Factorization-based (TD)DFT for the full system of electrons and nuclei: From mixed quantum-classical algorithms to multi-component TDDFT

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האוניברסיטה העברית בירושלים
THE HEBREW UNIVERSITY OF JERUSALEM

Theorem T-II

Electronic equation of motion

$$\Bigg(\underbrace{\hat{T}_e + \hat{W}_{ee} + \hat{V}_e^{ext}\left(\underline{\underline{r}}, t\right) + \hat{V}_{en}\left(\underline{\underline{r}}, \underline{\underline{R}}\right)}_{\hat{H}_{BO}(t)} + \sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu - A_\nu\left(\underline{\underline{R}}, t\right)\right)^2$$

$$+ \sum_{\nu}^{N_n} \frac{1}{M_\nu}\left(\frac{-i\nabla_\nu \chi\left(\underline{\underline{R}}, t\right)}{\chi\left(\underline{\underline{R}}, t\right)} + A_\nu\left(\underline{\underline{R}}, t\right)\right)\left(-i\nabla_\nu - A_\nu\right) - \in\left(\underline{\underline{R}}, t\right)\Bigg)\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) = i\partial_t \Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right)$$

Nuclear equation of motion

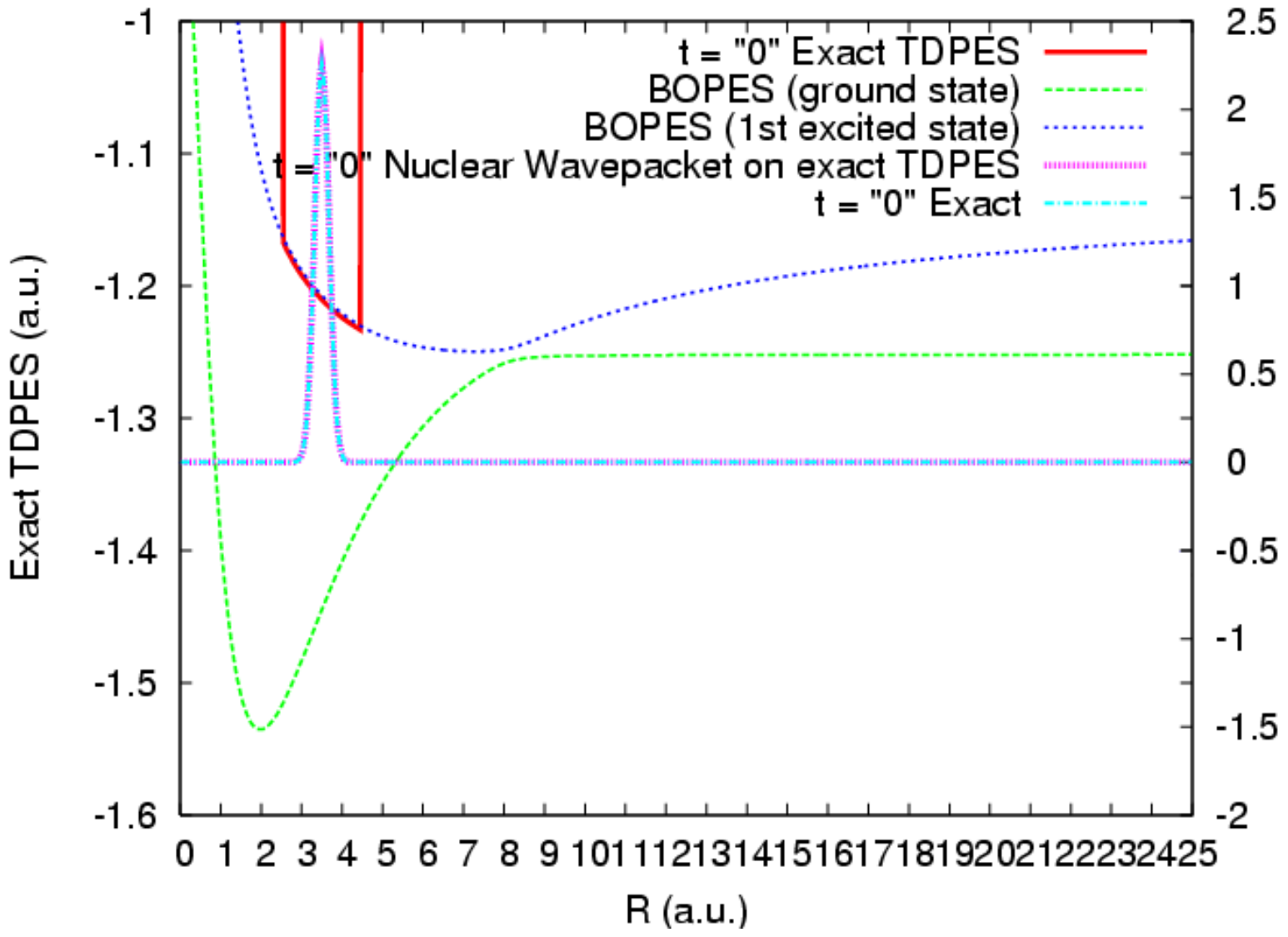
$$\left(\sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu\left(\underline{\underline{R}}, t\right)\right)^2 + \hat{W}_{nn}\left(\underline{\underline{R}}\right) + \hat{V}_n^{ext}\left(\underline{\underline{R}}, t\right) + \in\left(\underline{\underline{R}}, t\right)\right)\chi\left(\underline{\underline{R}}, t\right) = i\partial_t \chi\left(\underline{\underline{R}}, t\right)$$

How does the exact time-dependent PES look like?

Example: Splitting of nuclear wave packet when going through an avoided crossing (Zewail experiment)

A. Abedi, F. Agostini, Y. Suzuki, E.K.U.Gross,
PRL 110, 263001 (2013)

F. Agostini, A. Abedi, Y. Suzuki, E.K.U. Gross,
Mol. Phys. 111, 3625 (2013)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BOPES (1st excited state)
t = "0" Nuclear Wavepacket on exact TDPES
t = "0" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
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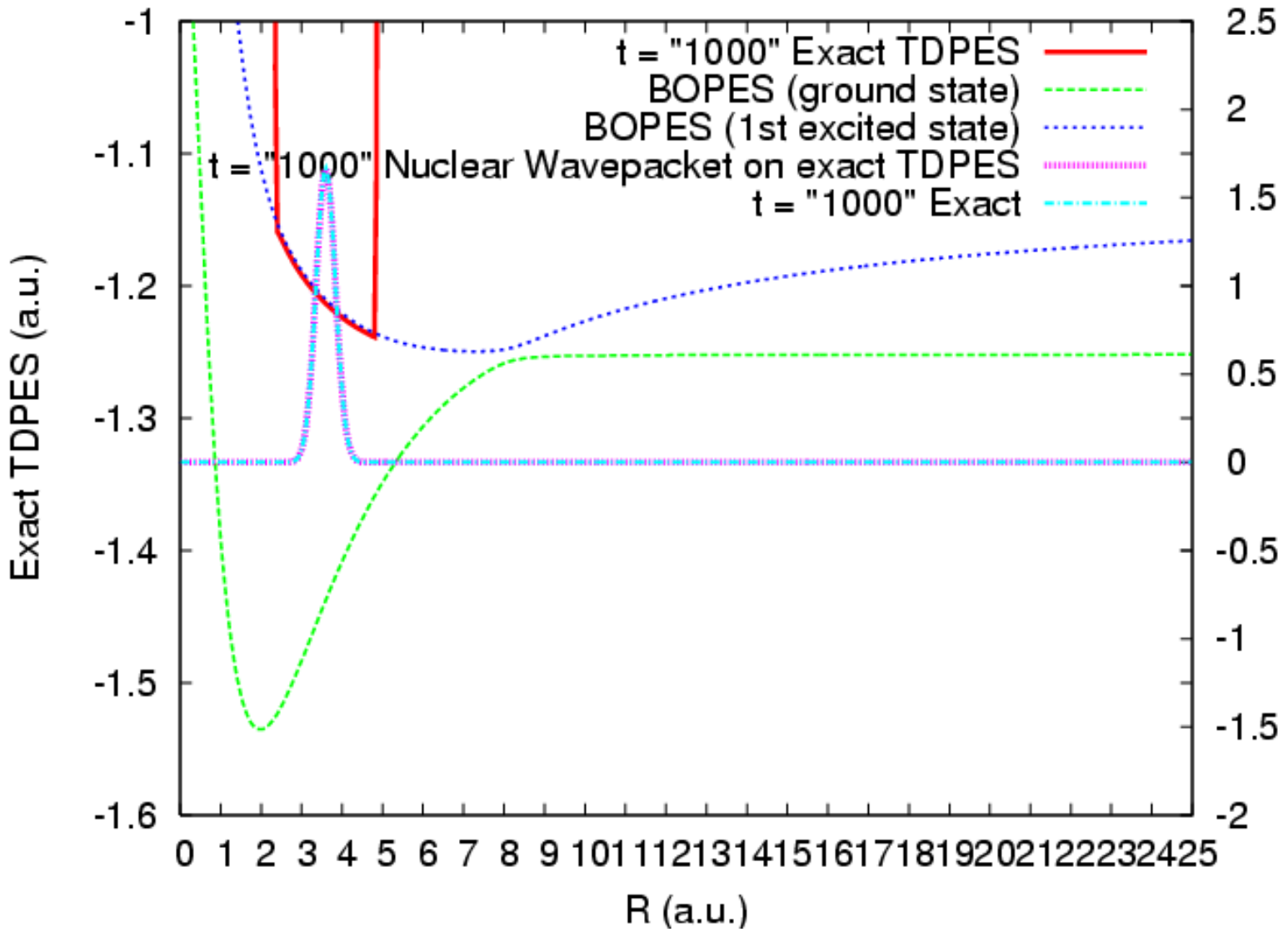
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R (a.u.)
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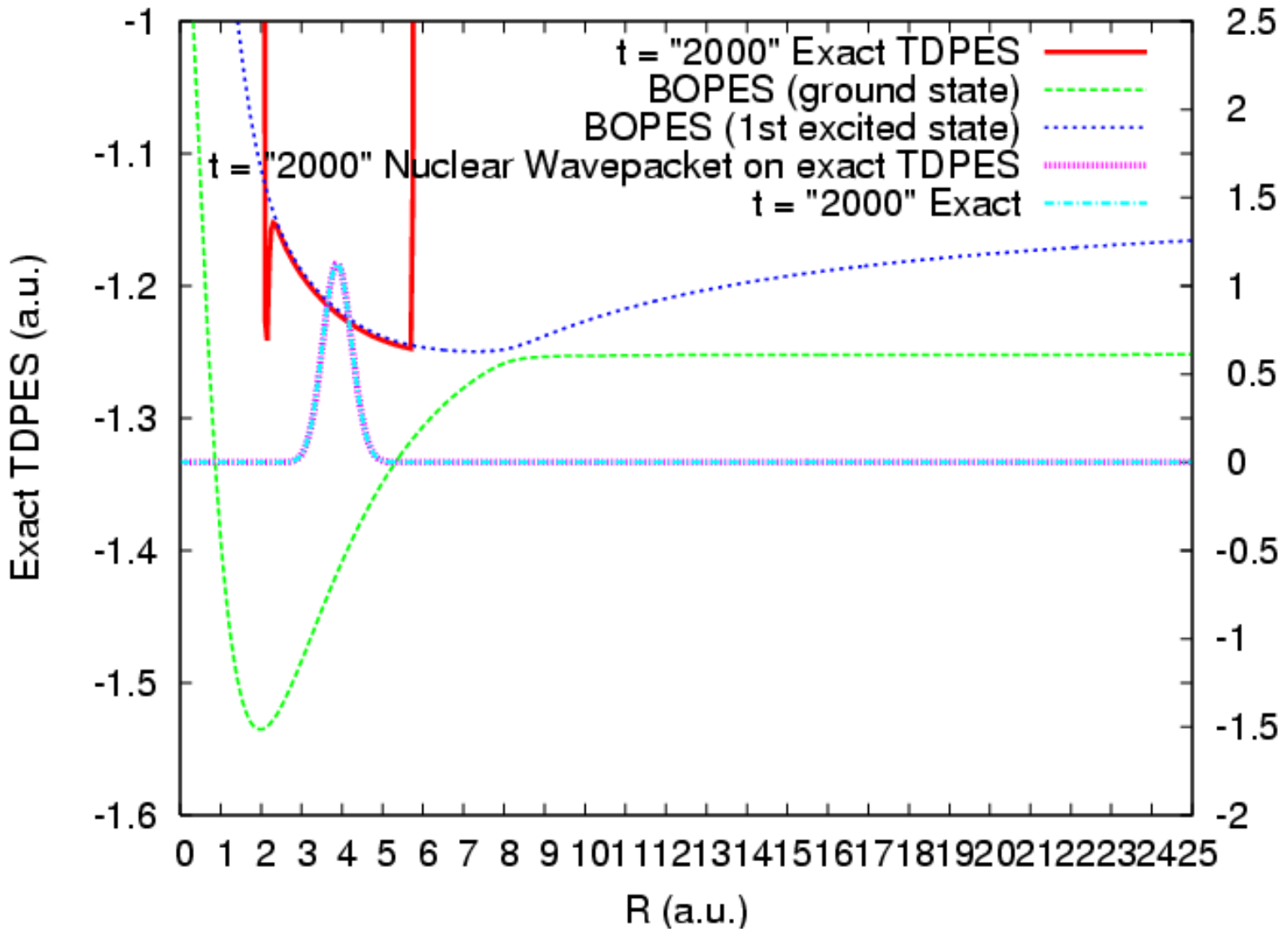
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R (a.u.)
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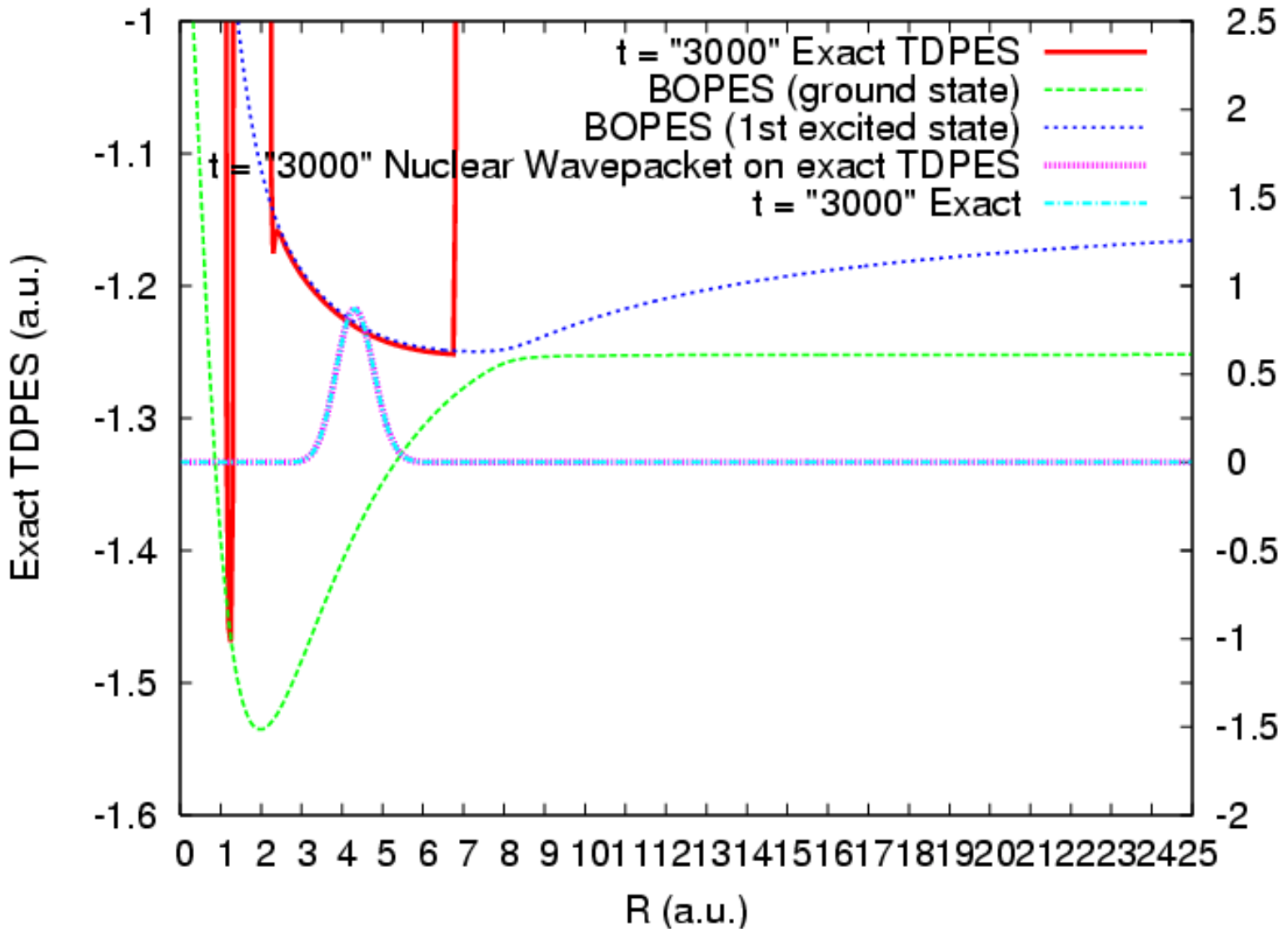
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BOPES (1st excited state)
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R (a.u.)
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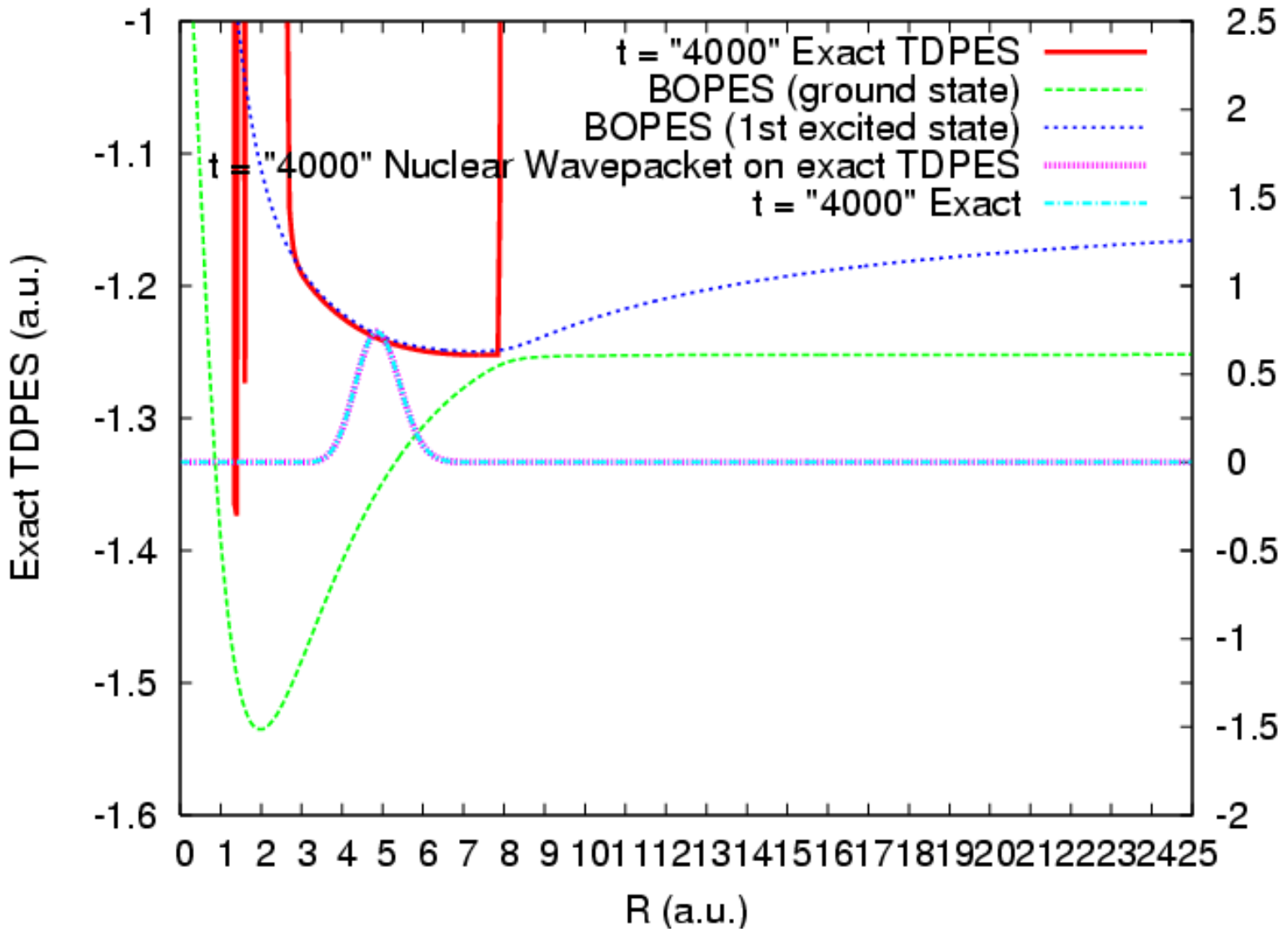
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R (a.u.)
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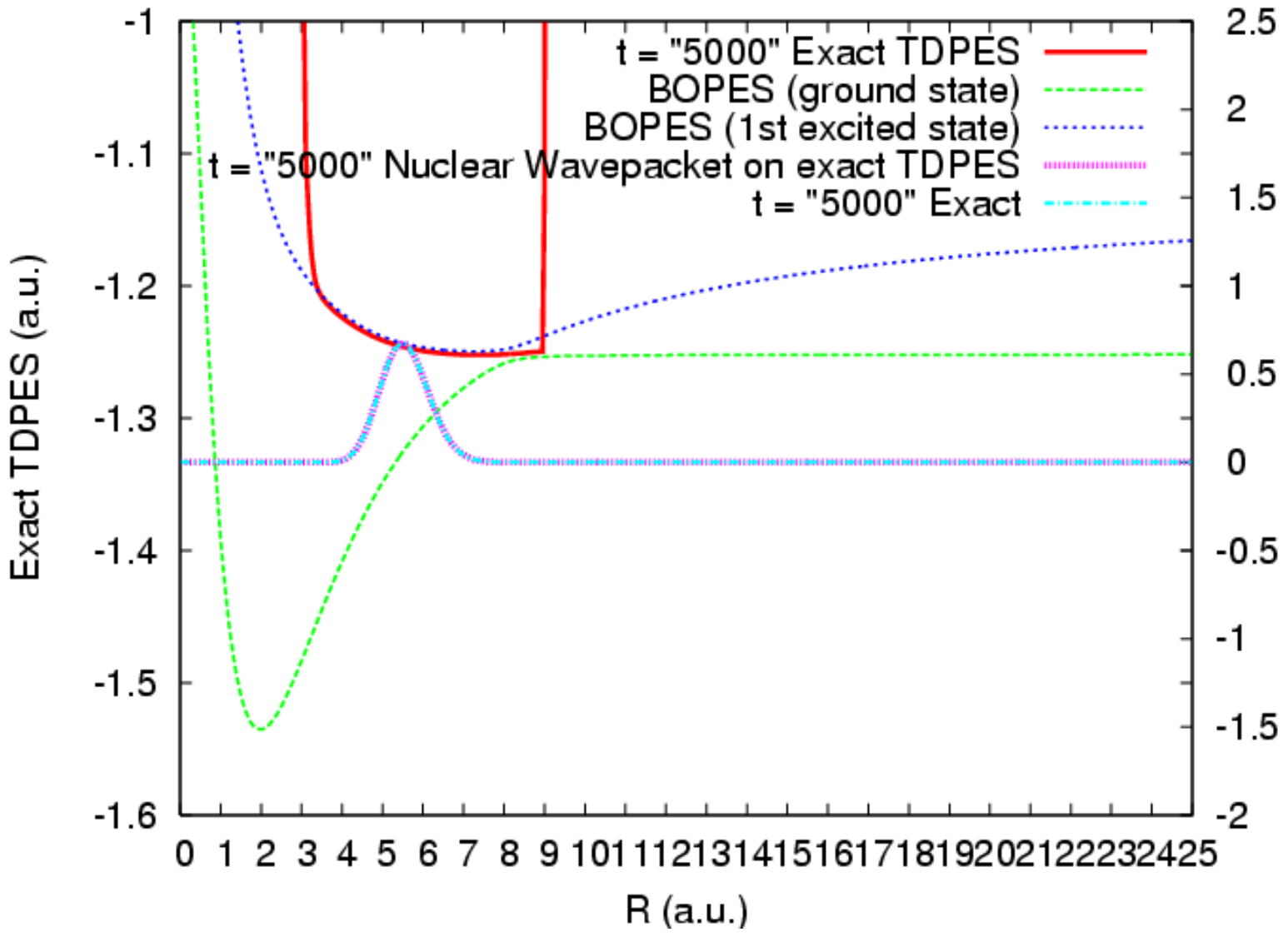
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t = "5000" Exact
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R (a.u.)
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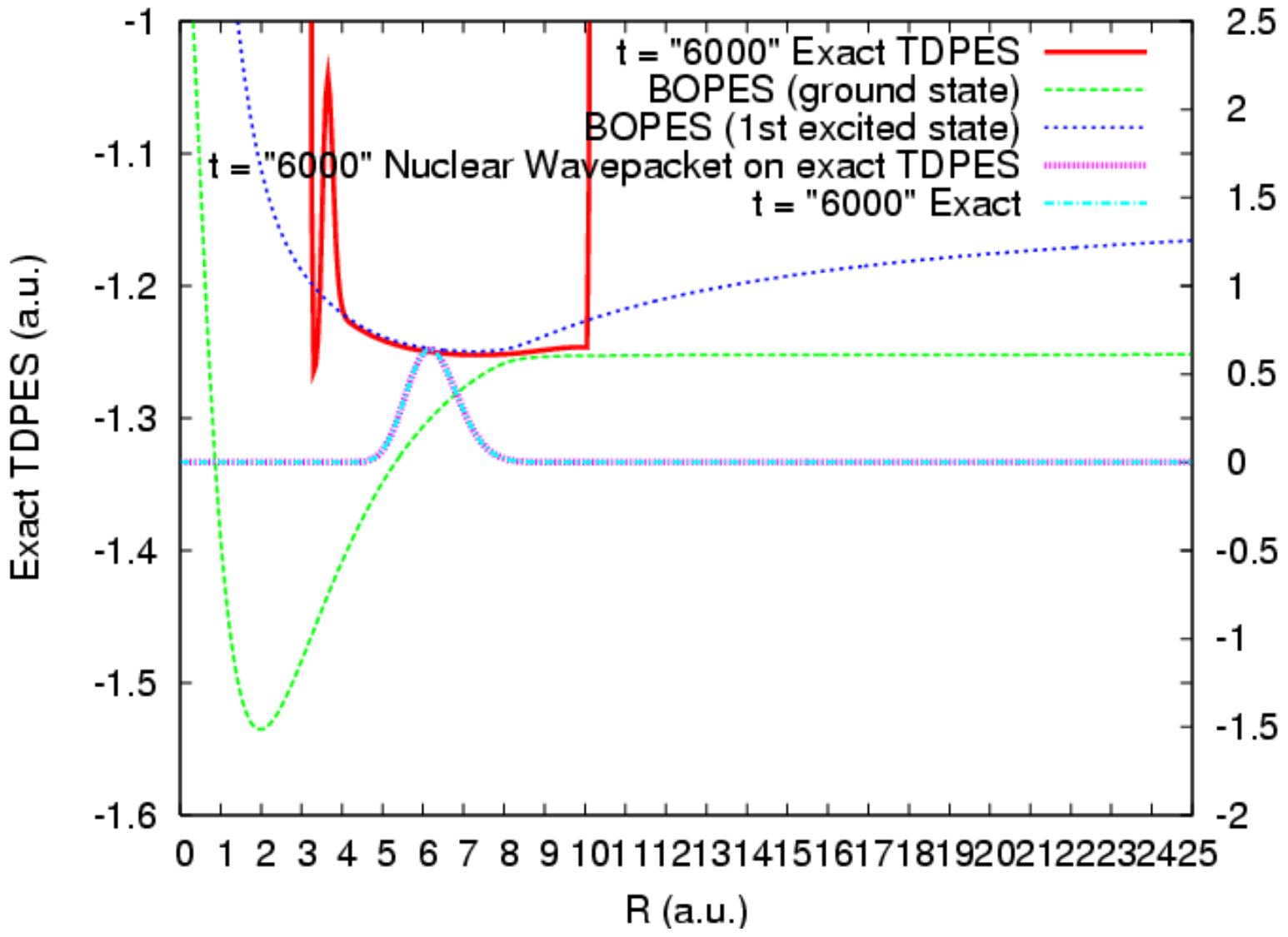
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t = "6000" Exact
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R (a.u.)
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-1.6
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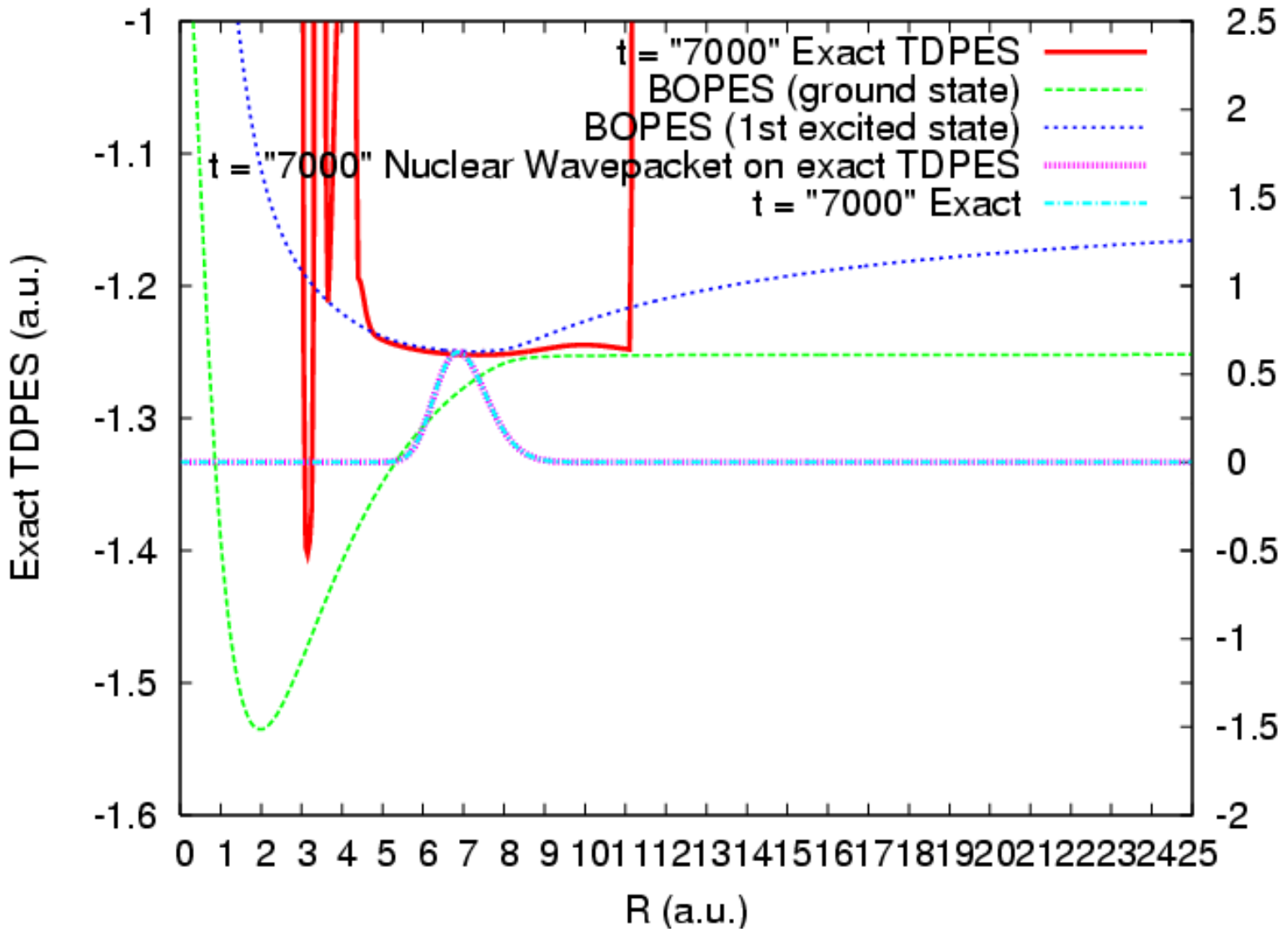
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BOPES (1st excited state)
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t = "7000" Exact
Exact TDPES (a.u.)
R (a.u.)
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-1.3
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-1.6
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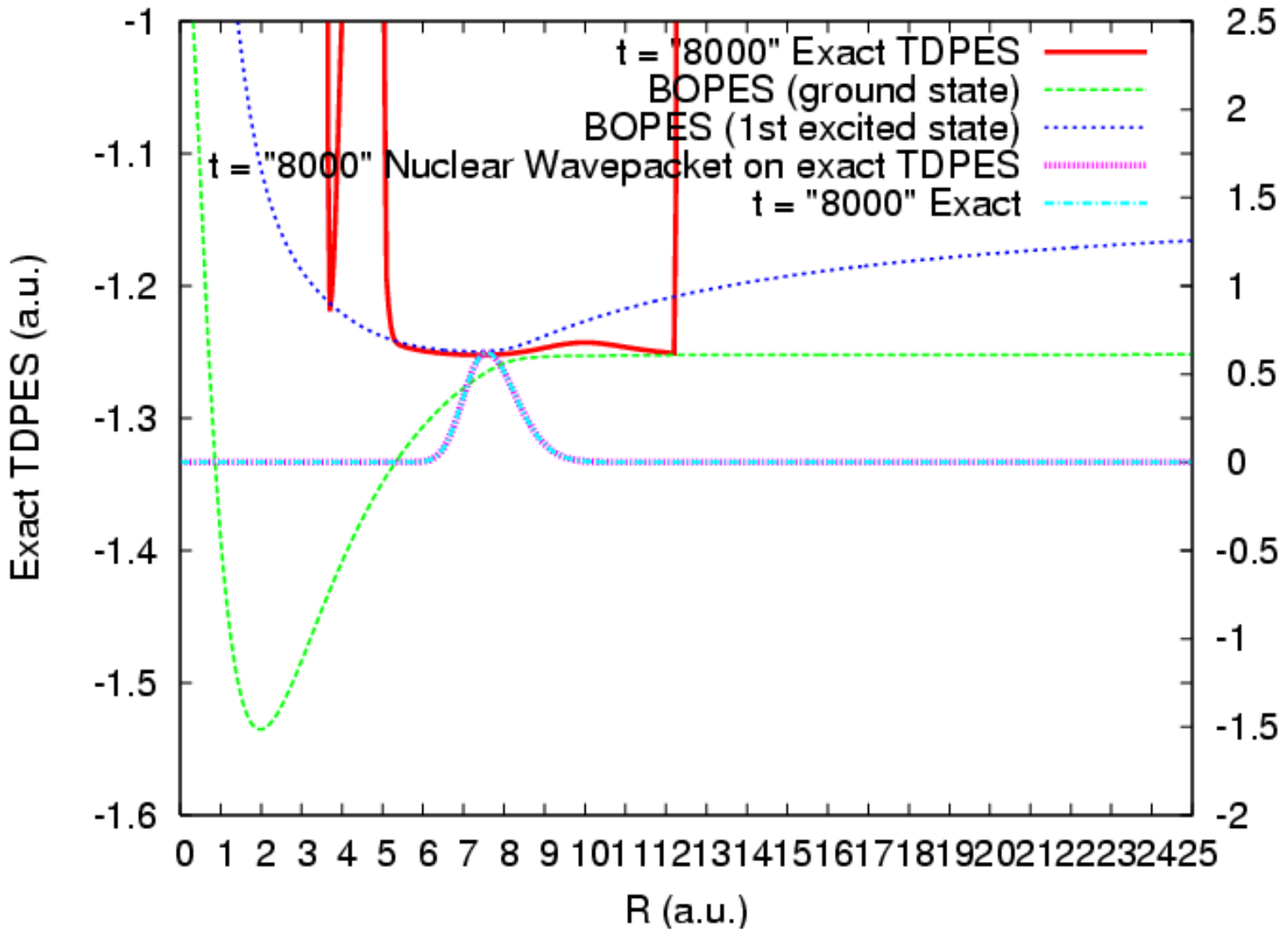
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R (a.u.)
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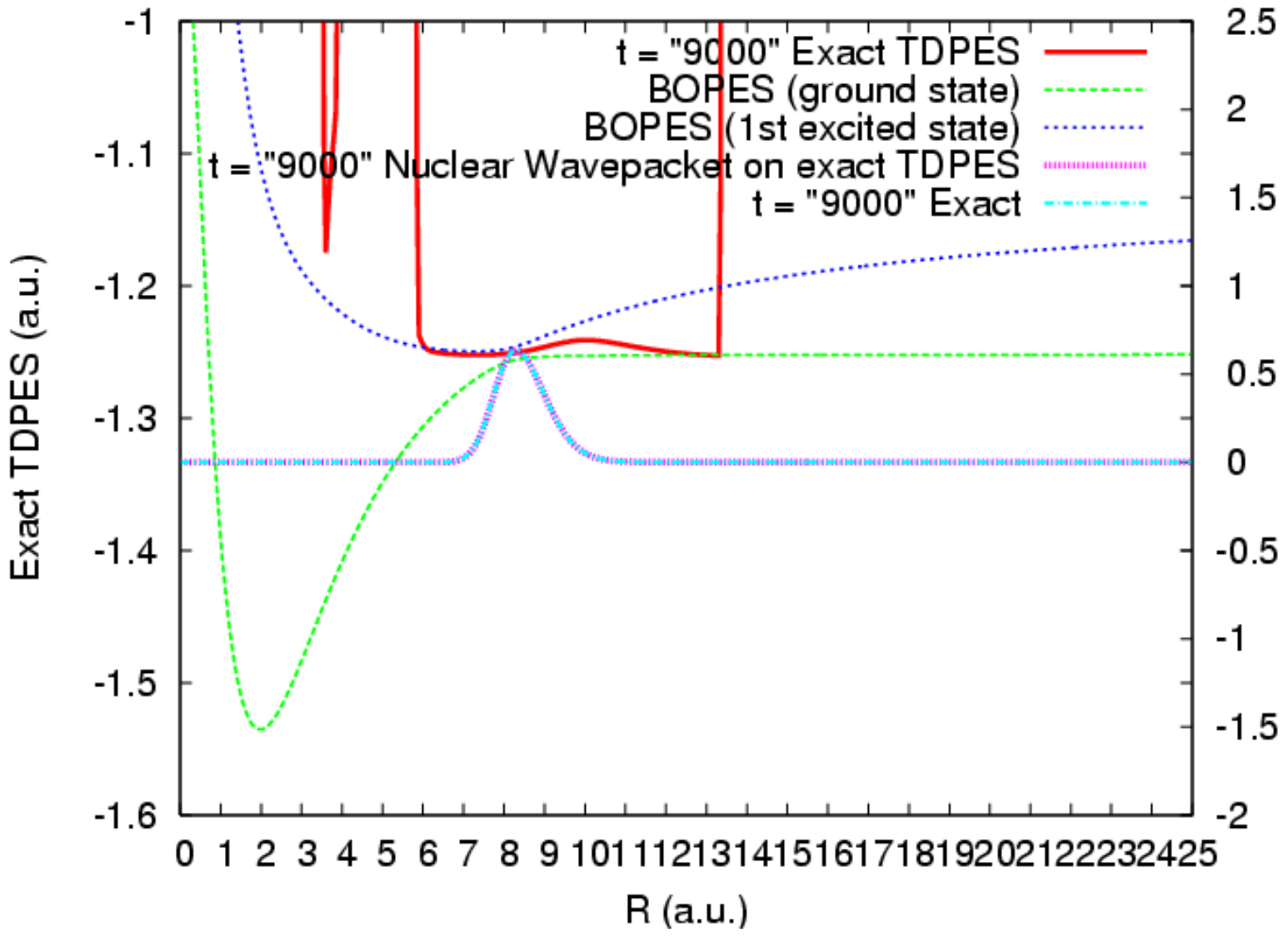
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R (a.u.)
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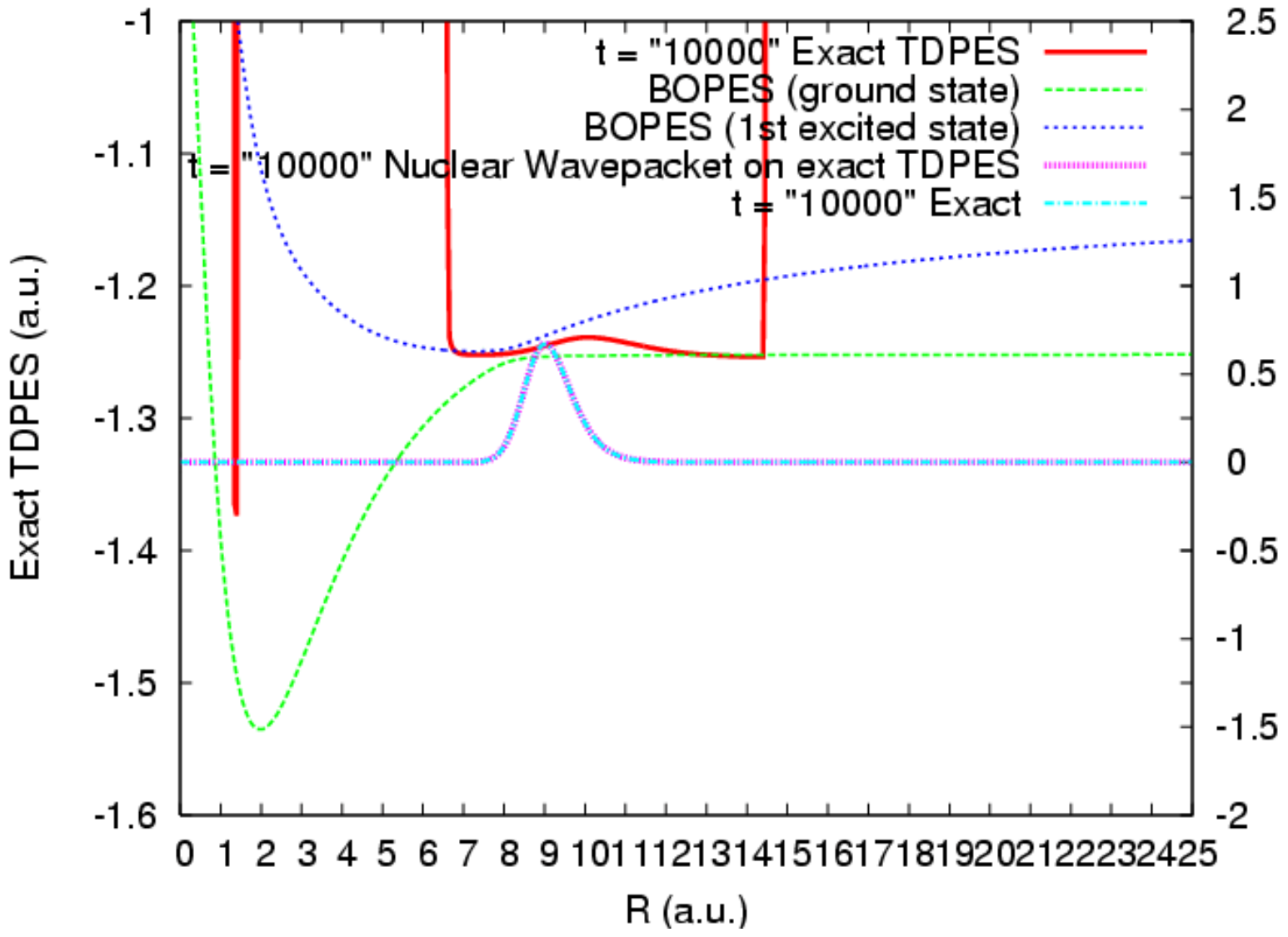
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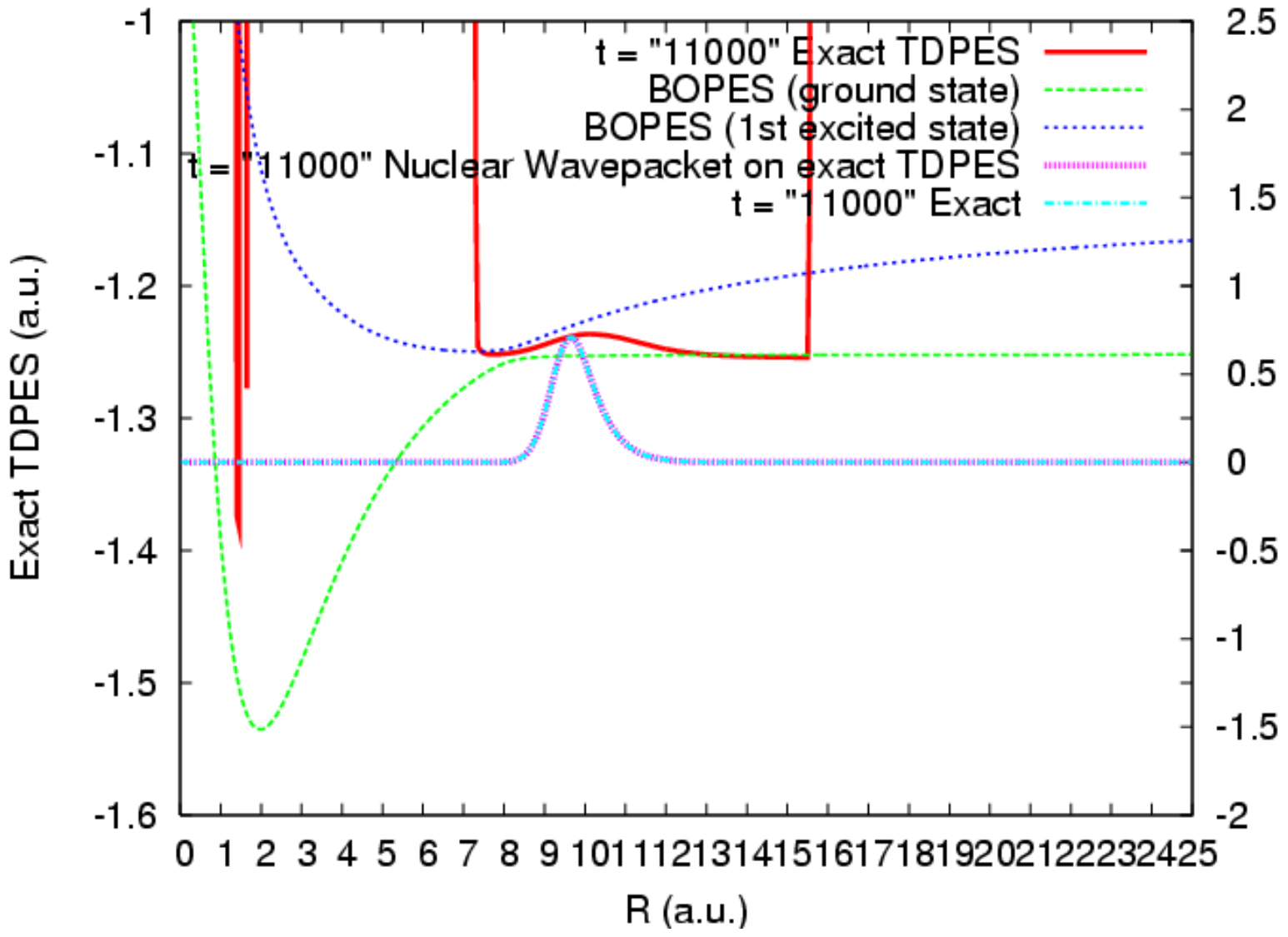
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R (a.u.)
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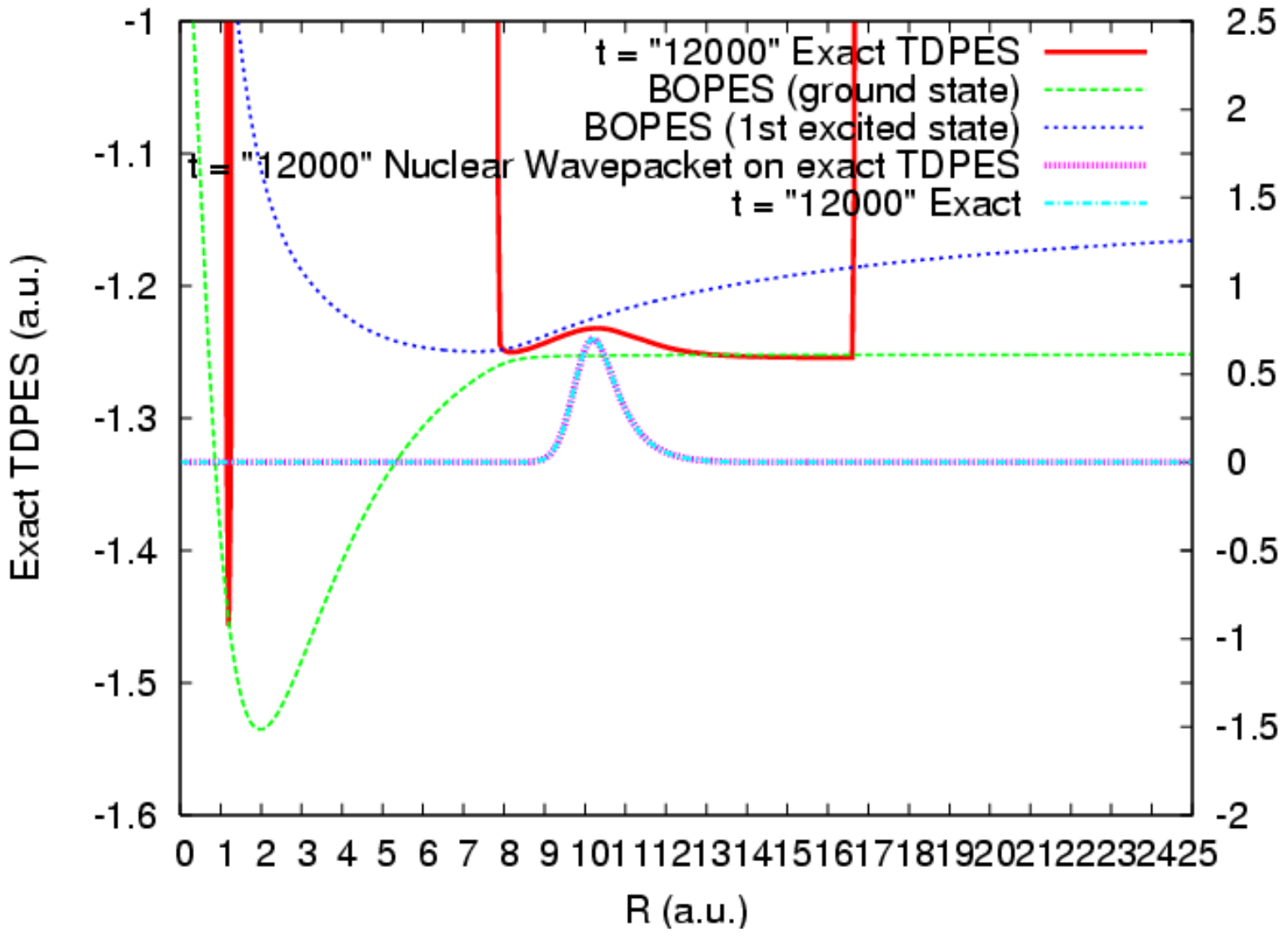
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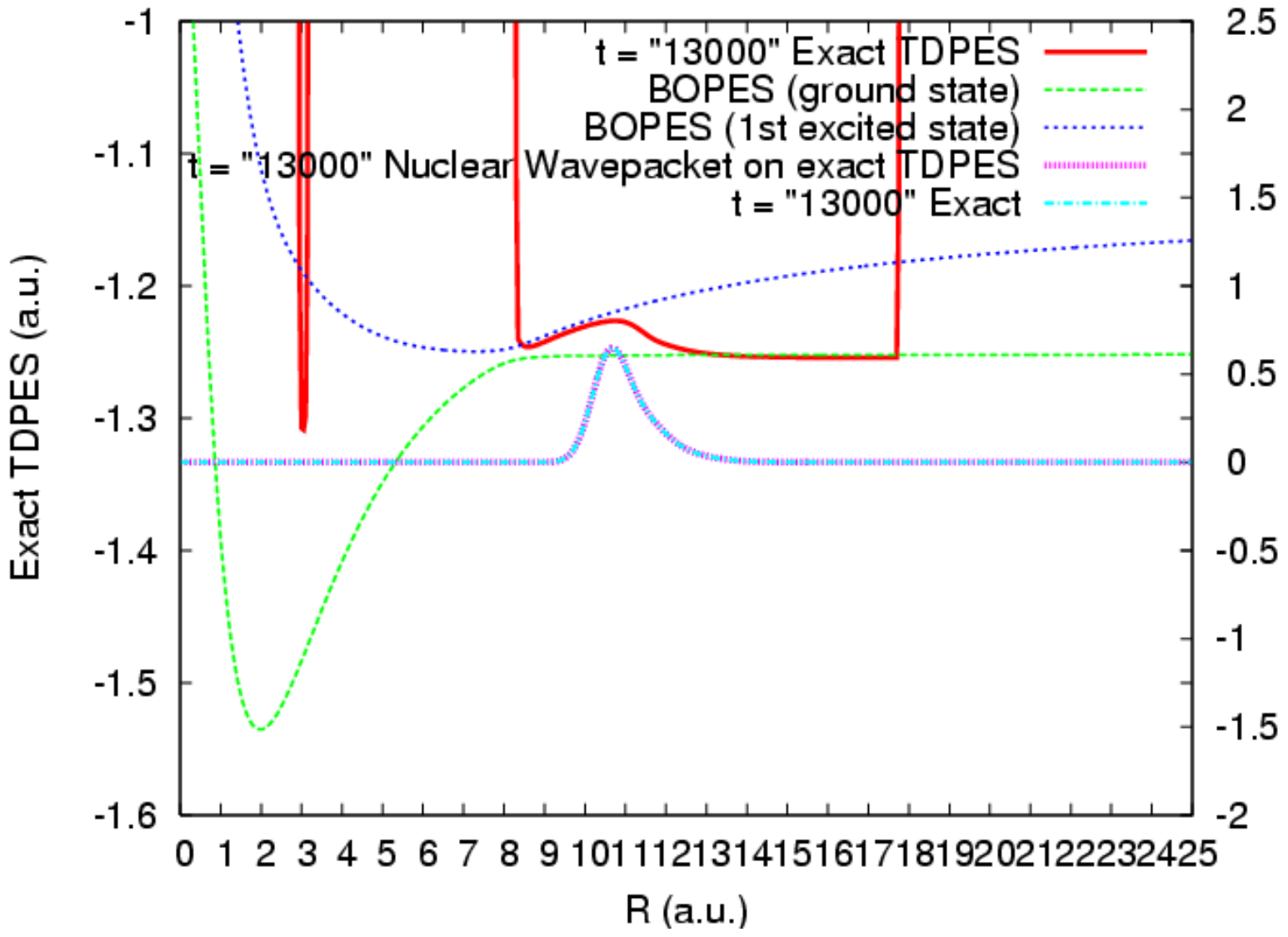
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R (a.u.)
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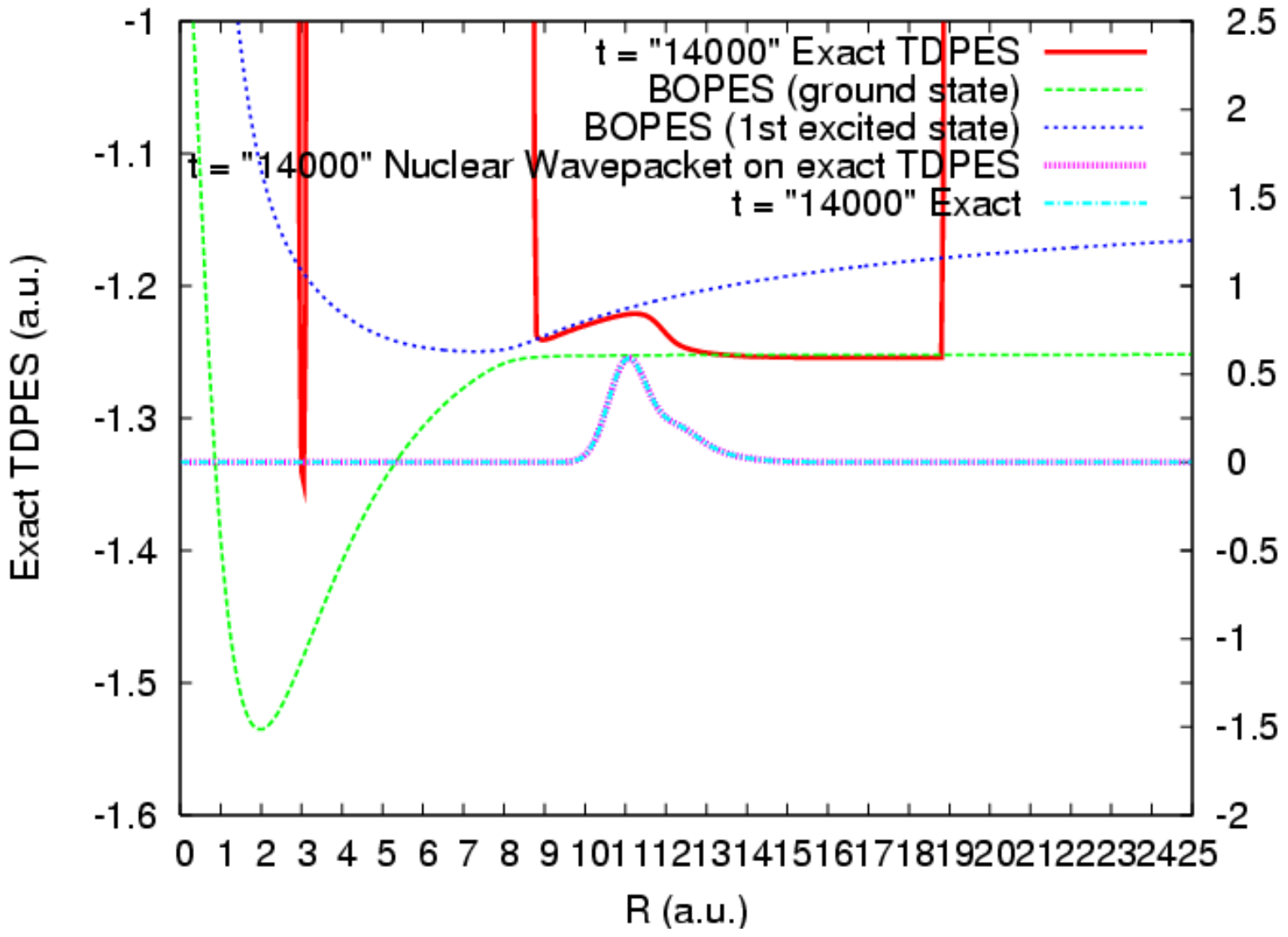
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R (a.u.)
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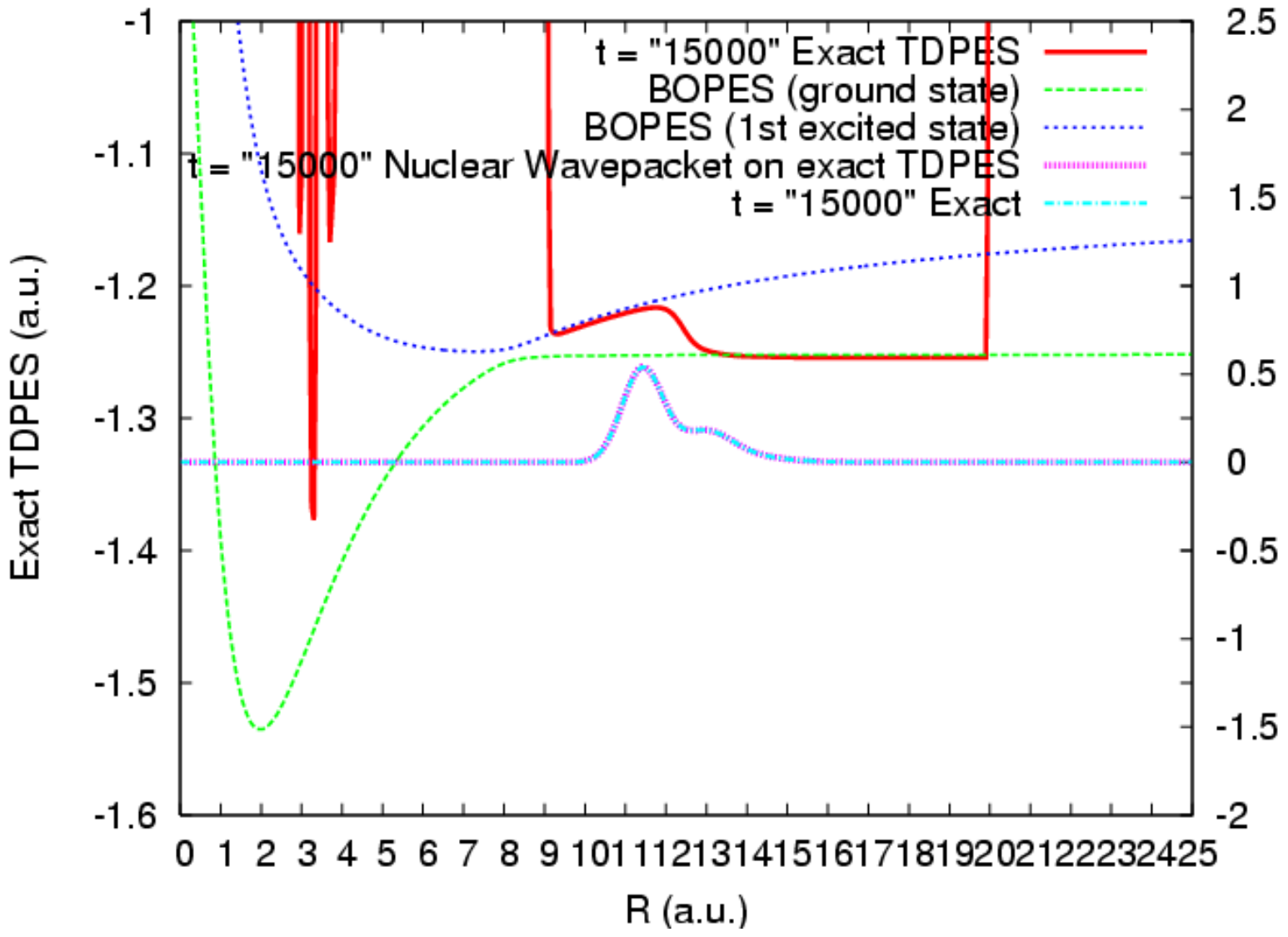
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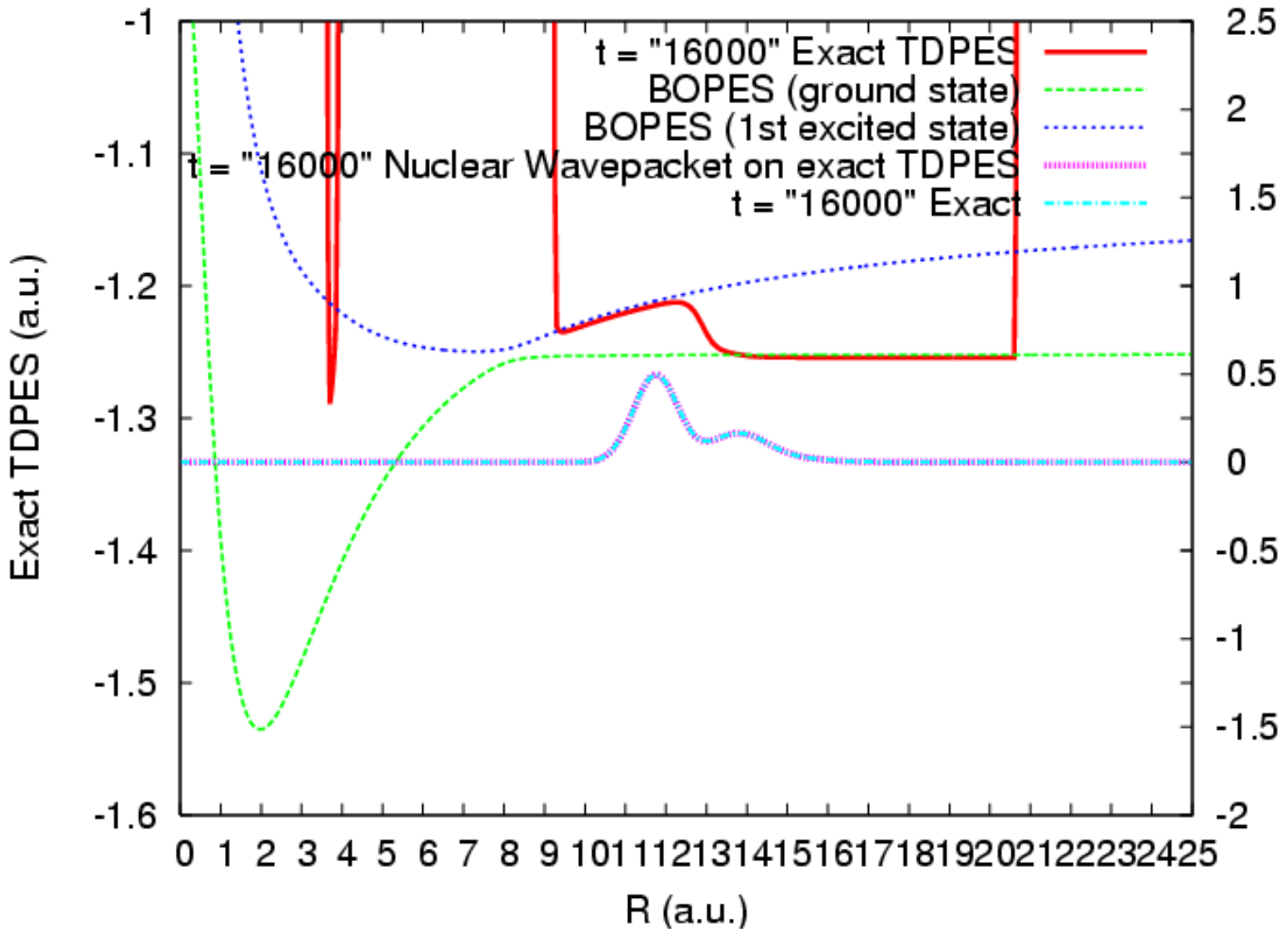
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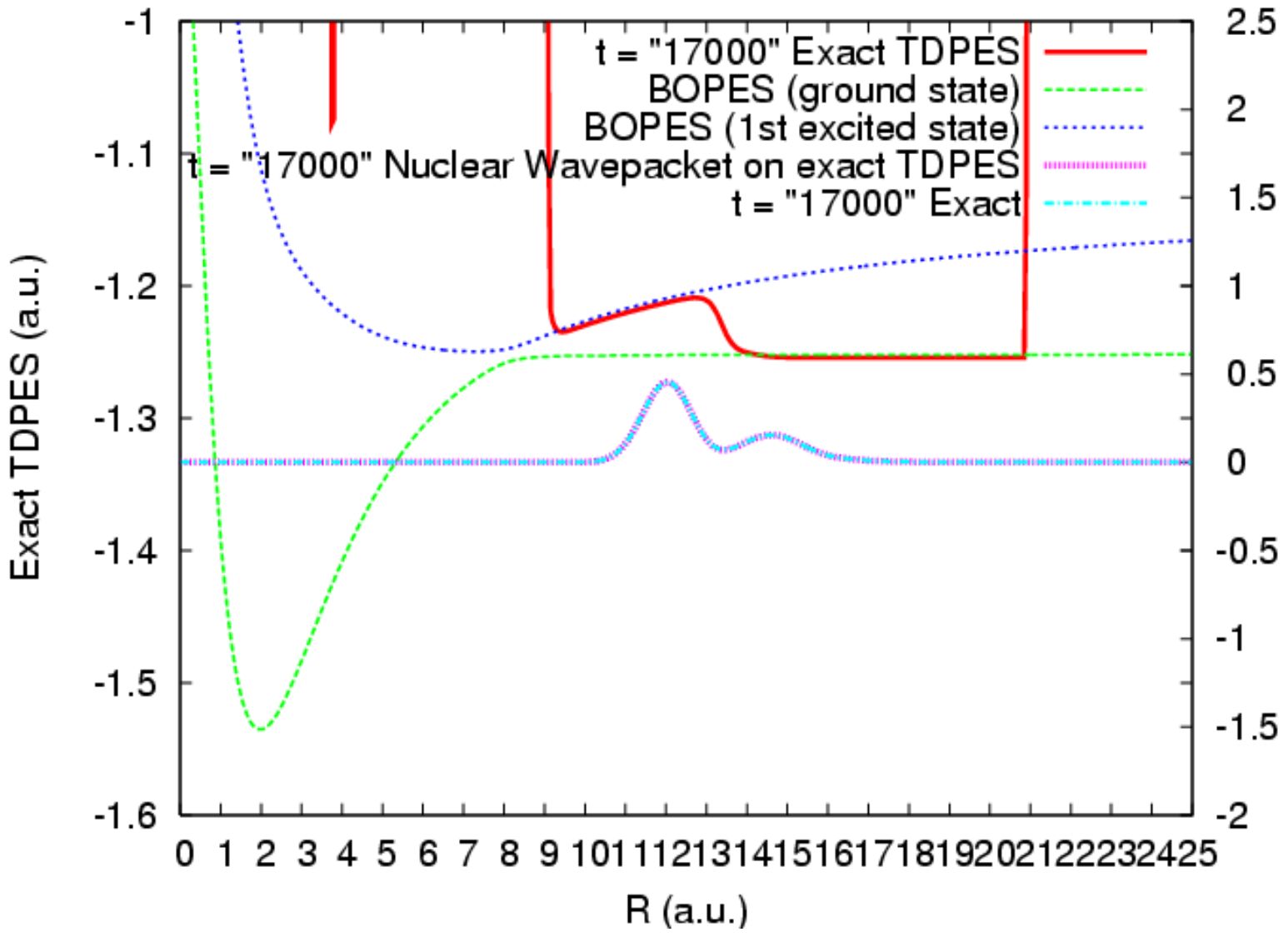
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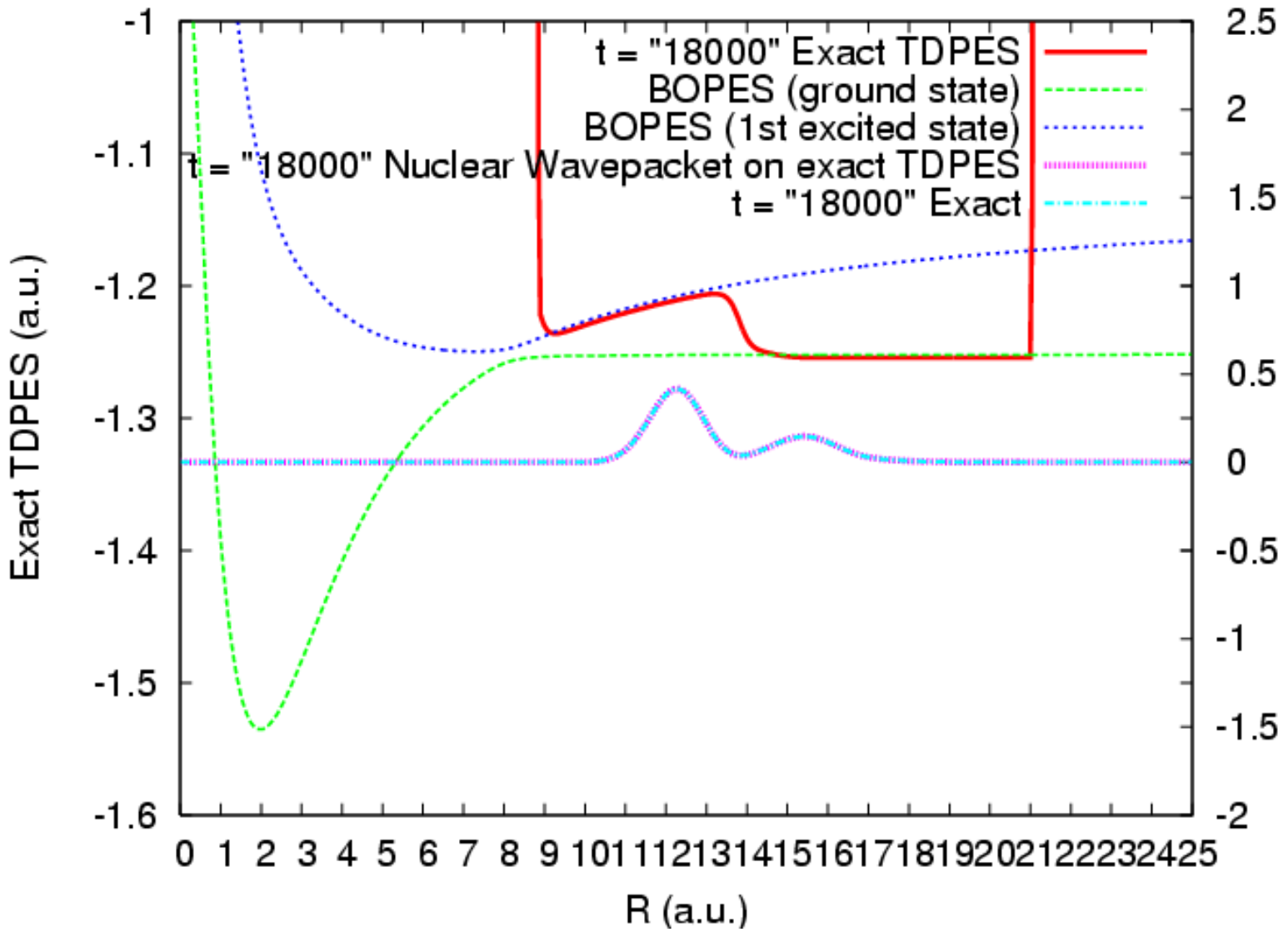
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t = "18000" Exact
Exact TDPES (a.u.)
R (a.u.)
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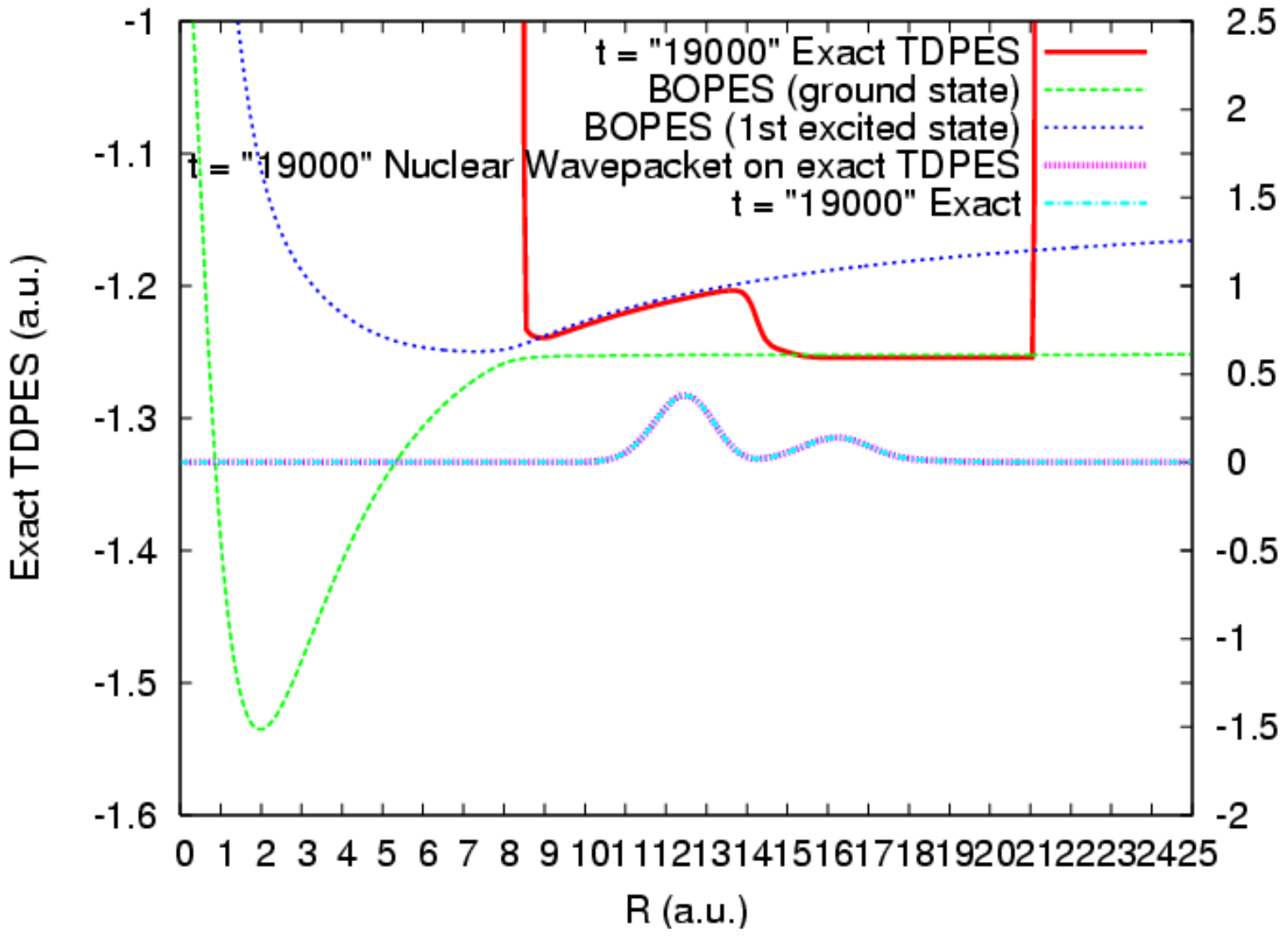
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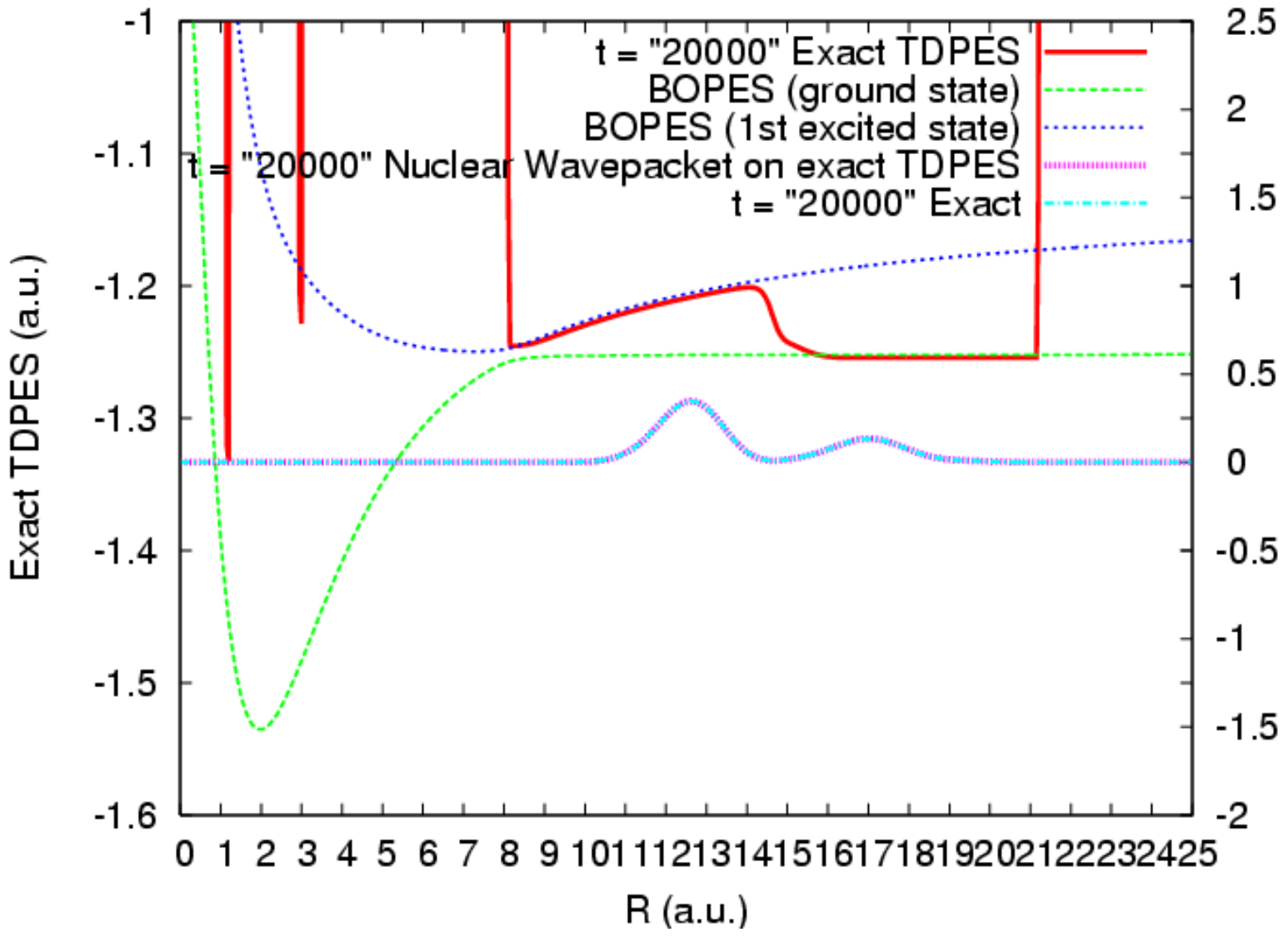
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0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

Theorem T-II

Electronic equation of motion

$$\Big(\underbrace{\hat{T}_e + \hat{W}_{ee} + \hat{V}_e^{ext}(\underline{\underline{r}},t) + \hat{V}_{en}(\underline{\underline{r}},\underline{\underline{R}})}_{\hat{H}_{BO}(t)} + \sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu - A_\nu(\underline{\underline{R}},t)\right)^2$$

$$+\sum_{\nu}^{N_n}\frac{1}{M_\nu}\left(\frac{-i\nabla_\nu\chi(\underline{\underline{R}},t)}{\chi(\underline{\underline{R}},t)} + A_\nu(\underline{\underline{R}},t)\right)\left(-i\nabla_\nu - A_\nu\right) - \in(\underline{\underline{R}},t)\Big)\Phi_{\underline{\underline{R}}}(\underline{\underline{r}}) = i\partial_t\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},t)$$

Nuclear equation of motion

$$\left(\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu(\underline{\underline{R}},t)\right)^2 + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{V}_n^{ext}(\underline{\underline{R}},t) + \in(\underline{\underline{R}},t)\right)\chi(\underline{\underline{R}},t) = i\partial_t\chi(\underline{\underline{R}},t)$$

Solve by swarm of nuclear trajectories (characteristics)

New MD schemes:

Treat the nuclear motion with classical trajectories, but retain the quantum treatment of the electronic degrees of freedom.

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

F. Agostini, S.K. Min, A. Abedi, E.K.U. Gross, JCTC 12, 2127 (2016)

F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, JPCL 8, 3048 (2017)

New MD schemes:

Treat the nuclear motion with classical trajectories, but retain the quantum treatment of the electronic degrees of freedom.

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

F. Agostini, S.K. Min, A. Abedi, E.K.U. Gross, JCTC 12, 2127 (2016)

F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, JPCL 8, 3048 (2017)

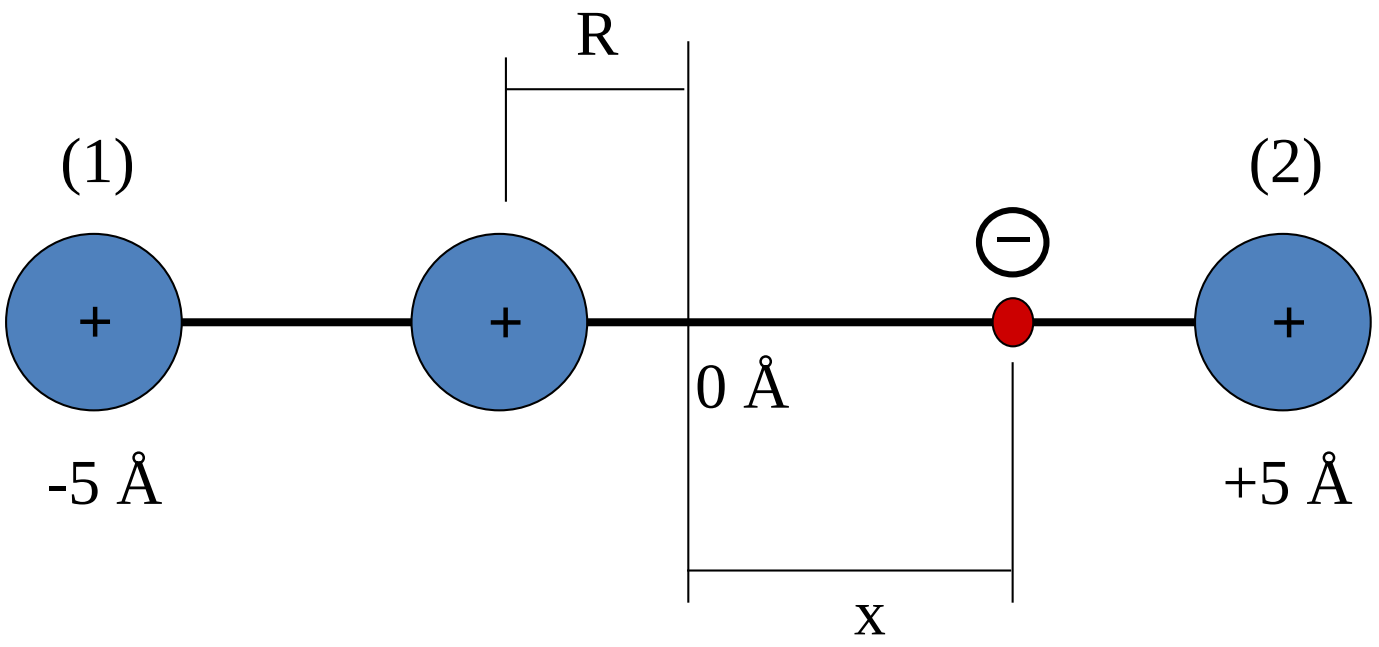
Second step: "Density-functionalization“ of electronic equation: Two very different ways of doing this:

- **Solve linear-response TDDFT along the trajectories**
- **Replace electronic EoM by real-time TDKS equation**

First test: Propagate classical nuclei on the exact TDPES for an exactly solvable model

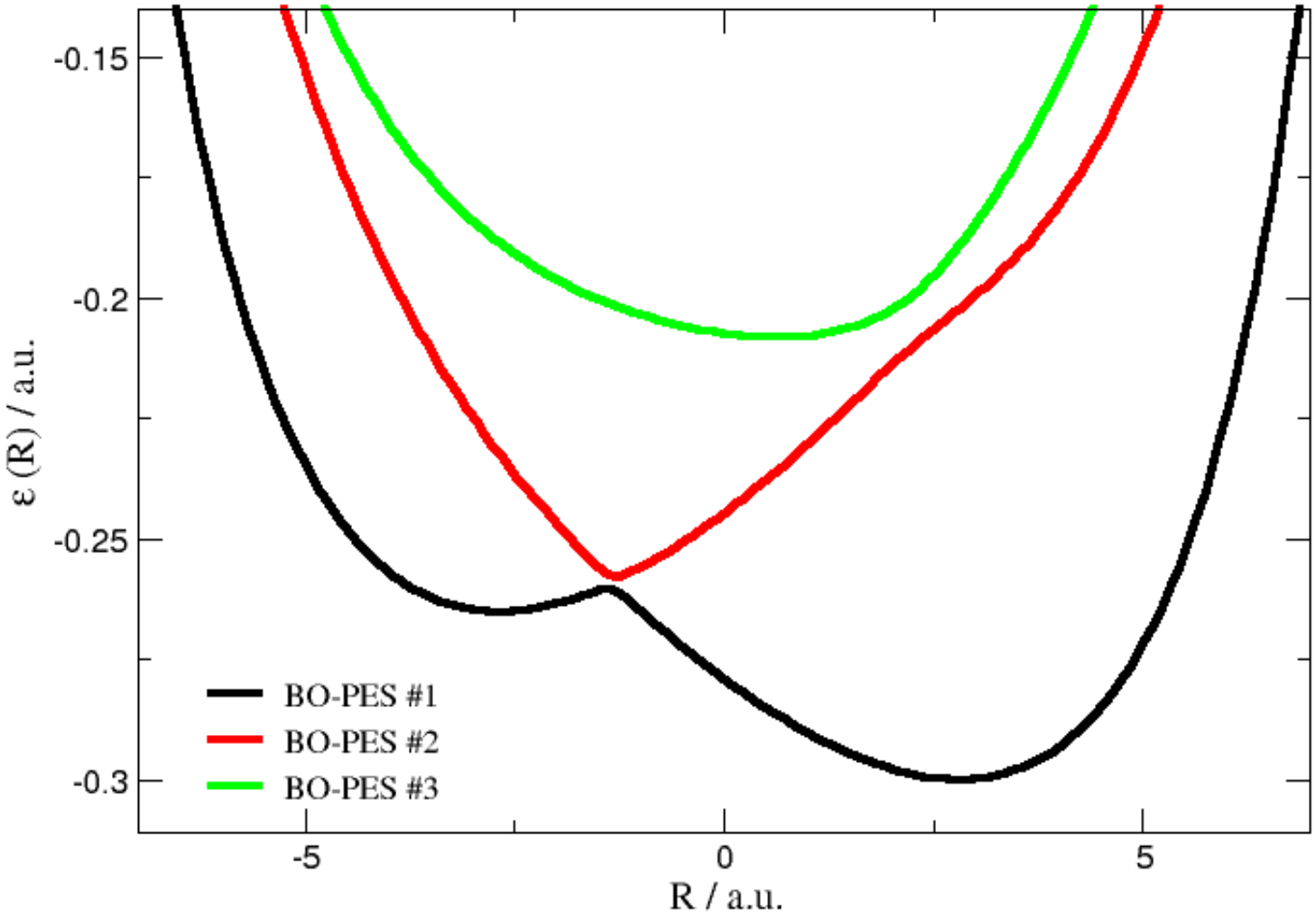
MODEL

S. Shin, H. Metiu, JCP 102, 9285 (1995), JPC 100, 7867 (1996)



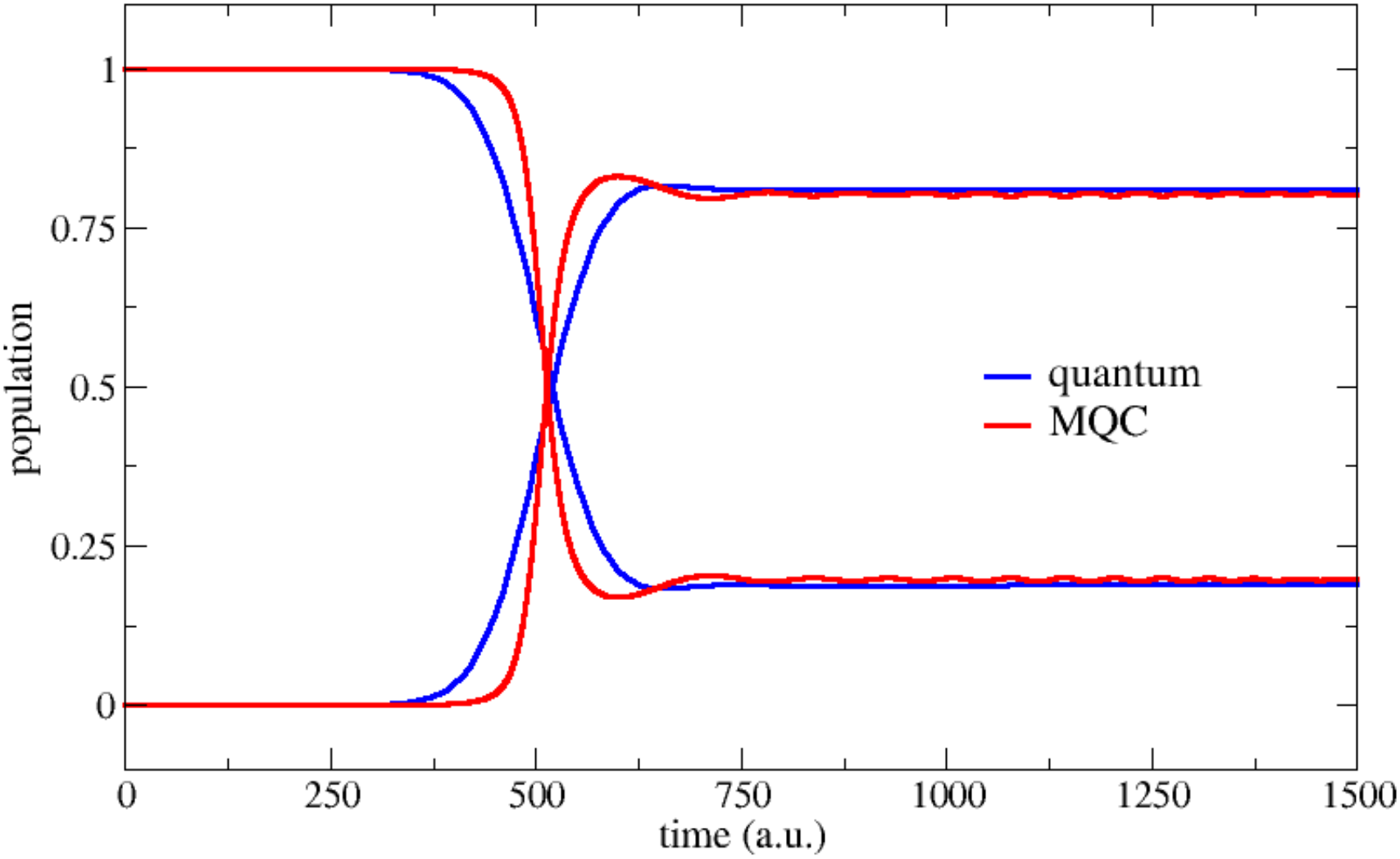
Nuclei (1) and (2) are heavy: Their positions are fixed

1D Shin-Metiu model

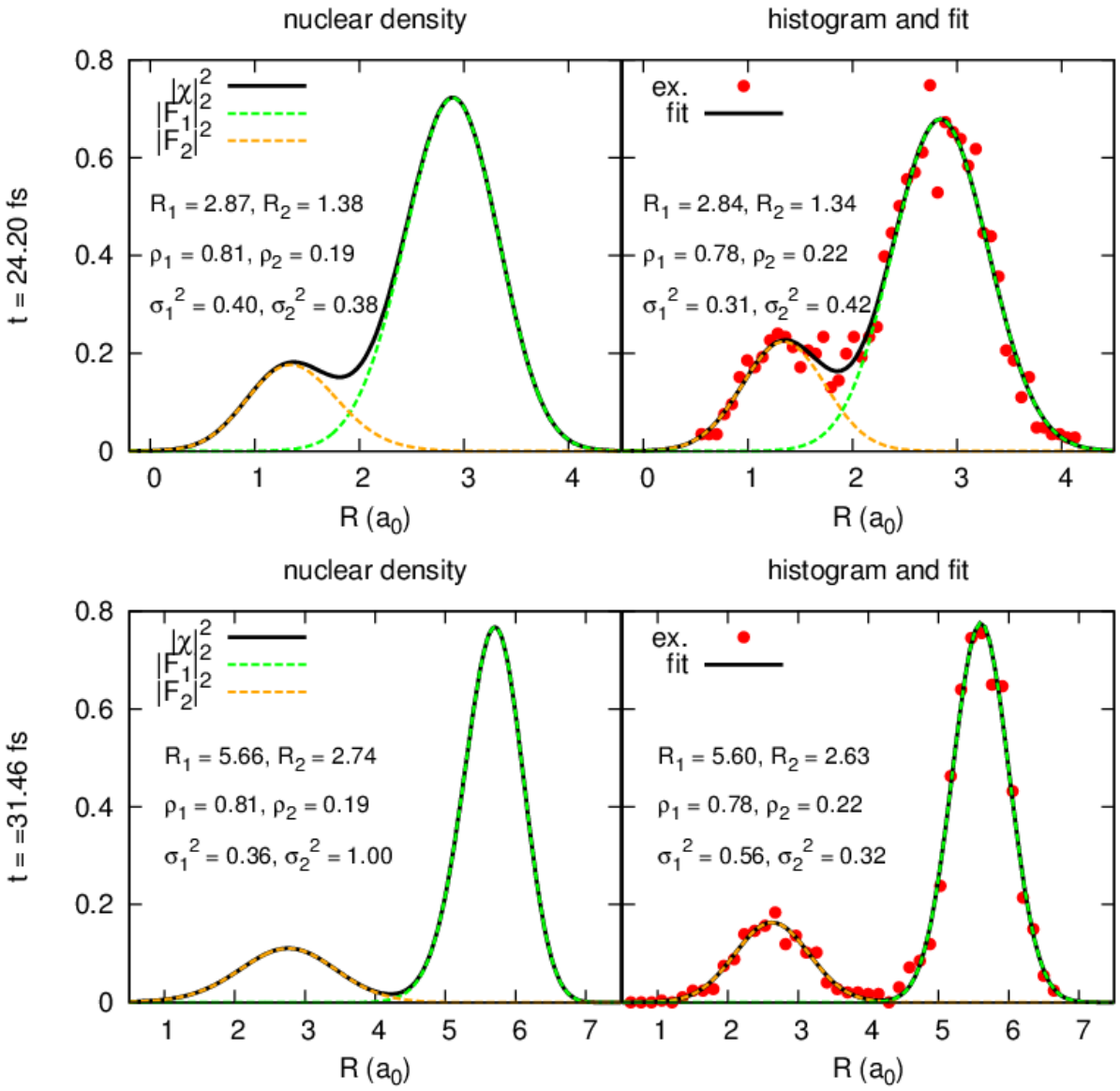


Shin-Metiu model

populations of the BO states as functions of time



Propagation of classical nuclei on exact TDPES



Construction of the Coupled-Trajectory Mixed Quantum Classical (CT-MQC) algorithm

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

$$\chi\left(\mathbf{R},t\right) = \left|\chi\left(\mathbf{R},t\right)\right| e^{(i/\hbar)S(\mathbf{R},t)}$$

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

Canonical momentum

$$M_\nu \mathbf{V}_\nu = \nabla_\nu S\left(\mathbf{R},t\right) + \mathbf{A}_\nu\left(\mathbf{R},t\right) \equiv \mathbf{P}_\nu$$

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Canonical momentum

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Quantum (Bohm) potential (neglected for the time being)

Evaluate derivatives along the trajectories

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_\nu \mathbf{V}_\nu \nabla_\nu$$

$$\Rightarrow \quad \dot{P}_\nu(t)\Big|_{\mathbf{R}^{(I)}(t)} = -\nabla_\nu \left(\varepsilon(\mathbf{R},t) + \sum_{\nu'=1}^{N_n} \mathbf{A}_{\nu'}(\mathbf{R},t) \cdot \frac{\mathbf{P}_{\nu'}(\mathbf{R},t)}{M_\nu} \right) + \dot{\mathbf{A}}_\nu(\mathbf{R},t)\Big|_{\mathbf{R}^{(I)}(t)}$$

$$\varepsilon(\mathbf{R},t) = \left\langle \Phi_{\mathbf{R}}(t) \middle| \hat{H}_{BO} + \hat{U}_{en}^{coup} - i\hbar\partial_t \middle| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}}$$

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

$$A_\nu(\mathbf{R},t) = \left\langle \Phi_{\mathbf{R}}(t) \middle| -i\hbar\nabla_\nu \middle| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}}$$

To evaluate the time-dependent potential energy surface and the vector potential we need the electronic wave function $\Phi_R(r,t)$ (along the trajectories)

Born-Huang: $\Phi_{\mathbf{R}}(\mathbf{r},t) = \sum_k C_k(\mathbf{R},t)\,\varphi_{\mathbf{R}}^{(k)}(\mathbf{r})_{BO}$

We need:: $C_k^I(t) = C_k\left(R^I(t)\right)$

$$\dot{C}_k^{(I)}(t) = \frac{-i}{\hbar}\left[\varepsilon_{BO}^{(k)(I)}(t) - \sum_{\nu=1}^{N_n}\frac{i\mathbf{Q}_\nu^{(I)}(t)}{M_\nu}\cdot\mathbf{A}_\nu(t)\right]C_k^{(I)}(t)$$
$$-\sum_{\nu=1}^{N_n}\frac{i\mathbf{Q}_\nu^{(I)}(t)}{M_\nu}\nabla_\nu C_k^{(I)}(t) - \sum_{\nu=1}^{N_n}\frac{\mathbf{P}_\nu^{(I)}(t)+i\mathbf{Q}_\nu^{(I)}(t)}{M_\nu}\sum_j C_j^{(I)}(t)\,\mathbf{d}_{\nu,kj}^{(I)}$$

$$\mathbf{d}_{\nu,kj}^{(I)} = \left\langle \varphi_{\mathbf{R}^{(I)}(t)}^{(k)} \middle| \nabla_\nu \varphi_{\mathbf{R}^{(I)}(t)}^{(j)} \right\rangle_{\mathbf{r}}$$

$$\mathbf{Q}_\nu^{(I)}(t) := -\frac{\hbar\nabla_\nu\left|\chi^{(I)}(t)\right|}{\left|\chi^{(I)}(t)\right|}$$

“Quantum momentum”

The algorithm requires the BOPES ε_{BO} and the non-adiabatic coupling vectors $d_{\nu,kj}$ along the trajectories. Those are evaluated on the fly, where any electronic-structure method can be employed. We choose to evaluate these quantities with linear-response TDDFT.

Evaluation of the quantum momentum

$$\mathbf{Q}_{\nu}^{(I)}(t)=\frac{-\hbar\nabla_{\nu}\left|\chi^{(I)}(t)\right|}{\left|\chi^{(I)}(t)\right|}=\frac{-\hbar\nabla_{\nu}\left|\chi^{(I)}(t)\right|^{2}}{2\left|\chi^{(I)}(t)\right|^{2}}$$

$$g_{\sigma_{\nu}^{(J)}(t)}\left(\mathbf{R}_{\nu}-\mathbf{R}_{\nu}^{(J)}(t)\right)=\left(\frac{1}{2\pi\sigma_{\nu}^{(J)^{2}}(t)}\right)^{\frac{3}{2}}\exp\left(-\frac{\left[\mathbf{R}_{\nu}-\mathbf{R}_{\nu}^{(J)}(t)\right]^{2}}{2\sigma_{\nu}^{(J)^{2}}(t)}\right)$$

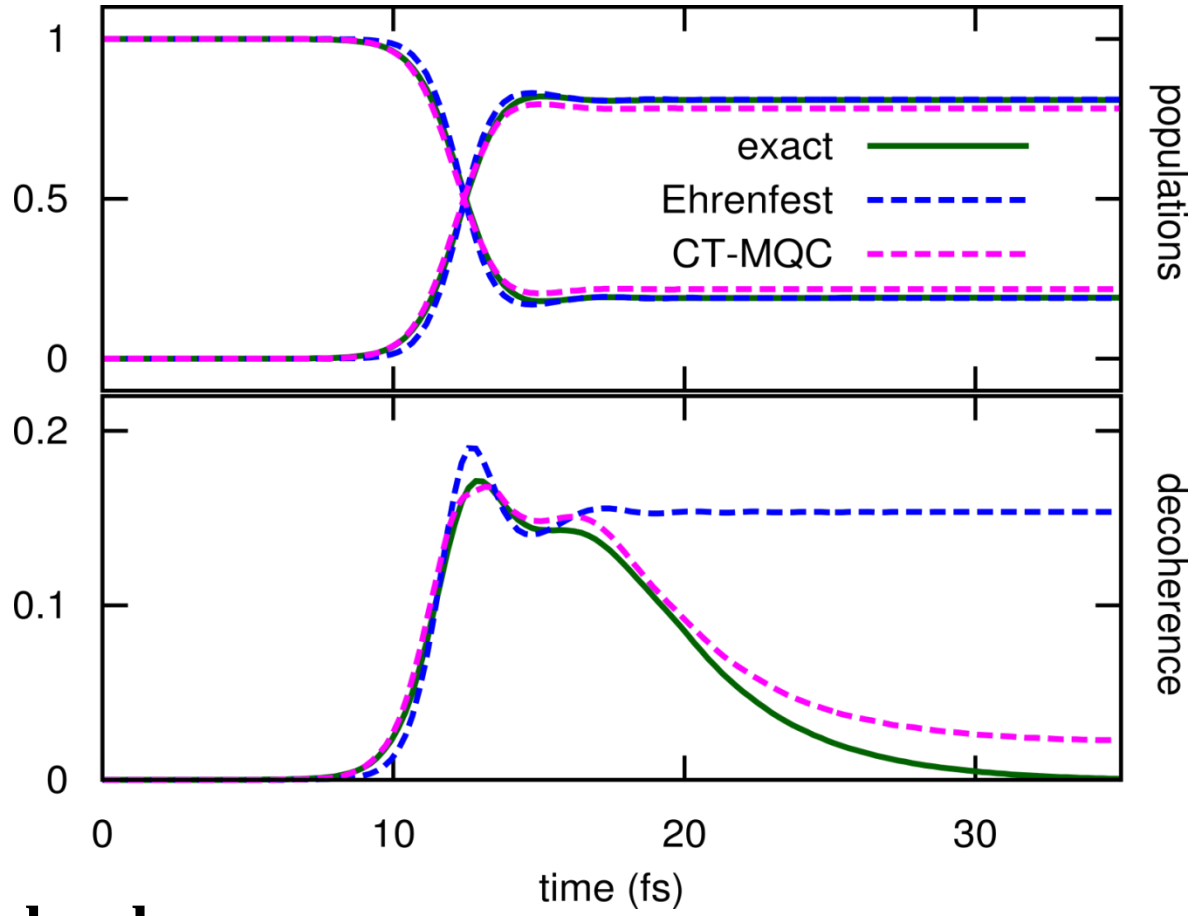
$$\left|\chi(\mathbf{R},t)\right|^{2}=\frac{1}{N_{tr}}\sum_{J=1}^{N_{tr}}\prod_{\nu=1}^{N_{n}}g_{\sigma_{\nu}^{(J)}(t)}\left(\mathbf{R}_{\nu}-\mathbf{R}_{\nu}^{(J)}(t)\right)$$

$$\left|\chi^{(I)}(t)\right|^{2}=\frac{1}{N_{tr}}\sum_{J=1}^{N_{tr}}\prod_{\nu=1}^{N_{n}}g_{\sigma_{\nu}^{(J)}(t)}\left(\mathbf{R}_{\nu}^{(I)}(t)-\mathbf{R}_{\nu}^{(J)}(t)\right)$$

$$\mathbf{Q}_\nu^{(I)}(t) = \frac{1}{N_{tr}} \sum_{J=1}^{N_{tr}} W_\nu^{IJ}(t) \left[\mathbf{R}_\nu^{(I)}(t) - \mathbf{R}_\nu^{(J)}(t) \right]$$

$$W_\nu^{IJ}(t) = \frac{\hbar \prod_{\nu'} g_{\sigma_{\nu'}^{(J)}(t)} \left(\mathbf{R}_{\nu'}^{(I)}(t) - \mathbf{R}_{\nu'}^{(J)}(t) \right)}{2\sigma_{\nu'}^{(J)^2}(t) \sum_K \prod_{\nu'} g_{\sigma_{\nu'}^{(K)}(t)} \left(\mathbf{R}_{\nu'}^{(I)}(t) - \mathbf{R}_{\nu'}^{(K)}(t) \right)}$$

Evaluating $Q_\nu^{(I)}(t)$ for the trajectory I requires knowledge of the positions of all trajectories, necessary to perform the summation. The trajectories become thus coupled through the quantum momentum.

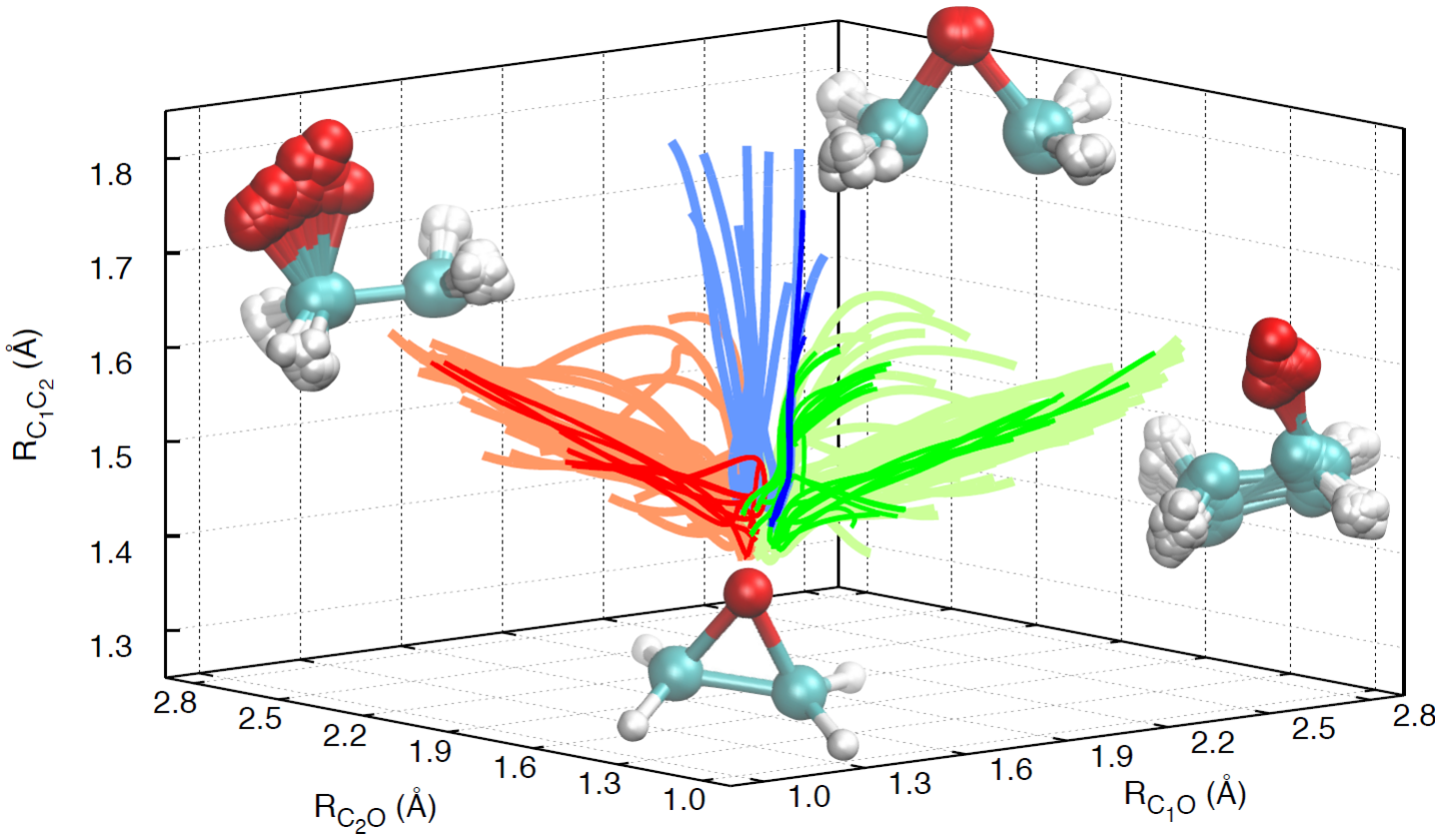


Measure of decoherence:

Quantum: $\int d\underline{\underline{\mathbf{R}}} \left|C_1\left(\underline{\underline{\mathbf{R}}}, t\right)\right|^2 \left|C_2\left(\underline{\underline{\mathbf{R}}}, t\right)\right|^2 \left|\chi\left(\underline{\underline{\mathbf{R}}}, t\right)\right|^2$

Trajectories $\boldsymbol{N_{traj}^{-1}} \sum_{\boldsymbol{I}} \left|\boldsymbol{C_1^{(I)}(t)}\right|^2 \left|\boldsymbol{C_2^{(I)}(t)}\right|^2$

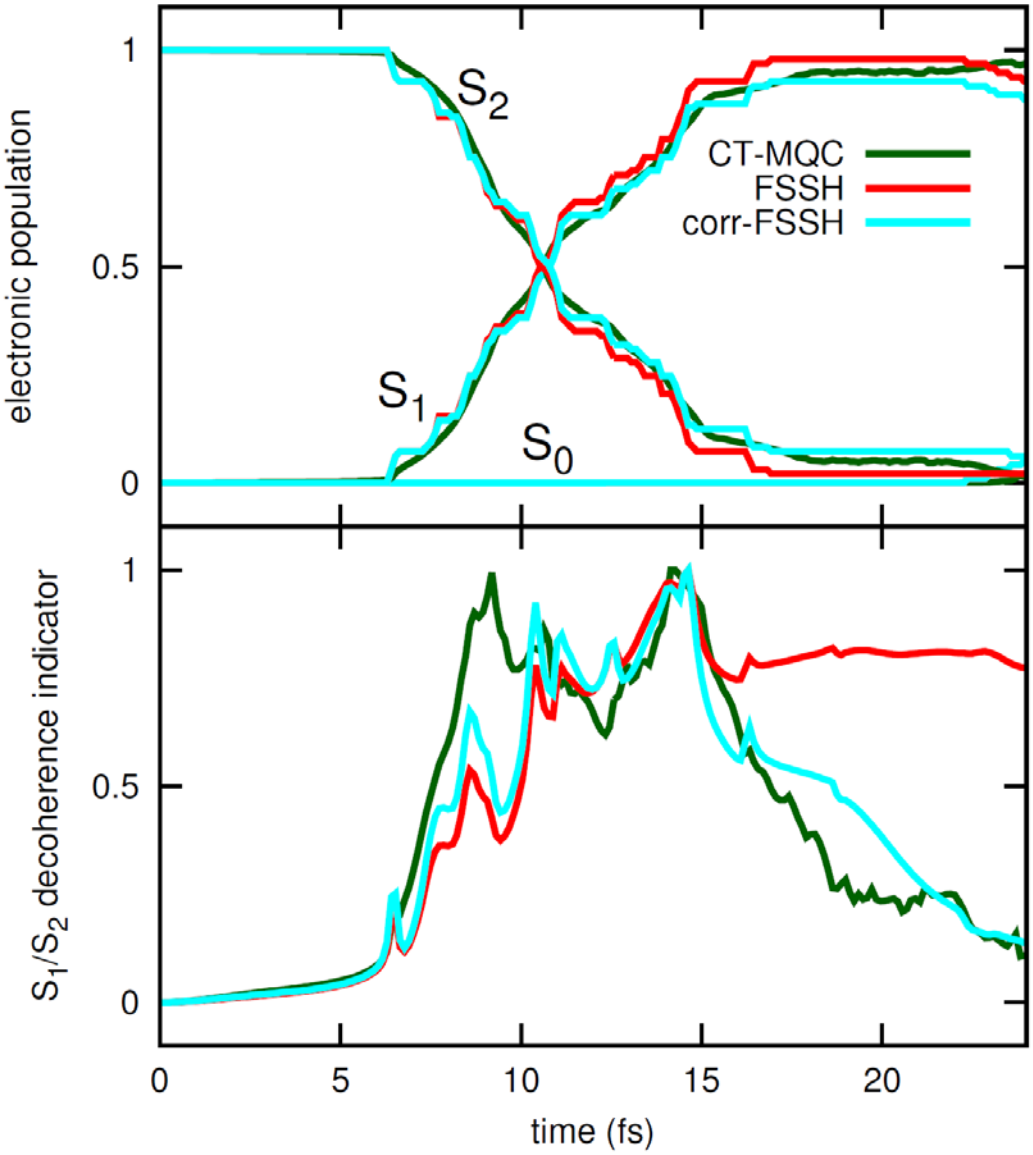
Photo-induced ring opening in Oxirane



Identification of the three groups of trajectories that, starting from the initial geometries, yield right-open (red) or left-open (green) ring structures and CC-extended bond geometry (blue).

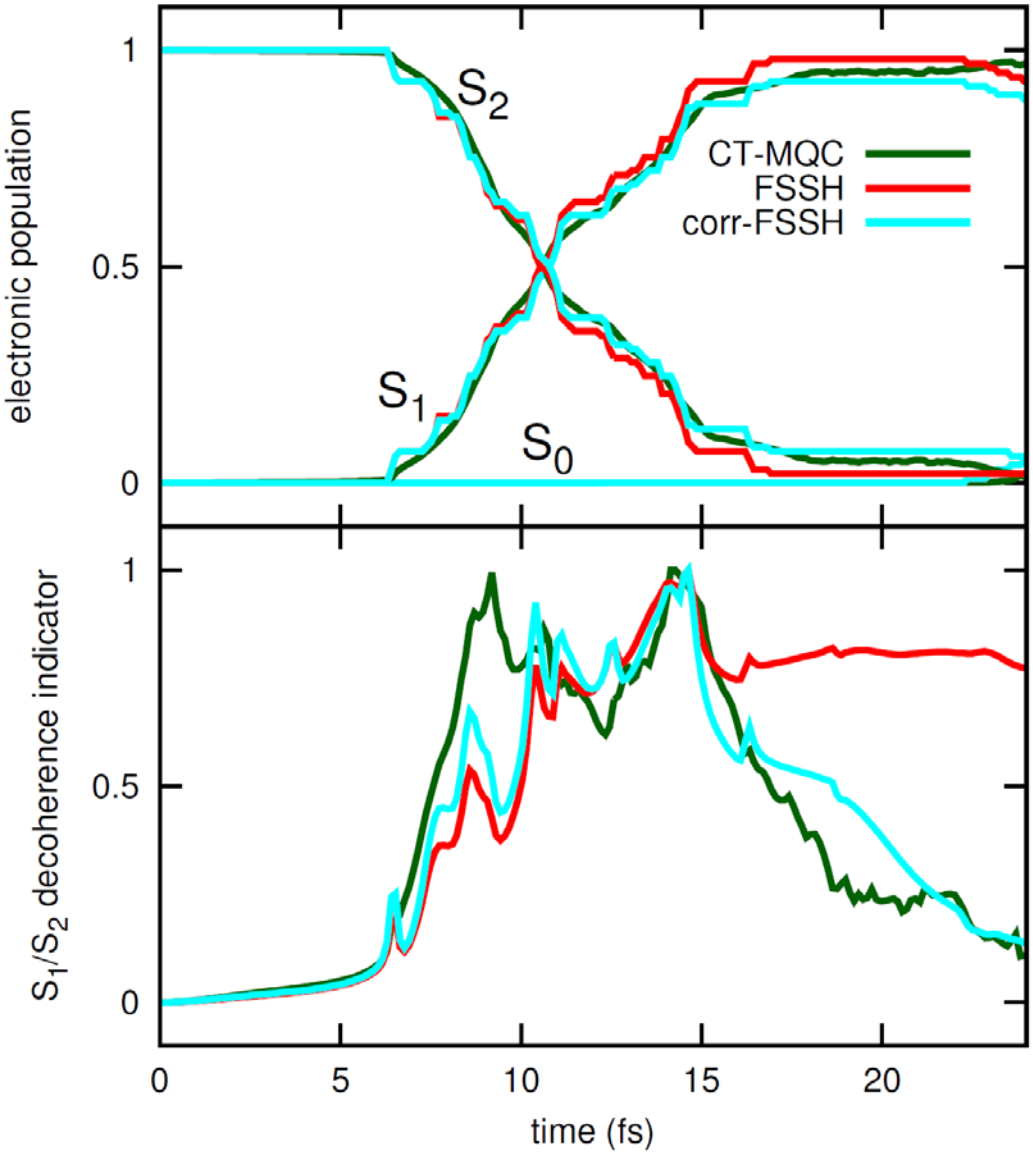
<u>Result</u>: Probability of ring-opening by oxygen motion is about 4 times larger than the C-C-bond stretch. Light colors identify CT-MQC trajectories and darker colors corr-FSSH trajectories.

F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, J.Phys.Chem. Lett. 8, 3048 (2017)



Upper panel: electronic populations of S0, S1 and S2 as functions of time. Lower panel: indicator of decoherence for the element S1=S2. Three sets of results are compared, based on the CT-MQC algorithm (dark-green lines), FSSH (red lines) and corr-FSSH (cyan lines).

F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, J.Phys.Chem. Lett. 8, 3048 (2017)



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Algorithm implemented in CPMD

F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, J.Phys.Chem. Lett. 8, 3048 (2017)

- **Starting from the right Schrödinger for the nuclei (the one that comes from the exact factorization), the resulting mixed quantum classical algorithms gives the effects of surface hopping and of decoherence for free.**

- **Mixed quantum-classical algorithm very efficient for field-free propagation because time-step is determined by nuclear time-scale.**

- **In the presence of long optical or XUV laser pulses, the time-step is determined by electron dynamics (atto-secs). Then real-time TDKS is advantageous.**

TDDFT for the complete electron-nuclear system

$$n\left(\boldsymbol{r},\underline{\underline{\boldsymbol{R}}},t\right)=N\int d\boldsymbol{r}_2\ldots d\boldsymbol{r}_N\left|\Psi\left(\boldsymbol{r},\boldsymbol{r}_2,\ldots\underline{\underline{\boldsymbol{R}}},t\right)\right|^2=\left|\chi\left(\underline{\underline{\boldsymbol{R}}},t\right)\right|^2\rho_{\underline{\underline{\boldsymbol{R}}}}(\boldsymbol{r},\boldsymbol{t})$$

1-1 correspondence: $V_{en}\left(\boldsymbol{r},\underline{\underline{\boldsymbol{R}}},t\right)\overset{1-1}{\longleftrightarrow}n\left(\boldsymbol{r},\underline{\underline{\boldsymbol{R}}},t\right)$

TDKS equations:

The time-dependent conditional density of the interacting system of interest can be calculated as density

$$\rho_R\left(rt\right)=\sum_{j=1}^{N}\left|\varphi_R^{(j)}\left(rt\right)\right|^2$$

of an auxiliary non-interacting (KS) system

$$i\hbar\frac{\partial}{\partial t}\varphi_R^{(j)}\left(rt\right)=\left(-\frac{\hbar^2\nabla^2}{2m}+v_S\left[\rho_R,\chi\right]\left(rt\right)\right)\varphi_R^{(j)}\left(rt\right)$$

To be solved in parallel with the nuclear equation of motion:

$$\left[\sum_{\mu} -\frac{1}{2M_\mu}\nabla_\mu^2 + V_{ext}\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right) + \varepsilon\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right)\right]\chi\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right) = i\frac{\partial}{\partial t}\chi\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right)$$

$$\varepsilon\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right) = \varepsilon^{BO}\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right) + \varepsilon_{geo}\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right)$$

Functionals: For $\varepsilon^{BO}\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right)$ use standard GS-DFT functionals as adiabatic approximation, i.e. evaluate GS functional at $\rho_{\underline{\boldsymbol{R}}}(\boldsymbol{r},\boldsymbol{t})$.

For $\varepsilon_{geo}\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right)$ use:

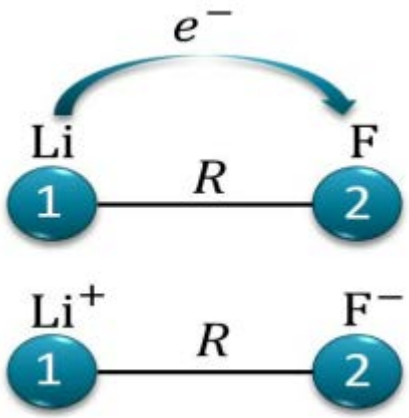
$$\varepsilon_{geo}\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right) = \int \frac{f\left[\rho_{\underline{\boldsymbol{R}}}(\boldsymbol{r},\boldsymbol{t})\right]}{2M_\mu}\left(\nabla_\mu \rho_{\underline{\boldsymbol{R}}}(\boldsymbol{r},\boldsymbol{t})\right)^2 d\boldsymbol{r}$$

TDKS potential:

$$v_s\left(\boldsymbol{r},\underline{\boldsymbol{R}},t\right) = \frac{\delta}{\delta\rho_{\underline{\boldsymbol{R}}}(\boldsymbol{r},\boldsymbol{t})}\int \left|\chi\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right)\right|^2\left(\varepsilon^{BO}\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right) + \varepsilon_{geo}\left(\underline{\boldsymbol{R}},\boldsymbol{t}\right)\right)d\underline{\boldsymbol{R}}$$

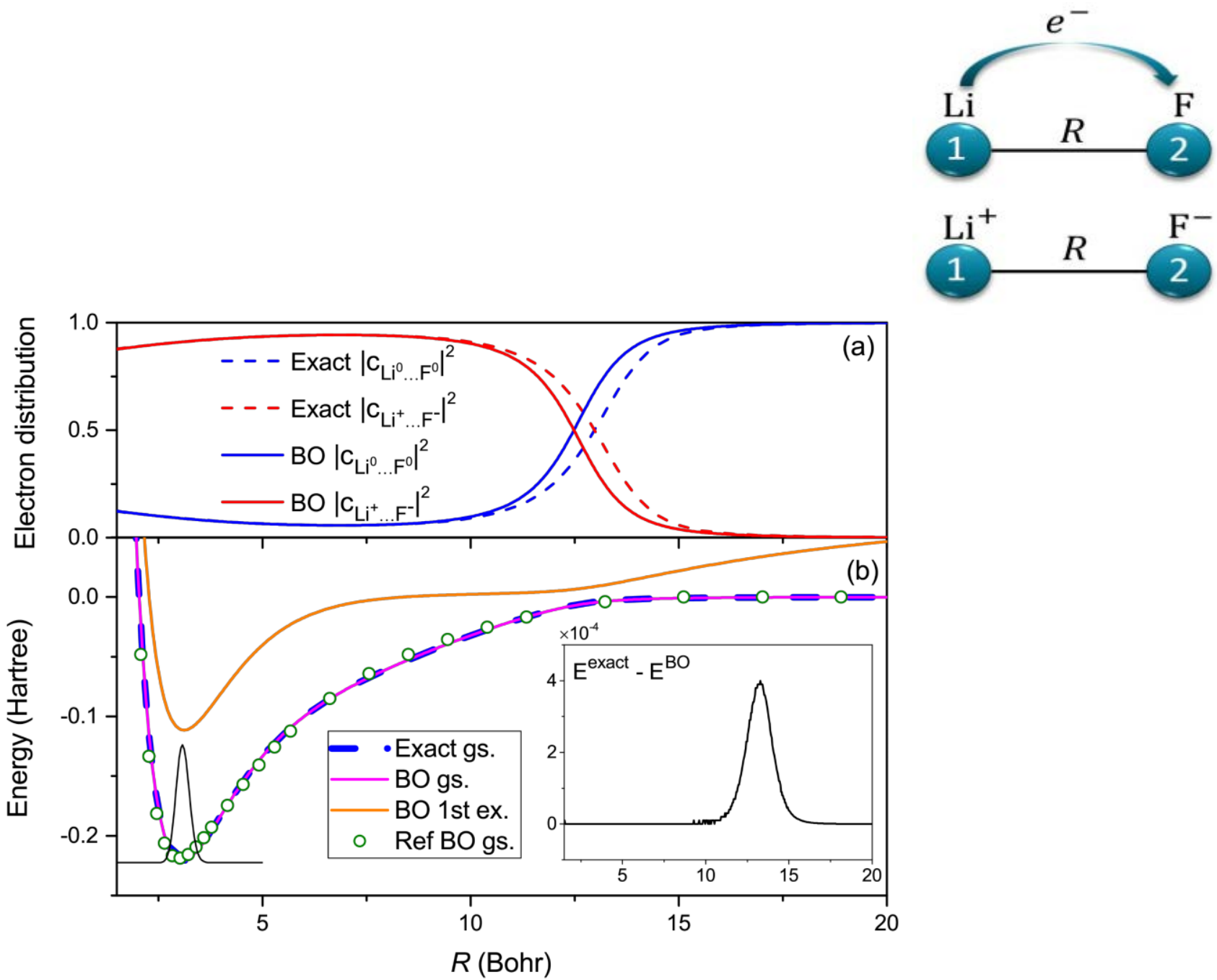
Test for simple model system: $\hat{H} = -\frac{1}{2M}\frac{d^2}{dR^2} + \boldsymbol{H}^{BO}(R)$

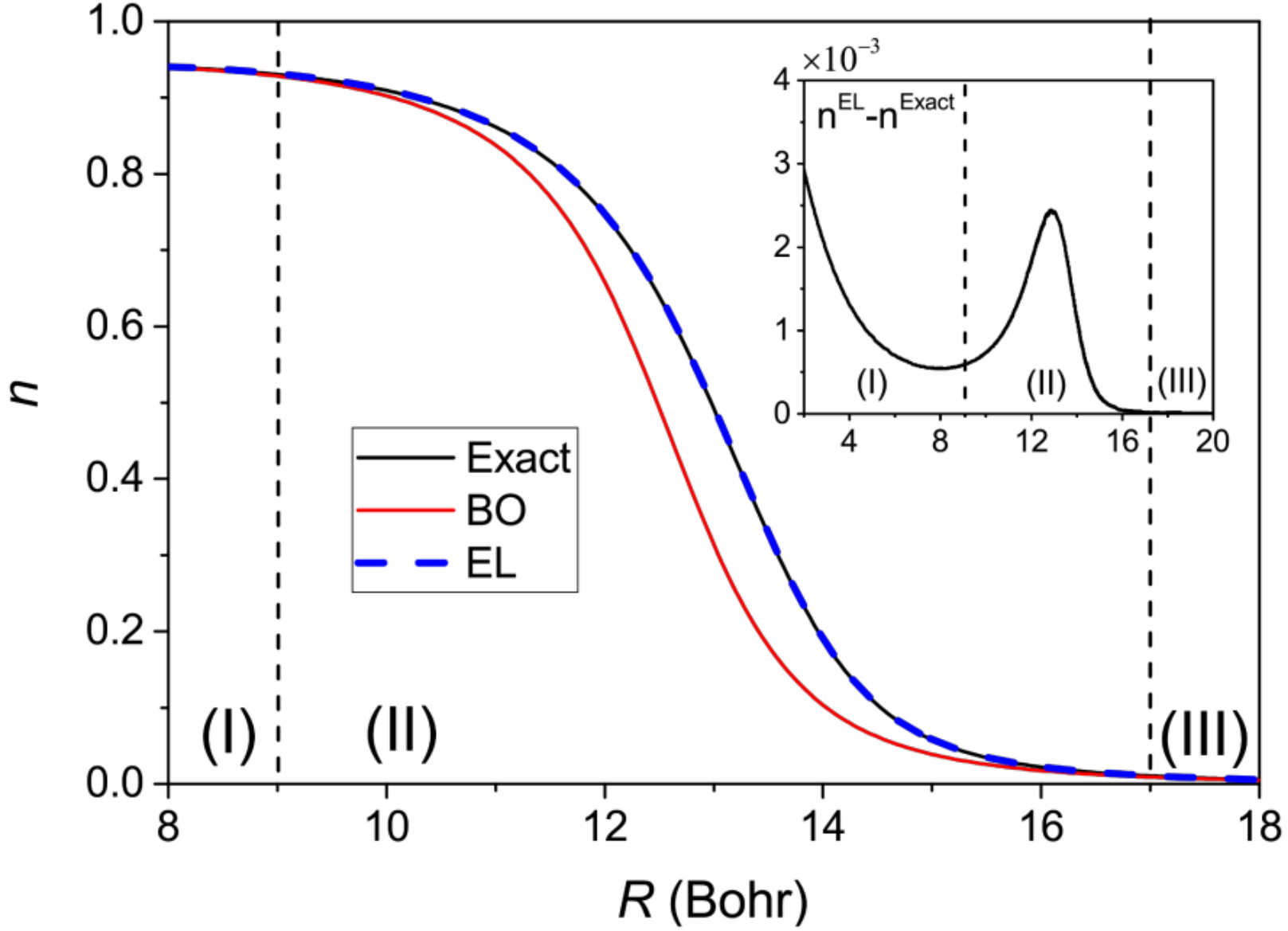
$$\boldsymbol{H}^{BO} = \begin{bmatrix} 2\varepsilon_1(R) + U_1 & -\sqrt{2}\tau(R) & 0 \\ -\sqrt{2}\tau(R) & \varepsilon_1(R) + \varepsilon_2(R) & -\sqrt{2}\tau(R) \\ 0 & -\sqrt{2}\tau(R) & 2\varepsilon_2(R) + U_2 \end{bmatrix}$$



$$\rho_R = |c_{Li^+\ldots F^-}(R)|^2 - |c_{Li^-\ldots F^+}(R)|^2$$

Chen Li, R. Requist, E.K.U. Gross, JCP 148, 084110 (2018)


e^-
Li
F
1
R
2
Li^+
F^-
1
R
2
Electron distribution
1.0
0.5
0.0
(a)
Exact $|c_{Li^0...F^0}|^2$
Exact $|c_{Li^+...F^-}|^2$
BO $|c_{Li^0...F^0}|^2$
BO $|c_{Li^+...F^-}|^2$
Energy (Hartree)
0.0
-0.1
-0.2
(b)
Exact gs.
BO gs.
BO 1st ex.
Ref BO gs.
$\times 10^{-4}$
$E^{exact} - E^{BO}$
4
2
0
5
10
15
20
5
10
15
20
R (Bohr)


1.0
0.8
0.6
0.4
0.2
0.0
n
8
10
12
14
16
18
R (Bohr)
(I)
(II)
(III)
Exact
BO
EL
×10^−3
4
3
2
1
0
n^EL-n^Exact
(I)
(II)
(III)
4
8
12
16
20

Summary of exact factorization

- $\Psi\left(\underline{\underline{r}},\underline{\underline{\underline{R}}},t\right)=\Phi_{\underline{\underline{\underline{R}}}}\left(\underline{\underline{r}},t\right)\cdot\chi\left(\underline{\underline{\underline{R}}},t\right)$ **is exact**

  A. Abedi, N.T. Maitra, E.K.U. Gross, PRL 105, 123002 (2010)

- **Exact Berry phase vanishes in some cases and is finite in others**

  S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, PRL 113, 263004 (2014)

- **TD-PES shows jumps betweeen BO-PES resembling surface hopping**

  A. Abedi, F. Agostini, Y. Suzuki, E.K.U.Gross, PRL 110, 263001 (2013)

- **mixed quantum classical algorithm**

  S.K. Min, F Agostini, E.K.U. Gross, PRL 115, 073001 (2015)

- **Application: Ring opening of oxirane**

  F. Agostini, S.K. Min, I. Tavernelli E.K.U. Gross, JPCL 8, 3048 (2017)

- **multi-component DFT for electrons and nuclei**

  Ryan Requist, E.K.U. Gross, PRL 117, 193001 (2016)

Other applications

- **Inverse factorisation:** $\Psi\left(\underline{\underline{r}},\underline{\underline{\underline{R}}},t\right)=\Phi_{\underline{\underline{r}}}\left(\underline{\underline{\underline{R}}},t\right)\cdot\chi\left(\underline{\underline{r}},t\right)$ **and electronic PES**

  Y. Suzuki, A. Abedi, N. Maitra, K. Yamashita, E.K.U. Gross, Phys. Rev. A 89, 040501(R) (2014)

- **Factorisation for electrons only: Description of processes involving "slow" and "fast" electrons such as HHG and ionisation. Concept of an exact single-active-electron potential.** **A. Schild, E.K.U.G., PRL 118, 163202 (2017)**

- **Exact TD-PES of systems driven by CW lasers are piecewise identical with Floquet surfaces with steps in between.**

  T. Fiedlschuster, E.K.U. Gross, R. Schmidt, Phys Rev A 95 , 063424 (2017)

- **Quantum interferences treated in mixed quantum-classical algorithm using exact time-dependent PES**

  B. Curchod, F. Agostini, E.K.U. Gross, JCP 145, 034103 (2016)

- **Ab-initio electron-phonon interaction:**

$$\hat{H}_{e-ph}=\sum_{k,q,\lambda}M_{\lambda}\left(k,q\right)\hat{c}^{\dagger}_{k-q}\hat{c}_{k}\left(\hat{b}^{\dagger}_{q\lambda}+\hat{b}_{-q\lambda}\right)$$

Take-home messages

Exact factorization useful to settle conceptual issues such as

- **unique classical force on nuclei (even when the nuclear WP splits)**
- **defines "exact geometric phase" without recourse to BO approx**

Exact factorization useful to develop practical algorithms

- **Starting from the right Schrödinger for the nuclei (the one that comes from the exact factorization), the resulting mixed quantum-classical algorithm does not need surface hopping nor decoherence corrections.**

- **Treating the non-adiabatic terms in the exact electronic EoM by 1^{st}-order perturbation theory provides an accurate and numerically efficient way to calculate electronic flux densities and vibrational circular dichroism.**