

Excited States and Nonadiabatic Dynamics CyberTraining School/Workshop 2023

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Basic Concepts and Terminology of Nonadiabatic Dynamics

Born-Oppenheimer Approximation



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

$$\widehat{H}(\widehat{\boldsymbol{r}}, \widehat{\boldsymbol{R}}) \Psi_{n}(\boldsymbol{r}, \boldsymbol{R}) = E_{n} \Psi_{n}(\boldsymbol{r}, \boldsymbol{R})$$

Includes el-el and el-nucl interactions

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

This is an electron-nuclear (vibronic) wavefunction

<u>Born-Oppenheimer approximation</u>: 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

$$\widehat{H}(\widehat{\pmb{r}},\widehat{\pmb{R}})\Psi_{\mathrm{n}}(\pmb{r},\pmb{R})=E_n\Psi_n(\pmb{r},\pmb{R})$$
BO approximation

$$\widehat{H}(\widehat{\boldsymbol{r}}; \boldsymbol{R}(t)) \Psi_{n}(\boldsymbol{r}; \boldsymbol{R}) = E_{n}(\boldsymbol{R}) \Psi_{n}(\boldsymbol{r}; \boldsymbol{R}(t))$$

Coordinates of nuclei are parameters

Energy – is a function of these parameters: potential

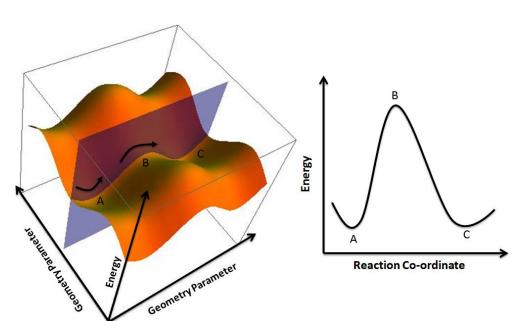
energy surface

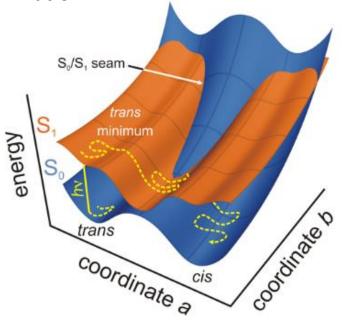
Potential energy surfaces (PES)



$$E_n(\mathbf{R}) = \langle \Psi_{n}(\mathbf{r}, \mathbf{R}) | \widehat{H}_{el}(\mathbf{r}, \mathbf{R}) | \Psi_{n}(\mathbf{r}, \mathbf{R}) \rangle_{\mathbf{r}} + V_{nn}(\mathbf{R})$$

- 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





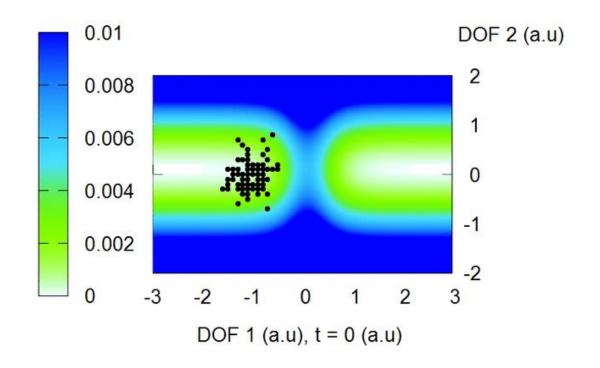
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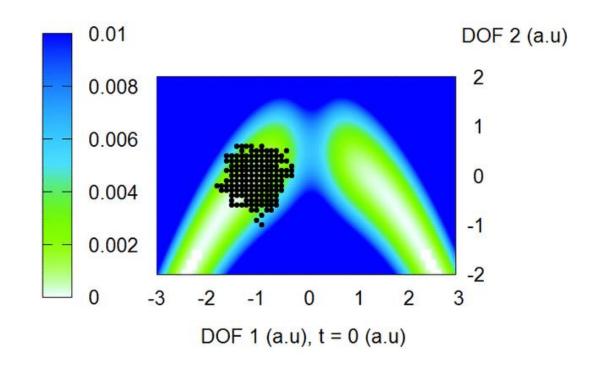
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Potential energy surfaces define the reactive dynamics



Credit: Brendan Smith





Tiers of approximation to the molecular Hamiltonian



Disregard the form of the wavefunction for now

Everything is operators!

Exact TD-SE

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

Electronic DOFs are still operators (quantum)

TD-SE with the BO

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

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)

(CPA)

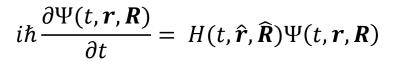
TD-SE with the classical path approximation
$$i\hbar \frac{\partial \Psi(t, \boldsymbol{r}, \boldsymbol{R})}{\partial t} = \left[T(\boldsymbol{P}) + \widehat{H}_{el}(\hat{\boldsymbol{r}}; \boldsymbol{R}(t)) + \widehat{V}_{nn}(\boldsymbol{R}(t))\right] \Psi(t, \boldsymbol{r}, \boldsymbol{R})$$

Nuclear DOFs are time-dependent variables

Kinetic energy is a function of momentum

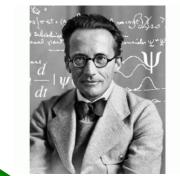
Adiabatic Approximation. Adiabatic and Nonadiabatic Dynamics





$$\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_{i} \chi_{i}(t, \mathbf{R}) \Phi_{i}(\mathbf{r}; \mathbf{R}(t)) \mathbf{A}$$

Except for in the exact factorization ansatz!



Adiabatic approximation: keep only one term

Adiabatic Dynamics

1 term is sufficient

Where is the BO approximation?

Reaction coordinate

Need more than 1 state
Non-Adiabatic Dynamics



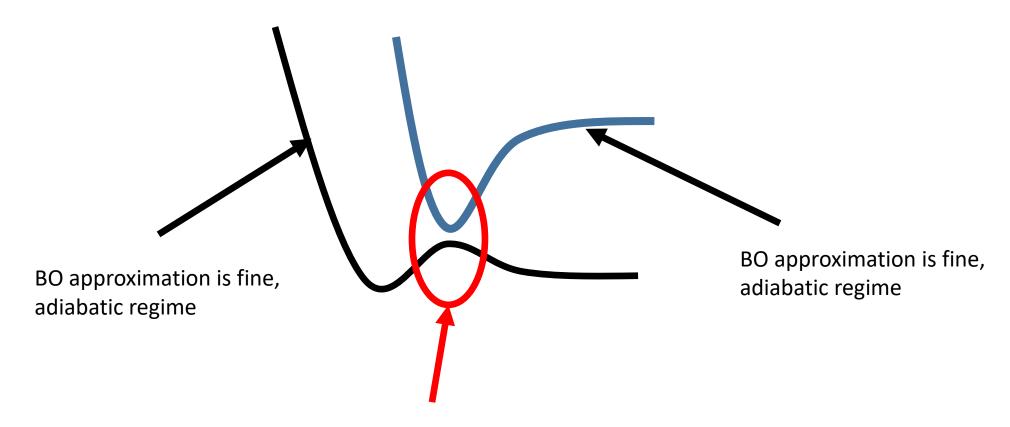
When NA dynamics is needed: Failure of the Born-Oppenheimer Approximation



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

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

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



Tiers of approximations to the wavefunction



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

Nonadiabatic

Adiabatic

Exact factorization

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

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.

$\Psi(t, \mathbf{r}, \mathbf{R}) = \chi(t, \mathbf{R}) \Phi_{\mathbf{R}}(t, \mathbf{r})$ $\int d\mathbf{r} |\Phi_{\mathbf{R}}(\mathbf{r}, t)| = 1, \forall \mathbf{R}$ $\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_{i} \chi_{i}(t, \mathbf{R}) \Phi_{i}(\mathbf{r}; \mathbf{R})$ $\Psi(t, \mathbf{r}, \mathbf{R}) = \chi(t, \mathbf{R}) \Phi(\mathbf{r}; \mathbf{R})$





Wavepacket-dressed trajectories

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

$$\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_{i} \chi_{i}(t, \mathbf{R}) \Phi_{i}(\mathbf{r}; \mathbf{R}(t)) \qquad \qquad \Psi(t, \mathbf{r}, \mathbf{R}) = \chi(t, \mathbf{R}) \Phi(\mathbf{r}; \mathbf{R}(t))$$

Bare trajectories

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

$$\Psi(t, \mathbf{r}; \mathbf{R}(\mathbf{t})) = \sum_{i} c_i(t) \Phi_i(\mathbf{r}; \mathbf{R}(t))$$



$$\Psi(t, \mathbf{r}; \mathbf{R}(\mathbf{t})) = c(t)\Phi(\mathbf{r}; \mathbf{R}(t))$$

Terminology: Adiabatic and Diabatic States



Adiabatic

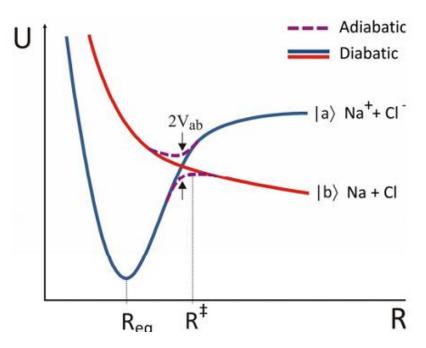
- unique
- eigenstates of molecular Hamiltonian:
- not always chemically-intuitive

Adiabatic (Hamiltonian is diagonal): $\langle \psi_{adi,i} | \widehat{H}_{el} | \psi_{adi,i} \rangle = 0, \forall i \neq j$

(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):
$$\langle \psi_{dia,i} | \nabla_{\mathbf{R}} | \psi_{dia,j} \rangle = 0, \forall \mathbf{R}$$



Examples of Deriving Equations of Motion with Different Approximations



Example 1: BO with quantum nuclei

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

$$\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_{i} \chi_{i}(t, \mathbf{R}) \Phi_{i}(\mathbf{r}; \mathbf{R})$$

Example 2: BO with wavepacket-dressed trajectories

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

$$\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_{i} \chi_{i}(t, \mathbf{R}) \Phi_{i}(\mathbf{r}; \mathbf{R}(t))$$

Case 1: Compute the action of \widehat{T} on Ψ



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

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

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

We keep all terms, because Φ is a function of R

Project on an arbitrary state Φ_i :

$$\langle \Phi_{i} | \hat{T} | \chi_{j} \Phi_{j} \rangle_{r} = \langle \Phi_{i} | \Phi_{j} \rangle_{r} \hat{T} \chi_{j} - \left(\sum_{\alpha} \frac{\hbar^{2}}{M_{\alpha}} \langle \Phi_{i} | \nabla_{\alpha} \Phi_{j} \rangle_{r} \nabla_{\alpha} \chi_{j} \right) + \langle \Phi_{i} | \hat{T} | \Phi_{j} \rangle_{r} \chi_{j}$$

$$\langle \Phi_{i} | \hat{T} | \chi_{j} \Phi_{j} \rangle_{r} = \delta_{ij} \hat{T} \chi_{j} - \left(\sum_{\alpha} \frac{\hbar^{2}}{M_{\alpha}} \langle \Phi_{i} | \nabla_{\alpha} \Phi_{j} \rangle_{r} \nabla_{\alpha} \chi_{j} \right) + \langle \Phi_{i} | \hat{T} | \Phi_{j} \rangle_{r} \chi_{j}$$

$$\langle \Phi_{i} | \hat{H}_{nucl} | \chi_{j} \Phi_{j} \rangle_{r} = \langle \Phi_{i} | \hat{H}_{nucl} | \Phi_{j} \rangle_{r} \chi_{j} = \langle \Phi_{i} | E_{j}(\mathbf{R}) | \Phi_{j} \rangle_{r} \chi_{j} = E_{j}(\mathbf{R}) \langle \Phi_{i} | \Phi_{j} \rangle_{r} \chi_{j} = E_{j}(\mathbf{R}) \delta_{ij} \chi_{j}$$

$$\langle \Phi_{i} | \hat{T} + \hat{H}_{nucl} | \Psi \rangle = \sum_{j} \langle \Phi_{i} | \hat{T} + \hat{H}_{nucl} | \chi_{j} \Phi_{j} \rangle_{r} = \sum_{j} \left[\delta_{ij} \hat{T} \chi_{j} - \left(\sum_{\alpha} \frac{\hbar^{2}}{M_{\alpha}} \langle \Phi_{i} | \nabla_{\alpha} \Phi_{j} \rangle_{r} \nabla_{\alpha} \chi_{j} \right) + \langle \Phi_{i} | \hat{T} | \Phi_{j} \rangle_{r} \chi_{j} + E_{j}(\mathbf{R}) \delta_{ij} \right]$$

Compute the LHS: Case 1



$$\left\langle \Phi_i \middle| \frac{\partial}{\partial t} \middle| \chi_j \Phi_j \right\rangle_r = \left\langle \Phi_i \middle| \Phi_j \right\rangle_r \frac{\partial}{\partial t} \chi_j + \left\langle \Phi_i \middle| \frac{\partial}{\partial t} \middle| \Phi_j \right\rangle_r \chi_j = \delta_{ij} \frac{\partial}{\partial t} \chi_j$$

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

Now, combine the two parts of the equation:

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

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

$$i\hbar\frac{\partial}{\partial t}\chi_{i} = \left[\hat{T} + E_{i}(\mathbf{R}) + \left\langle\Phi_{i}\middle|\hat{T}\middle|\Phi_{i}\right\rangle\right]\chi_{i} - i\hbar\sum_{j,\alpha}\left\langle\Phi_{i}\middle|\nabla_{\alpha}\Phi_{j}\right\rangle\frac{(-i\hbar\nabla_{\alpha})\chi_{j}}{M_{\alpha}} - \sum_{j\neq i,\alpha}\frac{\hbar^{2}}{2M_{\alpha}}\left\langle\Phi_{i}\middle|\nabla_{\alpha}^{2}\Phi_{j}\right\rangle\chi_{j}$$

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

Nonadiabatic dynamics



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

$$\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_{i} \chi_{i}(t, \mathbf{R}) \Phi_{i}(\mathbf{r}, \mathbf{R})$$

Diagonal BO correction to the PES! (ZPE of electrons)

In the adiabatic basis

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

$$D_{ii,\alpha}^{(1)} = \langle \Phi_i | \nabla_{\alpha} \Phi_j \rangle$$

first-order nonadiabatic couplings (NAC) - vector

Describes how a nuclear DOF α couples electronic state i and j This is what determines the rates of nonadiabatic transitions.

$$D_{ij,\alpha}^{(2)} = \left\langle \Phi_i \middle| \nabla_{\alpha}^2 \Phi_j \right\rangle$$

second-order NAC - scalar

In the diabatic basis

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

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

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

Case 2: Compute the action of \widehat{T} on Ψ



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

$$\widehat{T}(\chi_i \Phi_i) = (\widehat{T}\chi_i) \Phi_i$$

because Φ is only a function of time, not R

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

Compute the LHS

$$\left\langle \Phi_{i} \middle| \frac{\partial}{\partial t} \middle| \chi_{j} \Phi_{j} \right\rangle = \left\langle \Phi_{i} \middle| \Phi_{j} \right\rangle_{r} \frac{\partial}{\partial t} \chi_{j} + \left\langle \Phi_{i} \middle| \frac{\partial}{\partial t} \middle| \Phi_{j} \right\rangle \chi_{j} = \delta_{ij} \frac{\partial}{\partial t} \chi_{j} + \left\langle \Phi_{i} \middle| \frac{\partial}{\partial t} \middle| \Phi_{j} \right\rangle \chi_{j}$$

$$i\hbar \left\langle \Phi_{i} \middle| \frac{\partial}{\partial t} \middle| \Psi \right\rangle_{r} = i\hbar \sum_{j} \left\langle \Phi_{i} \middle| \frac{\partial}{\partial t} \middle| \chi_{j} \Phi_{j} \right\rangle_{r} = i\hbar \sum_{j} \delta_{ij} \frac{\partial}{\partial t} \chi_{j} + i\hbar \sum_{j} \left\langle \Phi_{i} \middle| \frac{\partial}{\partial t} \middle| \Phi_{j} \right\rangle \chi_{j} = i\hbar \frac{\partial}{\partial t} \chi_{i} + i\hbar \sum_{j} \left\langle \Phi_{i} \middle| \frac{\partial}{\partial t} \middle| \Phi_{j} \right\rangle \chi_{j}$$

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

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

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

Summary



Example 1: BO with quantum nuclei

Example 2: BO with wavepacket-dressed trajectories

$$\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_{i} \chi_{i}(t, \mathbf{R}) \Phi_{i}(\mathbf{r}; \mathbf{R})$$

$$\Psi(t, \mathbf{r}, \mathbf{R}) = \sum_{i} \chi_{i}(t, \mathbf{R}) \Phi_{i}(\mathbf{r}; \mathbf{R}(t))$$

Nonadiabatic, adiabatic basis

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

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

Nonadiabatic, diabatic basis

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

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

Adiabatic, adiabatic basis

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

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

Adiabatic, diabatic basis

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

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

Wavefunction and selection of representation



 $|\Psi\rangle$ Abstract wavefunction

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

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

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

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

Indeed

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

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

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

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

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

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

Different Hilbert spaces:

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

Shorthand notation. Adiabatic and Diabatic Representations



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

Shorthand notation for the entire basis:

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

Matrix elements (scalars)



 $A_{i,i} = \langle \psi_i | \hat{A} | \psi_i \rangle \leftrightarrow A = \langle \psi | \hat{A} | \psi \rangle$



Matrix

Basis:

Adiabatic (Hamiltonian is diagonal):
$$\langle \psi_{adi,i} | \widehat{H}_{el} | \psi_{adi,j} \rangle = 0, \forall i \neq j$$

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

Diabatic (NACs are exactly zero):

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

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

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

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

TD-SE in the Shorthand notation



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

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

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \widehat{H} |\Psi(t)\rangle$$
$$|\psi\rangle = (|\psi_1\rangle, |\psi_2\rangle, ..., |\psi_N\rangle)$$
$$C = (c_1, c_2, ..., c_N)^T$$

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

$$i\hbar \frac{\partial}{\partial t} |\psi_{rep}(t)\rangle C_{rep} + i\hbar |\psi_{rep}(t)\rangle \frac{\partial}{\partial t} C_{rep} = \widehat{H} |\psi_{rep}(t)\rangle C_{rep}$$

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

Projecting:

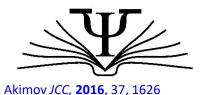
$$i\hbar S_{rep} \frac{\partial}{\partial t} C_{rep} = \left[\left\langle \psi_{rep}(t) | \widehat{H} | \psi_{rep}(t) \right\rangle - i\hbar \left\langle \psi_{rep}(t) | \frac{\partial}{\partial t} | \psi_{rep}(t) \right\rangle \right] C_{rep}$$



Transformations. Ehrenfest Dynamics. Some Implementation Detail In Libra

Libra as a workhorse of our developments





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

Implementation in Libra classes



Wavefunction language

$$|\Psi(t)\rangle = |\psi_{adi}(t)\rangle C_{adi}(t) = |\psi_{dia}(t)\rangle C_{dia}(t)$$

Density matrix language

$$\hat{\rho} = |\Psi\rangle\langle\Psi|$$

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

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

So the conversions of the density matrices is:

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

- ndia, nadi, ndof, ntraj
- ampl_dia, ampl_adi
- dm adi, dm dia

Coefficient transformation:

$$C_{dia} = UC_{adi} \leftrightarrow C_{adi} = U^{-1}C_{dia} \leftrightarrow C_{adi} = U^{+}SC_{dia}$$
 $H_{dia}U = SUH_{adi}$ and also computes derivative couplings and adiabatic gradients

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

nHamiltonian

- ampl_dia2adi
- ampl_adi2dia

compute_adiabatic()

compute_diabatic()

Implementation in the nHamiltonian class



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

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

$H_{dia} = \langle \boldsymbol{\psi}_{dia} | \widehat{H} | \boldsymbol{\psi}_{dia} \rangle$ Hamiltonian matrix elements

Scalar NACs
$$D_{adi} = \left\langle \psi_{adi} \middle| \frac{\partial}{\partial t} \middle| \psi_{adi} \right\rangle \quad \text{"Vibronic" Hamiltonian}$$

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

CMATRIX* ham_dia, nac_dia_nvib_dia CMATRIX* ham_adi, nac_adi, hvib_adi $H_{vib,dia} = H_{dia} - i\hbar D_{dia}$

Unitary (similarity) transformation

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

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

Time-overlaps (transition density matrices) $\langle \psi_{dia}(t - \Delta t) | \psi_{dia}(t) \rangle = St_{dia}(t - \Delta t, t) \approx I$

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

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

First-order derivative coupling vectors -

vector CiviAIRIX* dinam ado, d1ham dia

$$m{D}_{adi} \equiv \langle m{\psi}_{adi} |
abla m{\psi}_{adi}
angle$$
 - compute_adiabatic()

$$\langle \psi_{dia} | \psi_{dia} \rangle = S$$
 The diabatic basis is not necessarily $\langle \psi_{adi} | \psi_{adi} \rangle = I$ orthonormal

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

How to compute NACs?

$$U^{+} \nabla H_{dia} U - \left(\widetilde{D}_{dia}^{+} H_{adi} + H_{adi} \widetilde{D}_{dia} \right) = \nabla H_{adi} - \left(D_{adi}^{+} H_{adi} + H_{adi} D_{adi} \right)$$

$$\widetilde{\nabla H_{dia}} - \left(\widetilde{D}_{dia}^{+}\widetilde{H}_{dia} + \widetilde{H}_{dia}\widetilde{D}_{dia}\right) = \nabla H_{adi} - \left(D_{adi}^{+}H_{adi} + H_{adi}D_{adi}\right)$$

Then use special structure of the matrix

Nonadiabatic Couplings



Properties of the NACs

$$\overline{\mathbf{D}}_{dia}^{+} + \overline{\mathbf{D}}_{dia} = \nabla S$$

$$\overline{\mathbf{D}}_{adi} + \overline{\mathbf{D}}_{adi}^{+} = \nabla S_{adi} = 0 \to (D_{adi}^{\alpha})^{+} = -D_{adi}$$

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

This is a well-known property!

$$D^{lpha}_{rep,ij} \equiv \langle \psi_{rep,i} |
abla_{lpha} \psi_{rep,j}
angle$$
 is a scalar

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

$$\overline{m{D}}_{rep} \equiv \langle m{\psi}_{rep} | m{\nabla} m{\psi}_{rep} \rangle$$
 understood as a vector of matrices $D_{rep}^{lpha} = \langle m{\psi}_{rep} | m{\nabla}_{lpha} m{\psi}_{rep} \rangle$

Important observations

the equation becomes an identity when U = I

$$\begin{split} \widetilde{V_{\alpha}H_{dia}} - \left((D_{adi}^{\alpha})^{+}\widetilde{H}_{dia} + \widetilde{H}_{dia}\widetilde{D}_{dia}^{\alpha} \right) &= V_{\alpha}H_{adi} - \left((D_{adi}^{\alpha})^{+}H_{adi} + H_{adi}D_{adi}^{\alpha} \right) \\ U^{+} \langle \psi_{dia} | V_{\alpha}H | \psi_{dia} \rangle U & \langle \psi_{adi} | V_{\alpha}H | \psi_{adi} \rangle \end{split}$$

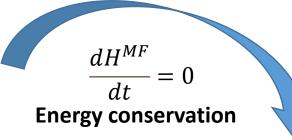
Quantum-Classical Hamiltonian and Ehrenfest forces



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

TD-SE for the amplitudes

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



nHamiltonian

- Ehrenfest_energy_adi
- Ehrenfest_energy_dia

$$\dot{\mathbf{R}} = M^{-1}\mathbf{P}$$

$$\mathbf{P} = f^{MF}(\mathbf{R}, \Psi_{\text{rep}})$$

Enforcing the "classical" form of equations of motion for nuclear DOFs $\dot{\mathbf{P}} = f^{MF}(\mathbf{R}, \Psi_{\text{rep}})$

nHamiltonian

- Ehrenfest forces adi
- Ehrenfest forces dia
- Ehrenfest forces tens adi
- Ehrenfest forces tens dia

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

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

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



Integrators and Local Diabatization

Trivial Crossing Problem

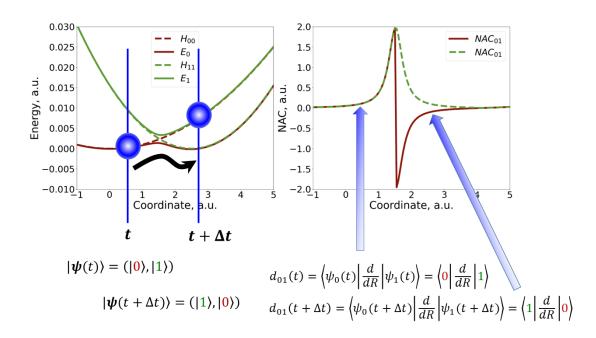


We want to solve

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

in the adiabatic basis:

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



Formal solution:

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

After projection:

$$C_{adi}(t + \Delta t) = \left| \psi_{adi}(t + \Delta t) \right| \left[\int_{0}^{\Delta t} d\tau \exp \left(-\frac{i\tau}{\hbar} \widehat{H}(t + \tau) \right) \right] \left| \psi_{adi}(t) \right\rangle C_{adi}(t)$$

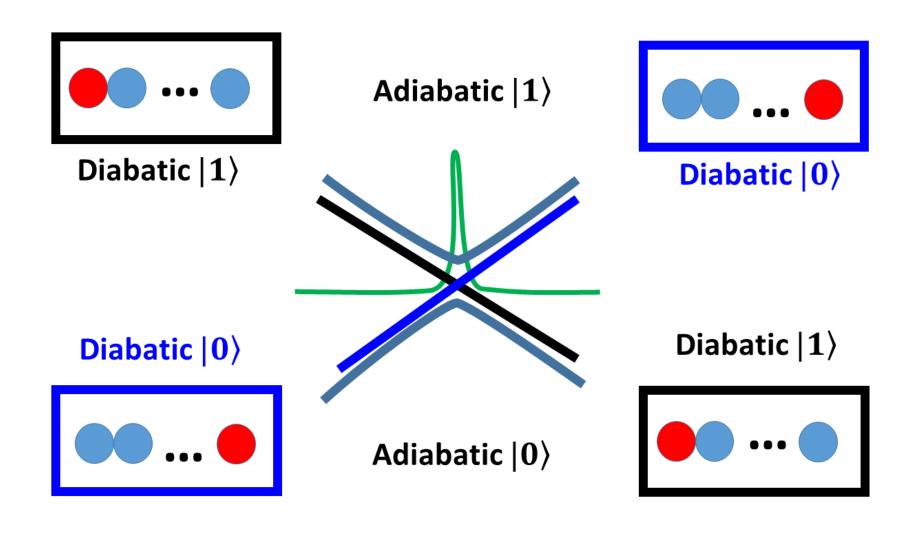
Consider the change of C_{adi} non-adiabatic dynamics

However, the bases $|\psi_{adi}(t)\rangle$ and $|\psi_{adi}(t+\Delta t)\rangle$ 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 Δt or due to inconsistency of energy and NAC (due to approximations)



Local Diabatization (LD) Approach



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

$$\left|\widetilde{\boldsymbol{\psi}}_{adi}(t)\right\rangle = \left|\boldsymbol{\psi}_{adi}(t)\right\rangle T(t)$$

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:

$$\begin{split} |\Psi(t)\rangle &= \big|\widetilde{\pmb{\psi}}_{adi}(t)\big\rangle \tilde{C}_{adi}(t) = |\pmb{\psi}_{adi}(t)\rangle C_{adi}(t) \\ C_{adi}(t) &= T(t)\tilde{C}_{adi}(t) \end{split}$$

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:

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

 $T(t + \Delta t) = [T^+(t)P(t, t + \Delta t)]^{-1}$ but this leads to fast accumulation of errors

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

$$T(t) = I$$

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

Lowdin normalization in the LD approach



However, this transformation will not preserve the wavefunction norm:

$$T(t + \Delta t) = [P(t, t + \Delta t)]^{-1}$$
$$|\psi_{adi}(t + \Delta t)\rangle = |\widetilde{\psi}_{adi}(t + \Delta t)\rangle T^{-1}(t + \Delta t)$$

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

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: $A = (T^+(t + \Delta t)T(t + \Delta t))^{-1/2}$

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

$$T(t) = I$$

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

Back to Integrating the TD-SE



$$U(t, t + \Delta t) = \left| \psi_{adi} \left(t + \Delta t \right) \right| \left[\int_{0}^{\Delta t} d\tau \exp \left(-\frac{i\tau}{\hbar} \hat{H}(t + \tau) \right) \right] |\psi_{adi}(t)\rangle$$

$$\left[\int_{0}^{\Delta t} d\tau \exp \left(-\frac{i\tau}{\hbar} \hat{H}(\tau) \right) \right] \approx \left[\exp \left(-\frac{i\Delta t}{2\hbar} \left[\hat{H}(t) + \hat{H}(t + \Delta t) \right] \right) \right] \approx \left[\exp \left(-\frac{i\Delta t}{2\hbar} \hat{H}(t + \Delta t) \right) \right] \left[\exp \left(-\frac{i\Delta t}{2\hbar} \hat{H}(t) \right) \right]$$

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

Using properties of the local-diabatic basis:

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

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

$$A(t) = \left\langle \psi_{adi}(t) \middle| \left[\exp \left(-\frac{i\Delta t}{2\hbar} \widehat{H}(t) \right) \right] \middle| \psi_{adi}(t) \right\rangle$$

Working the Liouville's space: propagation of density matrix

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

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

$$\widetilde{H} = \langle\widetilde{\pmb{\psi}}|\widehat{H}|\widetilde{\pmb{\psi}}\rangle = T^+\langle\underline{\pmb{\psi}}|\widehat{H}|\pmb{\psi}\rangle T$$

$$N\times N \text{ matrix}$$

Vectorized form of the QCLE

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

$$N^2 \times N^2 \text{ matrix} \qquad N^2 \times 1 \text{ vecto}$$

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:

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



Trajectory Surface Hopping (TSH) methods in Libra

TSH in the nutshell



Initialization

Nuclear dynamics

Stationary adiabatic states

Non-adiabatic Couplings

Electronic Dynamics

Decoherence 1

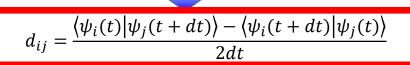
Proposed Hops Decoherence 2

Accept Hops

Change of state/Velocity rescaling

$$\dot{p_i} = -\frac{\partial H}{\partial r_i} \, \dot{r_i} = \frac{\partial H}{\partial p_i}$$

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



$$\Psi(\mathbf{r}, \mathbf{R}, \mathbf{t}) = \sum_{i} c_{i}(t) \psi_{i}(\mathbf{r}; \mathbf{R}(\mathbf{t})) \qquad i\hbar \frac{\partial c_{i}(\mathbf{t})}{\partial t} = \sum_{j} (E_{i} \delta_{ij} - i\hbar d_{ij}) c_{j}$$

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

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

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

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:

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

- 0 don't:
- 1 compute H_{adi} from H_{dia} by solving $H_{dia}U = SUH_{adi}$
- 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 $U: H_{dia} = SUH_{adi}U^{-1} = SUH_{adi}U^{+}S$

force method

how to compute nuclear forces:

- 0 don't
- 1 state-specific, adiabatic forces: $-\frac{\partial E_{adi}}{\partial \mathbf{r}}$
- 2 Ehrenfest forces

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

0 – using only diabatic properties; 1 – using adiabatic properties

Options for the Dynamics



dyn_control_params

- force_method

enforce_state_following

anforce state following

enforced_state_index

time_overlap_method

how to compute nuclear forces:

0 - don't

1 – state-specific, adiabatic forces: $-\frac{\partial E_{adi}}{\partial \mathbf{R}}$

2 – Ehrenfest forces

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

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.

How to get the time-overlaps $P_{adi}(t-\Delta t,t)=\langle \pmb{\psi}_{adi}(t-\Delta t)|\pmb{\psi}_{adi}(t)\rangle$ 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]

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

- 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

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

$$d\left(t + \frac{\Delta t}{2}\right) \approx \frac{1}{\Delta t} \int_{0}^{dt} \left\langle \boldsymbol{\psi}(t') \middle| \frac{\partial}{\partial t'} \middle| \boldsymbol{\psi}(t') \right\rangle dt' = \frac{1}{\Delta t} \int_{0}^{dt} T^{+}(t') \frac{\partial}{\partial t'} T(t') dt' = \frac{\log[T(t + \Delta t)]}{\Delta t}$$
$$T(t + \Delta t) = S'(t, t + \Delta t) = \left\langle \boldsymbol{\psi}(t) \middle| \boldsymbol{\psi}(t + \Delta t) \right\rangle$$

- 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

$$P_{i \to j}^{P} = \exp\left(-\frac{\pi}{4\sqrt{a^{2}}} \sqrt{\frac{2}{b^{2} + \sqrt{|b^{4} + sign(\mathbf{F}_{i}^{T}\mathbf{F}_{j})|}}}\right) \qquad P_{i \to f}^{P}(t, \mathbf{F}_{i}^{T}\mathbf{F}_{j}) = \exp\left(-\frac{\pi}{4\sqrt{a^{2}}} \sqrt{\frac{2}{b^{2} + \sqrt{|b^{4} + sign(\mathbf{F}_{i}^{T}\mathbf{F}_{j})|}}}\right) \qquad \text{Akin}$$

$$P_{i \to f}^{P}(t, \mathbf{F}_{i}^{T}\mathbf{F}_{j}) = \exp\left(-\frac{\pi}{4\sqrt{a^{2}}} \sqrt{\frac{2}{|b^{4} + sign(\mathbf{F}_{i}^{T}\mathbf{F}_{j})|}}\right) \qquad |\mathbf{F}_{i}^{T}\mathbf{F}_{j}^{T}| = \exp\left(-\frac{\pi}{4\sqrt{a^{2}}} \sqrt{\frac{2}{|b^{4} + sign(\mathbf{F}_{i}^{T}\mathbf{F}_{j})|}}\right) \qquad |\mathbf{F}_{i}^{T}\mathbf{F}_{j}^{T}\mathbf{F}_{j}^{T}| = \exp\left(-\frac{\pi}{4\sqrt{a^{2}}} \sqrt{\frac{2}{|b^{4} + sign(\mathbf{F}_{i}^{T}\mathbf{F}_{j})|}}\right) \qquad |\mathbf{F}_{i}^{T}\mathbf{F}_{j}^{T}\mathbf{F}_{j}^{T}| = \exp\left(-\frac{\pi}{4\sqrt{a^{2}}} \sqrt{\frac{2}{|b^{4} + sign(\mathbf{F}_{i}^{T}\mathbf{F}_{j})|}}\right) \qquad |\mathbf{F}_{i}^{T}\mathbf{F}_{j}^{T}\mathbf{F}_{j}^{T}\mathbf{F}_{j}^{T}| = \exp\left(-\frac{\pi}{4\sqrt{a^{2}}} \sqrt{\frac{2}{|b^{4} + sign(\mathbf{F}_{i}^{T}\mathbf{F}_{j})|}}\right) \qquad |\mathbf{F}_{i}^{T}\mathbf{F}_{j}$$

$$\frac{1}{\sqrt{\mu}}|\boldsymbol{F}_i - \boldsymbol{F}_j| \to \sqrt{(\boldsymbol{F}_i - \boldsymbol{F}_j)^T M^{-1}(\boldsymbol{F}_i - \boldsymbol{F}_j)}$$
Multidimensional version
$$\frac{1}{\sqrt{\mu}}|\boldsymbol{F}_i \boldsymbol{F}_j| \to \sqrt{|\boldsymbol{F}_i^T M^{-1} \boldsymbol{F}_j|}$$

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

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

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

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

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

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

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

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

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



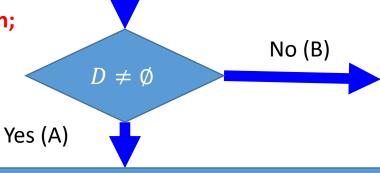
Advance "coherence time": $t_i = t_i + \Delta t$, $\forall i$

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 $t_i \ge T[\tau_i]$, add i to set $D: D = D \cup \{i\}$

int dish_decoherence_event_option;

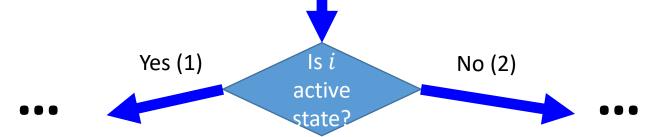
- 0 direct compare
- 1 -Poisson



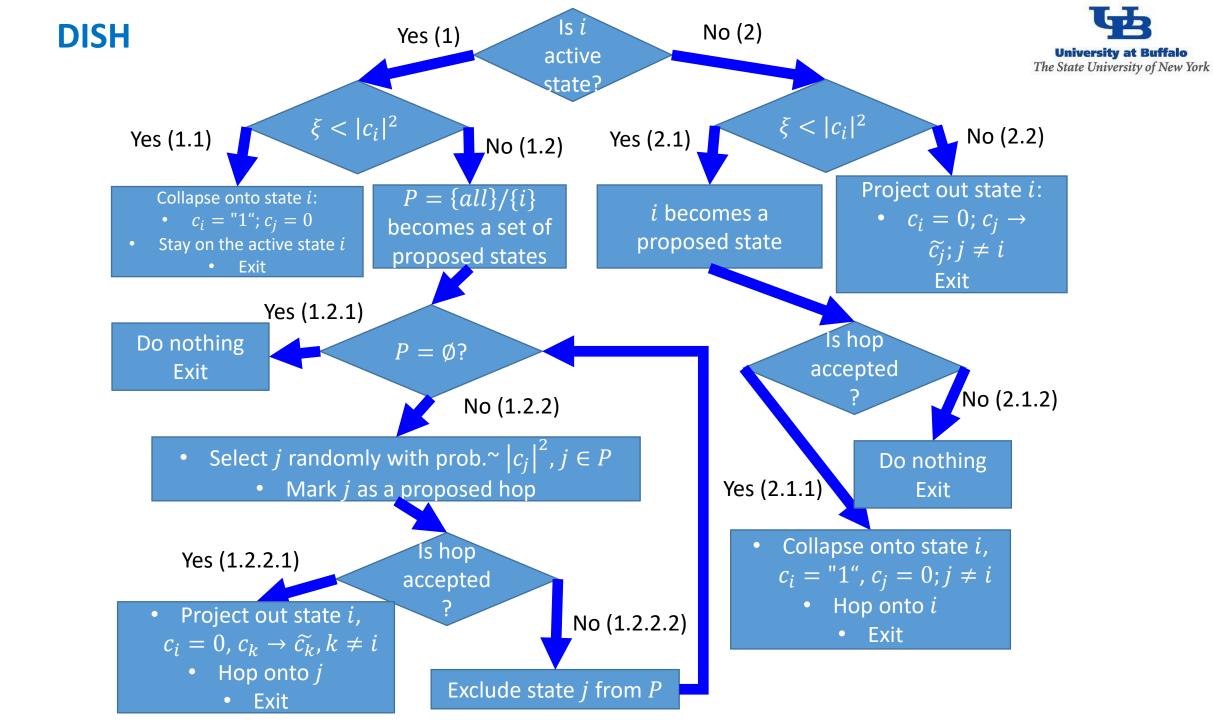
Continue coherent evolution:

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

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



Finish scheme in panel (b)



Hop Acceptance Probabilities



int hop_acceptance_algo;

Options:

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

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

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

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

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

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

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

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

SDM

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

gradually change the amplitudes

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

$$C'_{f} = C_{f} \frac{1 - \sum_{i \neq f} |C'_{i}|^{2}}{|C_{f}|^{2}}$$

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

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

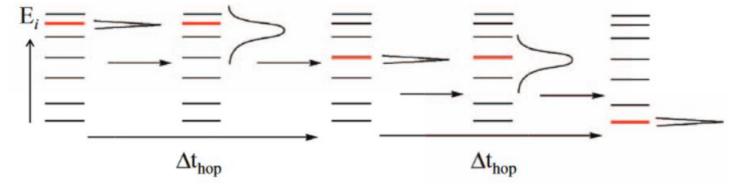
int collapse_option;

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



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 (D. Wenjun Ouvang, and Joseph E. Subotnik

Propagate extra set of variables

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

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

These variables define the rates for wavefunction collapse

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

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





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

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

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

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

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

Also compute the probability to reset the moments as

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

Decoherence: BCSH and MF-SD

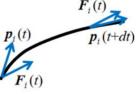


BCSH

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

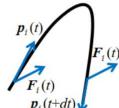
In this approach, decoherence correction is interpreted as a way to enforce the self-consistency of the TD-SE with the quantum-classical trajectories rather than as a common view of a decay of overlap of wavepackets moving on different PE surfaces. Namely:

- 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

$$\operatorname{sign}\left\{\boldsymbol{F}_{i}(t)\cdot\boldsymbol{p}_{i}(t)\right\} = \operatorname{sign}\left\{\boldsymbol{F}_{i}(t)\cdot\boldsymbol{p}_{i}(t+dt)\right\}$$



reflection

$$\operatorname{sign}\left\{\boldsymbol{F}_{i}(t)\cdot\boldsymbol{p}_{i}(t)\right\} = -\operatorname{sign}\left\{\boldsymbol{F}_{i}(t)\cdot\boldsymbol{p}_{i}(t+dt)\right\}$$

MF-SD

This method is essentially like Ehrenfest,

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

The probability of such a collapse is given by the quantum amplitude of the state and by the decoherence time to collapse onto a particular state k. $P_i = \frac{\rho_{ii}}{\tau_i} \Delta t$

The decoherence time is given by

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

Decoherence times



DISH

Decoherence interval

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

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

SDM/EDC

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

Granucci, G.; Persico, N.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

$$\tau_{ij}^{-1} = \sqrt{\frac{5\langle \delta E_{ij}^2 \rangle}{12\hbar^2}} \begin{array}{c} \text{Akimov, A. V.; Prezhdo, O. V. \textit{J.}} \\ \text{\textit{Phys. Chem. Lett. } \textbf{2013}, \textit{4}, \textit{3857}} \\ \text{Smith, B.; Akimov, A. V. \textit{J.}} \\ \text{\textit{Chem.Phys. } \textbf{2019}, 151, 124107} \end{array}$$

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.

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

schwartz_decoherence_inv_alpha

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

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

2004, Zhu, Jasper, Truhlar

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

$$\tau_{ij}^{SCDM} = \frac{\hbar}{|H_{ii}^{dia} - H_{jj}^{dia}|} + \frac{\hbar}{4E_{vib}}$$
Natural decay of mixing
$$\frac{1}{H_{ii}^{dia} - H_{jj}^{dia}} + \frac{\hbar}{4E_{vib}}$$
Self-consistent decay of mixing
$$\frac{1}{H_{ii}^{dia} - H_{jj}^{dia}} + \frac{1}{4E_{vib}}$$
Self-consistent decay of mixing
$$\frac{1}{H_{ii}^{dia} - H_{jj}^{dia}} + \frac{1}{4E_{vib}}$$
Self-consistent decay of mixing
$$\frac{1}{H_{ii}^{dia} - H_{jj}^{dia}} + \frac{1}{4E_{vib}}$$
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$$\frac{1}{H_{ii}^{dia} - H_{ii}^{dia}} + \frac{1}{4E_{vib}}$$
Self-consistent decay of mixing
$$\frac{1}{H_{ii}^{dia} - H_{ii}^{dia}} + \frac{1}{4E_{vib}}$$
Self-consistent decay of mixing
$$\frac{1}{H_{ii}^{dia} - H_{ii}^{dia}} + \frac{1}{4E_{vib}}$$
Self-consistent decay of mixing

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

2005, Jasper, Truhlar

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

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







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

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

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

2006, Larsen, Bedard-Hearn, Schwartz

$$\frac{1}{\tau_i^{BLS_i}} = \sqrt{\frac{1}{4\hbar^2} (\mathbf{F}^{MF} - \mathbf{F}_i)^T A^{-1} (\mathbf{F}^{MF} - \mathbf{F}_i)}$$

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



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

 $\chi_{a} = \left(\frac{2Re\left[\alpha_{a}\right]}{\pi}\right)^{1/4} \exp\left(-\alpha(x-x_{a})^{2} + \frac{iP_{a}x}{\hbar}\right)$ $|\sigma_{ij}| = \left|\frac{Re\left[2\alpha_{i}\right]^{1/4}Re\left[2\alpha_{j}\right]^{1/4}}{\left(\alpha_{i} + \alpha_{i}^{*}\right)^{1/2}}\right| \exp\left(-Re\left[\frac{\alpha_{i}\alpha_{j}^{*}(x_{i} - x_{j})^{2}}{\alpha_{i} + \alpha_{j}^{*}}\right]\right)$ Exclude the momentum difference terms

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

2012, Jaeger, Fisher, Prezhdo DISH

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

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

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. J. Chem. Phys. 137. 22A545.

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

2017, Gu and Franco

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

As a purity decay rate

$$\widehat{H} = \widehat{H}_S + \widehat{H}_B + \widehat{H}_{SB} \qquad \widehat{H}_{SB} = \sum_{\alpha} \widehat{S}_{\alpha} \otimes \widehat{B}_{\alpha}$$

$$\widehat{H}_{SB} = \sum_{a} \widehat{S}_{a} \otimes \widehat{B}_{a}$$

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

$$\Delta_{ab}^{X} = \langle \hat{X}_{a}\hat{X}_{b} \rangle - \langle \hat{X}_{a} \rangle \langle \hat{X}_{b} \rangle, X = S, B$$

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

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

Other ways of computing Decoherence times



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

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

2019, Sifain, Wang, Tretiak, Prezhdo

Dephasing-informed correction

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

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

2020, Esch, Levine

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

Pairwise decoherence scheme

2021, Vindel-Zandbergen et al.

In the context of exact factorization approach

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

$$\tau_i^{SHXF,-1} = \sum_j \mathbf{Q}^T M^{-1} (\mathbf{F}_i - \mathbf{F}_j) |c_j|^2$$
$$\mathbf{Q} = -\hbar \frac{\nabla |\chi|}{|\chi|}$$

Phase corrections



2011, Shenvi-Subotnik-Yang int do_ssy

A Gaussian $g_n(x)$ moving on the surface n would acquire an additional phase with respect to Gaussian $g_m(x)$ moving on the surface

$$m \text{ such that: } \frac{g_m(x=x_n(t))}{g_n(x=x_n(t))} = \exp(\Delta \phi) = \exp(i\hbar t \, P_n^T M^{-1} (P_m - P_n)).$$
 Shenvi, N., Subotnik, J.E., Yang, W., 2011. J. Chem. Phys. 135. 024101.

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

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

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

2019, Miao, Subotnik: Generalization to multiple states:

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

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

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

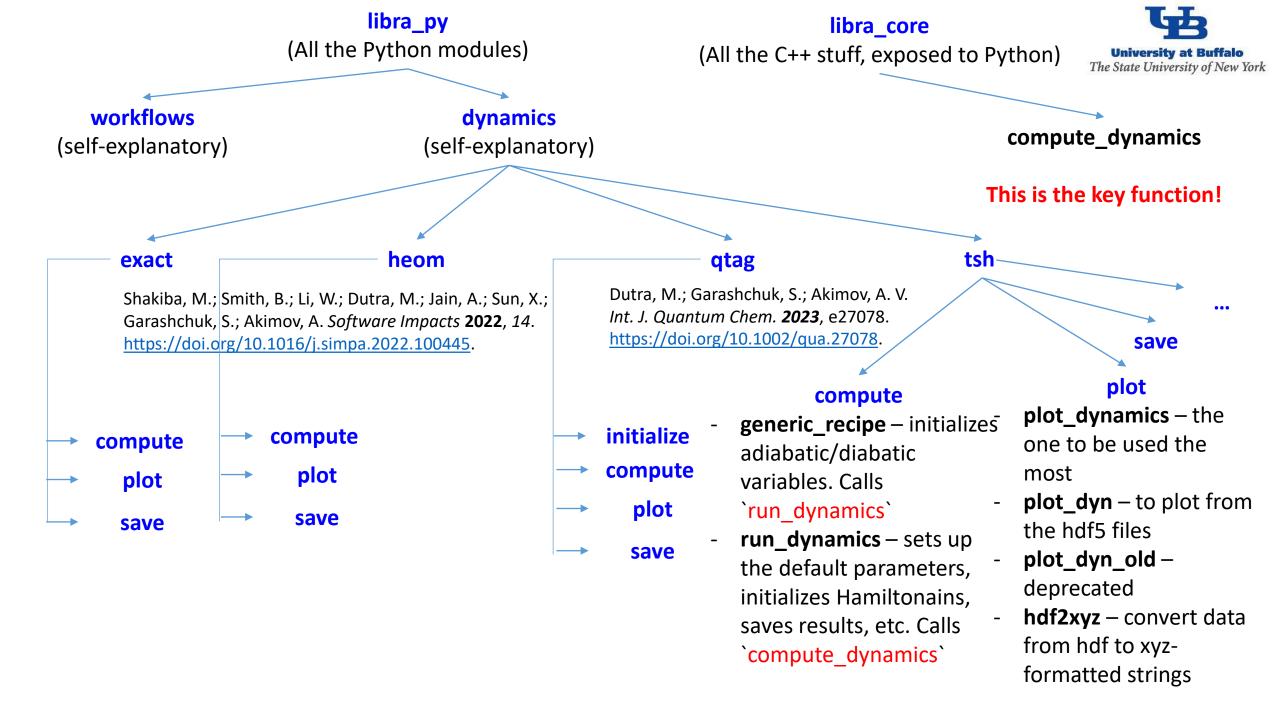
2016, Zhu: in terms of QCLE

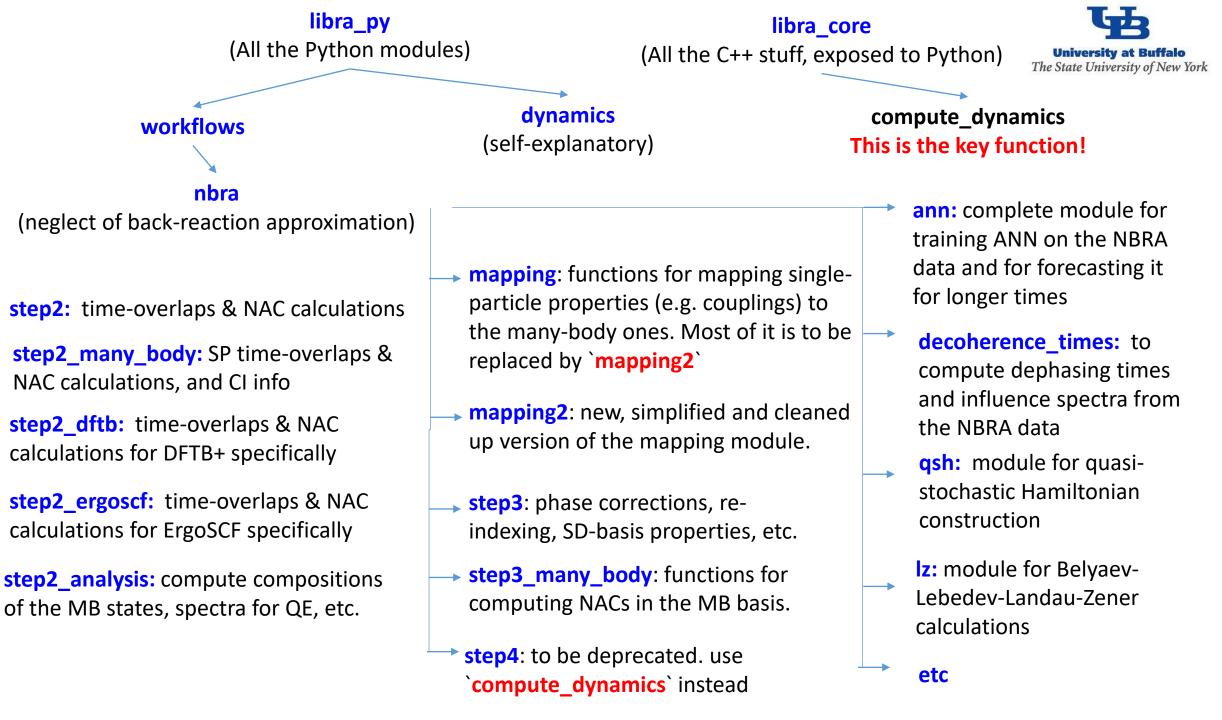
$$\begin{split} &i\hbar\frac{d\rho_{nm}(\textbf{\textit{R}},\textbf{\textit{P}})}{dt} = \sum_{i} \left[[E_{n}\delta_{ni} - i\hbar d_{ni}]\rho_{im} - \rho_{ni}[E_{m}\delta_{im} - i\hbar d_{im}] \right] \\ &= (E_{n} - E_{m})\rho_{nm} - i\hbar \sum_{i} [\rho_{im}d_{ni} - \rho_{ni}d_{im}] \end{split}$$

$$\begin{split} i\hbar\frac{d\rho_{nm}}{dt} \\ &= 2\big(\sqrt{E-E_m}-\sqrt{E-E_n}\big)\sqrt{E-E_{eff}}\rho_{nm} - i\hbar\sum_i[\rho_{im}d_{ni}-\rho_{ni}d_{im}] \\ E_{eff} &= \sum_i\rho_{ii}E_i \end{split}$$
 Zhu, C., 2016. Sci. Rep. 6. 24198.



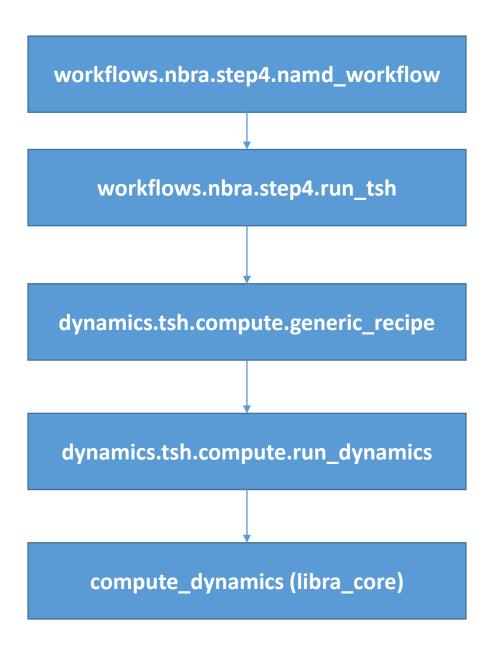
Structure of Libra package Atomistic Workflows





Brief Overview of the Deprecated step4





Parallelization, multiple methods/initial conditions

Initialization of nuclear variables

Initialization of electronic variables, transformation to the desired representation, nHamiltonian object construction and initialization

Initialization of default parameters, writing files, computing some observables, thermostat variables, iteration over nuclear timesteps

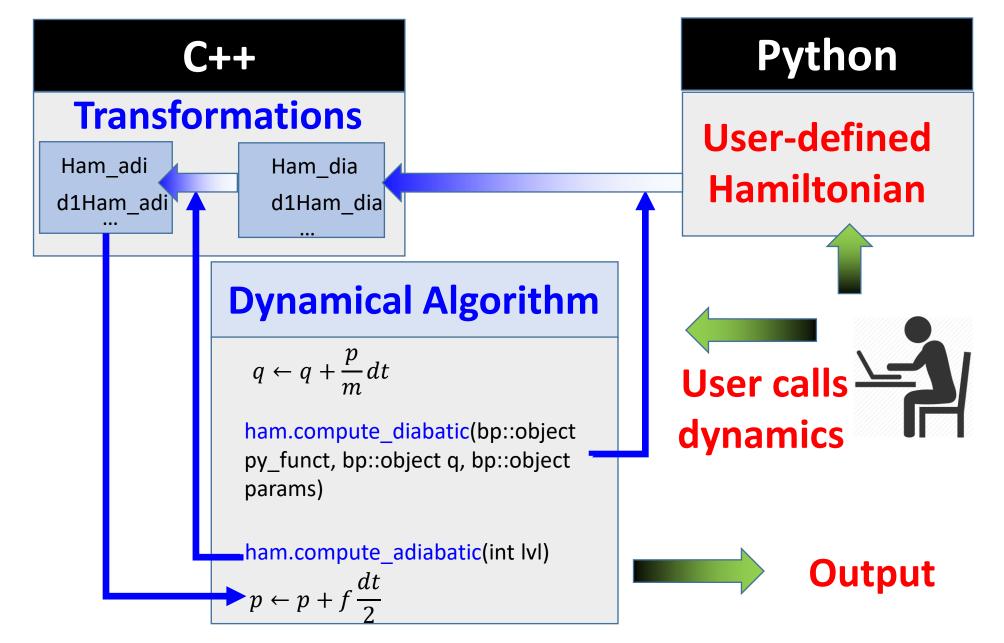
TSH/Ehrenfest and decoherence algorithms, trajectory coupling, Hamiltonian properties updates (calling external Python functions)



More on the nHamiltonian class. Making Interfaces

How `compute_dynamics` works





Different ways of computing matrix elements. Example of H_{dia}^{vib}



Blue = Required Input

Green = Output

Green with D = Can be set up directly via Python function call

Function	Q	P	H _{dia}	D _{dia}	d _{dia}	H_{dia}^{vib}
nHamiltonian::compute_diabatic(bp ::object py_funct)			D	D	D	D
nHamiltonian:: compute_nac_dia ()						
nHamiltonian:: compute_hvib_dia ()						

Different ways of computing matrix elements. Example of H_{adi}^{vib}



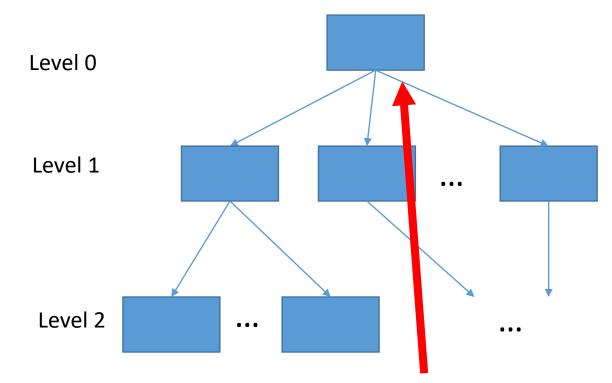
Function	Q	P	S	H_{dia}	∇H_{dia}	D_{dia}	U	H_{adi}	∇H_{adi}	Dadi	d_{adi}	H_{adi}^{vib}
nHamiltonian:: compute_diabatic (bp::object py_funct)			D	D	D	D						
nHamiltonian:: compute_adiabatic ()												
nHamiltonian::compute_adiabatic(bp::obj ect py_funct)							D	D	D	D	D	D
nHamiltonian:: compute_nac_adi()												
nHamiltonian:: compute_hvib_adi ()												

nHamiltonian class as a hierarchical data type to handle multiple trajectories



nHamiltonian

- level
- ic
- nHamiltonian* parent
- vector<nHamiltonian*> children
- nnucl, nadi, ndia
- 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
- ampl_dia2adi
- ampl_adi2dia



int entanglement_opt

A selector of a method to couple the trajectories in this ensemble.

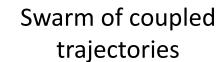
- 0: no coupling [default]
- 1: ETHD
- 2: ETHD3 (experimental)
- 22: another flavor of ETHD3 (experimental)

Packing variables for multiple trajectories



Individual trajectory

Swarm of uncoupled trajectories



$$p \leftarrow p + f \frac{dt}{2}$$

$$p \leftarrow p + f \frac{dt}{2}$$
 \leftarrow +

$$q \leftarrow q + M^{-1}pdt \leftarrow +$$





Forces update







$$p \leftarrow p + f \frac{di}{2}$$



Keep the Dynamical Workflow Fixed



User defines how to run the dynamical simulation

```
for i in range(500):
    propagate_el(Cdia, Cadi, Hvib, Sdia, 0.5*dt, rep)
    p = p + 0.5*f*dt
    q = q + dt*p/m
    compute_model(model, Hdia, Sdia, d1ham_dia, dc1_dia, q, params)
    ham.compute_adiabatic(1);
    f = compute_frc(ham, Cdia, Cadi, rep)
    p = p + 0.5*f*dt
    Hvib = compute_Hvib(Hdia, Hadi, dc1_dia, dc1_adi, p, m, rep)
    propagate_el(Cdia, Cadi, Hvib, Sdia, 0.5*dt, rep)

Etot = compute_etot(ham, p, Cdia, Cadi, m, rep)
```

User defines what function to use to compute entries in the Hamiltonian object (diabatic/adiabatic Ham, overlap matrix, derivatives, etc.) - NEXT

Example: Model Calculations



```
Initialize Python objects
def model2(q, params):
  obj = tmp()
  obj.ham dia = CMATRIX(2,2); obj.ovlp dia = CMATRIX(2,2);
  obj.d1ham_dia = CMATRIXList(); obj.d1ham_dia.append( CMATRIX(2,2))
  obj.dc1 dia = CMATRIXList(); obj.dc1 dia.append( CMATRIX(2,2))
 x = q.get(0)
  x0,k,D,V = params["x0"], params["k"], params["D"], params["V"]
                                                                     Set matrix elements according to
  obj.ovlp dia.set(0,0, 1.0+0.0j); obj.ovlp dia.set(0,1, 0.0+0.0j);
  obj.ovlp dia.set(1,0,0.0+0.0j); obj.ovlp dia.set(1,1,1.0+0.0j);
  obj.ham dia.set(0,0, k*x*x*(1.0+0.0j)); obj.ham dia.set(0,1, V*(1.0+0.0j));
  obj.ham dia.set(1,0, V*(1.0+0.0j));
                                         obj.ham dia.set(1,1, (k*(x-x0)**2 + D)*(1.0.
  for i in [0]:
    obj.d1ham dia[i].set(0,0, 2.0*k*x*(1.0+0.0j)); obj.d1ham dia[i].set(0,1, 0.0+0.0j);
    obj.d1ham dia[i].set(1,0, 0.0+0.0j);
                                                  obj.d1ham dia[i].set(1,1,2.0*k*(x-x0)*(1.0+0.0i));
    obj.dc1 dia[i].set(0,0, 0.0+0.0j); obj.dc1 dia[i].set(0,1,-0.1+0.0j);
    obj.dc1 dia[i].set(1,0, 0.1+0.0j); obj.dc1 dia[i].set(1,1, 0.0+0.0j);
```

return obj

Example: Atomistic Calculations



```
def model atomistic(q, params, indx):
                                                                                   Initialize Python objects
  natoms = params["natoms"]; ndof = q.num of rows; ndia = params["ndia"]
  params[ "output filename" ] = "detailed.out"
  obj = tmp()
  obj.ham dia = CMATRIX(1,1);
  obj.ovlp dia = CMATRIX(1,1);
                                  obj.ovlp dia.set(0,0, 1.0+0.0j)
  obj.d1ham dia = CMATRIXList();
  for i in xrange(ndof):
                                                                          Prepare and Run external program
    obj.d1ham dia.append( CMATRIX(1,1) )
  os.system("mkdir wd/job "+str(indx))
  os.system("cp dftb in.hsd wd/job "+str(indx)) #+"/dftb in.hsd")
  os.chdir("wd/job "+str(indx))
  create input.update coordinates(q, params)
  os.system("srun %s < dftb in.hsd > out" % (exe name) ) # DFTB calculations are run here!
  dftb forces = parse output.get forces(params)
                                                                            Set matrix elements according to
  os.chdir("../../")
  for i in xrange(ndof):
                                                                                               your model
    obj.d1ham_dia[i].set(0,0, dftb_forces[i]*(-1.0+0.0j))
    obj.dc1 dia[i].set(0, 0, 0.0+0.0j)
return obj
```