Libra Summer School and Workshop 2024
TSH: Part 3

Alexey Akimov

University at Buffalo, SUNY

July 9, 2024

TSH in the nutshell

Initialization

Nuclear dynamics
$$\dot{p}_i = -\frac{\partial H}{\partial r_i} \quad \dot{r}_i = \frac{\partial H}{\partial p_i}$$

Stationary adiabatic states
$$\hat{H}_{el}\psi_i = E_i\psi_i$$

Non-adiabatic Couplings
$$d_{ij} = \frac{\langle\psi_i(t)|\psi_j(t+dt)\rangle - \langle\psi_i(t+dt)|\psi_j(t)\rangle}{2dt}$$

Electronic Dynamics
$$\Psi(r,R,t) = \sum_i c_i(t)\psi_i(r;R(t)) \qquad i\hbar\frac{\partial c_i(t)}{\partial t} = \sum_j\left(E_i\delta_{ij} - i\hbar d_{ij}\right)c_j$$

NBRA

Decoherence 1
$$c_i \rightarrow c_i \exp\left(-\frac{\Delta t}{\tau_{ij}}\right), \forall i \neq j \qquad \text{as in SDM}$$

Proposed Hops Decoherence 2
$$P_{i\rightarrow j} = \Delta t * Re\left(\frac{2\frac{p}{m}d_{ij}c_i^*c_j}{c_i^*c_i}\right) \qquad \text{or as in DISH}$$

Accept Hops
based on energy conservation or
$$P_{i\rightarrow f}^A = \min\left(1, exp\left(-\frac{\Delta E}{k_B T}\right)\right)$$

Change of state/Velocity rescaling
change active electronic state, rescale velocity
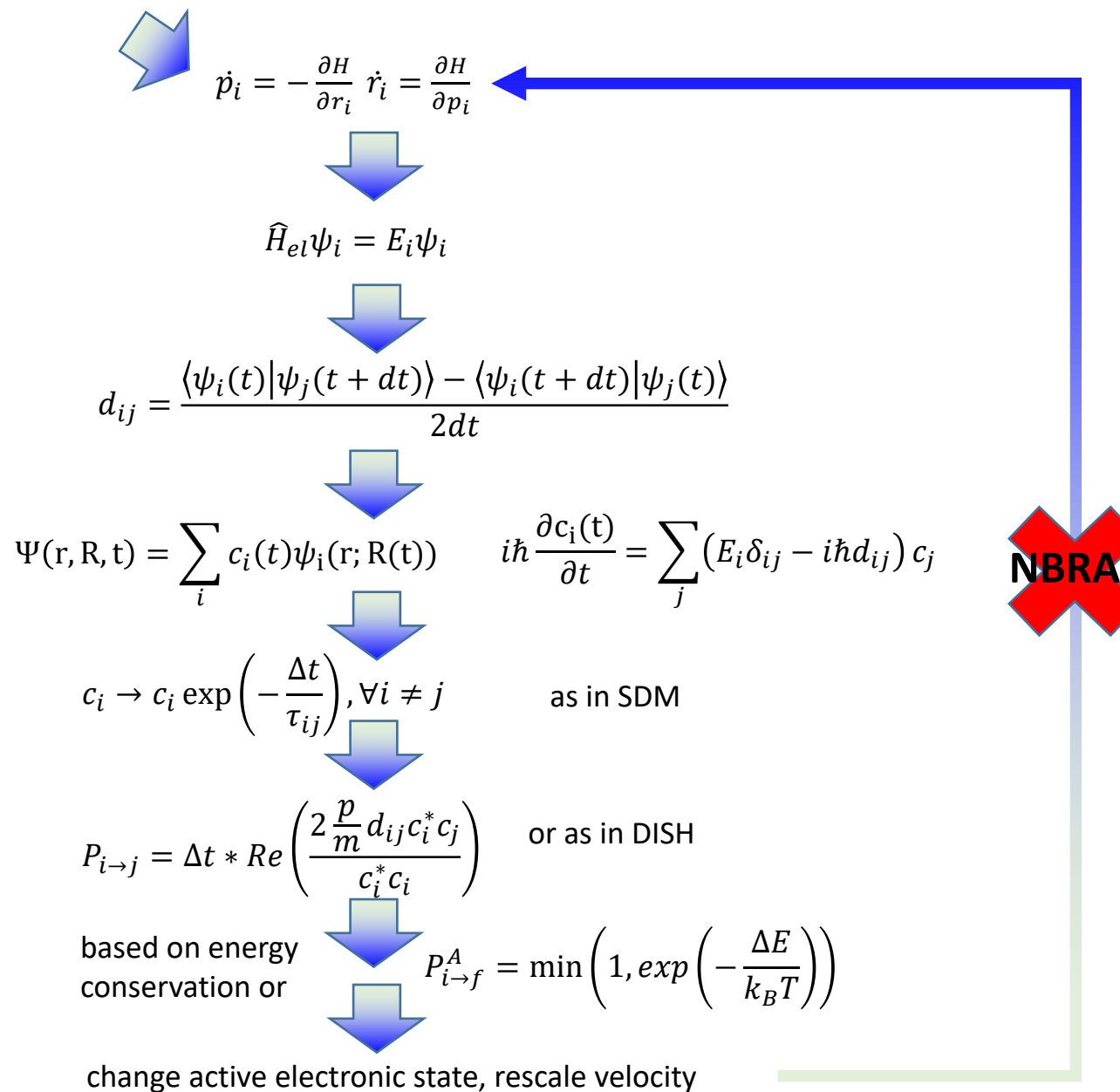
Trajectory Surface Hopping (TSH) methods
in Libra

Options for the Dynamics: Forces

dyn_control_params

- **force_method**   how to compute nuclear forces:

  0 – don't compute it – typical for the NBRA workflows

  [1 – state-specific forces]: $\boldsymbol{F_{adi},i} = -\frac{\partial E_{adi,i}}{\partial \boldsymbol{R}} = -\nabla_n H_{adi,i,i}$ for the active adiabatic state i

  2 – Ehrenfest forces (mean-field = MF)

  3 – QTSH forces – the off-diagonal contributions of the Ehrenfest force $f_{adi,n}^{QTSH} \equiv \frac{1}{C_{adi}^+ C_{adi}} C_{adi}^+ F_{adi,n}^{QTSH} C_{adi}$

- **rep_force**   0 – using only diabatic properties;   [1 – using adiabatic properties]

$$f_n^{MF} \equiv f_{n,dia}^{MF} = \frac{1}{C_{dia}^+ S C_{dia}} C_{dia}^+ F_{dia,n}^{HF} C_{dia} = f_{n,adi}^{MF} = \frac{1}{C_{adi}^+ C_{adi}} C_{adi}^+ F_{adi,n}^{HF} C_{adi}$$

nHamiltonian

- Ehrenfest_forces_dia
- Ehrenfest_forces_adi
- Ehrenfest_forces_tens_dia
- Ehrenfest_forces_tens_adi

$$F_{dia,n}^{MF} = -\langle \boldsymbol{\psi}_{dia} | \nabla_n H | \boldsymbol{\psi}_{dia} \rangle = \left[-\nabla_n H_{dia} + D_{dia,n}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia,n} \right]$$

$$F_{adi,n}^{MF} = -\langle \boldsymbol{\psi}_{adi} | \nabla_n H | \boldsymbol{\psi}_{adi} \rangle = \left[-\nabla_n H_{adi} + D_{adi,n}^+ H_{adi} + H_{adi} D_{adi,n} \right]$$

$$F_{adi,n}^{QTSH} = -\langle \boldsymbol{\psi}_{adi} | \nabla_n H | \boldsymbol{\psi}_{adi} \rangle = \left[D_{adi,n}^+ H_{adi} + H_{adi} D_{adi,n} \right]$$

Note on the Ehrenfest force calculations:

In the normal approach, when we rely on the TD-SE integrator that uses NACs, the force tensor is computed as:

$$F_{adi,n}^{MF} = -\langle \boldsymbol{\psi}_{adi} | \nabla_n H | \boldsymbol{\psi}_{adi} \rangle = \left[-\nabla_n H_{adi} + D_{adi,n}^+ H_{adi} + H_{adi} D_{adi,n} \right]$$

However, when the local diabatization integrators are used, the NACs vanish, $D_{adi} \approx 0$, so the force tensor becomes just:

$$F_{adi,n}^{MF,LD} = -\langle \boldsymbol{\psi}_{adi} | \nabla_n H | \boldsymbol{\psi}_{adi} \rangle \approx -\nabla_n H_{adi}$$

dyn_control_params

- **enforce_state_following**

Whether we want to enforce nuclear dynamics to be on a given state, regardless of the TSH transitions: [0 – no]; 1 – yes (the dynamics is governed by the given PES, but the hopping may still be happening). The option 1 can be used for NBRA for the excited-state surfaces.

- **enforced_state_index**

If we enforce the nuclear dynamics to be on a given state, what is the index of that state [any integer > 0, default = 0]
The default value of 0 enforces the nuclear dynamics to be on the ground state.

Options for the Dynamics: Time-overlaps and NACs

dyn_control_params

- **time_overlap_method**

How to get the time-overlaps $P_{adi}(t - \Delta t, t) = \langle \boldsymbol{\psi}_{adi}(t - \Delta t) | \boldsymbol{\psi}_{adi}(t) \rangle$ in the dynamics.
[0] - based on the wavefunctions (the Hamiltonian shall have the basis_transform variables updated): $P_{adi}(t - \Delta t, t) = U^+(t - \Delta t) P_{dia}(t - \Delta t, t) U(t)$
1 - based on external calculations (the Hamiltonian shall have the time_overlap_adi member updated) - use for NBRA

- **nac_update_method**

How to update NACs and vibronic Hamiltonian before electronic TD-SE propagation.
- 0: don't update them (e.g. for simplest NAC)
- [1]: update according to changed momentum and existing derivative couplings

$$d_{ij} = \sum_n D_{ij,n}^{adi} \frac{P_n}{M_n}$$

- 2: update according to time-overlaps (only time-derivative NACs)

- **nac_algo**

How to compute time-derivative NACs (if nac_update_method==2)
- (-1): don't update, e.g. we use NACs from somewhere else [default]
- 0: use HST formula: $d_{ij}\left(t + \frac{\Delta t}{2}\right) = \frac{St_{ij}(t,t+\Delta t]) - St_{ij}^+(t,t+\Delta t])}{2\Delta t}$
- 1: use NPI of Meek and Levine $\quad T(t + \Delta t) = S'(t, t + \Delta t) = \langle \boldsymbol{\psi}(t) | \boldsymbol{\psi}(t + \Delta t) \rangle$

Meek, G. A.; Levine, B. G. *J. Phys. Chem. Lett.* **2014**, *5*, 2351.

$$d\left(t + \frac{\Delta t}{2}\right) \approx \frac{1}{\Delta t} \int_0^{dt} \left\langle \boldsymbol{\psi}(t') \left| \frac{\partial}{\partial t'} \right| \boldsymbol{\psi}(t') \right\rangle dt' = \frac{1}{\Delta t} \int_0^{dt} T^+(t') \frac{\partial}{\partial t'} T(t') dt' = \frac{\log[T(t + \Delta t)]}{\Delta t}$$

Hop Proposal Probability

dyn_control_params

- **tsh_method**

  - [-1]: adiabatic dynamics, no hops [default]
  - 0: Fewest Switches Surface Hopping (FSSH)
  - 1: Global Flux Surface Hopping (GFSH)
  - 2: Markov-State Surface Hopping (MSSH)
  - 3: Landau-Zener (LZ) options
  - 4: Zhu-Nakamura (ZN) options
  - 5: DISH (see decoherence)
  - 6: MASH
  - 7: FSSH2
  - 8: FSSH3

FSSH3:
Akimov, A. V. *Mol. Phys.* **2024**, *to appear in press*

LZ:
(1) Tully, J. C. *J. Chem. Phys.* **1990**, 93, 1061, 1071
(2) Belyaev, A. K.; Lebedev, O. V. *Phys. Rev. A* **2011**, 84, 014701

FSSH:
Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061

GFSH:
Wang, L.; Trivedi, D.; Prezhdo, O. V. *JCTC* **2014**, 10, 3598

MSSH:
Akimov, A. V.; Trivedi, D.; Wang, L.; Prezhdo, O. V. *J. Phys. Soc. Jpn.* **2015**, 84, 094002

MASH:
(1) Mannouch, J. R.; Richardson, J. O. A *JCP* **2023**, 158, 104111
(2) Runeson, J. E.; Manolopoulos, D. E. A *JCP* **2023**, 159, 094115.
(3) E. Runeson, J.; P. Fay, T.; E. Manolopoulos, D. *PCCP* **2024**, 26, 4929–4938.

FSSH2:
Araujo, L.; Lasser, C.; Schmidt, B. *J. Chem. Theory Comput.* **2024**, *20*, 3413–3419

ZN:
(1) Zhu, C., Nakamura, H., Re, N., Aquilanti, V., 1992. J. Chem. Phys. 97, 1892
(2) Hanasaki, K., Kanno, M., Niehaus, T.A., Kono, H., 2018. J. Chem. Phys. 149. 244117
(3) Yu, L., Xu, C., Lei, Y., Zhu, C., Wen, Z., 2014. Phys. Chem. Chem. Phys. 16. 25883.

FSSH and MSSH Hop Proposal Probability

FSSH

$$P_{i\to *}(t, t+\Delta t) = \sigma\left(\frac{\rho_{ii}(t) - \rho_{ii}(t+\Delta t)}{\rho_{ii}(t)}\right) \approx \sigma\left(\frac{-\dot{\rho}_{ii}(t)\Delta t}{\rho_{ii}(t)}\right) = \sigma\left(-\frac{\Delta\rho_{ii}(t)}{\rho_{ii}(t)}\right) = \sigma\left(-\frac{\rho_{ii}(t+\Delta t) - \rho_{ii}(t)}{\rho_{ii}(t)}\right)$$

$$\sigma(x) = xH(x) = \begin{cases} x, x \geq 0 \\ 0, otherwise \end{cases}$$

$$P_{i\to *}(t, t+\Delta t) \approx \sigma\left(\frac{-\dot{\rho}_{ii}(t)\Delta t}{\rho_{ii}(t)}\right) = 2\sigma\left(\frac{\sum_{j=0}^{N-1} Re(\rho_{ij}^* d_{ij})\Delta t}{\rho_{ii}}\right) \approx \sum_{j=0}^{N-1} \sigma\left(\frac{2Re(\rho_{ij}^* d_{ij})\Delta t}{\rho_{ii}}\right)$$

References:

$$P_{i\to j}^{FSSH} = \sigma\left(\frac{2Re(\rho_{ij}^* d_{ij})\Delta t}{\rho_{ii}}\right)$$

Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061

$$P_{i\to j}^{FSSH} = max\left(0, \frac{2Re(\rho_{ij}^* d_{ij})\Delta t}{\rho_{ii}}\right) \qquad P_{i\to j}^{P} = max\left(0, \frac{\Delta t}{\hbar P_{ii}} Im[P_{i,j}H_{j,i}^{vib} - H_{i,j}^{vib}P_{j,i}]\right)$$

Fabiano, E.; Keal, T. W.; Thiel, W. *Chem. Phys.* **2008**, *349* (1), 334–347.

MSSH

$$P_{i\to f}^{P,MSSH}(t, t+\Delta t) = P_{ff}(t+\Delta t)$$ Akimov, A. V.; Trivedi, D.; Wang, L.; Prezhdo, O. V. *J. Phys. Soc. Jpn.* **2015**, 84, 094002

GFSH and FSSH-2 Hop Proposal Probability

FSSH-2

GFSH – starts with considering the changes of populations of all states

Total flux out of state i is the same as in the FSSH

$$\Delta\rho_{ii}(t) = \rho_{ii}(t + \Delta t) - \rho_{ii}(t)$$

$$P_{i\to*}(t, t + \Delta t) \approx \sigma\left(\frac{-\dot{\rho}_{ii}(t)\Delta t}{\rho_{ii}(t)}\right) = \sigma\left(-\frac{\Delta\rho_{ii}(t)}{\rho_{ii}(t)}\right) \qquad \sum_{i=0}^{N-1}\rho_{ii} = 1$$

$i \in A: \Delta\rho_{ii} < 0$

$i \in B: \Delta\rho_{ii} > 0$

$$P_{i\to*}(t, t + \Delta t) = \sigma\left(-\frac{\Delta\rho_{ii}(t)}{\rho_{ii}(t)}\right) = \sigma\left(-\frac{\rho_{ii}(t+\Delta t)-\rho_{ii}(t)}{\rho_{ii}(t)}\right) =$$

$$\sigma\left(-\frac{\left(1-\sum_{j\neq i}\rho_{jj}(t+\Delta t)\right)-\left(1-\sum_{j\neq i}\rho_{jj}(t)\right)}{\rho_{ii}(t)}\right) = \sigma\left(\frac{\sum_{j\neq i}\left(\rho_{jj}(t+\Delta t)-\rho_{jj}(t)\right)}{\rho_{ii}(t)}\right) =$$

$$P_{i\to j}^{GFSH} = \frac{\Delta\rho_{jj}}{\rho_{ii}}\frac{\Delta\rho_{ii}}{\sum_{k\in A}\Delta\rho_{kk}}, i \in A, j \in B$$

$$\sigma\left(\sum_{j\neq i}\frac{\rho_{jj}(t+\Delta t)-\rho_{jj}(t)}{\rho_{ii}(t)}\right)$$

$$P_{i\to*} = -\frac{\Delta\rho_{ii}}{\rho_{ii}} \text{ - total flux out of state } i$$

$$P_{i\to j}^{FSSH-2} = \frac{\rho_{jj}(t+\Delta t)-\rho_{jj}(t)}{\rho_{ii}(t)} \text{ - the interpretation is}$$

$$P(j|i) = \frac{\Delta\rho_{jj}}{\sum_{k\in A}(-\Delta\rho_{kk})} = -\frac{\Delta\rho_{jj}}{\sum_{k\in A}\Delta\rho_{kk}} -$$

conditional probability of ending up in state j if left from state i

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

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

$$P_{i\to i}^{GFSH} = P(j|i)P_{i\to*}$$

$$P_{i\to i}^{FSSH-2} = 1 - \sum_{j\neq i}P_{i\to j}^{FSSH-2}$$

Wang, L.; Trivedi, D.; Prezhdo, O. V. *JCTC* **2014**, 10, 3598

Araujo, L.; Lasser, C.; Schmidt, B. *J. Chem. Theory Comput.* **2024**, *20*, 3413–3419

FSSH-3 Hop Proposal Probability

FSSH-3

$$\boldsymbol{\rho}(t) = \left(\rho_{00}(t), \rho_{11}(t), \ldots, \rho_{N-1,N-1}(t)\right)^T$$

$$\frac{\boldsymbol{\rho}(t+\Delta t) - \boldsymbol{\rho}(t)}{\Delta t} = J(t, t+\Delta t)\boldsymbol{\rho}(t)$$

$\boldsymbol{y} = \boldsymbol{Jx}$ — the problem to solve

$\boldsymbol{J}_0 = \min_J \|\boldsymbol{y} - \boldsymbol{Jx}\|_2^2$ - solve the optimization problem

$\boldsymbol{J}_0 = (\boldsymbol{yx}^T)(\boldsymbol{xx}^T)^{-1}$ - the formal solution

$$P_{i \to j}^{FSSH-3} = \sigma\left(-\frac{\Delta\rho_{ii}(t)}{\rho_{ii}(t)}\right)\frac{\sigma(J_{j,i})}{\sum_k \sigma(J_{k,i})}, \forall j \neq i$$

$$P_{i \to i}^{FSSH-3} = 1 - \sigma\left(-\frac{\Delta\rho_{ii}(t)}{\rho_{ii}(t)}\right)$$

There are two options:

$\boldsymbol{x} = \boldsymbol{\rho}(t).$ $\boldsymbol{y} = \frac{\Delta\boldsymbol{\rho}}{\Delta t} = \frac{\boldsymbol{\rho}(t+\Delta t) - \boldsymbol{\rho}(t)}{\Delta t}$ Initial guess for $\boldsymbol{J} = \boldsymbol{0}$

$\boldsymbol{x} = \boldsymbol{\rho}(t).$ $\boldsymbol{y} = \boldsymbol{\rho}(t + \Delta t)$ Initial guess for $\boldsymbol{J} = \boldsymbol{I}$

dyn_control_params

The size of the vectorized density matrix in equations to determine hopping probabilities/fluxes
- 0: N elements - only populations; the matrices are overdetermined [default]
- 1: N^2 elements - first N elements are populations, then Re and Im parts of upper-triangular coherences
that is rho_{0,1}, rho_{0,2}, … rho_{0,N-1}, rho_{1,2}, … rho_{1,N-1}, … rho_{N-2,N-1}

- **fssh3_size_option**

The approach to determine the hopping probabilities:
- 0: based on master equation, rho(t+dt) = J * rho(t); J matrix contains hopping probabilities directly [default]
- 1: based on kinetic approach, drho/dt = J * rho; J matrix contains fluxes

- **fssh3_approach_option**

- **fssh3_dt** The time-step of the optimization procedure in the FSSH3 calculations. Default: 0.001

- **fssh3_max_steps** The maximal number of steps in the FSSH3 optimization step. Default: 1000

- **fssh3_err_tol** FSSH3 error tolerance. Default: 1e-7

MASH Hop Proposal Probability

1. Initialization of electronic amplitudes:

Initial conditions sampling algorithm:
1) Make N-1 uniformly distributed random cuts of the [0, 1] interval $\{0 < \xi_i < 1\}$. Sort them such that $\xi_{i+1} \geq \xi_i$
2) The population of i-th state is the distance between cuts: $p_i = \xi_i - \xi_{i-1}$. Find the maximal value and the index.
3) Swap the index of the target active state with the corresponding maximal-population index, do the same for the populations
4) The generated point (a vector of populations) would be considered belonging to the basin of the active state of interest
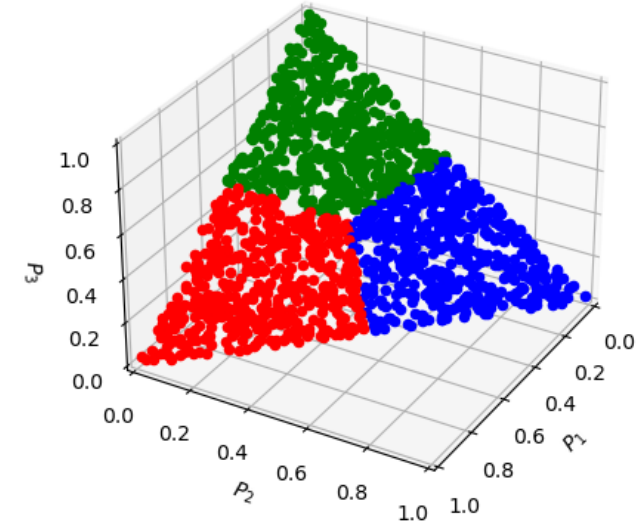
2. Hop proposal probability:

$$P_{*\to j} = 1, \exists j: \rho_{jj} = \max_i(\rho_{ii})$$

$$P_{*\to k} = 0, \forall k \neq j$$

Proposed hops to the states with the largest population

(1) Mannouch, J. R.; Richardson, J. O. A *JCP* **2023**, 158, 104111
(2) Runeson, J. E.; Manolopoulos, D. E. A *JCP* **2023**, 159, 094115.
(3) E. Runeson, J.; P. Fay, T.; E. Manolopoulos, D. *PCCP* **2024**, 26, 4929–4938.

3. Observables (population estimators):

$$P_n^{MASH,rep} = \alpha_N |c_n^{rep}|^2 + \beta_N$$

These are the SE populations

$$P_n^{SH,adi} = \frac{N_n}{N}$$ - works in adiabatic basis

$$P_n^{SH,dia}$$ - works if the adiabatic SH population is transformed according to Tempelaar

```
NSTATES = model_params["nstates"]

dyn_general = { "nsteps":2500, "ntraj":25, "nstates":NSTATES,
        "dt":10.0, "num_electronic_substeps":1, "isNBRA":0, "is_nbra":0,
        "progress_frequency":0.1, "which_adi_states":range(NSTATES), "which_dia_states":range(NSTATES),
        "mem_output_level":3,
        "properties_to_save":[ "timestep", "time", "q", "p", "f", "Cadi", "Cdia", "Epot_ave", "Ekin_ave", "Etot_ave",
        "se_pop_adi", "se_pop_dia", "sh_pop_adi", "sh_pop_dia", "mash_pop_adi", "mash_pop_dia"],
        "prefix":"adiabatic_md", "prefix2":"adiabatic_md"
        }
```

$$\alpha_N = \frac{N-1}{\sum_{k=1}^{N} 1/k - 1}; \beta_N = \frac{1-\alpha_N}{N}$$

Computing state populations in Libra

Diagonal elements of the density matrices $\boldsymbol{P}_{rep}$: $p_n^{SE,rep} = \boldsymbol{P}_{rep,n,n}$

$p_n^{SE,adi} = \left|c_{n,adi}\right|^2$ - adiabatic SE populations – "quantum" populations

$p_n^{SE,dia} = \left|c_{n,dia}\right|^2$ - diabatic SE populations – "quantum" populations

$$|\Psi(t)\rangle = |\boldsymbol{\psi}_{adi}(t)\rangle \boldsymbol{C}_{adi}(t) = |\boldsymbol{\psi}_{dia}(t)\rangle \boldsymbol{C}_{dia}(t) \qquad \boldsymbol{H}_{dia}\boldsymbol{U} = \boldsymbol{S}\boldsymbol{U}\boldsymbol{H}_{adi}$$

$$\boldsymbol{C}_{adi}\boldsymbol{C}_{adi}^+ = \boldsymbol{P}_{adi} \;\; \blacktriangleright \;\; \boldsymbol{P}_{dia} = \boldsymbol{U}^+\boldsymbol{S}\boldsymbol{P}_{adi}\boldsymbol{S}\boldsymbol{U}$$

$p_n^{SH,adi} = \frac{N_n}{N}$ - adiabatic SH populations – counting trajectories

$p_n^{SH,dia}$ - ???

This is a mixture of the SH populations and SE coherences

For each trajectory: $\boldsymbol{P}_{dia} = \boldsymbol{U}^+\boldsymbol{S}\widetilde{\boldsymbol{P}}_{adi}\boldsymbol{S}\boldsymbol{U}$

$$\tilde{P}_{adi,k,l} = \delta_{k,l}\delta_{k,a} + (1 - \delta_{k,l})c_k c_l^*$$

Active state index for the given trajectory

Tempelaar, R.; Reichman, D. R. JCP **2018**, *148*, 102309.
Bondarenko, A. S.; Tempelaar, R. JCP **2023**, *158*, 054117.

Hop Proposal Probability

Landau-Zener (LZ):

Hopping only at the gap minimum!

$$P_{i \to j}^{P} = \exp\left(-\frac{2\pi}{\hbar}\gamma^{LZ}\right)$$

$$\gamma^{LZ} = \frac{\left|H_{ij}^{dia}\right|^2}{\boldsymbol{v^T}\left(\nabla\left|H_{ii}^{dia} - H_{jj}^{dia}\right|\right)}$$

dyn_control_params

- **rep_lz**   The representation to compute LZ probabilities.
  Options:
  - 0: diabatic, Eq. 1 of the Belyaev-Lebedev paper, crossing point is determined by the sign change of the diabatic gap [default]
  - 1: adiabatic, Eq. 3 of the Belyaev-Lebedev paper, crossing point is determined by the sign change of the diabatic gap
  - 2: adiabatic, Eq. 3 of the Belyaev-Lebedev paper, crossing point is determined by the sign change of the NAC

(1) Tully, J. C. *J. Chem. Phys.* **1990**, 93, 1061, 1071
(2) Belyaev, A. K.; Lebedev, O. V. *Phys. Rev. A* **2011**, 84, 014701

Zhu-Nakamura (ZN):

Hopping only at the gap minimum!

$$a^2 = \frac{\hbar^2}{2\mu}\frac{\sqrt{\left|\boldsymbol{F}_i^T \boldsymbol{F}_j\right|}\left|\boldsymbol{F}_i - \boldsymbol{F}_j\right|}{\left(2H_{ij}^{dia}\right)^3}$$

$$b^2 = \left(E - E_i(\boldsymbol{R} = \boldsymbol{R}_c)\right)\frac{\left|\boldsymbol{F}_i - \boldsymbol{F}_j\right|}{\sqrt{\left|\boldsymbol{F}_i \boldsymbol{F}_j\right|}\left(2H_{ij}^{dia}\right)}$$

$$P_{i \to j}^{P} = \exp\left(-\frac{\pi}{4\sqrt{a^2}}\sqrt{\frac{2}{b^2 + \sqrt{\left|b^4 + sign(\boldsymbol{F}_i^T \boldsymbol{F}_j)\right|}}}\right)$$

Multidimensional version

$$\begin{cases} \frac{1}{\sqrt{\mu}}\left|\boldsymbol{F}_i - \boldsymbol{F}_j\right| \to \sqrt{\left(\boldsymbol{F}_i - \boldsymbol{F}_j\right)^T M^{-1}\left(\boldsymbol{F}_i - \boldsymbol{F}_j\right)} \\ \frac{1}{\sqrt{\mu}}\sqrt{\left|\boldsymbol{F}_i^T \boldsymbol{F}_j\right|} \to \sqrt{\left|\boldsymbol{F}_i^T M^{-1}\boldsymbol{F}_j\right|} \end{cases}$$

(1) Zhu, C., Nakamura, H., Re, N., Aquilanti, V., 1992. J. Chem. Phys. 97, 1892
(2) Hanasaki, K., Kanno, M., Niehaus, T.A., Kono, H., 2018. J. Chem. Phys. 149. 244117
(3) Yu, L., Xu, C., Lei, Y., Zhu, C., Wen, Z., 2014. Phys. Chem. Chem. Phys. 16. 25883.

Hop Acceptance Probabilities

- **hop_acceptance_algo**

Options:
- 0: accept all proposed hops [default]

$$P_{i \to f}^{A} = 1$$

- 10: based on adiabatic energy - accept only those hops that can obey the energy conservation with
    adiabatic potential energies
- 11: based on diabatic energy - same as 10, but we use diabatic potential energies

Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061

$$P_{i \to f}^{A} = \Theta\big(E_{kin} + E_f - E_f\big)$$

- 20: based on derivative coupling vectors - accept only those hops that can obey the energy conservation
    by rescaling nuclear velocities along the directions of derivative couplings for the quantum nuclear DOFs
- 21: based on difference of state-specific forces - same as 20, but the rescaling is done along the vector
    parallel to the difference of adiabatic forces on initial and target states

Prezhdo, O. V.; Duncan, W. R.; Prezhdo, V. V. *Prog. Surf. Sci.* **2009**, *84*, 30

$$P_{i \to f}^{A} = \min\left(1, exp\left(-\frac{\Delta E}{k_B T}\right)\right)$$

- 31: accept hops with the probability taken from the quantum Boltzmann distribution
- 32: accept hops with the probability taken from the classical Maxwell-Boltzmann distribution
- 33: accept hops with the probability taken from the updated quantum Boltzmann distribution (experimental)

Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107

$$P_{i \to f}^{A} = 1 - \left[\text{erf}\left(\left(\frac{\Delta E}{k_B T}\right)^{\frac{1}{2}}\right) - \sqrt{\frac{4}{\pi}\left(\frac{\Delta E}{k_B T}\right)^{\frac{1}{2}}} \exp\left(-\frac{\Delta E}{k_B T}\right) \right]$$

- 40: based on possibility to conserve energy using tcnbra_ekin variables (experimental for TC-NBRA)

$$P_{i \to f}^{A} = \Theta\big(E_{i(t+\Delta t)}^{tr}(t + \Delta t) + e_{kin,i}^{tr}(t + \Delta t) - e_{kin,j}^{tr}(t + \Delta t)\big)$$

Akimov, A. V. *J. Phys. Chem. Lett.* **2023**, *14*, 11673–11683

Momentum Rescaling

dyn_control_params

- **momenta_rescaling_algo**

$$P_n^{(j)} = P_n^{(i)} - \gamma t_{n,ij}$$

$$a_{ij} = \frac{1}{2} t_{ij}^T M^{-1} t_{ij}$$
$$b_{ij} = t_{ij}^T M^{-1} P^{(i)}$$
$$c_{ij} = E_i - E_j$$

$$\Delta_{ij} = b_{ij}^2 + 4a_{ij}c_{ij}$$

$\Delta_{ij} < 0$
Frustrated hop

$\Delta_{ij} \geq 0$
Accepted hop

Options:

 - 0: don't rescale [default]

 - 100: based on adiabatic energy, don't reverse on frustrated hops
 - 101: based on adiabatic energy, reverse on frustrated hops
 - 110: based on diabatic energy, don't reverse on frustrated hops
 - 111: based on diabatic energy, reverse on frustrated hops

 - 200: along derivative coupling vectors, don't reverse on frustrated hops
 - 201: along derivative coupling vectors, reverse on frustrated hops
 - 210: along difference of state-specific forces, don't reverse on frustrated hops
 - 211: along difference of state-specific forces, reverse on frustrated hops

 - 40: does not rescale velocities, but rescales tcnbra_ekin variables

Reversal or not

$b_{ij} < 0$
$$\gamma_{ij} = \frac{b_{ij} + \sqrt{\Delta_{ij}}}{2a_{ij}}$$

$b_{ij} \geq 0$
$$\gamma_{ij} = \frac{b_{ij} - \sqrt{\Delta_{ij}}}{2a_{ij}}$$

$$t_{n,ij} = D_{adi,ij}^n$$

$$t_{n,ij} = F_{adi,i}^n - F_{adi,j}^n$$

TC-NBRA rescaling of effective kinetic energy:

$$e_{kin}^{tr}(t) \rightarrow e_{kin}^{tr}(t + \Delta t) = e_{kin}^{tr}(t) + E_{i(t)} - E_{i(t+\Delta t)}$$

Akimov, A. V. *J. Phys. Chem. Lett.* **2023**, *14*, 11673–11683

dyn_control_params

- **use_Jasper_Truhlar_criterion**
Options:
- 0: don't use this criterion (naive handling)
- 1: use it [default]

use_Jasper_Truhlar_criterion = 1

$\Delta_{ij} < 0$
Frustrated hop

the velocities are reversed along the direction $\boldsymbol{D}_{adi,a,j}$ if
a) $\left(\boldsymbol{F}_a^T \boldsymbol{D}_{aj}\right)\left(\boldsymbol{F}_j^T \boldsymbol{D}_{aj}\right) < 0$
b) $\left(\boldsymbol{v}^T \boldsymbol{D}_{aj}\right)\left(\boldsymbol{F}_j^T \boldsymbol{D}_{aj}\right) < 0$
where a - is the active state index;
Only in effect, if
`momenta_rescaling_algo == 201`

Reversal

Otherwise

No Reversal

use_Jasper_Truhlar_criterion = 0

$\Delta_{ij} < 0$
Frustrated hop
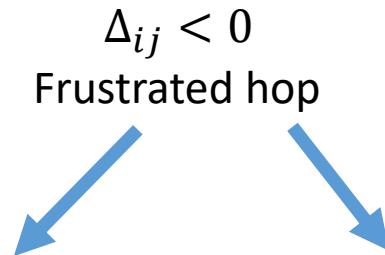
No reversal for momenta_rescaling_algo: 100, 110, 200, 210

Reversal for momenta_rescaling_algo: 101, 111, 201, 211

Decoherence Options

dyn_control_params

- **decoherence_algo**

  - [-1]: no decoherence [default]
    - 0: SDM and alike
    - 1: instantaneous decoherence options (ID-S, ID-A, ID-C, ID-F)
    - 2: AFSSH
    - 3: BCSH of Linjun Wang
    - 4: MF-SD of Bedard-Hearn, Larsen, Schwartz
    - 5: SHXF of Min
    - 6: MQCXF
    - 7: DISH, rev2023
    - 8: diabatic IDA, experimental

DISH_rev2023: Zhang, Q.; Shao, X.; Li, W.; Mi, W.; Pavanello, M.; Akimov, A. V. *J. Phys.: Condens. Matter* **2024**, *36*, 385901.

SHXF and MQCXF:
Ha, J.-K.; Lee, I. S.; Min, S. K. *J. Phys. Chem. Lett.* **2018**, 9, 1097
Han, D.; Akimov, A.V. *J. Chem. Theory Comput.* **2024,** 20, 5022–5042

SDM: Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114.

mSDM: Smith, B.; Akimov, A. V. *J. Chem. Phys.* **2019**, *151*, 124107.

ID-A: Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. *J. Chem. Phys.* **2013**, *138*, 224111.

ID-F: Zhang, Q.; Shao, X.; Li, W.; Mi, W.; Pavanello, M.; Akimov, A. V. *J. Phys.: Condens. Matter* **2024**, *36*, 385901.

A-FSSH:
Landry, B. R.; Subotnik, J. E. *The Journal of Chemical Physics* **2012**, *137*, 22A513.
Jain, A.; Herman, M. F.; Ouyang, W.; Subotnik, J. E. *The Journal of Chemical Physics* **2015**, *143*, 134106.
Jain, A.; Alguire, E.; Subotnik, J. E. *J. Chem. Theory Comput.* **2016**, *12*, 5256–5268.

BCSH: Xu, J.; Wang, L. *J. Chem. Phys.* **2019**, 150, 164101.

MF-SD: Bedard-Hearn, M. J.; Larsen, R. E.; Schwartz, B. J. *J. Chem. Phys.* **2005**, 123, 234106.

DISH:
Jaeger, H. M.; Fischer, S.; Prezhdo, O. V. *J. Chem. Phys.* **2012**, 137, 22A545
Akimov, A. V. *J. Chem. Phys.* **2021**, 155, 134106.

Decoherence: SDM and ID

SDM   Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114.

gradually change the amplitudes

$$C_i' = C_i \exp\left(-\frac{\Delta t}{\tau_{if}}\right), \forall i \neq f \qquad C_f' = C_f \sqrt{\frac{1 - \sum_{i \neq f}|C_i'|^2}{|C_f|^2}}$$
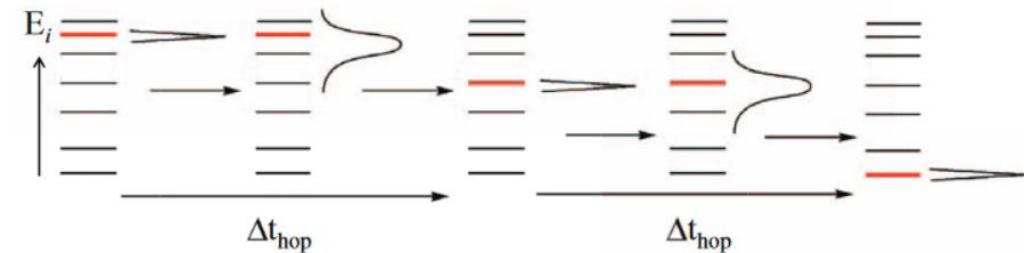
dyn_control_params

- **sdm_norm_tolerance**

  Corresponds to the "tol" parameter in the sdm function. It controls how much the norm of the old state can be larger than 1.0 before the code stops with the error message [default: 0.0]

  Note: only matters if decoherence_algo == 0

ID-A   Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. *J. Chem. Phys.* **2013**, *138*, 224111.

Wavefunction reduction

$$C_f = 1, C_i = 0, \forall i \neq f$$

dyn_control_params

- **collapse_option**   How to collapse wavefunction amplitudes in the decoherence schemes:

  - 0: by rescaling the magnitude of the amplitude vector elements, but preserving "phase" [default]
  - 1: by resetting the amplitudes to 1.0+0.0j. This option changes phase

- **instantaneous_decoherence_variant**

  Option to control the instantaneous decoherence methodology, only used with decoherence_algo == 1
  - 0: ID-S – on the successful hop
  - 1: ID-A [default] - if the proposed hop is not successful, we project back to the initial state if the proposed hop is accepted - we project onto that state
  - 2: ID-C - consistent ID - an experimental algorithm
  - 3: ID-A, new: if the proposed hop is not successful, we project out the proposed states if the proposed hop is accepted - we project onto that state
  - 4: ID-F, new: if the proposed hop is not successful, we project out the proposed states but we don't do anything if the hop is successful

Zhang, Q.; Shao, X.; Li, W.; Mi, W.; Pavanello, M.; Akimov, A. V. *J. Phys.: Condens. Matter* **2024**, *36*, 385901.

Decoherence: A-FSSH

(1) Landry, B. R.; Subotnik, J. E. *The Journal of Chemical Physics* **2012**, *137*, 22A513.
(2) Jain, A.; Herman, M. F.; Ouyang, W.; Subotnik, J. E. *The Journal of Chemical Physics* **2015**, *143*, 134106.
(3) Jain, A.; Alguire, E.; Subotnik, J. E. *J. Chem. Theory Comput.* **2016**, *12*, 5256–5268.

Propagate extra set of variables

$$\delta\vec{R} = \mathrm{Tr}_N[(\vec{R} - \vec{R}_{\mathrm{SH}})\rho]$$

$$\delta\vec{P} = \mathrm{Tr}_N[(\vec{P} - \vec{P}_{\mathrm{SH}})\rho]$$

These variables define the rates for wavefunction collapse

$$\frac{1}{\tau_d^{n\lambda}} = -\frac{\frac{d}{dt}|\sigma_{n\lambda}|}{|\sigma_{n\lambda}|}$$

$$\simeq \frac{\delta\vec{F}_{nn}\cdot(\delta\vec{R}_{nn} - \delta\vec{R}_{\lambda\lambda})}{2\hbar} - \frac{2|\vec{F}_{\lambda n}\cdot(\delta\vec{R}_{nn} - \delta\vec{R}_{\lambda\lambda})|}{\hbar}$$

$$\frac{d}{dt}\delta\vec{R}_{jk} = \left[-\frac{i}{\hbar}\mathbf{V} - \mathbf{T}, \delta\vec{R}\right]_{jk} + \frac{\delta\vec{P}_{jk}}{\vec{m}}$$

$$\frac{d}{dt}\delta\vec{P}_{jk} = \left[-\frac{i}{\hbar}\mathbf{V} - \mathbf{T}, \delta\vec{P}\right]_{jk} + \frac{1}{2}(\delta\vec{F}\sigma + \sigma\delta\vec{F})_{jk}$$

5. Compute the probability to collapse the amplitudes for the state $n \neq i$ (where i is the active surface) as

$$\gamma_n^{collapse} = dt\left(\frac{(F_{nn} - F_{ii})\delta x_{nn}}{2\hbar} - \frac{2|F_{in}\delta x_{nn}|}{\hbar}\right). \quad (A10)$$

Also compute the probability to reset the moments as

$$\gamma_n^{reset} = -dt\left(\frac{(F_{nn} - F_{ii})\delta x_{nn}}{2\hbar}\right). \quad (A11)$$

Decoherence: DISH

University at Buffalo
The State University of New York

Hops are the consequences of decoherence

1. Coherence interval for state i: $\frac{1}{\tau_i} = \sum_{j \neq i} \rho_{jj} r_{ij}$; $\rho_{jj} = |c_j|^2$; r_{ij} - pure dephasing time for the pair of states i and j

2. The time at which decoherence event takes place is distributed exponentially: $P(t) \sim \exp\left(-\frac{t}{\tau_i}\right)$, which corresponds to the Poisson distribution of the number of events to take place in a given time interval.

3. At decoherence event: coherent superposition $\Psi = \sum_i c_i \psi_i$ is projected in the following way:

   - with the probability $|c_i|^2$, the superposition is collapsed on the pure state ψ_i (set $c_i = 1$, set $c_j = 0, \forall j \neq i$)
       -- but do this only if the hop to this state + velocity rescaling associated with this transition is possible
   - with the probability $1 - |c_i|^2$, the state ψ_i is projected out from the superposition (reset $c_i = 0$, renormalize others)

What if the decohered state is the active state?
 - If we collapse on this state – fine;
 - If we project out the state from the superposition – the SE and SH
populations become inconsistent (e.g. say the ground state is active, but $c_0 = 0$)

   if the decohered state turns out to be the active one, we project the corresponding amplitude out only if a successful hop to any other state can occur. The hop to any other state j is proposed with the probability $|c_j|^2$ and if the hop into this state is successful, the superposition is collaped onto this new state and the hop occurs.

Note: DISH is invoked by tsh_method==5 (hopping scheme) and decoherence_algo==-1 (no additional decoherence)

DISH

Initialize "coherence time" for each state $t_i = 0, \forall i$

Advance "coherence time": $t_i = t_i + \Delta t, \forall i$

Initialize set of "decohering" states: $D = \emptyset$
For all states i:
- compute coherence interval for this state $\tau_i^{-1} = \sum_{j \neq i} \rho_{jj}(t) \tau_{ij}^{-1}$
  - If $t_i \geq T[\tau_i]$, add i to set D: $D = D \cup \{i\}$

int dish_decoherence_event_option;
- 0 – direct compare
- 1 - Poisson

$D \neq \emptyset$

No (B)

Continue coherent evolution:
$$c(t + \Delta t) = \exp\left(-\frac{iH}{\hbar}\Delta t\right) c(t)$$

Yes (A)

- Select a single decohered state, i, our of the set randomly
- reset $t_i = 0$
- don't change the variables for other states
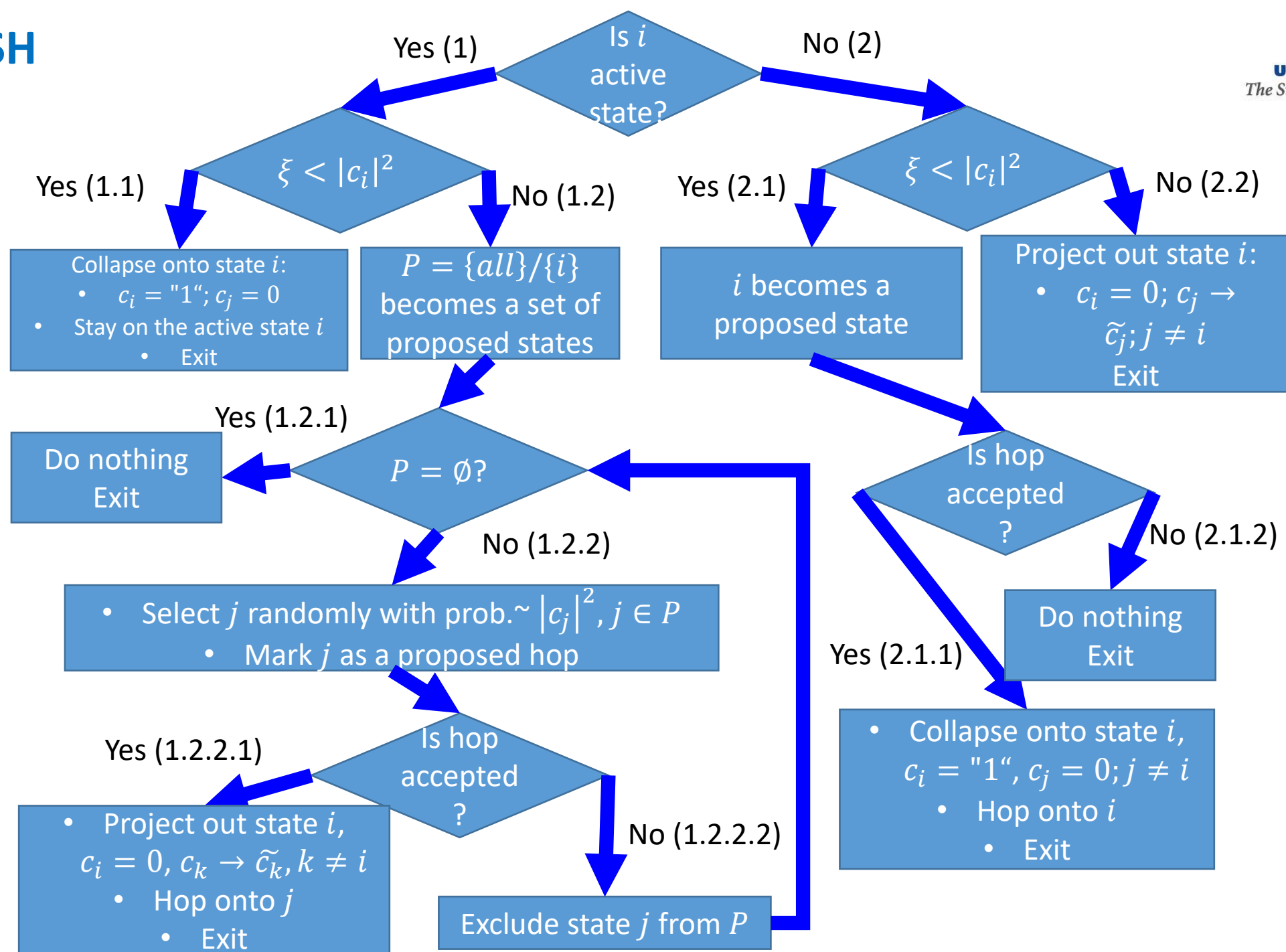
Yes (1)

Is i active state?

No (2)

$\cdots$

$\cdots$

Finish scheme in panel (b)

DISH

University at Buffalo
The State University of New York

Is i active state?

Yes (1)

No (2)

$\xi < |c_i|^2$

Yes (1.1)

No (1.2)

$\xi < |c_i|^2$

Yes (2.1)

No (2.2)

Collapse onto state i:
- $c_i = $ "1"; $c_j = 0$
- Stay on the active state i
  - Exit

$P = \{all\}/\{i\}$ becomes a set of proposed states

i becomes a proposed state

Project out state i:
- $c_i = 0; c_j \to \widetilde{c_j}; j \neq i$

Exit

Yes (1.2.1)

Do nothing
Exit

$P = \emptyset$?

No (1.2.2)

Is hop accepted?

No (2.1.2)

Do nothing
Exit

- Select j randomly with prob.~ $|c_j|^2, j \in P$
  - Mark j as a proposed hop

Yes (2.1.1)

Yes (1.2.2.1)

Is hop accepted?

No (1.2.2.2)

Exclude state j from P

- Project out state i,
  $c_i = 0, c_k \to \widetilde{c_k}, k \neq i$
  - Hop onto j
    - Exit

- Collapse onto state i,
  $c_i = $ "1", $c_j = 0; j \neq i$
  - Hop onto i
    - Exit

Decoherence: DISH_rev2023

Another problem:

In the limit of infinite decoherence time (overcoherent, or FSSH limit), no decoherence events would be determined and hence no hops would be happening.

In this situation, the TD-SE populations could indicate the population transfer, but the TSH populations won't change.

Hence, the new approach (DISH revision of 2023) simply applies the wavefunction collapse/projection out correction to the TD-SE wavefunction, similar to IDA or SDM, except that if a state "i" is decided to experience a decoherence event, the wavefunction is collapsed onto this state with the probability of $|c_i|^2$ and with the probability $1 - |c_i|^2$ the state is projected out from the coherent superposition. In this case, it doesn't matter if the decoherent state is an active state or not.

Projector operator introduced in the original DISH paper of Jaeger et al.:

DISH_rev2023 only applies this operator to the electronic part (regardless whether the projection can be consistent with the energy conservation, which is already broken in the NBRA anyways)

$$\hat{L}_i = \begin{cases} \dfrac{1}{|c_i|^2} |\psi_i\rangle\langle\psi_i|, \xi_i < |c_i|^2 \\ \dfrac{1}{1 - |c_i|^2} (\hat{I} - |\psi_i\rangle\langle\psi_i|), \xi_i \geq |c_i|^2 \end{cases}$$

Decoherence: BCSH and MF-SD

BCSH

In this approach, decoherence correction is interpreted as a way to enforce the self-consistency of the TD-SE with the quantum-classical trajectories rather than as a common view of a decay of overlap of wavepackets moving on different PE surfaces. Namely:

• at every nonadiabatic interaction region, there is a possibility of the wavepacket branching into reflecting and transmitting wavepackets on different surfaces.
• the idea is to eliminate the wavepackets that go in the opposite direction with the main wavepacket on the active state.
• the correction is applied only at the reflection points (not the reflection of active trajectory, but the reflection of the wavepacket on other surfaces in comparison to that of the active surface)
• the reflection is judged as:
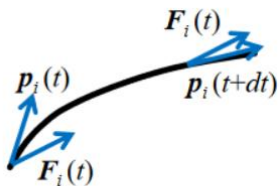
no reflection

$$\text{sign}\left\{ \boldsymbol{F}_i(t) \cdot \boldsymbol{p}_i(t) \right\} = \text{sign}\left\{ \boldsymbol{F}_i(t) \cdot \boldsymbol{p}_i(t+dt) \right\}$$
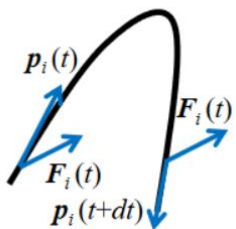
reflection

$$\text{sign}\left\{ \boldsymbol{F}_i(t) \cdot \boldsymbol{p}_i(t) \right\} = -\text{sign}\left\{ \boldsymbol{F}_i(t) \cdot \boldsymbol{p}_i(t+dt) \right\}$$

MF-SD

This method is essentially like Ehrenfest,

but there is always a probability to collapse the coherent superposition to a pure state.

The probability of such a collapse is given by the quantum amplitude of the state and by the decoherence time to collapse onto a particular state k.

$$P_i = \frac{\rho_{ii}}{\tau_i} \Delta t$$

The decoherence time is given by

$$\tau_i^{-2} = \frac{1}{4\hbar^2} (\boldsymbol{F}_{MF} - \boldsymbol{F}_i)^T \alpha^{-1} (\boldsymbol{F}_{MF} - \boldsymbol{F}_i)$$

Decoherence: XFSH and MQCXF

$$i\hbar \frac{d}{dt}|\Phi_{\boldsymbol{R}}(t)\rangle = \left[\widehat{H}_{BO}(\boldsymbol{R}(t)) + \widehat{H}_{XF}(\boldsymbol{R}, t)\right]|\Phi_{\boldsymbol{R}}(t)\rangle$$

$$\dot{\boldsymbol{P}} = \boldsymbol{F}$$

$$H_{XF} = -\sum_{\nu}\frac{i\hbar\mathcal{P}_{\nu}}{M_{\nu}}\cdot(\nabla_{\nu}\boldsymbol{CC}^{\dagger} + \boldsymbol{C}\nabla_{\nu}\boldsymbol{C}^{\dagger}) = \sum_{\nu}\frac{\mathcal{P}_{\nu}}{M_{\nu}}\cdot(\boldsymbol{\phi}_{\nu}\boldsymbol{CC}^{\dagger} - \boldsymbol{CC}^{\dagger}\boldsymbol{\phi}_{\nu}) = -\sum_{\nu}\frac{\mathcal{P}_{\nu}}{M_{\nu}}\cdot(\boldsymbol{\rho}\boldsymbol{\phi}_{\nu} - \boldsymbol{\phi}_{\nu}\boldsymbol{\rho})$$

$$\boldsymbol{F}(\boldsymbol{R}, t) = \boldsymbol{F}^{MF}(\boldsymbol{R}, t) + \boldsymbol{F}^{XF}(\boldsymbol{R}, t)$$

$$\boldsymbol{F}^{MF}(\boldsymbol{R}, t) = -\langle\Phi_{\boldsymbol{R}}(t)|\nabla\widehat{H}_{BO}|\Phi_{\boldsymbol{R}}(t)\rangle$$

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

$$F_{\nu}^{XF} = -\frac{i}{\hbar}\sum_{a,b}\rho_{aa}\rho_{bb}\sum_{\mu}(\phi_{\nu,bb} - \phi_{\nu,aa})(\phi_{\mu,bb} - \phi_{\mu,aa})\frac{\mathcal{P}_{\mu}}{M_{\mu}}$$

$$C_{j}(\boldsymbol{R}) = |C_{j}(\boldsymbol{R})|\exp(i\theta_{j}(\boldsymbol{R})/\hbar) \qquad \nabla_{\nu}\theta_{j} = \frac{i}{\hbar}\phi_{j\nu}$$

$$\mathcal{P}(\boldsymbol{R}, t) = -i\hbar\frac{\nabla|\chi(\boldsymbol{R},t)|}{|\chi(\boldsymbol{R},t)|} = -i\hbar\frac{\nabla|\chi|^{2}}{2|\chi|^{2}}$$

$$= \frac{i\hbar}{2}\sigma^{-2}(\boldsymbol{R} - \langle\boldsymbol{R}\rangle) \approx \frac{i\hbar}{2}\sigma^{-2}\sum_{i}\rho_{ii}(\boldsymbol{R}_{a} - \boldsymbol{R}_{i})$$

Both $\widehat{H}_{BO}(\boldsymbol{R}(t))$ and $\widehat{H}_{XF}(\boldsymbol{R}, t)$ are used   MFXF, aka EhXF   Only $\boldsymbol{F}^{MF}(\boldsymbol{R}, t)$

Both $\widehat{H}_{BO}(\boldsymbol{R}(t))$ and $\widehat{H}_{XF}(\boldsymbol{R}, t)$ are used   SHXF (DISH-XF)   Adiabatic forces of the active state

Both $\widehat{H}_{BO}(\boldsymbol{R}(t))$ and $\widehat{H}_{XF}(\boldsymbol{R}, t)$ are used   MQCXF   Both $\boldsymbol{F}^{MF}(\boldsymbol{R}, t)$ and $\boldsymbol{F}^{XF}(\boldsymbol{R}, t)$ are used

Decoherence times

University at Buffalo — The State University of New York

DISH

Decoherence interval

$$\tau_i^{-1} = \sum_{j \neq i} P_{jj} \tau_{ij}^{-1}$$

Jaeger, H. M.; Fischer, S.; Prezhdo, O. V. *J. Chem. Phys.* **2012**, *137*, 22A545

SDM/EDC

Granucci, G.; Persico, M. *JCP* **2007**, *126*, 134114.

$$\tau_{ij}^{EDC} = \frac{\hbar}{|E_i - E_j|}\left(C + \frac{\epsilon}{E_{kin}}\right)$$

dyn_control_params

- **decoherence_C_param**
- **decoherence_eps_param**

mSDM

$$\tau_{ij}^{-1} = \sqrt{\frac{5\langle \delta E_{ij}^2 \rangle}{12\hbar^2}}$$

Akimov, A. V.; Prezhdo, O. V. *JPCL*, **2013**, *4*, 3857
Smith, B.; Akimov, A. V. *JCP* **2019**, 151, 124107

dyn_control_params

- **decoherence_times_type**

  - [-1]: set all dephasing rates to zero [default]
  - 0: use the rates read out from the input
  - 1: use the energy-based decoherence method (EDC)
  - 2: Schwartz - mean-field Force-based decoherence
  - 3: Schwartz - pair-wise-based decoherences

Phase-informed Decoherence times

Sifain, A. E.; Wang, L.; Tretiak, S.; Prezhdo, O. V.

$$\tau_{ij}^{-1,PI} = \tau_{ij}^{-1}\frac{|E_i - E_j|}{\langle |E_i - E_j|\rangle}$$

dyn_control_params

- **dephasing_informed**
  - 0: don't apply [default]
  - 1: use it

MF-SD

Bedard-Hearn, M. J.; Larsen, R. E.; Schwartz, B. J. *JCP* **2005**, *123*, 234106.

$$\tau_i^{-2} = \frac{1}{4\hbar^2}(\boldsymbol{F}_{MF} - \boldsymbol{F}_i)^T \alpha^{-1}(\boldsymbol{F}_{MF} - \boldsymbol{F}_i)$$

dyn_control_params

- **schwartz_decoherence_inv_alpha**

$$\tau_{ij}^{-2} = \frac{1}{\hbar^2}(\boldsymbol{F}_i - \boldsymbol{F}_j)^T \alpha^{-1}(\boldsymbol{F}_i - \boldsymbol{F}_j)$$

Independent stochastic pairwise decoherence (**ISPD**)

Esch, M. P.; Levine, B. G. *JCP* **2020**, *152*, 234105.

Other ways of computing Decoherence times

2001, Hack, Truhlar

$$\frac{1}{\tau_{ij}^{NDM}} = \frac{\hbar}{\left|H_{ii}^{dia} - H_{jj}^{dia}\right|}\frac{E_{tot}}{E_{vib}}$$

Natural decay of mixing

Hack, M.D., Truhlar, D.G., **2001**, *JCP* 114, 9305.

2004, Zhu, Jasper, Truhlar

$$\tau_{ij}^{SCDM} = \frac{\hbar}{\left|H_{ii}^{dia} - H_{jj}^{dia}\right|} + \frac{\hbar}{4E_{vib}}$$

Self-consistent decay of mixing

Zhu, C., Jasper, A.W., Truhlar, D.G., **2004**, *JCP* 120, 5543.

2005, Jasper, Truhlar

$$\chi_a = \frac{1}{(2\pi\sigma_a^2)^{1/4}}\exp\left(-\frac{(x-x_a)^2}{4\sigma_a^2} - \frac{iP_a x}{\hbar}\right) \Rightarrow O_{ab}(t) = \langle\chi_a|\chi_b\rangle \Rightarrow \dot{O}_{ab} = -k_{ab}O_{ab} \Rightarrow$$

$$\frac{1}{\tau_{ab}} = k_{ab} = \frac{(x_a - x_b)(P_a - P_b)}{2m(\sigma_a^2 + \sigma_b^2)} + \frac{2\sigma_a^2\sigma_b^2(P_a - P_b)(F_a - F_b)}{\hbar^2(\sigma_a^2 + \sigma_b^2)}$$

Classical GWP center motion, etc.

$$\frac{1}{\tau_{ab}} = k_{ab} = \frac{\pi}{2}\frac{|F_a - F_b|}{|\bar{P}|} + \sqrt{\frac{(P_a - P_b)^2|E_a - E_b|}{4m\hbar^2\pi^2} + \left(\frac{\pi}{2}\frac{|F_a - F_b|}{|\bar{P}|}\right)^2}$$

$$\bar{P} = \frac{P_a + P_b}{2}$$

Jasper, A.W., Truhlar, D.G., **2005**, *JCP* 123, 064103

Parallel surfaces

$$\tau_{ab}^{Truhlar} = \frac{\hbar}{|E_a - E_b|}\sqrt{\frac{|\bar{P}|}{|P_a - P_b|}}$$

2006, Larsen, Bedard-Hearn, Schwartz

$$\frac{1}{\tau_i^{BLS,}} = \sqrt{\frac{1}{4\hbar^2}(F^{MF} - F_i)^T A^{-1}(F^{MF} - F_i)}$$

Larsen, R.E., Bedard-Hearn, M.J., Schwartz, B.J., **2006**, *JPCB* 110, 20055.

2007, Granucci, Persico

$$\tau_{ij}^{SDM} = \frac{\hbar}{|E_i - E_j|}\left(1 + \frac{C}{E_{kin}}\right)$$

Simplified decay of mixing

Granucci, G., Persico, M., **2007**, *JCP*, 126, 134114

Other ways of computing Decoherence times

2008, Cheng, Truhlar, et al

$$\tau_{ij}^{SCDM\prime} = \frac{C_1 \pi \hbar}{\left| H_{ii}^{dia} - H_{jj}^{dia} \right|} + \frac{C_2 \hbar}{4 E_{vib}}$$

2-parameters self-consistent decay of mixing

Cheng, S.C., Zhu, C., Liang, K.K., Lin, S.H., Truhlar, D.G., **2008** *JCP* 129. 024112

2011, Shenvi, Subotnik, Yang

Exclude the momentum difference terms

Shenvi, N., Subotnik, J.E., Yang, W., **2011**, *JCP* 134. 144102.

$$\chi_a = \left(\frac{2 Re[\alpha_a]}{\pi} \right)^{1/4} \exp\left(-\alpha(x - x_a)^2 + \frac{i P_a x}{\hbar} \right)$$

$$|\sigma_{ij}| = \left| \frac{Re[2\alpha_i]^{1/4} Re[2\alpha_j]^{1/4}}{(\alpha_i + \alpha_j^*)^{1/2}} \right| \exp\left(-Re\left[\frac{\alpha_i \alpha_j^*(x_i - x_j)^2}{\alpha_i + \alpha_j^*} \right] \right)$$

$$\frac{1}{\tau_{ij}^{SSY}} = -\frac{1}{|\sigma_{ij}|} \frac{d|\sigma_{ij}|}{dt} = Re\left[\frac{\alpha_i \alpha_j^*(x_i - x_j)^2}{\alpha_i + \alpha_j^*} (\dot{x}_i - \dot{x}_j) \right]$$

2012, Jaeger, Fisher, Prezhdo
DISH

$$\frac{1}{\tau_i^{DISH}} = \sum_{j \neq i} k_{ij}^{deph} |c_j|^2$$

Jaeger, H.M., Fischer, S., Prezhdo, O.V., **2012**, *JCP* 137. 22A545.

2013, Akimov, Prezhdo

$$k_{ij}^{deph} = \frac{1}{\hbar} \sqrt{\frac{5}{12} \langle \delta^2 E_{ij} \rangle}$$

So: $$\frac{1}{\tau_0^{DISH}} = \frac{|c_1|^2}{\hbar} \sqrt{\frac{5}{12} \langle \delta^2 E_{01} \rangle}$$

Akimov, A.V., Prezhdo, O.V., **2013**, *JPCL* 4, 3857.

2017, Gu and Franco
As a purity decay rate

Gu, B., Franco, I., **2017**, *JPCL* 8, 4289.
Gu, B., Franco, I., **2018**, *JPCL* 9, 773

$$\sigma(t) = Tr_S\{\rho\} = \sum_i p_i |i\rangle\langle i|$$

$$P(t) = Tr_S\{\sigma^2(t)\} = \exp\left(-\frac{t^2}{\tau_d^2} \right)$$

$$\tau_d = \frac{\hbar}{\sqrt{2 \sum_{ab} \Delta_{ab}^S \times \Delta_{ab}^B}}$$

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB} \qquad \hat{H}_{SB} = \sum_a \hat{S}_a \otimes \hat{B}_a$$

$$\Delta_{ab}^X = \langle \hat{X}_a \hat{X}_b \rangle - \langle \hat{X}_a \rangle \langle \hat{X}_b \rangle, X = S, B$$

For a 2-level system with constant diabatic coupling = pure dephasing limit:

$$\frac{1}{k^{deph}} = \frac{\hbar}{|c_0||c_1| \sqrt{2 \langle \delta^2 E_{01} \rangle}}$$

So: $$\frac{1}{\tau_d^{Gu-Franco}} = \frac{|c_0||c_1|}{\hbar} \sqrt{2 \langle \delta^2 E_{01} \rangle}$$

Other ways of computing Decoherence times

$$k_{ij}^{deph} = \frac{1}{\hbar}\sqrt{\frac{5}{12}\langle \delta^2 E_{ij}\rangle}$$

is a problematic at the points of zero gap (where coherence times should be infinite)

2019, Sifain, Wang, Tretiak, Prezhdo

Dephasing-informed correction

Sifain, A.E., Wang, L., Tretiak, S., Prezhdo, O.V., **2019**, *JCP* 150. 194104.

$$k_{ij}^{deph,corr}(t) = k_{ij}^{deph}\frac{|E_i(t) - E_j(t)|}{\langle|E_i - E_j|\rangle}$$

2020, Esch, Levine

$$\frac{1}{\tau_{ij}^{Esch-Levine}} = \sqrt{\frac{1}{4\hbar^2}(\boldsymbol{F}_i - \boldsymbol{F}_j)^T A^{-1}(\boldsymbol{F}_i - \boldsymbol{F}_j)}$$

Pairwise decoherence scheme

2021, Vindel-Zandbergen et al.

In the context of exact factorization approach

Vindel-Zandbergen, P., Ibele, L.M., Ha, J.-K., et al., **2021** *JCTC* 17, 3852.

$$\tau_i^{SHXF,-1} = \sum_j \boldsymbol{Q}^T M^{-1}(\boldsymbol{F}_i - \boldsymbol{F}_j)|c_j|^2$$

$$\boldsymbol{Q} = -\hbar\frac{\nabla|\chi|}{|\chi|}$$

Phase corrections

2011, Shenvi-Subotnik-Yang int do_ssy

A Gaussian $g_n(x)$ moving on the surface n would acquire an additional phase with respect to Gaussian $g_m(x)$ moving on the surface m such that: $\frac{g_m(x=x_n(t))}{g_n(x=x_n(t))} = \exp(\Delta\phi) = \exp(i\hbar t\, \boldsymbol{P}_n^T M^{-1}(\boldsymbol{P}_m - \boldsymbol{P}_n))$.

Shenvi, N., Subotnik, J.E., Yang, W., 2011. J. Chem. Phys. 135. 024101.

Such a phase difference can also be acquired if the effective Hamiltonian used in the TD-SE (coherent dynamics) is constructed

as: $H(state\ n\ is\ active) = \begin{pmatrix} -\boldsymbol{P}_n^T M^{-1}\boldsymbol{P}_n & -i\hbar\boldsymbol{P}_n^T \boldsymbol{d}_{nm} \\ i\hbar\boldsymbol{P}_n^T \boldsymbol{d}_{nm} & -\boldsymbol{P}_n^T M^{-1}\boldsymbol{P}_m \end{pmatrix}$

$E_n + \frac{1}{2}\boldsymbol{P}_n^T M^{-1}\boldsymbol{P}_n = E_m + \frac{1}{2}\boldsymbol{P}_m^T M^{-1}\boldsymbol{P}_m.$

2019, Miao, Subotnik: Generalization to multiple states:

Miao, G., Subotnik, J., 2019. J. Phys. Chem. A 123, 5428.

$$H_{ij}(state\ n\ is\ active) = -\boldsymbol{P}_n^T M^{-1}\boldsymbol{P}_i\delta_{ij} - i\hbar\boldsymbol{P}_n^T M^{-1}\boldsymbol{D}_{ij}$$

$$\boldsymbol{P}_n = \begin{cases} sign(\boldsymbol{P})\sqrt{\boldsymbol{P}^T\boldsymbol{P} + 2m(E_i(\boldsymbol{R}) - E_n(\boldsymbol{R}))}, if\ \boldsymbol{P}^T\boldsymbol{P} + 2m(E_i(\boldsymbol{R}) - E_n(\boldsymbol{R})) \geq 0 \\ 0, otherwise \end{cases}$$

2016, Zhu: in terms of QCLE

rep_tdse = 3;
electronic_integrator=0

rep_tdse = 3;
electronic_integrator=1

$i\hbar\frac{d\rho_{nm}(\boldsymbol{R},\boldsymbol{P})}{dt} = \sum_i [[E_n\delta_{ni} - i\hbar d_{ni}]\rho_{im} - \rho_{ni}[E_m\delta_{im} - i\hbar d_{im}]]$

$= (E_n - E_m)\rho_{nm} - i\hbar\sum_i [\rho_{im}d_{ni} - \rho_{ni}d_{im}]$
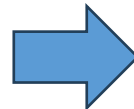
$i\hbar\frac{d\rho_{nm}}{dt}$

$= 2(\sqrt{E - E_m} - \sqrt{E - E_n})\sqrt{E - E_{eff}}\rho_{nm} - i\hbar\sum_i [\rho_{im}d_{ni} - \rho_{ni}d_{im}]$

$E_{eff} = \sum_i \rho_{ii}E_i$

Zhu, C., 2016. Sci. Rep. 6. 24198.