Describing photoexcitation in nonadiabatic molecular dynamics

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Centre for Computational Chemistry

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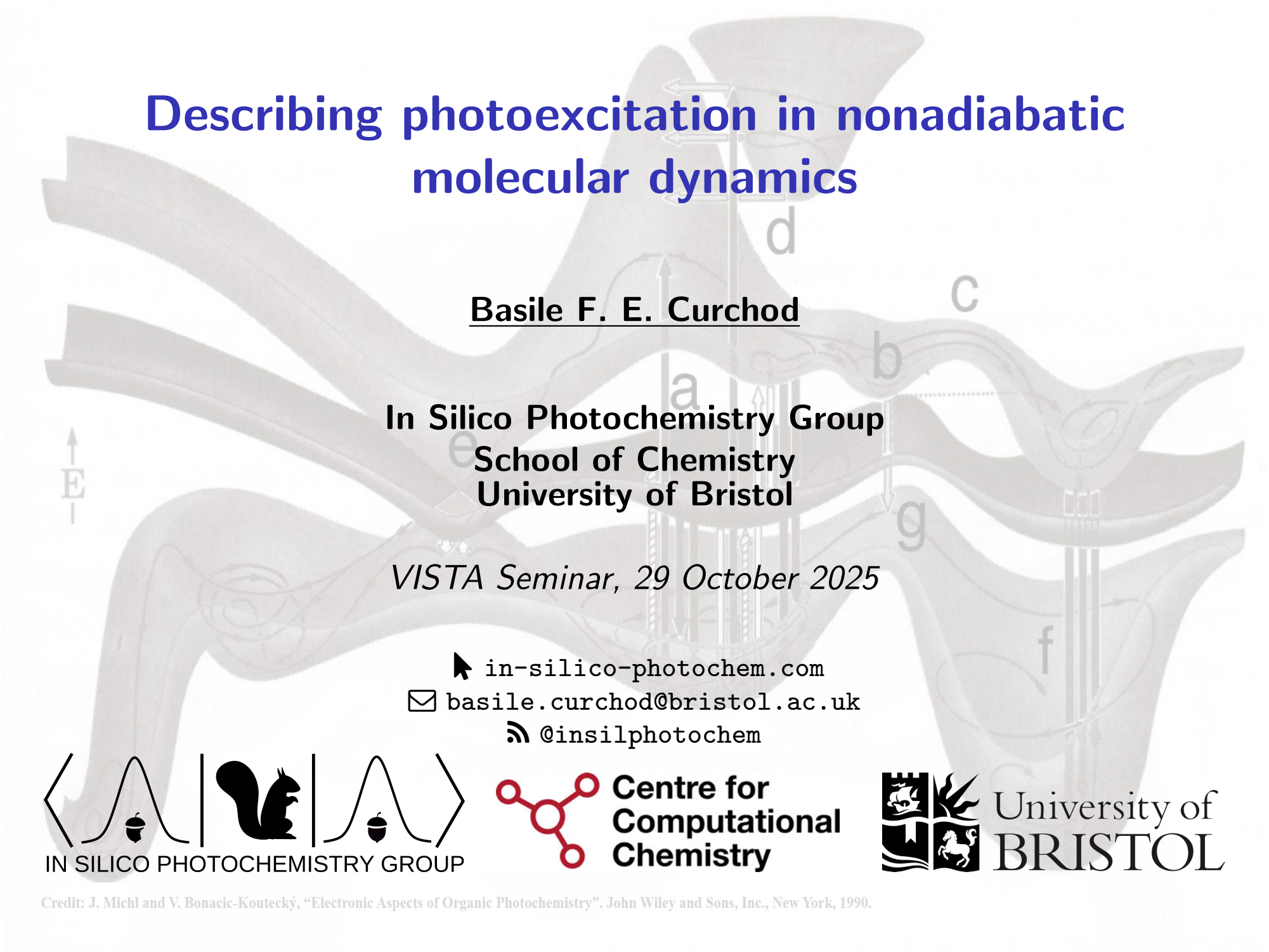
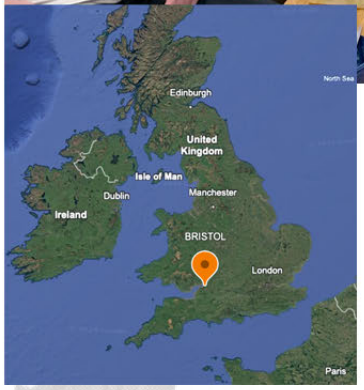


Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.



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Antonio Prlj (Ruđer Bošković Institute)
Lewis Hutton (Oxford)
Emanuele Marsili (Airbus)
Harry Stroud (U. Santiago de Compostela)
Kenzo Marmorat (ENS Paris)
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Terry Dillon & Andrew Rickard (U. of York)

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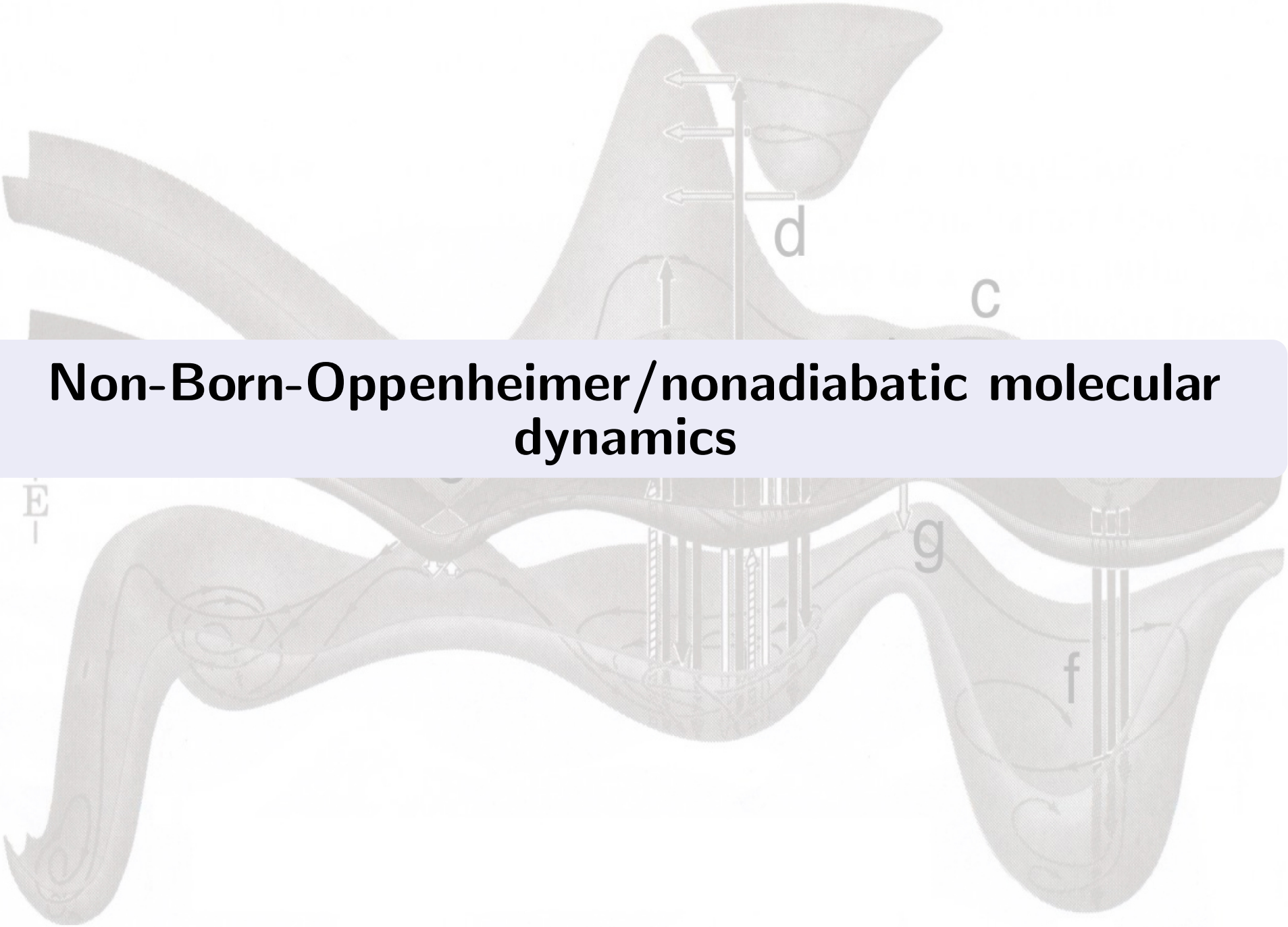
erc European Research Council Established by the European Commission

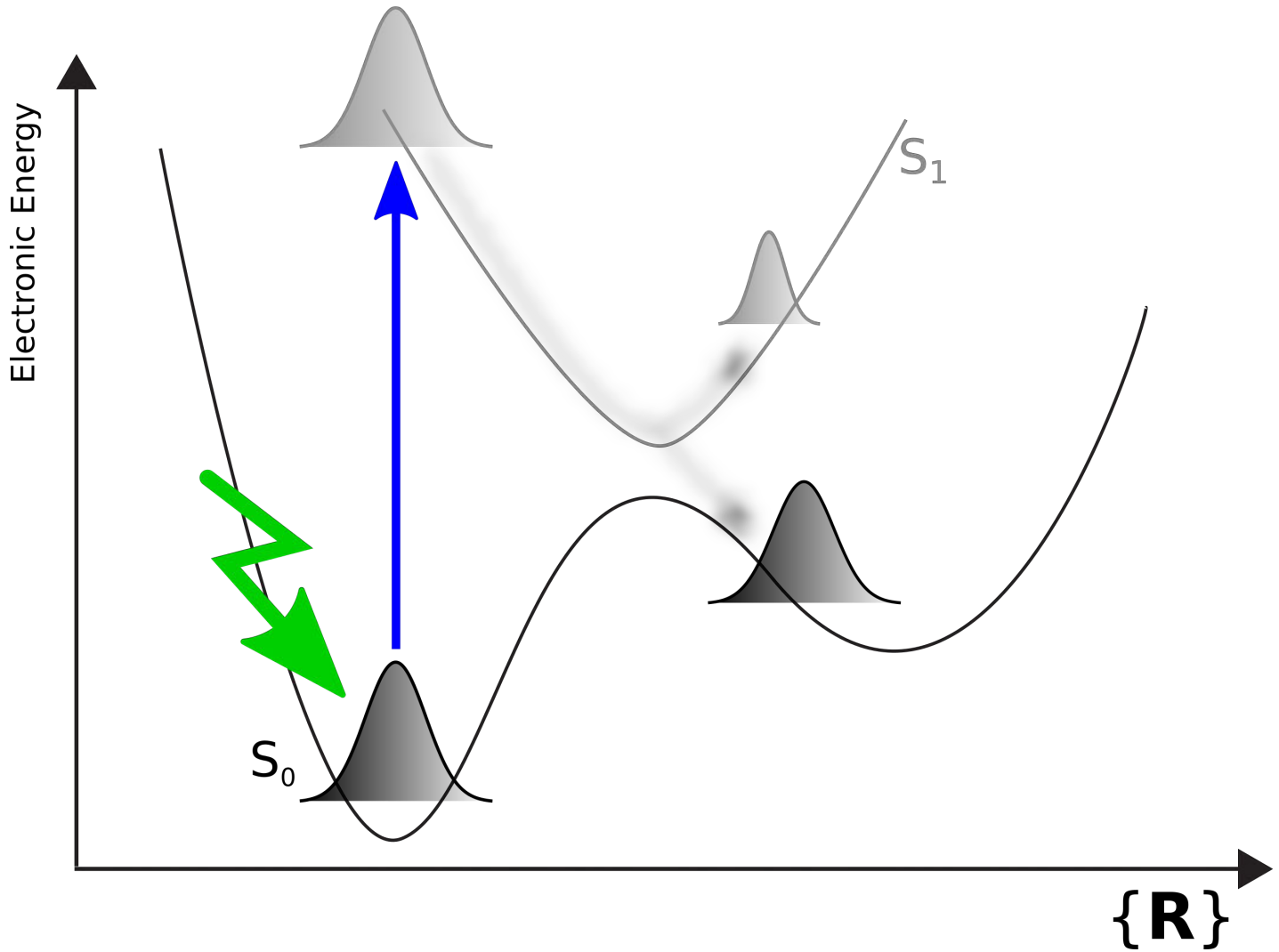
Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.



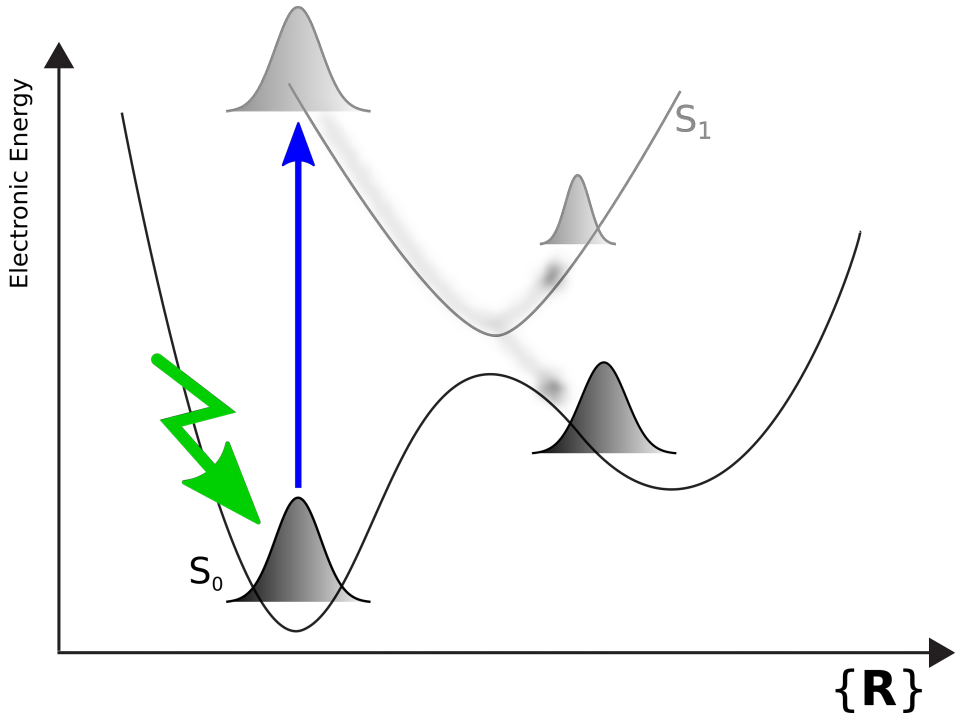
Non-Born-Oppenheimer/nonadiabatic molecular dynamics

Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

Dream: in silico photochemical experiment



Nonadiabatic dynamics - a theoretical challenge



$$i\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t) = \hat{H}_{mol}\Psi(\mathbf{r},\mathbf{R},t)$$

Born-Huang representation:

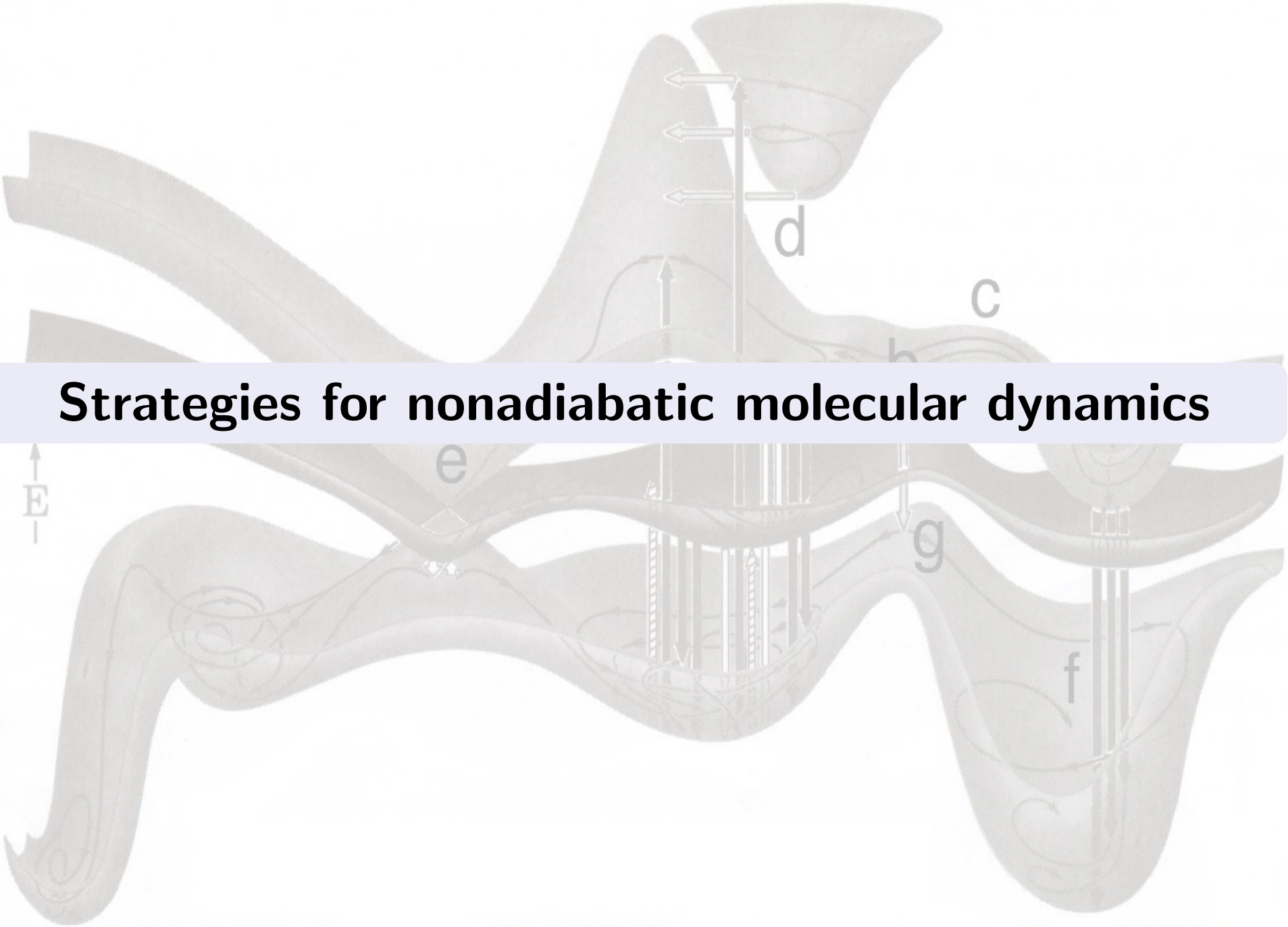
$\Psi(\mathbf{r},\mathbf{R},t) = \sum_J^\infty \Phi_J(\mathbf{r};\mathbf{R})\chi_J(\mathbf{R},t)$

A complete challenge for theoretical chemistry.

- Coupling between *electrons*, *nuclei*, and the *environment*.
- Electronic structure problem: $\Phi_J(\mathbf{r};\mathbf{R})$?
- Environment: $\hat{H}_{mol}$?
- Nuclear dynamics: $\chi_J(\mathbf{R},t)$?

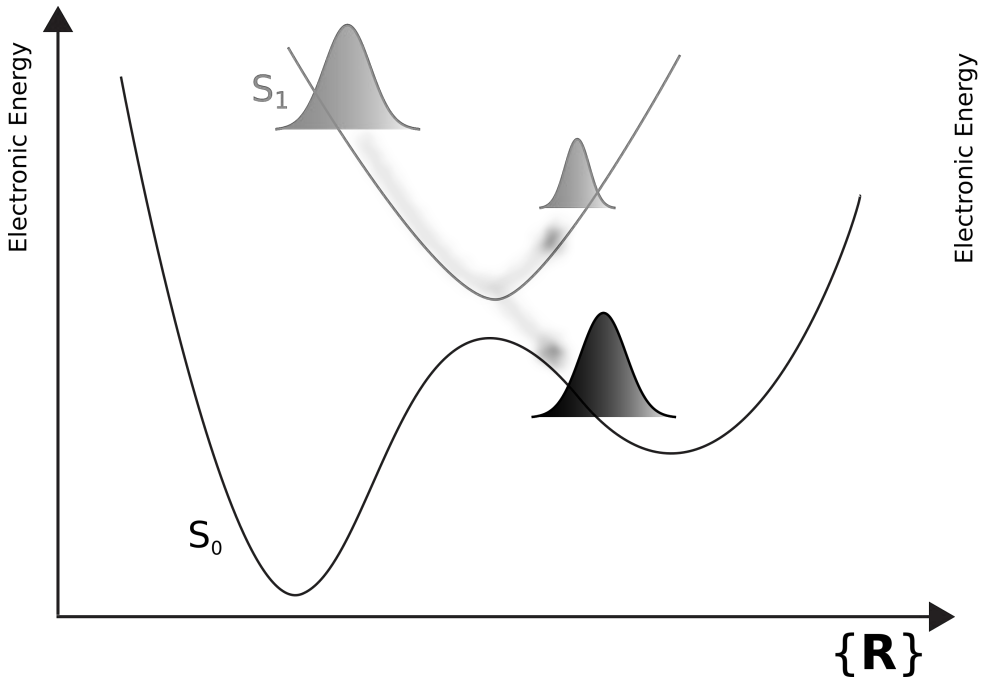
Goal: Devise robust strategies to provide, at least, a qualitative picture of photochemical processes for molecules in their full dimensionality.

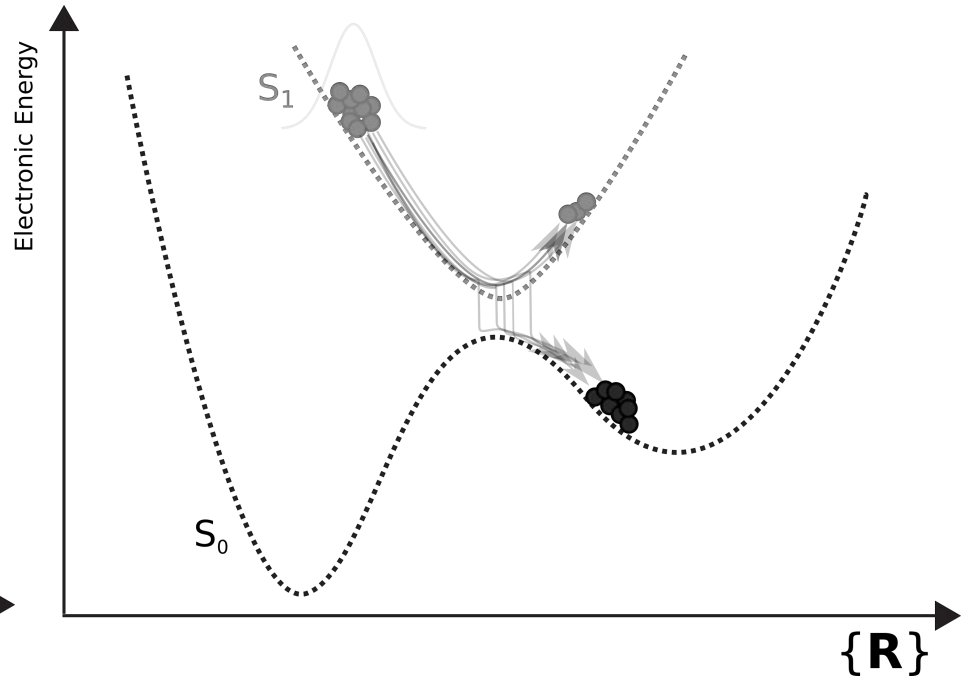
Strategies for nonadiabatic molecular dynamics



Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

From quantum to classical nuclei





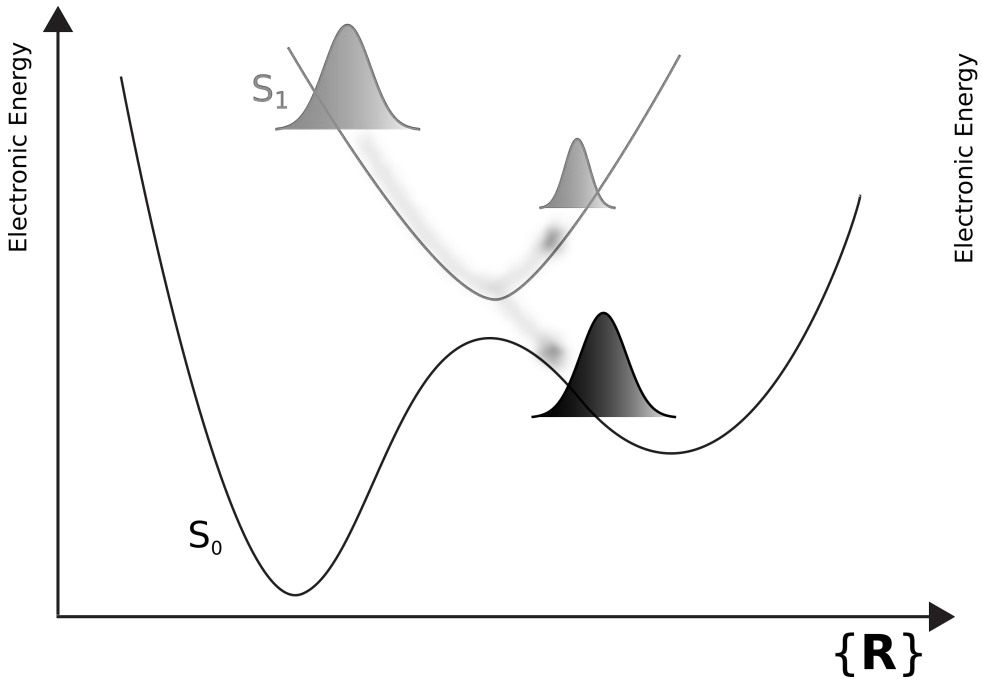
Nuclear Wavepacket Propagation
Limited number of nuclear DoFs
MCTDH

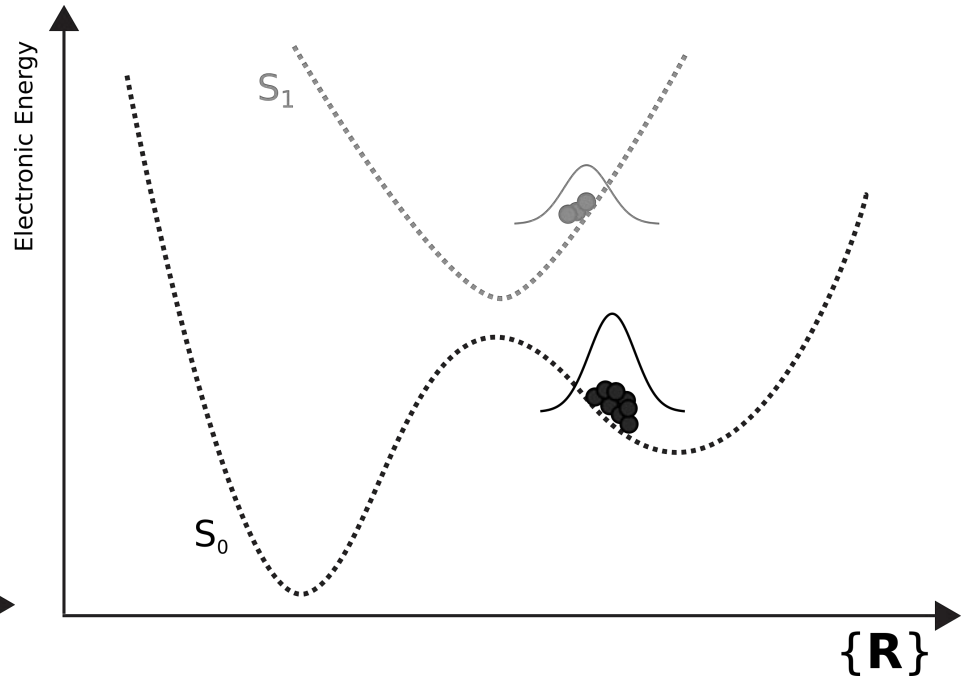
See for example: G. A. Worth, H.-D. Meyer, H. Köppel, L. S. Cederbaum, I. Burghardt, *Int. Rev. Phys. Chem.*, **27**, 569 (2008).

Classical Trajectory Approaches
Approximate nuclear dynamics
Trajectory Surface Hopping (TSH)

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

From quantum to classical nuclei





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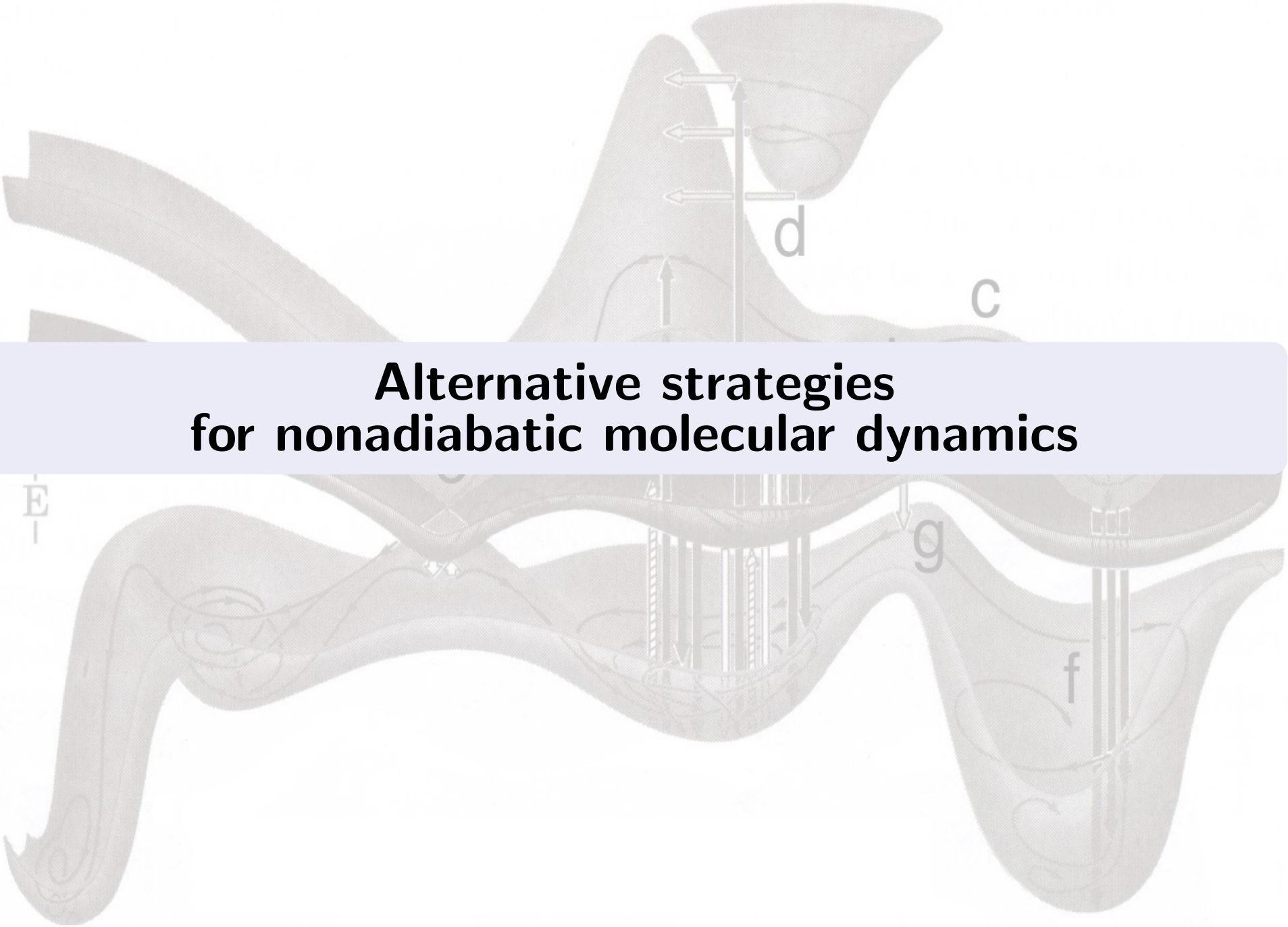
Classical Trajectory Approaches
Independent Trajectory Approximation
Trajectory Surface Hopping (TSH)

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

Alternative strategies for nonadiabatic molecular dynamics

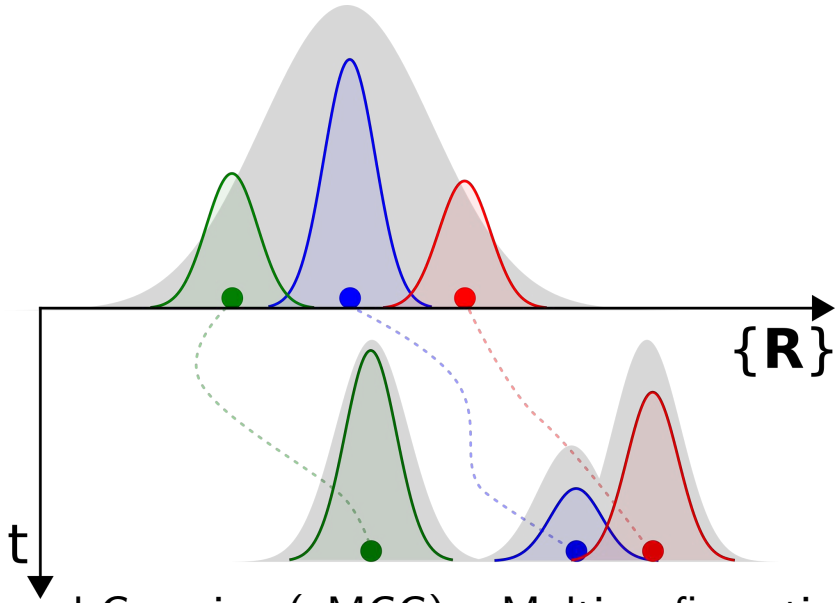


Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

Alternative methods for nonadiabatic dynamics

Nuclear wavefunction represented by trajectory basis functions (TBFs)

$$\chi_I(\mathbf{R},t) = \sum_k^{N_{TBFs}} C_k^I(t)\chi_k^I\left(\mathbf{R};\overline{\mathbf{R}}_k^I(t),\overline{\mathbf{P}}_k^I(t),\boldsymbol{\alpha}_k^I(t),\overline{\gamma}_k^I(t)\right)$$



variational MultiConfigurational Gaussian (vMCG) – Multiconfigurational Ehrenfest (MCE) – Ab Initio Multiple Cloning (AIMC) – Full Multiple Spawning (FMS)

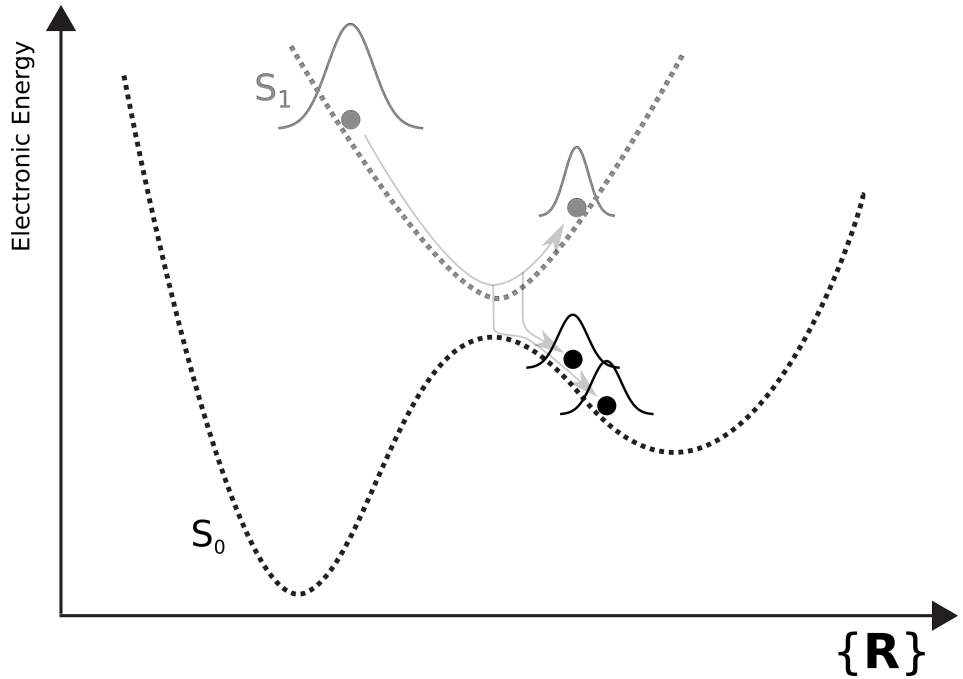
---

vMCG (Worth, Lasorne, Burghardt): *Faraday Discuss.*, **127**, 307 (2004); *Int. Rev. Phys. Chem.*, **34**, 269 (2015). **MCE** (Shalashilin): *J. Chem. Phys.*, **130**, 244101 (2009). **FMS** (Martínez): *J. Phys. Chem.*, **100**, 7884 (1996). **Other strategies**: Quantum Ehrenfest, DGAS, MCAD.

Full and Ab Initio Multiple Spawning

Nuclear wavefunction represented by trajectory basis functions (TBFs)

$$\chi_I(\mathbf{R}, t) = \sum_k^{N_{TBFs}(t)} C_k^I(t)\chi_k^I\left(\mathbf{R}; \overline{\mathbf{R}}_k^I(t), \overline{\mathbf{P}}_k^I(t), \alpha, \overline{\gamma}_k^I(t)\right)$$



Full/Ab Initio Multiple Spawning

M. Ben-Nun and T. J. Martínez, *Adv. Chem. Phys.*, **121**, 439 (2002). B. F. E. Curchod and T. J. Martínez, *Chem. Rev.*, **118**, 3305 (2018).

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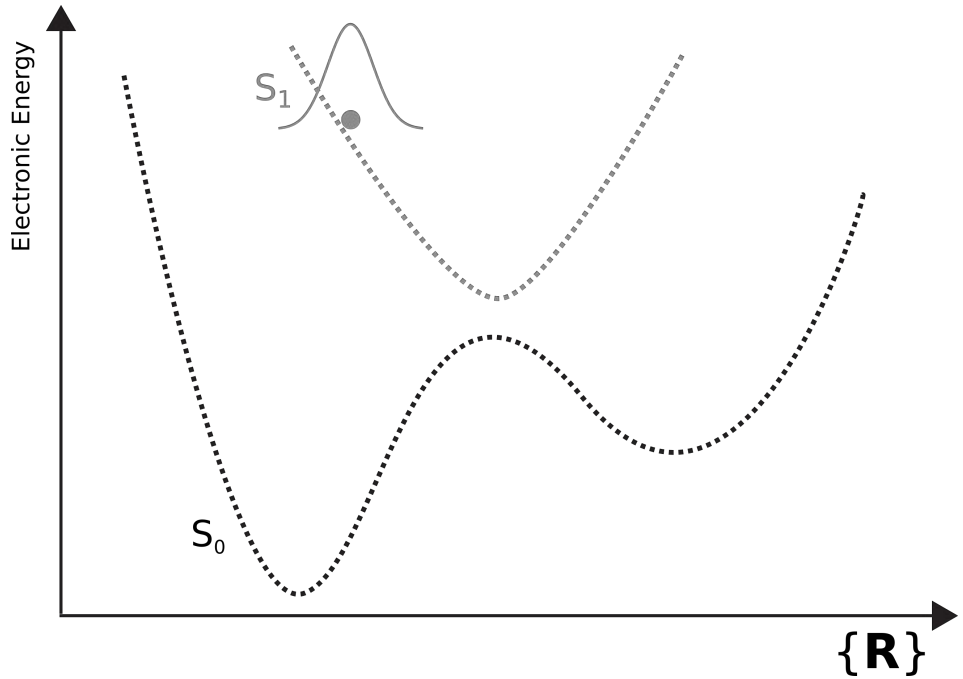

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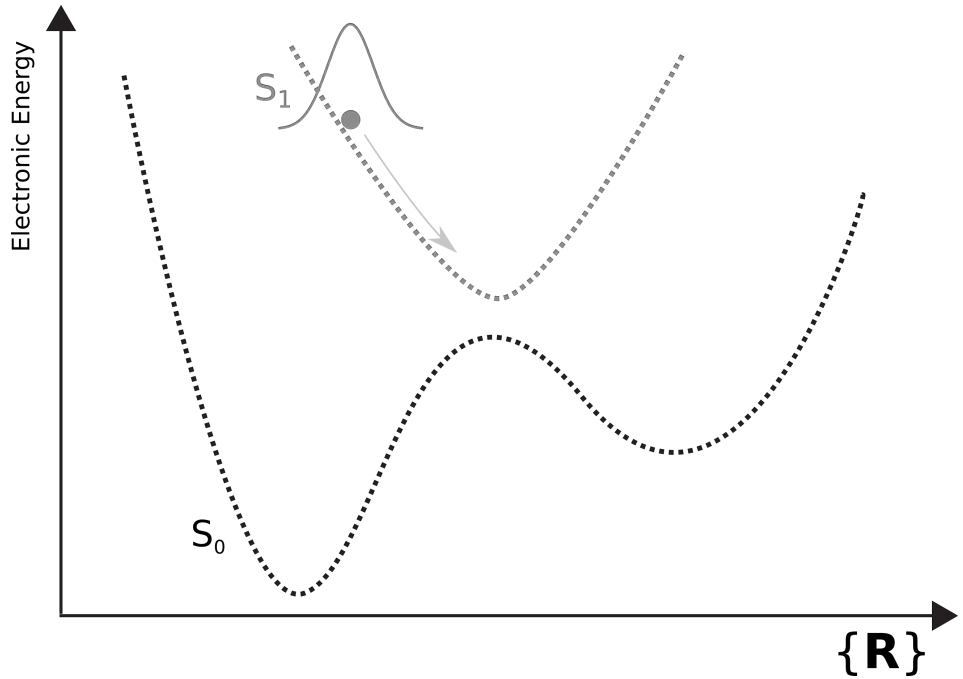

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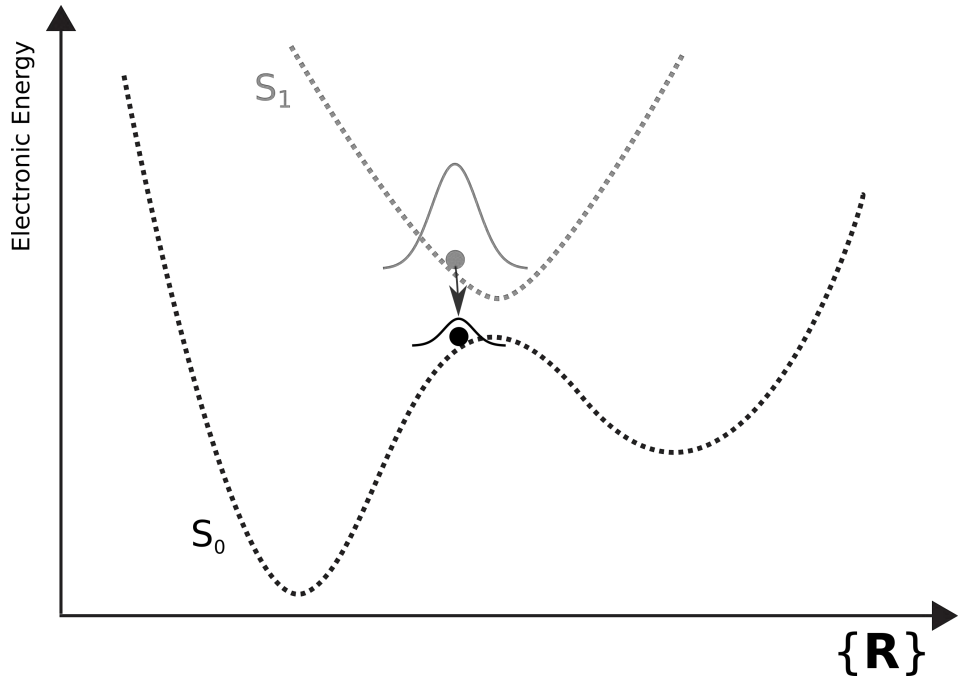

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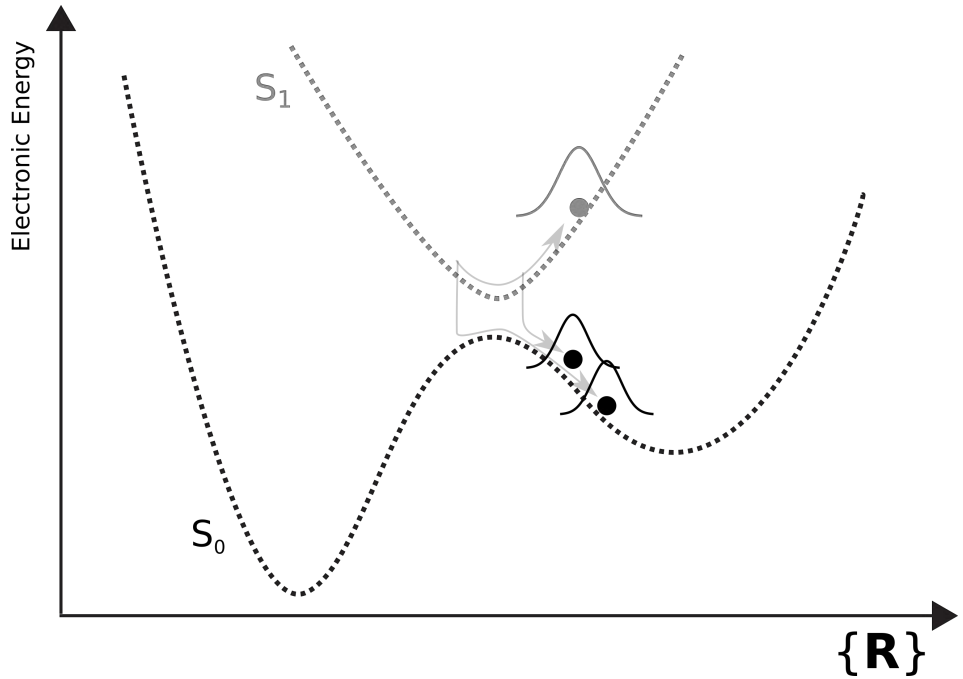

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Inserted into the Born-Huang representation, and then into the time-dependent molecular Schrödinger equation:

TDSE in an electronic and TBFs basis

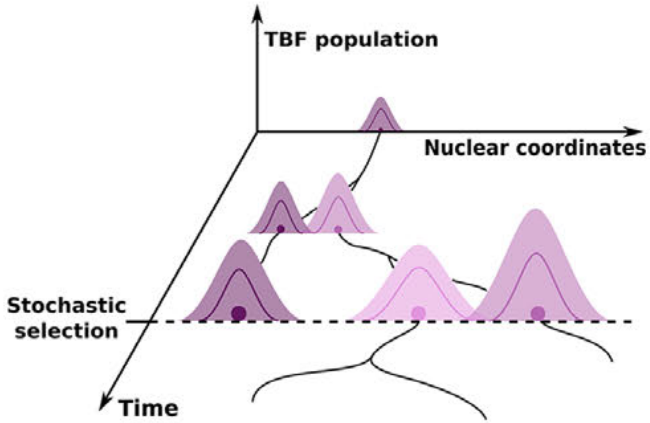
$$\frac{d}{dt}\mathbf{C}^I(t) = -i(\mathbf{S}_{II}^{-1})\left[\left[\mathbf{H}_{II} - i\dot{\mathbf{S}}_{II}\right]\mathbf{C}^I + \sum_{J\neq I}\mathbf{H}_{IJ}\mathbf{C}^J\right]$$

TBFs are coupled via the Hamiltonian matrix H.

FMS = exact couplings

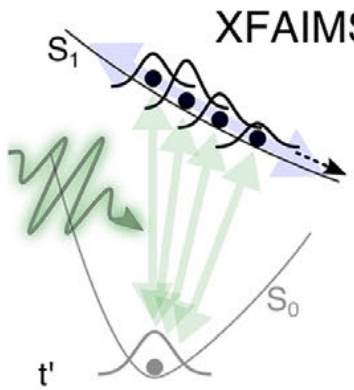
AIMS = approximate couplings

M. Ben-Nun and T. J. Martínez, *Adv. Chem. Phys.*, **121**, 439 (2002). B. F. E. Curchod and T. J. Martínez, *Chem. Rev.*, **118**, 3305 (2018).



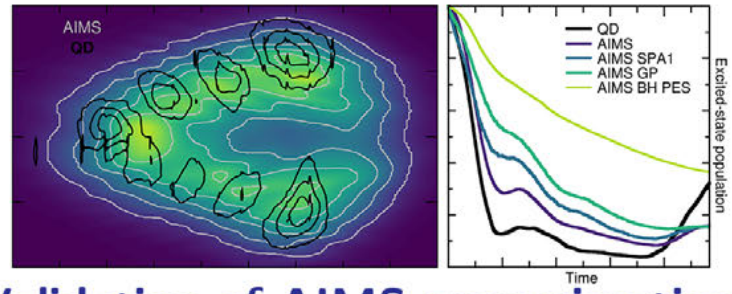
Making AIMS computationally cheaper

J. Phys. Chem. A, **124**, 6133 (2020)
J. Chem. Phys., **154**, 104110 (2021)
J. Chem. Phys., **154**, 211106 (2021)
J. Phys. Chem. Lett., **13**, 12011 (2022)



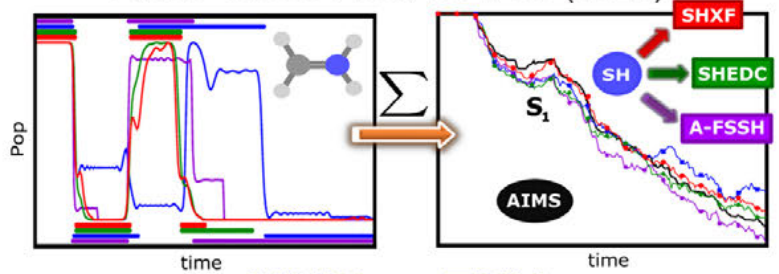
Inclusion of explicit laser pulses and intersystem crossings

J. Chem. Phys., **144**, 101102 (2016)
J. Chem. Phys., **145**, 191104 (2016)
J. Chem. Phys., **150**, 101101 (2019)



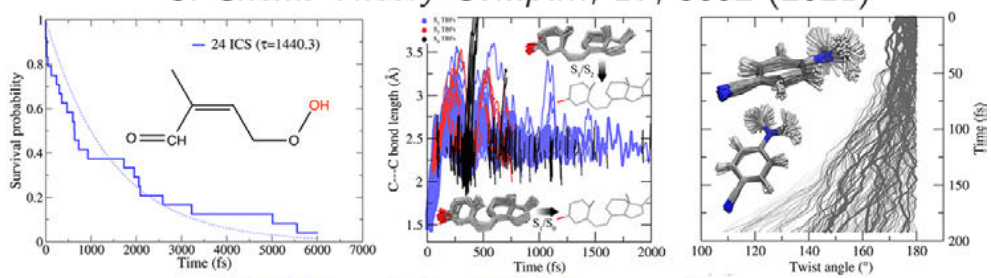
Validation of AIMS approximations

J. Chem. Phys., **148**, 134110 (2018)
J. Chem. Phys., **155**, 174119 (2021)
Theor. Chem. Acc., **142**, 66 (2023)



AIMS *vs* TSH

J. Phys. Chem. A, **123**, 3582 (2019)
Phys. Chem. Chem. Phys., **22**, 15183 (2020)
J. Chem. Theory Comput., **17**, 3852 (2021)



AIMS with GPU-accelerated electronic structure

J. Phys. Chem. Lett., **7**, 2444 (2016)
J. Phys. Chem. A, **121**, 265 (2017)

Take-home message:

A hierarchy of methods is available to perform excited-state dynamics!

Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

Hierarchy of nonadiabatic methods
– an analogy –

Full CI

...

CCSD(T)

CISD

MP2

Post-HF

(*multiple* Slater determinants)

Hartree Fock

(*single* Slater determinant)

Electronic wavefunction

Hierarchy of nonadiabatic methods
– an analogy –

Full CI

...

CCSD(T)

CISD

MP2

Post-HF

(*multiple* Slater determinants)

Hartree Fock

(*single* Slater determinant)

Electronic wavefunction

MCTDH

...

vMCG, MCE

(SS)AIMS, AIMC

AIMSWISS, CT-MQC

'Post-TSH'

(*coupled* trajectories)

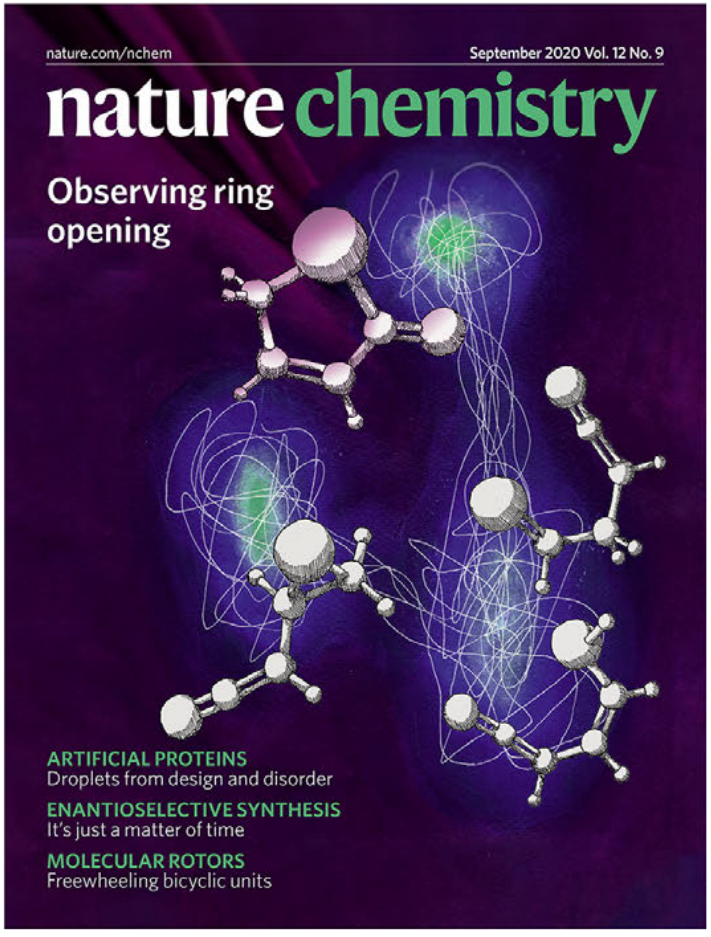
Trajectory surface hopping

(*independent* trajectories)

Nuclear wavefunctions*

A. Prlj, J. T. Taylor, J. Janoš, P. Slavíček, F. Agostini, B. F. E. Curchod, arxiv.2508.05263 (2025).

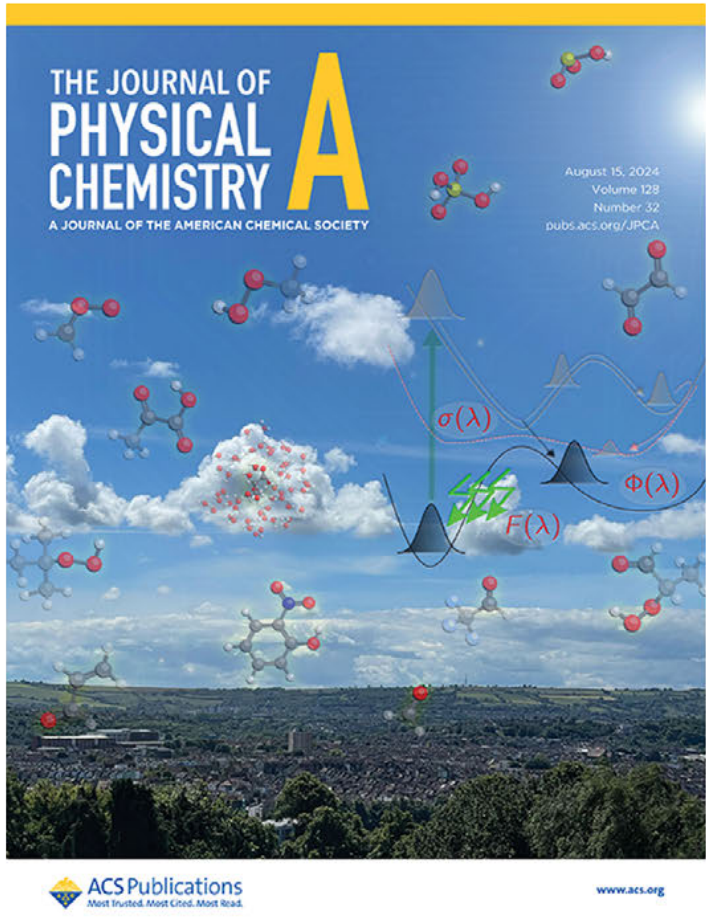
Time-resolved observables



Ultrafast spectroscopy

TR-PES, TR-UED, TR-XAS/XPS

Energy-resolved observables



Atmospheric chemistry

Photoabsorption cross-sections, quantum yields

B. F. E. Curchod, A. J. Orr-Ewing, *J. Phys. Chem. A*, **128**, 6613 (2024)

Prediction challenge: photochemistry of cyclobutanone

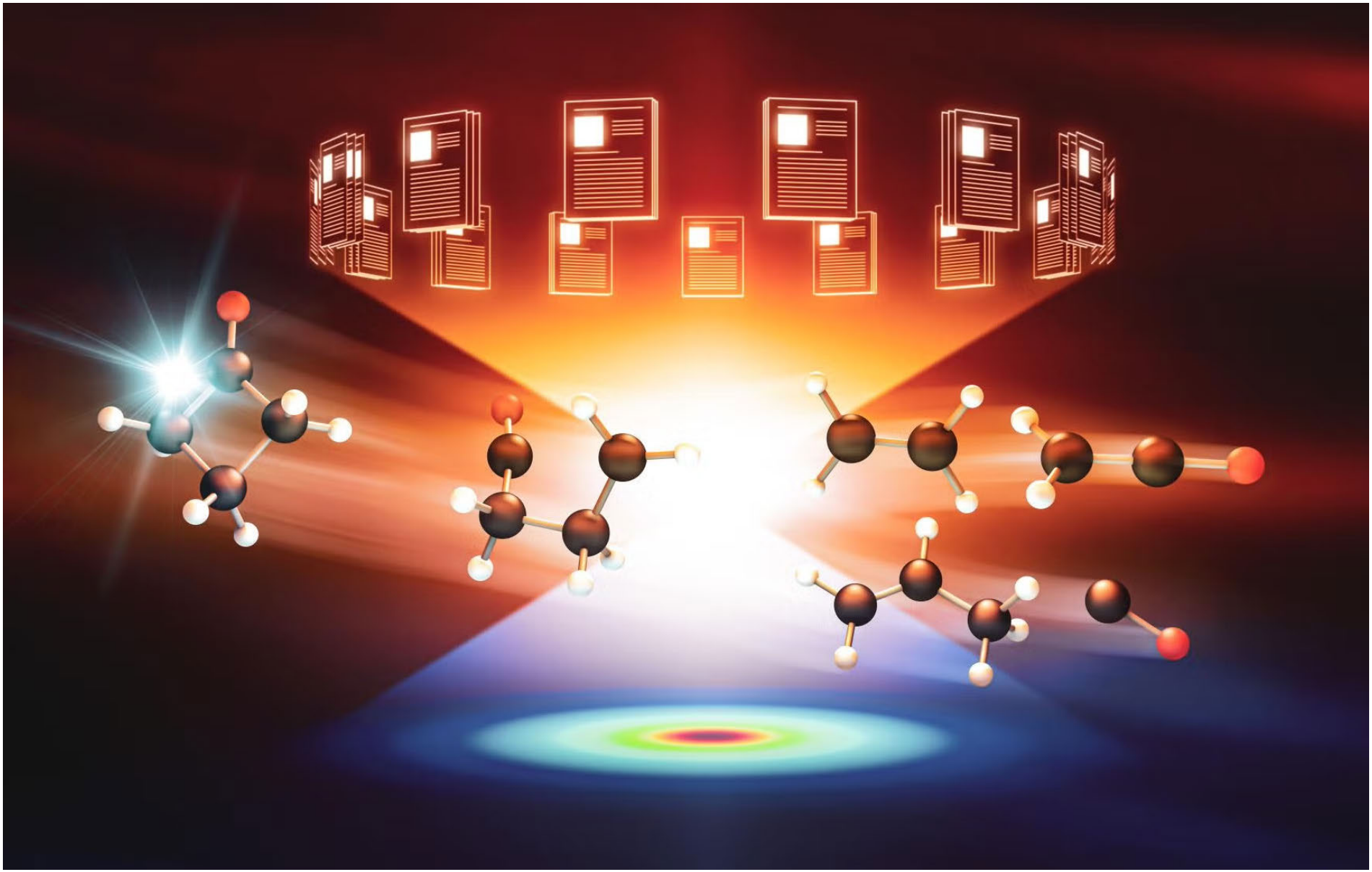
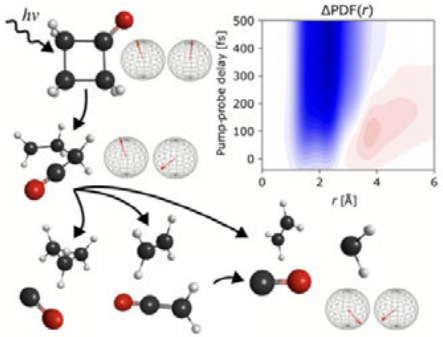


Image: Greg Stewart/SLAC National Accelerator Laboratory

Prediction Challenge: Cyclobutanone Photochemistry

The Journal of Chemical Physics

The simulation of photochemical molecular dynamics has been a major challenge to theoretical chemistry because of the need to simultaneously describe quantum mechanical effects of both nuclei and electrons. Numerous advances have been made over the past decade and many would agree that excited state simulations have demonstrated their value in the interpretation of experiments. However, one can question whether these simulations have been unambiguously predictive. True predictive capabilities would pave the way to rational design of light-driven molecular systems, with revolutionary implications for renewable solar energy (directly to electricity or to fuels), bioimaging, optogenetics, and photochemical synthesis. Thankfully, new ultrafast diffraction experiments1 have come on-line which provide both spatio-temporal resolution on the atomic scale, i.e. molecular movies. This provides a novel opportunity — a double-blind test of the accuracy of excited state simulations.

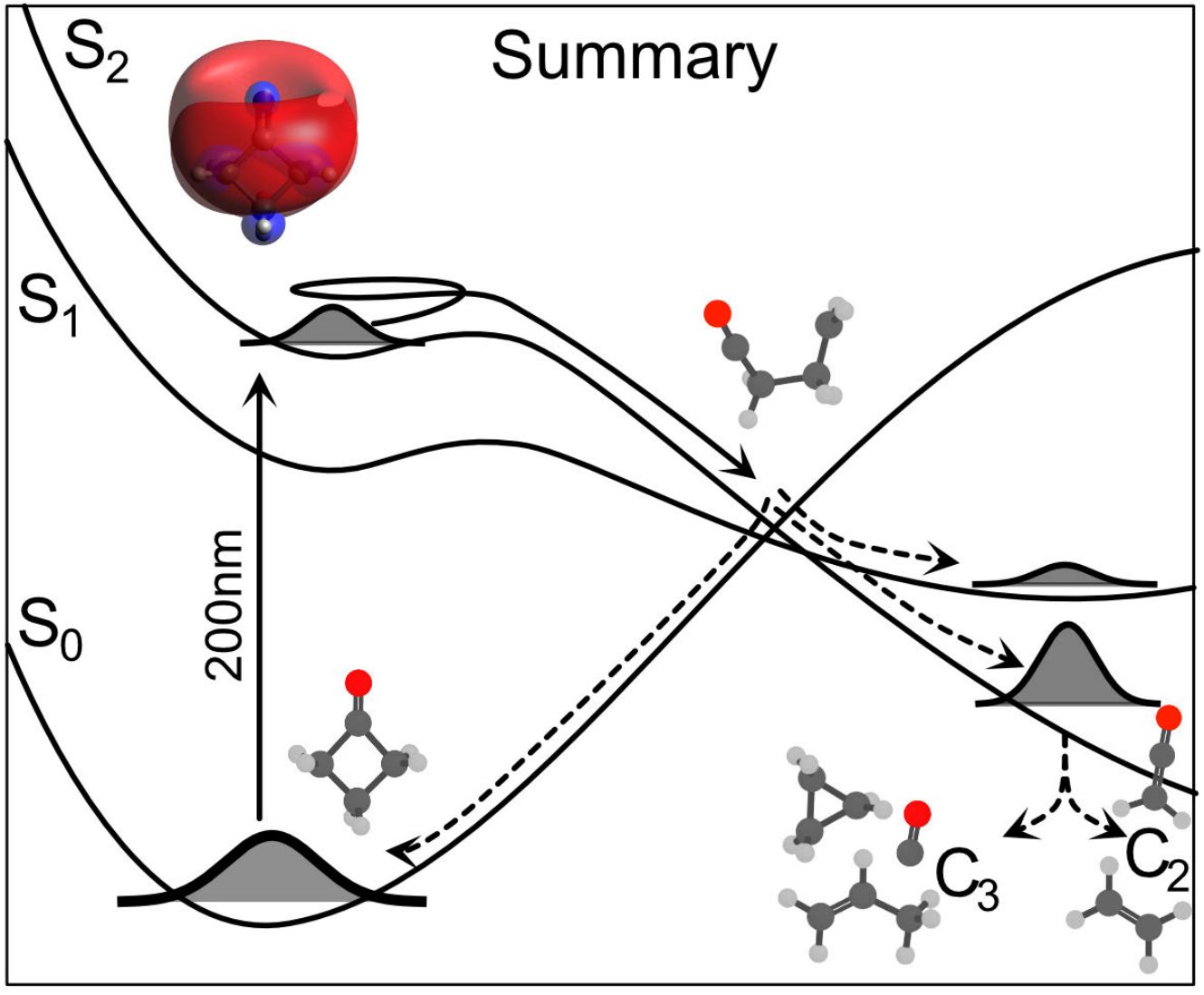


Based on intensive discussions during a CECAM workshop, we have arranged for such a test and challenge the community to predict the results of the experiment and prepare manuscripts for submission to a special issue in The Journal of Chemical Physics. To be considered, submissions must be received before the experimental results are revealed (no earlier than January 2024) and they must include direct predictions of the key experimental observables (details provided below). In the spirit of the challenge, we will be requiring contributors to upload their manuscript to arXiv prior to JCP submission. Upon submission to JCP, authors must then include the pre-print DOI in their cover letter and in their original manuscript (for reference during revisions). We are excited to see the outcome and rooting for the success of the simulations!

[1] M. Centurion, T. J. A. Wolf, and J. Yang, Ultrafast Imaging of Molecules with Electron Diffraction, Ann. Rev. Phys. Chem. **73**, 21 (2022).

Guest Editors: Todd Martínez, Thomas Wolf, Petr Slavíček, Graham Worth, Mario Barbatti, Basile Curchod, Sara Bonella, with JCP Editor David Manolopoulos.

15 contributed articles (74 researchers) – TSH, AIMS, MASH, LZSH, vMCG, MCTDH, LR-TDDFT, ADC(2), XMS-CASPT2, SA-CASSCF, MR-CIS, ...

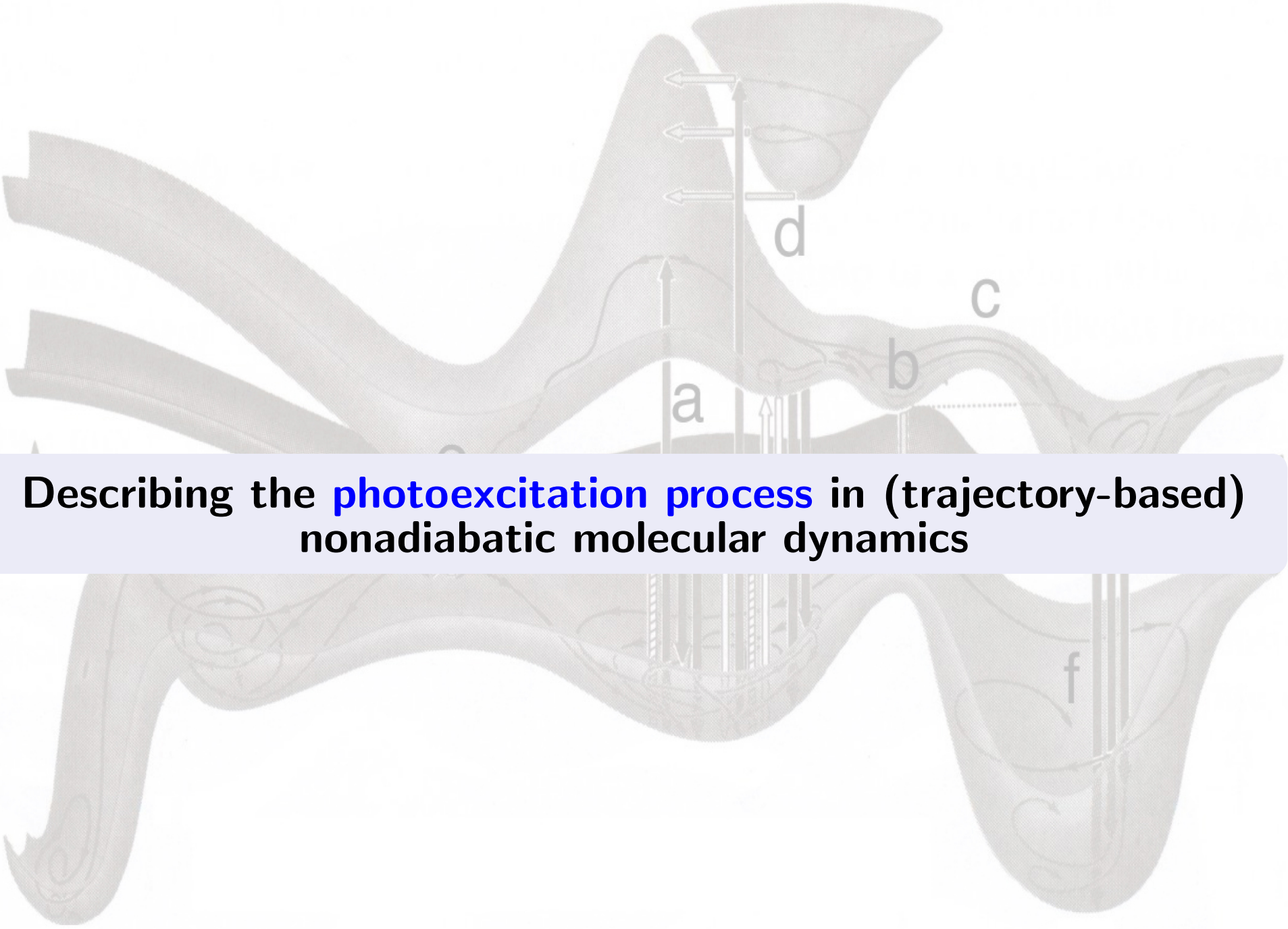


Perspective article on the prediction challenge, in preparation.

Some conclusions*

- The level of electronic-structure theory had by far the largest impact on the predicted photochemistry of cyclobutanone.
- Most (trajectory-based) nonadiabatic methods gave very similar results (population decays, photoproducts, experimental observables).
- Issues with the description of the photoexcitation process.

*valid for the photochemistry of cyclobutanone and MeV-UED signals.

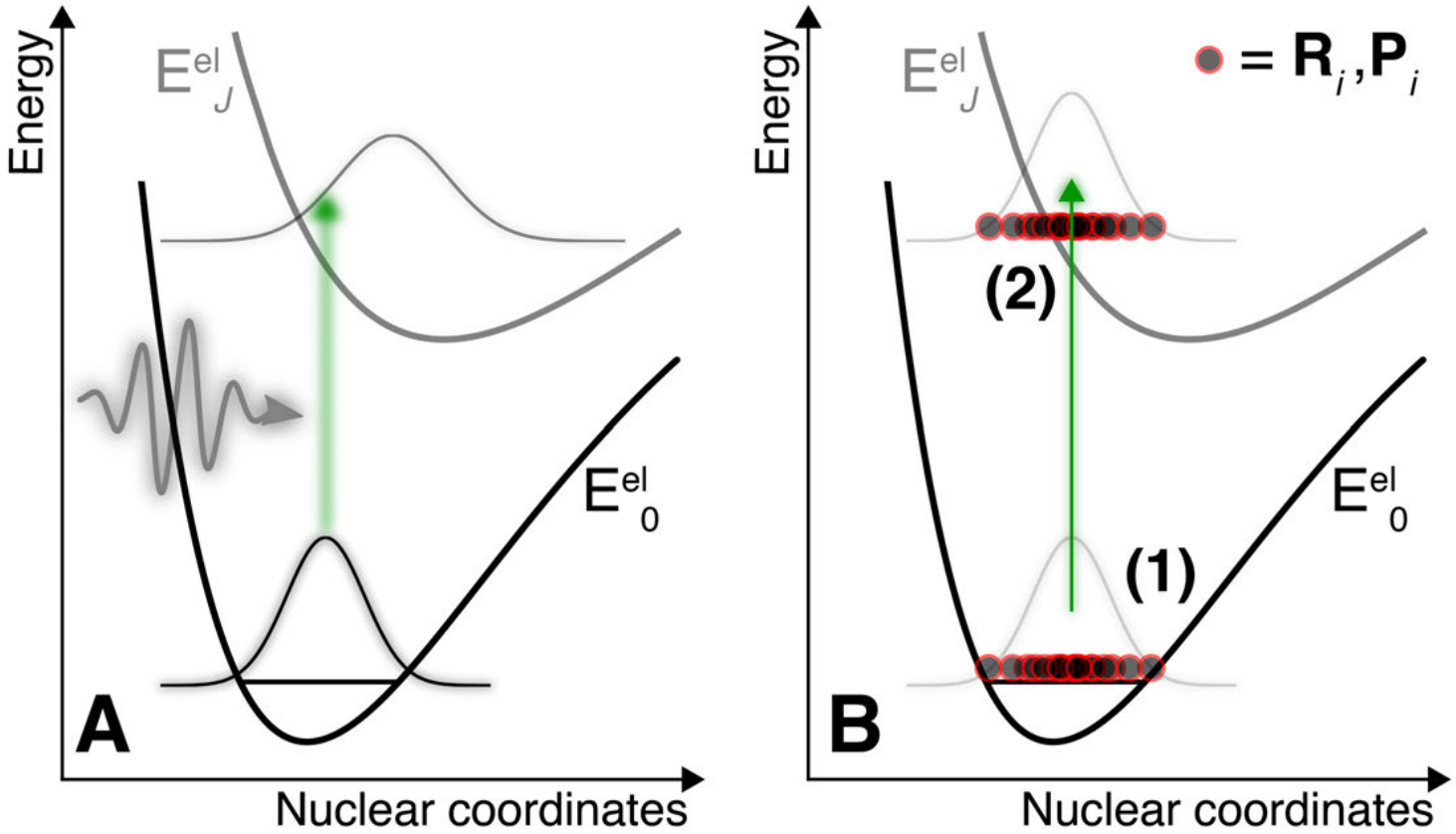


Describing the photoexcitation process in (trajectory-based) nonadiabatic molecular dynamics

Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

Photoexcitation process

Photoexcitation is often highly approximate in nonadiabatic molecular dynamics.



Approximations at the level of (1) the ground-state distribution and (2) the characteristics of the photoexcitation process.

J. Suchan, D. Hollas, B. F. E. Curchod, P. Slavíček, *Faraday Discuss.*, **212**, 307 (2018)
J. Janoš, P. Slavíček, B. F. E. Curchod, *Acc. Chem. Res.*, **58**, 261 (2025)

Photoexcitation process

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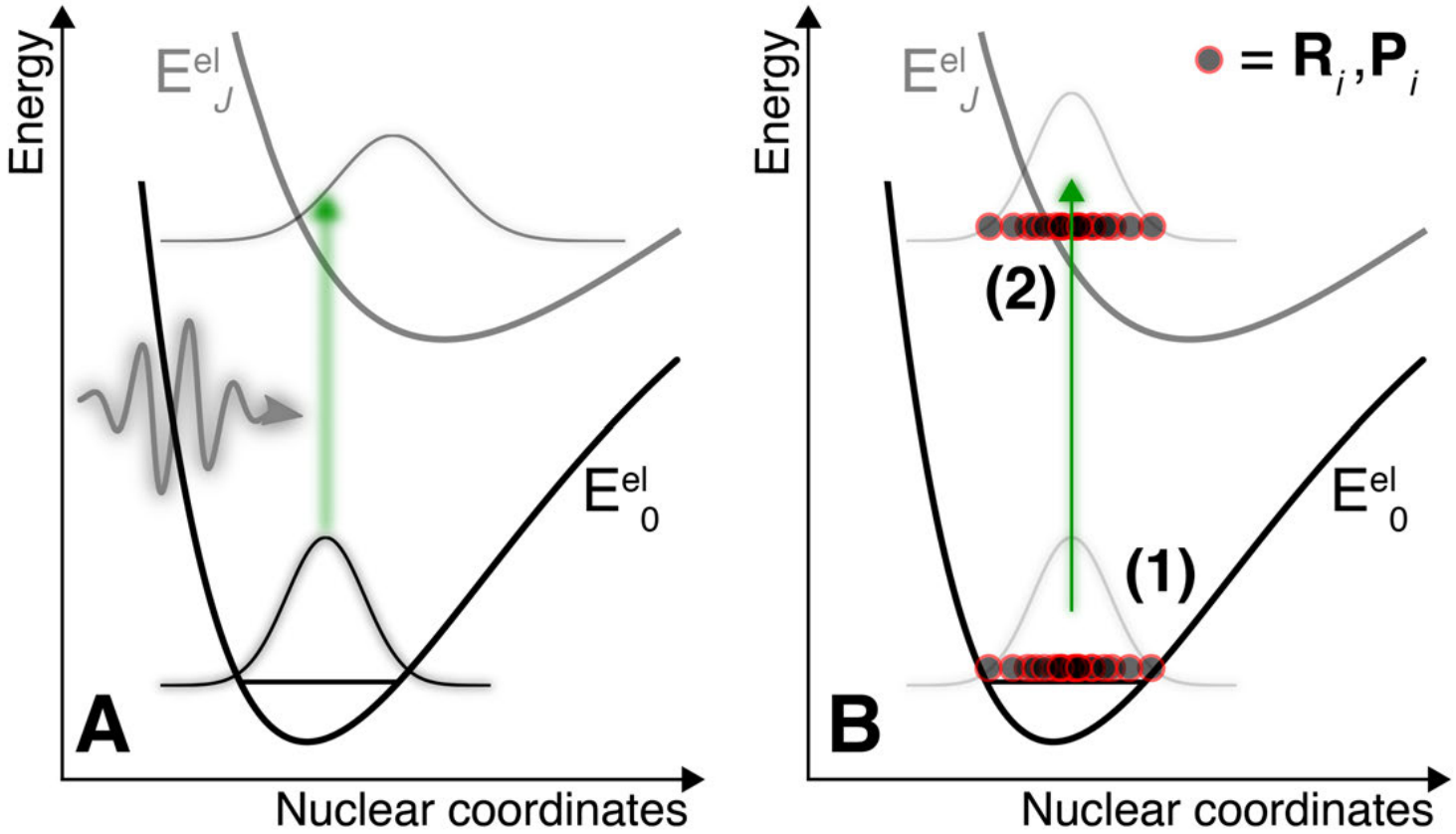

Trajectory-based nonadiabatic molecular dynamics starts from the definition of a set of initial conditions.

J. Suchan, D. Hollas, B. F. E. Curchod, P. Slavíček, *Faraday Discuss.*, **212**, 307 (2018)
J. Janoš, P. Slavíček, B. F. E. Curchod, *Acc. Chem. Res.*, **58**, 261 (2025)

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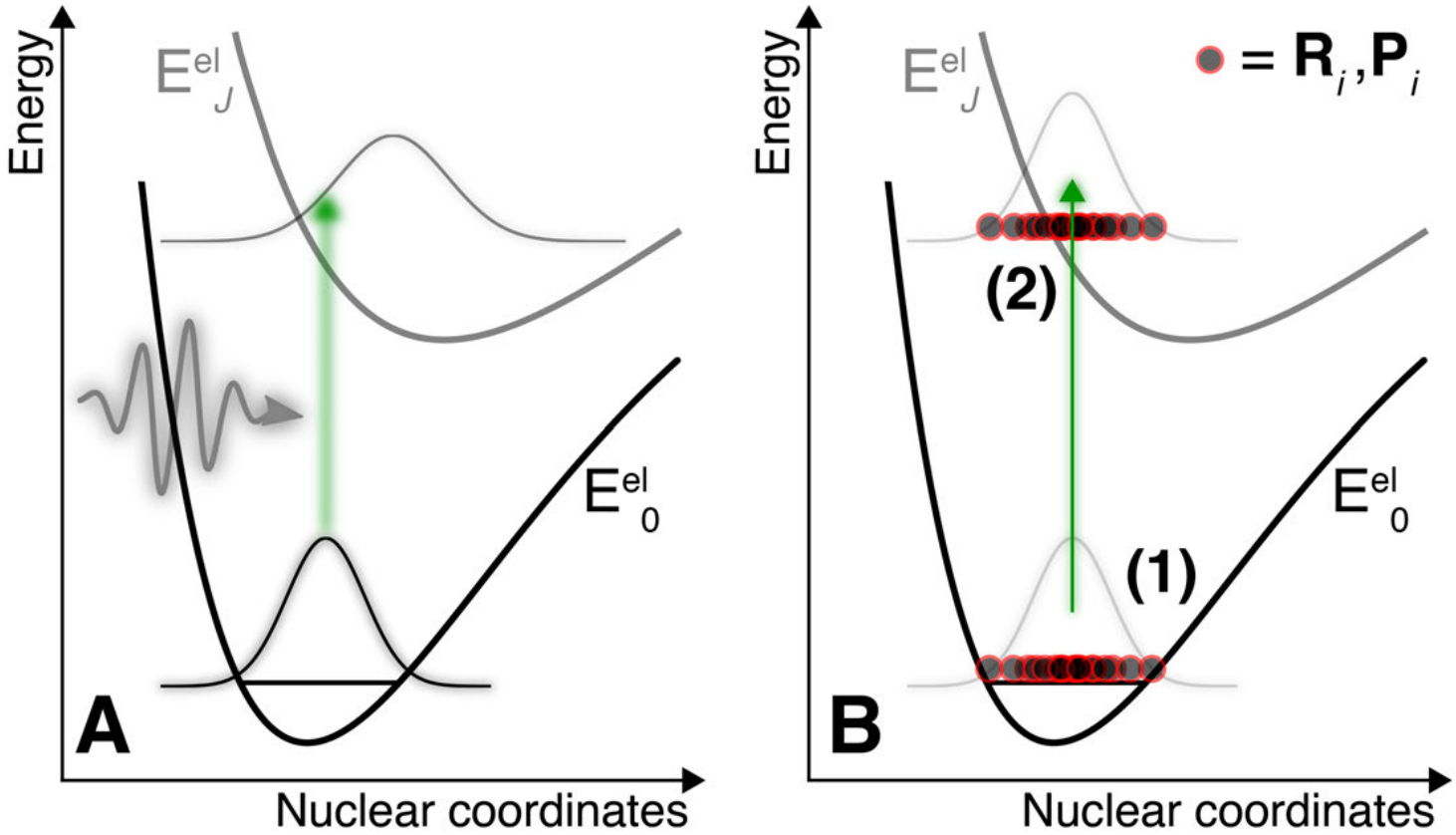


Descriptor for initial conditions: $\mathcal{D}_{\mathrm{IC}} = \{\mathbf{R}_i, \mathbf{P}_i, J_i, t_i\}_{i=1}^{N_{\mathrm{IC}}}$

J. Suchan, D. Hollas, B. F. E. Curchod, P. Slavíček, *Faraday Discuss.*, **212**, 307 (2018)
J. Janoš, P. Slavíček, B. F. E. Curchod, *Acc. Chem. Res.*, **58**, 261 (2025)

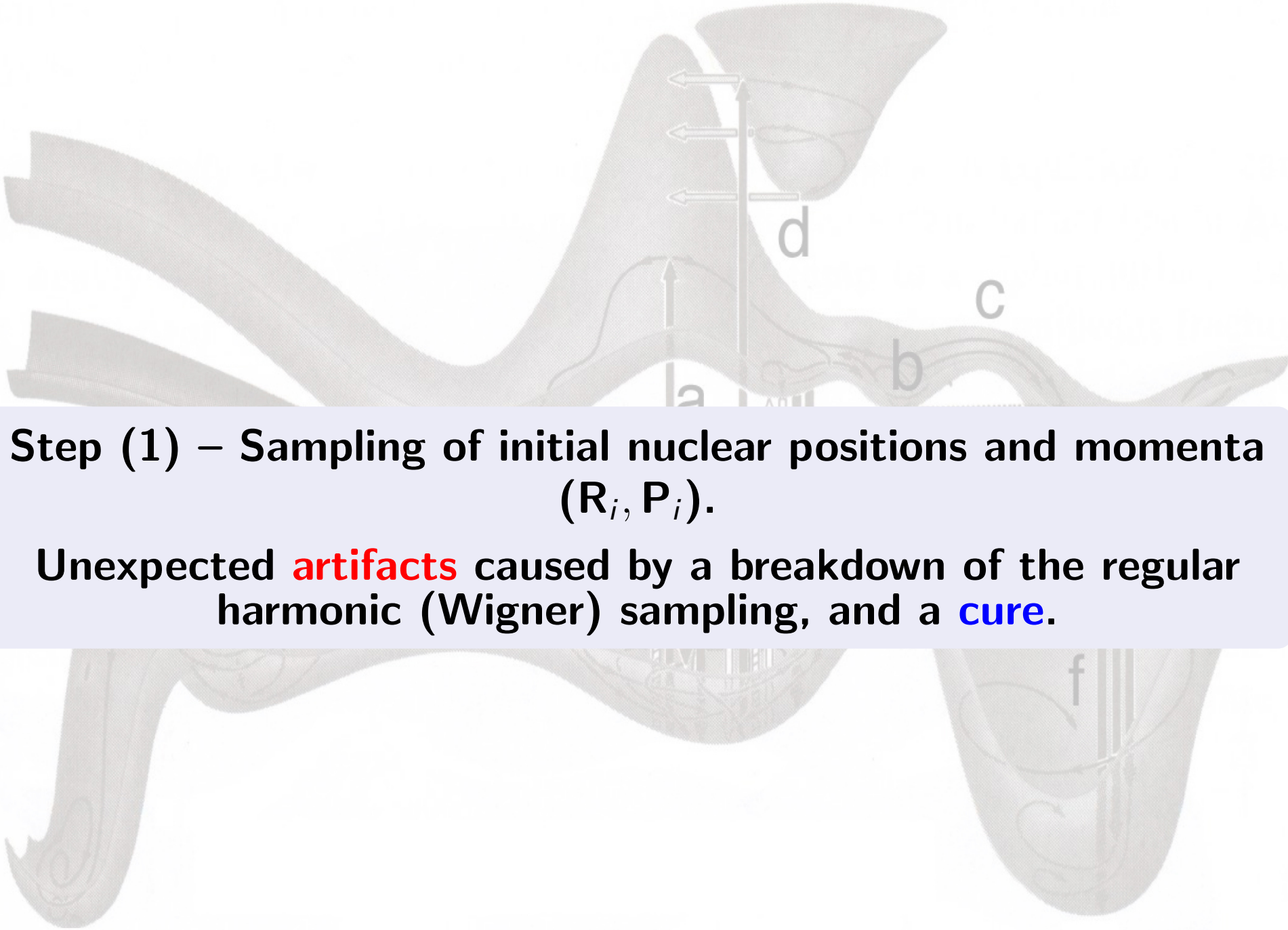
Typical approximations for the photoexcitation

Most applications of trajectory-based nonadiabatic dynamics use the following approximations:

- **Step (1)**: Sampling of initial nuclear positions and momenta $(\mathbf{R}_i, \mathbf{P}_i)$ based on an approximate ground-state distribution, e.g., harmonic (Wigner) distribution.
  - $\rightarrow$ Potential issue with flexible molecules.

- **Step (2)**: Photoexcitation mimicked by a sudden (vertical) excitation to a given electronic state J ($J_i = J$, and $t_i = 0$, $\forall i$) or an energy windowing around a specific excitation wavelength (any J within window can be taken as J_i, and $t_i = 0$, $\forall i$).
  - $\rightarrow$ Does not account adequately for the characteristics of the excitation source (e.g., laser pulse).

M. Persico, G. Granucci, *Theor. Chem. Acc.*, **133**, 1526 (2014)
J. Suchan, D. Hollas, B. F. E. Curchod, P. Slavíček, *Faraday Discuss.*, **212**, 307 (2018)
J. Janoš, P. Slavíček, B. F. E. Curchod, *Acc. Chem. Res.*, **58**, 261 (2025)



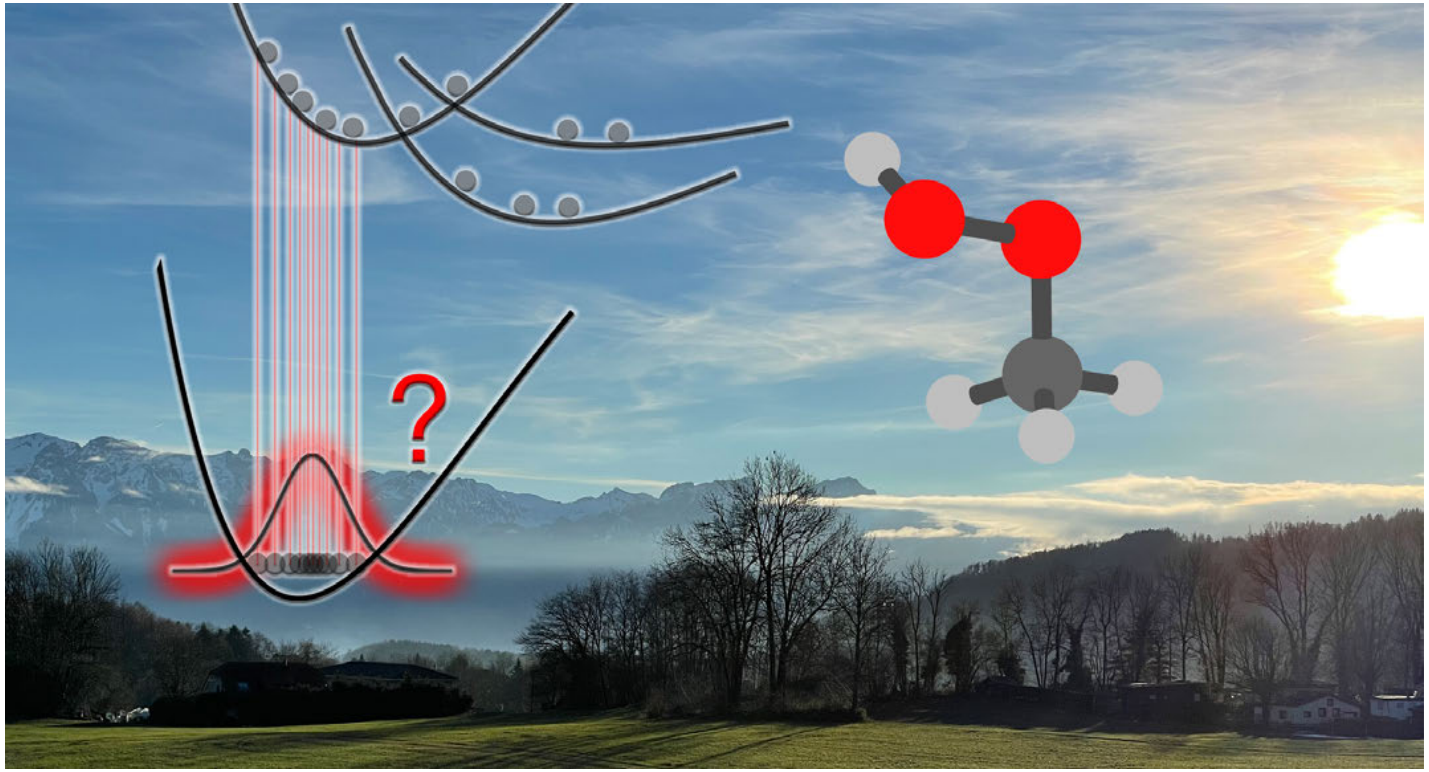
Step (1) – Sampling of initial nuclear positions and momenta $(\mathbf{R}_i, \mathbf{P}_i)$.

Unexpected artifacts caused by a breakdown of the regular harmonic (Wigner) sampling, and a cure.

Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

(1) – Possible artifacts with Wigner sampling

Context: calculation of a photoabsorption cross-section for methylhydroxyperoxide (MHP), important atmospheric volatile organic compound.



A. Prlj, E. Marsili, L. Hutton, D. Hollas, D. Shchepanovska, D. R. Glowacki, P. Slavíček, B. F. E. Curchod, *ACS Earth Space Chem.*, **6**, 207 (2022)
A. Prlj, D. Hollas, B. F. E. Curchod, *J. Phys. Chem. A*, **127**, 7400 (2023)

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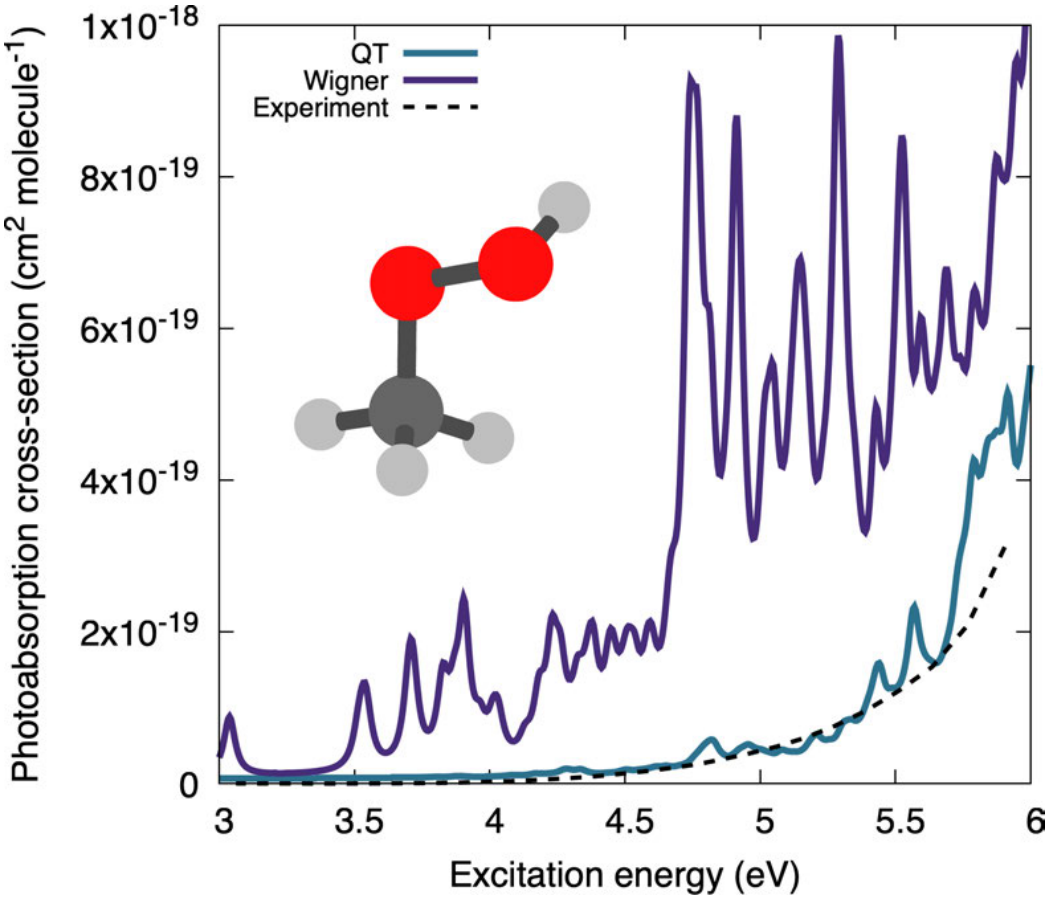

Nuclear ensemble approach – 500 sampled geometries. DFT/LR-TDDFT/TDA/PBE0/6-311G*

A. Prlj, E. Marsili, L. Hutton, D. Hollas, D. Shchepanovska, D. R. Glowacki, P. Slavíček, B. F. E. Curchod, *ACS Earth Space Chem.*, **6**, 207 (2022)
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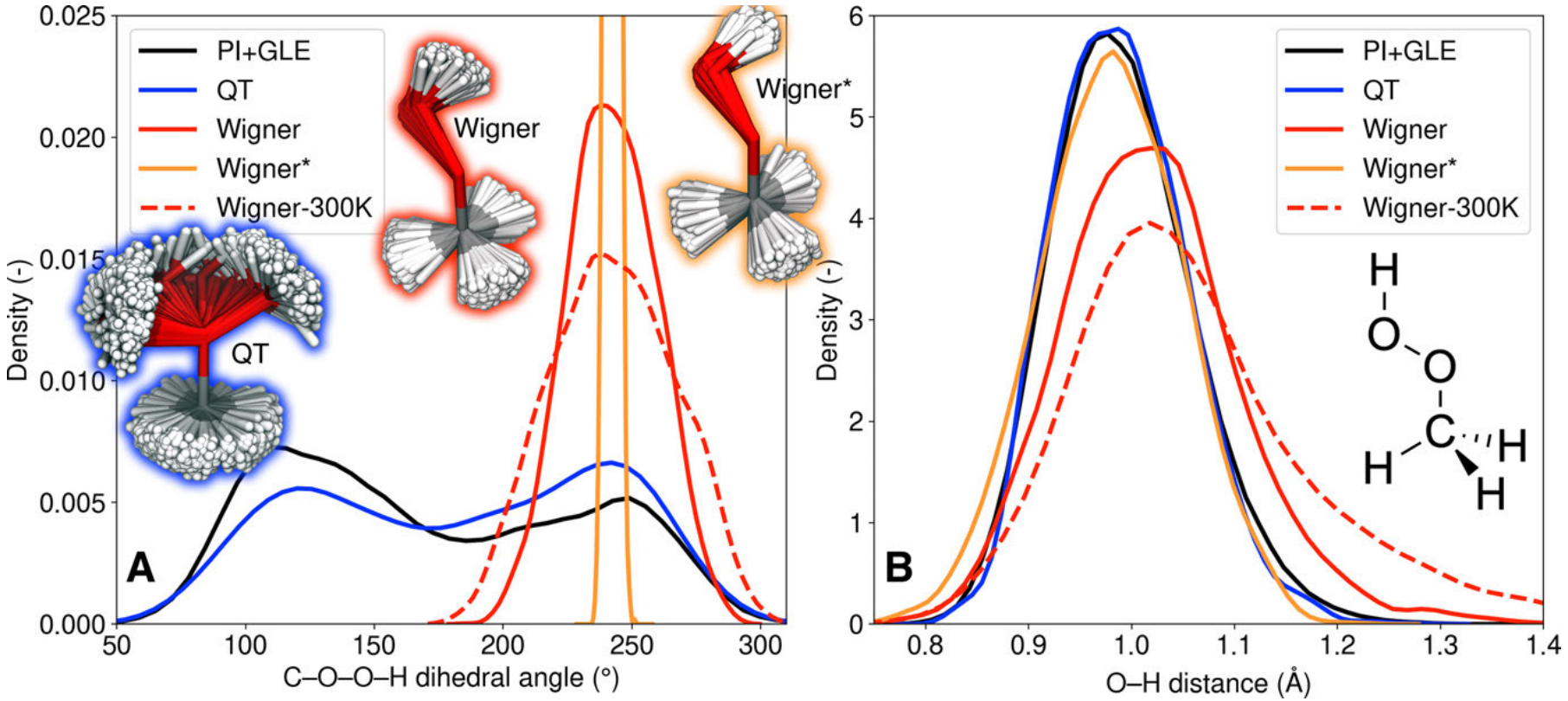
Use of harmonic (Wigner) sampling with rectilinear coordinates leads to an artificial O–H stretch caused by the C–O–O–H torsion.



Nuclear ensemble approach – 4000 sampled geometries for each distribution. MP2/aug-cc-pVDZ

The lowest-energy transition of MHP has a dark $n\sigma^*$(O–O) character, while the second lowest transition exhibits a brighter $n\sigma^*$(O–H) character.

A. Prlj, D. Hollas, B. F. E. Curchod, *J. Phys. Chem. A*, **127**, 7400 (2023); M. Ceriotti, G. Bussi, M. Parrinello, *Phys. Rev. Lett.*, **103**, 030603 (2009)

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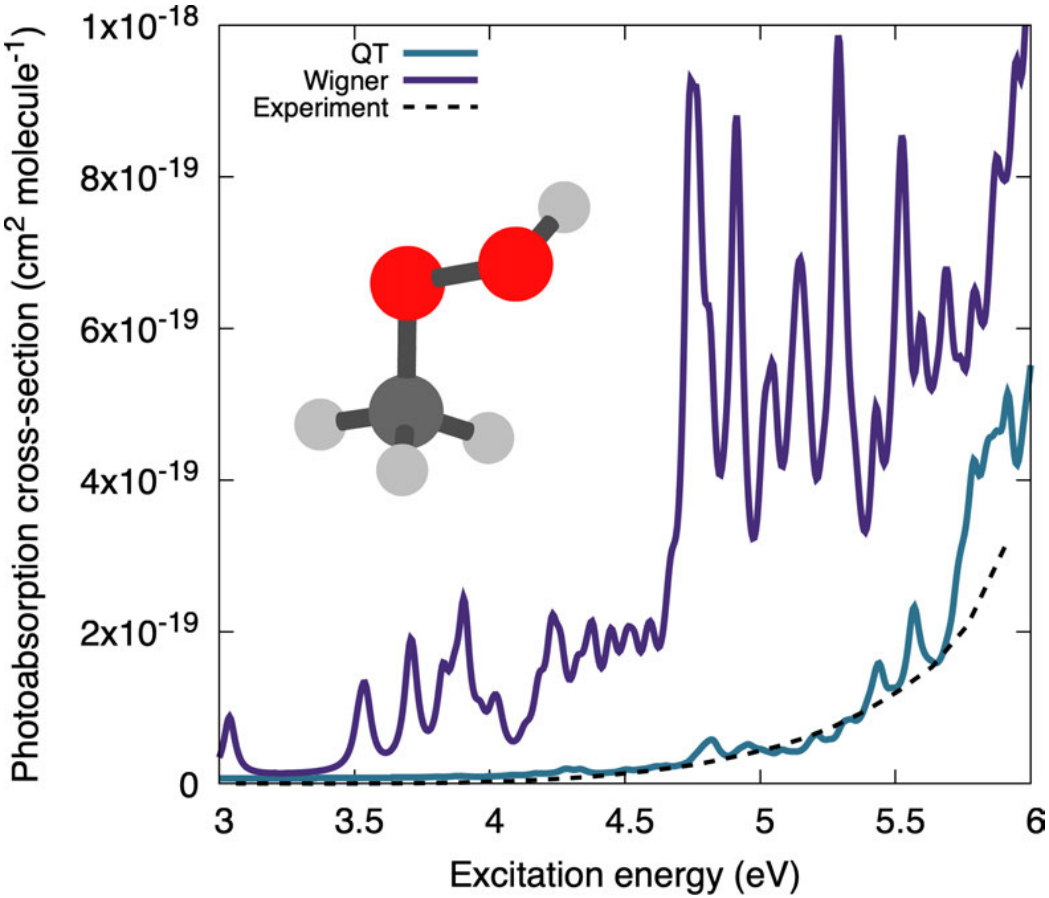

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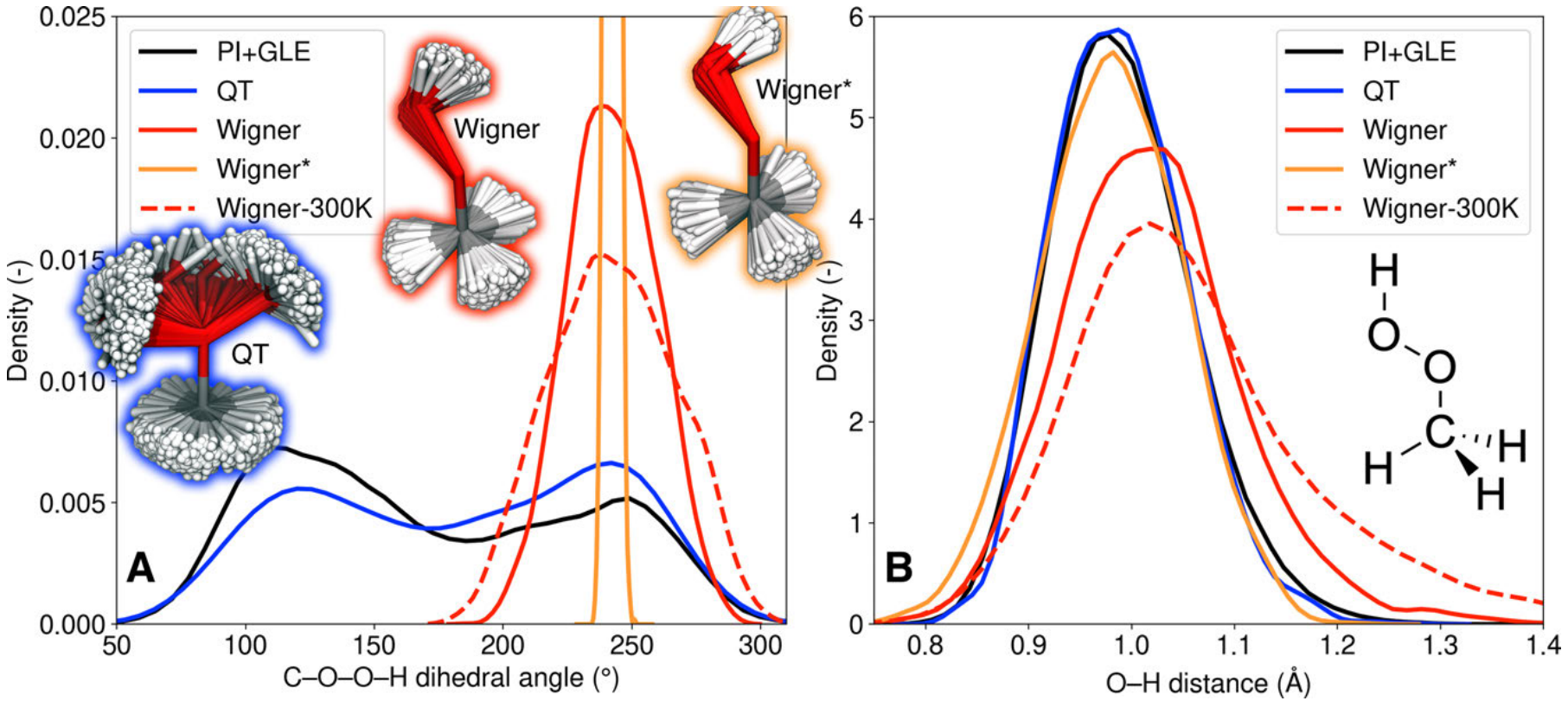

Nuclear ensemble approach – 4000 sampled geometries for each distribution. MP2/aug-cc-pVDZ

Effect on the outcome of the nonadiabatic molecular dynamics?

A. Prlj, D. Hollas, B. F. E. Curchod, *J. Phys. Chem. A*, **127**, 7400 (2023); M. Ceriotti, G. Bussi, M. Parrinello, *Phys. Rev. Lett.*, **103**, 030603 (2009)

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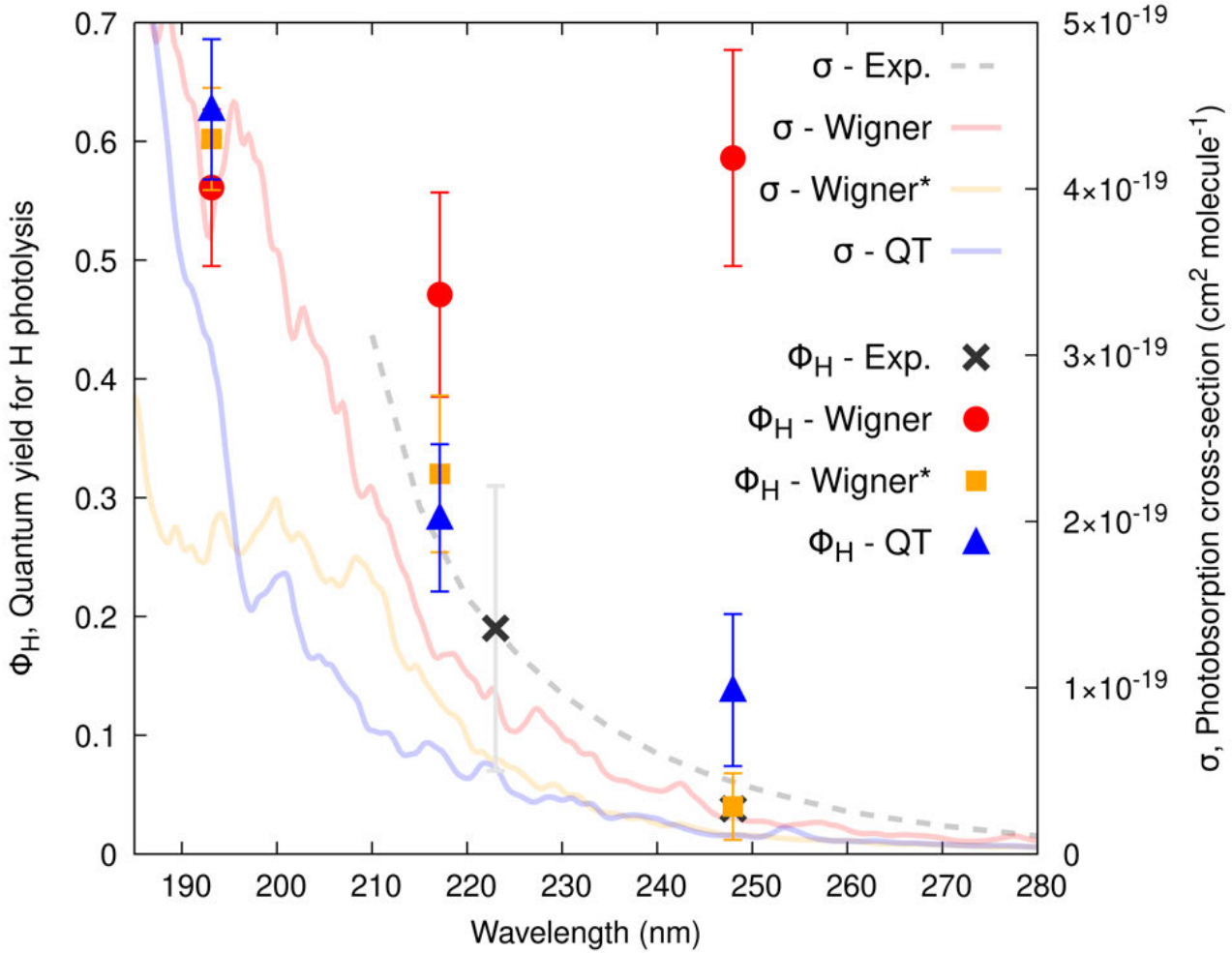

TSH/XMS(4)-CASPT2(8/6)/def2-SVPD (∼100 ICs per energy window from each distribution).

Inadequate sampling of the ground-state distribution for photoactive modes can lead to significant artifacts in the nonadiabatic molecular dynamics.

A. Prlj, D. Hollas, B. F. E. Curchod, *J. Phys. Chem. A*, **127**, 7400 (2023); M. Ceriotti, G. Bussi, M. Parrinello, *Phys. Rev. Lett.*, **103**, 030603 (2009)

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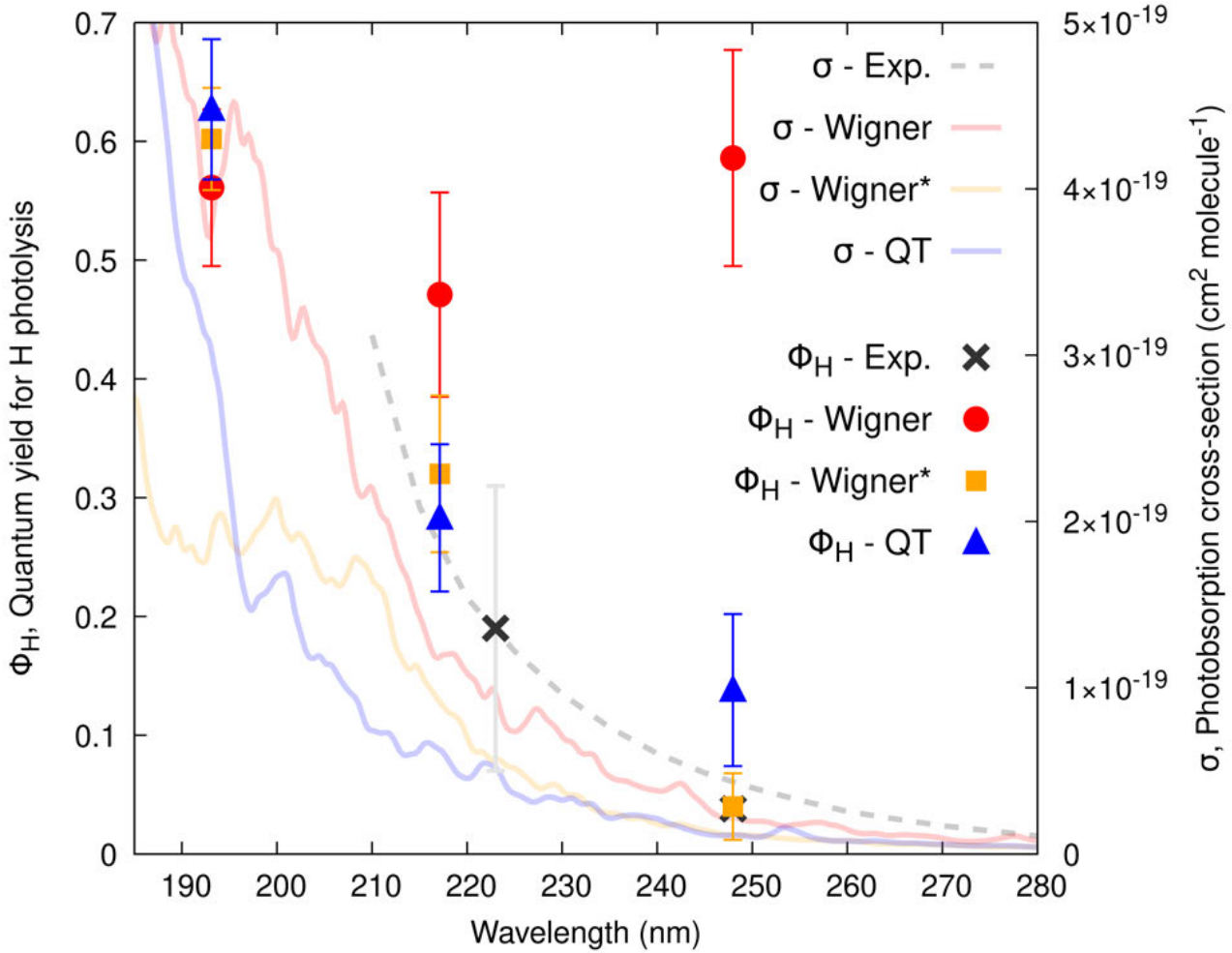

TSH/XMS(4)-CASPT2(8/6)/def2-SVPD (∼100 ICs per energy window from each distribution).

[XMS-CASPT2 oscillator strengths can be underestimated for dark transitions! See Bone et al., *J. Phys. Chem. A*, **129**, 9355 (2025)]

A. Prlj, D. Hollas, B. F. E. Curchod, *J. Phys. Chem. A*, **127**, 7400 (2023); M. Ceriotti, G. Bussi, M. Parrinello, *Phys. Rev. Lett.*, **103**, 030603 (2009)

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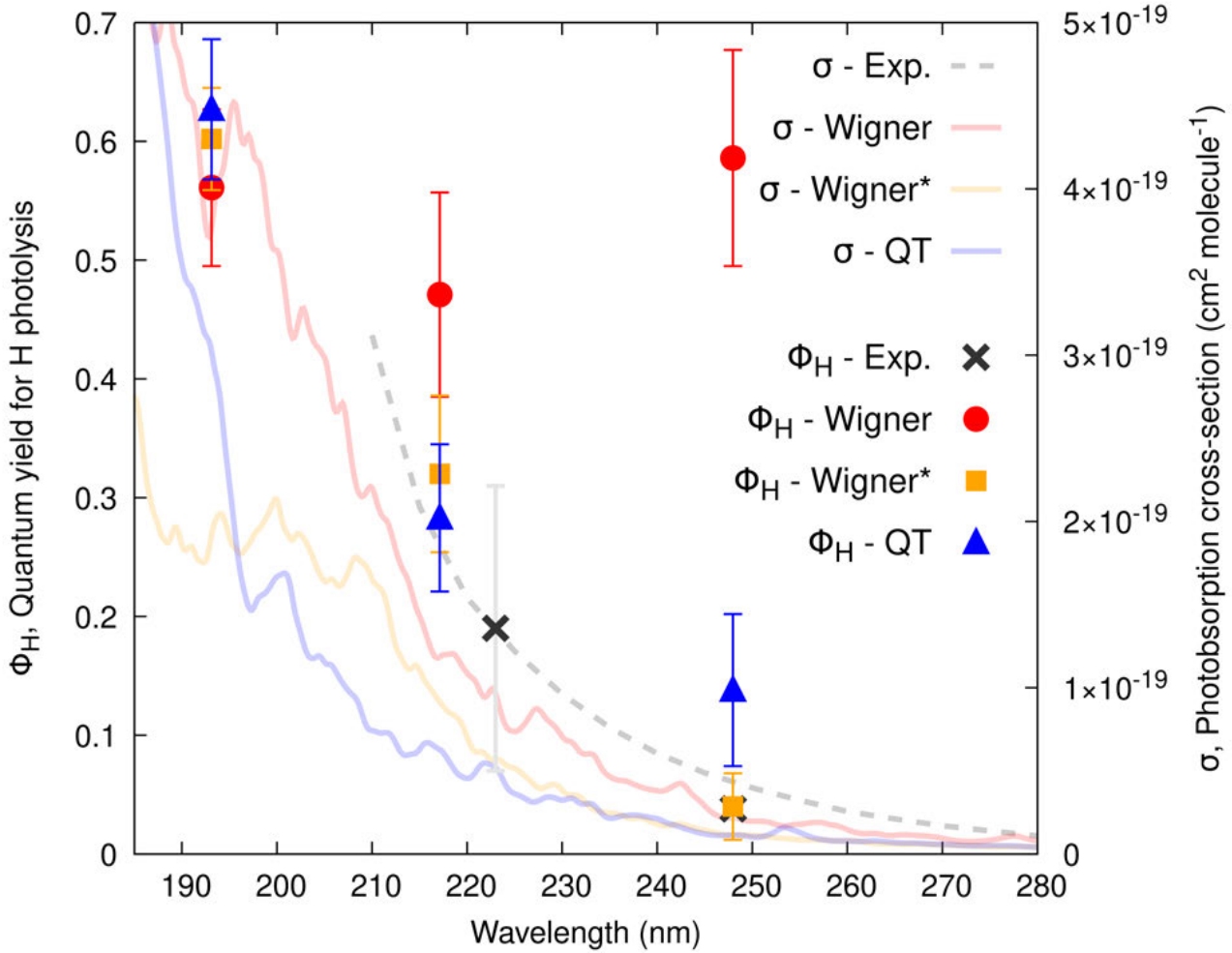
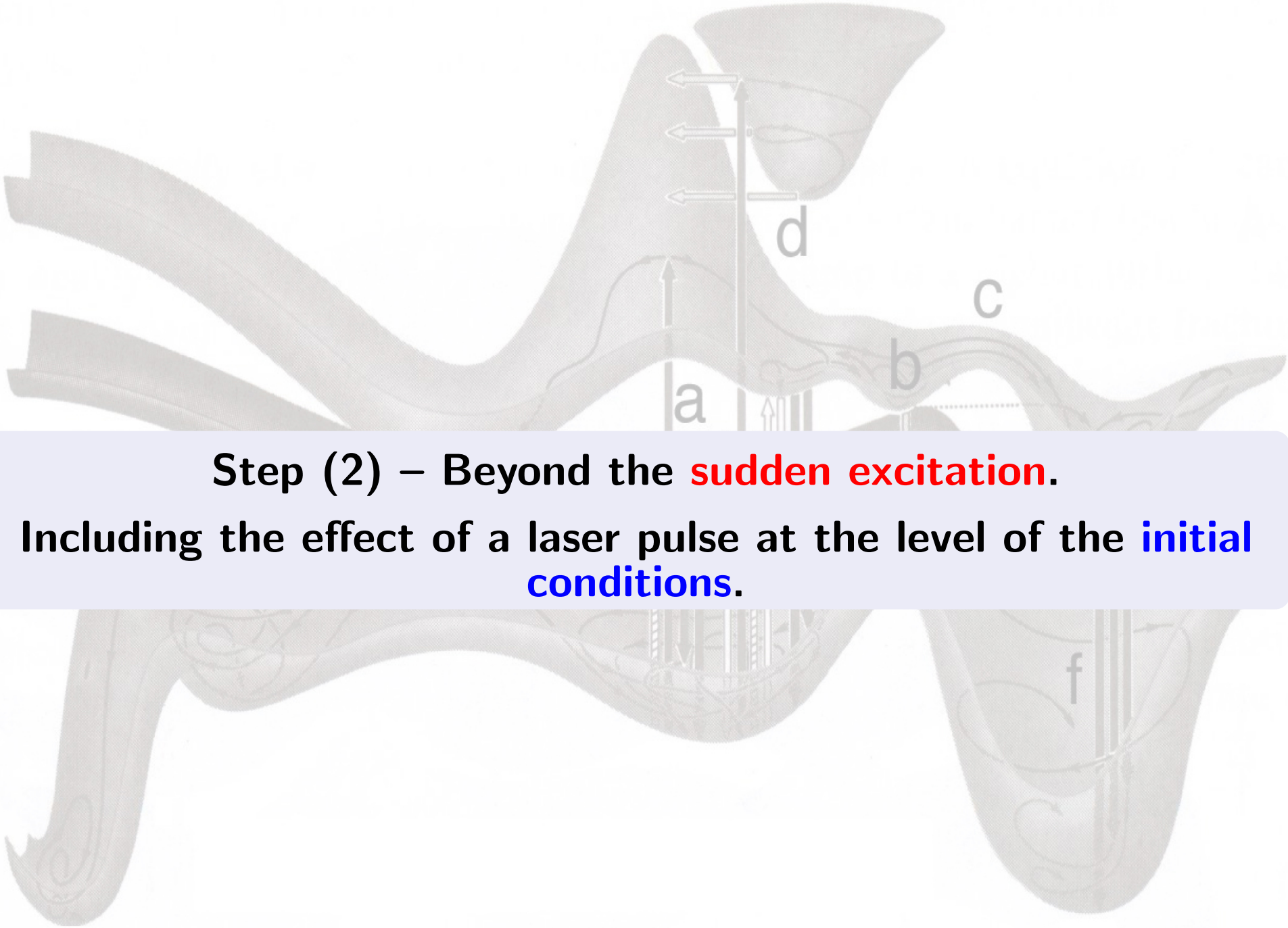


TSH/XMS(4)-CASPT2(8/6)/def2-SVPD (∼100 ICs per energy window from each distribution).

Sampling based on a quantum-thermostat Born-Oppenheimer molecular dynamics distribution appears to address this issue.

A. Prlj, D. Hollas, B. F. E. Curchod, *J. Phys. Chem. A*, **127**, 7400 (2023); M. Ceriotti, G. Bussi, M. Parrinello, *Phys. Rev. Lett.*, **103**, 030603 (2009)



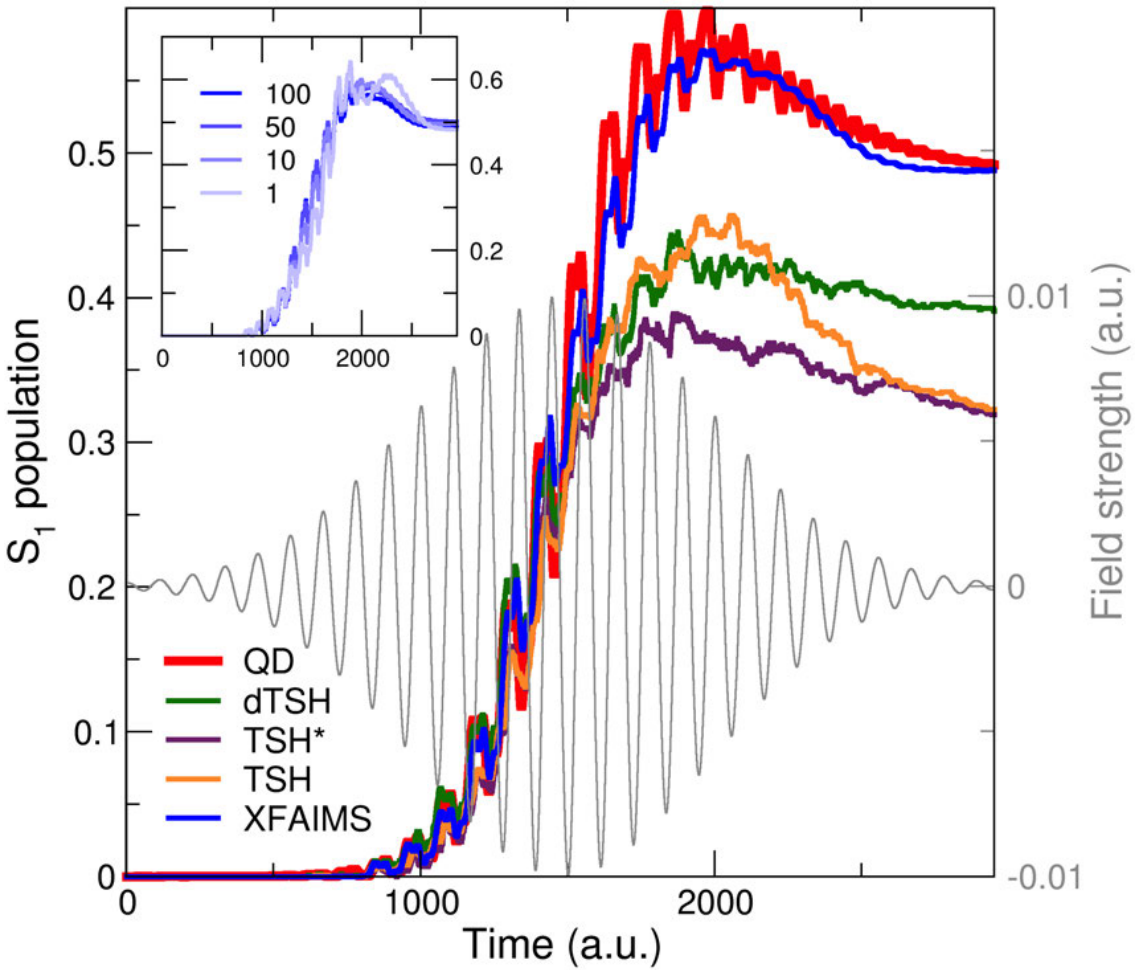
Step (2) – Beyond the sudden excitation.

Including the effect of a laser pulse at the level of the initial conditions.

Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

Beyond the sudden approximation?

Including explicitly a laser pulse in a trajectory-based simulation is challenging.



Photoexcitation of LiH with a long IR pulse.

Long pulses break the independent trajectory approximation of TSH (with and without decoherence correction).

XFAIMS can reproduce the exact QD result thanks to the coupling between TBFs, but the method is expensive.

B. Mignolet, B. F. E. Curchod, *J. Phys. Chem A*, **123**, 3582 (2019)

Beyond the sudden approximation?

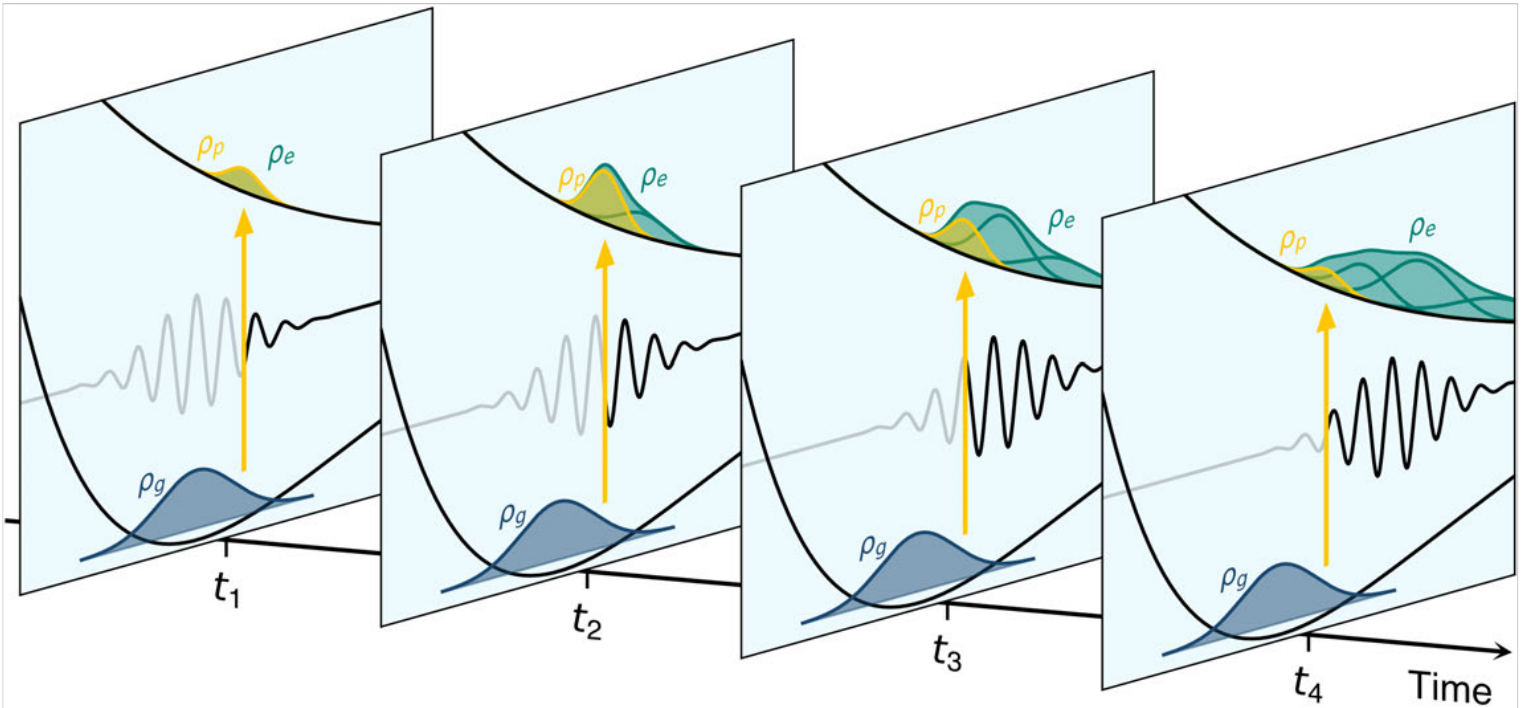
Including explicitly a laser pulse in a trajectory-based simulation is challenging.

Can we derive a simple approach to include – within the workflow of trajectory-based methods and at no cost – the effect of a laser pulse implicitly within the initial conditions?

Calculations of pump-probe signals using trajectory-based nonadiabatic dynamics approaches: Z. Li, J.-Y. Fang, C. C. Martens, *J. Chem. Phys.*, **104**, 6919 (1996) or M. Kowalewski, B. P. Fingerhut, K. E. Dorfman, K. Bennett, S. Mukamel, *Chem. Rev.*, **117**, 12165 (2017).

(2) – Including the laser pulse in the initial conditions

Promoted density approach (PDA) – Including explicitly the photoexcitation by a laser pulse at the level of the initial conditions for TSH or AIMS!



$$\rho_e^{\mathrm{cl}}(\mathbf{R},\mathbf{P},t) = \frac{1}{\hbar^2}\int_{-\infty}^{t} \mathrm{e}^{\mathcal{L}_e^{\mathrm{cl}}(t-t')} \underbrace{\left[|\vec{\mu}_{eg}(\mathbf{R})\cdot\vec{E}_0|^2 \mathcal{W}_E(t',\Delta E_{eg}^{\mathrm{el}}(\mathbf{R})/\hbar)\rho_g^{\mathrm{cl}}(\mathbf{R},\mathbf{P})\right]}_{\rho_p^{\mathrm{cl}}(\mathbf{R},\mathbf{P},t')} \mathrm{d}t'$$

J. Janoš, P. Slavíček, B. F. E. Curchod, *J. Phys. Chem. Lett.*, **15**, 10614 (2024); A. Martínez-Mesa, P. Saalfrank, *J. Chem. Phys.* **142**, 194107 (2015)

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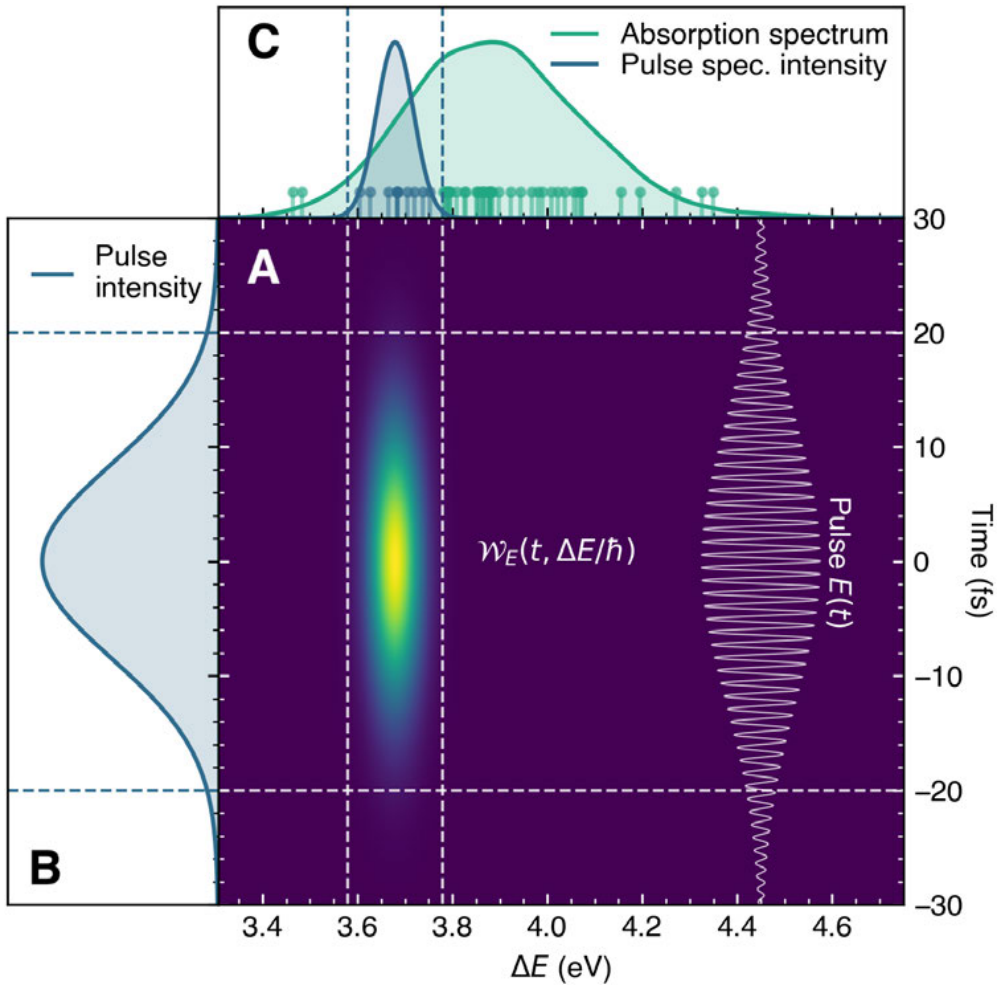

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Promoted density approach (PDA) – Including explicitly the photoexcitation by a laser pulse at the level of the initial conditions for TSH or AIMS!

Algorithm 1: The PDA algorithm used to sample the promoted density $\rho_p^{\mathrm{cl}}(\underline{\mathbf{R}}, \underline{\mathbf{P}}, t')$. The input consists of the ground-state nuclear position-momentum pairs $\{\underline{\mathbf{R}}_i, \underline{\mathbf{P}}_i\}$ with their corresponding excitation energies $\Delta E_i = \Delta E_{eg}^{\mathrm{el}}(\underline{\mathbf{R}}_i)$ and transition dipole moments $\vec{\mu}_i = \vec{\mu}_{eg}(\underline{\mathbf{R}}_i)$.

estimate maximum probability p_{max}
$j = 1$
while $j \leq N_p$ **do**
  randomly select $i \in \{1, \ldots, N_g\}$
  randomly select t'
  calculate probability $p = |\vec{\mu}_i \cdot \vec{E}_0|^2 \mathcal{W}_E(t', \Delta E_i)$
  if $p < 0$ **then**
    handle negative probabilities (see Section 6.4)
  end
  randomly select $\mathcal{R} \in [0, p_{\mathrm{max}}]$
  if $\mathcal{R} \leq p$ **then**
    accept $\{\underline{\mathbf{R}}_i, \underline{\mathbf{P}}_i, t'\}$ as an initial condition j
    $j = j + 1$
  end
end

Access to $\mathbf{R}_i, \mathbf{P}_i, J_i, t_i$

J. Janoš, P. Slavíček, B. F. E. Curchod, *J. Phys. Chem. Lett.*, **15**, 10614 (2024); A. Martínez-Mesa, P. Saalfrank, *J. Chem. Phys.* **142**, 194107 (2015)

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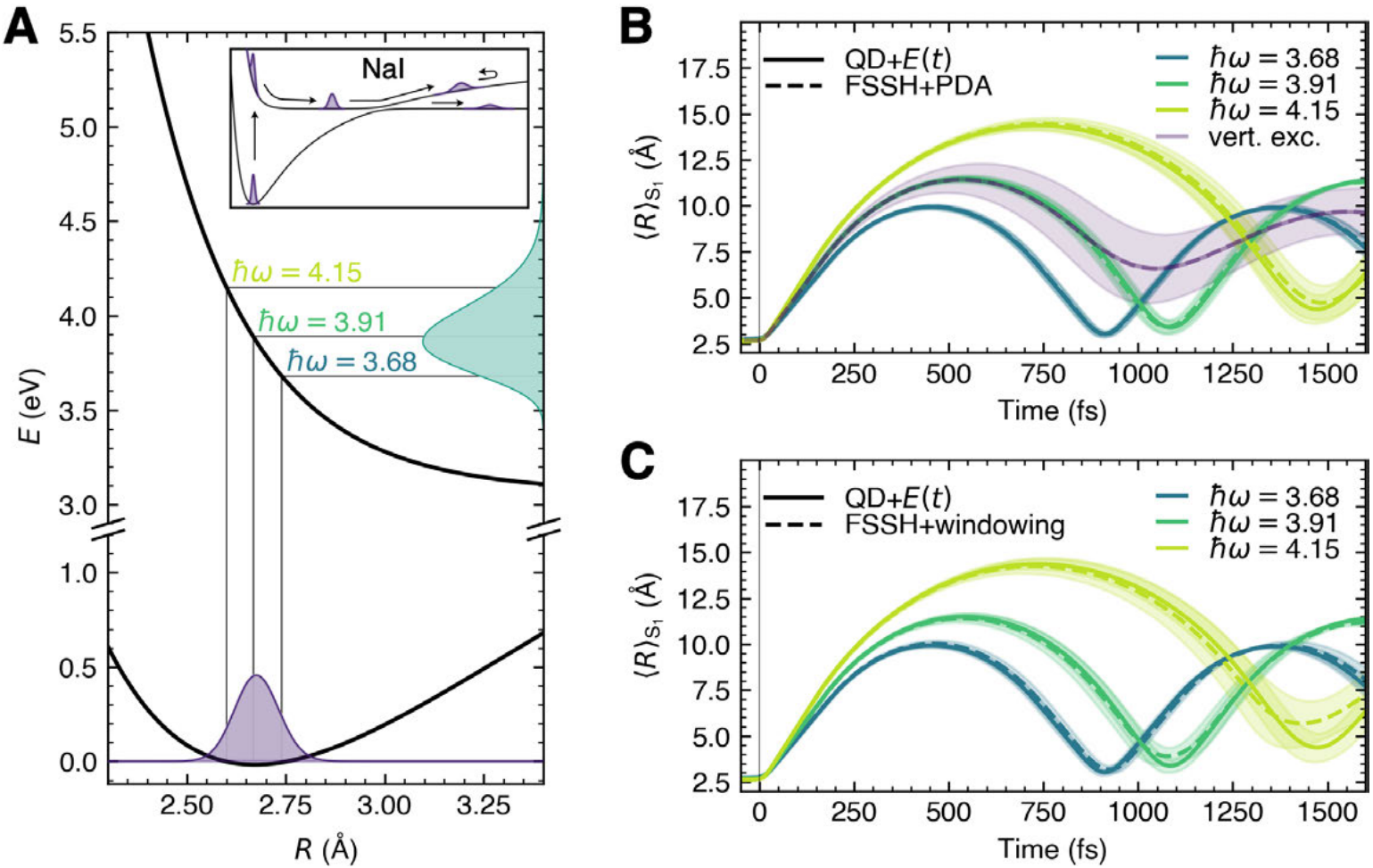

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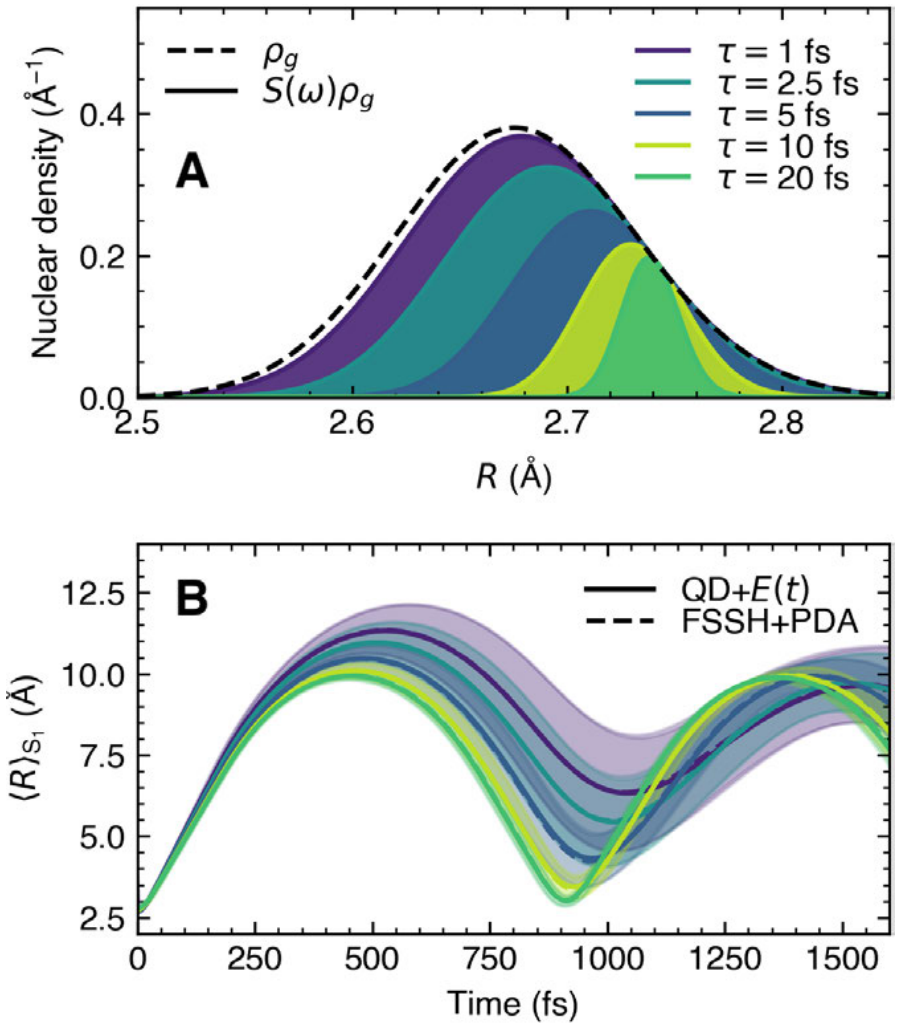

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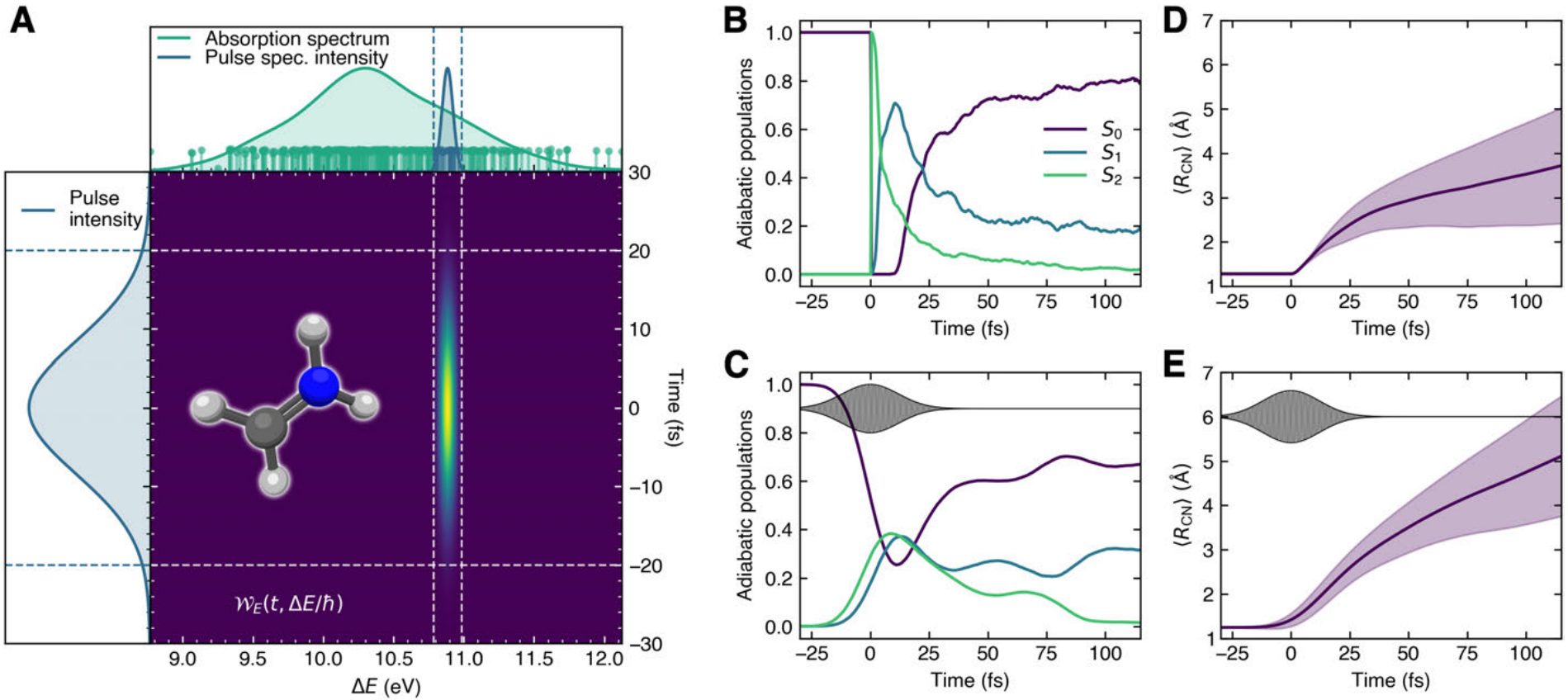


J. Janoš, P. Slavíček, B. F. E. Curchod, *J. Phys. Chem. Lett.*, **15**, 10614 (2024); A. Martínez-Mesa, P. Saalfrank, *J. Chem. Phys.* **142**, 194107 (2015)

(2) – Including the laser pulse in the initial conditions

Promoted density approach (PDA) – Including explicitly the photoexcitation by a laser pulse at the level of the initial conditions for TSH or AIMS!

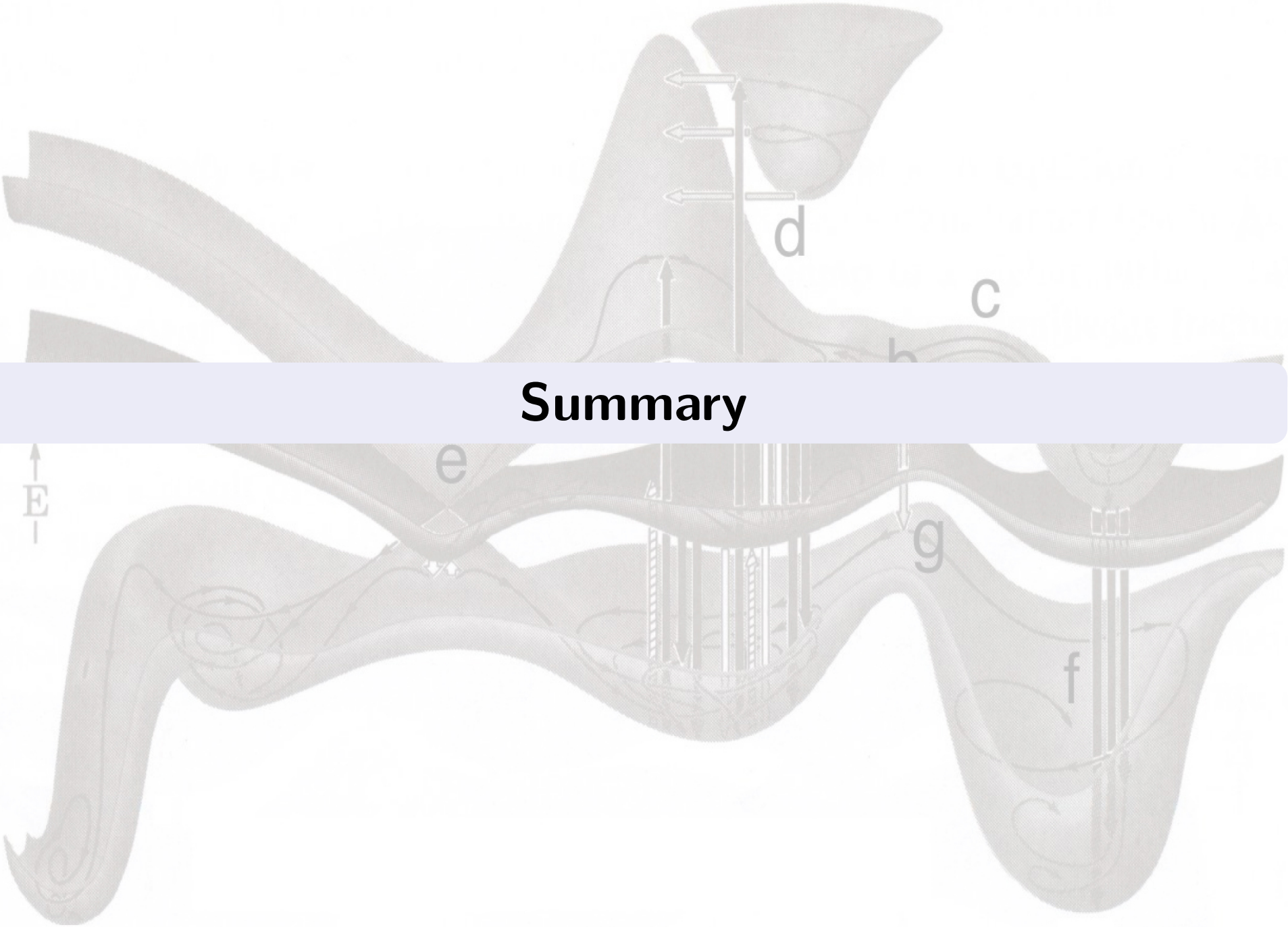
The promoted density approach comes at no additional costs!

- Sample $\{\mathbf{R}_i, \mathbf{P}_i\}$ as per usual and calculate absorption spectrum (using e.g., Newton-X, SHARC, or ABIN).
- PDA selects the proper initial conditions using the provided characteristics of the laser pulse (τ_{FWHM}, chirped, envelope type, frequency) and the properties of each initial condition ($\Delta E^{el}_{I,i}$, $f_{I,i}$), outputting a final set of initial conditions $\{\mathbf{R}_i, \mathbf{P}_i, J_i, t_i\}_{i=1}^{N_{\text{IC}}}$.
- Open-source code available:

```
$ pip install promdens
```

The framework of PDA also offers a theoretical justification for the energy-windowing approach, with specific recommendations for the weight assigned to each trajectory (PDAW).

Summary



Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

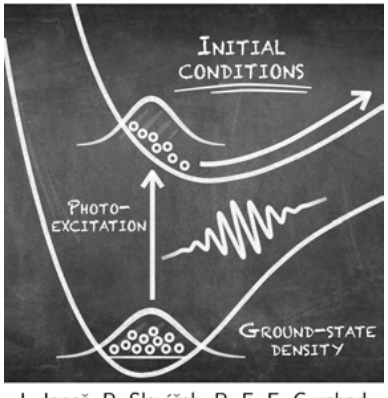
Trajectory-based nonadiabatic molecular dynamics, combined with state-of-the-art electronic-structure methods, has reached a level of maturity allowing us to tackle challenging photochemical problems.

Yet, its initialization process – i.e., sampling of the ground-state distribution and photoexcitation – is dramatically approximated in most photochemical applications.

Sampling of initial conditions: Quantum-thermostat ab initio molecular dynamics offers an alternative to harmonic Wigner sampling.

Photoexcitation process: Promoted density approach includes the effect of a laser pulse in the initial conditions at no additional cost.

Remaining challenges: electronic-structure methods, excitation with incoherent light, and adequate description of an environment for photochemistry.



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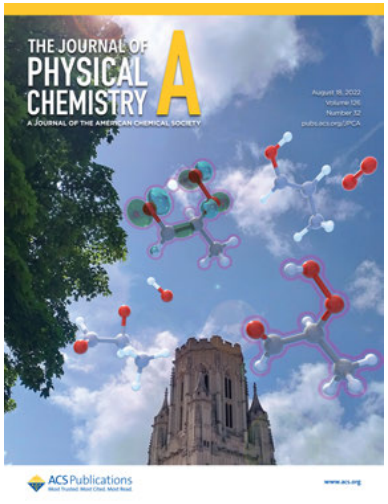

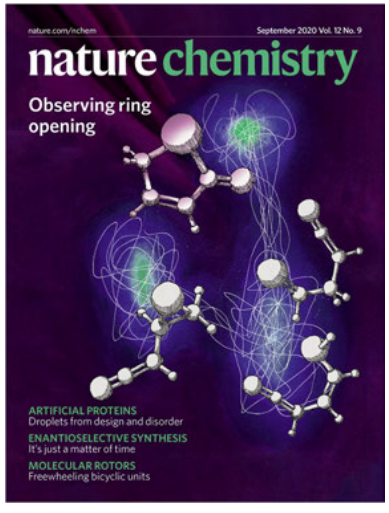

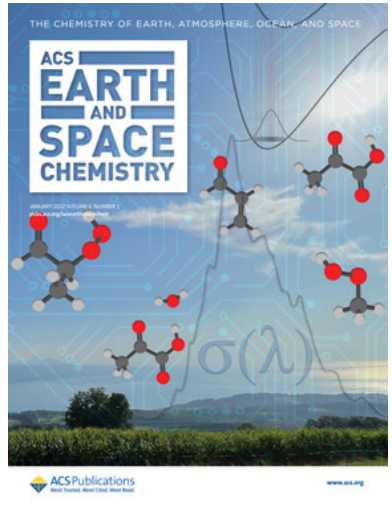

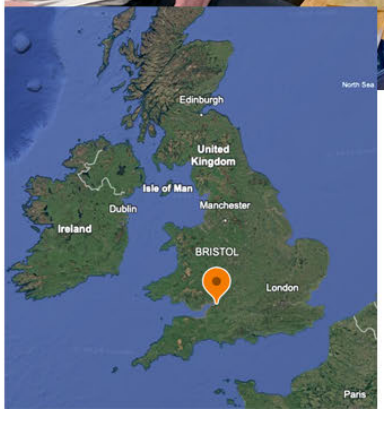

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Todd J. Martínez (Stanford U.)
Jan Verlet (Durham University)
Terry Dillon & Andrew Rickard (U. of York)

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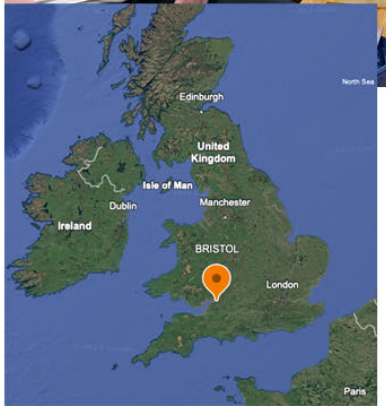
[Submitted on 7 Aug 2025]

Best practices for nonadiabatic molecular dynamics simulations

Antonio Prlj, Jack T. Taylor, Jiří Janoš, Petr Slavíček, Federica Agostini, Basile F. E. Curchod



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