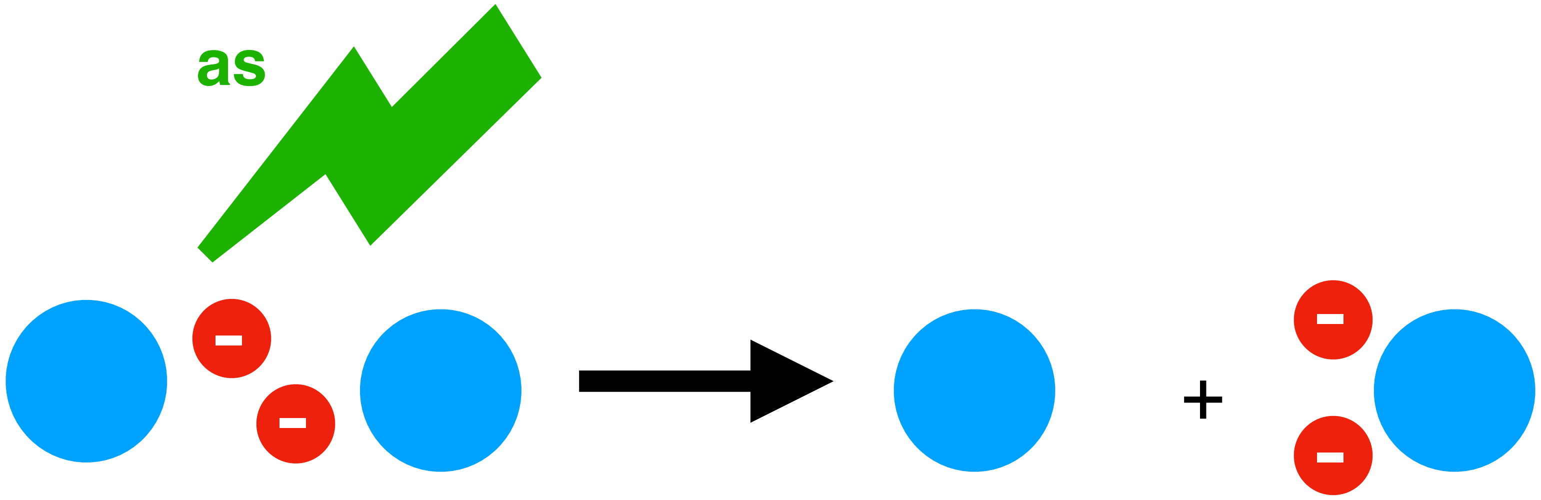
Challenges in attochemistry and its theoretical description



Morgane VACHER

CEISAM
Chimie et Interdisciplinarité
Synthèse, Analyse,
Modélisation

WPC Symposium 2025

Chemistry

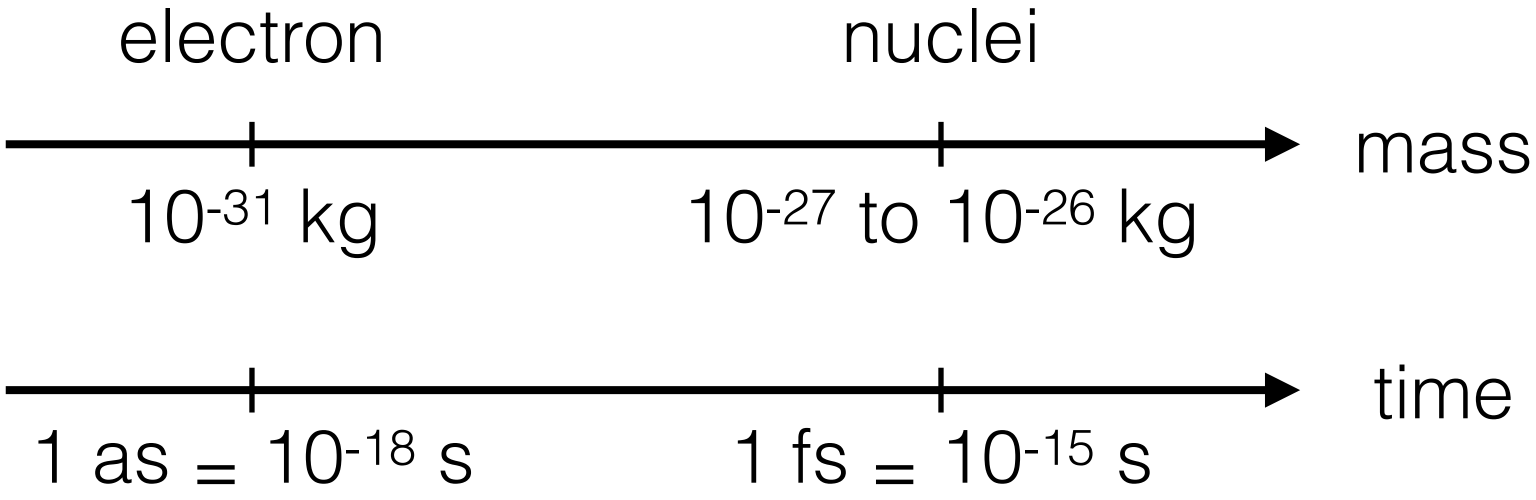
- Basic definitions

A molecule is a group of two or more atoms held together by attractive forces known as chemical bonds.

Every atom is composed of a nucleus and one or more electrons bound to the nucleus.

A chemical reaction is the transformation of one set of molecules to another, involving the forming and breaking of bonds between atoms.

- Order of magnitudes



electron

nuclei

mass

10^{-31} kg

10^{-27} to 10^{-26} kg

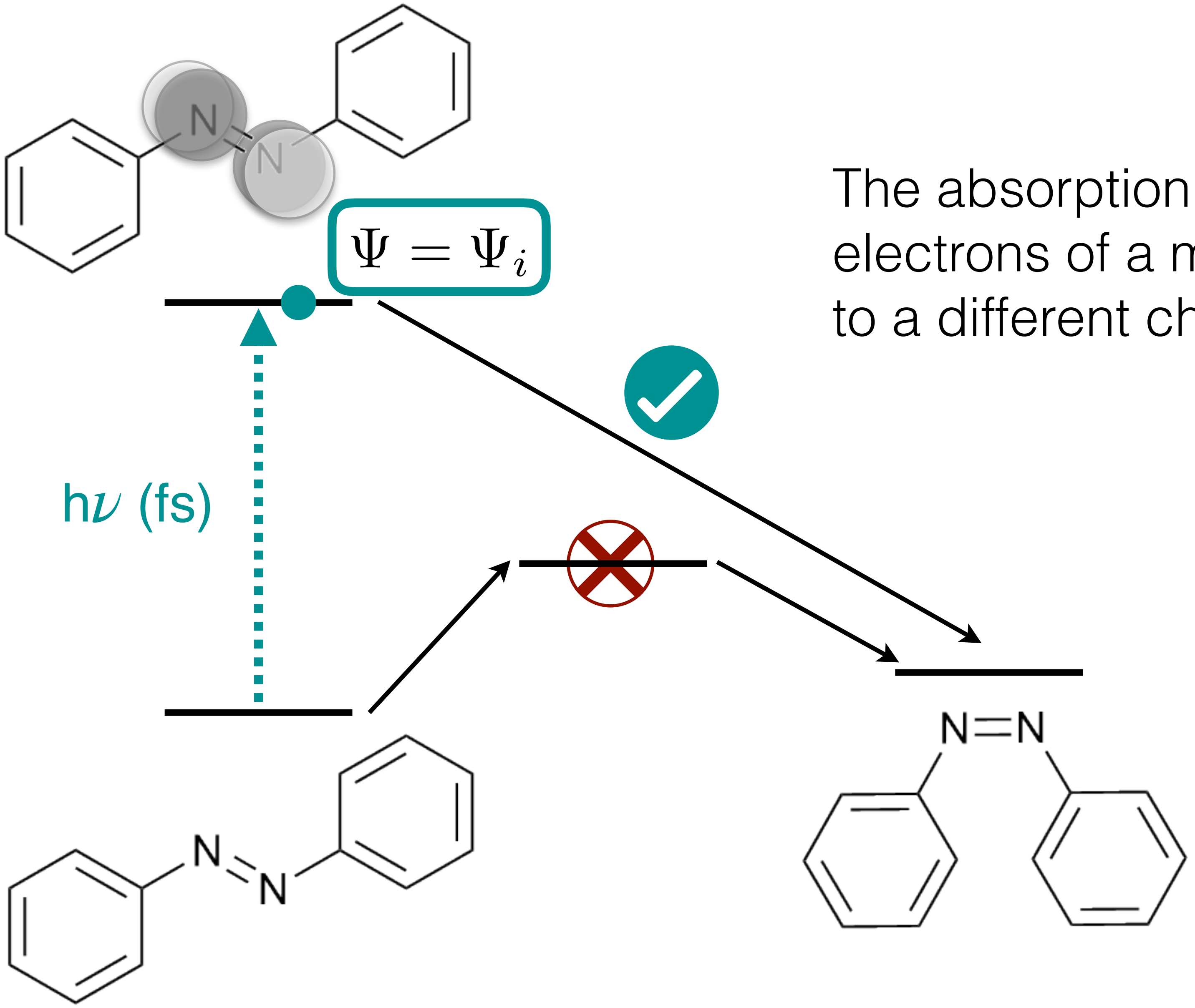
time

1 as = 10^{-18} s

1 fs = 10^{-15} s

The concept of photochemistry

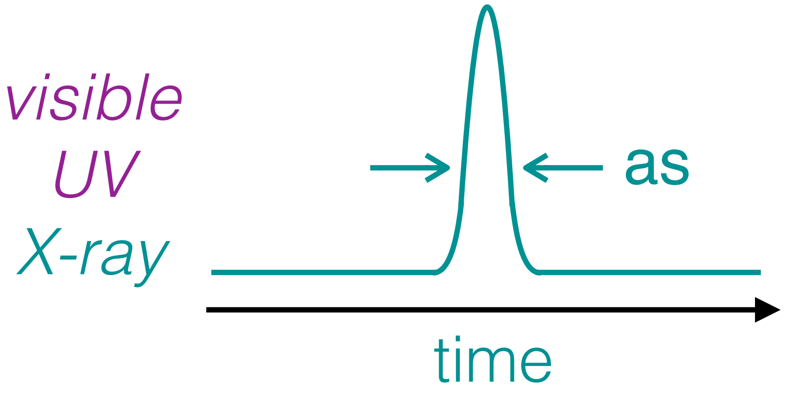
1 fs = 10^{-15} s



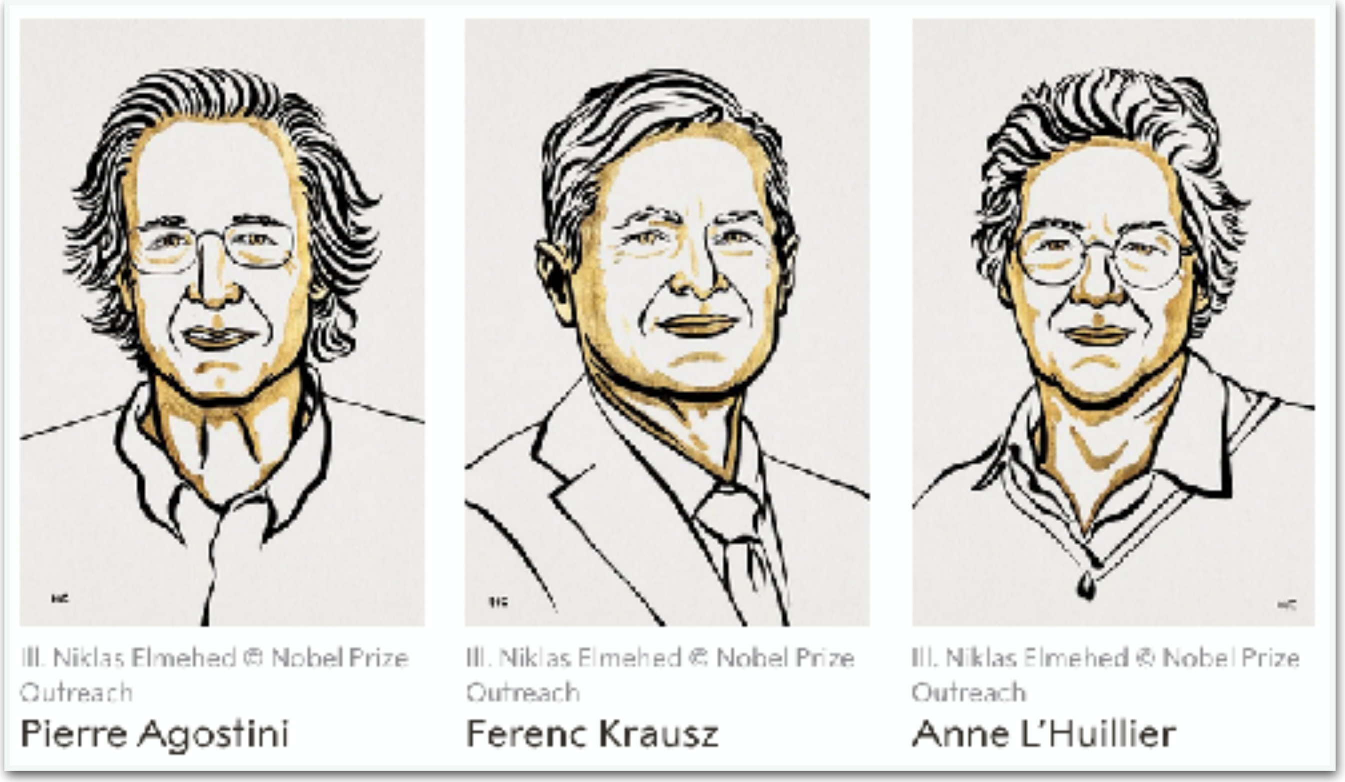
The absorption of light excites the electrons of a molecule and leads to a different chemical reactivity.

Photochemical reactions are limited by the number and nature of electronic excited states of molecules, and thus lack control and selectivity.

The birth of attosecond science



1 as = 10^{-18} s


Ill. Niklas Elmehed © Nobel Prize Outreach
Pierre Agostini

Ill. Niklas Elmehed © Nobel Prize Outreach
Ferenc Krausz

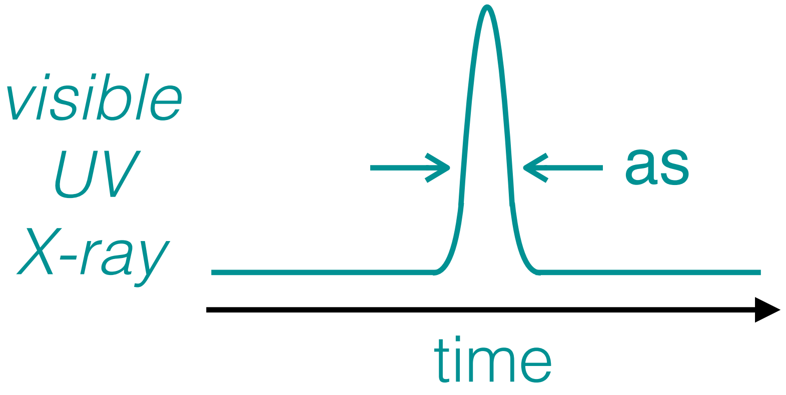
Ill. Niklas Elmehed © Nobel Prize Outreach
Anne L'Huillier

Nobel Prize in Physics 2023
for experimental methods that generate attosecond pulses of light for the study of electron dynamics in matter

Travers *et al.* Nature Photonics 13, 547-554 (2019)
Hassan *et al.* Nature 530, 66-70 (2016)
Paul *et al.* Science 292, 1689-1692 (2001)
Hentschel *et al.* Nature 414, 509-513 (2001)

The birth of attosecond science

attochemistry = attosecond pulses applied to molecules



1 as = 10^{-18} s

U.S. Department of Energy: « attosecond electronic motion within molecules » as one priority research opportunity (2017)

Travers *et al.* Nature Photonics 13, 547-554 (2019)
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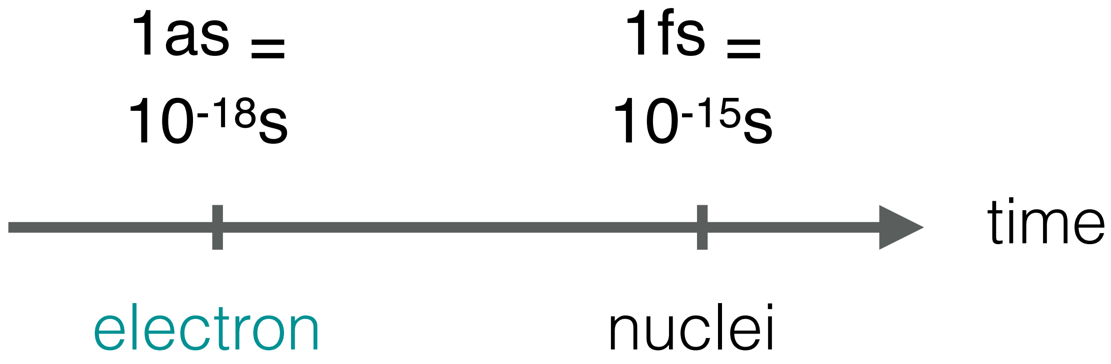


1as = 10^{-18}s

1fs = 10^{-15}s

time

electron

nuclei

nature

CHEMISTRY IN MOTION

Attosecond snapshots reveal dynamics of valence electrons

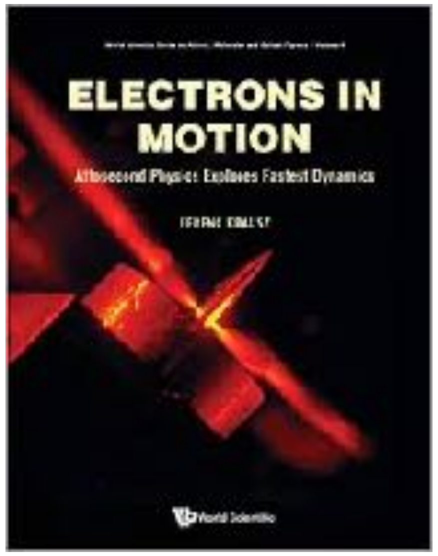
CITIZEN SCIENCE
Crowd-based supercomputing

OCEAN MONITORING
Tap into submarine cables

CHEMICAL REVIEWS

ULTRAFAST PROCESSES IN CHEMISTRY

THE JOURNAL OF PHYSICAL CHEMISTRY A



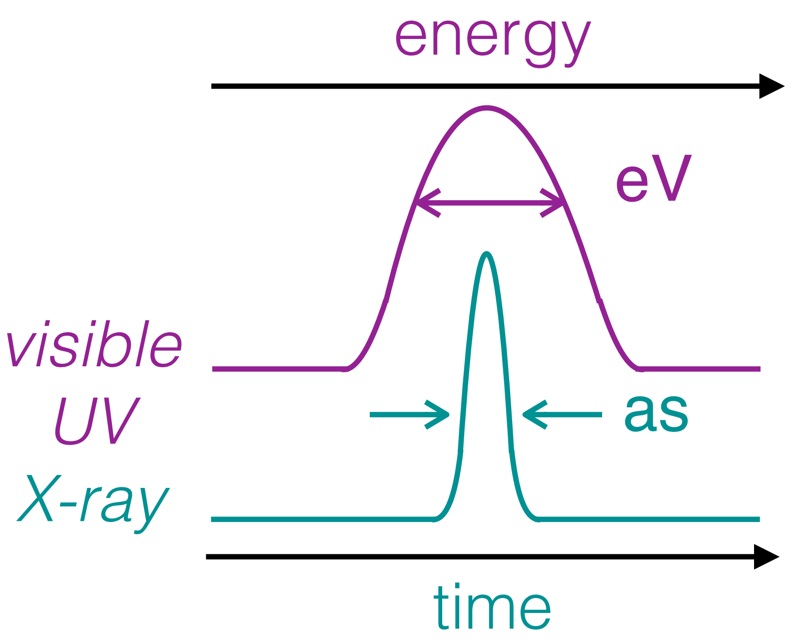
ELECTRONS IN MOTION

Attosecond Physics Explores Fastest Dynamics

World Scientific

The birth of attosecond science

attochemistry = attosecond pulses applied to molecules



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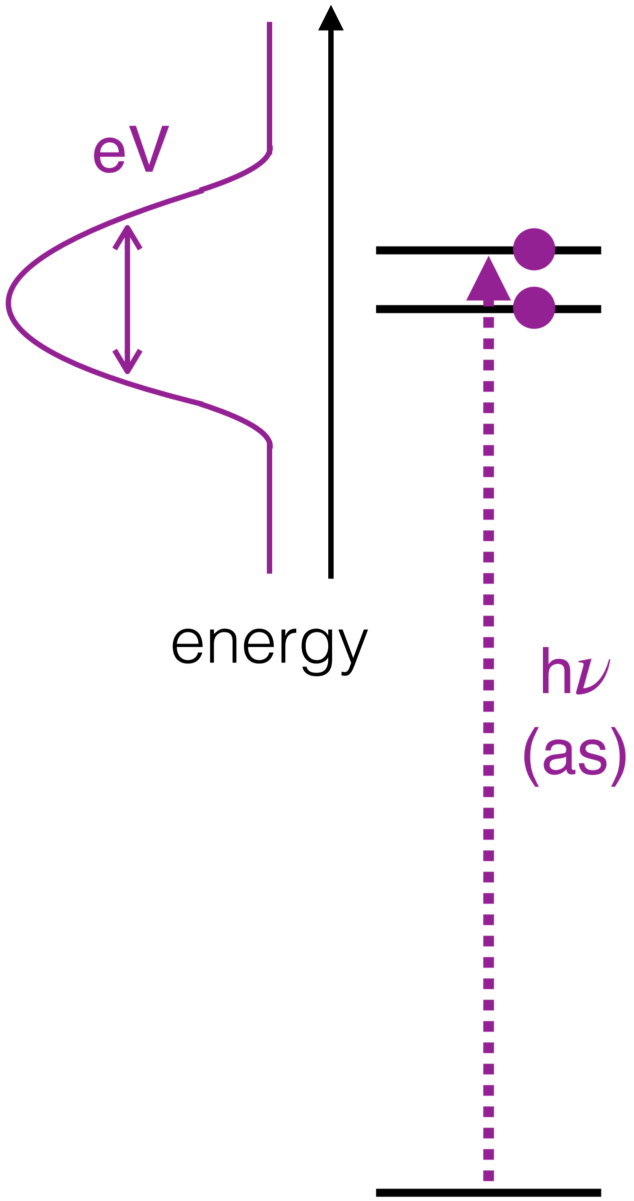


$$\boxed{\Psi = \sum_i c_i \exp(i\phi_i)\Psi_i}$$

Attosecond pulses excite **several** electronic states → electronic wavepacket

Travers *et al.* Nature Photonics 13, 547-554 (2019)
Hassan *et al.* Nature 530, 66-70 (2016)
Paul *et al.* Science 292, 1689-1692 (2001)
Hentschel *et al.* Nature 414, 509-513 (2001)

The birth of attosecond science

$$\Psi(\mathbf{r}, t=0) = c_0\psi_0(\mathbf{r}) + c_1\psi_1(\mathbf{r})$$

Electronic time-dependent
Schrödinger equation:

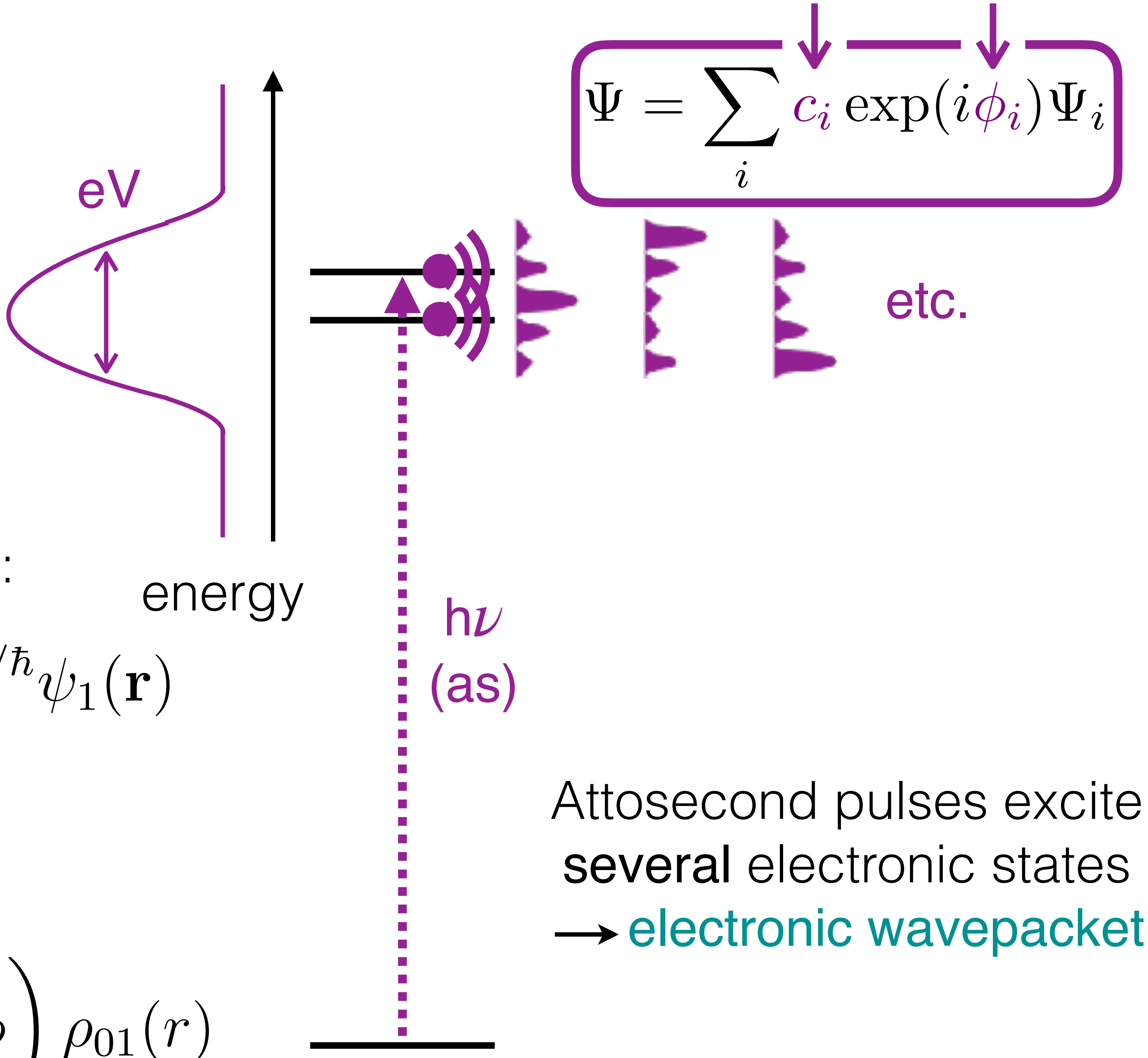
$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{\mathcal{H}}_e(\mathbf{r})\Psi(\mathbf{r},t)$$

Time-dependent electronic wavepacket:

$$\Psi(\mathbf{r},t) = c_0 e^{-iE_0 t/\hbar}\psi_0(\mathbf{r}) + c_1 e^{-iE_1 t/\hbar}\psi_1(\mathbf{r})$$

Time-dependent electronic density:

$$\rho(r,t) = |c_0|^2\rho_{00}(r) + |c_1|^2\rho_{11}(r) + 2|c_0||c_1|\cos\left(\frac{E_1 - E_0}{\hbar}t + \phi\right)\rho_{01}(r)$$



$$\boxed{\Psi = \sum_i c_i \exp(i\phi_i)\Psi_i}$$

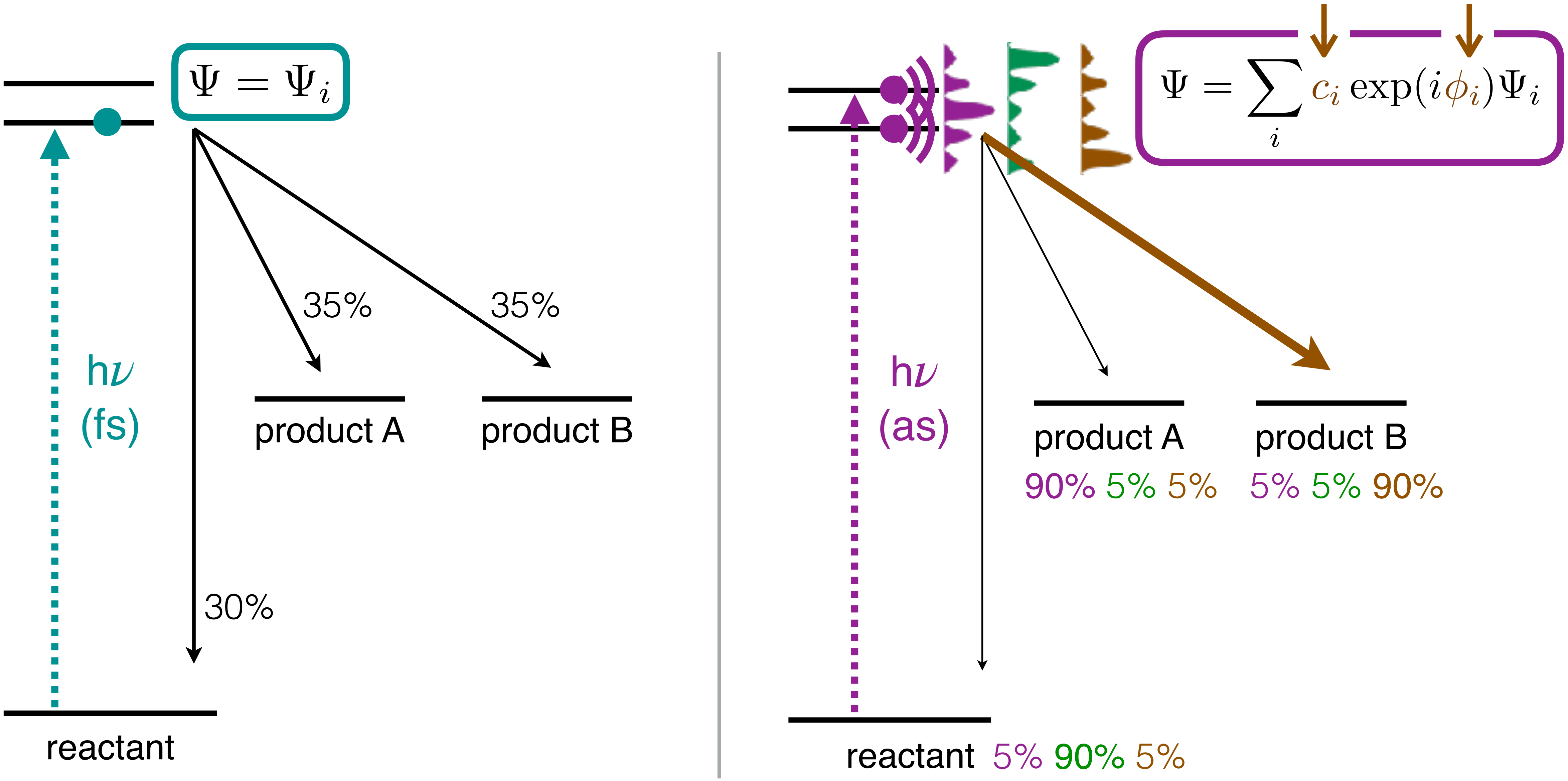
Attosecond pulses excite **several** electronic states
→ electronic wavepacket

What would be the chemical reactivity?

Breidbach and Cederbaum, J. Chem. Phys. 118, 9 (2003)
Lunnemann et al, Chem. Phys. Lett. 450, 232 (2008)

The concept of atto-photochemistry

The idea of « atto-photochemistry" is to bring the recent technological progress in attoscience to the field of photochemistry.



$\Psi = \Psi_i$

35%

35%

$h\nu$ (fs)

product A

product B

30%

reactant

$\Psi = \sum_i c_i \exp(i\phi_i)\Psi_i$

$h\nu$ (as)

product A

90% 5% 5%

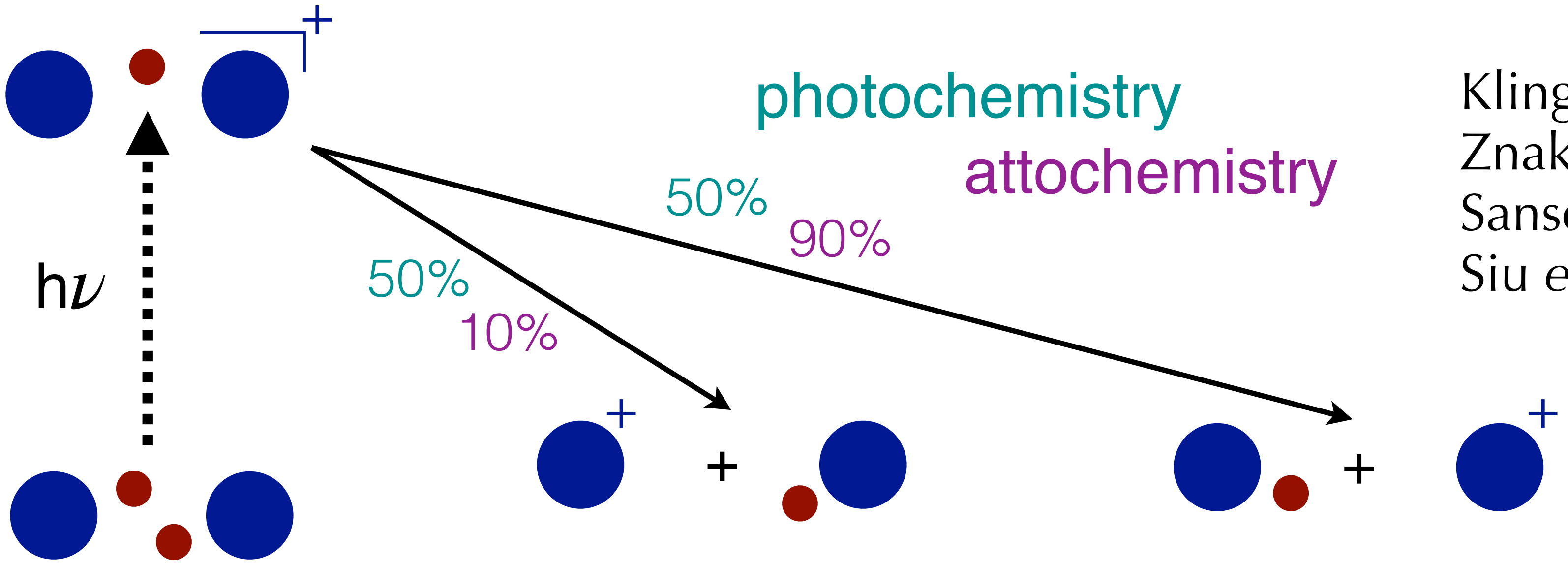
product B

5% 5% 90%

reactant 5% 90% 5%

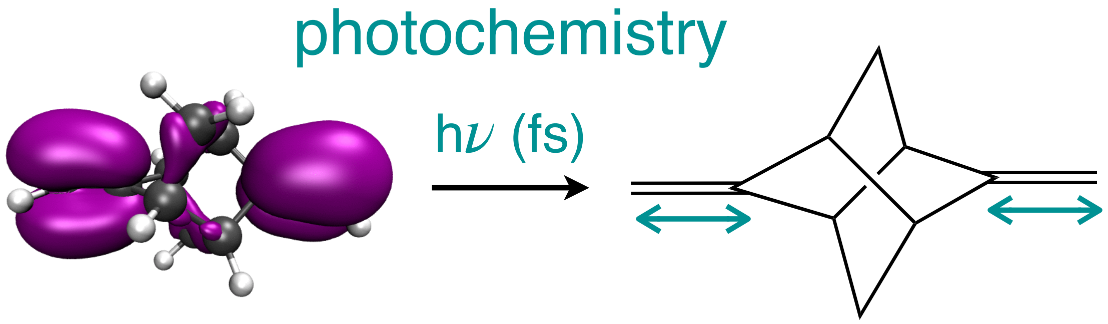
First steps towards atto-photochemistry

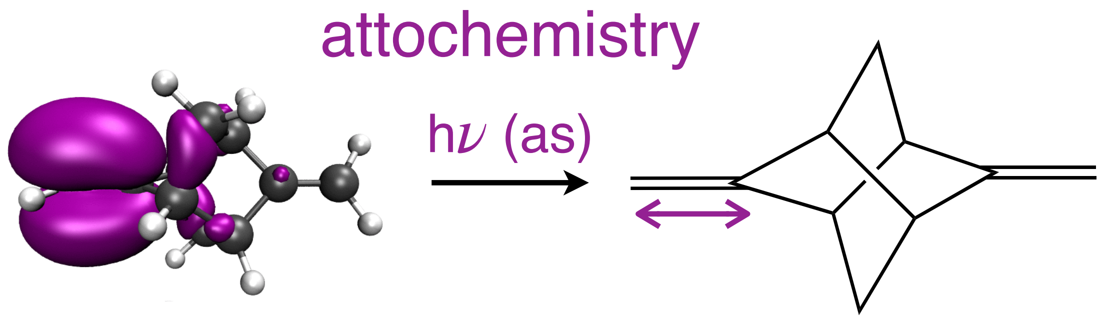
Experimental proof-of-concept in diatomics: H_2, CO, O_2



Kling *et al.* Science 312, 246-248 (2006)
Znakovskaya *et al.* PRL 103, 103002 (2009)
Sansone *et al.* Nature 465, 763-766 (2010)
Siu *et al.* PRA 84, 063412 (2011)

Theoretical preliminary results in polyatomic molecules





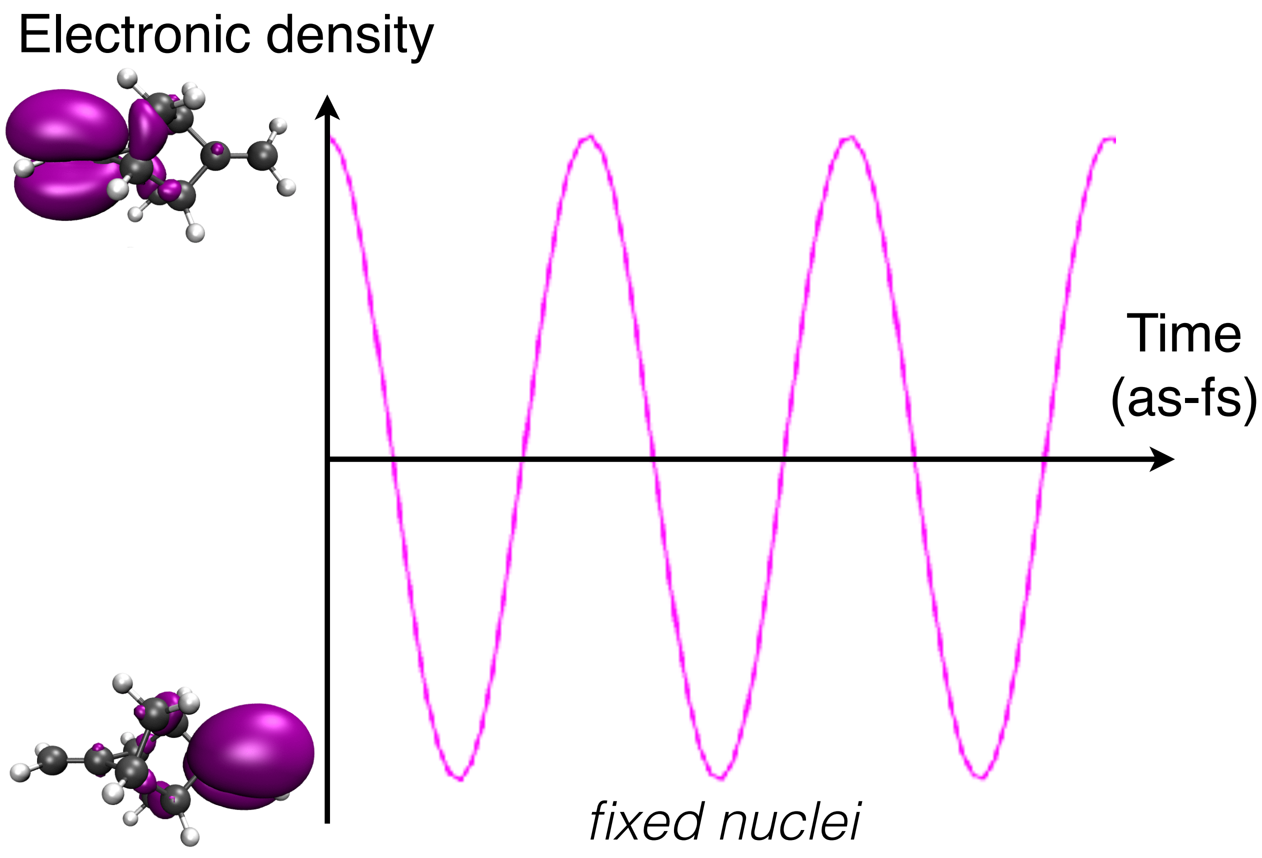
Vacher* *et al.* Faraday Discuss. 194 (2016)

The current goal is to explore the concept of
atto-photochemical reactions in polyatomic molecules.

Challenges of atto-photochemistry

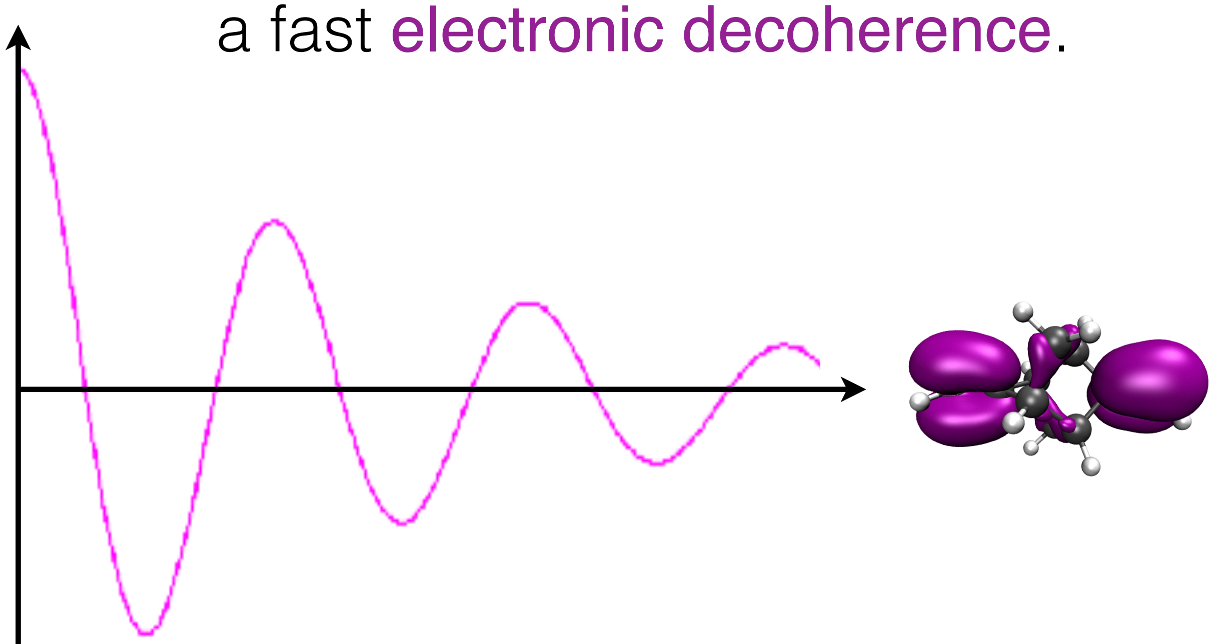
Scientific challenges - *for both theory and experiment*

1



fixed nuclei

The nuclear degrees of freedom leads to a fast electronic decoherence.



nuclei moving

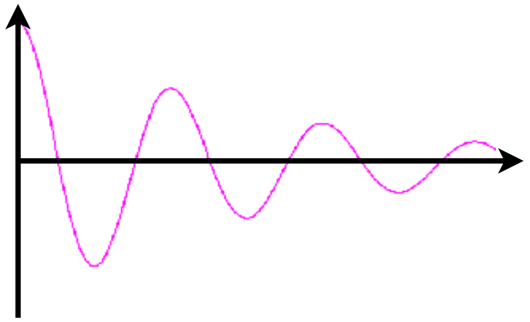
Cederbaum *et al.* Chem. Phys. Lett. 307, 205-210 (1999)
Remacle *et al.* Z. Anorg. Chem. 221, 647-661 (2007)

Vacher *et al.* Phys. Rev. A 92, 040502 (2015)
Vacher* *et al.* Phys. Rev. Lett. 118, 083001 (2017)

Challenges of atto-photochemistry

Scientific challenges - *for both theory and experiment*

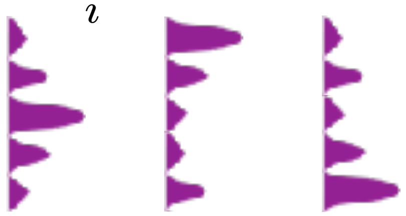
1



Is electronic coherence long enough to affect a chemical reaction?

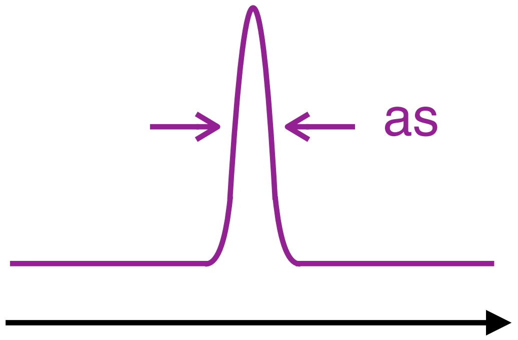
2

$$\Psi = \sum_i c_i \exp(i\phi_i)\Psi_i$$



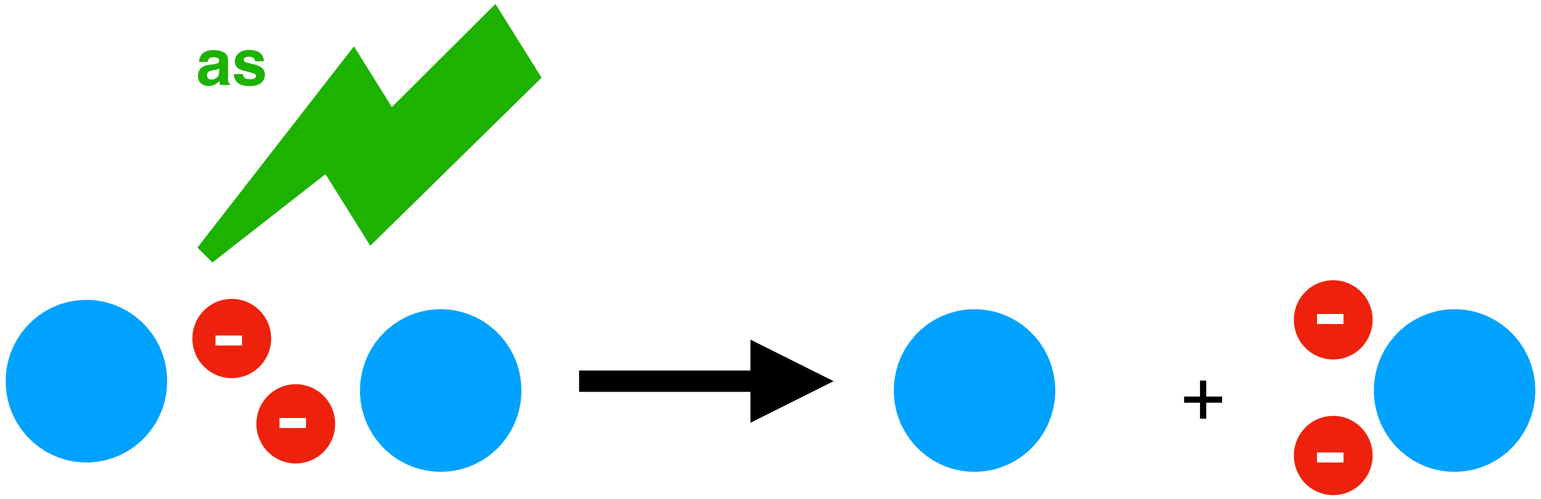
What electronic wavepacket will induce the desired reaction?

3



What pulse should excite the molecule?

Challenges in attochemistry and its theoretical description



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Coupled electron and nuclear dynamics

time-dependent
Schrödinger equation

$$i\hbar\frac{\partial\Phi}{\partial t} = \boxed{\hat{H}}\Phi$$

molecular Hamiltonian $\boxed{\hat{H}} = \hat{T}_n + \hat{T}_e + \hat{U}$

clampled-nucleus Hamiltonian $\hat{H}_{el}(\mathbf{r};\mathbf{R}) = \hat{T}_e(\mathbf{r}) + \hat{U}(\mathbf{r};\mathbf{R})$

For any given value of **R**, $\hat{H}_{el}\boxed{\psi_i(\mathbf{r};\mathbf{R})} = E_i(\mathbf{R})\boxed{\psi_i(\mathbf{r};\mathbf{R})}$

electronic eigenstates electronic eigenvalues

Born representation: $\Phi(\mathbf{r},\mathbf{R},t) = \sum_i^{\infty} \boxed{\chi_i(\mathbf{R},t)}\boxed{\psi_i(\mathbf{r};\mathbf{R})}$

nuclear function

$$\boxed{i\hbar\frac{\partial\chi_j}{\partial t} = [\hat{T}_n + E_j]\chi_j - \sum_i^{\infty}\hat{\Lambda}_{ji}\chi_i}$$

Worth and Cederbaum, *Annu. Rev. Phys. Chem.* **55**, 127:58 (2004)

Coupled electron and nuclear dynamics

$$i\hbar\frac{\partial\chi_j}{\partial t} = [\hat{T}_n + E_j]\chi_j - \sum_i^{\infty} \hat{\Lambda}_{ji}\chi_i$$

non-adiabatic coupling: $\hat{\Lambda}_{ij} = \frac{1}{2M}(2F_{ij}\cdot\nabla + G_{ij})$

$$F_{ij} = \langle\psi_i|\nabla\psi_j\rangle = \frac{\langle\psi_i|(\nabla\hat{H}_{el})|\psi_j\rangle}{E_j - E_i}$$

Group Born-Oppenheimer approximation

$$\Phi(\mathbf{r},\mathbf{R},t) = \sum_{i\in\{g\}} \chi_i(\mathbf{R},t)\psi_i(\mathbf{r};\mathbf{R})$$

$$i\hbar\frac{\partial\chi_j}{\partial t} = [\hat{T}_n + E_j]\chi_j - \sum_{i\in\{g\}} \hat{\Lambda}_{ji}^{(g)}\chi_i$$

Worth and Cederbaum, *Annu. Rev. Phys. Chem.* **55**, 127:58 (2004)

How to describe coupled electron-nuclear dynamics?

Born representation: $\Phi(\mathbf{r}, \mathbf{R}, t) = \sum_{i \in \{g\}} \chi_i(\mathbf{R}, t) \psi_i(\mathbf{r}; \mathbf{R})$

what basis of electronic states?

How to describe coupled electron-nuclear dynamics?

Basis of electronic states

- Adiabatic basis

$$i\hbar\frac{\partial\chi_j}{\partial t} = [\hat{T}_n + V_j]\chi_j - \sum_i \cancel{\hat{\Lambda}}_{ji}\chi_i$$

- Diabatic basis

$$\tilde{\psi} = S(R)\psi$$

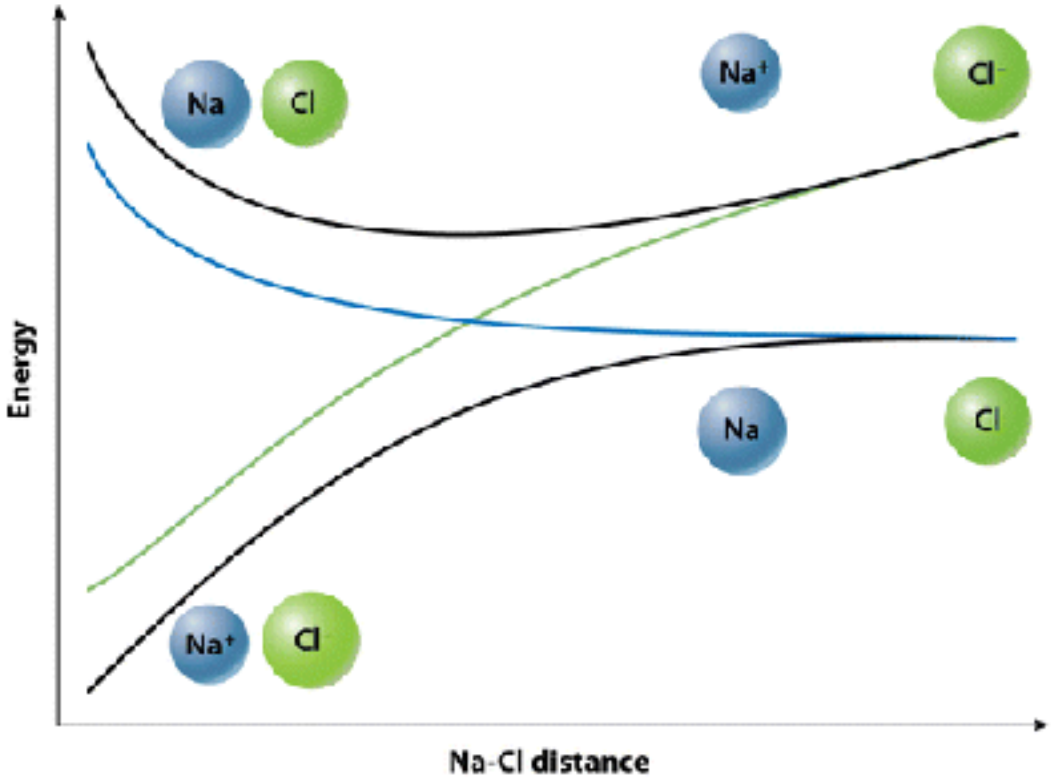
$$i\hbar\frac{\partial\tilde{\chi}_j}{\partial t} = \hat{T}_n\tilde{\chi}_j + \sum_i W_{ji}\tilde{\chi}_i$$

😊 no singularity of the derivative coupling

😓 how to find *S(R)* ?

😊 what comes out of standard quantum chemistry packages

😟 singularity of derivative coupling at conical intersection



Van Voorhis et al, *Annu. Rev. Phys. Chem.* **61**, 149 (2010)

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non-adiabatic coupling

$$F_{ij} = \langle\psi_i|\nabla\psi_j\rangle = \frac{\langle\psi_i|(\nabla\hat{H}_{el})|\psi_j\rangle}{E_j - E_i}$$

Thiel et al, *JCP* **110**, 9371 (1999), Köppel et al, *JCP* **115**, 2377 (2001)

How to describe coupled electron-nuclear dynamics?

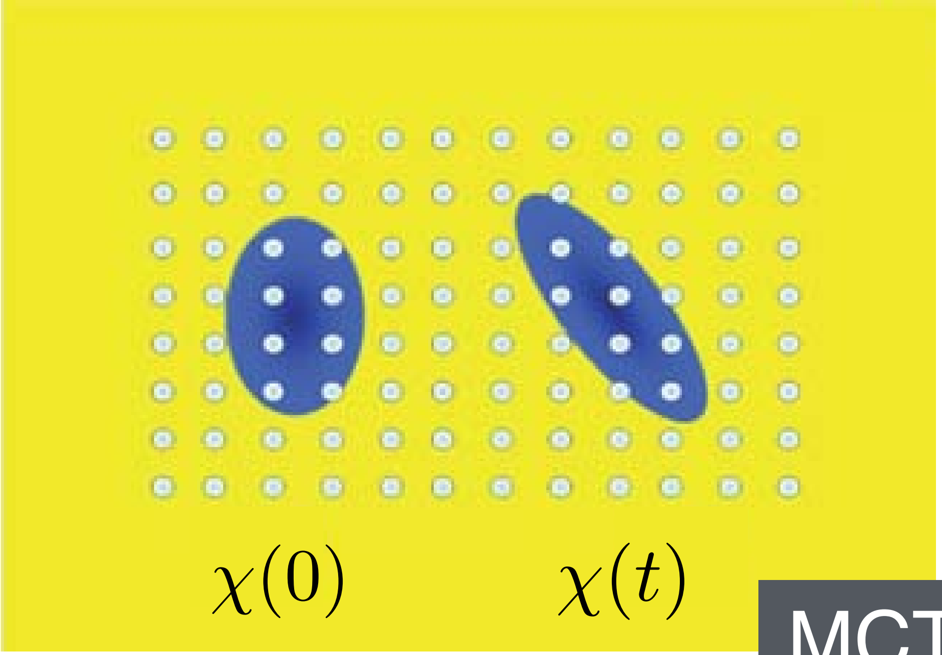
Born representation: $\Phi(\mathbf{r}, \mathbf{R}, t) = \sum_{i \in \{g\}} \chi_i(\mathbf{R}, t) \psi_i(\mathbf{r}; \mathbf{R})$

how to represent the nuclear wavefunction?

How to describe coupled electron-nuclear dynamics?

Representation of nuclear wavefunctions

Grid-based methods

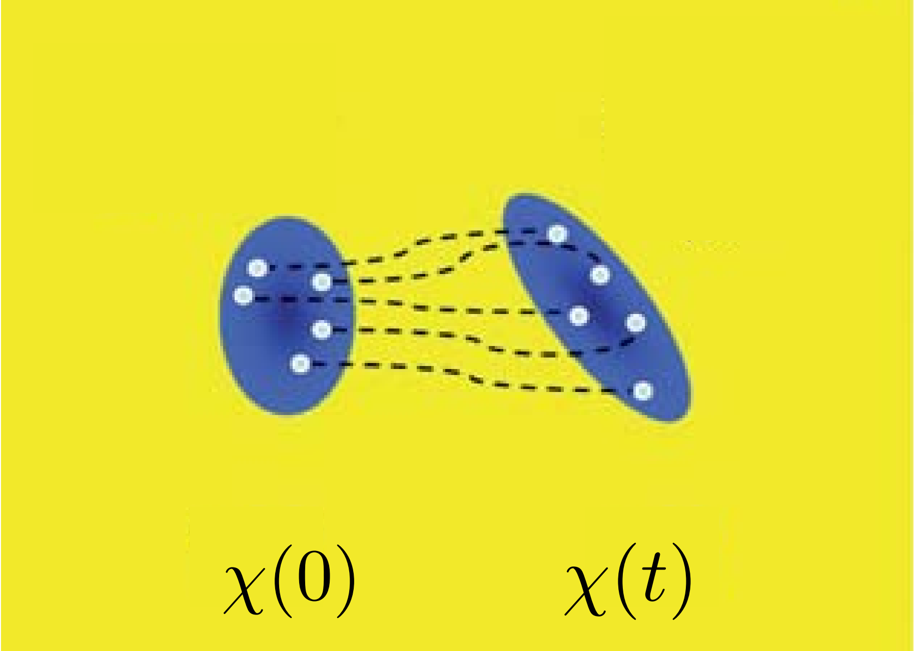


MCTDH

- 😊 numerical integration on a grid
- 😟 computation and fit of PES before any dynamics calculation
- 😭 p grid points per dimension, N dimensions: p^N grid points in total.

→ "exponential scaling" of the basis set with the number of degrees of freedom

Trajectory-based methods



- 😊 minimise the basis set size
- 😟 convergence with respect to the basis set size
- 😊 more intuitive picture
- 😊 local character of Basis Function (BF)

→ generate the PES "on-the-fly"

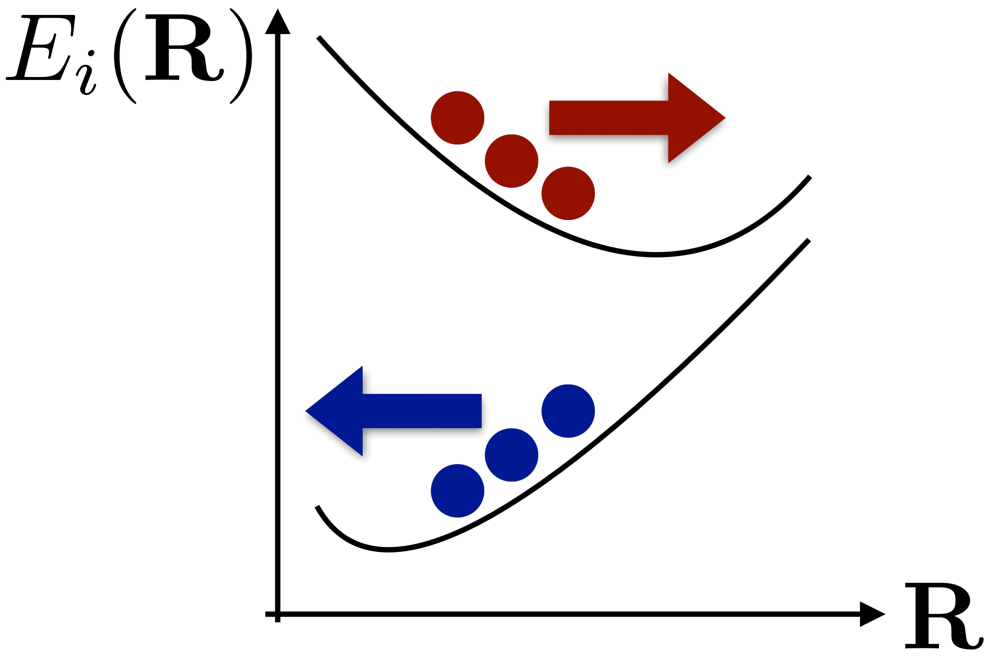
Shalashilin, *Faraday Discuss.* **153**, 105-116 (2011)

How to describe coupled electron-nuclear dynamics?

Representation of nuclear wavefunctions

Trajectory-based methods

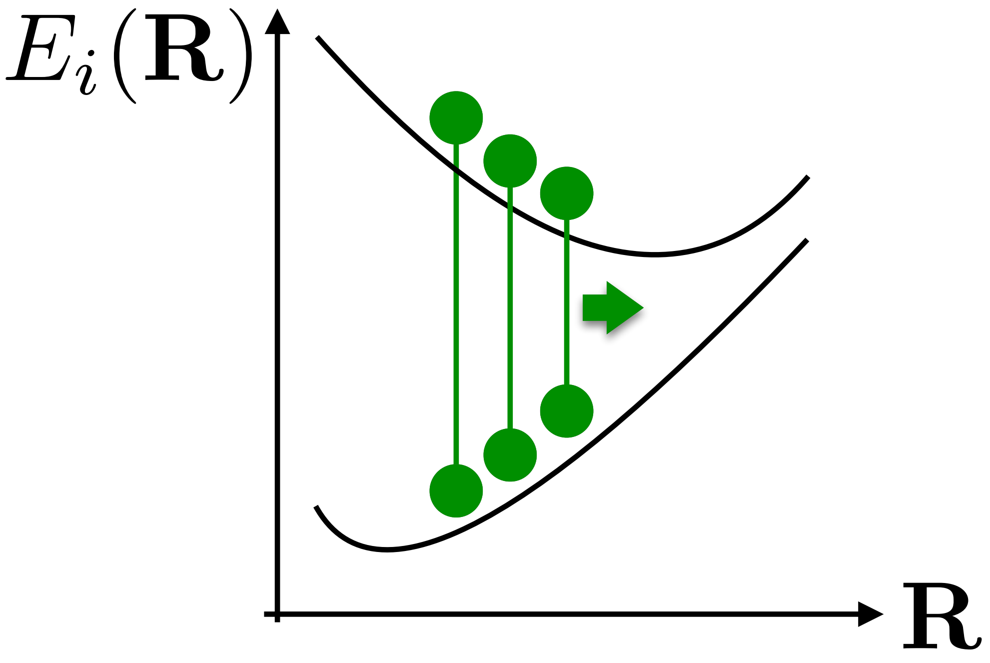
“multi-set” formalism



😊 BF able to adapt better to the different electronic states

😟 need more basis functions

“single-set” formalism

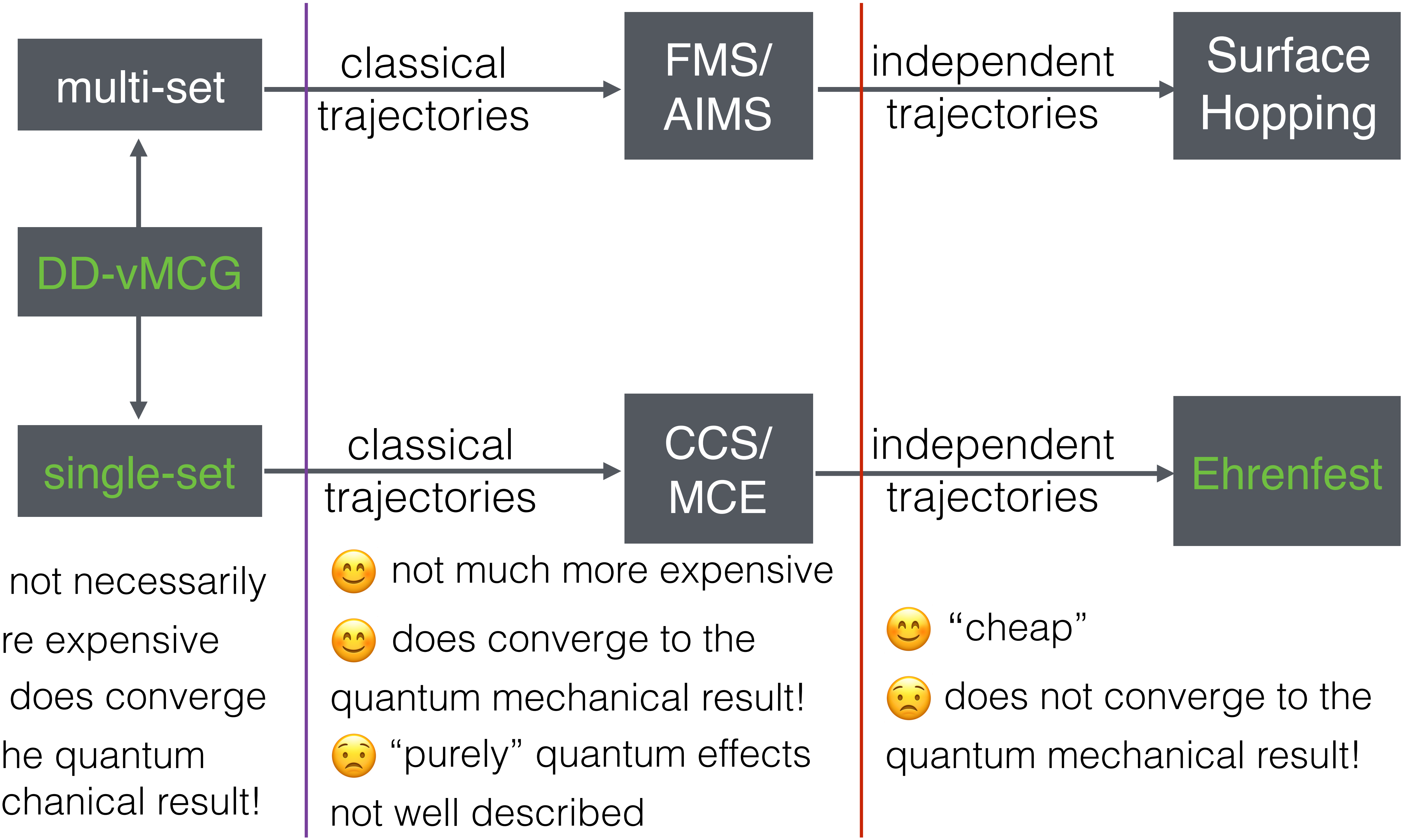


😊 need less basis functions

😟 BF constrained to move the same way for all electronic states

Shalashilin, *Faraday Discuss.* **153**, 105-116 (2011)

How to describe coupled electron-nuclear dynamics?



multi-set

classical trajectories

FMS/ AIMS

independent trajectories

Surface Hopping

DD-vMCG

single-set

classical trajectories

CCS/ MCE

independent trajectories

Ehrenfest

😐 not necessarily more expensive

😊 does converge to the quantum mechanical result!

😊 not much more expensive

😊 does converge to the quantum mechanical result!

😟 “purely” quantum effects not well described

😊 “cheap”

😟 does not converge to the quantum mechanical result!

DD-vMCG: direct dynamics variational multi-configuration Gaussian
FMS: full multiple spawning and **AIMS**: ab initio multiple spawning
CCS: coupled-coherent states and **MCE**: multi-configurational Ehrenfest

Vacher et al, *Theor. Chem. Acc.* **135**, 187 (2016)

The trajectory surface hopping method

- A mixed quantum-classical dynamics method

electron dynamics

$$\Phi(r,t;R(t)) = \sum_k C_k(t)\phi_k(r;R(t))$$

$$i\hbar\frac{\partial C_i}{\partial t} = \sum_k C_k\left(H^{el}_{ik} - i\hbar\langle\phi_i|\frac{\partial\phi_k}{\partial t}\rangle\right)$$

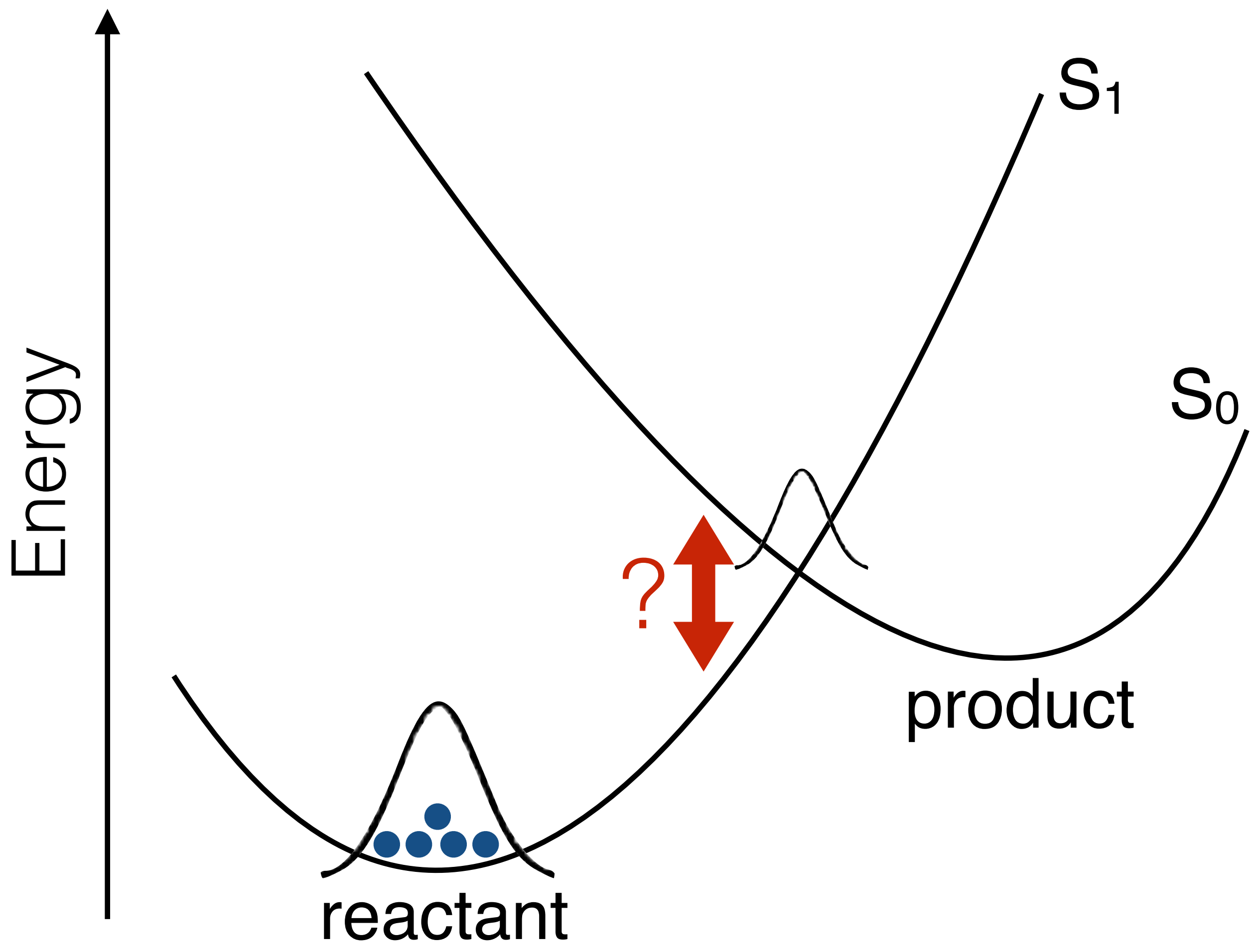
time-derivative non-adiabatic coupling

$$= \sum_k C_k\left(H^{el}_{ik} - i\hbar\frac{\partial R}{\partial t}\cdot\langle\phi_i|\frac{\partial\phi_k}{\partial R}\rangle\right)$$

time-independent non-adiabatic coupling vector

nuclear dynamics $\{R(t);P(t)\}$

$$\frac{dP(t)}{dt} = -\overrightarrow{\nabla}_R\langle\phi_i|H^{el}|\phi_i\rangle$$

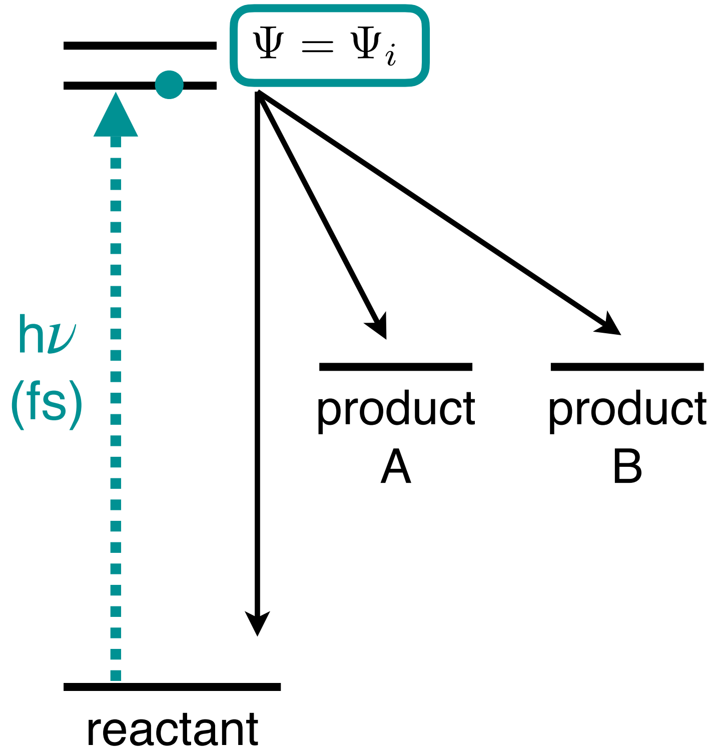


- Fewest switching algorithm

a stochastic procedure and a hopping probability to determine the « active » state

Which dynamics methods for attochemistry?

- Benchmark of dynamics methods in the case of femtochemistry



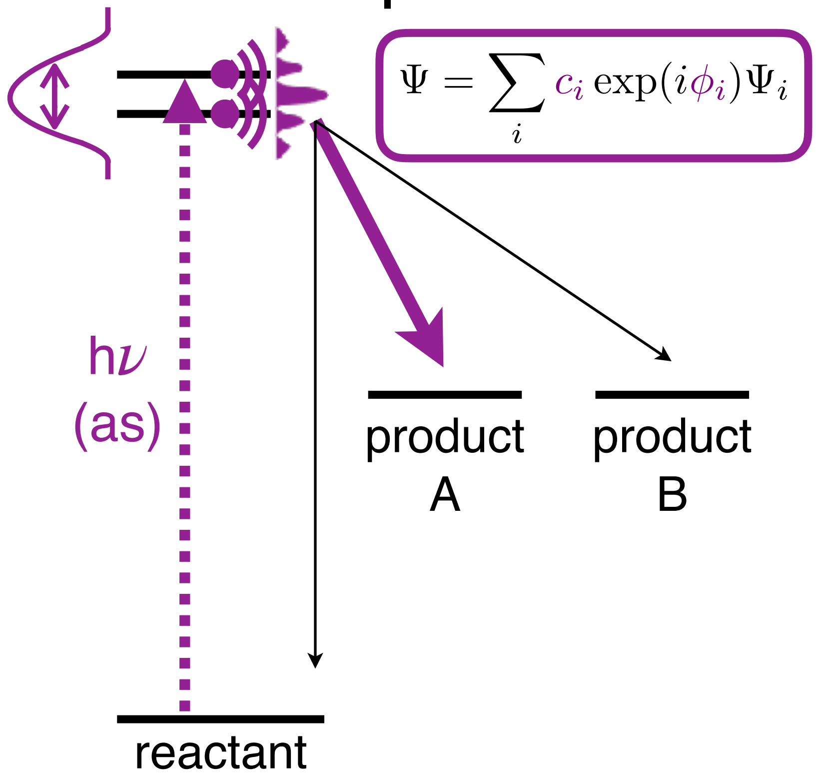
Ibele and Curchod, *Phys. Chem. Chem. Phys.* **22**, 15183-15196 (2020)

Janos and Slavicek, *J. Chem. Theory Comput.* **19**, 8273-8284 (2023)

Gomez, Spinlove and Worth, *Phys. Chem. Chem. Phys.* **26**, 1929-1844 (2024)

-> For most photochemical reactions, the surface hopping method works well.

- Mixed quantum-classical methods used in attochemistry



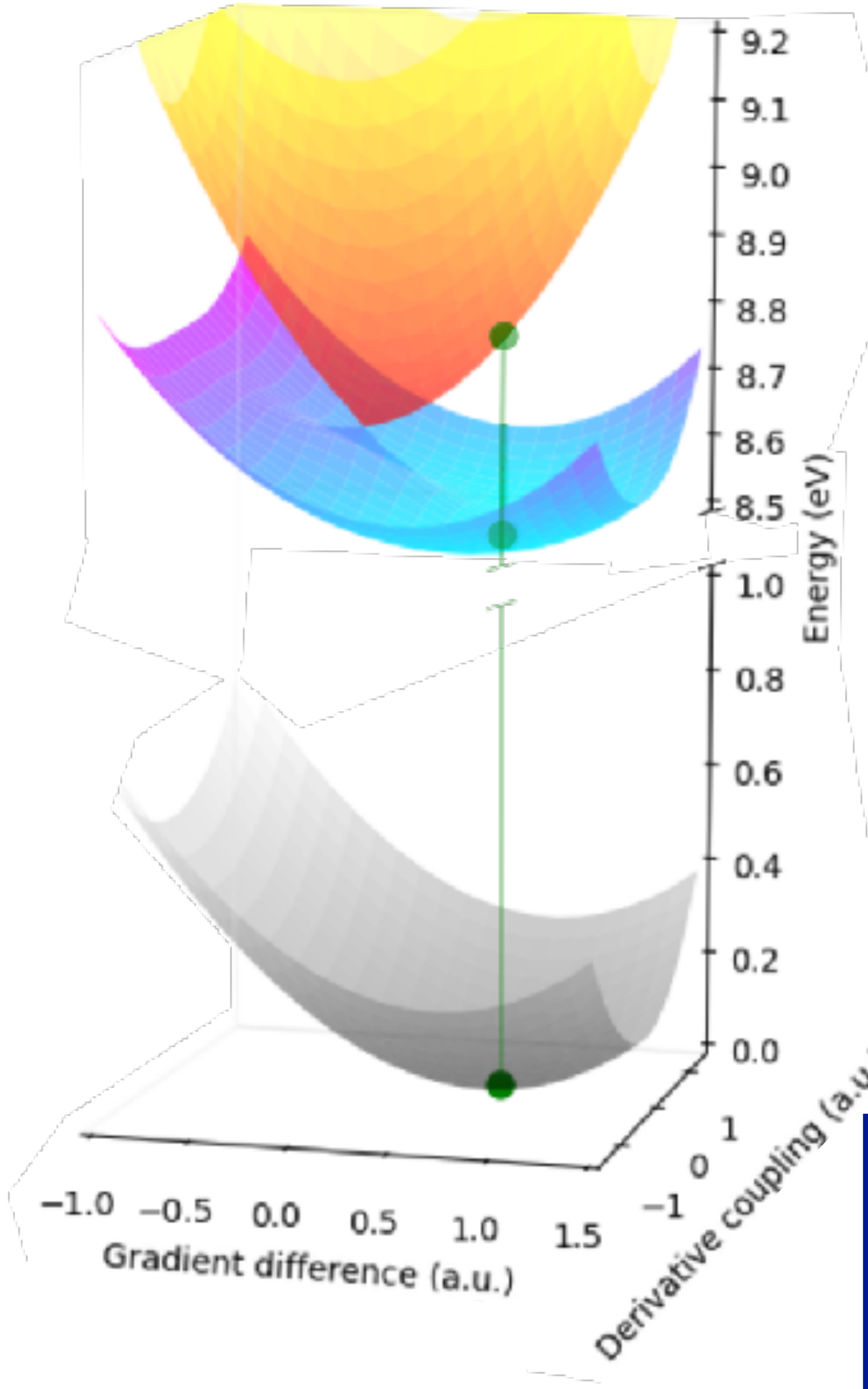
Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, **377**, 20170472 (2019)

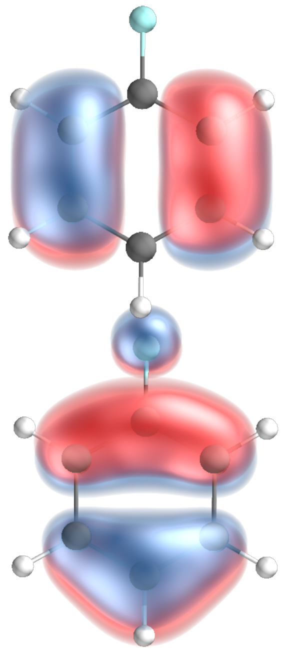
J. Phys. B: At. Mol. Opt. **53**, 164006 (2020)

Faraday Discuss. **228**, 349-377 (2021)

-> How valid are mixed quantum-classical methods for attochemistry?

Ionisation of fluoro-benzene as a model system





D₁ Ψ_A « antiquinoid »

D₀ Ψ_Q « quinoid »

4 initial electronic states considered:

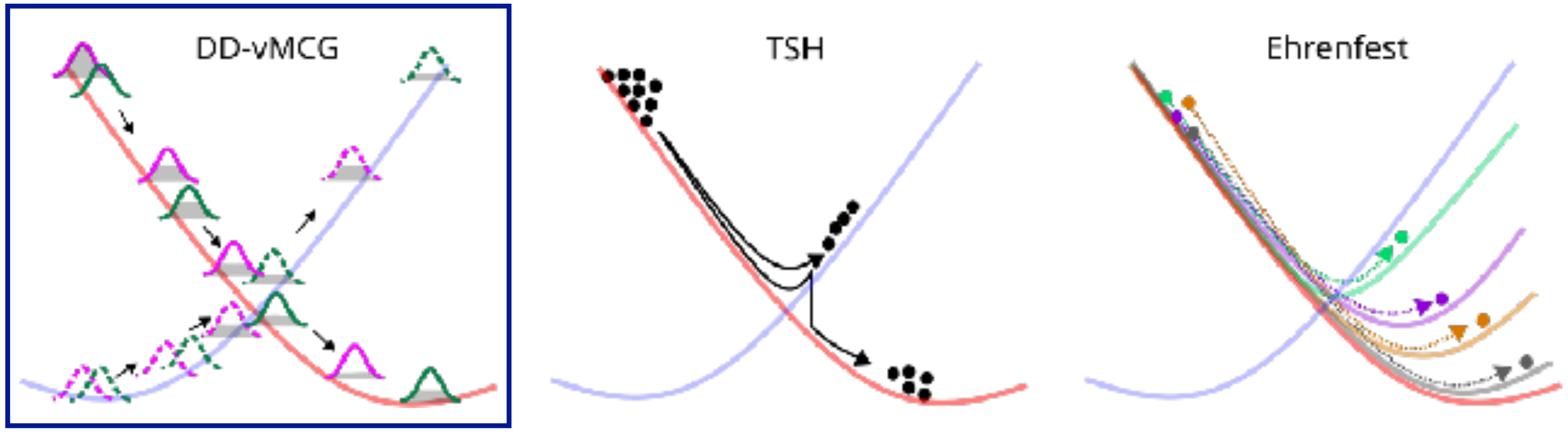
$$\Psi_Q$$

$$\Psi_A$$

$$\frac{1}{\sqrt{2}}(\Psi_Q + \Psi_A)$$

$$\frac{1}{\sqrt{2}}(\Psi_Q - \Psi_A)$$

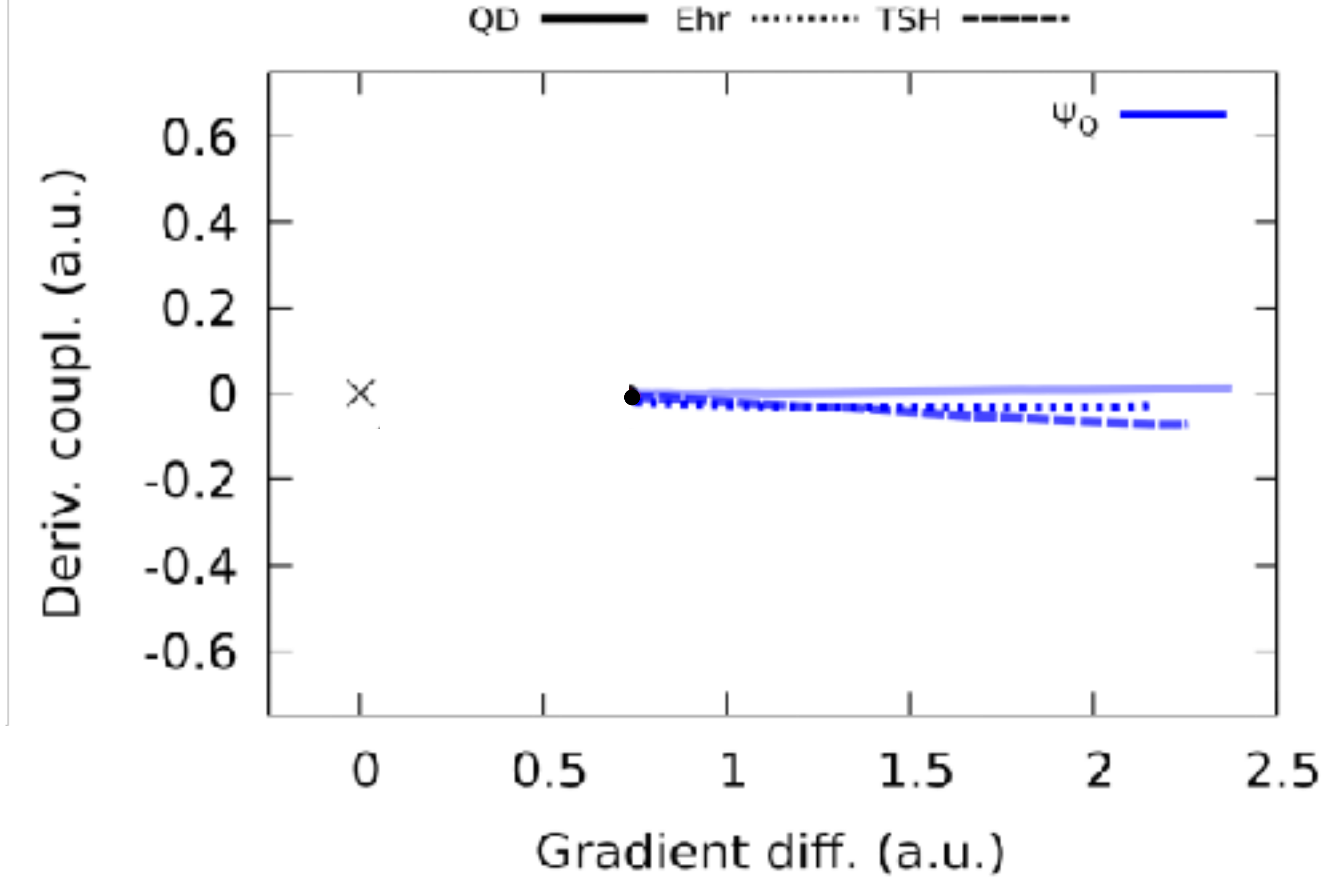
3 dynamics methods tested:



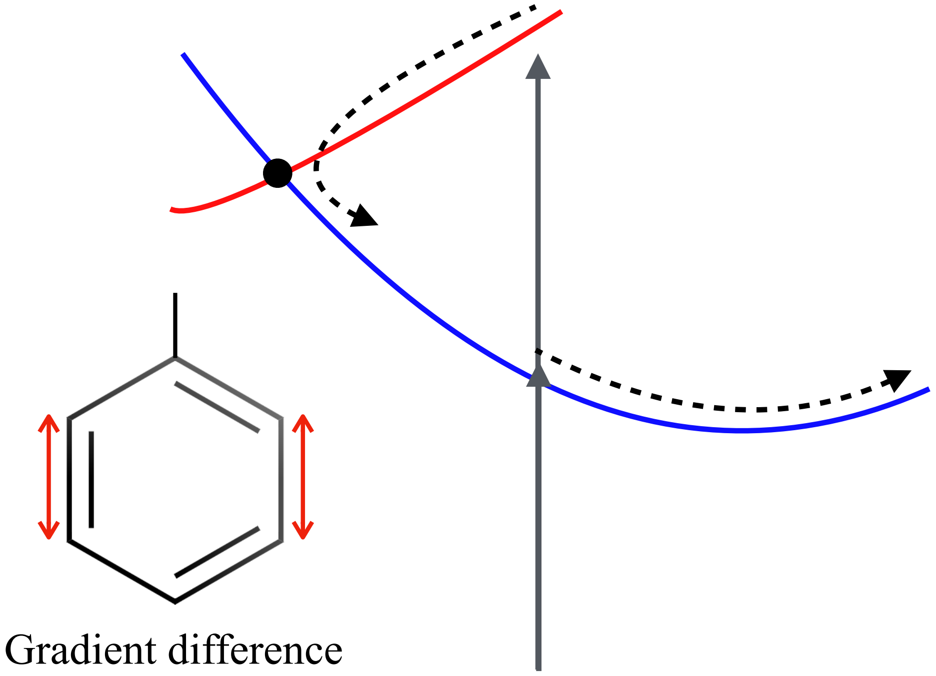
Tran, Ferté and Vacher, *J. Phys. Chem. Lett.* **15**, 3646-3652 (2024)

Dynamics upon ionisation to a single state

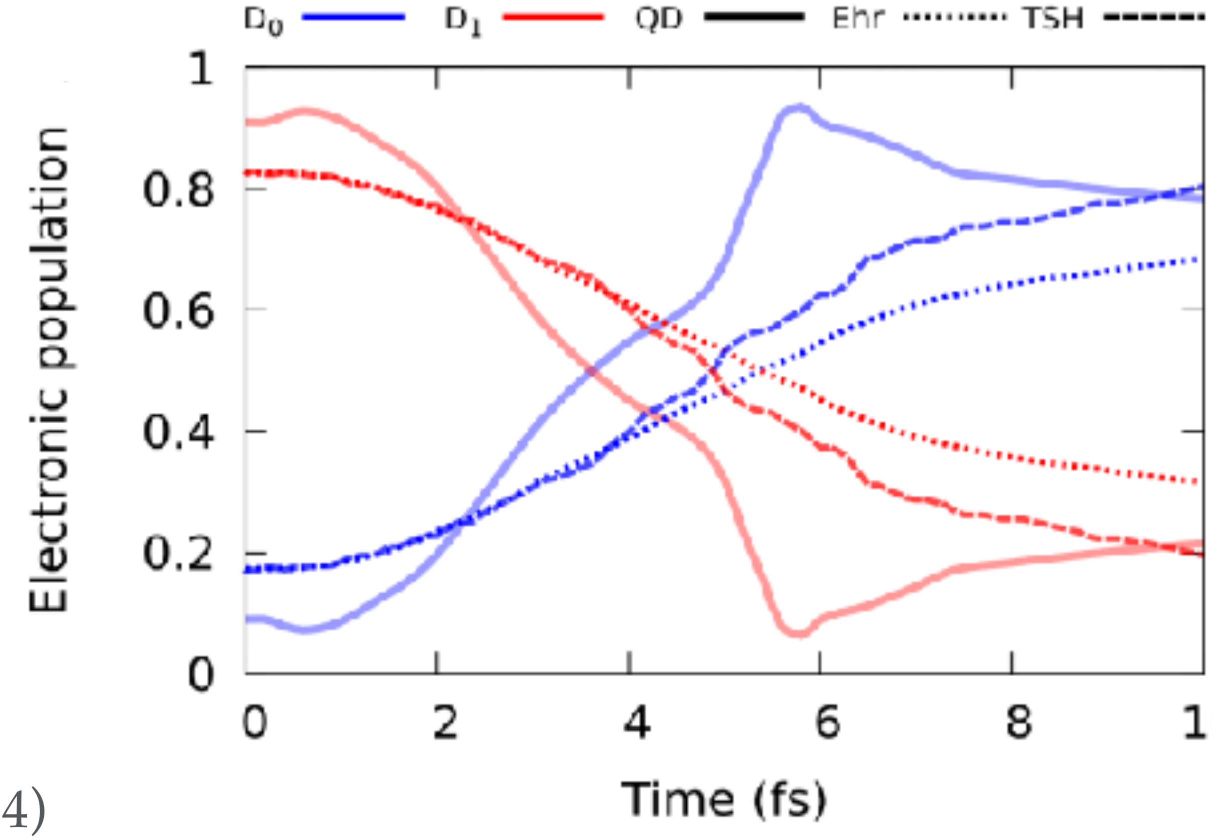
Average nuclear motion



Mixed quantum-classical methods reproduce the quantum dynamics induced by single electronic adiabatic states, as in standard photochemistry.



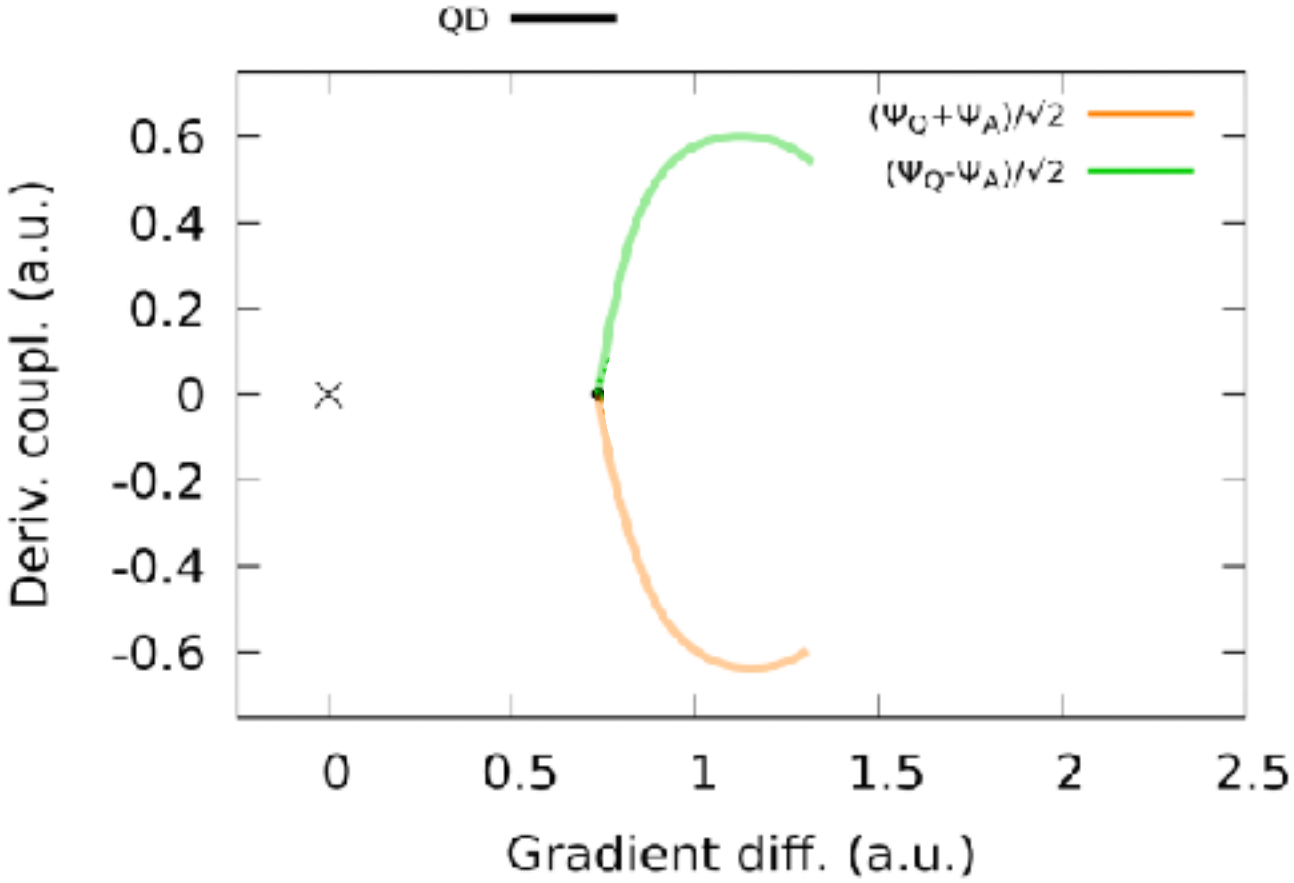
Electronic population decay



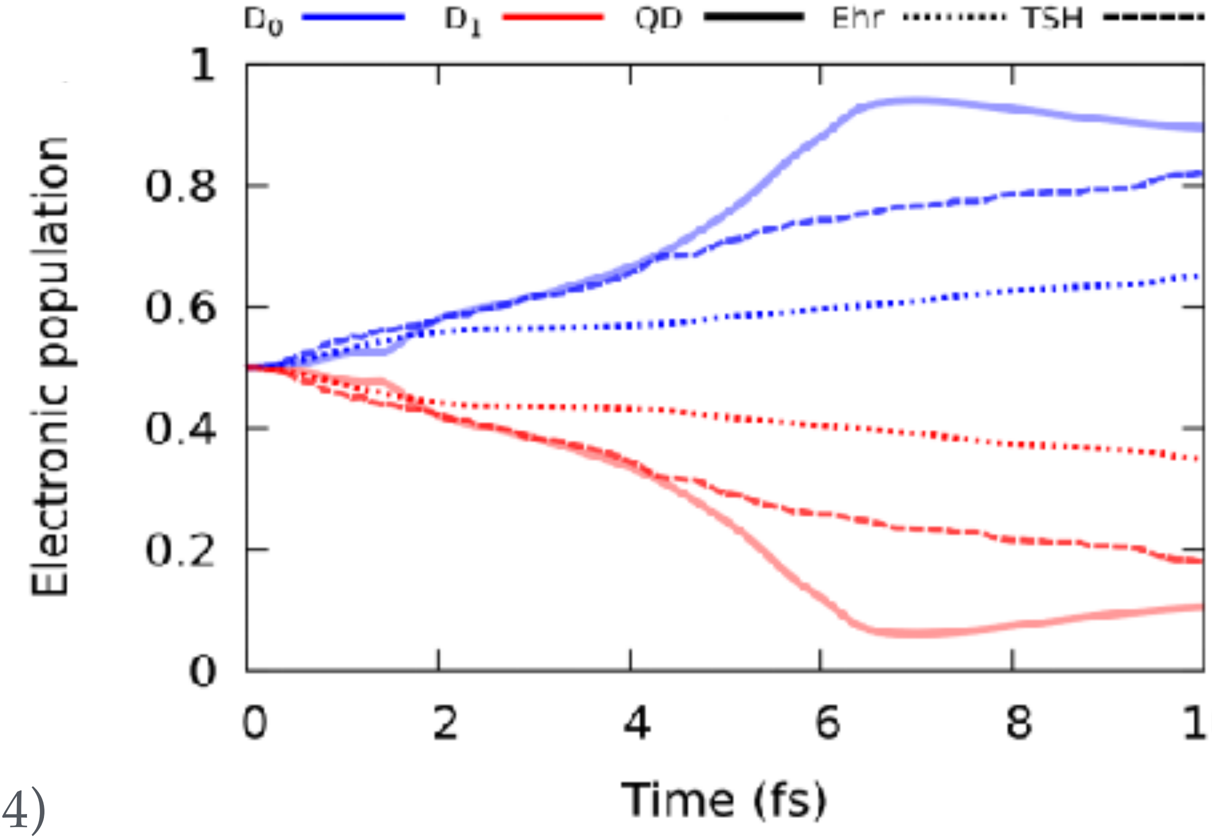
Tran, Ferté and Vacher, *J. Phys. Chem. Lett.* **15**, 3646-3652 (2024)

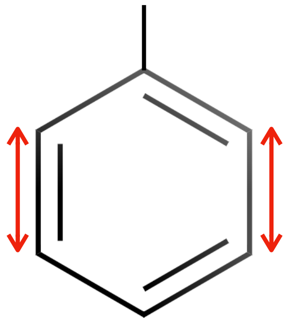
Dynamics upon ionisation to electronic wavepackets

Average nuclear motion

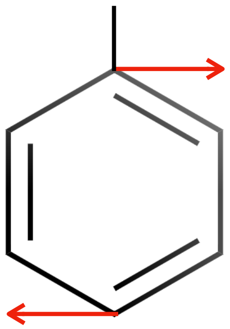


Electronic population decay





Gradient difference

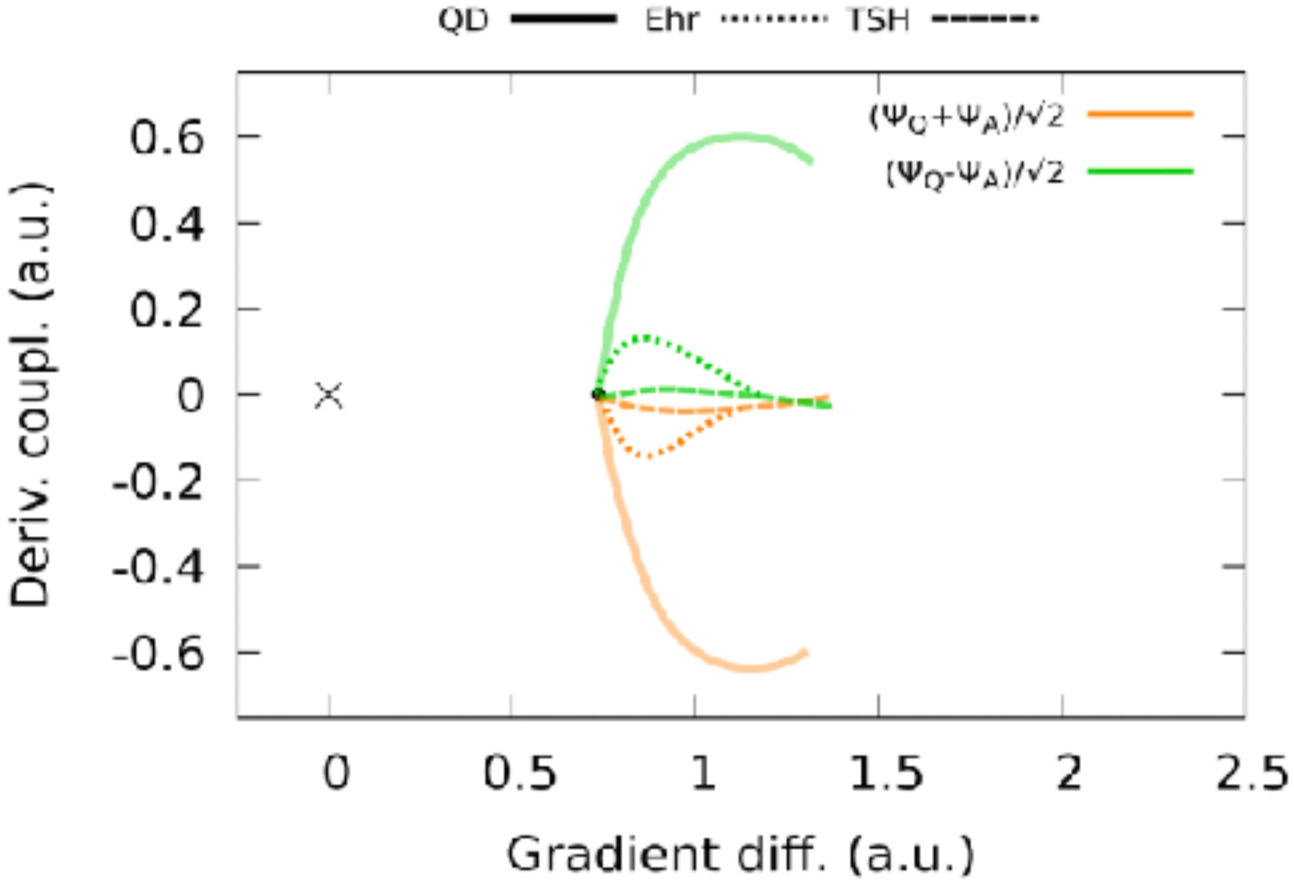


Derivative coupling

Tran, Ferté and Vacher, *J. Phys. Chem. Lett.* **15**, 3646-3652 (2024)

Dynamics upon ionisation to electronic wavepackets

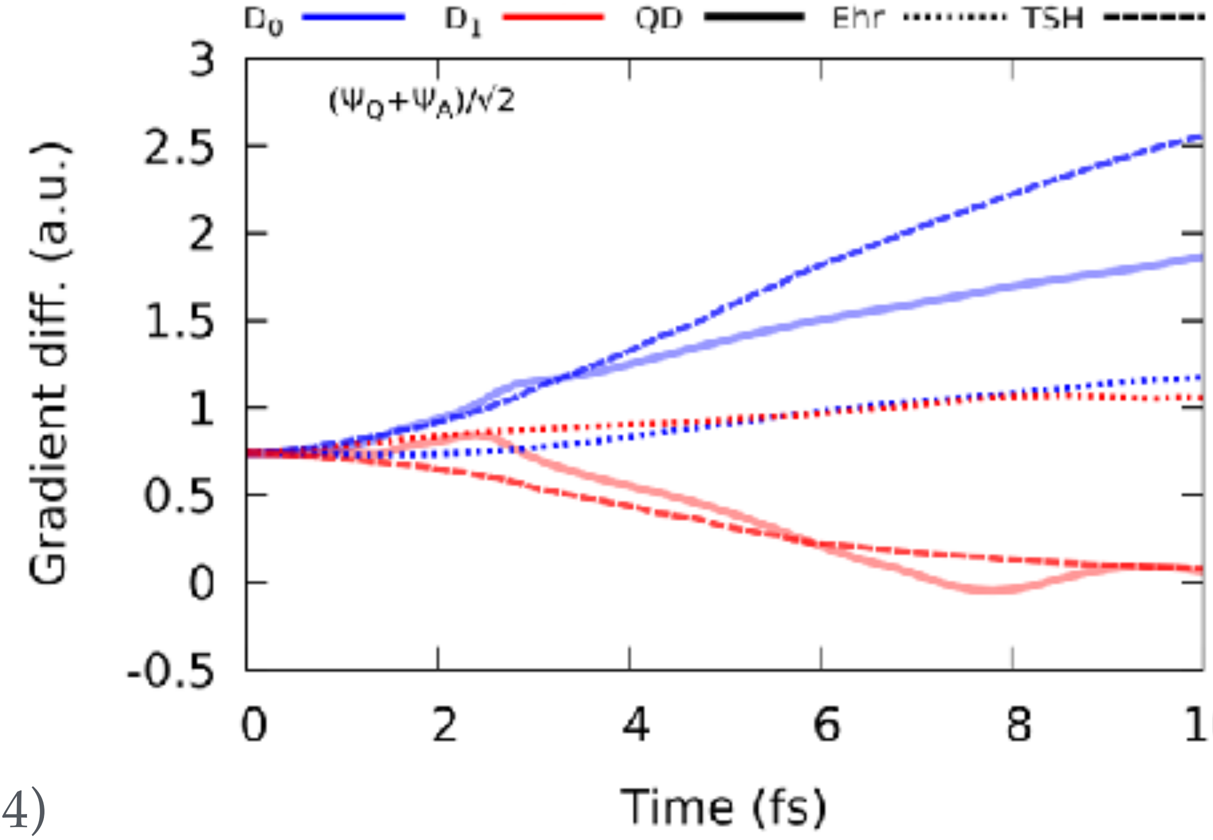
Average nuclear motion

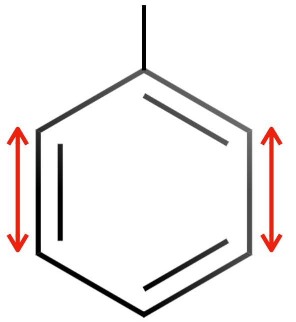


Accurate simulation of attochemical dynamics induced by electronic wavepackets thus requires a full quantum treatment.

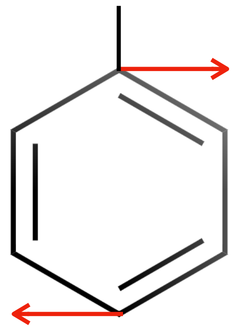
The most accurate dynamics method predicts the strongest attochemical control of the nuclear motion.

Nuclear motion on individual electronic states





Gradient difference



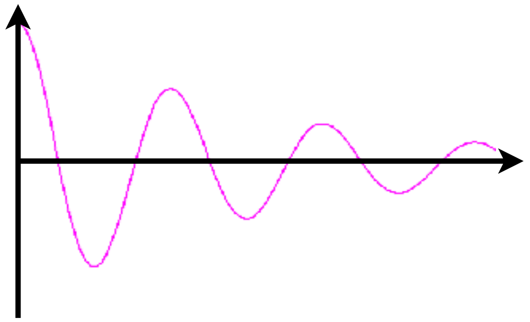
Derivative coupling

Tran, Ferté and Vacher, *J. Phys. Chem. Lett.* **15**, 3646-3652 (2024)

Challenges of atto-photochemistry

Scientific challenges - *for both theory and experiment*

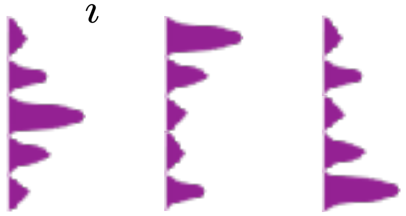
1



Is electronic coherence long enough to affect a chemical reaction?

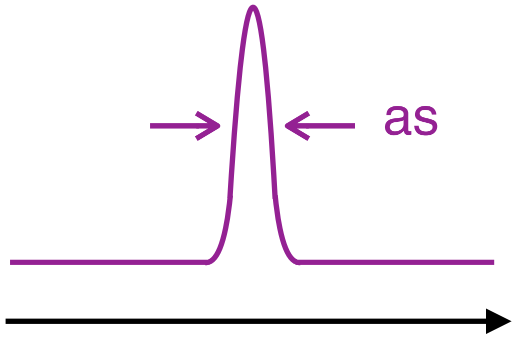
2

$$\Psi = \sum_i c_i \exp(i\phi_i)\Psi_i$$



What electronic wavepacket will induce the desired reaction?

3



What pulse should excite the molecule?

Theoretical challenges

4 Quantum treatment of electronic coherence

5 Inclusion of all nuclear degrees of freedom

6 Diabatisation of electronic states

Acknowledgements

Current team @CEISAM

Past members

Post-doc positions available

Thank you for your attention!

cnrs

CEISAM
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Modélisation

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