Nonadiabatic (Molecular) Dynamics

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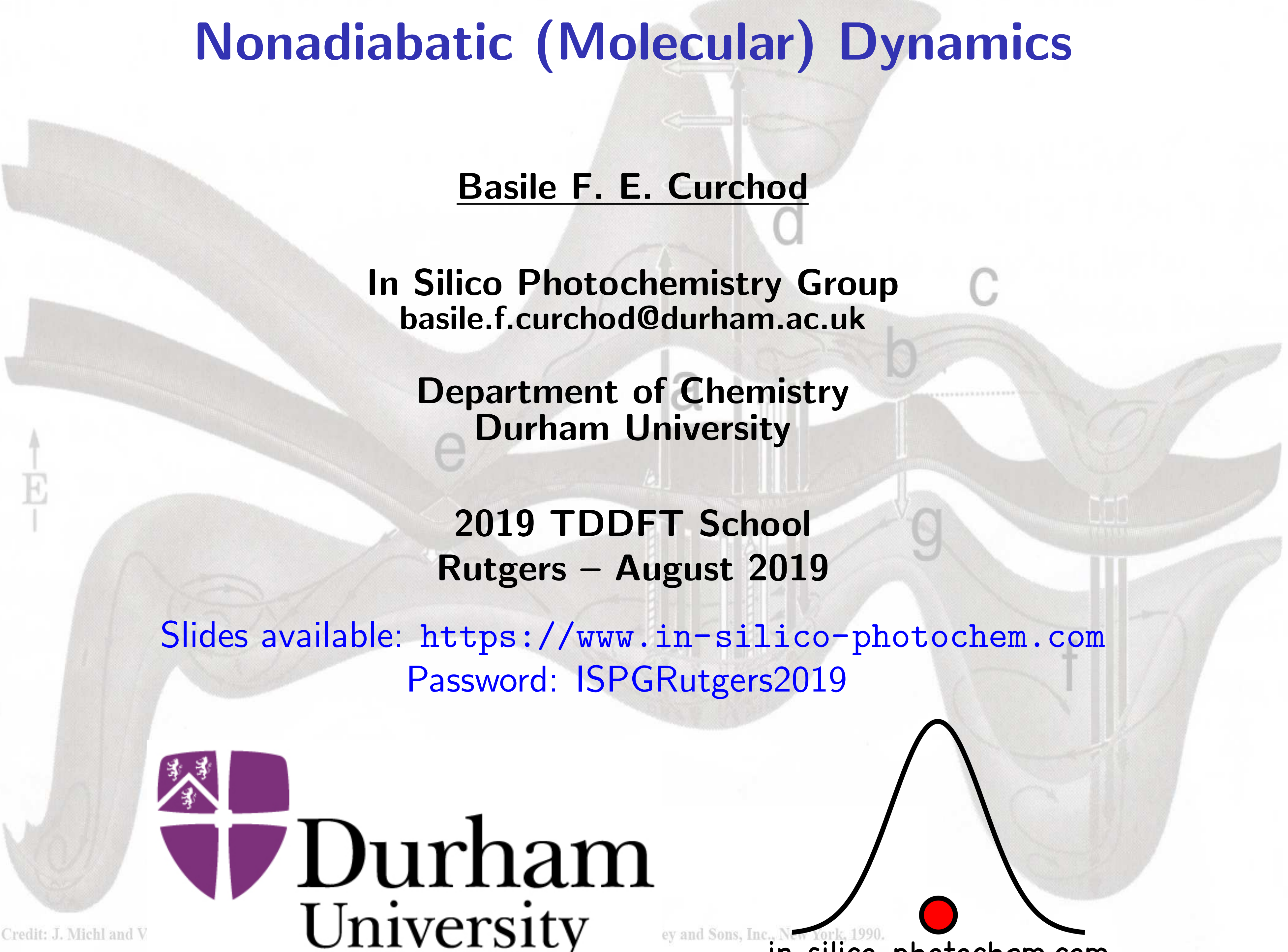
Slides available: `https://www.in-silico-photochem.com`
Password: ISPGRutgers2019



Credit: J. Michl and V ey and Sons, Inc., New York, 1990.

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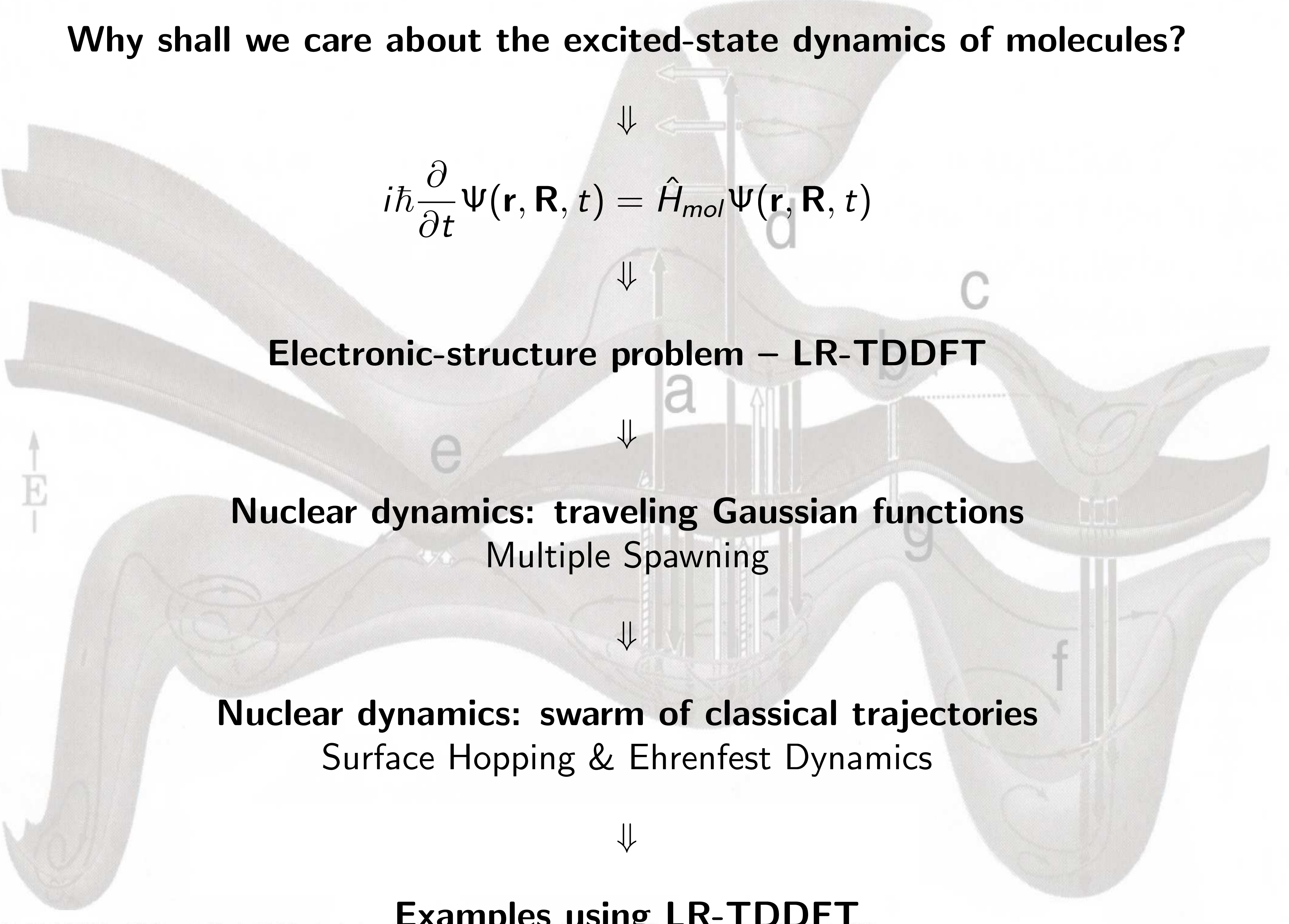
Why shall we care about the excited-state dynamics of molecules?



$$\Downarrow$$

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

$$\Downarrow$$

Electronic-structure problem – LR-TDDFT

$$\Downarrow$$

Nuclear dynamics: traveling Gaussian functions

Multiple Spawning

$$\Downarrow$$

Nuclear dynamics: swarm of classical trajectories

Surface Hopping & Ehrenfest Dynamics

$$\Downarrow$$

Examples using LR-TDDFT

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

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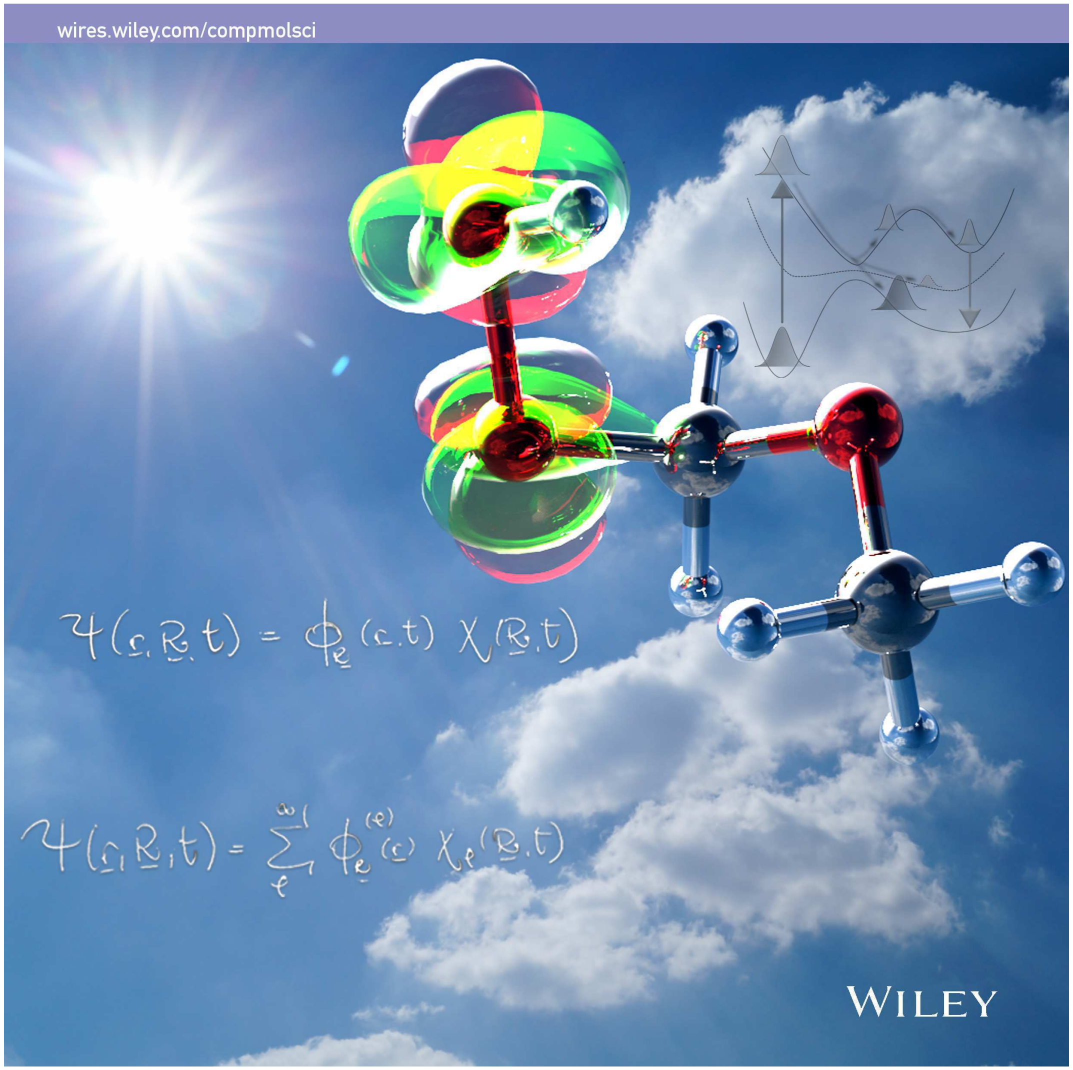
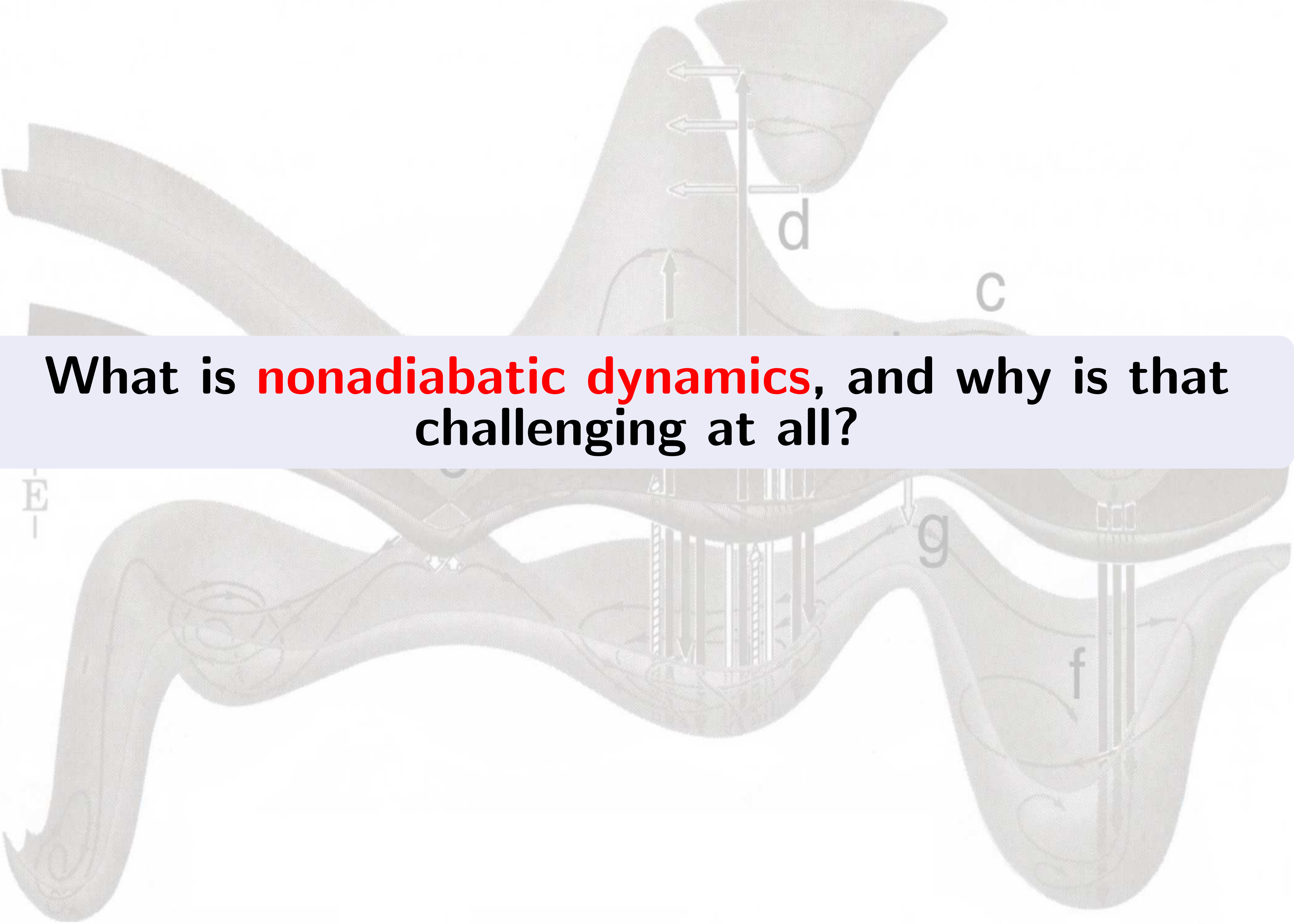
WIREs
COMPUTATIONAL MOLECULAR SCIENCE



For an Overview on Nonadiabatic Molecular Dynamics:

Federica Agostini and Basile F. E. Curchod, *WIREs Comp. Mol. Sci.*, e1417 (2019).

What is nonadiabatic dynamics, and why is that challenging at all?

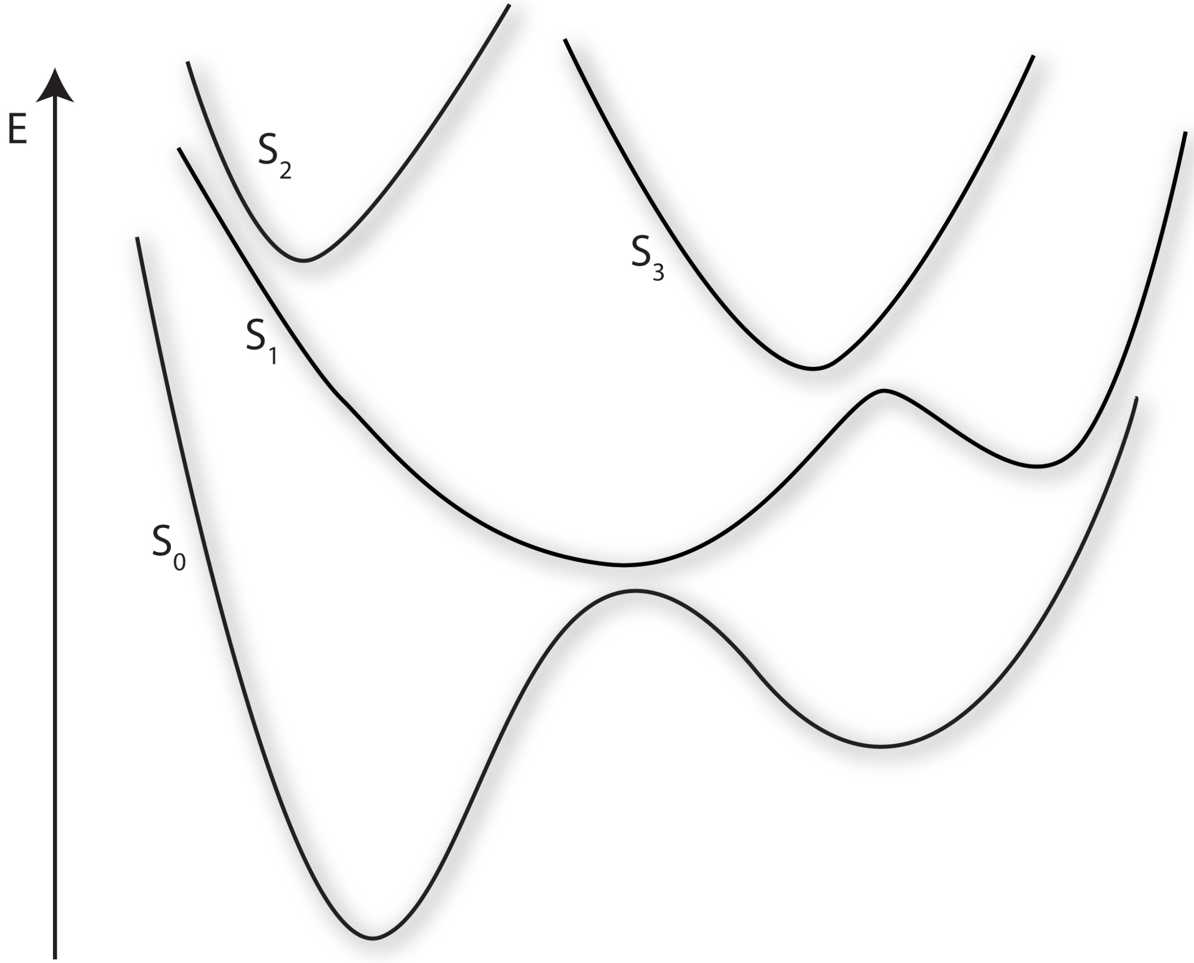


Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

Beyond Born-Oppenheimer

Born-Oppenheimer approximation (1927)

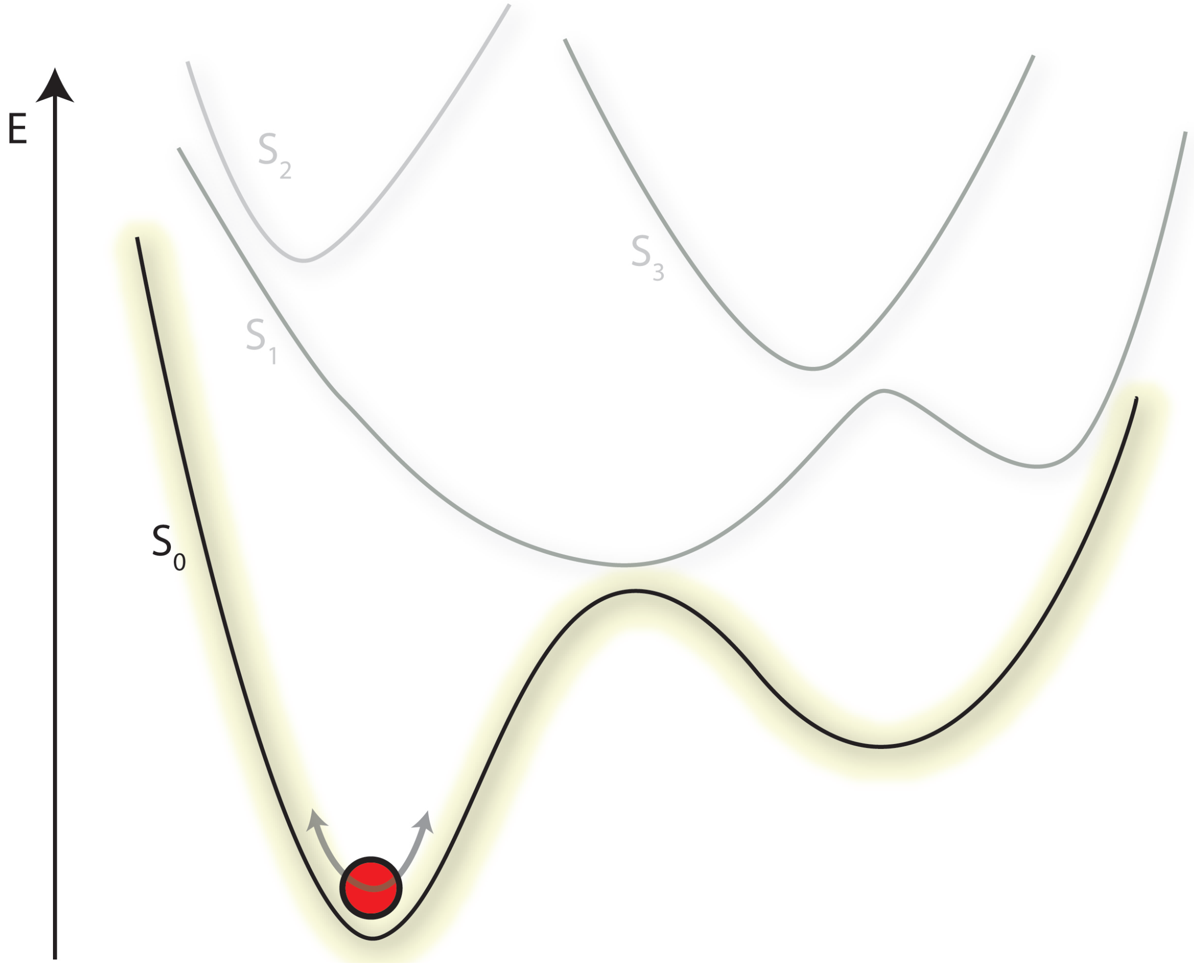
("Perspective on *Zur Quantentheorie der Molekeln*", Theor. Chem. Acc., 103, 173 (2000))



Beyond Born-Oppenheimer

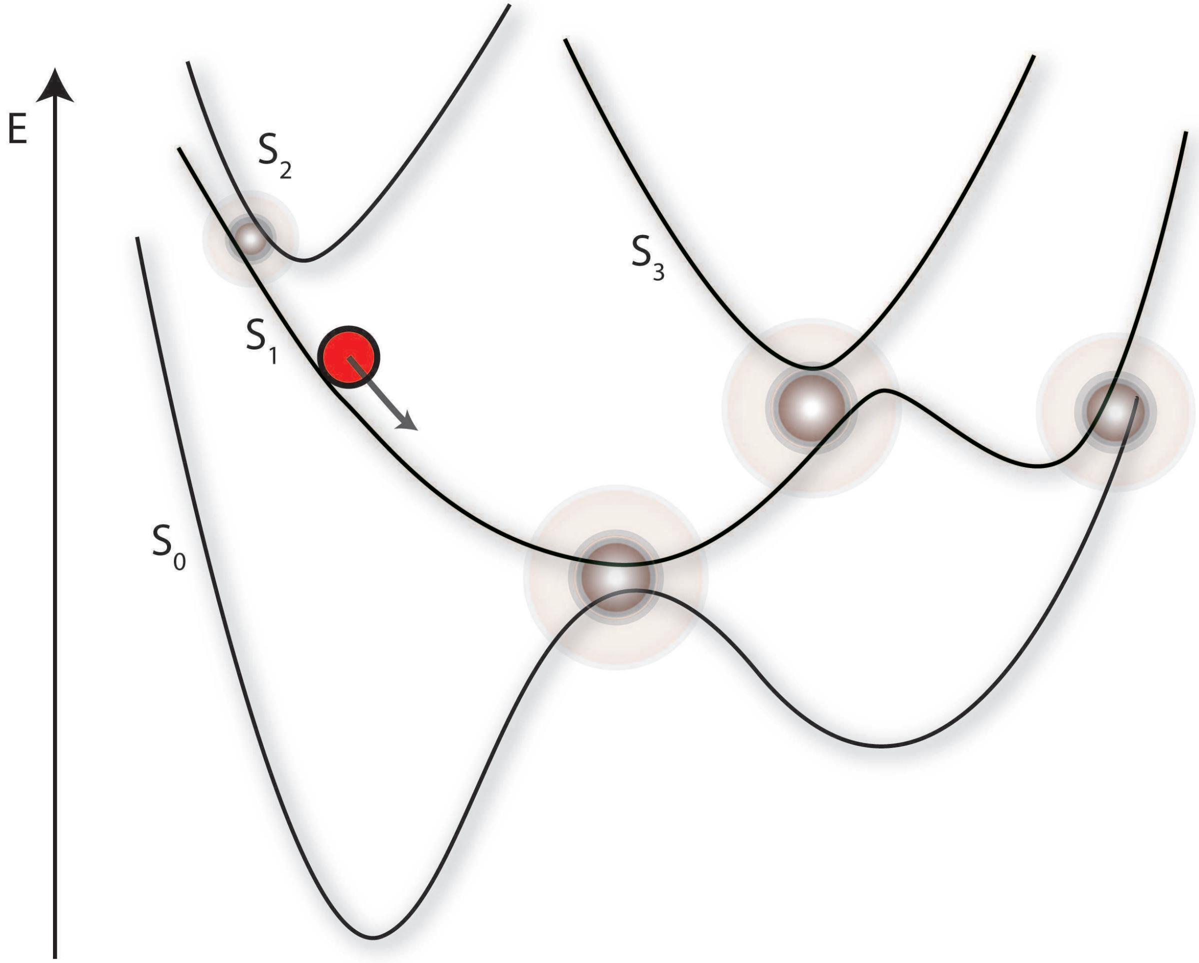
Born-Oppenheimer approximation:

neglects coupling between electronic states and nuclear motion



Beyond Born-Oppenheimer

Dynamics in electronically excited states:
nonadiabatic effects!



Importance of Electronic Excited States

Long-time exposure photography of fireflies...

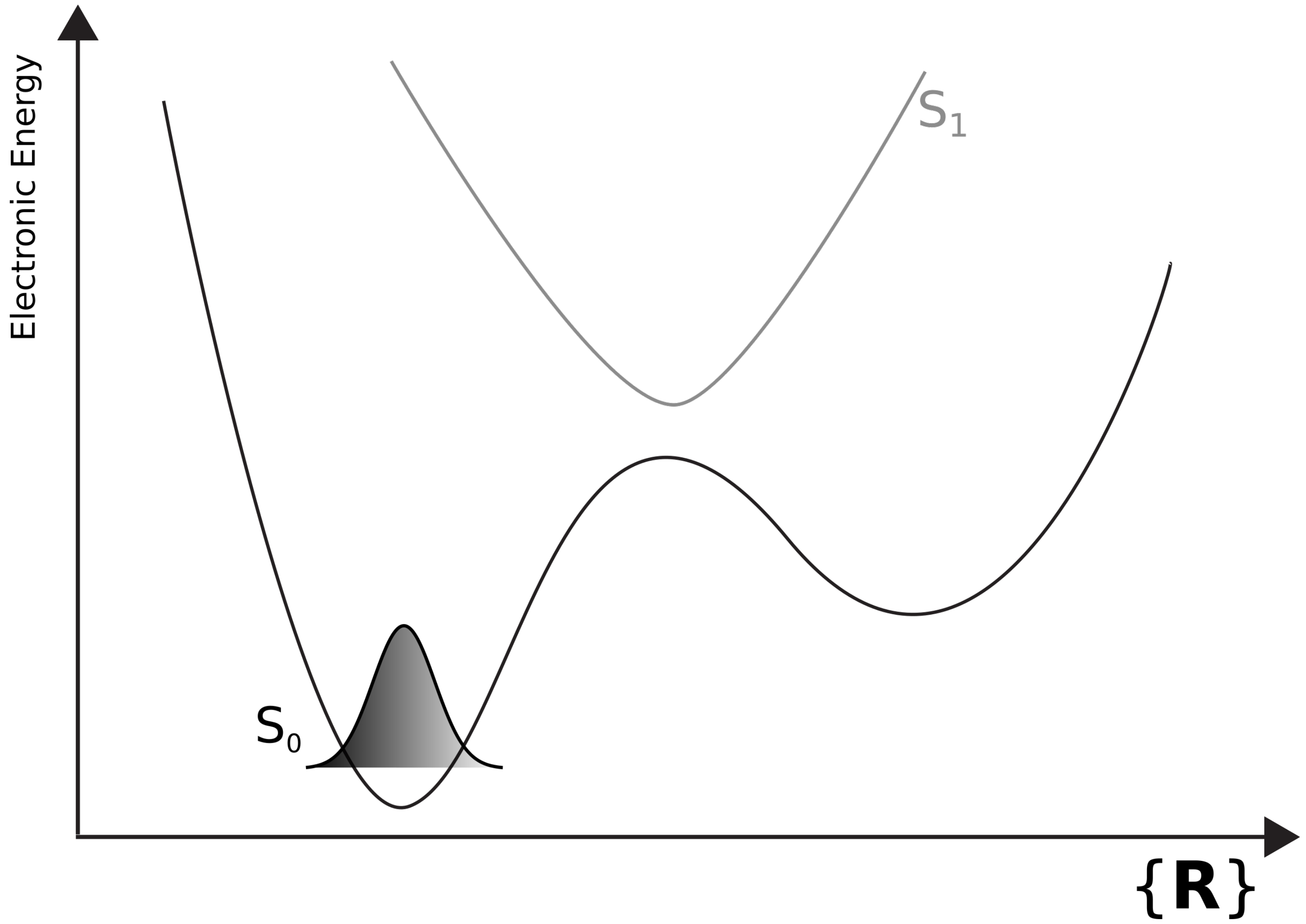
Picture by Tsuneaki Hiramatsu

Importance of Electronic Excited States

Now applying the Born-Oppenheimer approximation!

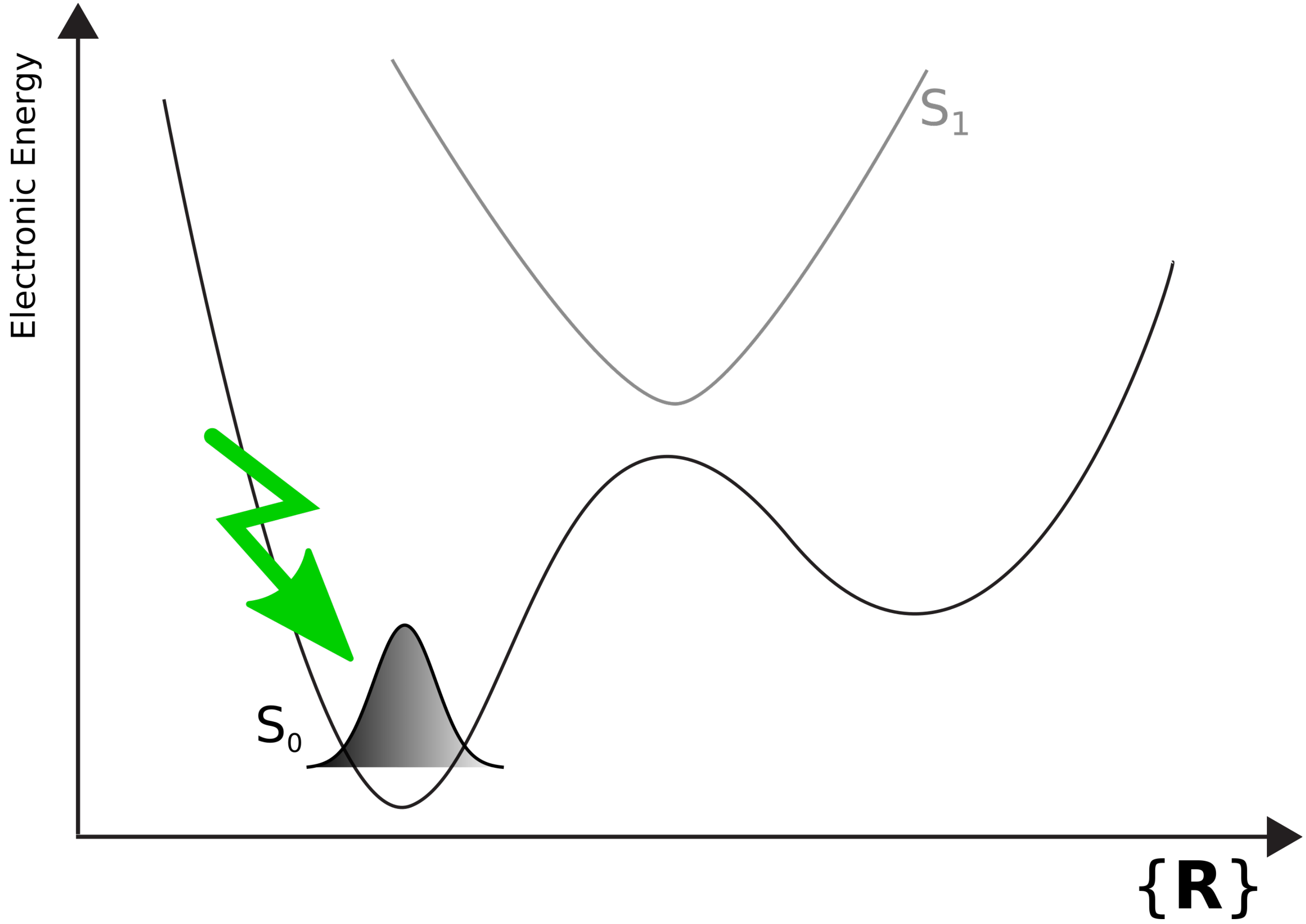
Dream: in silico photochemical experiment

Molecule initially in its electronic ground state



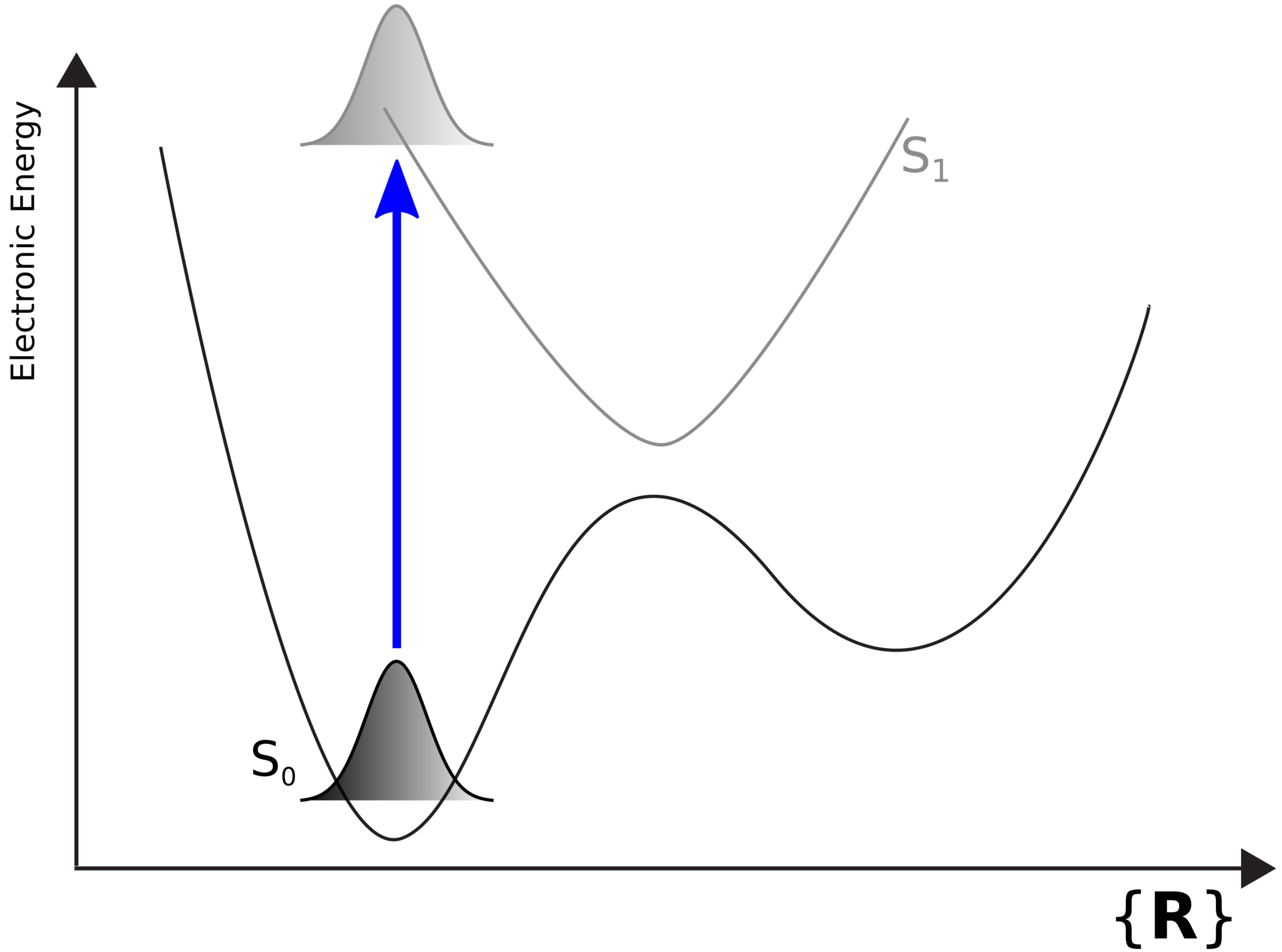
Dream: in silico photochemical experiment

Molecule absorbs a photon...



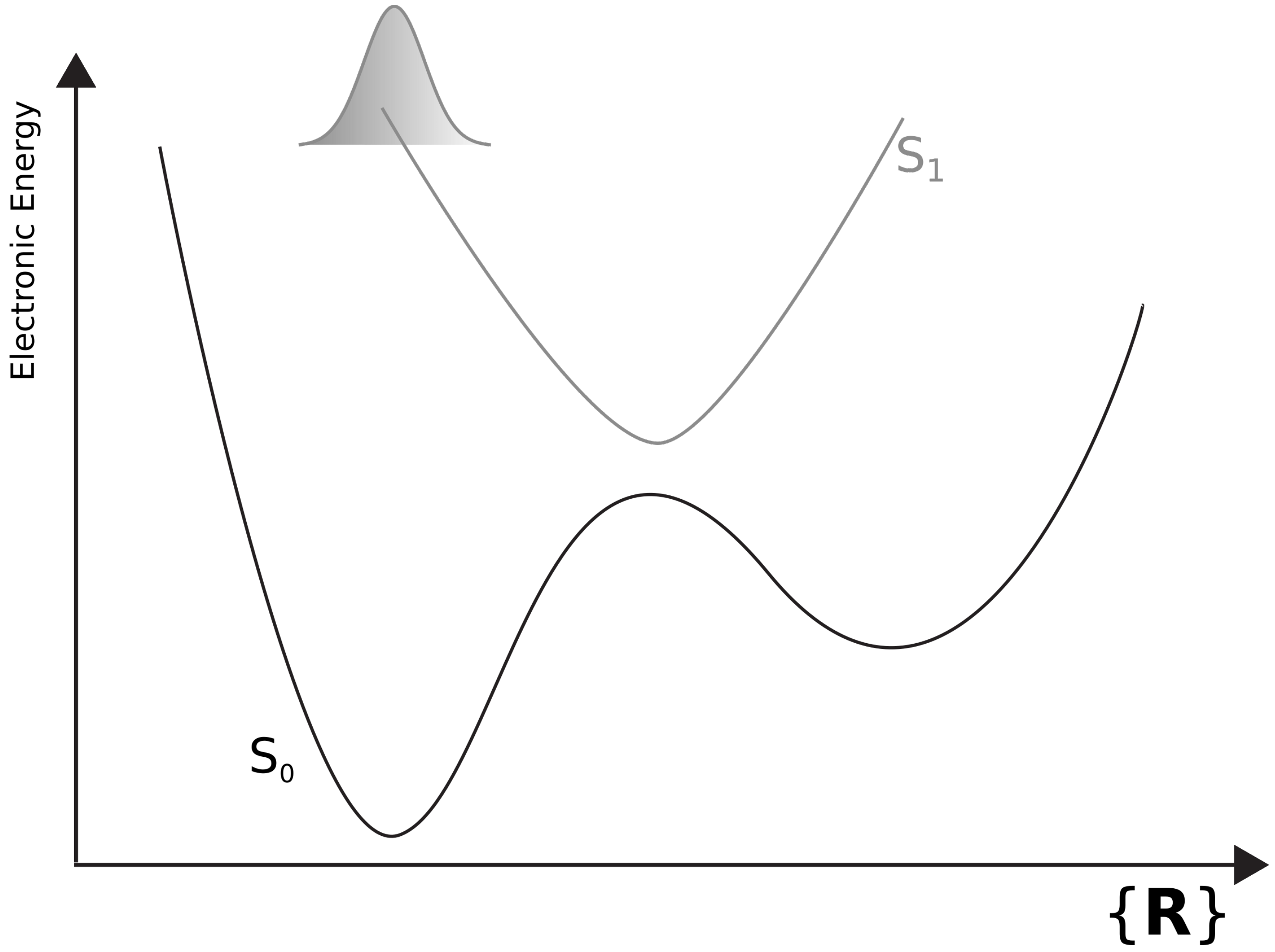
Dream: in silico photochemical experiment

... that leads to an electronic transition (here to S_1).



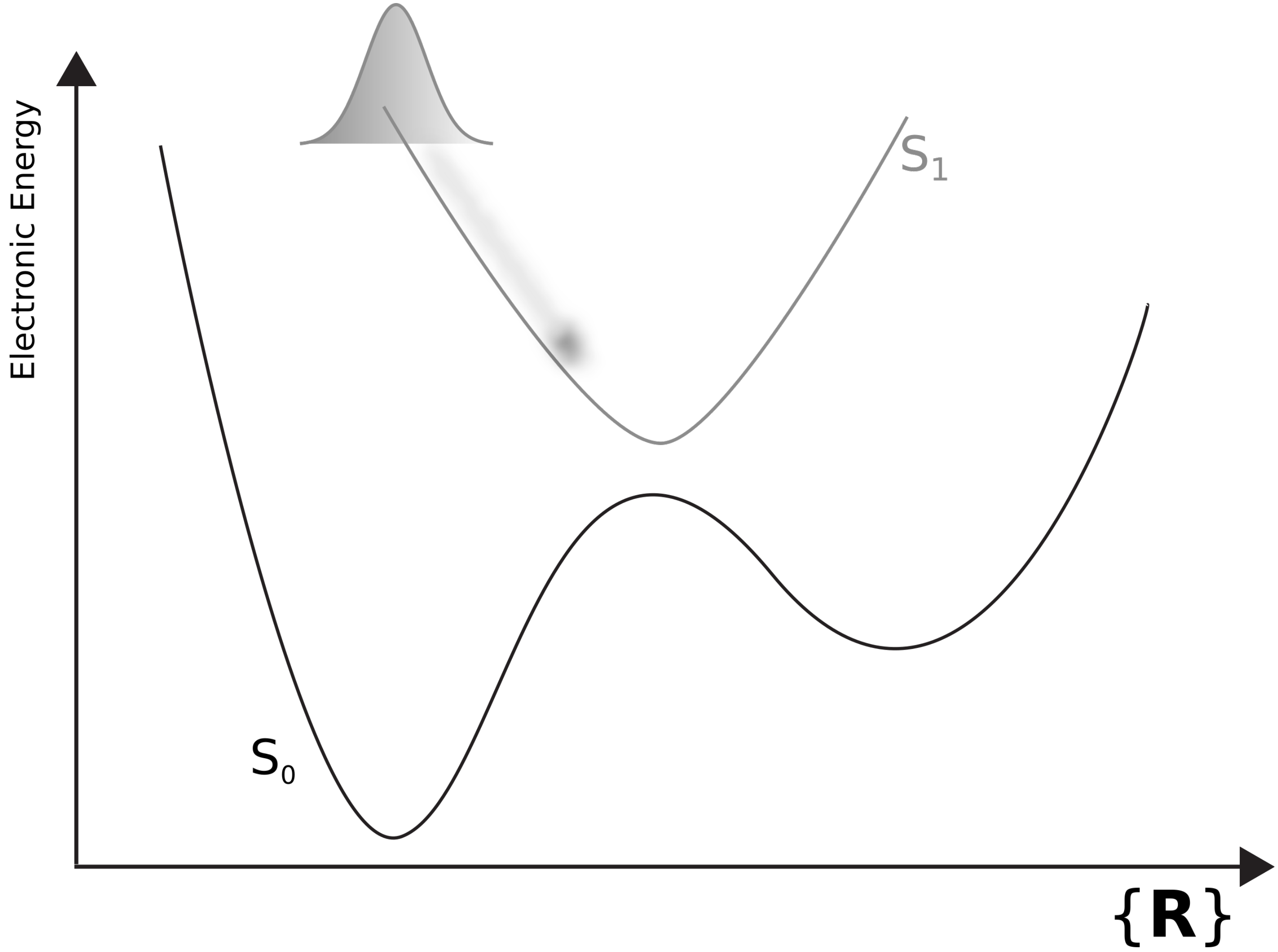
Dream: in silico photochemical experiment

Molecule is in S_1.



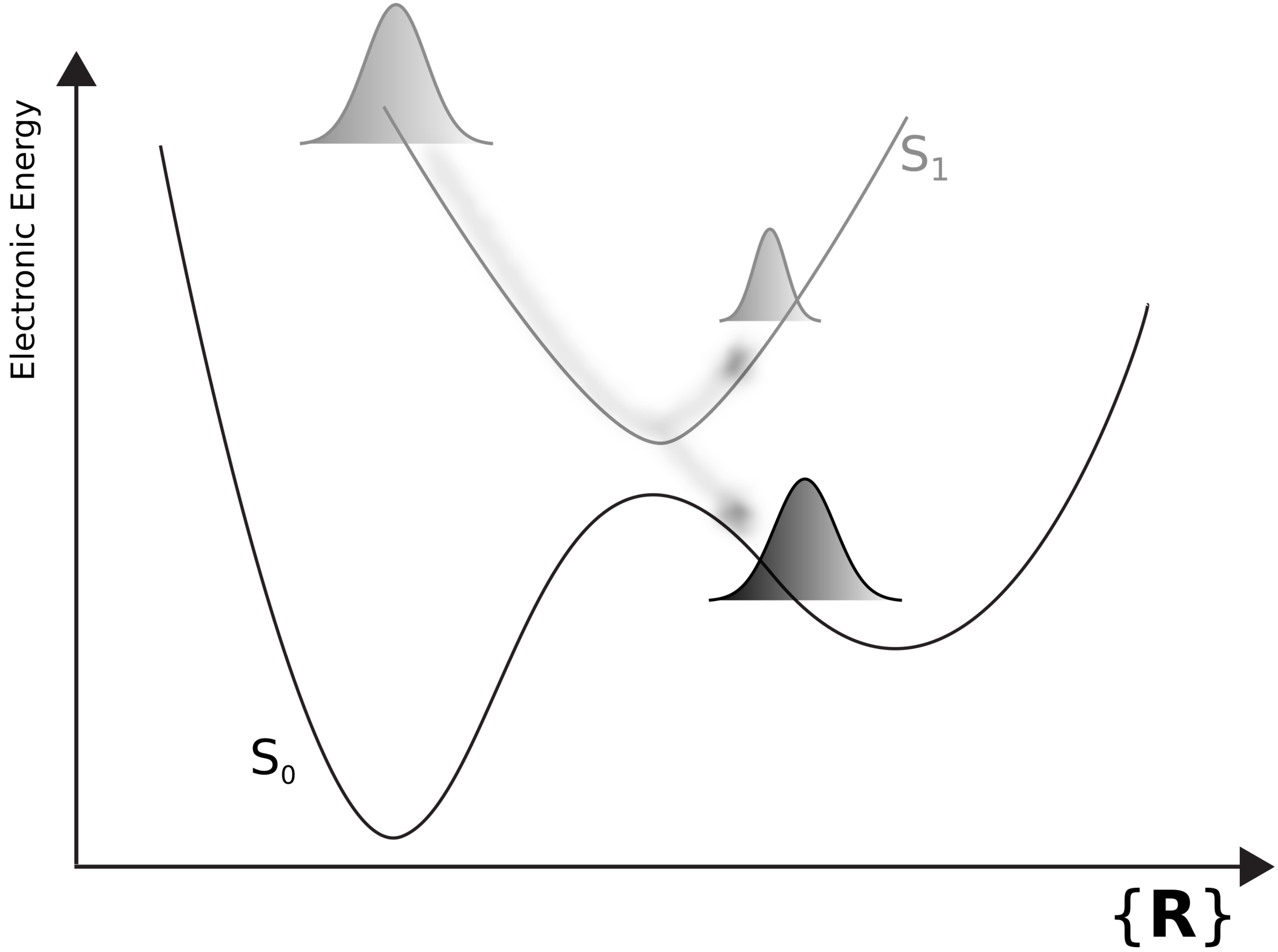
Dream: in silico photochemical experiment

Relaxation processes

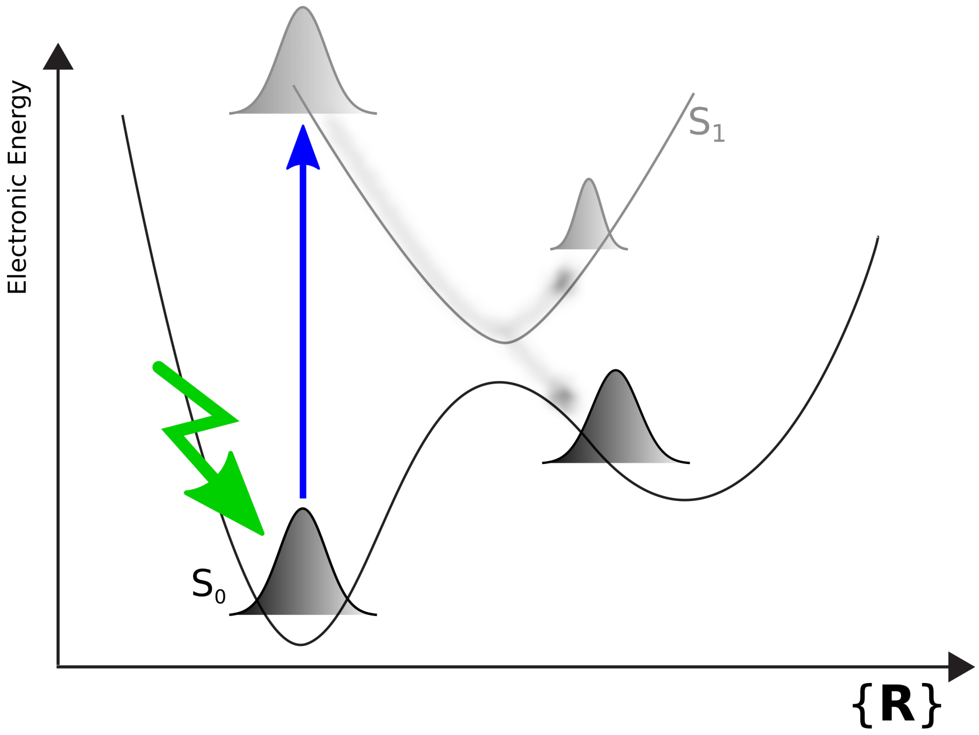


Dream: in silico photochemical experiment

Nonadiabatic processes



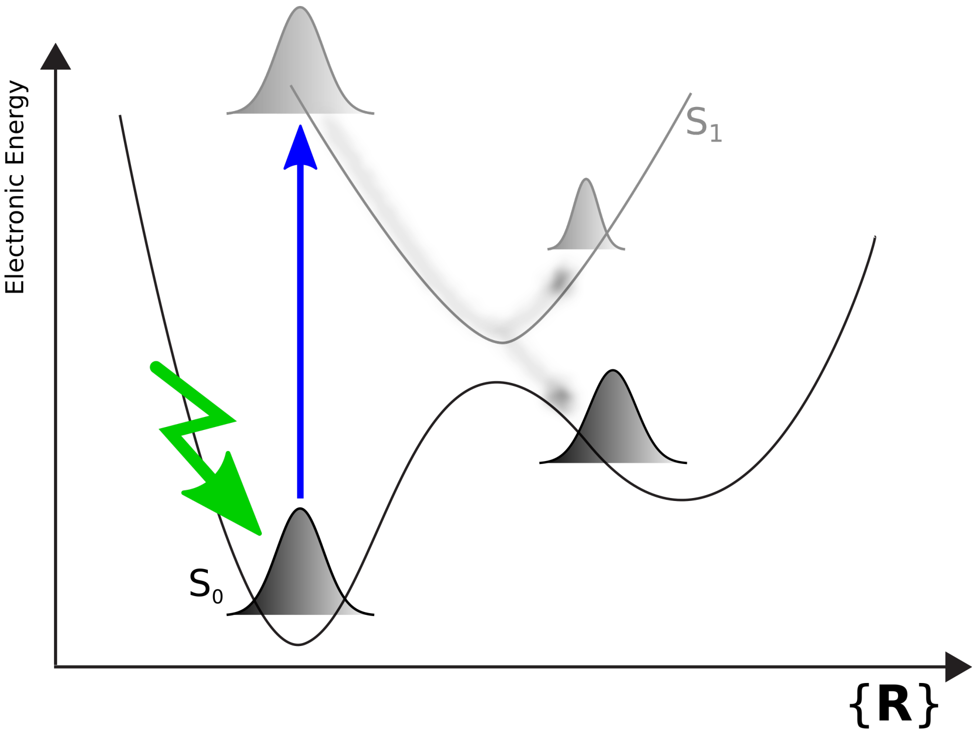
Nonadiabatic dynamics - a theoretical challenge



A complete challenge for theoretical chemistry.

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

Nonadiabatic dynamics - a theoretical challenge



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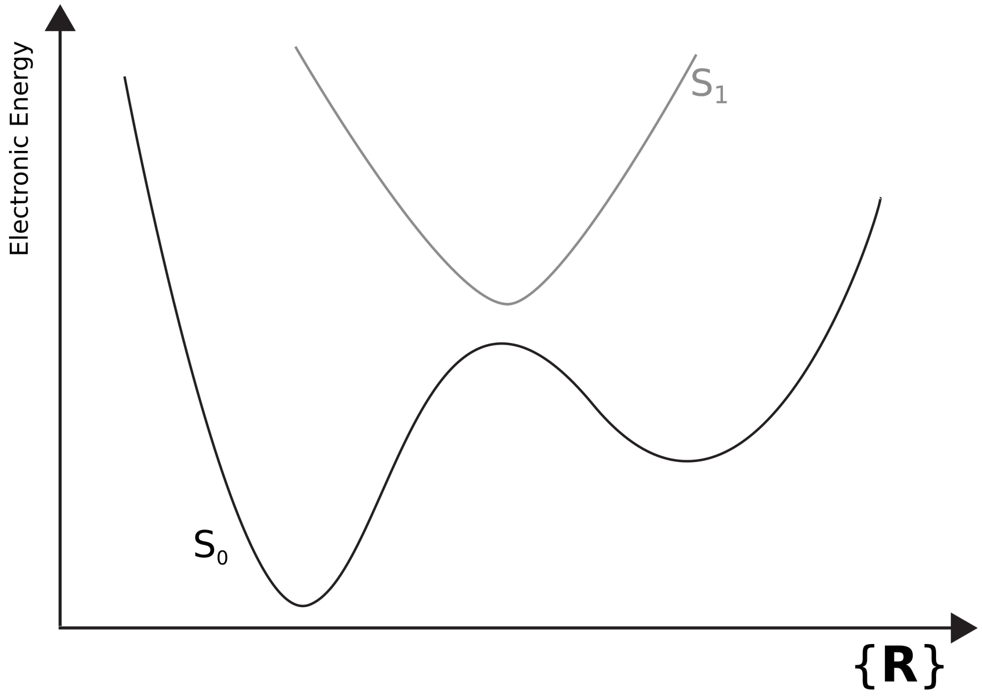

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Electronic energies: $E_J^{el}(\mathbf{R})$

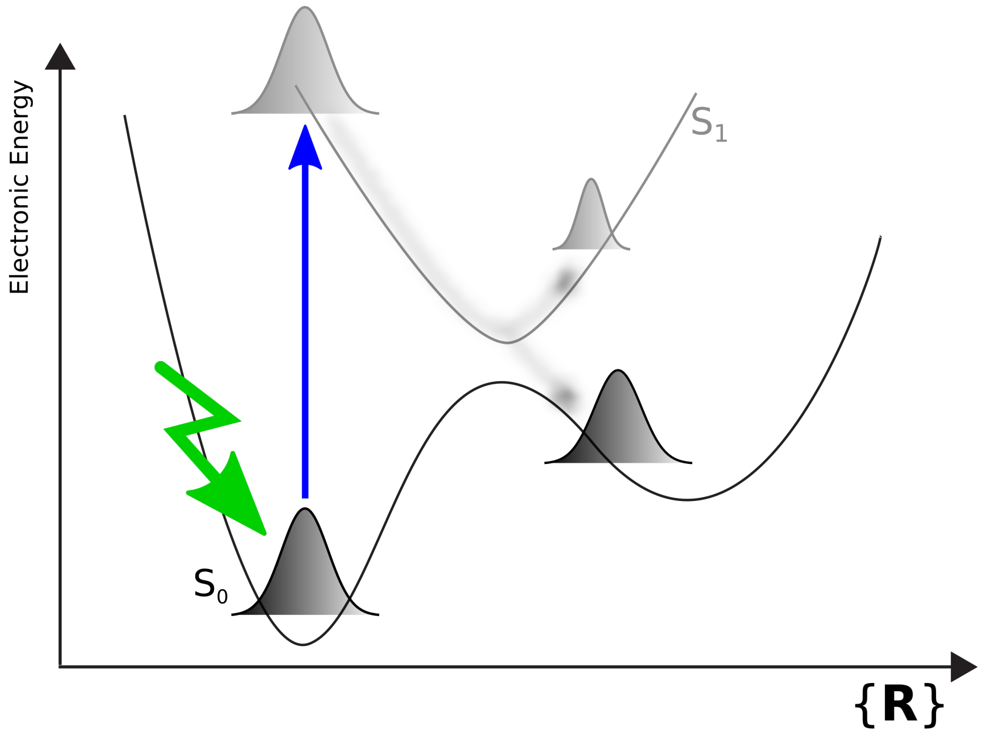
Nuclear forces: $\mathbf{F}_J = -\nabla_{\mathbf{R}} E_J^{el}(\mathbf{R})|_{\mathbf{R}=\mathbf{R}(t)}$

Nonadiabatic coupling vectors:

$$\mathbf{d}_{JI}(\mathbf{R}) = \langle \Phi_J | \nabla_{\mathbf{R}} | \Phi_I \rangle_{\mathbf{r}}$$

...

Nonadiabatic dynamics - a theoretical challenge



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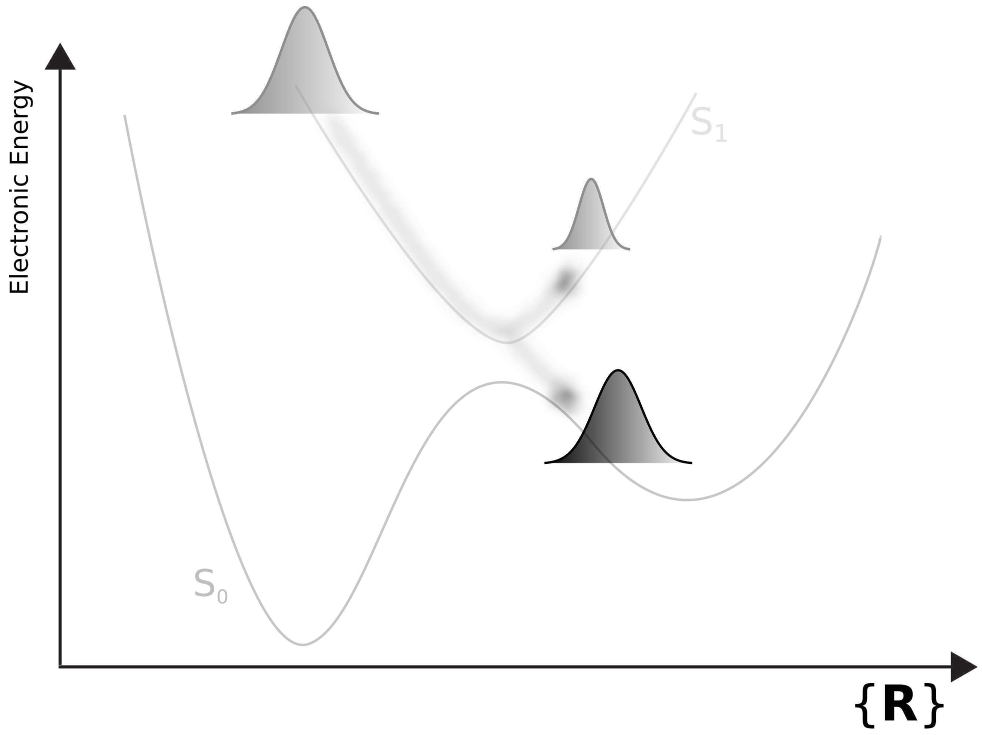
External electromagnetic field?
Solvent effects?

Nonadiabatic dynamics - a theoretical challenge



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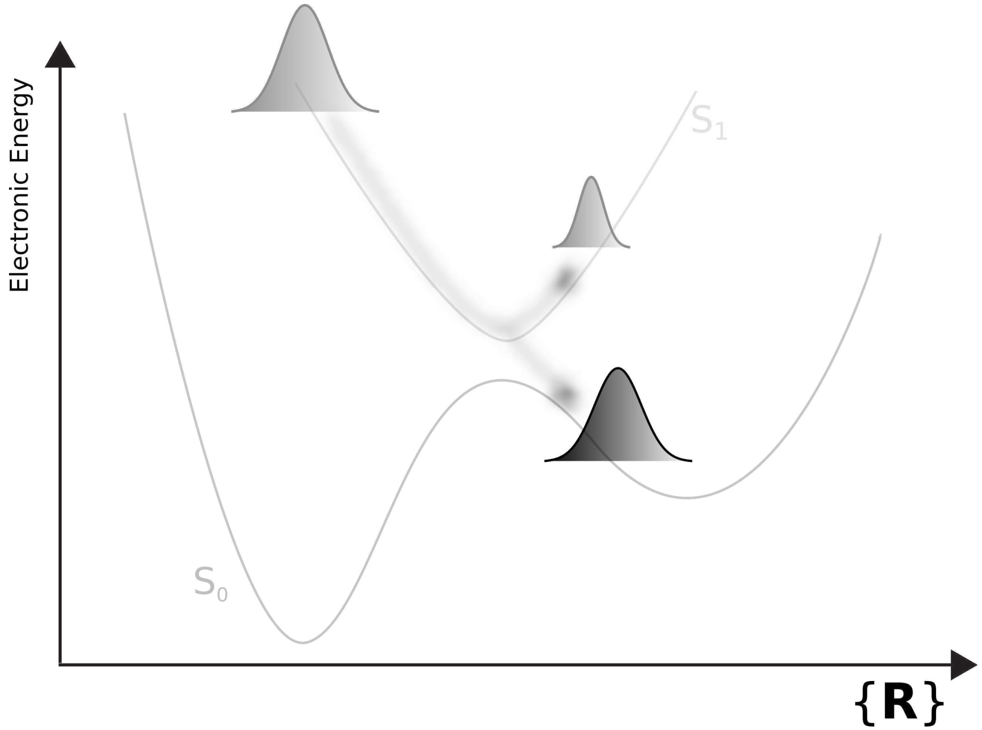
Quantum-mechanical treatment of the nuclei?
Classical approximation and trajectories?
How to account for nonadiabatic effects?

Nonadiabatic dynamics – A theoretical challenge



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

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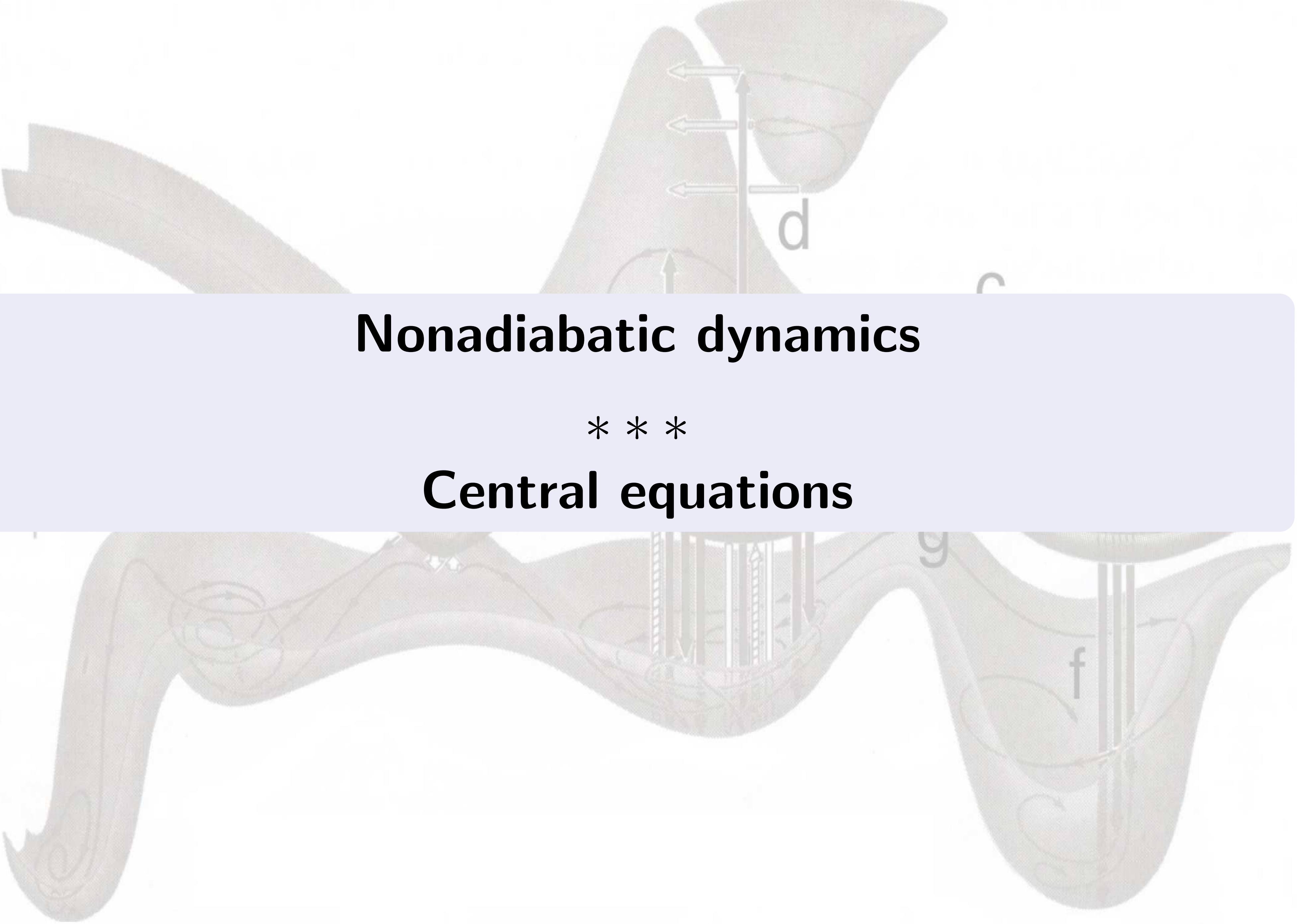
Such complexity implies a compromise between computational efficiency and nuclear-dynamics/electronic-structure accuracy.

Nonadiabatic dynamics

* * *

Central equations



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

Starting point

Time-dependent Schrödinger equation (TDSE):

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

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

$$\begin{aligned}\hat{H}(\mathbf{r},\mathbf{R}) &= -\sum_{\gamma}\frac{\hbar^2}{2M_\gamma}\nabla_\gamma^2 - \sum_i \frac{\hbar^2}{2}\nabla_i^2 + \sum_{i<j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_{\gamma,i}\frac{Z_\gamma}{|\mathbf{R}_\gamma-\mathbf{r}_i|} + \sum_{\gamma<\beta}\frac{Z_\gamma Z_\beta}{|\mathbf{R}_\gamma-\mathbf{R}_\beta|}\\ &= -\sum_{\gamma}\frac{\hbar^2}{2M_\gamma}\nabla_\gamma^2 + \hat{\mathcal{H}}_{el}(\mathbf{r},\mathbf{R})\end{aligned}$$

γ (i) is a label for the nuclei (electrons).

This wavefunction describes **both the electrons and the nuclei**.

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Representation of $\Psi(\mathbf{r}, \mathbf{R}, t)$

Different ways to express $\Psi(\mathbf{r}, \mathbf{R}, t)$:

Exact:

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow[\text{Huang}]{\text{Born-}} \sum_{J}^{\infty} \Phi_J(\mathbf{r}; \mathbf{R})\chi_J(\mathbf{R}, t)$$

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow[\text{Factorization}]{\text{Exact}} \Phi(\mathbf{r}; \mathbf{R}, t)\chi(\mathbf{R}, t)$$

Approximate:

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow[\text{Oppenheimer}]{\text{Born-}} \Phi_J(\mathbf{r}; \mathbf{R})\chi_J(\mathbf{R}, t)$$

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow{\text{TDSCF}} \Phi(\mathbf{r}, t)\chi(\mathbf{R}, t)$$

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Born-Huang representation

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

In this equation, $\{\Phi_J(\mathbf{r};\mathbf{R})\}$ describes a complete set of basis electronic functions which can be taken as solutions of the time-independent Schrödinger equation:

$$\hat{\mathcal{H}}_{el}(\mathbf{r},\mathbf{R})\Phi_J(\mathbf{r};\mathbf{R})=E_J^{el}(\mathbf{R})\Phi_J(\mathbf{r};\mathbf{R})$$

$\mathbf{R}$ is taken as a parameter.
Eigenfunctions of $\hat{\mathcal{H}}_{el}(\mathbf{r};\mathbf{R})$ are considered to be orthonormal, i.e. $\langle\Phi_J|\Phi_I\rangle_{\mathbf{r}}=\delta_{JI}$, $\forall\mathbf{R}$.

The time-dependence of the total molecular wavefunction is transferred to the nuclear wavefunctions.

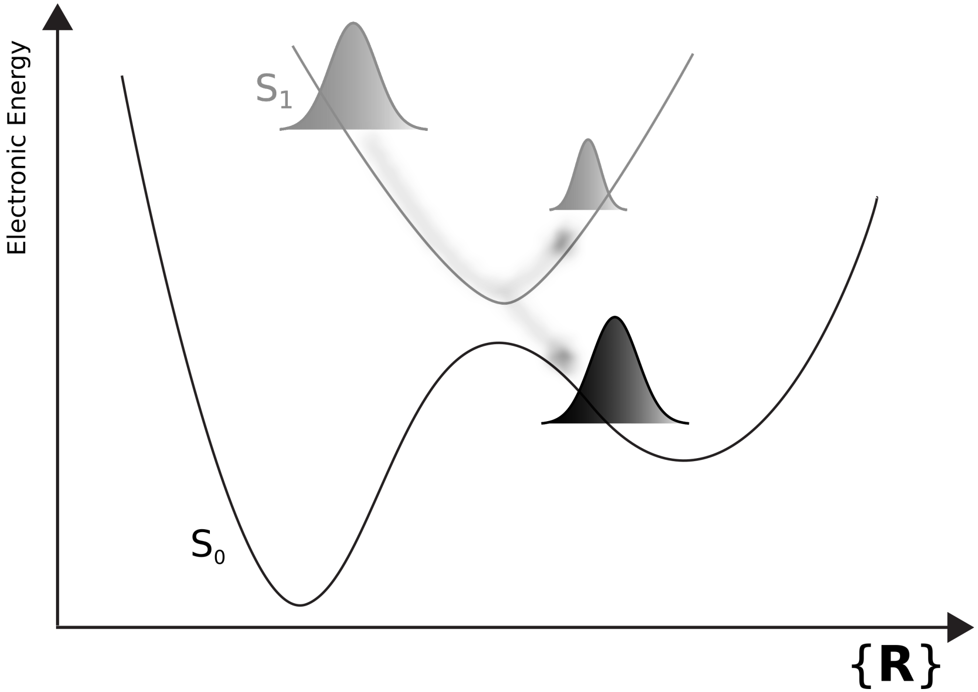
We now insert the Born-Huang representation into the TDSE...

Equations of motion for the nuclei

$$i\hbar\frac{\partial}{\partial t}\chi_I(\mathbf{R},t)=\left[-\sum_{\gamma}\frac{\hbar^2}{2M_\gamma}\nabla_\gamma^2+E_I^{el}(\mathbf{R})\right]\chi_I(\mathbf{R},t)+\sum_J^{\infty}\mathcal{C}_{IJ}(\mathbf{R})\chi_J(\mathbf{R},t)$$

This expression corresponds to an equation for time-dependent nuclear wavefunctions in each electronic state.

$E_I^{el}(\mathbf{R})$ represents the potential energy surface for the nuclei in electronic state I.



Equations of motion for the nuclei

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Important additional term: $\mathcal{C}_{IJ}(\mathbf{R})$! Nonadiabatic coupling terms:

$$\mathcal{C}_{IJ}(\mathbf{R}) = -\sum_\gamma \frac{\hbar^2}{2M_\gamma}\langle\Phi_I(\mathbf{R})|\frac{\partial^2}{\partial R_\gamma^2}|\Phi_J(\mathbf{R})\rangle_{\mathbf{r}} - \sum_\gamma \frac{\hbar}{M_\gamma}\langle\Phi_I(\mathbf{R})|\frac{\partial}{\partial R_\gamma}|\Phi_J(\mathbf{R})\rangle_{\mathbf{r}}\frac{\partial}{\partial R_\gamma}$$

Nonadiabatic coupling vectors: $\mathbf{d}_{IJ}(\mathbf{R}) = \langle\Phi_I(\mathbf{R})|\nabla_{\mathbf{R}}|\Phi_J(\mathbf{R})\rangle_{\mathbf{r}}$

Second-order nonadiabatic couplings: $D_{IJ}(\mathbf{R}) = \langle\Phi_I(\mathbf{R})|\nabla_{\mathbf{R}}^2|\Phi_J(\mathbf{R})\rangle_{\mathbf{r}}$

Equations of motion for the nuclei

$$i\hbar\frac{\partial}{\partial t}\chi_I(\mathbf{R},t) = \left[-\sum_\gamma \frac{\hbar^2}{2M_\gamma}\nabla_\gamma^2 + E_I^{el}(\mathbf{R})\right]\chi_I(\mathbf{R},t) + \sum_J^\infty \mathcal{C}_{IJ}(\mathbf{R})\chi_J(\mathbf{R},t)$$

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The nonadiabatic coupling terms couple the motion of the nuclei with the electronic states, and are crucial to describe the photochemistry of a molecule.