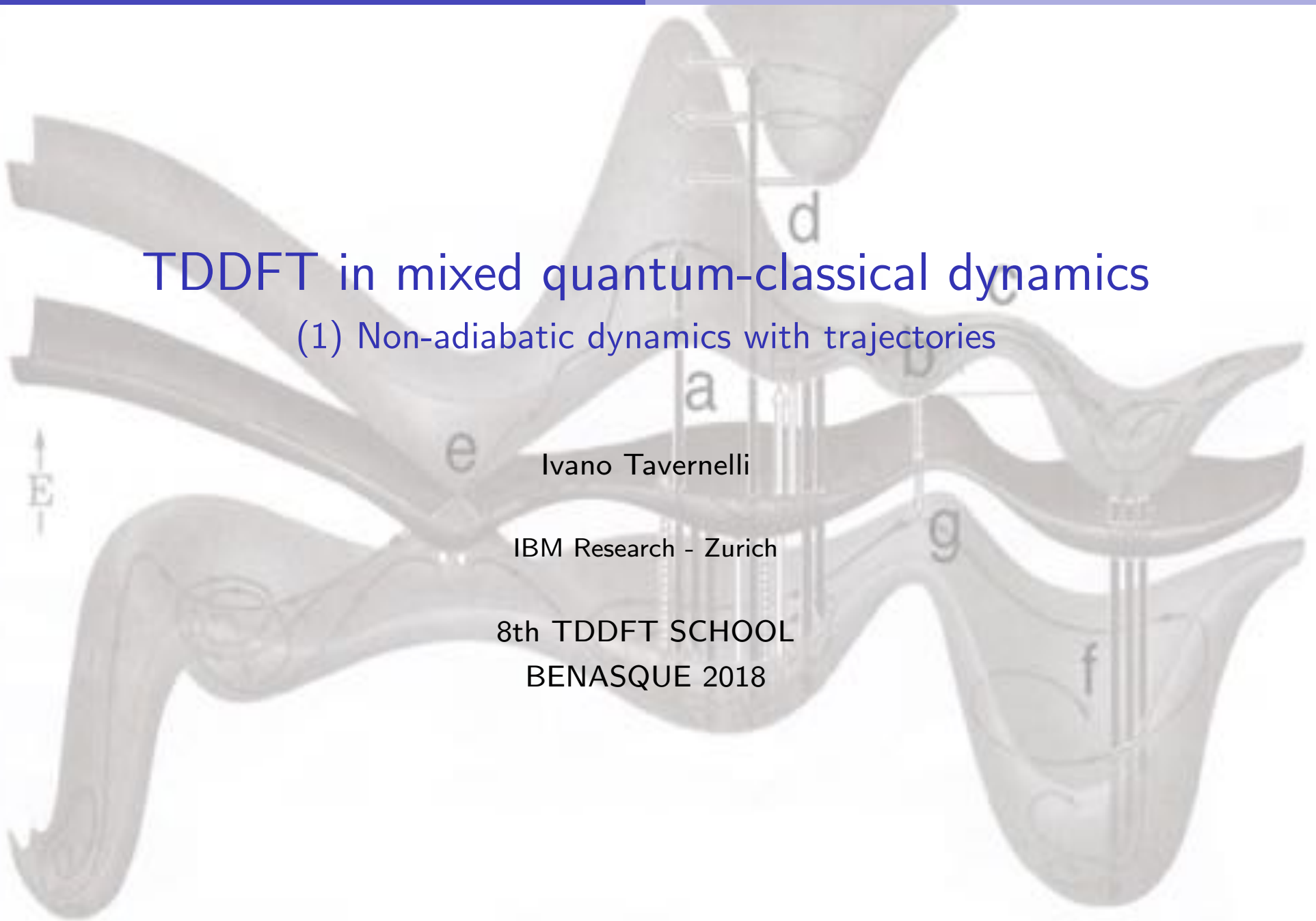


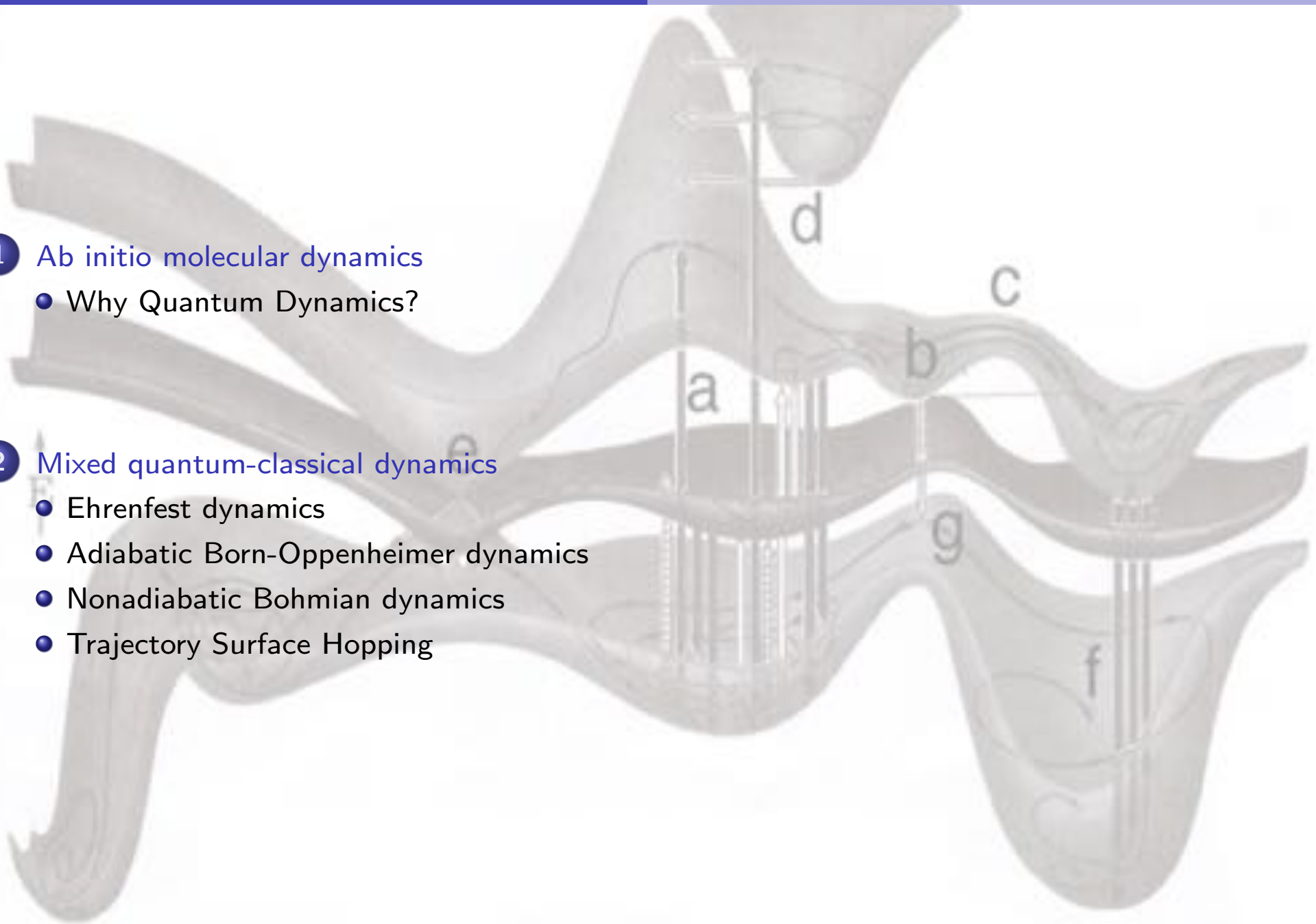
TDDFT in mixed quantum-classical dynamics

(1) Non-adiabatic dynamics with trajectories

Ivano Tavernelli

IBM Research - Zurich

8th TDDFT SCHOOL
BENASQUE 2018



1. Ab initio molecular dynamics
   - Why Quantum Dynamics?
2. Mixed quantum-classical dynamics
   - Ehrenfest dynamics
   - Adiabatic Born-Oppenheimer dynamics
   - Nonadiabatic Bohmian dynamics
   - Trajectory Surface Hopping

Recent review on TDDFT-based nonadiabatic dynamics

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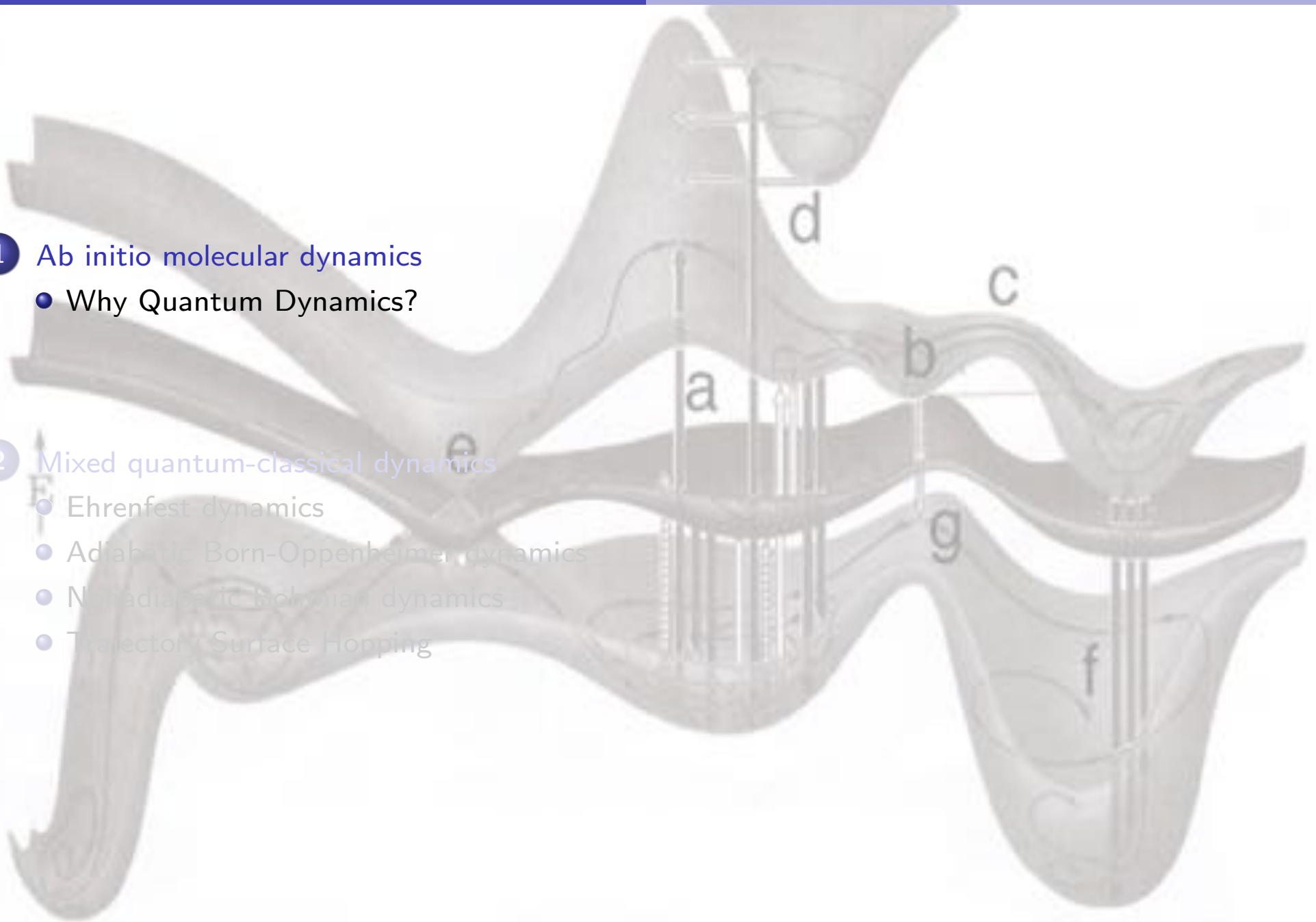
ChemPubSoc Europe

DOI: 10.1002/cphc.201200941

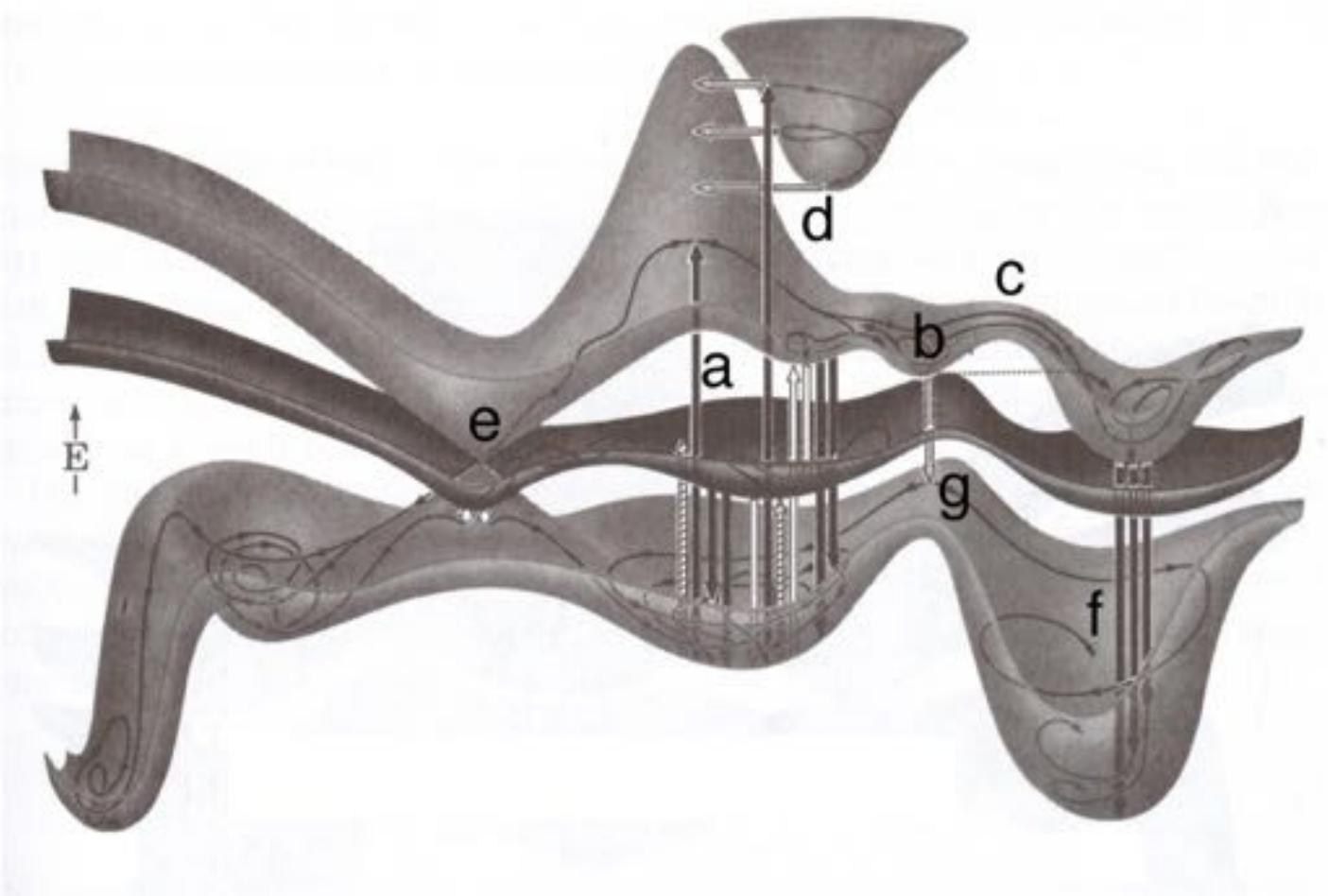
Trajectory-Based Nonadiabatic Dynamics with Time-Dependent Density Functional Theory

Basile F. E. Curchod, Ursula Rothlisberger, and Ivano Tavernelli*[a]

ChemPhysChem,**14**, 1314 (2013)



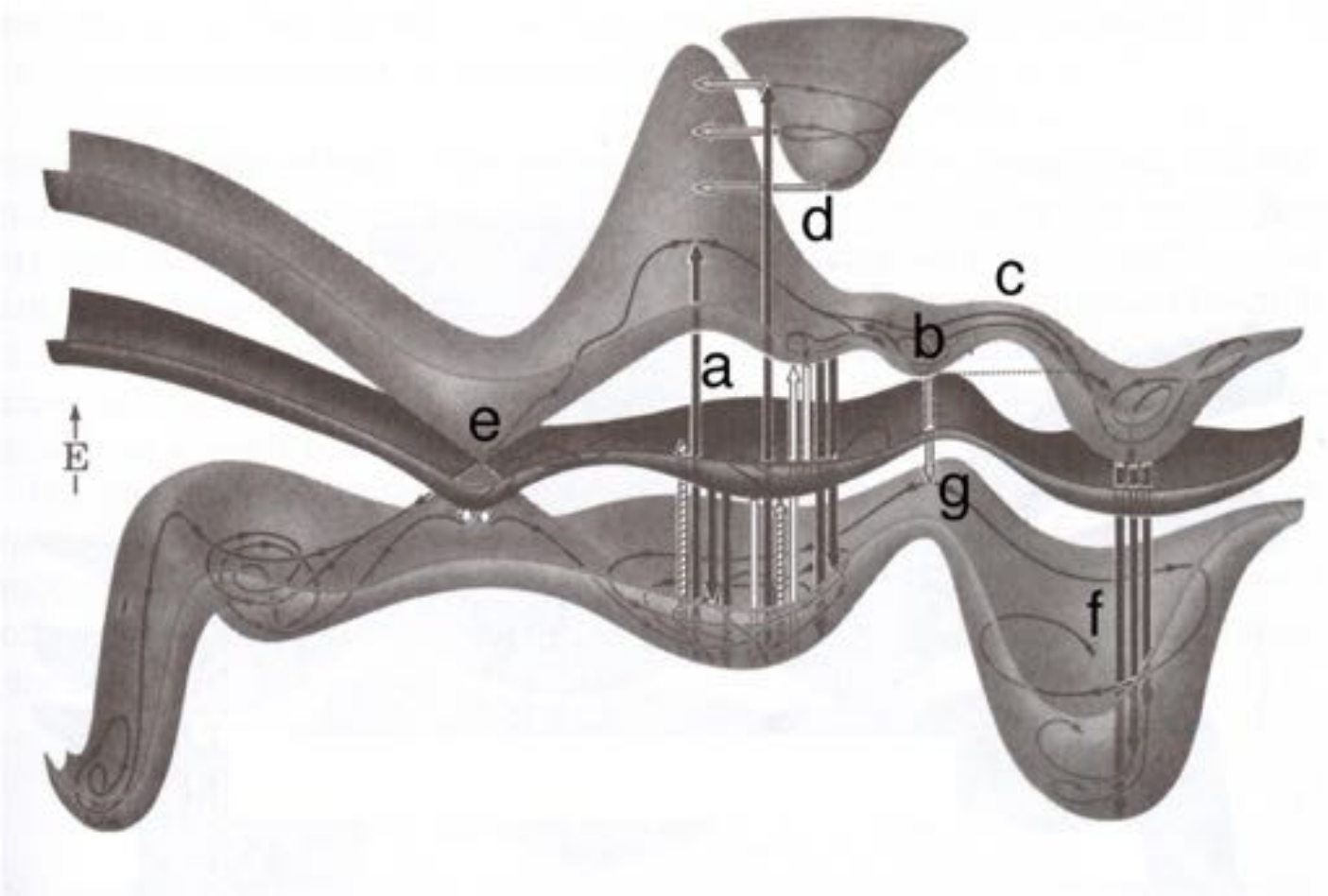
Reminder from last lecture: potential energy surfaces



We have electronic structure methods for electronic ground and excited states...

Now, we need to propagate the nuclei...

Reminder from last lecture: potential energy surfaces



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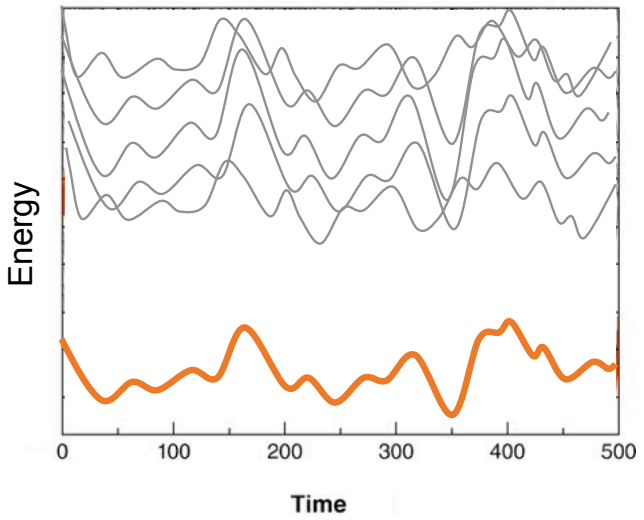
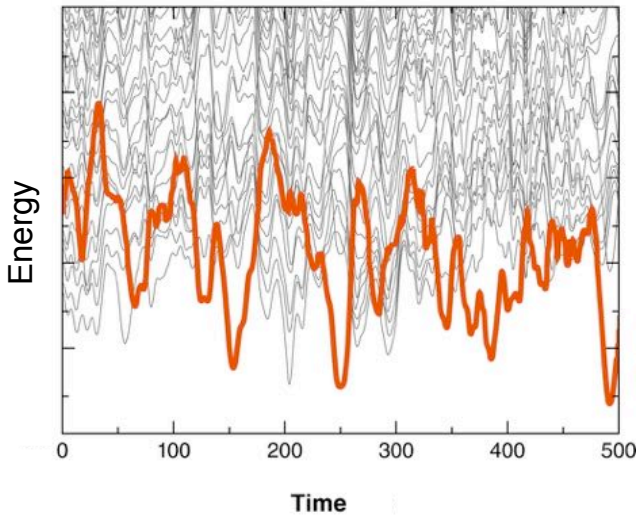
Now, we need to propagate the nuclei...

Why Quantum dynamics?





GS adiabatic dynamics (BO vs. CP)

BO $M_I \ddot{\boldsymbol{R}}_I(t) = -\nabla \min_\rho E_{KS}(\{\phi_i[\rho]\})$

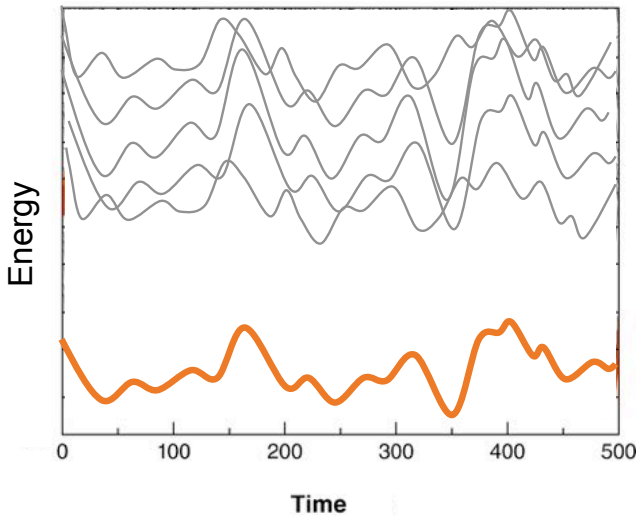
CP $\mu_i |\ddot{\phi}_i(t)\rangle = -\frac{\delta}{\delta\langle\phi_i|} E_{KS}(\{\phi_i(\boldsymbol{r})\}) + \frac{\delta}{\delta\langle\phi_i|}\{\text{constr.}\}$

$M_I \ddot{\boldsymbol{R}}_I(t) = -\nabla E_{KS}(\{\phi_i(t)\})$

ES nonadiabatic quantum dynamics

- Wavepacket dynamics (MCTDH)
- Trajectory-based approaches
  - Tully's trajectory surface hopping (TSH)
  - Bohmian dynamics (quantum hydrodyn.)
  - Semiclassical (WKB, DR)
  - Path integrals (Pechukas)
  - Mean-field solution (Ehrenfest dynamics)
- Density matrix, Liouvillian approaches, ...

Why Quantum dynamics?

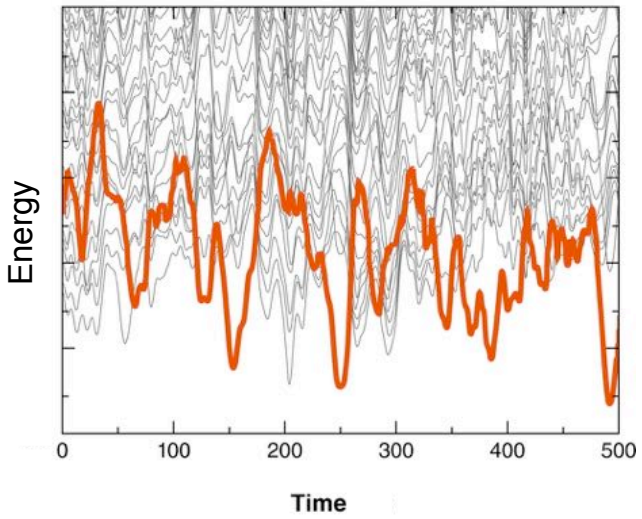


GS adiabatic dynamics

First principles Heaven

Ab initio MD with WF methods
Ab initio MD with DFT & TDDFT [CP]
classical MD
Coarse-grained MD
...

No principles World



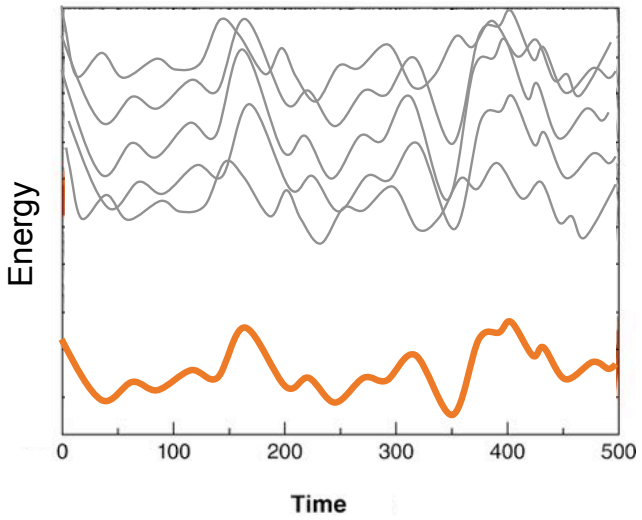
ES nonadiabatic quantum dynamics

First principles Heaven

Ab initio MD with WF methods
Ab initio MD with DFT & TDDFT [CP]
↓
Models
↓?

No principles World

Why Quantum dynamics?



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First principles Heaven
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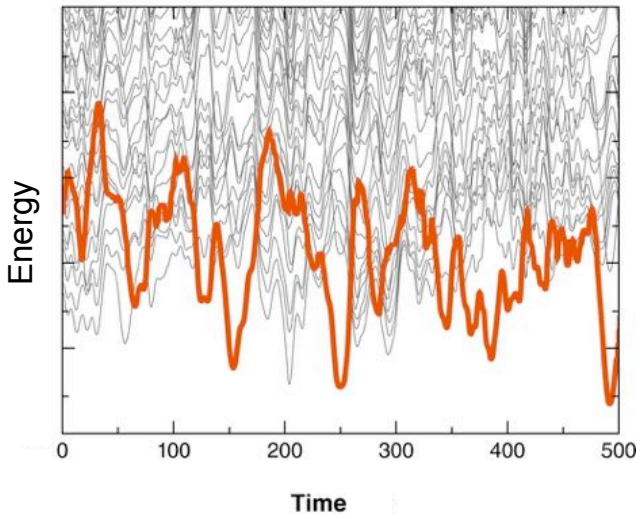
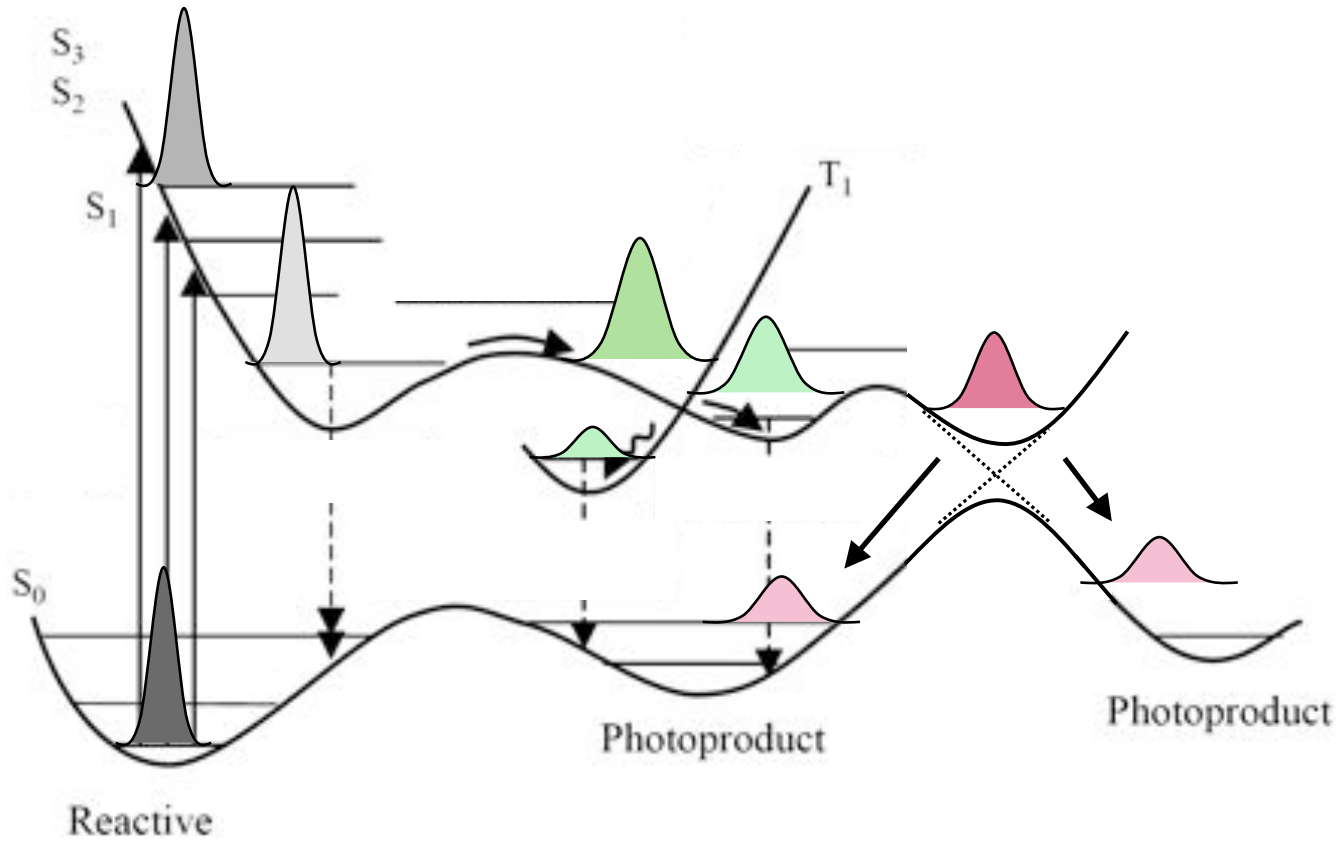


ES nonadiabatic quantum dynamics

- (-) We cannot get read of electrons
- (-) Nuclei keep some QM flavor
- (-) Accuracy is an issue
- (-) Size can be large (diffuse excitons)
- (+) Time scales are usually short ($< ps$)

Nonadiabatic effects requires quantum nuclear dynamics

The nuclear dynamics cannot be described by a single classical trajectory (like in the ground state -adiabatically separated- case)



Why trajectory-based approaches?

W1 In "conventional" nuclear wavepacket propagation potential energy surfaces are needed.

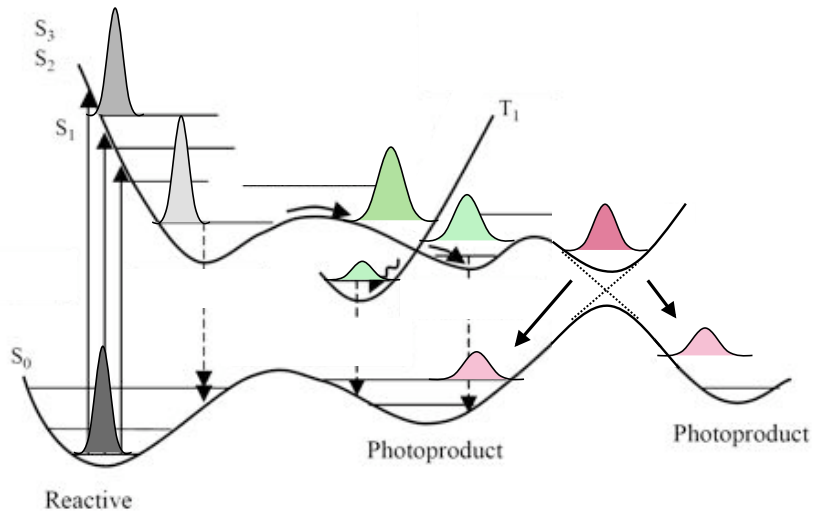
W2 Difficulty to obtain and fit potential energy surfaces for large molecules.

W3 Nuclear wavepacket dynamics is very expensive for large systems (6 degrees of freedom, 30 for MCTDH). Bad scaling.

T1 Trajectory based approaches can be run *on-the-fly* (no need to parametrize potential energy surfaces).

T2 Can handle large molecules in the full (unconstraint) configuration space.

T3 They offer a good **compromise** between accuracy and computational effort.



Starting point

The starting point is the molecular time-dependent Schrödinger equation :

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

where $\hat{H}$ is the molecular time-independent Hamiltonian and $\Psi(\boldsymbol{r},\boldsymbol{R},t)$ the total wavefunction (nuclear + electronic) of our system.

In mixed quantum-classical dynamics the nuclear dynamics is described by a swarm of classical trajectories (taking a "partial" limit $\hbar \to 0$ for the nuclear wf).

In this lecture we will discuss two main approximate solutions based on the following Ansätze for the total wavefucntion

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) \xrightarrow[\text{Huang}]{\text{Born-}} \sum_j^{\infty} \Phi_j(\boldsymbol{r};\boldsymbol{R})\Omega_j(\boldsymbol{R},t)$$

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) \xrightarrow{\text{Ehrenfest}} \Phi(\boldsymbol{r},t)\Omega(\boldsymbol{R},t)\exp\left[\frac{i}{\hbar}\int_{t_0}^{t} E_{el}(t')dt'\right]$$

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) \xrightarrow{\text{Exact Factorization}} \Phi_{\boldsymbol{R}}(\boldsymbol{r},t)\Omega(\boldsymbol{R},t); \quad \text{with} \quad \int d\boldsymbol{r}\ \Phi_{\boldsymbol{R}}(\boldsymbol{r},t) = 1,\ \forall \boldsymbol{R}.$$

Tarjectory-based quantum and mixed QM-CL solutions

We can "derive" the following trajectory-based solutions:

- Nonadiabatic Ehrenfest dynamics dynamics

  I. Tavernelli et al., *Mol. Phys.*, **103**, 963981 (2005).

- Adiabatic Born-Oppenheimer MD equations

- Nonadiabatic Bohmian Dynamics (NABDY)

  B. Curchod, IT, U. Rothlisberger, *PCCP*, **13**, 32313236 (2011)

- Nonadiabatic Trajectory Surface Hopping (TSH) dynamics
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  E. Tapavicza, I. Tavernelli, U. Rothlisberger, *PRL*, **98**, 023001 (2007)

- Time dependent potential energy surface approach
  based on the exact decomposition: $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \Omega(\boldsymbol{R}, t)\Phi(\boldsymbol{r}, t)$.

  A. Abedi, N. T. Maitra, E. K. U. Gross, *PRL*, **105**, 123002 (2010)

Ehrenfest dynamics

$$\Psi(\boldsymbol{r},\boldsymbol{R},t) \xrightarrow{\text{Ehrenfest}} \Phi(\boldsymbol{r},t)\Omega(\boldsymbol{R},t)\exp\left[\frac{i}{\hbar}\int_{t_0}^{t} E_{el}(t')dt'\right]$$

Inserting this representation of the total wavefunction into the molecular td Schrödinger equation and multiplying from the left-hand side by $\Omega^*(\boldsymbol{R},t)$ and integrating over $\boldsymbol{R}$ we get

$$i\hbar\frac{\partial\Phi(\boldsymbol{r},t)}{\partial t} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2\Phi(\boldsymbol{r},t) + \left[\int d\boldsymbol{R}\ \Omega^*(\boldsymbol{R},t)\hat{V}(\boldsymbol{r},\boldsymbol{R})\Omega(\boldsymbol{R},t)\right]\Phi(\boldsymbol{r},t)$$

where $\hat{V}(\boldsymbol{r},\boldsymbol{R}) = \sum_{i<j}\frac{e^2}{|\boldsymbol{r}_i-\boldsymbol{r}_j|} - \sum_{\gamma,i}\frac{e^2 Z_\gamma}{|\boldsymbol{R}_\gamma-\boldsymbol{r}_i|}$.
In a similar way, multiplying by $\Phi^*(\boldsymbol{r},t)$ and integrating over $\boldsymbol{r}$ we obtain

$$i\hbar\frac{\partial\Omega(\boldsymbol{R},t)}{\partial t} = -\frac{\hbar^2}{2}\sum_\gamma M_\gamma^{-1}\nabla_\gamma^2\Omega(\boldsymbol{R},t) + \left[\int d\boldsymbol{r}\ \Phi^*(\boldsymbol{r},t)\hat{\mathcal{H}}_{el}\Phi(\boldsymbol{r},t)\right]\Omega(\boldsymbol{R},t)$$

Conservation of energy has also to be imposed through the condition that $d\langle\hat{H}\rangle/dt \equiv 0$.

Note that both the electronic and nuclear parts evolve according to an average potential generated by the other component (in square brakets). These average potentials are time-dependent and are responsible for the feedback interaction between the electronic and nuclear components.

Ehrenfest dynamics - the nuclear equation

We start from the polar representation of the nuclear wavefunction

$$\Omega(\boldsymbol{R}, t) = A(\boldsymbol{R}, t) \exp\left[\frac{i}{\hbar} S(\boldsymbol{R}, t)\right]$$

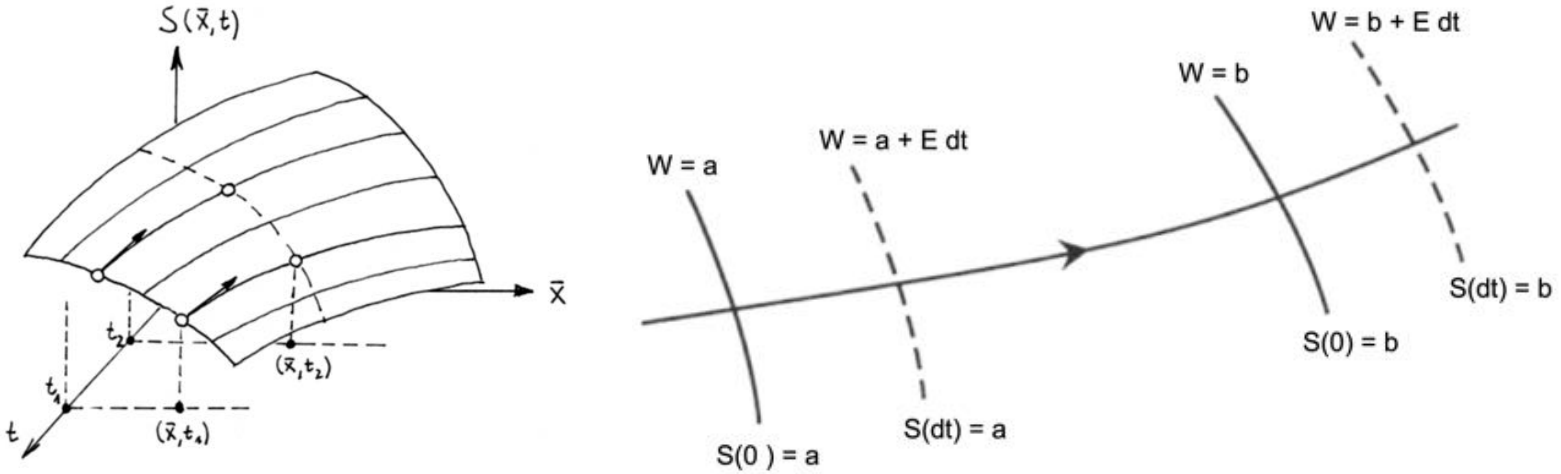
where the amplitude $A(\boldsymbol{R}, t)$ and the phase $S(\boldsymbol{R}, t)/\hbar$ are real functions.
Inserting this representation for $\Omega(\boldsymbol{R}, t)$ and separating the real and the imaginary parts one gets for the phase S in the classical limit $\hbar \to 0$

$$\frac{\partial S}{\partial t} = -\frac{1}{2}\sum_{\gamma} M_{\gamma}^{-1}\left(\nabla_{\gamma} S\right)^2 - \left[\int d\boldsymbol{r}\ \Phi^*(\boldsymbol{r}, t)\hat{\mathcal{H}}_{el}(\boldsymbol{r}, \boldsymbol{R})\Phi(\boldsymbol{r}, t)\right]$$

This has the form of the "Hamilton-Jacobi" (HJ) equation of classical mechanics, which establishes a relation between the partial differential equation for $S(\boldsymbol{R}, t)$ in configuration space and the trajectories of the corresponding (quantum) mechanical systems.

Ehrenfest dynamics - the nuclear equation

$$\frac{\partial S}{\partial t} = -\frac{1}{2}\sum_{\gamma} M_{\gamma}^{-1}\left(\nabla_{\gamma} S\right)^2 - \left[\int d\boldsymbol{r}\ \Phi^*(\boldsymbol{r},t)\hat{\mathcal{H}}_{el}(\boldsymbol{r},\boldsymbol{R})\Phi(\boldsymbol{r},t)\right]$$



Instead of solving the field equation for $S(\boldsymbol{R},t)$, find the equation of motion for the corresponding trajectories (*characteristics*).

Ehrenfest dynamics - the nuclear equation

The identification of $S(\boldsymbol{R}, t)$ with the "classical" action, defines a point-particle dynamics with Hamiltonian, H_{cl} and momenta

$$\boldsymbol{P} = \nabla_{\boldsymbol{R}} S(\boldsymbol{R}).$$

The solutions of this Hamiltonian system are curves (*characteristics*) in the $(\boldsymbol{R}, t)$-space, which are extrema of the action $S(\boldsymbol{R}, t)$ for given initial conditions $\boldsymbol{R}(t_0)$ and $\boldsymbol{P}(t_0) = \nabla_{\boldsymbol{R}} S(\boldsymbol{R})|_{\boldsymbol{R}(t_0)}$. Newton-like equation for the nuclear trajectories corresponding to the HJ equation

$$\frac{d\boldsymbol{P}_\gamma}{dt} = -\nabla_\gamma \left[\int d\boldsymbol{r}\ \Phi^*(\boldsymbol{r}, t) \hat{\mathcal{H}}_{el}(\boldsymbol{r}, \boldsymbol{R}) \Phi(\boldsymbol{r}, t) \right]$$

Ehrenfest dynamics

$$i\hbar \frac{\partial \Phi(\boldsymbol{r}; \boldsymbol{R}, t)}{\partial t} = \hat{\mathcal{H}}_{el}(\boldsymbol{r}; \boldsymbol{R}) \Phi(\boldsymbol{r}; \boldsymbol{R}, t)$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I \langle \hat{\mathcal{H}}_{el}(\boldsymbol{r}; \boldsymbol{R}) \rangle$$

Ehrenfest dynamics - the nuclear equation

The identification of $S(\boldsymbol{R}, t)$ with the "classical" action, defines a point-particle dynamics with Hamiltonian, H_{cl} and momenta

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Ehrenfest dynamics - Densityfunctionalization (ϕ_k: KS orbitals)

$$i\hbar \frac{\partial}{\partial t} \phi_k(\boldsymbol{r}, t) = -\frac{1}{2m_e} \nabla^2_{\boldsymbol{r}} \phi_k(\boldsymbol{r}, t) + v_{\text{eff}}[\rho, \Phi_0](\boldsymbol{r}, t)\, \phi_k(\boldsymbol{r}, t)$$

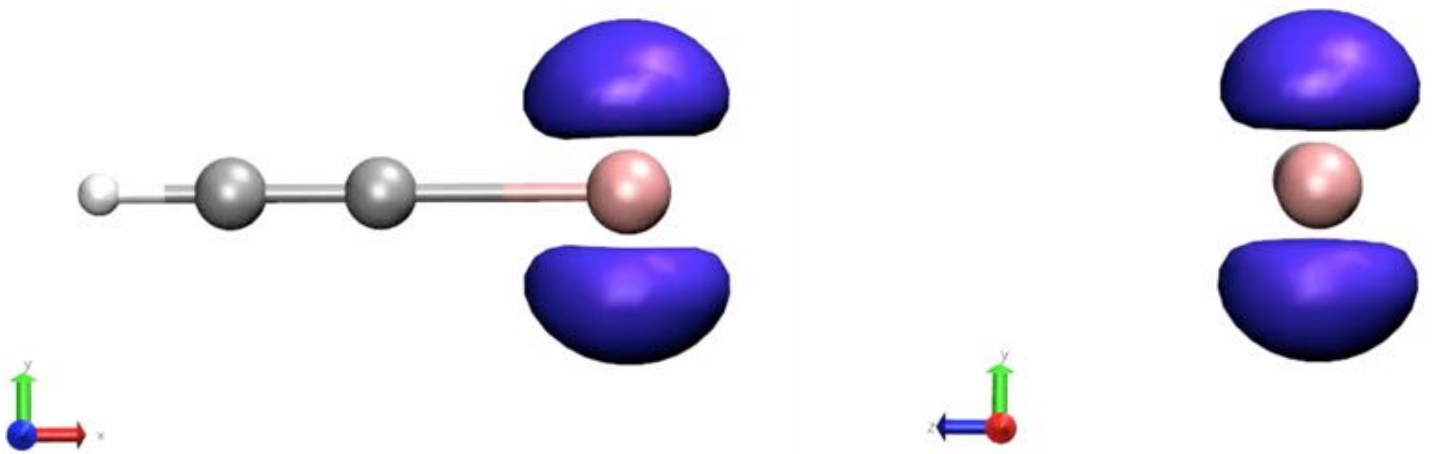
$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E[\rho(\boldsymbol{r}, t)]$$

Ehrenfest dynamics - Example

Ehrenfest dynamics

$$i\hbar\frac{\partial}{\partial t}\phi_k(\boldsymbol{r},t) = -\frac{1}{2m_e}\nabla^2_{\boldsymbol{r}}\phi_k(\boldsymbol{r},t) + v_{\text{eff}}[\rho,\Phi_0](\boldsymbol{r},t)\,\phi_k(\boldsymbol{r},t)$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I\langle\hat{\mathcal{H}}_{el}(\boldsymbol{r};\boldsymbol{R})\rangle$$



Ehrenfest dynamics and mixing of electronic states

Ehrenfest dynamics

$$i\hbar\frac{\partial\Phi(\boldsymbol{r};\boldsymbol{R},t)}{\partial t} = \hat{\mathcal{H}}_{el}(\boldsymbol{r};\boldsymbol{R})\Phi(\boldsymbol{r};\boldsymbol{R},t)$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I\langle\hat{\mathcal{H}}_{el}(\boldsymbol{r};\boldsymbol{R})\rangle$$

Consider the following expansion of $\Phi(\boldsymbol{r};\boldsymbol{R},t)$ in the *static* basis of electronic wavefucntions $\{\Phi_k(\boldsymbol{r};\boldsymbol{R})\}$

$$\Phi(\boldsymbol{r};\boldsymbol{R},t) = \sum_{k=0}^{\infty} c_k(t)\Phi_k(\boldsymbol{r};\boldsymbol{R})$$

The time-dependency is now on the set of coefficients $\{c_k(t)\}$ ($|c_k(t)|^2$ is the population of state k). Inserting in the Ehrenfest's equations...

Ehrenfest dynamics and mixing of electronic states

Ehrenfest dynamics

$$i\hbar\dot{c}_k(t) = c_k(t)E_k^{el} - i\hbar\sum_j c_j(t)D_{kj}$$

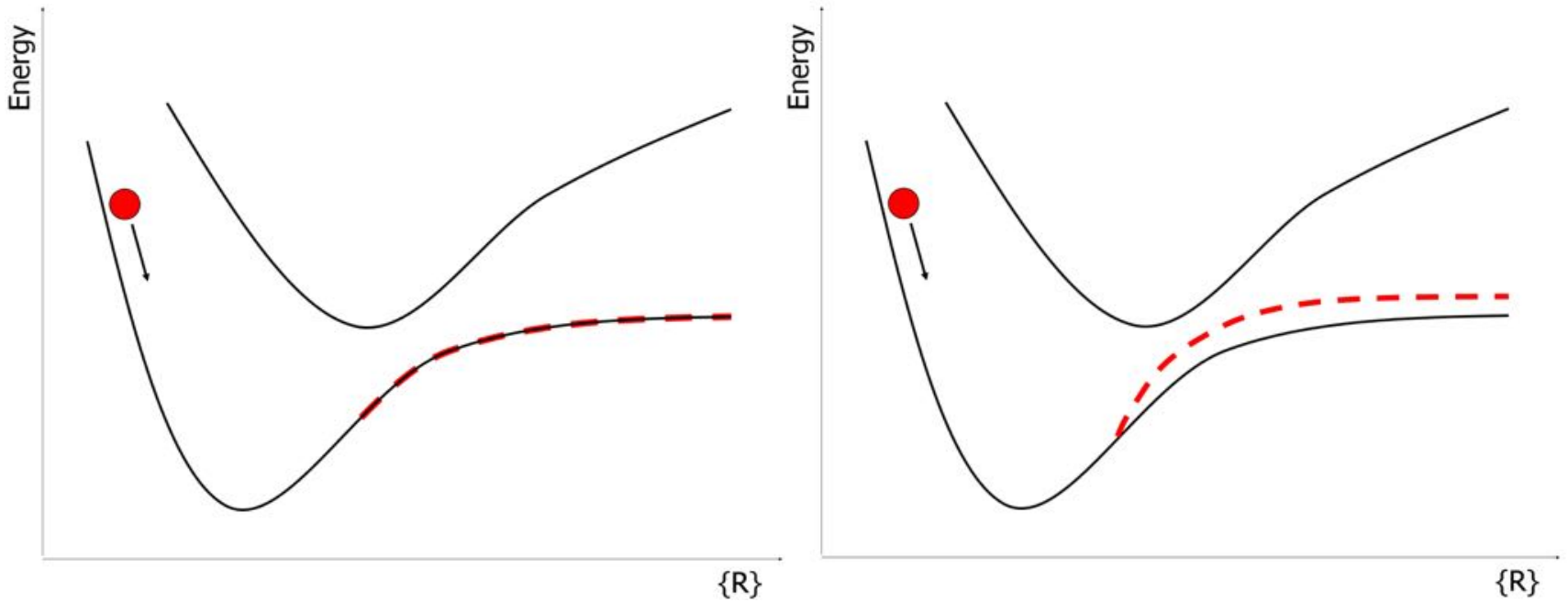
$$M_I\ddot{\mathbf{R}}_I = -\nabla_I\sum_{k=0}^{\infty}|c_k(t)|^2E_k^{el}$$

where

$$D_{kj} = \langle\Phi_k|\frac{\partial}{\partial t}|\Phi_j\rangle = \langle\Phi_k|\frac{\partial \boldsymbol{R}}{\partial t}\frac{\partial}{\partial \boldsymbol{R}}|\Phi_j\rangle = \dot{\mathbf{R}}\langle\Phi_k|\nabla|\Phi_j\rangle = \dot{\mathbf{R}}\cdot\mathbf{d}_{kj}$$

Thus we incorporate directly nonadiabatic effects.

Ehrenfest dynamics: the mean-field potential



$$i\hbar\dot{c}_k(t) = c_k(t)E_k^{el} - i\hbar\sum_j c_j(t)D_{kj}$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I\sum_{k=0}^{\infty}|c_k(t)|^2E_k^{el}$$

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Born-Oppenheimer approximation

$$\Psi(\boldsymbol{r}, \boldsymbol{R}, t) \xrightarrow[\text{Huang}]{\text{Born-}} \sum_{j}^{\infty} \Phi_j(\boldsymbol{r}; \boldsymbol{R}) \Omega_j(\boldsymbol{R}, t)$$

In this equation, $\{\Phi_j(\boldsymbol{r}; \boldsymbol{R})\}$ describes a complete basis of electronic states solution of the time-independent Schrödinger equation:

$$\hat{\mathcal{H}}_{el}(\boldsymbol{r}; \boldsymbol{R}) \Phi_j(\boldsymbol{r}; \boldsymbol{R}) = E_{el,j}(\boldsymbol{R}) \Phi_j(\boldsymbol{r}; \boldsymbol{R})$$

$\boldsymbol{R}$ is taken as a parameter.
Eigenfunctions of $\hat{\mathcal{H}}_{el}(\boldsymbol{r}; \boldsymbol{R})$ are considered to be orthonormal, i.e. $\langle \Phi_j | \Phi_i \rangle = \delta_{ij}$.

Born-Oppenheimer approximation

$$\Psi(\boldsymbol{r}, \boldsymbol{R}, t) \xrightarrow[\text{Huang}]{\text{Born-}} \sum_j^{\infty} \Phi_j(\boldsymbol{r}; \boldsymbol{R}) \Omega_j(\boldsymbol{R}, t)$$

Electrons are *static*. Use your favourite electronic structure method.

For the nuclei, insert this *Ansatz* into the molecular time-dependent Schrödinger equation

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

After left multiplication by $\Phi_k^*(\boldsymbol{r}; \boldsymbol{R})$ and integration over $\boldsymbol{r}$, we obtain the following equation (we used $\langle \Phi_j | \Phi_i \rangle = \delta_{ij}$) :

$$\left[-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_{el,k}(\boldsymbol{R}) \right] \Omega_k(\boldsymbol{R}, t) + \sum_j^{\infty} D_{kj} \Omega_j(\boldsymbol{R}, t) = i\hbar \frac{\partial}{\partial t} \Omega_k(\boldsymbol{R}, t)$$

Born-Oppenheimer approximation

$$\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + E_{el,k}(\boldsymbol{R})\right]\Omega_k(\boldsymbol{R},t) + \sum_j D_{kj}\Omega_j(\boldsymbol{R},t) = i\hbar\frac{\partial}{\partial t}\Omega_k(\boldsymbol{R},t)$$

- Equation for the nuclear "wavepacket", $\Omega(\boldsymbol{R},t)$, dynamics.
- $E_{el,k}(\boldsymbol{R})$ represents a potential energy surface for the nuclei.

Important additional term : D_{kj} ! NONADIABATIC COUPLING TERMS

$$D_{kj} = \int \Phi_k^*(\boldsymbol{r};\boldsymbol{R})\left[\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\right]\Phi_j(\boldsymbol{r};\boldsymbol{R})d\boldsymbol{r} + \sum_I \frac{1}{M_I}\left\{\int \Phi_k^*(\boldsymbol{r};\boldsymbol{R})\left[-i\hbar\nabla_I\right]\Phi_j(\boldsymbol{r};\boldsymbol{R})d\boldsymbol{r}\right\}\left[-i\hbar\nabla_I\right]$$

Born-Oppenheimer approximation

$$D_{kj} = \int \Phi_k^*(\boldsymbol{r};\boldsymbol{R}) \left[\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\right] \Phi_j(\boldsymbol{r};\boldsymbol{R}) d\boldsymbol{r} + \sum_I \frac{1}{M_I} \left\{\int \Phi_k^*(\boldsymbol{r};\boldsymbol{R}) \left[-i\hbar\nabla_I\right] \Phi_j(\boldsymbol{r};\boldsymbol{R}) d\boldsymbol{r}\right\} \left[-i\hbar\nabla_I\right]$$

If we neglect all the D_{kj} terms (diagonal and off-diagonal), we have the Born-Oppenheimer approximation.

$$\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + E_{el,k}(\boldsymbol{R})\right] \Omega_k(\boldsymbol{R},t) = i\hbar\frac{\partial}{\partial t}\Omega_k(\boldsymbol{R},t)$$

Mainly for ground state dynamics or for dynamics on states that do not couple with others. (Back to nonadiabatic dynamics later).

Born-Oppenheimer approximation: the nuclear trajectories

$$\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + E_{el,k}(\boldsymbol{R})\right]\Omega_k(\boldsymbol{R},t) = i\hbar\frac{\partial}{\partial t}\Omega_k(\boldsymbol{R},t)$$

Using a polar expansion for $\Omega_k(\boldsymbol{R},t)$, we may find a way to obtain classical equation of motions for the nuclei.

$$\Omega_k(\boldsymbol{R},t) = A_k(\boldsymbol{R},t)\exp\left[\frac{i}{\hbar}S_k(\boldsymbol{R},t)\right].$$

$A_k(\boldsymbol{R},t)$ represents an amplitude and $S_k(\boldsymbol{R},t)/\hbar$ a phase.

Further: insert the polar representation into the equation above, do some algebra, and separate real and imaginary part, we obtain an interesting set of equations:

Born-Oppenheimer approximation: the nuclear trajectories

$$\frac{\partial S_k}{\partial t} = \frac{\hbar^2}{2} \sum_I M_I^{-1} \frac{\nabla_I^2 A_k}{A_k} - \frac{1}{2} \sum_I M_I^{-1} (\nabla_I S_k)^2 - E_k$$

$$\frac{\partial A_k}{\partial t} = -\sum_I M_I^{-1} \nabla_I A_k \nabla_I S_k - \frac{1}{2} \sum_I M_I^{-1} A_k \nabla_I^2 S_k$$

Dependences of the functions S and A are omitted for clarity (k is a index for the electronic state; in principle there is only one state in the adiabatic case).

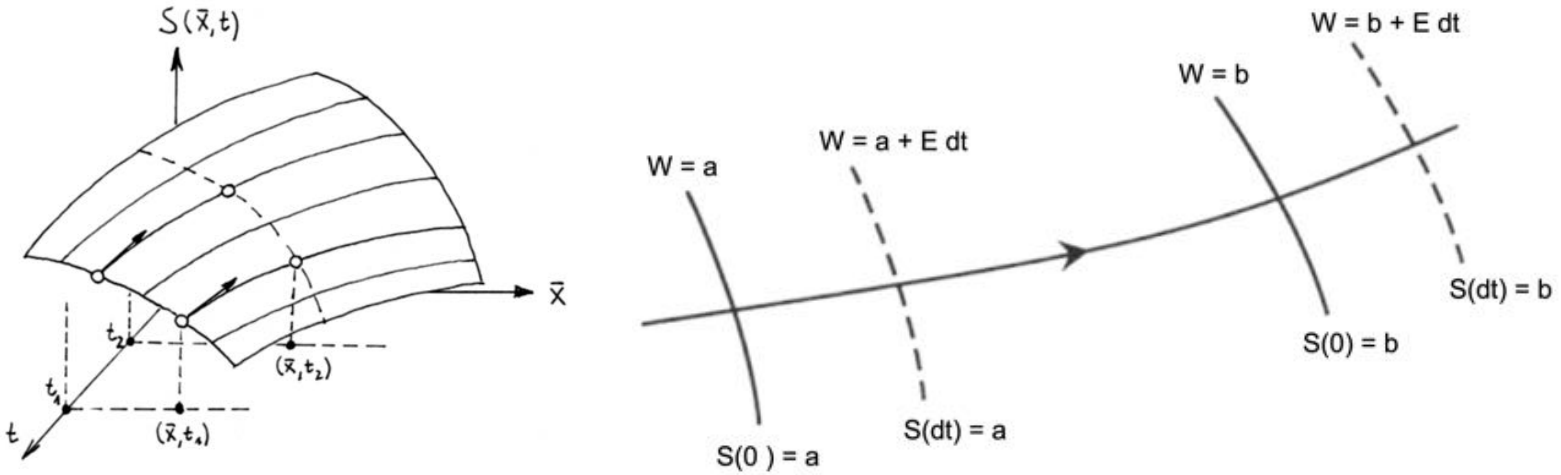
We have now a time-dependent equation for both the amplitude and the phase.
Since we are in the adiabatic case there is only one PES and the second equation becomes trivially a diffusion continuity equation.

The nuclear dynamics is derived from the real part ($\frac{\partial S_k}{\partial t}$). This equation has again the form of a *classical* Hamilton-Jacobi equation.

Born-Oppenheimer approximation: the nuclear trajectories

$$\frac{\partial S_k}{\partial t} = \frac{\hbar^2}{2} \sum_I M_I^{-1} \frac{\nabla_I^2 A_k}{A_k} - \frac{1}{2} \sum_I M_I^{-1} (\nabla_I S_k)^2 - E_k$$

$$\frac{\partial A_k}{\partial t} = -\sum_I M_I^{-1} \nabla_I A_k \nabla_I S_k - \frac{1}{2} \sum_I M_I^{-1} A_k \nabla_I^2 S_k$$



Instead of solving the field equation for $S(\boldsymbol{R}, t)$, find the equation of motion for the corresponding trajectories (*characteristics*).

Born-Oppenheimer approximation: the nuclear trajectories

$$\frac{\partial S_k}{\partial t} = \frac{\hbar^2}{2}\sum_I M_I^{-1}\frac{\nabla_I^2 A_k}{A_k} - \frac{1}{2}\sum_I M_I^{-1}\left(\nabla_I S_k\right)^2 - E_k$$

The classical limit is obtained by taking[1]: $\hbar \to 0$

$$\frac{\partial S_k}{\partial t} = -\frac{1}{2}\sum_I M_I^{-1}\left(\nabla_I S_k\right)^2 - E_k$$

These are the classical Hamilton-Jacobi equation and S is the classical action related to a particle.

$$S(t) = \int_{t_0}^{t} L(t')dt' = \int_{t_0}^{t} \left[E_{kin}(t') - E_{pot}(t')\right] dt'$$

The momentum of a particle I is related to

$$\nabla_I S = \boldsymbol{p}_I = \frac{\boldsymbol{v}_I}{M_I}$$

[1] Caution! This classical limit is subject to controversy...

Born-Oppenheimer approximation: the nuclear trajectories

Therefore, taking the gradient,

$$-\nabla_J \frac{\partial S_k}{\partial t} = \frac{1}{2}\nabla_J \sum_I M_I^{-1} \left(\nabla_I S_k\right)^2 + \nabla_J E_k$$

and rearranging this equation using $\nabla_J S_k / M_J = \boldsymbol{v}_J^k$, we obtain the (familiar) Newton equation:

$$M_J \frac{d}{dt} \boldsymbol{v}_J^k = -\nabla_J E_k$$

In Summary:

Adiabatic BO MD

$$\hat{\mathcal{H}}_{el}(\boldsymbol{r};\boldsymbol{R})\Phi_k(\boldsymbol{r};\boldsymbol{R}) = E_k^{el}(\boldsymbol{R})\Phi_k(\boldsymbol{r};\boldsymbol{R})$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_k^{el}(\boldsymbol{R}) = -\underset{min\Phi_k}{\nabla_I} \langle \Phi_k | \hat{\mathcal{H}}_{el} | \Phi_k \rangle$$

Mean-field vs. BO MD (adiabatic case)

Ehrenfest dynamics

$$i\hbar\frac{\partial\Phi(\boldsymbol{r};\boldsymbol{R},t)}{\partial t} = \hat{\mathcal{H}}_{el}(\boldsymbol{r};\boldsymbol{R})\Phi(\boldsymbol{r};\boldsymbol{R},t)$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I\langle\hat{\mathcal{H}}_{el}(\boldsymbol{r};\boldsymbol{R})\rangle$$

Explicit time dependence of the electronic wavefunction.

Born-Oppenheimer dynamics

$$\hat{\mathcal{H}}_{el}(\boldsymbol{r};\boldsymbol{R})\Phi_k(\boldsymbol{r};\boldsymbol{R}) = E_k^{el}(\boldsymbol{R})\Phi_k(\boldsymbol{r};\boldsymbol{R})$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I E_k^{el}(\boldsymbol{R}) = -\underset{min\Phi_k}{\nabla_I}\langle\Phi_k|\hat{\mathcal{H}}_{el}|\Phi_k\rangle$$

The electronic wavefunction are *static* (only implicit time-dependence.

Mean-field vs. BO MD (adiabatic case)

Method	Born-Oppenheimer MD	Ehrenfest MD
	adiabatic MD (one PES)	nonadiabatic MD (mean-field)
	Efficient propagation of the nuclei	Get the "real" dynamics of the electrons
	Adiabatic nuclear propagation	Propagation of nuclei & electrons
	$\delta t \sim$10-20 a.u. (0.25-0.5 fs)	$\delta t \sim$0.01 a.u. (0.25 as)
	Simple algorithm	Common propagation of the nuclei and the electrons implies more sophisticated algorithms

Exact quantum dynamics?

Can we derive "exact" quantum equations of motion for the nuclei?
(without taking the classical limit $\hbar \to 0$?)

Tarjectory-based quantum and mixed QM-CL solutions

We can "derive" the following trajectory-based solutions:

- Nonadiabatic Ehrenfest dynamics dynamics

  I. Tavernelli et al., *Mol. Phys.*, **103**, 963981 (2005).

- Adiabatic Born-Oppenheimer MD equations

- Nonadiabatic Bohmian Dynamics (NABDY)

  B. Curchod, IT*, U. Rothlisberger, *PCCP*, **13**, 32313236 (2011)

- Nonadiabatic Trajectory Surface Hopping (TSH) dynamics
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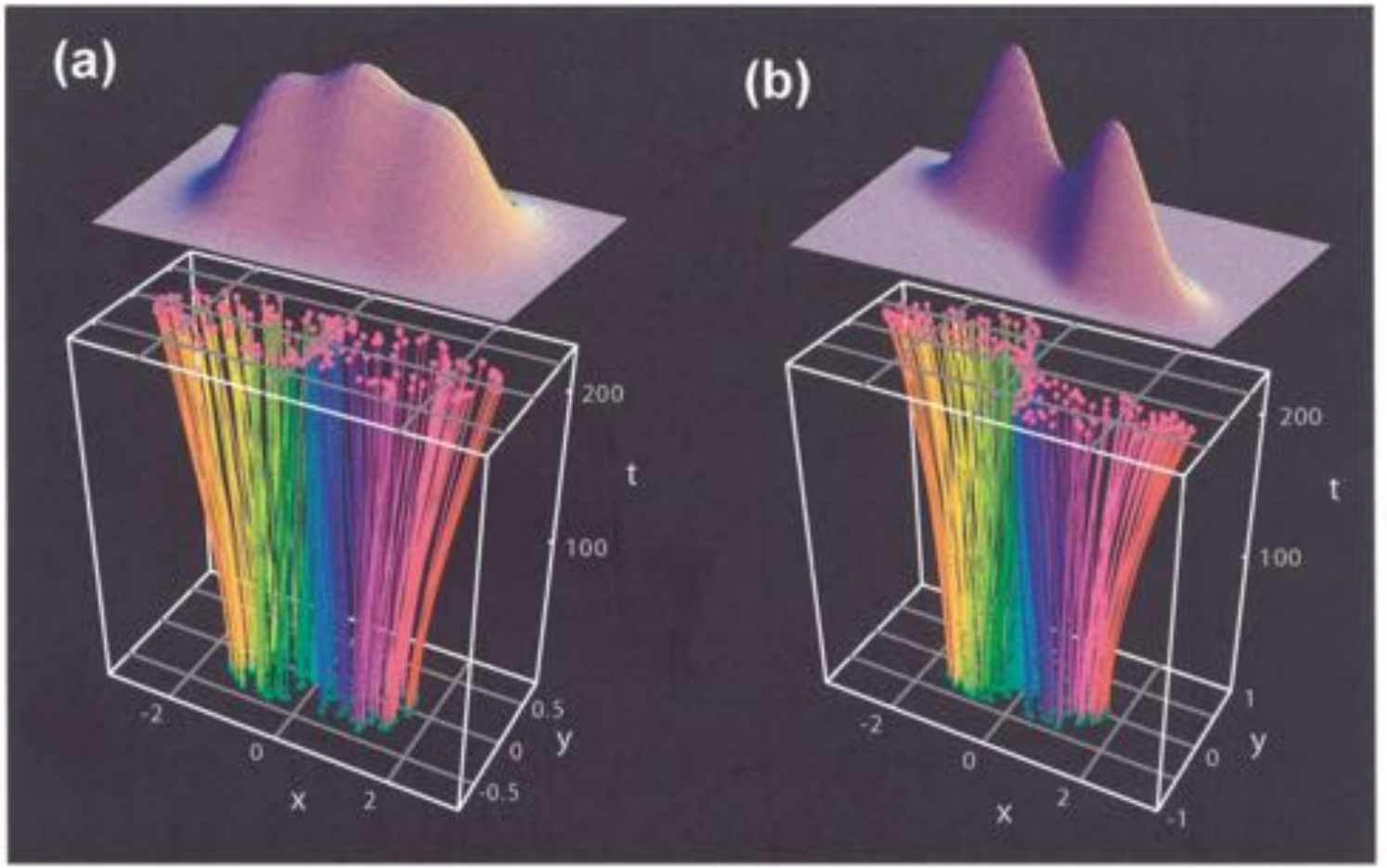
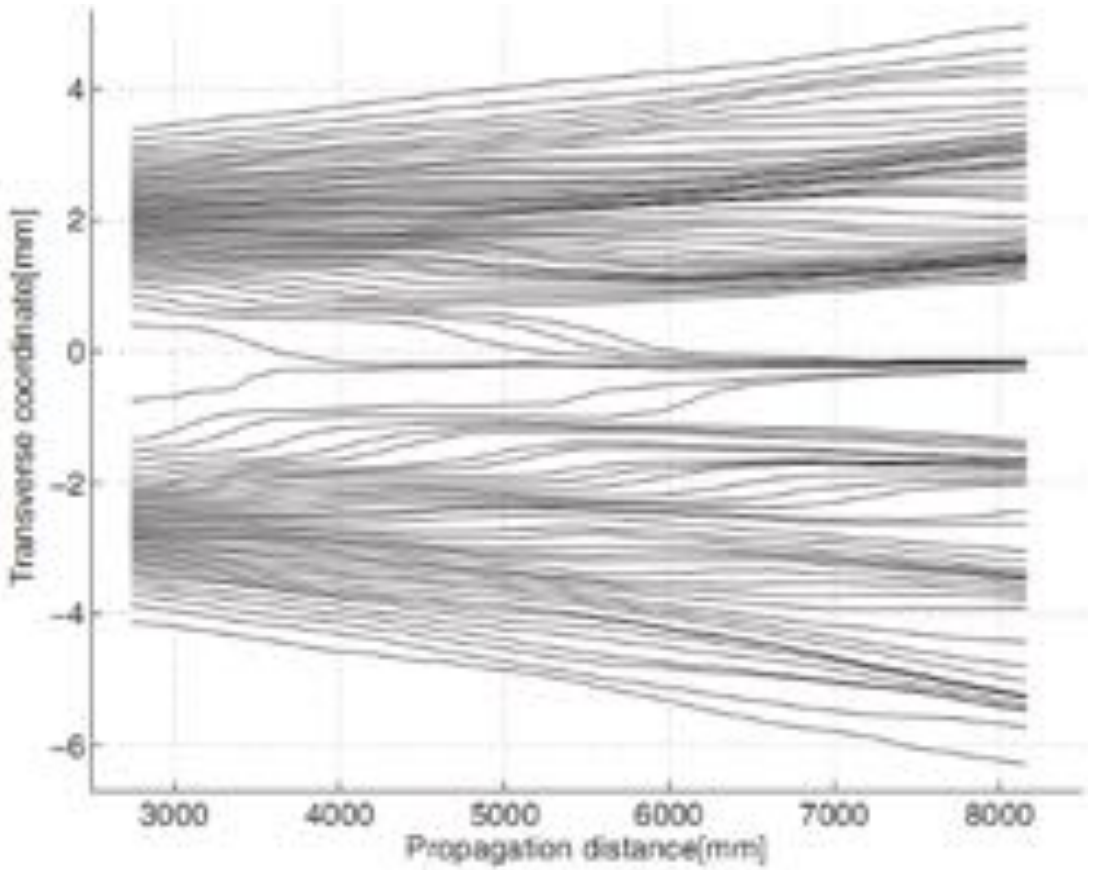
- Time dependent potential energy surface approach
  based on the exact decomposition: $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \Omega(\boldsymbol{R}, t)\Phi(\boldsymbol{r}, t)$.

  A. Abedi, N. T. Maitra, E. K. U. Gross, *PRL*, **105**, 123002 (2010)

Nonadiabatic dynamics: Multi-trajectory solutions



Nonadiabatic Bohmian dynamics



Pioneers in quantum hydrodynamics: D. Bohm, P. R. Holland, R. E. Wyatt, and many others.

NABDY: "exact" trajectory-based nonadiabatic dynamics

Using

- $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \sum_j^{\infty} \Phi_j(\boldsymbol{r}; \boldsymbol{R})\Omega_j(\boldsymbol{R}, t)$
- $\Omega_j(\boldsymbol{R}, t) = A_j(\boldsymbol{R}, t) \exp\left[\frac{i}{\hbar} S_j(\boldsymbol{R}, t)\right]$

in the exact time-dependent Schrödinger equation for the nuclear wavefucntion we get

$$
\begin{aligned}
-\frac{\partial S_j(\boldsymbol{R}, t)}{\partial t} =& \sum_{\gamma} \frac{1}{2M_\gamma} \left(\nabla_\gamma S_j(\boldsymbol{R}, t)\right)^2 + E_j^{el}(\boldsymbol{R}) - \sum_{\gamma} \frac{\hbar^2}{2M_\gamma} \frac{\nabla_\gamma^2 A_j(\boldsymbol{R}, t)}{A_j(\boldsymbol{R}, t)} \\
&+ \sum_{\gamma i} \frac{\hbar^2}{2M_\gamma} D_{ji}^{\gamma}(\boldsymbol{R}) \frac{A_i(\boldsymbol{R}, t)}{A_j(\boldsymbol{R}, t)} \Re\left[e^{i\phi}\right] - \sum_{\gamma, i\neq j} \frac{\hbar^2}{M_\gamma} \boldsymbol{d}_{ji}^{\gamma}(\boldsymbol{R}) \frac{\nabla_\gamma A_i(\boldsymbol{R}, t)}{A_j(\boldsymbol{R}, t)} \Re\left[e^{i\phi}\right] \\
&+ \sum_{\gamma, i\neq j} \frac{\hbar}{M_\gamma} \boldsymbol{d}_{ji}^{\gamma}(\boldsymbol{R}) \frac{A_i(\boldsymbol{R}, t)}{A_j(\boldsymbol{R}, t)} \nabla_\gamma S_i(\boldsymbol{R}, t) \Im\left[e^{i\phi}\right]
\end{aligned}
$$

and

$$
\begin{aligned}
\frac{\partial A_j(\boldsymbol{R}, t)}{\partial t} =& -\sum_{\gamma} \frac{1}{M_\gamma} \nabla_\gamma A_j(\boldsymbol{R}, t) \nabla_\gamma S_j(\boldsymbol{R}, t) - \sum_{\gamma} \frac{1}{2M_\gamma} A_j(\boldsymbol{R}, t) \nabla_\gamma^2 S_j(\boldsymbol{R}, t) \\
&+ \sum_{\gamma i} \frac{\hbar}{2M_\gamma} D_{ji}^{\gamma}(\boldsymbol{R}) A_i(\boldsymbol{R}, t) \Im\left[e^{i\phi}\right] - \sum_{\gamma, i\neq j} \frac{\hbar}{M_\gamma} \boldsymbol{d}_{ji}^{\gamma}(\boldsymbol{R}) \nabla_\gamma A_i(\boldsymbol{R}, t) \Im\left[e^{i\phi}\right] \\
&- \sum_{\gamma, i\neq j} \frac{1}{M_\gamma} \boldsymbol{d}_{ji}^{\gamma}(\boldsymbol{R}) A_i(\boldsymbol{R}, t) \nabla_\gamma S_i(\boldsymbol{R}, t) \Re\left[e^{i\phi}\right],
\end{aligned}
$$

where both $S_j(\boldsymbol{R}, t)$ and $A_j(\boldsymbol{R}, t)$ are real fields and $\phi = \frac{1}{\hbar}(S_i(\boldsymbol{R}, t) - S_j(\boldsymbol{R}, t))$.

NABDY: "exact" trajectory-based nonadiabatic dynamics

From the NABDY equations we can obtain a Newton-like equation of motion (using the HJ definition of the momenta $\nabla_\beta S_j(\boldsymbol{R}, t) = \boldsymbol{P}^j_\beta$)

$$M_\beta \frac{d^2 \boldsymbol{R}_\beta}{(dt^j)^2} = -\nabla_\beta \left[E^j_{el}(\boldsymbol{R}) + \mathcal{Q}_j(\boldsymbol{R}, t) + \sum\nolimits_i D_{ij}(\boldsymbol{R}, t) \right]$$

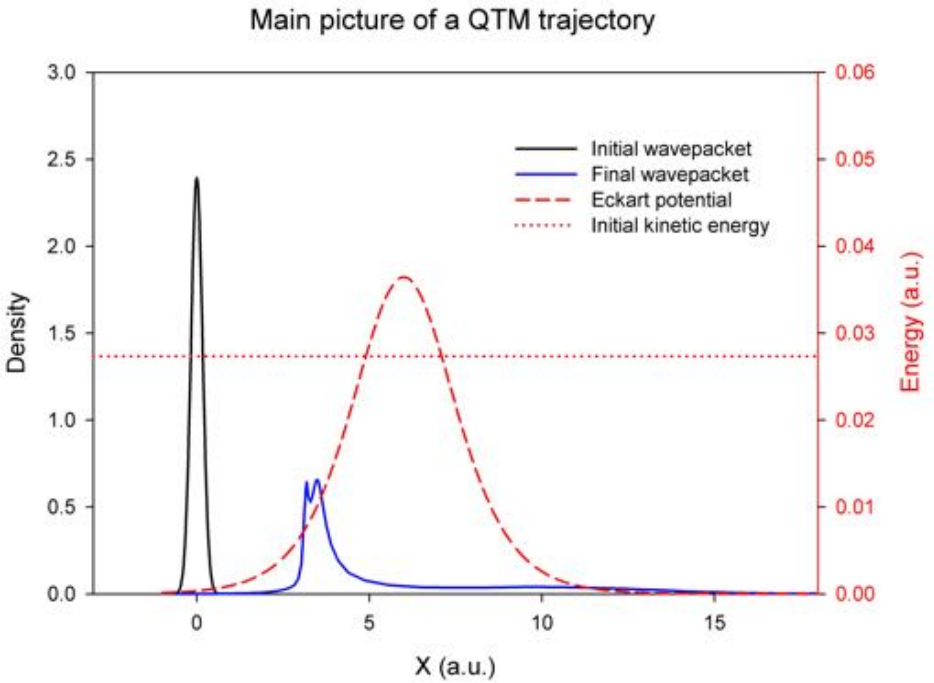
where $\mathcal{Q}_j(\boldsymbol{R}, t)$ is the quantum potential responsible for all coherence/decoherence "intrasurface" QM effects, and $\mathcal{D}_j(\boldsymbol{R}, t)$ is the *nonadiabatic* potential responsible for the amlpitude transfer among the different PESs.

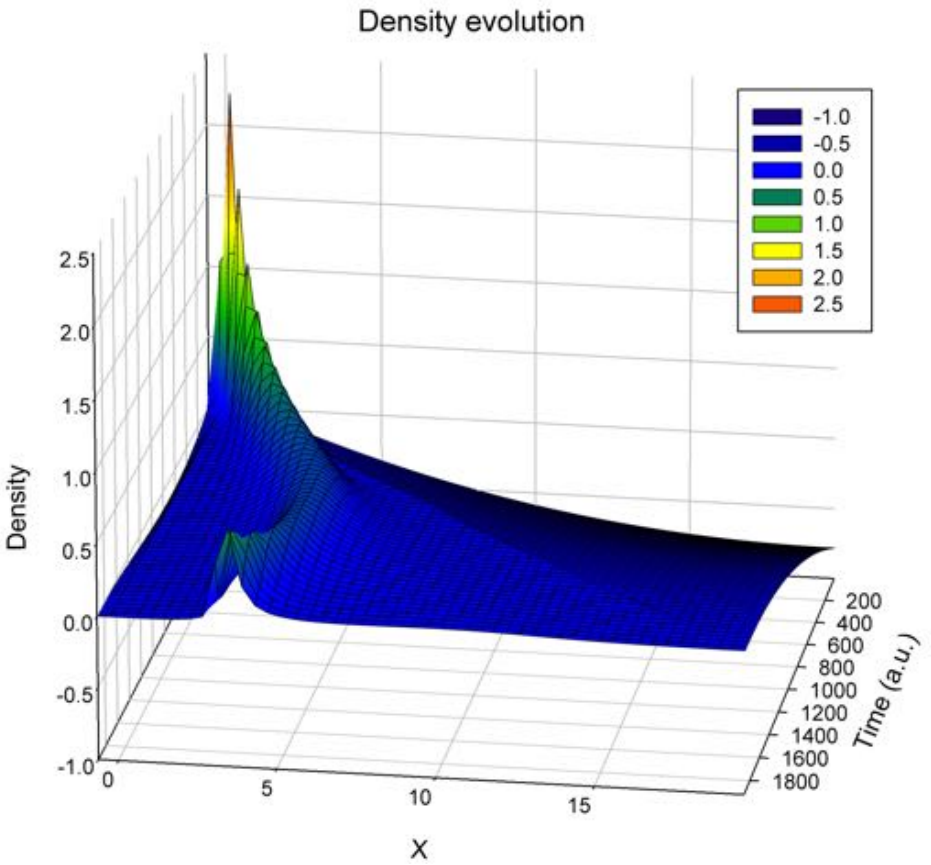
For more informations see:
B. Curchod, IT, U. Rothlisberger, *PCCP*, **13**, 3231 – 3236 (2011)

NABDY limitations

- Mainly numerical challenges
- Instabilities induced by the quantum potential
- Compute derivatives in the $3N$ dimensional($\mathbb{R}^{3N}$) configuration space

Gaussian wavepacket on an Eckart potential ($E_k = 3/4V$)





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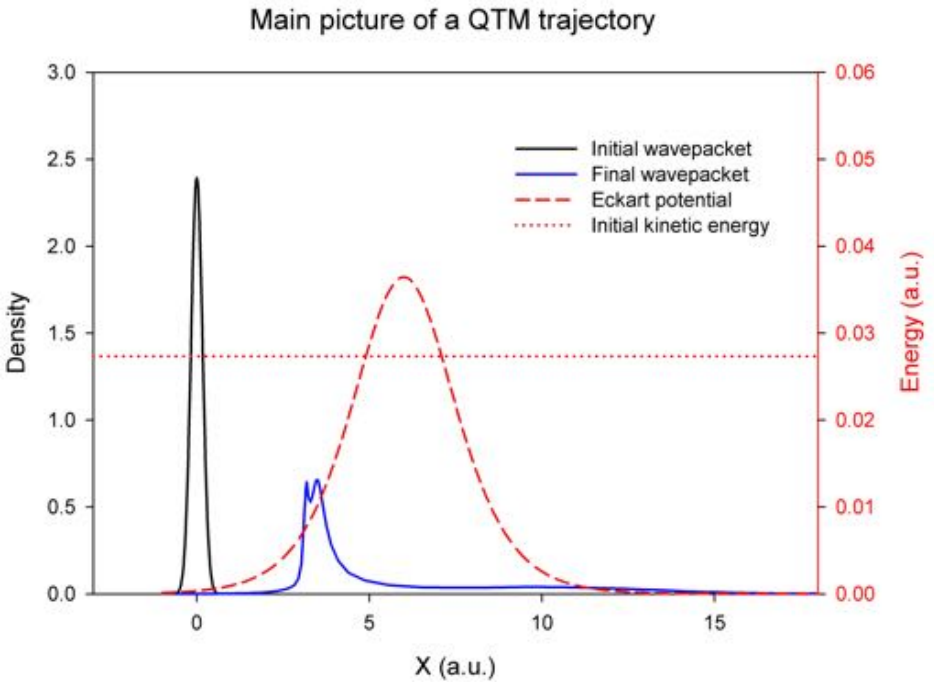
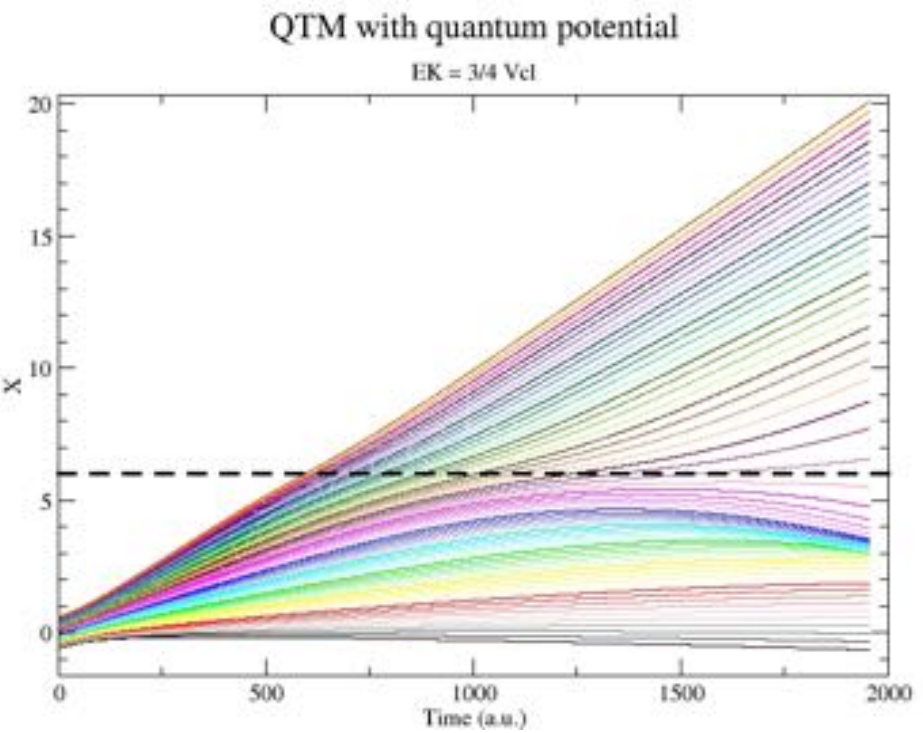
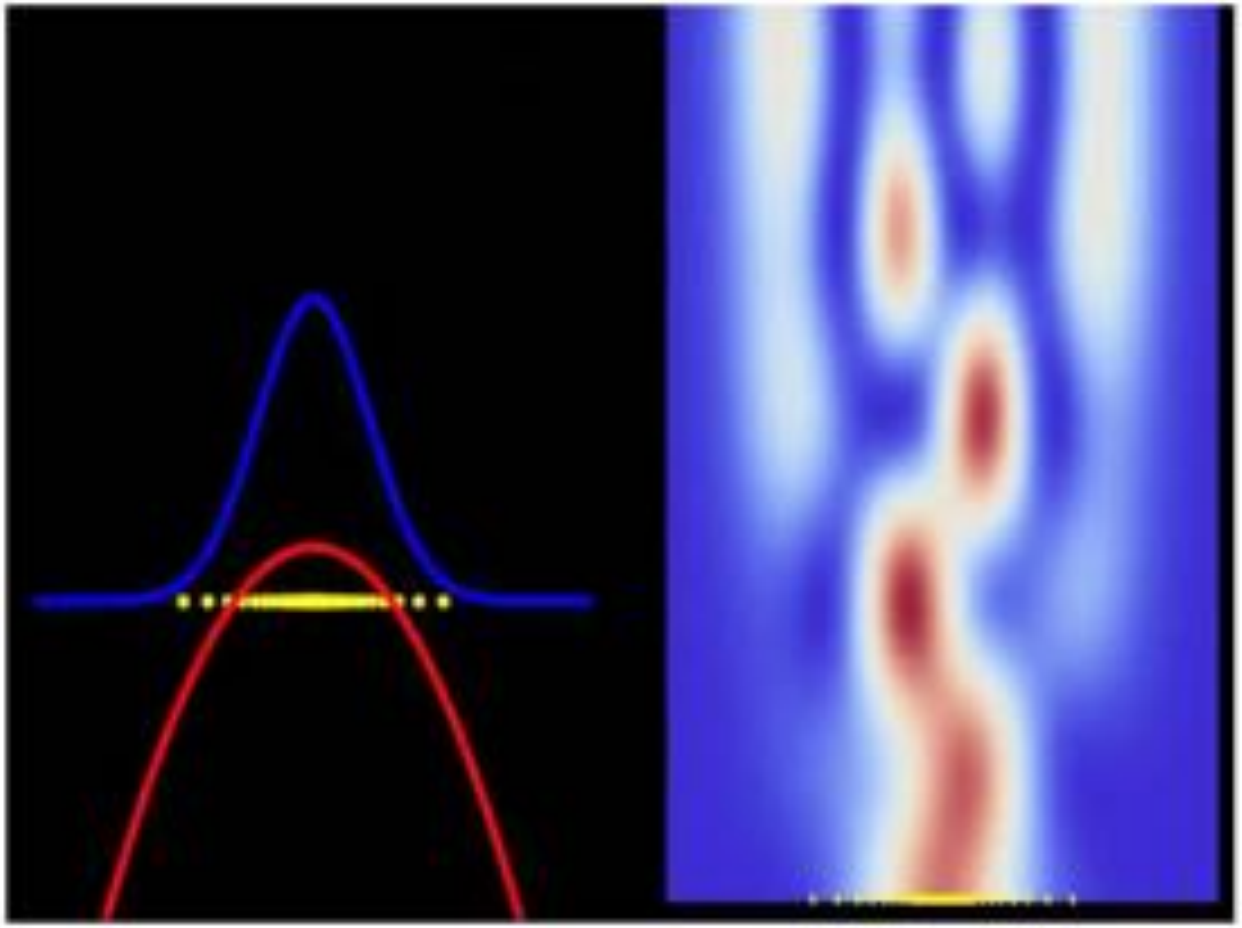
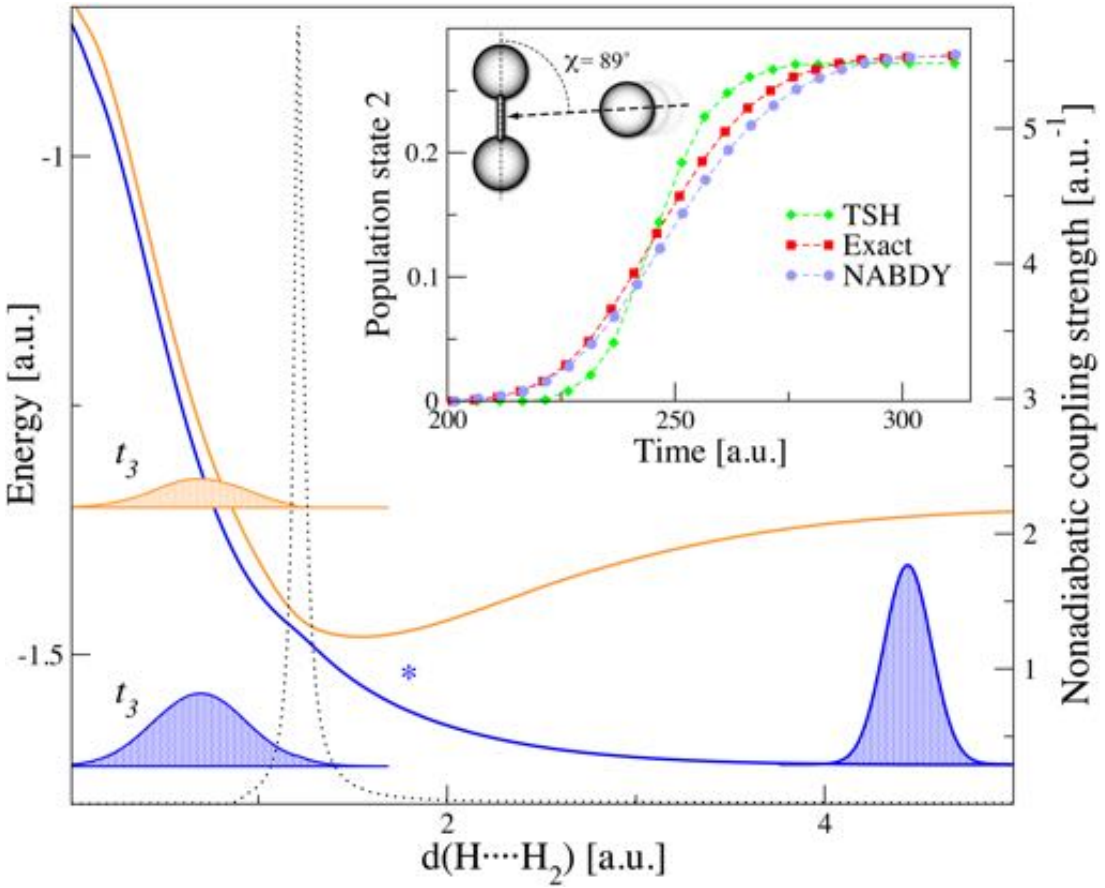






Bohmian Quantum Hydrodynamics: $H_2 + H$ collision



Current and future developments of NABDY:

- ✓ Extension to higher dimensions (configuration space)
- ✓ Off-grid propagation of the amplitudes
- Implementation in CPMD

[B.F.E. Curchod, IT, U.Rothlisberger, **PCCP**, 13, 3231 (2011)]

Bohmian dynamics in phase space

Study of the proton transfer dynamics in $N_2H_7^+$ (27-1 dimensions)

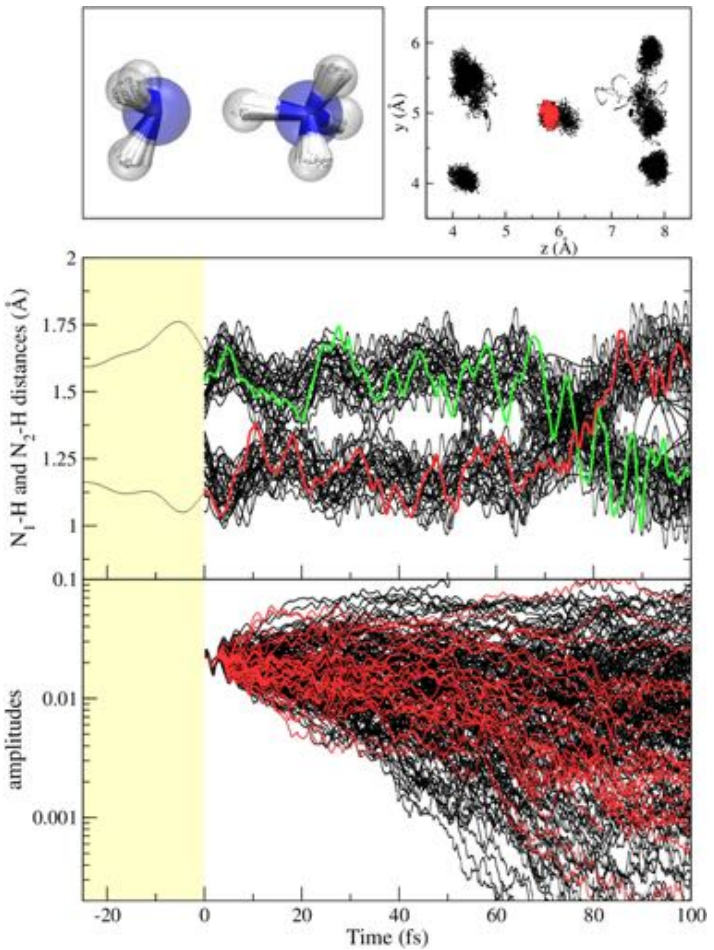
(N=9,M=20) fluid elements (FE) quantum dynamics.

Bohmian dynamics in phase space

Study of the proton transfer dynamics in $N_2H_7^+$ (27-1 dim. configuration space)

Fig. N-H distances for the central hydrogen atom.

Fig. Amplitudes associated to the hydrogen atoms.



I.T., *Phys. Rev. A*, **87**, 042501 (2014).

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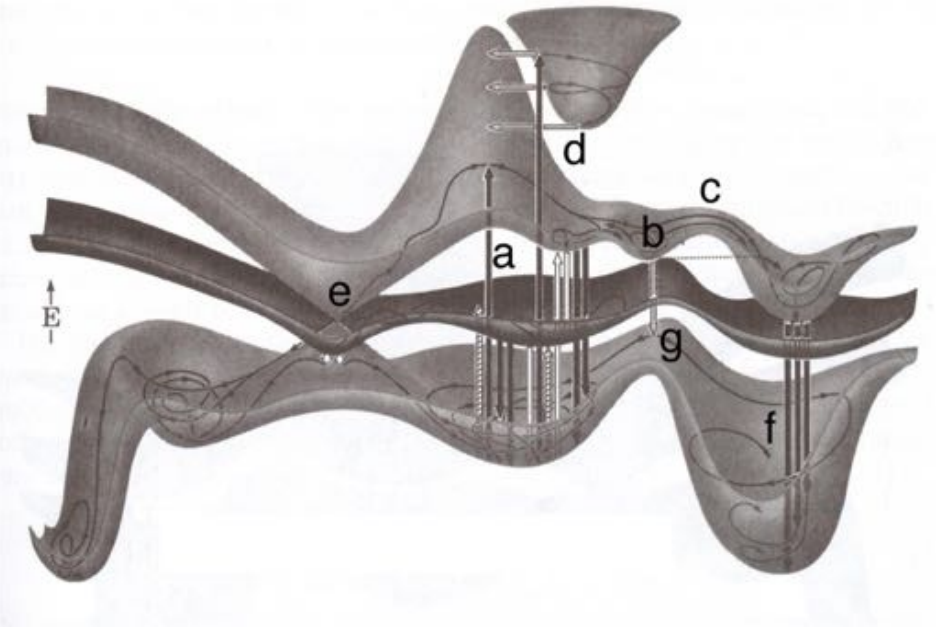
  A. Abedi, N. T. Maitra, E. K. U. Gross, *PRL*, **105**, 123002 (2010)

Applications in Photochemistry and Photophysics

Trajectory-based solutions of the "exact" nonadiabatic equations are still impractical.



Approximate solutions are available. Among the most popular is

Trajectory Surface Hopping (TSH)

The trajectory surface hopping dynamics (1)

TSH is a mixed quantum-classical theory

The classical component

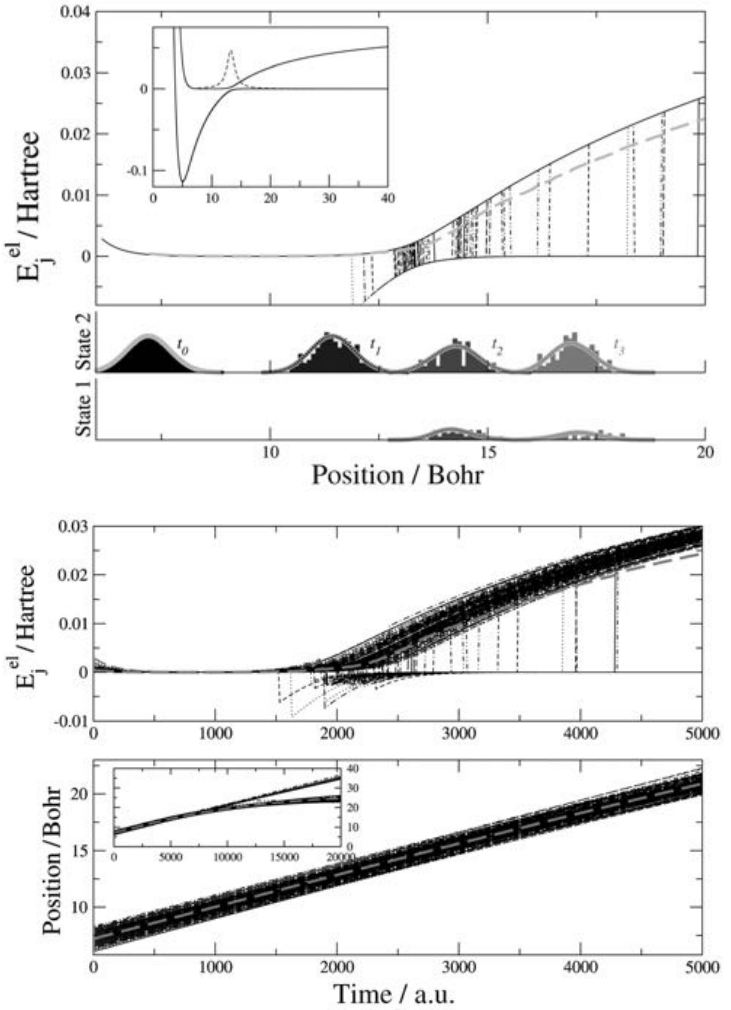
- ensemble of classical trajectories following Newton's equation of motion

$$\frac{d\boldsymbol{P}_j^{\beta}(t)}{dt^j} = -\nabla_{\beta} E_j^{el}(\boldsymbol{R}(t))$$

- trajectories are independent (ITA).

  No coherence
- density of trajectories (${}^{CL}\rho_j(\boldsymbol{R}(t), t)$) at each time step reproduces a 'classical distribution' on the different PESs.

$$\rho_k^{CL}(\boldsymbol{R}^{\alpha}, t^{\alpha}) = \frac{N_k^{\alpha}(\boldsymbol{R}^{\alpha}, dV, t^{\alpha})}{N_{tot}} \frac{1}{dV} \sim |\Omega_k(\boldsymbol{R}^{\alpha}, t^{\alpha})|^2$$



The trajectory surface hopping dynamics (2)

The quantum component

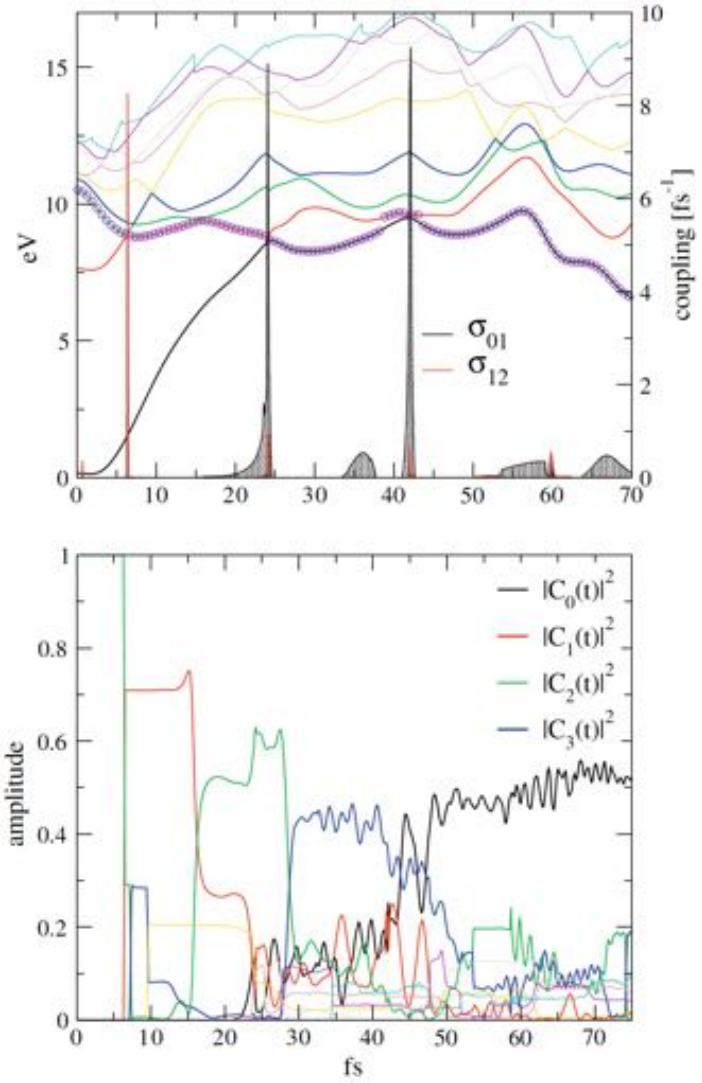
- To each trajectory there are quantum amplitudes ${}^{QM}C_j(\boldsymbol{R}(t),t)$ associated to each PES:
  $\{C_0(\boldsymbol{R}(t),t), C_1(\boldsymbol{R}(t),t), C_2(\boldsymbol{R}(t),t),\ldots\}$.
- They evolve according to

$$i\hbar\frac{dC_j}{dt} = C_j E_j^{el} - i\hbar\sum_i \left(\boldsymbol{d}_{ji}\cdot\dot{\boldsymbol{R}}C_i\right)$$

- ${}^{QM}C_j(\boldsymbol{R}(t),t)$ determine the surface hopping probabilities,

$$p_{i\leftarrow j}^{[\alpha]}(\Delta t) = -2\int_t^{t+\Delta t}\frac{\Re[C_i^{[\alpha]}(\tau)C_j^{[\alpha]*}(\tau)\dot{\boldsymbol{R}}(\tau)\cdot\boldsymbol{d}_{ij}(\boldsymbol{R}(\tau))]}{C_j^{[\alpha]}(\tau)C_j^{[\alpha]*}(\tau)}\,d\tau$$

so that: ${}^{QM}C_j^2(\boldsymbol{R}(t),t) \equiv {}^{CL}\rho_j(\boldsymbol{R}(t),t)$.



Tully's surface hopping - Summary

Tully's surface hopping

$$i\hbar\dot{C}_k^\alpha(t) = \sum_j C_j^\alpha(t)(H_{kj} - i\hbar\dot{\boldsymbol{R}}^\alpha \cdot \boldsymbol{d}_{kj}^\alpha)$$

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I E_k^{el}(\boldsymbol{R})$$

$$\sum_{I\leq k-1} g_{jI}^\alpha < \zeta < \sum_{I\leq k} g_{jI}^\alpha \ ,$$

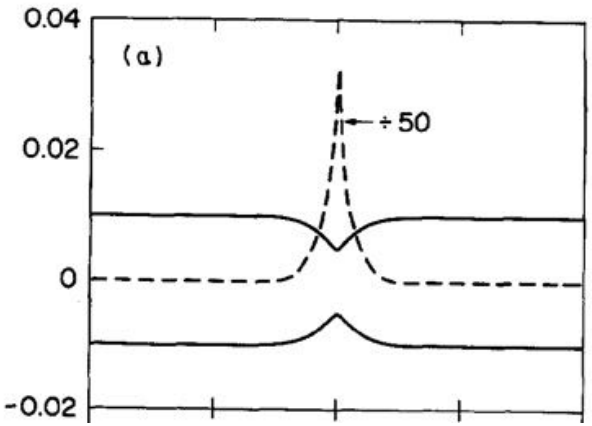
Some warnings:

1. Evolution of classical trajectories (no QM effects – such as tunneling – are possible).
2. Rescaling of the nuclei velocities after a surface hop (to ensure energy conservation) is still a matter of debate.
3. Depending on the system studied, many trajectories could be needed to obtain a complete statistical description of the non-radiative channels.

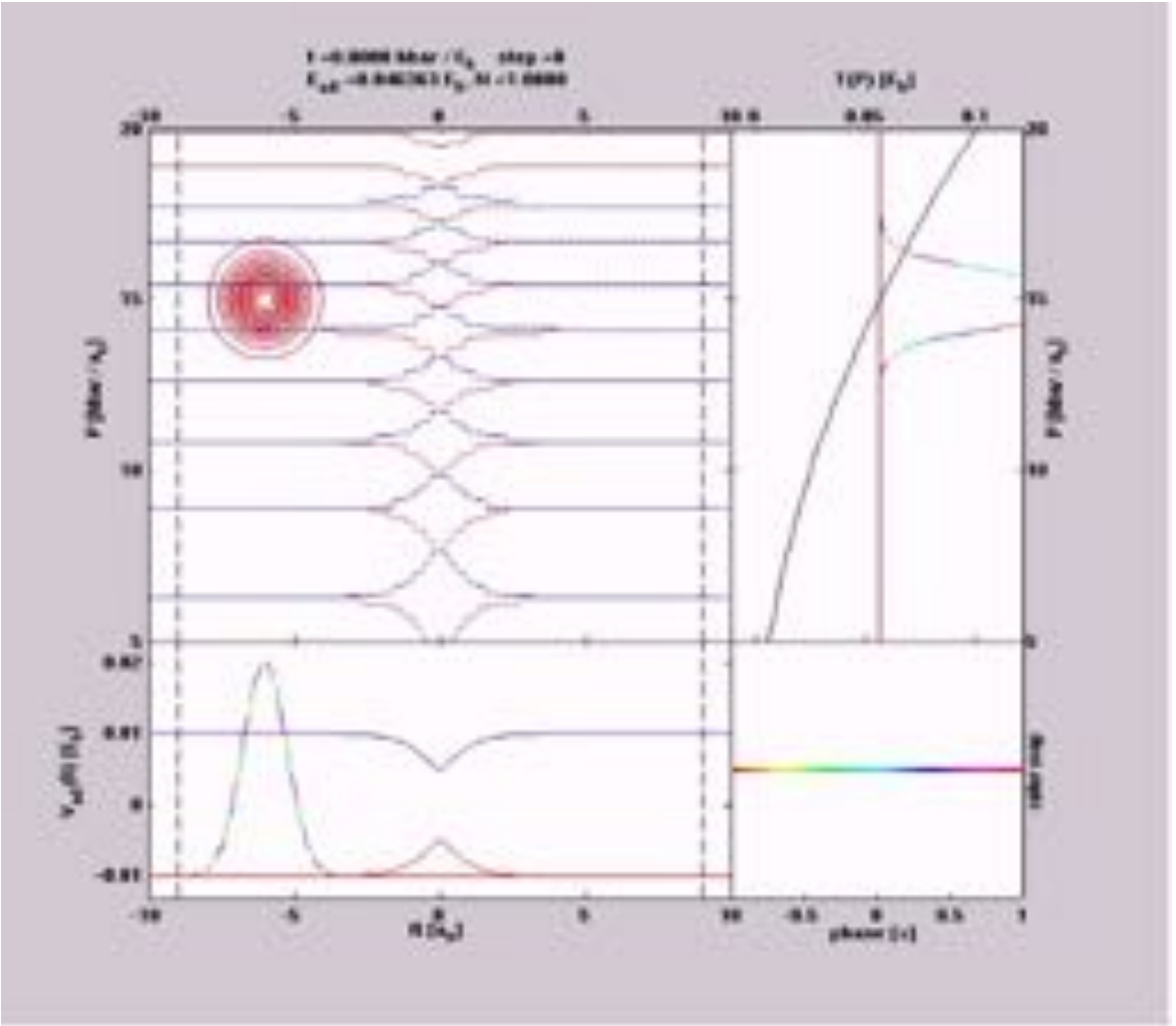
For more details (and warnings) about Tully's surface hopping, see G. Granucci and M. Persico, J Chem Phys 126, 134114 (2007).

Tully's surface hopping - Examples

1D systems



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



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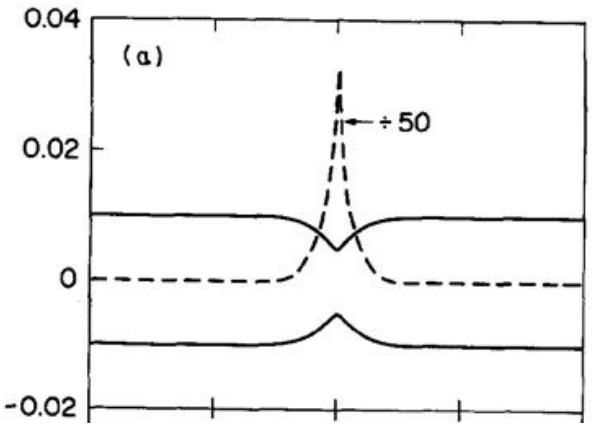

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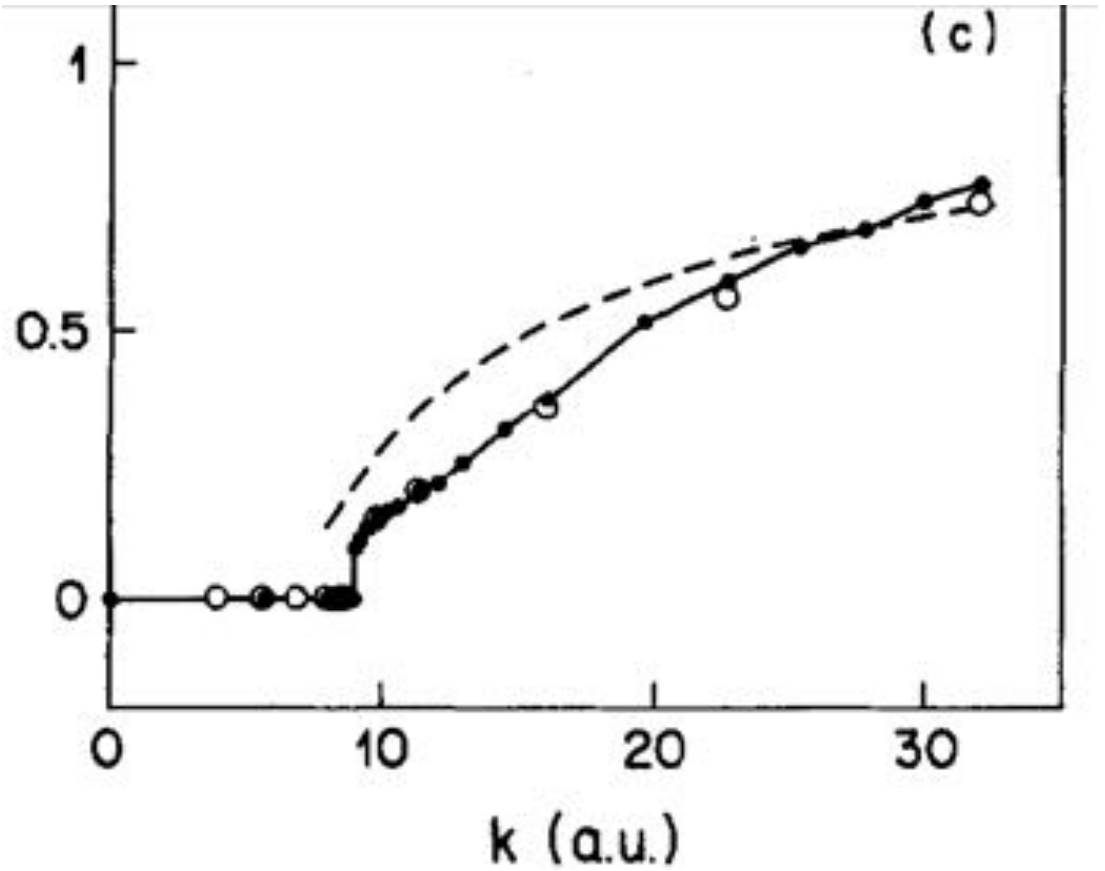
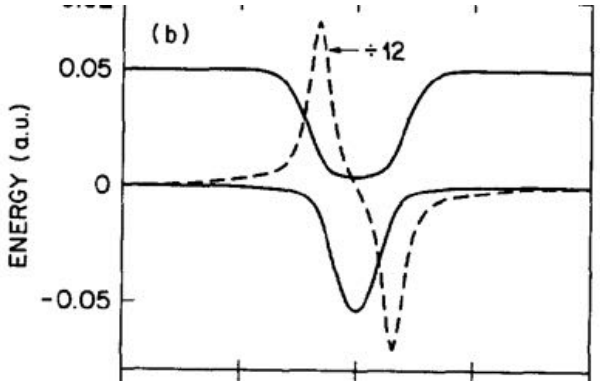


On the right: population of the upper state (k=mom)

- exact
- TSH
  - Landau-Zener

Tully's surface hopping - Examples

1D systems



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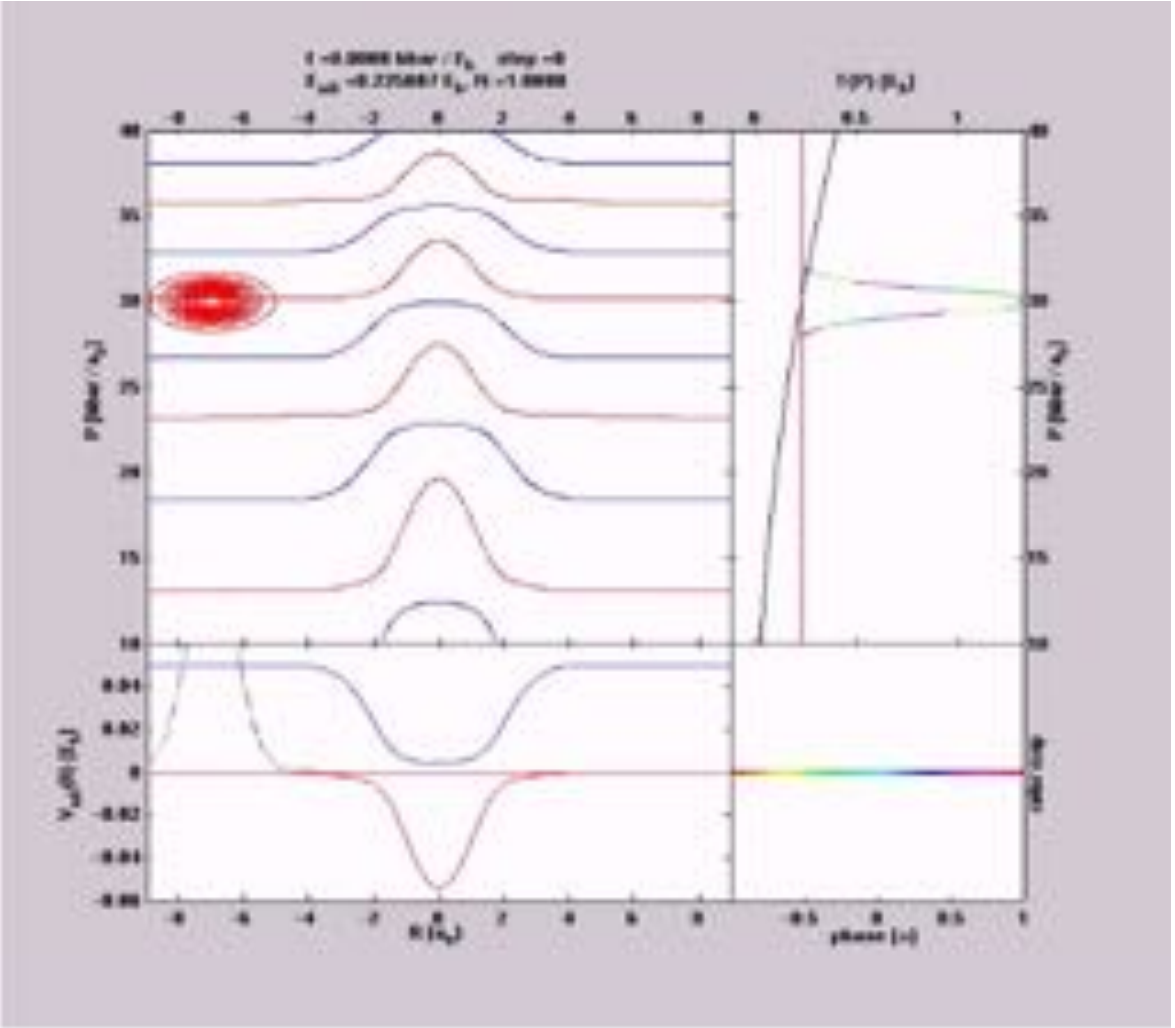

Tully's surface hopping - Examples

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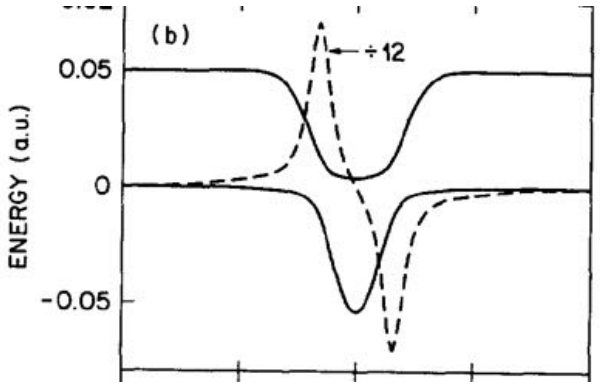

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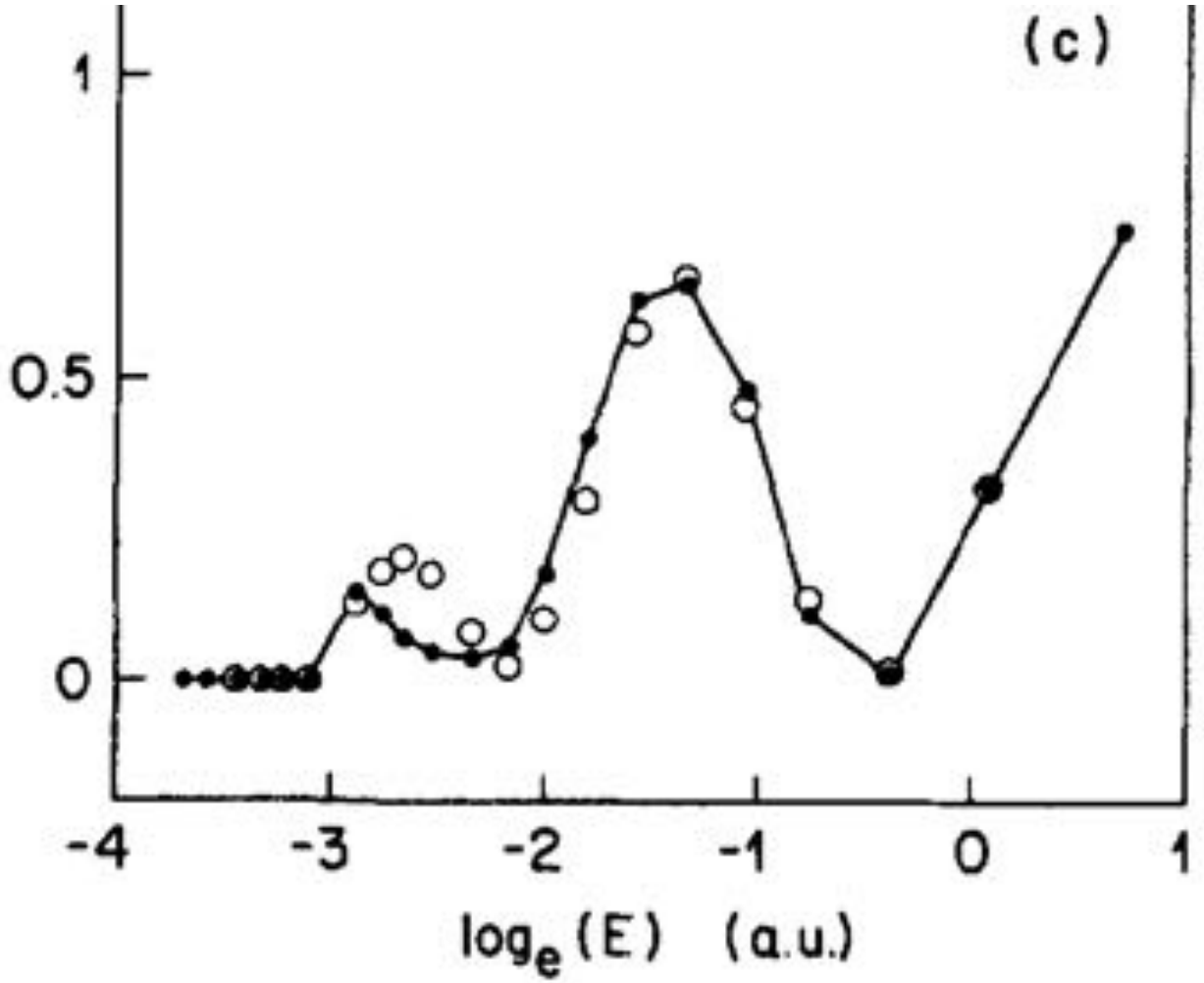
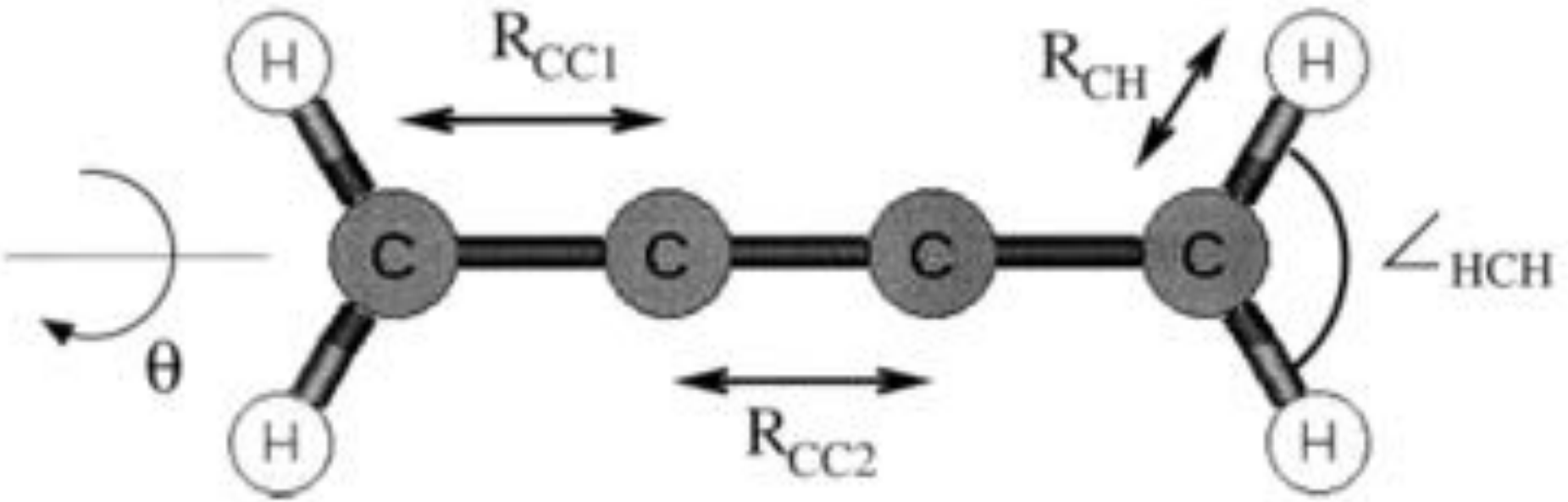


Comparison with wavepacket dynamics

Butatriene molecule: dynamics of the radical cation in the first excited state.



JPCA,107,621 (2003)

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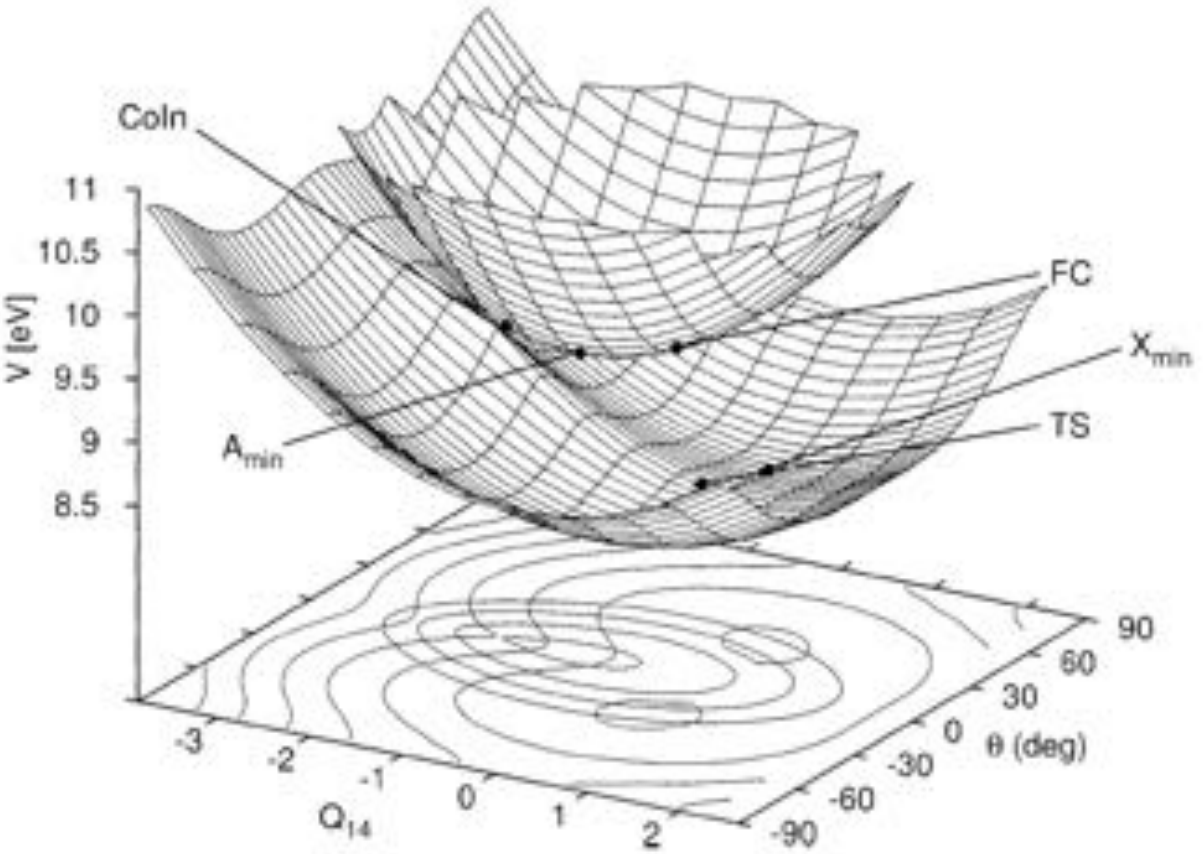
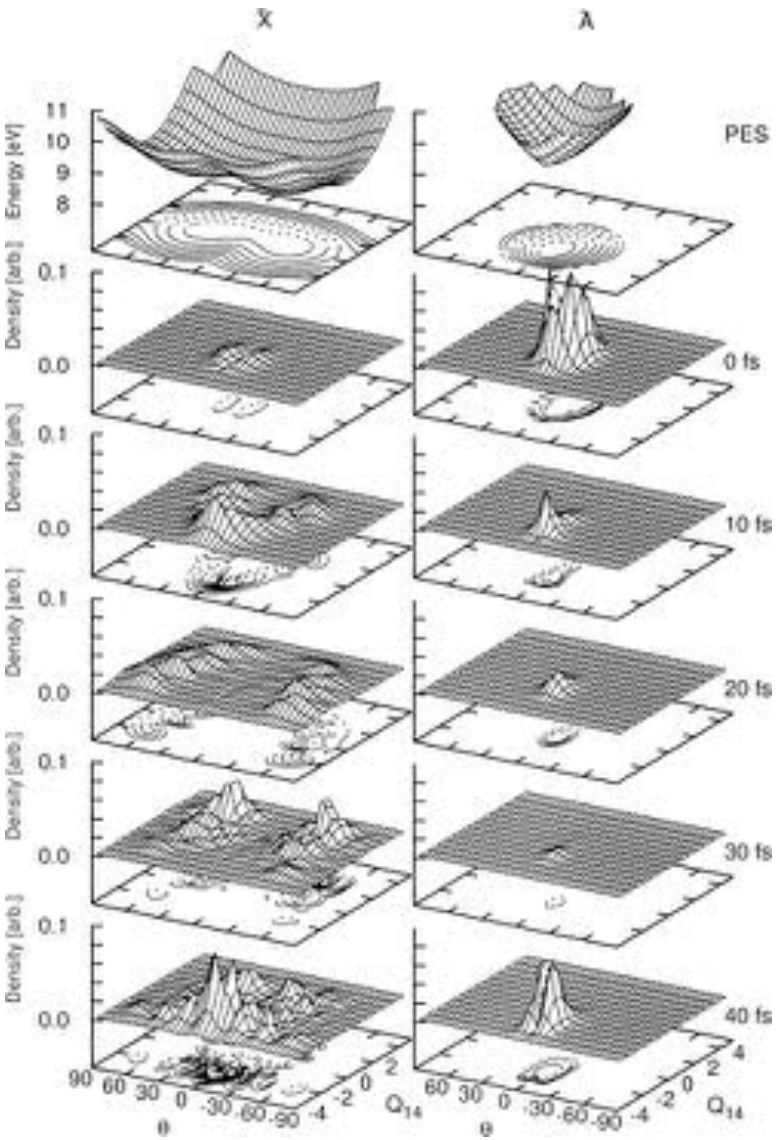


JPCA,107,621 (2003)

CASSCF PESs for the radical cation (Q_{14}: symmetric stretch, θ: torsional angle).

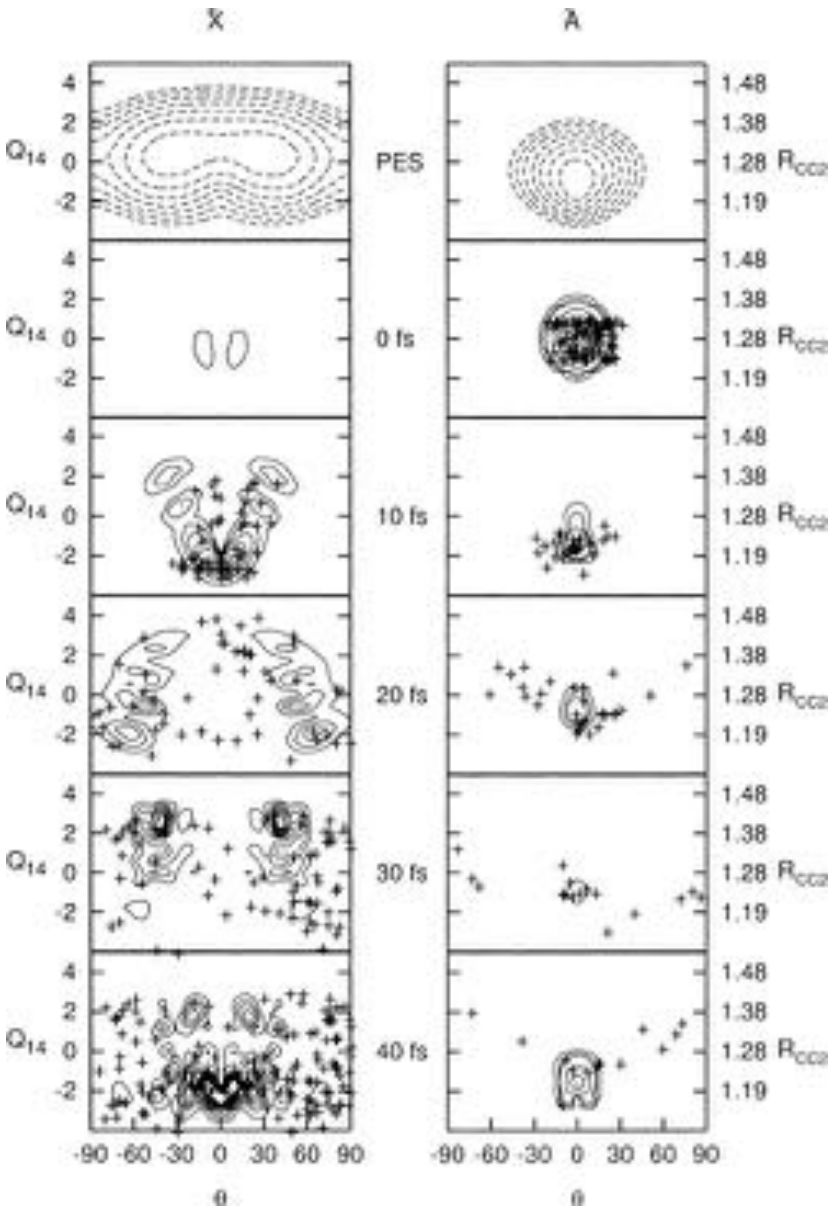
Comparison with wavepacket dynamics



Nuclear wavepacket dynamics on fitted potential energy surfaces (using MCTDH with 5 modes). Reappearing of the wavepacket in S_1 after $\sim$ 40fs.

JPCA,107,621 (2003)

Comparison with wavepacket dynamics



On-the-fly dynamics with 80 trajectories (crosses).

Trajectories are not coming back close to the conical intersection.

What is the reason for this discrepancy? The independent trajectory approximation?, i.e. the fact that trajectories are not correlated?
(Or it has to do with differences in the PESs?)

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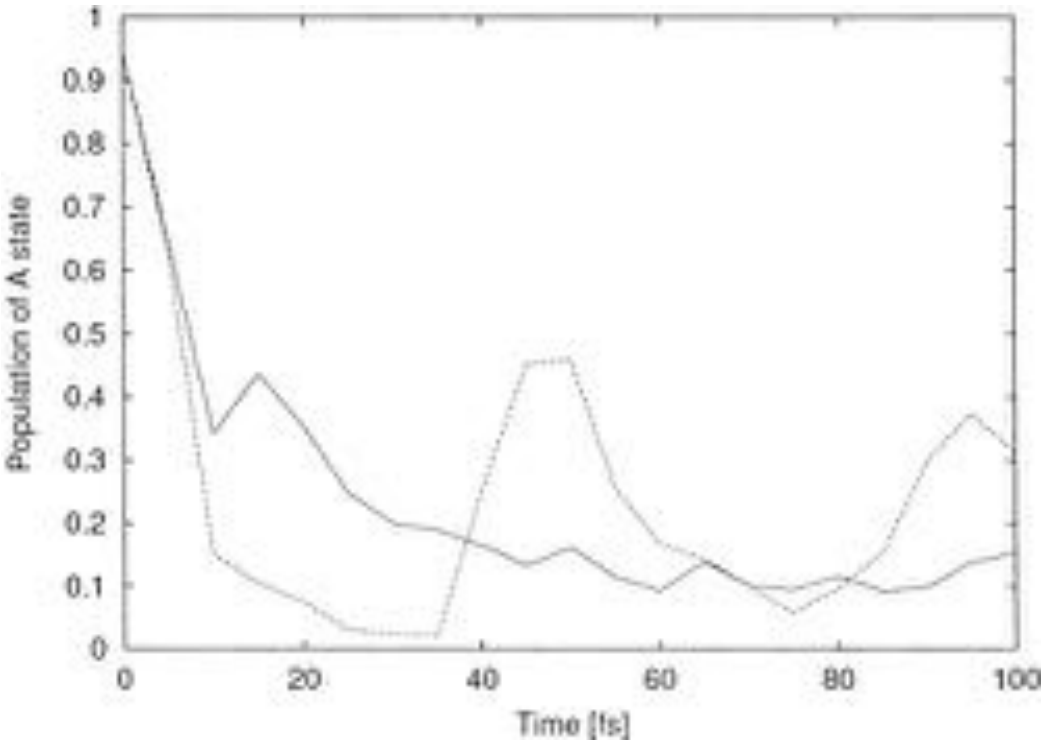
Comparison with wavepacket dynamics



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JPCA,107,621 (2003)

Tarjectory-based quantum and mixed QM-CL solutions

We can "derive" the following trajectory-based solutions:

- Nonadiabatic Ehrenfest dynamics dynamics

  I. Tavernelli et al., *Mol. Phys.*, **103**, 963981 (2005).

- Adiabatic Born-Oppenheimer MD equations

- Nonadiabatic Bohmian Dynamics (NABDY)

  B. Curchod, IT, U. Rothlisberger, *PCCP*, **13**, 32313236 (2011)

- Nonadiabatic Trajectory Surface Hopping (TSH) dynamics
  [ROKS: N. L. Doltsinis, D. Marx, *PRL*, **88**, 166402 (2002)]
  C. F. Craig, W. R. Duncan, and O. V. Prezhdo, *PRL*, **95**, 163001 (2005)
  E. Tapavicza, I. Tavernelli, U. Rothlisberger, *PRL*, **98**, 023001 (2007)

- Time dependent potential energy surface approach

  based on the exact decomposition: $\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \Omega(\boldsymbol{R}, t)\Phi(\boldsymbol{r}, t)$.

  A. Abedi, N. T. Maitra, E. K. U. Gross, *PRL*, **105**, 123002 (2010)

Coupled-trajectories mixed quantum-classical (CT-MQC)

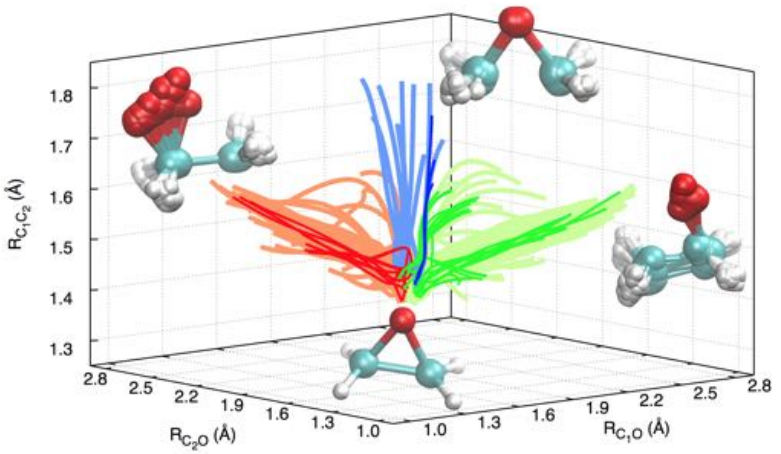
Why do we need another trajectory based approach?

Requirements:

- Existence of an exact limit - tuneable parameters
- Description of quantum coherence/decoherence effects
- Simple trajectory-based implementation
- Densityfunctionalization
- Parallelization

CT-MQC literature:

1. F. Agostini et al., *J. Chem. Theory Comput.* **12**, 2127-2143 (2016),
2. S.K. Min, et al., *J. Chem. Phys. Lett.*, **8**, 3048 (2017)



Derivation of the CT-MQC dynamics

The starting point is the exact factorization theorem, which prescribes

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

as solution of the td-SE $\quad i\hbar\partial_t\Psi(\boldsymbol{r},\boldsymbol{R},t)=\hat{H}(\boldsymbol{r},\boldsymbol{R})\Psi(\boldsymbol{r},\boldsymbol{R},t).$

The equations of motion (EOM) are

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

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

- $\epsilon(\boldsymbol{R},t)=\langle\Phi_{\boldsymbol{R}}(t)|\hat{H}_{BO}+\hat{U}_{en}^{coup}-i\hbar\partial_t|\Phi_{\boldsymbol{R}}(t)\rangle_{\boldsymbol{r}}$ is the td-PES.
- $\hat{U}_{en}^{coup}[\Phi_{\boldsymbol{R}},\chi]=\sum_\nu[(-i\hbar\nabla_\nu-\boldsymbol{A}_\nu)^2/2M_\nu+(-i\hbar\nabla_\nu\chi/\chi+\boldsymbol{A}_\nu)(-i\hbar\nabla_\nu+\boldsymbol{A}_\nu)/M_\nu]$
- $\boldsymbol{A}_\nu(\boldsymbol{R},t)=\langle\Phi_{\boldsymbol{R}}(t)|-i\hbar\nabla_\nu\Phi_{\boldsymbol{R}}(t)\rangle_{\boldsymbol{r}}$ is a td vector quantum potential.

A. Abedi et al, *Phys. Rev. Lett.***105**, 123002 (2010), A. Abedi et al, *J. Chem. Phys.* 2012, **13**, 22A530 (2012).

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Implementation of the CT-MQC dynamics

Mixed quantum-classical limit

(i) Newton EOM with forces from the td vector $\boldsymbol{A}_\nu(\boldsymbol{R},t)$ and scalar td $\epsilon(\boldsymbol{R},t)$ potentials

(ii) Born-Huang representation for the electronic wavefunction

$$\Phi_{\boldsymbol{R}}(\boldsymbol{r},t) = \sum_I C_I(\boldsymbol{R},t)\varphi_{\boldsymbol{R}}^{(I)}(\boldsymbol{r})$$

(iii) Classical limit for the vector quantum potential (part of $\hat{U}_{en}^{coup}[\Phi_{\boldsymbol{R}},\chi]$): $-i\hbar\nabla_\nu\chi(\boldsymbol{R})/\chi(\boldsymbol{R})$

(iv) Swarm of (correlated) trajectories to compute properties of the nu-wavefunction, $\chi(\boldsymbol{R})$.
$\rightarrow$ Gaussian wavepackets moving with the trajectories.

The electronic and nuclear equations in the MQC-limit of the EXF are

State populations: $\dot{C}_I^{(\alpha)}(t) = \dot{C}_{\text{Eh.}\,I}^{(\alpha)}(t) + \dot{C}_{\text{qm}\,I}^{(\alpha)}(t)$

Nuclear forces: $\mathbf{F}_\nu^{(\alpha)}(t) = \mathbf{F}_{\text{Eh.}\,\nu}^{(\alpha)}(t) + \mathbf{F}_{\text{qm}\,\nu}^{(\alpha)}(t)$

F. Agostini et al., *J. Chem. Theory Comput.* **12**, 2127-2143 (2016), S.K. Min, et al., *J. Chem. Phys. Lett.*, **8**, 3048 (2017)

Implementation of the CT-MQC dynamics

The Ehrenfest-like terms

$$\dot{C}^{(\alpha)}_{\mathrm{Eh.}\,I}(t) = \frac{-i}{\hbar}\epsilon^{(I)(\alpha)}_{BO} C^{(\alpha)}_{I}(t) - \sum_{k} C^{(\alpha)}_{k}(t) \sum_{\nu=1}^{N_n} \frac{\mathbf{P}^{(\alpha)}_{\nu}(t)}{M_\nu} \cdot \mathbf{d}^{(\alpha)}_{\nu,lk}$$

$$\mathbf{F}^{(\alpha)}_{\mathrm{Eh.},\nu}(t) = -\sum_{k} \left| C^{(\alpha)}_{k}(t) \right|^2 \nabla_\nu \epsilon^{(k),(\alpha)}_{BO} - \sum_{k,I} C^{(\alpha)\,*}_{I}(t) C^{(\alpha)}_{k}(t) \left(\epsilon^{(k),(\alpha)}_{BO} - \epsilon^{(I),(\alpha)}_{BO} \right) \mathbf{d}^{(\alpha)}_{\nu,lk},$$

$\epsilon^{(I)(\alpha)}_{BO}$	adiabatic PES I evaluated at $\alpha-$th trajectory,
$\mathbf{d}^{(\alpha)}_{\nu,lk}$	NACV ($\langle \varphi^{(I)(\alpha)} \vert \nabla_\nu \varphi^{(k)(\alpha)} \rangle_{\boldsymbol{r}}$) for trajectory α,
$\mathbf{P}^{(\alpha)}_{\nu}(t)$	classical momentum along the $\alpha-$th trajectory.

I, k is the state indices, α the trajectory index, and ν is the index over the nuclei.

F. Agostini, et al. *J. Chem. Theory Comput.* **12**, 2127-2143 (2016).
S.K. Min, et al., *J. Chem. Phys. Lett.*, **8**, 3048 (2017)

Implementation of the CT-MQC dynamics

Quantum momentum terms (from exact factorization)

$$\dot{C}^{(\alpha)}_{\mathrm{qm}\,I}(t) = -\sum_{\nu=1}^{N_n} \frac{\boldsymbol{\mathcal{P}}^{(\alpha)}_{\nu}(t)}{\hbar M_\nu} \cdot \left[\sum_k \left|C^{(\alpha)}_k(t)\right|^2 \mathbf{f}^{(\alpha)}_{k,\nu}(t) - \mathbf{f}^{(\alpha)}_{I,\nu}(t)\right] C^{(\alpha)}_I(t),$$

$$\mathbf{F}^{(\alpha)}_{\mathrm{qm}\,\nu}(t) = -\sum_I \left|C^{(\alpha)}_I(t)\right|^2 \left(\sum_{\nu'=1}^{N_n} \frac{2}{\hbar M_{\nu'}} \boldsymbol{\mathcal{P}}^{(\alpha)}_{\nu'}(t) \cdot \mathbf{f}^{(\alpha)}_{I,\nu'}(t)\right) \left[\sum_k \left|C^{(\alpha)}_k(t)\right|^2 \mathbf{f}^{(\alpha)}_{k,\nu}(t) - \mathbf{f}^{(\alpha)}_{I,\nu}(t)\right]$$

$\mathbf{f}^{(\alpha)}_{\mathbf{k},\nu}(\mathbf{t})$ integrated forces $= -\int^t dt' \nabla_\nu \varepsilon^{(k),(\alpha)}_{BO}$

$\boldsymbol{\mathcal{P}}^{(\alpha)}_{\nu}(t)$ quantum momentum $= -\frac{\hbar}{2} \frac{\nabla_\nu |\chi^{(\alpha)}(t)|^2}{|\chi^{(\alpha)}(t)|^2}$.

It induces coupling between the trajectories (beyond the *ind. traj. appr. (ITA)*).

I, k are state indices, α the trajectory index, and ν the index over the nuclei.

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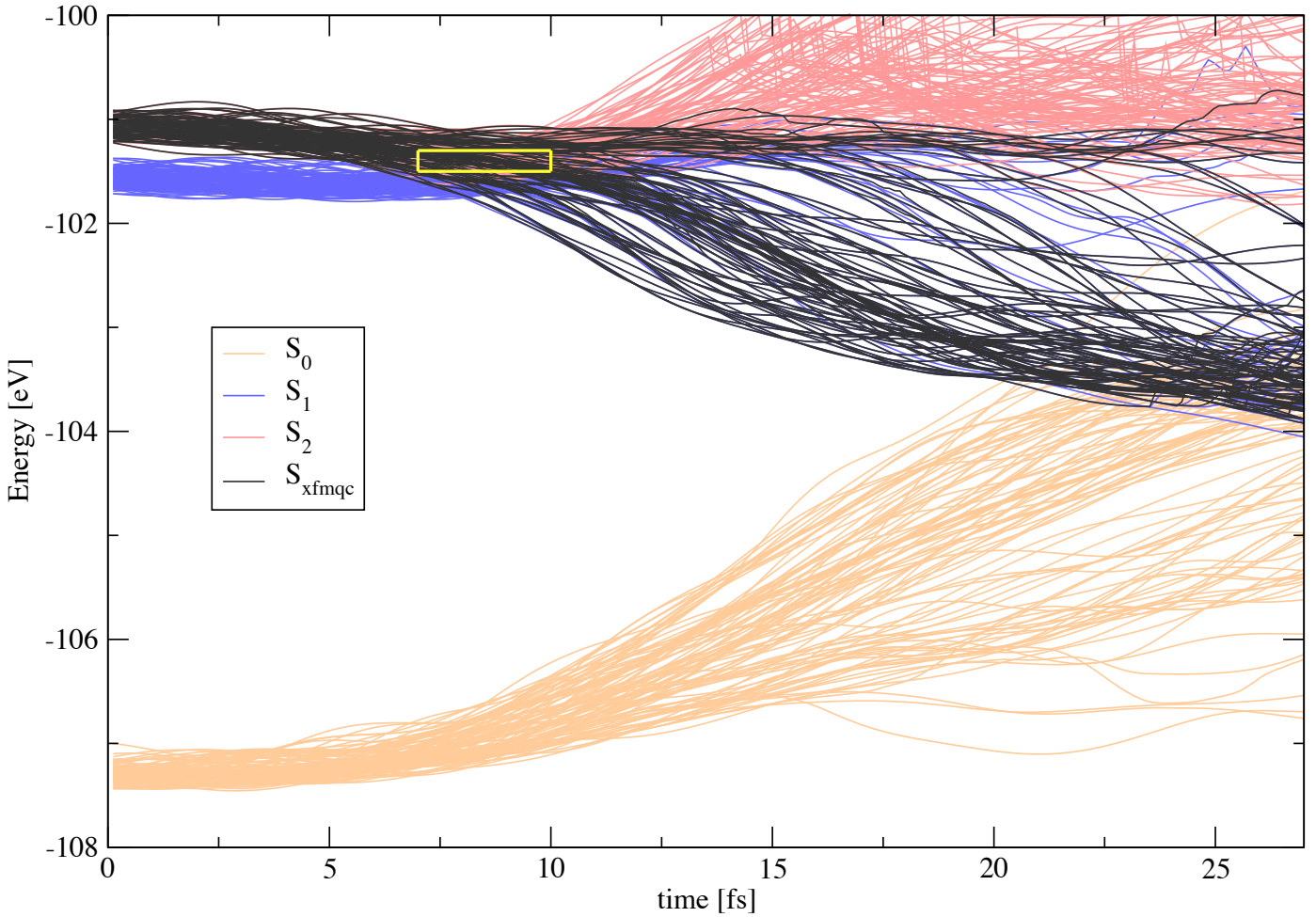
CT-MQC dynamics: time-dependent potential energy lines



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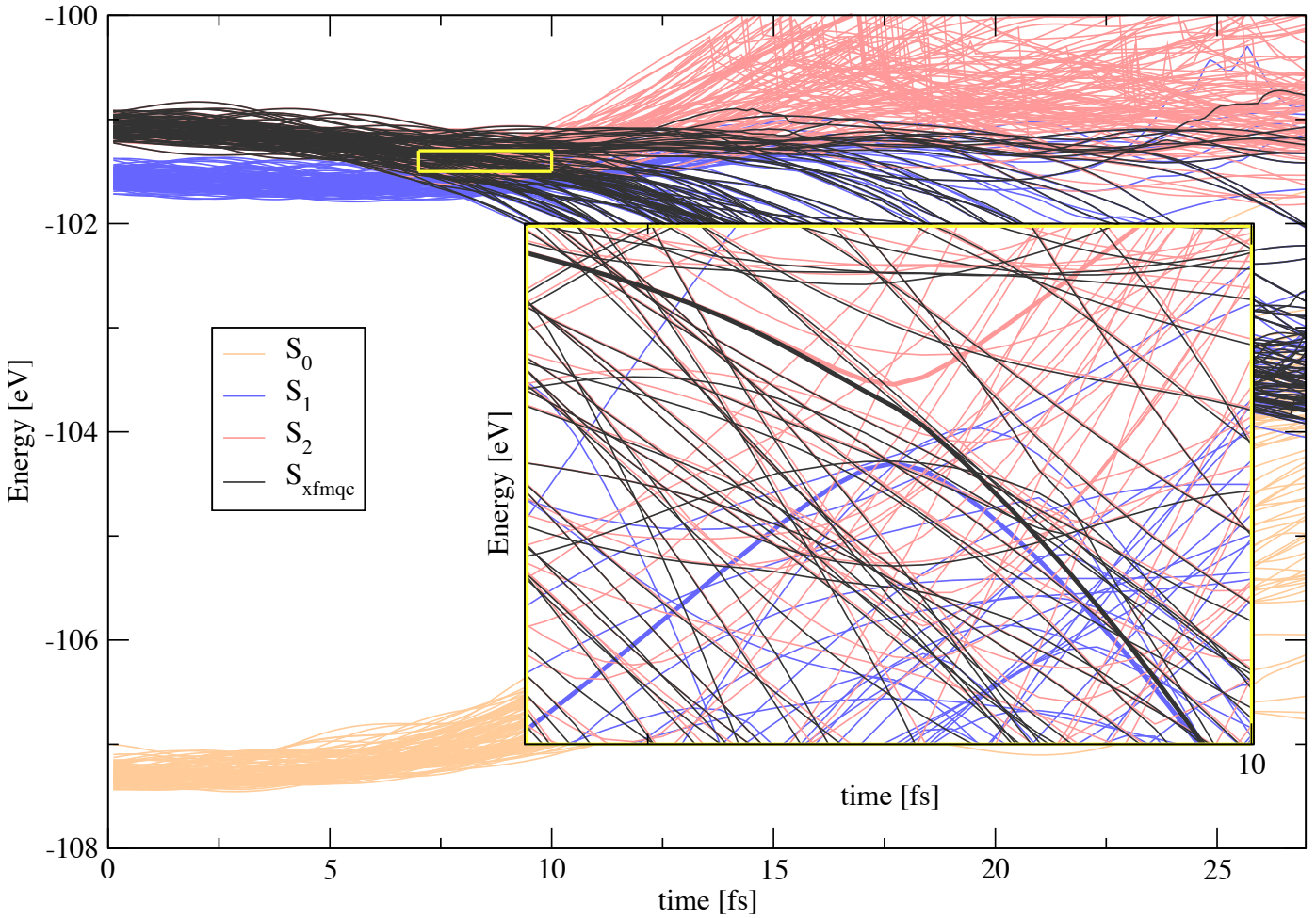

Further extensions: nuclear quantum (tunneling) effects in CT-MQC

The quantum potential

$$\mathcal{Q}(\boldsymbol{R},t) = -\sum_{\nu} \frac{\hbar}{2M_\nu} \frac{\nabla_\nu^2 |\chi(\boldsymbol{R},t)|}{|\chi(\boldsymbol{R},t)|}$$

can be derived computed suing the Gaussian associated to the trajectories

$$|\chi(\boldsymbol{R},t|^2 = \frac{1}{N_{tr}} \sum_{I=1}^{N_{tr}} \prod_{\nu=1}^{N_{nu}} G_{\sigma_{I,\nu}}(\boldsymbol{R}_\nu; \boldsymbol{R}_\nu^{(I)}(t))$$

where $G_{\sigma_{I,\nu}}(\boldsymbol{R}_\nu; \boldsymbol{R}_\nu^{(I)}(t))$ are normalized Gaussians centred at the classical trajectory $\boldsymbol{R}^{(I)}(t)$ with variance $\sigma_{I,\nu}$,

$$\sigma_{I,\nu} = \frac{\sqrt{\overline{\mathcal{D}^2}_{I,\nu} - \overline{\mathcal{D}}_{I,\nu}^2}}{n_{tr}^{(I)}}, \quad \overline{\mathcal{D}}_{I,\nu} = \frac{1}{n_{tr}^{(I)}} \sum_{J}^{n_{tr}^{(I)}} |\boldsymbol{R}_\nu^{(I)} - \boldsymbol{R}_\nu^{(J)}|, \quad \overline{\mathcal{D}^2}_{I,\nu} = \frac{1}{n_{tr}^{(I)}} \sum_{J}^{n_{tr}^{(I)}} |\boldsymbol{R}_\nu^{(I)} - \boldsymbol{R}_\nu^{(J)}|^2$$

F. Agostini, IT, G. Ciccotti, *Eur. Phys. J. B* **91**, 139 (2018).

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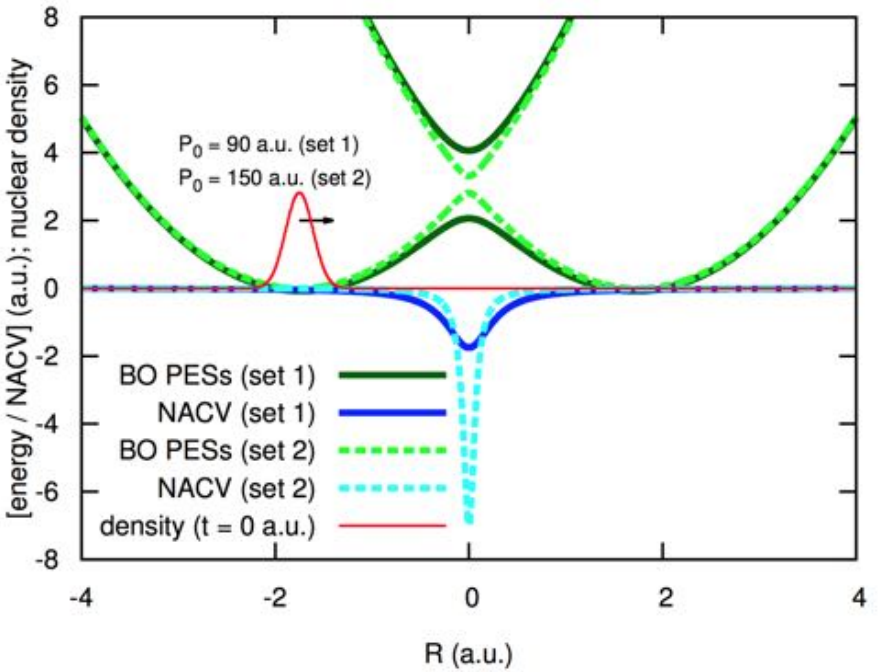

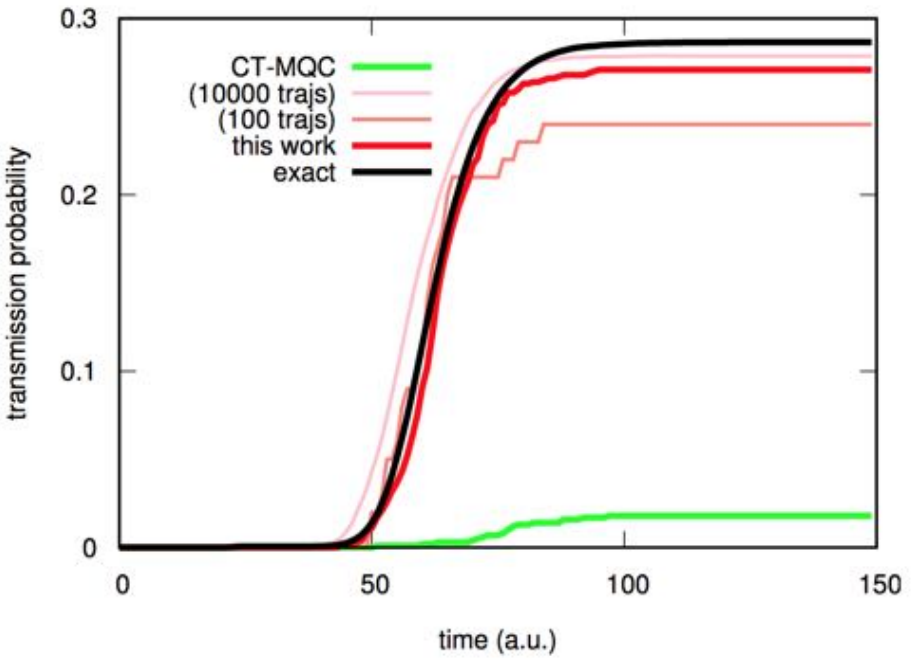

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Green: CT-MQC with no quantum potential.

Red: CT-MQC with quantum potential.