Interacting trajectory ensemble in the framework of exact factorization

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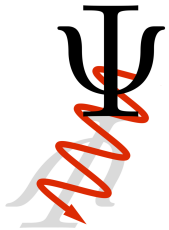


VISTA, May 11th 2022

Non-adiabatic dynamics

Born-Huang expansion

$$\Psi(q,x,t) = \sum_{\alpha} \psi^{\alpha}_{BO}(x,t) \times \phi^{\alpha}(q;x)$$

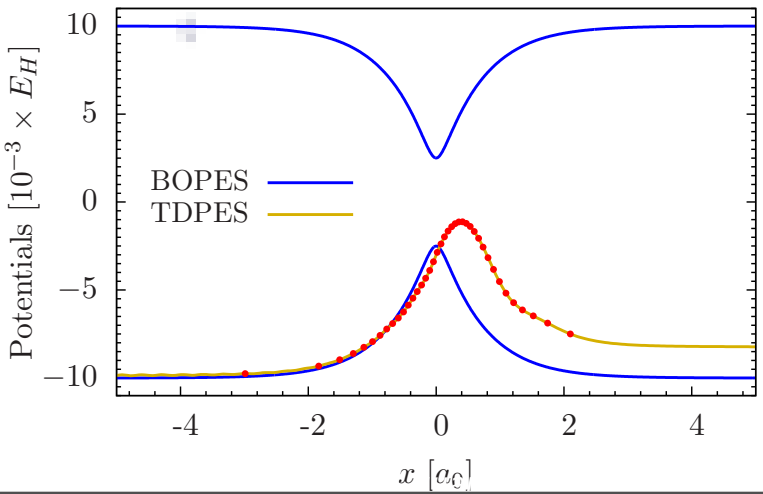
$$\begin{cases} i\hbar\partial_t \psi^{\alpha}_{BO} = \left[\hat{T} + \epsilon^{\alpha}_{BO}(x)\right] \psi^{\alpha}_{BO} \\ \qquad\qquad + \sum_{\beta} \mathcal{F}_{\alpha\beta}(x)\, \psi^{\beta}_{BO} \\ \\ \hat{H}^{\alpha}_{BO}(x)\phi^{\alpha} = \epsilon^{\alpha}_{BO}(x)\phi^{\alpha} \end{cases}$$

Exact Factorization

$$\Psi(q,x,t) = \psi(x,t) \times \phi(q,t;x)$$

$$\begin{cases} i\hbar\partial_t \psi = \left[\sum_{\nu=1}^{3N_n} \frac{[-i\hbar\nabla_\nu + A_\nu(x,t)]^2}{2M_\nu} + \epsilon(x,t)\right] \psi \\ \\ i\hbar\partial_t \phi = \left[\hat{H}_{BO}(x) + \hat{U}_{en}[\phi,\psi] - \epsilon(x,t)\right] \phi \end{cases}$$

Abedi, Maitra & Gross, Phys. Rev. Lett. 105, 123002 (2010)



Unambiguous Ehrenfest-like force on nuclei

$\Rightarrow$ CT-MQC

Abedi, Agostini & Gross, EPL 106 3 33001 (2014)

Problem with nuclear quantum effects?

Hydrodynamics equations (Gauge choice: $A_\nu = 0$)

$$i\hbar \frac{\partial \psi(x,t)}{\partial t}\bigg|_x = \left[\frac{[-i\hbar\partial_x]^2}{2m} + \epsilon(x,t)\right]\psi(x,t)$$

$$\begin{cases} \text{Polar form:} \quad \psi(x,t) = R(x,t)e^{iS(x,t)/\hbar} \qquad R(x,t),\ S(x,t)\ \in \mathbb{R} \\ \text{Trajectories follow density:} \quad J(x,t) = R^2(x,t)\,\dot{x} \\ \text{Lagrangian frame:} \quad \dfrac{d}{dt} = \dfrac{\partial}{\partial t}\bigg|_x + \dot{x}\dfrac{\partial}{\partial x} = \dfrac{\partial}{\partial t}\bigg|_{x_0} \end{cases}$$

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$$\Longrightarrow \begin{cases} \boxed{\dfrac{\partial R^2(x,t)}{\partial t}\bigg|_{x_0} = -R^2(x,t)\dfrac{\partial}{\partial x}\left[\dot{x}\right]} & \text{Continuity eq.} \\ \boxed{m\ddot{x} = \dfrac{\partial \epsilon(x,t)}{\partial x} - \dfrac{\partial Q_\psi(x,t)}{\partial x}} & \text{e.o.m. for } \boxed{x = x(x_0,t)} \end{cases}$$

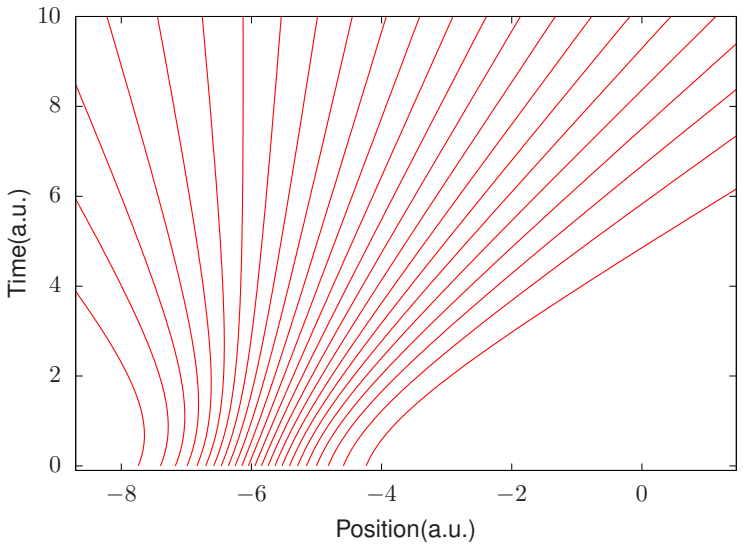
Quantum Potential: $Q_\psi(x,t) = -\dfrac{\hbar^2}{2m\,R(x,t)}\dfrac{\partial^2 R(x,t)}{\partial x^2}$

Wave-free Quantum potential

Free gaussian wavepacket:

$$x = x(C,t)\ , \qquad C(x_0) = \int_{-\infty}^{x_0} \rho_0(x'_0)\, dx'_0$$

$$\boxed{R^2(x,t) = \frac{1}{x'}}\ , \qquad x' = \frac{\partial x}{\partial C}$$



$$\boxed{m\ddot{x} = \frac{\partial \epsilon(x,t)}{\partial x} \underbrace{-\frac{\hbar^2}{4m}\left(\frac{x''''}{x'^4} - 8\frac{x'''x''}{x'^5} + 10\frac{x''^3}{x'^6}\right)}_{f_Q}}$$

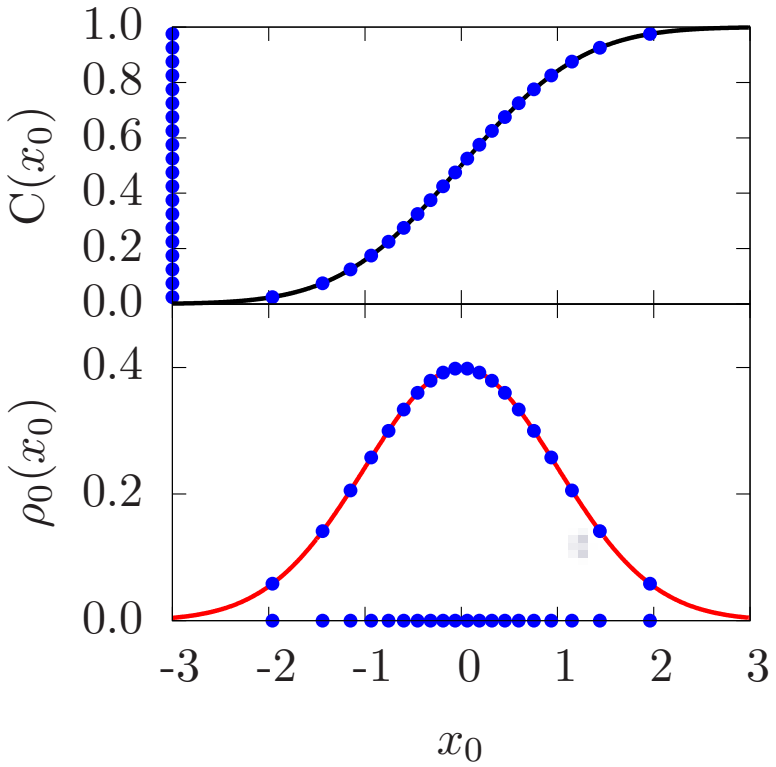
f_Q is the Quantum force

Poirier, Chem. Phys. 370 (1-3), 4-14 (2010)
Schiff & Poirier, J. Chem. Phys. 136 (3), 031102 (2012)

Numerical implementation

Initialization:

- Initial trajectory distribution follows the initial density profile



- Before starting, relaxation step

Cruz-Rodríguez *et al.*, Chem. Phys. 503 39-49 (2018)

Propagation:

Quantum force as trajectory interaction:

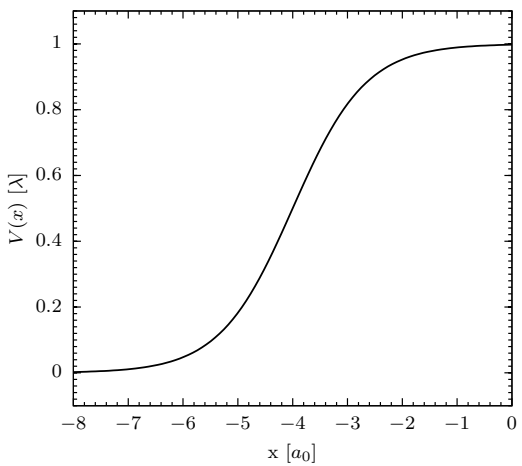
$$f_Q = f_Q(\overbrace{x_{n-2}, x_{n-1}, x_n, x_{n+1}, x_{n+2}}^{5 \text{ neighbors}})$$

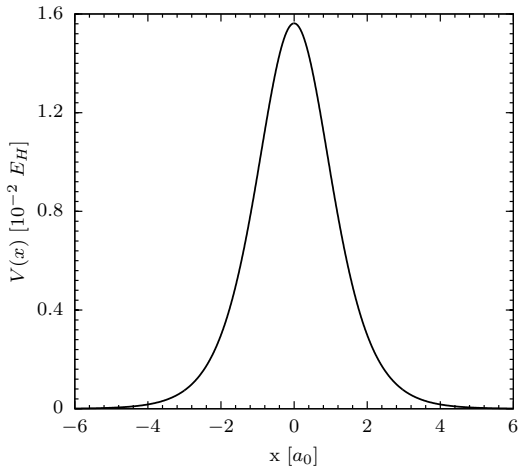
Hall *et al.*, Phys. Rev. X 4 041013 (2014)

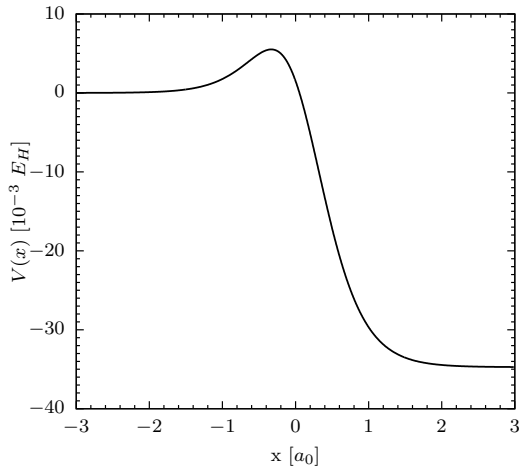
Integrator : Bulirsch-Stoer

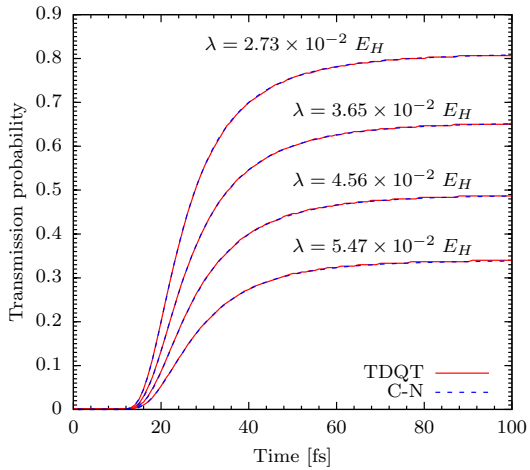
- **No smoothing** (artificial viscosity force)
- **No fitting** (moving weighted least squares)
- **No regridding** (ALE frame)

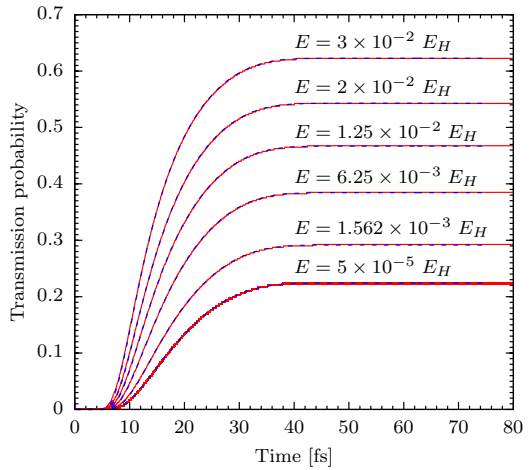
Adiabatic potentials

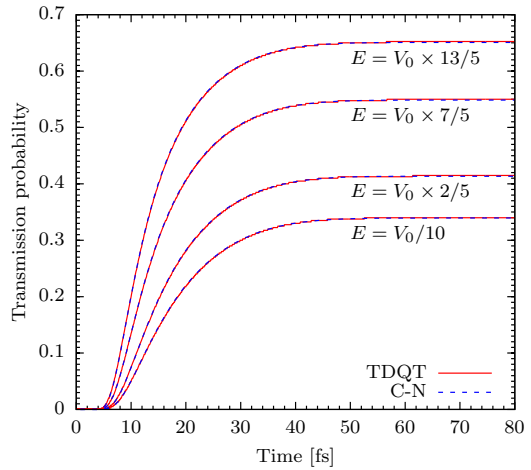












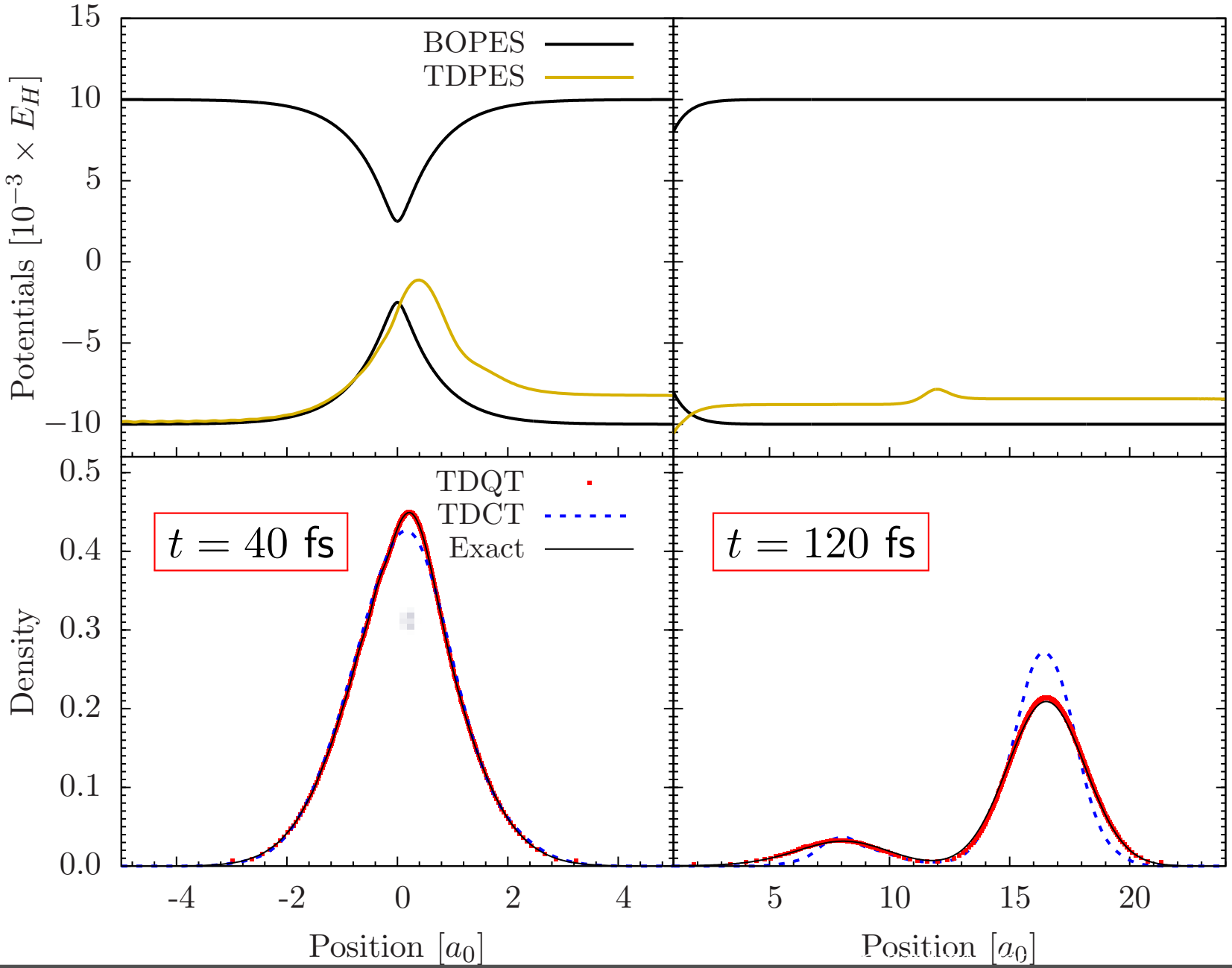
TDQT in EF framework: Proof of principle

- $\Psi(x,t)$ and $\phi(q,t;x)$ are computed exactly on a fixed grid $\{x_i\}$ at discrete times $\{t_j\}$
- Values $\epsilon(x_i,t_j)$ are deduced
- $\dfrac{\partial \epsilon}{\partial x}$ is approximated by finite differences

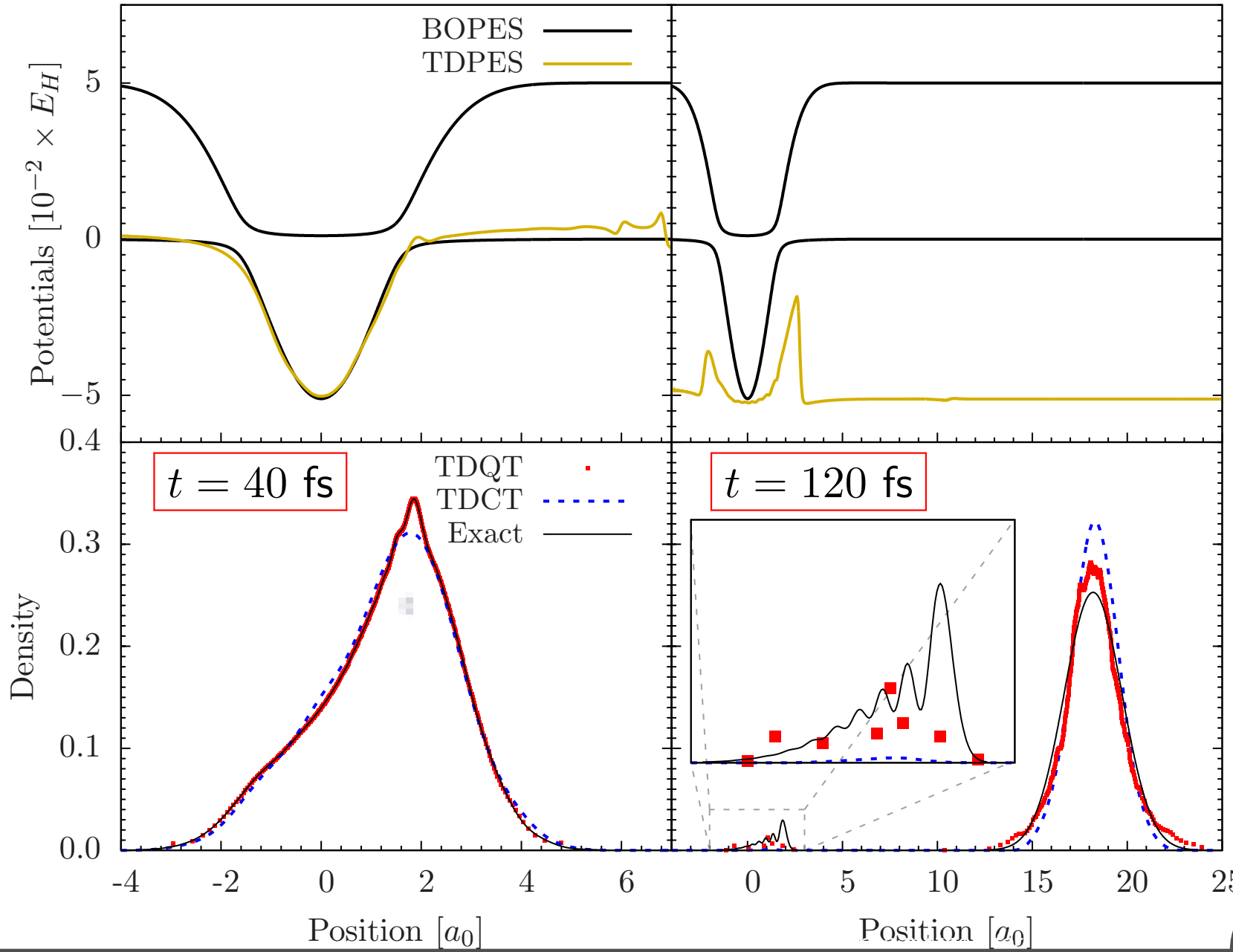
  ☞ linear time and spatial interpolations

- Quantum and classical trajectories are evolved on the pre-determined TDPES

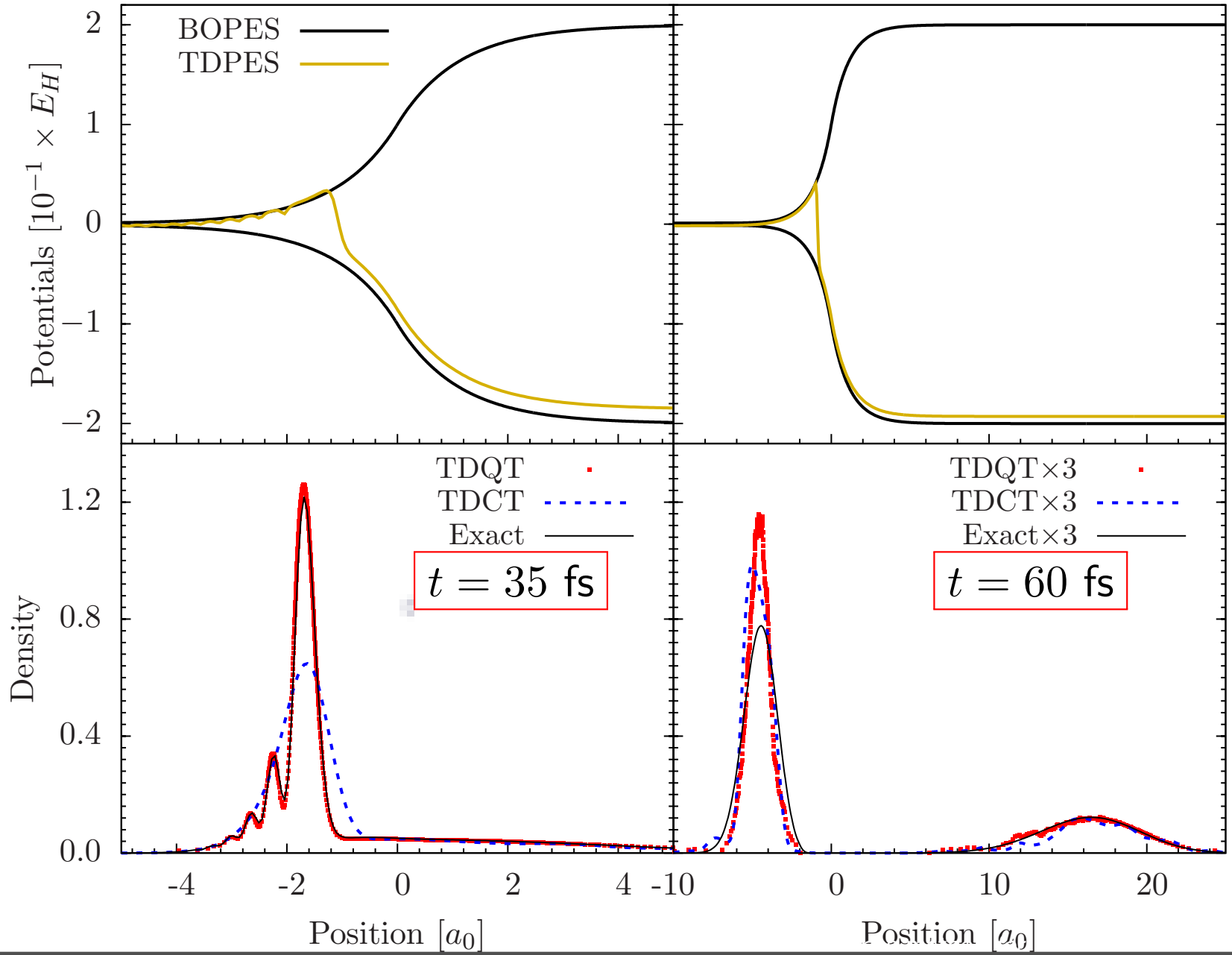
Non-adiabatic potentials: Tully 1, $k_0 = 10\ \hbar a_0^{-1}$



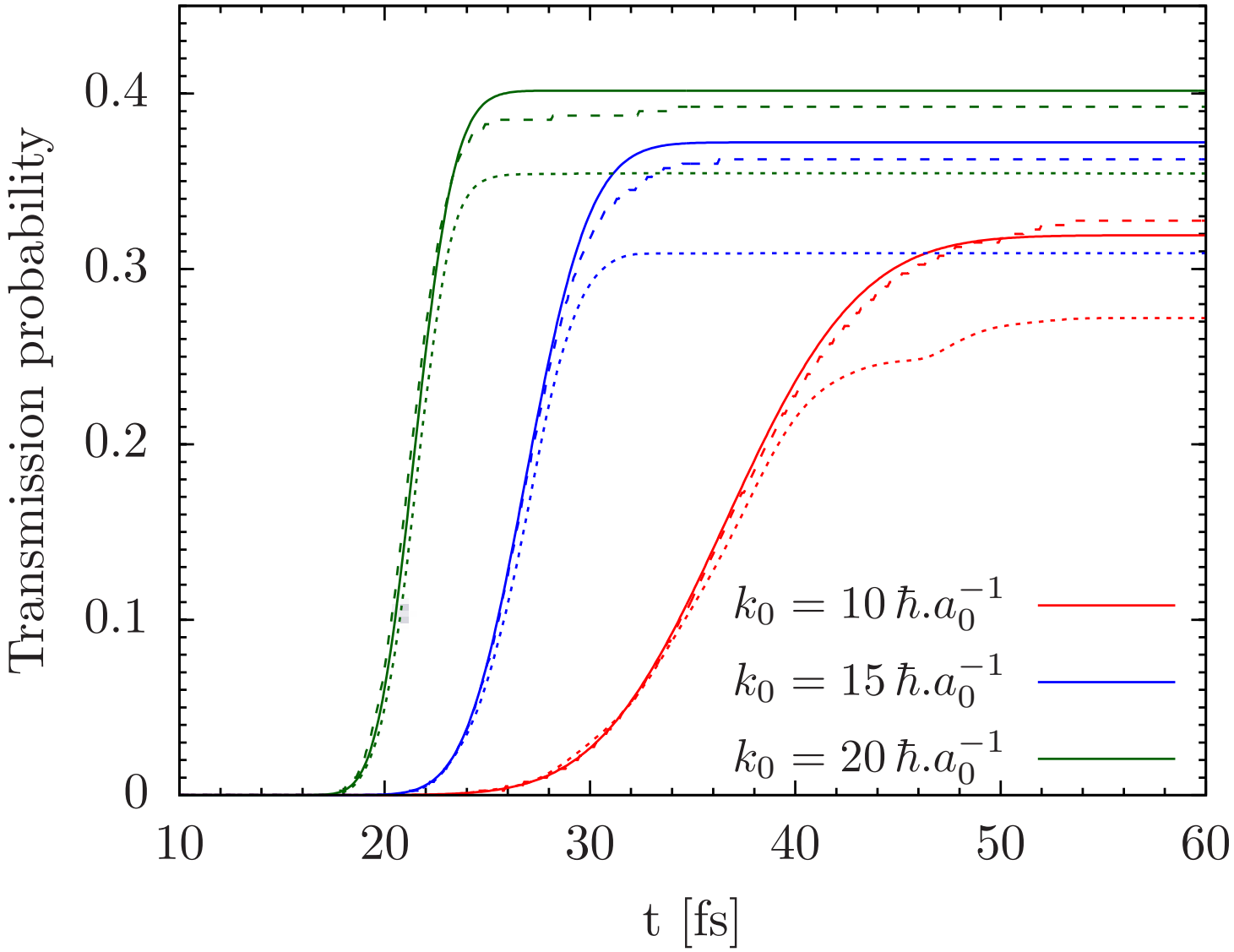
Non-adiabatic potentials: Tully 2, $k_0 = 10\ \hbar a_0^{-1}$



Non-adiabatic potentials: Tully 3, $k_0 = 10\ \hbar a_0^{-1}$



Non-adiabatic potentials: Tully 3



Conclusion

- Quantum trajectories are very sensitive to the accuracy of the TDPES
- Improvement over classical trajectories already clear
- Interacting trajectories remained stable
- This work inspires future developments of a full-fledged algorithm

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