# *Electron-nuclear correlation to the realtime time-dependent density functional theory from mixed-quantum classical equations based on the exact factorization*

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# Decoherence correction based on exact factorization (XF)

## Mixed quantum-classical (MQC) approach from XF

The MQC equation from XF gives an explicit form of the decoherence due to the electron-nuclear correlation.

***XFMQC equations of motion***

[Agostini, F; Min, S. K.; Abedi, A.; Gross, E. K. U., *JCTC*, **2016**.]

$$\mathbf{F}_\nu = -\langle \Phi_{\underline{\underline{\mathbf{R}}}}(t)|\nabla_\nu \hat{H}_{BO}|\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}} + \sum_{\nu'} \frac{2i\mathscr{P}_{\nu'}}{M_{\nu'}} \cdot \left(\mathbf{A}_{\nu'}\mathbf{A}_\nu - \Re\langle \nabla_{\nu'}\Phi_{\underline{\underline{\mathbf{R}}}}(t)|\nabla_\nu \Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}}\right)$$

$$i\frac{d\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)}{dt} = \left(\hat{H}_{BO} - \sum_\nu \frac{\mathscr{P}_\nu}{M_\nu}\cdot(\mathbf{A}_\nu + i\nabla_\nu) + \sum_\nu \frac{1}{2M_\nu}(\mathbf{A}_\nu + i\nabla_\nu)\cdot(\mathbf{A}_\nu + i\nabla_\nu)\right)\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$$

***XF ansatz***

[Abedi, A.; Maitra, N. T.; Gross, E. K. U. *PRL*, **2010**.]

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

*Partial normalization condition (PNC)*

$$\langle \Phi_{\underline{\underline{\mathbf{R}}}}(t)|\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}} = 1 \text{ for all } \underline{\underline{\mathbf{R}}} \text{ and } t$$

***New terms beyond the Ehrenfest propagation!***

***td vector potential*** $\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}},t) = \langle \Phi_{\underline{\underline{\mathbf{R}}}}(t)| -i\nabla_\nu \Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}}$

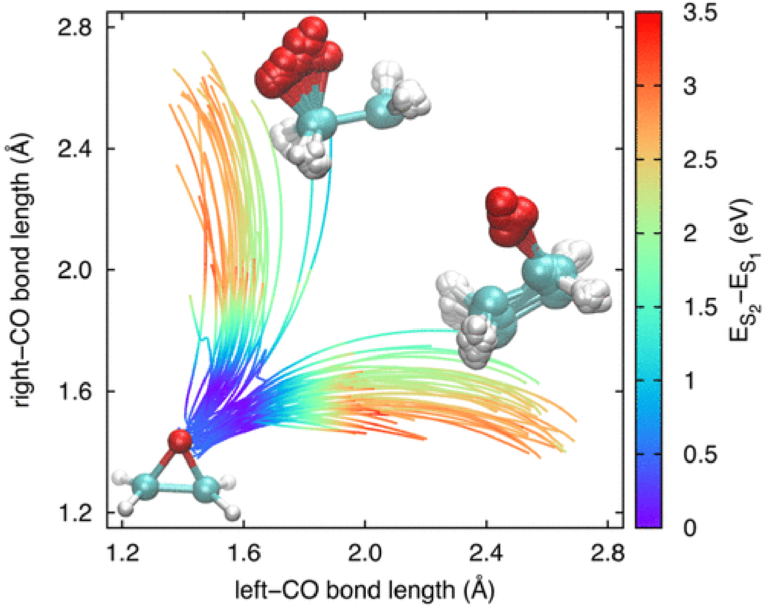
***quantum momentum*** $\mathscr{P}_\nu(\underline{\underline{\mathbf{R}}},t) = -i\frac{\nabla_\nu|\chi(\underline{\underline{\mathbf{R}}},t)|}{|\chi(\underline{\underline{\mathbf{R}}},t)|}$

# Nonadiabatic dynamics simulations from exact factorization

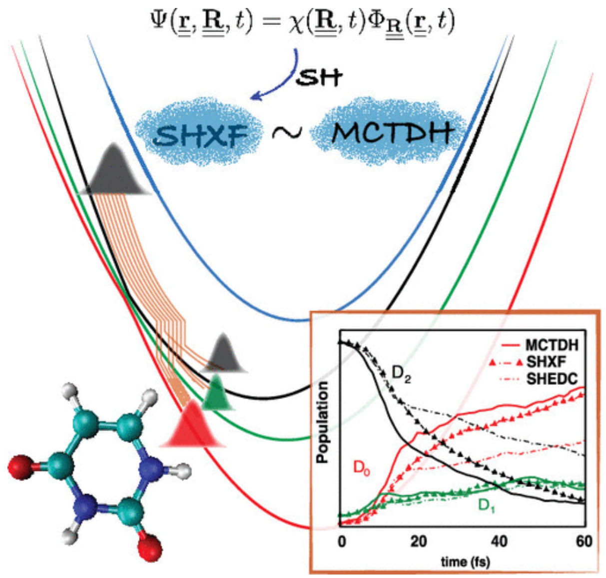
## Various nonadiabatic dynamics methods based on XF

[Villaseco Arribas, E.; Vindel-Zandbergen, P.; Roy, S.; Maitra, N. T. *PCCP*, **2023**.]

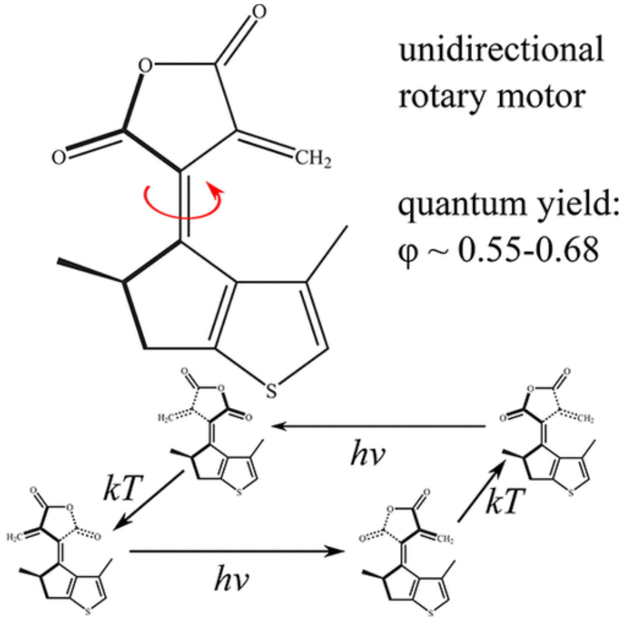
| | MQC | SH | Ehrenfest |
|---|---|---|---|
| Coupled Trajectories | CT-MQC<br>[Min, S.K.; Agostini, F; Gross, E.K.U. *PRL*, **2015**.] | CTSH<br>[Pieroni, C.; Agostini, F.; *JCTC*, **2021**.] | CT-MQCe<br>[Gossel, G. H.; Agostini, F.; Maitra, N. T.; *JCTC*, **2018**.] |
| Independent Trajectories | MQCXF<br>[Ha, J.-K.; Min, S. K., *JCP*, **2022**.] | DISH-XF (SHXF)<br>[Ha, J.-K.; Lee, I.S.; Min, S.K., *JPCL*, **2018**.] | EhXF |




A ring-opening reaction (CT-MQC)
[Min, S. K.; Agostini; F.; Tavernelli, I.; Gross, E. K. U., *JPCL*, **2017**.]




Nonadiabatic dynamics containing a multistate conical intersection (SHXF)
[Vindel-Zandbergen, P.; Matsika, S.; Maitra, N. T. *JPCL*, **2022**.]




Simulations of a molecular rotor (SHXF)
[Filatov, M.; Paolino, M.; Min, S. K.; Kim, K. S. *JPCL*, **2018**.]

# RT-TDDFT dynamics for simulating condensed systems

**Semiclassical dynamics with realtime time-dependent density functional theory (RT-TDDFT)**

In a semiclassical dynamics using RT-TDDFT, the many-body electronic problem is bypassed with TDDFT, and nuclei is propagated with the Ehrenfest force.

[Kolesov, G.; Grånäs, O.; Hoyt, R.; Vinichenko, D.; Kaxiras, E. *JCTC*, **2016**.]

Many-body TDSE $$i\partial_t \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t) = \hat{H}_{BO}(\underline{\underline{\mathbf{r}}},t;\underline{\underline{\mathbf{R}}})\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$$

td Kohn-Sham (TDKS) equation $$i\frac{\partial \psi_j(\mathbf{r},t)}{\partial t} = \left[-\frac{1}{2}\nabla^2 + v + v_H + v_{xc}\right]\psi_j(\mathbf{r},t) = \hat{h}_{KS}[\rho]\psi_j(\mathbf{r},t)$$

Nuclear equation $$\mathbf{F}_\nu = -\nabla_\nu E[\rho]$$

# Hermitian construction of the ENC operator

**How to add the electron-nuclear correlation (ENC) to the TDKS equation?**

It is natural to ask the correspondence between the XFMQC and TDKS equation.

XFMQC

$$i\frac{d\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)}{dt} = \left(\hat{H}_{BO} - \boxed{\sum_\nu \frac{\mathscr{P}_\nu}{M_\nu}\cdot(\mathbf{A}_\nu + i\nabla_\nu) + \sum_\nu \frac{1}{2M_\nu}(\mathbf{A}_\nu + i\nabla_\nu)\cdot(\mathbf{A}_\nu + i\nabla_\nu)}\right)\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$$

↕

TDKS

$$i\frac{\partial\psi_j(\mathbf{r},t)}{\partial t} = \hat{h}_{KS}[\rho]\psi_j(\mathbf{r},t) + \boxed{\;?\;}$$

# Hermitian construction of the ENC operator

## How to add the electron-nuclear correlation (ENC) to the TDKS equation?

One crude approximation to generate a decoherence correction is to replace the many-body quantities to the one-body counterpart.

$$\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t) \mapsto \psi^{j}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t),$$

$$\hat{H}_{BO} \mapsto \hat{h}_{KS},$$

$$\mathbf{A}_{\nu}(\underline{\underline{\mathbf{R}}},t) = \langle \Phi_{\underline{\underline{\mathbf{R}}}}(t)| -i\nabla_{\nu}\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}} \mapsto \mathbf{a}^{j}_{\nu}(\underline{\underline{\mathbf{R}}},t) = \langle \psi^{j}_{\underline{\underline{\mathbf{R}}}}(t)| -i\nabla_{\nu}\psi^{j}_{\underline{\underline{\mathbf{R}}}}(t)\rangle$$

Then the resulting equation is the following.

$$i\partial_t \psi^{j}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) = \hat{h}_{KS}\psi^{j}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) - \sum_{\nu} \frac{\mathscr{P}_{\nu}}{M_{\nu}} \cdot (\mathbf{a}^{j}_{\nu} + i\nabla_{\nu})\psi^{j}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)$$

However, this violates the orthogonality of TDKS orbitals.

$$\partial_t \langle \psi^{i}_{\underline{\underline{\mathbf{R}}}}(t)|\psi^{j}_{\underline{\underline{\mathbf{R}}}}(t)\rangle = \sum_{\nu} \frac{i\mathscr{P}_{\nu}}{M_{\nu}} \cdot \left[(\mathbf{a}^{i}_{\nu} + \mathbf{a}^{j}_{\nu})\delta_{ij} - 2\langle \psi^{i}_{\underline{\underline{\mathbf{R}}}}(t)| -i\nabla_{\nu}\psi^{j}_{\underline{\underline{\mathbf{R}}}}(t)\rangle\right] \neq 0$$

# Hermitian construction of the ENC operator

## Hermitian form of the ENC operator

The violation of orthogonality is from the non-Hermiticity of the ENC operator.

$$\hat{H}_{en}^{(1)} = -\sum_{\nu} \frac{\mathscr{P}_{\nu}}{M_{\nu}} \cdot (\mathbf{A}_{\nu} + i\nabla_{\nu}) \qquad \hat{H}_{en}^{(2)} = \sum_{\nu} \frac{1}{2M_{\nu}} (\mathbf{A}_{\nu} + i\nabla_{\nu}) \cdot (\mathbf{A}_{\nu} + i\nabla_{\nu})$$

Stable propagation is guaranteed in the conventional RT-TDDFT dynamics since it is described with the Hermitian operator.

Equivalent time evolution, but Hermitian using the density representation

[Han, D.; Ha, J.-K.; Min, S. K. *JCTC*, **2023**.]

$$i|\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle = \left[ -i\sum_{\nu} \frac{\mathscr{P}_{\nu}}{M_{\nu}} \cdot \nabla_{\nu}\hat{\Gamma}_{\underline{\underline{\mathbf{R}}}}(t) - \sum_{\nu} \frac{\nabla_{\nu}^{2}\hat{\Gamma}_{\underline{\underline{\mathbf{R}}}}(t) + \nabla_{\nu}\hat{\Gamma}_{\underline{\underline{\mathbf{R}}}}(t) \cdot \nabla_{\nu}\hat{\Gamma}_{\underline{\underline{\mathbf{R}}}}(t)}{2M_{\nu}} \right] |\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle$$

$$= \left( \hat{\tilde{H}}_{en}^{(1)} + \hat{\tilde{H}}_{en}^{(2)} \right) |\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle$$

Density operator $\hat{\Gamma}_{\underline{\underline{\mathbf{R}}}} = |\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle\langle\Phi_{\underline{\underline{\mathbf{R}}}}(t)|$

# Hermitian construction of the ENC operator

## Equivalence of time evolution

Only the partial normalization condition is used for derivation. $\langle\Phi_{\underline{\underline{\mathbf{R}}}}(t)|\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}} = 1$ for all $\underline{\underline{\mathbf{R}}}$ and $t$

$$
\begin{aligned}
H_{en}^{(1)}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle &= -\sum_\nu \frac{\mathscr{P}_\nu}{M_\nu}\cdot(\mathbf{A}_\nu + i\nabla_\nu)|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle \\
&= -\sum_\nu \frac{\mathscr{P}_\nu}{M_\nu}\cdot\Big(\langle\Phi_{\underline{\underline{\mathbf{R}}}}| - i\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + i|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\Big) \\
&= -i\sum_\nu \frac{\mathscr{P}_\nu}{M_\nu}\cdot\Big(\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + |\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\Big) \\
&= -i\sum_\nu \frac{\mathscr{P}_\nu}{M_\nu}\cdot\nabla_\nu\Gamma_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle \\
&= \tilde{H}_{en}^{(1)}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle.
\end{aligned}
$$

$$
\begin{aligned}
H_{en}^{(2)}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle &= \sum_\nu \frac{1}{2M_\nu}(\mathbf{A}_\nu + i\nabla_\nu)\cdot(\mathbf{A}_\nu + i\nabla_\nu)|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle \\
&= \sum_\nu \frac{1}{2M_\nu}\Big[((\langle\Phi_{\underline{\underline{\mathbf{R}}}}| - i\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + i\nabla_\nu)\cdot((\langle\Phi_{\underline{\underline{\mathbf{R}}}}| - i\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + i\nabla_\nu)\Big]|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle \\
&= \sum_\nu \frac{1}{2M_\nu}\Big[-\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + \langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle \\
&\quad + \langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\cdot|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + \langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu^2\Phi_{\underline{\underline{\mathbf{R}}}}\rangle|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + \langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - |\nabla_\nu^2\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\Big] \\
&= \sum_\nu \frac{1}{2M_\nu}\Big[\Big(-|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - |\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\cdot|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\Big) \\
&\quad + \Big(2|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + 2|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\cdot|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + |\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu^2\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - |\nabla_\nu^2\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\Big)\Big] \\
&= \sum_\nu \frac{1}{2M_\nu}\Big[\Big(-|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - |\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\cdot|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\Big) \\
&\quad + \Big(2|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - |\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\nabla_\nu^2\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - |\nabla_\nu^2\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\Big)\Big] \\
&= \sum_\nu \frac{1}{2M_\nu}\Big[\Big(-|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - |\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\cdot|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle \\
&\quad - |\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - |\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\Big) \\
&\quad + \Big(-|\nabla_\nu^2\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - 2|\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\cdot\langle\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle - |\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\nabla_\nu^2\Phi_{\underline{\underline{\mathbf{R}}}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\Big)\Big] \\
&= \sum_\nu \frac{1}{2M_\nu}\Big(-\nabla_\nu\Gamma_{\underline{\underline{\mathbf{R}}}}\cdot\nabla_\nu\Gamma_{\underline{\underline{\mathbf{R}}}} - \nabla_\nu^2\Gamma_{\underline{\underline{\mathbf{R}}}}\Big)|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle \\
&= \tilde{H}_{en}^{(2)}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle,
\end{aligned}
$$

* Here, all operations are done with respect to the electronic degrees of freedom.

# TDKS equation based on XF

## The ENC Hamiltonian as a perturbation

To derive the ENC term in the TDKS equation, consider the ENC Hamiltonian as a perturbation to the original action.

$$\mathscr{A} = \int_{t_0}^{t_1} dt \langle \Phi_{\underline{\underline{\mathbf{R}}}} | i\partial_t - \hat{H}_{BO} - \hat{\hat{H}}_{en}^{(1)} | \Phi_{\underline{\underline{\mathbf{R}}}} \rangle_{\underline{\underline{\mathbf{r}}}}.$$

$$\mathscr{A} = \mathscr{B} - \int_{t_0}^{t_1} dt \int d\mathbf{r} \rho_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) v(\mathbf{r},t) - \mathscr{C}$$

ENC action $\mathscr{C} = \int_{t_0}^{t_1} dt \langle \Phi_{\underline{\underline{\mathbf{R}}}} | \hat{\hat{H}}_{en}^{(1)} | \Phi_{\underline{\underline{\mathbf{R}}}} \rangle_{\underline{\underline{\mathbf{r}}}} = 0$

$$\hat{\hat{H}}_{en}^{(1)} = -i \sum_{\nu} \frac{\mathscr{P}_{\nu}}{M_{\nu}} \cdot \nabla_{\nu} \hat{\Gamma}_{\underline{\underline{\mathbf{R}}}}$$

$$\langle \Phi_{\underline{\underline{\mathbf{R}}}} | \hat{\hat{H}}_{en}^{(1)} \Phi_{\underline{\underline{\mathbf{R}}}} \rangle_{\underline{\underline{\mathbf{r}}}} = -i \sum_{\nu} \frac{\mathscr{P}_{\nu}}{M_{\nu}} \cdot \nabla_{\nu} \langle \Phi_{\underline{\underline{\mathbf{R}}}} | \hat{\Gamma}_{\underline{\underline{\mathbf{R}}}} \Phi_{\underline{\underline{\mathbf{R}}}} \rangle_{\underline{\underline{\mathbf{r}}}} = 0$$

***PNC*** $\langle \Phi_{\underline{\underline{\mathbf{R}}}}(t) | \Phi_{\underline{\underline{\mathbf{R}}}}(t) \rangle_{\underline{\underline{\mathbf{r}}}} = 1$ for all $\underline{\underline{\mathbf{R}}}$ and $t$

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*cf. A similar approach has been employed where the ENC Hamiltonian is considered as a perturbation in the static perturbation theory. The 1st order term does not change the energy but does the wave function.*

Nuclear-velocity perturbation theory based on XF [Scherrer, A.; Agostini, F.; Sebastiani, D.; Gross, E. K. U.; Vuilleumier, R. *JCP*, **2015**.]

$$\epsilon(\mathbf{R},t) = \left\langle \varphi_{\mathbf{R}}^{(0)} \right| \hat{H}_{BO} + \sum_{\nu=1}^{N_n} \boldsymbol{\lambda}_{\nu}(\mathbf{R},t) \cdot (-i\hbar\nabla_{\nu}) \left| \varphi_{\mathbf{R}}^{(0)} \right\rangle_{\mathbf{r}} = \epsilon_{BO}^{(0)}(\mathbf{R})$$

$$\boldsymbol{\lambda}_{\nu}(\mathbf{R},t) = \frac{1}{M_{\nu}} \frac{-i\hbar\nabla_{\nu}\chi(\mathbf{R},t)}{\chi(\mathbf{R},t)}$$

$$\varphi_{\mathbf{R}}(\mathbf{r},t) = \varphi_{\mathbf{R}}^{(0)}(\mathbf{r}) + \sum_{e\neq 0} \frac{\left\langle \varphi_{\mathbf{R}}^{(e)} \right| -i\hbar \sum_{\nu,\alpha} \lambda_{\alpha}^{\nu}(\mathbf{R},t) \partial_{\alpha}^{\nu} \varphi_{\mathbf{R}}^{(0)} \Big\rangle_{\mathbf{r}}}{\epsilon_{BO}^{(0)}(\mathbf{R}) - \epsilon_{BO}^{(e)}(\mathbf{R})} \varphi_{\mathbf{R}}^{(e)}(\mathbf{r})$$

# TDKS equation based on XF

## The ENC Hamiltonian as a perturbation

The ENC action can be expressed in terms of density or 1RDM, which is constructed from the TDKS orbital of the reference.

$$\int d\mathbf{r}\rho_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) = N_e\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\hat{\Gamma}_{\underline{\underline{\mathbf{R}}}}\Phi_{\underline{\underline{\mathbf{R}}}}\rangle \qquad \gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},\mathbf{r}',t) = \sum_j^{occ}\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\psi^{j*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)$$

1RDM(1-body reduced density matrix)

$$\mathscr{C} = \int_{t_0}^{t_1} dt\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\hat{\hat{H}}^{(1)}_{en}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle_{\underline{\underline{\mathbf{r}}}} = \int_{t_0}^{t_1} dt\left(-i\sum_\nu\frac{\mathscr{P}_\nu}{M_\nu N_e}\cdot\int d\mathbf{r}\nabla_\nu\rho_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\right) = \int_{t_0}^{t_1} dt\left(-i\sum_\nu\frac{\mathscr{P}_\nu}{M_\nu N_e}\cdot\frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\nabla_\nu|\gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},\mathbf{r}',t)|^2\right)$$

Then ENC term is derived, taking a functional derivative with respect to the reference TDKS orbital.

$$\frac{\delta\mathscr{A}}{\delta\psi^{i*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)} = \frac{\delta\mathscr{B}}{\delta\rho_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)}\psi^i_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) - v(\mathbf{r},t)\psi^i_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) - \int d\mathbf{r}'\left(-i\sum_\nu\frac{\mathscr{P}_\nu}{M_\nu N_e}\cdot\nabla_\nu\gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},\mathbf{r}',t)\psi^i_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\right) = \frac{\delta\mathscr{B}}{\delta\rho_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)}\psi^i_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) - v(\mathbf{r},t)\psi^i_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) - \hat{h}_{en}\psi^i_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)$$

$$\hat{h}_{en}[\gamma_{\underline{\underline{\mathbf{R}}}}]\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) \equiv \int d\mathbf{r}'\left(-i\sum_\nu\frac{\mathscr{P}_\nu}{M_\nu N_e}\cdot\nabla_\nu\gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},\mathbf{r}',t)\right)\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)$$

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$$\begin{aligned}\iint\nabla_\nu|\gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},\mathbf{r}',t)|^2 d\mathbf{r}'d\mathbf{r} &= \sum_{jk}^{occ}\int d\mathbf{r}\nabla_\nu\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\psi^{k*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\int d\mathbf{r}'\psi^{j*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\psi^k_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t) + \sum_{jk}^{occ}\int d\mathbf{r}\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\nabla_\nu\psi^{k*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\int d\mathbf{r}'\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\psi^{k*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\\
&+\sum_{jk}^{occ}\int d\mathbf{r}\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\psi^{k*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\int d\mathbf{r}'\nabla_\nu\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\psi^{k*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t) + \sum_{jk}^{occ}\int d\mathbf{r}\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\psi^{k*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\int d\mathbf{r}'\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\nabla_\nu\psi^{k*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\\
&=\sum_j^{occ}\int d\mathbf{r}\left(\nabla_\nu\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\psi^{j*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) + \psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\nabla_\nu\psi^{j*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\right) + \sum_j^{occ}\int d\mathbf{r}'\left(\nabla_\nu\psi^{j*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t) + \psi^{j*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\nabla_\nu\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\right)\\
&=2\int d\mathbf{r}\nabla_\nu\rho(\mathbf{r},t)\end{aligned}$$

$$\rho_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) = \sum_j^{occ}\psi_j(\mathbf{r},t)\psi_j^*(\mathbf{r},t)$$

# TDKS equation based on XF

## XF-TDKS equations

The resultant coupled equations are given as

*Exchange operator with respect to electronic coordinates*

$$i\frac{\partial \psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)}{\partial t} = \left(\hat{h}_{KS}[\rho_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)] + \hat{h}_{en}[\gamma_{\underline{\underline{\mathbf{R}}}}]\right)\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) \quad \hat{h}_{en}[\gamma_{\underline{\underline{\mathbf{R}}}}]\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t) \equiv \int d\mathbf{r}'\left(-i\sum_\nu \frac{\mathscr{P}_\nu}{M_\nu N_e}\cdot\nabla_\nu\gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},\mathbf{r}',t)\right)\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)$$

$$\mathbf{F}_\nu = -\nabla_\nu E[\rho_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)] - i\sum_{\nu'}\frac{\mathscr{P}_{\nu'}}{M_{\nu'}N_e}\cdot\iint d\mathbf{r}d\mathbf{r}'\nabla_{\nu'}\gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},\mathbf{r}',t)\nabla_\nu\gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',\mathbf{r},t)$$

*Gauge condition of the XFMQC equation*

$$\mathbf{F}_\nu = \dot{\mathbf{A}}_\nu = \sum_i(\langle\dot{\psi}^i_{\underline{\underline{\mathbf{R}}}}| -i\nabla_\nu\psi^i_{\underline{\underline{\mathbf{R}}}}\rangle + \langle\psi^i_{\underline{\underline{\mathbf{R}}}}| -i\nabla_\nu\dot{\psi}^i_{\underline{\underline{\mathbf{R}}}}\rangle)$$

Now, the orthonormality is guaranteed with the electronic propagation.

$$\begin{aligned}\partial_t\langle\psi^i_{\underline{\underline{\mathbf{R}}}}(t)|\psi^j_{\underline{\underline{\mathbf{R}}}}(t)\rangle &= \iint d\mathbf{r}d\mathbf{r}'\sum_\nu\frac{\mathscr{P}_\nu}{M_\nu N_e}\cdot\nabla_\nu\gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',\mathbf{r},t)\psi^{i*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\\ &+\iint d\mathbf{r}d\mathbf{r}'\left[-\sum_\nu\frac{\mathscr{P}_\nu}{M_\nu N_e}\cdot\nabla_\nu\gamma_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},\mathbf{r}',t)\psi^{i*}_{\underline{\underline{\mathbf{R}}}}(\mathbf{r},t)\psi^j_{\underline{\underline{\mathbf{R}}}}(\mathbf{r}',t)\right]\\ &=0\end{aligned}$$

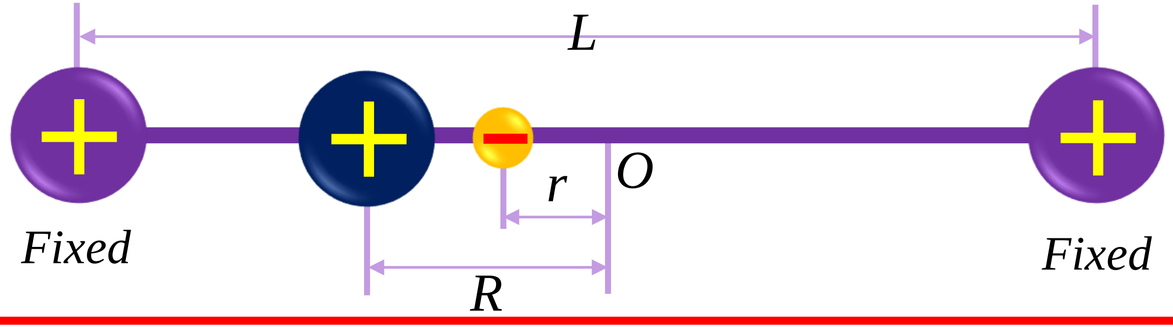
# Real-space and real-time propagation with the ENC Hamiltonian

## MQC dynamics of the Shin-Metiu model

The new ENC operator are tested with the MQC dynamics of Shin-Metiu model using the Crank-Nicolson propagator. The MQC dynamics is compared with the quantum dynamics (QD) with the numerical grid method.

***Shin-Metiu model*** [Shin, S.; Metiu, H. *JCP*, **1995**.]

$$\hat{H}(r,R) = -\frac{1}{2M}\frac{\partial^2}{\partial R^2} - \frac{1}{2}\frac{\partial^2}{\partial r^2} + \frac{1}{|\frac{L}{2}-R|} + \frac{1}{|\frac{L}{2}+R|} - \frac{\mathrm{erf}(|R-r|/R_c)}{|R-r|} - \frac{\mathrm{erf}(|r-\frac{L}{2}|/R_r)}{|r-\frac{L}{2}|} - \frac{\mathrm{erf}(|r+\frac{L}{2}|/R_r)}{|r+\frac{L}{2}|}$$



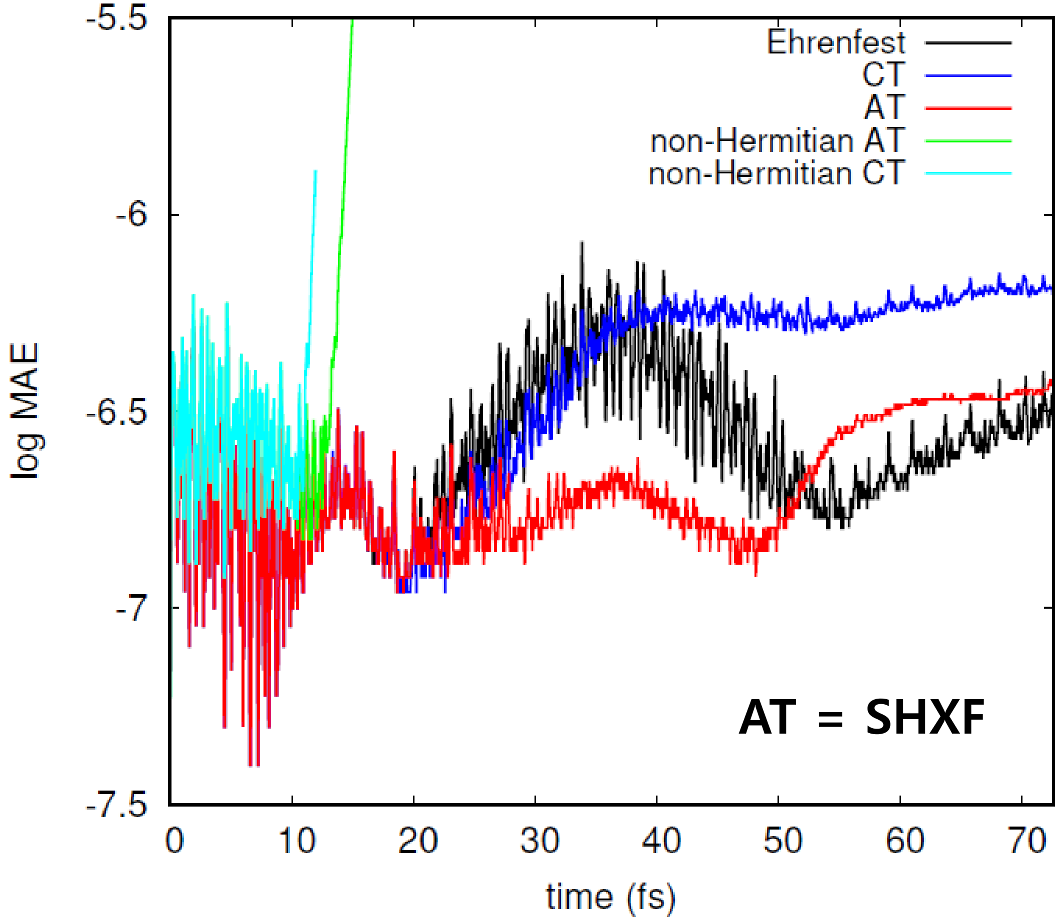

***Crank-Nicolson propagation***

$$\left(1+\frac{i\Delta t\hat{H}(\underline{\mathbf{r}},t;\underline{\underline{\mathbf{R}}})}{2}\right)\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}},t+\Delta t) = \left(1-\frac{i\Delta t\hat{H}(\underline{\mathbf{r}},t;\underline{\underline{\mathbf{R}}})}{2}\right)\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}},t)$$

# Real-space and real-time propagation with the ENC Hamiltonian

## MQC dynamics of the Shin-Metiu model

Stability of the nonadiabatic dynamics with the new Hermitian ENC operator is confirmed by monitoring the mean absolute error (MAE) of the norm from unity.




$$\frac{1}{N_{traj}}\sum_{\underline{\underline{\mathbf{R}}}}\left|1-\langle\Phi_{\underline{\underline{\mathbf{R}}}}(t)|\Phi_{\underline{\underline{\mathbf{R}}}}(t)\rangle_{\underline{\underline{\mathbf{r}}}}\right|$$

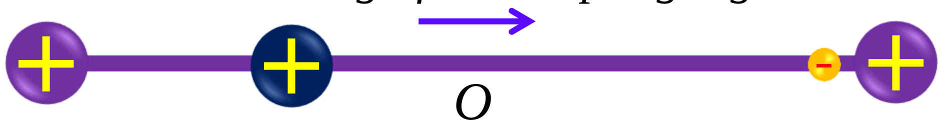
*Non-Hermitian propagations show divergent MAEs, and eventually halt due to their instability.*

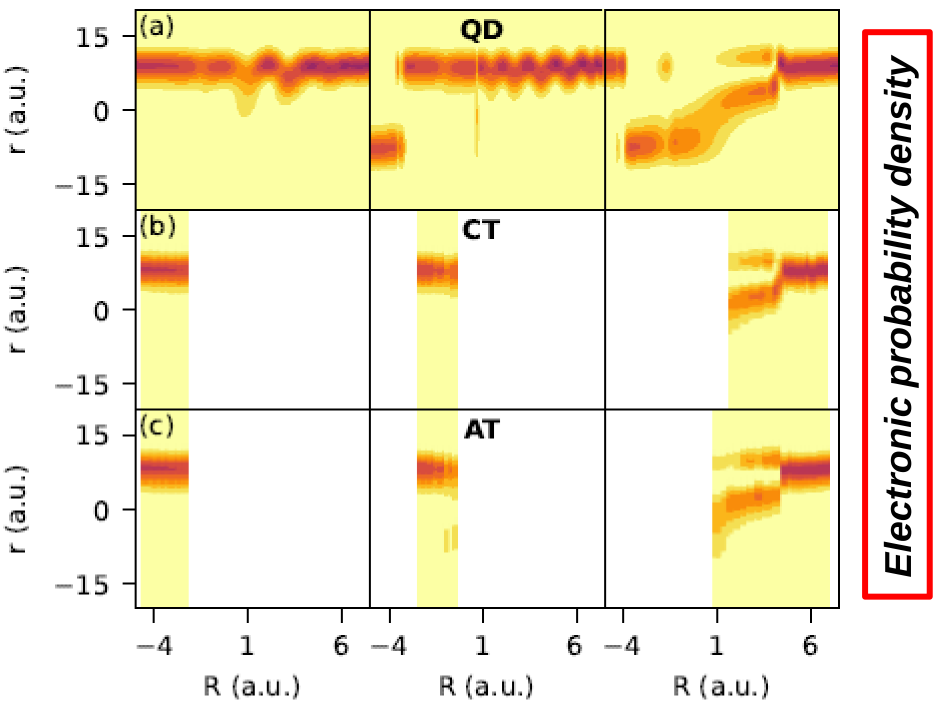
# Real-space and real-time propagation with the ENC Hamiltonian

## MQC dynamics of the Shin-Metiu model

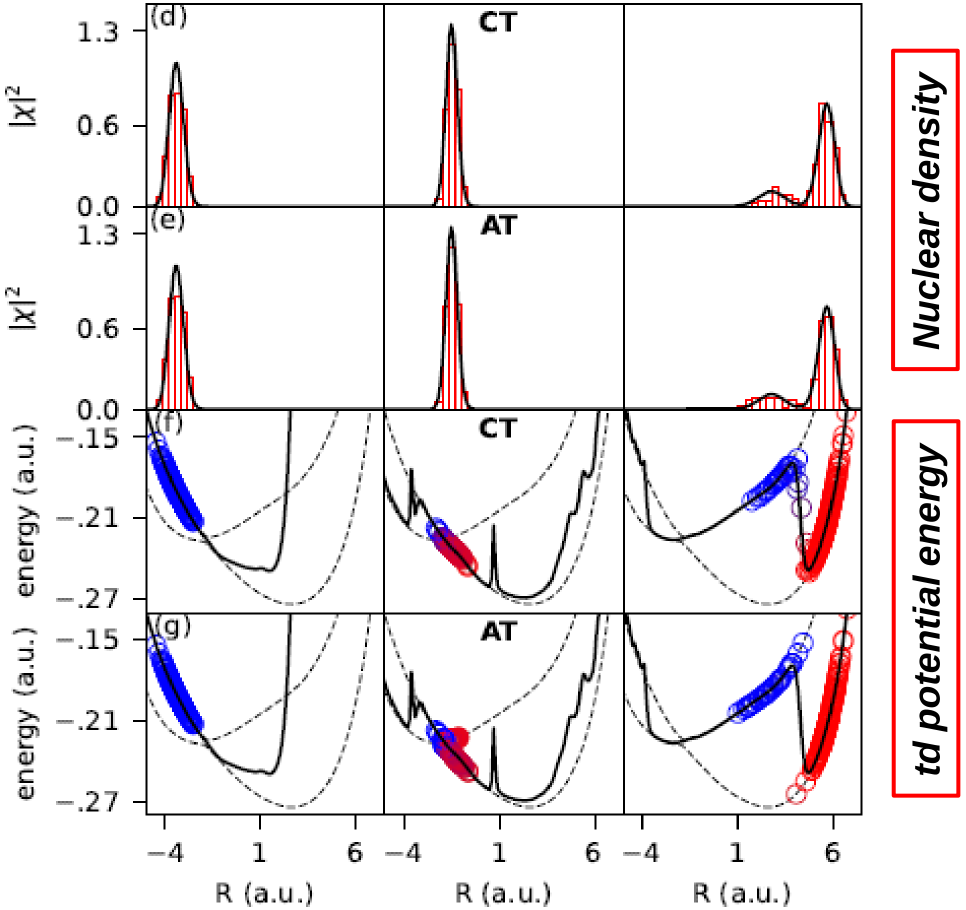
- Overall, CT/AT(SHXF) dynamics well reproduce the QD profile in the classically sampled region.
- In CT, the force behaves continuously, giving the potential "step" present in QD. While, in AT, this step is not shown due to its simplification of the force.

*First crossing of the coupling region*




$|\Phi_R(r,t)|^2$

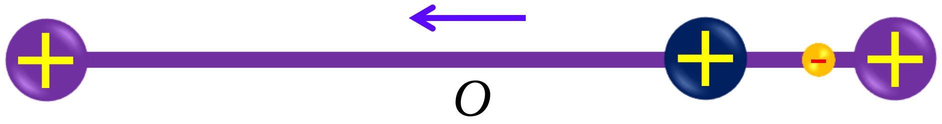



$\langle \Phi_R(t)|\hat{H}|\Phi_R(t)\rangle_r$

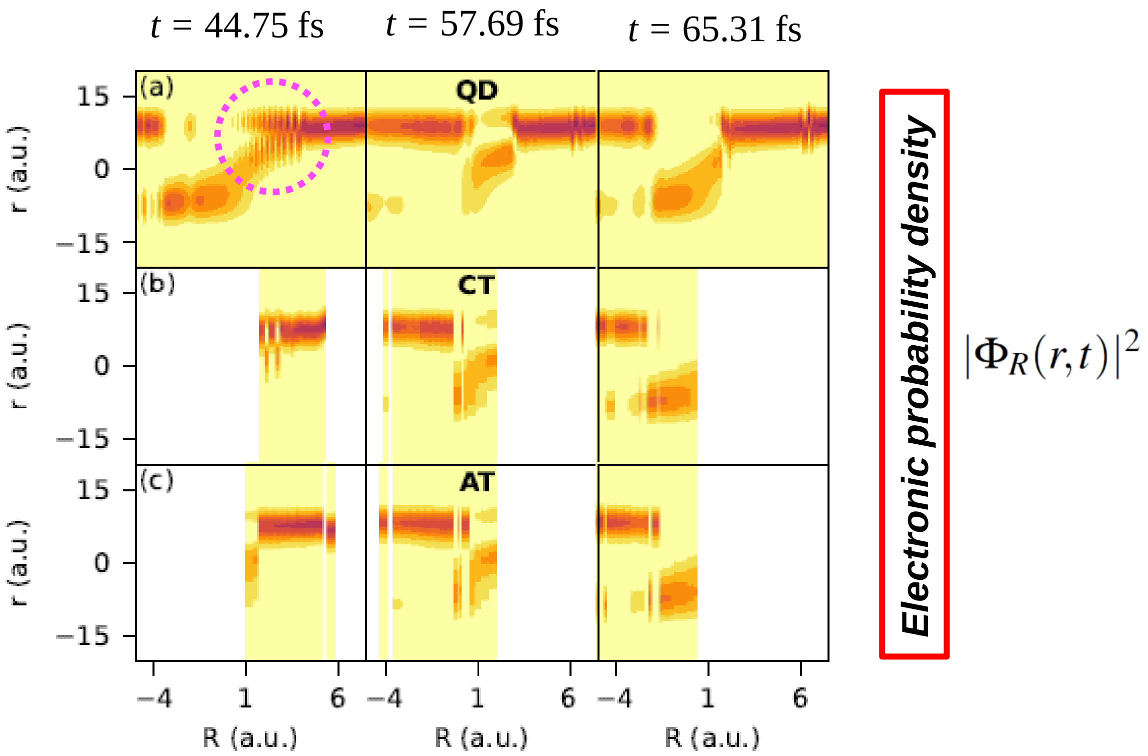
# Real-space and real-time propagation with the ENC Hamiltonian

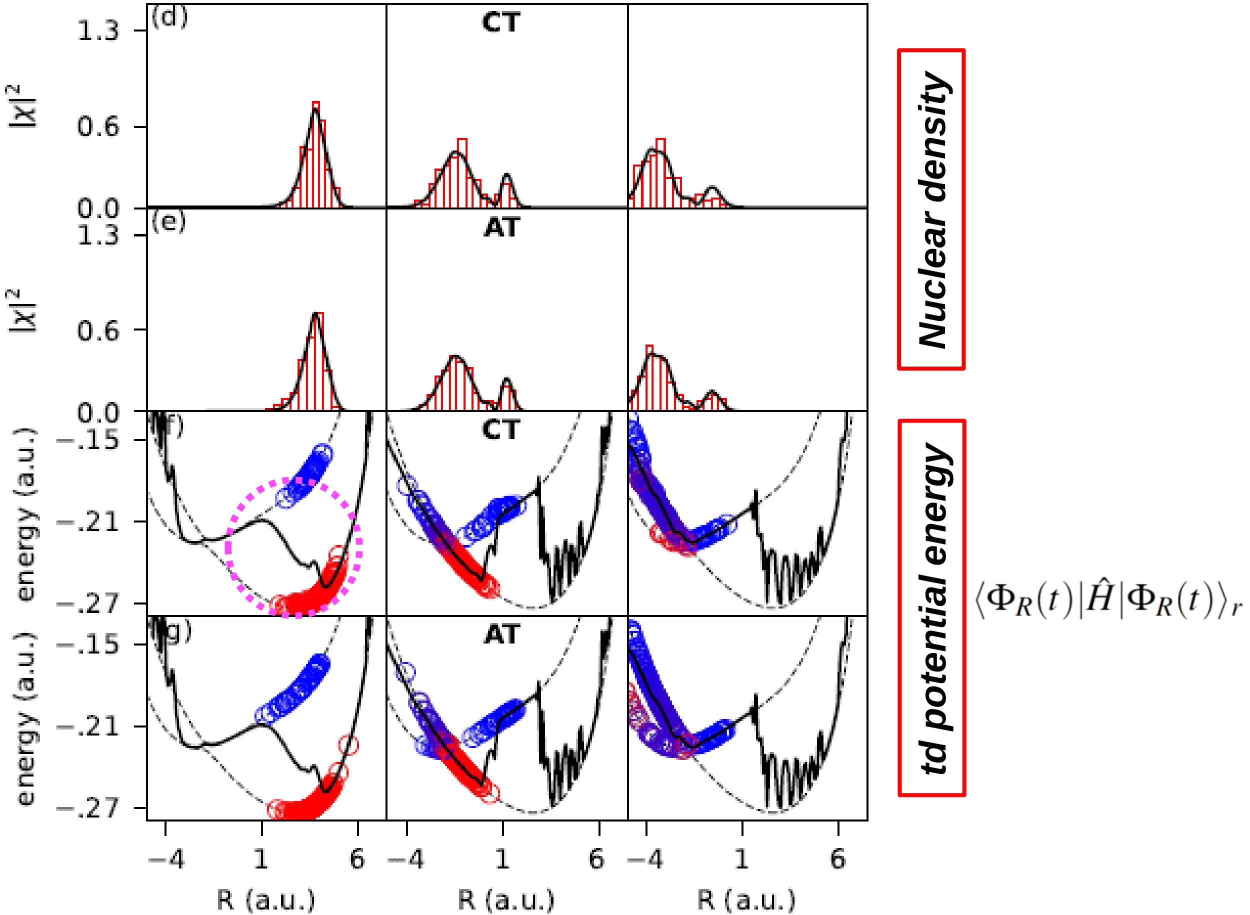
## MQC dynamics of the Shin-Metiu model

*Second crossing of the coupling region*




- The MQC dynamics cannot describe the quantum inference, since the wave nature is lost from the trajectory-based approximation.
- The td potential energy is no longer reproduced, and nuclear positions on each adiabatic state behave independently.

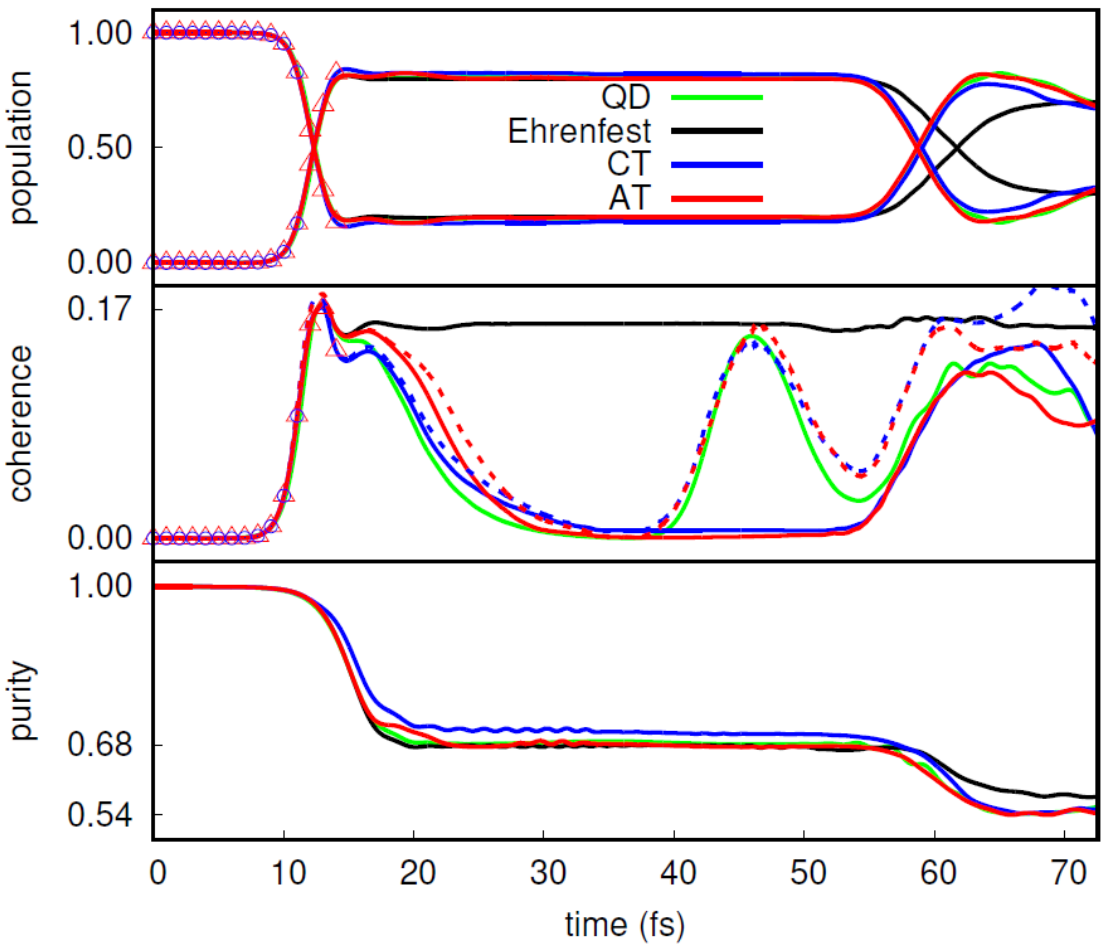


# Real-space and real-time propagation with the ENC Hamiltonian

## MQC dynamics of the Shin-Metiu model

| | |
|---|---|
| ***Adiabatic population*** | $\rho_{ll}(t) = \langle \phi^l_{\underline{\mathbf{R}}} \vert \Phi_{\underline{\mathbf{R}}} \rangle \langle \Phi_{\underline{\mathbf{R}}} \vert \phi^l_{\underline{\mathbf{R}}} \rangle = \vert C_l \vert^2$ |
| ***Coherence (solid)*** | $\vert\rho_{lk}\vert^2(t) = \vert C_l(t)\vert^2 \vert C_k(t)\vert^2$ |
| ***Coherence (dashed)*** | $\langle w_{lk}(t)\rangle = \sum_R w_l^R(t) w_k^R(t)$ |
| Gaussian-smeared density | $w_l^R(t) = \sum_{R'} \rho_{ll}^{R'}(t) g^{RR'}(t) / \sum_{R' \in \mathscr{D}(R)} g^{RR'}(t)$ |
| | $g^{RR'}(t) = \exp((R(t) - R'(t))^2/\sigma^2)$ |
| ***Purity*** | $P(t) = \int d\underline{\mathbf{r}} d\underline{\mathbf{r}}' \bar{\Gamma}(\underline{\mathbf{r}}, \underline{\mathbf{r}}', t) \bar{\Gamma}(\underline{\mathbf{r}}', \underline{\mathbf{r}}, t)$ |
| | $\bar{\Gamma}(\underline{\mathbf{r}}, \underline{\mathbf{r}}', t) = \int d\underline{\mathbf{R}} \vert\chi(\underline{\mathbf{R}}, t)\vert^2 \Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}, t) \Phi^*_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}', t)$ |



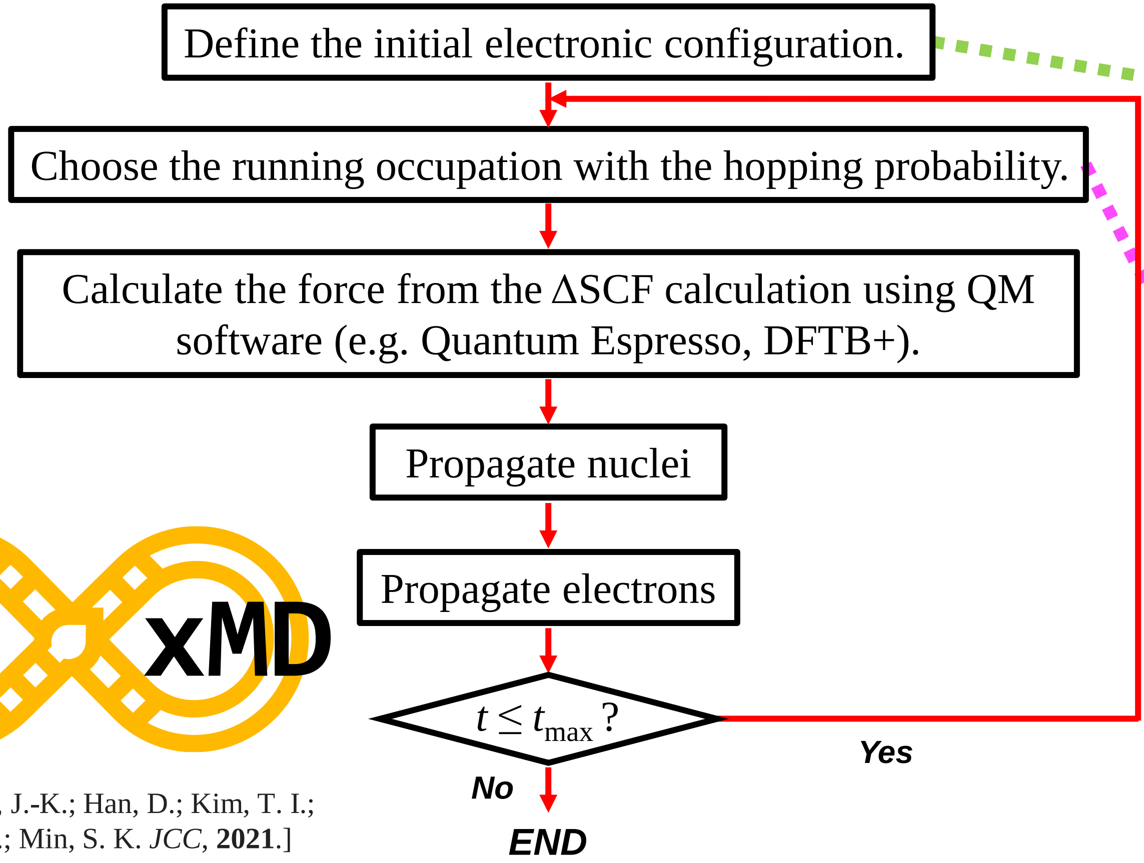

- The population of all methods shows consistency except for the Ehrenfest dynamics during the 2nd crossing.
- The Ehrenfest dynamics fails to capture the decoherence completely.
- The MQC dynamics cannot capture the 2nd coherence peak from the quantum interference. However, its revised coherence indicator considering neighboring trajectories can explain it.
- Purities indicate the state mixing correctly when the population exchange occurs. However, they behave similarly in all methods, so it is insufficient to be a measure of quality of a nonadiabatic dynamics.

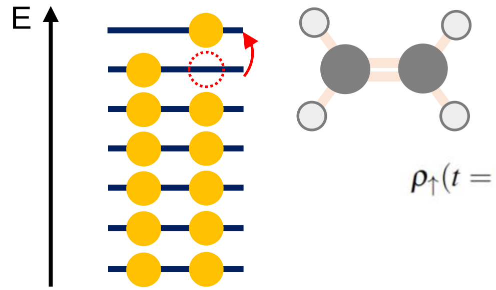
# Practical implementation of the XF-TDKS equation

## Orbital-based surface hopping through exact factorization (OSHXF)

Electronic equation $\dot{\rho}^{\mathbf{\underline{\underline{R}}}}_{lk} = -i(\varepsilon_l - \varepsilon_k)\rho^{\mathbf{\underline{\underline{R}}}}_{lk} - \sum_m (\tau^{\mathbf{\underline{\underline{R}}}}_{lm}\rho^{\mathbf{\underline{\underline{R}}}}_{mk} - \rho^{\mathbf{\underline{\underline{R}}}}_{lm}\tau^{\mathbf{\underline{\underline{R}}}}_{mk}) + \sum_\nu \frac{i\mathscr{P}_\nu}{M_\nu N_e} \cdot \sum_m (\mathbf{F}^\nu_{ml} + \mathbf{F}^\nu_{mk})\rho^{\mathbf{\underline{\underline{R}}}}_{lm}\rho^{\mathbf{\underline{\underline{R}}}}_{mk}$ ⬅ XF-TDKS

Nuclear equation $\mathbf{F}_\nu = -\nabla_\nu E_r$ $r$ : running occupation




$r$= (2, 2, 2, 2, 2, 1, 1)

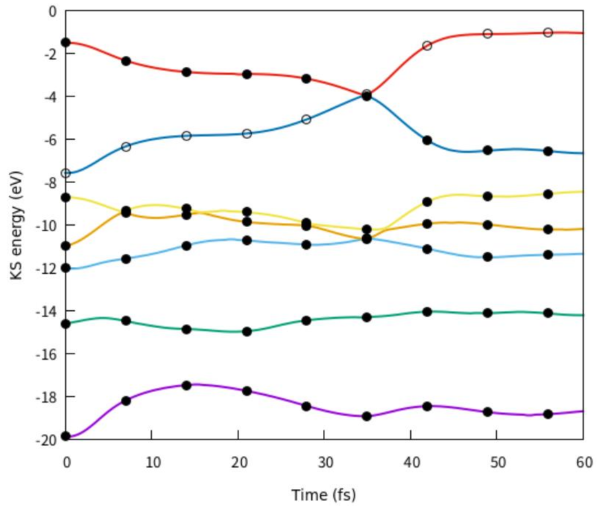
$$\rho_\uparrow(t=0) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

***Hopping probability***

$$P_{l \to k} = \frac{2\Re\left(\rho^{\mathbf{\underline{\underline{R}}}}_{lk}\tau^{\mathbf{\underline{\underline{R}}}}_{lk}\right)}{\rho^{\mathbf{\underline{\underline{R}}}}_{ll}}\Delta t$$

*From orbital l to k*

● Occupied ○ Vacant



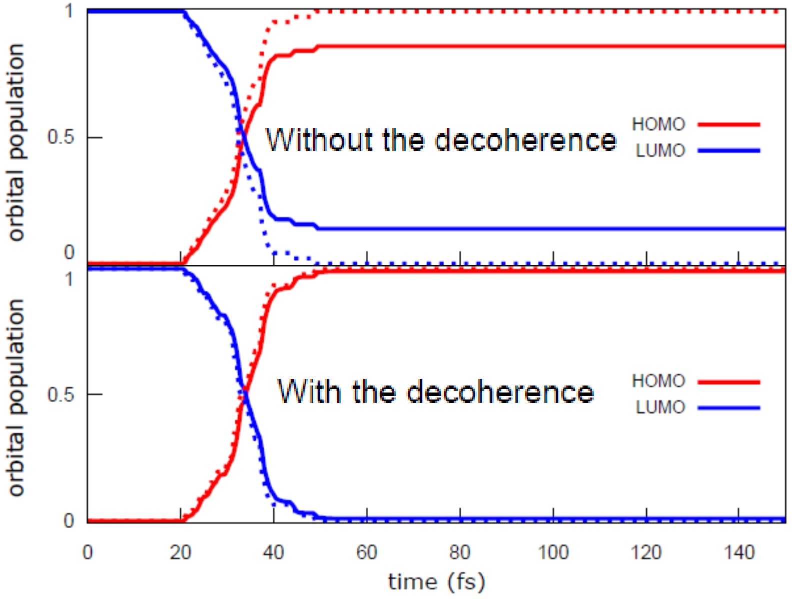

UNI xMD

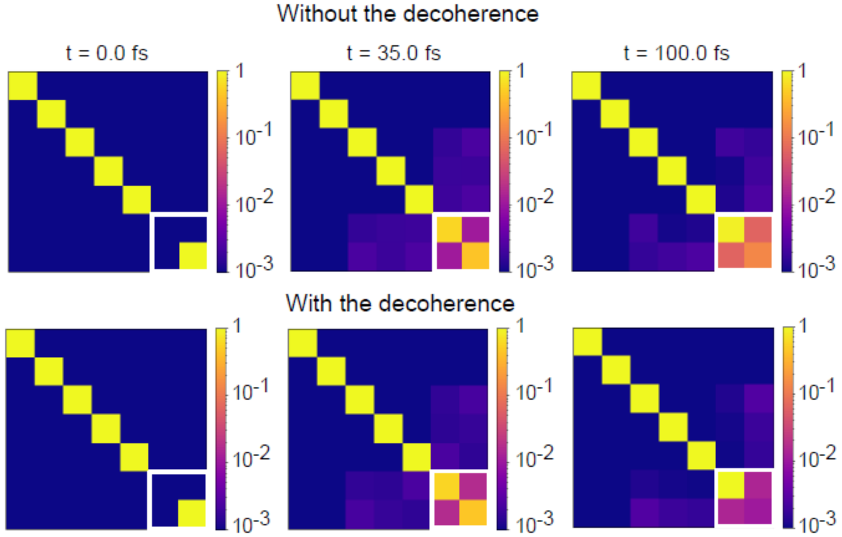
[Lee, I. S.; Ha, J.-K.; Han, D.; Kim, T. I.; Moon, S. W.; Min, S. K. *JCC*, **2021**.]

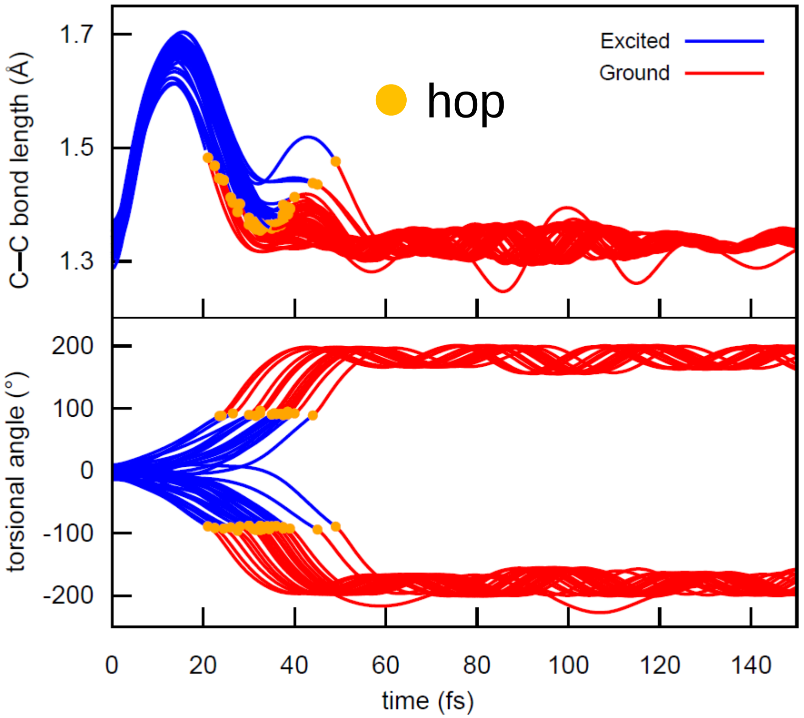
# Practical implementation of the XF-TDKS equation

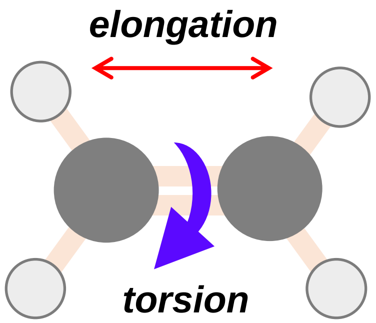
## Orbital-based surface hopping through exact factorization (OSHXF)

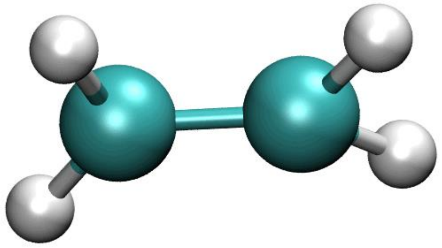
- Excited-state dynamics of an ethylene molecule in vacuum are conducted while the initial electronic configuration is the HOMO → LUMO configuration.
- The elongation and torsion occur simultaneously. All trajectories deactivate to the ground state through the twisted $CH_2$ structures of the conical intersection.
- Without the decoherence correction, the density matrix cannot recover to that of the ground-state configuration.



# *Conclusion*

- **The Hermitian-type electron-nuclear correlation operator from XF is derived, giving equivalent time evolution.**

- **The decoherence correction for the TDKS equation is deduced based on XF.**

- **Combining with SHXF and the XF-TDKS equation, the OSHXF method has been developed.**

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