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CyberTraining: Modeling Quantum Dynamics of Excited States in Materials in the Era of Machine Learning, 2026

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https://compchem-cybertraining.github.io/Cyber_Training_Workshop_2026/

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Part 4: Algorithms and Methods for NA-MD

The general NA-MD workflow

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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

$$\hat{H}_{el}\psi_i = E_i\psi_i$$

analytical models or electronic structure codes

Non-adiabatic Couplings

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

Integrate Coherent Electronic Dynamics

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

NBRA

Decoherence 1

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

as in SDM

Proposed Hops Decoherence 2

$$P_{i\rightarrow j} = \Delta t * Re\left(\frac{2\frac{p}{m}d_{ij}c_i^* c_j}{c_i^* c_i}\right)$$

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

NAC: Hammes-Schiffer, S.; Tully, J. C. *JCP* **1994**, *101*, 4657

Phase tracking: Akimov, A. V. *JPCL* **2018** 9, 6096

Local Diabatization: Granucci, G.; Persico, M.; Toniolo, A. *JCP* **2001**, *114*, 10608; Plasser, F.; Granucci, G.; Pittner, J. et al. *JCP* **2012**, 137, 22A514; Shakiba, M.; Akimov, A. V. *TCA* **2023**, 142, 68

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Part 4.1: Integrating Nuclear EOM

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Options for the Dynamics: Forces

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dyn_control_params

- **force_method** how to compute nuclear forces:
  0 – don't compute it – typical for the NBRA workflows
  [1 – state-specific forces]: $\boldsymbol{F_{adi,\mathrm{i}}} = -\frac{\partial E_{adi,i}}{\partial \boldsymbol{R}} = -\nabla_n H_{adi,i,i}$ for the active adiabatic state *i*
  2 – Ehrenfest forces (mean-field = MF)
  3 – QTSH forces – the off-diagonal contributions of the Ehrenfest force $f_{adi,n}^{QTSH} \equiv \frac{1}{C_{adi}^{+} C_{adi}} C_{adi}^{+} F_{adi,n}^{QTSH} C_{adi}$
  4 - KC-RPMD force

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

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

nHamiltonian

- Ehrenfest_forces_dia
- Ehrenfest_forces_adi
- Ehrenfest_forces_tens_dia
- Ehrenfest_forces_tens_adi

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

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

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

Options for the Dynamics: Forces

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.

QTSH Forces

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$$\boldsymbol{P} = \boldsymbol{M}\dot{\boldsymbol{q}} = \boldsymbol{p} - 2\hbar \sum_{i,j:i<j} \beta_{ij}\boldsymbol{h}_{ij}$$

$\boldsymbol{P}$ – kinematic momentum; $\boldsymbol{p}$ – canonical momentum

use_qtsh

[0 – don't use non-classical force, $\boldsymbol{F}^{(nc)}$]
1 - use

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

$\dot{\boldsymbol{q}} = \boldsymbol{M}^{-1}\boldsymbol{p}$ - other methods

$$\dot{\boldsymbol{P}} = \boldsymbol{F}_a + \boldsymbol{F}^{(nc)} \quad \Leftrightarrow \quad \dot{\boldsymbol{P}} = -\nabla V_{aa} + 2Re[(c^+)^T \boldsymbol{h}^+ H_{vib} c] + \boldsymbol{F}^D$$

$$\boldsymbol{F}_a = -\nabla V_{aa}$$

qtsh_force_option

Nonclassical force options in the adiabatic QTSH. Only used with `use_qtsh == 1`
Options:

- 0: Considering only the first-order force, i.e., off-diagonal Ehrenfest force, $\boldsymbol{F}^{(1)}$
- 1: The whole force including the second-order term is used [default], $\boldsymbol{F}^{(2)}$

$$\boldsymbol{F}^{(nc)} = \boldsymbol{F}^{(1)} + \boldsymbol{F}^{(2)} + \boldsymbol{F}^D$$

$$\boldsymbol{F}^{(1)} = 2\sum_{i,j:i<j} (V_{ii} - V_{jj})\alpha_{ij}\boldsymbol{h}_{ij}$$

$$\boldsymbol{F}^{(2)} = -2\hbar \sum_{i,j:i<j} \sum_{k=0}^{N-1} (\beta_{ik}d_{kj} - d_{ik}\beta_{kj})\,\boldsymbol{h}_{ij}$$

$$\boldsymbol{F}^D = 2\hbar \sum_{i,j:i<j} \beta_{ij} \frac{\dot{\boldsymbol{z}}\nabla_{\boldsymbol{z}} g}{g(\boldsymbol{z})} \boldsymbol{h}_{ij}$$

(not computed explicitly, but replaced by decoherence option)

Part 4.2: Electronic Hamiltonian

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Hamiltonian Options

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dyn_control_params

- **ham_update_method**

how to update Ham:
- 0 – don't;
- [1 – update H_{dia}]; - calls an external Python function that computes this matrix; common choice for model Hamiltonians (**common for model problems**)
- 2 – update H_{adi} - the Python function directly gives this matrix, we may not have the diabatic properties in this case; suitable for the atomistic on-the-fly NA-MD calculations or NBRA NA-MD calculations (**for NBRA or on-the-fly calculations**)

- **ham_transform_method**

how to update Ham via transformation :
0 – don't, so one doesn't override the adiabatic properties read from the files; typical for the atomistic workflows (e.g. with the ham_update_method == 2)
[1 – compute H_{adi} from H_{dia} by solving $H_{dia}U = SUH_{adi}$] (**common for model problems**)

To be implemented

2 – compute H_{adi} from H_{dia} by using a provided U: $H_{adi} = (SU)^{-1}H_{dia}U = U^{+}H_{dia}U$
3 – compute H_{dia} from H_{adi} by using a provided U: $H_{dia} = SUH_{adi}U^{-1} = SUH_{adi}U^{+}S$
4 - compute H_{dia} from H_{adi} by using a local diabatization approach

Computing time-overlaps and NACs

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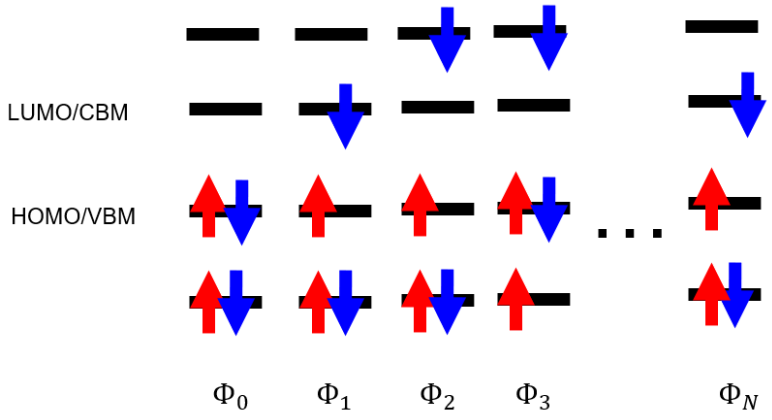
Single-particle description of excited states



Single-particle states $\Psi_i \approx \Phi_i$

- Usually okay for lower excited states
- For less symmetric systems

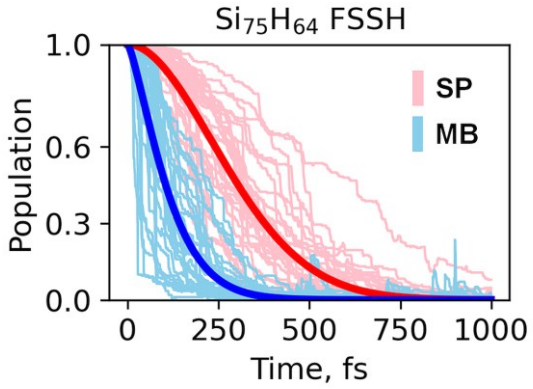
da Silva Oliboni, R.; et al *JPCC* **2016**, *120*, 27688

Akimov, A. V.; Prezhdo, O. V. *JCTC* **2013**, *9*, 4959

Oberhofer, H.; Blumberger, J. *PCCP* **2012**, *14*, 13846

Many-body description generally accelerates the dynamics

$$\Psi = c_0\Phi_0 + c_1\Phi_1 + c_2\Phi_2 + \cdots$$



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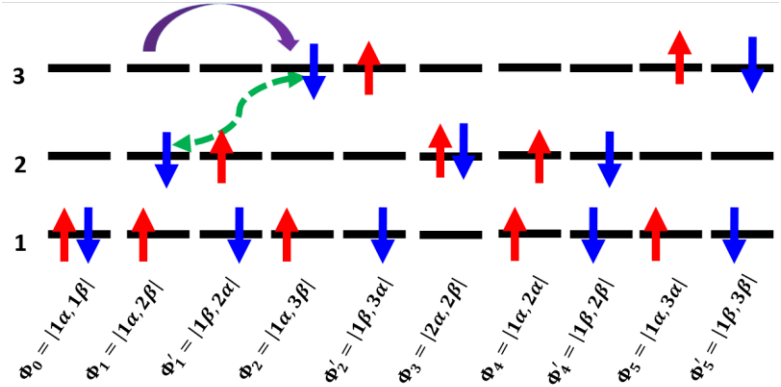
Brendan Smith

Mohammad Shakiba

Spin-adapted configurations



$$S_0 = \Phi_0 \qquad S_1 = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_1')$$

$$S_2 = \frac{1}{\sqrt{2}}(\Phi_2 - \Phi_2')$$

	Φ_0	Φ_1	Φ_1'	Φ_2	Φ_2'	Φ_3	Φ_4	Φ_4'	Φ_5	Φ_5'
Φ_0	0	d_{12}	$-d_{12}$	d_{13}	$-d_{13}$	0	0	0	0	0
Φ_1		0	0	d_{23}	0	d_{12}	0	0	0	0
Φ_1'			0	0	d_{23}	$-d_{12}$	0	0	0	0
Φ_2				0	0	0	0	0	0	0
Φ_2'					0	0	0	0	0	0
Φ_3						0	0	0	0	0
Φ_4							0	0	0	0
Φ_4'								0	0	0
Φ_5									0	0
Φ_5'										0

	S_0	S_1	S_2
S_0	0	$\sqrt{2}d_{12}$	$\sqrt{2}d_{12}$
S_1		0	d_{23}
S_2			0

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New approach: CI tools

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https://github.com/compchem-cybertraining/Tutorials_Libra/tree/master/15_citools

Canonical ordering: $(-i) < (+i) < (-j) < (+j) \quad \text{for} \quad i < j,$

$$|\mathbf{d}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{p_1}(1) & \chi_{p_2}(1) & \cdots & \chi_{p_N}(1) \\ \chi_{p_1}(2) & \chi_{p_2}(2) & \cdots & \chi_{p_N}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{p_1}(N) & \chi_{p_2}(N) & \cdots & \chi_{p_N}(N) \end{vmatrix}.$$

$$|\mathbf{d}\rangle = \mathrm{sgn}(\pi)\, |\mathbf{d}^{\mathrm{can}}\rangle,$$

$$\mathrm{sgn}(\pi) = \begin{cases} +1 & \text{even permutation,} \\ -1 & \text{odd permutation,} \end{cases}$$

$$\mathbf{d}^{\mathrm{can}} = \mathrm{sort}(\mathbf{d}).$$

$$\begin{aligned} |D_0\rangle &= |40^\alpha, 40^\beta\rangle && \text{(ground state)} \\ |D_1\rangle &= |41^\alpha, 40^\beta\rangle && \text{(excitation } 40 \to 41\text{)} \\ |D_2\rangle &= |41^\beta, 40^\alpha\rangle && \text{(spin complement)} \\ |D_3\rangle &= |42^\alpha, 40^\beta\rangle && \text{(excitation } 40 \to 42\text{)} \\ |D_4\rangle &= |42^\beta, 40^\alpha\rangle && \text{(spin complement)} \end{aligned}$$

$$\begin{aligned} |\mathrm{CSF}_0\rangle &= |40^\alpha, 40^\beta\rangle && \text{(ground-state)} \\ |\mathrm{CSF}_1\rangle &= \frac{1}{\sqrt{2}}\left(|41^\alpha, 40^\beta\rangle - |41^\beta, 40^\alpha\rangle\right) && \text{(excitation } 40 \to 41\text{)} \\ |\mathrm{CSF}_2\rangle &= \frac{1}{\sqrt{2}}\left(|42^\alpha, 40^\beta\rangle - |42^\beta, 40^\alpha\rangle\right) && \text{(excitation } 40 \to 42\text{)} \end{aligned}$$

$$[|\mathrm{CSF}_0\rangle \quad |\mathrm{CSF}_1\rangle \quad |\mathrm{CSF}_2\rangle] = \underbrace{\begin{bmatrix} |D_0\rangle \\ |D_1\rangle \\ |D_2\rangle \\ |D_3\rangle \\ |D_4\rangle \end{bmatrix}}_{\text{rows of T}} \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & 0 & -\frac{1}{\sqrt{2}} \end{bmatrix}}_{T \text{ matrix}}$$

$$\langle D_0|\frac{\partial}{\partial t}|D_1\rangle = -\langle D_0|\frac{\partial}{\partial t}|D_2\rangle$$

$$\langle D_0|\frac{\partial}{\partial t}|D_1\rangle \sim \langle HOMO|\frac{\partial}{\partial t}|LUMO\rangle$$

$$\langle D_0|\frac{\partial}{\partial t}|D_3\rangle \sim \langle HOMO|\frac{\partial}{\partial t}|LUMO+1\rangle$$

$$\langle CSF_0|\frac{\partial}{\partial t}|CSF_1\rangle = \sqrt{2}\langle D_0|\frac{\partial}{\partial t}|D_1\rangle$$

$$\langle CSF_0|\frac{\partial}{\partial t}|CSF_2\rangle = \sqrt{2}\langle D_0|\frac{\partial}{\partial t}|D_3\rangle$$

$$\langle CSF_1|\frac{\partial}{\partial t}|CSF_2\rangle = \langle D_1|\frac{\partial}{\partial t}|D_3\rangle$$

Pushing the size further: xTB (in CP2k)

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$$\psi^{KS}_{\boldsymbol{k},i}(t) = \sum_j U_{\boldsymbol{k},ji}(t)\beta_{\boldsymbol{k},j}(t) \qquad \beta_{\boldsymbol{k},a}(\boldsymbol{r}) = \frac{1}{\sqrt{N}}\sum_{\boldsymbol{t}} e^{i\boldsymbol{k}\boldsymbol{t}}\phi_a(\boldsymbol{r}-\boldsymbol{t})$$

$$St^B_{\boldsymbol{k},a,\boldsymbol{k}',b} = \langle\beta_{\boldsymbol{k},a}|\beta_{\boldsymbol{k}',b}\rangle = \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}'\boldsymbol{R}}\frac{1}{N}\sum_{\boldsymbol{t}} e^{i(\boldsymbol{k}'-\boldsymbol{k})\boldsymbol{t}} St^{AO}_{ab}(\boldsymbol{R})$$

Same k-point $$St^B_{\boldsymbol{k},a,\boldsymbol{k},b} = \langle\beta_{\boldsymbol{k},a}|\beta_{\boldsymbol{k},b}\rangle = \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\boldsymbol{R}} S_{ab}(\boldsymbol{R})$$

Gamma k-point $$St^B_{\boldsymbol{k},a,\boldsymbol{k},b} = \langle\beta_{\boldsymbol{k},a}|\beta_{\boldsymbol{k},b}\rangle = \langle\phi_a|\phi_b\rangle = St^{AO}_{ab}$$

Want to compute these guys

Previously: cube files, numerically

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Current:

- numpy.muptiprocessing
- Libint2; using *molden* format
- xTB implementation if CP2k

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https://github.com/compchem-cybertraining/Tutorials_Libra/blob/master/14_molecular_integrals/4_libint2_advanced

Part 4.3: Nonadiabatic Couplings

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Initialization

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as in SDM

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or as in DISH

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Options for the Dynamics: Time-overlaps and NACs

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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 $T(t+\Delta t)=S'(t,t+\Delta t)=\langle \boldsymbol{\psi}(t)|\boldsymbol{\psi}(t+\Delta t)\rangle$

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

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

Part 4.4: Integrating Electronic EOM

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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

$$\hat{H}_{el}\psi_i = E_i\psi_i$$

analytical models or electronic structure codes

Non-adiabatic Couplings

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

Integrate Coherent Electronic Dynamics

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

NBRA

Decoherence 1

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

as in SDM

Proposed Hops Decoherence 2

$$P_{i\rightarrow j} = \Delta t * Re\left(\frac{2\frac{p}{m}d_{ij}c_i^* c_j}{c_i^* c_i}\right)$$

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

NAC: Hammes-Schiffer, S.; Tully, J. C. *JCP* **1994**, *101*, 4657

Phase tracking: Akimov, A. V. *JPCL* **2018** 9, 6096

Local Diabatization: Granucci, G.; Persico, M.; Toniolo, A. *JCP* **2001**, *114*, 10608; Plasser, F.; Granucci, G.; Pittner, J. et al. *JCP* **2012**, 137, 22A514; Shakiba, M.; Akimov, A. V. *TCA* **2023**, 142, 68

SDM: Granucci, G.; Persico, M. *JCP* **2007**, *126*, 134114; **mSDM**: Smith, B. A.; Akimov, A. V. *JCP*, **2019**, 151, 124107; **IDA**: Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. *JCP* **2013**, *138*, 224111.

FSSH: Tully, J. C. *JCP*, **1990**, 93, 1061

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

Options for the Dynamics: TD-SE and Hamiltonian

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dyn_control_params

- **rep_tdse**

how to evolve electronic DOFs: 0 - C_{dia}; [1 - C_{adi}]; 2 - P_{dia}; 3 - P_{adi}

- **hvib_update_method**

How to update $H_{vib,dia}$ and $H_{vib.adi}$
- 0: don't update them, e.g. if it is read externally – useful for NBRA workflows
- [1]: update according to regular formula: $H_{vib,rep} = H_{rep} - i\hbar d_{ij,rep}$

$$i\hbar \frac{\partial \mathrm{c_i(t)}}{\partial t} = \sum_j \left(E_i \delta_{ij} - i\hbar d_{ij}\right) c_j = \sum_j H_{ij}^{vib} c_j$$

Formally, the solution is:

$$C(t + \Delta t) = \exp\left(-\frac{i\Delta t}{\hbar} H^{vib,rep}\right) C(t)$$

- **electronic_integrator = 5**

$$H_{ij}^{vib,adi} = E_i \delta_{ij} - i\hbar d_{ij}$$
$$H_{ij}^{vib,dia} = H_{ij}^{dia} - i\hbar d_{ij}^{dia}$$

In theory, but more complicated in reality…

$d_{ij}^{dia} = 0$ only for exactly diabatic states;
non-zero for quasi-diabatic states

there is a trivial crossing problem + phase arbitrariness

Trivial Crossing Problem

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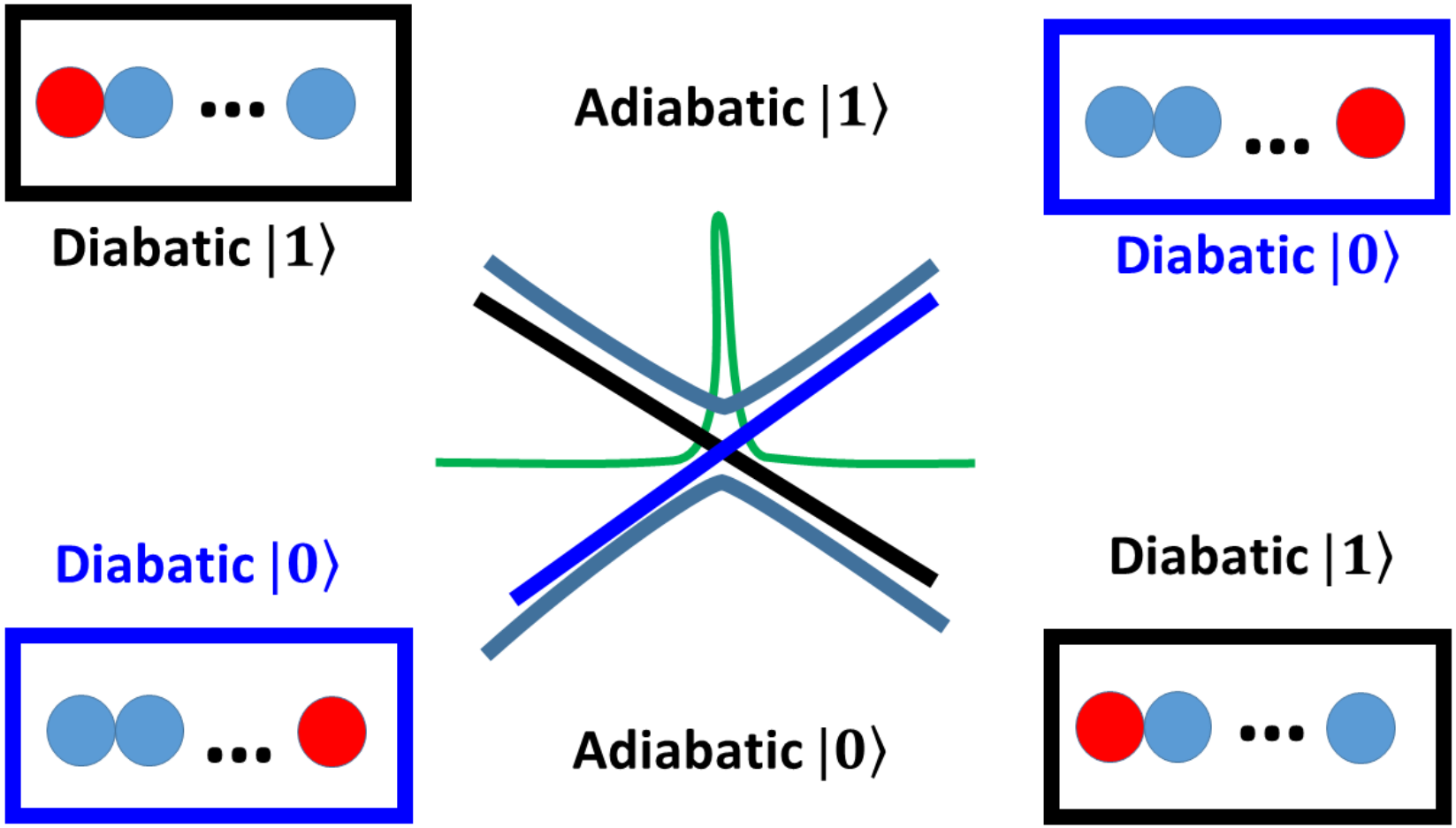
Arises because of finite Δt or due to inconsistency of energy and NAC (due to approximations)



Not accounting for state tracking can result in – unphysical long-distance charge transfer (e.g. bad carrier mobilities)

Giannini, S.; Carof, A.; Blumberger, J. *JPCL* **2018**, *9*, 3116–3123; Bai, X.; Qiu, J.; Wang, L. *JCP* **2018**, *148*, 104106.

State Tracking Options

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state_tracking_algo

State tracking algorithm:

- -1: use LD approach, it includes phase correction too [default]
- 0: no state tracking
- 1: method of Kosuke Sato (may fail by getting trapped into an infinite loop)
- 2: Munkres-Kuhn (Hungarian) algorithm
- 21: ChatGPT-generated Munkres-Kuhn (Hungarian) algorithm
- 3: experimental stochastic algorithm, the original version with elimination (known problems)
- 32: experimental stochastic algorithms with all permutations (too expensive)
- 33: the improved stochastic algorithm with good scaling and performance, on par with the mincost
- 4: force-based tracking

- 5: SVD-reformulated LD approach of Granucci and Persico

Shakiba, M.; Akimov, A. V. *Theor Chem Acc* **2023**, *142* (8), 68.

$$T(t) = I$$

$$T(t+\Delta t) = P^{-1}(t, t+\Delta t)([P^{-1}(t, t+\Delta t)]^{+} P^{-1}(t, t+\Delta t))^{-1/2}$$

Note: $T = T_{LD}^{-1}$ Granucci G, Persico M, Toniolo A *J. Chem. Phys.* **2001**, 114, 10608

Fernandez-Alberti, S.; Roitberg, A. E.; Nelson, T.; Tretiak, S. *J. Chem. Phys.* **2012**, *137*, 014512

$$S(t, t+\Delta t) = \langle \boldsymbol{\psi}(t) | \boldsymbol{\psi}(t+\Delta t) \rangle \leftrightarrow S_{ij}(t, t+\Delta t) = \langle \psi_i(t) | \psi_j(t+\Delta t) \rangle$$

Cost matrix: $C_{ij} = -S_{ij}^2$

Solution (states' reordering): $Tr(C) \to min$ same as $Tr(S_{ij}^2) \to max$

Akimov, A.V. *JPCL* **2024** 15, 11944

Cost matrix: $C_{ij} = -\left|\frac{1}{2}\left(1 - sign\left(\Delta E_{ji}(t)\right) sign\left(\Delta \tilde{E}_{ji}(t+\Delta t)\right)\right)\right|^2$

Solution: $Tr(C) \to min$

$S = U\sigma V^{+}$ (SVD decomposition of the S matrix)

$$T = UV^{+}$$

Basis of Local Diabatization

Shakiba, M.; Akimov, A. V. *Theor Chem Acc* **2023**, *142* (8), 68.

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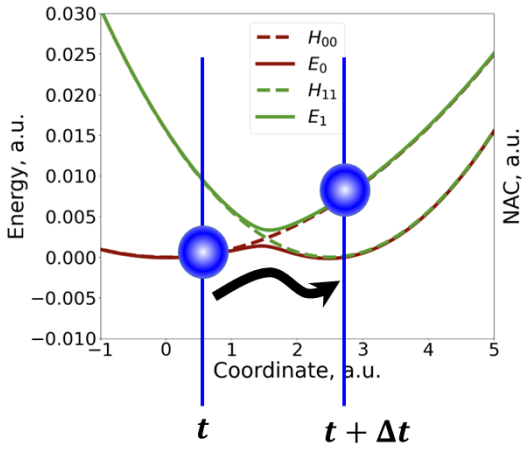
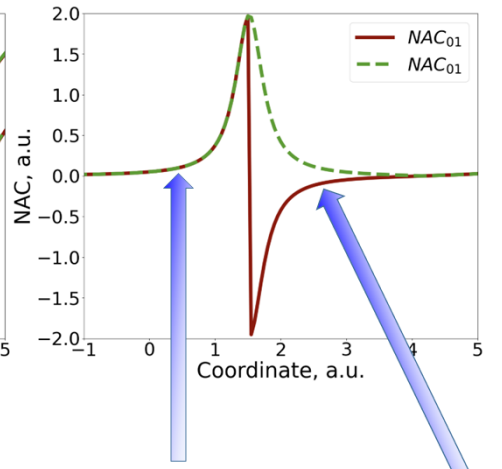
We want to solve

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$$

in the adiabatic basis:

$$|\Psi(t)\rangle = |\boldsymbol{\psi}_{adi}(t)\rangle C_{adi}(t)$$





$|\boldsymbol{\psi}(t)\rangle = (|0\rangle, |1\rangle)$

$|\boldsymbol{\psi}(t+\Delta t)\rangle = (|1\rangle, |0\rangle)$

$d_{01}(t) = \left\langle \psi_0(t)\left|\frac{d}{dR}\right|\psi_1(t)\right\rangle = \left\langle 0\left|\frac{d}{dR}\right|1\right\rangle$

$d_{01}(t+\Delta t) = \left\langle \psi_0(t+\Delta t)\left|\frac{d}{dR}\right|\psi_1(t+\Delta t)\right\rangle = \left\langle 1\left|\frac{d}{dR}\right|0\right\rangle$

Formal solution:

$$|\Psi(\mathrm{t}+\Delta\mathrm{t})\rangle = \left[\int_0^{\Delta t} d\tau \exp\left(-\frac{i\tau}{\hbar}\hat{H}(t+\tau)\right)\right]|\Psi(\mathrm{t})\rangle = |\boldsymbol{\psi}_{adi}(\mathrm{t}+\Delta\mathrm{t})\rangle C_{adi}(t+\Delta\mathrm{t})$$

Consider the change of C_{adi} non-adiabatic dynamics

After projection:

$$C_{adi}(t+\Delta t) = \left\langle \boldsymbol{\psi}_{adi}(t+\Delta t)\right|\left[\int_0^{\Delta t} d\tau \exp\left(-\frac{i\tau}{\hbar}\hat{H}(t+\tau)\right)\right]|\boldsymbol{\psi}_{adi}(\mathrm{t})\rangle C_{adi}(t)$$

However, the bases $|\boldsymbol{\psi}_{adi}(t)\rangle$ and $|\boldsymbol{\psi}_{adi}(t+\Delta t)\rangle$ may change their relative order (e.g. in trivial crossing situations) or acquire a spurious phase difference. **Consider this as the adiabatic dynamics (e.g. adiabatic charge transfer)**

Derivation of Local Diabatization (LD) Approach

Introduce the dynamically-consistent (local diabatic) basis, $|\tilde{\boldsymbol{\psi}}_{adi}(t)\rangle$: $\langle\tilde{\boldsymbol{\psi}}_{adi}(t)|\tilde{\boldsymbol{\psi}}_{adi}(t+\Delta t)\rangle \approx I$

The idea: these basis functions preserve their identity as much as possible

Introduce the **basis re-projection** matrix, $T(t)$: it describes the adiabatic dynamics of the basis

$$|\tilde{\boldsymbol{\psi}}_{adi}(t)\rangle = |\boldsymbol{\psi}_{adi}(t)\rangle T(t)$$

Closely related to the one in the LD of Granucci et al.

$$T = T_{LD}^{-1}$$

Granucci G, Persico M, Toniolo A *J. Chem. Phys.* **2001**, 114, 10608

The wavefunction should stay invariant w.r.t. the choice of the basis:

$$|\Psi(t)\rangle = |\tilde{\boldsymbol{\psi}}_{adi}(t)\rangle\tilde{C}_{adi}(t) = |\boldsymbol{\psi}_{adi}(t)\rangle C_{adi}(t)$$

$$C_{adi}(t) = T(t)\tilde{C}_{adi}(t)$$

Use the definitions above:

$$T^{+}(t)\langle\boldsymbol{\psi}(t)|\boldsymbol{\psi}(t+\Delta t)\rangle T(t+\Delta t) = T^{+}(t)P(t, t+\Delta t)T(t+\Delta t) \approx I$$

Time-overlap (transition density matrix):

$$P(t, t+\Delta t) = \langle\boldsymbol{\psi}(t)|\boldsymbol{\psi}(t+\Delta t)\rangle$$

Solving for the re-projection matrix:

$$T(t+\Delta t) = [T^{+}(t)P(t, t+\Delta t)]^{-1}$$

but this leads to fast accumulation of errors

so, should not evolve the re-projection matrix globally, only locally:

Local diabatization assumption

$$T(t) = I$$
$$T(t+\Delta t) = P^{-1}(t, t+\Delta t)$$

Lowdin normalization in the LD approach

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However, this transformation will not preserve the wavefunction norm:

$$T(t+\Delta t) = [P(t, t+\Delta t)]^{-1}$$

$$|\boldsymbol{\psi}_{adi}(t+\Delta t)\rangle = \left|\widetilde{\boldsymbol{\psi}}_{adi}(t+\Delta t)\right\rangle T^{-1}(t+\Delta t)$$

$$Tr[\langle\boldsymbol{\psi}(t+\Delta t)|\boldsymbol{\psi}(t+\Delta t)\rangle] = Tr\left[(T^{-1})^{+}\left\langle\widetilde{\boldsymbol{\psi}}(t+\Delta t)\middle|\widetilde{\boldsymbol{\psi}}(t+\Delta t)\right\rangle T^{-1}\right] =$$
$$Tr\left[\left\langle\widetilde{\boldsymbol{\psi}}(t+\Delta t)\middle|\widetilde{\boldsymbol{\psi}}(t+\Delta t)\right\rangle T^{-1}(T^{-1})^{+}\right] = Tr\left[\left\langle\widetilde{\boldsymbol{\psi}}(t+\Delta t)\middle|\widetilde{\boldsymbol{\psi}}(t+\Delta t)\right\rangle T^{-1}(T^{+})^{-1}\right] =$$
$$Tr\left[\left\langle\widetilde{\boldsymbol{\psi}}(t+\Delta t)\middle|\widetilde{\boldsymbol{\psi}}(t+\Delta t)\right\rangle (T^{+}T)^{-1}\right] \neq Tr\left[\left\langle\widetilde{\boldsymbol{\psi}}(t+\Delta t)\middle|\widetilde{\boldsymbol{\psi}}(t+\Delta t)\right\rangle\right].$$

Normalize the T matrix: $T \to \tilde{T} = TA$ such that $\tilde{T}^{+}(t+\Delta t)\tilde{T}(t+\Delta t) = A^{+}T^{+}(t+\Delta t)T(t+\Delta t)A = I$

The matrix A can be chosen as: $A = \left(T^{+}(t+\Delta t)T(t+\Delta t)\right)^{-1/2}$

So the normalized matrix is: $\tilde{T}(t+\Delta t) = T(t+\Delta t)\left(T^{+}(t+\Delta t)T(t+\Delta t)\right)^{-1/2}$

Local diabatization with Lowdin normalization

$$T(t) = I$$
$$T(t+\Delta t) = P^{-1}(t, t+\Delta t)([P^{-1}(t, t+\Delta t)]^{+}P^{-1}(t, t+\Delta t))^{-1/2}$$

F-tracking approach

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Akimov, A.V. *JPCL* **2024** 15, 11944

$$F_{i,\alpha} = -\frac{\partial E_i}{\partial R_\alpha}$$ so

Change of the coordinate under the action of given force:

$$\Delta R_\alpha = M_\alpha^{-1} P_\alpha \Delta t + \frac{1}{2} M_\alpha^{-1} F_\alpha \Delta t^2$$

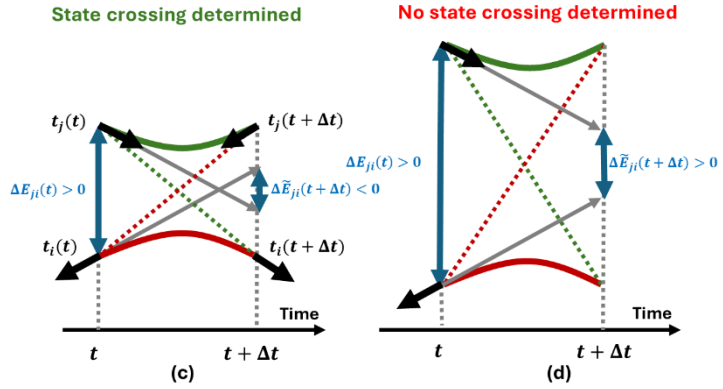
Change of energy:

$$\Delta E_i(t+\Delta t) = -\sum_\alpha F_{i,\alpha}(t)\Delta R_\alpha = -\sum_\alpha F_{i,\alpha}(t)\left[M_\alpha^{-1} P_\alpha\left(t+\frac{\Delta t}{2}\right)\Delta t + \frac{1}{2} M_\alpha^{-1} F_{i,\alpha}(t)\Delta t^2\right]$$

Change of energy gap:

$$\Delta\tilde{E}_{ji}(t+\Delta t) = \Delta E_{ji}(t) + \Delta E_j - \Delta E_i = \Delta E_{ji}(t) - \sum_\alpha \left[F_{j,\alpha}(t) - F_{i,\alpha}(t)\right] M_\alpha^{-1} P_\alpha\left(t+\frac{\Delta t}{2}\right)\Delta t - \frac{1}{2}\sum_\alpha \left[F_{j,\alpha}^2(t) - F_{i,\alpha}^2(t)\right] M_\alpha^{-1}\Delta t^2$$

The idea: Need to consider the extrapolated change of the energy gap under the motion with given forces compared to the actual gap change



Gap is smaller - $\Delta\tilde{E}_{ji}$ changes sign

Gap is large - $\Delta\tilde{E}_{ji}$ does not change sign

Cost matrix to be used in the Munkres-Kuhn (Hungarian) maximization algorithm

$$C_{ij} = \left|\frac{1}{2}\left(1 - sign\left(\Delta E_{ji}(t)\right) sign\left(\Delta\tilde{E}_{ji}(t+\Delta t)\right)\right)\right|^2$$

$\Delta\tilde{E}_{ji}$ - changes sign: $C_{ij} = 1$ → favors state index permutation

$\Delta\tilde{E}_{ji}$ - does not change sign: $C_{ij} = 0$

Diagonal elements: $\Delta\tilde{E}_{ji} = 0$: $C_{ij} = 0.25$

Simple phase correction approach

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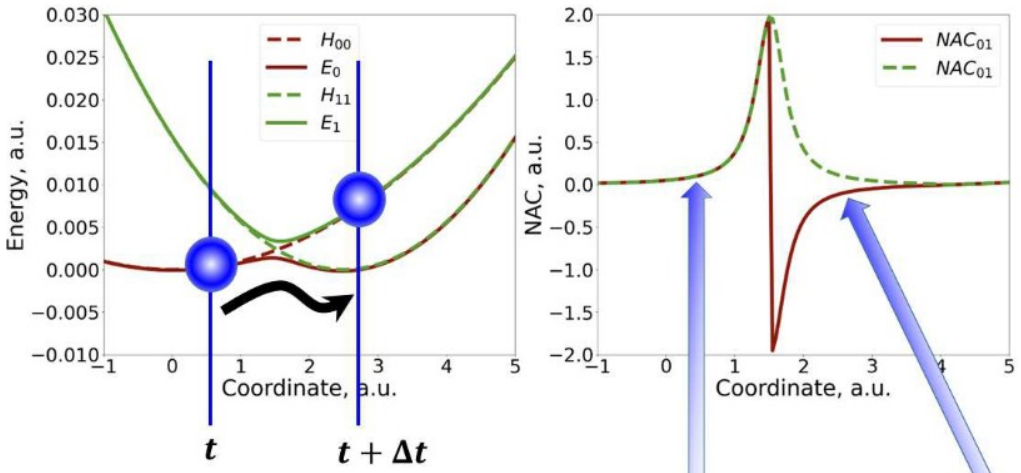
Akimov, A.V. *JPCL* **2024** 15, 11944

- We still assume time-overlaps are not available, but the tNACs are
- The available tNACs may still have inconsistent phases
- The F-tracking of the states does not fix the phase fluctuations in tNACs
- **Can we use the tNAC data to fix the signs?**

do_nac_phase_correction

Options:
- 0: no correction [default]
- 1: do this correction

The idea: while passing the intersection, we want the tNAC not change its sign (be continuous).



$$|\psi(t)\rangle = (|0\rangle, |1\rangle)$$

$$|\psi(t+\Delta t)\rangle = (|1\rangle, |0\rangle)$$

$$d_{01}(t) = \left\langle \psi_0(t) \middle| \frac{d}{dR} \middle| \psi_1(t) \right\rangle = \left\langle 0 \middle| \frac{d}{dR} \middle| 1 \right\rangle$$

$$d_{01}(t+\Delta t) = \left\langle \psi_0(t+\Delta t) \middle| \frac{d}{dR} \middle| \psi_1(t+\Delta t) \right\rangle = \left\langle 1 \middle| \frac{d}{dR} \middle| 0 \right\rangle$$

$$s_{ij} = sign\left(d_{ij}(t-\Delta t)\right) sign\left(d_{ij}(t)\right), i > j$$

$$d_{ij}(t) \rightarrow \tilde{d}_{ij}(t) = d_{ij}(t) s_{ij}$$

$$d_{ji}(t) \rightarrow \tilde{d}_{ji}(t) = d_{ji}(t) s_{ij}$$

Limitation: if the crossing region is not localized, the tNAC may be changing sign in a continuous way. Then the sign alignment may be incorrect.

Simple phase correction approach

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

Hammes-Schiffer, S.; Tully, J. C. *J. Chem. Phys.* **1994**, *101*, 4657–4667

But states are defined only up to a complex phase!

Phase correction:

AVA. *J. Phys. Chem. Lett.* **2018** 9, 6096

$$f_i=\frac{\langle\psi_i(t)|\psi_i(t')\rangle}{\sqrt{|\langle\psi_i(t)|\psi_i(t')\rangle|}}$$

$$|\tilde{\psi}_i(t')\rangle=f_i^*|\psi_i(t')\rangle \qquad C_{adi,i}\rightarrow\tilde{C}_{adi,i}=f_iC_{adi,i}$$

Indeed:

$$|\psi_i(t)\rangle=e^{i\phi(t)}|\chi_i(t)\rangle$$
$$|\psi_i(t')\rangle=e^{i\phi(t')}|\chi_i(t')\rangle$$

Then:

$$|\tilde{\psi}_i(t')\rangle=f_i^*|\psi_i(t')\rangle=e^{-i[\phi(t')-\phi(t)]}e^{i\phi(t')}|\chi_i(t')\rangle=e^{i\phi(t)}|\chi_i(t')\rangle$$

do_phase_correction

Options:
- 0: no phase correction
- 1: according to our phase correction algorithm [default]

phase_correction_tol

The minimal magnutude of the matrix element for which we'll be computing the phase correction

If the overlap is zero, then we don't really care about the phase, but if it is not, then this parameter sets out threshold for when we do. [default: 1e-3]

Summary of Electronic Integrators

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dyn_control_params

- **electronic_integrator**

rep_tdse = 0 (diabatic):

-1 - No propagation
0 - Lowdin exp_ with 2-point Hvib_dia
1 - based on QTAG propagator
2 - based on modified QTAG propagator (Z at two times)
3 - non-Hermitian integrator with 2-point Hvib_dia

rep_tdse = 1 (adiabatic):

-1 - No propagation
0 - LD, with crude splitting, with exp_ [default]
1 - LD, with symmetric splitting, with exp_
2 - LD, original, with exp_
3 - 1-point, Hvib integration, with exp_
4 - 2-points, Hvib integration, with exp_
5 - 3-points, Hvib, integration with the second-point correction of Hvib, with exp_
6 - same as 4, but without projection matrices (T_new = I)

10 - same as 0, but with rotations
11 - same as 1, but with rotations
12 - same as 2, but with rotations
13 - same as 3, but with rotations
14 - same as 4, but with rotations
15 - same as 5, but with rotations

rep_tdse = 2 (diabatic, density matrix formalism):

0 - mid-point Hvib with the second-point correction of Hvib

rep_tdse = 3 (adiabatic, density matrix formalism):

0 - mid-point Hvib with the second-point correction of Hvib
1 - Zhu Liouvillian

10 - same as 0, but with rotations

Back to Integrating the TD-SE

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$$U(t,t+\Delta t) = \left\langle \boldsymbol{\psi}_{adi}\,(t+\Delta t)\right| \left[\int_0^{\Delta t} d\tau \exp\left(-\frac{i\tau}{\hbar}\hat{H}(t+\tau)\right)\right] \left|\boldsymbol{\psi}_{adi}(\mathrm{t})\right\rangle$$

Crude splitting:

$$\left[\int_0^{\Delta t} d\tau \exp\left(-\frac{i\tau}{\hbar}\widehat{H}(\tau)\right)\right] \approx \left[\exp\left(-\frac{i\Delta t}{2\hbar}\left[\widehat{H}(t)+\widehat{H}(t+\Delta t)\right]\right)\right] \approx \left[\exp\left(-\frac{i\Delta t}{2\hbar}\widehat{H}(t+\Delta t)\right)\right]\left[\exp\left(-\frac{i\Delta t}{2\hbar}\widehat{H}(t)\right)\right]$$

$$U(t,t+\Delta t) \approx \left\langle \boldsymbol{\psi}_{adi}\,(t+\Delta t)\right| \left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t+\Delta t)\right)\right]\left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t)\right)\right] \left|\boldsymbol{\psi}_{adi}(\mathrm{t})\right\rangle$$

Using properties of the local-diabatic basis:

$$\left|\tilde{\boldsymbol{\psi}}_{adi}(t+\Delta t)\right\rangle\left\langle\tilde{\boldsymbol{\psi}}_{adi}\,(t)\right| \approx \left|\tilde{\boldsymbol{\psi}}_{adi}(t)\right\rangle\left\langle\tilde{\boldsymbol{\psi}}_{adi}\,(t+\Delta t)\right| \approx \hat{I}$$

$$U(t,t+\Delta t) \approx \langle\boldsymbol{\psi}_{adi}(t+\Delta t)|\left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t+\Delta t)\right)\right]\tilde{\boldsymbol{\psi}}_{adi}(t+\Delta t)\rangle\langle\tilde{\boldsymbol{\psi}}_{adi}(t)|\left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t)\right)\right]|\boldsymbol{\psi}_{adi}(\mathrm{t})\rangle = \langle\boldsymbol{\psi}_{adi}(t+\Delta t)|\left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t+\Delta t)\right)\right]\boldsymbol{\psi}_{adi}(t+\Delta t)\rangle T(t+\Delta t)T^{+}(t)\langle\boldsymbol{\psi}_{adi}(t)|\left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t)\right)\right]|\boldsymbol{\psi}_{adi}(\mathrm{t})\rangle = A(t+\Delta t)T(t+\Delta t)\,A(t)$$

$$A(t) = \left\langle \boldsymbol{\psi}_{adi}\,(t)\right|\left[\exp\left(-\frac{i\Delta t}{2\hbar}\widehat{H}(t)\right)\right]\left|\boldsymbol{\psi}_{adi}(\mathrm{t})\right\rangle = \exp\left(-\frac{i\Delta t}{2\hbar}H(t)\right)$$

Note: this **should be the electronic Hamiltonian**, **not the vibronic Hamiltonian**!

Back to Integrating the TD-SE: Another integrator

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Symmetric splitting:

$$U(t,t+\Delta t)=\left\langle \boldsymbol{\psi}_{adi}\,(t+\Delta t)\right|\left[\exp\left(-\frac{i\Delta t}{4\hbar}\widehat{H}(t)\right)\right]\left[\exp\left(-\frac{i\Delta t}{2\hbar}\widehat{H}(t+\Delta t)\right)\right]\left[\exp\left(-\frac{i\Delta t}{4\hbar}\widehat{H}(t)\right)\right]|\boldsymbol{\psi}_{\mathrm{adi}}(\mathrm{t})\rangle$$

$$\begin{aligned}&U(t,t+\Delta t)\\&=\left\langle \boldsymbol{\psi}_{adi}\,(t+\Delta t)\right|\left|\widetilde{\boldsymbol{\psi}}_{adi}(t+\Delta t)\right\rangle\left\langle\widetilde{\boldsymbol{\psi}}_{adi}\,(t)\right|\left[\exp\left(-\frac{i\Delta t}{4\hbar}\widehat{H}(t)\right)\right]\left|\widetilde{\boldsymbol{\psi}}_{adi}(t)\right\rangle\left\langle\widetilde{\boldsymbol{\psi}}_{adi}\,(t+\Delta t)\right|\exp\left(-\frac{i\Delta t}{2\hbar}\widehat{H}(t+\Delta t)\right)\Big]\left|\widetilde{\boldsymbol{\psi}}_{adi}(t\right.\\&\left.+\Delta t)\right\rangle\left\langle\widetilde{\boldsymbol{\psi}}_{adi}\,(t)\right|\Big[\exp\left(-\frac{i\Delta t}{4\hbar}\widehat{H}(t)\right)\Big]|\boldsymbol{\psi}_{\mathrm{adi}}(\mathrm{t})\rangle\end{aligned}$$

$$\begin{aligned}&U(t,t+\Delta t)\\&=\left\langle \boldsymbol{\psi}_{adi}\,(t+\Delta t)\right|\left|\boldsymbol{\psi}_{adi}(t+\Delta t)\right\rangle T(t+\Delta t)T^{+}(t)\left\langle\boldsymbol{\psi}_{adi}\,(t)\right|\left[\exp\left(-\frac{i\Delta t}{4\hbar}\widehat{H}(t)\right)\right]|\boldsymbol{\psi}_{adi}(t)\rangle T(t)T^{+}(t\\&+\Delta t)\left\langle \boldsymbol{\psi}_{adi}\,(t+\Delta t)\right|\left[\exp\left(-\frac{i\Delta t}{2\hbar}\widehat{H}(t+\Delta t)\right)\right]|\boldsymbol{\psi}_{adi}(t+\Delta t)\rangle T(t+\Delta t)T^{+}(t)\left\langle\boldsymbol{\psi}_{adi}\,(t)\right|\left[\exp\left(-\frac{i\Delta t}{4\hbar}\widehat{H}(t)\right)\right]|\boldsymbol{\psi}_{\mathrm{adi}}(\mathrm{t})\rangle\\&=T(t+\Delta t)B(t)T^{+}(t+\Delta t)A(t+\Delta t)T(t+\Delta t)B(t)\end{aligned}$$

$$B(t)=\left\langle \boldsymbol{\psi}_{adi}\,(t)\right|\left[\exp\left(-\frac{i\Delta t}{4\hbar}\widehat{H}(t)\right)\right]|\boldsymbol{\psi}_{adi}(t)\rangle=\exp\left(-\frac{i\Delta t}{4\hbar}H(t)\right)=A^{1/2}$$

Rotation-based Integrators for TD-SE

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$$i\hbar\frac{\partial C}{\partial t} = XC \qquad X_{ij} = Re[X_{ij}] + iIm[X_{ij}] \qquad C(t+\Delta t) = \exp(iL\Delta t)C(t).$$

$$iL \equiv \dot{C}\frac{\partial}{\partial C} = \sum_i \dot{C}_i \frac{\partial}{\partial C_i}$$

$$iL = -\frac{i}{\hbar}\sum_i\sum_j X_{ij}C_j\frac{\partial}{\partial C_i} = -\frac{i}{\hbar}\sum_{i,j} X_{ij}C_j\frac{\partial}{\partial C_i} = -\frac{i}{\hbar}\sum_i X_{ii}C_i\frac{\partial}{\partial C_i} - \frac{i}{\hbar}\sum_{i,j:i>j}\left[X_{ij}C_j\frac{\partial}{\partial C_i}\right] - \frac{i}{\hbar}\sum_{i,j:i<j}\left[X_{ij}C_j\frac{\partial}{\partial C_i}\right]$$
$$= -\frac{i}{\hbar}\sum_i X_{ii}C_i\frac{\partial}{\partial C_i} - \frac{i}{\hbar}\sum_{i,j:i>j}\left[X_{ij}C_j\frac{\partial}{\partial C_i}\right] - \frac{i}{\hbar}\sum_{i,j:i>j}\left[X_{ji}C_i\frac{\partial}{\partial C_j}\right] = -\frac{i}{\hbar}\sum_i X_{ii}C_i\frac{\partial}{\partial C_i} - \frac{i}{\hbar}\sum_{i,j:i>j}\left[X_{ij}C_j\frac{\partial}{\partial C_i} + X_{ji}C_i\frac{\partial}{\partial C_j}\right]$$

$$iL = -\frac{i}{\hbar}\sum_i X_{ii}C_i\frac{\partial}{\partial C_i} - \frac{i}{\hbar}\sum_{i,j:i>j}\left[Re(X_{ij})\left[C_j\frac{\partial}{\partial C_i} + C_i\frac{\partial}{\partial C_j}\right] + iIm(X_{ij})\left[C_j\frac{\partial}{\partial C_i} - C_i\frac{\partial}{\partial C_j}\right]\right] = \sum_i iL_i^{(1)} + \sum_{i,j:i>j} iL_{ij}^{(2)} + \sum_{i,j:i>j} iL_{ij}^{(3)}$$

$$iL_i^{(1)} = -\frac{i}{\hbar}X_{ii}C_i\frac{\partial}{\partial C_i} \qquad iL_{ij}^{(2)} = \frac{Im(X_{ij})}{\hbar}\left[C_j\frac{\partial}{\partial C_i} - C_i\frac{\partial}{\partial C_j}\right] \qquad iL_{ij}^{(3)} = -\frac{iRe(X_{ij})}{\hbar}\left[C_j\frac{\partial}{\partial C_i} + C_i\frac{\partial}{\partial C_j}\right]$$

Rotation-based Integrators for TD-SE: Action of the operators

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$$\exp\left(iL_i^{(1)}\Delta t\right)C_i = \exp\left(-\frac{i\Delta t}{\hbar}X_{ii}\right)C_i \qquad A = \frac{Im(X_{ij})\Delta t}{\hbar} \qquad B = \frac{Re(X_{ij})\Delta t}{\hbar}$$

$$\exp\left(iL_{ij}^{(2)}\Delta t\right)\begin{pmatrix}C_i\\C_j\end{pmatrix} = \begin{pmatrix}C_i\\C_j\end{pmatrix} + A\begin{pmatrix}C_j\\-C_i\end{pmatrix} + \frac{A^2}{2!}\begin{pmatrix}-C_i\\-C_j\end{pmatrix} + \frac{A^3}{3!}\begin{pmatrix}-C_j\\C_i\end{pmatrix} + \frac{A^4}{4!}\begin{pmatrix}C_i\\C_j\end{pmatrix}\ldots = \begin{pmatrix}1-\frac{A^2}{2!}+\frac{A^4}{4!}\ldots & A-\frac{A^3}{3!}+\cdots\\ -A+\frac{A^3}{3!}+\cdots & 1-\frac{A^2}{2!}+\frac{A^4}{4!}\ldots\end{pmatrix}\begin{pmatrix}C_i\\C_j\end{pmatrix} = \begin{pmatrix}\cos(A) & \sin(A)\\ -\sin(A) & \cos(A)\end{pmatrix}\begin{pmatrix}C_i\\C_j\end{pmatrix}$$

$$\exp\left(iL_{ij}^{(3)}\Delta t\right)\begin{pmatrix}C_i\\C_j\end{pmatrix} = \begin{pmatrix}C_i\\C_j\end{pmatrix} - iB\begin{pmatrix}C_j\\C_i\end{pmatrix} + \frac{(-iB)^2}{2!}\begin{pmatrix}C_i\\C_j\end{pmatrix} + \frac{(-iB)^3}{3!}\begin{pmatrix}C_j\\C_i\end{pmatrix} + \frac{(-iB)^4}{4!}\begin{pmatrix}C_i\\C_j\end{pmatrix} + \cdots = \begin{pmatrix}1-\frac{B^2}{2!}+\frac{B^4}{4!}+\cdots & -iB+\frac{(-iB)^3}{3!}+\cdots\\ -iB+\frac{(-iB)^3}{3!}+\cdots & 1-\frac{B^2}{2!}+\frac{B^4}{4!}+\cdots\end{pmatrix}\begin{pmatrix}C_i\\C_j\end{pmatrix} = \begin{pmatrix}\cos(B) & -i\sin(B)\\ -i\sin(B) & \cos(B)\end{pmatrix}\begin{pmatrix}C_i\\C_j\end{pmatrix}$$

Rotation-based Integrators for TD-SE: Overall Factorization

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$$\exp(iL\Delta t) = \exp\left(\left\{\sum_i iL_i^{(1)} + \sum_{i,j:i>j} iL_{ij}^{(2)} + \sum_{i,j:i>j} iL_{ij}^{(3)}\right\}\Delta t\right) \approx \left\{\prod_i \exp\left(iL_i^{(1)}\frac{\Delta t}{2}\right)\right\}\left\{\prod_{i,j:i>j} \exp\left(iL_{ij}^{(3)}\frac{\Delta t}{2}\right)\right\}\left\{\prod_{i,j:i>j} \exp\left(iL_{ij}^{(2)}\frac{\Delta t}{2}\right)\right\}\left\{\prod_{o\{i,j:i>j\}} \exp\left(iL_{ij}^{(2)}\frac{\Delta t}{2}\right)\right\}\left\{\prod_{o\{i,j:i>j\}} \exp\left(iL_{ij}^{(3)}\frac{\Delta t}{2}\right)\right\}\left\{\prod_{o\{i\}} \exp\left(iL_i^{(1)}\frac{\Delta t}{2}\right)\right\}$$

$$\exp\left(iL_0^{(1)}\frac{\Delta t}{2}\right)\exp\left(iL_1^{(1)}\frac{\Delta t}{2}\right)\exp\left(iL_2^{(1)}\frac{\Delta t}{2}\right)\exp\left(iL_{01}^{(3)}\frac{\Delta t}{2}\right)\exp\left(iL_{02}^{(3)}\frac{\Delta t}{2}\right)\exp\left(iL_{12}^{(3)}\frac{\Delta t}{2}\right)$$

$$\exp\left(iL_{01}^{(2)}\frac{\Delta t}{2}\right)\exp\left(iL_{02}^{(2)}\frac{\Delta t}{2}\right)\exp\left(iL_{12}^{(2)}\frac{\Delta t}{2}\right)\exp\left(iL_{12}^{(2)}\frac{\Delta t}{2}\right)\exp\left(iL_{02}^{(2)}\frac{\Delta t}{2}\right)\exp\left(iL_{01}^{(2)}\frac{\Delta t}{2}\right)$$

$$\exp\left(iL_{12}^{(3)}\frac{\Delta t}{2}\right)\exp\left(iL_{02}^{(3)}\frac{\Delta t}{2}\right)\exp\left(iL_{01}^{(3)}\frac{\Delta t}{2}\right)\exp\left(iL_2^{(1)}\frac{\Delta t}{2}\right)\exp\left(iL_1^{(1)}\frac{\Delta t}{2}\right)\exp\left(iL_0^{(1)}\frac{\Delta t}{2}\right)$$

Working the Liouville's space: propagation of density matrix

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$$i\hbar\frac{\partial\hat{\rho}}{\partial t}=\left[\hat{H},\hat{\rho}\right]$$

$$\frac{\partial\tilde{\rho}_{ij}}{\partial t}=-\frac{i}{\hbar}\sum_{a,b}\tilde{L}_{ij,ab}\tilde{\rho}_{ab}$$

$N\times N$ matrix

$$\tilde{L}_{ij,ab}=\tilde{H}_{ia}\delta_{bj}-\tilde{H}_{bj}\delta_{ai}$$

$$\tilde{H}=\langle\tilde{\boldsymbol{\psi}}|\hat{H}|\tilde{\boldsymbol{\psi}}\rangle=T^{+}\langle\boldsymbol{\psi}|\hat{H}|\boldsymbol{\psi}\rangle T$$

Vectorized form of the QCLE

$$\frac{\partial vec(\tilde{\rho})}{\partial t}=-i\tilde{L}*vec(\tilde{\rho})$$

$N^2\times N^2$ matrix $\quad N^2\times 1$ vector

For the "closed" quantum systems, there is a direct correspondence between wavefunction and density matrix, so:

$$\rho_{adi}=C_{adi}C_{adi}^{+}=T\tilde{C}_{adi}\tilde{C}_{adi}^{+}T^{+}=T\tilde{\rho}_{adi}T^{+}$$

$$\tilde{\rho}_{adi}=T^{-1}\rho_{adi}(T^{+})^{-1}=T^{+}\rho_{adi}T$$

So, the final expression:

$$\rho(t+\Delta t)=T(t+\Delta t)vec^{-1}\left\{\left[\int_0^{\Delta t}d\tau\exp\left(-\frac{i\tau}{\hbar}\tilde{L}(t+\tau)\right)\right]vec\big(\rho(t)\big)T\right\}T^{+}(t+\Delta t)$$

Additional flags for the Integrators

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dyn_control_params

- **assume_always_consistent**

If set to True (1), we will force the reprojection matrix T_new to be the identity matrix. This effectively removes basis-reprojection (local diabatization) approach and turns on the "naive" approach where no trivial crossings exist.

- [0]: No - we do want to use the LD approaches by default.
- 1: Yes - one may need to turn on additional state tracking and phase correction methods

- **ampl_transformation_method**

Whether transform the amplitudes by the T transformation matrix
- 0: do not transform by the T matrix (naive, but potentially correct approach)
- 1: do transform it (as in LD, but maybe not needed if we directly transform basis)

Part 4.5: Hop Proposal Probabilities

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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

$$\hat{H}_{el}\psi_i = E_i\psi_i$$

analytical models or electronic structure codes

Non-adiabatic Couplings

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

Integrate Coherent Electronic Dynamics

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

NBRA

Decoherence 1

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

as in SDM

Proposed Hops Decoherence 2

$$P_{i\to j} = \Delta t * Re\left(\frac{2\frac{p}{m}d_{ij}c_i^* c_j}{c_i^* c_i}\right)$$

or as in DISH

Accept Hops

based on energy conservation or

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

Change of state/Velocity rescaling

change active electronic state, rescale velocity

NAC: Hammes-Schiffer, S.; Tully, J. C. *JCP* **1994**, *101*, 4657

Phase tracking: Akimov, A. V. *JPCL* **2018** 9, 6096

Local Diabatization: Granucci, G.; Persico, M.; Toniolo, A. *JCP* **2001**, *114*, 10608; Plasser, F.; Granucci, G.; Pittner, J. et al. *JCP* **2012**, 137, 22A514; Shakiba, M.; Akimov, A. V. *TCA* **2023**, 142, 68

SDM: Granucci, G.; Persico, M. *JCP* **2007**, *126*, 134114; **mSDM**: Smith, B. A.; Akimov, A. V. *JCP*, **2019**, 151, 124107; **IDA**: Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. *JCP* **2013**, *138*, 224111.

FSSH: Tully, J. C. *JCP*, **1990**, 93, 1061

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

Hop Proposal Probability

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

$$\sigma(x) = xH(x) = \begin{cases} x, x \geq 0 \\ 0, otherwise \end{cases} \qquad P_{i\to j}^{FSSH} = \sigma\left(\frac{2Re\left(\rho_{ij}^{*} d_{ij}\right)\Delta t}{\rho_{ii}}\right)$$

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

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

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

$$P_{i\to f}^{P,MSSH}(t, t+\Delta t) = P_{ff}(t+\Delta t)$$

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

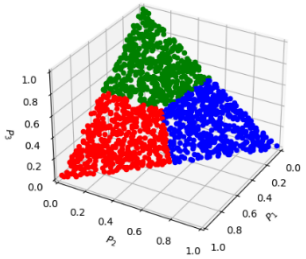
$$P_{i\to j}^{FSSH-2} = \min\left(\sigma\left(-\frac{\rho_{ii}(t+\Delta t)-\rho_{ii}(t)}{\rho_{ii}(t)}\right), \sigma\left(\frac{\rho_{jj}(t+\Delta t)-\rho_{jj}(t)}{\rho_{ii}(t)}\right)\right), \forall j \neq i$$

FSSH3:
Akimov, A. V. *Mol. Phys.* **2024**, *Mol. Phys.* e2376893

$$P_{i\to j}^{FSSH-3} = \sigma\left(-\frac{\Delta\rho_{ii}(t)}{\rho_{ii}(t)}\right)\frac{\sigma\left(J_{j,i}\right)}{\sum_k \sigma\left(J_{k,i}\right)}, \forall j \neq i \qquad \boldsymbol{J}_0 = \min_{\boldsymbol{J}} \|\boldsymbol{y} - \boldsymbol{J}\boldsymbol{x}\|_2^2$$

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.

$$P_{*\to j} = 1, \exists j: \rho_{jj} = \max_i(\rho_{ii})$$
$$P_{*\to k} = 0, \forall k \neq j$$



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.

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 and MSSH Hop Proposal Probability

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FSSH

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

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

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

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

$$P_{i\to j}^{FSSH}=max\left(0,\frac{2Re\left(\rho_{ij}^{*}d_{ij}\right)\Delta t}{\rho_{ii}}\right)$$

$$P_{i\to j}^{P}=\max\left(0,\frac{\Delta t}{\hbar P_{ii}}Im\left[P_{i,j}H_{j,i}^{vib}-H_{i,j}^{vib}P_{j,i}\right]\right)$$

References:

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

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

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

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

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

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

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

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

$$P(j|i) = \frac{\Delta\rho_{jj}}{\sum_{k\in A}(-\Delta\rho_{kk})} = -\frac{\Delta\rho_{jj}}{\sum_{k\in A}\Delta\rho_{kk}}$$ - conditional probability of ending up in state j if left from state i

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

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

FSSH-2

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

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

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

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

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

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

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

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

FSSH-3 Hop Proposal Probability

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

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FSSH-3

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

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

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

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

$\boldsymbol{y} = \boldsymbol{J}\boldsymbol{x}$ - the problem to solve

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

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

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

- **fssh3_size_option**

  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_approach_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_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

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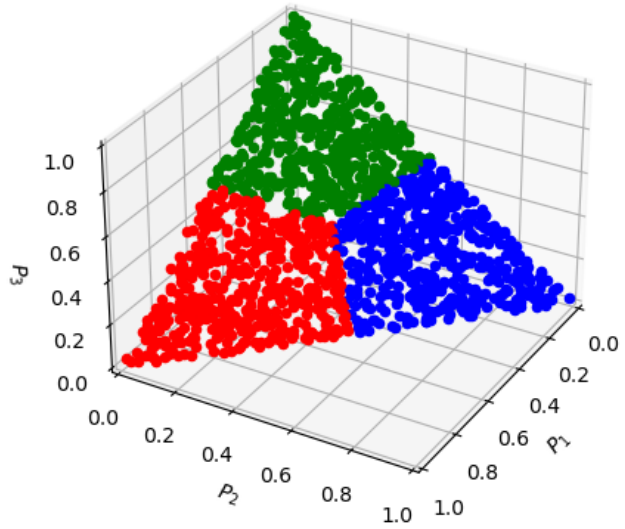
1. Initialization of electronic amplitudes:

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):

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

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

```
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"
              }
```

Hop Proposal Probability

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Landau-Zener (LZ):

Hopping only at the gap minimum!

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

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

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!

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

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

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

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.

Part 4.6: Hop Acceptance

University at Buffalo
The State University of New York

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

$$\hat{H}_{el}\psi_i = E_i\psi_i$$

analytical models or electronic structure codes

Non-adiabatic Couplings

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

Integrate Coherent Electronic Dynamics

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

NBRA

Decoherence 1

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

as in SDM

Proposed Hops Decoherence 2

$$P_{i\rightarrow j} = \Delta t * Re\left(2\frac{p}{m}d_{ij}c_i^*c_j\right)$$

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

NAC: Hammes-Schiffer, S.; Tully, J. C. *JCP* **1994**, *101*, 4657

Phase tracking: Akimov, A. V. *JPCL* **2018** 9, 6096

Local Diabatization: Granucci, G.; Persico, M.; Toniolo, A. *JCP* **2001**, *114*, 10608; Plasser, F.; Granucci, G.; Pittner, J. et al. *JCP* **2012**, 137, 22A514; Shakiba, M.; Akimov, A. V. *TCA* **2023**, 142, 68

SDM: Granucci, G.; Persico, M. *JCP* **2007**, *126*, 134114; **mSDM**: Smith, B. A.; Akimov, A. V. *JCP*, **2019**, 151, 124107; **IDA**: Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. *JCP* **2013**, *138*, 224111.

FSSH: Tully, J. C. *JCP*, **1990**, 93, 1061

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

Hop Acceptance Probabilities

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Options:

- 0: accept all proposed hops [default]

$$P^A_{i\to f} = 1$$

- 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

- 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

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

$$P^A_{i\to f} = \Theta\left(E_{kin} + E_f - E_f\right)$$

- 31: accept hops with the probability taken from the quantum Boltzmann distribution

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

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

- 32: accept hops with the probability taken from the classical Maxwell-Boltzmann distribution

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

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

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

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

$$P^A_{i\to f} = \Theta\left(E^{tr}_{i(t+\Delta t)}(t+\Delta t) + e^{tr}_{kin,i}(t+\Delta t) - e^{tr}_{kin,j}(t+\Delta t)\right)$$

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

Part 4.7: Momentum Rescaling and Reversal

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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

$$\hat{H}_{el}\psi_i = E_i\psi_i$$

analytical models or electronic structure codes

Non-adiabatic Couplings

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

Integrate Coherent Electronic Dynamics

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

NBRA

Decoherence 1

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

as in SDM

Proposed Hops Decoherence 2

$$P_{i\rightarrow j} = \Delta t * Re\left(\frac{2\frac{p}{m}d_{ij}c_i^* c_j}{c_i^* c_i}\right)$$

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

NAC: Hammes-Schiffer, S.; Tully, J. C. *JCP* **1994**, *101*, 4657

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FSSH: Tully, J. C. *JCP*, **1990**, 93, 1061

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

Momentum Rescaling

University at Buffalo
The State University of New York

$$\boldsymbol{P}_n^{(j)} = \boldsymbol{P}_n^{(i)} - \gamma \boldsymbol{t}_{n,ij}$$

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

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

$\Delta_{ij} < 0$ Frustrated hop

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

Reversal or not

$b_{ij} < 0$

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

$b_{ij} \geq 0$

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

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

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

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

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

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

TC-NBRA rescaling of effective kinetic energy:

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

Momentum Reversal on Frustrated Hops: Jasper-Truhlar Criterion

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dyn_control_params

Jasper, A. W.; Truhlar, D. G. Chem. Phys. Lett. 2003, 369, 60– 67

- **use_Jasper_Truhlar_criterion**

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

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

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

Part 4.8: Decoherence Corrections

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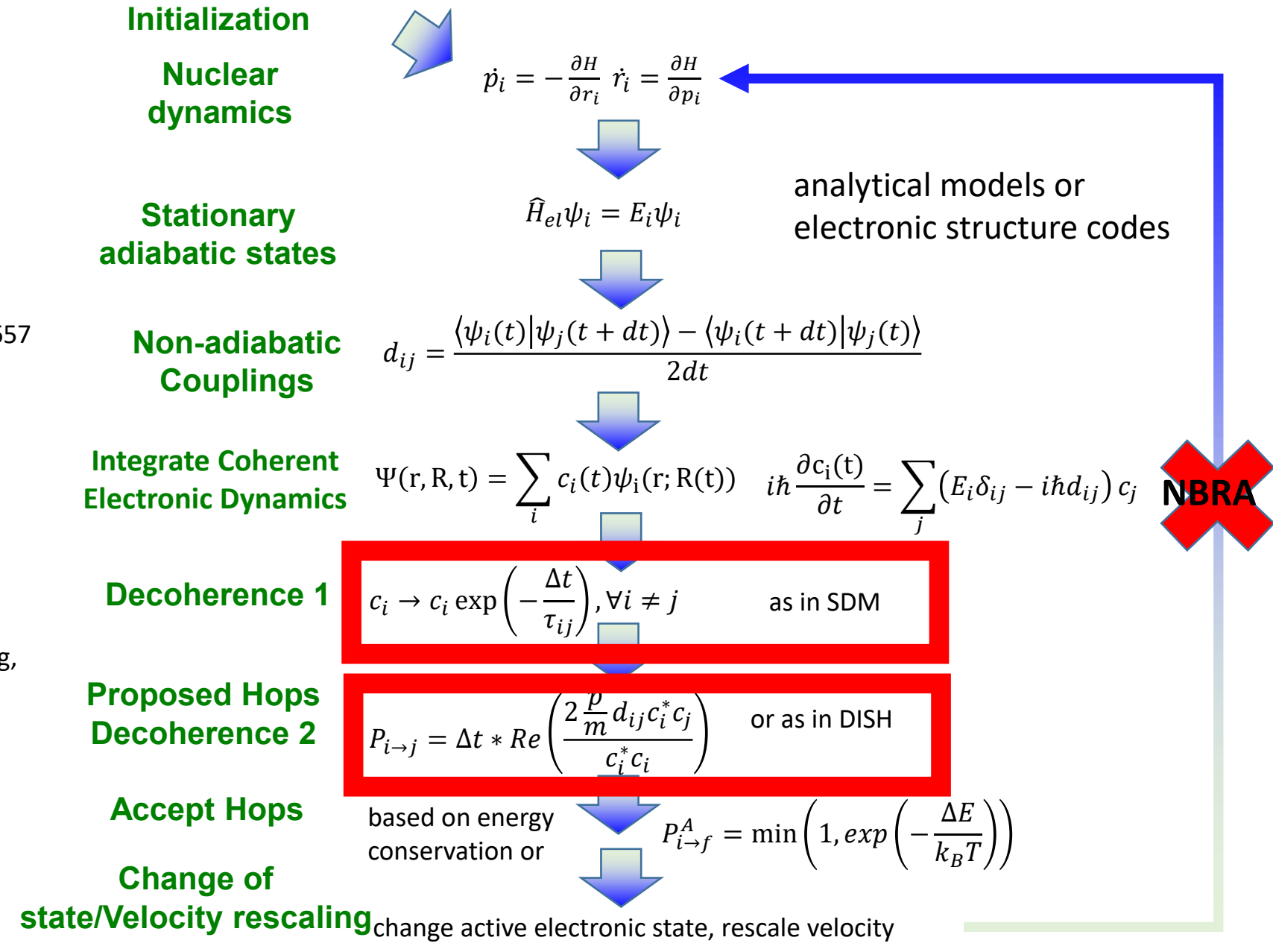

NAC: Hammes-Schiffer, S.; Tully, J. C. *JCP* **1994**, *101*, 4657

Phase tracking: Akimov, A. V. *JPCL* **2018** 9, 6096

Local Diabatization: Granucci, G.; Persico, M.; Toniolo, A. *JCP* **2001**, *114*, 10608; Plasser, F.; Granucci, G.; Pittner, J. et al. *JCP* **2012**, 137, 22A514; Shakiba, M.; Akimov, A. V. *TCA* **2023**, 142, 68

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

Decoherence Options

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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
    - 9: simple decoherence, experimental (in progress)

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

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The State University of New York

SDM

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

gradually change the amplitudes

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

Implicit: energy-based decoherence (**EDC**) is used:

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

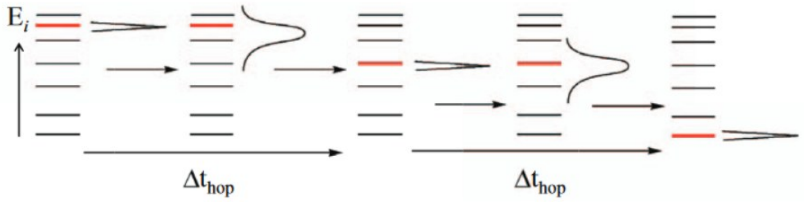
mSDM (modified SDM)

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

The only difference is that the decoherence times defined as:

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

ID - instantaneous_decoherence_variant



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

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

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

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

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

Decoherence: BCSH and MF-SD

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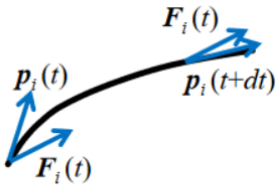
Branching-corrected SH (BCSH)

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

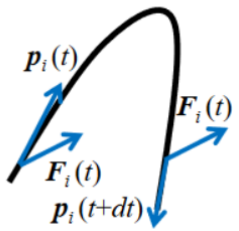
* decoherence is a way to enforce the self-consistency, so:

• 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

$$\text{sign}\{F_i(t)\cdot p_i(t)\} = \text{sign}\{F_i(t)\cdot p_i(t+dt)\}$$



reflection

$$\text{sign}\{F_i(t)\cdot p_i(t)\} = -\text{sign}\{F_i(t)\cdot p_i(t+dt)\}$$

MF-SD

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

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: DISH

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

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?

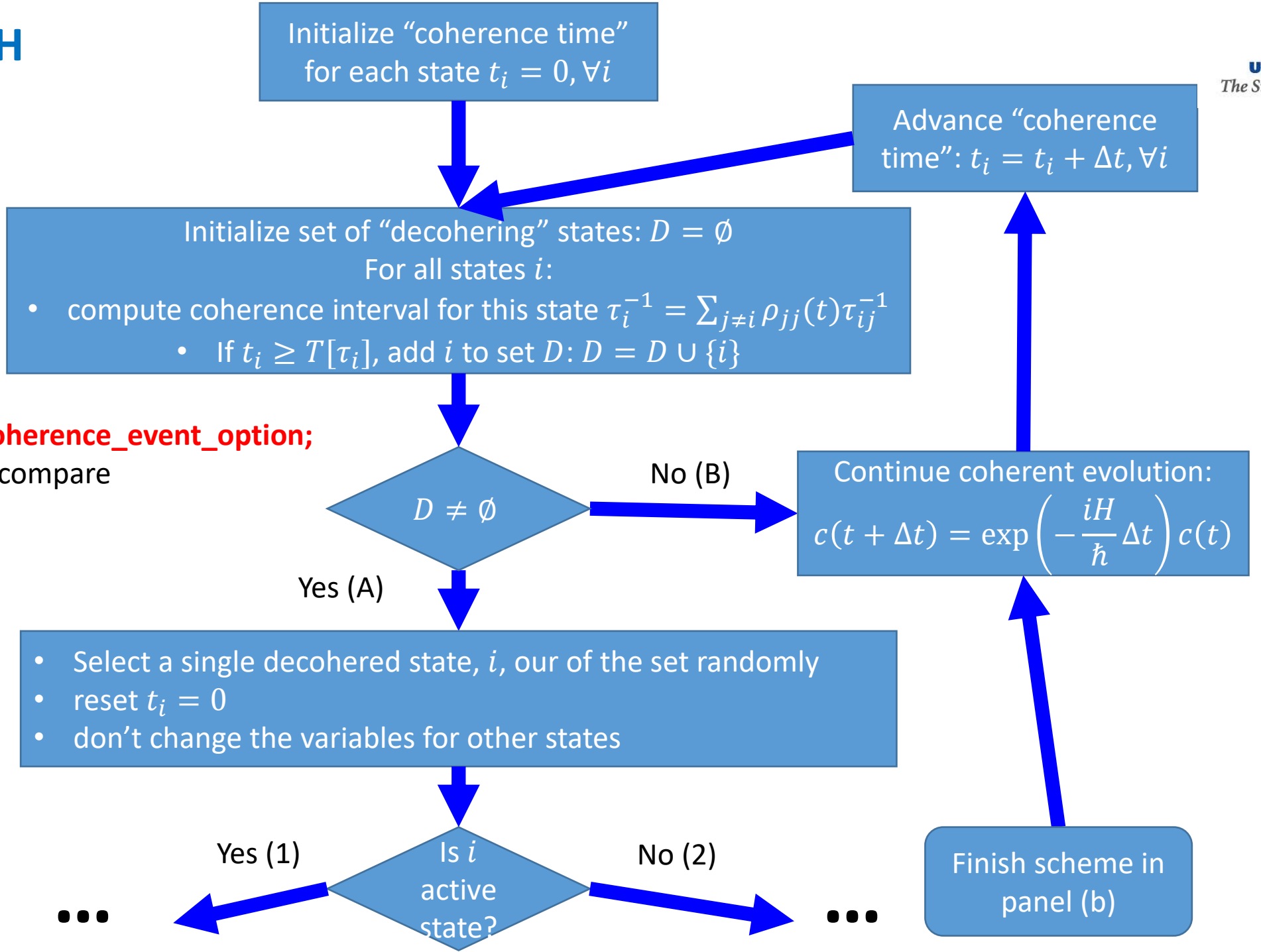
Akimov, A. V. *J. Chem. Phys.* **2021**, 155, 134106.

- 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)

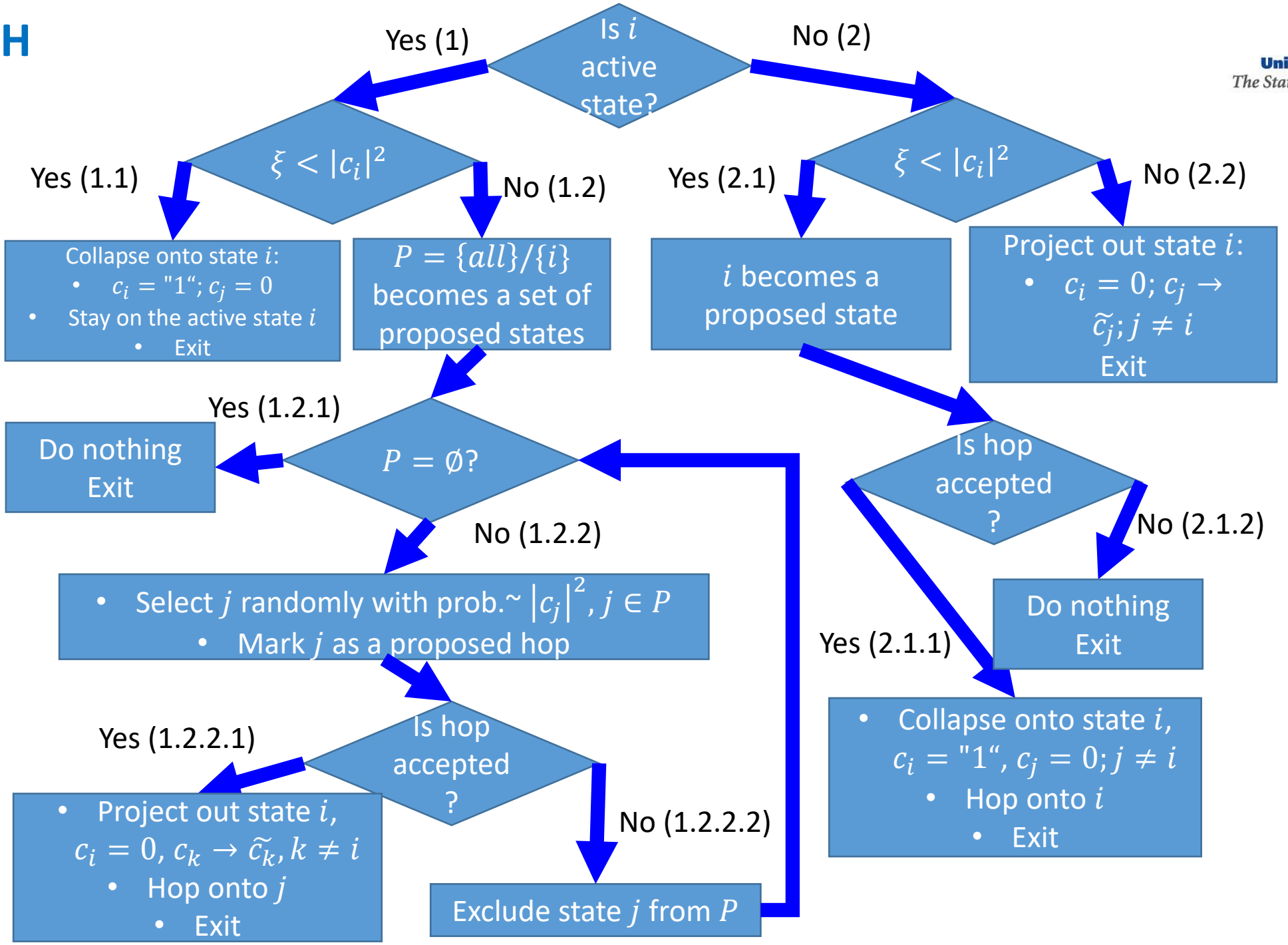
DISH



int dish_decoherence_event_option;

- 0 – direct compare
- 1 -Poisson

DISH


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:
• $c_i = 0$; $c_j \rightarrow \tilde{c_j}; j \neq i$
Exit
Yes (1.2.1)
Do nothing
Exit
$P = \emptyset$?
No (1.2.2)
Is hop accepted ?
No (2.1.2)
Do nothing
Exit
Yes (2.1.1)
• Select j randomly with prob.~ $|c_j|^2, j \in P$
• Mark j as a proposed hop
• Collapse onto state i, $c_i =$ "1", $c_j = 0; j \neq i$
• Hop onto i
• Exit
Yes (1.2.2.1)
Is hop accepted ?
No (1.2.2.2)
• Project out state i, $c_i = 0, c_k \rightarrow \tilde{c_k}, k \neq i$
• Hop onto j
• Exit
Exclude state j from P

Decoherence: DISH_rev2023

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

First revision: Akimov, A. V. *J. Chem. Phys.* **2021**, 155, 134106. **tsh_method = 5**

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)

Branched-out revision: Zhang, Q.; Shao, X.; Li, W.; Mi, W.; Pavanello, M.; Akimov, A. V. *J. Phys.: Condens. Matter* **2024**, *36*, 385901. **tsh_method = * ; decoherence_algo = 7**

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.:

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

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

Decoherence: XFSH and MQCXF

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

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

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

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

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

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

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

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

$$C_j(\boldsymbol{R}) = \left|C_j(\boldsymbol{R})\right|\exp\left(i\theta_j\,(\boldsymbol{R})/\hbar\right) \qquad \nabla_{\nu}\theta_j = \frac{i}{\hbar}\phi_{j\nu}$$

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

Both $\hat{H}_{BO}(\boldsymbol{R}(t))$ and $\hat{H}_{XF}(\boldsymbol{R},t)$ are used	MFXF, aka EhXF	Only $\boldsymbol{F}^{MF}(\boldsymbol{R},t)$
Both $\hat{H}_{BO}(\boldsymbol{R}(t))$ and $\hat{H}_{XF}(\boldsymbol{R},t)$ are used	SHXF (DISH-XF)	Adiabatic forces of the active state
Both $\hat{H}_{BO}(\boldsymbol{R}(t))$ and $\hat{H}_{XF}(\boldsymbol{R},t)$ are used	MQCXF	Both $\boldsymbol{F}^{MF}(\boldsymbol{R},t)$ and $\boldsymbol{F}^{XF}(\boldsymbol{R},t)$ are used

Part 4.9: Computing Decoherence Times

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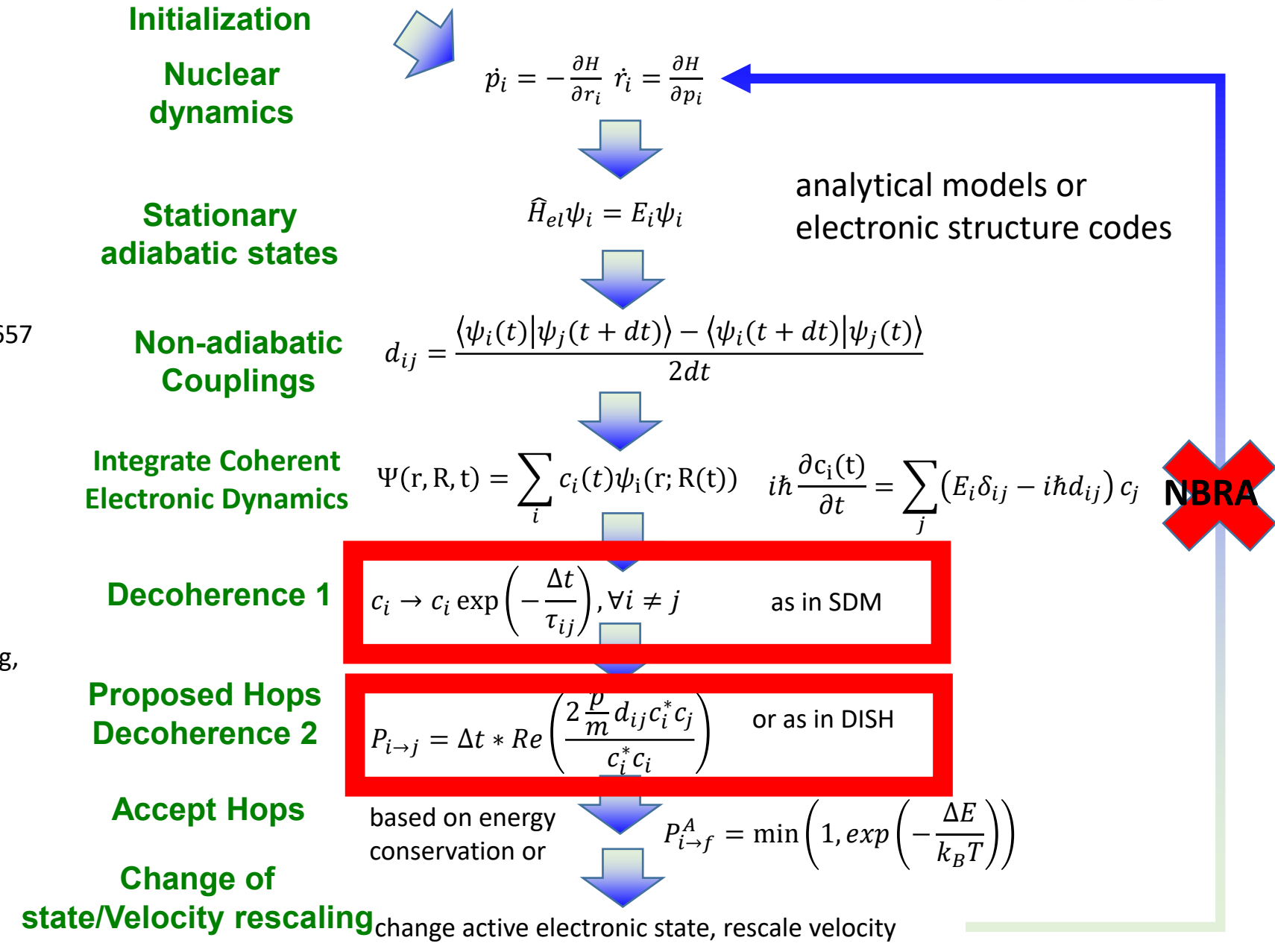

NAC: Hammes-Schiffer, S.; Tully, J. C. *JCP* **1994**, *101*, 4657

Phase tracking: Akimov, A. V. *JPCL* **2018** 9, 6096

Local Diabatization: Granucci, G.; Persico, M.; Toniolo, A. *JCP* **2001**, *114*, 10608; Plasser, F.; Granucci, G.; Pittner, J. et al. *JCP* **2012**, 137, 22A514; Shakiba, M.; Akimov, A. V. *TCA* **2023**, 142, 68

SDM: Granucci, G.; Persico, M. *JCP* **2007**, *126*, 134114; **mSDM**: Smith, B. A.; Akimov, A. V. *JCP*, **2019**, 151, 124107; **IDA**: Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. *JCP* **2013**, *138*, 224111.

FSSH: Tully, J. C. *JCP*, **1990**, 93, 1061

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

Decoherence times

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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.

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

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 (Schwartz 1), using inv_alpha
- 3: Schwartz - pair-wise-based decoherence, (Schwartz 2), using inv_alpha
- 4: Schwartz - mean-field Force-based decoherence (Schwartz 1), but using interaction width
- 5: Gu-Franco

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**

Independent stochastic pairwise decoherence (ISPD)

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

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

Part 4.10: Additional Options and Recipes

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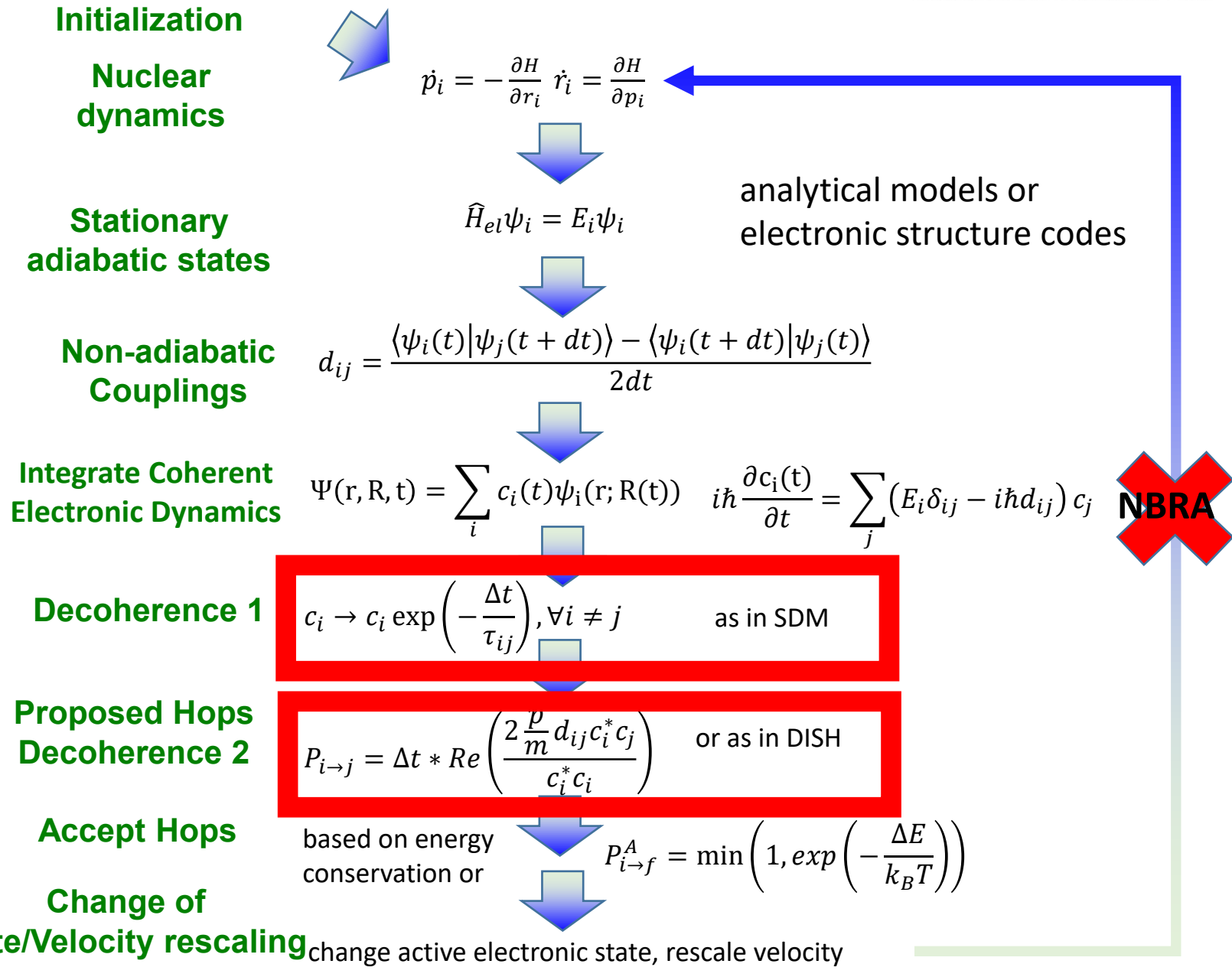

NAC: Hammes-Schiffer, S.; Tully, J. C. *JCP* **1994**, *101*, 4657

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

Other ways of computing Decoherence times

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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.

$$\frac{1}{\tau_{ab}} = k_{ab} = \frac{\pi}{2}\frac{|\boldsymbol{F}_a - \boldsymbol{F}_b|}{|\bar{\boldsymbol{P}}|} + \sqrt{\frac{(\boldsymbol{P}_a - \boldsymbol{P}_b)^2|E_a - E_b|}{4m\hbar^2\pi^2} + \left(\frac{\pi}{2}\frac{|\boldsymbol{F}_a - \boldsymbol{F}_b|}{|\bar{\boldsymbol{P}}|}\right)^2} \qquad \bar{\boldsymbol{P}} = \frac{\boldsymbol{P}_a + \boldsymbol{P}_b}{2}$$

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

Parallel surfaces

$$\tau_{ab}^{Truhlar} = \frac{\hbar}{|E_a - E_b|}\sqrt{\frac{|\bar{\boldsymbol{P}}|}{|\boldsymbol{P}_a - \boldsymbol{P}_b|}}$$

2006, Larsen, Bedard-Hearn, Schwartz

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

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

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2008, Cheng, Truhlar, et al

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

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

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

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

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

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

2012, Jaeger, Fisher, Prezhdo
DISH

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

2013,Akimov, Prezhdo

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

So:

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

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

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

2017, Gu and Franco

As a purity decay rate

$$\sigma(t) = Tr_S\{\rho\} = \sum_i p_i |i\rangle\langle i| \quad \Rightarrow \quad P(t) = Tr_S\{\sigma^2(t)\} = \exp\left(-\frac{t^2}{\tau_d^2}\right)$$

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

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

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

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

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

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

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

2020, Esch, Levine $$\frac{1}{\tau_{ij}^{Esch-Levine}} = \sqrt{\frac{1}{4\hbar^2}\left(\boldsymbol{F}_i - \boldsymbol{F}_j\right)^T A^{-1}\left(\boldsymbol{F}_i - \boldsymbol{F}_j\right)}$$ 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.

$$\tau_i^{SHXF,-1} = \sum_j \boldsymbol{Q}^T M^{-1}\left(\boldsymbol{F_i} - \boldsymbol{F_j}\right)\left|c_j\right|^2$$

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

Shenvi-Subotnik-Yang (SSY) Phase correction

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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: $\frac{g_m(x=x_n(t))}{g_n(x=x_n(t))} = \exp(\Delta\phi) = \exp\left(i\hbar t\, \boldsymbol{P}_n^T M^{-1}(\boldsymbol{P}_m - \boldsymbol{P}_n)\right)$.

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.

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

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

2016, Zhu: in terms of QCLE

rep_tdse = 3;
electronic_integrator=0

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

rep_tdse = 3;
electronic_integrator=1

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

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

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

Setting up parameters controlling dynamics

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```
#=============== Some automatic variables, related to the settings above ===================
dyn_general = { "nsteps":NSTEPS*2, "ntraj":250, "nstates":NSTATES, "dt":DT*units.fs2au, "nfiles": NSTEPS,
                "decoherence_rates":rates, "ave_gaps": gaps,
                "progress_frequency":0.1, "which_adi_states":range(NSTATES), "which_dia_states":range(NSTATES),
                "mem_output_level":2,
                "properties_to_save":[ "timestep", "time","se_pop_adi", "sh_pop_adi" ],
                "prefix":F"NBRA", "isNBRA":0
              }
```

```
# Uncomment one of the options in each of the categories below:
#====== How to update Hamiltonian ==================
#dyn_general.update({"ham_update_method":0}) # don't update any Hamiltonians
#dyn_general.update({"ham_update_method":1})  # recompute only diabatic Hamiltonian, common choice for model Hamiltonians
dyn_general.update({"ham_update_method":2})  # recompute only adiabatic Hamiltonian; use with file-based or on-the-fly workflows
```

```
#====== How to transform the Hamiltonians between representations ============
dyn_general.update( {"ham_transform_method":0 }) # don't do any transforms; usually for NBRA or on-the-fly workflows,
                                                 # so you don't override the read values
#dyn_general.update( {"ham_transform_method":1 }) # diabatic->adiabatic according to internal diagonalization
#dyn_general.update( {"ham_transform_method":2 }) # diabatic->adiabatic according to internally stored basis transformation matr
#dyn_general.update( {"ham_transform_method":3 }) # adiabatic->diabatic according to internally stored basis transformation matr
#dyn_general.update( {"ham_transform_method":4 }) # adiabatic->diabatic according to local diabatization method
```

Composite schemes

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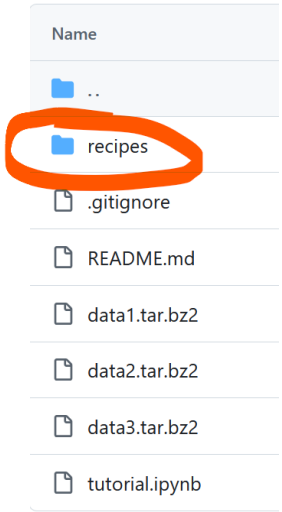
How to evolve electronic amplitudes	Electron-nuclear dynamics	Hop proposal	Decoherence correction	Decoherence times
	XF variants	GFSH	SDM/mSDM	DISH
	MF	FSSH	IDA/IDF	EDC
With SSY	Adiabatic	FSSH-2	BCSH	Schwartz 1
Without SSY	QTSH	FSSH-3	DISH (rev)	Schwartz 2
			XF	

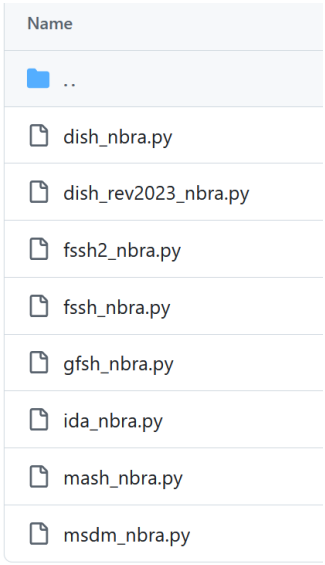
Decoherence time hyperparameters

As a result: SSY-GFSH-mSDM, etc.

```
(libra) alexvakimov@Hegel:~/SOFTWARE/libra/_build$ vi ../src/libra_py/dynamics/tsh/recipes/
Display all 542 possibilities? (y or n)
README.md                          dish_gu_franco_fssh_h_minus.py      fssh2_g_jt.py                  sdm_edc_fssh_h_plus.py
__init__.py                        dish_gu_franco_fssh_h_minus_ssy.py  fssh2_g_jt_ssy.py              sdm_edc_fssh_h_plus_ssy.py
bcsh_fssh2_g_jt.py                 dish_gu_franco_fssh_h_plus.py       fssh2_g_minus.py               sdm_edc_fssh_v_jt.py
bcsh_fssh2_g_jt_ssy.py             dish_gu_franco_fssh_h_plus_ssy.py   fssh2_g_minus_ssy.py           sdm_edc_fssh_v_jt_ssy.py
bcsh_fssh2_g_minus.py              dish_gu_franco_fssh_v_jt.py         fssh2_g_plus.py                sdm_edc_fssh_v_minus.py
bcsh_fssh2_g_minus_ssy.py          dish_gu_franco_fssh_v_jt_ssy.py     fssh2_g_plus_ssy.py            sdm_edc_fssh_v_minus_ssy.py
bcsh_fssh2_g_plus.py               dish_gu_franco_fssh_v_minus.py      fssh2_h_jt.py                  sdm_edc_fssh_v_plus.py
bcsh_fssh2_g_plus_ssy.py           dish_gu_franco_fssh_v_minus_ssy.py  fssh2_h_jt_ssy.py              sdm_edc_fssh_v_plus_ssy.py
bcsh_fssh2_h_jt.py                 dish_gu_franco_fssh_v_plus.py       fssh2_h_minus.py               sdm_edc_gfsh_g_jt.py
bcsh_fssh2_h_jt_ssy.py             dish_gu_franco_fssh_v_plus_ssy.py   fssh2_h_minus_ssy.py           sdm_edc_gfsh_g_jt_ssy.py
bcsh_fssh2_h_minus.py              dish_gu_franco_gfsh_g_jt.py         fssh2_h_plus.py                sdm_edc_gfsh_g_minus.py
bcsh_fssh2_h_minus_ssy.py          dish_gu_franco_gfsh_g_jt_ssy.py     fssh2_h_plus_ssy.py            sdm_edc_gfsh_g_minus_ssy.py
bcsh_fssh2_h_plus.py               dish_gu_franco_gfsh_g_minus.py      fssh2_v_jt.py                  sdm_edc_gfsh_g_plus.py
```

Recipes






```
from recipes import dish_rev2023_nbra, fssh_nbra, fssh2_nbra, gfsh_
```

```
#============== Select the method =====================
# UNCOMMENT AS NEEDED

#dish_rev2023_nbra.load(dyn_general); prf = "DISH"  # DISH
#fssh_nbra.load(dyn_general); prf = "FSSH"  # FSSH
#fssh2_nbra.load(dyn_general); prf = "FSSH2"  # FSSH2
#gfsh_nbra.load(dyn_general); prf = "GFSH"  # GFSH
#ida_nbra.load(dyn_general); prf = "IDA"  # IDA
#mash_nbra.load(dyn_general); prf = "MASH"  # MASH
#msdm_nbra.load(dyn_general); prf = "MSDM"  # MSDM
```

```
from liblibra_core import *

def load(dyn_general):

    # Uncomment one of the options in each of the categories below:
    #====== How to update Hamiltonian ==================
    #dyn_general.update({"ham_update_method":0}) # don't update any Hamiltonians
    #dyn_general.update({"ham_update_method":1})  # recompute only diabatic Hamilto
    dyn_general.update({"ham_update_method":2})  # recompute only adiabatic Hamilto


    #====== How to transform the Hamiltonians between representations ============
    dyn_general.update( {"ham_transform_method":0 }) # don't do any transforms; usu
                                                     # so you don't override the r
    #dyn_general.update( {"ham_transform_method":1 }) # diabatic->adiabatic accordi
    #dyn_general.update( {"ham_transform_method":2 }) # diabatic->adiabatic accordi
    #dyn_general.update( {"ham_transform_method":3 }) # adiabatic->diabatic accordi
    #dyn_general.update( {"ham_transform_method":4 }) # adiabatic->diabatic accordi

    #====== How do get the time-overlaps in the dynamics ========
    dyn_general.update( {"time_overlap_method":0 })  # don't update time-overlaps -
    #dyn_general.update( {"time_overlap_method":1 }) # explicitly compute it from t

    #================== How to compute NACs ==============================
    dyn_general.update({"nac_update_method":0 })  # just read from files
    #dyn_general.update({"nac_update_method":1})  # explicit NAC calculations - let
    #dyn_general.update({"nac_update_method":2, "nac_algo":0})  # HST algo
    #dyn_general.update({"nac_update_method":2, "nac_algo":1})  # NPI algo
```

Part 4.11: Observables and Properties

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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

$$\hat{H}_{el}\psi_i = E_i\psi_i$$

analytical models or electronic structure codes

Non-adiabatic Couplings

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

Integrate Coherent Electronic Dynamics

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

NBRA

Decoherence 1

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

as in SDM

Proposed Hops Decoherence 2

$$P_{i\to j} = \Delta t * Re\left(\frac{2\frac{p}{m}d_{ij}c_i^* c_j}{c_i^* c_i}\right)$$

or as in DISH

Accept Hops

based on energy conservation or

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

Change of state/Velocity rescaling

change active electronic state, rescale velocity

NAC: Hammes-Schiffer, S.; Tully, J. C. *JCP* **1994**, *101*, 4657

Phase tracking: Akimov, A. V. *JPCL* **2018** 9, 6096

Local Diabatization: Granucci, G.; Persico, M.; Toniolo, A. *JCP* **2001**, *114*, 10608; Plasser, F.; Granucci, G.; Pittner, J. et al. *JCP* **2012**, 137, 22A514; Shakiba, M.; Akimov, A. V. *TCA* **2023**, 142, 68

SDM: Granucci, G.; Persico, M. *JCP* **2007**, *126*, 134114; **mSDM**: Smith, B. A.; Akimov, A. V. *JCP*, **2019**, 151, 124107; **IDA**: Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. *JCP* **2013**, *138*, 224111.

FSSH: Tully, J. C. *JCP*, **1990**, 93, 1061

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

Properties and variables

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"properties_to_save": […, "states",
"SH_pop",
"SH_pop_raw",
"se_pop_adi",
"se_pop_dia",
"sh_pop_adi",
"D_adi",
"D_adi_raw",
"D_dia",
"D_dia_raw",
"q",
"p",
"f",
"Cadi",
"Cdia",
"q_mm",
"p_mm",
"hvib_adi",
"hvib_dia",
"St",
"basis_transform",
"projector", …]

```
#=============== Some automatic variables, related to the settings above ==================
dyn_general = { "nsteps":NSTEPS*2, "ntraj":250, "nstates":NSTATES, "dt":DT*units.fs2au, "nfiles": NSTEPS,
                "decoherence_rates":rates, "ave_gaps": gaps,
                "progress_frequency":0.1, "which_adi_states":range(NSTATES), "which_dia_states":range(NSTATES),
                "mem_output_level":2,
                "properties_to_save":[ "timestep", "time","se_pop_adi", "sh_pop_adi" ],
                "prefix":F"NBRA", "isNBRA":0
              }
```

"mem_output_level": -1
1 – 1D: e.g. `time[timestep]` or `Epot_ave[timestep]`
2 – 2D: e.g. `se_pop_adi[timestep, istate]` or `states[timestep, itraj]`
3 – 3D: e.g. Cadi[timestep, istate, itraj]
4 – 4D: e.g. St
5 - 5D: only `dc1_adi[timestep, itraj, idof, istate, jstate]` so far

1D data

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["timestep",	Time axis (integer steps)
"time",	Time axis (a.u. of time)
"Ekin_ave",	Average kinetic energy
"Epot_ave",	Average potential energy
"Etot_ave",	Average total energy
"dEkin_ave",	Fluctuation of average kinetic energy
"dEpot_ave",	Fluctuation of average potential energy
"dEtot_ave",	Fluctuation of average total energy
“Etherm”,	Thermostat energy
“E_NHC”,	System + thermostat energy
“tcnbra_ekin”,	TC-NBRA kinetic energy - averaged over all trajectories
“tcnbra_thermostat_energy”,	TC-NBRA thermostat energy
“Ekin_ave_qtsh”,	Average kinetic energy in QTSH
“ekin_aux_var”]	KC-RPMD auxiliary electronic variable kinetic energy

2D data

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["states",	Trajectory-resolved instantaneous adiabatic states, nsteps x ntraj
"states_dia",	Trajectory-resolved instantaneous diabatic states, nsteps x ntraj
"se_pop_adi",	Average adiabatic SE populations, nsteps x nstates, $p_i^{SE,adi}(t) = \frac{1}{N_{traj}} \sum_{j=1}^{N_{traj}} \left\| c_{i,j}^{adi}(t) \right\|^2$
"se_pop_dia",	Average diabatic SE populations, nsteps x nstates, $p_i^{SE,dia}(t) = \frac{1}{N_{traj}} \sum_{j=1}^{N_{traj}} \left\| c_{i,j}^{dia}(t) \right\|^2$
"sh_pop_adi",	Average adiabatic SH populations, nsteps x nstates, $p_i^{SH,adi}(t) = \frac{N_i^{adi}(t)}{N_{traj}}$
"sh_pop_dia",	Average diabatic SH populations, nsteps x nstates, $p_i^{SH,dia}(t) = \frac{N_i^{dia}(t)}{N_{traj}}$
"sh_pop_adi_TR",	Average adiabatic SH populations from the Tempelaar and Reichman's method, nsteps x nstates
"sh_pop_dia_TR",	Average diabatic SH populations from the Tempelaar and Reichman's method, nsteps x nstates
"mash_pop_adi",	Average adiabatic MASH populations, nsteps x nstates
"mash_pop_dia",	Average diabatic MASH populations, nsteps x nstates
"fssh3_average_errors",	Average errors from FSSH3, nsteps x 5
"y_aux_var",	Trajectory-resolved auxiliary electronic variable coordinate in kc-RPMD, nsteps x 1
"p_aux_var",	Trajectory-resolved auxiliary electronic variable momentum, nsteps x 1
"f_aux_var"	Trajectory-resolved auxiliary electronic variable force, nsteps x 1
]	

3D data

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["coherence_adi",	Average coherence indicator matrices, nsteps x nstates x nstates
"coherence_dia",	
"q", "p", "f",	Trajectory-resolved coordinates, momenta, and forces, nsteps x ntraj x ndof
"Cadi", "Cdia",	Trajectory-resolved (a)diabatic TD-SE amplitudes, nsteps x ntraj x nstates (complex)
"p_quant",	Trajectory-resolved quantum momenta, nsteps x ntraj x ndof
"wp_quant",	Trajectory-resolved width parameters for quantum momenta, nsteps x ntraj x ndof
"VP",	Trajectory-resolved exact vector potential, nsteps x ntraj x ndof
"f_xf",	Trajectory-resolved decoherence forces based on XF, nsteps x ntraj x ndof
"qtsh_f_nc",	Trajectory-resolved nonclassical forces in QTSH, nsteps x ntraj x ndof
"ave_decoherence_rates"	Trajectory-averaged decoherence rates, nsteps x nstates x nstates
]	

4D data

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[“hvia_adi", “hvib_dia”,	Trajectory-resolved vibronic (a)diabatic Hamiltonian, nsteps x ntraj x nstates x nstates (complex)
“St”,	Trajectory-resolved time-overlaps of the adiabatic states, nsteps x ntraj x nstates x nstates (complex)
“basis_transform”,	Trajectory-resolved diabatic-to-adiabatic transformation matrices, nsteps x ntraj x nstates x nstates (complex)
“projector”,	Trajectory-resolved projector matrices (from the raw adiabatic to consistent adiabatic), nsteps x ntraj x nstates x nstates (complex)
“q_aux”, “p_aux”,	Trajectory-resolved auxiliary coordinates/momenta for XF methods, nsteps x ntraj x nstates x ndofs
“nab_phase”,	Trajectory-resolved nabla_phase for XF methods, nsteps x ntraj x nstates x ndofs
“energy_gaps”,	Trajectory-resolved energy gaps, nsteps x ntraj x nstates x nstates
“mean_energy_gaps”,	Trajectory-resolved running-average (mean) energy gaps
“energy_gaps2”,	Trajectory-resolved energy gaps squared
“mean_energy_gaps2”	Trajectory-resolved running-average (mean) energy gaps squared
“energy_gap_fluctuations”,	Trajectory-resolved energy gap fluctuations
“energy_gap_correlations”	Trajectory-resolved gap correlation functions

]

Computing state populations in Libra

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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

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

$$\boldsymbol{H}_{dia}\boldsymbol{U} = \boldsymbol{S}\boldsymbol{U}\boldsymbol{H}_{adi}$$

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

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

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

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

This is a mixture of the SH populations and SE coherences

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

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.