# *Excited States and Nonadiabatic Dynamics*
# *CyberTraining School/Workshop 2023*

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June 12, 2023

# *Basic Concepts and Terminology of Nonadiabatic Dynamics*

# Born-Oppenheimer Approximation

$$\hat{H}(\hat{\boldsymbol{r}},\hat{\boldsymbol{R}},t)=\hat{T}(\hat{\boldsymbol{R}})+\hat{H}_{el}(\hat{\boldsymbol{r}},\hat{\boldsymbol{R}},t)+\hat{V}_{nn}(\hat{\boldsymbol{R}},t)$$

$$\hat{H}(\hat{\boldsymbol{r}},\hat{\boldsymbol{R}})\Psi_{\mathrm{n}}(\boldsymbol{r},\boldsymbol{R})=E_n\Psi_n(\boldsymbol{r},\boldsymbol{R})$$

Includes el-el and el-nucl interactions

This is an **electron-nuclear (vibronic)** Hamiltonian

This is an **electron-nuclear (vibronic)** wavefunction

**Born-Oppenheimer approximation**: a general **time-scale separation** approximation = there are fast and slow degrees of freedom, in general. **Enables factorization $X(fast,slow)\approx x(slow)y(fast;slow)$** the adiabatic approximation applied to **electrons and nuclei**

- Nuclei are heavier than electrons, so nuclei are seeing by electrons as static entities
- Electrons move in the field created by immobile nuclei and themselves
- $m_{nucl}\gg m_{elec}$, so treat nuclei classically, and electrons – quantum-mechanically

$$\boxed{\hat{H}(\hat{\boldsymbol{r}},\hat{\boldsymbol{R}})}\Psi_{\mathrm{n}}(\boldsymbol{r},\boldsymbol{R})=E_n\Psi_n(\boldsymbol{r},\boldsymbol{R})\quad\Rightarrow\quad\boxed{\hat{H}(\hat{\boldsymbol{r}};\boldsymbol{R}(t))}\Psi_{\mathrm{n}}(\boldsymbol{r};\boldsymbol{R})=E_n(\boldsymbol{R})\Psi_n(\boldsymbol{r};\boldsymbol{R}(t))$$

**BO approximation**

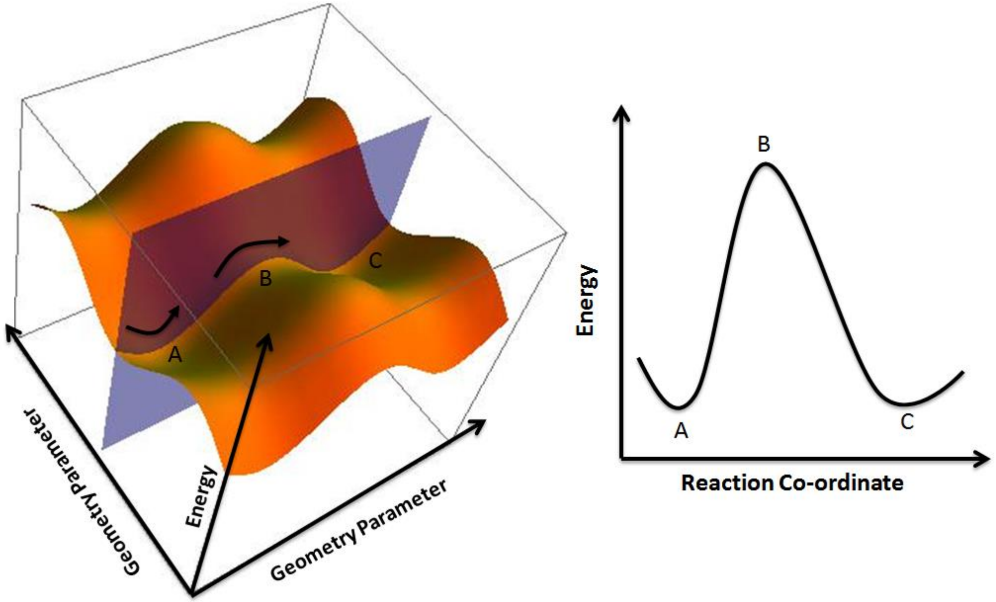
Coordinates of nuclei are the dynamical variables
Energy - is a number

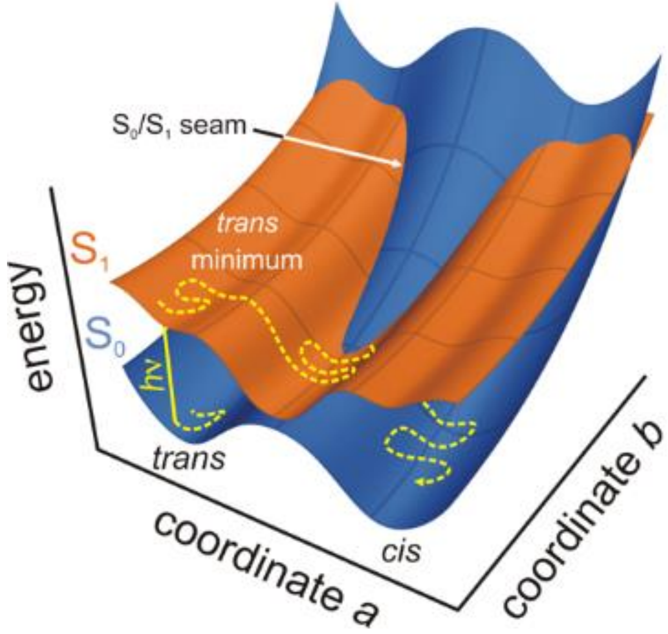
Coordinates of nuclei are parameters
Energy – is a function of these parameters: **potential energy surface**

# Potential energy surfaces (PES)

$$E_n(\boldsymbol{R}) = \left\langle \Psi_{\mathrm{n}}(\mathbf{r},\mathbf{R}) \middle| \hat{H}_{el}(\boldsymbol{r},\boldsymbol{R}) \middle| \Psi_{\mathrm{n}}(\mathbf{r},\mathbf{R}) \right\rangle_{\boldsymbol{r}} + V_{nn}(\boldsymbol{R})$$

- Energy of a given state as a function of nuclear coordinates
- Multidimensional, but one is often interested in lower-dimensional cuts (profiles)
- Topology: minima, maxima, barriers, saddle points
- Reaction coordinate – a collective transformation of all atoms
- Present only as a consequence of the BO approximation





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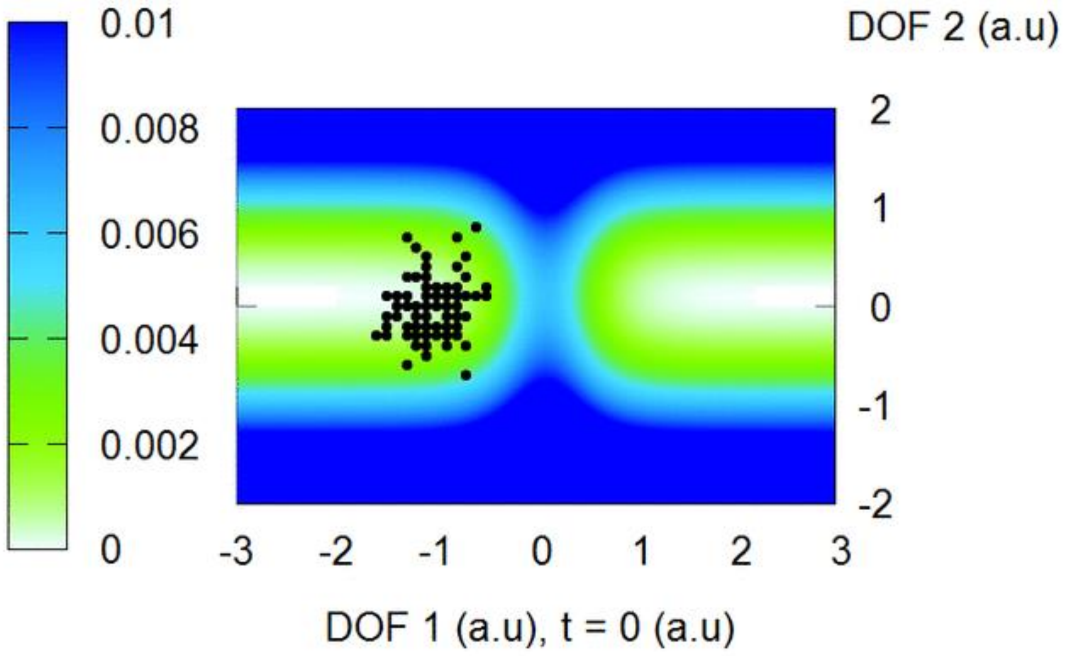
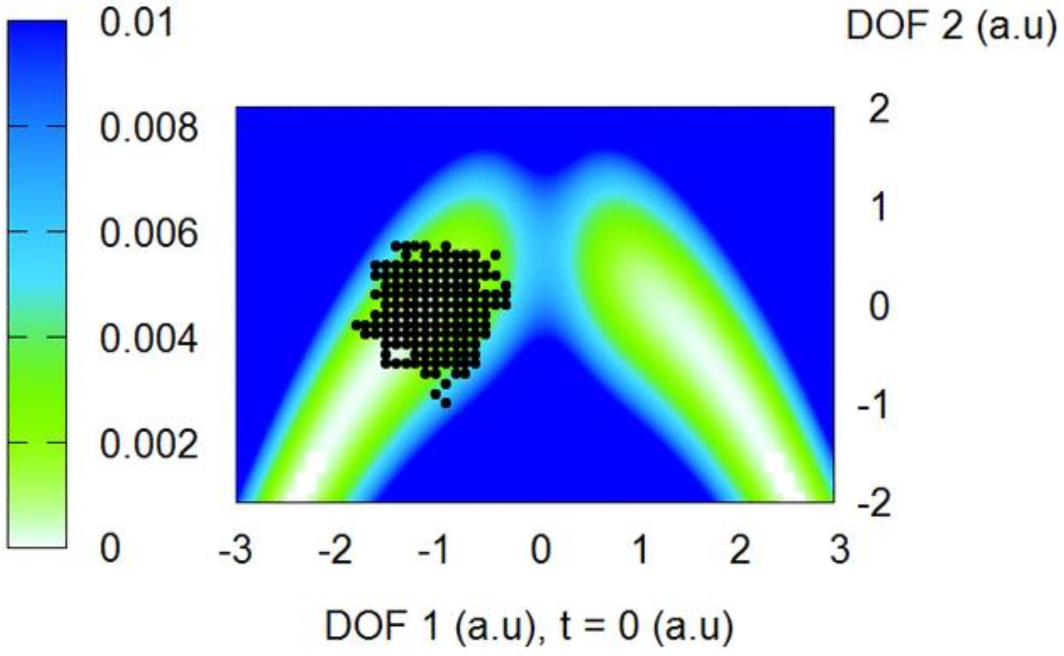
# Potential energy surfaces define the reactive dynamics

Credit: Brendan Smith





# Tiers of approximation to the molecular Hamiltonian

Disregard the form of the wavefunction for now

Everything is operators!

Exact TD-SE

$$i\hbar \frac{\partial \Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = \left[\hat{T}(\hat{\boldsymbol{R}}) + \hat{H}_{el}(\hat{\boldsymbol{r}},\hat{\boldsymbol{R}}) + \hat{V}_{nn}(\hat{\boldsymbol{R}})\right]\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

Electronic DOFs are still operators (quantum)

TD-SE with the BO

$$i\hbar \frac{\partial \Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = \left[\hat{T}(\hat{\boldsymbol{R}}) + \hat{H}_{el}(\hat{\boldsymbol{r}};\boldsymbol{R}) + \hat{V}_{nn}(\boldsymbol{R})\right]\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

Nuclear DOFs are variables – could be independent (quantum) or could be time-dependent (classical path)

In general, we still have nuclear kinetic energy operator (for quantum nuclei)

TD-SE with the classical path approximation (CPA)

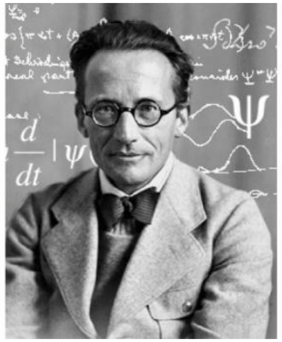
$$i\hbar \frac{\partial \Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = \left[T(\boldsymbol{P}) + \hat{H}_{el}(\hat{\boldsymbol{r}};\boldsymbol{R}(t)) + \hat{V}_{nn}(\boldsymbol{R}(t))\right]\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

Nuclear DOFs are time-dependent variables

Kinetic energy is a function of momentum

# Adiabatic Approximation. Adiabatic and Nonadiabatic Dynamics

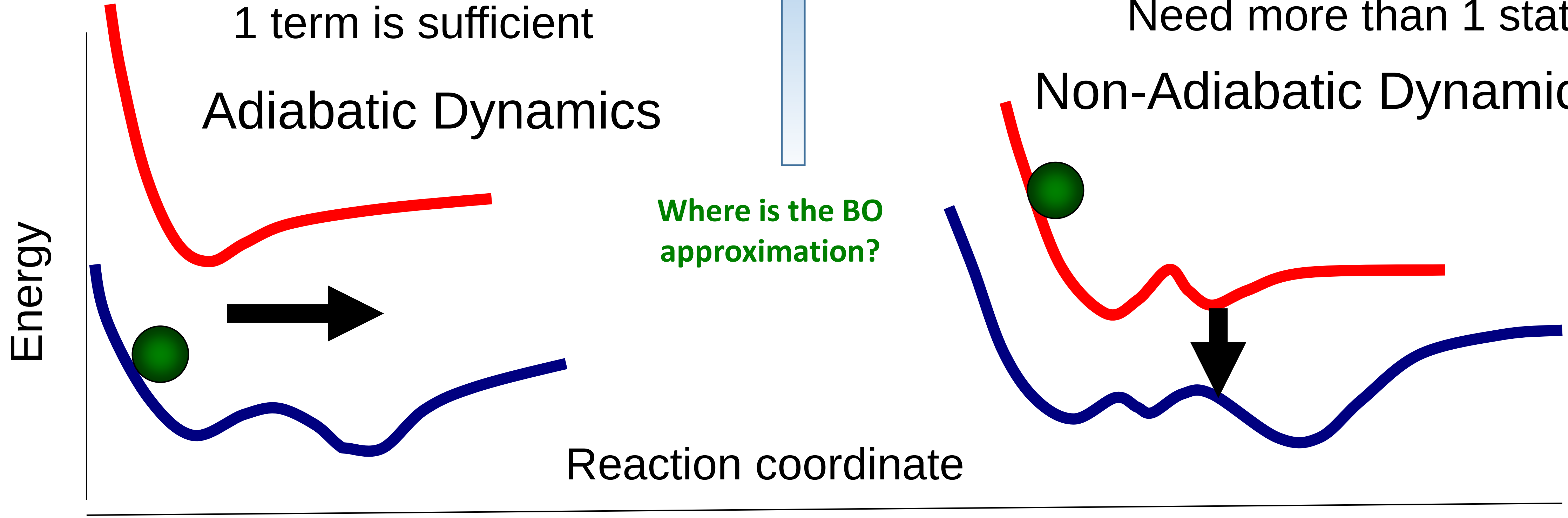
$$i\hbar\frac{\partial\Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = H(t,\hat{\boldsymbol{r}},\hat{\boldsymbol{R}})\Psi(t,\boldsymbol{r},\boldsymbol{R})$$



$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R}(t))$$

Except for in the exact factorization ansatz!

**Adiabatic approximation:** keep only one term



1 term is sufficient

Adiabatic Dynamics

**Where is the BO approximation?**

Need more than 1 state

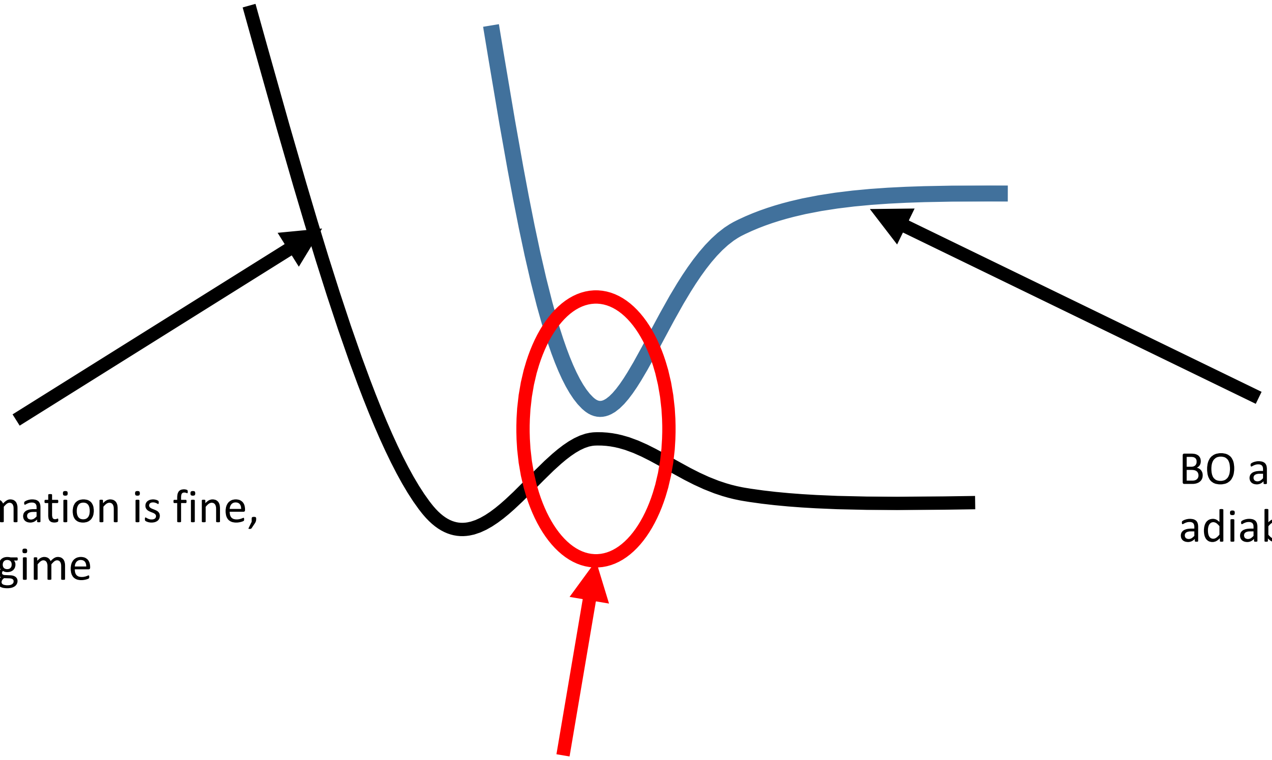
Non-Adiabatic Dynamics

# When NA dynamics is needed: Failure of the Born-Oppenheimer Approximation

$E_{kin} \gg |E_i - E_j|$

$v = \frac{p}{m}$

- light atoms (e.g. H – quantum nuclear effects)
- high-energy (momentum) – e.g. colliding particles
- degeneracies of quantum states (bond-breaking, plasmas, metals)



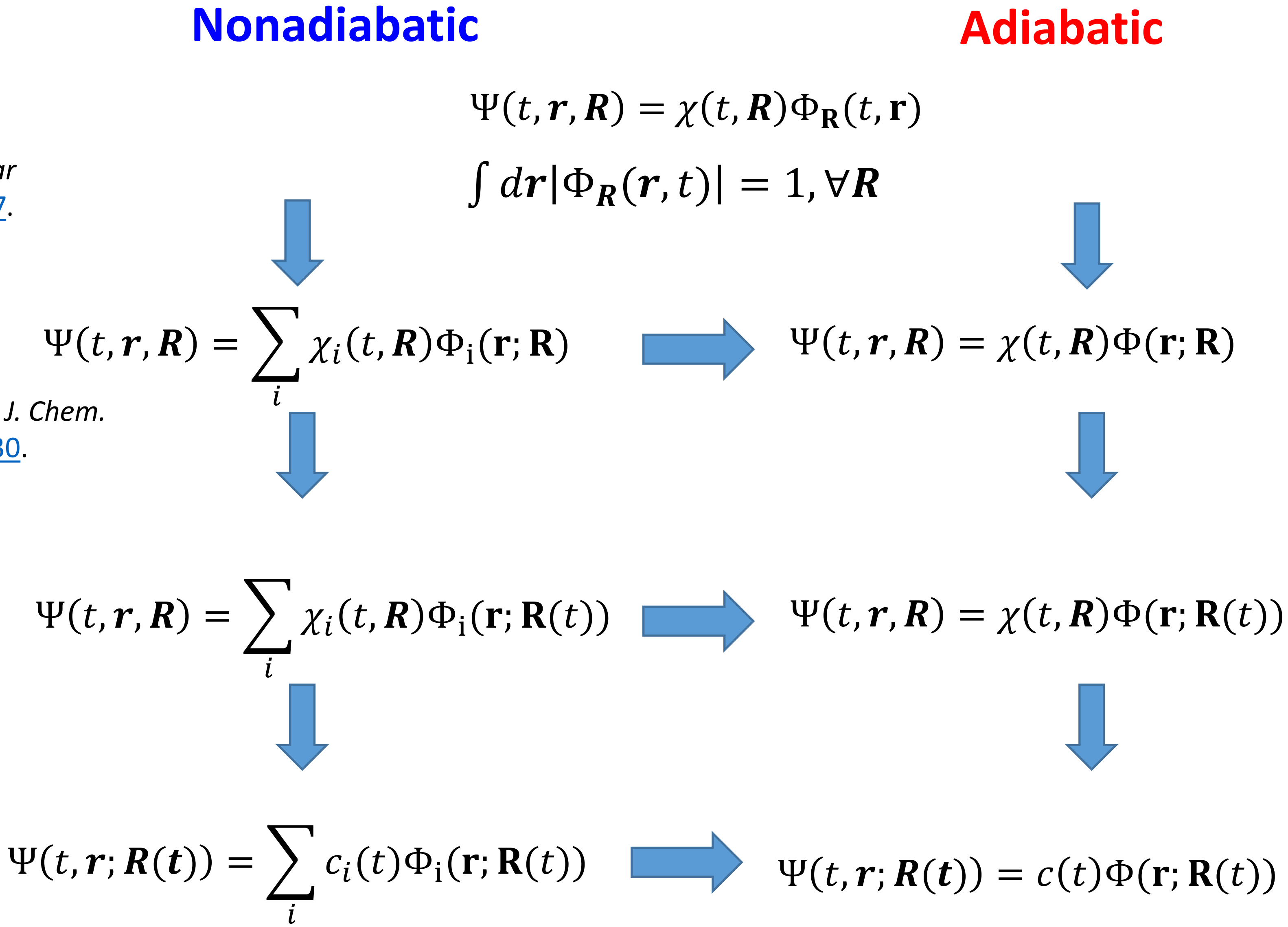
BO approximation is fine, adiabatic regime

BO approximation is fine, adiabatic regime

BO approximation breaks down here, non-adiabatic regime

# Tiers of approximations to the wavefunction

The solution largely depends on the approximation we make to represent the total wavefunction $\Psi(t,\boldsymbol{r},\boldsymbol{R})$



**Nonadiabatic**

**Adiabatic**

### Exact factorization

Agostini, F.; Curchod, B. F. E. *WIREs Computational Molecular Science* **2019**, *9*, e1417. https://doi.org/10.1002/wcms.1417.

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \chi(t,\boldsymbol{R})\Phi_{\mathbf{R}}(t,\mathbf{r})$$

$$\int d\boldsymbol{r}|\Phi_{\boldsymbol{R}}(\boldsymbol{r},t)| = 1, \forall \boldsymbol{R}$$

### Quantum nuclei, with BO approximation (AIMS, QTAG, etc.)

Makhov, D. V.; Glover, W. J.; Martinez, T. J.; Shalashilin, D. V. *J. Chem. Phys.* **2014**, *141*, 054110. https://doi.org/10.1063/1.4891530.

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_\mathrm{i}(\mathbf{r};\mathbf{R}) \quad\Rightarrow\quad \Psi(t,\boldsymbol{r},\boldsymbol{R}) = \chi(t,\boldsymbol{R})\Phi(\mathbf{r};\mathbf{R})$$

### Wavepacket-dressed trajectories

Dutra, M.; Garashchuk, S.; Akimov, A. V. *Int. J. Quantum Chem.* **2023** e27078. https://doi.org/10.1002/qua.27078.

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_\mathrm{i}(\mathbf{r};\mathbf{R}(t)) \quad\Rightarrow\quad \Psi(t,\boldsymbol{r},\boldsymbol{R}) = \chi(t,\boldsymbol{R})\Phi(\mathbf{r};\mathbf{R}(t))$$

### Bare trajectories

Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061–1071. https://doi.org/10.1063/1.459170.

$$\Psi(t,\boldsymbol{r};\boldsymbol{R}(\boldsymbol{t})) = \sum_i c_i(t)\Phi_\mathrm{i}(\mathbf{r};\mathbf{R}(t)) \quad\Rightarrow\quad \Psi(t,\boldsymbol{r};\boldsymbol{R}(\boldsymbol{t})) = c(t)\Phi(\mathbf{r};\mathbf{R}(t))$$

# Terminology: Adiabatic and Diabatic States

## Adiabatic

- unique
- eigenstates of molecular Hamiltonian:
- not always chemically-intuitive

Adiabatic (Hamiltonian is diagonal):

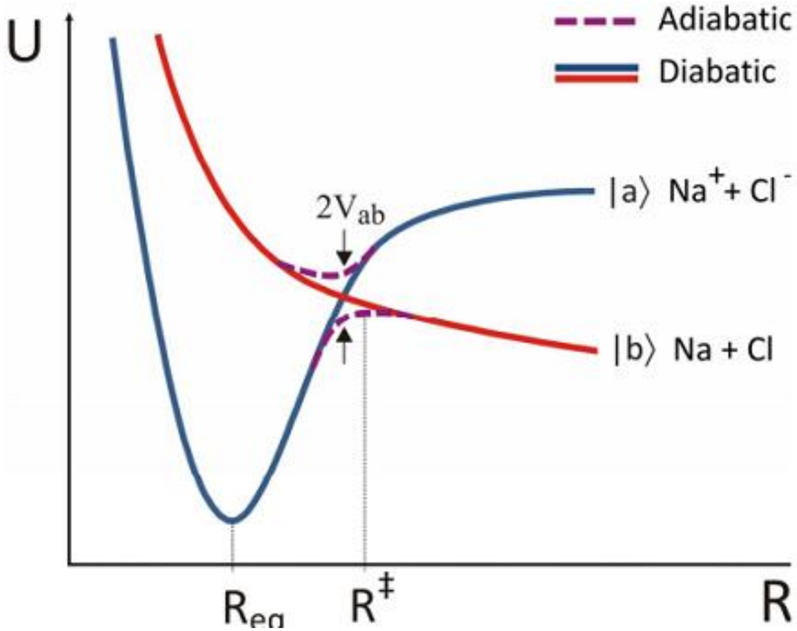
$$\langle \psi_{adi,i} | \hat{H}_{el} | \psi_{adi,j} \rangle = 0, \forall i \neq j$$

## (Quasi-)Diabatic

- non-unique, infinite # of possibilities
- Is not an eigenstate of molecular Hamiltonian
- usually chosen to be chemically-intuitive

Diabatic (NACs are exactly zero):

$$\langle \psi_{dia,i} | \nabla_{\boldsymbol{R}} | \psi_{dia,j} \rangle = 0, \forall \boldsymbol{R}$$



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# Examples of Deriving Equations of Motion with Different Approximations

## Example 1: BO with quantum nuclei

$$i\hbar\frac{\partial\Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = H(t,\hat{\boldsymbol{r}},\widehat{\boldsymbol{R}})\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R})$$

## Example 2: BO with wavepacket-dressed trajectories

$$i\hbar\frac{\partial\Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = H(t,\hat{\boldsymbol{r}},\widehat{\boldsymbol{R}})\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R}(\boldsymbol{t}))$$

# Case 1: Compute the action of $\widehat{T}$ on $\Psi$

$$\nabla^2(AB) = \nabla\big(\nabla(AB)\big) = \nabla\big((\nabla \mathrm{A})\mathrm{B} + A\nabla B\big) = (\nabla^2 \mathrm{A})\mathrm{B} + 2(\nabla \mathrm{A})(\nabla \mathrm{B}) + A\nabla^2 B$$

$$\left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\right)\chi_j\Phi_j = \left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\chi_j\right)\Phi_j - \left(2\sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla_\alpha\Phi_j\nabla_\alpha\chi_j\right) + \left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\Phi_j\right)\chi_j$$

$$\hat{T}\chi_j\Phi_j = (\hat{T}\chi_j)\Phi_j - \left(\sum_\alpha\frac{\hbar^2}{M_\alpha}\nabla_\alpha\Phi_j\nabla_\alpha\chi_j\right) + (\hat{T}\Phi_j)\chi_j$$

**We keep all terms, because $\boldsymbol{\Phi}$ is a function of $\boldsymbol{R}$**

## Project on an arbitrary state $\Phi_i$:

$$\langle\Phi_i|\hat{T}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \langle\Phi_i|\Phi_j\rangle_{\boldsymbol{r}}\hat{T}\chi_j - \left(\sum_\alpha\frac{\hbar^2}{M_\alpha}\langle\Phi_i|\nabla_\alpha\Phi_j\rangle_{\boldsymbol{r}}\nabla_\alpha\chi_j\right) + \langle\Phi_i|\hat{T}|\Phi_j\rangle_{\boldsymbol{r}}\chi_j$$

$$\langle\Phi_i|\hat{T}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \delta_{ij}\hat{T}\chi_j - \left(\sum_\alpha\frac{\hbar^2}{M_\alpha}\langle\Phi_i|\nabla_\alpha\Phi_j\rangle_{\boldsymbol{r}}\nabla_\alpha\chi_j\right) + \langle\Phi_i|\hat{T}|\Phi_j\rangle_{\boldsymbol{r}}\chi_j$$

$$\langle\Phi_i|\widehat{H}_{nucl}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \langle\Phi_i|\widehat{H}_{nucl}|\Phi_j\rangle_{\boldsymbol{r}}\chi_j = \langle\Phi_i|E_j(\boldsymbol{R})|\Phi_j\rangle_{\boldsymbol{r}}\chi_j = E_j(\boldsymbol{R})\langle\Phi_i|\Phi_j\rangle_{\boldsymbol{r}}\chi_j = E_j(\boldsymbol{R})\delta_{ij}\chi_j$$

$$\langle\Phi_i|\hat{T} + \widehat{H}_{nucl}|\Psi\rangle = \sum_j\langle\Phi_i|\hat{T} + \widehat{H}_{nucl}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \sum_j\left[\delta_{ij}\hat{T}\chi_j - \left(\sum_\alpha\frac{\hbar^2}{M_\alpha}\langle\Phi_i|\nabla_\alpha\Phi_j\rangle_{\boldsymbol{r}}\nabla_\alpha\chi_j\right) + \langle\Phi_i|\hat{T}|\Phi_j\rangle_{\boldsymbol{r}}\chi_j + E_j(\boldsymbol{R})\delta_{ij}\right]$$

# Compute the LHS: Case 1

$$\left\langle \Phi_i \middle| \frac{\partial}{\partial t} \middle| \chi_j \Phi_j \right\rangle_{\boldsymbol{r}} = \langle \Phi_i | \Phi_j \rangle_{\boldsymbol{r}} \frac{\partial}{\partial t}\chi_j + \cancel{\left\langle \Phi_i \middle| \frac{\partial}{\partial t} \middle| \Phi_j \right\rangle_{\boldsymbol{r}}} \chi_j = \delta_{ij}\frac{\partial}{\partial t}\chi_j$$

$$i\hbar\left\langle \Phi_i \middle| \frac{\partial}{\partial t} \middle| \Psi \right\rangle_{\boldsymbol{r}} = i\hbar\sum_j \left\langle \Phi_i \middle| \frac{\partial}{\partial t} \middle| \chi_j \Phi_j \right\rangle_{\boldsymbol{r}} = i\hbar\sum_j \delta_{ij}\frac{\partial}{\partial t}\chi_j = i\hbar\frac{\partial}{\partial t}\chi_i$$

## Now, combine the two parts of the equation:

$$i\hbar\frac{\partial\Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = H(t,\boldsymbol{r},\boldsymbol{R})\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i(\boldsymbol{R}) + \langle \Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i - \sum_{j,\alpha}\frac{\hbar^2}{M_\alpha}\langle \Phi_i|\nabla_\alpha\Phi_j\rangle\nabla_\alpha\chi_j - \sum_{j\neq i,\alpha}\frac{\hbar^2}{2M_\alpha}\langle \Phi_i|\nabla_\alpha^2\Phi_j\rangle\chi_j$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i(\boldsymbol{R}) + \langle \Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i - i\hbar\sum_{j,\alpha}\langle \Phi_i|\nabla_\alpha\Phi_j\rangle\frac{(-i\hbar\nabla_\alpha)\chi_j}{M_\alpha} - \sum_{j\neq i,\alpha}\frac{\hbar^2}{2M_\alpha}\langle \Phi_i|\nabla_\alpha^2\Phi_j\rangle\chi_j$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i(\boldsymbol{R}) + \langle \Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i - i\hbar\sum_{j,\alpha}\langle \Phi_i|\nabla_\alpha\Phi_j\rangle\frac{\hat{p}_\alpha\chi_j}{M_\alpha} - \sum_{j\neq i,\alpha}\frac{\hbar^2}{2M_\alpha}\langle \Phi_i|\nabla_\alpha^2\Phi_j\rangle\chi_j$$

# Nonadiabatic dynamics

This is what defines the evolution of nuclear component of the wavefunction and populations of all electronic states.

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_\mathrm{i}(\mathbf{r},\mathbf{R})$$

**Diagonal BO correction to the PES!**

**(ZPE of electrons)**

In the **adiabatic basis**

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i\big(\boldsymbol{R}(t)\big) + \langle\Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i - i\hbar\sum_{j,\alpha} D^{(1)}_{ij,\alpha}\frac{\hat{p}_\alpha\chi_j}{M_\alpha} - \sum_{j\neq i,\alpha}\frac{\hbar^2}{2M_\alpha}D^{(2)}_{ij,\alpha}\chi_j$$

$D^{(1)}_{ij,\alpha} = \langle\Phi_i|\nabla_\alpha\Phi_j\rangle$ first-order nonadiabatic couplings (NAC) - vector

Describes how a nuclear DOF $\alpha$ couples electronic state $i$ and $j$

This is what determines the rates of nonadiabatic transitions.

$D^{(2)}_{ij,\alpha} = \langle\Phi_i|\nabla^2_\alpha\Phi_j\rangle$ second-order NAC - scalar

In the **diabatic basis**

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle + \langle\Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i$$

Nuclear dynamics on state *i* is defined by the probability density: $P_i(t,\boldsymbol{R}) = |\langle\Phi_i|\Psi\rangle_{\boldsymbol{r}}|^2 = |\chi_i(t,\boldsymbol{R})|^2$

Population of a state $i$: $P_i(t) = \left|\langle\Phi_i|\Psi\rangle_{\boldsymbol{r},\boldsymbol{R}}\right|^2 = |\chi_i(t)|^2$

# Case 2: Compute the action of $\hat{T}$ on $\Psi$

$$\left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\right)\chi_j\Phi_j = \left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\chi_j\right)\Phi_j - \left(2\sum_\alpha \cancel{\frac{\hbar^2}{2M_\alpha}\nabla_\alpha\Phi_j\nabla_\alpha\chi_j}\right) + \left(\sum_\alpha -\cancel{\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\Phi_j}\right)\chi_j$$

$$\hat{T}(\chi_j\Phi_j) = (\hat{T}\chi_j)\Phi_j$$

**because $\Phi$ is only a function of time, not $\boldsymbol{R}$**

$$\langle\Phi_i|\hat{T}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \delta_{ij}\hat{T}\chi_j$$

$$\langle\Phi_i|\hat{T}+\hat{H}_{nucl}|\Psi\rangle = \sum_j\langle\Phi_i|\hat{T}+\hat{H}_{nucl}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \sum_j\left[\delta_{ij}\hat{T}\chi_j + E_j(\boldsymbol{R})\delta_{ij}\right]$$

Compute the LHS

$$\left\langle\Phi_i\middle|\frac{\partial}{\partial t}\middle|\chi_j\Phi_j\right\rangle = \langle\Phi_i|\Phi_j\rangle_{\boldsymbol{r}}\frac{\partial}{\partial t}\chi_j + \left\langle\Phi_i\middle|\frac{\partial}{\partial t}\middle|\Phi_j\right\rangle\chi_j = \delta_{ij}\frac{\partial}{\partial t}\chi_j + \left\langle\Phi_i\middle|\frac{\partial}{\partial t}\middle|\Phi_j\right\rangle\chi_j$$

$$i\hbar\left\langle\Phi_i\middle|\frac{\partial}{\partial t}\middle|\Psi\right\rangle_{\boldsymbol{r}} = i\hbar\sum_j\left\langle\Phi_i\middle|\frac{\partial}{\partial t}\middle|\chi_j\Phi_j\right\rangle_{\boldsymbol{r}} = i\hbar\sum_j\delta_{ij}\frac{\partial}{\partial t}\chi_j + i\hbar\sum_j\left\langle\Phi_i\middle|\frac{\partial}{\partial t}\middle|\Phi_j\right\rangle\chi_j = i\hbar\frac{\partial}{\partial t}\chi_i + i\hbar\sum_j\left\langle\Phi_i\middle|\frac{\partial}{\partial t}\middle|\Phi_j\right\rangle\chi_j$$

$$\boxed{i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i(\boldsymbol{R}(t))\right]\chi_i - \boxed{i\hbar\sum_j\left\langle\Phi_i\middle|\frac{\partial}{\partial t}\middle|\Phi_j\right\rangle\chi_j}}$$

This terms appears because $\Phi$ is an implicit function of time, via $\boldsymbol{R}(t)$

$$\left\langle\Phi_i\middle|\frac{\partial}{\partial t}\middle|\Phi_j\right\rangle = \sum_{j,\alpha}\left\langle\Phi_i\middle|\frac{\partial}{\partial\boldsymbol{R}_\alpha}\middle|\Phi_j\right\rangle\frac{\partial\boldsymbol{R}_\alpha}{\partial t} = \sum_{j,\alpha}D^{(1)}_{ij,\alpha}\frac{\boldsymbol{P}_\alpha}{M_\alpha}$$

# Summary

## Example 1: BO with quantum nuclei

## Example 2: BO with wavepacket-dressed trajectories

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R})$$

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R}(\boldsymbol{t}))$$

### Nonadiabatic, adiabatic basis

$$i\hbar\frac{\partial}{\partial t}\chi_i = [\hat{T} + E_i(\boldsymbol{R}(t)) + \langle\Phi_i|\hat{T}|\Phi_i\rangle]\chi_i - i\hbar\sum_{j,\alpha} D^{(1)}_{ij,\alpha}\frac{\hat{p}_\alpha\chi_j}{M_\alpha} - \sum_{j\neq i,\alpha}\frac{\hbar^2}{2M_\alpha}D^{(2)}_{ij,\alpha}\chi_j$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = [\hat{T} + E_i(\boldsymbol{R}(t))]\chi_i - i\hbar\sum_{j,\alpha} D^{(1)}_{ij,\alpha}\frac{\boldsymbol{P}_\alpha}{M_\alpha}\chi_j$$

### Nonadiabatic, diabatic basis

$$i\hbar\frac{\partial}{\partial t}\chi_i = [\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle + \langle\Phi_i|\hat{T}|\Phi_i\rangle]\chi_i$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = [\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle]\chi_i$$

### Adiabatic, adiabatic basis

$$i\hbar\frac{\partial}{\partial t}\chi = [\hat{T} + E_i(\boldsymbol{R}(t)) + \langle\Phi_i|\hat{T}|\Phi_i\rangle]\chi$$

$$i\hbar\frac{\partial}{\partial t}\chi = [\hat{T} + E_i(\boldsymbol{R}(t))]\chi$$

### Adiabatic, diabatic basis

$$i\hbar\frac{\partial}{\partial t}\chi = [\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle + \langle\Phi_i|\hat{T}|\Phi_i\rangle]\chi$$

$$i\hbar\frac{\partial}{\partial t}\chi = [\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle]\chi$$

# Wavefunction and selection of representation

$|\Psi\rangle$ Abstract wavefunction

$\{|\boldsymbol{r}\rangle : \hat{\boldsymbol{r}}|\boldsymbol{r}\rangle = \boldsymbol{r}|\boldsymbol{r}\rangle\}$ Position states (Hilbert space)

$\{|\boldsymbol{k}\rangle : \widehat{\boldsymbol{k}}|\boldsymbol{k}\rangle = \boldsymbol{k}|\boldsymbol{k}\rangle\}$ Momentum states (Hilbert space)

$\Psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\Psi\rangle$ Wavefunction in a **position representation** – representation in the basis of position states

$$1 = \int d\boldsymbol{r}'|\boldsymbol{r}'\rangle\langle\boldsymbol{r}'|$$ Complete basis

Indeed

$$|\Psi\rangle = \int d\boldsymbol{r}'|\boldsymbol{r}'\rangle\langle\boldsymbol{r}'|\Psi\rangle = \int d\boldsymbol{r}'\,|\boldsymbol{r}'\rangle\Psi(\boldsymbol{r}')$$

$\Psi(\boldsymbol{r}')$ is essentially an expansion coefficient in the basis of coordinate states $\{|\boldsymbol{r}\rangle\}$
Can be regarded as DVR (grid representation of the wavefunction)

$\Psi(\boldsymbol{k}) = \langle \boldsymbol{k}|\Psi\rangle$ Likewise, the **momentum representation** of a wavefunction

Different Hilbert spaces:

$\Psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\Psi\rangle; |\boldsymbol{r}\rangle, |\Psi\rangle \in \mathcal{H}_{\boldsymbol{r}}$ only electrons

$\Psi(\boldsymbol{R}) = \langle \boldsymbol{R}|\Psi\rangle; |\boldsymbol{R}\rangle, |\Psi\rangle \in \mathcal{H}_{\boldsymbol{R}}$ only nuclei

$\Psi(\boldsymbol{r},\boldsymbol{R}) = \langle \boldsymbol{r},\boldsymbol{R}|\Psi\rangle; |\Psi\rangle \in \mathcal{H}_r \otimes \mathcal{H}_{\boldsymbol{R}}$both electrons and nuclei

$\Psi(\boldsymbol{r}) = \langle \boldsymbol{R}|\Psi\rangle; |\Psi\rangle \in \mathcal{H}_r \otimes \mathcal{H}_{\boldsymbol{R}}$ projection on $|\boldsymbol{R}\rangle \in \mathcal{H}_{\boldsymbol{R}}$; $\Psi(\boldsymbol{r};\boldsymbol{R}) \in \mathcal{H}_r$ operator of electronic DOF (electronic coordinate operator), but a function of nuclear DOF - $\boldsymbol{R}$

# Shorthand notation. Adiabatic and Diabatic Representations

$\psi_i(\boldsymbol{r}) = \langle \boldsymbol{r}|i\rangle = \langle \boldsymbol{r}|\psi_i\rangle$ electronic coordinates, i-th basis state

Shorthand notation for the entire basis: $|\boldsymbol{\psi}\rangle = (|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_N\rangle)$

Matrix elements (scalars) → $A_{ij} = \langle \psi_i|\hat{A}|\psi_j\rangle \leftrightarrow A = \langle \boldsymbol{\psi}|\hat{A}|\boldsymbol{\psi}\rangle$ ← Matrix

**Basis:**

Adiabatic (Hamiltonian is diagonal):

$\langle \psi_{adi,i}|\widehat{H}_{el}|\psi_{adi,j}\rangle = 0, \forall i \neq j$

Diabatic (NACs are exactly zero):

$\langle \psi_{dia,i}|\nabla_{\boldsymbol{R}}|\psi_{dia,j}\rangle = 0, \forall \boldsymbol{R}$

$$|\boldsymbol{\psi}_{adi}\rangle = |\boldsymbol{\psi}_{dia}\rangle U$$

$H_{adi} = \langle \boldsymbol{\psi}_{adi}|\widehat{H}_{el}|\boldsymbol{\psi}_{adi}\rangle$ Hamiltonians $H_{dia} = \langle \boldsymbol{\psi}_{dia}|\widehat{H}_{el}|\boldsymbol{\psi}_{dia}\rangle$

Transformation between bases $H_{dia}U = SUH_{adi}$ $H_{adi} = U^{+}H_{dia}U = \widetilde{H}_{dia}$

Wavefunction should be invariant w.r.t. the basis representation

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

# TD-SE in the Shorthand notation

Wavefunction should be invariant w.r.t. the basis representation

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

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

$$|\boldsymbol{\psi}\rangle = \left(|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_N\rangle\right)$$

$$C = (c_1, c_2, \dots, c_N)^T$$

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

$$i\hbar\frac{\partial}{\partial t}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle C_{rep} + i\hbar|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle\frac{\partial}{\partial t}C_{rep} = \hat{H}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle C_{rep}$$

Projecting:

$$i\hbar\langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\frac{\partial}{\partial t}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle C_{rep} + i\hbar\langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle\frac{\partial}{\partial t}C_{rep} = \langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\hat{H}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle C_{rep}$$

$$\boxed{i\hbar S_{rep}\frac{\partial}{\partial t}C_{rep} = \left[\langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\hat{H}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle - i\hbar\langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\frac{\partial}{\partial t}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle\right]C_{rep}}$$

# *Transformations. Ehrenfest Dynamics.*

## *Some Implementation Detail In Libra*

# Libra as a workhorse of our developments

University at Buffalo
*The State University of New York*

Akimov *JCC,* **2016**, 37, 1626

Implemented in **Libra:** **https://quantum-dynamics-hub.github.io/libra/index.html**
**https://github.com/Quantum-Dynamics-Hub/libra-code**

Examples& Tutorials: **https://github.com/compchem-cybertraining**

Some of the implemented methods:

| **Methods** | **Paper** |
|---|---|
| Surface hopping schemes | Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061 (FSSH); Wang, L., et al. *JCTC* **2014**, 10, 3598 (GFSH); Akimov, A. V. et al. *J. Phys. Soc. Jpn.* **2015**, 84, 094002 (MSSH) |
| Decoherence schemes | Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114 (SDM); Nelson, T. et al. *J. Chem. Phys.* **2013**, *138*, 224111. (ID-A, ID-S); Jaeger, H. M. et al. *J. Chem. Phys.* **2012**, *137*, 22A545 (DISH) |
| Dephasing times calculations | Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107<br>Akimov, A. V.; Prezhdo, O. V. *J. Phys. Chem. Lett.* **2013**, *4*, 3857<br>Sifain, A. E.; Wang, L.; Tretiak, S.; Prezhdo, O. V.<br>Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114. |
| Neglect of back-reaction (NBRA) | Prezhdo, O. V.; Duncan, W. R.; Prezhdo, V. V. *Prog. Surf. Sci.* **2009**, *84*, 30 |
| Boltzmann-corrected Ehrenfest | Bastida, A. et al. *Chem. Phys. Lett.* **2006**, *417*, 53<br>Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107 |
| Phase corrections | Akimov, A. V *J. Phys. Chem. Lett.* **2018**, *9*, 6096 |
| State tracking | Fernandez-Alberti, S.; et al. *J. Chem. Phys.* **2012**, *137*, 014512 (mincost); Temen, S.; AVA. *JPCL* **2021**, 12, 10587-10597 (stochastic) |
| Interfaces with ES codes | DFTB+ (Smith, B.; AVA *JPCL*. **2020**, 11, 1456), QE (Pradhan et al. *JPCM,* **2018**, 30, 484002), CP2K (Smith, B. A. et al. JCTC, 2021, 17, 678), Gaussian, GAMESS (Sato et al. *PCCP,* **2018**, 20, 25275) |
| Exact dynamics | Kosloff, D. and Kosloff, R. J. Chem. Phys. **1983**, *52*, 35-53 (SOFT); Colbert, D. T. and Miller, W. H. **1992**, *96*, 1982-1991 (Colert-Miller DVR) |
| HEOM | Temen et al. *Int. J. Quant. Chem.,* **2020**, 120, e26373 |

# Implementation in Libra classes

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

Density matrix language $\hat{\rho} = |\Psi\rangle\langle\Psi|$

**dyn_variables**

- ndia, nadi, ndof, ntraj
- ampl_dia, ampl_adi
- dm_adi, dm_dia

$$P_{adi} = \langle\boldsymbol{\psi}_{adi}|\hat{\rho}|\boldsymbol{\psi}_{adi}\rangle = \langle\boldsymbol{\psi}_{adi}|\boldsymbol{\psi}_{adi}\rangle C_{adi}C_{adi}^{+}\langle\boldsymbol{\psi}_{adi}|\boldsymbol{\psi}_{adi}\rangle = IC_{adi}C_{adi}^{+}I = C_{adi}C_{adi}^{+}$$

$$P_{dia} = \langle\boldsymbol{\psi}_{dia}|\hat{\rho}|\boldsymbol{\psi}_{dia}\rangle = \langle\boldsymbol{\psi}_{dia}|\boldsymbol{\psi}_{dia}\rangle C_{dia}C_{dia}^{+}\langle\boldsymbol{\psi}_{dia}|\boldsymbol{\psi}_{dia}\rangle = SC_{dia}C_{dia}^{+}S$$

So the conversions of the density matrices is:

$$UP_{dia}U^{+} = U^{+}SC_{dia}C_{dia}^{+}SU = C_{adi}C_{adi}^{+} = P_{adi} \Rightarrow P_{dia} = U^{-1}P_{adi}(U^{-1})^{+} = U^{+}SP_{adi}(U^{+}S)^{+} = U^{+}SP_{adi}SU$$

Coefficient transformation:

**nHamiltonian**

$$C_{dia} = UC_{adi} \leftrightarrow C_{adi} = U^{-1}C_{dia} \leftrightarrow C_{adi} = U^{+}SC_{dia}$$

- ampl_dia2adi
- ampl_adi2dia

$$H_{dia}U = SUH_{adi}$$

and also computes derivative couplings and adiabatic gradients

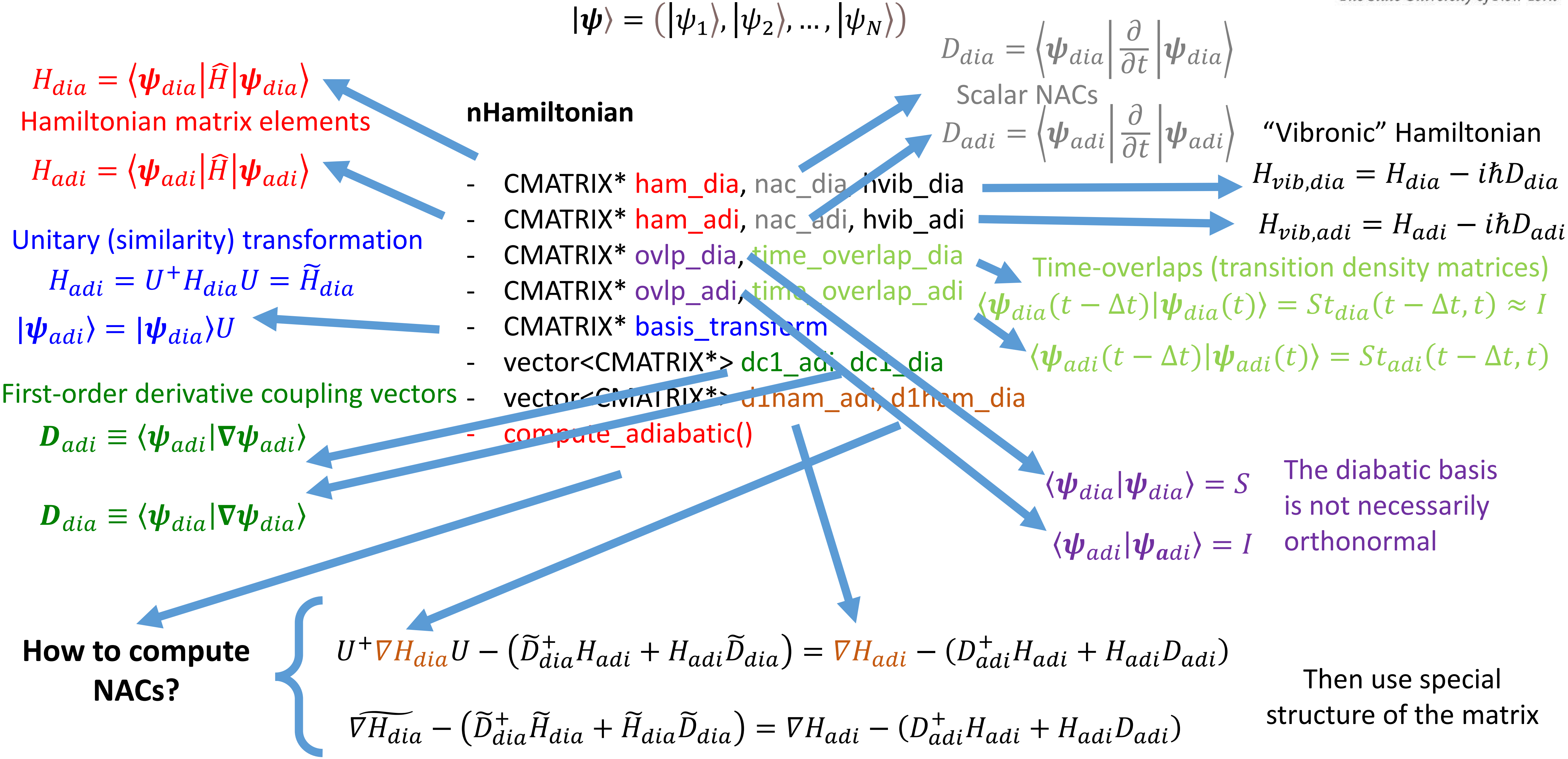
- compute_adiabatic()

computes $H_{dia}$, $D_{dia}$, and $\nabla H_{dia}$ according to given methods (e.g. Python modules with Hamiltonian models)

- compute_diabatic()

# Implementation in the nHamiltonian class

University at Buffalo
The State University of New York



$$|\boldsymbol{\psi}\rangle = (|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_N\rangle)$$

**nHamiltonian**

- CMATRIX* ham_dia, nac_dia, hvib_dia
- CMATRIX* ham_adi, nac_adi, hvib_adi
- CMATRIX* ovlp_dia, time_overlap_dia
- CMATRIX* ovlp_adi, time_overlap_adi
- CMATRIX* basis_transform
- vector<CMATRIX*> dc1_adi, dc1_dia
- vector<CMATRIX*> d1ham_adi, d1ham_dia
- compute_adiabatic()

$$H_{dia} = \langle \boldsymbol{\psi}_{dia} | \hat{H} | \boldsymbol{\psi}_{dia} \rangle$$

Hamiltonian matrix elements

$$H_{adi} = \langle \boldsymbol{\psi}_{adi} | \hat{H} | \boldsymbol{\psi}_{adi} \rangle$$

Unitary (similarity) transformation

$$H_{adi} = U^{+} H_{dia} U = \tilde{H}_{dia}$$

$$|\boldsymbol{\psi}_{adi}\rangle = |\boldsymbol{\psi}_{dia}\rangle U$$

First-order derivative coupling vectors

$$\boldsymbol{D}_{adi} \equiv \langle \boldsymbol{\psi}_{adi} | \boldsymbol{\nabla} \boldsymbol{\psi}_{adi} \rangle$$

$$\boldsymbol{D}_{dia} \equiv \langle \boldsymbol{\psi}_{dia} | \boldsymbol{\nabla} \boldsymbol{\psi}_{dia} \rangle$$

$$D_{dia} = \left\langle \boldsymbol{\psi}_{dia} \middle| \frac{\partial}{\partial t} \middle| \boldsymbol{\psi}_{dia} \right\rangle$$

Scalar NACs

$$D_{adi} = \left\langle \boldsymbol{\psi}_{adi} \middle| \frac{\partial}{\partial t} \middle| \boldsymbol{\psi}_{adi} \right\rangle$$

“Vibronic” Hamiltonian

$$H_{vib,dia} = H_{dia} - i\hbar D_{dia}$$

$$H_{vib,adi} = H_{adi} - i\hbar D_{adi}$$

Time-overlaps (transition density matrices)

$$\langle \boldsymbol{\psi}_{dia}(t-\Delta t) | \boldsymbol{\psi}_{dia}(t) \rangle = St_{dia}(t-\Delta t, t) \approx I$$

$$\langle \boldsymbol{\psi}_{adi}(t-\Delta t) | \boldsymbol{\psi}_{adi}(t) \rangle = St_{adi}(t-\Delta t, t)$$

$$\langle \boldsymbol{\psi}_{dia} | \boldsymbol{\psi}_{dia} \rangle = S$$

$$\langle \boldsymbol{\psi}_{adi} | \boldsymbol{\psi}_{adi} \rangle = I$$

The diabatic basis is not necessarily orthonormal

**How to compute NACs?**

$$\left\{ \begin{array}{l} U^{+} \nabla H_{dia} U - (\tilde{D}_{dia}^{+} H_{adi} + H_{adi} \tilde{D}_{dia}) = \nabla H_{adi} - (D_{adi}^{+} H_{adi} + H_{adi} D_{adi}) \\ \widetilde{\nabla H_{dia}} - (\tilde{D}_{dia}^{+} \tilde{H}_{dia} + \tilde{H}_{dia} \tilde{D}_{dia}) = \nabla H_{adi} - (D_{adi}^{+} H_{adi} + H_{adi} D_{adi}) \end{array} \right.$$

Then use special structure of the matrix

# Nonadiabatic Couplings

Properties of the NACs

$$\bar{\boldsymbol{D}}^+_{dia} + \bar{\boldsymbol{D}}_{dia} = \nabla S$$

$$\bar{\boldsymbol{D}}_{adi} + \bar{\boldsymbol{D}}^+_{adi} = \boldsymbol{\nabla} S_{adi} = 0 \rightarrow (D^\alpha_{adi})^+ = -D_{adi}$$

This is a well-known property!

$$D^\alpha_{adi} = \widetilde{D}^\alpha_{dia} + U^+ S \nabla_\alpha U$$

$D^\alpha_{rep,ij} \equiv \langle \psi_{rep,i} | \nabla_\alpha \psi_{rep,j} \rangle$ is a scalar

$\boldsymbol{D}_{rep,ij} \equiv \langle \psi_{rep,i} | \nabla \psi_{rep,j} \rangle$ understood as a column-vector

$\bar{\boldsymbol{D}}_{rep} \equiv \langle \boldsymbol{\psi}_{rep} | \boldsymbol{\nabla} \boldsymbol{\psi}_{rep} \rangle$ understood as a vector of matrices $D^\alpha_{rep} = \langle \boldsymbol{\psi}_{rep} | \nabla_\alpha \boldsymbol{\psi}_{rep} \rangle$

Important observations

the equation becomes an identity when $U = I$

$$\underbrace{\widetilde{\nabla_\alpha H_{dia}} - \left((D^\alpha_{adi})^+ \widetilde{H}_{dia} + \widetilde{H}_{dia} \widetilde{D}^\alpha_{dia}\right)}_{U^+ \langle \boldsymbol{\psi}_{dia} | \nabla_\alpha H | \boldsymbol{\psi}_{dia} \rangle U} = \underbrace{\nabla_\alpha H_{adi} - \left((D^\alpha_{adi})^+ H_{adi} + H_{adi} D^\alpha_{adi}\right)}_{\langle \boldsymbol{\psi}_{adi} | \nabla_\alpha H | \boldsymbol{\psi}_{adi} \rangle}$$

# Quantum-Classical Hamiltonian and Ehrenfest forces

University at Buffalo
The State University of New York

$$H^{MF}(\boldsymbol{R},\boldsymbol{P};\Psi) = \frac{\langle\Psi|H^{qc}(\boldsymbol{R},\boldsymbol{P})|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{1}{2}\boldsymbol{P}^T M^{-1}\boldsymbol{P} + \frac{C_{adi}^{+}H_{adi}C_{adi}}{C_{adi}^{+}C_{adi}} = \frac{1}{2}\boldsymbol{P}^T M^{-1}\boldsymbol{P} + \frac{C_{dia}^{+}H_{dia}C_{dia}}{C_{dia}^{+}SC_{dia}}$$

**nHamiltonian**
- Ehrenfest_energy_adi
- Ehrenfest_energy_dia

TD-SE for the amplitudes

$$i\hbar S\frac{dC_{rep}}{dt} = \left(H_{rep} - i\hbar d_{rep}\right)C_{rep}$$

$$\frac{dH^{MF}}{dt} = 0$$

**Energy conservation**

Enforcing the “classical” form of equations of motion for nuclear DOFs

$$\dot{\boldsymbol{R}} = M^{-1}\boldsymbol{P}$$
$$\dot{\boldsymbol{P}} = f^{MF}\left(\boldsymbol{R},\Psi_{\mathrm{rep}}\right)$$

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

**nHamiltonian**
- Ehrenfest_forces_adi
- Ehrenfest_forces_dia
- Ehrenfest_forces_tens_adi
- Ehrenfest_forces_tens_dia

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

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

# *Integrators and Local Diabatization*

# Trivial Crossing Problem

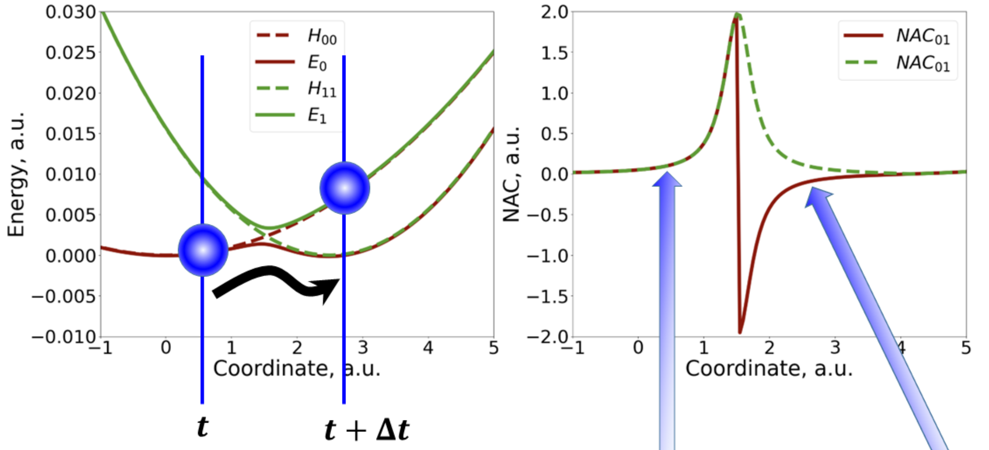
University at Buffalo
The State University of New York

We want to solve

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

in the adiabatic basis:

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



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

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

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

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

Formal solution:

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

After projection:

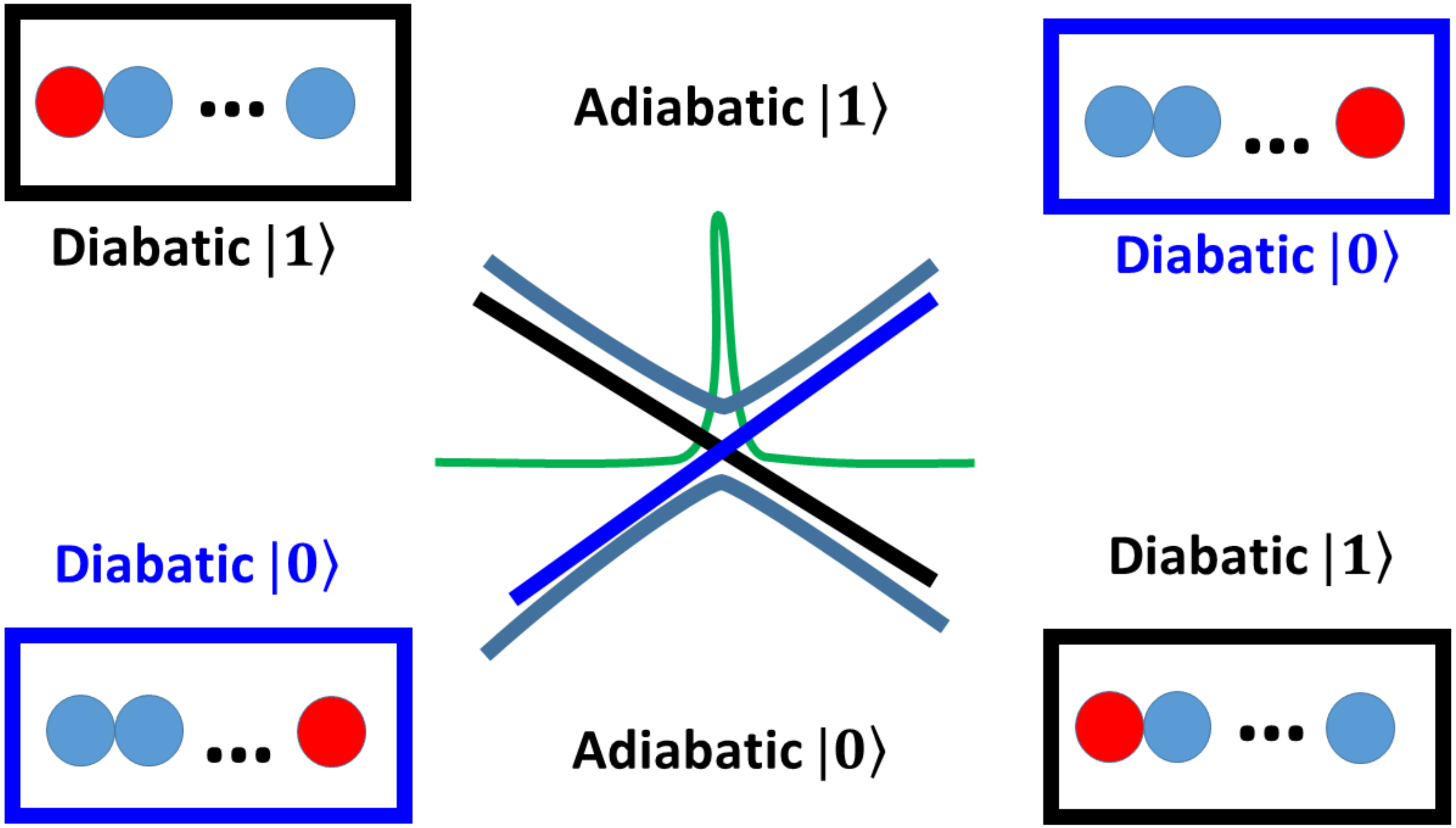
$$C_{adi}(t+\Delta t) = \left\langle \boldsymbol{\psi}_{adi}(t+\Delta t) \right| \left[\int_0^{\Delta t} d\tau \exp\left(-\frac{i\tau}{\hbar}\hat{H}(t+\tau)\right)\right] |\boldsymbol{\psi}_{adi}(\mathrm{t})\rangle C_{adi}(t)$$

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

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)**

# Trivial Crossing Problem

Arises because of finite $\Delta t$ or due to inconsistency of energy and NAC (due to approximations)



# 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

However, this transformation will not preserve the wavefunction norm:

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

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

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

Normalize the $T$ matrix: $T \rightarrow \tilde{T} = TA$ 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 normalizaiton**

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

# Back to Integrating the TD-SE

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

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

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

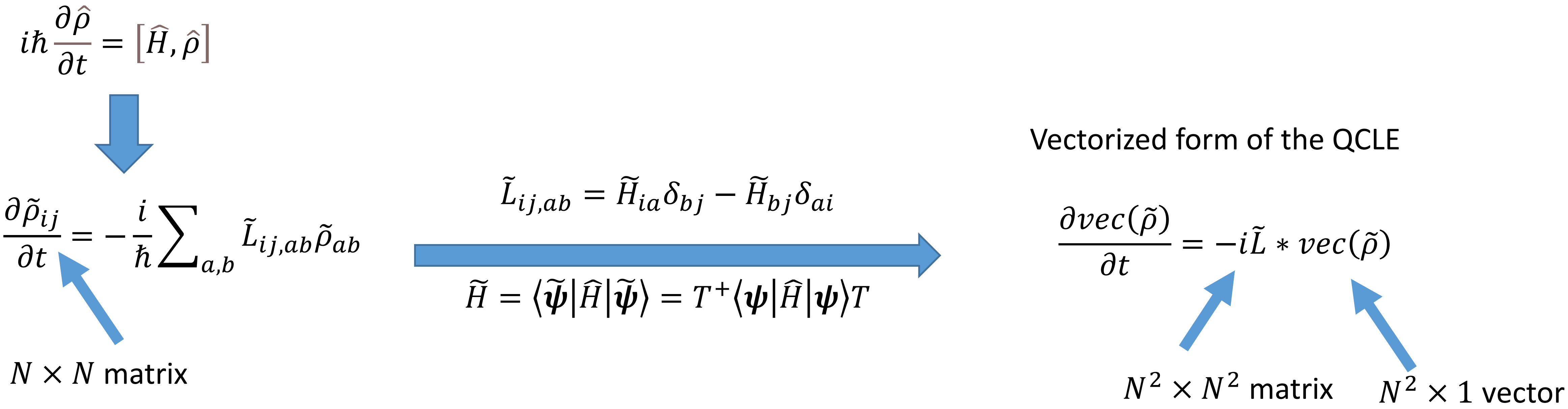
Using properties of the local-diabatic basis:

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

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

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

# Working the Liouville's space: propagation of density matrix



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

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

$N \times N$ 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

$N^2 \times 1$ vector

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

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

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

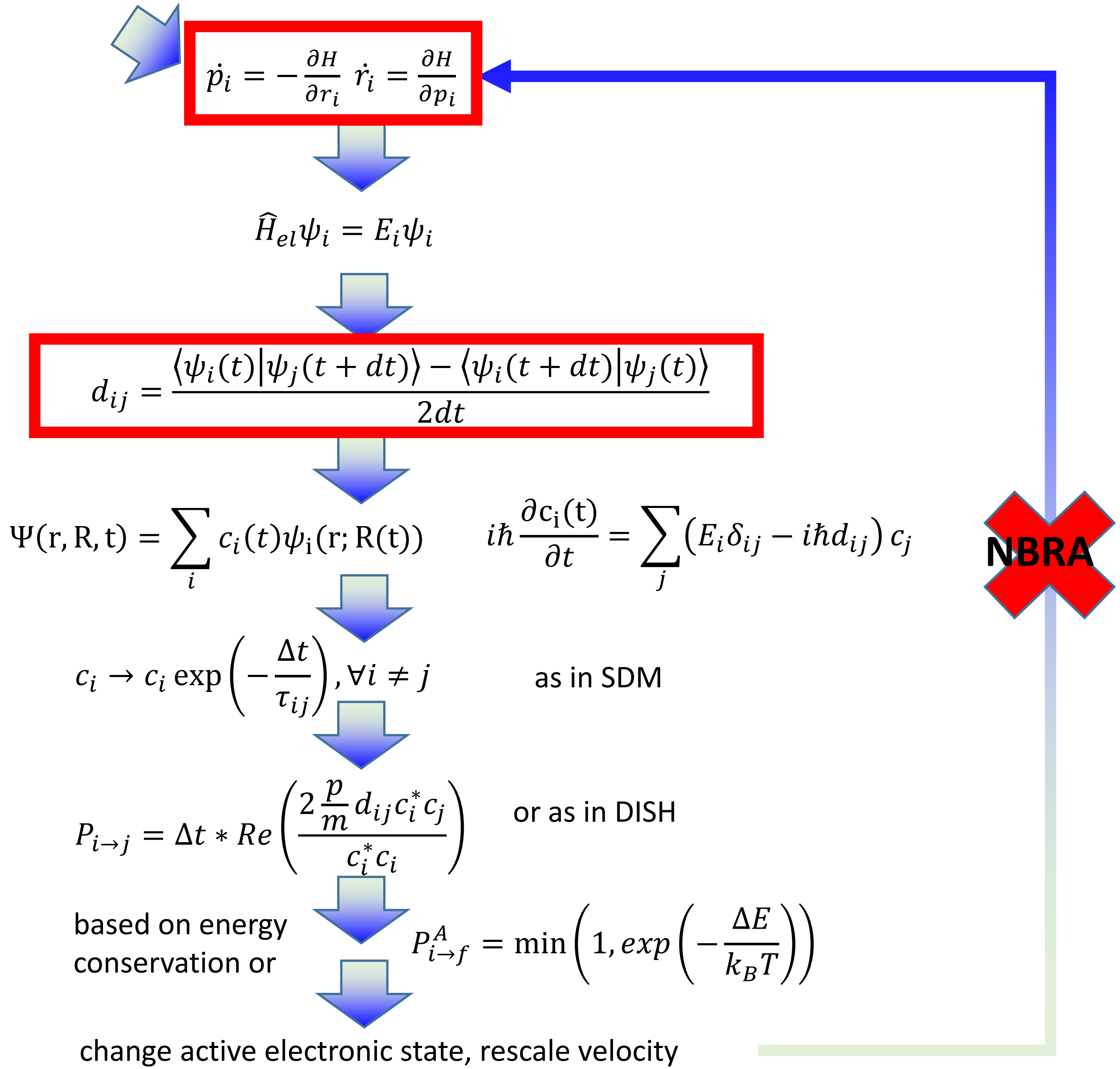
So, the final expression:

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

# *Trajectory Surface Hopping (TSH) methods*

# *in Libra*

# TSH in the nutshell



**Initialization**

**Nuclear dynamics**

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

**Stationary adiabatic states**

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

**Non-adiabatic Couplings**

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

**Electronic Dynamics**

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

**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

# Options for the Dynamics

**dyn_control_params**

| | |
|---|---|
| - rep_tdse | how to evolve electronic DOFs: 0 - $C_{dia}$; 1 - $C_{adi}$; 2 - $P_{dia}$; 3 - $P_{adi}$ |
| - ham_update_method | how to update Ham: 0 – don't; 1 – update $H_{dia}$; 2 – update $H_{adi}$ |
| - ham_transform_method | how to update Ham via transformation : $H_{dia}U = SUH_{adi}$<br>0 – don't;<br>1 – compute $H_{adi}$ from $H_{dia}$ by solving $H_{dia}U = SUH_{adi}$<br>2 – compute $H_{adi}$ from $H_{dia}$ by using a provided $U$: $H_{adi} = (SU)^{-1}H_{dia}U = U^{+}H_{dia}U$<br>3 – compute $H_{dia}$ from $H_{adi}$ by using a provided $U$: $H_{dia} = SUH_{adi}U^{-1} = SUH_{adi}U^{+}S$ |
| - force_method | how to compute nuclear forces:<br>0 – don't<br>1 – state-specific, adiabatic forces: $-\frac{\partial E_{adi}}{\partial \mathbf{R}}$<br>2 – Ehrenfest forces |
| - rep_force | $f_{n,dia}^{\mathrm{MF}} = \frac{1}{C_{dia}^{+}SC_{dia}} C_{dia}^{+}F_{dia,n}^{HF}C_{dia} = f_{n,adi}^{MF} = \frac{1}{C_{adi}^{+}C_{adi}} C_{adi}^{+}F_{adi,n}^{HF}C_{adi}$<br>0 – using only diabatic properties; 1 – using adiabatic properties |

# Options for the Dynamics

**dyn_control_params**

- force_method

how to compute nuclear forces:
0 – don’t
1 – state-specific, adiabatic forces: $-\frac{\partial E_{adi}}{\partial \boldsymbol{R}}$
2 – Ehrenfest forces

- enforce_state_following

Wheather we want to enforce nuclear dynamics to be on a given state, regardlenss of the TSH transitions: 0 - no [ default ]; 1 - yes

- 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.

- 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) [ default ]$P_{adi}(t-\Delta t, t) = U^{+}(t-\Delta t)P_{dia}(t-\Delta t, t)U(t)$
1 - based on external calculations (the Hamiltonian shall have the time_overlap_adi member updated) - use for NBRA

# Options for the Dynamics

**dyn_control_params**

- 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 [ default ]

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

- 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

Meek, G. A.; Levine, B. G. *J. Phys. Chem. Lett.* **2014**, *5*, 2351. https://doi.org/10.1021/jz5009449.

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

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

- 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)
- 1: update according to regular formula: $H_{vib,rep} = H_{rep} - i\hbar d_{ij,rep}$

# Hop Proposal Probability

**tsh_method;**

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

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

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

$$P^P_{i\to f} = \max\left(0, \frac{\Delta P_{ff}}{P_{ff}}\frac{\Delta P_{jj}}{\sum_{k\in A}\Delta P_{kk}}\right). i \in A, j \in B$$

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

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

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

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

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

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

Multidimensional version

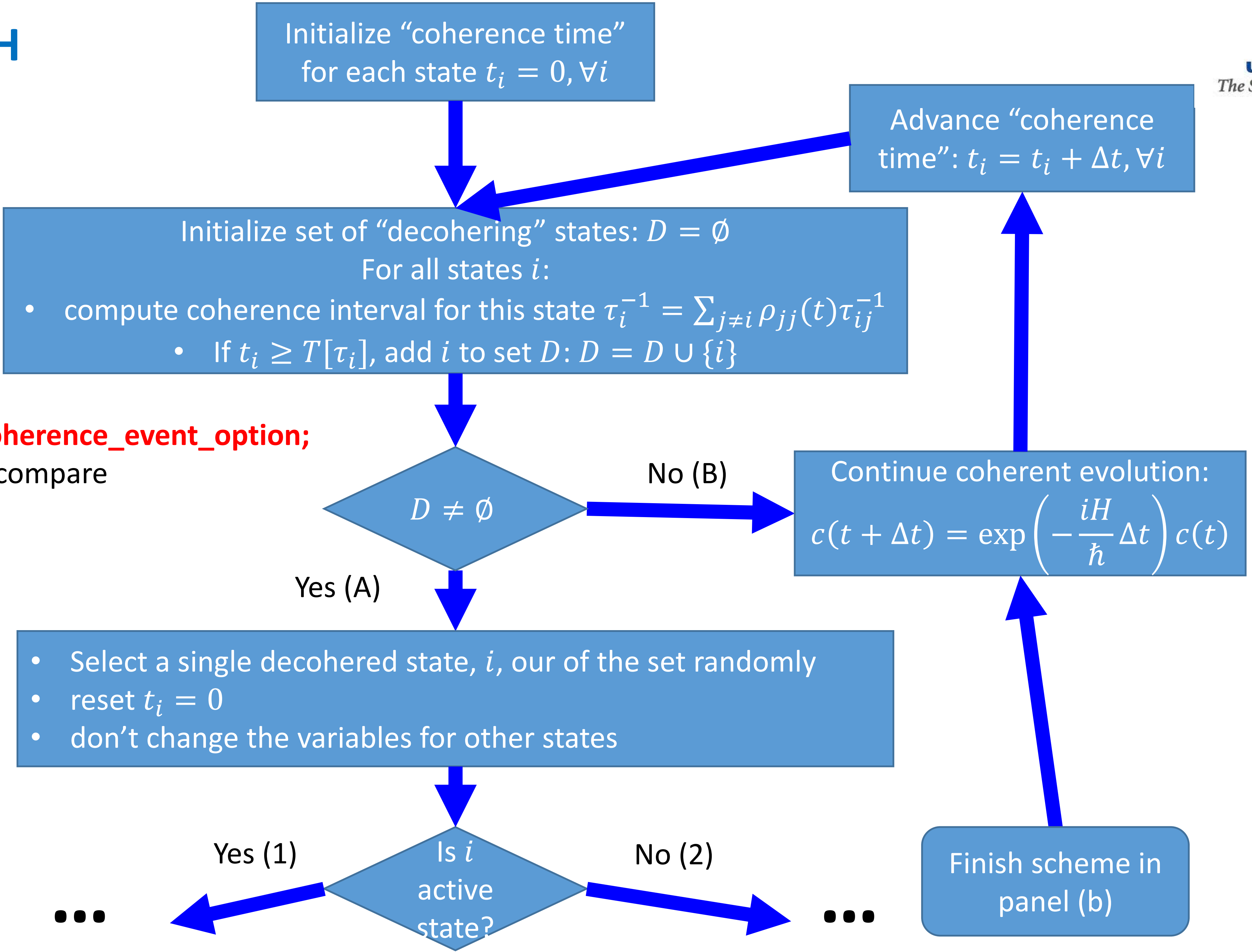
$$\begin{cases} \frac{1}{\sqrt{\mu}}\left|\boldsymbol{F}_i-\boldsymbol{F}_j\right| \to \sqrt{\left(\boldsymbol{F}_i-\boldsymbol{F}_j\right)^T M^{-1}\left(\boldsymbol{F}_i-\boldsymbol{F}_j\right)} \\ \frac{1}{\sqrt{\mu}}\left|\boldsymbol{F}_i\boldsymbol{F}_j\right| \to \sqrt{\left|\boldsymbol{F}_i{}^T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

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

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

# DISH

University at Buffalo
*The State University of New York*



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

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

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

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

$D \neq \emptyset$

No (B)

Continue coherent evolution:

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

Yes (A)

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

Is $i$ active state?

Yes (1)

No (2)

…

…

Finish scheme in panel (b)

# DISH

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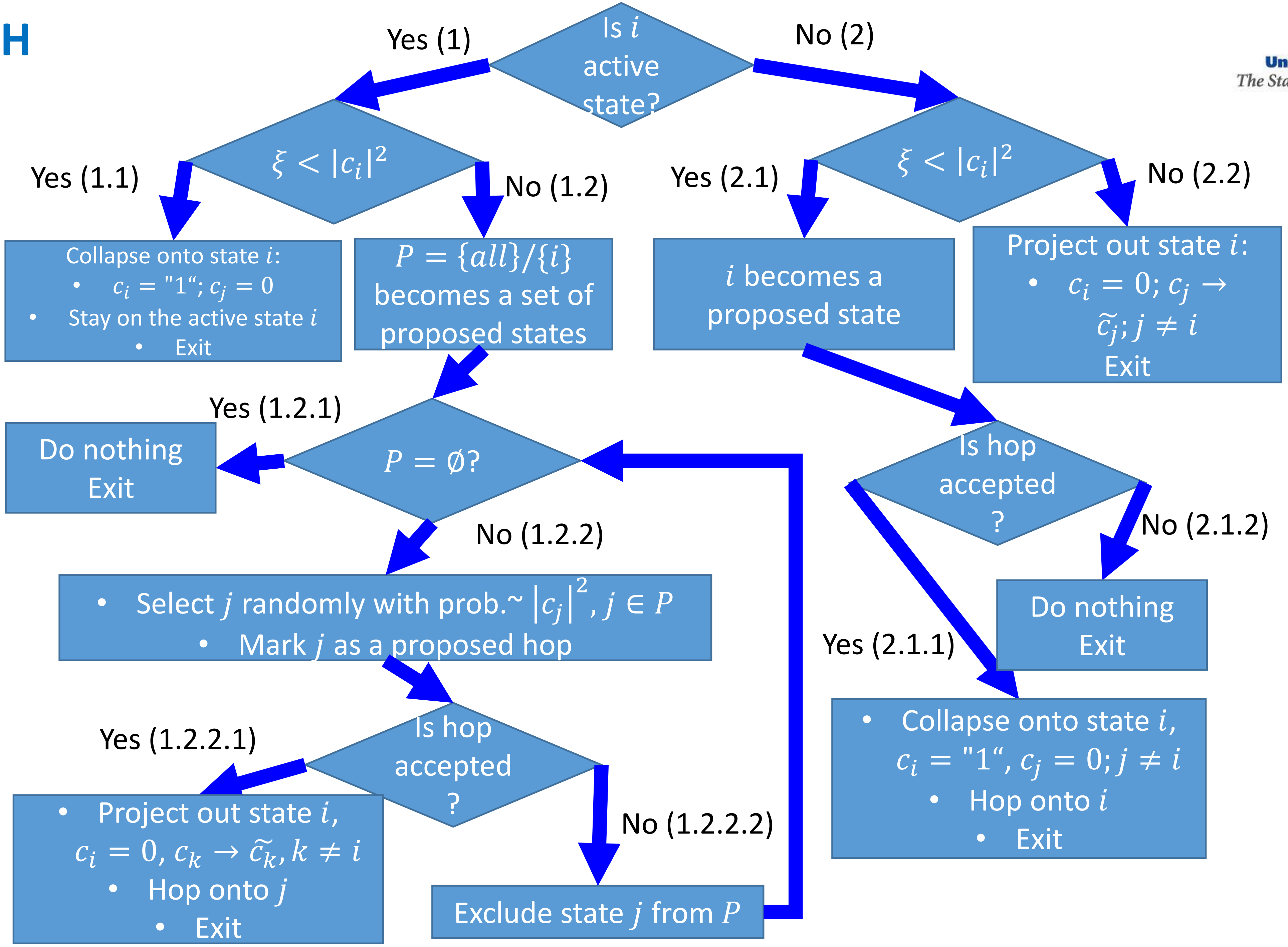


Is $i$ active state?

Yes (1)

$\xi < |c_i|^2$

Yes (1.1)

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

No (1.2)

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

$P = \emptyset?$

Yes (1.2.1)

Do nothing
Exit

No (1.2.2)

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

Is hop accepted ?

Yes (1.2.2.1)

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

No (1.2.2.2)

Exclude state $j$ from $P$

No (2)

$\xi < |c_i|^2$

Yes (2.1)

$i$ becomes a proposed state

Is hop accepted ?

Yes (2.1.1)

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

No (2.1.2)

Do nothing
Exit

No (2.2)

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

Exit

# Hop Acceptance Probabilities

**int hop_acceptance_algo;**

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 DOF
- 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

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

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

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

(experimental)

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

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

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

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

# Momentum Rescaling

**int momenta_rescaling_algo;**

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

# Decoherence: SMD, ID-A

**double decoherence_algo;**
Options:

- [-1]: no decoherence [ default ]
  - 0: SDM and alike
  - 1: instantaneous decoherence options (ID-S, ID-A, ID-C)
  - 2: AFSSH
  - 3: BCSH of Linjun Wang
  - 4: MF-SD of Bedard-Hearn, Larsen, Schwartz

**int 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

**int instantaneous_decoherence_variant;**
- 0: ID-S
- 1: ID-A [default]
- 2: ID-C - consistent ID - an experimental algorithm

## SDM

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

gradually change the amplitudes

$$C_i' = C_i \exp\left(-\frac{\Delta t}{\tau_{if}}\right), \forall i \neq f$$

$$C_f' = C_f \sqrt{\frac{1 - \sum_{i \neq f} |C_i'|^2}{|C_f|^2}}$$

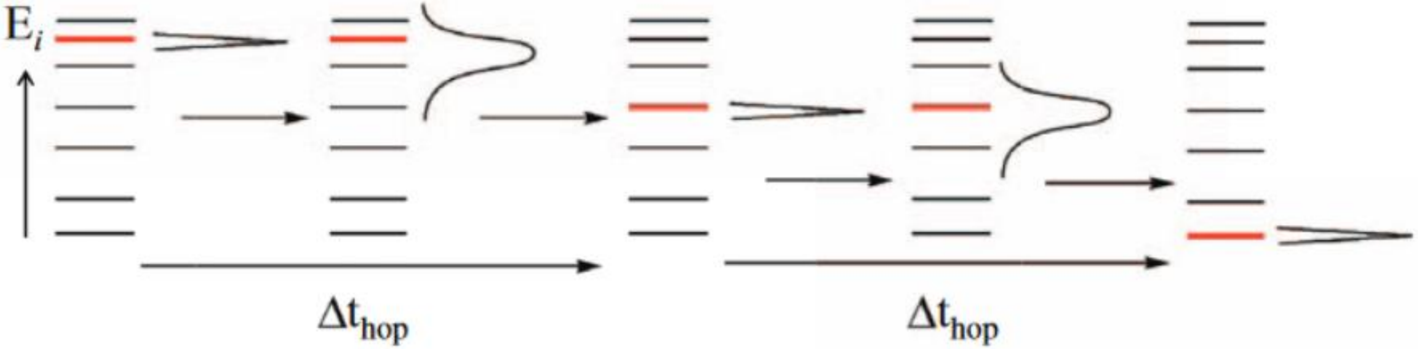
## ID-A

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

- on a successful hop (ID-S)
- on an attempted hop (ID-A)
- at every timestep (ID-C)

Wavefunction reduction

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



# Decoherence: A-FSSH

**Surface hopping, transition state theory and decoherence. I. Scattering theory and time-reversibility**

Cite as: J. Chem. Phys. **143**, 134106 (2015); https://doi.org/10.1063/1.4930548
Submitted: 17 June 2015 . Accepted: 24 August 2015 . Published Online: 02 October 2015

Amber Jain, Michael F. Herman, Wenjun Ouyang, and Joseph E. Subotnik

Propagate extra set of variables

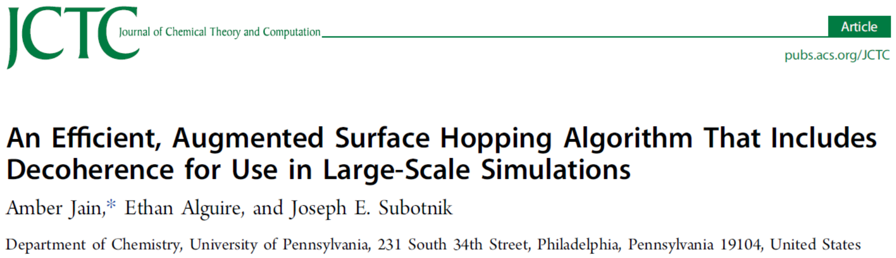
$$\boldsymbol{\delta}\vec{\mathbf{R}} = \mathrm{Tr}_N[(\vec{R} - \vec{R}_{SH})\boldsymbol{\rho}]$$

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

These variables define the rates for wavefunction collapse

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

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



JCTC Journal of Chemical Theory and Computation

Article

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**An Efficient, Augmented Surface Hopping Algorithm That Includes Decoherence for Use in Large-Scale Simulations**

Amber Jain,* Ethan Alguire, and Joseph E. Subotnik

Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104, United States

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

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

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

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

Also compute the probability to reset the moments as

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

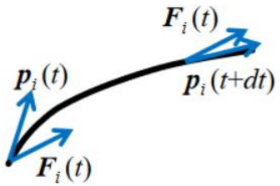
# Decoherence: BCSH and MF-SD

## BCSH

Xu, J.; Wang, L. *J. Chem. Phys.* **2019**, 150, 164101. https://doi.org/10.1063/1.5090927.

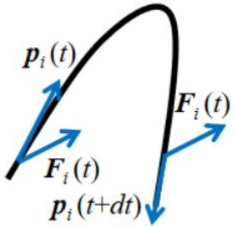
In this approach, decoherence correction is interpreted as a way to enforce the self-consistency of the TD-SE with the quantum-classical trajectories rather than as a common view of a decay of overlap of wavepackets moving on different PE surfaces. Namely:

- at every nonadiabatic interaction region, there is a possibility of the wavepacket branching into reflecting and transmitting wavepackets on different surfaces.
- the idea is to eliminate the wavepackets that go in the opposite direction with the main wavepacket on the active state.
- the correction is applied only at the reflection points (not the reflection of active trajectory, but the reflection of the wavepacket on other surfaces in comparison to that of the active surface)
- the reflection is judged as:



**no reflection**

$$\mathrm{sign}\{\boldsymbol{F}_i(t)\cdot\boldsymbol{p}_i(t)\}=\mathrm{sign}\{\boldsymbol{F}_i(t)\cdot\boldsymbol{p}_i(t+dt)\}$$



**reflection**

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

## MF-SD

This method is essentially like Ehrenfest,

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

The probabilitiy 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 times

## 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

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

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

**decoherence_C_param;**

**decoherence_eps_param;**

**decoherence_times_type;**

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

## mSDM

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

Akimov, A. V.; Prezhdo, O. V. *J. Phys. Chem. Lett.* **2013**, *4*, 3857
Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107

## Phase-informed Decoherence times

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

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

**dephasing_informed;**

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

## MF-SD

Bedard-Hearn, M. J.; Larsen, R. E.; Schwartz, B. J. *J. Chem. Phys.* **2005**, *123* (23), 234106. https://doi.org/10.1063/1.2131056.

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

**schwartz_decoherence_inv_alpha**

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

Independent stochastic pairwise decoherence (**ISPD**)

Esch, M. P.; Levine, B. G. *J. Chem. Phys.* **2020**, *152* (23), 234105. https://doi.org/10.1063/5.0010081.

# Other ways of computing Decoherence times

**2001, Hack, Truhlar**

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

Natural decay of mixing

Hack, M.D., Truhlar, D.G., 2001. J. Chem. Phys. 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. J. Chem. Phys. 120, 5543.

**2005, Jasper, Truhlar**

$$\chi_a = \frac{1}{(2\pi\sigma_a^2)^{1/4}}\exp\left(-\frac{(x-x_a)^2}{4\sigma_a^2} - \frac{iP_a x}{\hbar}\right)$$

$$O_{ab}(t) = \langle\chi_a|\chi_b\rangle$$

$$\dot{O}_{ab} = -k_{ab}O_{ab}$$

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

Classical GWP center motion, etc.

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

$$\overline{\boldsymbol{P}} = \frac{\boldsymbol{P}_a + \boldsymbol{P}_b}{2}$$

Jasper, A.W., Truhlar, D.G., 2005. J. Chem. Phys. 123. 064103

Parallel surfaces

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

**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. J. Phys. Chem. B 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. J. Chem. Phys. 126. 134114

# Other ways of computing Decoherence times

University at Buffalo
The State University of New York

**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. J. Chem. Phys. 129. 024112

**2011, Shenvi, Subotnik, Yang**

Exclude the momentum difference terms

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

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

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

Shenvi, N., Subotnik, J.E., Yang, W., 2011. J. Chem. Phys. 134. 144102.

**2012, Jaeger, Fisher, Prezhdo**
**DISH**

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

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

**2013,Akimov, Prezhdo**

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

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

Akimov, A.V., Prezhdo, O.V., 2013. J. Phys. Chem. Lett. 4, 3857.

**2017, Gu and Franco**

As a purity decay rate

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

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

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

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

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

Gu, B., Franco, I., 2017. J. Phys. Chem. Lett. 8, 4289.
Gu, B., Franco, I., 2018. J. Phys. Chem. Lett. 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

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

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

**2019, Sifain, Wang, Tretiak, Prezhdo**

Dephasing-informed correction

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

Sifain, A.E., Wang, L., Tretiak, S., Prezhdo, O.V., 2019. J. Chem. Phys. 150. 194104.

**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

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

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

Vindel-Zandbergen, P., Ibele, L.M., Ha, J.-K., et al., 2021. J. Chem. Theory Comput. 17, 3852.

# Phase corrections

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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.

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

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

**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.