

Trajectory-based approaches to excited-state dynamics

Federica Agostini

federica.agostini@u-psud.fr

Laboratoire de Chimie Physique
University Paris-Sud, Orsay

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Multiscale dynamics in molecular systems

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Summary

(1) Introduction on excited-state dynamics

- (a) Molecular processes involving electronic excited states
- (b) The time-dependent Schrödinger equation

(2) The molecular time-dependent Schrödinger equation

- (a) Expansion in the adiabatic basis: Born-Huang expansion
- (b) The Born-Oppenheimer approximation
- (c) The classical limit in the Born-Oppenheimer approximation
- (d) Beyond the Born-Oppenheimer approximation
- (e) The trajectory-based (quantum-classical) approach

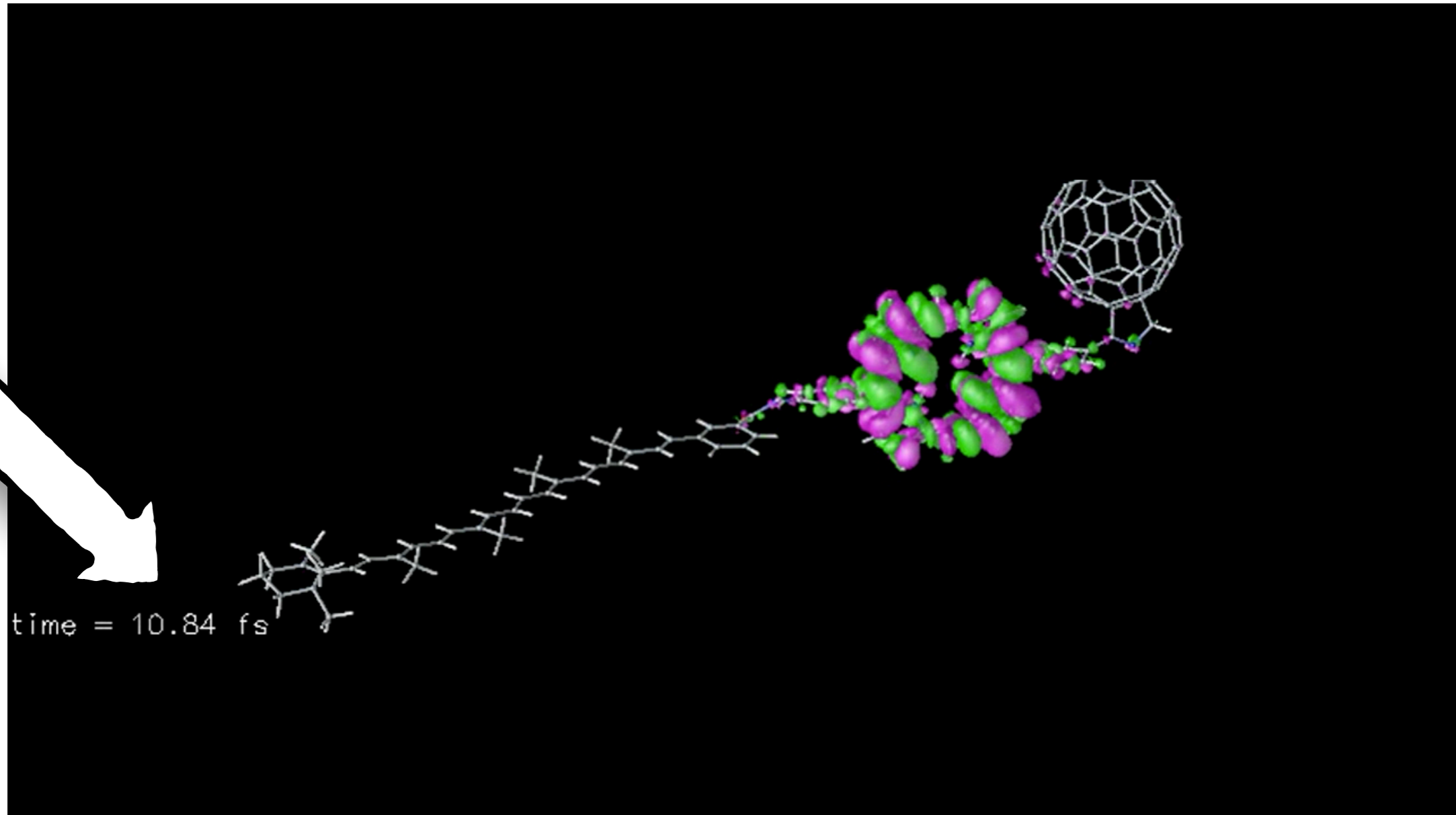
(3) Trajectory-based approaches to excited-state molecular dynamics

- (a) Sampling of the initial conditions
- (b) The concept of classical force in nonadiabatic dynamics
- (c) Trajectory surface hopping
- (d) An example: Photo-dynamics of thiophene with TSH
- (e) Trajectory surface hopping: A model study
- (f) Trajectory surface hopping: Photo-induced ring opening
- (g) Trajectory surface hopping: Intersystem crossing
- (h) Available codes & References

(4) Other methods for excited-state, nonadiabatic dynamics

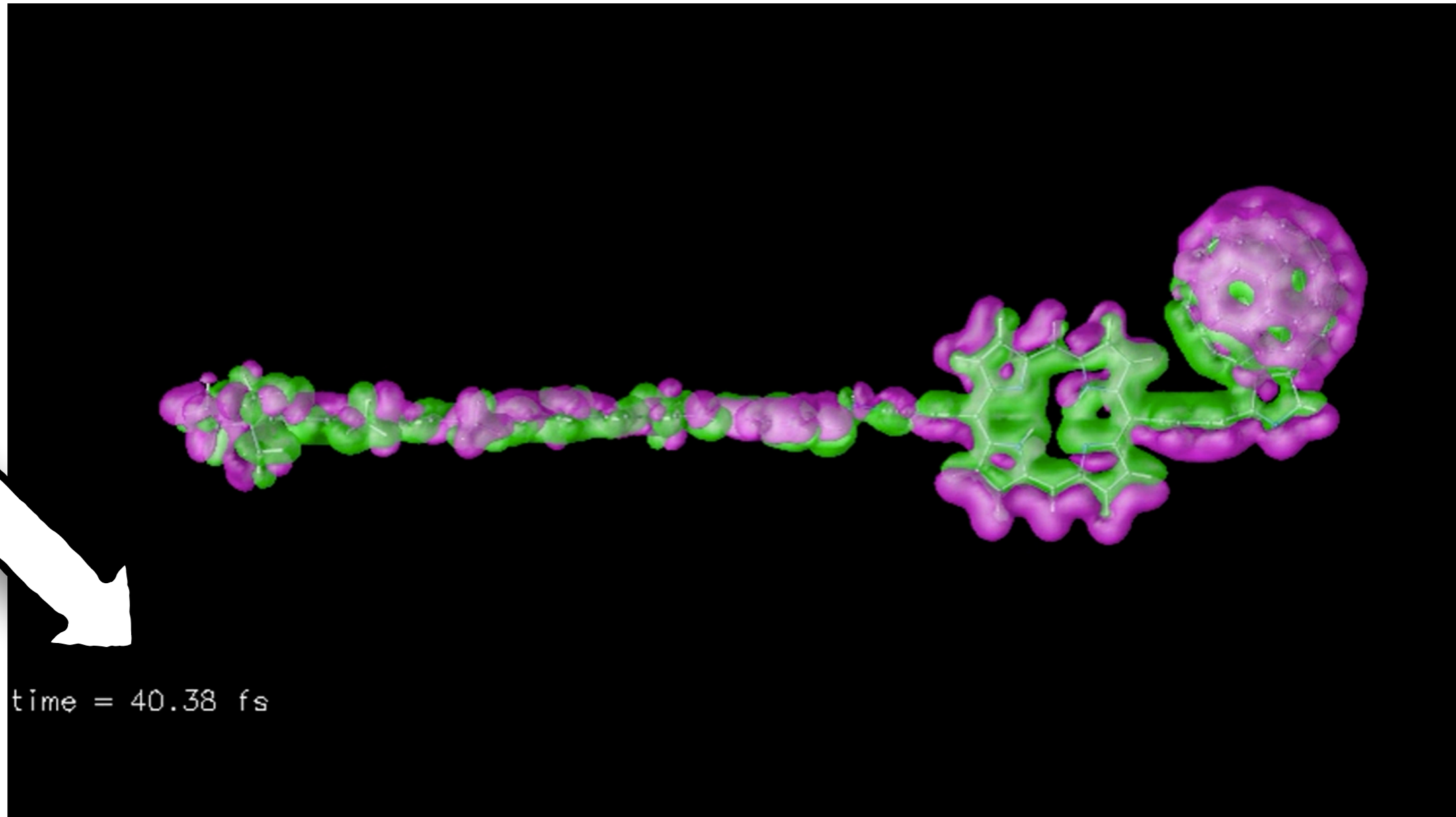
(1) Introduction on excited-state dynamics

Molecular processes involving electronic excited states



triad carotene-porphyrin-fullerene: photo-excitation of the porphyrin and following electronic dynamics (at fixed nuclear positions)

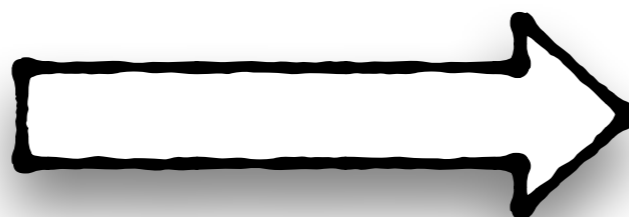
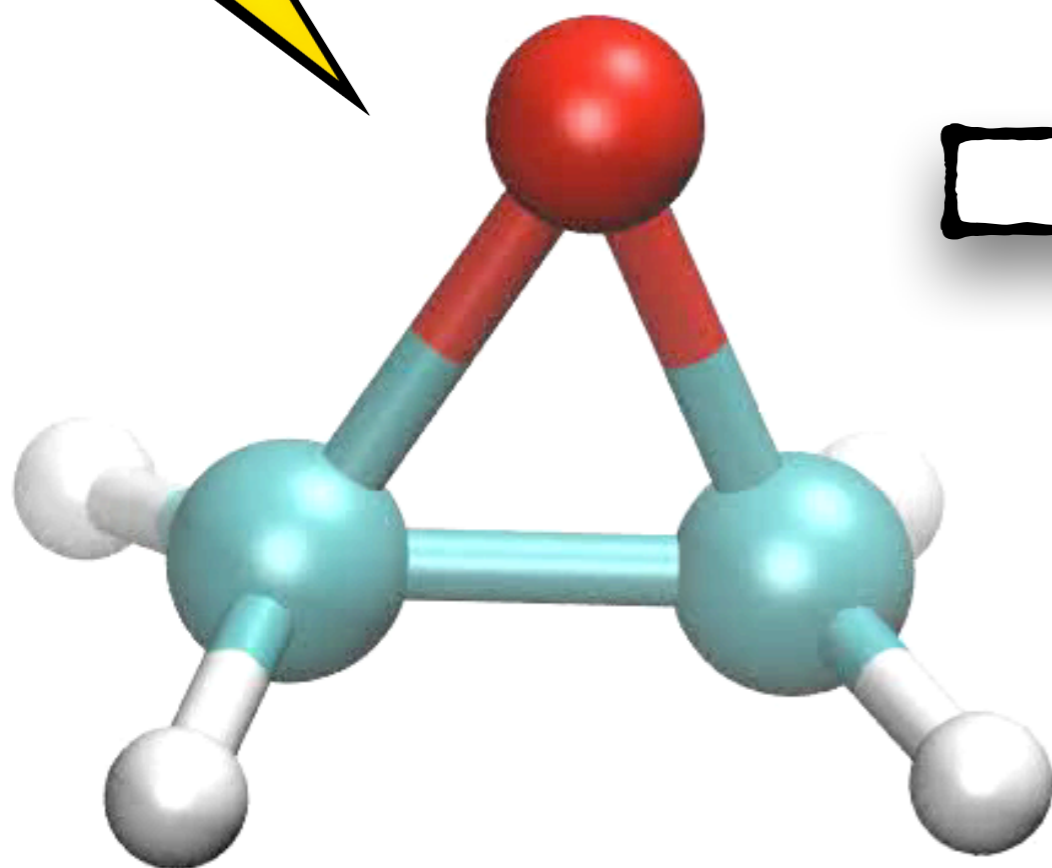
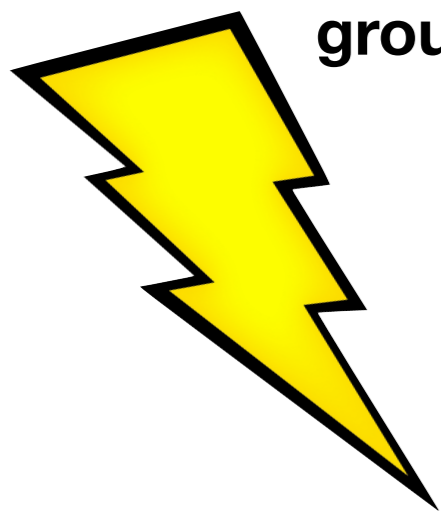
Molecular processes involving electronic excited states



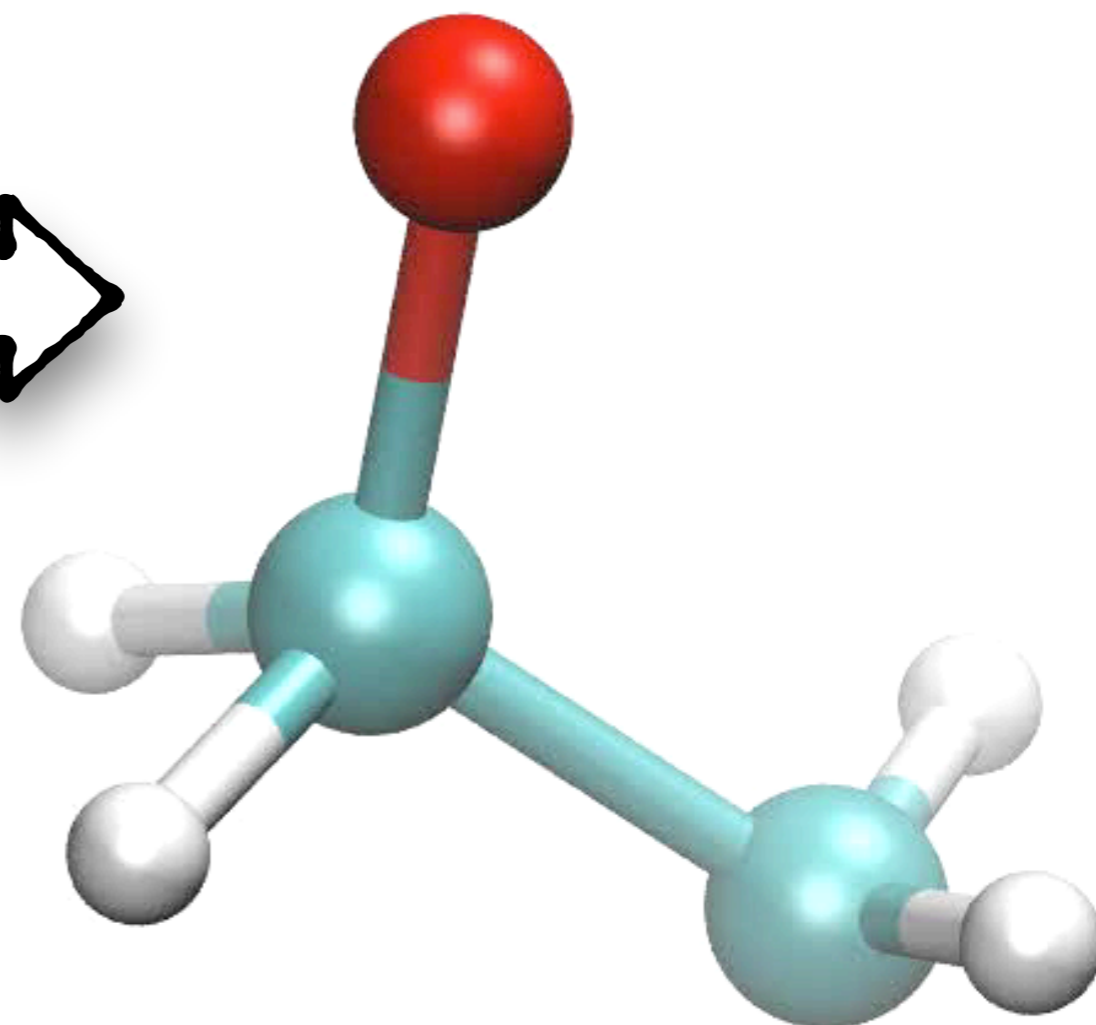
triad carotene-porphyrin-fullerene: photo-excitation of the porphyrin and following ultrafast electron-nuclear dynamics

Molecular processes involving electronic excited states

ground-state (adiabatic) vs. excited-state (nonadiabatic) dynamics



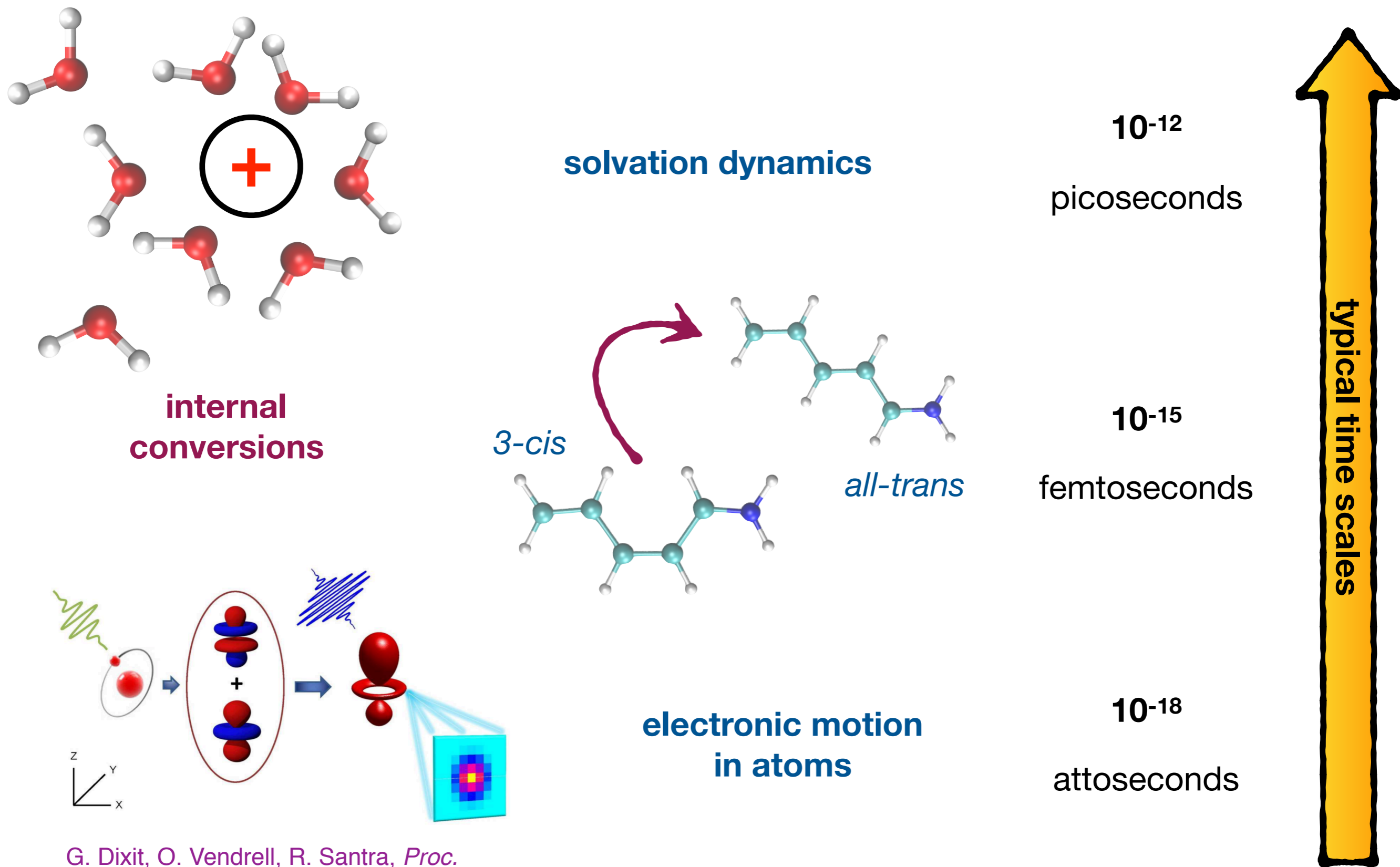
ring opening within 35 fs



dynamics in the electronic ground state
(before photo-excitation)

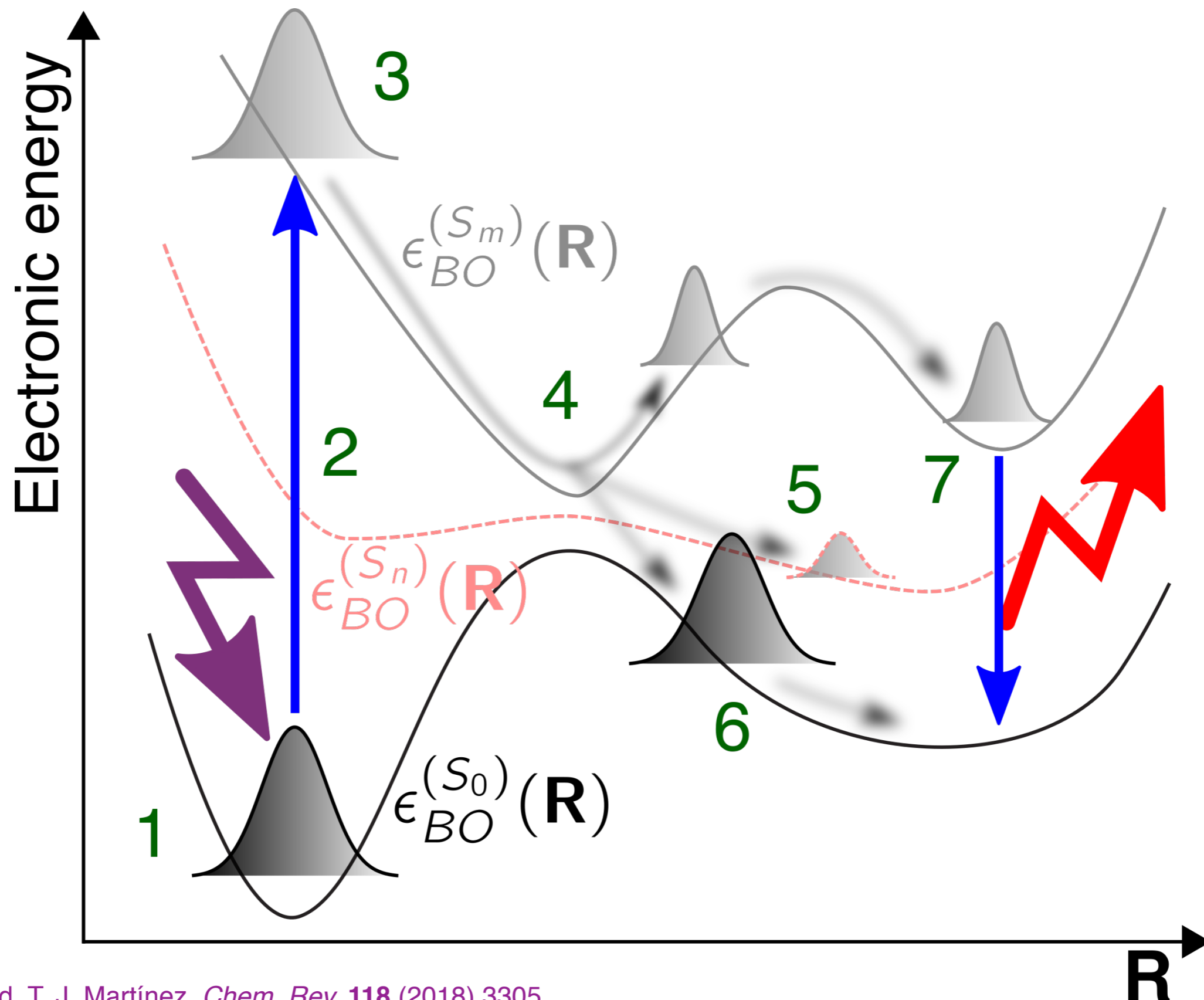
dynamics in the electronic excited states
(after photo-excitation)

Molecular processes involving electronic excited states



G. Dixit, O. Vendrell, R. Santra, *Proc. Nat. Ac. Science* **109** (2012) 11636.

Molecular processes involving electronic excited states



The time-dependent Schrödinger equation

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

$$\hat{H} = \underbrace{\sum_{\nu} \frac{-\hbar^2}{2M_{\nu}} \nabla_{\nu}^2}_{\hat{T}_n} + \underbrace{\sum_i \frac{-\hbar^2}{2m} \nabla_i^2}_{\hat{T}_e} + \underbrace{\sum_{\nu} \sum_{\mu < \nu} \frac{Z_{\nu} Z_{\mu} e^2}{4\pi\epsilon_0 R_{\nu\mu}}}_{\hat{V}_{nn}} + \underbrace{\sum_i \sum_{j < i} \frac{e^2}{4\pi\epsilon_0 r_{ij}}}_{\hat{V}_{ee}} - \underbrace{\sum_{\nu} \sum_i \frac{Z_{\nu} e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_{\nu}|}}_{\hat{V}_{en}}$$

need for approximations

photo-dissociation of NaI



photo-induced ring-opening
in oxirane

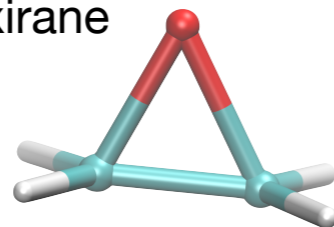


photo-isomerization of
azobenzene

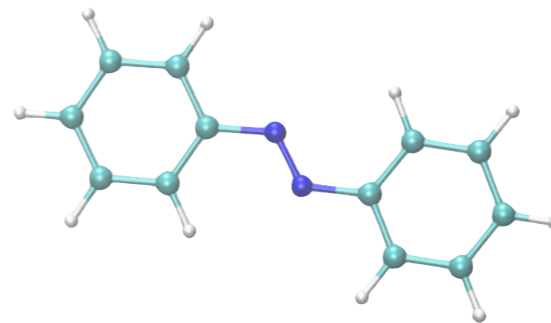
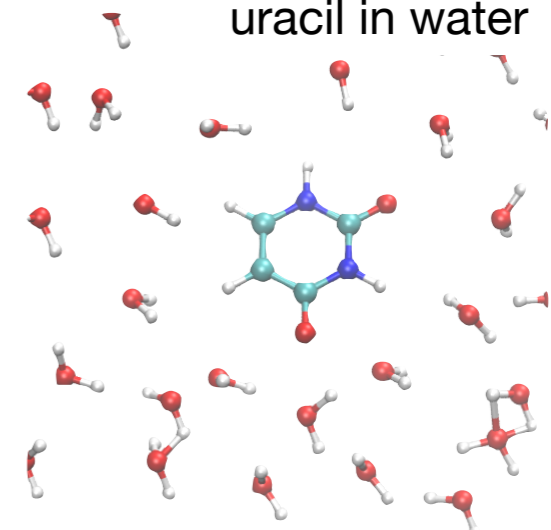


photo-ionization of
uracil in water



system size

(2) The molecular time-dependent Schrödinger equation

Expansion in the adiabatic basis: Born-Huang expansion

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

$$\hat{H}=\hat{T}_n(\mathbf{R})+\hat{H}_{BO}(\mathbf{r},\mathbf{R})$$

representation of the molecular wavefunction on a basis

$$\Psi(\mathbf{r},\mathbf{R},t)=\sum_k\chi_k(\mathbf{R},t)\varphi_{\mathbf{R}}^{(k)}(\mathbf{r})$$

$\mathbf{r}=\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_{N_{el}};$
 $\mathbf{R}=\mathbf{R}_1,\mathbf{R}_2,\dots,\mathbf{R}_{N_n}$

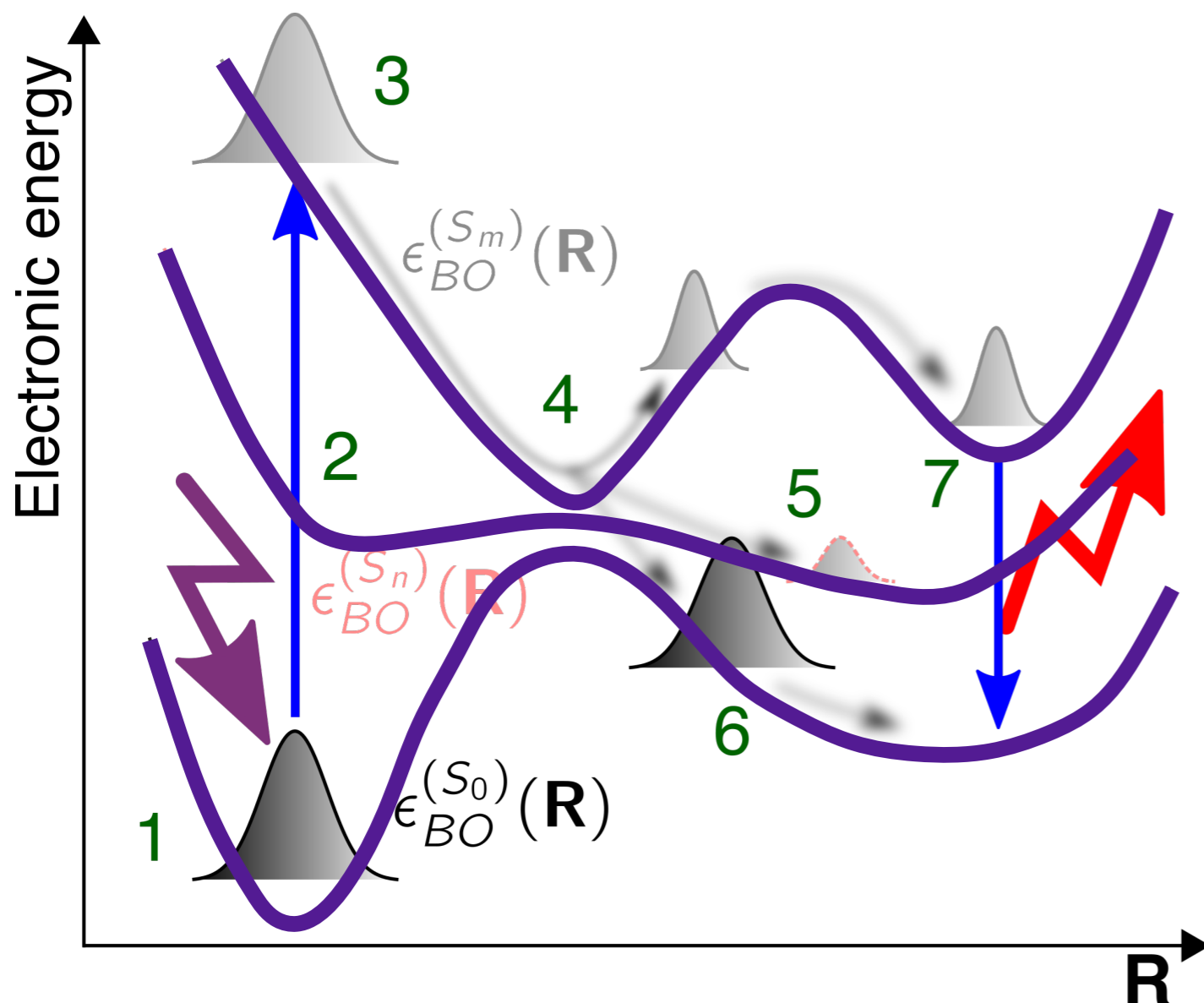
*parametric dependence on
the nuclear configuration*

how is the adiabatic basis defined?

Expansion in the adiabatic basis: Born-Huang expansion

$$\hat{H}_{BO}(\mathbf{r}, \mathbf{R})\varphi_{\mathbf{R}}^{(k)}(\mathbf{r}) = \epsilon_{BO}^{(k)}(\mathbf{R})\varphi_{\mathbf{R}}^{(k)}(\mathbf{r})$$

adiabatic (or Born-Oppenheimer) potential energy surfaces (PESs)



$$k = S_0, S_1, S_2, \dots, T_1, T_2, \dots$$

Expansion in the adiabatic basis: Born-Huang expansion

inserting the Born-Huang expansion into the molecular TDSE
(and projecting on an adiabatic state):

$$i\hbar\partial_t\chi_l(\mathbf{R}, t) = \left[\sum_{\nu} \frac{-\hbar^2\nabla_{\nu}^2}{2M_{\nu}} + \epsilon_{BO}^{(l)}(\mathbf{R}) \right] \chi_l(\mathbf{R}, t) \\ + \sum_k \left(\sum_{\nu} \frac{-i\hbar}{M_{\nu}} \mathbf{d}_{lk,\nu}(\mathbf{R}) \cdot (-i\hbar\nabla_{\nu}) + \frac{-\hbar^2}{2M_{\nu}} D_{lk,\nu}(\mathbf{R}) \right) \chi_k(\mathbf{R}, t)$$

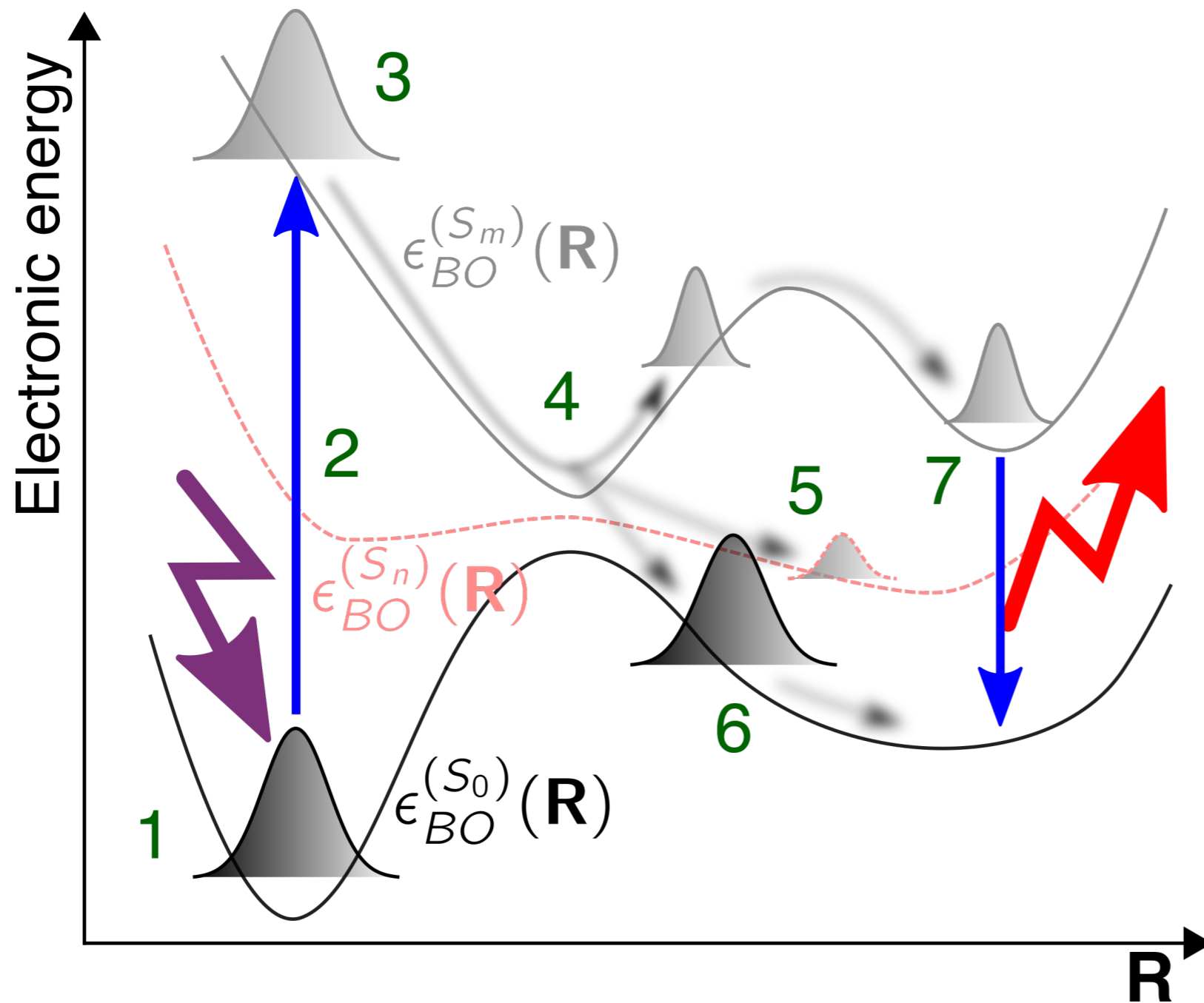
with

$$\mathbf{d}_{lk,\nu}(\mathbf{R}) = \left\langle \varphi_{\mathbf{R}}^{(l)} \left| \nabla_{\nu} \varphi_{\mathbf{R}}^{(k)} \right. \right\rangle_{\mathbf{r}} ; \quad D_{lk,\nu}(\mathbf{R}) = \left\langle \varphi_{\mathbf{R}}^{(l)} \left| \nabla_{\nu}^2 \varphi_{\mathbf{R}}^{(k)} \right. \right\rangle_{\mathbf{r}}$$

*nonadiabatic coupling vector
(or derivative coupling)*

*second-order nonadiabatic
coupling*

Expansion in the adiabatic basis: Born-Huang expansion



small energy gap between
two adiabatic PESs



large nonadiabatic couplings

$$d_{lk,\nu}(\mathbf{R}) = \frac{\langle \varphi_{\mathbf{R}}^{(l)} | (\nabla_{\nu} \hat{H}_{BO}(\mathbf{r}, \mathbf{R})) | \varphi_{\mathbf{R}}^{(k)} \rangle_{\mathbf{r}}}{\epsilon_{BO}^{(l)}(\mathbf{R}) - \epsilon_{BO}^{(k)}(\mathbf{R})}$$

nuclear density



sum over adiabatic
contributions

$$|\chi(\mathbf{R}, t)|^2 = \sum_k |\chi_k(\mathbf{R}, t)|^2$$

Derivation of the expression of the nonadiabatic couplings

We start from the expression

$$\partial_R \left\langle \varphi_R^{(l)} \left| \hat{H}_{BO}(R) \right| \varphi_R^{(k)} \right\rangle_r = 0 \text{ if } l \neq k$$

valid since the adiabatic states are eigenstates of the Hamiltonian \hat{H}_{BO} . We apply the derivative operator to each term on the left-hand side,

$$\begin{aligned} 0 &= \left\langle \partial_R \varphi_R^{(l)} \left| \hat{H}_{BO}(R) \right| \varphi_R^{(k)} \right\rangle_r + \left\langle \varphi_R^{(l)} \left| \left(\partial_R \hat{H}_{BO}(R) \right) \right| \varphi_R^{(k)} \right\rangle_r + \left\langle \varphi_R^{(l)} \left| \hat{H}_{BO}(R) \right| \partial_R \varphi_R^{(k)} \right\rangle_r \\ &= d_{kl}^*(R) \epsilon_{BO}^{(k)}(R) + \left\langle \varphi_R^{(l)} \left| \left(\partial_R \hat{H}_{BO}(R) \right) \right| \varphi_R^{(k)} \right\rangle_r + d_{lk}(R) \epsilon_{BO}^{(l)}(R) \\ &= -d_{lk}(R) \epsilon_{BO}^{(k)}(R) + \left\langle \varphi_R^{(l)} \left| \left(\partial_R \hat{H}_{BO}(R) \right) \right| \varphi_R^{(k)} \right\rangle_r + d_{lk}(R) \epsilon_{BO}^{(l)}(R), \end{aligned}$$

where the relation $d_{kl}^*(R) = -d_{lk}(R)$ has been used. Isolating the term $d_{lk}(R)$ one gets

$$d_{lk}(R) = \frac{\left\langle \varphi_R^{(l)} \left| \left(\partial_R \hat{H}_{BO}(R) \right) \right| \varphi_R^{(k)} \right\rangle_r}{\epsilon_{BO}^{(l)}(R) - \epsilon_{BO}^{(k)}(R)}.$$

The Born-Oppenheimer approximation

$$i\hbar\partial_t\chi_l(\mathbf{R}, t) = \left[\sum_{\nu} \frac{-\hbar^2\nabla_{\nu}^2}{2M_{\nu}} + \epsilon_{BO}^{(l)}(\mathbf{R}) \right] \chi_l(\mathbf{R}, t) + \sum_k \left(\sum_{\nu} \frac{-i\hbar}{M_{\nu}} \mathbf{d}_{lk,\nu}(\mathbf{R}) \cdot (-i\hbar\nabla_{\nu}) + \frac{-\hbar^2}{2M_{\nu}} D_{lk,\nu}(\mathbf{R}) \right) \chi_k(\mathbf{R}, t)$$

the equations for the coefficients decouple if the nonadiabatic couplings are neglected

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only one term can be considered in the Born-Huang expansion

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \chi_{S_0}(\mathbf{R}, t) \varphi_{\mathbf{R}}^{(S_0)}(\mathbf{r}) + \sum_{k \neq S_0} \chi_k(\mathbf{R}, t) \varphi_{\mathbf{R}}^{(k)}(\mathbf{r})$$

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~~$$+ \sum_k \left(\sum_{\nu} \frac{-i\hbar}{M_{\nu}} \mathbf{d}_{lk,\nu}(\mathbf{R}) \cdot (-i\hbar\nabla_{\nu}) + \frac{-\hbar^2}{2M_{\nu}} D_{lk,\nu}(\mathbf{R}) \right) \chi_k(\mathbf{R}, t)$$~~

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The Born-Oppenheimer approximation

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*in the BO approximation, the molecular wavefunction is represented as a **single** product of an adiabatic electronic state and a time-dependent nuclear wavefunction*

$$\Psi(\mathbf{r}, \mathbf{R}, t) \simeq \chi_{S_0}(\mathbf{R}, t)\varphi_{\mathbf{R}}^{(S_0)}(\mathbf{r})$$

this approximation is valid if the nonadiabatic couplings are small, namely if the energy gap between PESs is large

$$\left| \epsilon_{BO}^{(S_0)}(\mathbf{R}) - \epsilon_{BO}^{(S_k)}(\mathbf{R}) \right| \gg \tau_n^{-1} \quad \forall k \neq 0$$

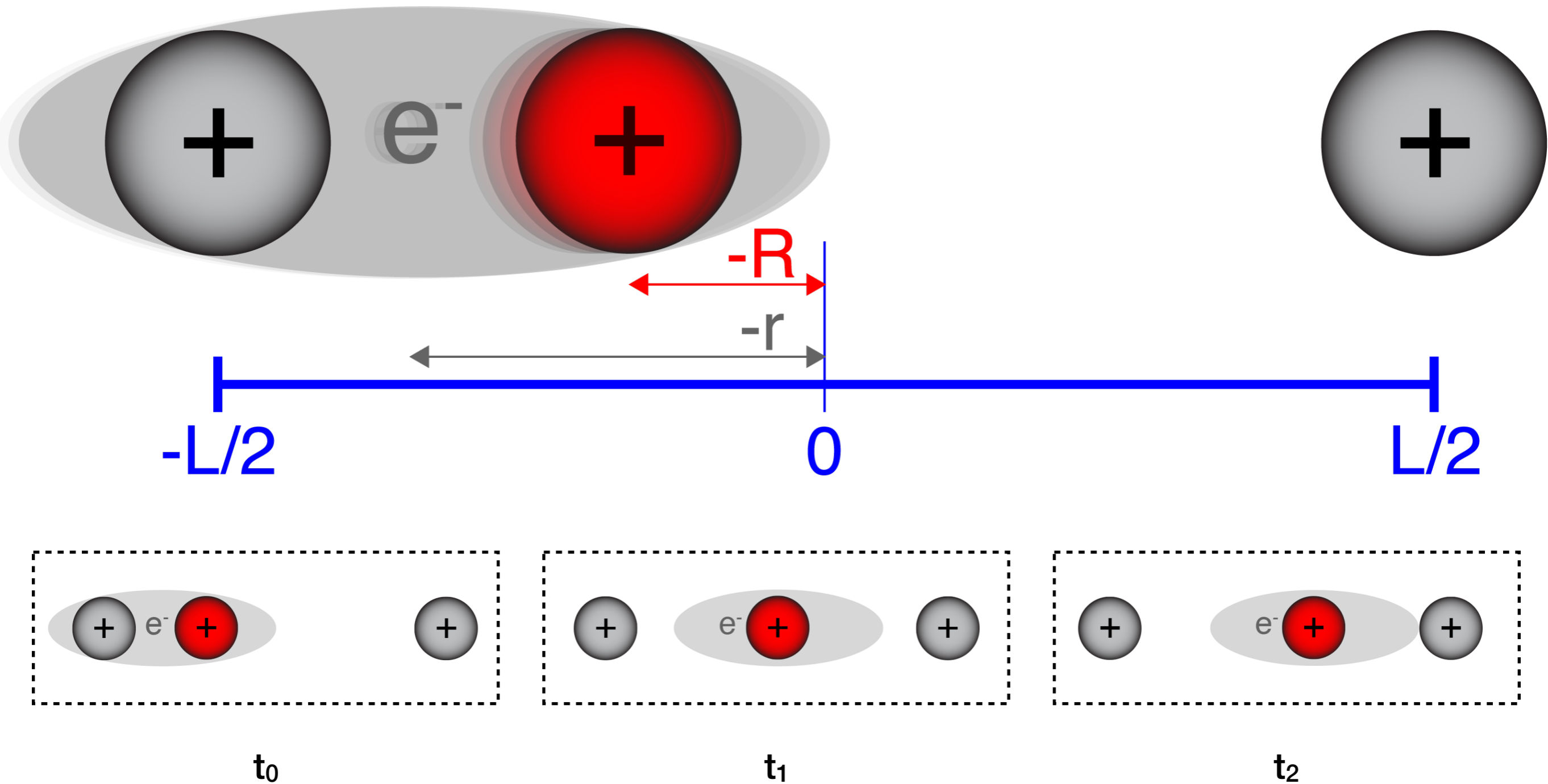
The Born-Oppenheimer approximation

$$i\hbar\partial_t\Psi(\mathbf{r}, \mathbf{R}, t) = \left[\sum_{\nu} \frac{-\hbar^2\nabla_{\nu}^2}{2M_{\nu}} + \hat{H}_{BO}(\mathbf{r}, \mathbf{R}) \right] \Psi(\mathbf{r}, \mathbf{R}, t)$$

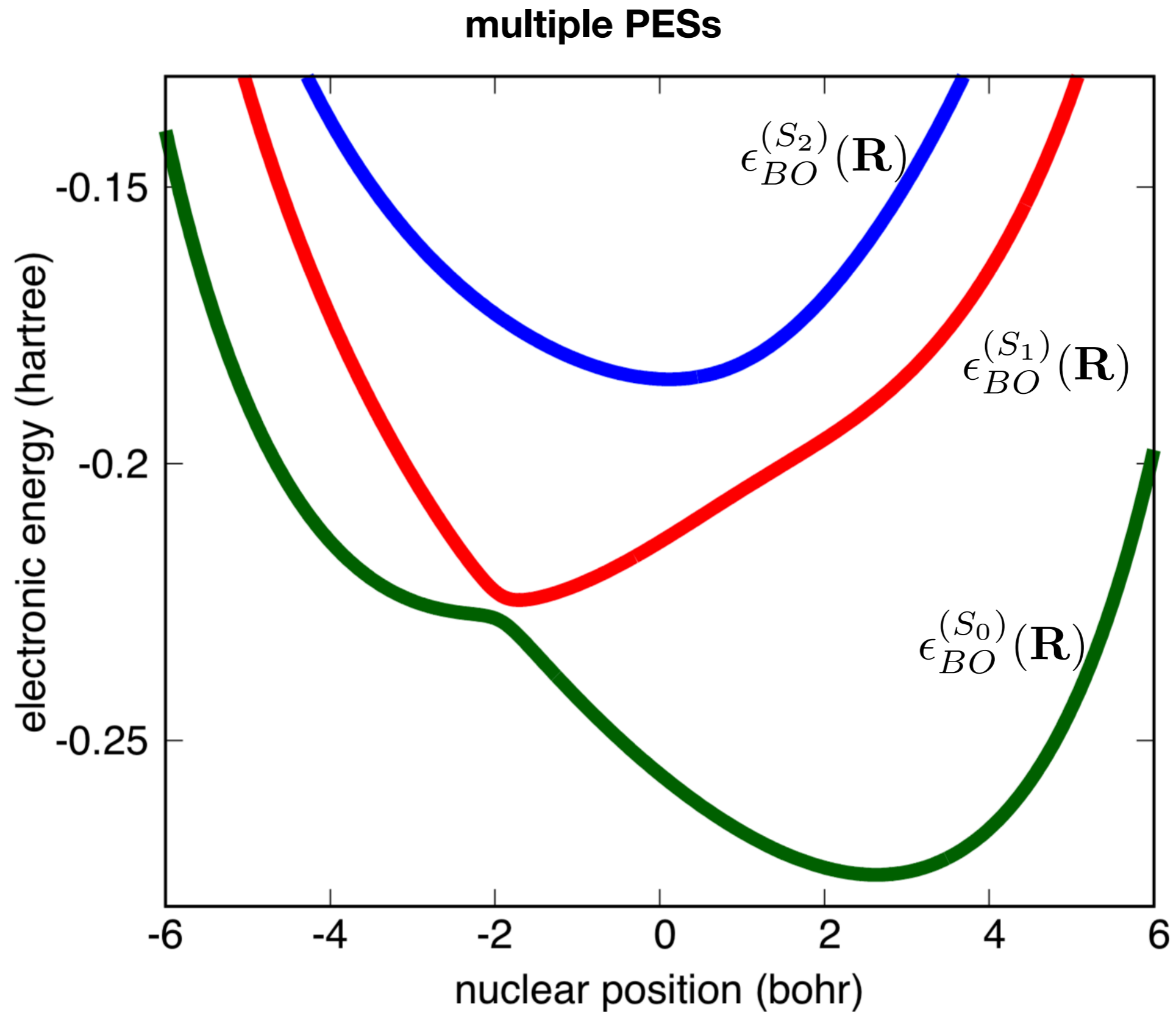
from the TDSE for the molecular wavefunction to
a new TDSE for the nuclear wavefunction only
because the electronic state is static $\varphi_{\mathbf{R}}^{(S_0)}(\mathbf{r})$.

$$i\hbar\partial_t\chi_{S_0}(\mathbf{R}, t) = \left[\sum_{\nu} \frac{-\hbar^2\nabla_{\nu}^2}{2M_{\nu}} + \epsilon_{BO}^{(S_0)}(\mathbf{R}) \right] \chi_{S_0}(\mathbf{R}, t)$$

The Born-Oppenheimer approximation

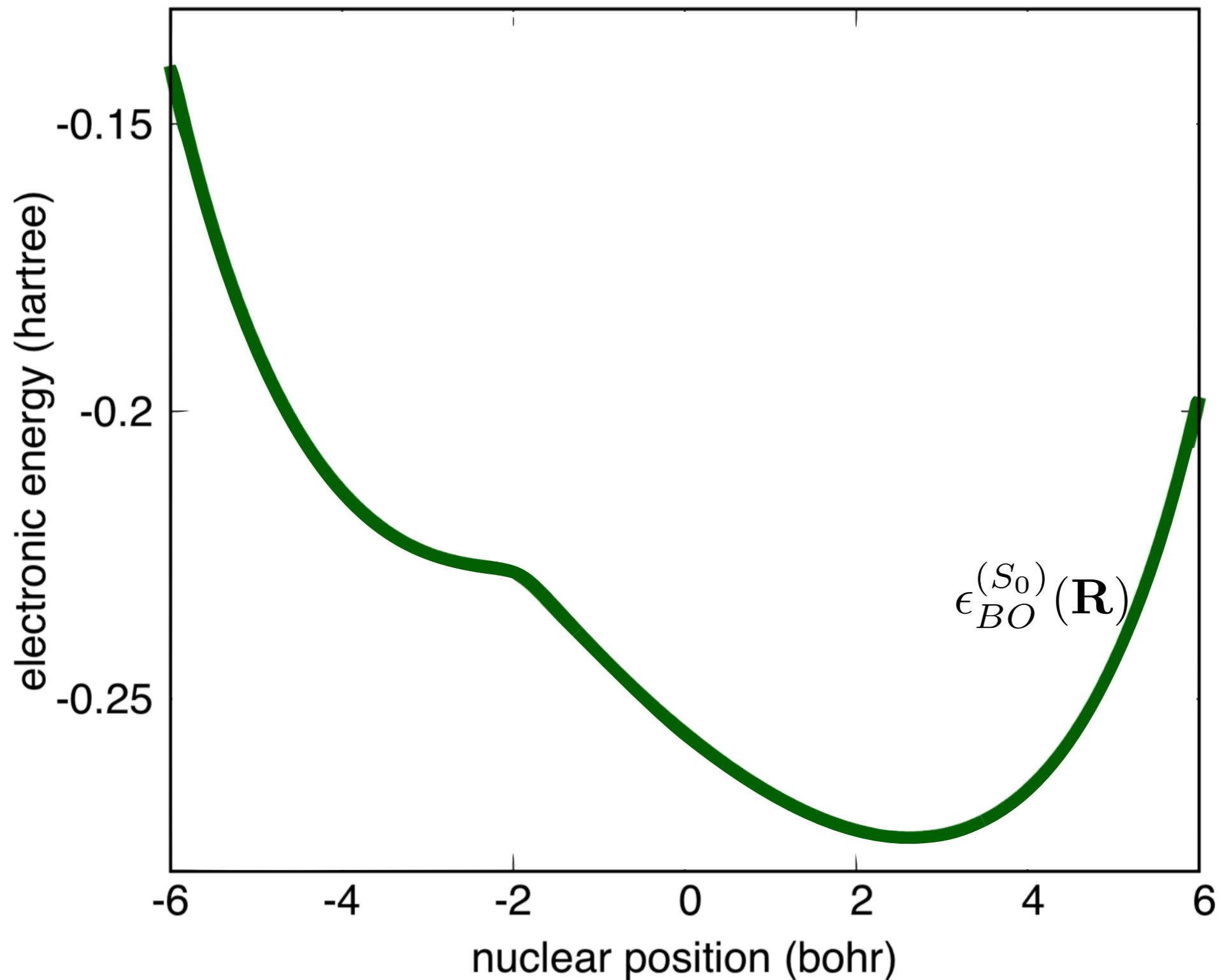


The Born-Oppenheimer approximation



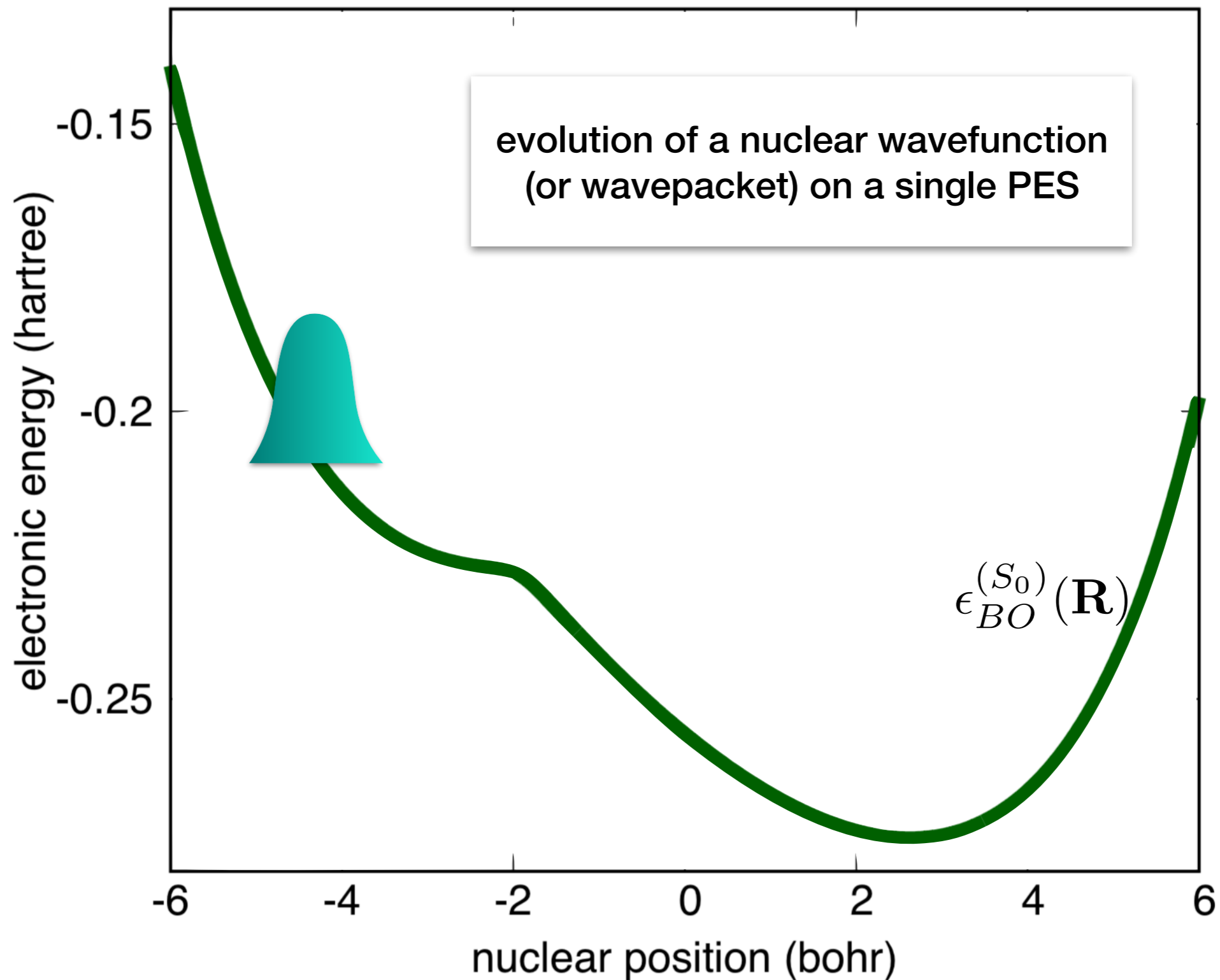
The Born-Oppenheimer approximation

dynamics on a single PESs (BO approximation)



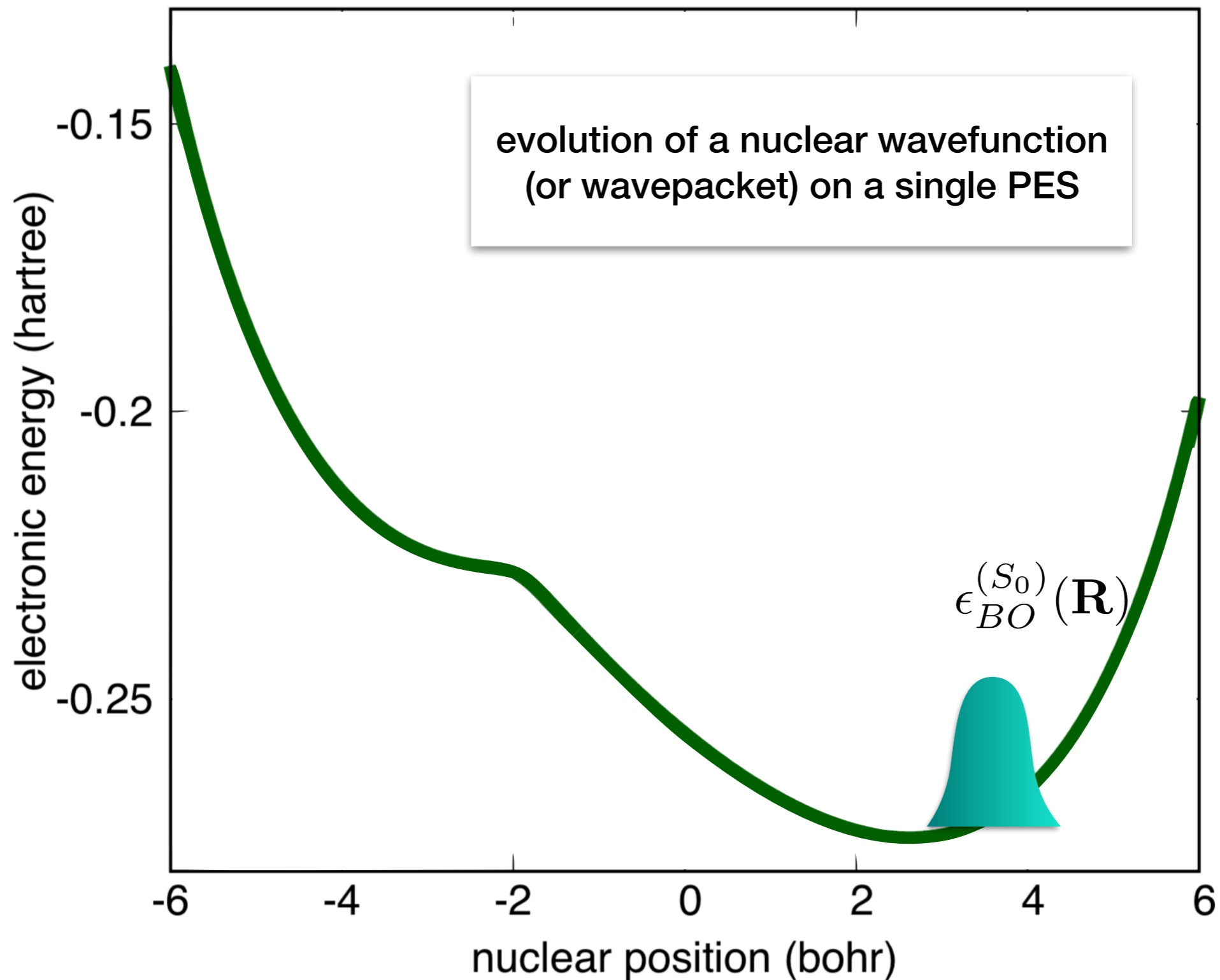
The Born-Oppenheimer approximation

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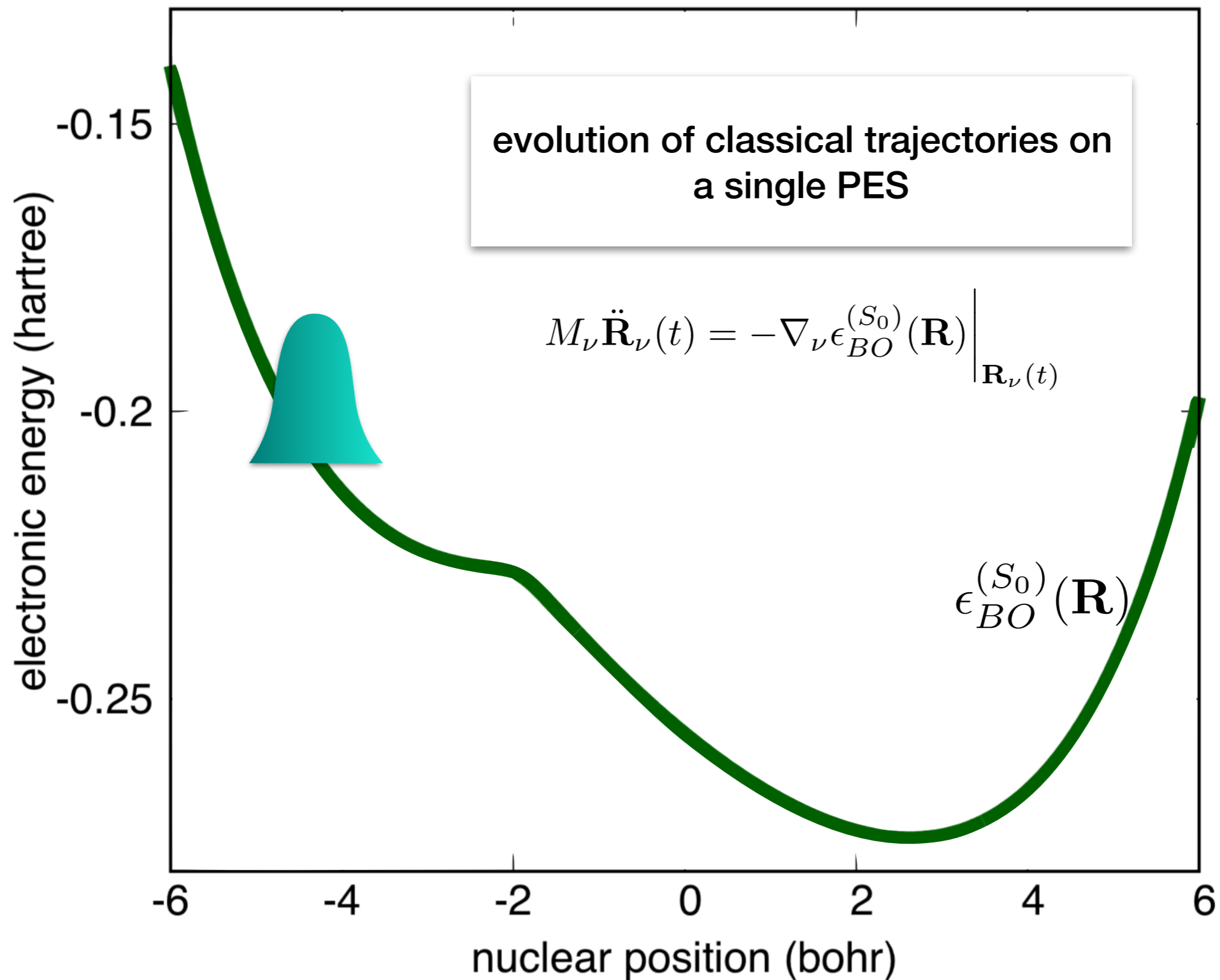
The Born-Oppenheimer approximation

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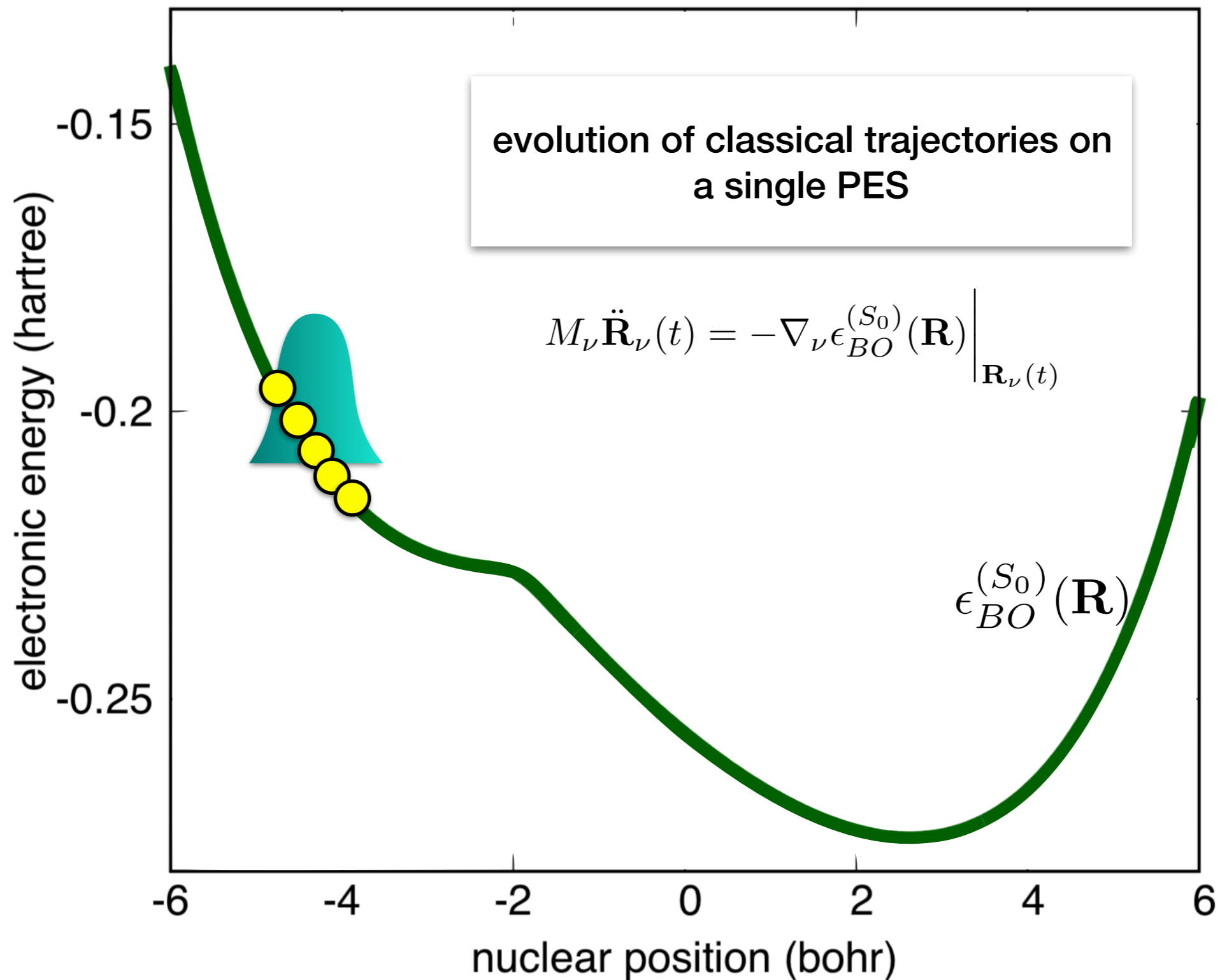
The classical limit in the Born-Oppenheimer approximation

single PESs (BO approximation)



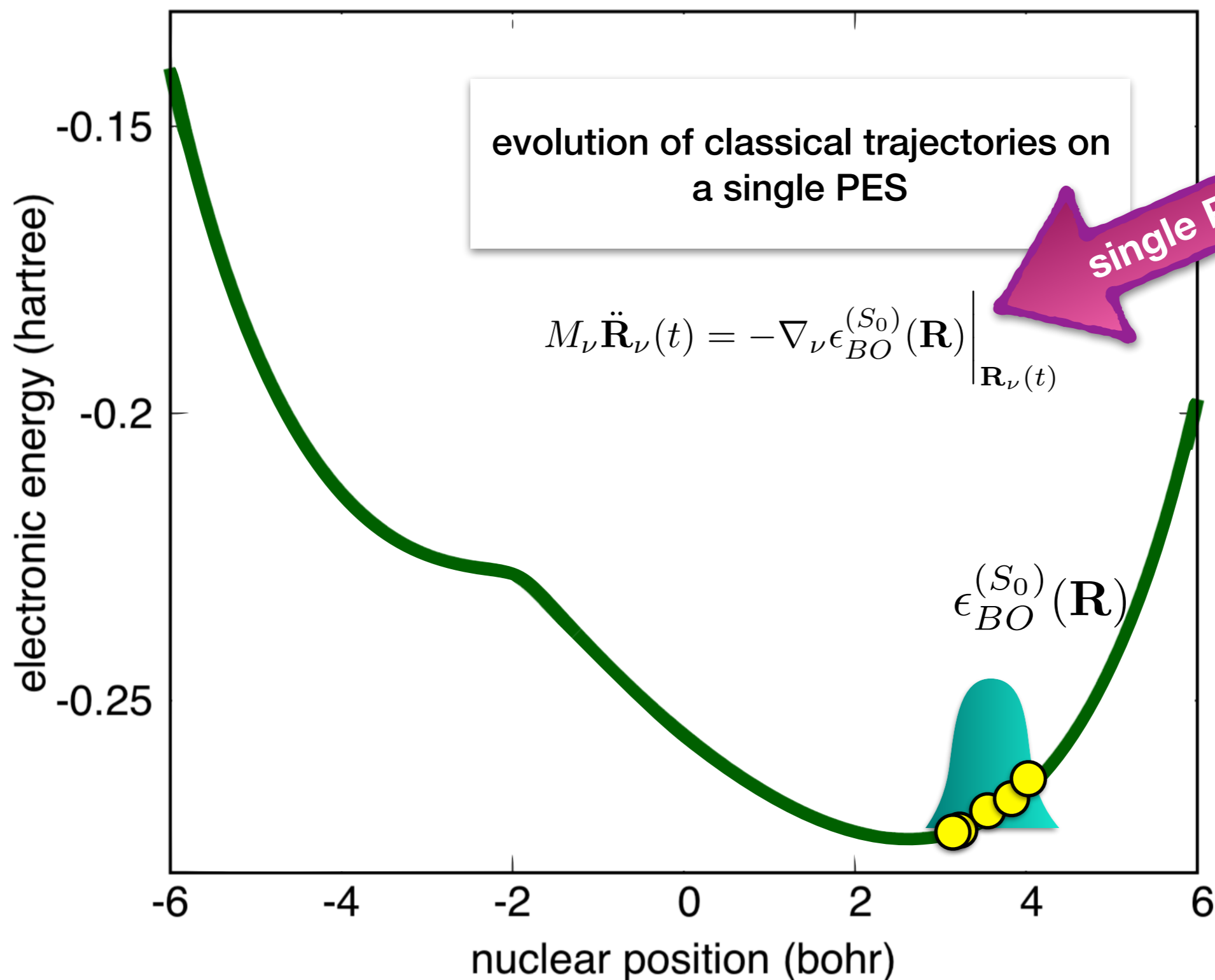
The classical limit in the Born-Oppenheimer approximation

single PESs (BO approximation)

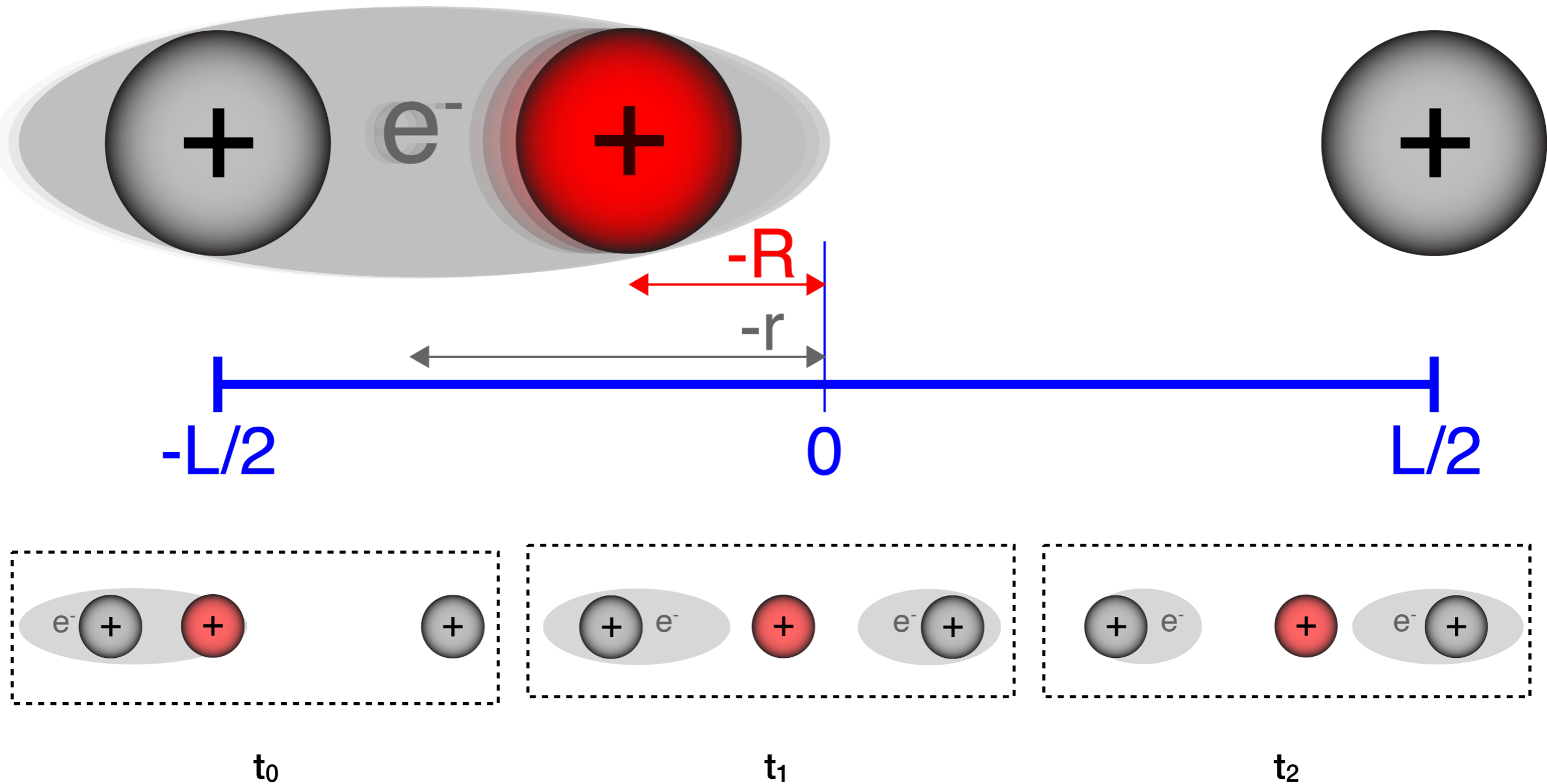


The classical limit in the Born-Oppenheimer approximation

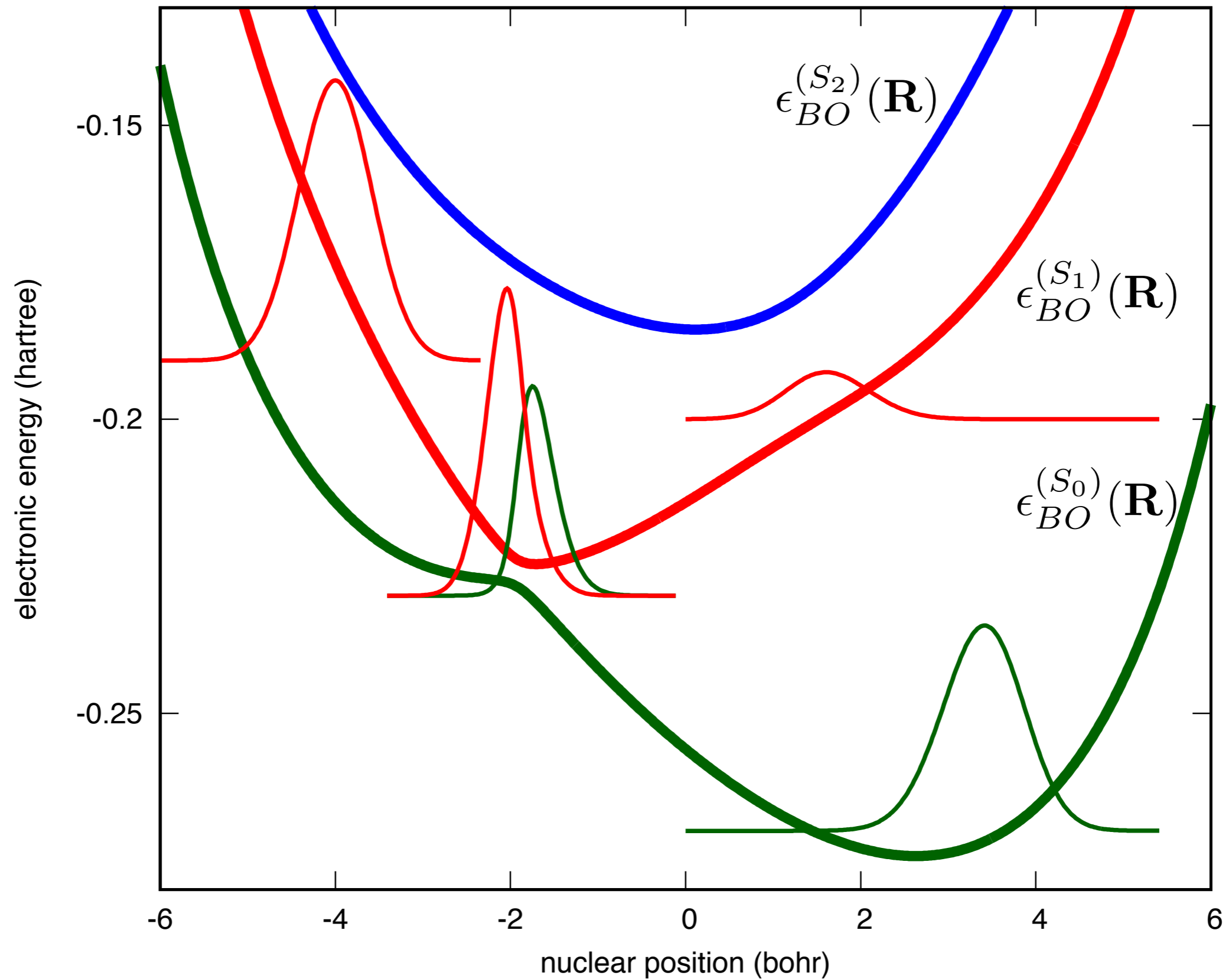
single PESs (BO approximation)



Beyond the Born-Oppenheimer approximation

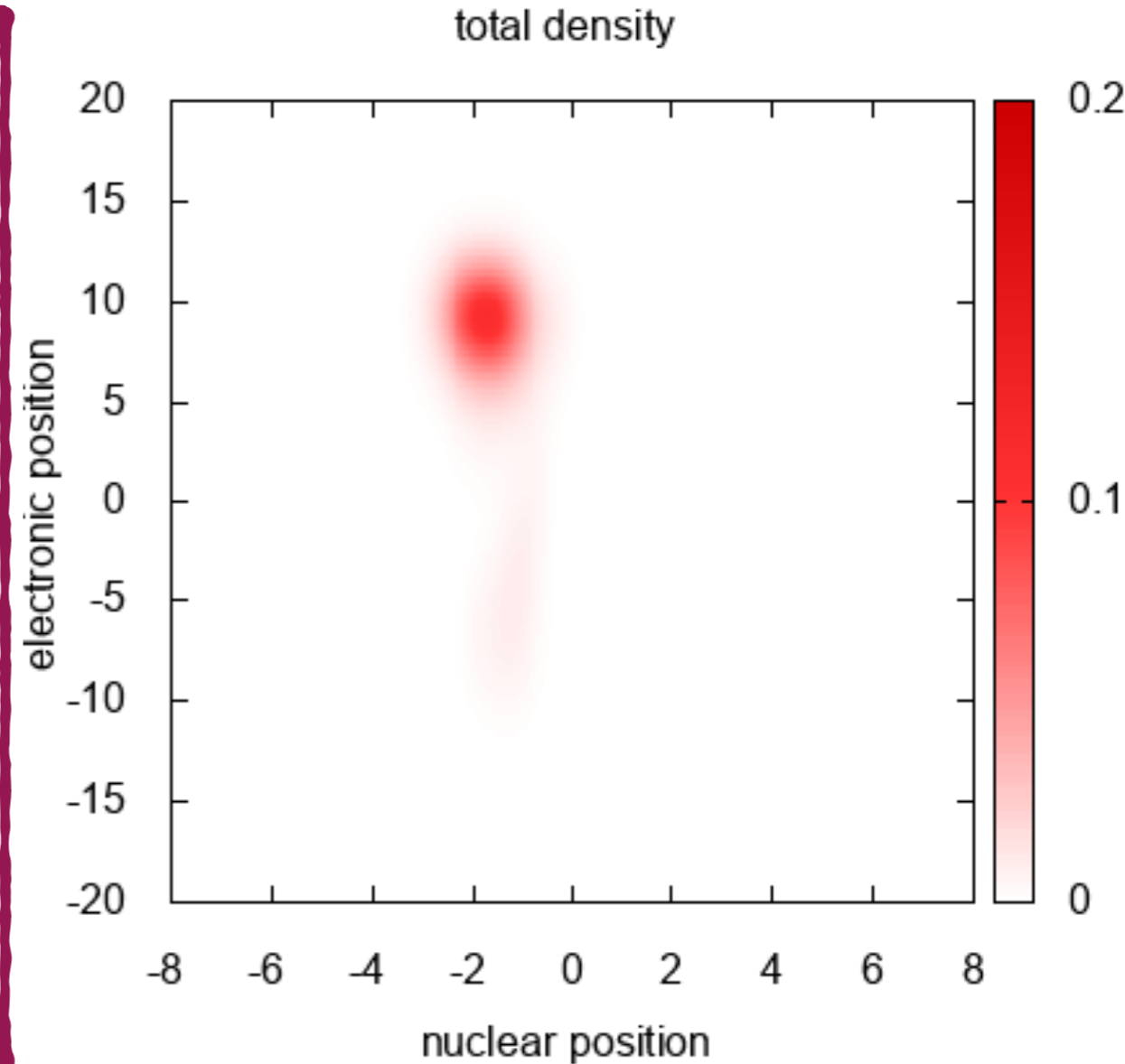
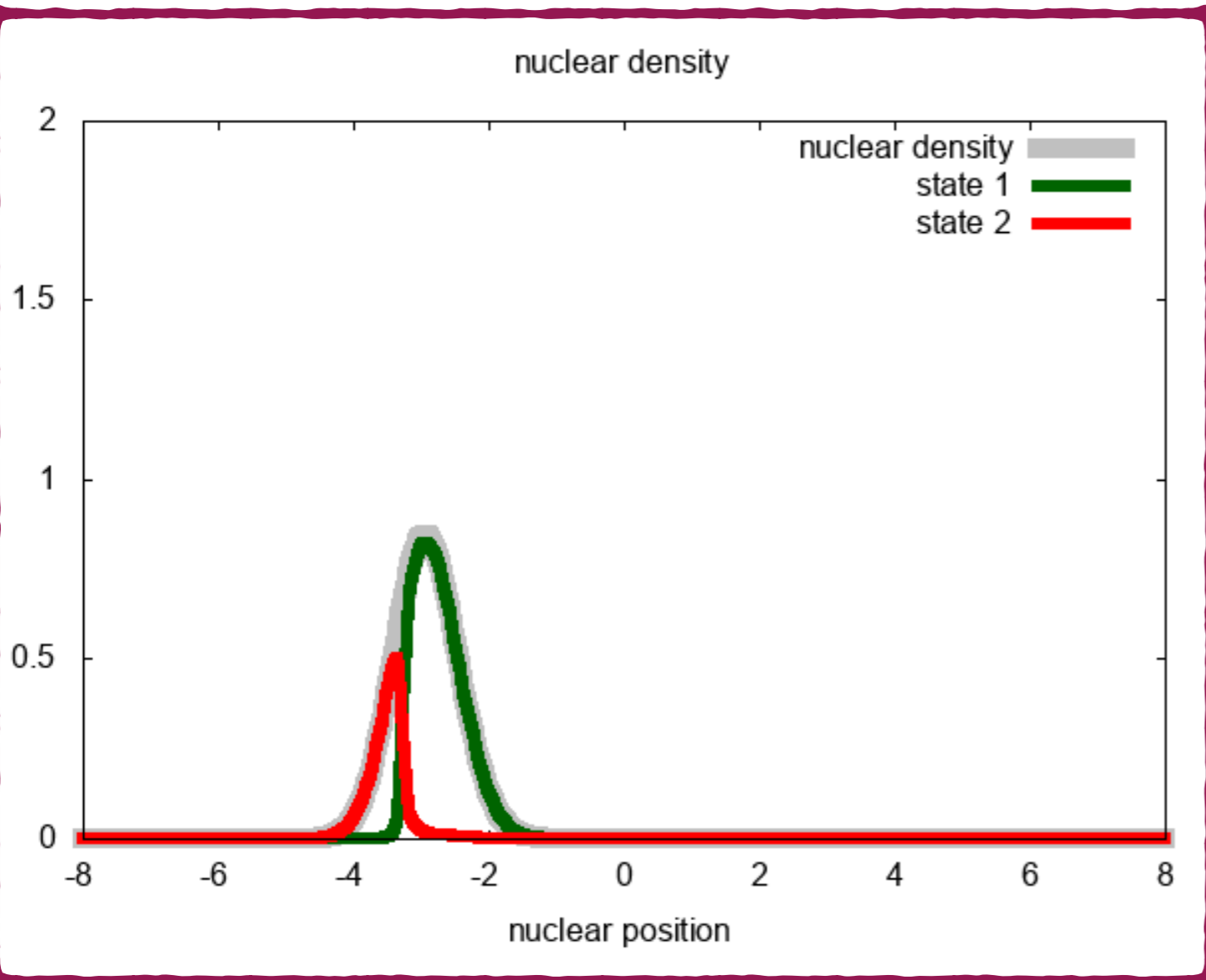


Beyond the Born-Oppenheimer approximation



Beyond the Born-Oppenheimer approximation

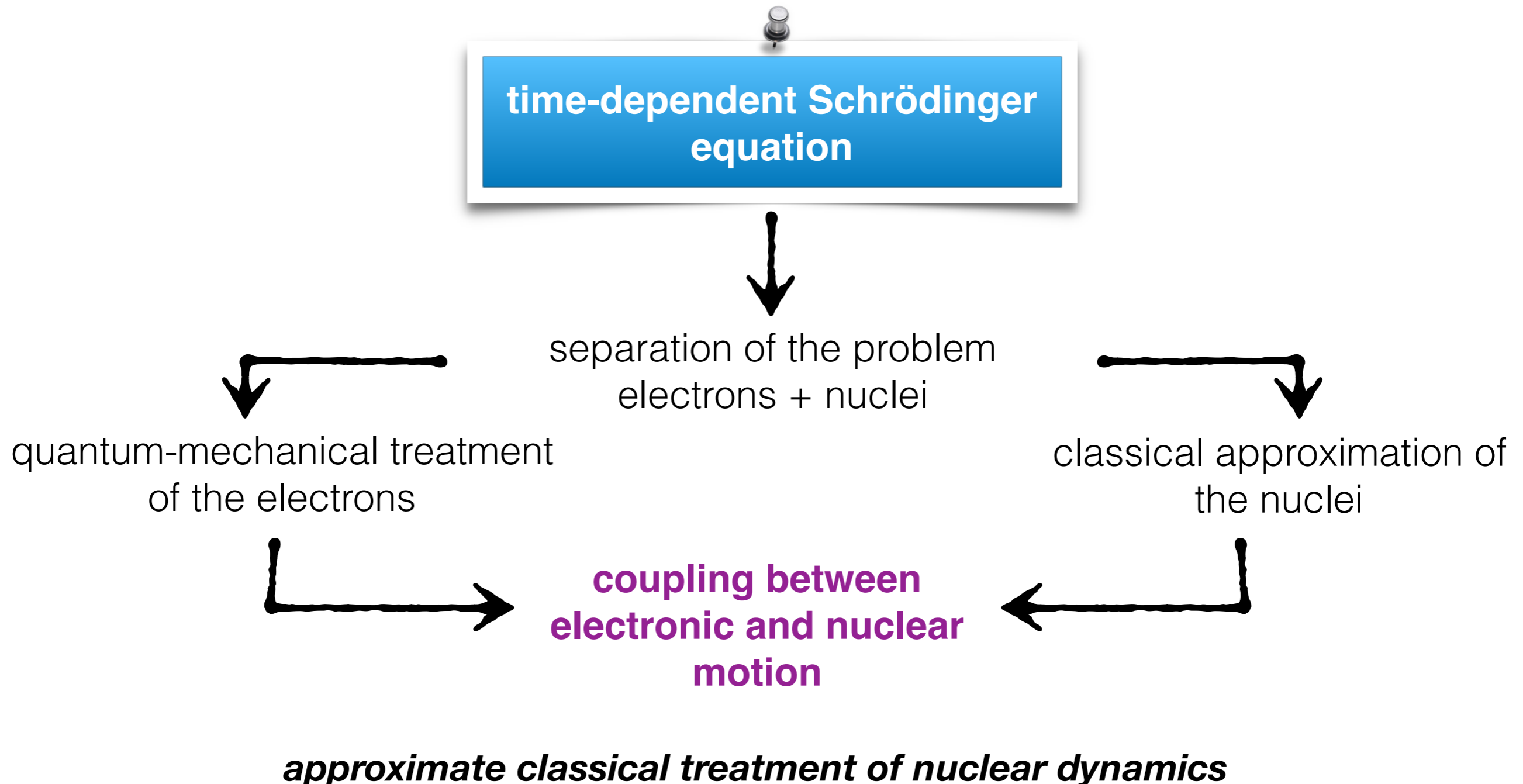
$$i\hbar\partial_t\chi_l(\mathbf{R}, t) = \left[\sum_{\nu} \frac{-\hbar^2\nabla_{\nu}^2}{2M_{\nu}} + \epsilon_{BO}^{(l)}(\mathbf{R}) \right] \chi_l(\mathbf{R}, t) + \sum_k \left(\sum_{\nu} \frac{-i\hbar}{M_{\nu}} \mathbf{d}_{lk,\nu}(\mathbf{R}) \cdot (-i\hbar\nabla_{\nu}) + \frac{-\hbar^2}{2M_{\nu}} D_{lk,\nu}(\mathbf{R}) \right) \chi_k(\mathbf{R}, t)$$



The trajectory-based (quantum-classical) approach

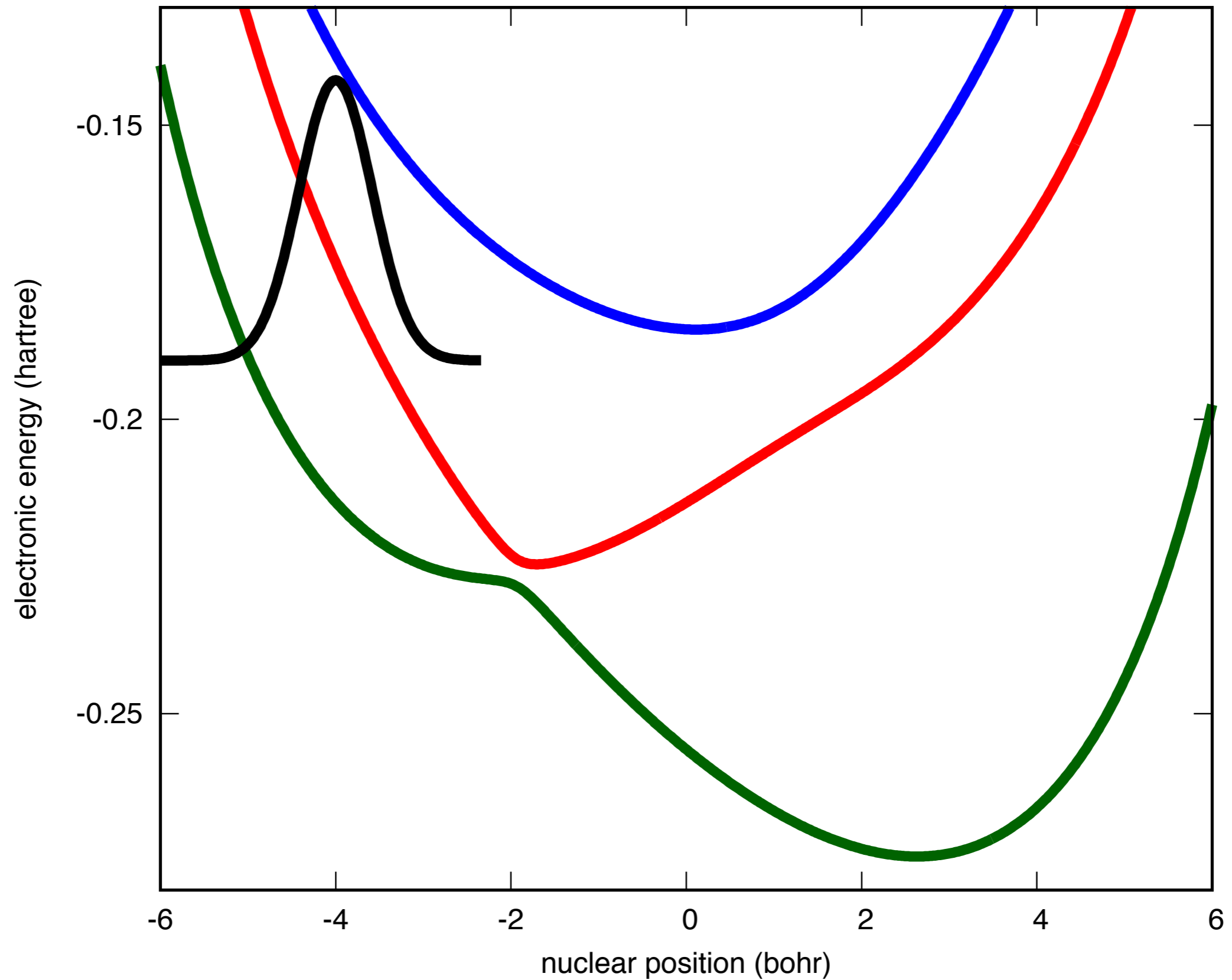
quantum-classical methods

seperation of the problem into two sets of degrees of freedom, electrons and nuclei



(3) Trajectory-based approaches to excited-state molecular dynamics

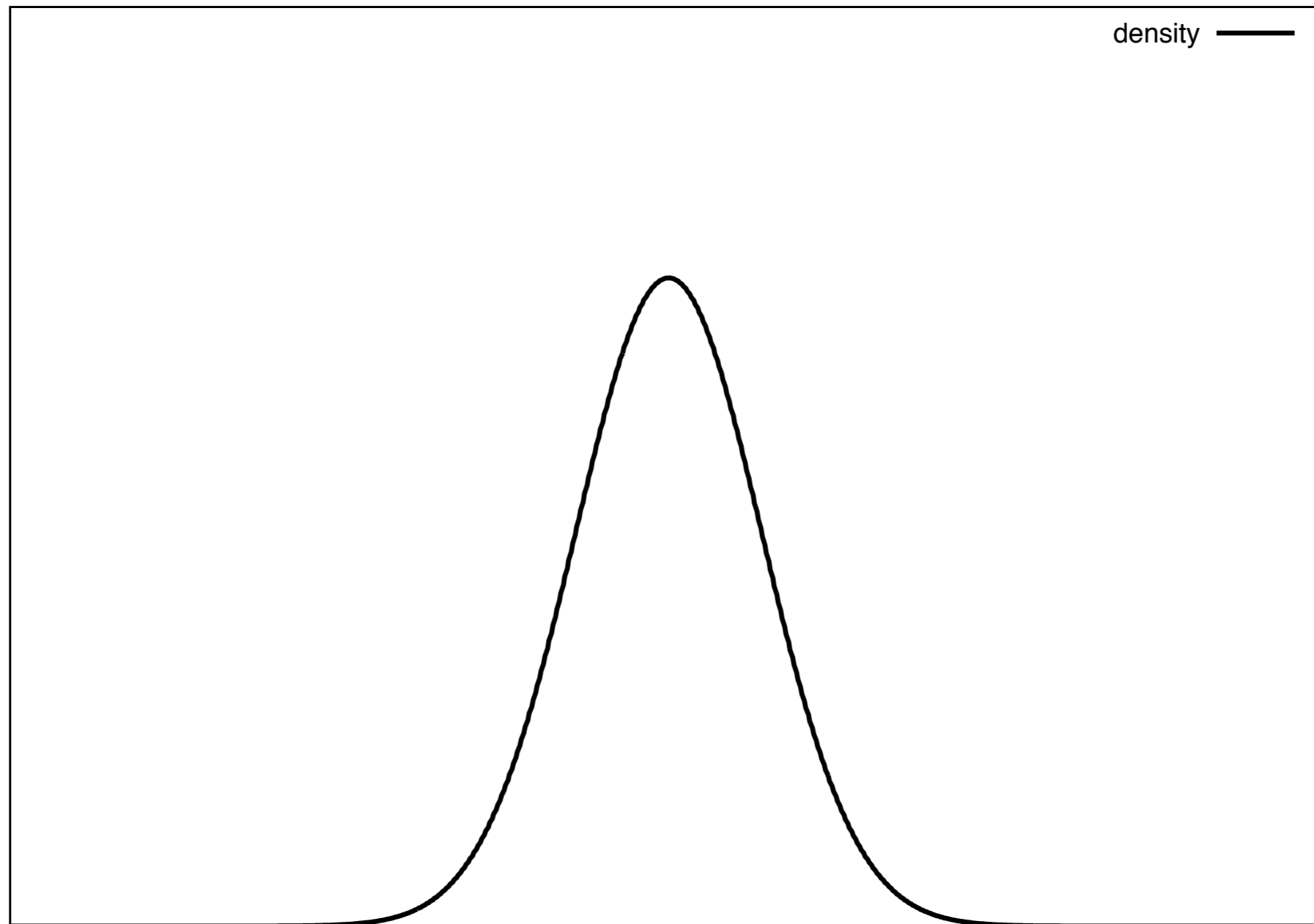
Sampling of the initial conditions



Sampling of the initial conditions

**MODEL
SYSTEM**

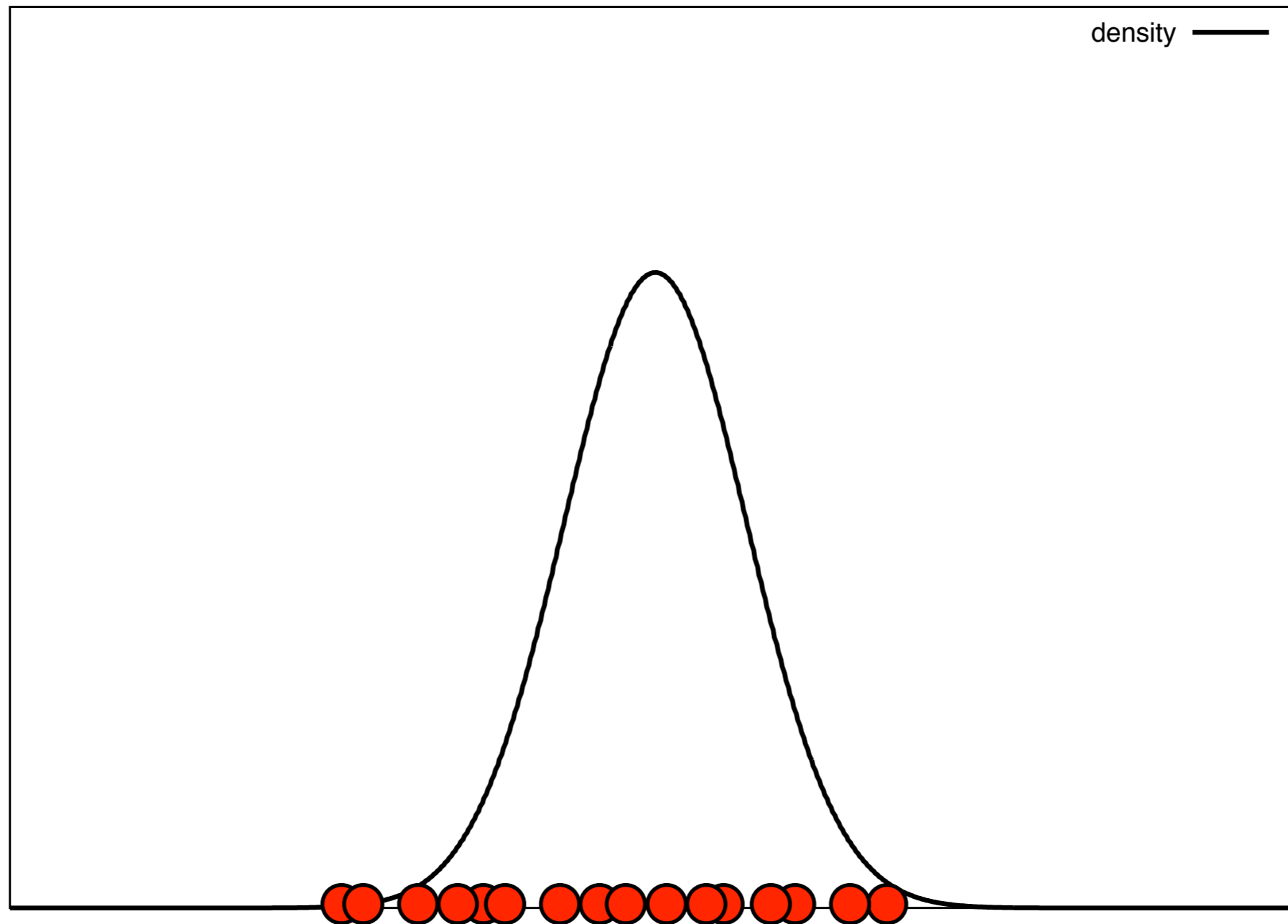
quantum mechanical nuclear distribution



Sampling of the initial conditions

**MODEL
SYSTEM**

quantum mechanical nuclear distribution

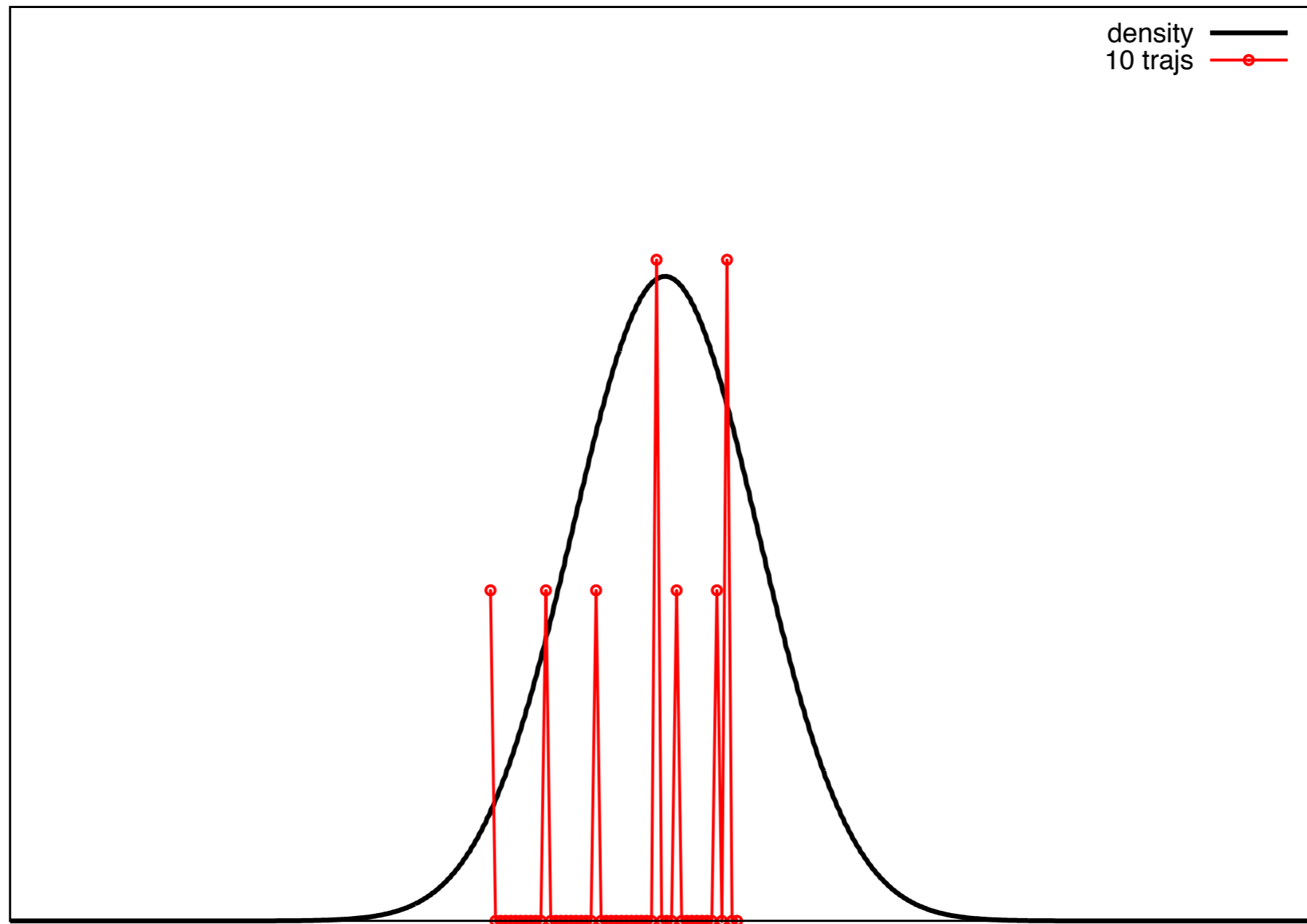


classical nuclear distribution

Sampling of the initial conditions

MODEL
SYSTEM

quantum mechanical nuclear distribution

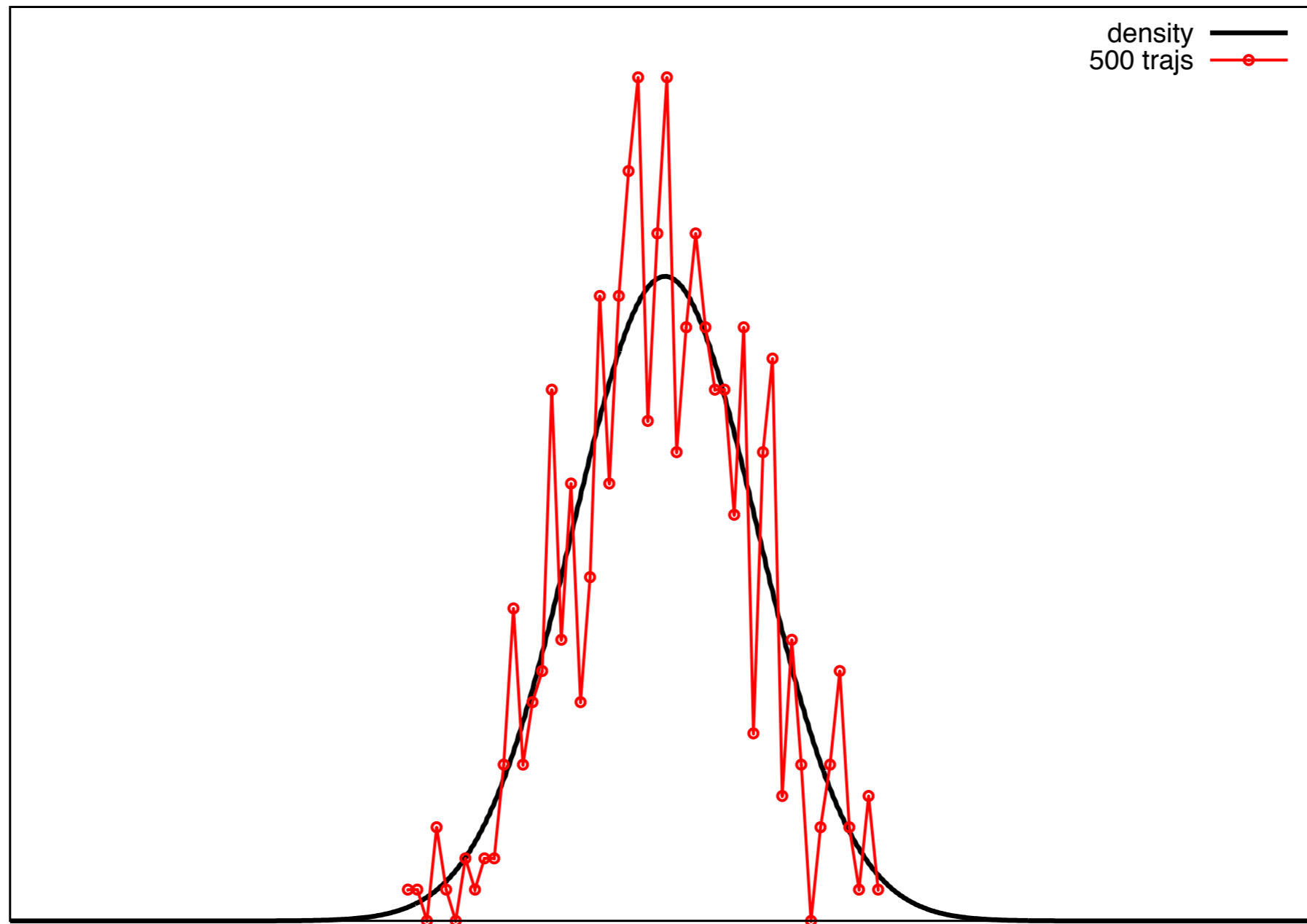


distribution of 10 trajectories

Sampling of the initial conditions

MODEL
SYSTEM

quantum mechanical nuclear distribution

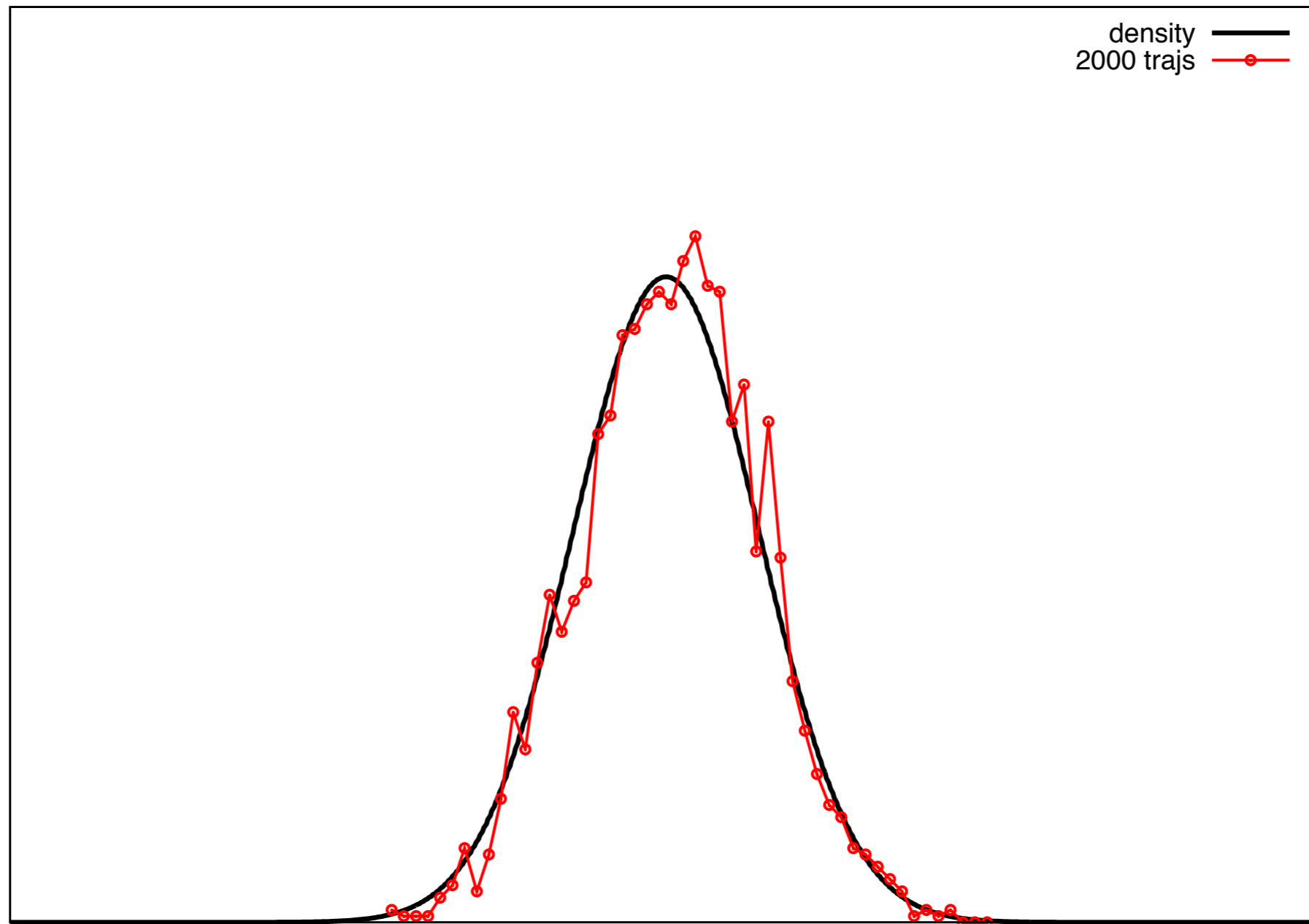


distribution of 500 trajectories

Sampling of the initial conditions

MODEL
SYSTEM

quantum mechanical nuclear distribution

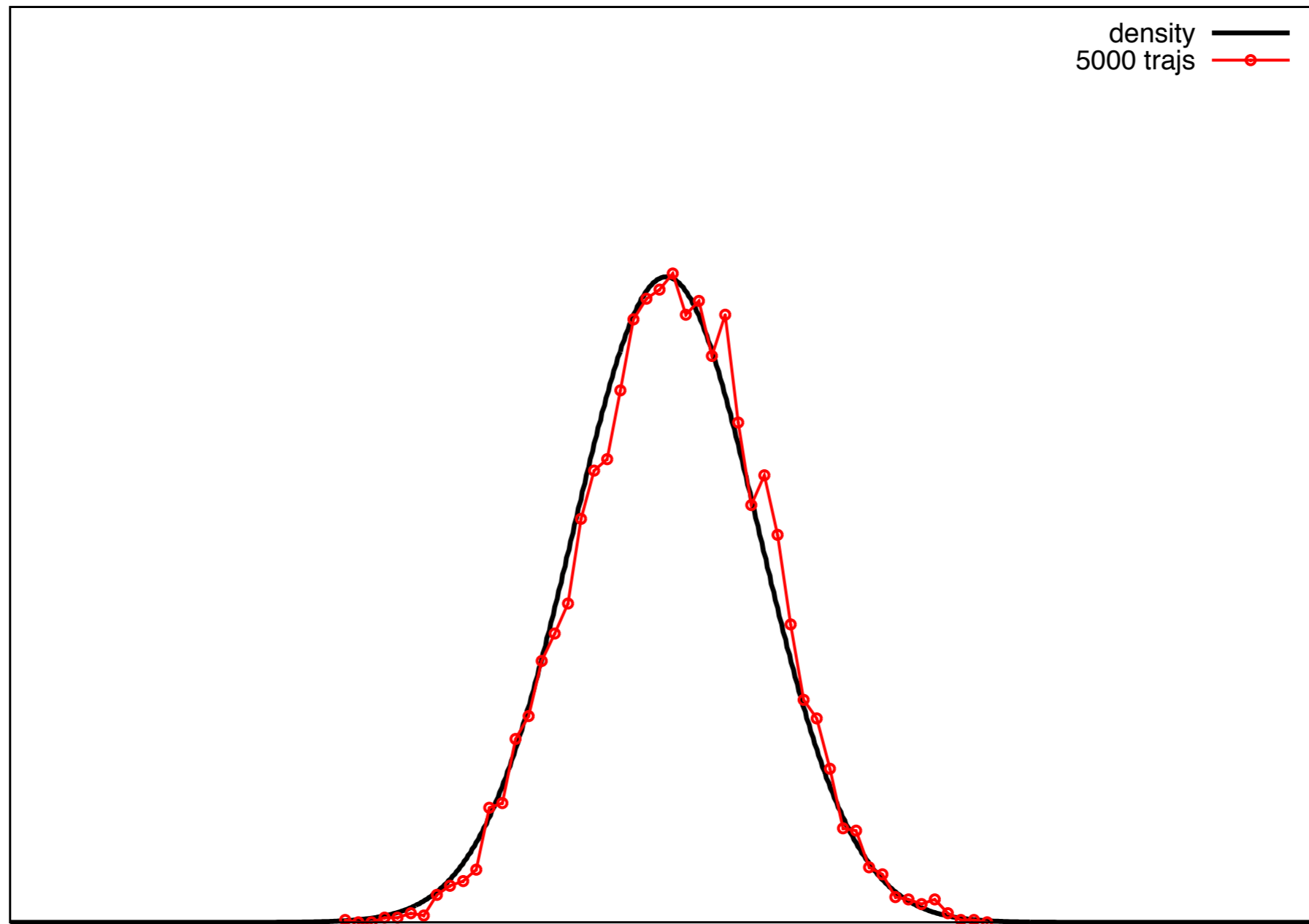


distribution of 2000 trajectories

Sampling of the initial conditions

MODEL
SYSTEM

quantum mechanical nuclear distribution

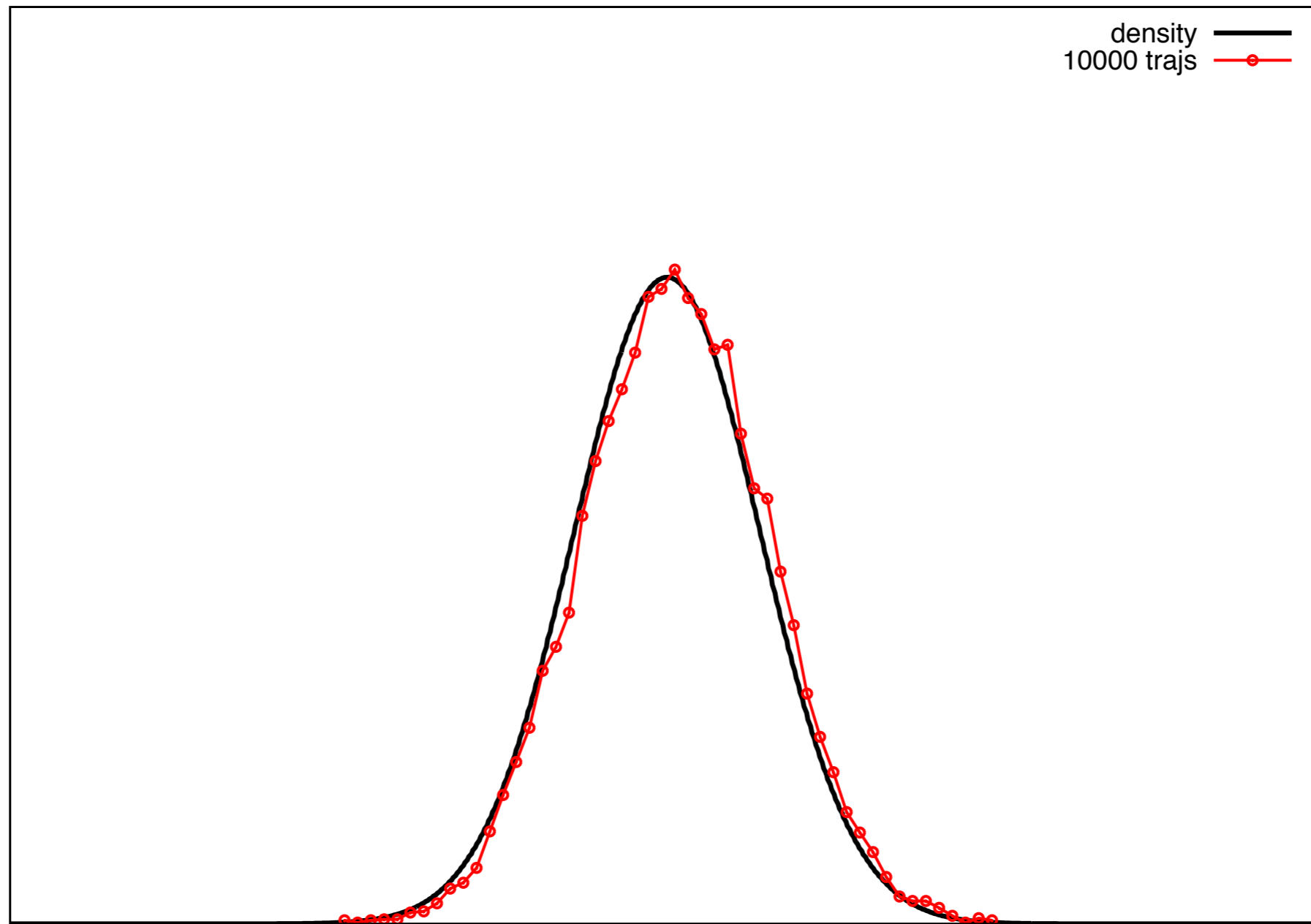


distribution of 5000 trajectories

Sampling of the initial conditions

MODEL
SYSTEM

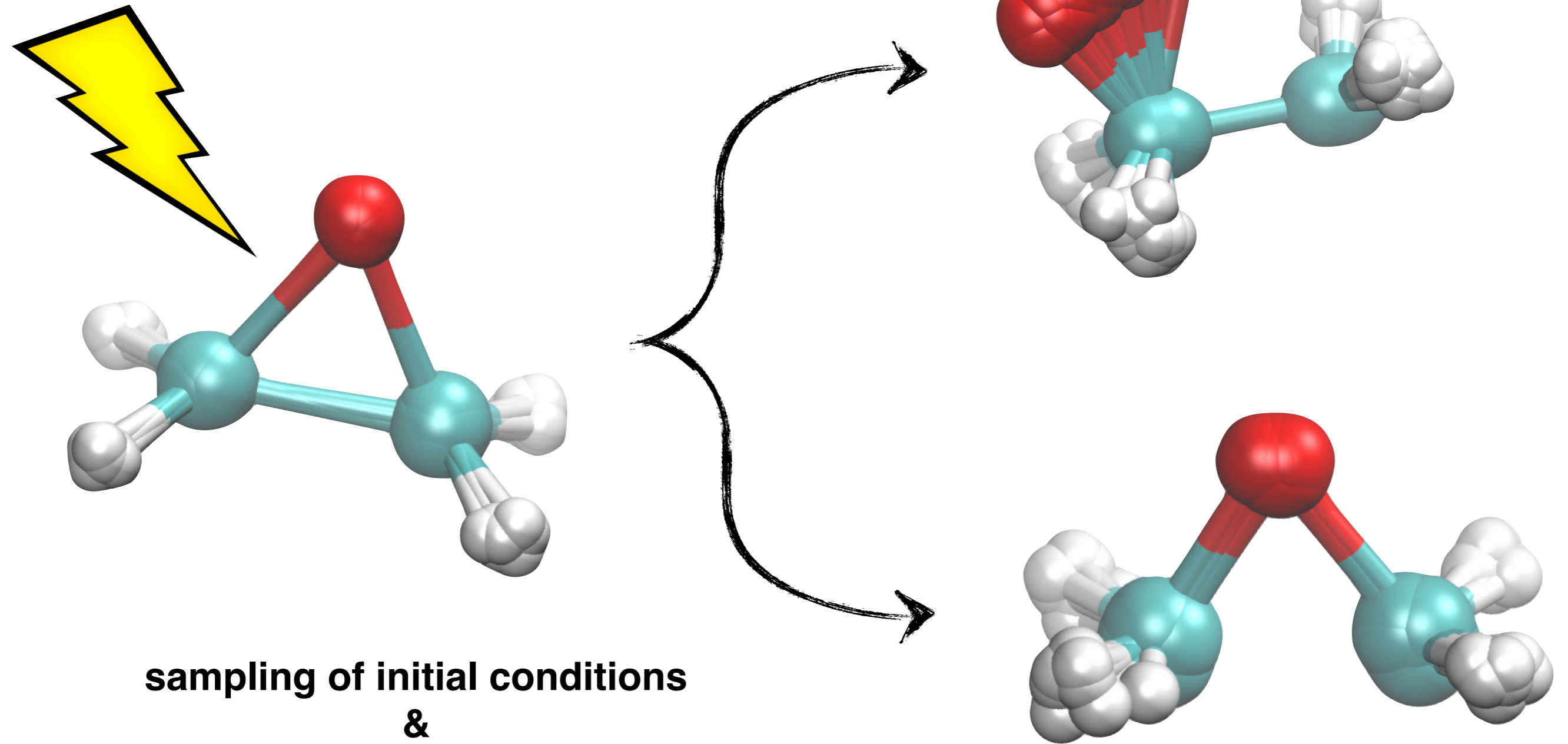
quantum mechanical nuclear distribution



distribution of 10000 trajectories

Sampling of the initial conditions

**REAL
SYSTEM**



**sampling of initial conditions
&
evolution of N copies of the same system**

Sampling of the initial conditions

Wigner distribution

$$\rho(\mathbf{R}, \mathbf{P}) = \frac{1}{(2\pi\hbar)^f} \int d\mathbf{z} \left\langle \mathbf{R} + \frac{\mathbf{z}}{2} \left| \hat{\rho} \right| \mathbf{R} - \frac{\mathbf{z}}{2} \right\rangle e^{-\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{z}}; \quad \hat{\rho} = |\psi\rangle \langle \psi|$$

in the case (and only in the case) of a Gaussian-shaped (initial) nuclear wavefunction

$$\chi(R, t=0) = \left(\frac{1}{\pi\sigma^2} \right)^{1/4} \exp \left[-\frac{(R - R_0)^2}{2\sigma^2} \right] \exp \left[\frac{i}{\hbar} P_0 (R - R_0) \right]$$

Wigner transform

1D example

$$\chi_W(R, P, t=0) = \frac{1}{\pi\hbar} \exp \left[-\frac{(R - R_0)^2}{\sigma^2} \right] \exp \left[-\frac{\sigma^2 (P - P_0)^2}{\hbar^2} \right]$$

Gaussian sampling
around R_0 with variance σ

Gaussian sampling
around P_0 with variance \hbar/σ

Derivation of the Wigner function for a Gaussian

Starting from the expression of the nuclear wavefunction at time $t = 0$

$$\chi(R, t = 0) = \left(\frac{1}{\pi\sigma^2} \right)^{1/4} \exp \left[-\frac{(R - R_0)^2}{2\sigma^2} \right] \exp \left[\frac{i}{\hbar} P_0 (R - R_0) \right]$$

we insert it into the definition of the Wigner function

$$\begin{aligned} \chi_W(R, P, t = 0) &= \frac{1}{(2\pi\hbar)} \int dz \chi\left(R + \frac{z}{2}, t = 0\right) \chi^*\left(R - \frac{z}{2}, t = 0\right) e^{-\frac{i}{\hbar} P z} \\ &= \frac{1}{(2\pi\hbar)} \sqrt{\frac{1}{\pi\sigma^2}} e^{-\frac{(R-R_0)^2}{\sigma^2}} \int dz e^{-\frac{z^2}{4\sigma^2} - \frac{i}{\hbar} (P - P_0) z}. \end{aligned}$$

Completing the square in the exponent of the integrand function, i.e., $-\frac{z^2}{4\sigma^2} - \frac{i}{\hbar} (P - P_0) z - \frac{\sigma^2 (P - P_0)^2}{\hbar^2}$,

$$\chi_W(R, P, t = 0) = \frac{1}{\pi\hbar} \exp \left[-\frac{(R - R_0)^2}{\sigma^2} \right] \exp \left[-\frac{\sigma^2 (P - P_0)^2}{\hbar^2} \right].$$

Sampling of the initial conditions

The Wigner distribution...

- is a one-to-one transformation from a quantum-mechanical distribution in configuration space to a quantum-mechanical distribution in phase space
 - * *possibility to account for quantum effects, e.g., zero-point energy, in the distribution of initial conditions*
- is a Gaussian distribution in phase space only for a Gaussian distribution in configuration space
 - * *sampling easy to implement: Box-Muller transform to generate independent normally-distributed numbers (i.e., initial conditions) starting from uniformly-distributed random numbers; normal modes to determine the width of the distribution.*
- presents negative regions in general cases, thus non-standard sampling techniques are required
- is normally used in the harmonic approximation

Sampling of the initial conditions

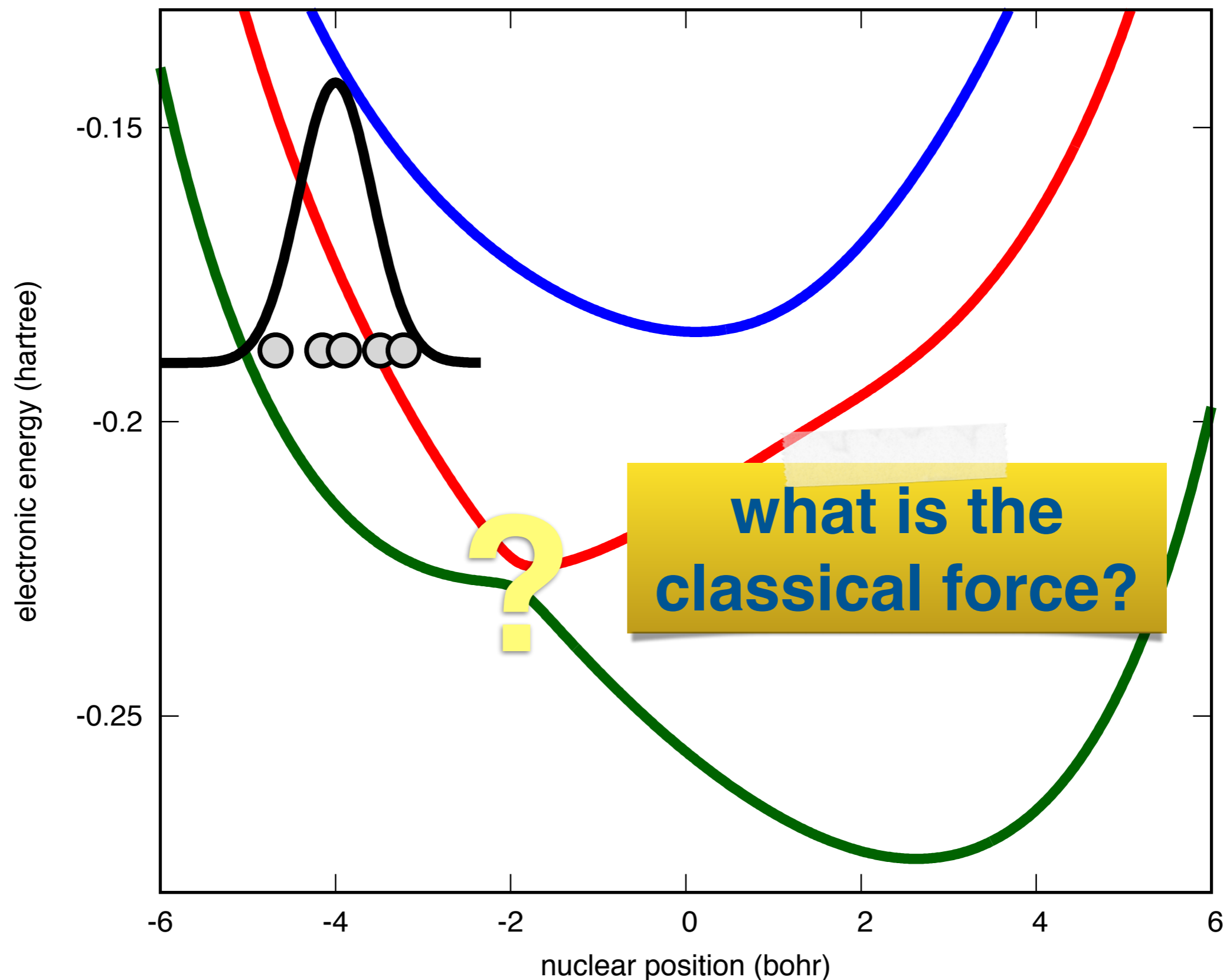
The classical Boltzmann distribution...

$$\rho(R, P) \propto \exp \left[-\frac{H(R, P)}{k_B T} \right]$$

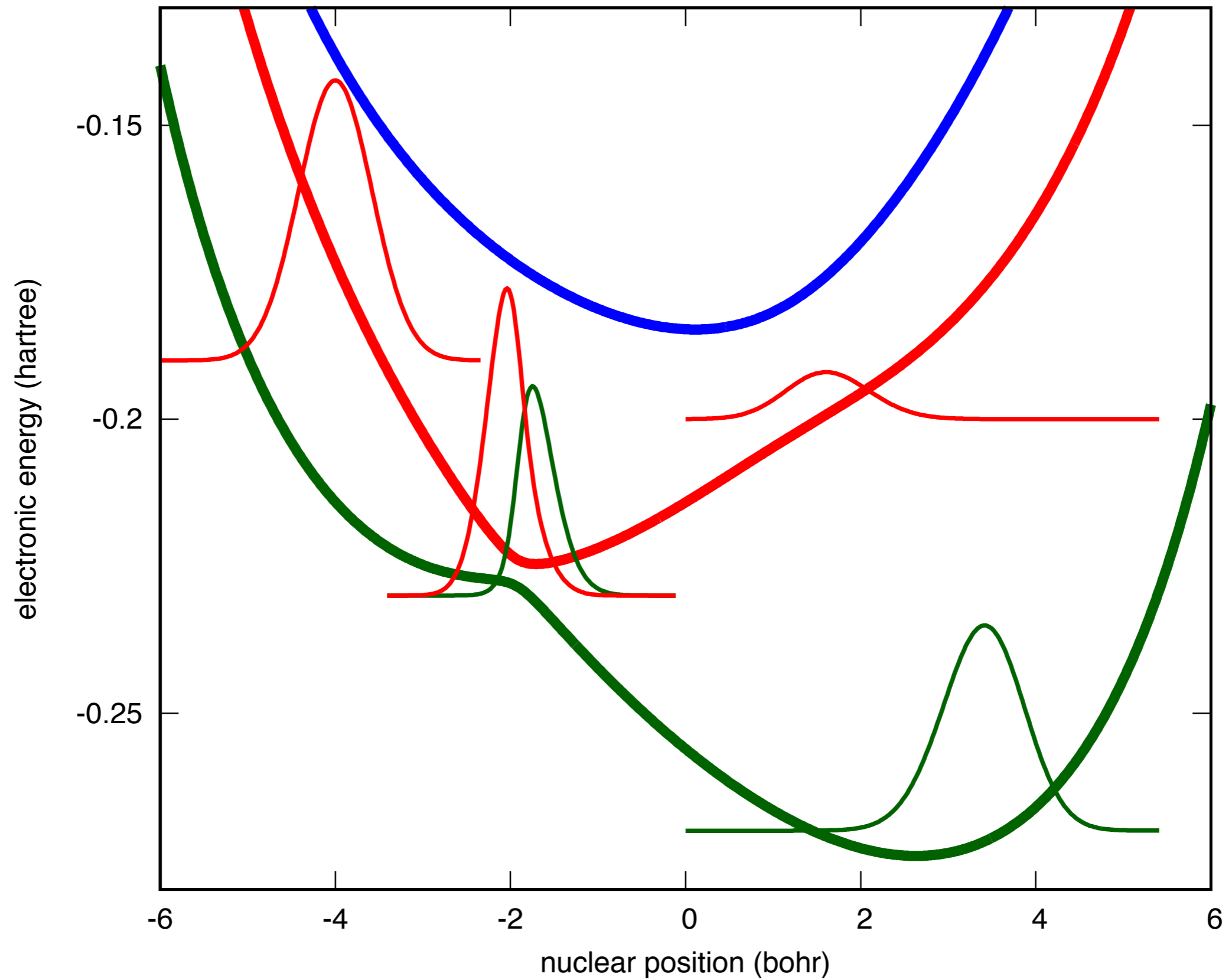
$$H(R, P) = \frac{P^2}{2M} + V(R) \longrightarrow \text{with } V(R) = \epsilon_{BO}^{(S_0)}(R)$$

- can be sampled via *ab initio* molecular dynamics in the electronic ground state in the NVT ensemble
- can be sampled via Monte Carlo methods
- does not account for quantum effects
- can account for anharmonicity in the potential energy surface

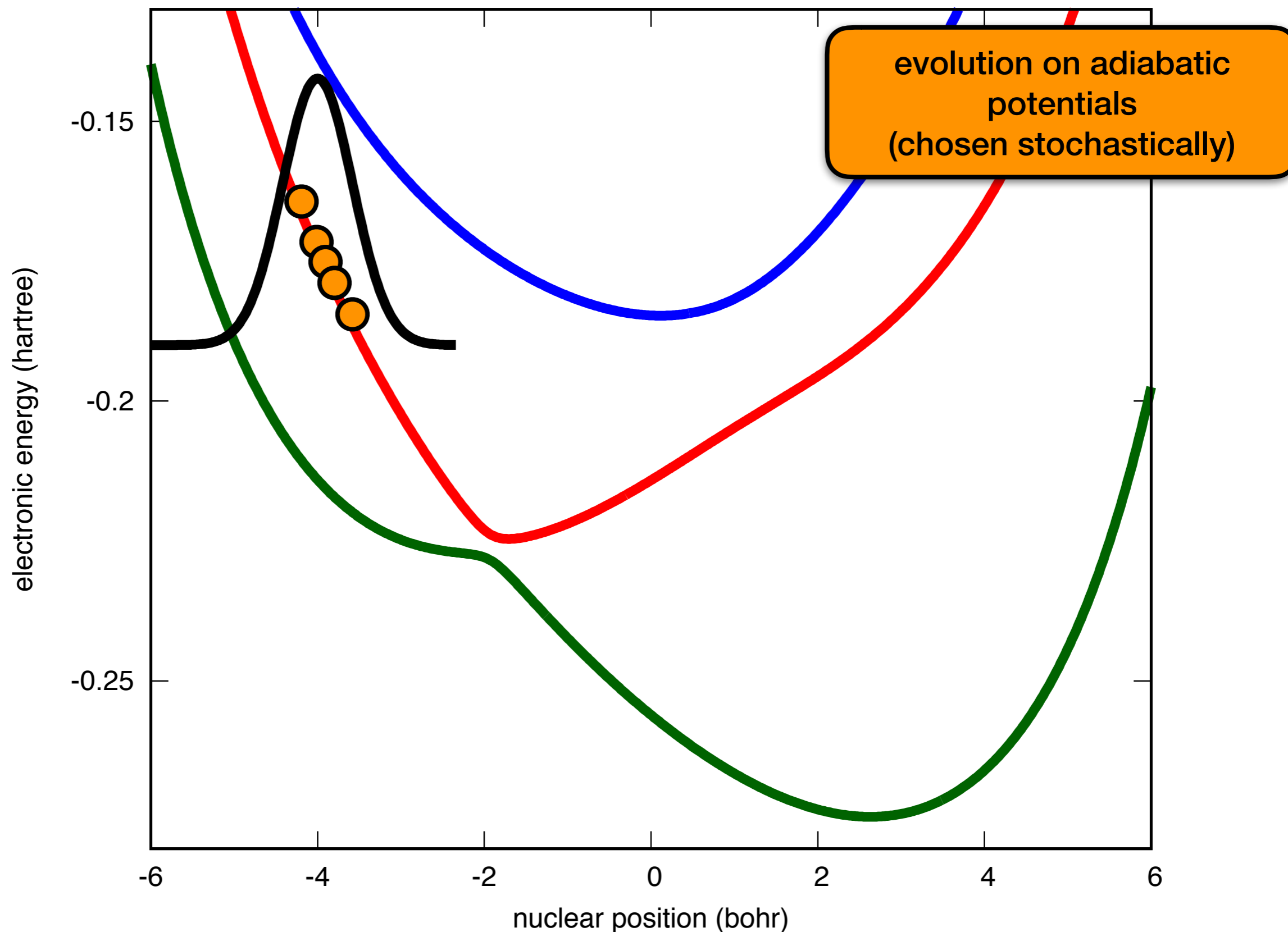
The concept of classical force in nonadiabatic dynamics



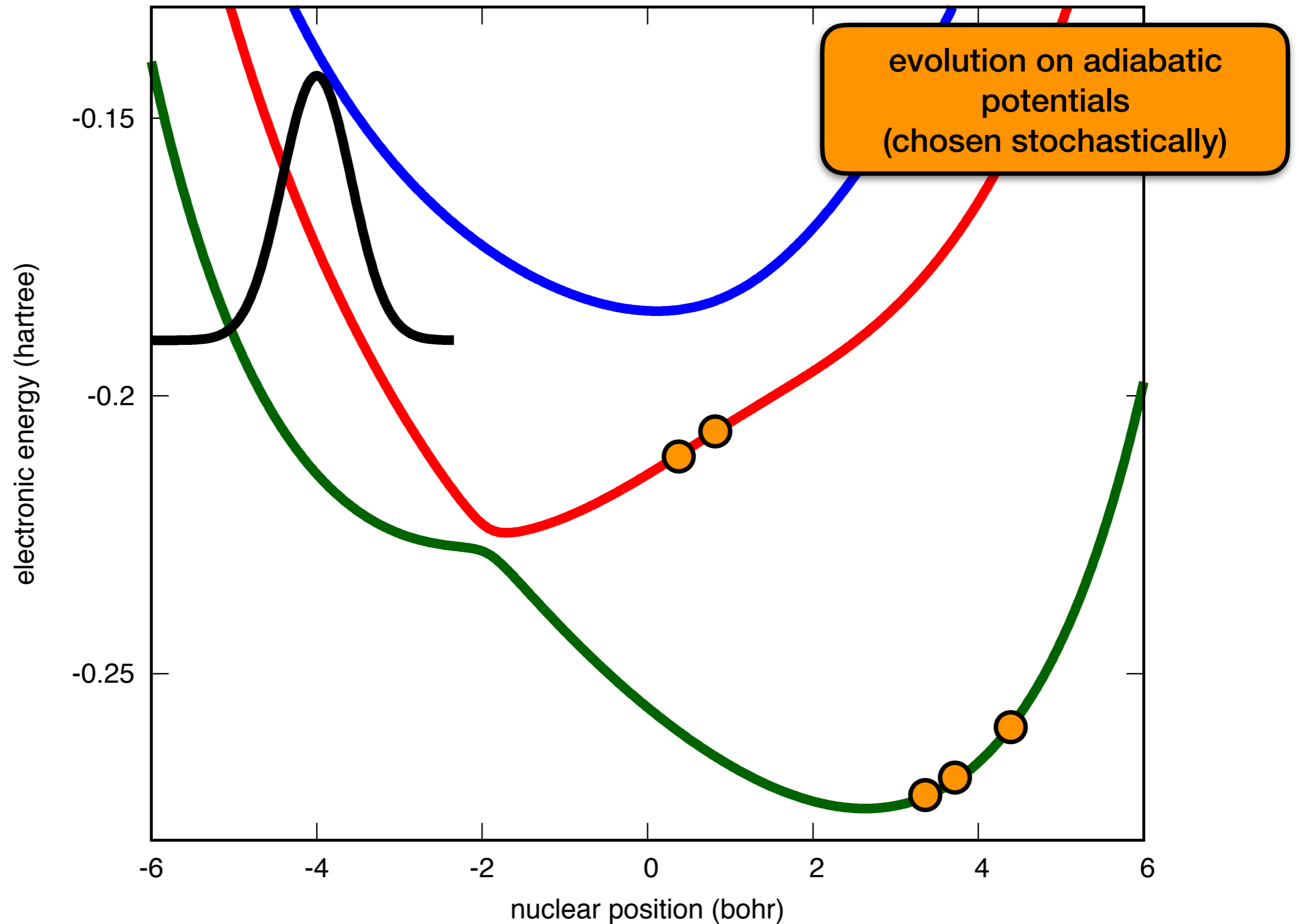
Trajectory surface hopping



Trajectory surface hopping



Trajectory surface hopping



Trajectory surface hopping

The ideas behind the trajectory surface hopping algorithm...

- the nuclei evolve along classical trajectories, therefore an implicit time dependence (via the trajectory) appears in the electronic Schrödinger equation
- we suppose that the electronic equation is “given” (see next slide), and the coupling to the nuclei is simply expressed via the dependence of the electronic Hamiltonian on the trajectory
- a nonadiabatic event, i.e., what happens at an avoided crossing or conical intersection, is represented as a trajectory jump
- the “jump” is a stochastic event that takes place according to some probability (we will see in the following the fewest-switches procedure)

Trajectory surface hopping

TSH algorithm: the nuclear evolution equations

$$\dot{\mathbf{R}}_{cl,\nu}(t) = \frac{\mathbf{P}_{cl,\nu}(t)}{M_\nu}$$

$$\dot{\mathbf{P}}_{cl,\nu}(t) = \mathbf{F}_\nu^{\text{TSH}}(t) = -\nabla_\nu \epsilon_{BO}^* \left(\mathbf{R}_{cl}(t) \right)$$

*at every time step the state * has to be selected: for instance, if the trajectory at time t is evolving on the surface k, the probability to jump to a state l is evaluated from*

$$\mathcal{P}_{k \rightarrow l}(t, t + dt) = \max \left[0, \frac{-2 dt \Re[C_k^*(t)C_l(t)]}{|C_k(t)|^2} \sum_\nu \dot{\mathbf{R}}_{cl,\nu}(t) \cdot \mathbf{d}_{lk,\nu}(\mathbf{R}_{cl}(t)) \right]$$

- velocity rescaling: the discontinuity in the potential energy after a jump has occurred has to be “balanced” by a discontinuity in the kinetic energy to impose energy conservation along a trajectory
- frustrated hop: if a trajectory does not have enough kinetic energy for a jump towards a potential surface that is higher in energy, the hop does not occur

Trajectory surface hopping

TSH algorithm: the electronic evolution equation

(1) introduce the electronic Schrödinger equation as

$$i\hbar\partial_t\Phi(\mathbf{r}, \mathbf{R}_{cl}(t), t) = \hat{H}_{BO}(\mathbf{r}, \mathbf{R}_{cl}(t))\Phi(\mathbf{r}, \mathbf{R}_{cl}(t), t)$$

(2) Born-Huang-like expansion of the electronic wavefunction

$$\Phi(\mathbf{r}, \mathbf{R}_{cl}(t), t) = \sum_k C_k(t)\phi_{\mathbf{R}_{cl}(t)}^{(k)}(\mathbf{r})$$

(3) eigenvalues of the electronic Hamiltonian

$$\left[\hat{T}_e(\mathbf{r}) + \hat{V}(\mathbf{r}, \mathbf{R}_{cl}(t))\right]\phi_{\mathbf{R}_{cl}(t)}^{(k)}(\mathbf{r}) = \epsilon_{BO}^{(k)}(\mathbf{R}_{cl}(t))\phi_{\mathbf{R}_{cl}(t)}^{(k)}(\mathbf{r})$$

(4) equations for the expansion coefficients

$$\dot{C}_k(t) = -\frac{i}{\hbar}\epsilon_{BO}^{(k)}(\mathbf{R}_{cl}(t))C_k(t) - \sum_l \dot{\mathbf{R}}_{cl}(t) \cdot \mathbf{d}_{kl}(\mathbf{R}_{cl}(t))C_l(t)$$

Derivation of the expression of the electronic evolution equation

Given the expression of the electronic wavefunction in the adiabatic basis $\Phi(r, R_{cl}(t), t) = \sum_k C_k(t) \phi_{R_{cl}(t)}^{(k)}(r)$, the electronic time-dependent Schrödinger equation is

$$i\hbar \partial_t \sum_k C_k(t) \phi_{R_{cl}(t)}^{(k)}(r) = \left(\hat{T}_e(r) + \hat{V}(r, R_{cl}(t)) \right) \sum_k C_k(t) \phi_{R_{cl}(t)}^{(k)}(r).$$

The action of the time derivative on the left-hand side gives

$$i\hbar \partial_t \sum_k C_k(t) \phi_{R_{cl}(t)}^{(k)}(r) = i\hbar \sum_k \dot{C}_k(t) \phi_{R_{cl}(t)}^{(k)}(r) + i\hbar \sum_k C_k(t) \dot{R}_{cl}(t) \partial_R \phi_{R_{cl}(t)}^{(k)}(r)$$

where the chain rule $\partial_t = \dot{R}_{cl}(t) \partial_R$ has been used in the second term on the right-hand side. When projecting the electronic time-dependent Schrödinger equation on $\phi_{R_{cl}(t)}^{(l)}(r)$, one gets

$$i\hbar \dot{C}_l(t) + i\hbar \sum_k C_k(t) \dot{R}_{cl}(t) \left\langle \phi_{R_{cl}(t)}^{(l)} \left| \partial_R \phi_{R_{cl}(t)}^{(k)} \right. \right\rangle_r = C_l(t) \epsilon_{BO}^{(l)}(R_{cl}(t)),$$

and rearranging

$$\dot{C}_l(t) = -\frac{i}{\hbar} \epsilon_{BO}^{(l)}(R_{cl}(t)) C_l(t) - i\hbar \sum_k C_k(t) \dot{R}_{cl}(t) d_{lk}(R_{cl}(t)).$$

Trajectory surface hopping

What do we need from electronic-structure theory?

$$\mathbf{F}_{\nu}^{\text{TSH}}(t) = -\nabla_{\nu} \epsilon_{BO}^* \left(\mathbf{R}_{cl}(t) \right)$$

$$\mathcal{P}_{k \rightarrow l}(t, t + dt) = \max \left[0, \frac{-2 dt \Re[C_k^*(t) C_l(t)]}{|C_k(t)|^2} \sum_{\nu} \dot{\mathbf{R}}_{cl, \nu}(t) \cdot \mathbf{d}_{lk, \nu}(\mathbf{R}_{cl}(t)) \right]$$

$$\dot{C}_k(t) = -\frac{i}{\hbar} \epsilon_{BO}^{(k)}(\mathbf{R}_{cl}(t)) C_k(t) - \sum_{\nu} \dot{\mathbf{R}}_{cl, \nu}(t) \cdot \sum_l \mathbf{d}_{kl, \nu}(\mathbf{R}_{cl}(t)) C_l(t)$$

ENERGIES, GRADIENTS, NONADIABATIC COUPLINGS
at the instantaneous (classical) nuclear positions

on-the-fly dynamics

we do not need to know electronic properties everywhere in nuclear configuration space

Trajectory surface hopping

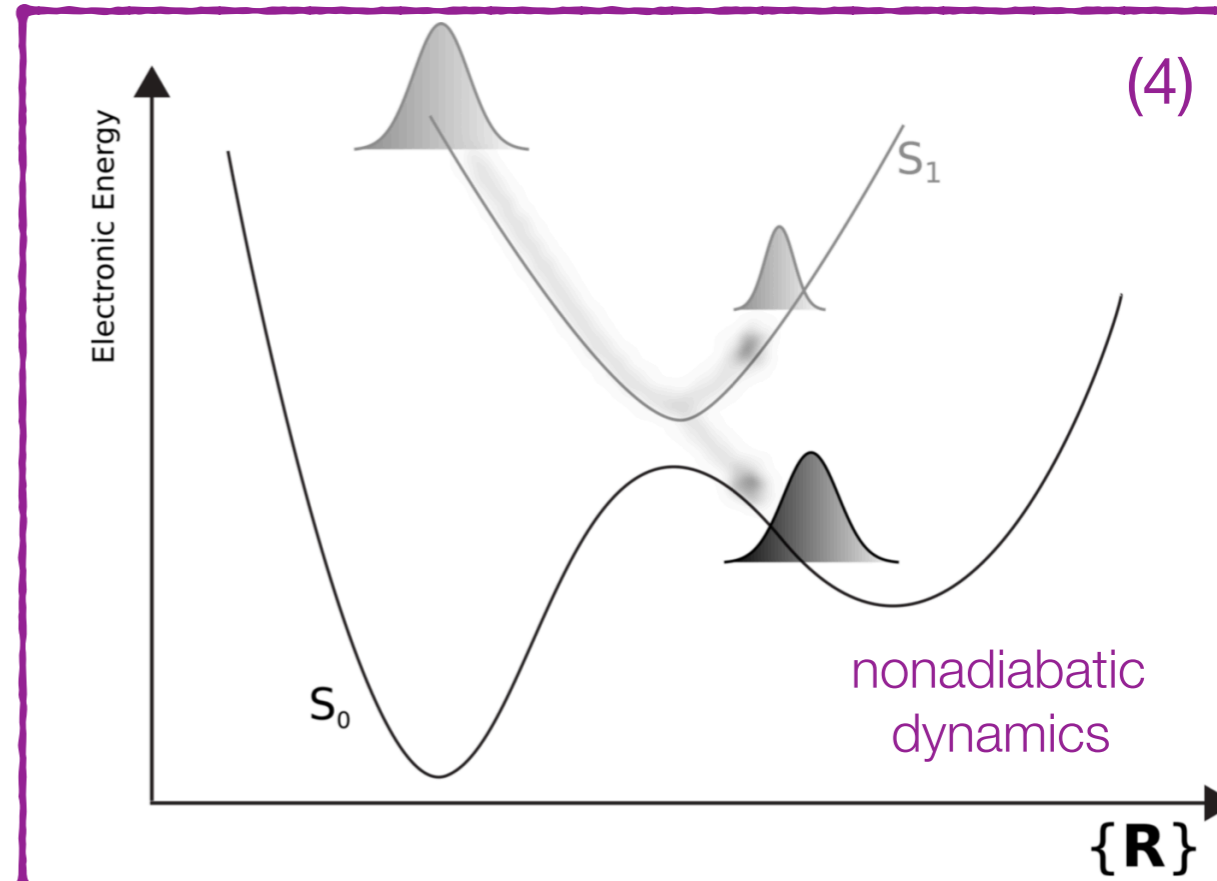
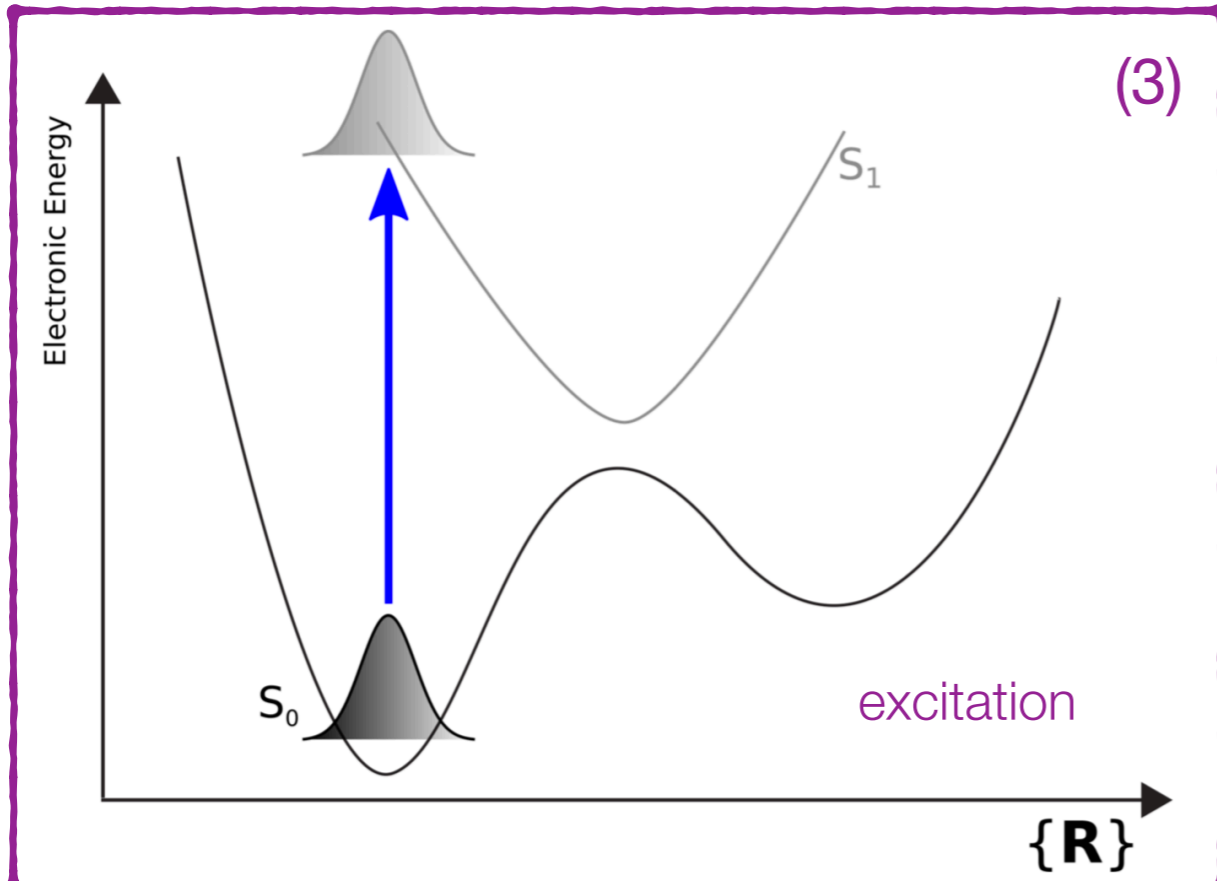
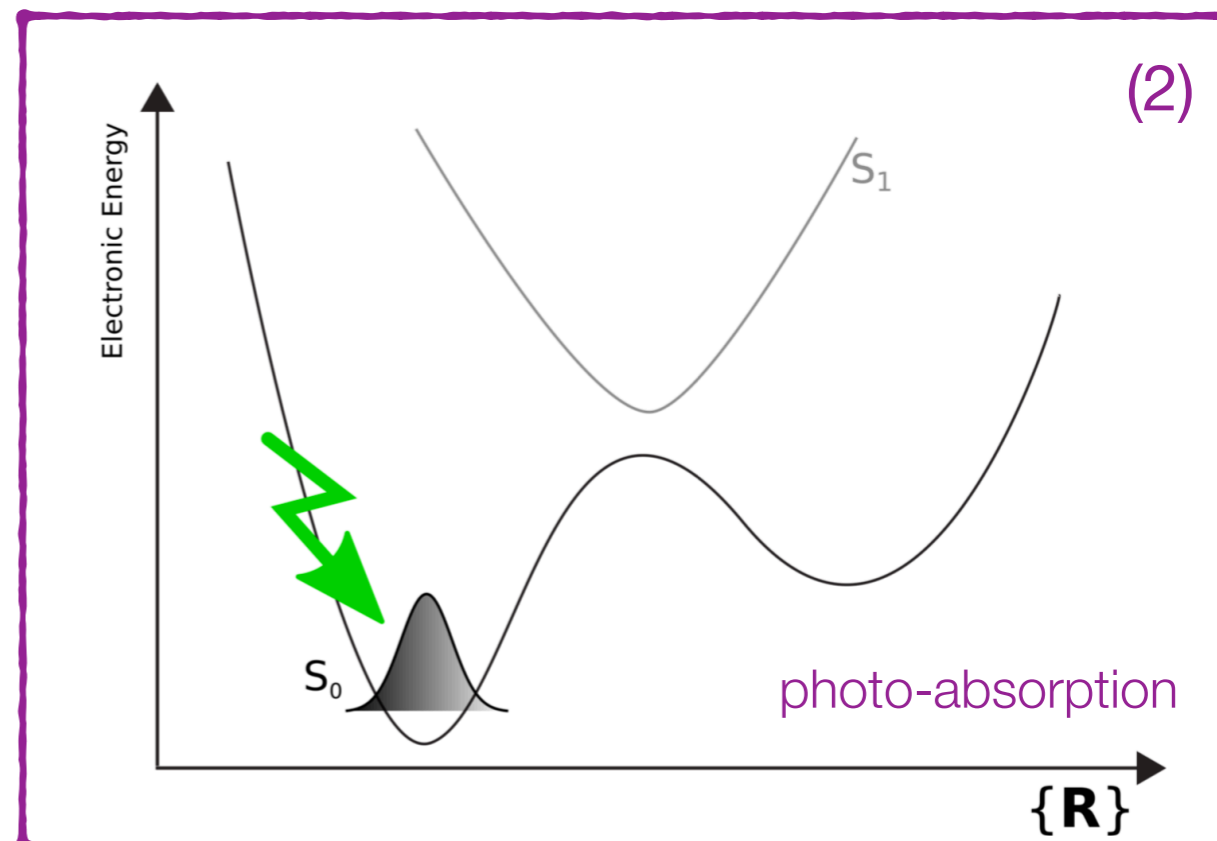
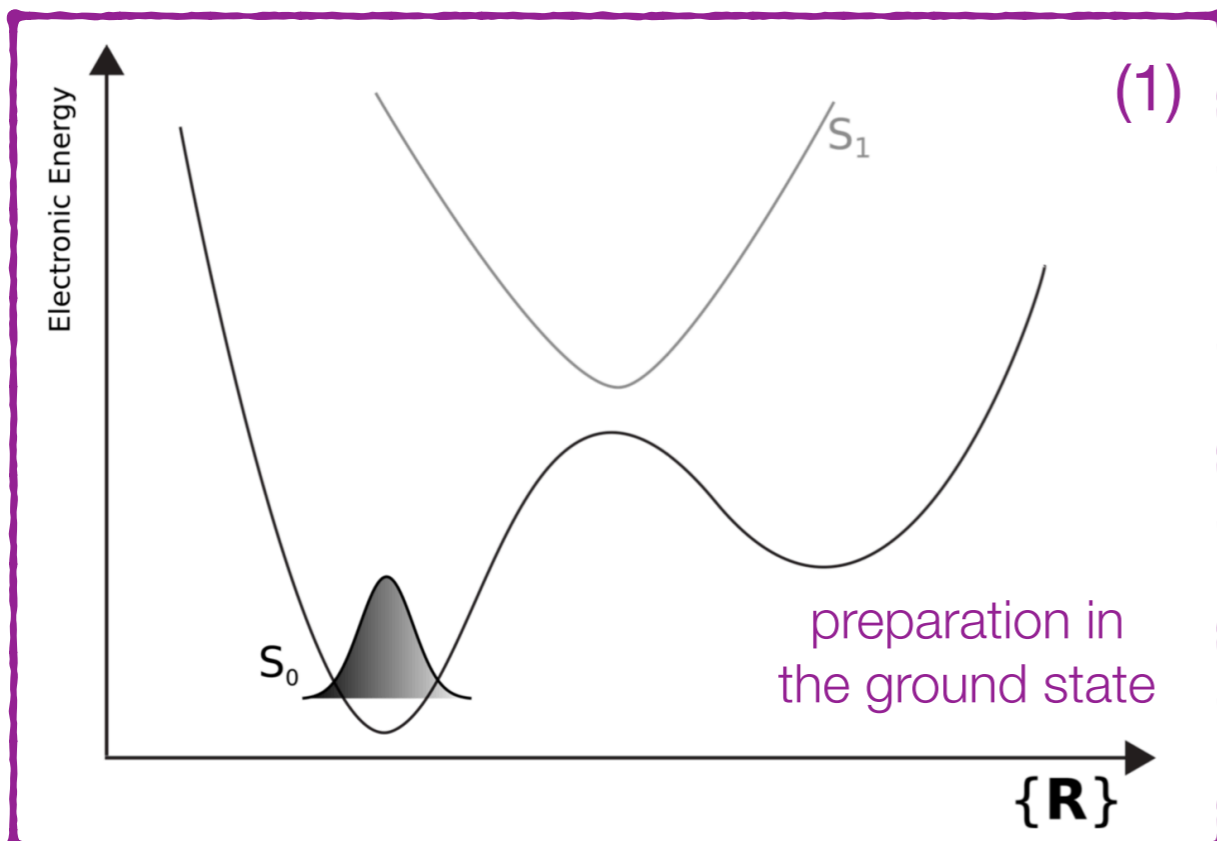
✦ PROS

- intuitive, easy implementation, widely used (therefore already implemented in many codes)
- independent trajectories, thus easy to parallelize
- suitable for on-the-fly dynamics
- good for big systems (tens of atoms, depending on the electronic structure method)
- possibility to combine it with QM/MM (available in some codes)
- widely used to treat spin-orbit coupling

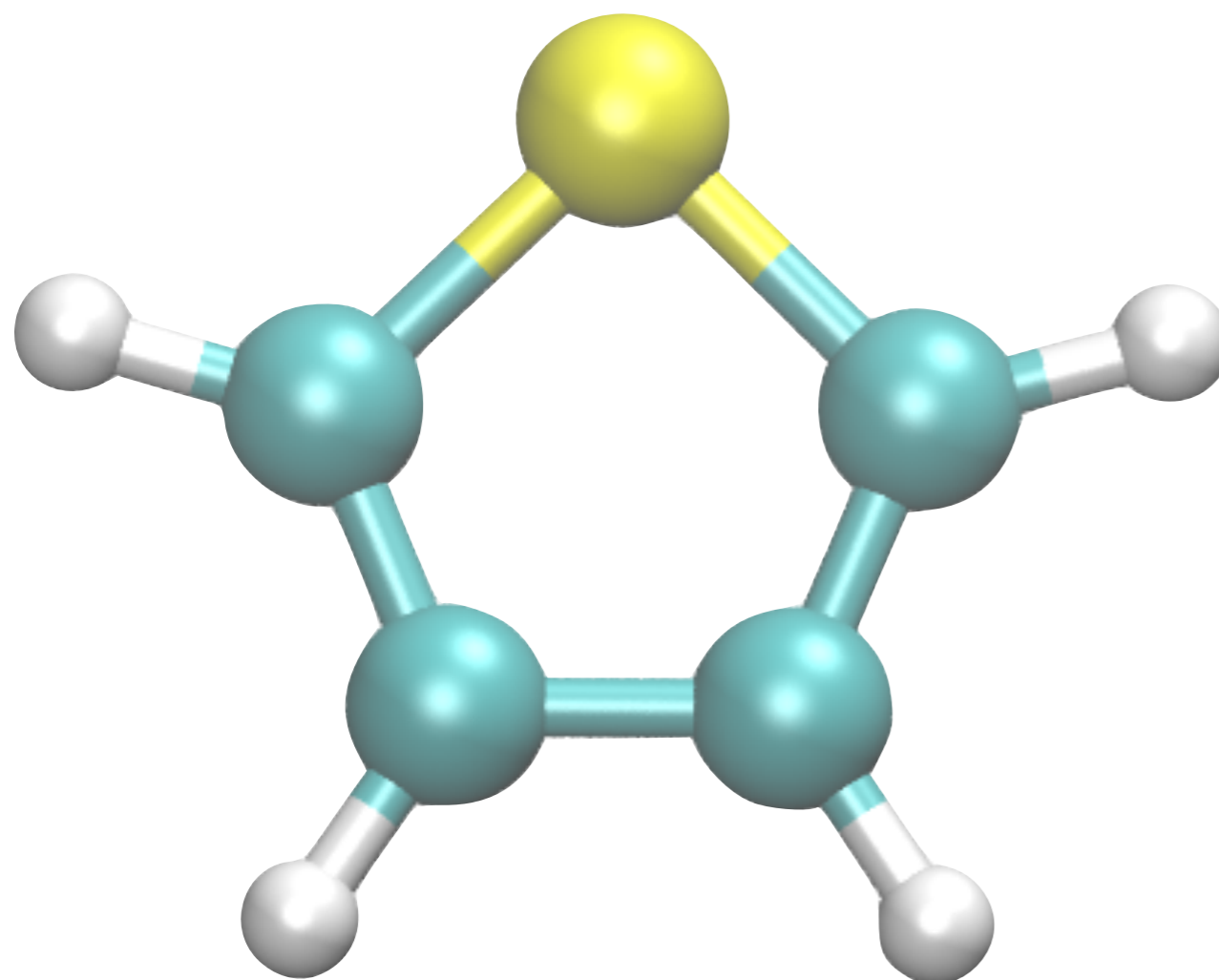
✦ CONS

- *ad hoc* method (approximations not well controlled)
- wrong description of quantum decoherence, but easy *ad hoc* cures
- not a unique way of treating spin-orbit coupling

An example: Photo-dynamics of thiophene with TSH



An example: Photo-dynamics of thiophene with TSH



Thiophene: geometry optimized with Gaussian09 at the DFT level (ω B97X-D) with basis set 6-31G*.

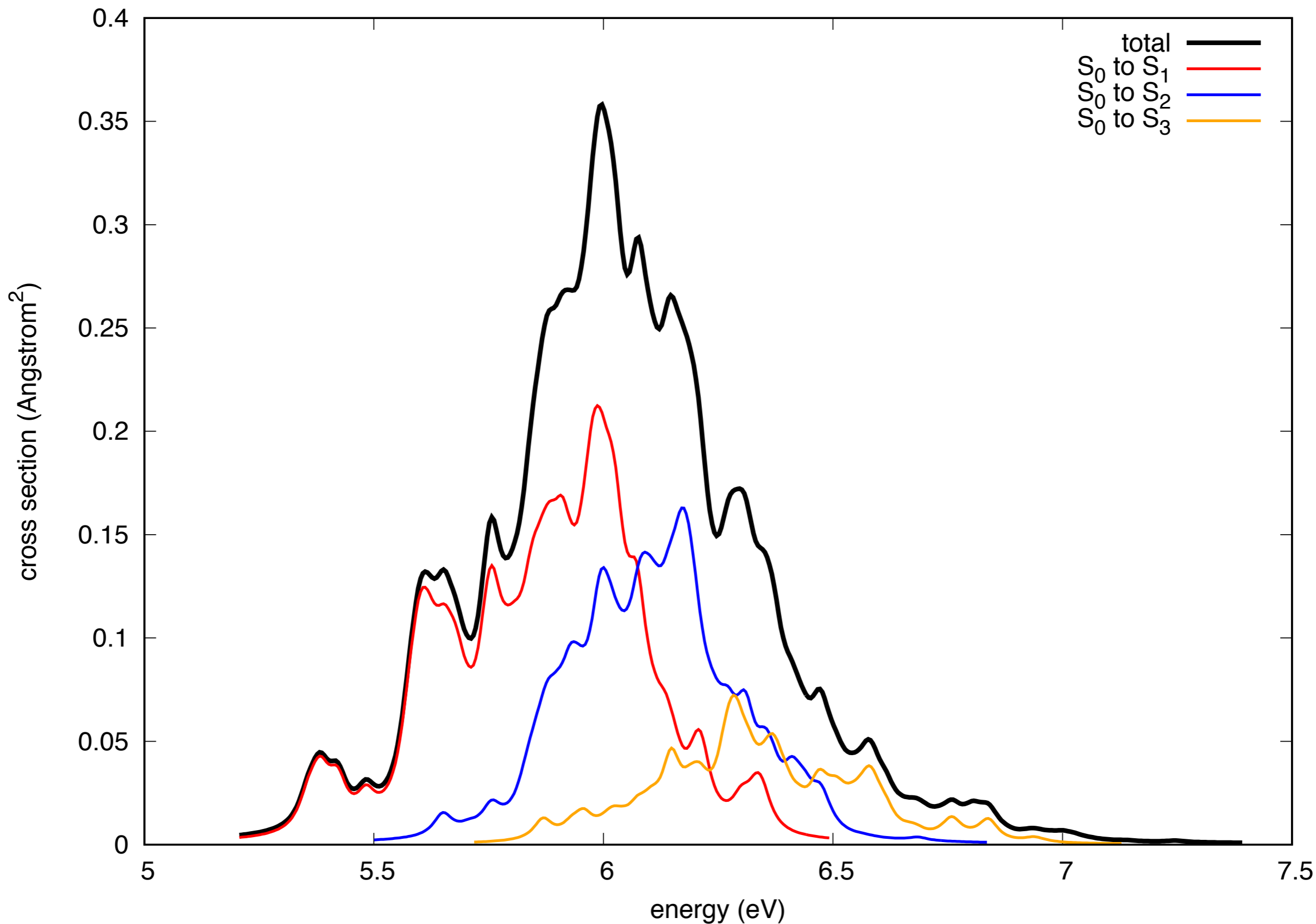
Frequencies (cm⁻¹)

460
583
623
697
736
769
862
898
902
943
1069
1118
1129
1299
1430
1496
1609
3247
3262
3295
3298

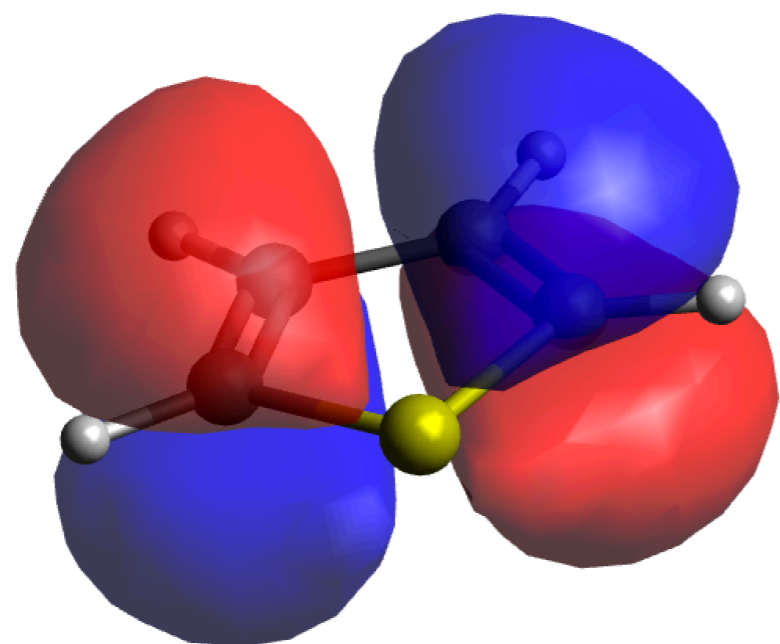
(1)

we are in the minimum of the potential because all frequencies are positive (real)

An example: Photo-dynamics of thiophene with TSH



An example: Photo-dynamics of thiophene with TSH

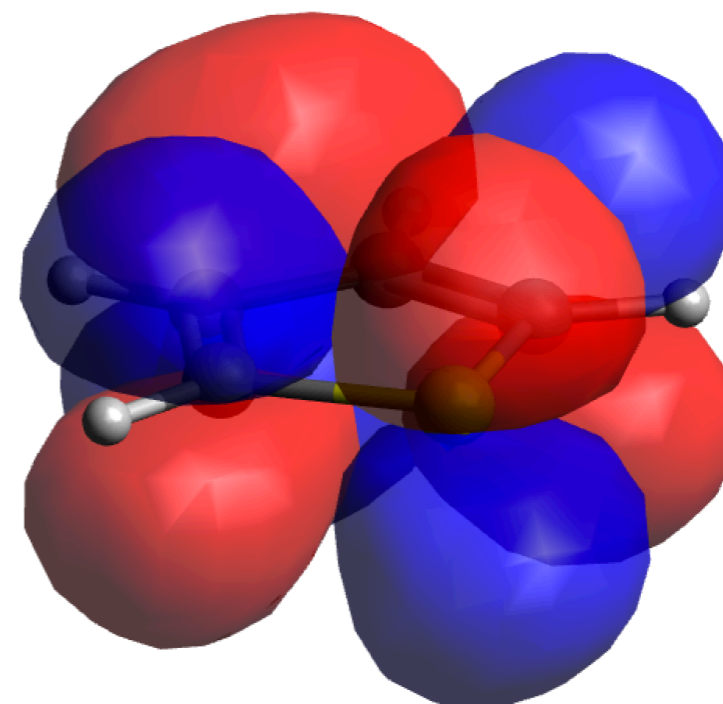


HOMO

$E = 6.1 \text{ eV}$
 $f = 0.09$

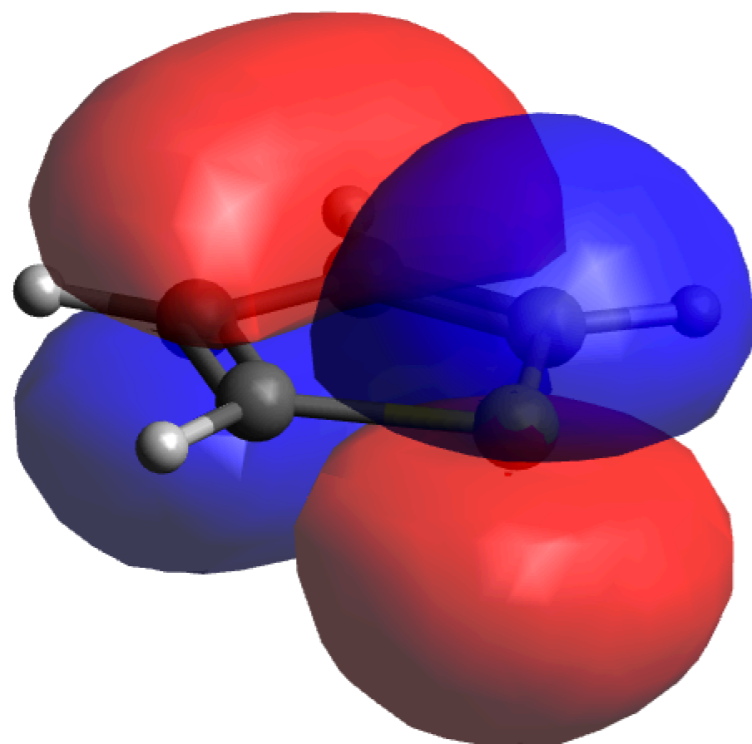


$S_0 \text{ to } S_1$



LUMO

(3)

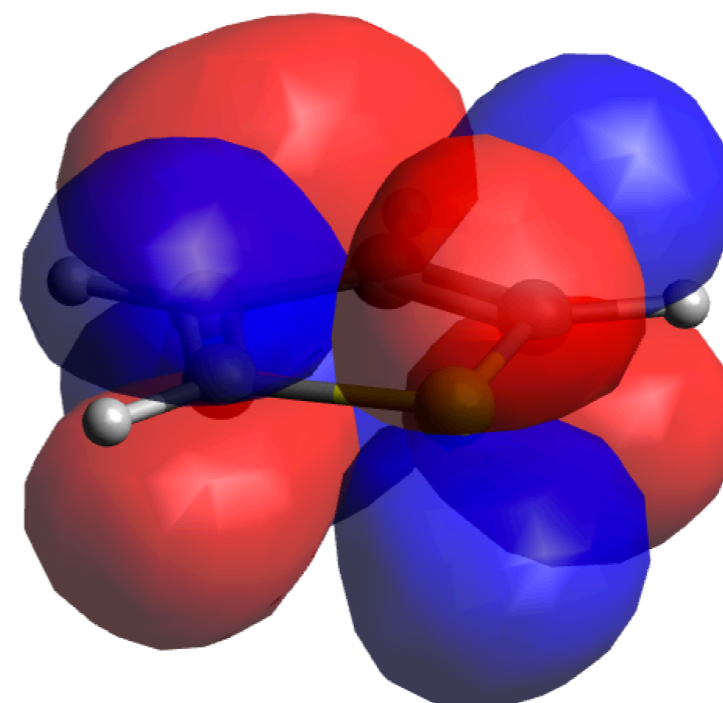


HOMO-1

$E = 6.2 \text{ eV}$
 $f = 0.10$

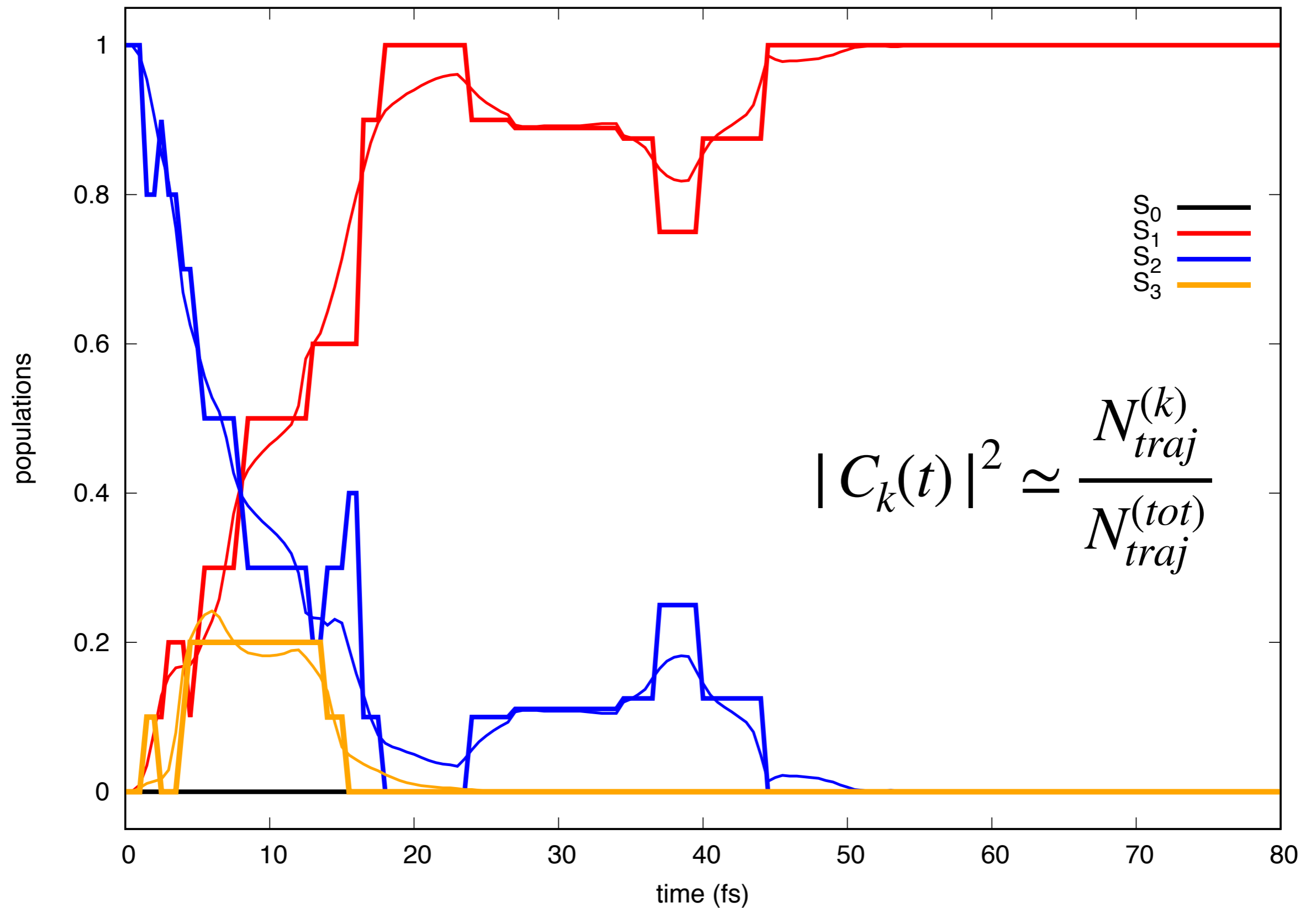


$S_0 \text{ to } S_2$



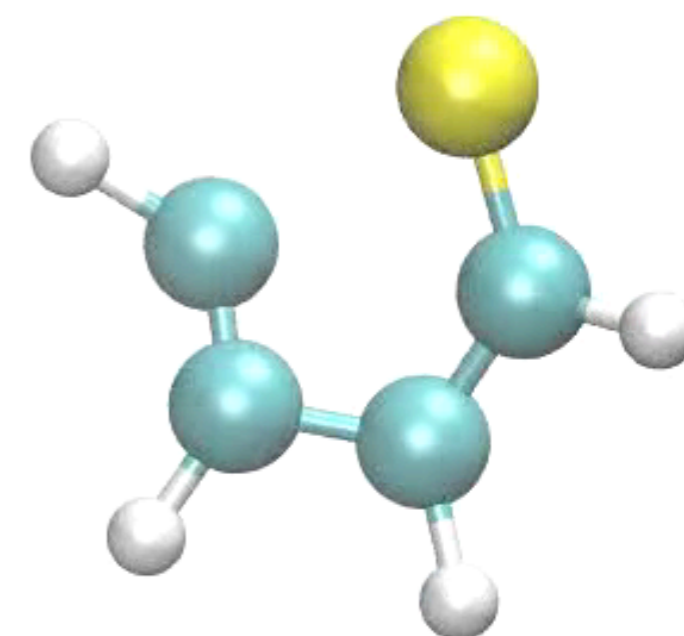
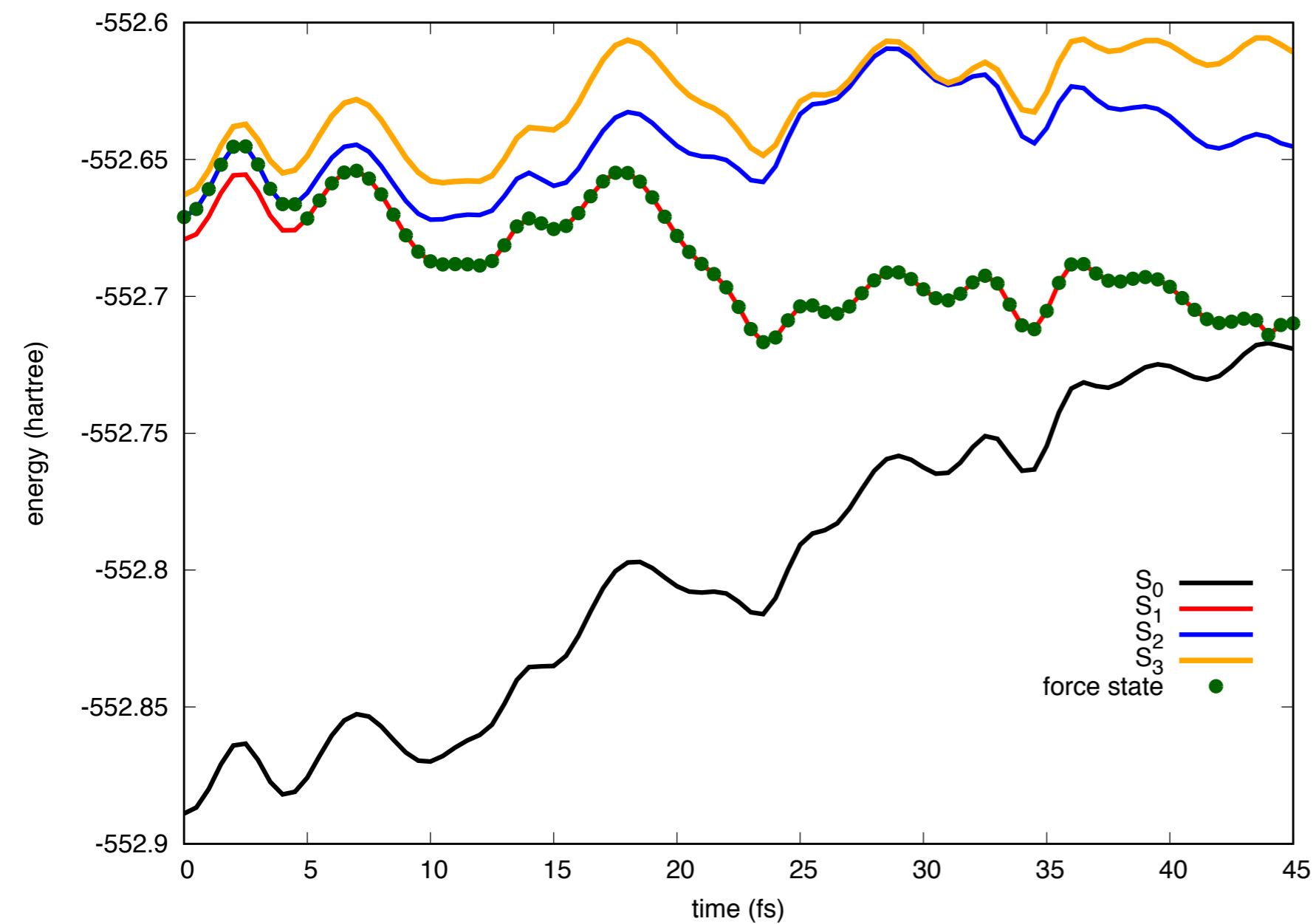
LUMO

An example: Photo-dynamics of thiophene with TSH



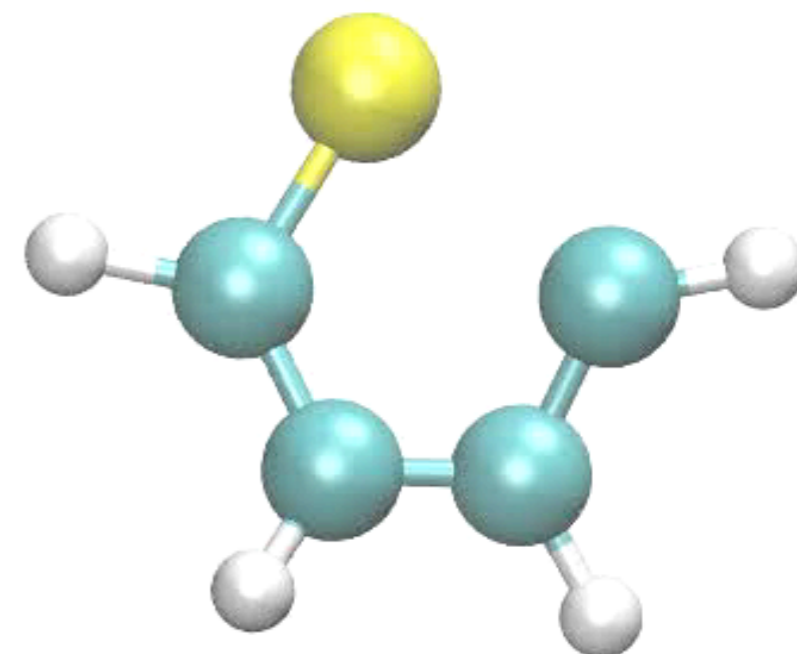
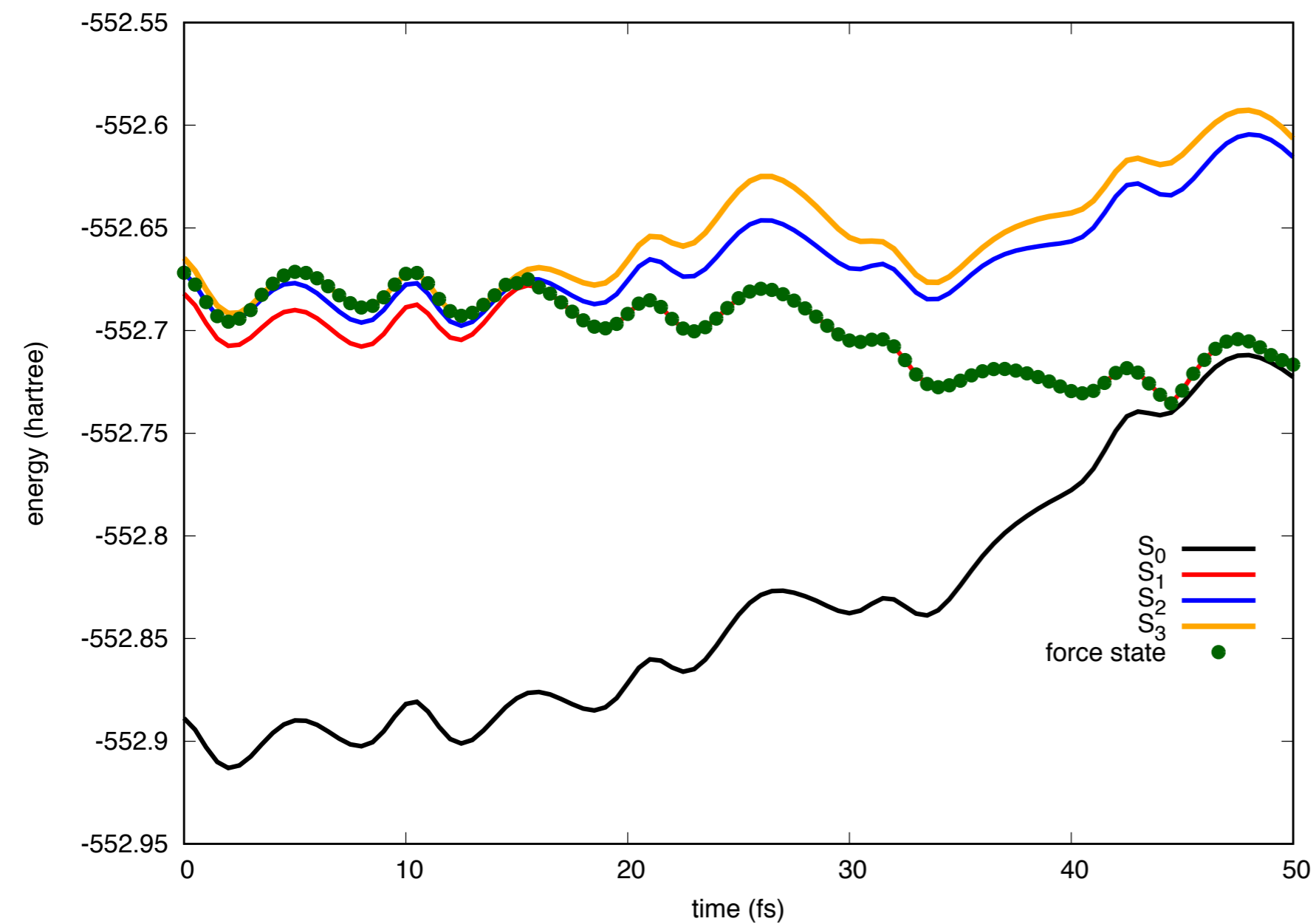
An example: Photo-dynamics of thiophene with TSH

(4)



An example: Photo-dynamics of thiophene with TSH

(4)



Available codes & References

- **CPMD**
 - TSH based on linear-response TDDFT
 - <http://www.cpmd.org>
- **NEWTON-X**
 - interface for TSH dynamics with different electronic-structure packages
 - <http://www.newtonx.org>
- **SHARC**
 - interface for TSH dynamics with different electronic-structure packages
 - <https://sharc-md.org>

BOOKS AND BOOK CHAPTERS

- Domcke, W., Yarkony, D., & Köppel, H. (Eds.). (2004). *Conical intersections: Electronic structure, dynamics & spectroscopy* (Vol. 15). World Scientific Pub Co Inc.
- Baer, M. (2006). *Beyond Born-Oppenheimer: Electronic Nonadiabatic Coupling Terms and Conical Intersections*. John Wiley & Sons, Inc.
- Gatti, F., Lasorne, B., Meyer, H.-D., & Nauts, A. (2017). *Applications of quantum dynamics in chemistry* (Vol. 98). Springer.
- Agostini, F., Curchod, B. F. E., Vuilleumier, R., Tavernelli, I., & Gross, E. K. U. (2018). *TDDFT and quantum-classical dynamics: A universal tool describing the dynamics of matter*. In W. Andreoni & S. Yip (Eds.), *Handbook of materials modeling* (p. 1-47) Springer Netherlands.

REVIEWS AND OVERVIEWS

TSH: Barbatti, M. (2011). *WIREs Comput. Mol. Sci.*, **1**, 620-633; Persico, M., & Granucci, G. (2014). *Theor. Chem. Acc.*, **133**, 1-28.

TRAJECTORY-BASED METHODS: Crespo-Otero, R., & Barbatti, M. (2018). *Chem. Rev.*, **118**, 7026-7068.

EXCITED-STATE DYNAMICS: Agostini, F., & Curchod, B. F. E (2019). *WIREs Comput. Mol. Sci.*, **9**, e1417.

Other methods for excited-state, nonadiabatic dynamics

Methods to solve the time-dependent Schrödinger equation

Quantum dynamics (not really an approximation method)

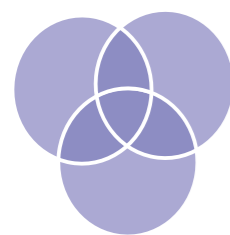
- representation of the molecular wavefunction or of the BO wavefunctions on a time-independent grid
- representation of the BO wavefunctions on a time-independent basis set
- representation of the BO wavefunctions on a time-dependent basis set

Semiclassical dynamics

- path-integral representation of the quantum-mechanical propagator
- initial-value representation for phase-space representation

Quantum dynamics with trajectories

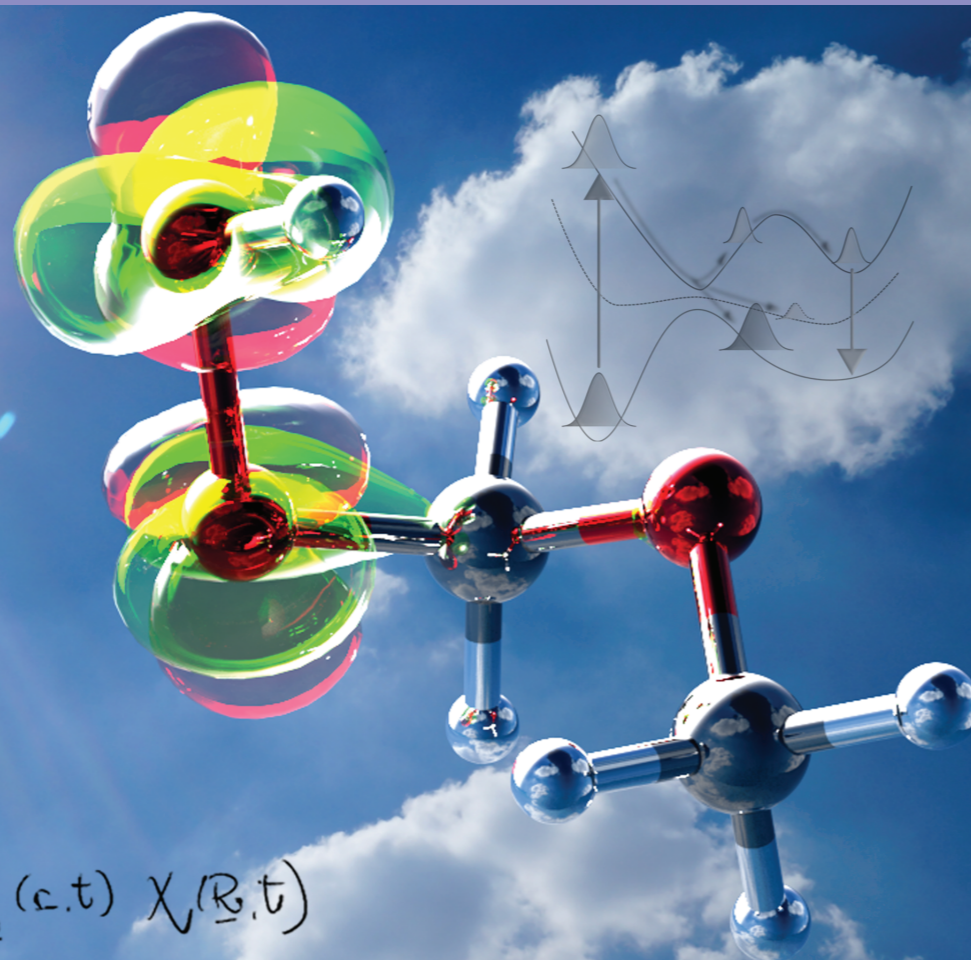
- trajectory surface hopping (Persico, Granucci, Barbatti, Subotnik, Gonzalez, Tavernelli)
- Ehrenfest and multi-configuration Ehrenfest dynamics (Robb, de la Lande, Shalashilin)
- full and ab initio multiple spawning (Martinez, Curchod)
- ab initio multiple cloning (Shalashilin, Tretiak)
- direct dynamics vMCG (Lasorne, Worth)
- exact factorization and CT-MQC (Gross, Agostini, Min)
- (Bohmian) quantum trajectories (Tavernelli, Albareda)



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$$\Psi(\underline{r}, \underline{R}, t) = \phi_e(\underline{r}, t) \chi(\underline{R}, t)$$

$$\Psi(\underline{r}, \underline{R}, t) = \sum_e^{\omega} \phi_e^{(e)}(\underline{r}) \chi_e(\underline{R}, t)$$

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OVERVIEW

Different flavors of nonadiabatic molecular dynamics

Federica Agostini & Basile F. E. Curchod
WIREs Computational Molecular Science

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