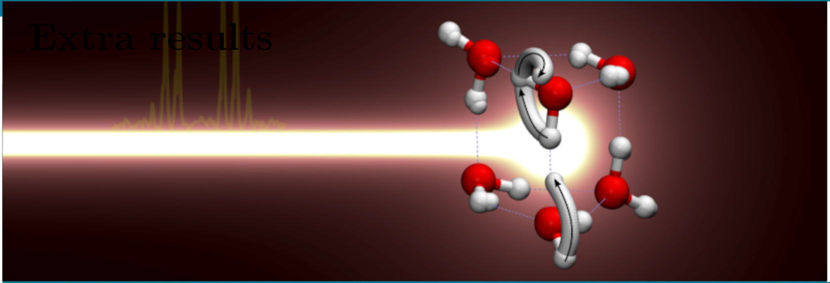


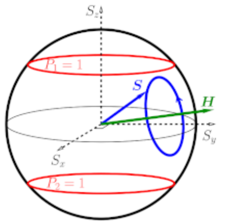
FNSNF Swiss National Science Foundation

ETH zürich

We are looking for new students, postdocs and collaborators

Extra results





Spin-mapping nonadiabatic dynamics [Johan Runeson]

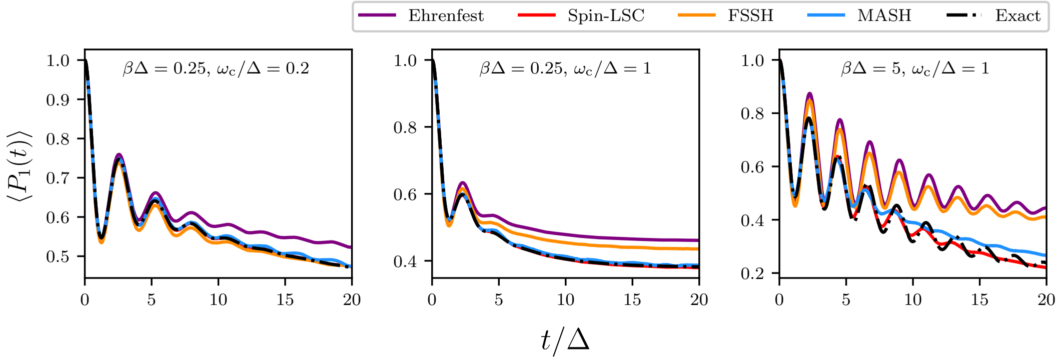
$$\mathcal{H} = \frac{p^2}{2m} + V_0 + H_x S_x + H_y S_y + H_z S_z$$
$$= \frac{p^2}{2m} + V_0 + \sum_{nm} \frac{1}{2}(X_n X_m + P_n P_m - \gamma) H_{nm}$$

$\gamma_{\text{Ehrenfest}} = 0$ $\gamma_{\text{MMST}} = 1$ $\gamma_{\text{Stock}} \approx 0.6$ $\gamma_{\text{SQC}} = 0.666\ldots$

$\gamma_{\text{SU(2)}} = \sqrt{3} - 1 = 0.732\ldots$ $\gamma_{\text{SU}(N)} = \frac{2}{N}\left(\sqrt{N+1} - 1\right)$

- Runeson & J.O.R. "Generalized spin mapping for quantum-classical dynamics." *J. Chem. Phys.* **152**, 084110 (2020).

More spin-boson models (again!)



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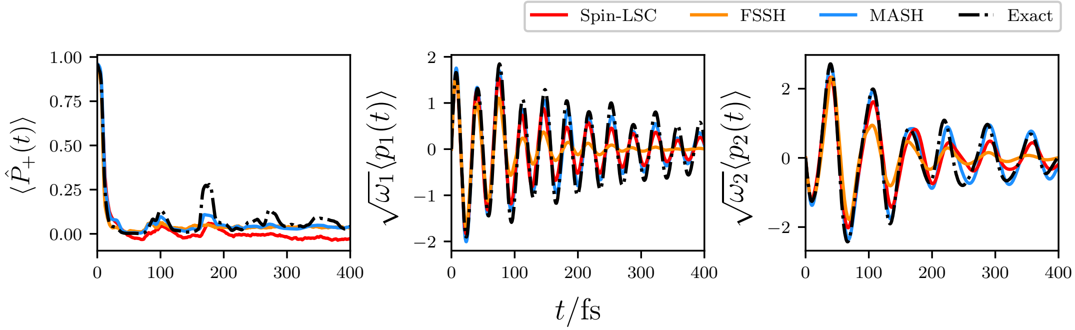
3-mode pyrazine model



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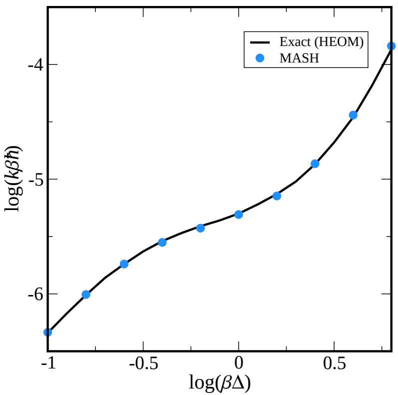

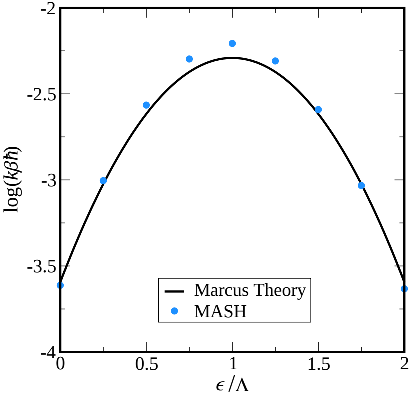

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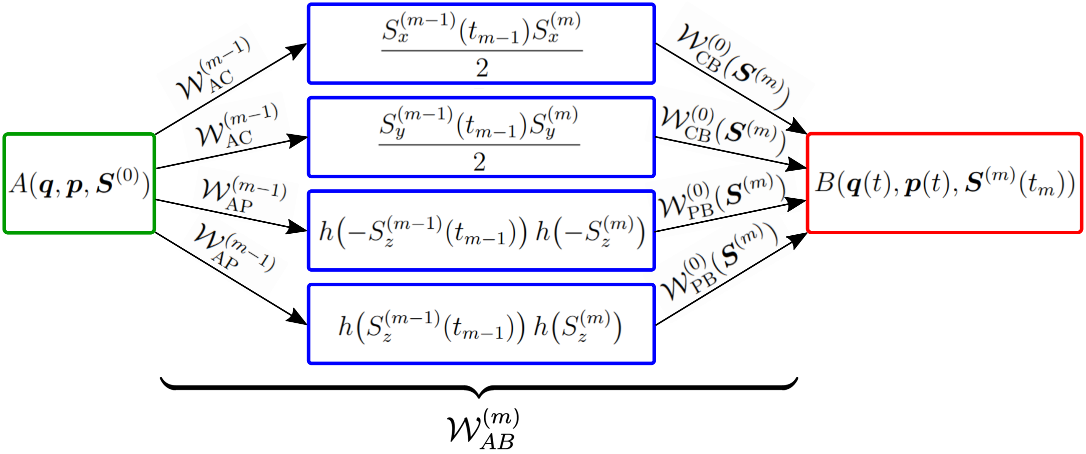
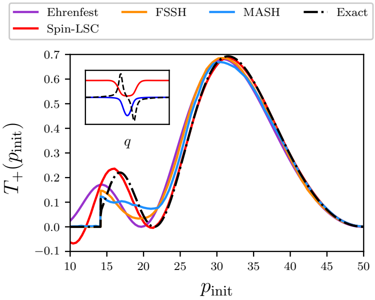
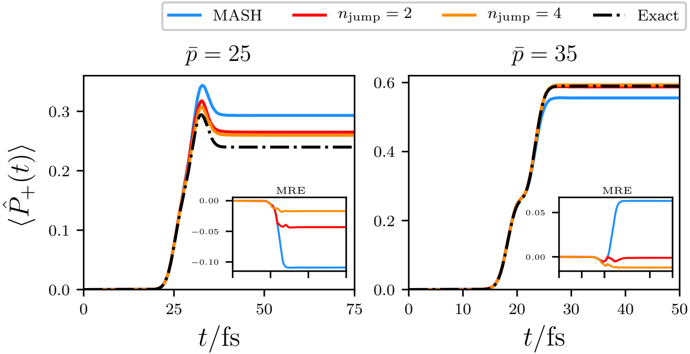
Quantum jump and decoherence corrections



- Mannouch & J.O.R. "A mapping approach to surface hopping." *J. Chem. Phys.* **158**, 104111

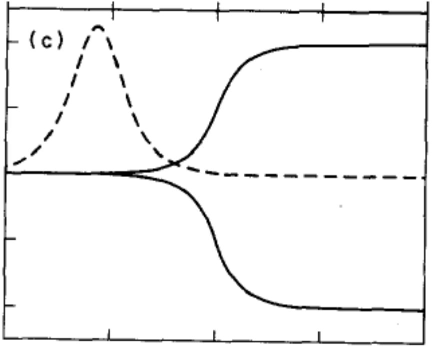
Results for Tully 2

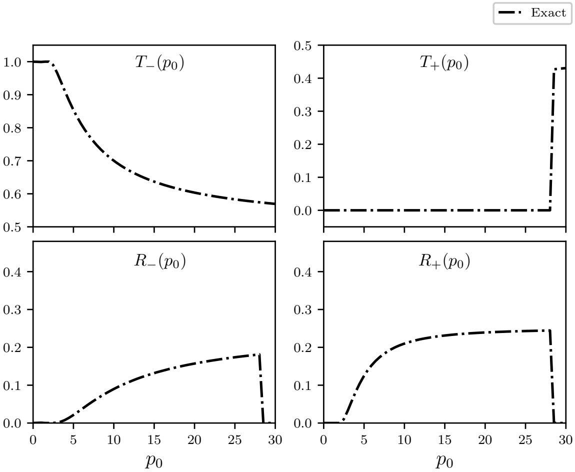




- Mannouch & J.O.R. "A mapping approach to surface hopping." *J. Chem. Phys.* **158**, 104111 (2023).

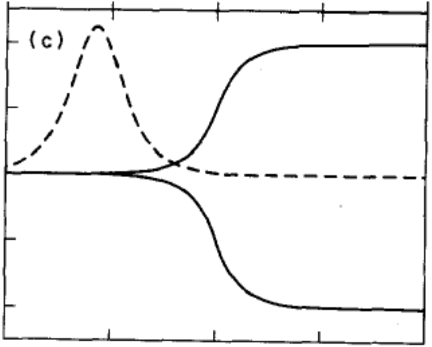
Results for Tully 3

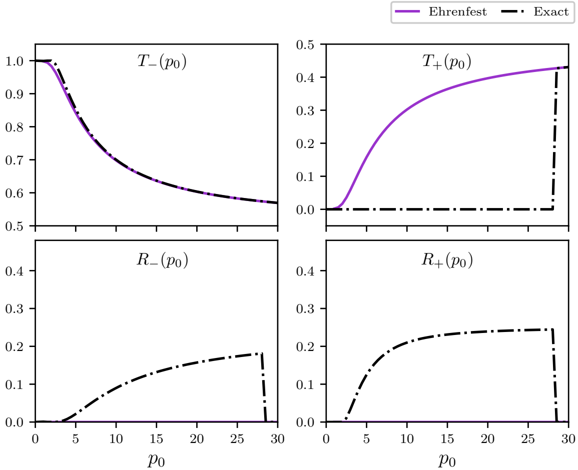




- Mannouch & J.O.R. "A mapping approach to surface hopping." *J. Chem. Phys.* **158**, 104111 (2023).

Results for Tully 3





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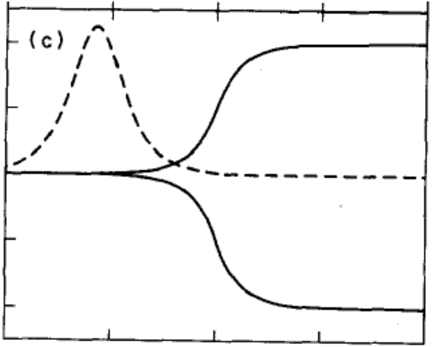

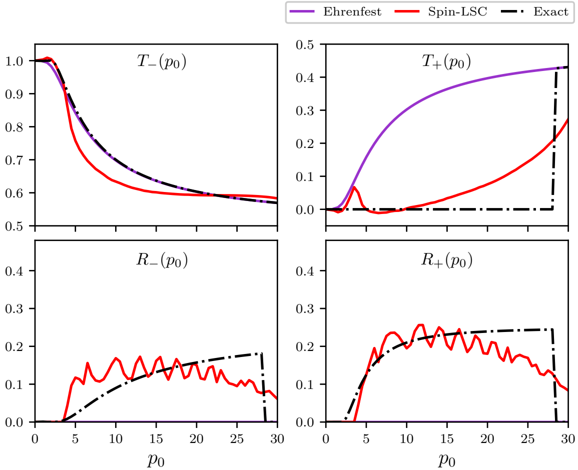

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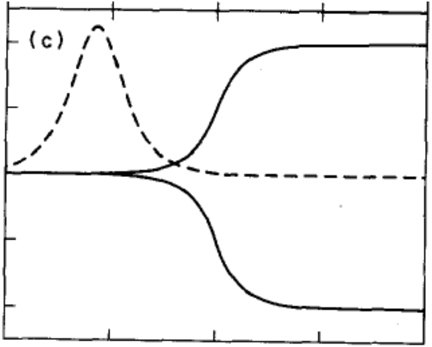

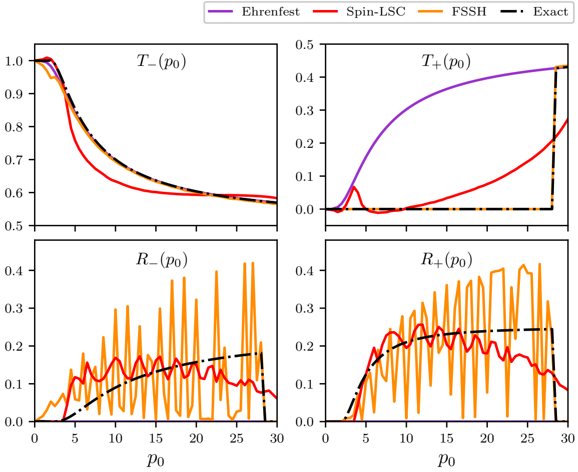

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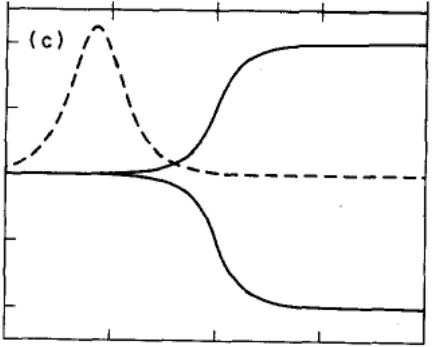

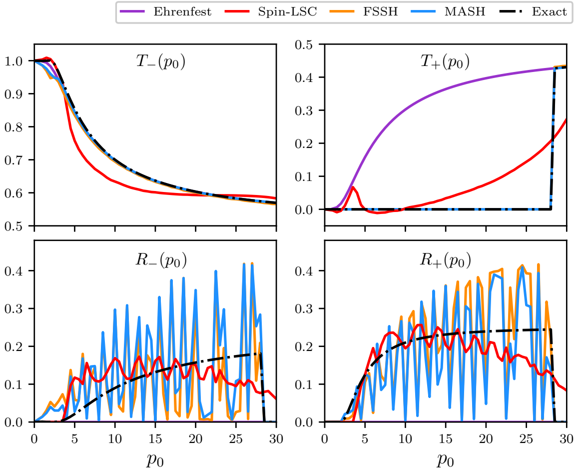

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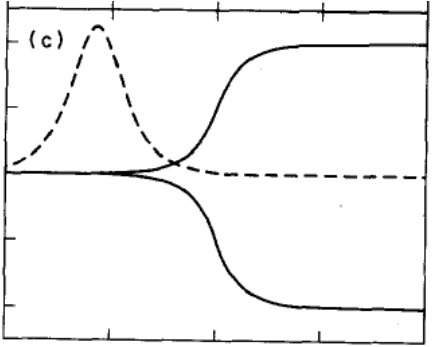

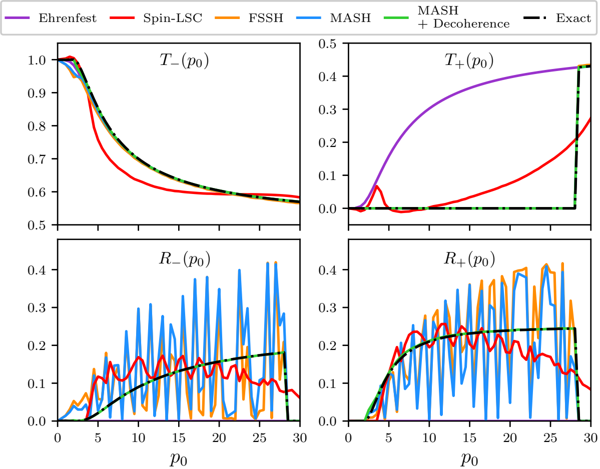

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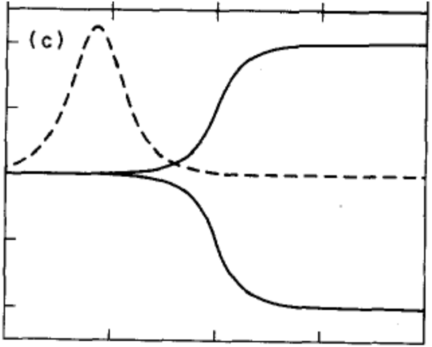
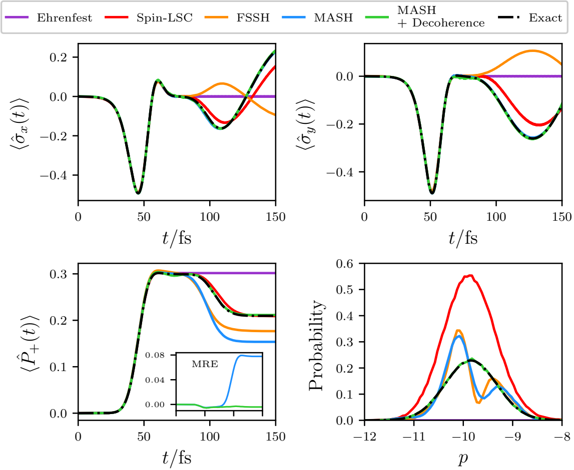
Wavepacket results for Tully 3





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