Exact factorization of the time-dependent electron-nuclear wavefunction

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Coupling between electronic and nuclear motion:

Situations where the electronic and the nuclear motions are strongly coupled and the quantum features of the nuclear motion become substantial:

- molecules in strong laser pulses
- light "nuclei"; muon, positron, ...
- electron-phonon interaction
- branching ratio of the chemical reactions at the conical intersection

System

N_e electrons, $(\mathbf{r_1}...\mathbf{r_{Ne}}) \equiv \underline{\underline{\mathbf{r}}}$

N_n nuclei, $(\mathbf{R_1}...\mathbf{R_{N_n}}) \equiv \underline{\underline{\mathbf{R}}}$, masses $M_1...M_{N_n}$ and charges $Z_1...Z_{N_n}$

$$\hat{H} = \hat{H}^{BO}_{\underline{\underline{\mathbf{R}}}} + \hat{V}^{e}_{ext}(\underline{\underline{\mathbf{r}}}, t) + \hat{T}_n(\underline{\underline{\mathbf{R}}}) + \hat{V}^{n}_{ext}(\underline{\underline{\mathbf{R}}}, t)$$

$\hat{H}^{BO}_{\underline{\underline{\mathbf{R}}}}$ is the traditional Born-Oppenheimer electronic Hamiltonian,

$$\hat{H}^{BO}_{\underline{\underline{\mathbf{R}}}} = \hat{T}_e(\underline{\underline{\mathbf{r}}}) + \hat{W}_{ee}(\underline{\underline{\mathbf{r}}}) + \hat{V}_{en}(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) + \hat{W}_{nn}(\underline{\underline{\mathbf{R}}})$$

Time-dependent schrödinger equation

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

- exact numerical solution
  - provides the complete information on the system
  - only for very small systems like H_2^+
  - lacks the intuitive picture that potential energy surfaces can provide
- approximate methods: nuclear wavepacket dynamics on BO surfaces, Ehrenfest dynamics of nuclei, surface hopping (Tully)
  - applicable to larger systems
  - based on potential energy surfaces picture or forces acting on nuclei
  - approximations are introduced in early stages $\rightarrow$ mean-field or non-correlated $\rightarrow$ don't work in many situations

Born-Oppenheimer approximation

Solve

$$\hat{H}^{BO}_{\underline{\underline{\mathbf{R}}}}\Phi^{BO}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}) = \epsilon^{BO}(\underline{\underline{\mathbf{R}}})\Phi^{BO}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}})$$

for each fixed nuclear configuration , $\underline{\underline{R}}$.

Approximate the full electron-nuclear wave function:

$$\Psi^{BO}(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}) = \Phi^{BO}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}})\chi^{BO}(\underline{\underline{\mathbf{R}}})$$

Nuclear equation:

$$\Big(\sum_{\nu=1}^{N_n} \frac{1}{2M_\nu}(-i\nabla_\nu + \mathbf{A}_\nu)^{\mathbf{2}} + \hat{W}_{nn}(\underline{\underline{\mathbf{R}}}) + \hat{V}^{ext}_n(\underline{\underline{\mathbf{R}}}) + \epsilon^{BO}(\underline{\underline{\mathbf{R}}})\Big)\chi^{BO}(\underline{\underline{\mathbf{R}}}) = E\chi^{BO}(\underline{\underline{\mathbf{R}}})$$

Vector potential

$$\mathbf{A}_\nu^{\mathbf{BO}}(\underline{\underline{\mathbf{R}}}) = \int \mathbf{\Phi}_{\underline{\underline{\mathbf{R}}}}^{\mathbf{BO}*}(\underline{\mathbf{r}})(-\mathbf{i}\nabla_\nu)\mathbf{\Phi}_{\underline{\underline{\mathbf{R}}}}^{\mathbf{BO}}(\underline{\mathbf{r}})\ \mathbf{d}\underline{\mathbf{r}}$$

geometrical phase

$$\gamma^{BO}(C) = \oint_C \mathbf{A}_\nu^{\mathbf{BO}}(\underline{\underline{\mathbf{R}}}) \cdot \mathbf{d}\underline{\underline{\mathbf{R}}}$$

Question: Is the appearance of Berry phases a consequence of the Born-Oppenheimer approximation or does it survive in the exact treatment?

Vector potential

$$\mathbf{A}_\nu^{\mathbf{BO}}(\underline{\underline{\mathbf{R}}}) = \int \Phi_{\underline{\underline{\mathbf{R}}}}^{\mathbf{BO}*}(\underline{\mathbf{r}})(-\mathbf{i}\nabla_\nu)\Phi_{\underline{\underline{\mathbf{R}}}}^{\mathbf{BO}}(\underline{\mathbf{r}})\ \mathbf{d}\underline{\mathbf{r}}$$

geometrical phase

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Question: Is the appearance of Berry phases a consequence of the Born-Oppenheimer approximation or does it survive in the exact treatment?

Born-Oppenheimer expansion

Expand full electron-nuclear wave function in complete set of BO states:

$$\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t) = \sum_j \Phi^{BO}_{\underline{\underline{\mathbf{R}}},j}(\underline{\mathbf{r}})\chi_j(\underline{\underline{\mathbf{R}}}, t)$$

Insert the expansion in the full time-dependent Schödinger equation$\rightarrow$standard non-adiabatic coupling terms from $\hat{T}_n$ acting on $\Phi^{BO}_{\underline{\underline{\mathbf{R}}},j}$.

- Numerically very hard:
  - Need many-electron BO wavefunction
  - Non-adiabatic coupling terms become infinitely large in the vicinity of conical intersections
- $\chi_j(\underline{\underline{\mathbf{R}}}, t)$ looses nice interpretation as "nuclear wavefunction"

Goal: show that $\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) = \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)\chi(\underline{\underline{\mathbf{R}}}, t)$ can be made **Exact**

- Concept of Exact time-dependent potential energy surface
- Concept of Exact time-dependent vector potential

G. Hunter, Int. J. Quantum Chem. 9, 237 (1975)
Nikitas I. Gidopoulos, E. K. U. Gross, arXiv:cond-mat/0502433

Theorem

(a)The exact solution of

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

can be written as a single product

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

where $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$ satisfies the partial normalization condition

$$\int d\underline{\underline{\mathbf{r}}}|\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)|^2 = 1$$

for each fixed $\underline{\underline{\mathbf{R}}}$, at any time t.

A. A., N.T. Maitra, E.K.U. Gross, Phys. Rev. Lett. 105, 123002 (2010)

Immediate Consequences:

1– The diagonal $\Gamma(\underline{\underline{\mathbf{R}}}, t)$ of the nuclear $N_n - body$ density matrix is identical with $|\chi(\underline{\underline{\mathbf{R}}}, t)|^2$

proof: $\Gamma(\underline{\underline{\mathbf{R}}}, t) = \int d\underline{\underline{\mathbf{r}}} |\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)|^2 = \int d\underline{\underline{\mathbf{r}}} |\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)|^2 |\chi(\underline{\underline{\mathbf{R}}}, t)|^2 = |\chi(\underline{\underline{\mathbf{R}}}, t)|^2$

2– $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)$ and $\chi(\underline{\underline{\mathbf{R}}}, t)$ are unique up to within the gauge transformation :

$$\tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t) := e^{i\theta(\underline{\underline{\mathbf{R}}}, t)} \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)$$

$$\tilde{\chi}(\underline{\underline{\mathbf{R}}}, t) := e^{-i\theta(\underline{\underline{\mathbf{R}}}, t)} \chi(\underline{\underline{\mathbf{r}}}, t)$$

Immediate Consequences:

proof: Let $\Phi_{\underline{\underline{\mathbf{R}}}} \cdot \chi$ and $\tilde{\Phi}_{\underline{\underline{\mathbf{R}}}} \cdot \tilde{\chi}$ be two different representations of an exact wave function $\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t)$

$$\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}, t) = \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)\chi(\underline{\underline{\mathbf{R}}}, t) = \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)\tilde{\chi}(\underline{\underline{\mathbf{R}}}, t)$$

$$\rightarrow \frac{\chi}{\tilde{\chi}} = \frac{\tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}}{\Phi_{\underline{\underline{\mathbf{R}}}}} := g(\underline{\underline{\mathbf{R}}}, t) \rightarrow |\tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)|^2 = |g(\underline{\underline{\mathbf{R}}}, t)|^2 |\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)|^2$$

$$\int d\underline{\mathbf{r}} |\tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)|^2 = |g(\underline{\underline{\mathbf{R}}}, t)|^2 \int d\underline{\mathbf{r}} |\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)|^2$$

$$\rightarrow |g(\underline{\underline{\mathbf{R}}}, t)|^2 = 1 \rightarrow g(\underline{\underline{\mathbf{R}}}, t) = e^{i\theta(\underline{\underline{\mathbf{R}}}, t)}$$

$$\rightarrow \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t) = e^{i\theta(\underline{\underline{\mathbf{R}}}, t)} \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t) \qquad \tilde{\chi}(\underline{\underline{\mathbf{R}}}, t) = e^{-i\theta(\underline{\underline{\mathbf{R}}}, t)} \chi(\underline{\underline{\mathbf{R}}}, t)$$

Proof of part (a):

Given the exact electron-nuclear wavefunction $\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)$

Choose $\chi(\underline{\underline{\mathbf{R}}}, t) := e^{iS(\underline{\underline{\mathbf{R}}},t)} \sqrt{\int d\underline{\underline{\mathbf{r}}} |\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)|^2}$

with some real-valued function $S(\underline{\underline{\mathbf{R}}}, t)$

$$\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t) := \Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t)/\chi(\underline{\underline{\mathbf{R}}}, t)$$

Then, by construction, $\int d\underline{\underline{\mathbf{r}}} |\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)|^2 = 1$

Equations

(b) The wavefunctions $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$ and $\chi(\underline{\underline{\mathbf{R}}},t)$ satisfy:

(1) electronic equation

$$\left(\hat{H}^{BO}_{\underline{\underline{\mathbf{R}}}}+\hat{V}^{e}_{ext}(\underline{\underline{\mathbf{r}}},t)+\hat{U}^{coup}_{en}[\chi,\Phi_{\underline{\underline{\mathbf{R}}}}]-\epsilon(\underline{\underline{\mathbf{R}}},t)\right)\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)=i\partial_t\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$$

(2) nuclear equation

$$\left(\sum_{\nu=1}^{N_n}\frac{1}{2M_\nu}(-i\nabla_\nu+\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}},t))^2+\hat{V}^{n}_{ext}(\underline{\underline{\mathbf{R}}},t)+\epsilon(\underline{\underline{\mathbf{R}}},t)\right)\chi(\underline{\underline{\mathbf{R}}},t)=i\partial_t\chi(\underline{\underline{\mathbf{R}}},t)$$

EXACT time-dependent potential energy surface

$$\epsilon(\underline{\underline{\mathbf{R}}},t)=\int d\underline{\underline{\mathbf{r}}}\Phi^{*}_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)\left[H^{BO}_{\underline{\underline{\mathbf{R}}}}+\hat{V}^{e}_{ext}(t)+\sum_{\nu=1}^{N_n}\frac{(-i\nabla_\nu-\mathbf{A}_\nu)^2}{2M_\nu}-i\partial_t\right]\Phi^{*}_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$$

EXACT time-dependent vector potential

$$\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}},\mathbf{t})=\int\mathbf{\Phi}^{*}_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},\mathbf{t})(-\mathbf{i}\nabla_\nu)\mathbf{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},\mathbf{t})\mathbf{d}\underline{\underline{\mathbf{r}}}$$

EXACT electron-nuclear correlation operator

$$\hat{U}^{coup}_{en}[\chi,\Phi_{\underline{\underline{\mathbf{R}}}}]=\sum_{\nu=1}^{N_n}\frac{1}{M_\nu}\left[\frac{(-i\nabla_\nu-\mathbf{A}_\nu)^2}{2}+\left(\frac{-i\nabla_\nu\chi}{\chi}+\mathbf{A}_\nu\right)(-i\nabla_\nu-\mathbf{A}_\nu)\right]$$

Observations

- Electronic equation is nonlinear in $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}},t)$ and contains $\chi(\underline{\underline{\mathbf{R}}},t)$
- There is an alternative, equally exact, representation $\Psi = \Phi_{\underline{\mathbf{r}}}(\underline{\underline{\mathbf{R}}},t)\chi(\underline{\mathbf{r}},t)$ (electrons move on the nuclear energy surface)
- Both equations are form-invariant under the gauge transformation

$$\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}},t) \rightarrow \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}},t) = e^{i\theta(\underline{\underline{\mathbf{R}}},t)}\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}},t)$$

$$\chi(\underline{\underline{\mathbf{R}}},t) \rightarrow \tilde{\chi}(\underline{\underline{\mathbf{R}}},t) = e^{-i\theta(\underline{\underline{\mathbf{R}}},t)}\chi(\underline{\underline{\mathbf{R}}},t)$$

$$\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}},t) \rightarrow \tilde{\mathbf{A}}_\nu(\underline{\underline{\mathbf{R}}},t) = \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}},t) + \nabla_\nu\theta(\underline{\underline{\mathbf{R}}},t)$$

$$\epsilon(\underline{\underline{\mathbf{R}}},t) \rightarrow \tilde{\epsilon}(\underline{\underline{\mathbf{R}}},t) = \epsilon(\underline{\underline{\mathbf{R}}},t) + \partial_t\theta(\underline{\underline{\mathbf{R}}},t)$$

Basic idea of the proof part (b)

- first step: we apply Frenkel's stationary action principle, $\delta \int_{t_0}^{t_1} dt \langle \Psi | \hat{H} - i\partial_t | \Psi \rangle = 0$, to the product wavefunction and require the action to be stationary with respect to variations in $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}}, t)$ and $\chi(\underline{\underline{\mathbf{R}}}, t)$, subject to the normalization condition

$$\frac{\delta}{\delta \Phi_{\underline{\underline{\mathbf{R}}}}{}^*(\underline{\mathbf{r}})} \left(\frac{\int_{t_0}^{t_1} dt \langle \Psi | \hat{H} - i\partial_t | \Psi \rangle}{\langle \Phi\chi | \Phi\chi \rangle} \right) = 0$$

$$\frac{\delta}{\delta \chi^*(\underline{\underline{\mathbf{R}}})} \left(\frac{\int_{t_0}^{t_1} dt \langle \Psi | \hat{H} - i\partial_t | \Psi \rangle}{\langle \Phi\chi | \Phi\chi \rangle} \right) = 0$$

- second step: prove the implication: Φ, χ satisfy $Eqs.1, 2 \Longrightarrow \Psi := \Phi\chi$ satisfies $\hat{H}\Psi = i\partial_t \Psi$.

- $\epsilon(\underline{\underline{\mathbf{R}}}, t)$, $\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, \mathbf{t})$ and $\hat{U}_{en}^{coup}[\chi, \Phi_{\underline{\underline{\mathbf{R}}}}]$ mediate the coupling between the nuclear and the electronic degrees of freedom in a formally **exact** way

- Vector potential appears in the exact treatment.

Does it produce a real effect or can it be made disappear by a suitable gauge transformation?

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Does it produce a real effect or can it be made disappear by a suitable gauge transformation?

Vector potential as the difference of paramagnetic nuclear velocity fields derived from the full and nuclear wavefunctions:

$$\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}},t) = \frac{Im\left\langle \Psi(t)\right| \nabla_\nu \Psi(t)\rangle_{\underline{\underline{\mathbf{r}}}}}{|\chi(\underline{\underline{\mathbf{R}}},t)|^2} - \frac{Im(\chi^*\nabla_\nu\chi)}{|\chi(\underline{\underline{\mathbf{R}}},t)|^2}$$

$Im(\chi^*\nabla_\nu\chi) + |\chi|^2\mathbf{A}_\nu \rightarrow$ **reproduce the exact nuclear current density.**

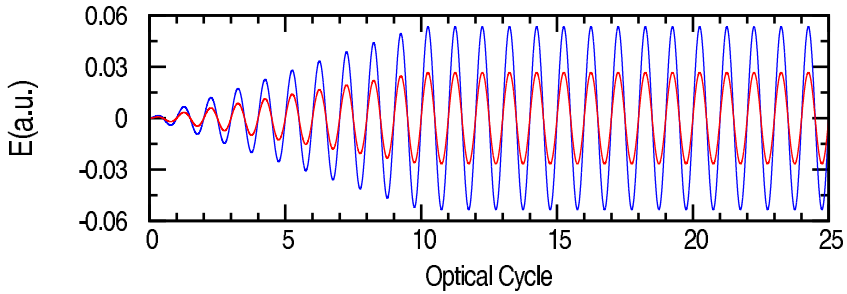
$\chi(\underline{\underline{\mathbf{R}}},t) \rightarrow$ **proper nuclear many-body wavefunction:**

- Its absolute-value squared gives the exact nuclear (N-body) density
- Its phase yields the correct nuclear (N-body) current density.

Time-Dependent Potential Energy Surfaces

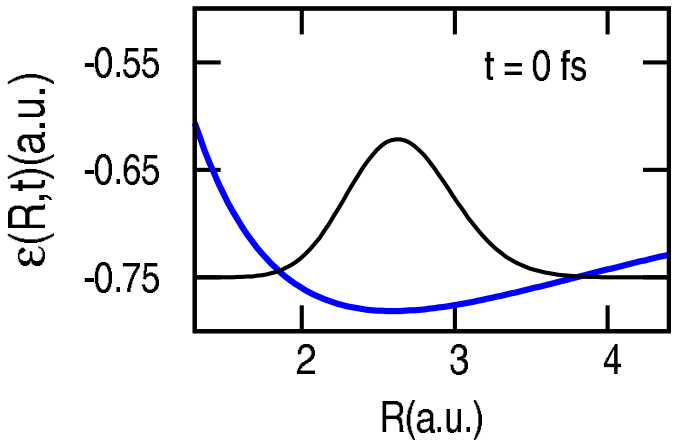
Example: $1D - H_2^+$ in strong laser field

1D-model (soft Coulomb potentials)



$$\hat{H}(t) = -\frac{1}{M}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_e}\frac{\partial^2}{\partial z^2} - \frac{1}{\sqrt{1+(z-R/2)^2}} - \frac{1}{\sqrt{1+(z+R/2)^2}} + \frac{1}{\sqrt{0.03+R^2}} + \hat{V}_{laser}(z,t)$$

- H_2^+ *molecular ion exposed to* $\lambda = 228$ *nm laser field*
- $E(t) = E_0 f(t)\sin(\omega t)$, *for two peak intensities,* $I_1 = |E_0|^2 = 10^{14} W/cm^2$ *(dashed) and* $I_2 = |E_0|^2 = 2.5 \times 10^{13} W/cm^2$ (solid)
- $f(t)$ *is chosen such that the field is linearly ramped from zero to its maximum strength at* $t = 7.6$ *fs and thereafter held constant*



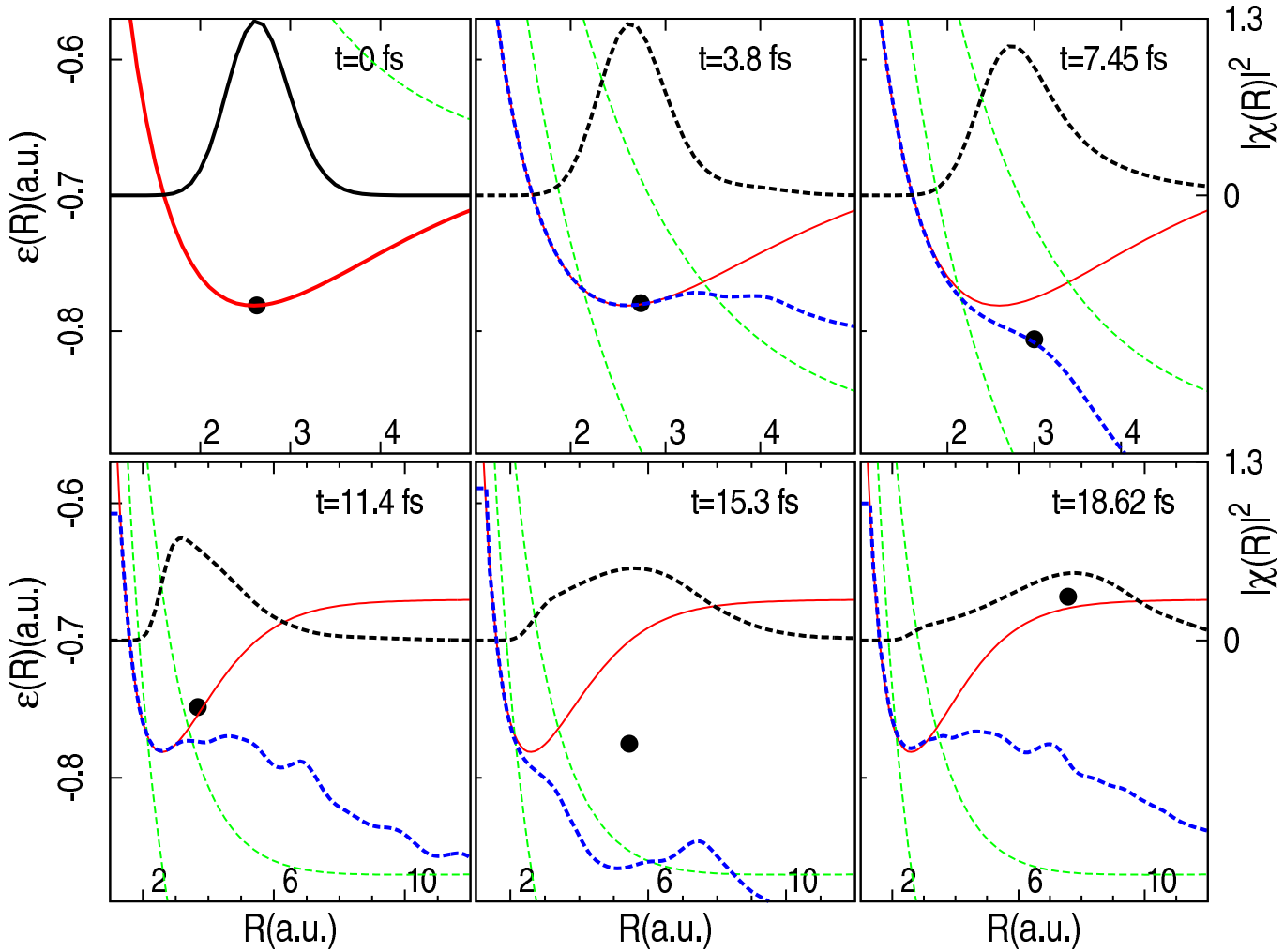
Example: $1D - H_2^+$ in strong laser field

exact solution of $i\partial_t \Psi(r,R,t) = \hat{H}\Psi(r,R,t)$

Compared with:

- Hartree approximation (TDSCF): $\Psi_H(r,R,t) = \chi(R,t)\phi(r,t)$
- Standard Ehrenfest dynamics
- "Exact Ehrenfest dynamics" where the forces on nuclei are calculated from the *exact* TDPES

Results: $I_1 = 10^{14}\mathrm{W/cm}^2$



Snapshots of the TDPES (blue lines) and nuclear density (black) at times indicated. The circles indicate the position and energy of the classical particle in the exact-Ehrenfest calculation. For reference, the ground-state BO surface is shown as the thin red line.

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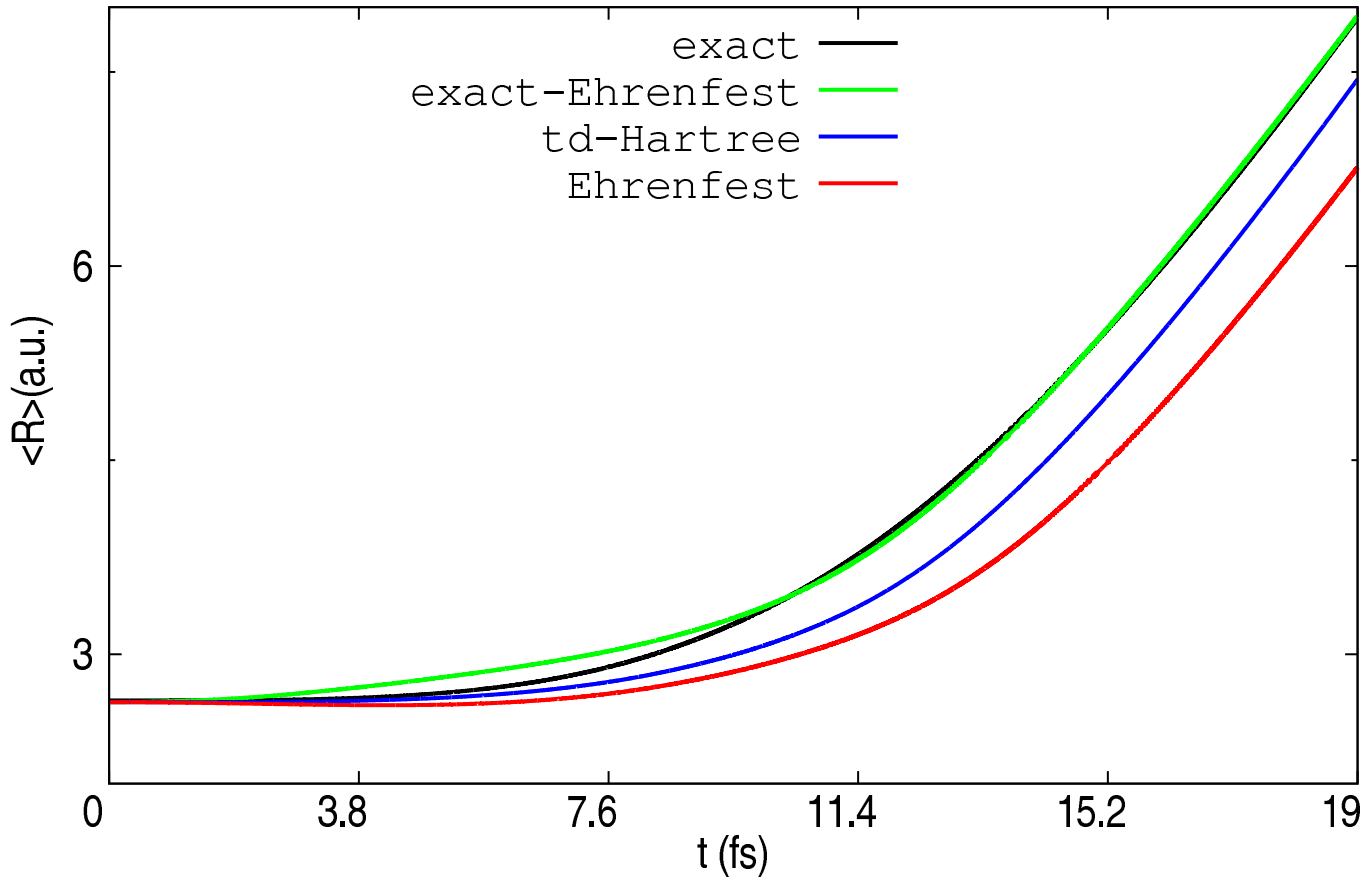
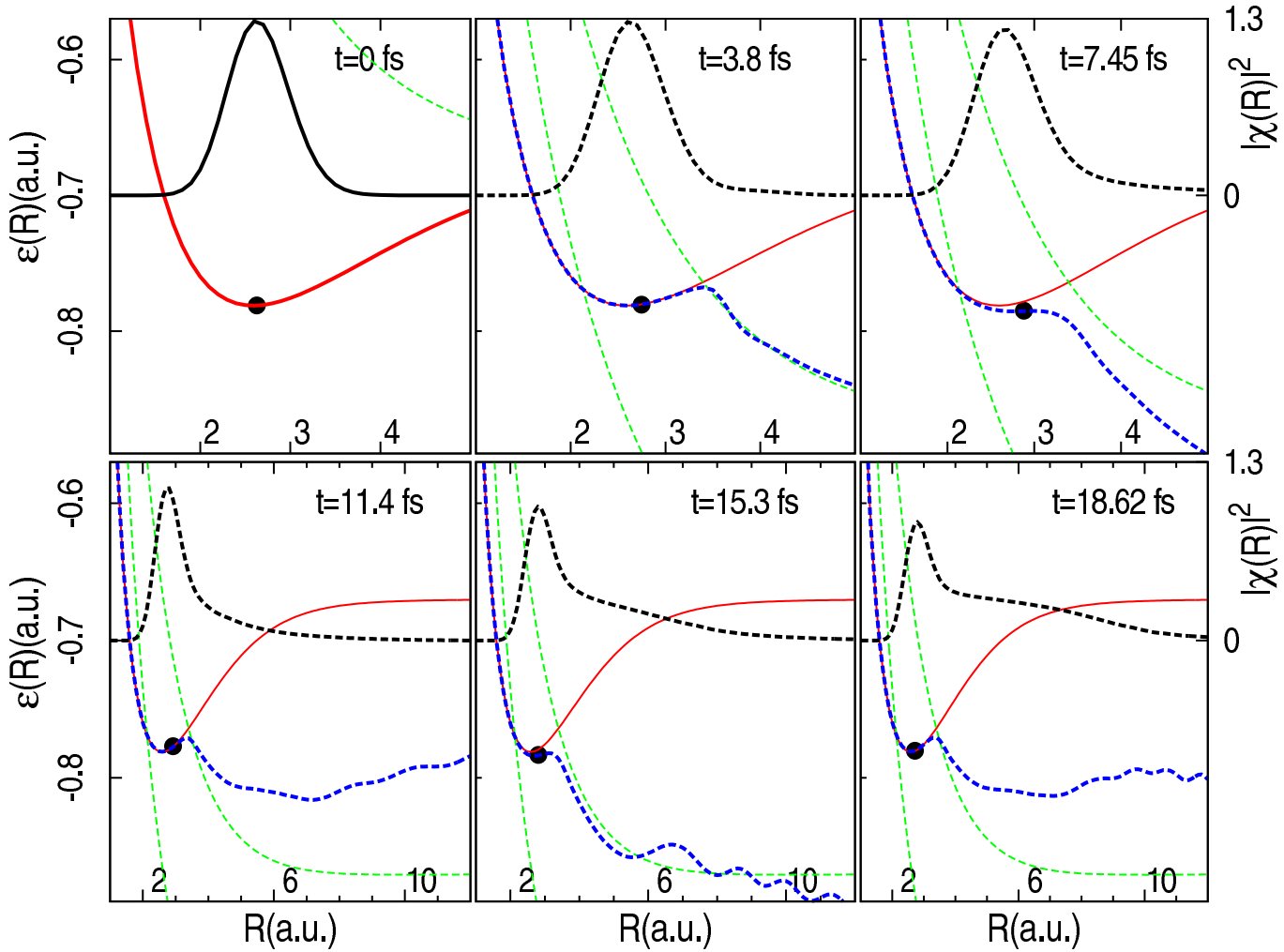


The internuclear separation $\langle R \rangle(t)$

Results: $I_2 = 2.5 \times 10^{13}$



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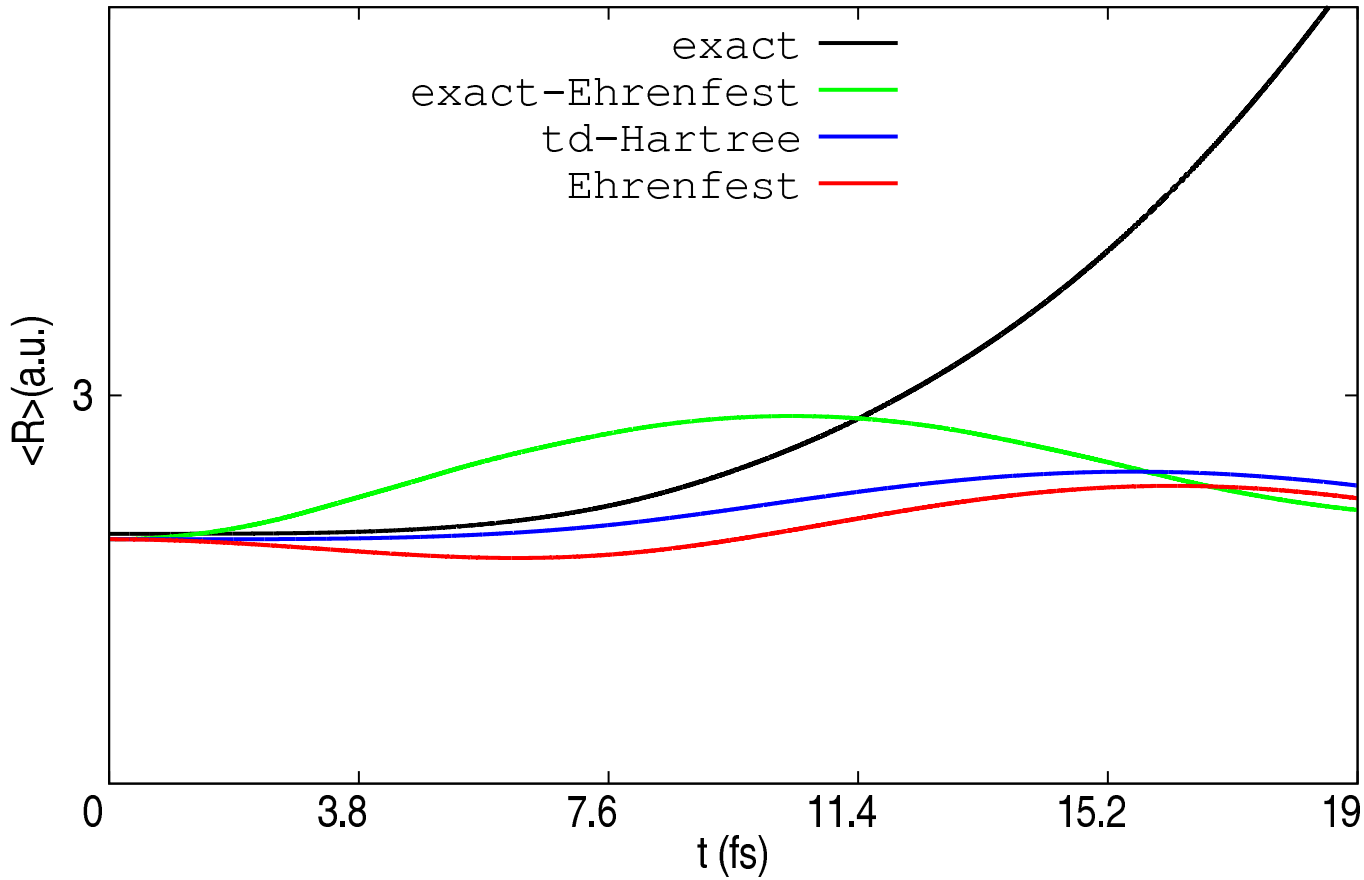
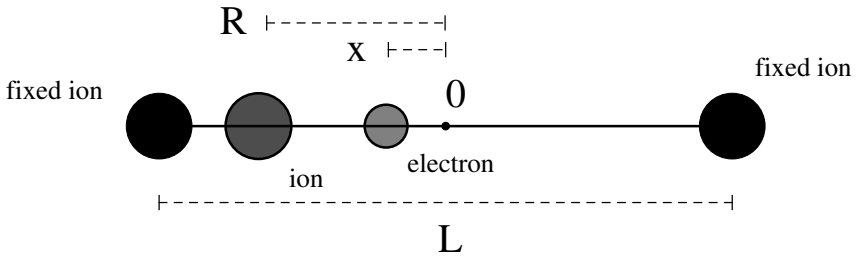
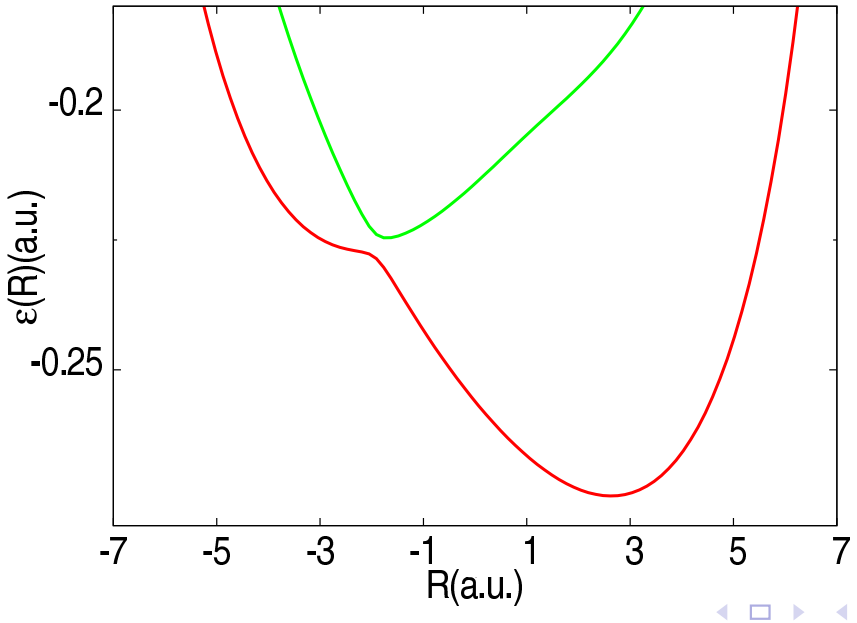


The internuclear separation $\langle R \rangle(t)$

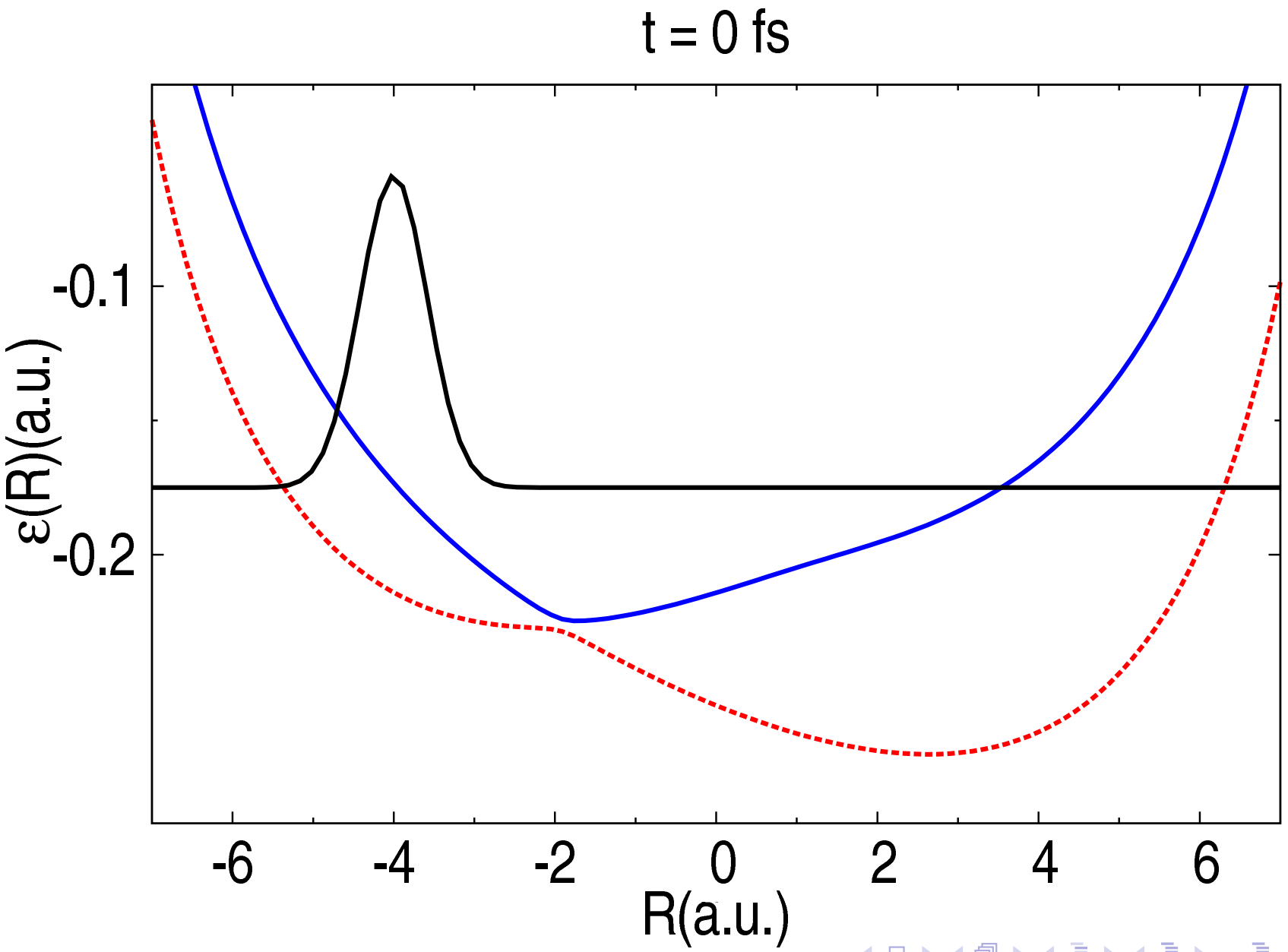
Model (S. Shin and H. Metiu, JCP **102** 1995)



$$\hat{H}(x,R) = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2M}\frac{\partial^2}{\partial R^2} + \frac{1}{|L/2-R|} + \frac{1}{|L/2+R|} - \frac{\mathrm{erf}(|R-x|/R_f)}{|R-x|} - \frac{\mathrm{erf}\left(|x-L/2|/R_{c_1}\right)}{|x-L/2|} - \frac{\mathrm{erf}\left(|x+L/2|/R_{c_2}\right)}{|x+L/2|}$$



Time-Dependent potential energy surfaces



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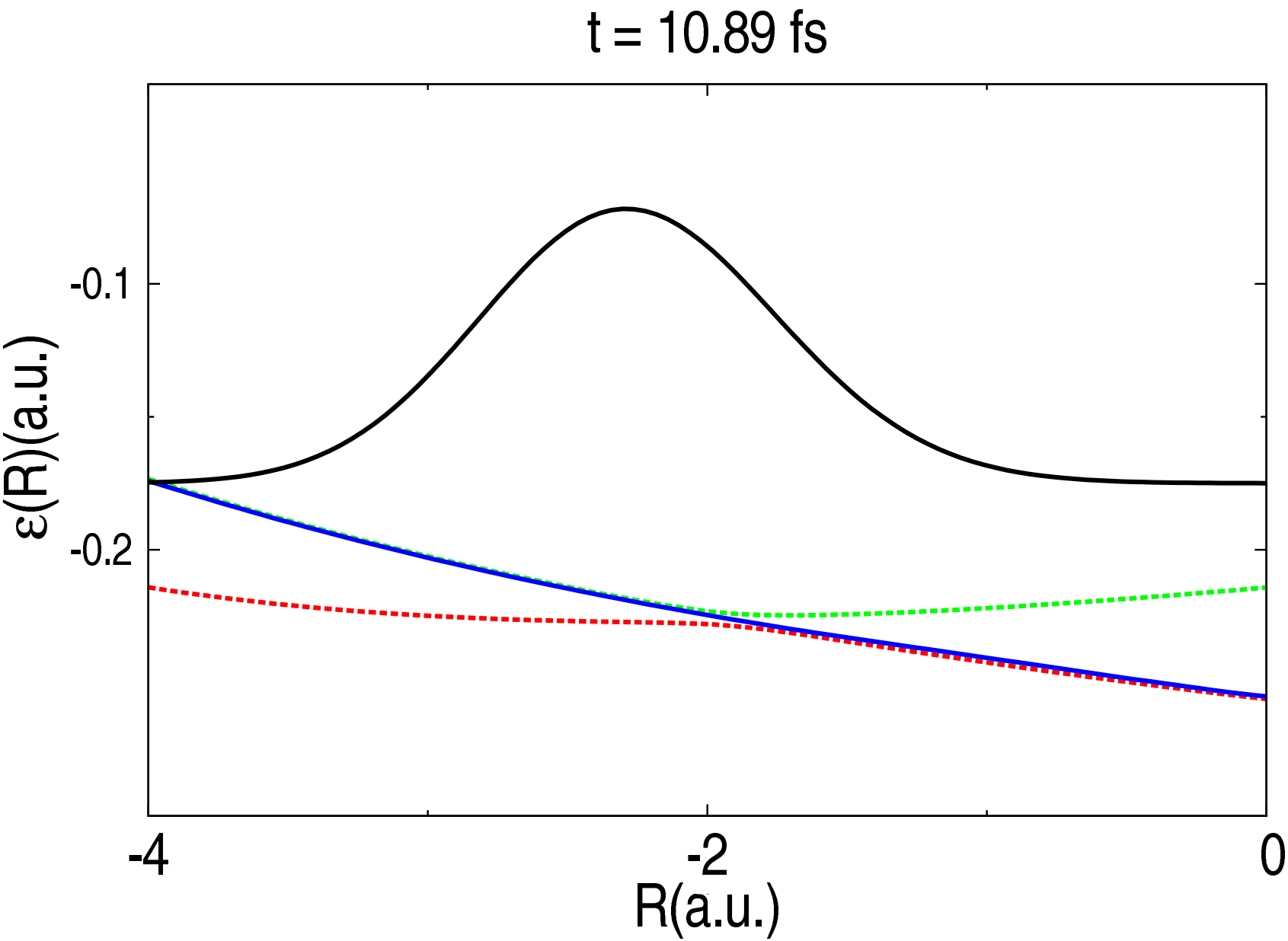

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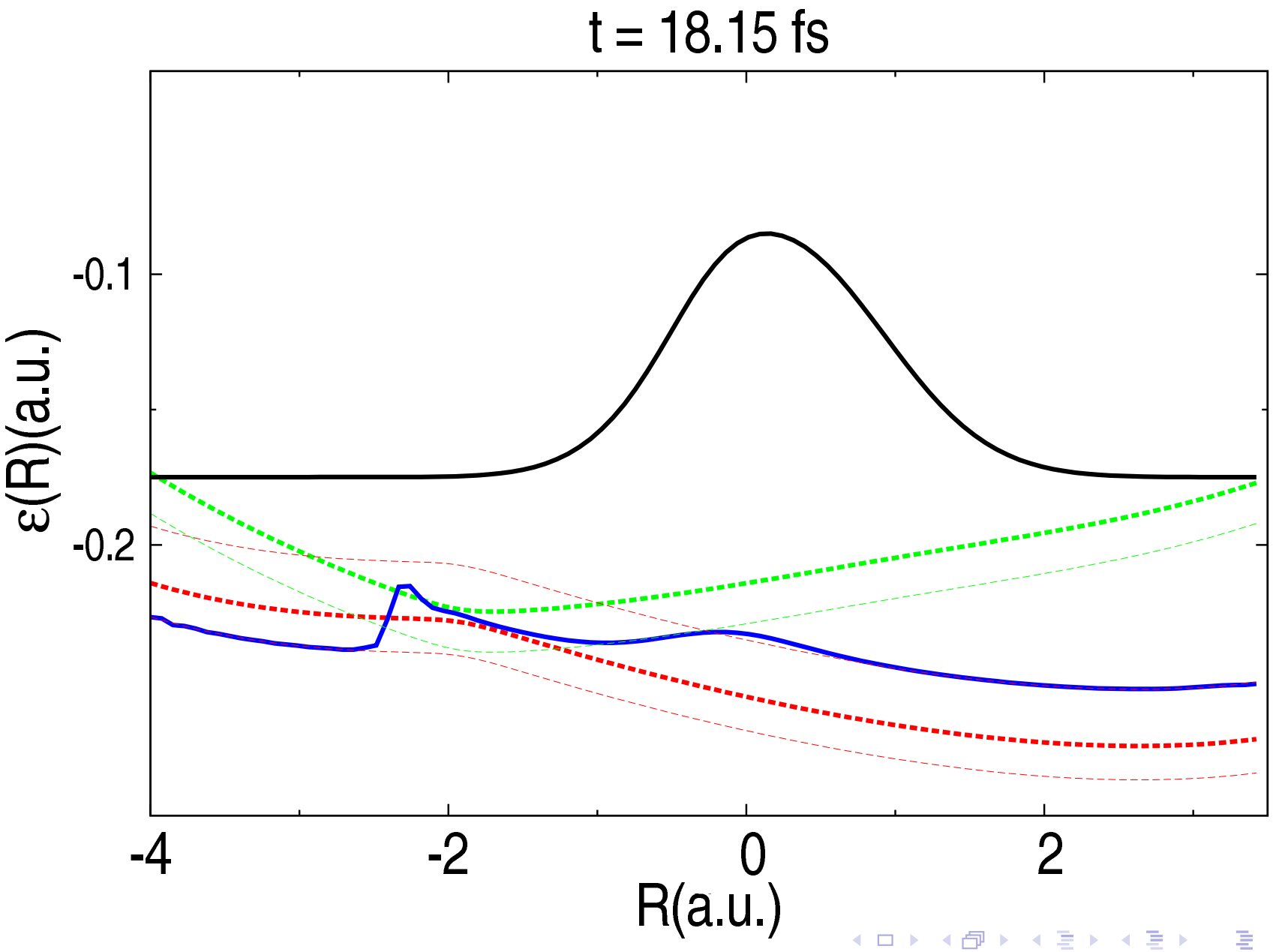

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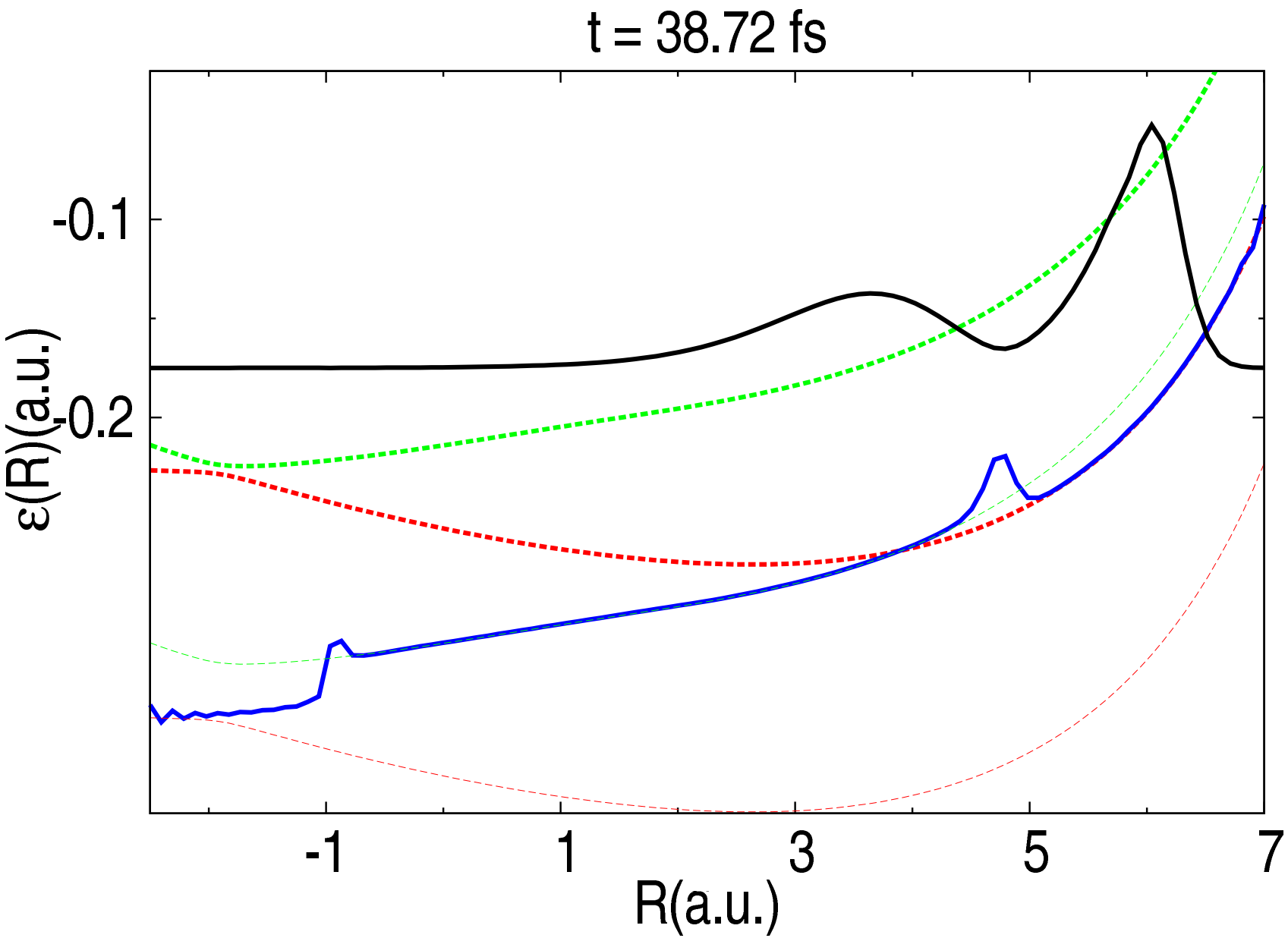


Analysis of the step

$$\Psi(r,R,t) = \chi_1(R,t)\phi_R^{(1)}(r) + \chi_2(R,t)\phi_R^{(2)}(r)$$
$$\Phi_R(r,t) = F_1(R,t)\phi_R^{(1)}(r) + F_2(R,t)\phi_R^{(2)}(r)$$

where $F_k(R,t) = \frac{e^{i\theta}\chi_k(R,t)}{\sqrt{|\chi_1(R,t)|^2+|\chi_2(R,t)|^2}}$

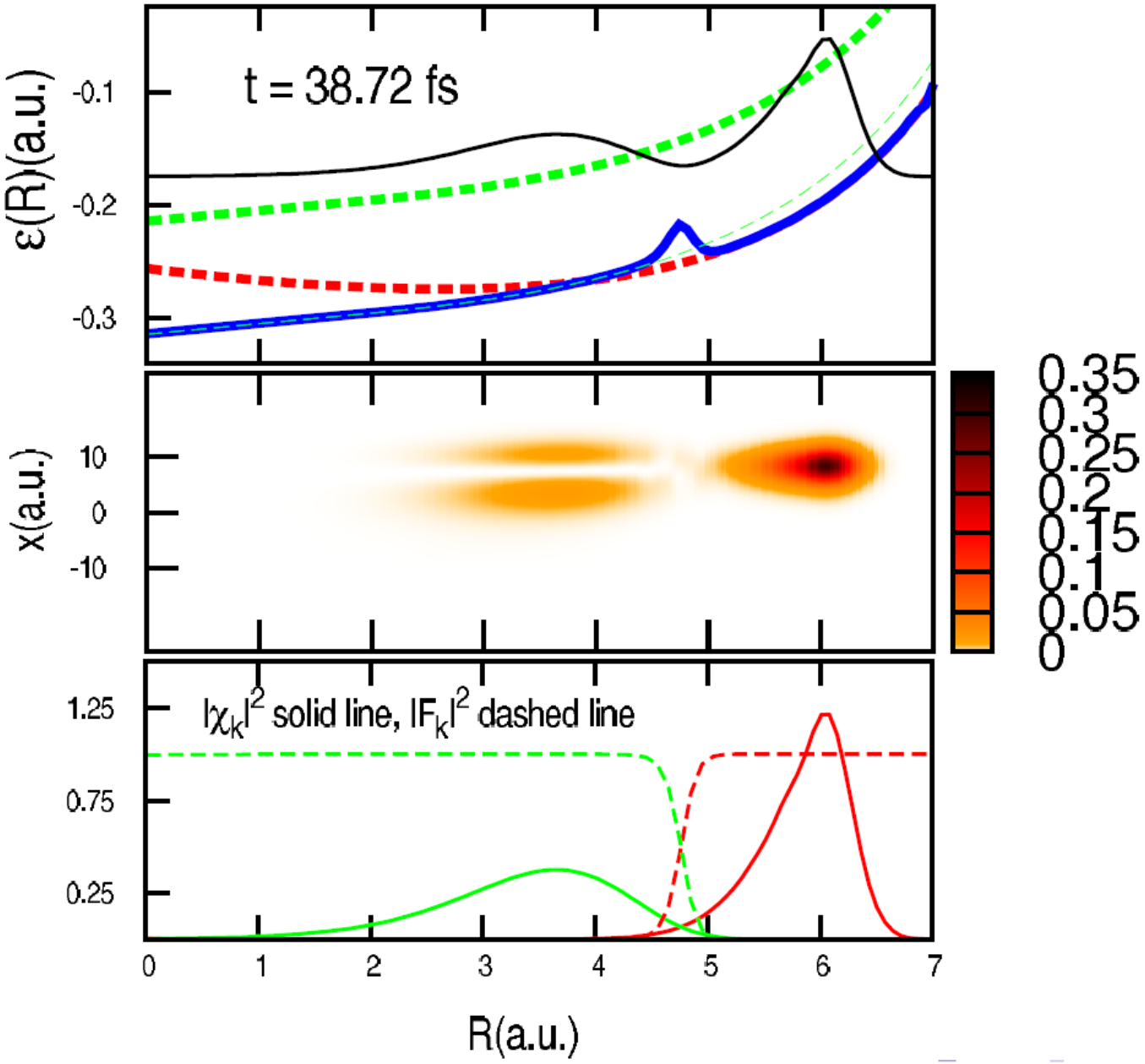
$$\epsilon(R,t) = |F_1|^2\left(\epsilon_{BO}^{(1)} + \dot{\gamma}_1\right) + |F_2|^2\left(\epsilon_{BO}^{(2)} + \dot{\gamma}_2\right)$$

at R_0, the cross-over of $|\chi_1|$ and $|\chi_2|$, where $|\chi_1(R_0,t)| = |\chi_2(R_0,t)| = |X(t)|$, regardless of $|X(t)|$'s value, $|F_1|^2$ and $|F_2|^2$ are always $|F_1(R_0,t)|^2 = |F_2(R_0,t)|^2 = 1/2$, R_0 being the center of the region where steps form

$$\Delta R = \frac{2}{\alpha}$$

$$\alpha(t) = \frac{\left(\nabla_R |\chi_1(R,t)|\right)_{R_0} - \left(\nabla_R |\chi_2(R,t)|\right)_{R_0}}{|X(t)|}$$

Analysis of the step



Summary

- We have shown $\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}, t) = \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t) \cdot \chi(\underline{\underline{\mathbf{R}}}, t)$ is an exact representation of the complete electron-nuclear wavefunction if $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)$ and $\chi(\underline{\underline{\mathbf{R}}}, t)$ satisfy the right equations

- Proper definition of the of Exact time-dependent potential energy surfaces

- Proper definition of the of Exact time-dependent vector potential

- We have shown that the TDPES is a useful tool to interpret different dissociation mechanisms

- We have investigated the structure of the TDPES in the presence of strong non-adiabatic coupling (avoided-crossing)

THANKS!

Equations

electronic equation

$$\left(\hat{H}^{BO}_{\underline{\underline{\mathbf{R}}}} + \hat{V}^{e}_{ext}(\underline{\underline{\mathbf{r}}}, t) + \hat{U}^{coup}_{en} - \epsilon(\underline{\underline{\mathbf{R}}}, t)\right)\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t) = i\partial_t \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)$$

nuclear equation

$$\left(\sum_{\nu=1}^{N_n} \frac{1}{2M_\nu}(-i\nabla_\nu + \mathbf{A}_\nu)^2 + \hat{V}^{n}_{ext}(\underline{\underline{\mathbf{R}}}, t) + \epsilon(\underline{\underline{\mathbf{R}}}, t)\right)\chi(\underline{\underline{\mathbf{R}}}, t) = i\partial_t \chi(\underline{\underline{\mathbf{R}}}, t)$$

gauge transformation

$$\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t) \rightarrow \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t) = e^{i\theta(\underline{\underline{\mathbf{R}}}, t)}\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}, t)$$

$$\chi(\underline{\underline{\mathbf{R}}}, t) \rightarrow \tilde{\chi}(\underline{\underline{\mathbf{R}}}, t) = e^{-i\theta(\underline{\underline{\mathbf{R}}}, t)}\chi(\underline{\underline{\mathbf{R}}}, t)$$

$$\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t) \rightarrow \tilde{\mathbf{A}}_\nu(\underline{\underline{\mathbf{R}}}, t) = \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}, t) + \nabla_\nu \theta(\underline{\underline{\mathbf{R}}}, t)$$

$$\epsilon(\underline{\underline{\mathbf{R}}}, t) \rightarrow \tilde{\epsilon}(\underline{\underline{\mathbf{R}}}, t) = \epsilon(\underline{\underline{\mathbf{R}}}, t) + \partial_t \theta(\underline{\underline{\mathbf{R}}}, t)$$

Static limit

$$\Psi(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}},t) = e^{-iEt}\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})\chi(\underline{\underline{\mathbf{R}}}) = [e^{-i\epsilon(\underline{\underline{\mathbf{R}}})t}\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})][e^{-i(E-\epsilon(\underline{\underline{\mathbf{R}}}))t}\chi(\underline{\underline{\mathbf{R}}})]$$

Electronic equation:

$$\left(\hat{H}^{BO}_{\underline{\underline{\mathbf{R}}}} + \hat{U}^{coup}_{en}\right)\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}) = \epsilon(\underline{\underline{\mathbf{R}}})\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})$$

Nuclear equation:

$$\left(\sum_{\nu=1}^{N_n}\frac{1}{2M_\nu}(-i\nabla_\nu + \mathbf{A}_\nu)^2 + \hat{\mathbf{V}}^{\mathbf{ext}}_{\mathbf{n}}(\underline{\underline{\mathbf{R}}}) + \epsilon(\underline{\underline{\mathbf{R}}})\right)\chi(\underline{\underline{\mathbf{R}}}) = \mathbf{E}\chi(\underline{\underline{\mathbf{R}}})$$

- $\epsilon(\underline{\underline{\mathbf{R}}}) =< \Phi_{\underline{\underline{\mathbf{R}}}}|\hat{H}^{BO}_{\underline{\underline{\mathbf{R}}}} + \sum_{\nu=1}^{N_n}\frac{(-i\nabla_\nu - \mathbf{A}_\nu)^2}{2M_\nu}|\Phi_{\underline{\underline{\mathbf{R}}}} >_e$
  exact potential energy surface is gauge invariant
- neglecting the $1/M_\nu$ terms in the electronic equation leads to the BO electronic equation and potential energy surfaces
- The static decomposition was shown first by Hunter (G. Hunter, Int. J. Quantum Chem. 9, 237 (1975))

Vector potential

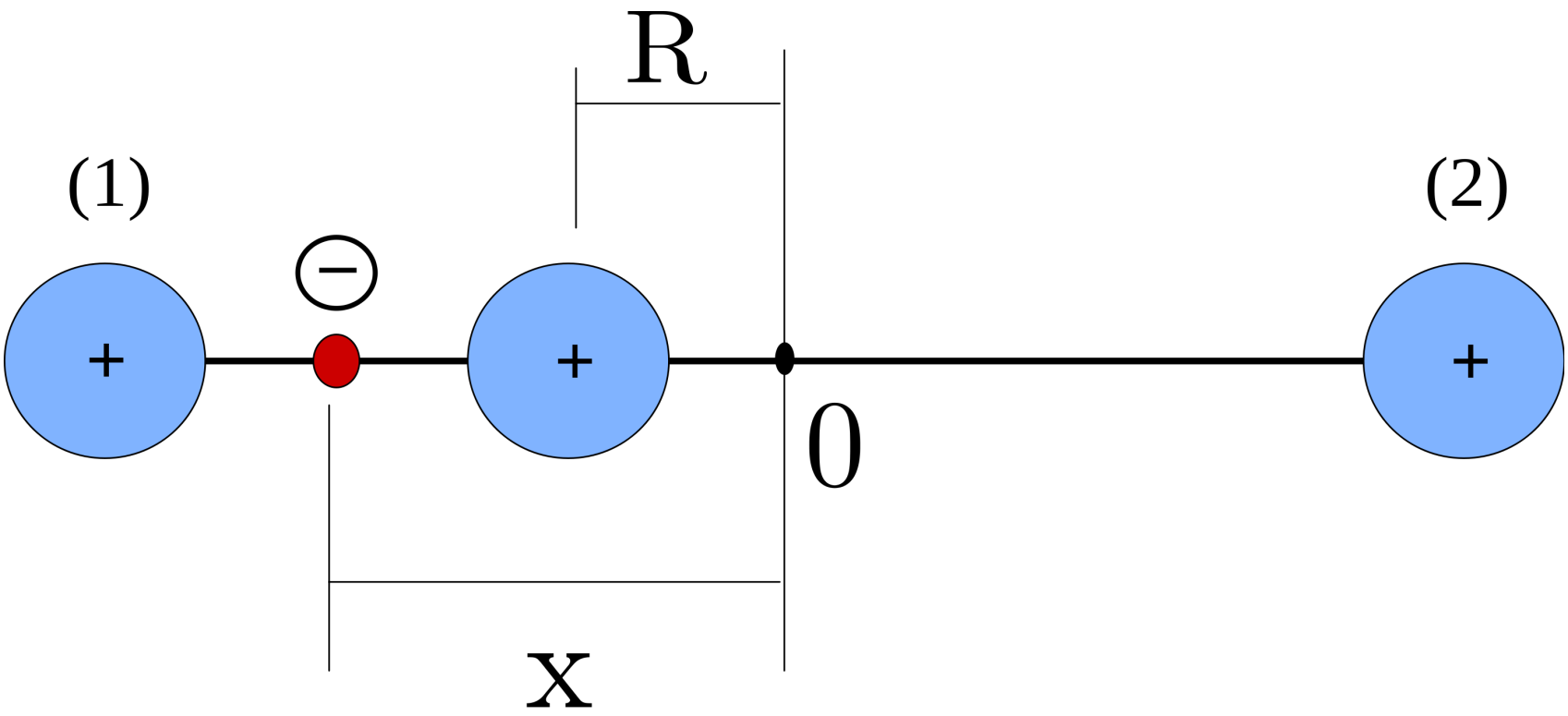
$$\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}},t) = \frac{Im\langle\Psi|\nabla_\nu\Psi\rangle_{\underline{\underline{\mathbf{r}}}}}{|\chi(\underline{\underline{R}},t)|^2} - \nabla_\nu S(\underline{\underline{\mathbf{R}}})$$

where $\chi(\underline{\underline{\mathbf{R}}}) := e^{iS(\underline{\underline{\mathbf{R}}})}|\chi(\underline{\underline{\mathbf{R}}})|$

For a non current carrying molecular ground state

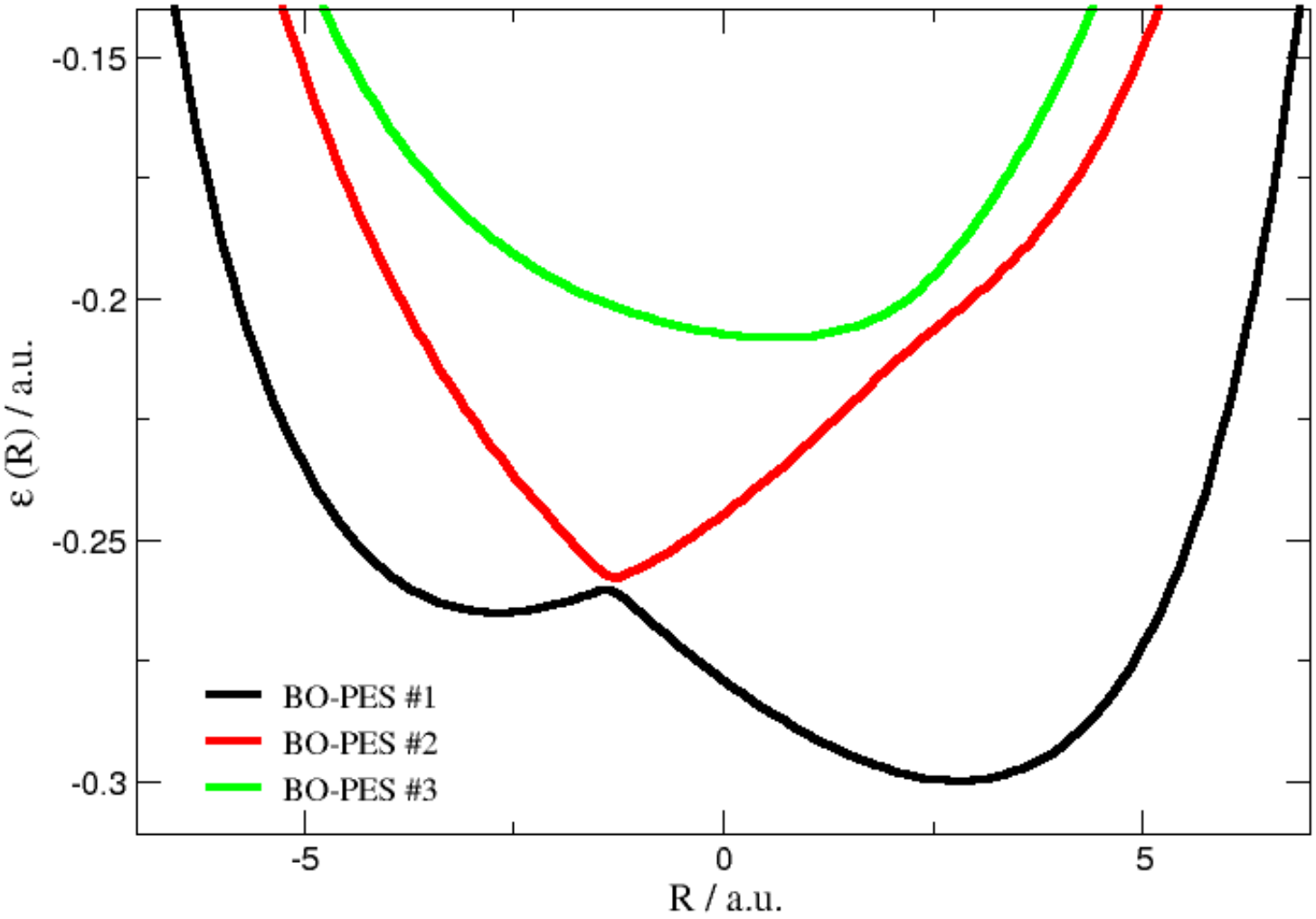
$$\mathbf{A}_\nu(\underline{\underline{\mathbf{R}}}) = -\nabla_\nu S(\underline{\underline{\mathbf{R}}})$$

Model (Horia metiu)



Nuclei (1) and (2) are heavy: their positions are fixed

Adiabatic potential energy surfaces



Exact potential energy surfaces