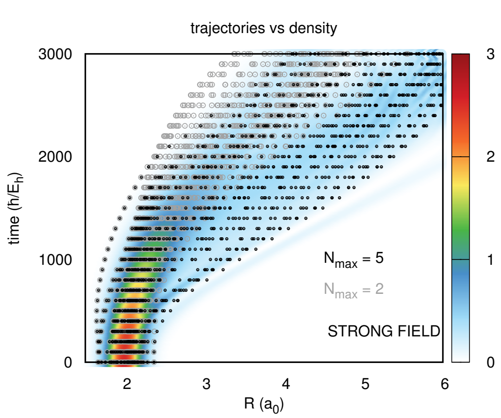
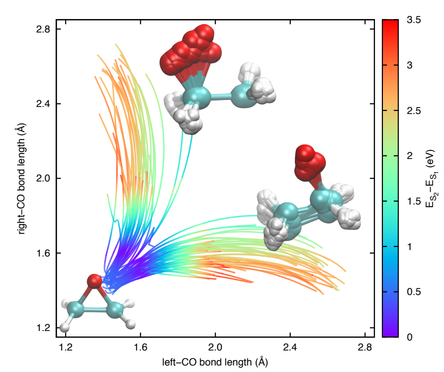
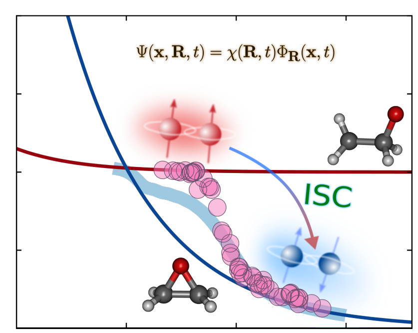
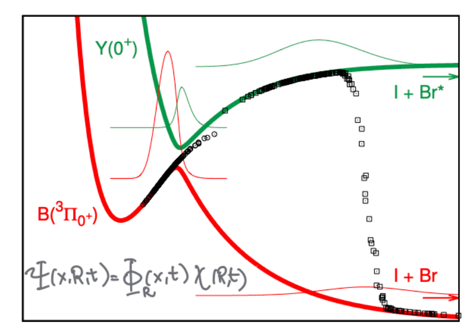
Theory and simulation of ultrafast processes in molecules with the exact factorization









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VISTA webinar — April 27, 2022

Overview

Preparation of the initial state

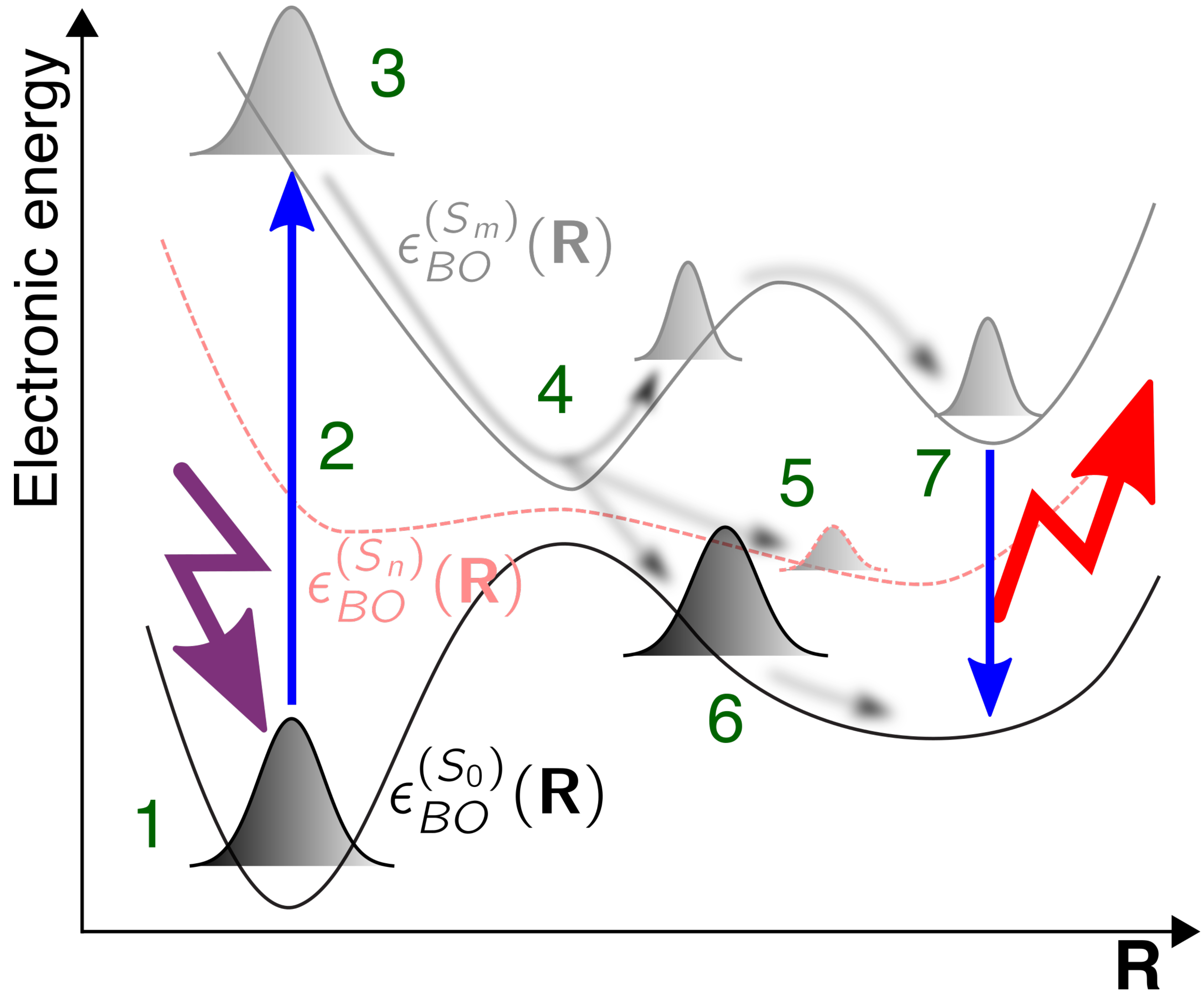
Excitation by photo-absorption

Creation of an excited nuclear wavepacket

Non-radiative relaxation via internal conversion or intersystem crossing

Formation of photoproducts

Radiative relaxation via fluorescence or phosphorescence



Courtesy of Basile Curchod

Summary

- An introduction on nonadiabatic dynamics with trajectories
- Exact factorization of the electron-nuclear wavefunction and its classical limit
- The concept of classical force from the exact factorization
- Some studies on photo-isomerization, intersystem crossing, Floquet-driven dynamics

About nonadiabatic dynamics

$$i\hbar\partial_t\Psi(r,R,t) = \left(\hat{T}_n + \hat{H}_{el}\right)\Psi(r,R,t)$$

resolution strategies based on representing $\Psi(r,R,t)$ as:

$$\sum_k \chi_k(R,t)\varphi_k(r;R) = \mathrm{BH}$$

DD-vMCG, AIMS, AIMC, TSH

$$\chi(R,t)\Phi(r,t;R) = \mathrm{EF}$$

CT-MQC(/TSH), SHXF, EH

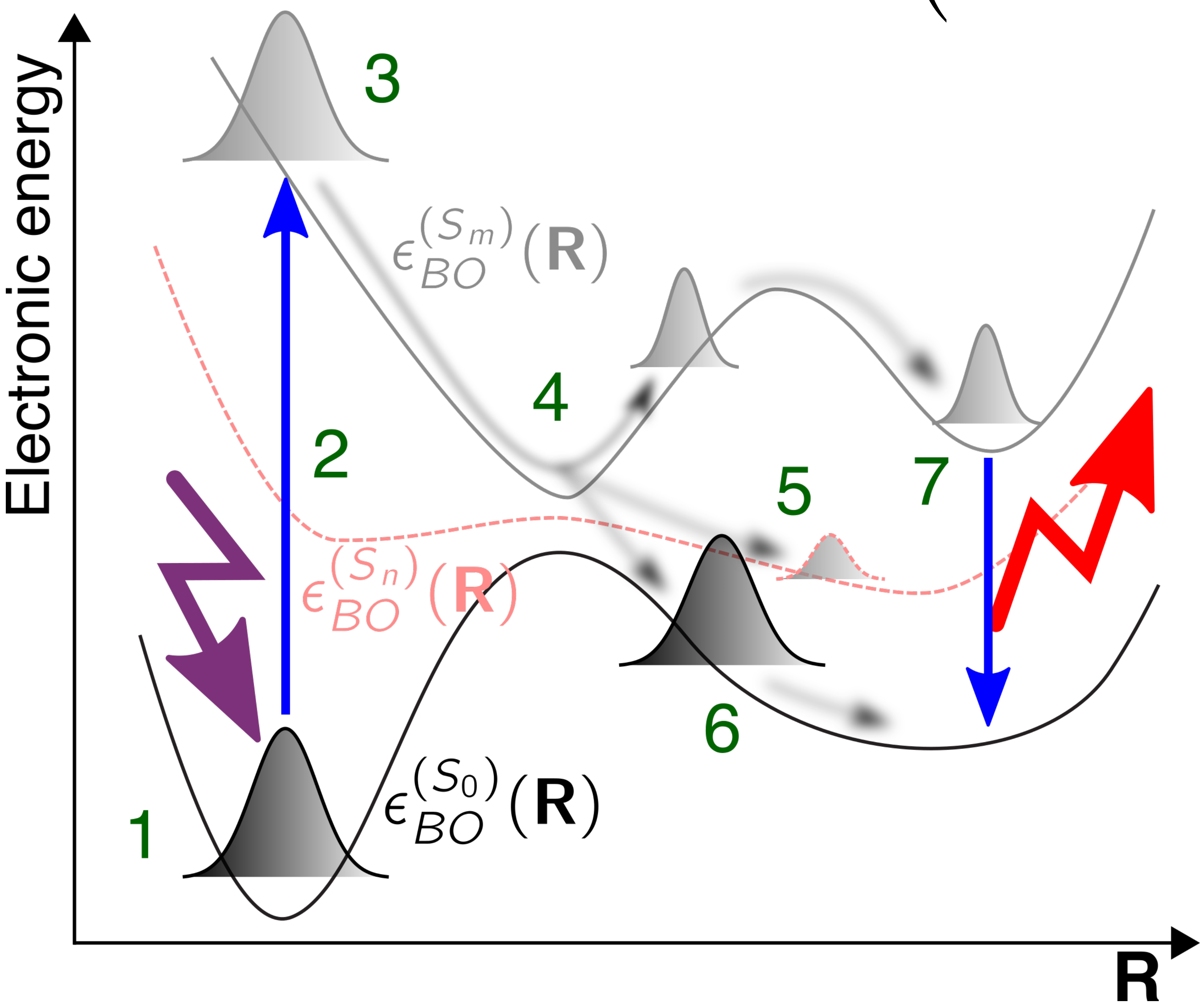
and if we only keep one term in the Born-Huang expansion or if we neglect the time-dependence in the electronic wavefunction of the exact factorization, we recover the Born-Oppenheimer limit

$$\chi_{BO}(R,t)\varphi_{BO}(r;R) = \mathrm{BO}$$

Abedi, Maitra, Gross, *Phys. Rev. Lett.* (2010); Agostini, Curchod, *WIREs Overview* (2019); Crespo-Otero, Barbatti, *Chem. Rev.* (2018).

About nonadiabatic dynamics with trajectories

$$i\hbar\partial_t\Psi(r,R,t) = \left(\hat{T}_n + \hat{H}_{el}\right)\Psi(r,R,t)$$



$\hat{H}_{el}(\mathbf{r},\mathbf{R})$ encodes the **electronic structure problem**
[energies, gradients, nonadiabatic coupling, spin-orbit coupling, transition dipole moments]

$\hat{T}_n(\mathbf{R}) + \hat{H}_{el}(\mathbf{r},\mathbf{R})$ generates the **coupled electron-nuclear dynamics**
[quantum trajectories, semiclassical dynamics, trajectory-basis functions, independent or coupled classical trajectories]

Exact factorization of the molecular wavefunction

$$i\hbar\partial_t \underbrace{\chi(R,t)\Phi(r,t;R)}_{\text{EF}} = \left(\hat{T}_n + \hat{H}_{el}\right)\underbrace{\chi(R,t)\Phi(r,t;R)}_{\text{EF}}$$

$$i\hbar\partial_t\Phi(r,t;R) = \left[\hat{H}_{el} + \hat{U}_{en}[\Phi,\chi] - \epsilon(R,t)\right]\Phi(r,t;R)$$

$$i\hbar\partial_t\chi(R,t) = \left[\frac{[-i\hbar\nabla_R + A(R,t)]^2}{2M} + \epsilon(R,t)\right]\chi(R,t)$$

expansion in the adiabatic electronic basis with coefficients $C_k(R_\alpha(t),t)$

classical limit & trajectory-based description $R_\alpha(t)$ with forces $F_\alpha(t)$

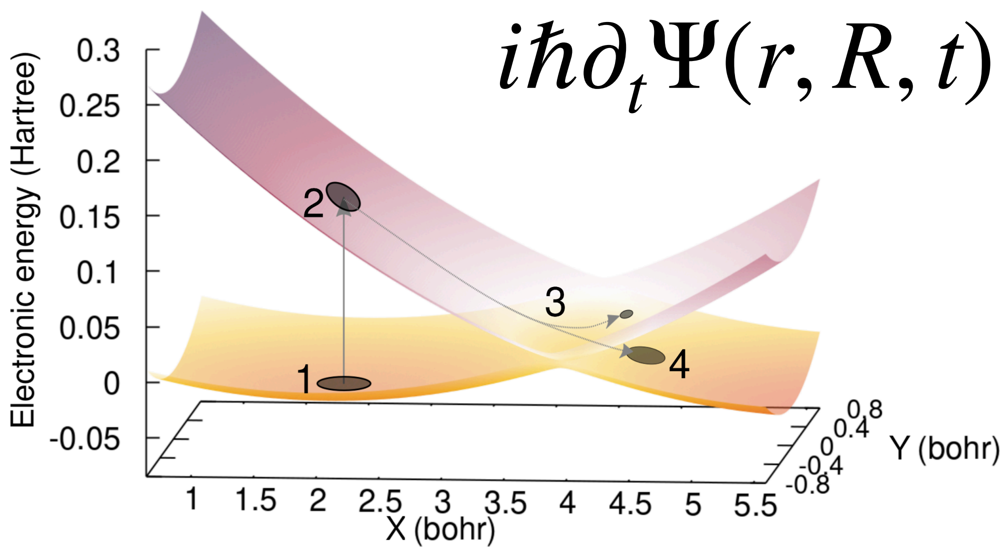
$$\dot{C}_k\big(R_\alpha(t),t\big) = \dot{C}_k^{\mathrm{mf}}\big(R_\alpha(t),t\big) + \dot{C}_k^{\mathrm{ct}}\big(R_\alpha(t),t;\underline{R}(t)\big)$$

$$F_\alpha\big(t\big) = F_\alpha^{\mathrm{mf}}\big(t\big) + F_\alpha^{\mathrm{ct}}\big(t;\underline{R}(t)\big)$$

CT-MQC

Abedi, Maitra, Gross, *Phys. Rev. Lett.* (2010); Min, Agostini, Gross, *Phys. Rev. Lett.* (2015).

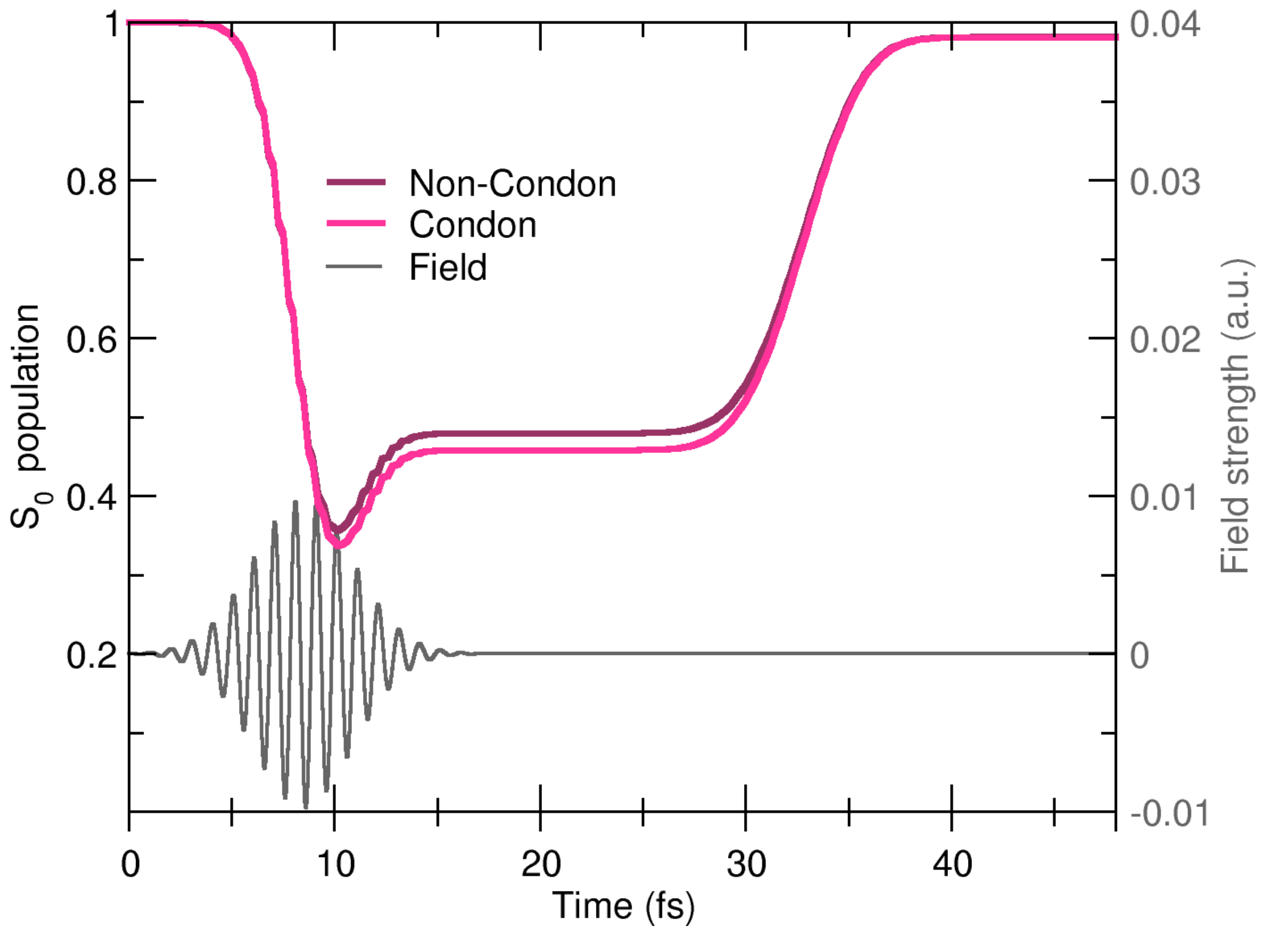
The classical force in the exact factorization

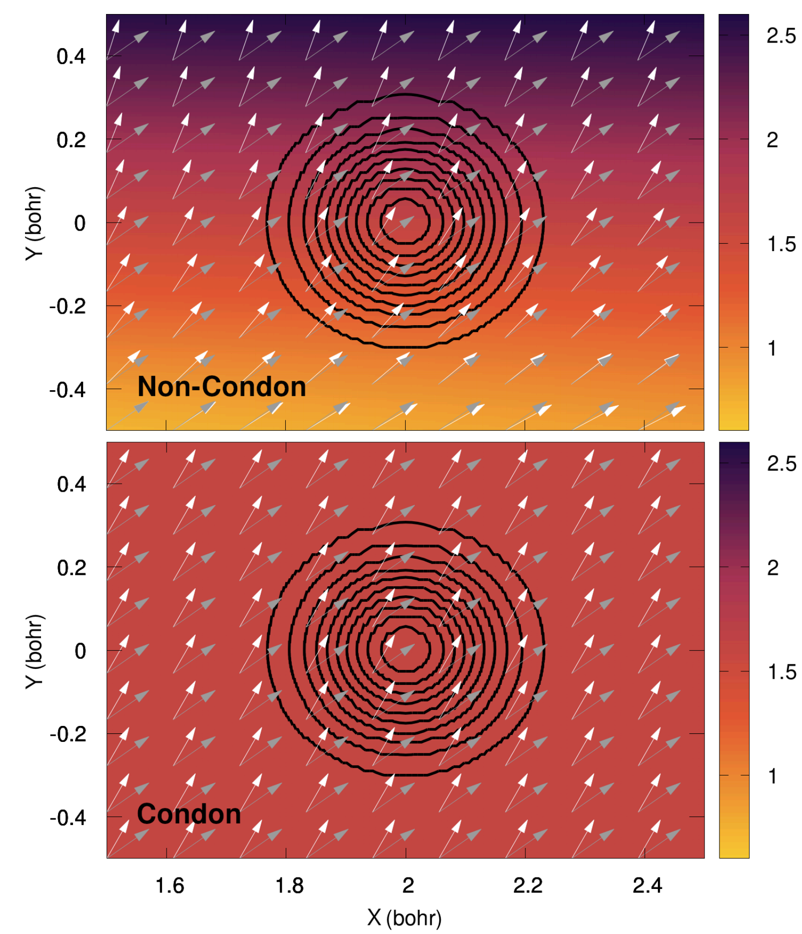


$$i\hbar\partial_t\Psi(r,R,t) = \left(\hat{T}_n + \hat{H}_{el} + \hat{V}(t)\right)\Psi(r,R,t)$$

$$\hat{V}(t) = -\hat{\mu}\cdot E(t)$$

- $E_0 = 0.065\ E_h/(ea_0);\ \Omega = 0.15\ E_h/\hbar$
- laser pulse duration $\sim 15\ fs$
- linear approximation for $\mu(R)$

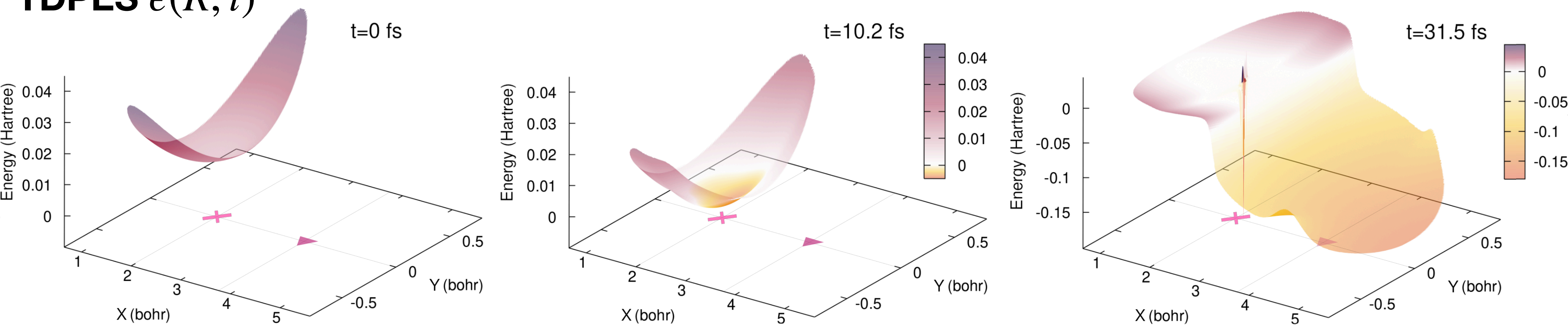


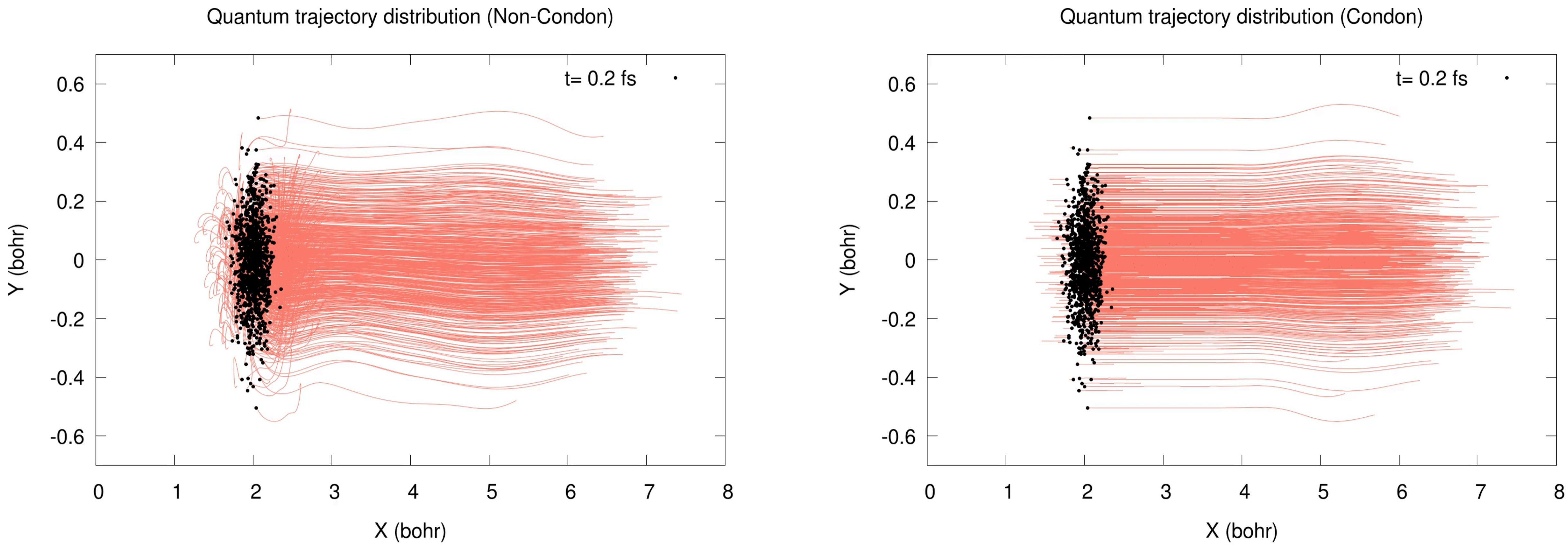


Ibele, Curchod, Agostini, *J. Phys. Chem. A* (2022).

The classical force in the exact factorization

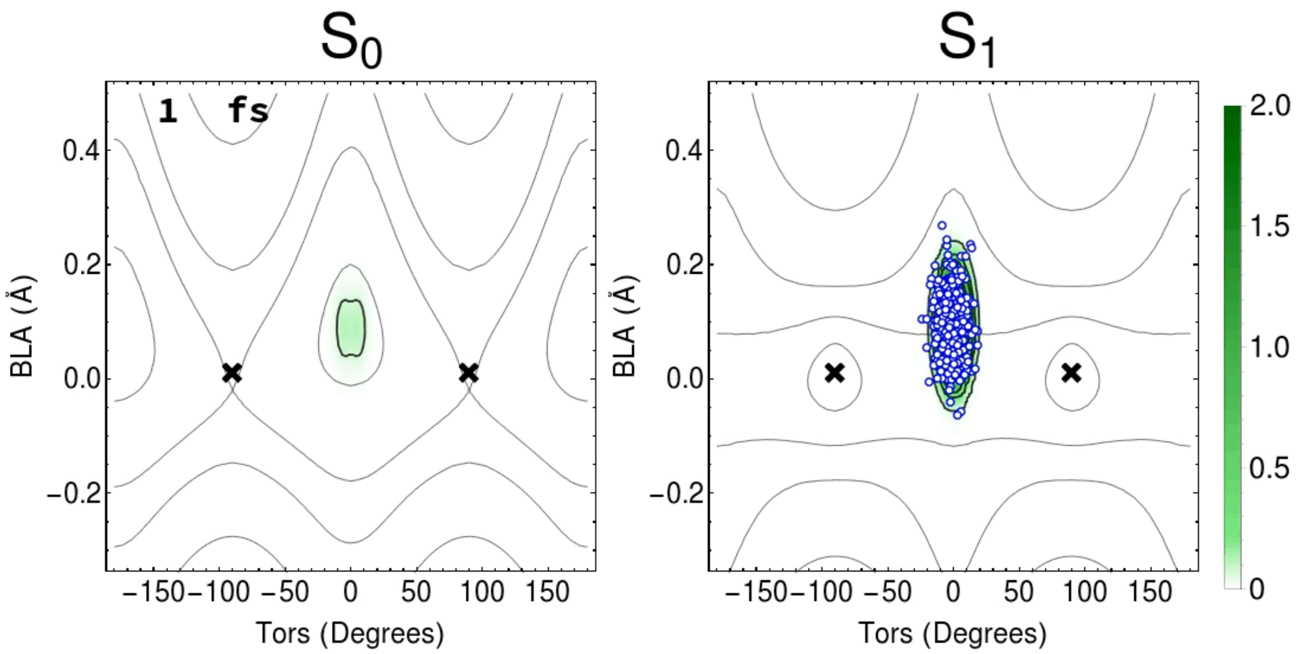
TDPES $\epsilon(R,t)$

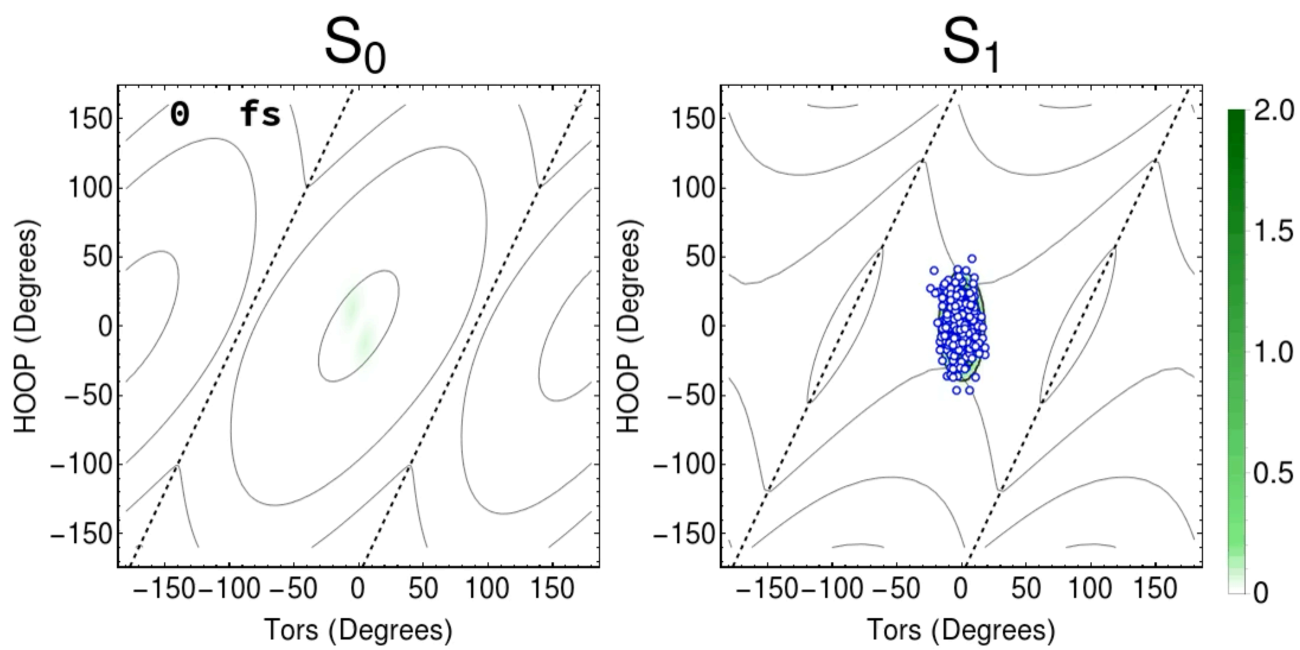




Ibele, Curchod, Agostini, *J. Phys. Chem. A* (2022).

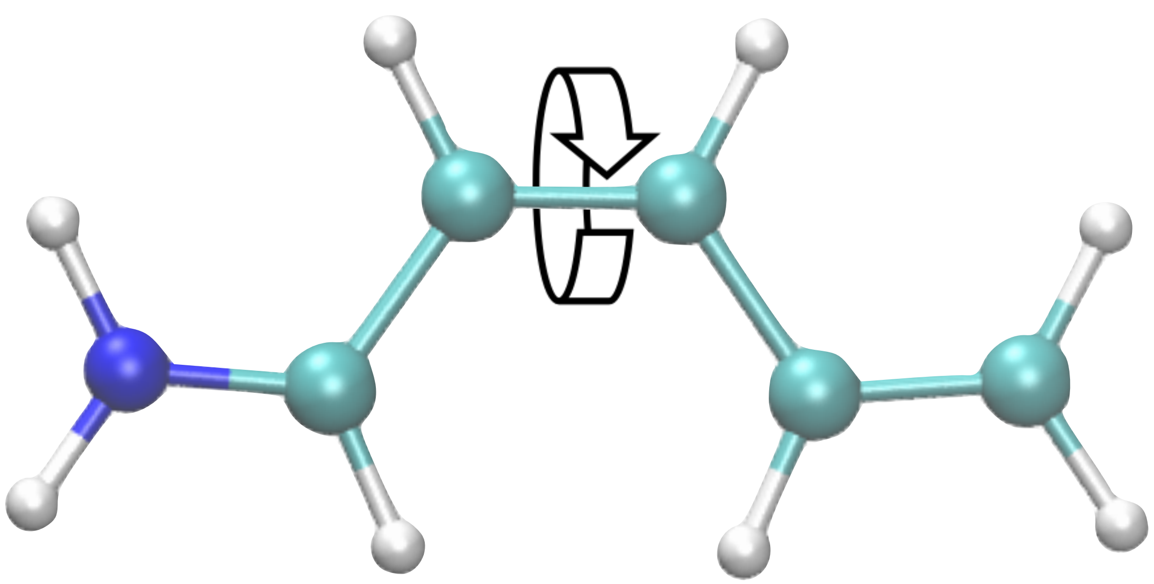
Photo-isomerization of a retinal chromophore model

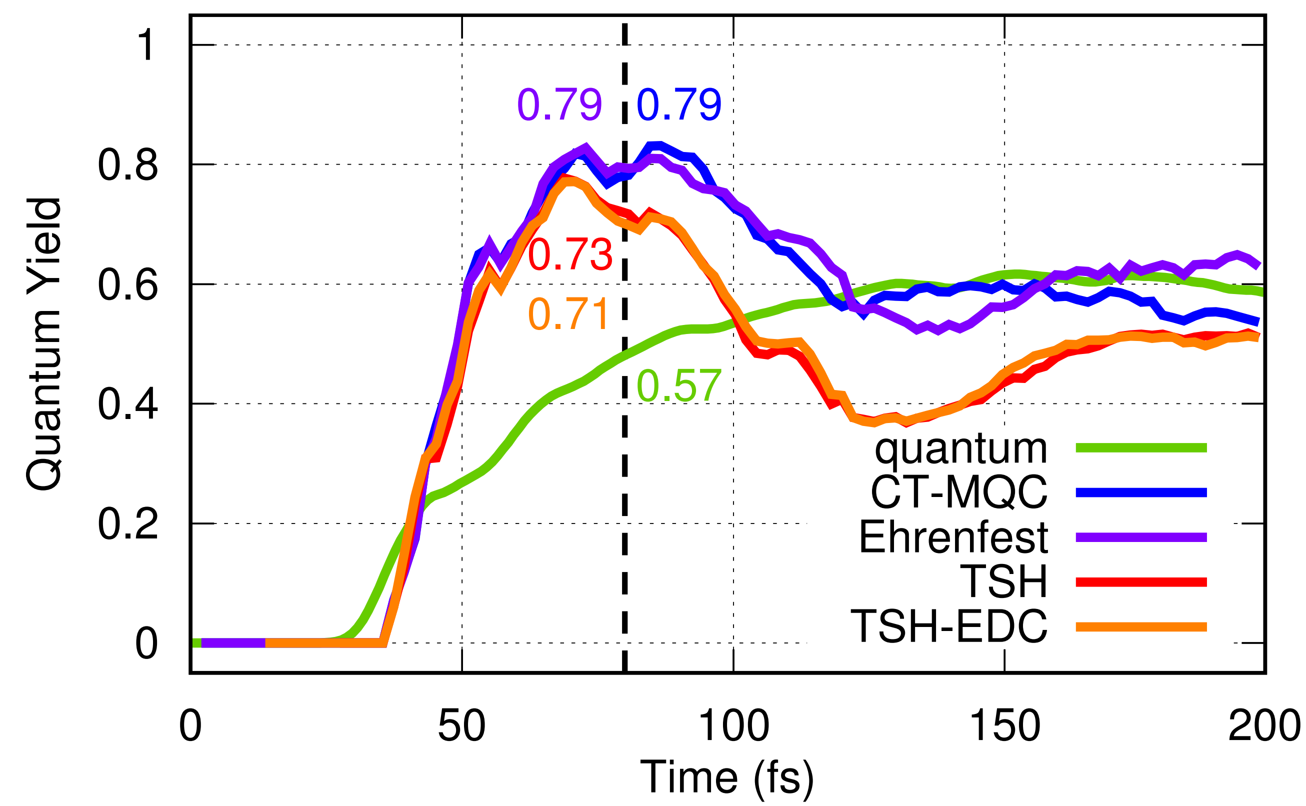




CT-MQC

rotation around the CC double bond in PSB3





Marsili, Olivucci, Lauvergnat, Agostini, *J. Chem. Theory Comput.* (2020).

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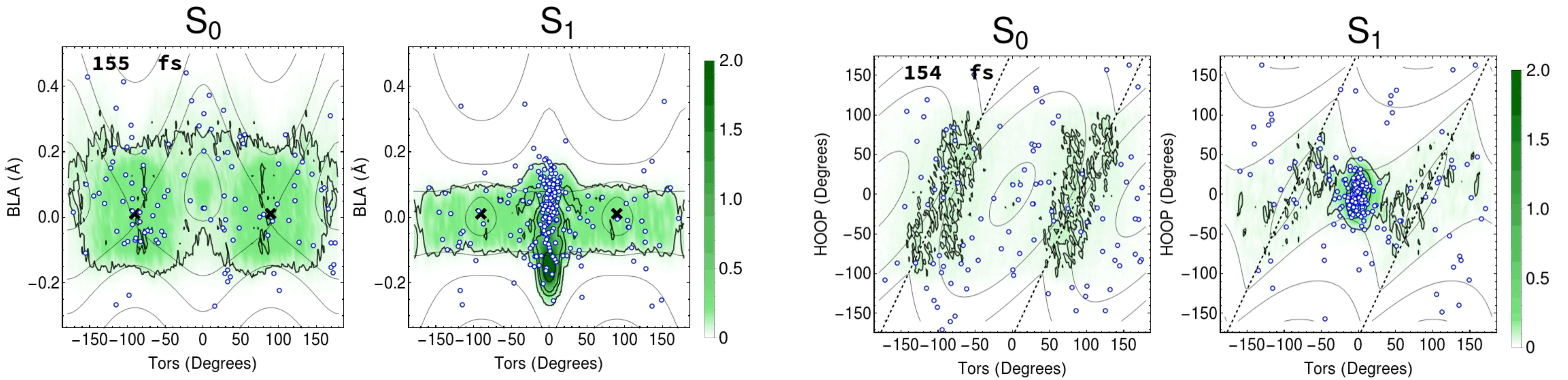
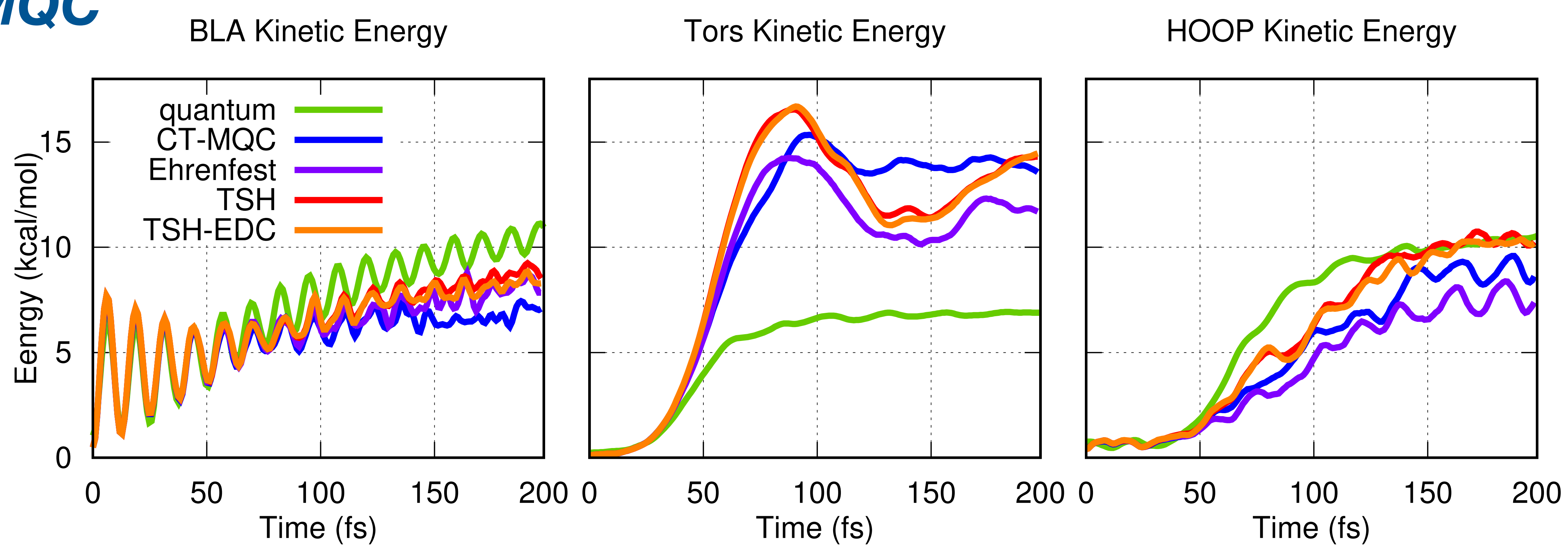


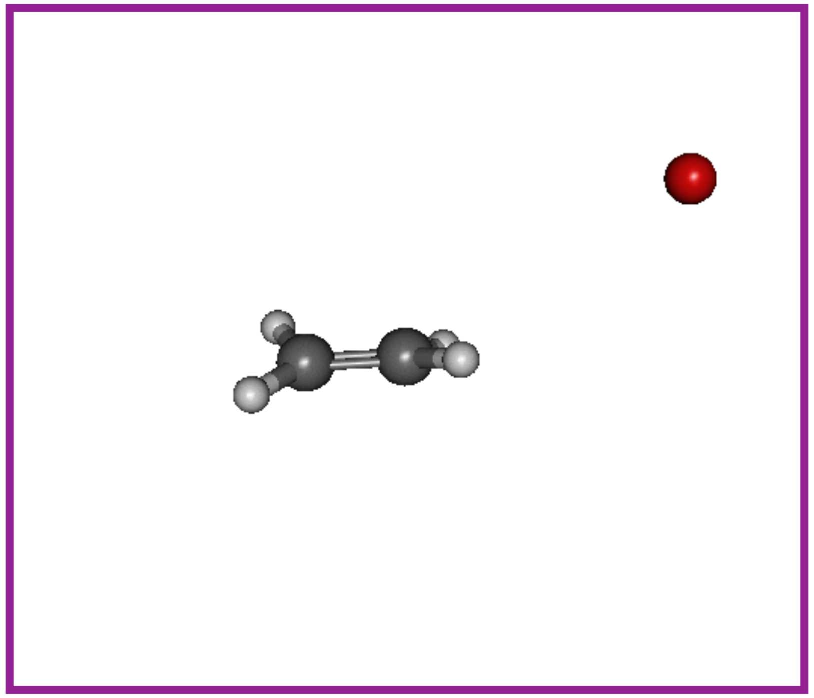
CT-MQC



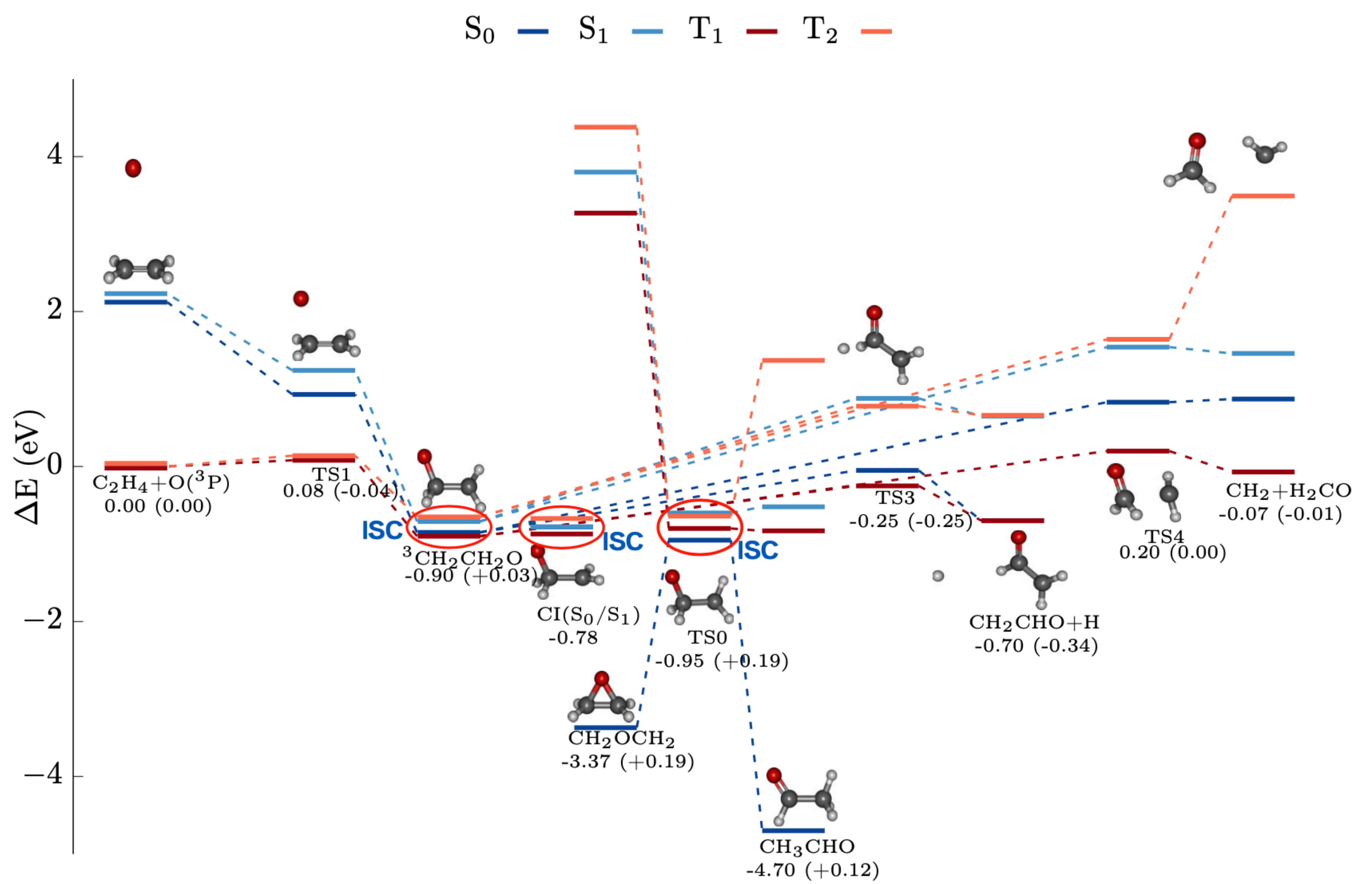
Marsili, Olivucci, Lauvergnat, Agostini, *J. Chem. Theory Comput.* (2020); Pieroni, Marsili, Lauvergnat, Agostini, *J. Chem. Phys.* (2021).

Intersystem crossing in a collision reaction

$$i\hbar\partial_t\chi(R,t)\Phi(x,t;R) = \left(\hat{T}_n + \hat{H}_{el} + \hat{H}_{SOC}\right)\chi(R,t)\Phi(x,t;R)$$



calculations with SHARC based on CASSCF with OpenMolcas



Talotta, Morisset, Rougeau, Lauvergnat, Agostini, *J. Phys. Chem A* (2021).

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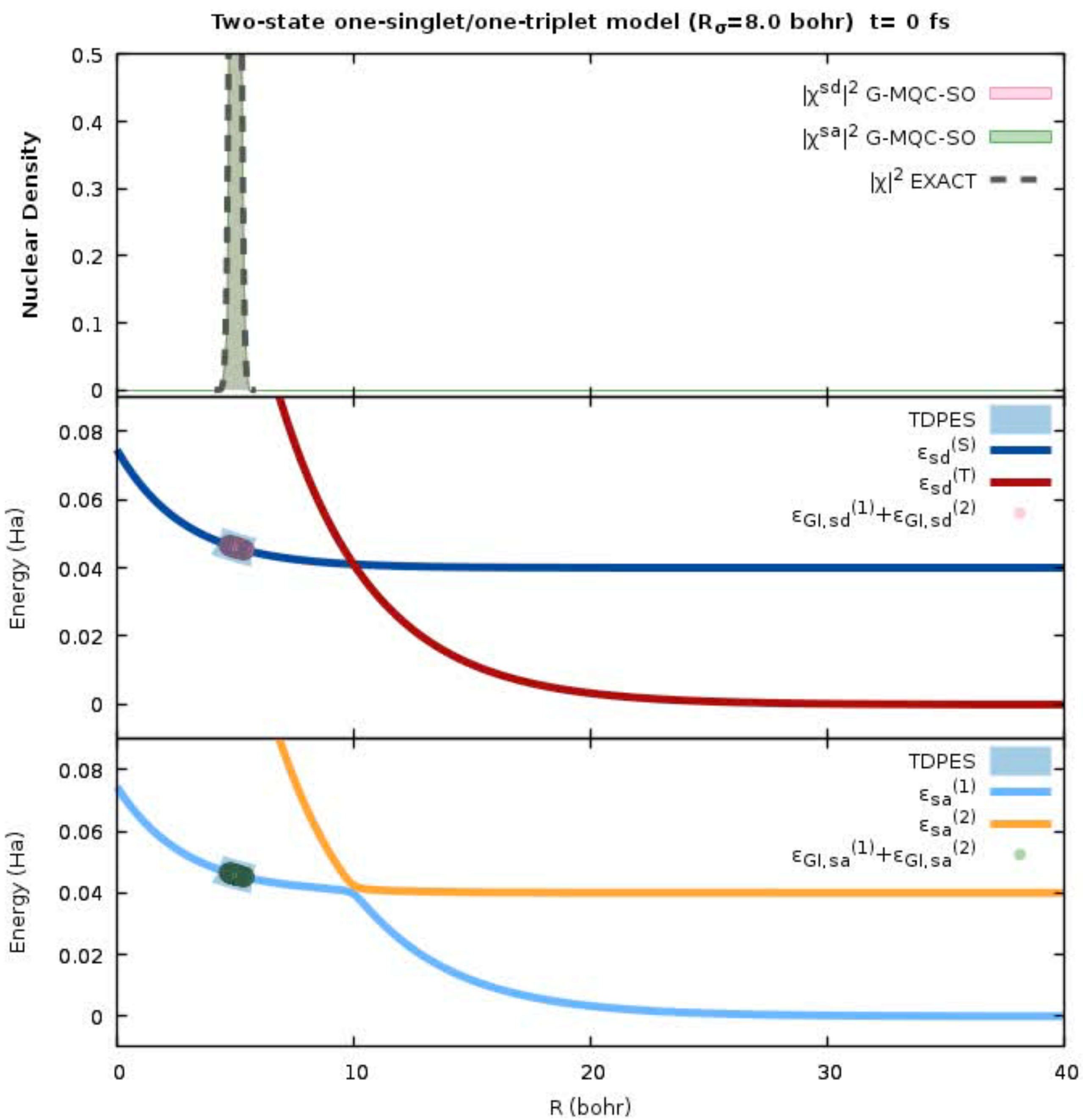
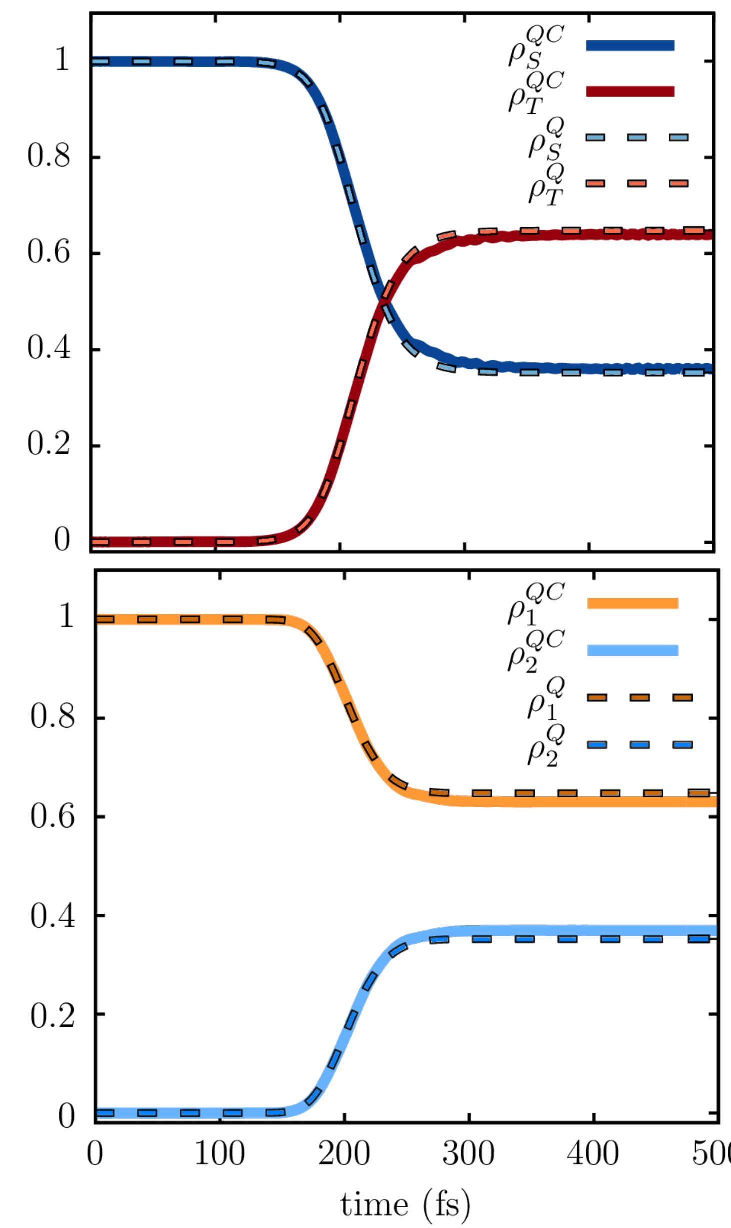




spin-diabatic basis (eigenstates of $\hat{H}_{el}$)

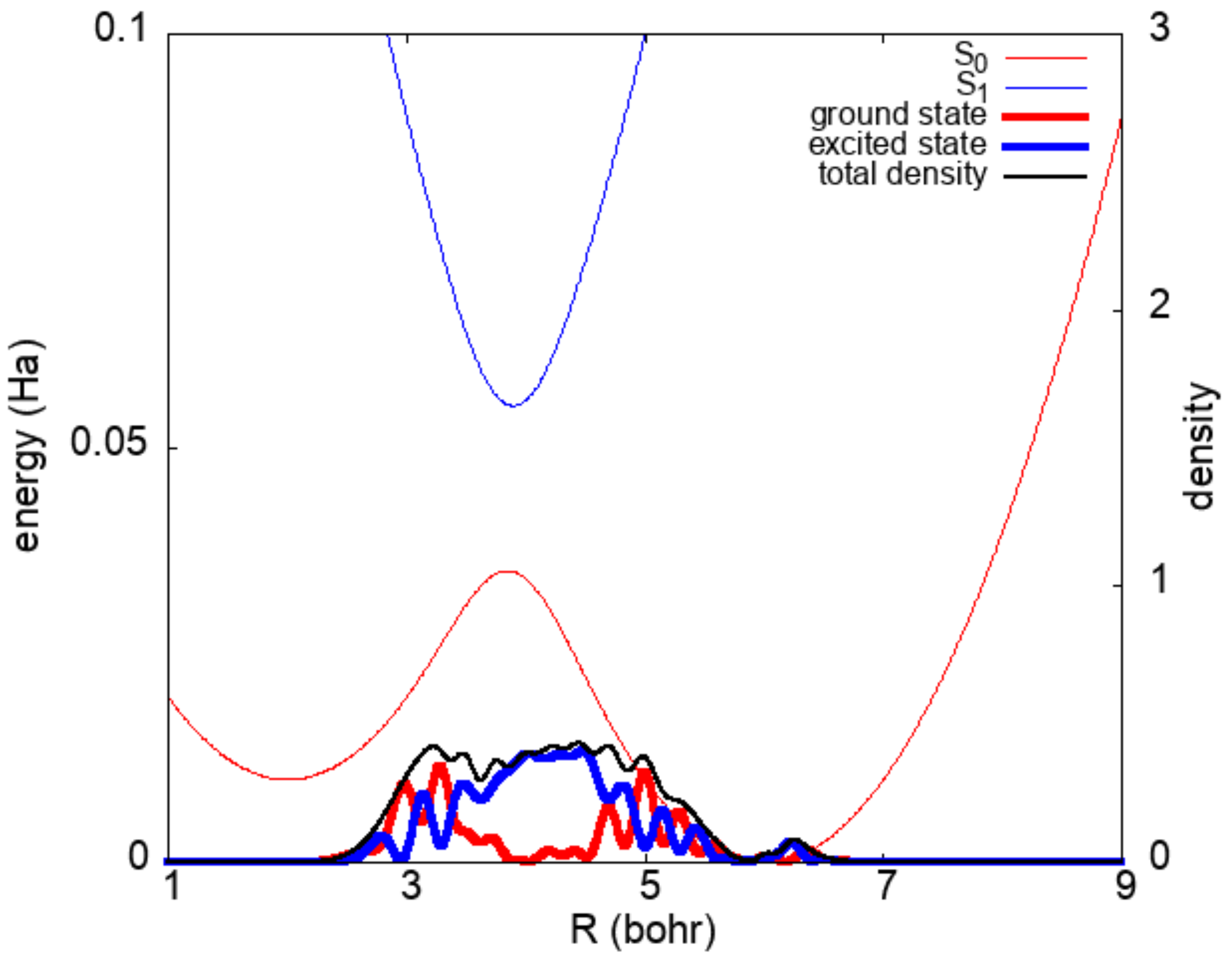
spin-adiabatic basis (eigenstates of $\hat{H}_{el} + \hat{H}_{SOC}$)

G-CT-MQC

Talotta, Morisset, Rougeau, Lauvergnat, Agostini, *Phys. Rev. Lett. (2020); J. Chem. Theory Comput.* (2020).

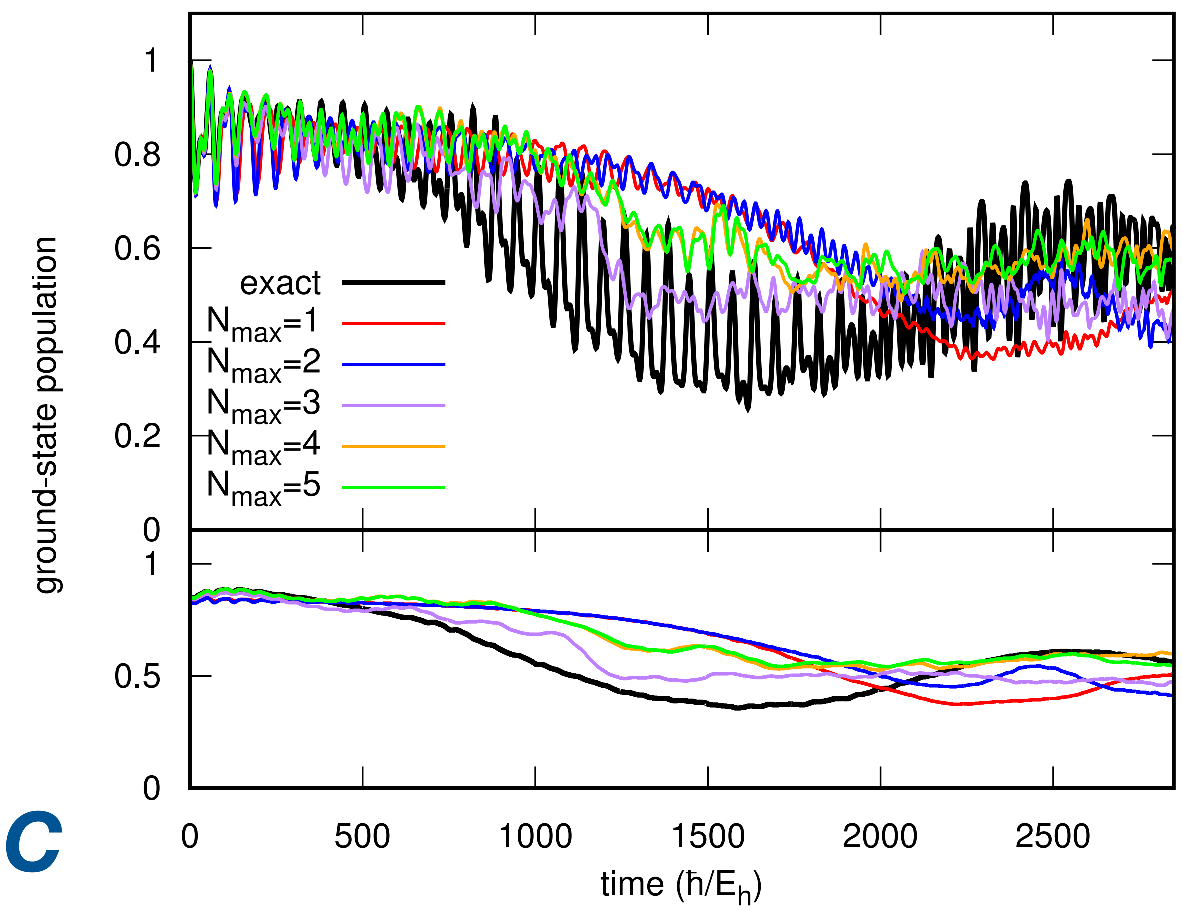
Floquet-driven nonadiabatic dynamics

$$i\hbar\partial_t\chi(R,t)\Phi(r,t;R) = \left(\hat{T}_n + \hat{H}_{el} + \hat{V}(t)\right)\chi(R,t)\Phi(r,t;R)$$



$$\hat{V}(t) = -\hat{\mu}E_0\cos(\Omega t)$$

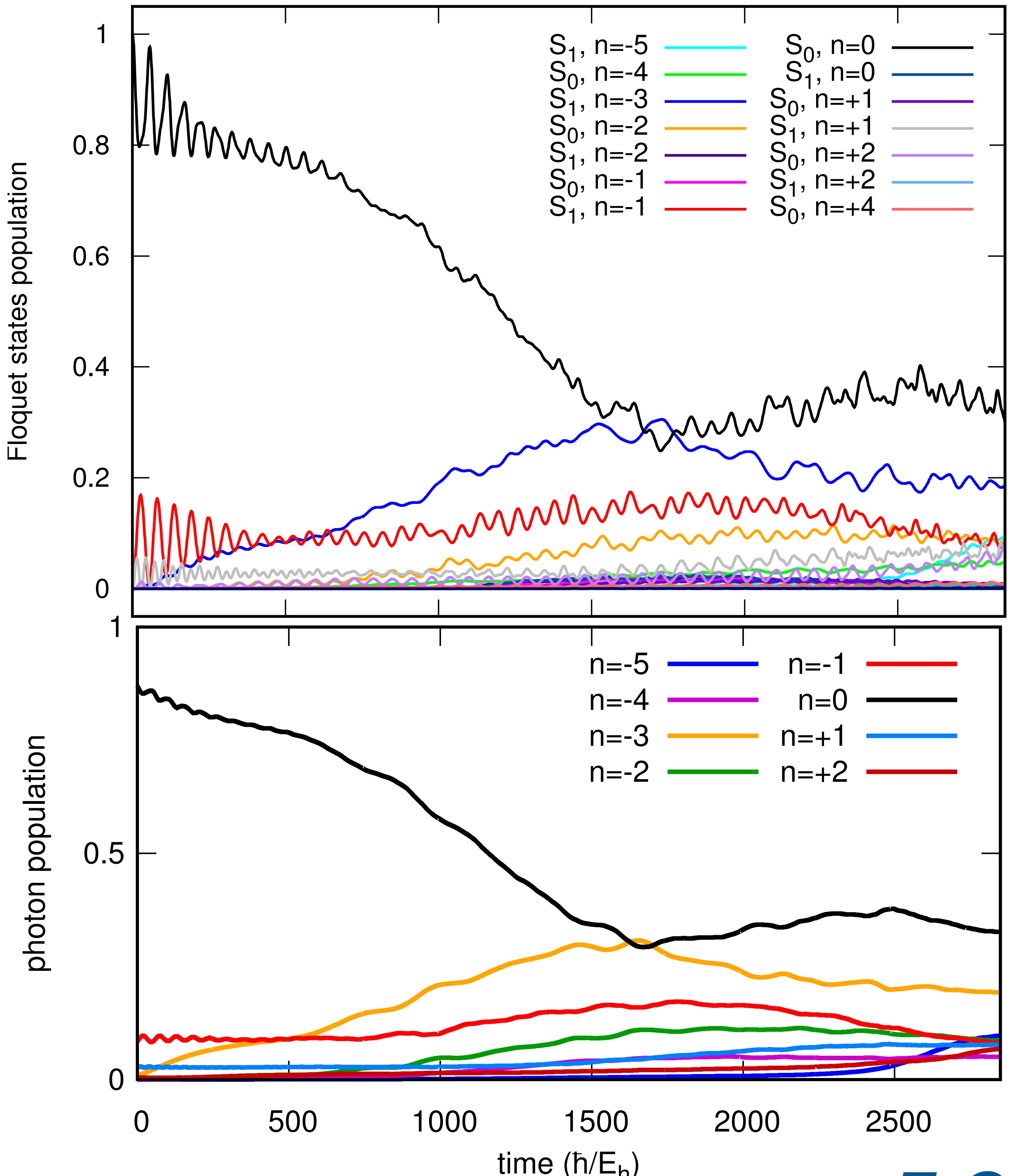
- $E_0 = 0.5\ E_h/(ea_0);\ \Omega = 0.05\ E_h/\hbar$
- linear approximation for $\mu(R)$
- dynamics of $3000\ \hbar/E_h \simeq 75\ fs$

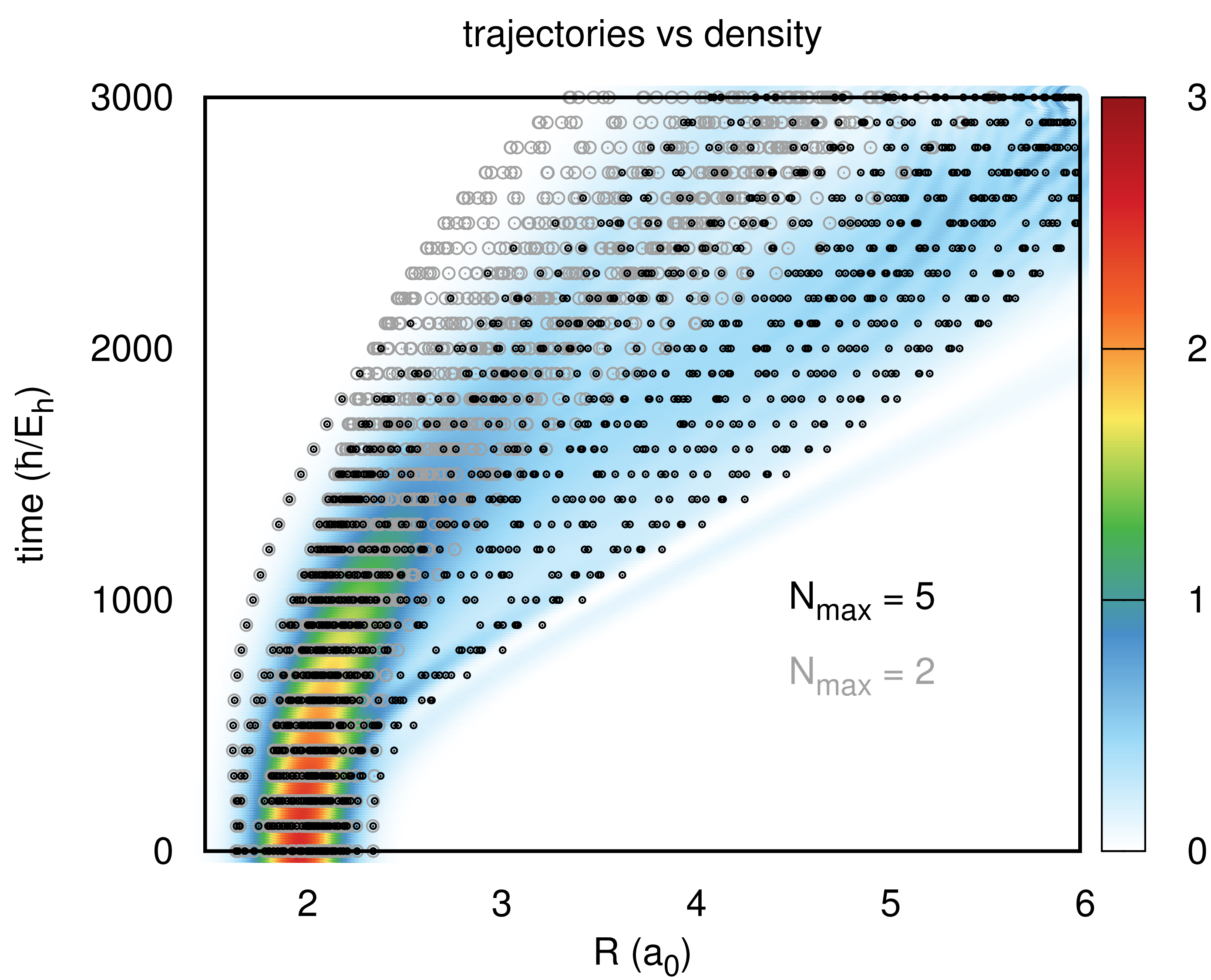


F-CT-MQC

Schirò, Eich, Agostini, *J. Chem. Phys.* (2021).

Floquet-driven nonadiabatic dynamics





F-CT-MQC

Schirò, Eich, Agostini, *J. Chem. Phys.* (2021).

Conclusions

- From the Born-Huang representation to the exact factorization for nonadiabatic dynamics
- Important of identifying the classical force in a trajectory-based description of nonadiabatic dynamics
- Some application of coupled-trajectory mixed quantum classical algorithm

G-CTMQC: Pieroni, Agostini, *J. Chem. Theory Comput.* (2021).
SHORT REVIEW ON EF: *Agostini, Gross, Eur. Phys. J. B* (2021).

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Florian Eich (HQS Karlsruhe)

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Job offer

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Two-year postdoc position at the University of Montpellier (south of France) in collaboration with the University Paris-Saclay on the combination of the exact factorization with a quantum-trajectory approach.

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Partners: David Lauvergnat david.lauvergnat@universite-paris-saclay.fr
Federica Agostini federica.agostini@universite-paris-saclay.fr

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