Nuclear quantum effects in electronic (non-)adiabatic dynamics

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Outline

- Exact factorization of the electron-nuclear wavefunction and trajectory-based scheme
- Nuclear dynamics (TDSE) by Hamilton-Jacobi (with quantum potential) and the continuity equation for the nuclear density
- The approximate algorithm:
  - nuclear density as the sum of travelling Gaussians
  - Hamilton-Jacobi by the method of characteristics
- An illustrative example for two phenomena:
  - an adiabatic tunnelling process
  - a strong non-adiabatic process

Exact factorization

A. Abedi, N. T. Maitra, E. K. U. Gross, *Phys. Rev. Lett.* **105** (2010) 123002; *J. Chem. Phys.* **137** (2012) 22A530.

Exact factorization of the electron-nuclear wavefunction

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

contains electronic kinetic energy and all interaction potentials

EF

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

$$i\hbar\partial_t\Phi_\mathbf{R}(\mathbf{r},t) = \left[\hat{H}_{BO} + \hat{U}_{en}(\mathbf{R},t) - \epsilon(\mathbf{R},t)\right]\Phi_\mathbf{R}(\mathbf{r},t)$$

$$i\hbar\partial_t\chi(\mathbf{R},t) = \left[\sum_{\nu=1}^{N_n} \frac{[-i\hbar\nabla_\nu + \mathbf{A}_\nu(\mathbf{R},t)]^2}{2M_\nu} + \epsilon(\mathbf{R},t)\right]\chi(\mathbf{R},t)$$

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Exact factorization of the electron-nuclear wavefunction

→ **partial normalization condition**

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

→ **electron-nuclear coupling operator**

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

→ **time-dependent vector potential**

$$\mathbf{A}_{\nu}[\Phi_{\mathbf{R}};\mathbf{R},t] = \langle\Phi_{\mathbf{R}}(t)|\,-i\hbar\nabla_{\nu}\Phi_{\mathbf{R}}(t)\rangle_{\mathbf{r}}$$

→ **time-dependent potential energy surface**

$$\epsilon[\Phi_{\mathbf{R}};\mathbf{R},t] = \langle\Phi_{\mathbf{R}}(t)|\,\hat{H}_{BO}+\hat{U}_{en}-i\hbar\partial_t\,|\Phi_{\mathbf{R}}(t)\rangle_{\mathbf{r}}$$

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Nuclear dynamics via Hamilton-Jacobi and continuity equations

F. Agostini, I. Tavernelli, G. Ciccotti, *Eur. J. Phys. B,* special issue in honour of Hardy Gross (accepted).

The polar form of the nuclear wavefunction

$$\chi(\mathbf{R},t) = \sqrt{\Gamma(\mathbf{R},t)}\exp\left[\frac{i}{\hbar}S(\mathbf{R},t)\right]$$

the nuclear time-dependent Schrödinger equation becomes

Hamilton-Jacobi equation with quantum potential

$\mathcal{Q}(\mathbf{R},t)$

$$\partial_t S = -\sum_\nu \frac{[\nabla_\nu S + \mathbf{A}_\nu]^2}{2M_\nu} - \left(\epsilon + \sum_\nu \frac{-\hbar^2}{2M_\nu}\frac{\nabla_\nu^2\sqrt{\Gamma}}{\sqrt{\Gamma}}\right)$$

quantum potential

continuity equation

$$\partial_t \Gamma = -\sum_\nu \nabla_\nu \cdot \left(\Gamma \frac{\nabla_\nu S + \mathbf{A}_\nu}{M_\nu}\right)$$

nuclear probability current

F. Agostini, I. Tavernelli, G. Ciccotti, *Eur. J. Phys. B,* special issue in honour of Hardy Gross (accepted).

Hamilton-Jacobi and the method of characteristics

$$F\left(S, \boldsymbol{\nabla} S, S_t, \mathbf{R}, t\right) \equiv F\left(S, \mathbf{P}, E, \mathbf{R}, t\right) = E + H\left(\mathbf{P}, \mathbf{R}, t\right) = 0$$

$$dF = F_S\,\dot{S} + F_{\mathbf{P}} \cdot \dot{\mathbf{P}} + F_E\,E + F_{\mathbf{R}} \cdot \dot{\mathbf{R}} + F_t\,\dot{t} = 0$$

i.e., orthogonality of the general gradient of *F* and the parametric equations of the Hamilton-Jacobi characteristics

$$\partial_{R_\nu} F(\mathbf{P}, S_t, \mathbf{R}, t) = \partial_{R_\nu} H\left(\mathbf{P}, \mathbf{R}, t\right)$$
$$\partial_t F(\mathbf{P}, S_t, \mathbf{R}, t) = \partial_t H\left(\mathbf{P}, \mathbf{R}, t\right)$$
$$\partial_{P_\nu} F(\mathbf{P}, S_t, \mathbf{R}, t) = \partial_{P_\nu} H\left(\mathbf{P}, \mathbf{R}, t\right)$$
$$\partial_E F(\mathbf{P}, S_t, \mathbf{R}, t) = 1$$
$$\partial_S F(\mathbf{P}, S_t, \mathbf{R}, t) = 0,$$

$\nu = 1, \ldots, N_n$

$$\dot{\mathbf{R}}(s) = F_{\mathbf{P}}$$
$$\dot{t}(s) = 1$$
$$\dot{\mathbf{P}}(s) = -F_S\,\mathbf{P} - F_{\mathbf{R}}$$
$$\dot{E} = F_t = -\partial_t H$$
$$\dot{S} = F_{\mathbf{P}} \cdot \dot{\mathbf{P}} + F_E\,E$$

($\dot{t}(s) = 1$ and $\dot{E} = F_t = -\partial_t H$): trivial

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Hamilton-Jacobi and the method of characteristics

$$\dot{\mathbf{R}}_\nu = \boldsymbol{\nabla}_{P_\nu} H_n = \frac{\mathbf{P}_\nu(t) + \mathbf{A}_\nu(\mathbf{R},t)}{M_\nu}$$

$$\dot{\mathbf{P}}_\nu = -\boldsymbol{\nabla}_{R_\nu} H_n = -\boldsymbol{\nabla}_{R_\nu}\left[\sum_{\nu'} \frac{[\nabla_{\nu'} S + \mathbf{A}_{\nu'}]^2}{2M_{\nu'}} - (\epsilon + \mathcal{Q})\right]$$

$$\dot{S} = \sum_{\nu=1}^{N_n} \mathbf{P}_\nu(t) \cdot \frac{\mathbf{P}_\nu(t) + \mathbf{A}_\nu(\mathbf{R},t)}{M_\nu} - H_n$$

The solution of the Hamilton-Jacobi equation, $S(\mathbf{R},t)$, is obtained by integrating the ODEs for an infinite number of initial conditions, to determine the value of S at time t and position $\mathbf{R}$, thus obtaining $S(\mathbf{R},t)$.

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Nuclear density as travelling Gaussians

S. K. Min, F. Agostini, E. K. U. Gross, *Phys. Rev. Lett.*, **115** (2015) 073001.

Nuclear density and quantum potential

$$\Gamma(\mathbf{R},t) = |\chi(\mathbf{R},t)|^2 = \frac{1}{N_{tr}} \sum_{I=1}^{N_{tr}} \prod_{\nu=1}^{N_n} G_{\sigma_{I,\nu}}\left(\mathbf{R}_\nu; \mathbf{R}_\nu^{(I)}(t)\right)$$

$G_{\sigma I,\nu}$ is a normalized Gaussian centered at $R_\nu^{(I)}(t)$ with variance σ_I related to the number of trajectories $R_\nu^{(J)}(t)$ falling in a sphere of given (small) radius centered at $R_\nu^{(I)}(t)$

$$\sigma_{I,\nu} = \frac{\sqrt{\overline{\boldsymbol{\mathcal{D}}^2}_{I,\nu} - \overline{\boldsymbol{\mathcal{D}}}^2_{I,\nu}}}{n_{tr}^{(I)}}$$

$$\overline{\boldsymbol{\mathcal{D}}}_{I,\nu} = \frac{1}{n_{tr}^{(I)}} \sum_{J=1}^{n_{tr}^{(I)}} \left|\mathbf{R}_\nu^{(I)}(t) - \mathbf{R}_\nu^{(J)}(t)\right|$$

$$\overline{\boldsymbol{\mathcal{D}}^2}_{I,\nu} = \frac{1}{n_{tr}^{(I)}} \sum_{J=1}^{n_{tr}^{(I)}} \left|\mathbf{R}_\nu^{(I)}(t) - \mathbf{R}_\nu^{(J)}(t)\right|^2$$

TO NOTE: the initial conditions are sampled from the chosen density at *t=0* and so the weight is far from uniform — larger weights in the regions of high probability at *t=0*
(a concession to semiclassical approximation)

S. K. Min, F. Agostini, E. K. U. Gross, *Phys. Rev. Lett.*, **115** (2015) 073001.

Illustrative examples

F. Agostini, I. Tavernelli, G. Ciccotti, *Eur. J. Phys. B,* special issue in honour of Hardy Gross (accepted).

Illustrative model

$$\hat{H} = \frac{\hat{P}^2}{2M} + \begin{pmatrix} V_+(R) & d \\ d & V_-(R) \end{pmatrix}$$

$V_\pm(R) = aR^2 \pm bR + c$
with $a = 1.0\ au, b = 3.5\ au, c = 3.0625\ au,$
$d = 1.0\ au$ (set 1), $0.25\ au$ (set 2)

eigenvalues and eigenvectors

$$E_\pm(R) = \frac{V_+(R) + V_-(R)}{2} \pm \frac{1}{2}\sqrt{\left(V_+(R) - V_-(R)\right)^2 + 4d^2}$$

$$|\pm; R\rangle = N(R)\left(|\uparrow\rangle + \frac{E_\pm(R) - V_+(R)}{d}|\downarrow\rangle\right)$$

$$N(R) = d/\sqrt{d^2 + \left(E_\pm(R) - V_+(R)\right)^2}$$

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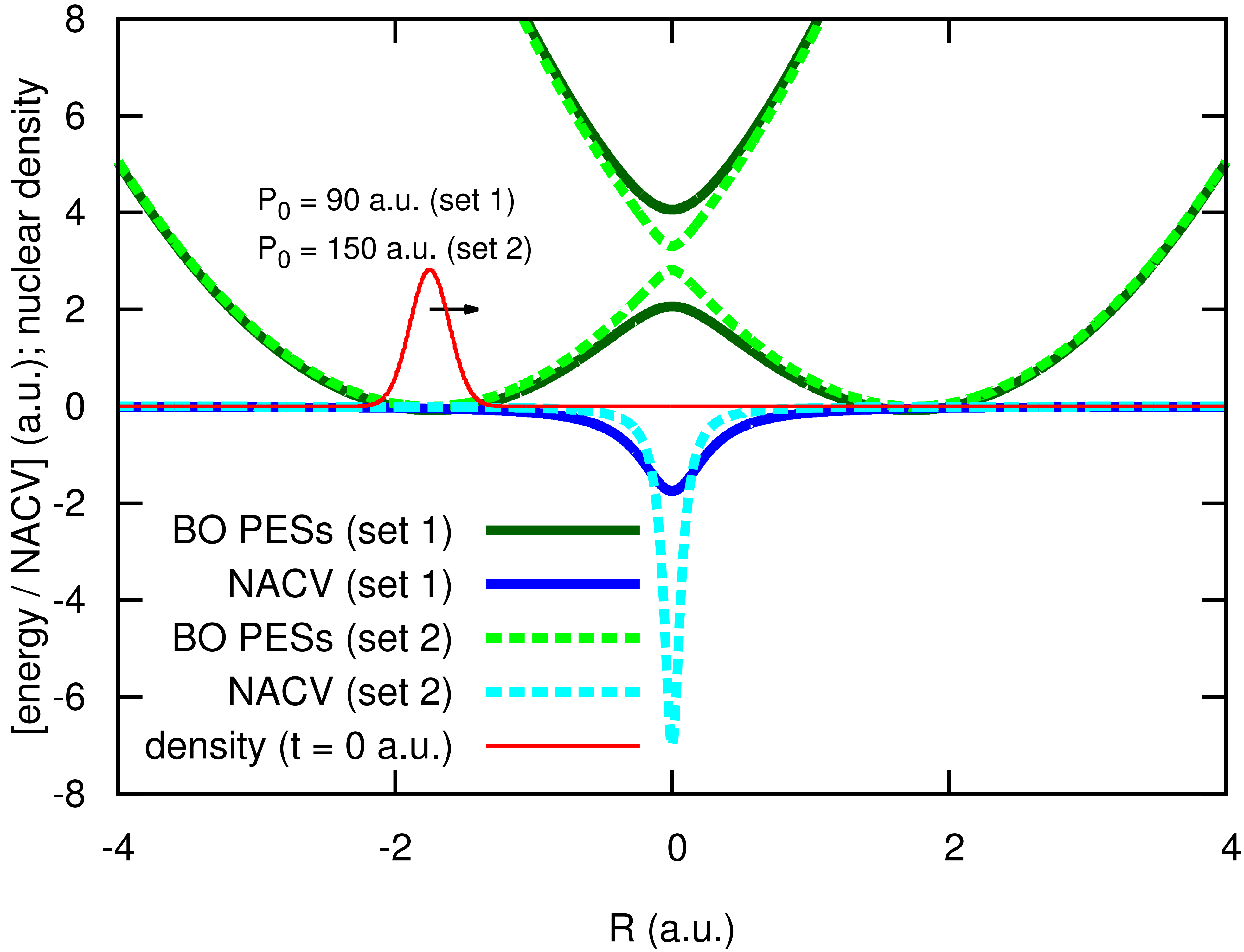
Illustrative model



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Illustrative model: exact quantum dynamics

INITIAL CONDITION

$$\begin{pmatrix} \Psi_+(R,t=0) \\ \Psi_-(R,t=0) \end{pmatrix} = \begin{pmatrix} 0 \\ \sqrt[4]{\frac{1}{\pi\sigma^2}}\, e^{-\frac{(R-R_0)^2}{2\sigma^2}} e^{\frac{i}{\hbar}P_0(R-R_0)} \end{pmatrix}$$

$$\text{with } R_0 = -1.75\ au, \sigma = 0.2\ au,$$

$$P_0 = 90.0\ au\ (\text{set } 1),\ 150.0\ au\ (\text{set } 2)$$

FULL EVOLUTION OPERATOR

$$e^{-\frac{i}{\hbar}\hat{H}dt} \simeq e^{-\frac{i}{\hbar}\hat{H}_{el}\frac{dt}{2}} e^{-\frac{i}{\hbar}\frac{\hat{P}^2}{2M}dt} e^{-\frac{i}{\hbar}\hat{H}_{el}\frac{dt}{2}}$$

$$\text{with } dt = 0.1\ au$$

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Illustrative model: exact quantum dynamics

using Pauli matrices…

$$\hat{H}_{el}(R) = \begin{pmatrix} V_+(R) & d \\ d & V_-(R) \end{pmatrix} = \alpha(R)\hat{\sigma}_x + \beta(R)\hat{\sigma}_z + \gamma(R)\hat{I}$$

&

$$\gamma(R) + \beta(R) = V_+(R)$$
$$\gamma(R) - \beta(R) = V_-(R)$$
$$\alpha(R) = d$$

… the action of the evolution operator containing the electronic Hamiltonian is

$$e^{-\frac{i}{\hbar}\frac{dt}{2}\hat{H}_{el}} = \begin{pmatrix} e^{-\frac{i}{\hbar}\frac{dt}{2}[\gamma(R)+\beta(R)]}\cos\left(\frac{\alpha(R)dt}{2\hbar}\right) & -ie^{-\frac{i}{\hbar}\frac{dt}{2}[\gamma(R)-\beta(R)]}\sin\left(\frac{\alpha(R)dt}{2\hbar}\right) \\ -ie^{-\frac{i}{\hbar}\frac{dt}{2}[\gamma(R)+\beta(R)]}\sin\left(\frac{\alpha(R)dt}{2\hbar}\right) & e^{-\frac{i}{\hbar}\frac{dt}{2}[\gamma(R)-\beta(R)]}\cos\left(\frac{\alpha(R)dt}{2\hbar}\right) \end{pmatrix}$$

Illustrative model: trajectory-based quantum dynamics

from the electronic equation of the exact factorization

derivation of ODEs for the electronic wavefunction

Runge-Kutta algorithm to evolve

$$\left(\begin{array}{c} \Phi_{\mathbf{R},+}(t) \\ \Phi_{\mathbf{R},-}(t) \end{array} \right)$$

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from the nuclear equation of the exact factorization

solution per characteristics of the quantum Hamilton-Jacobi equation

Velocity-Verlet algorithm to evolve

$$\mathbf{R}(t), \mathbf{P}(t)$$

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Illustrative model: trajectory-based quantum dynamics

from the electronic equation
of the exact factorization

↓

derivation of
ODEs for the
electronic wavefunction

from the nuclear equation
of the exact factorization

↓

solution per characteristics
of the quantum Hamilton-Jacobi
equation

COUPLED-TRAJECTORY MIXED QUANTUM-CLASSICAL (WITH QUANTUM POTENTIAL)

Runge-Kutta algorithm to evolve

$$\begin{pmatrix} \Phi_{\mathbf{R},+}(t) \\ \Phi_{\mathbf{R},-}(t) \end{pmatrix}$$

Velocity-Verlet algorithm to evolve

$$\mathbf{R}(t), \mathbf{P}(t)$$

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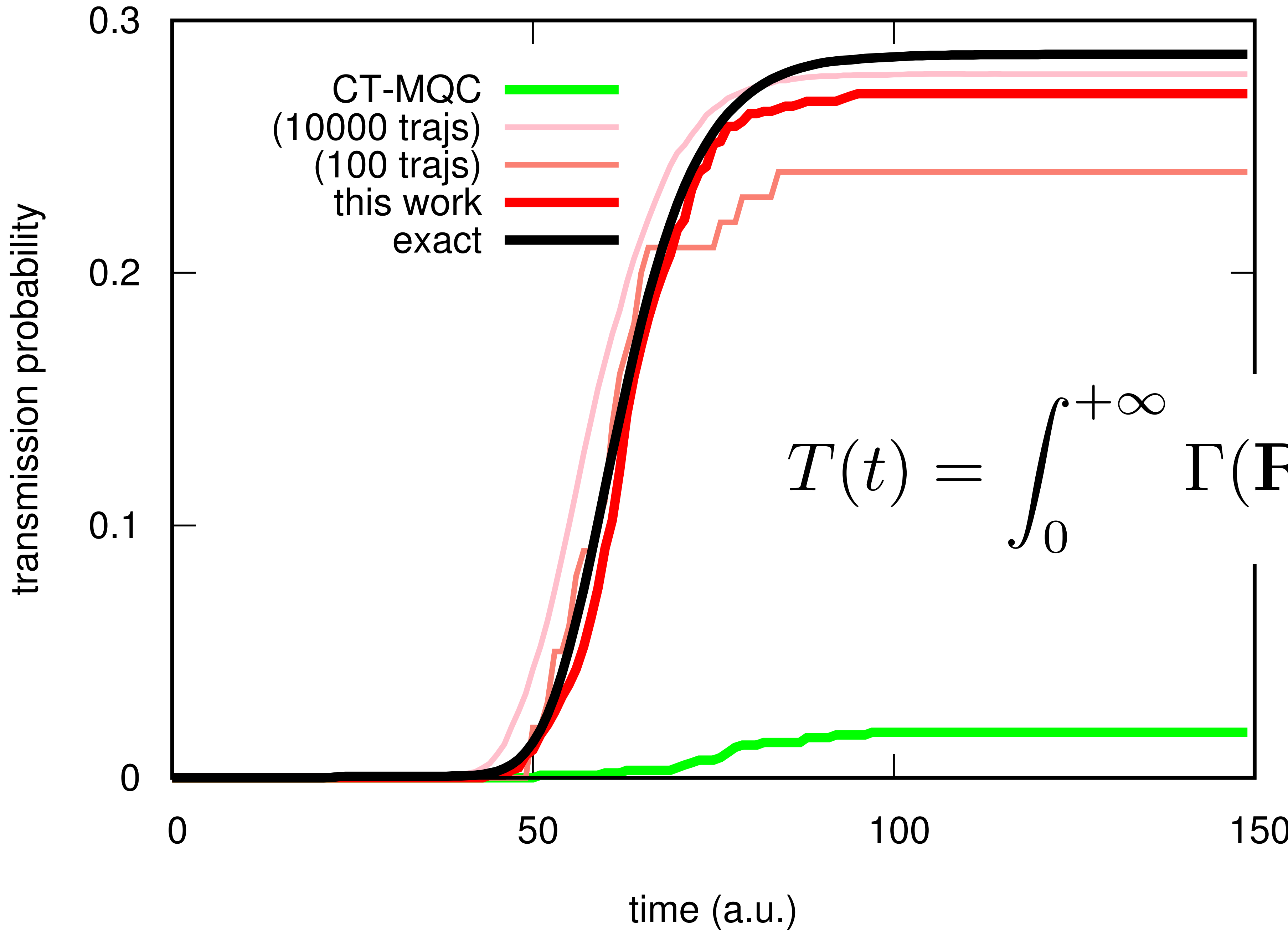
Adiabatic tunnelling process



$$T(t) = \int_0^{+\infty} \Gamma(\mathbf{R}, t)\, d\mathbf{R}$$

Transmission probability across the barrier of the ground-state potential.

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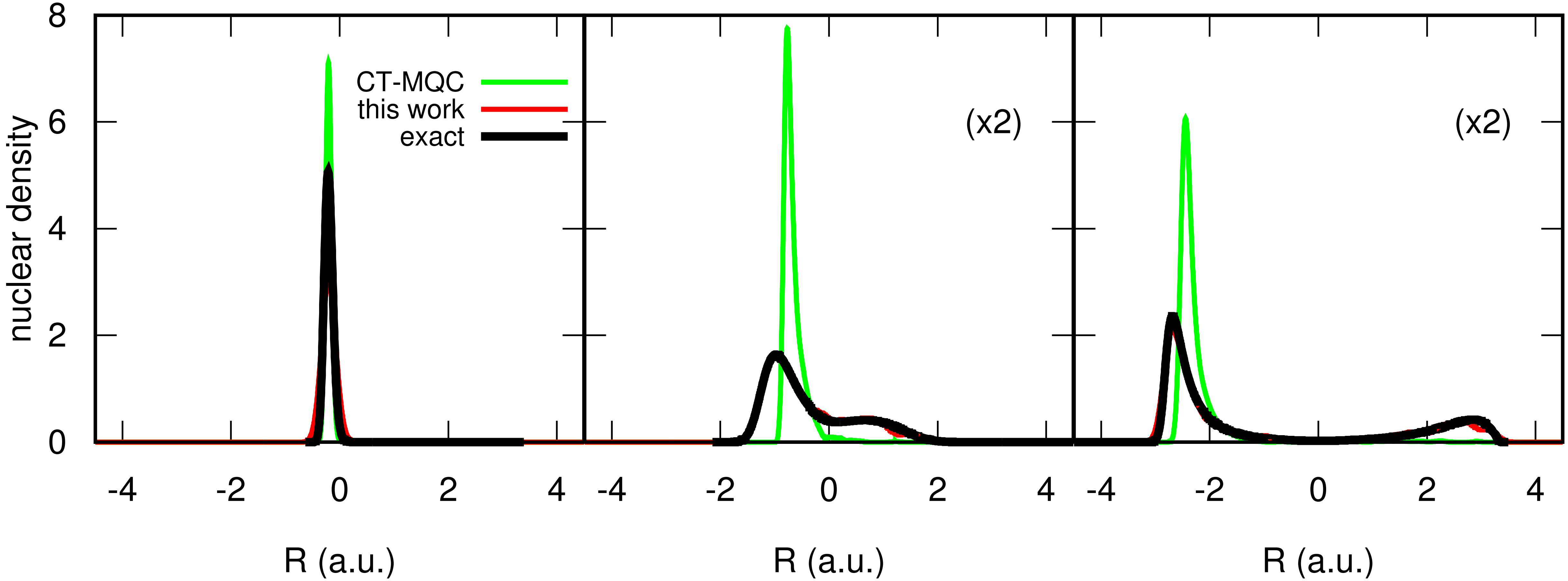
Adiabatic tunnelling process

$$\Gamma(\mathbf{R},t) = |\Psi_+(\mathbf{R},t)|^2 + |\Psi_-(\mathbf{R},t)|^2$$



Snapshots at t = 50,100,140 au (from left to right) of the nuclear density.

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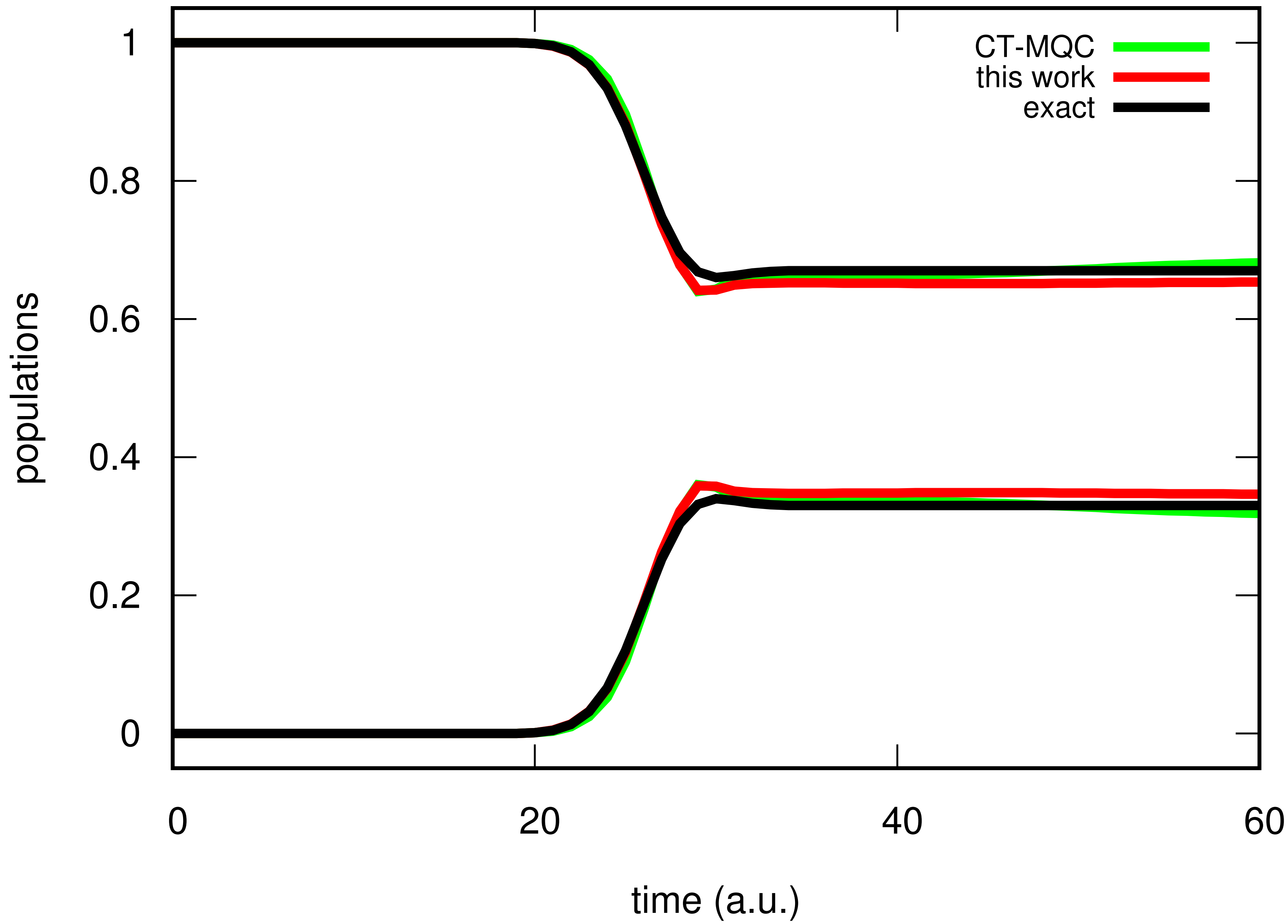
Strong nonadiabatic process



Population of the two electronic adiabatic states considered in the process.

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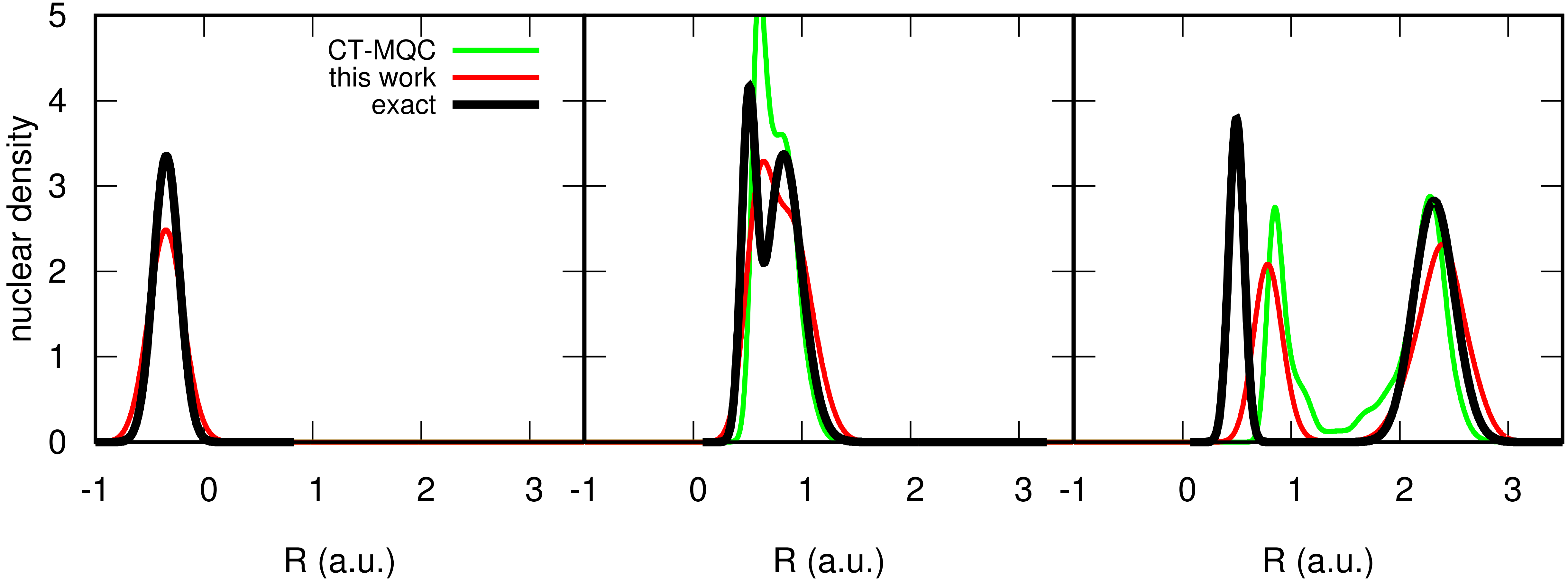
Strong nonadiabatic process

$$\Gamma(\mathbf{R},t) = \left|\Psi_+(\mathbf{R},t)\right|^2 + \left|\Psi_-(\mathbf{R},t)\right|^2$$



Snapshots at t=20,40,60 au (from left to right) of the nuclear density.

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Conclusions & Perspectives

- The zero order estimate of nuclear dynamics can describe qualitatively the tunnelling effect
- An iterative reconstruction of the nuclear dynamics could permit to solve exactly the nuclear quantum evolution
- Non-adiabatic effects are well reproduced
- The computational cost still prohibitive is forbidding challenging applications. However, fast processes (like photo-excitations) and small molecules may give an interesting starting point

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