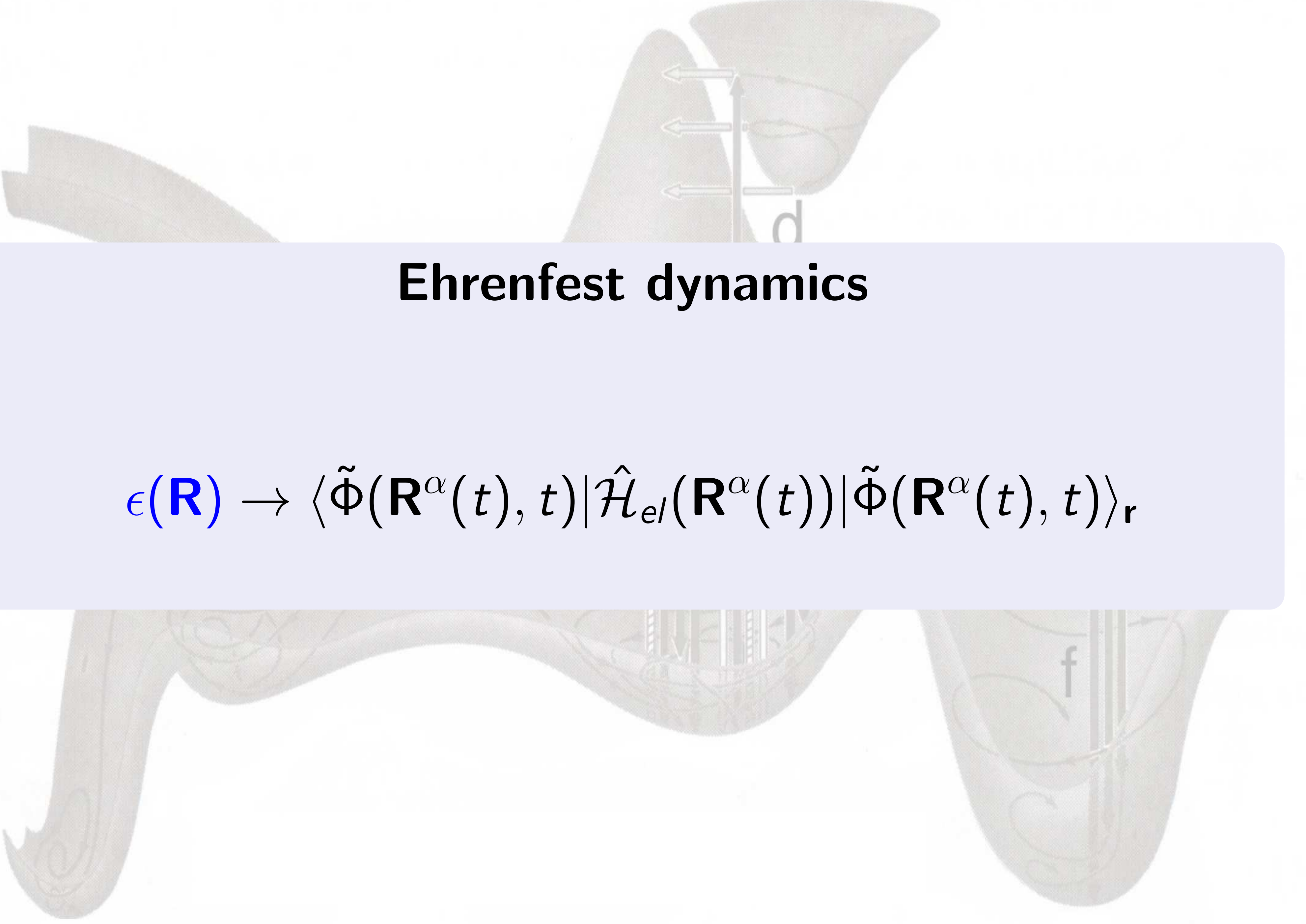


Ehrenfest dynamics

$$\epsilon(\mathbf{R}) \rightarrow \langle \tilde{\Phi}(\mathbf{R}^{\alpha}(t), t) | \hat{\mathcal{H}}_{el}(\mathbf{R}^{\alpha}(t)) | \tilde{\Phi}(\mathbf{R}^{\alpha}(t), t) \rangle_{\mathbf{r}}$$

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

Ehrenfest dynamics

In Ehrenfest dynamics, the potential energy $\epsilon(\mathbf{R})$ used to evolve a trajectory is the average electronic energy as computed from the time-dependent electronic wavefunction:

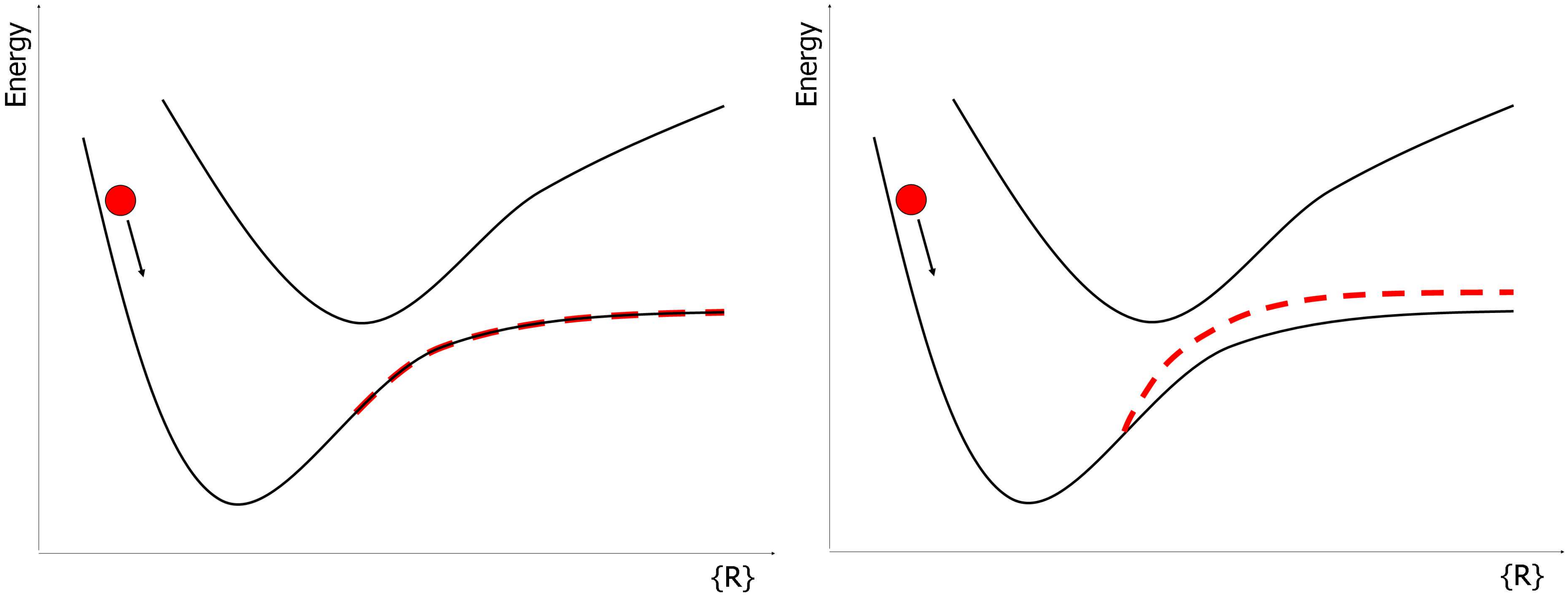
Ehrenfest dynamics

$$i\hbar\dot{c}_I^\alpha(t) = \sum_J c_J^\alpha(t)\left(E_J^{el}(\mathbf{R}^\alpha(t))\delta_{IJ} - i\hbar\dot{\mathbf{R}}^\alpha \cdot \mathbf{d}_{IJ}(\mathbf{R}^\alpha(t))\right)$$

$$\begin{aligned}\mathbf{F}^\alpha &= -\nabla_{\mathbf{R}}\langle\tilde{\Phi}(\mathbf{R}^\alpha(t),t)|\hat{\mathcal{H}}_{el}(\mathbf{R}^\alpha(t))|\tilde{\Phi}(\mathbf{R}^\alpha(t),t)\rangle_{\mathbf{r}} \\ &= -\nabla_{\mathbf{R}}\left(\sum_{IJ} c_I^\alpha(t)^* c_J^\alpha(t)\langle\Phi_I(\mathbf{R}^\alpha(t))|\hat{\mathcal{H}}_{el}(\mathbf{R}^\alpha(t))|\Phi_J(\mathbf{R}^\alpha(t))\rangle_{\mathbf{r}}\right)\end{aligned}$$

One can perform Ehrenfest dynamics by using the time-dependent Kohn-Sham equation instead of the time-dependent electronic Schrödinger equation!!!

Nuclear dynamics with a mean potential



$$i\hbar \dot{c}_I^\alpha(t) = \sum_J c_J^\alpha(t)\left(E_J^{el}(\mathbf{R}^\alpha(t))\delta_{IJ} - i\hbar\dot{\mathbf{R}}^\alpha\cdot\mathbf{d}_{IJ}(\mathbf{R}^\alpha(t))\right)$$

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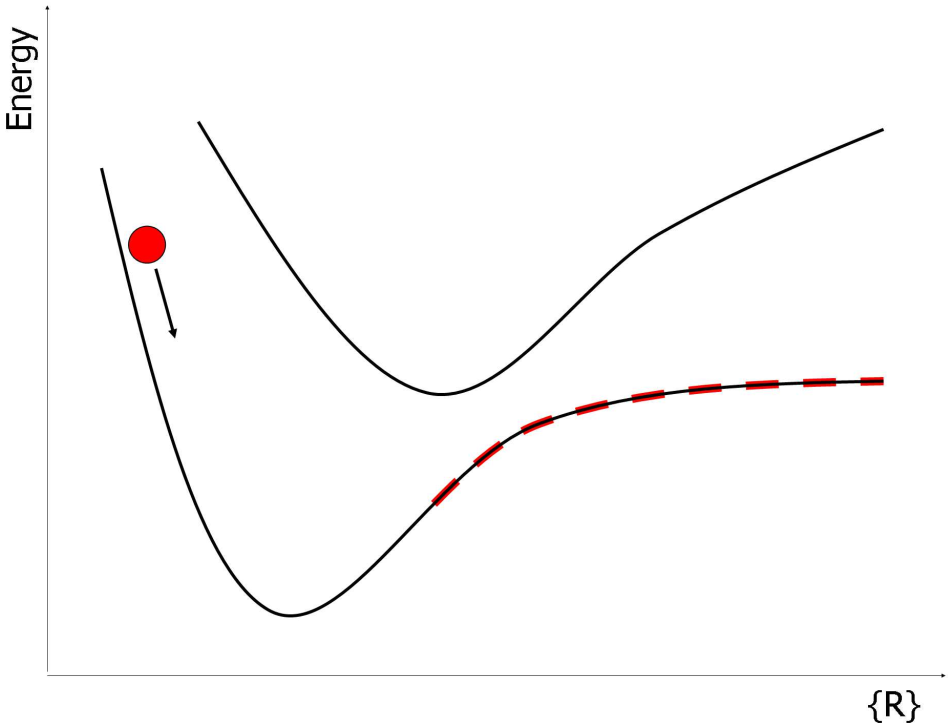
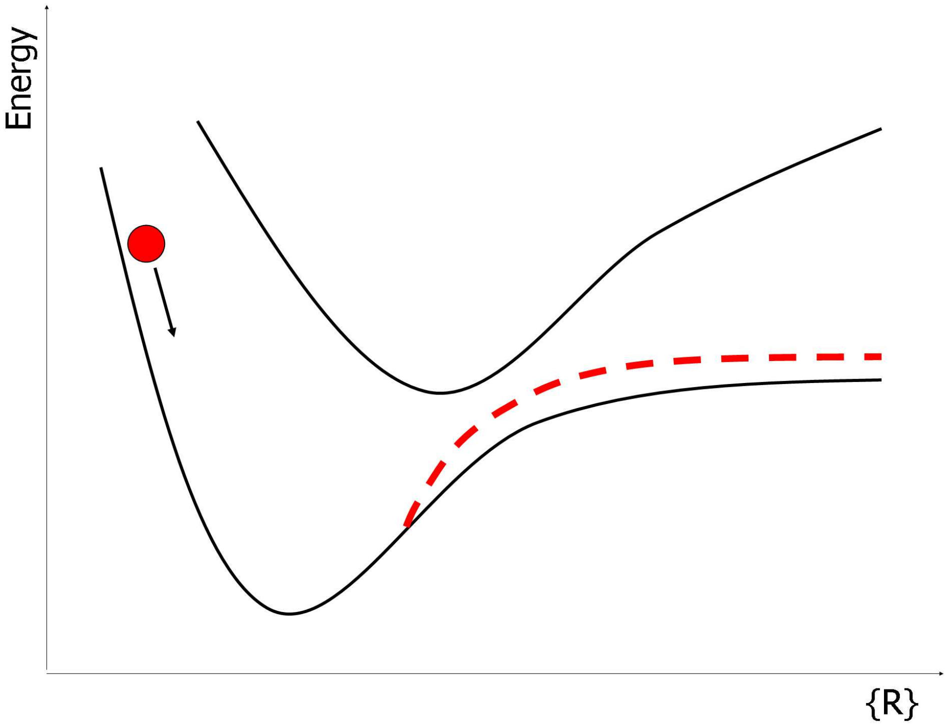
Nuclear dynamics with a mean potential



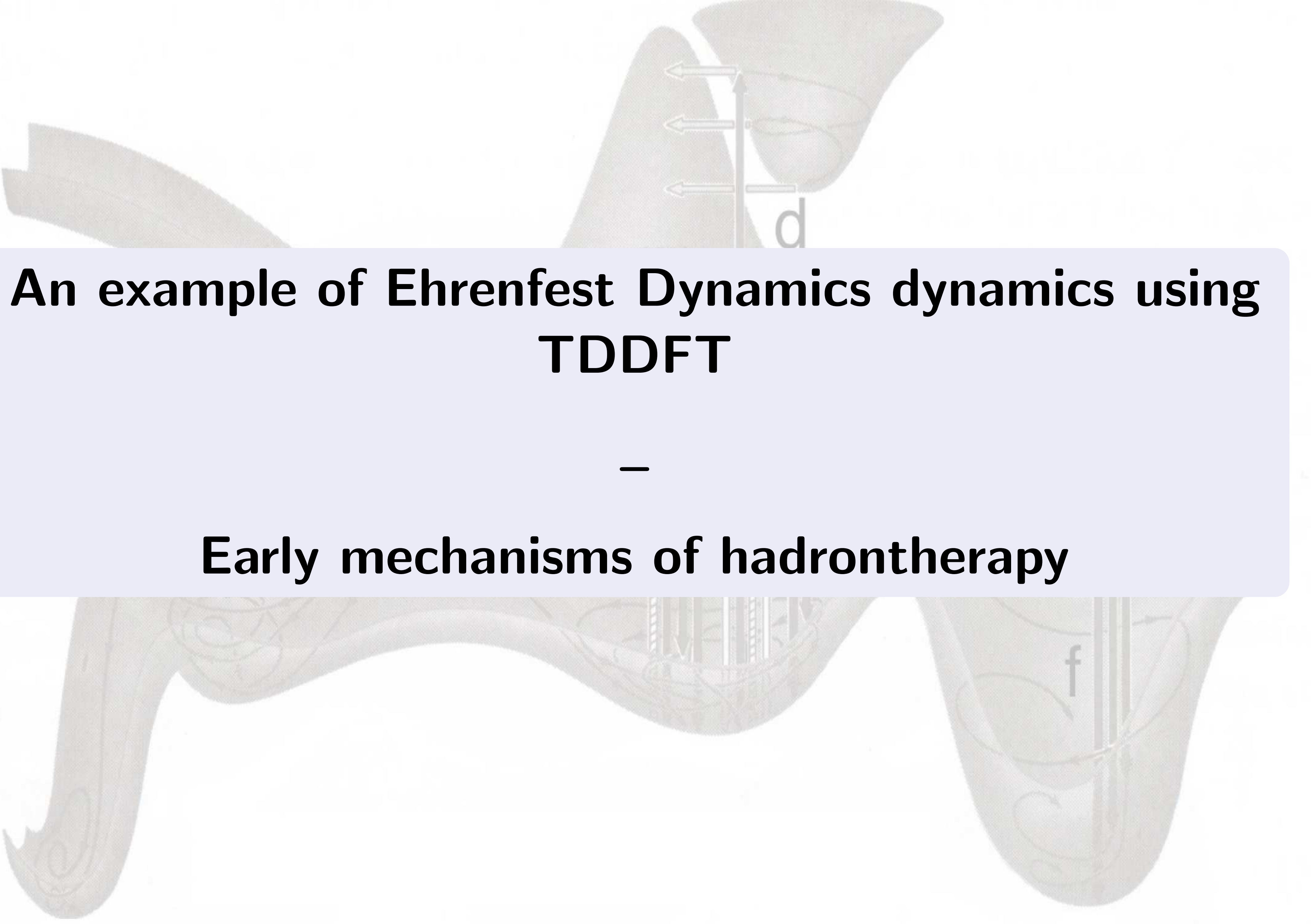


- Approximate account for nonadiabatic effects – mean-field dynamics.
- Produce physical nonadiabatic dynamics only if the different electronic states important for the dynamics have similar potential energy surfaces, or for short-time dynamics.

An example of Ehrenfest Dynamics dynamics using TDDFT

–

Early mechanisms of hadrontherapy

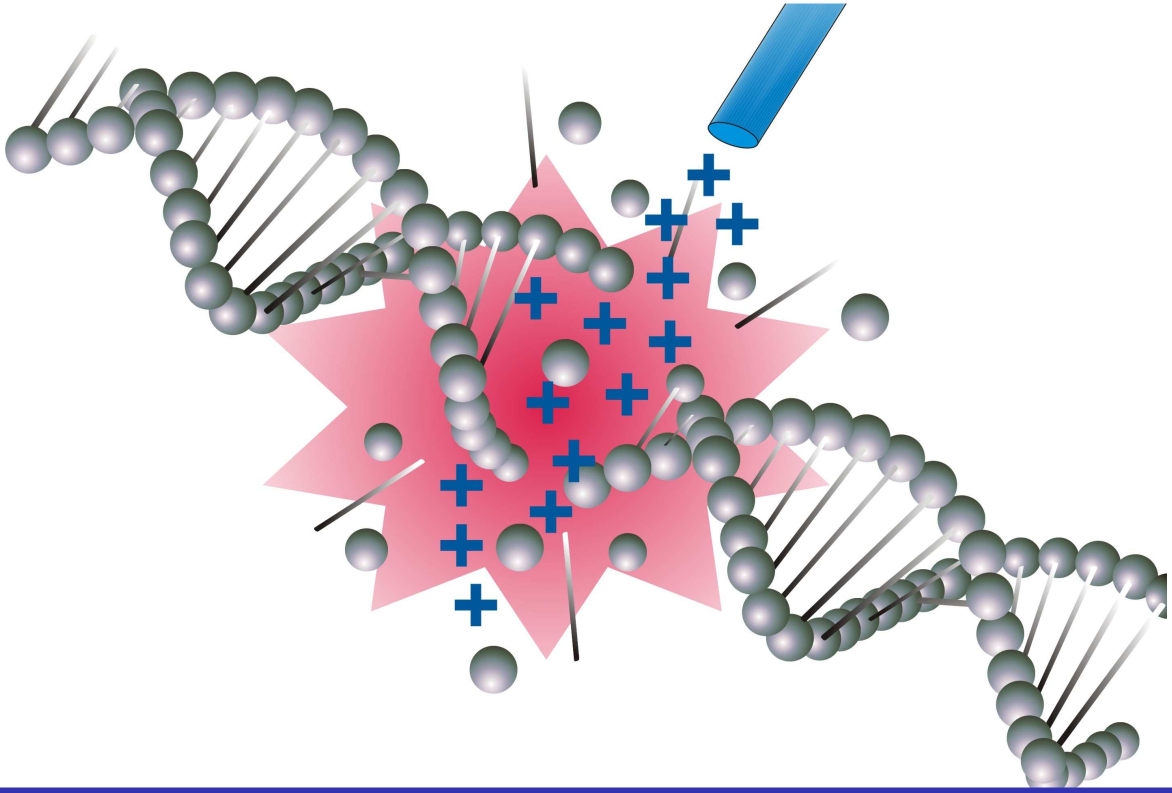


Credit: J. Michl and V. Bonacic-Koutecký, “Electronic Aspects of Organic Photochemistry”. John Wiley and Sons, Inc., New York, 1990.

Hadrontherapy

"Process of irradiating a malignant tumor with ionizing radiation with the aim of damaging the DNA of the cancerous cells."

- When high-energy photons are used: X-ray therapy.
- When hadronic matter is used (H or C): **Hadrontherapy**.



Hadrontherapy

> *"Process of irradiating a malignant tumor with ionizing radiation with the aim of damaging the DNA of the cancerous cells."*
>
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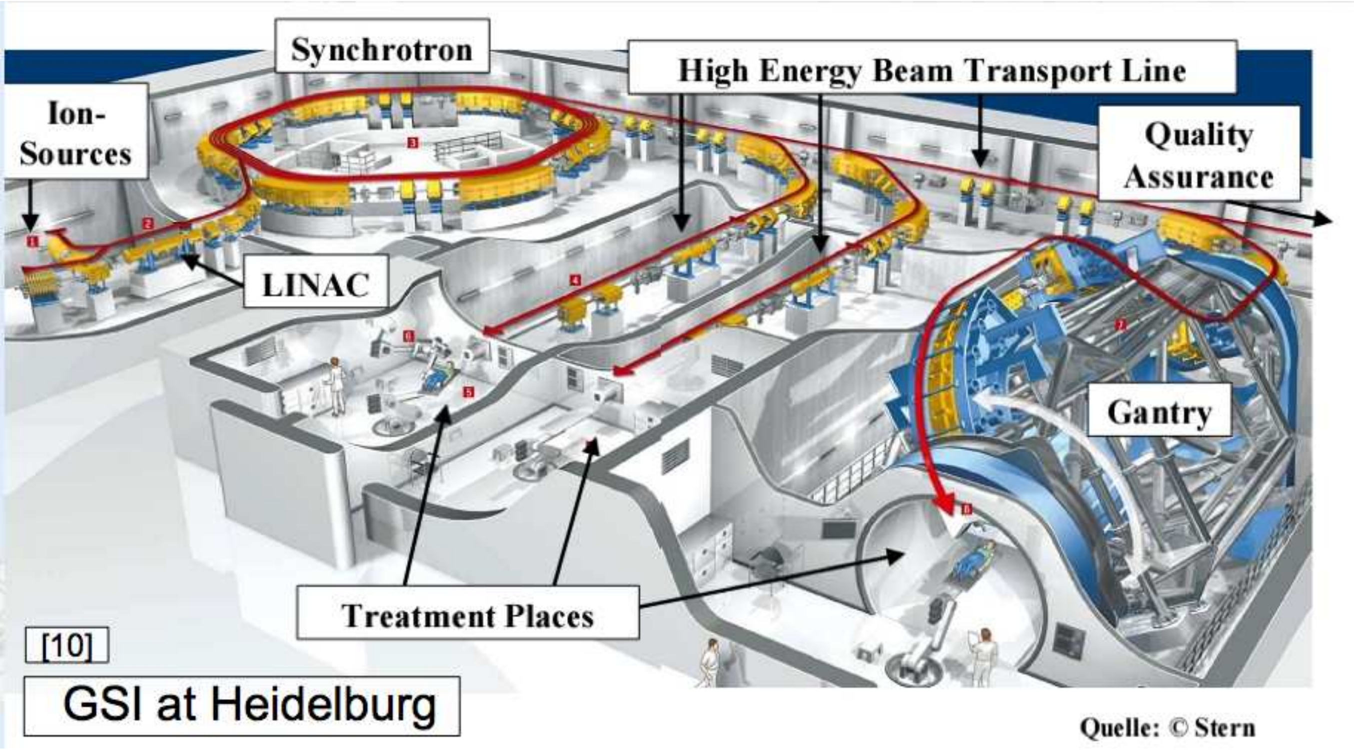


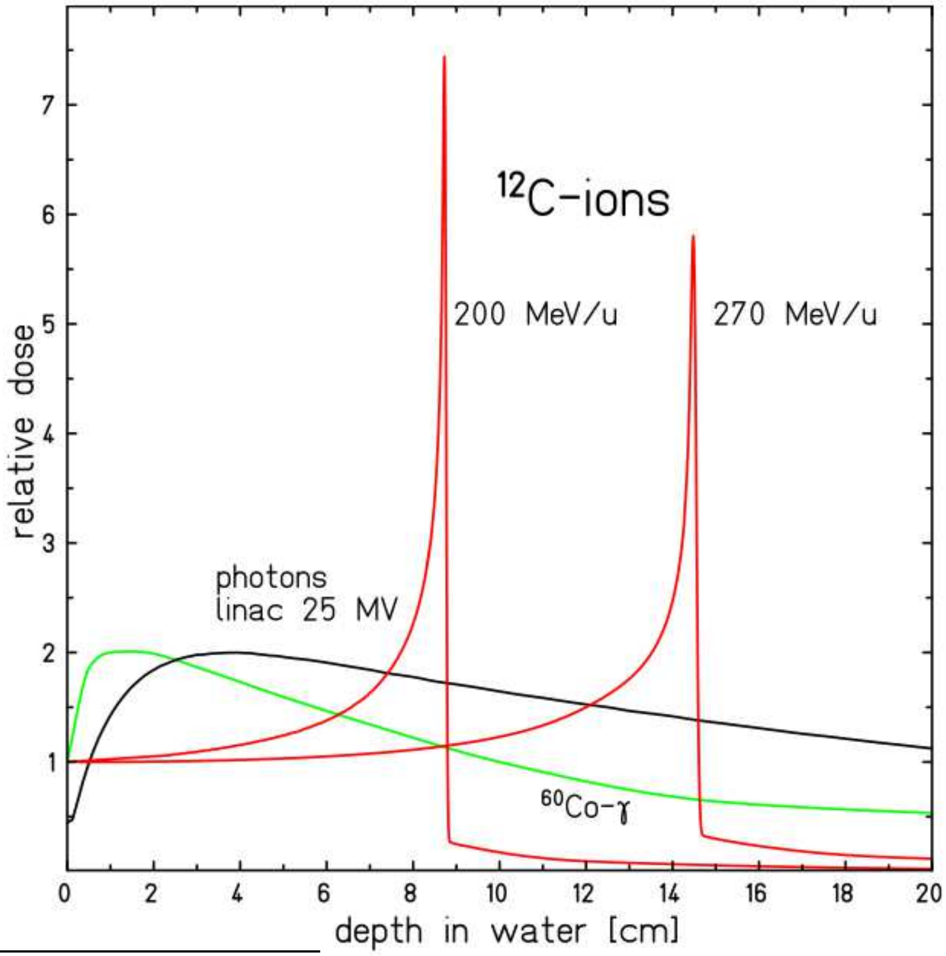
[10]

GSI at Heidelburg

Quelle: © Stern

Hadrontherapy - The idea

The main advantage of heavily-charged ion beams is their favorable depth-dose profile, also known as Bragg curve [3].



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[3] Rev. Mod. Phys. **82**, 383 (2010).

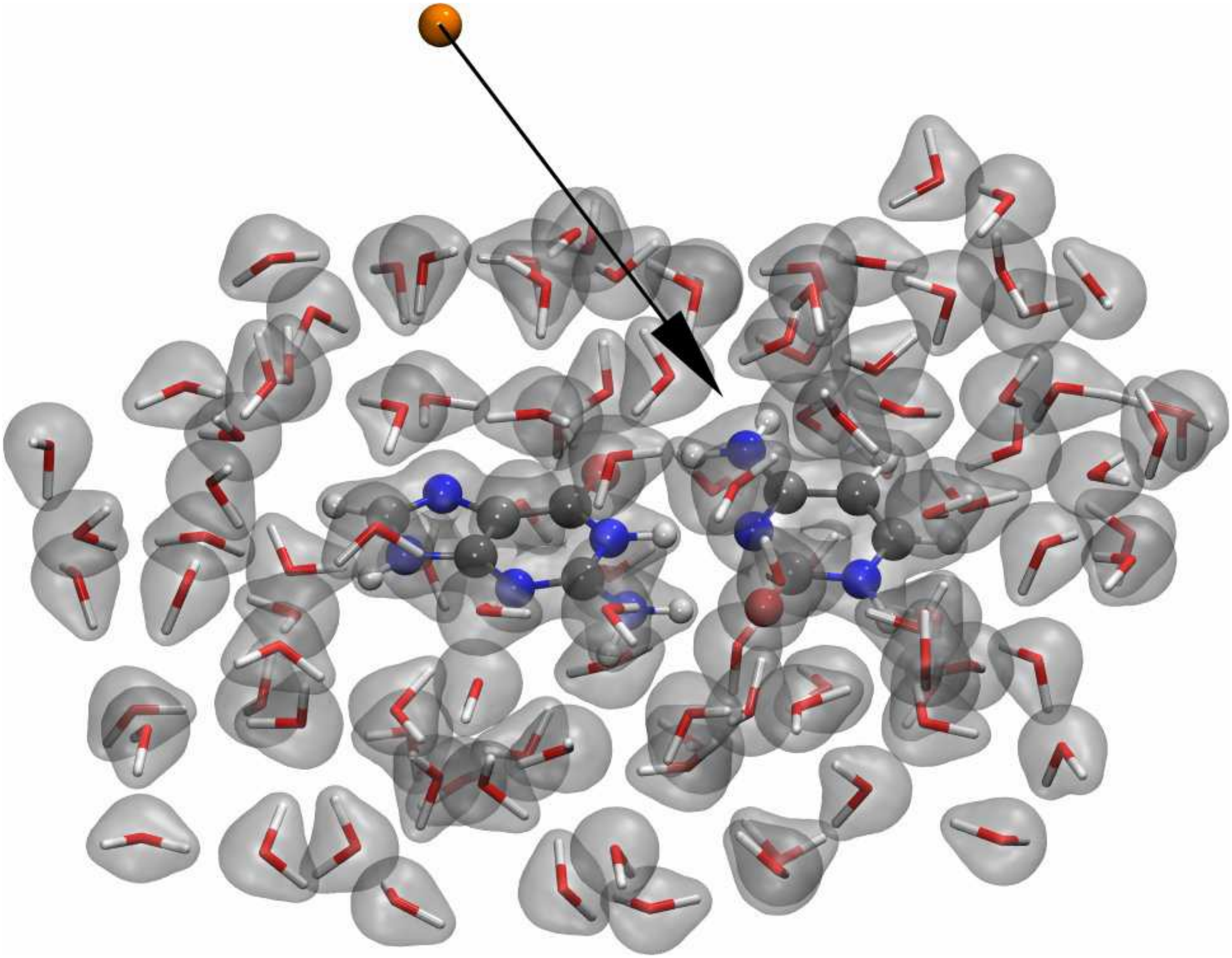
Setup

Ehrenfest dynamics with TDDFT

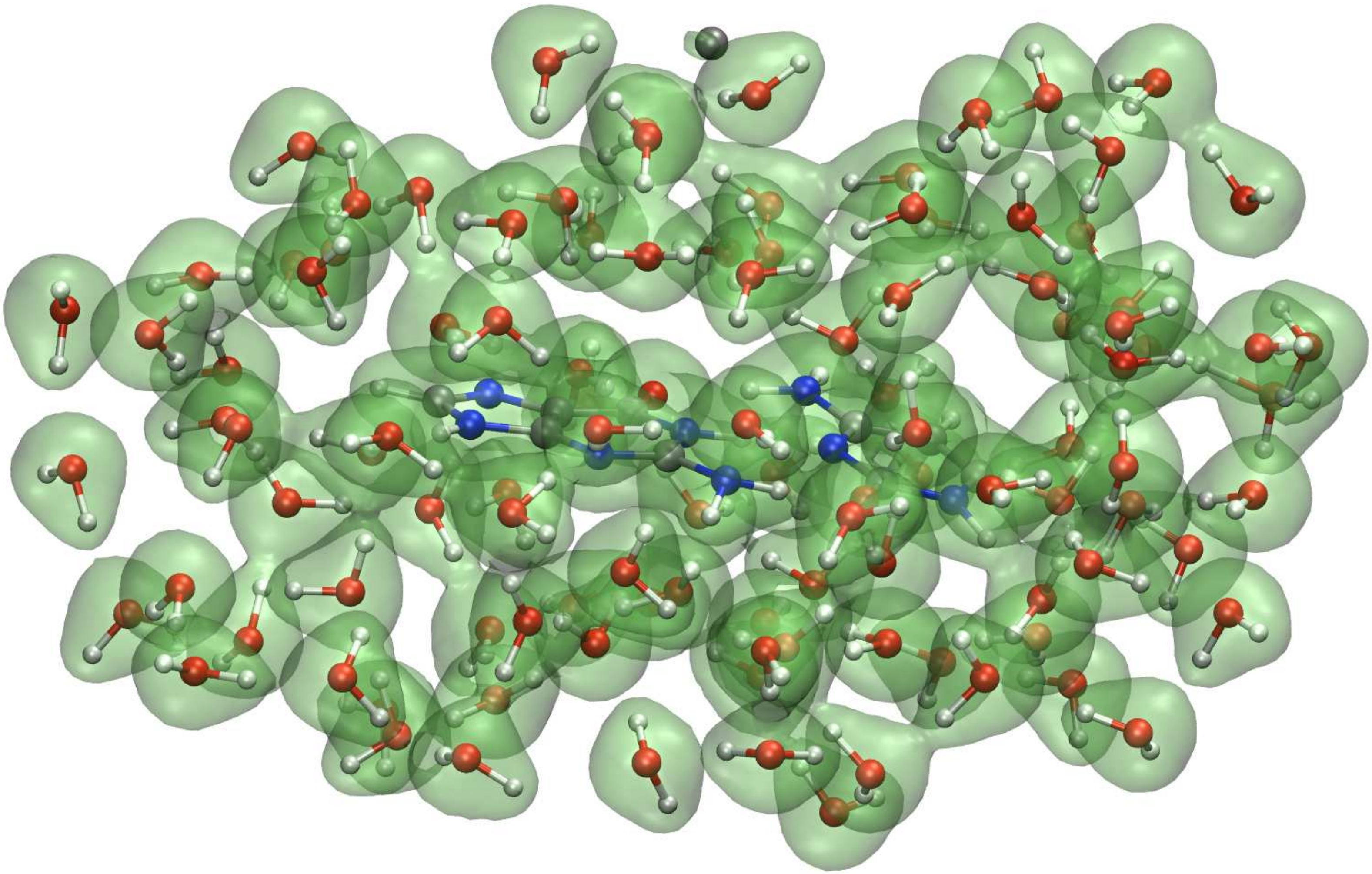
- Guanine-Cytosine base pair + 107 water molecules.
- Full system treated at the Ehrenfest/TDDFT level of theory (PBE functional).
- Projectile: C^{4+}.
- Speed of the ion in the Bragg peak: $\sim 0.79\%$ of c
  $\Rightarrow$ relativistic effects are negligible!
- Projectile added on a corner of the box, with a velocity computed to cross the bubble with no direct collision.
- Time step = 0.24 as. Total duration of the dynamics: 1 fs.
- And the final setup is...

Unpublished results.

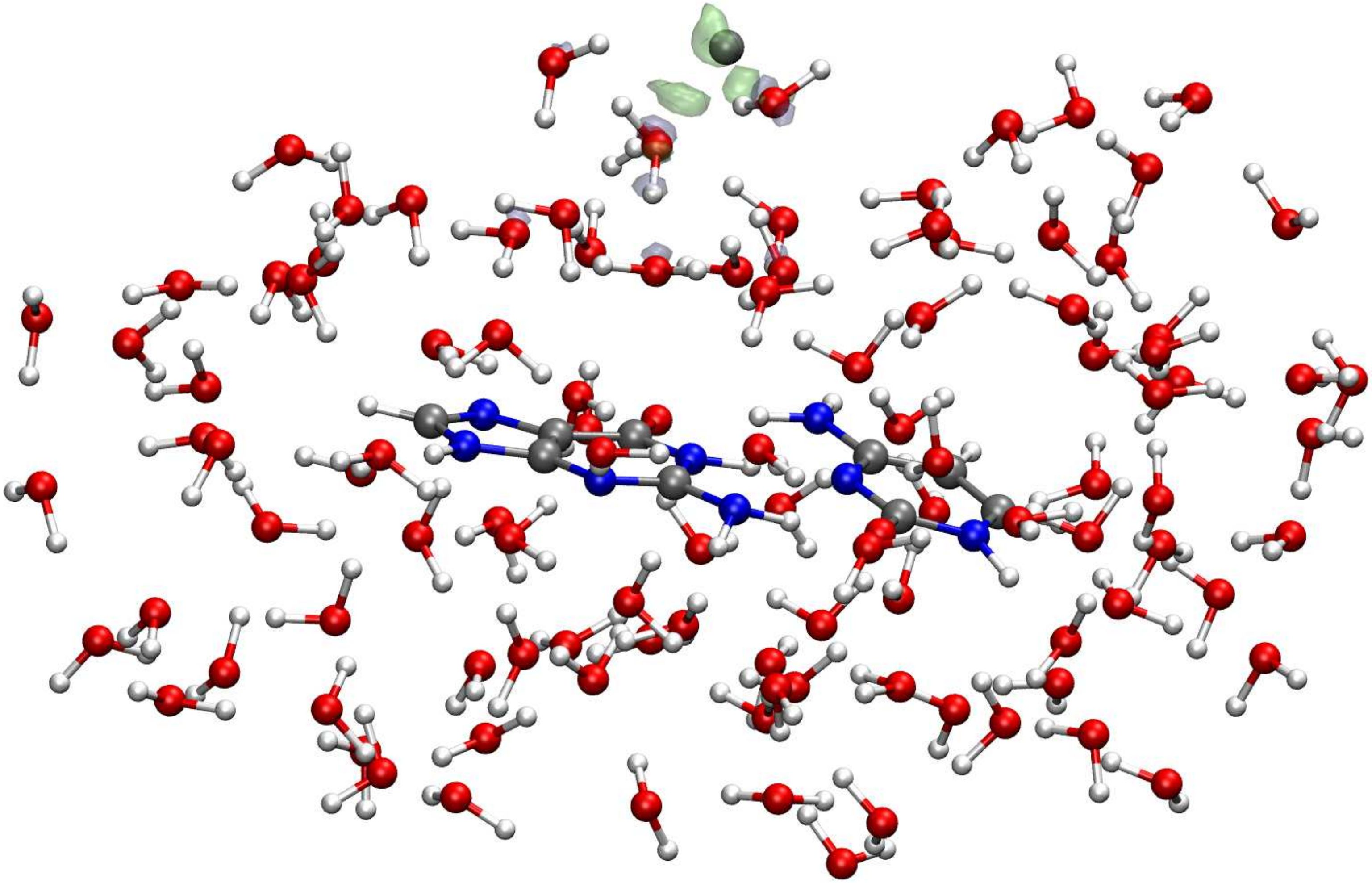
Setup



Electron extraction from C^{4+} - $[\rho(\mathbf{r},t)]$

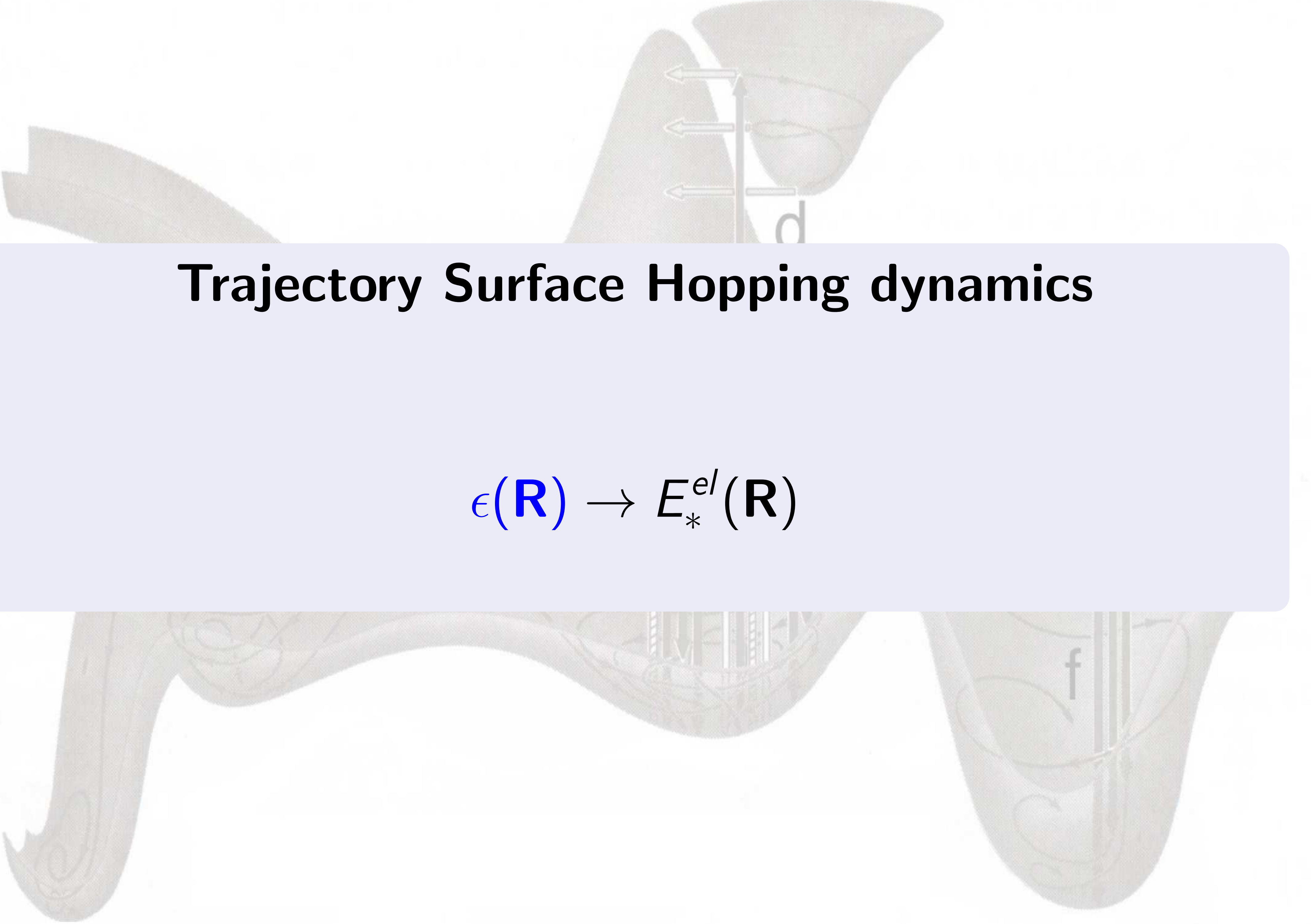


Electron extraction from C^{4+} - $\left[\rho(\mathbf{r},t) - \rho_0^{(\text{no } C^{4+})}(\mathbf{r})\right]$



Trajectory Surface Hopping dynamics

$$\epsilon(\mathbf{R}) \rightarrow E_*^{el}(\mathbf{R})$$



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

Trajectory Surface Hopping dynamics

Trajectory Surface Hopping (TSH) invokes that the PES, $E_*^{el}(\mathbf{R})$, from which the nuclear forces are computed can be chosen based on a set of rules after each nuclear integration time step:

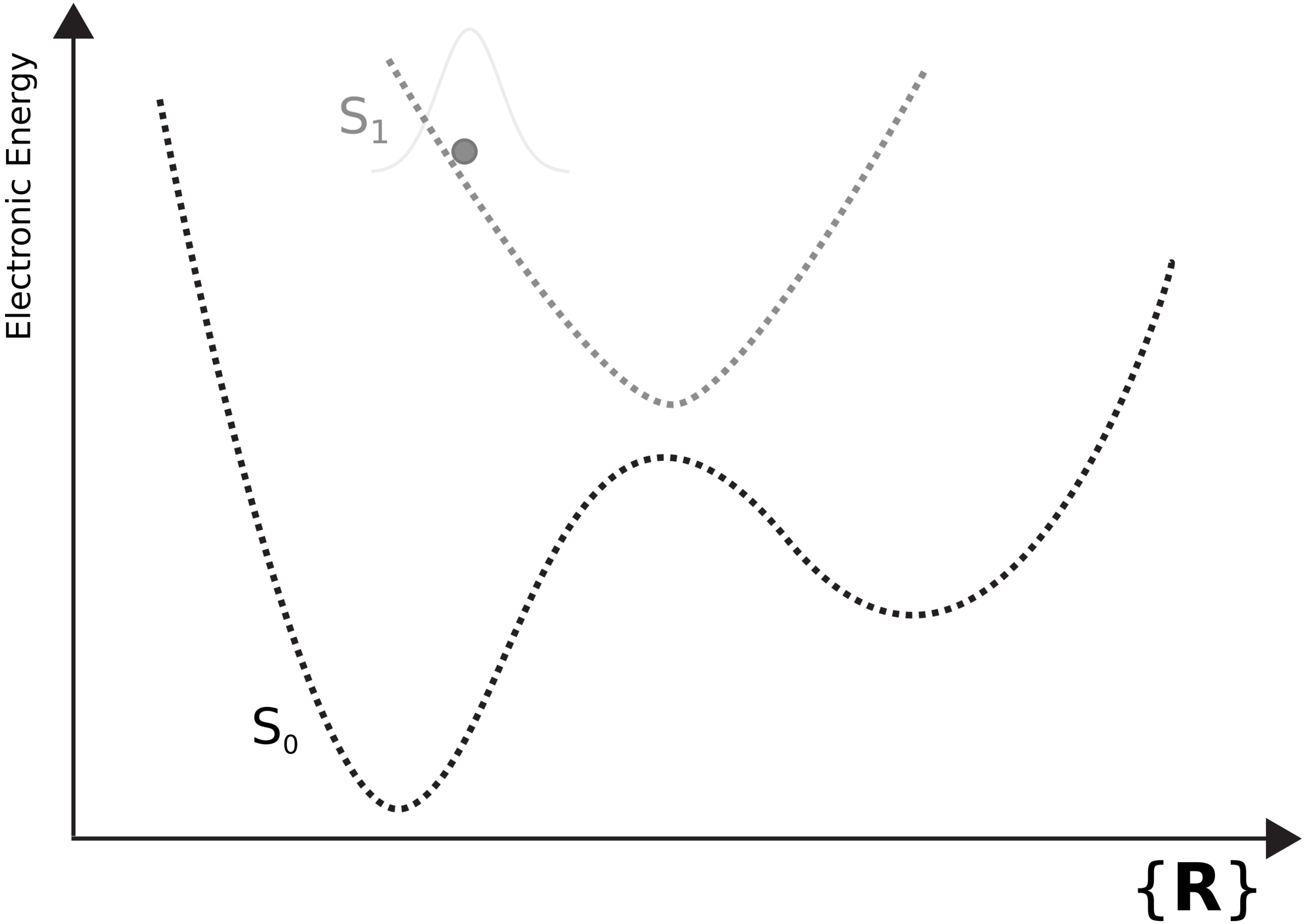
Trajectory Surface Hopping dynamics

$$i\hbar\dot{c}_I^\alpha(t) = \sum_J c_J^\alpha(t)\left(E_J^{el}(\mathbf{R}^\alpha(t))\delta_{IJ} - i\hbar\dot{\mathbf{R}}^\alpha(t)\cdot\mathbf{d}_{IJ}(\mathbf{R}^\alpha(t))\right)$$

$$\mathbf{F}^\alpha = -\nabla_{\mathbf{R}}E_*^{el}(\mathbf{R})|_{\mathbf{R}=\mathbf{R}^\alpha(t)}$$

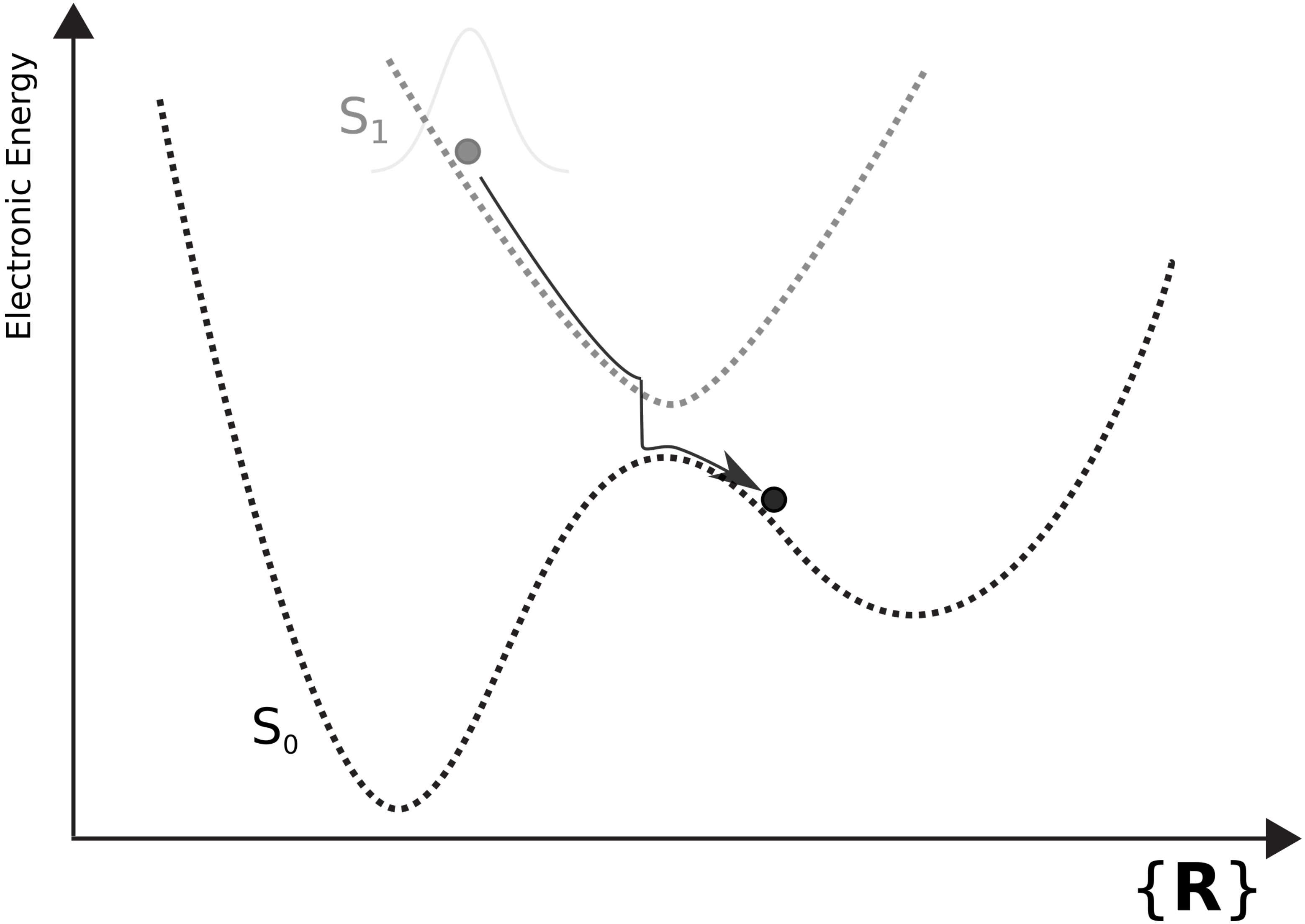
In TSH, a trajectory α evolves adiabatically on a given potential energy surface but can *hop* after each nuclear time step if nonadiabatic effects are detected.

Trajectory Surface Hopping – a pictorial introduction



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

Trajectory Surface Hopping – a pictorial introduction



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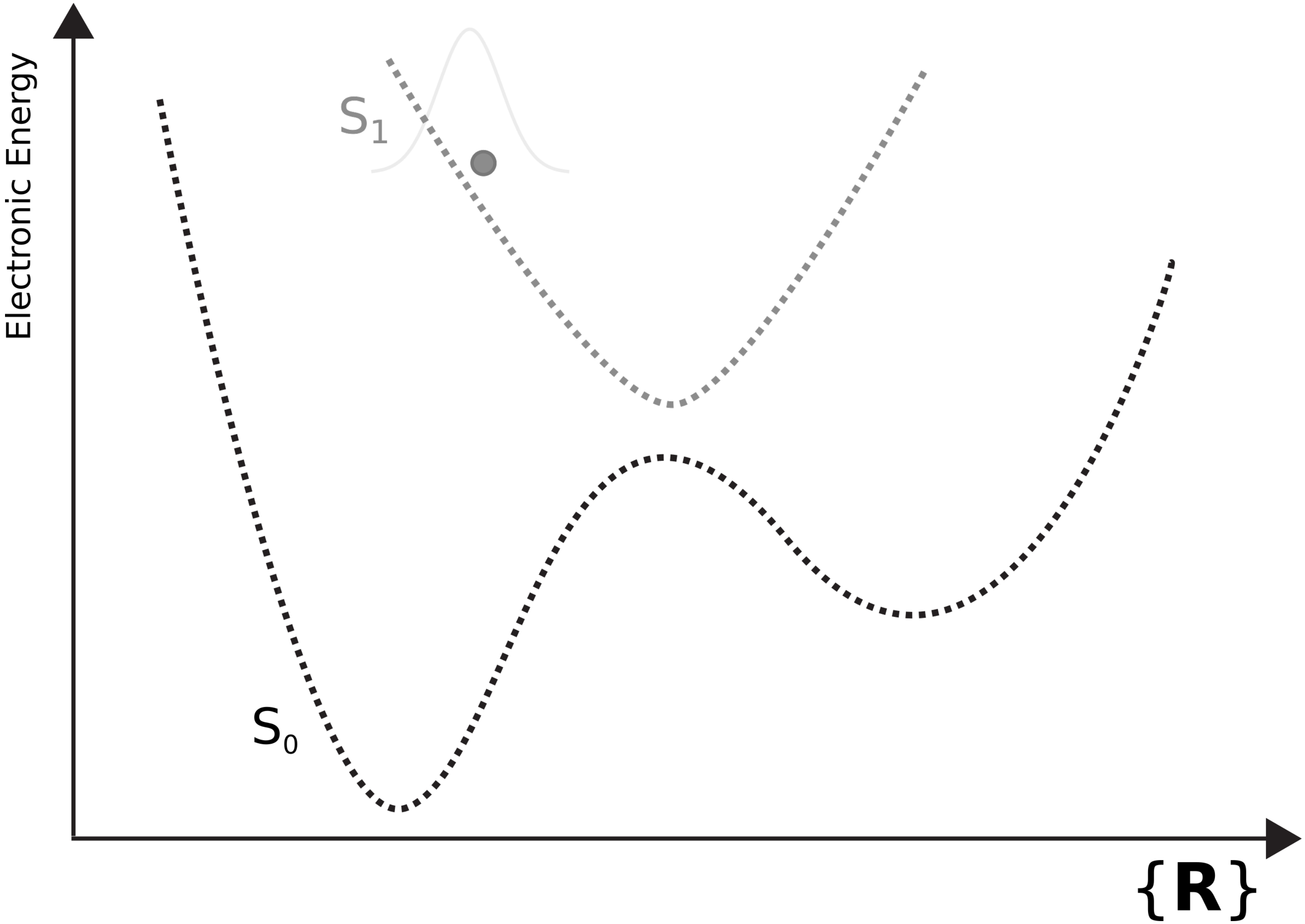
Trajectory Surface Hopping – a pictorial introduction



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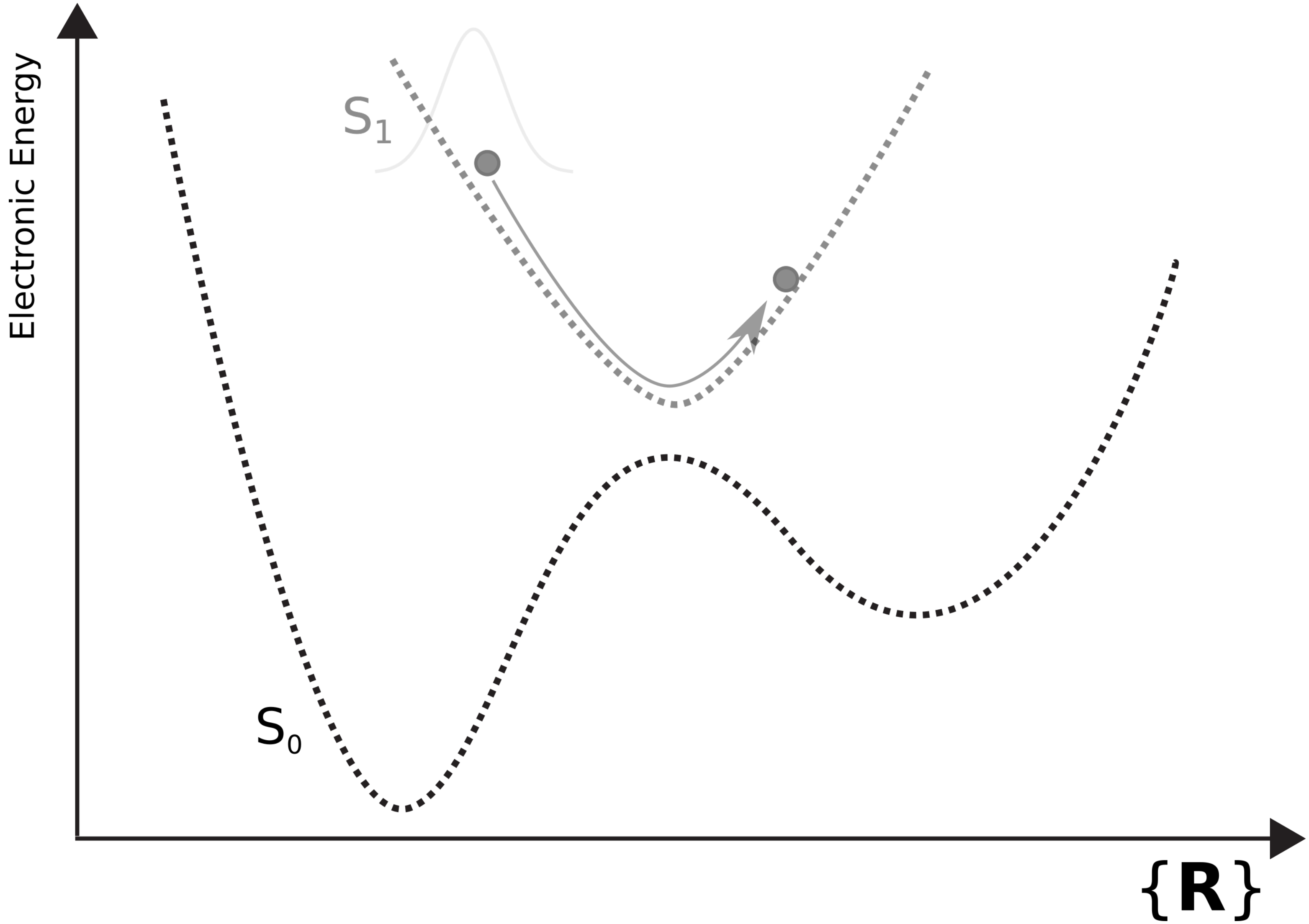
Trajectory Surface Hopping – a pictorial introduction



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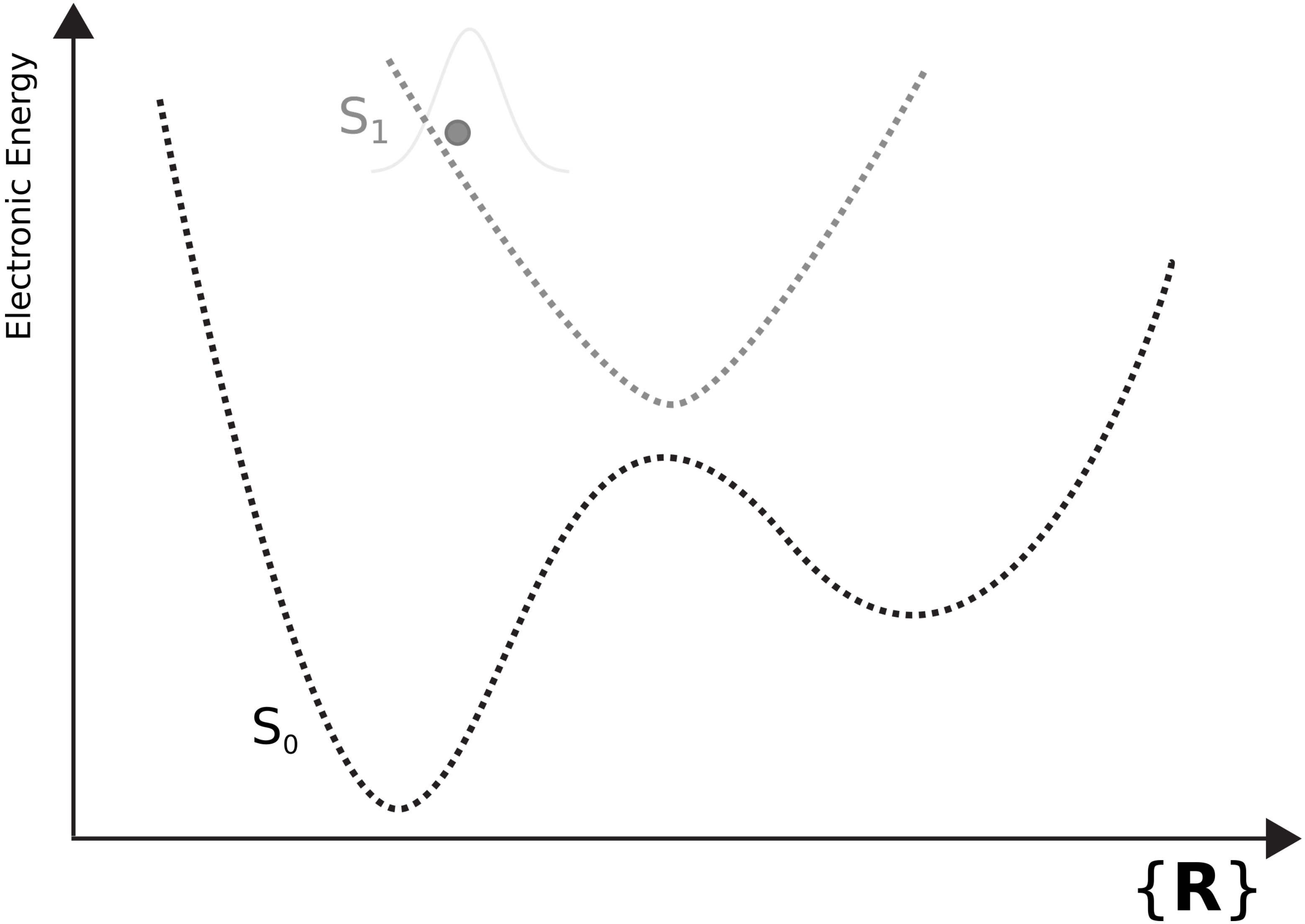
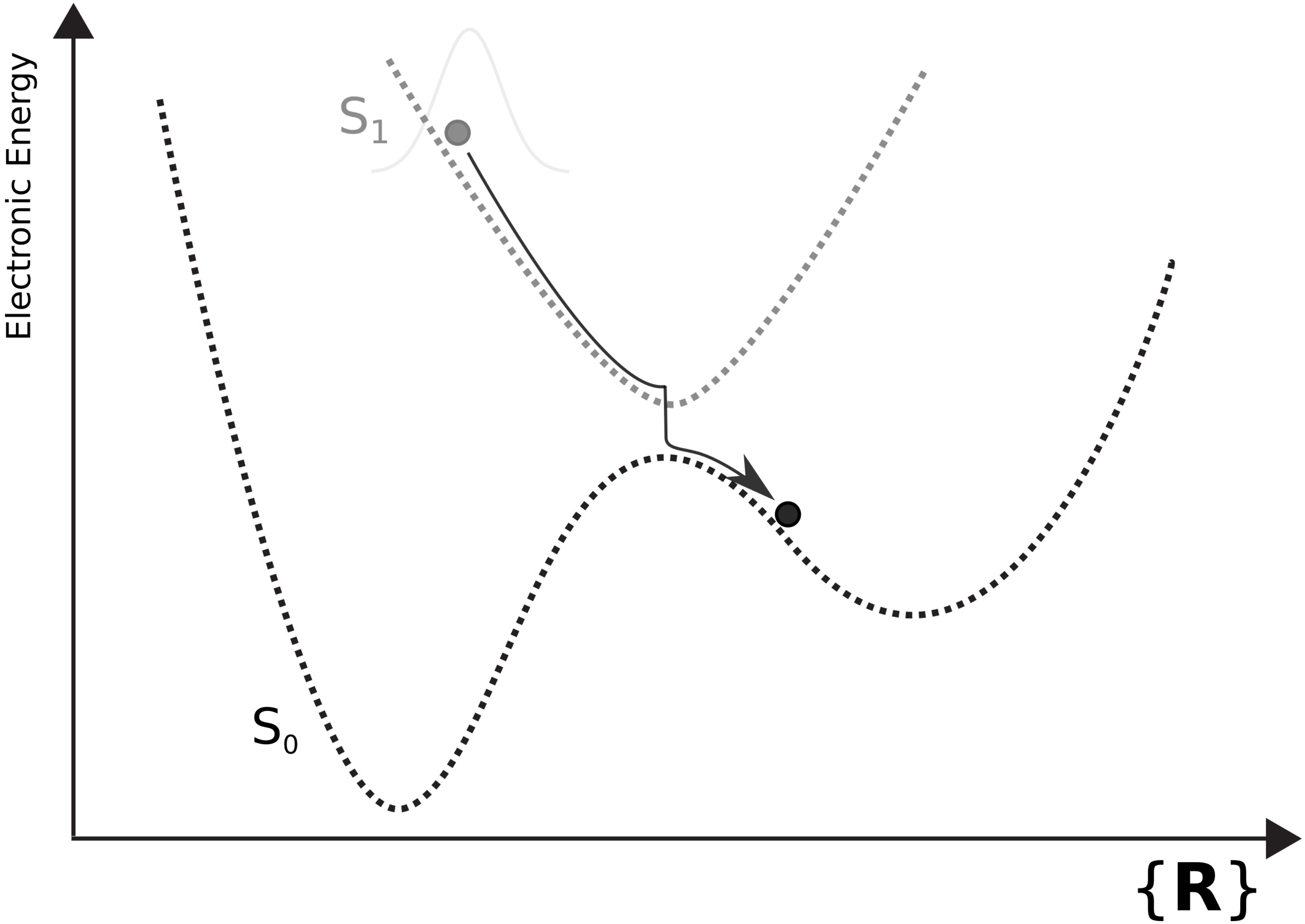
Trajectory Surface Hopping – a pictorial introduction



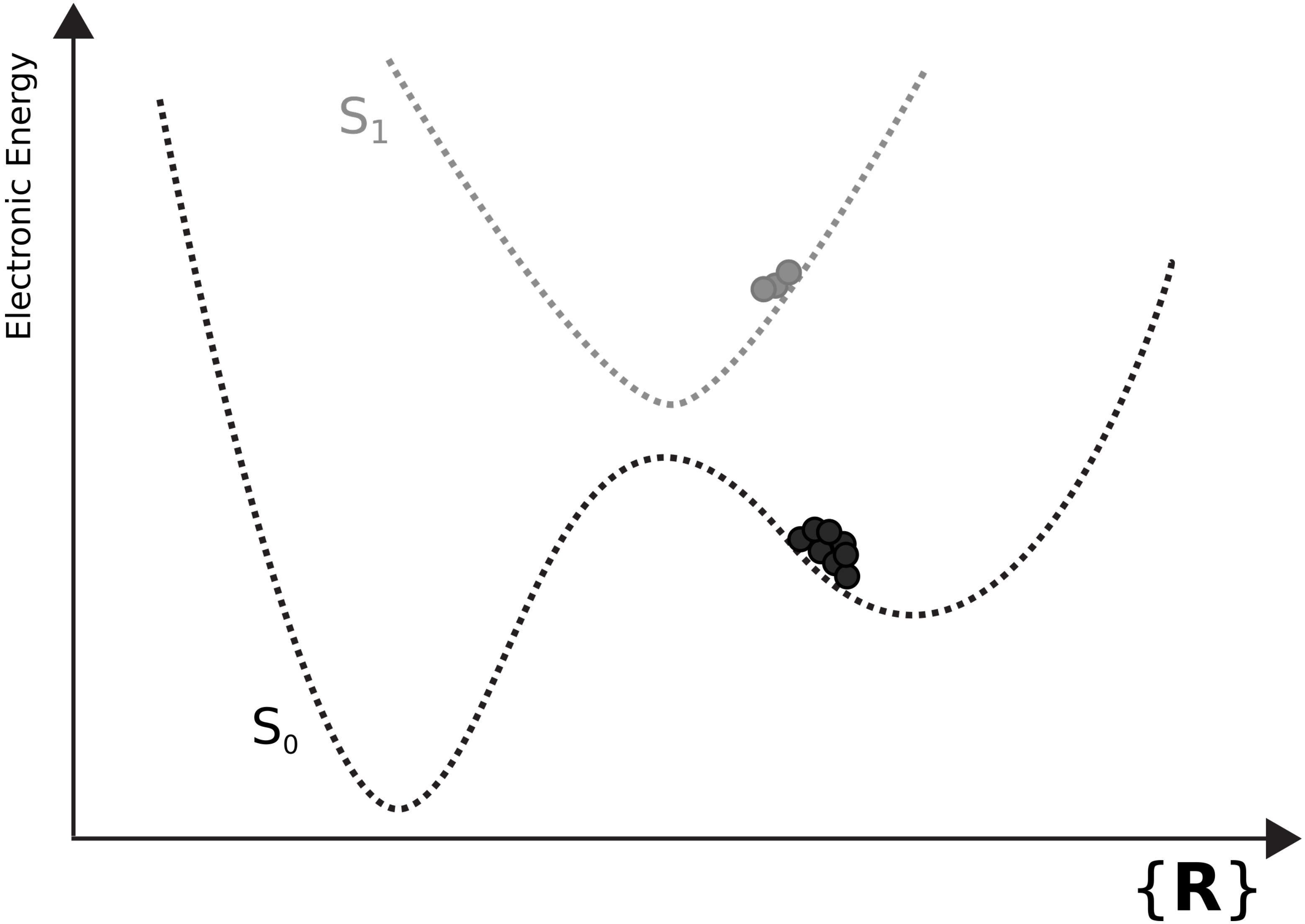
J. C. Tully, *J. Chem. Phys.*, **93**, 1061 (1990).

Trajectory Surface Hopping – a pictorial introduction



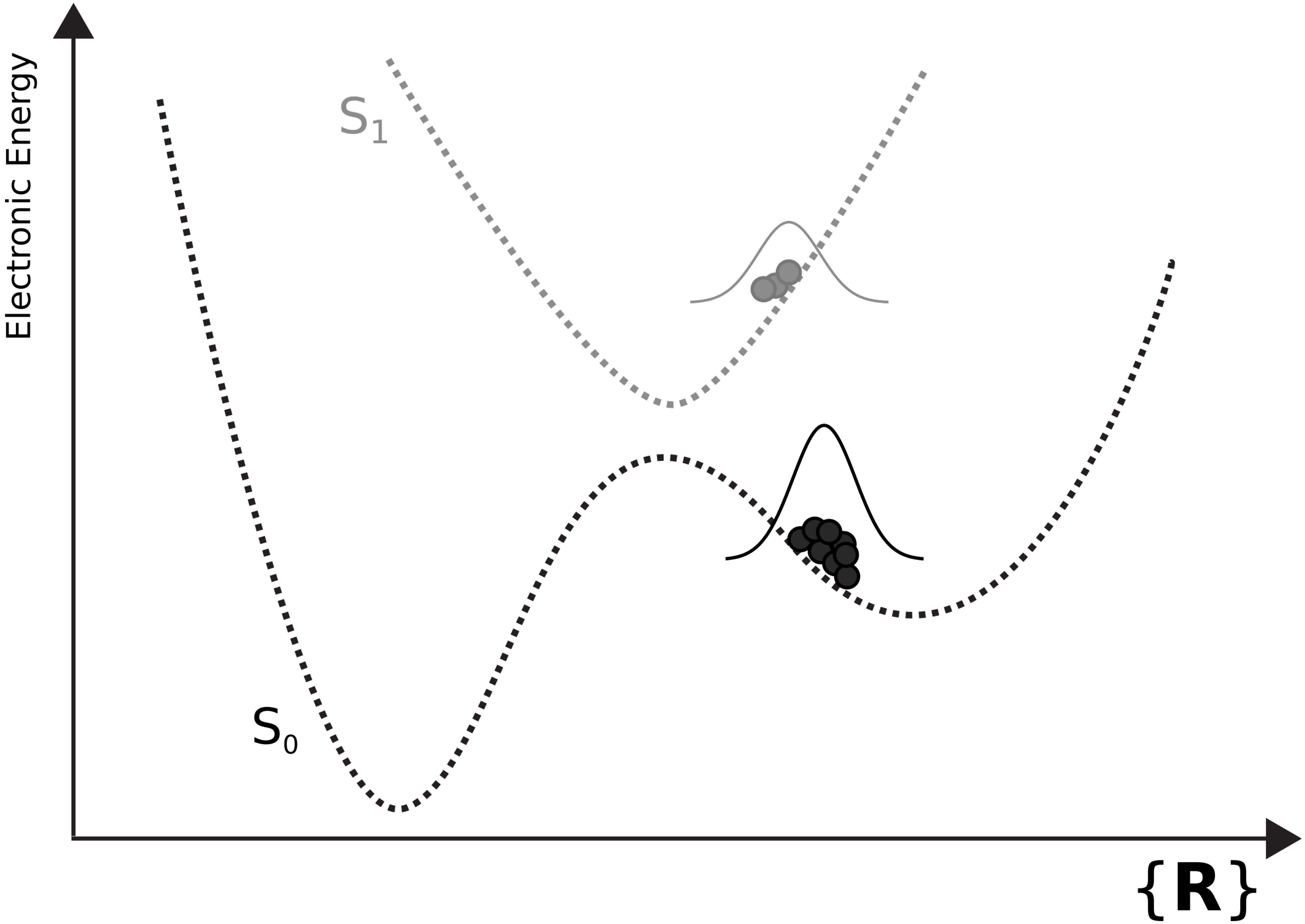
J. C. Tully, *J. Chem. Phys.*, **93**, 1061 (1990).

Trajectory Surface Hopping – a pictorial introduction



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

Trajectory Surface Hopping – a pictorial introduction



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

What is the prescription for a hop to occur?

Tully devised in 1990 the *fewest switches* algorithm, which provides a possible prescription for a trajectory to hop from one state to the other after each time step:

$$\mathcal{P}^{\alpha}_{K\to I} = \max\left[0, \frac{-2\,dt}{\left|c^{\alpha}_{K}(t)\right|^2}\,\Re\left[c^{\alpha *}_{K}(t)c^{\alpha}_{I}(t)\right]\dot{\mathbf{R}}^{\alpha}(t)\cdot\mathbf{d}_{IK}\left(\mathbf{R}^{\alpha}(t)\right)\right].$$

A hop occurs from electronic K to another electronic state I if

$$\sum_{J}^{I-1}\mathcal{P}^{\alpha}_{K\to J} \leq \zeta \leq \sum_{J}^{I}\mathcal{P}^{\alpha}_{K\to J}\,,$$

where ζ is a random number generated uniformly in the interval $[0:1]$. If a hop occurs, the nuclear forces will now be obtained from $E^{el}_{*}(\mathbf{R}) = E^{el}_{I}(\mathbf{R})$.

An important point of the TSH algorithm is that it requires a large number of *independent* trajectories, or independent TSH runs, to converge the hopping algorithm, as well as the sampling of initial conditions.

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

Trajectory Surface Hopping dynamics – central equations

Trajectory Surface Hopping dynamics

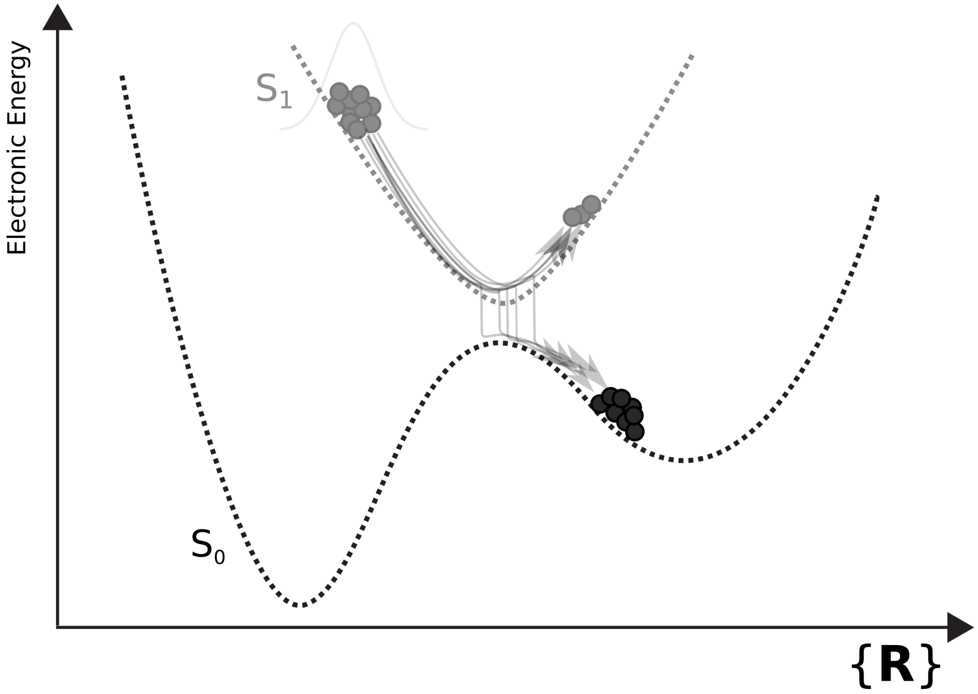
$$i\hbar\dot{c}_I^\alpha(t) = \sum_J c_J^\alpha(t)\left(E_J^{el}(\mathbf{R}^\alpha(t))\delta_{IJ} - i\hbar\dot{\mathbf{R}}^\alpha(t)\cdot\mathbf{d}_{IJ}(\mathbf{R}^\alpha(t))\right)$$

$$\mathbf{F}^\alpha = -\nabla_{\mathbf{R}}E_*^{el}(\mathbf{R})|_{\mathbf{R}=\mathbf{R}^\alpha(t)}$$

$$\sum_J^{I-1}\mathcal{P}_{K\to J}^\alpha \leq \zeta \leq \sum_J^{I}\mathcal{P}_{K\to J}^\alpha\,,$$

Multiple independent trajectories α have to be propagated.

Trajectory Surface Hopping dynamics – some warnings



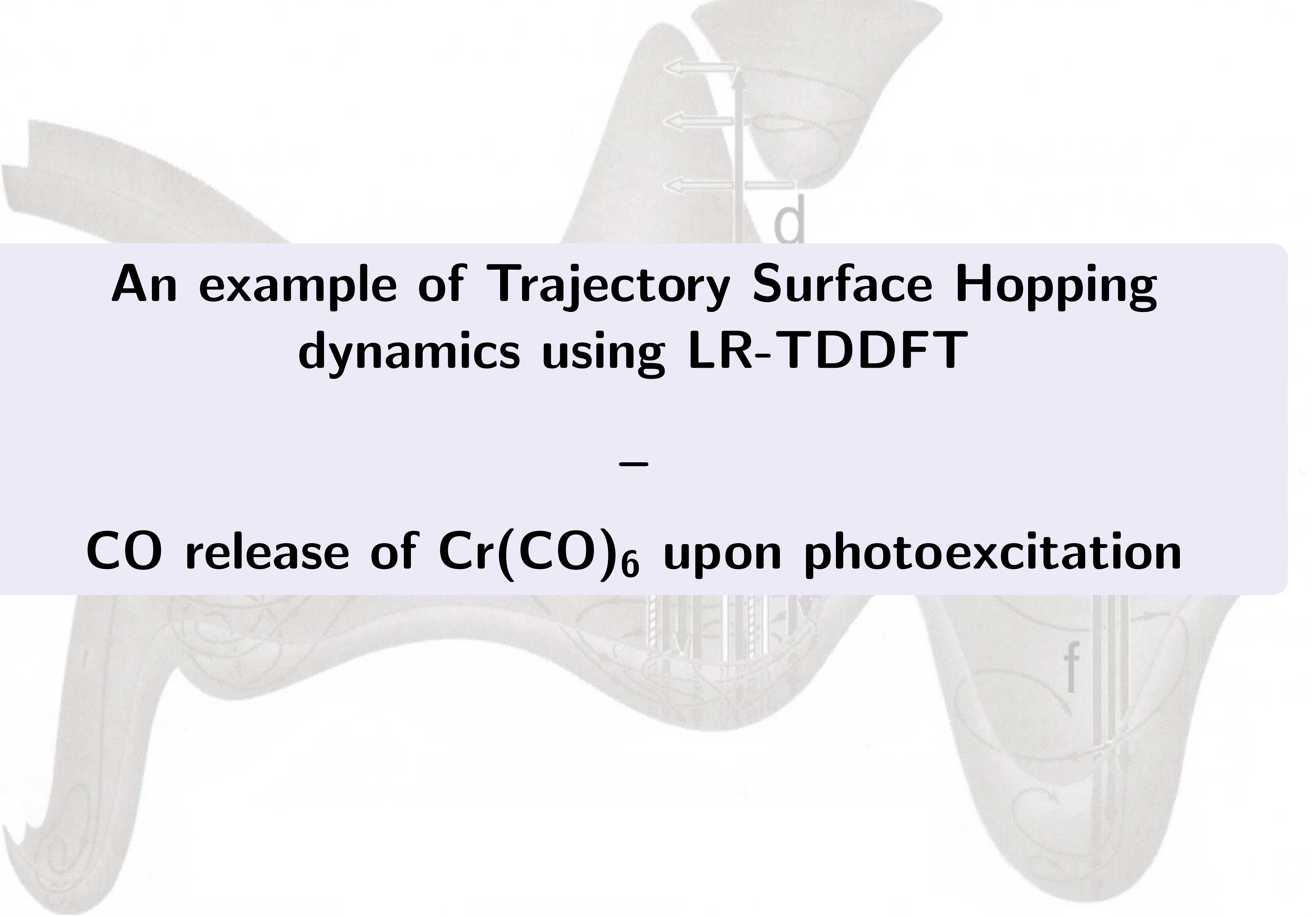
- Rescaling of the nuclei velocities after a hop is still a matter of debate.
- Depending on the system studied, a lot of trajectories could be needed to obtain a complete statistical description of the non-radiative relaxation.
- TSH cannot adequately describe the decoherence of nuclear wavepackets...

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

An example of Trajectory Surface Hopping dynamics using LR-TDDFT

–

CO release of $Cr(CO)_6$ upon photoexcitation



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

$Cr(CO)_6$ - CO photodissociation

Experimentally, it is well-known that light-irradiation of carbonyl organometallic complexes leads to dissociation of a CO ligand and subsequent replacement by a solvent molecule.

$$\mathrm{Mo(CO)_6} + \mathrm{THF} \xrightarrow{\text{light}} \mathrm{Mo(CO)_5THF} + \mathrm{CO}$$

This mechanism is used in the lab to produce interesting initial reactants for more complex reactions.

$Cr(CO)_6$ - CO photodissociation

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This mechanism is used in the lab to produce interesting initial reactants for more complex reactions.

Study of $Cr(CO)_6$ photodissociation using trajectory surface hopping to understand the electronic excited states involved.

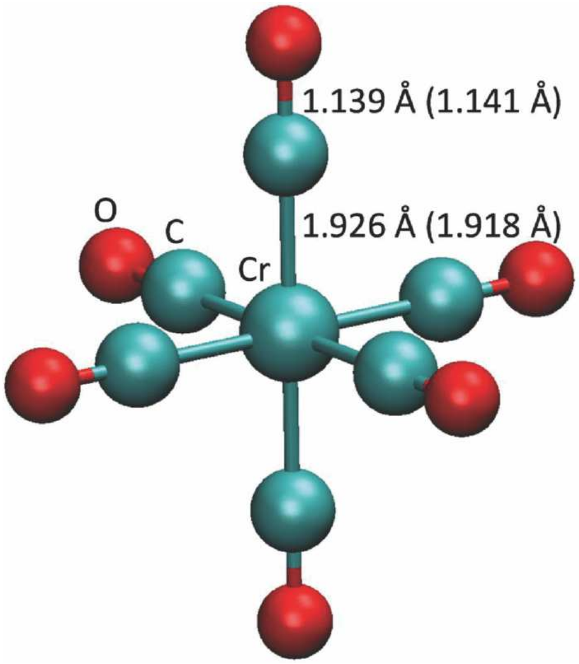
JCP, **134**, 164305 (2011)

$Cr(CO)_6$ - CO photodissociation

Study of $Cr(CO)_6$ photodissociation using trajectory surface hopping

Computational details

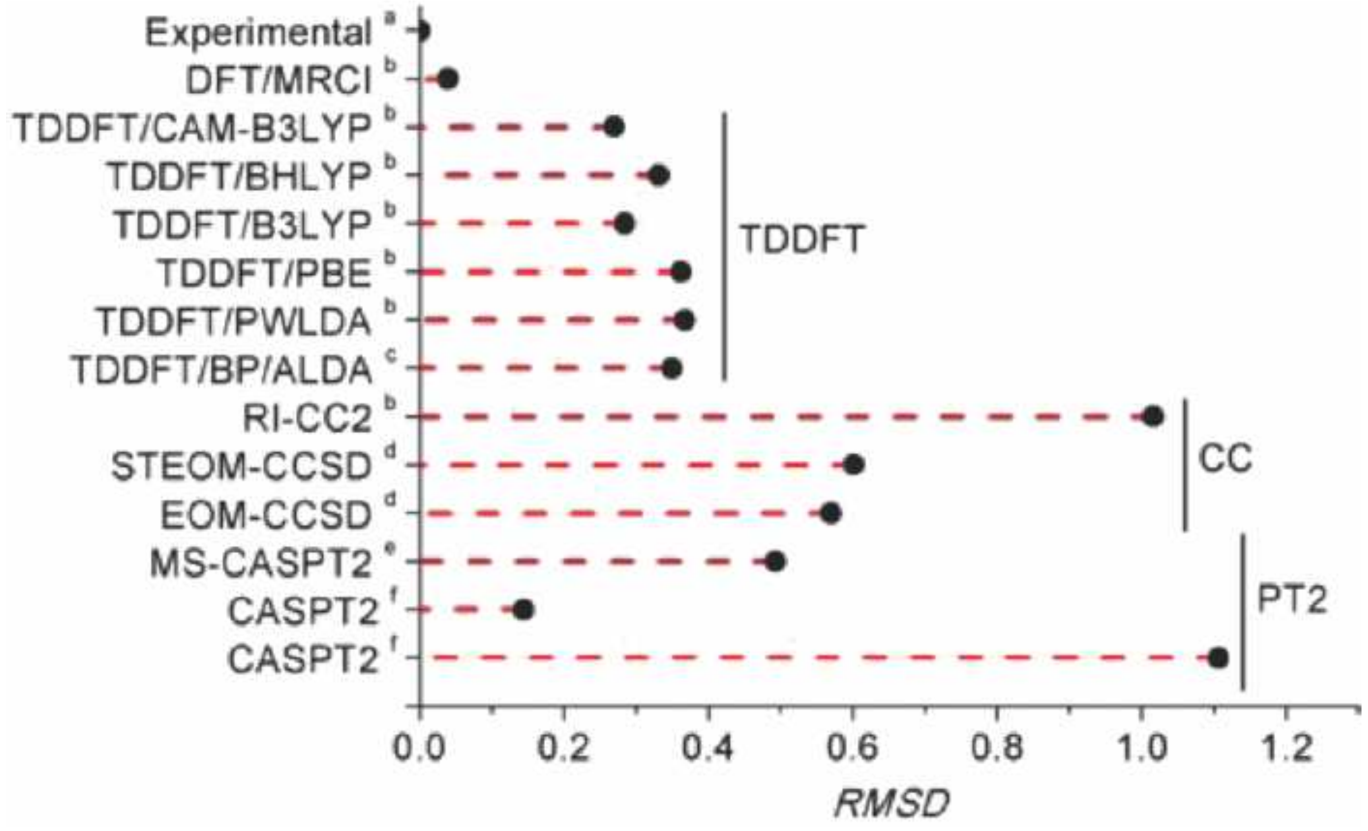
- Gas phase system
- LR-TDDFT/B3LYP for 5 lowest excited state
- TSH dynamics
- $\sim$ 30 trajectories
- $\sim$ 200 fs per trajectory



JCP, **134**, 164305 (2011)

$Cr(CO)_6$ - Comparison between methods

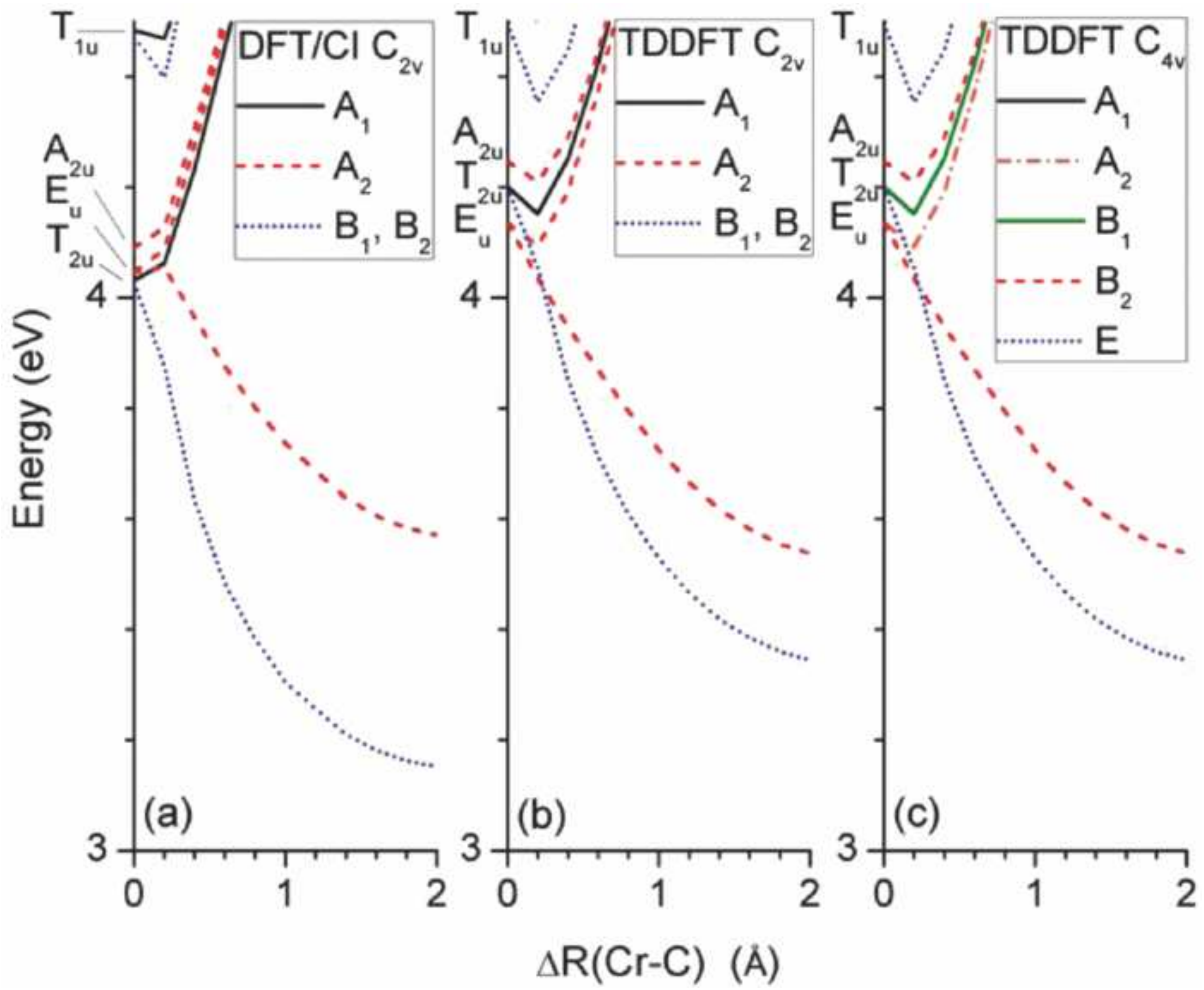
The root mean square deviation between experimental and theoretical excitation energies and oscillator stengths for two selected states.



CASPT2: importance of the active space.

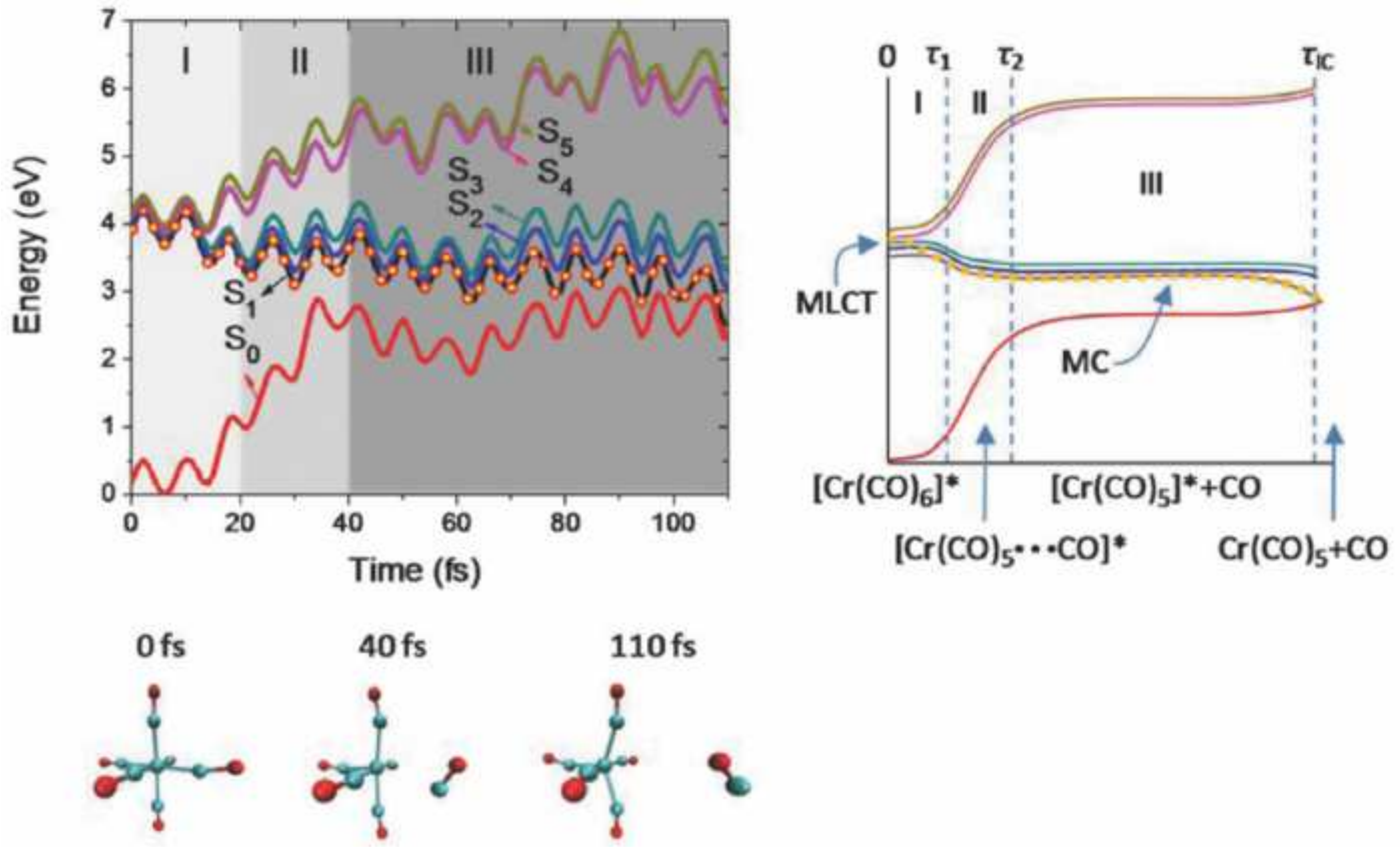
$Cr(CO)_6$ - Potential energy surfaces

Validation of the potential energy surfaces



$Cr(CO)_6$ - Trajectory surface hopping

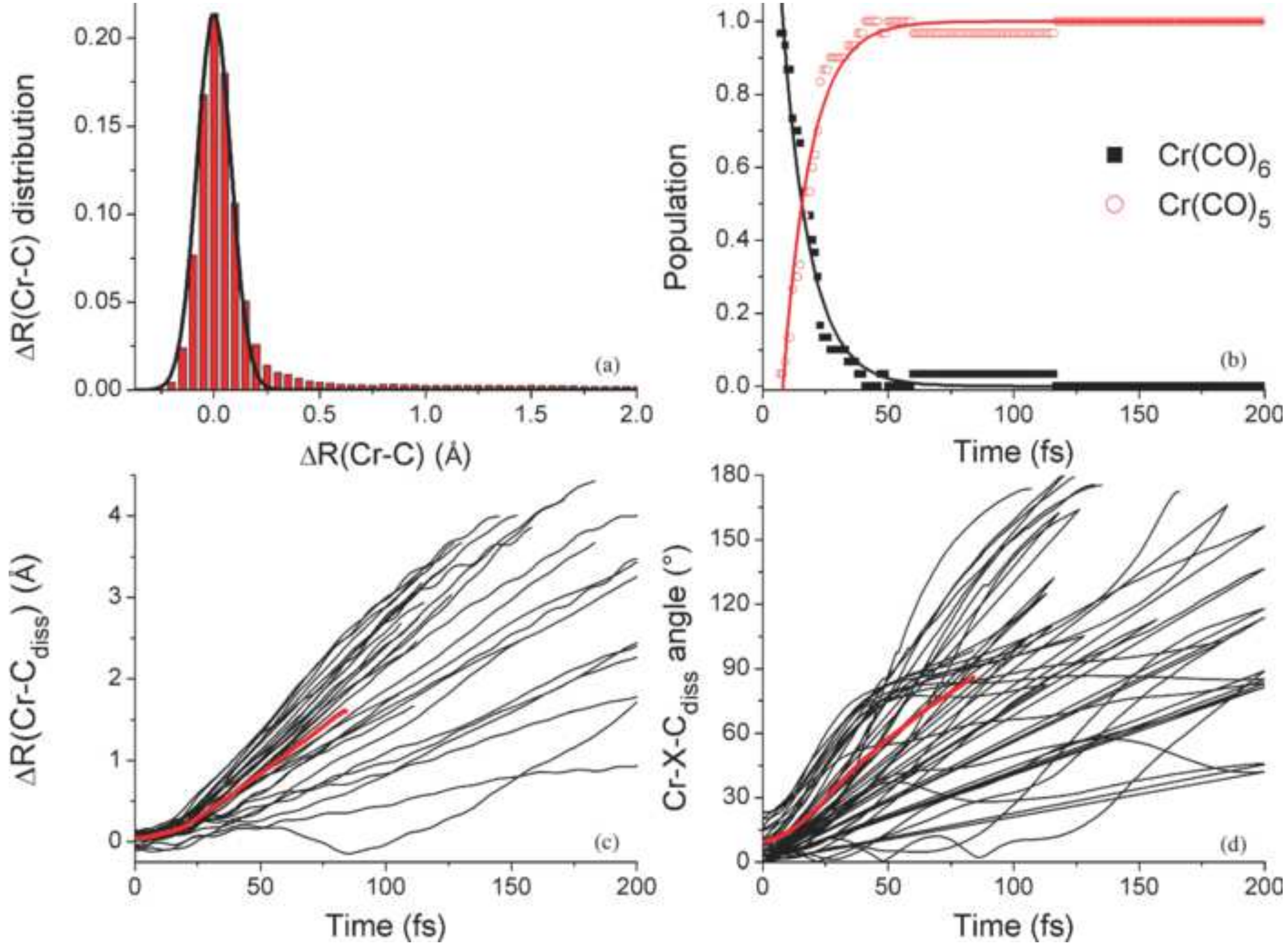
General trends of the nonadiabatic trajectories



Three steps: Hops within the large density of states - bands splitting - dynamics of the $Cr(CO)_5$ fragment and relaxation towards S_0.

$Cr(CO)_6$ - Trajectory surface hopping

Different observables along the dynamics



$Cr(CO)_6$ - Trajectory surface hopping

Comparison with experimental findings

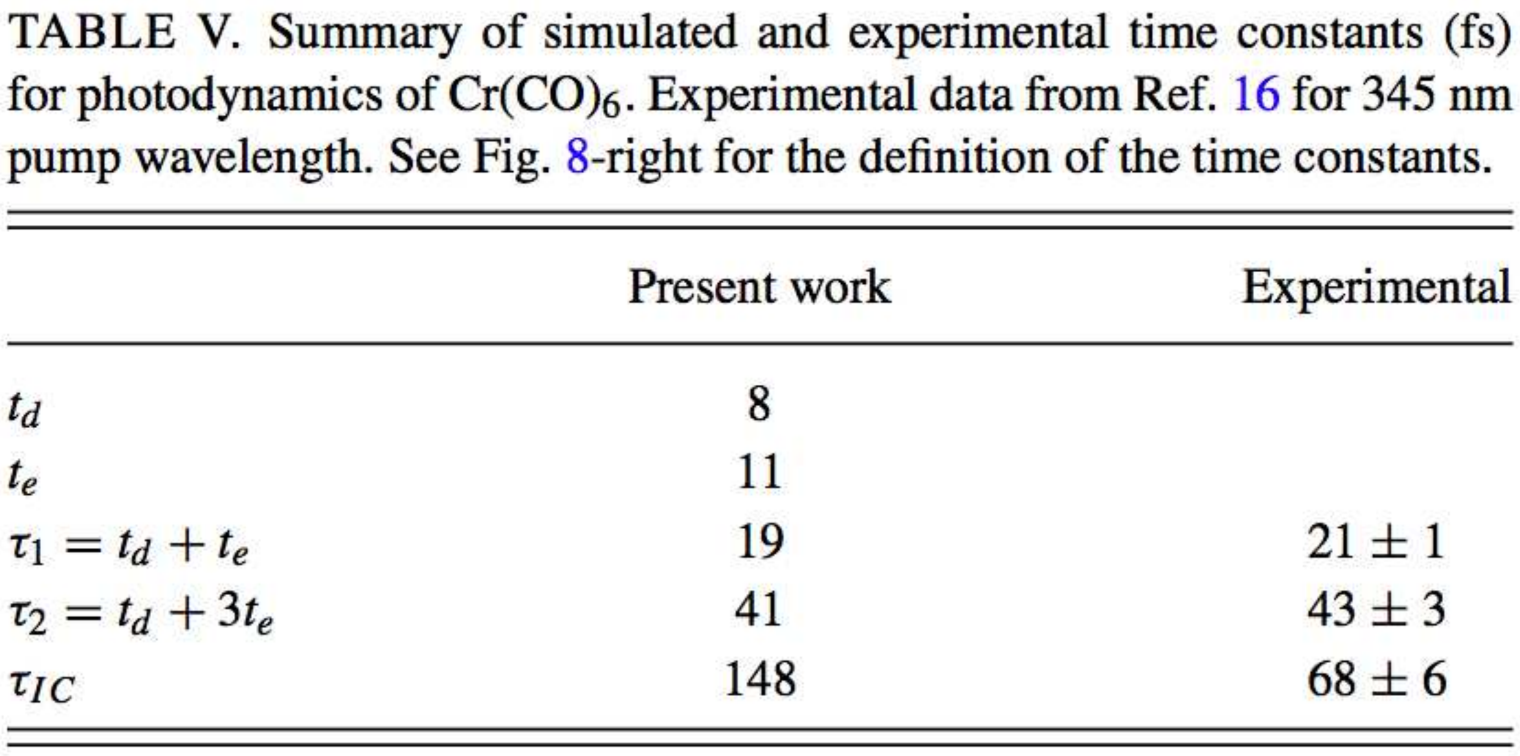


TABLE V. Summary of simulated and experimental time constants (fs) for photodynamics of $Cr(CO)_6$. Experimental data from Ref. 16 for 345 nm pump wavelength. See Fig. 8-right for the definition of the time constants.

	Present work	Experimental
t_d	8	
t_e	11	
$\tau_1 = t_d + t_e$	19	21 ± 1
$\tau_2 = t_d + 3t_e$	41	43 ± 3
τ_{IC}	148	68 ± 6

t_d is the latency time before any dissociation takes place and t_e is the exponential time constant

τ_1: Time when the dissociation starts. τ_2: Time when $Cr(CO)_5$ population dominates ($3t_e$ corresponds to 95% of the exponential decay distribution). τ_{IC}: Excited state lifetime.