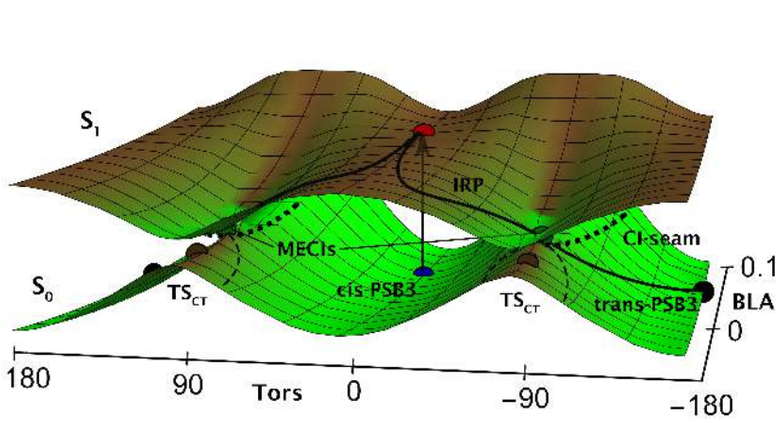
université PARIS-SACLAY

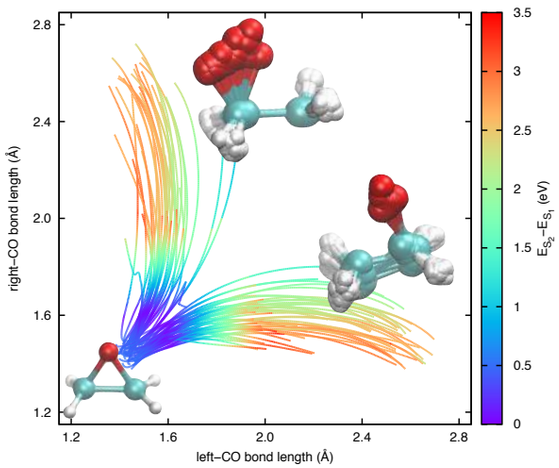
FACULTÉ DES SCIENCES D'ORSAY

Institut de Chimie Physique

Dynamics of electrons and nuclei in molecules

Beyond the Born-Oppenheimer approximation





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GDR NBODY

Lille — January 8-10, 2020

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Summary

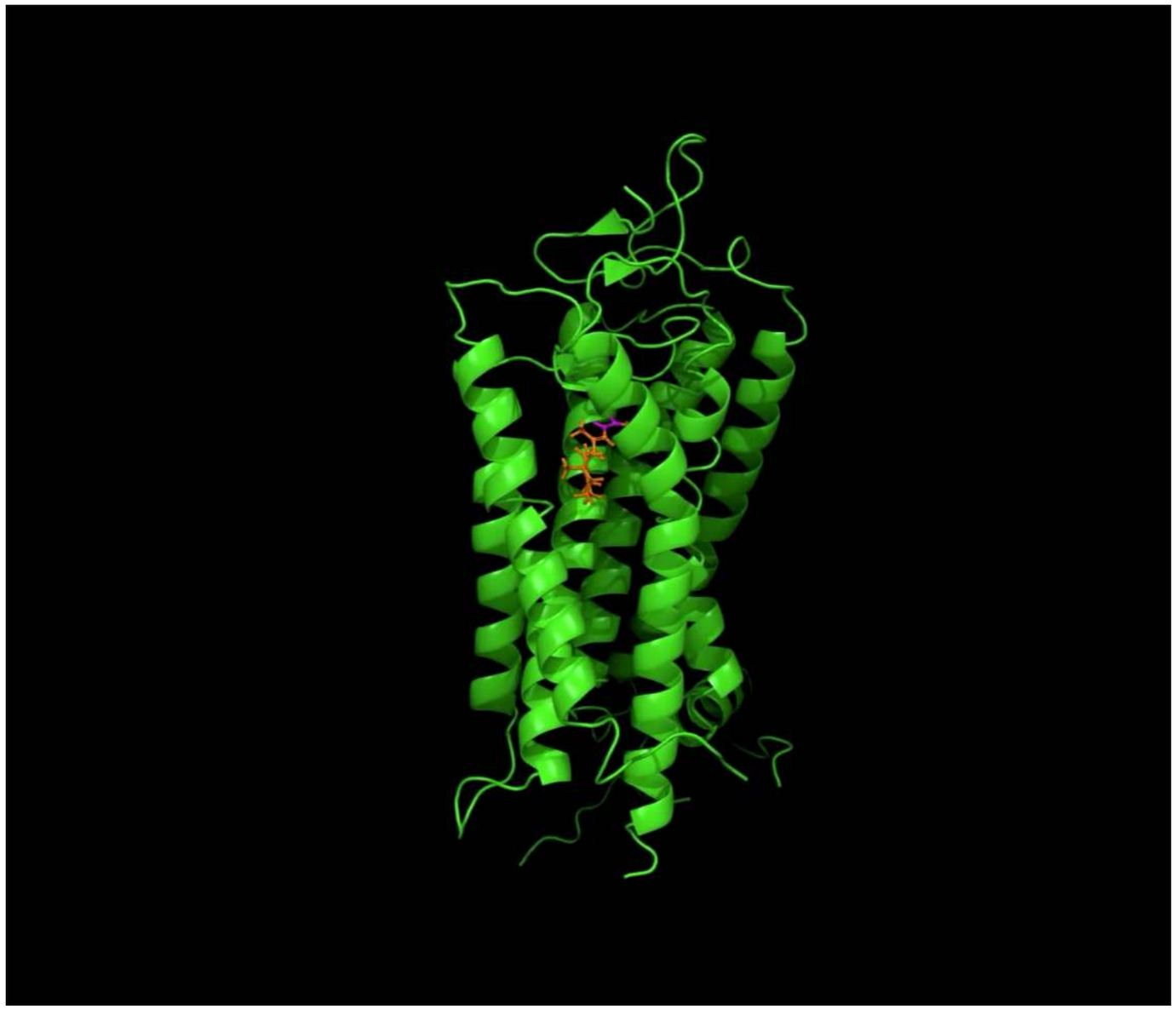
“N-body” problem (electrons & nuclei) + ultrafast dynamics

- photo-activated ultrafast phenomena in a nutshell
- the quantum-mechanical problem & approximations
- trajectory-based approches to excited-state dynamics
- exact factorization of the electron-nuclear wavefunction
- an overview on the applications

What happens to a molecule after photo-excitation?

cis-trans isomerization of the retinal chromophore in the rhodopsin protein as the first step in the process of vision

one of the fastest photochemical reactions known in nature (200 fs)

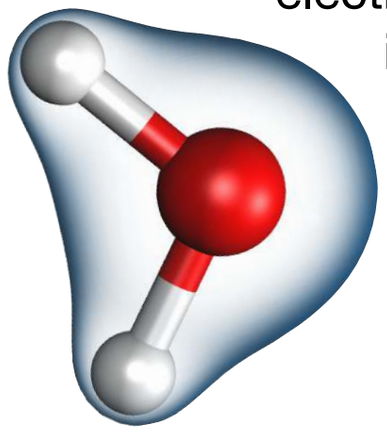


theoretical description need to go beyond the Born-Oppenheimer approximtion

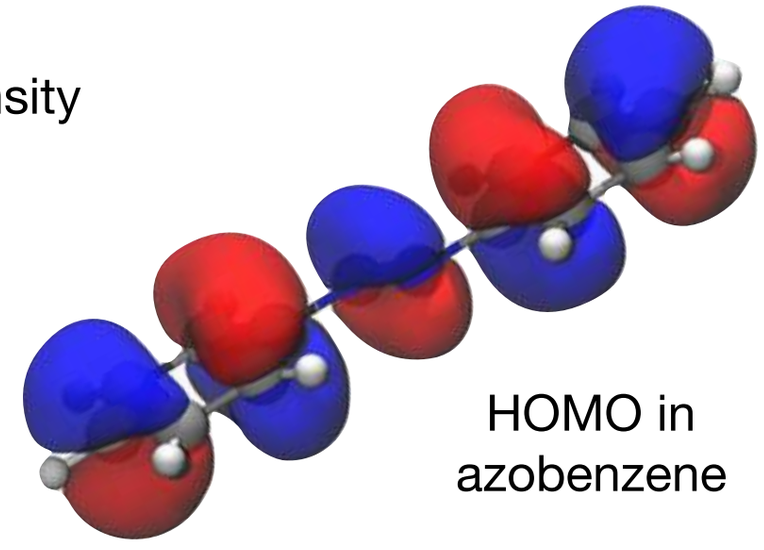
The molecular basis of vision - Computational Chemistry
YouTube / CompChemist

Simulations of light-matter interaction phenomena

systems of interacting electrons and nuclei



electronic density in water



HOMO in azobenzene

microscopic quantum mechanical description

electronic excited-state effects

nuclear quantum effects

Simulations of light-matter interaction phenomena

systems of interacting electrons and nuclei

microscopic quantum mechanical description

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

electronic excited-state effects

nuclear quantum effects

Simulations of light-matter interaction phenomena

systems of interacting electrons and nuclei

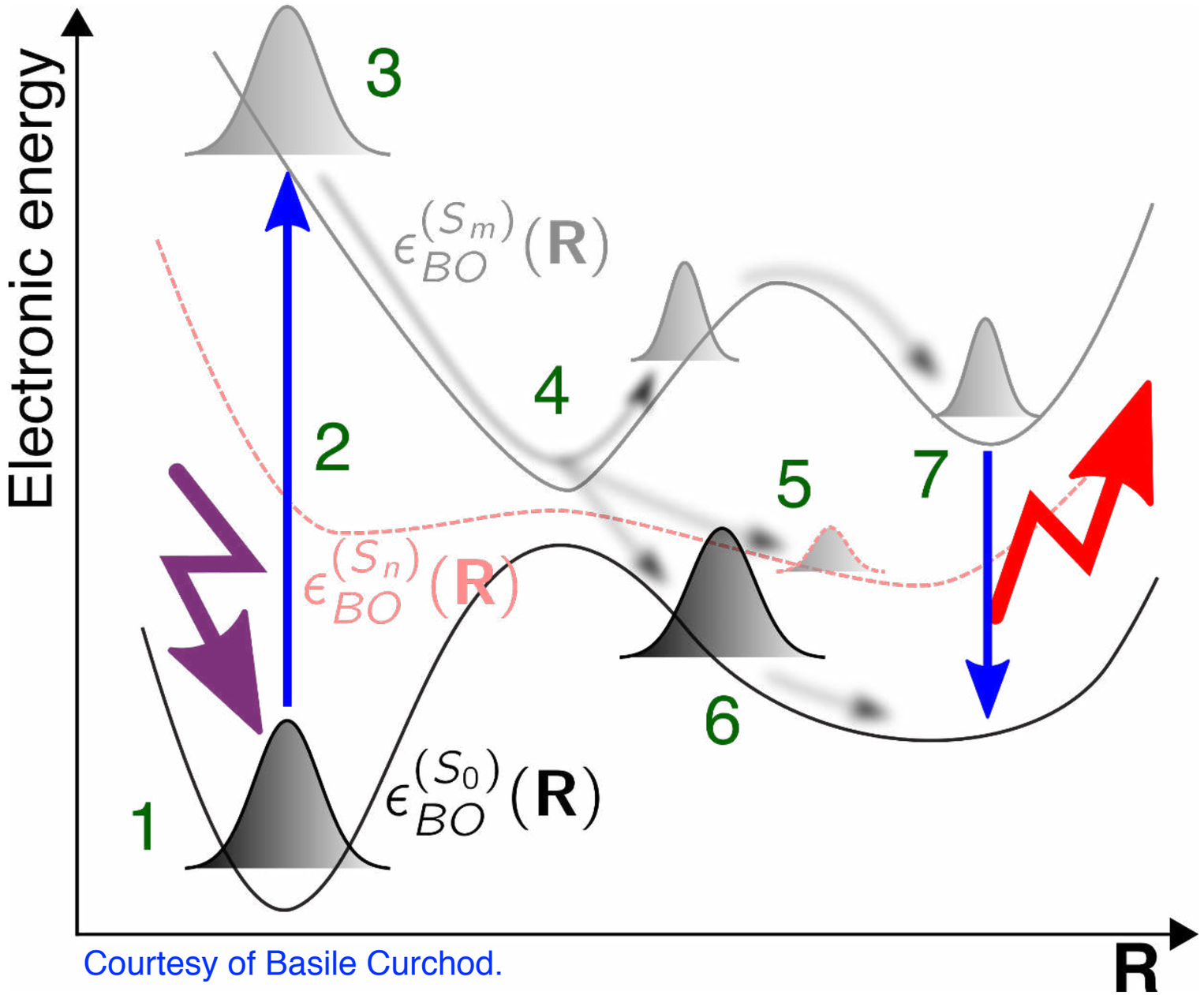
microscopic quantum mechanical description

electronic excited-state effects

quantum chemistry

nuclear quantum effects

nuclear dynamics



Courtesy of Basile Curchod.

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

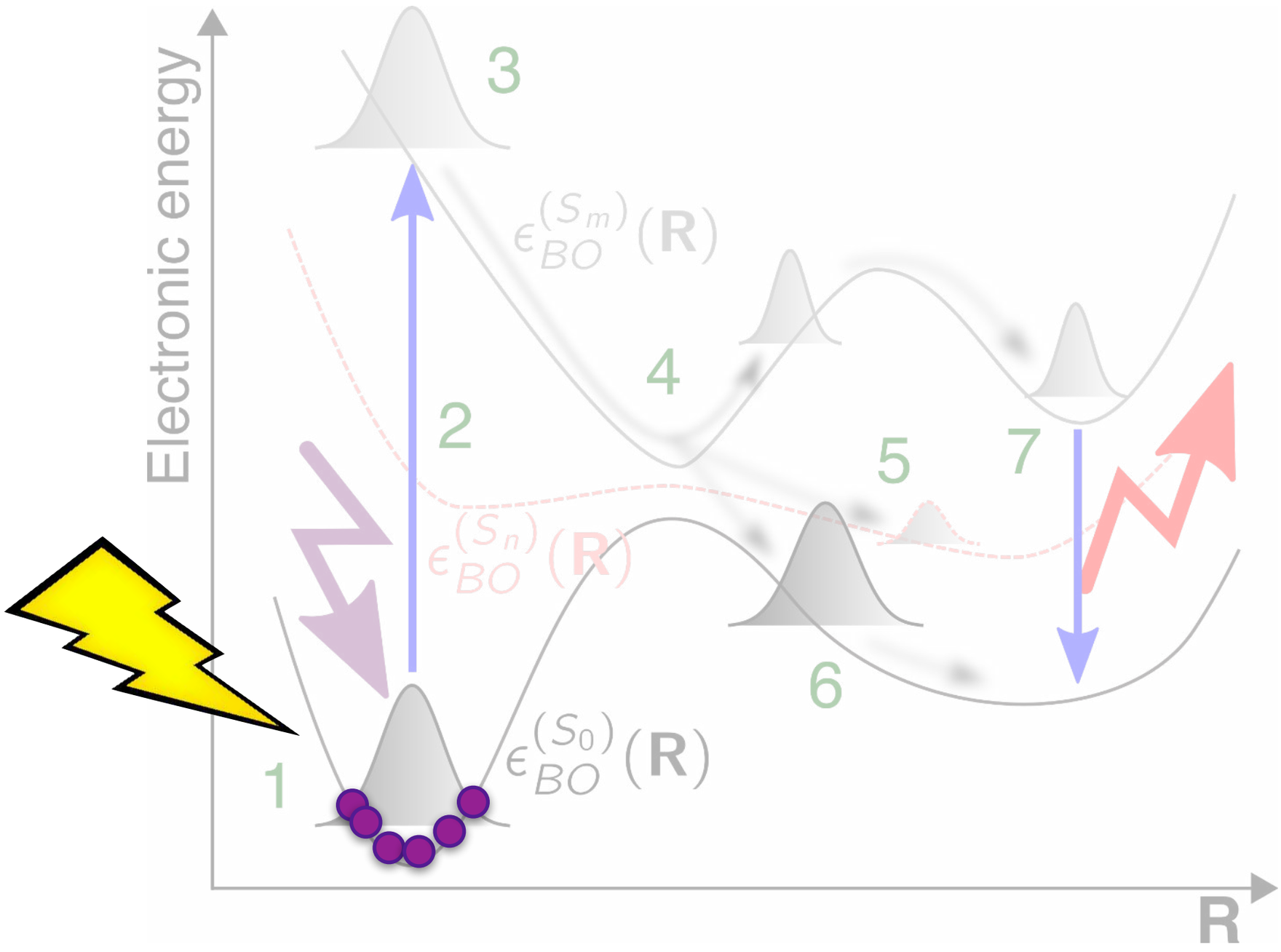
Ab initio molecular dynamics simulations

electronic excited-state effects

quantum chemistry

nuclear quantum effects

nuclear **classical-like** dynamics



Ab initio molecular dynamics simulations

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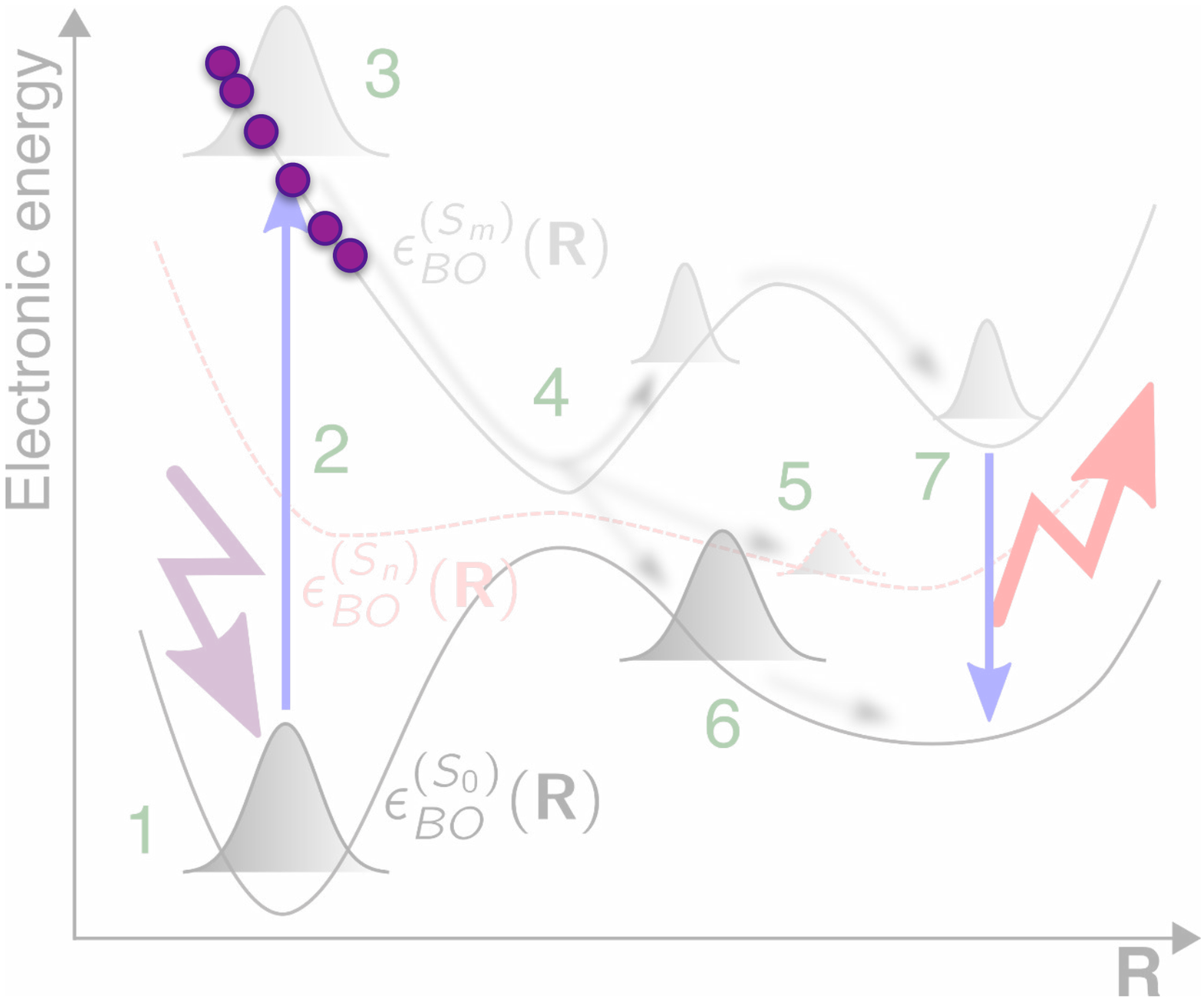

Ab initio molecular dynamics simulations

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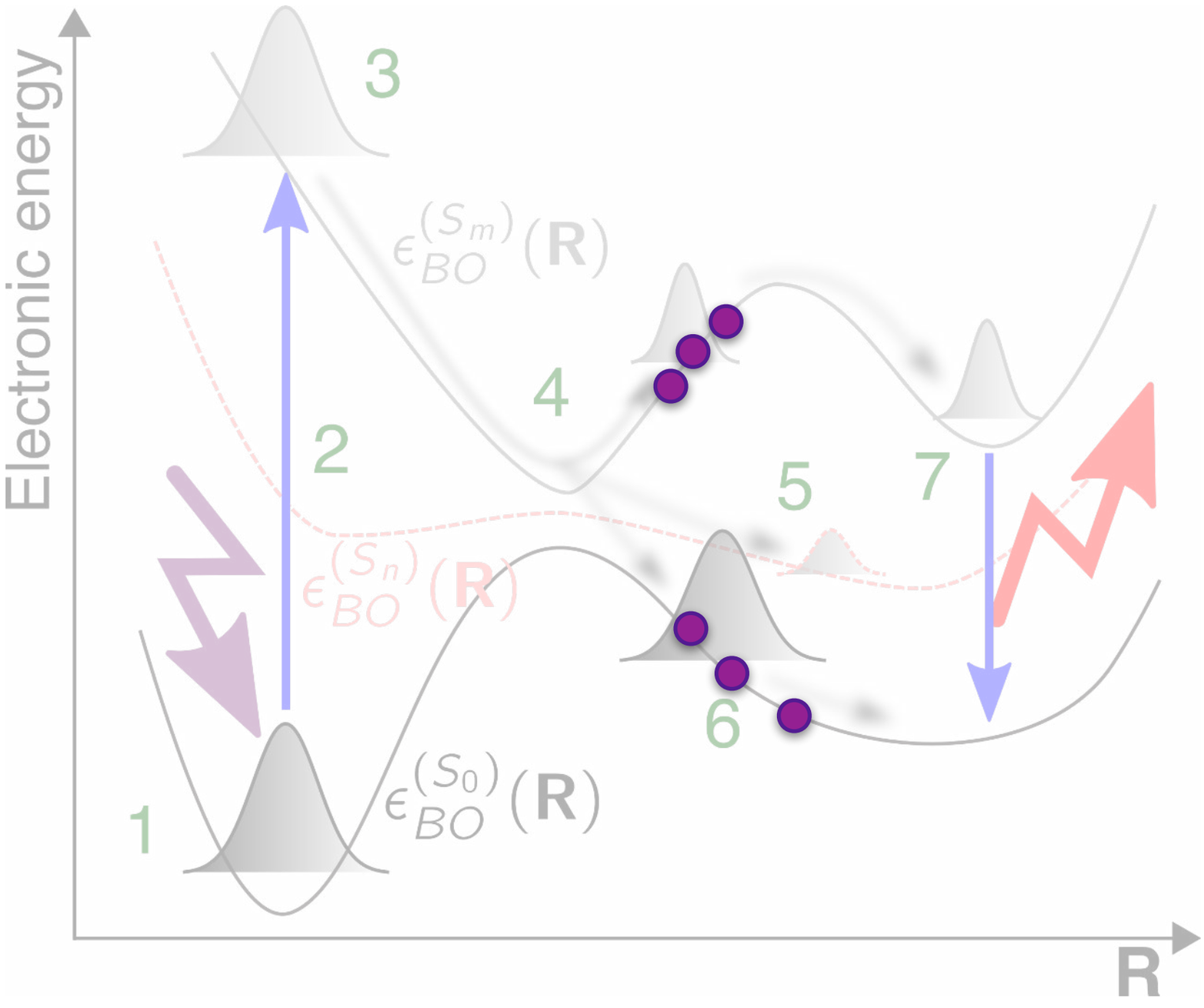

Ab initio molecular dynamics simulations

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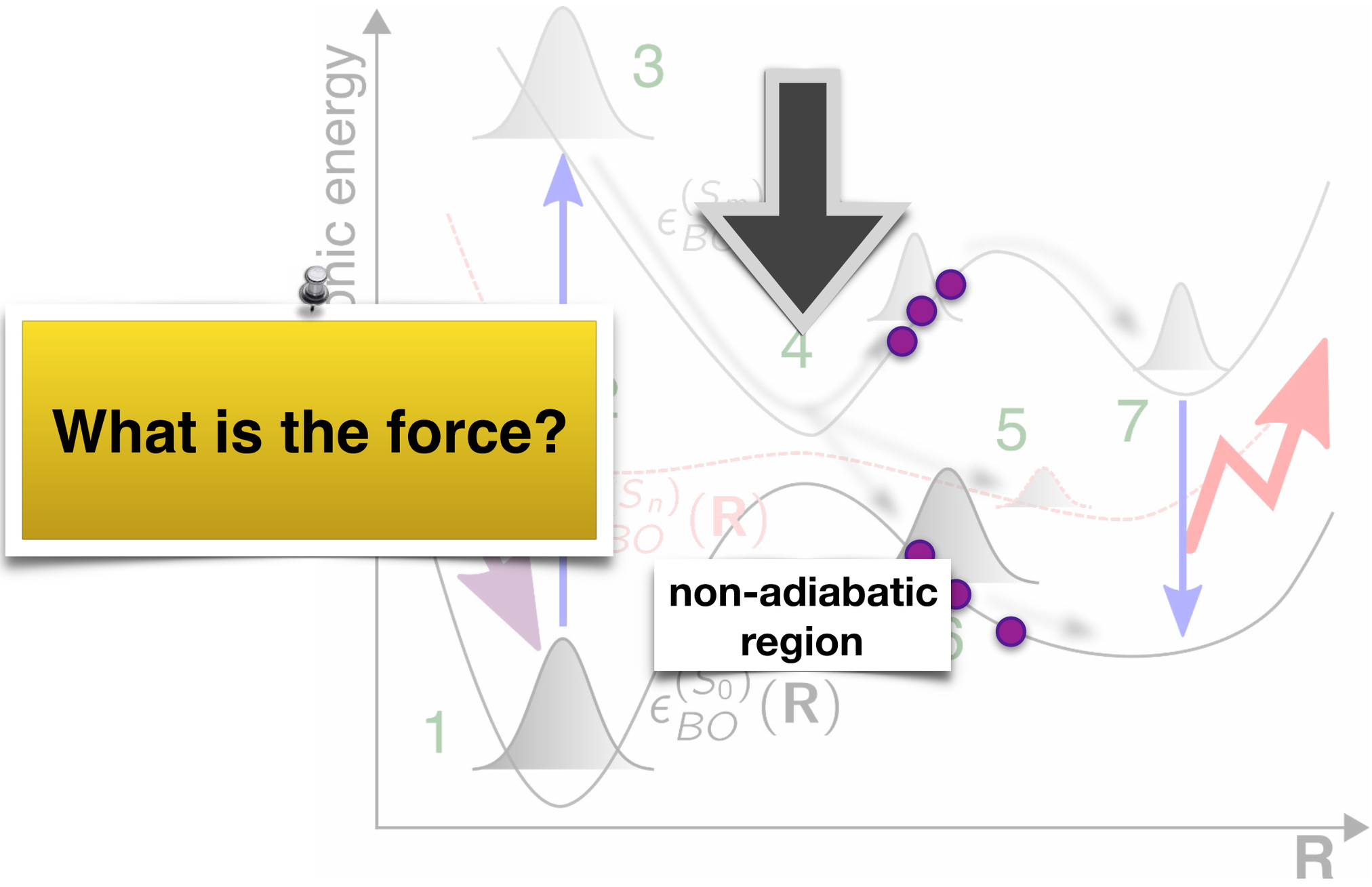
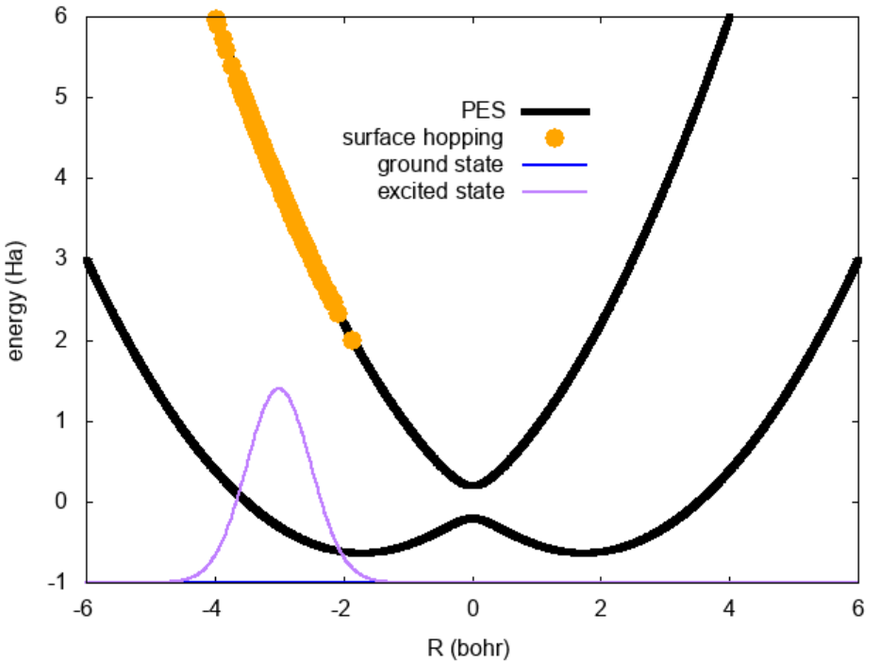


What is the force?

Determining classical-like forces

COMPARISON OF QUANTUM AND CLASSICAL DYNAMICS
(model system for photo-excited dynamics)

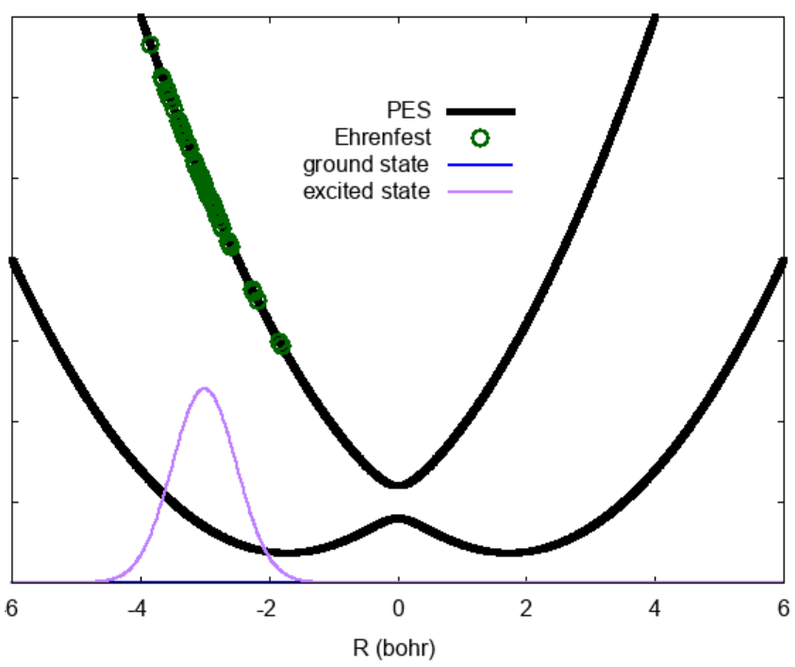
surface hopping



trajectories jump stochastically

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

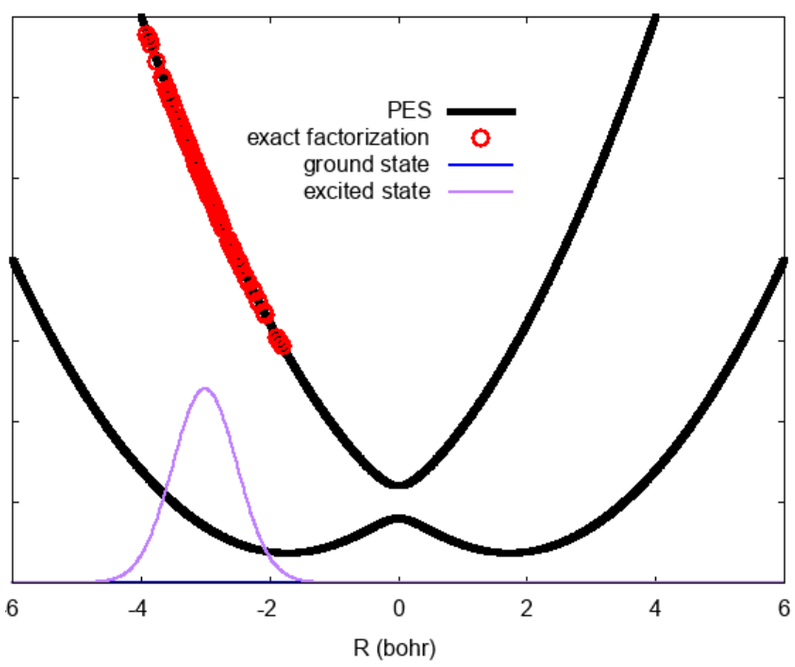
Ehrenfest dynamics



trajectories follow an average potential

J. C. Tully, *Farad. Discuss.* **110** (1998) 407.

exact factorization



trajectories evolve with the exact force

Exact factorization of the electron-nuclear wavefunction

$$P^{(J)}(x,y) = P_y^{(C)}(x)\, P^{(M)}(y)$$

axiom of probability theory

$$|\Psi(\mathbf{r},\mathbf{R})|^2 = |\Phi_{\mathbf{R}}(\mathbf{r})|^2\, |\chi(\mathbf{R})|^2$$

probabilistic interpretation of the squared modulus of the wavefunction

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

Hunter, *Int. J. Quantum Chem.* **9** (1975)

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

Abedi, Maitra, Gross, *Phys. Rev. Lett.* **105** (2010)

$$i\hbar\partial_t \Phi_{\mathbf{R}}(\mathbf{r},t)\chi(\mathbf{R},t) = \left[\hat{T}_n + \hat{H}_{el}\right] \Phi_{\mathbf{R}}(\mathbf{r},t)\chi(\mathbf{R},t)$$

electronic equation

nuclear equation

FA, B. F. E. Curchod, WIREs Comput. Mol. Sci. (2019); FA, B. F. E. Curchod, R. Vuilleumier, I. Tavernelli, E. K. U. Gross, *Handbook of Materials Modeling. Vol. 1: Theory and Modeling*, Springer (2018).

Exact factorization of the electron-nuclear wavefunction

quantum-mechanical solution based on quantum chemistry

explicit coupling to the nuclear equation

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

$$i\hbar\partial_t \chi(\mathbf{R},t) = \left[\sum_{\nu=1}^{N_n} \frac{[-i\hbar\nabla_\nu + \mathbf{A}_\nu(\mathbf{R},t)]^2}{2M_\nu} + \epsilon(\mathbf{R},t)\right]\chi(\mathbf{R},t)$$

classical solution based on trajectories

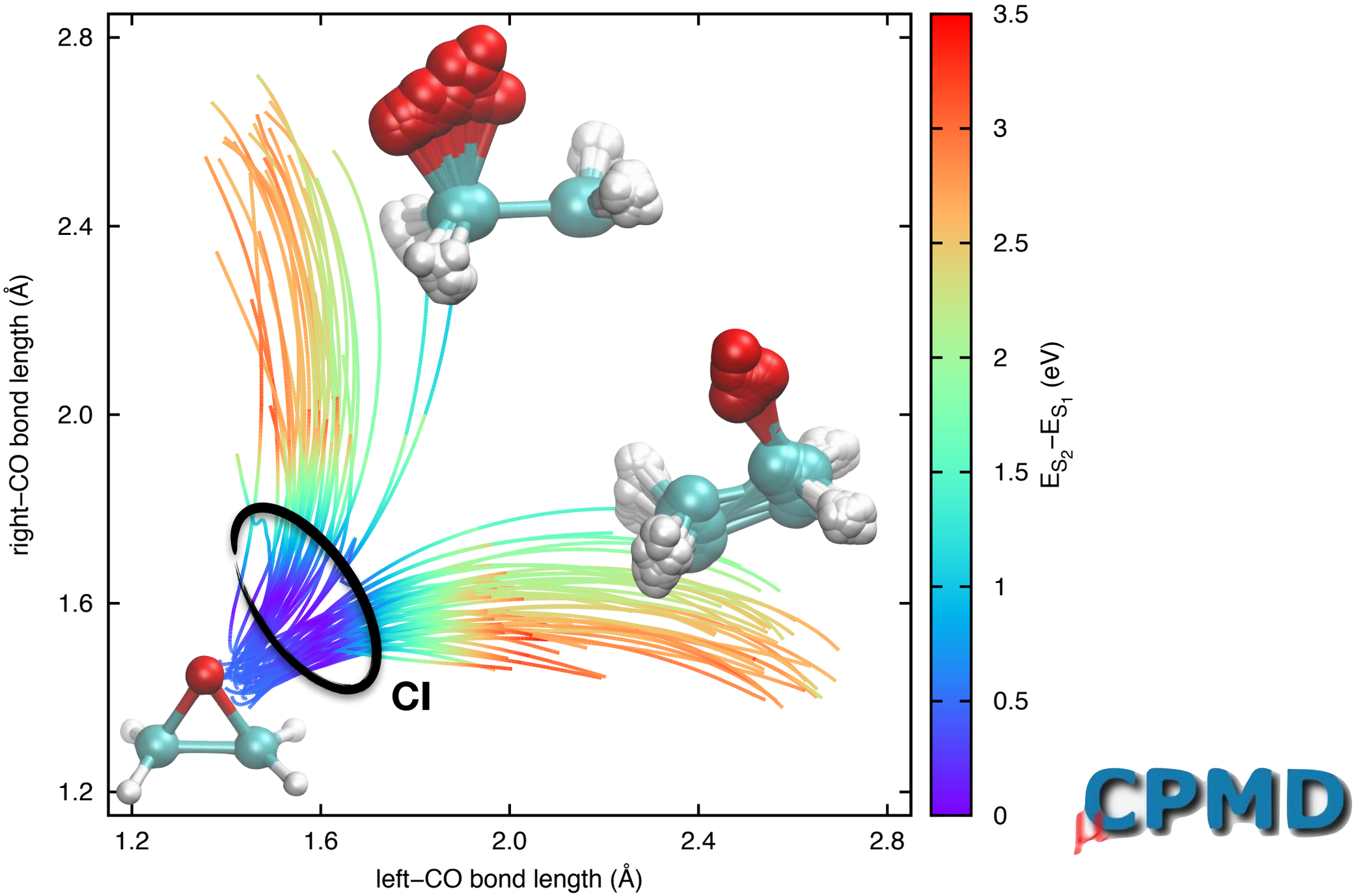
nuclear time-dependent Schrödinger equation

time-dependent potentials

A. Abedi, FA, Y. Suzuki and E. K. U. Gross, *Phys. Rev. Lett.* (2013); S. K. Min, FA, E. K. U. Gross, *Phys. Rev. Lett.* (2015); FA, Eur. Phys. J. B (2018); B. F. E. Cuchod, FA, I. Tavernelli, Eur. Phys. J. B (2018).

Photo-induced ring-opening in Oxirane

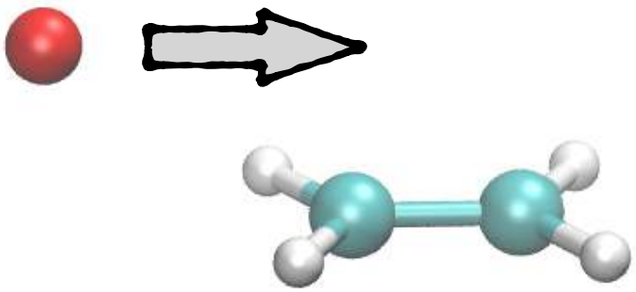
internal conversion = non-radiative relaxation



S. K. Min, FA, I. Tavernelli, E. K. U. Gross, *J. Phys. Chem. Lett.* (2017); B. F. E. Curchod, FA, I. Tavernelli, *Europhys. J. B* (2108); FA, E. K. U. Gross, in *Quantum Chemistry and Dynamics of Excited States: Methods and Applications* (in press).

Spin-orbit interactions in ultrafast phenomena

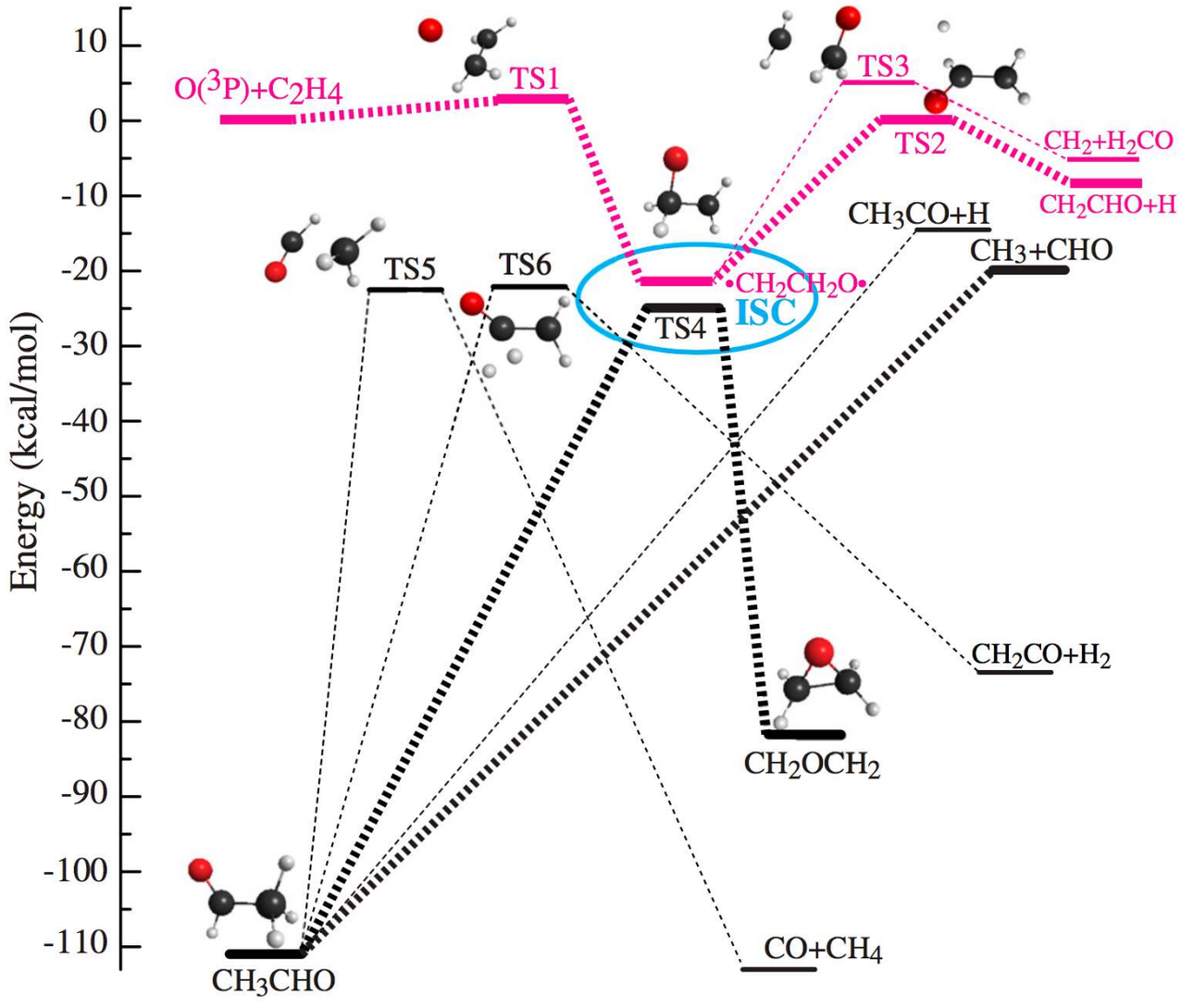
$$i\hbar\partial_t \Psi(\mathbf{x}, \mathbf{R}, t) = \left[\hat{T}_n + \hat{H}_{el} + \hat{H}_{SO}\right] \Psi(\mathbf{x}, \mathbf{R}, t)$$



collision dynamics

$O(^3P) + C_2H_4$
including couplings
between
states of different spin
multiplicity, e.g., singlets
and triplets

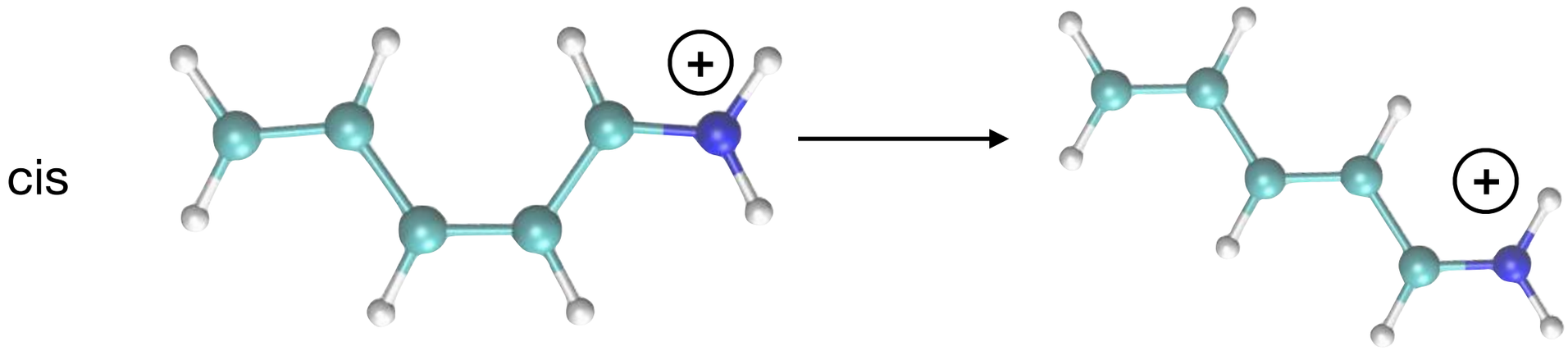
intersystem crossing

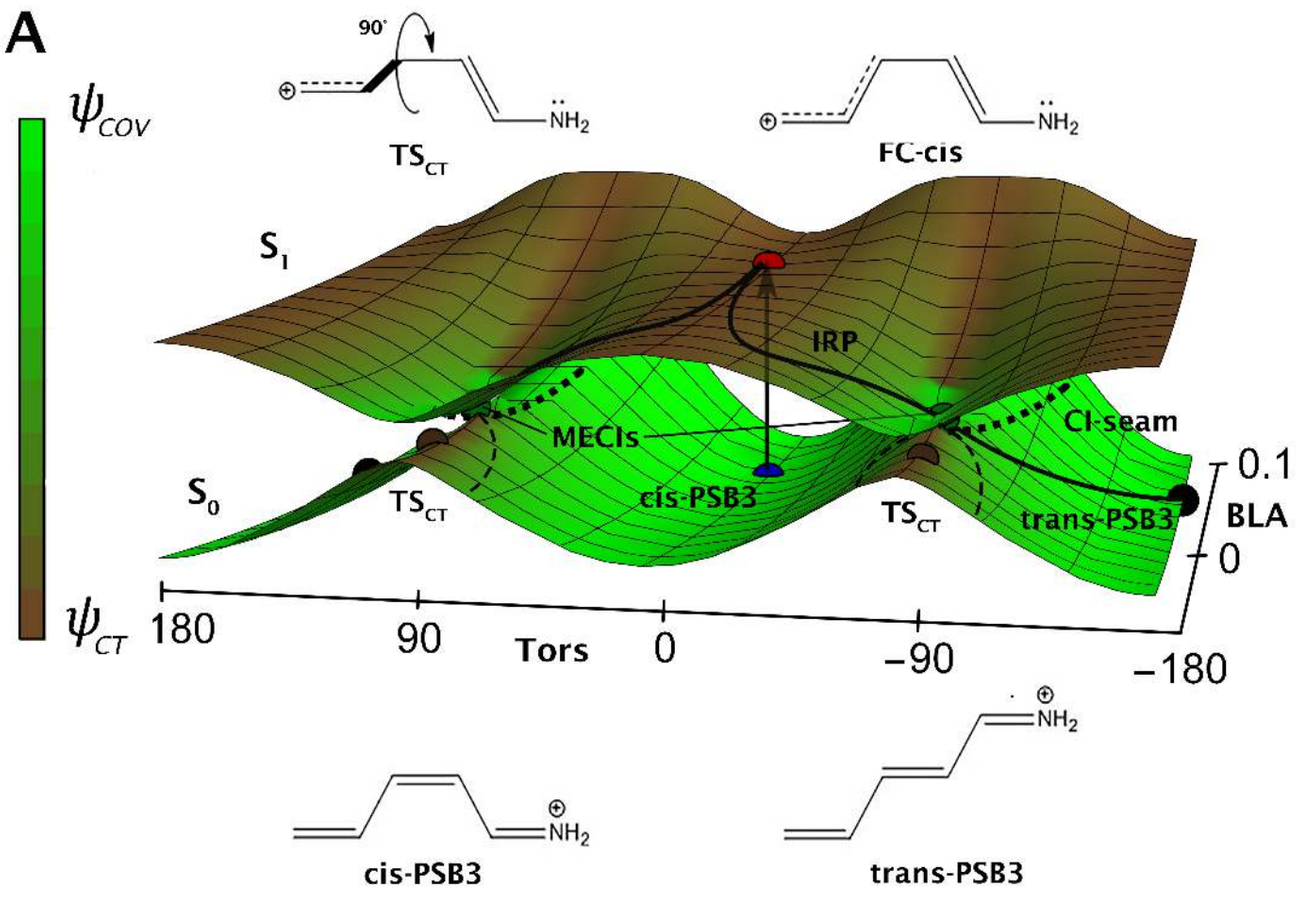


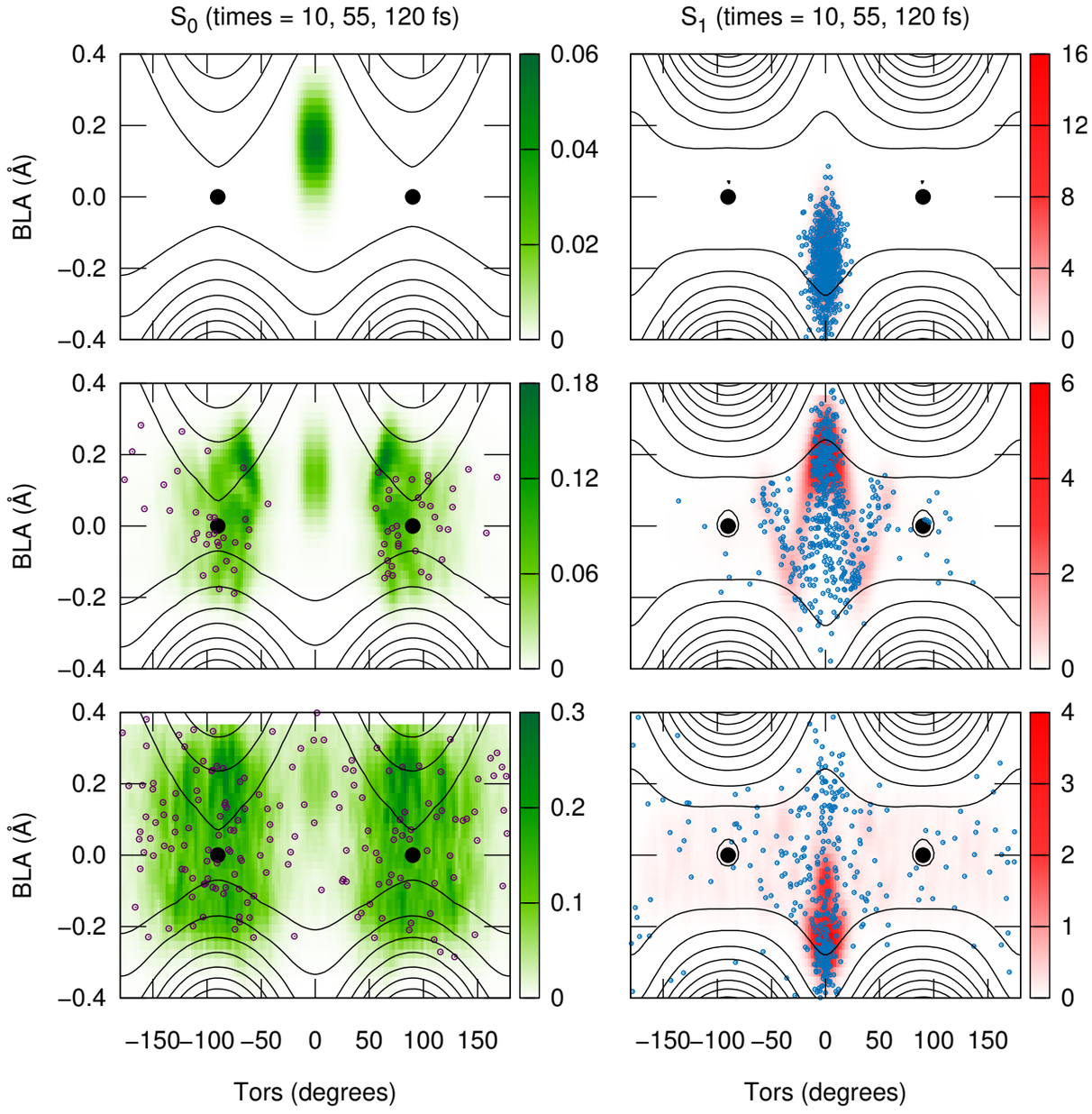
B. Fu, et al., *Proc. Nat. Ac. Sci.* **109** (2012) 9733.

F. Talotta, S. Morisset, N. Rougeau, D. Lauvergnat, FA, Phys. Rev. Lett. (in press).

Photo-isomerization of a retinal model







E. Marsili, et al., *J. Phys. Chem. A* **123** (2019) 1710.

E. Marsili, M. Olivucci, D. Lauvergnat, FA, *in preparation*.