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Libra Summer School and Workshop 2024

TSH: Part 2

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TSH in the nutshell

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Initialization

Nuclear dynamics

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

Stationary adiabatic states

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

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

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

Decoherence 1

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

as in SDM

Proposed Hops Decoherence 2

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

or as in DISH

Accept Hops

based on energy conservation or

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

Change of state/Velocity rescaling

change active electronic state, rescale velocity

NBRA

Integrators and Local Diabatization

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Options for the Dynamics: TD-SE and Hamiltonian

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dyn_control_params

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

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

- **ham_transform_method** — how to update Ham via transformation :
  - 0 – don't, so one doesn't override the adiabatic properties read from the files; typical for the atomistic workflows (e.g. with the ham_update_method == 2)
  - [1 – compute H_{adi} from H_{dia} by solving $H_{dia}U = SUH_{adi}$] (common for model problems)
  - 2 – compute H_{adi} from H_{dia} by using a provided U: $H_{adi} = (SU)^{-1}H_{dia}U = U^{+}H_{dia}U$
  - 3 – compute H_{dia} from H_{adi} by using a provided U: $H_{dia} = SUH_{adi}U^{-1} = SUH_{adi}U^{+}S$
  - 4 - compute H_{dia} from H_{adi} by using a local diabatization approach

  To be implemented

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

Trivial Crossing Problem

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

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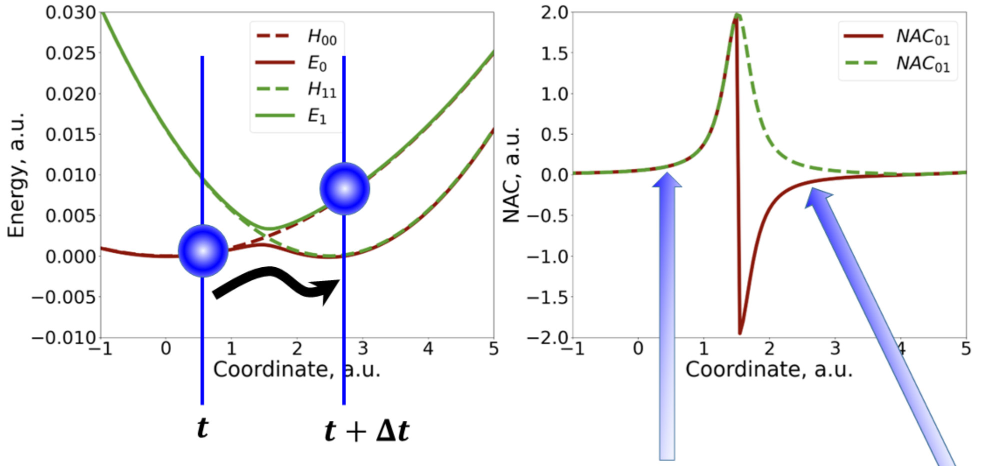
We want to solve

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

in the adiabatic basis:

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



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

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

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

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

Formal solution:

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

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

After projection:

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

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

Trivial Crossing Problem

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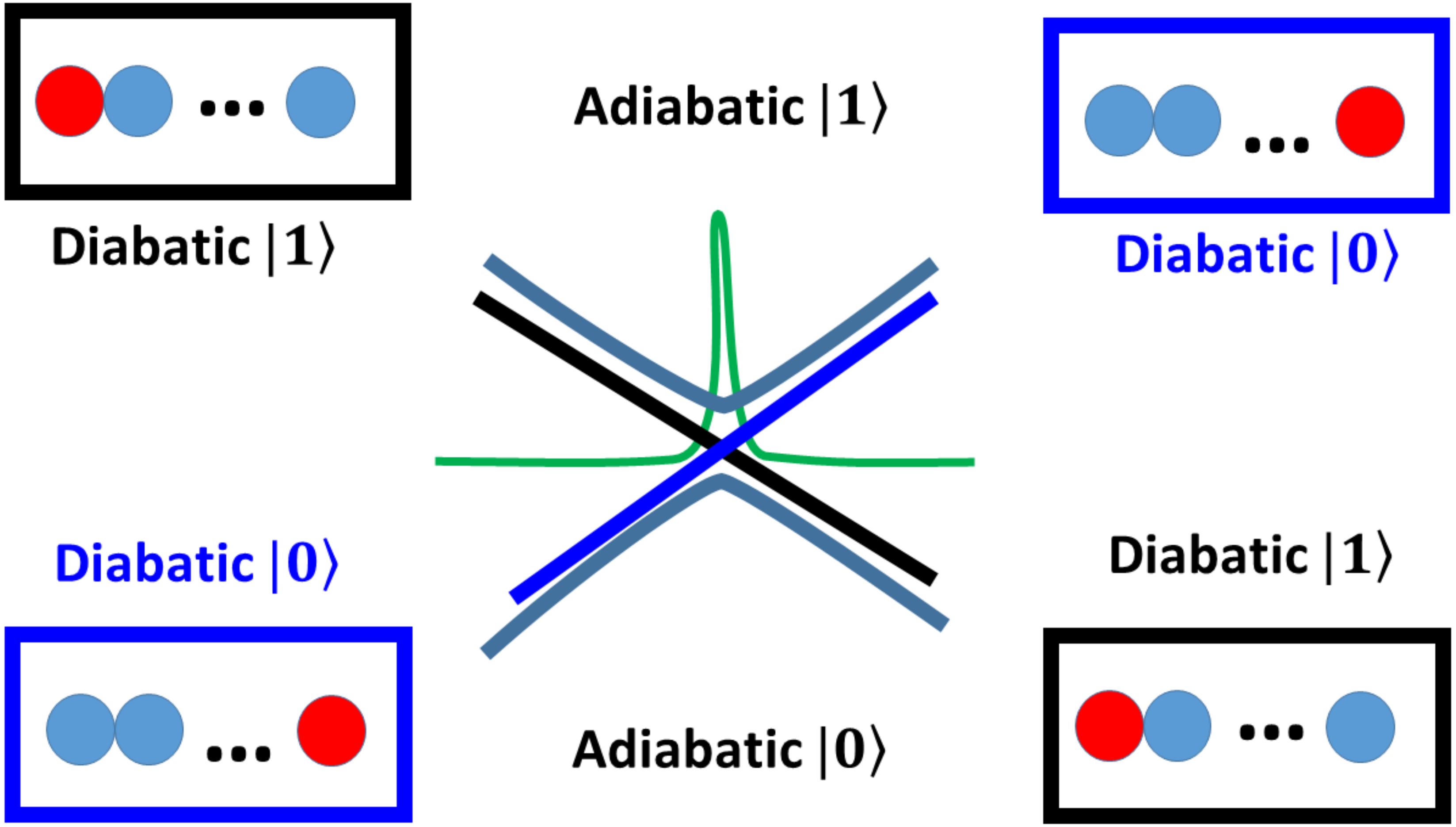
Arises because of finite Δt or due to inconsistency of energy and NAC (due to approximations)



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

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

Local Diabatization (LD) Approach

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

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

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

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:

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

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

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 normalization

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

Back to Integrating the TD-SE

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

Crude splitting:

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

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

Using properties of the local-diabatic basis:

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

$$U(t,t+\Delta t) \approx \langle \boldsymbol{\psi}_{adi}(t+\Delta t)| \left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t+\Delta t)\right)\right] |\tilde{\boldsymbol{\psi}}_{adi}(t+\Delta t)\rangle\langle\tilde{\boldsymbol{\psi}}_{adi}(t)| \left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t)\right)\right] |\boldsymbol{\psi}_{adi}(\mathrm{t})\rangle = \langle \boldsymbol{\psi}_{adi}(t+\Delta t)| \left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t+\Delta t)\right)\right] \boldsymbol{\psi}_{adi}(t+\Delta t)\rangle T(t+\Delta t) T^{-1}(t) \langle \boldsymbol{\psi}_{adi}(t)| \left[\exp\left(-\frac{i\Delta t}{2\hbar}\hat{H}(t)\right)\right] |\boldsymbol{\psi}_{adi}(\mathrm{t})\rangle = A(t+\Delta t) T(t+\Delta t)\, A(t)$$

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

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

Back to Integrating the TD-SE: Another integrator

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Symmetric splitting:

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

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

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

$$= T(t+\Delta t)B(t)T^{+}(t+\Delta t)A(t+\Delta t)T(t+\Delta t)B(t)$$

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

Rotation-based Integrators for TD-SE

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$$i\hbar\frac{\partial C}{\partial t} = XC$$

$$X_{ij} = Re[X_{ij}] + iIm[X_{ij}]$$

$$C(t+\Delta t) = \exp(iL\Delta t)C(t).$$

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

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

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

$$iL_i^{(1)} = -\frac{i}{\hbar}X_{ii}C_i\frac{\partial}{\partial C_i}$$

$$iL_{ij}^{(2)} = \frac{Im(X_{ij})}{\hbar}\left[C_j\frac{\partial}{\partial C_i} - C_i\frac{\partial}{\partial C_j}\right]$$

$$iL_{ij}^{(3)} = -\frac{iRe(X_{ij})}{\hbar}\left[C_j\frac{\partial}{\partial C_i} + C_i\frac{\partial}{\partial C_j}\right]$$

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

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

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

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

Rotation-based Integrators for TD-SE: Overall Factorization

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

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

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

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

Working the Liouville's space: propagation of density matrix

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

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

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

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

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

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

So, the final expression:

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

Overview of Electronic Integrators

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dyn_control_params

- **electronic_integrator**

rep_tdse = 0 (diabatic):

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

rep_tdse = 1 (adiabatic):

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

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

rep_tdse = 2 (diabatic, density matrix formalism):

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

rep_tdse = 3 (adiabatic, density matrix formalism):

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

10 - same as 0, but with rotations

Additional flags for the Integrators

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dyn_control_params

- **assume_always_consistent**

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

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

- **ampl_transformation_method**

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