The exact factorization: A predictive first-principles approach to non-adiabatic dynamics

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Hamiltonian for the complete system of N_e electrons with coordinates $(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) \equiv \underline{\underline{\mathbf{r}}}$ and N_n nuclei with coordinates $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{\mathbf{R}}}$

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

with $\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla_\nu^2}{2M_\nu}$ $\hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m}$ $\hat{W}_{nn} = \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$

$$\hat{W}_{ee} = \frac{1}{2}\sum_{\substack{j,k \\ j\neq k}}^{N_e} \frac{1}{|r_j - r_k|} \qquad \hat{V}_{en} = \sum_{j=1}^{N_e}\sum_{\nu=1}^{N_n} -\frac{Z_\nu}{|r_j - R_\nu|}$$

Hamiltonian for the complete system of N_e electrons with coordinates $(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) \equiv \underline{\underline{r}}$ and N_n nuclei with coordinates $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{R}}$

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$$\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla_\nu^2}{2M_\nu} \qquad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m} \qquad \hat{W}_{nn} = \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$$

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Time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\underline{r}, \underline{\underline{R}}, t) = \left(H(\underline{r}, \underline{\underline{R}}) + V_{laser}(\underline{r}, \underline{\underline{R}}, t)\right)\psi(\underline{r}, \underline{\underline{R}}, t)$$

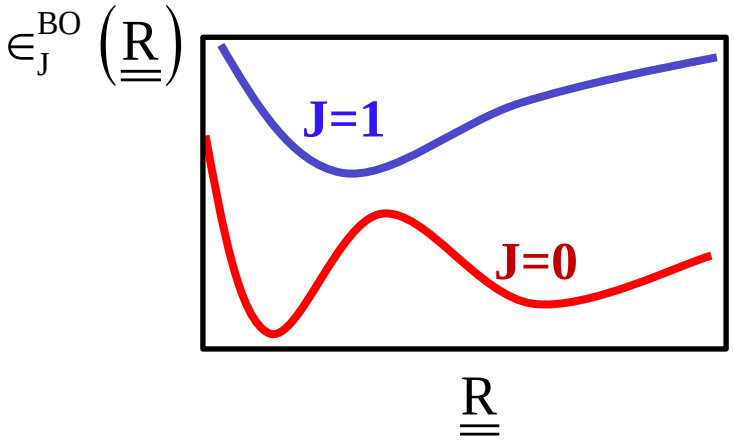
$$V_{laser}(\underline{r}, \underline{\underline{R}}, t) = \left(\sum_{j=1}^{N_e} r_j - \sum_{\nu=1}^{N_n} Z_\nu R_\nu\right) \cdot E \cdot f(t) \cdot \cos\omega t$$

Born-Oppenheimer

solve

$$\left(\hat{T}_e(\underline{\underline{r}}) + \hat{W}_{ee}(\underline{\underline{r}}) + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{V}_{en}(\underline{\underline{r}}, \underline{\underline{R}})\right)\Phi^{BO}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right) = \in^{BO}_{J}\left(\underline{\underline{R}}\right)\Phi^{BO}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right)$$

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



Born-Huang expansion of the full electron-nuclear wave function

Expand full molecular wave function in complete set of BO states:

$$\Psi\left(\underline{\underline{r}},\underline{\underline{\underline{R}}},t\right)=\sum_{J}\Phi^{BO}_{\underline{\underline{\underline{R}}},J}\left(\underline{\underline{r}}\right)\cdot\chi_{J}\left(\underline{\underline{\underline{R}}},t\right)$$

and insert expansion in the full Schrödinger equation → standard non-adiabatic coupling terms from T_n acting on $\Phi^{BO}_{\underline{\underline{\underline{R}}},J}\left(\underline{\underline{r}}\right)$.

Plug Born-Huang expansion in full TDSE:

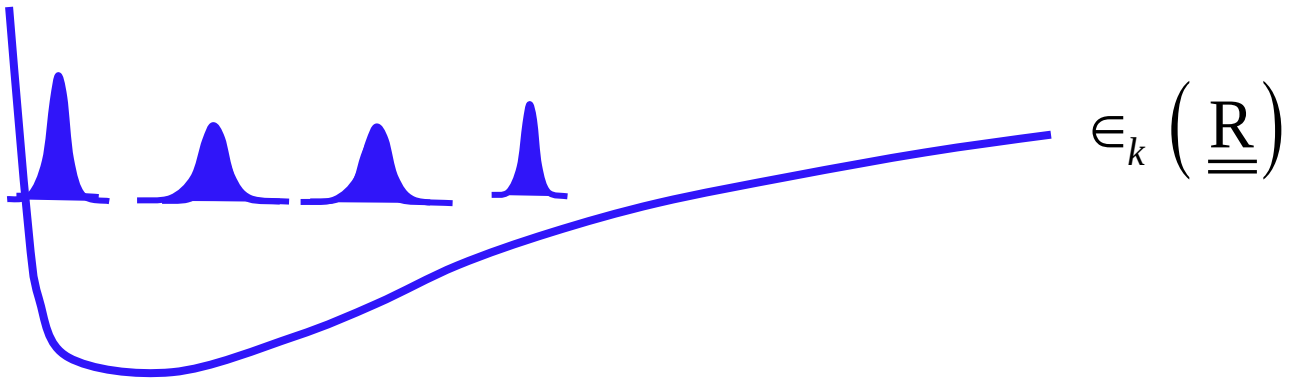
$$i\partial_t \chi_k\left(\underline{\underline{R}},t\right) = T_n \chi_k\left(\underline{\underline{R}},t\right) + \in_k\left(\underline{\underline{R}}\right)\chi_k\left(\underline{\underline{R}},t\right)$$

$$+\sum_{j\alpha}\left(\frac{\hbar^2}{M_\alpha}\right)\underbrace{\left\langle \phi^{BO}_{\underline{\underline{R}},k}\left|-i\nabla_{\underline{\underline{R}}_\alpha}\right|\phi^{BO}_{\underline{\underline{R}},j}\right\rangle}_{\text{NAC-1}}\left(-i\nabla_{\underline{\underline{R}}_\alpha}\chi_j\left(\underline{\underline{R}},t\right)\right)$$

$$+\sum_{j\alpha}\left(-\frac{\hbar^2}{2M_\alpha}\right)\underbrace{\left\langle \phi^{BO}_{\underline{\underline{R}},k}\left|\nabla^2_{\underline{\underline{R}}_\alpha}\right|\phi^{BO}_{\underline{\underline{R}},j}\right\rangle}_{\text{NAC-2}}\chi_j\left(\underline{\underline{R}},t\right)$$

Plug Born-Huang expansion in full TDSE:

$$i\partial_t \chi_k\left(\underline{\underline{R}},t\right) = T_n \chi_k\left(\underline{\underline{R}},t\right) + \in_k\left(\underline{\underline{R}}\right)\chi_k\left(\underline{\underline{R}},t\right)$$

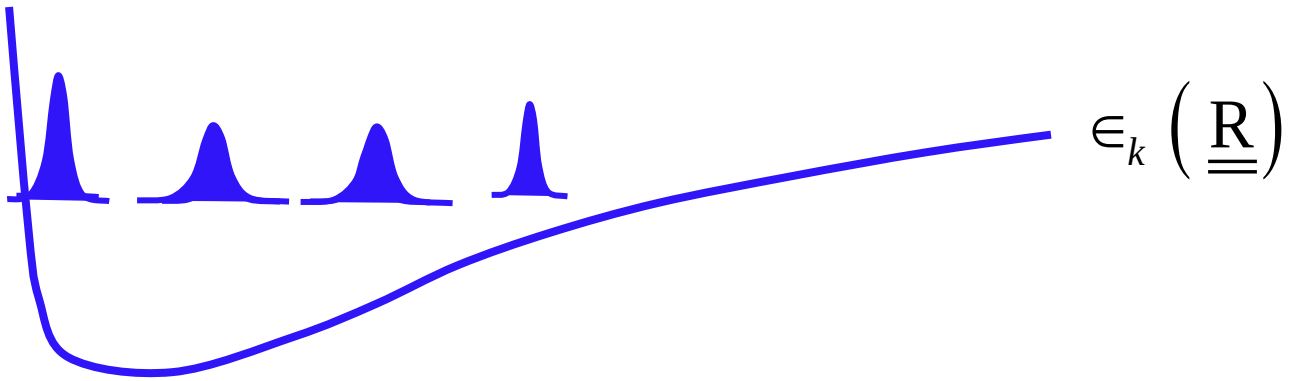


$$\Psi^{adiab}\left(\mathbf{R},\mathbf{r},t\right) \approx \chi_k\left(\mathbf{R},t\right)\Phi_k^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)$$

Adiabatic approximation

Plug Born-Huang expansion in full TDSE:

$$i\partial_t \chi_k\left(\underline{\underline{R}},t\right) = T_n \chi_k\left(\underline{\underline{R}},t\right) + \in_k\left(\underline{\underline{R}}\right)\chi_k\left(\underline{\underline{R}},t\right)$$

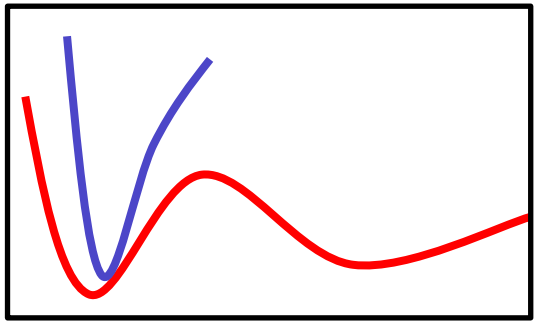


$$\Psi^{adiab}\left(\mathbf{R},\mathbf{r},t\right) \approx \chi_k\left(\mathbf{R},t\right)\Phi_k^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)$$ **Adiabatic approximation**

In calculations of vibrational spectra one usually makes two approximations:

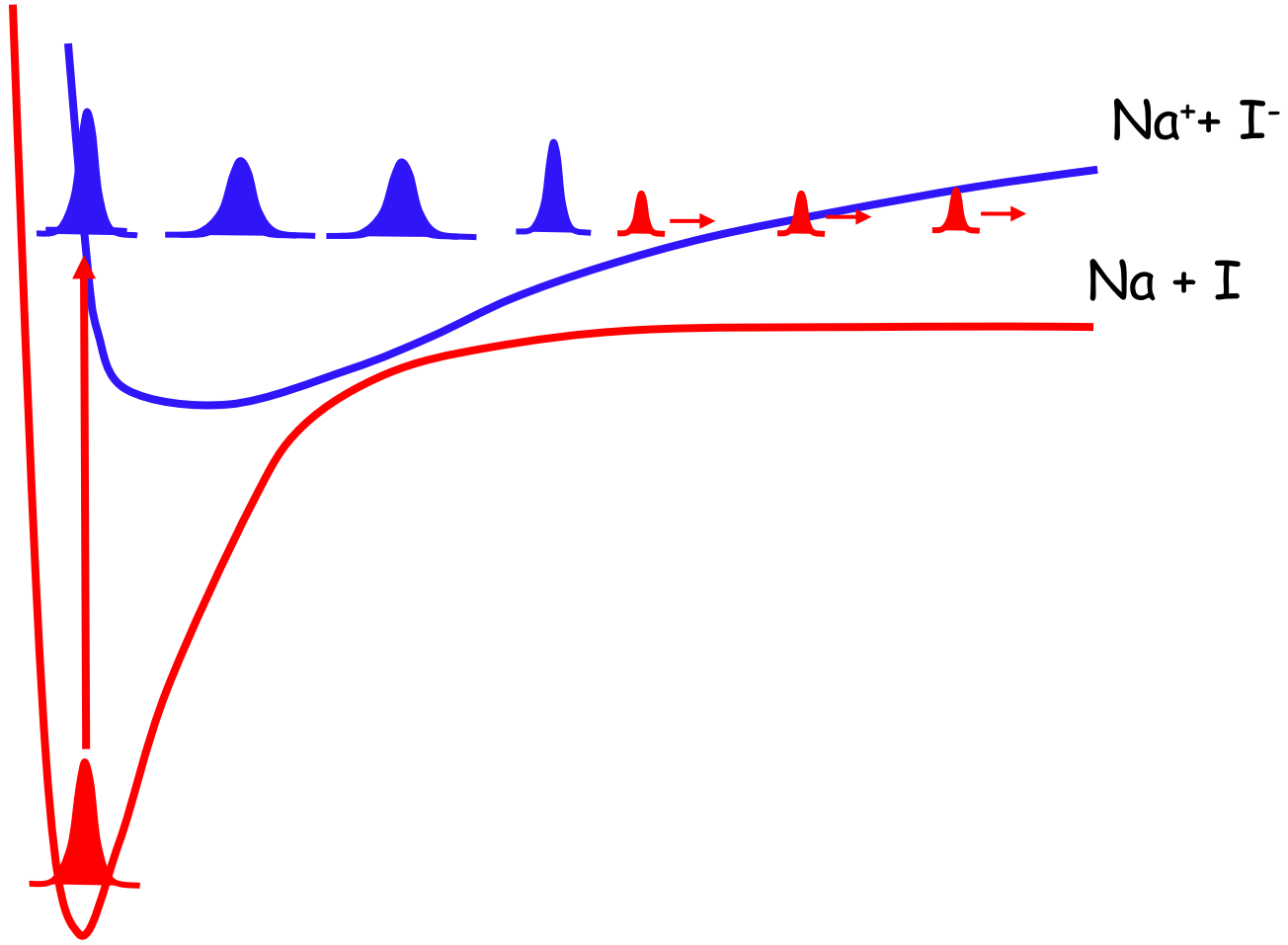
- **Adiabatic approximation**
- **Harmonic approximation**

Vibrational spectra are usually very well described within the adiabatic approach, but not always! (Hammes-Schiffer)



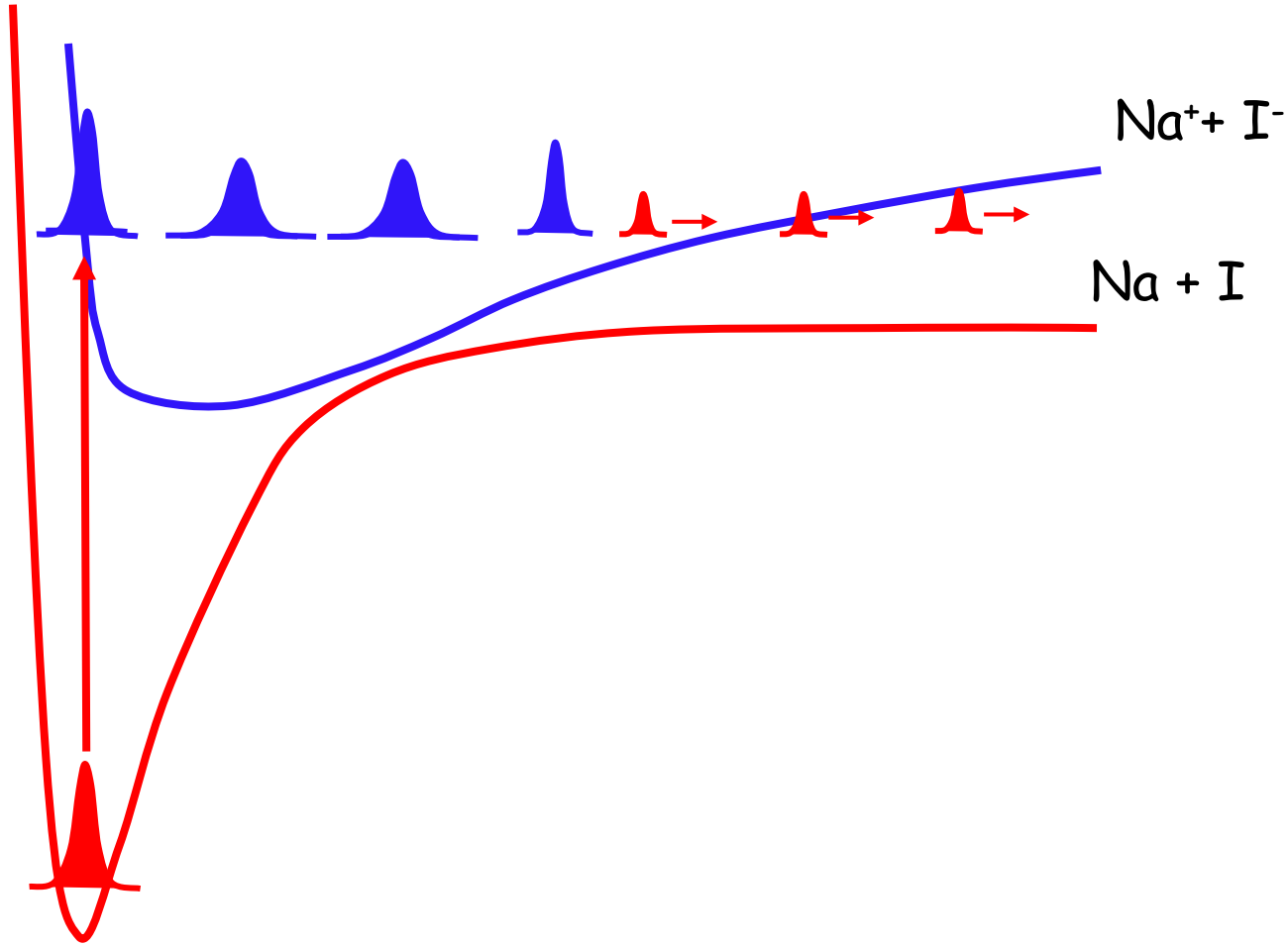
Dramatic failures of the adiabatic approximation:

- **Zewail experiments**
- **Calculation of electronic currents associated with nuclear motion**



$$\Psi\left(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}},t\right) \approx \chi_0\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{0,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right) + \chi_1\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{1,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right)$$

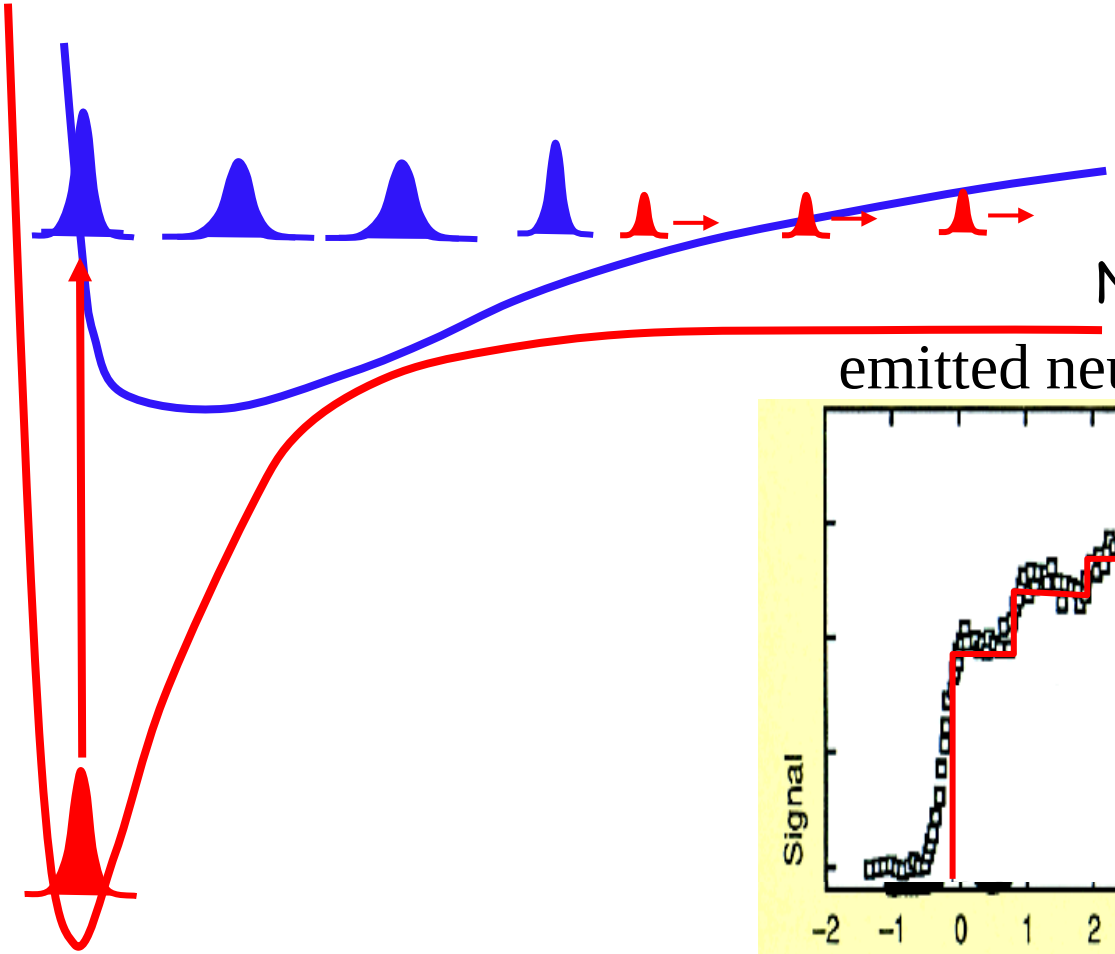
Two BO potential energy surfaces of equal importance



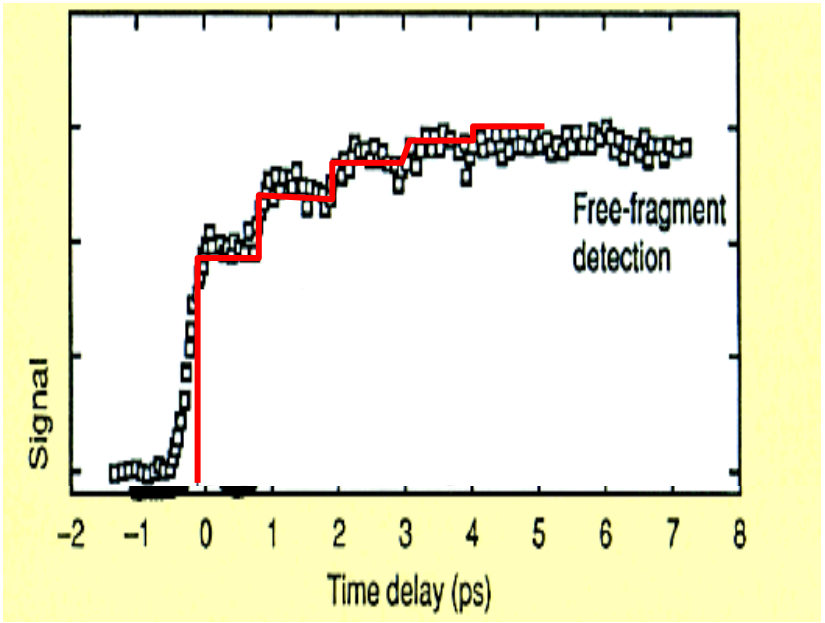
$$\Psi\left(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}},t\right) \approx \chi_0\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{0,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right) + \chi_1\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{1,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right)$$

Nuclear Density:

$$\Gamma\left(\underline{\underline{\mathbf{R}}},t\right) = \int\left|\Psi\left(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}},t\right)\right|^2 d\underline{\underline{\mathbf{r}}} = \left|\chi_1\left(\underline{\underline{\mathbf{R}}},t\right)\right|^2 + \left|\chi_0\left(\underline{\underline{\mathbf{R}}},t\right)\right|^2$$



emitted neutral Na atoms



$$\Psi\left(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}},t\right) \approx \chi_0\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{0,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right) + \chi_1\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{1,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right)$$

Nuclear Density:

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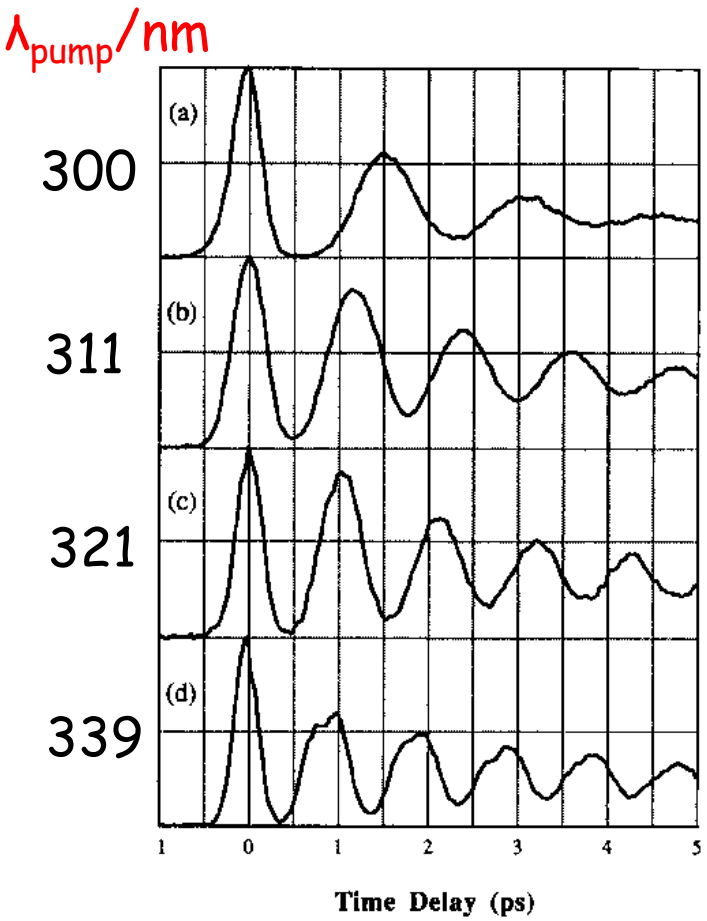
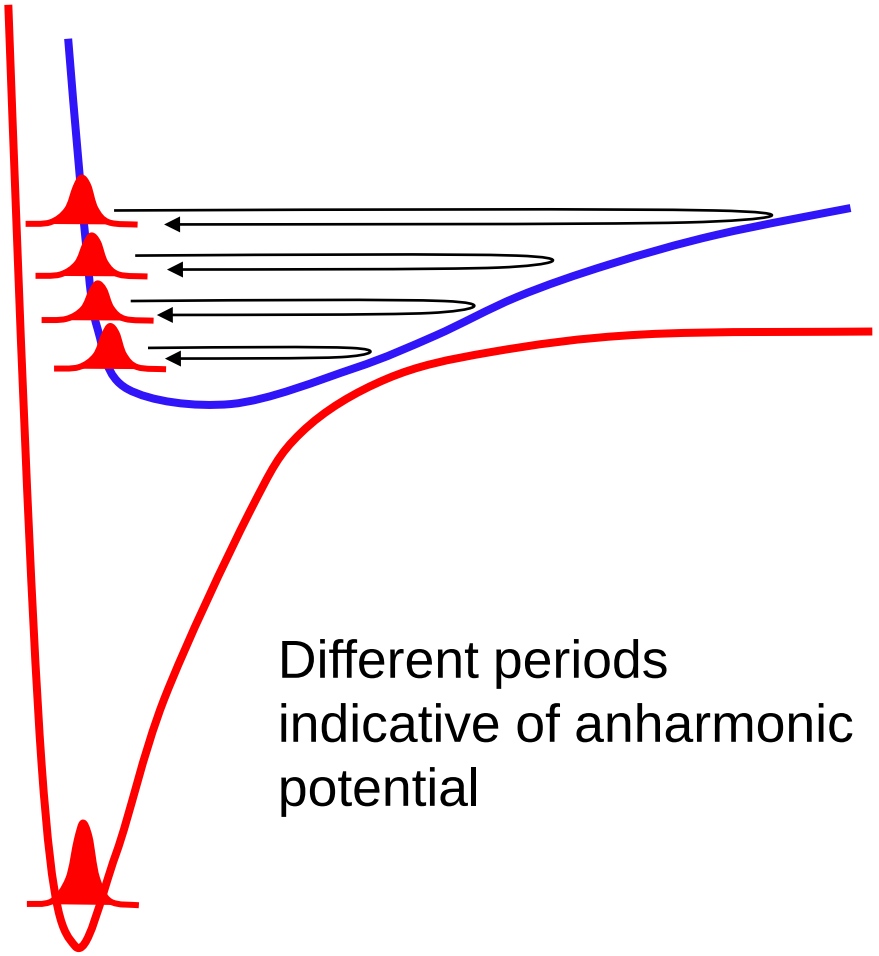
Effect of tuning pump wavelength (exciting to different points on excited surface)





Different periods indicative of anharmonic potential

T.S. Rose, M.J. Rosker, A. Zewail, JCP **91**, 7415 (1989)

Most dramatic failure of the adiabatic approximation: Calculation of electronic flux density associated with nuclear motion

Adiabatic approximation (dynamics on a single BO-PES)

$$\Psi\left(\mathbf{R},\mathbf{r},t\right)\approx\chi^{BO}\left(\mathbf{R},t\right)\Phi^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)$$

with non-degenerate, real-valued BO state $\Phi^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)$

Time-dependent electronic (N-body, or one-body) density:

$$\rho^{BO}\left(\mathbf{r},t\right)=\int\left|\chi^{BO}\left(\mathbf{R},t\right)\right|^{2}\left|\Phi^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)\right|^{2}d\mathbf{R}$$

very close to true TD density

$$\mathbf{j}^{BO}\left(\mathbf{r},t\right)=\int\mathrm{Im}\left(\Psi^{*}\partial_{\mathbf{r}}\Psi\right)d\mathbf{R}=\int\left|\chi^{BO}\left(\mathbf{R},t\right)\right|^{2}\mathrm{Im}\left(\Phi^{BO*}\partial_{\mathbf{r}}\Phi^{BO}\right)d\mathbf{R}=0$$

completely wrong!! Dramatic failure of adiabatic approximation

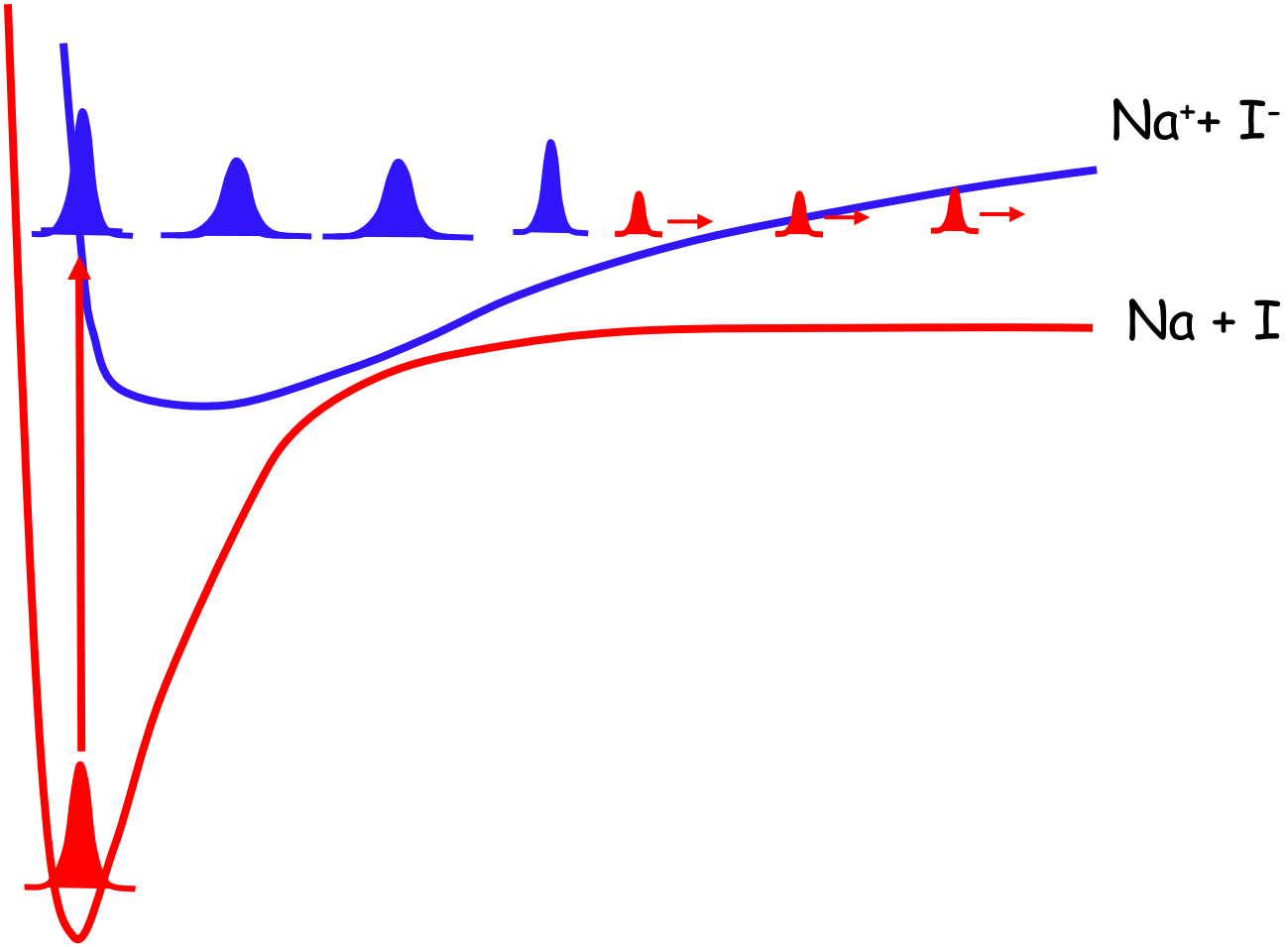
- **When the adiabatic approximation fails one has to go back to the Born-Huang expansion.**

- **When only two (or few) surfaces are important (like in Zewail experiment) that's feasible.**

<u>Problem</u>: Born-Huang expansion not feasible for larger molecules or solids

For large systems one would like to (one has to) treat the nuclear motion with classical trajectories.

But what's the right classical force when the nuclear wave packet splits?



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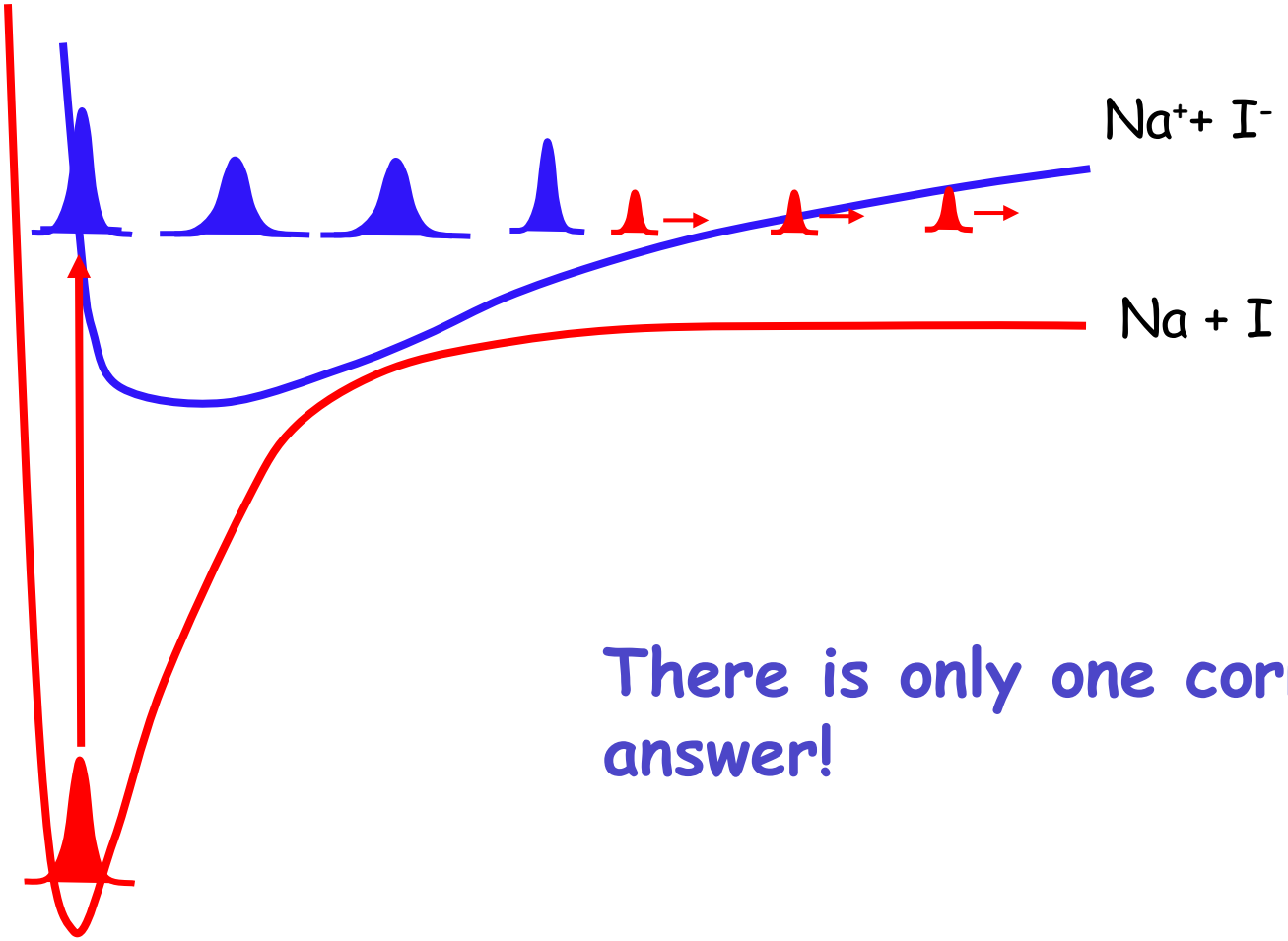


There is only one correct answer!

The exact factorisation

The exact factorisation

"Exactification" $\Psi^{\text{exact}}\left(\underline{\underline{r}},\underline{\underline{R}},t\right)=\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}},t\right)\cdot\chi\left(\underline{\underline{R}},t\right)$

of the adiabatic approximation

$$\Psi^{\text{adiab}}\left(\underline{\underline{r}},\underline{\underline{R}},t\right)=\Phi^{\text{BO}}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\cdot\chi\left(\underline{\underline{R}},t\right)$$

Outline

- **Show that the factorisation**

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

  is an exact representation of the electron-nuclear wave function

- **Concept of exact and unique time-dependent PES and the exact classical force on the nuclei**

- **Nuclear-velocity perturbation theory**
  -- electronic currents associated with nuclear motion
  -- vibrational circular dichroism

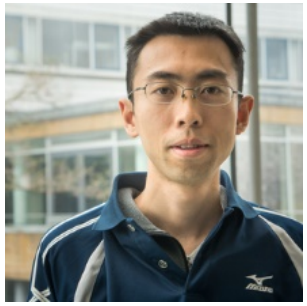
- **Novel mixed quantum-classical algorithm for nonadiabatic dynamics (no surface hopping, no decoherence correction)**

THANKS!

Axel Schild

Ali Abedi

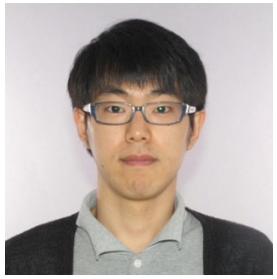
Federica Agostini



Chen Li

Basile Curchod

Ivano Tavernelli



Seung Kyu Min

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Rodolphe Vuilleumier

Ryan Requist

Nikitas Gidopoulos

Theorem I

The exact solution of

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

can be written in the form

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

where $\int d\underline{\underline{r}} \left|\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right)\right|^2 = 1$ **for any fixed** $\underline{\underline{R}}, t$.

A. Abedi, N.T. Maitra, E.K.U.G., PRL 105, 123002 (2010)
JCP 137, 22A530 (2012)

Theorem II

$\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},t)$ and $\chi(\underline{\underline{R}},t)$ satisfy the following equations

Eq. ❶

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

Eq. ❷

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

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

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

Eq. ❷

Exact TD vector potential

Exact TDPES

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

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

JCP 137, 22A530 (2012)

Exact Berry connection

$$A_\nu\left(\underline{\underline{R}},t\right)=\int d\underline{\underline{r}}\;\Phi^*_{\underline{\underline{R}}}\left(\underline{\underline{r}},t\right)\;\left(-i\nabla_\nu\right)\;\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}},t\right)$$

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

$$\chi\left(\underline{\underline{R}},t\right):=e^{i\theta\left(\underline{\underline{R}},t\right)}\left|\chi\left(\underline{\underline{R}},t\right)\right|$$

$$A_\nu\left(\underline{\underline{R}},t\right)=\mathrm{Im}\left\{\int d\underline{\underline{r}}\;\Psi^*\left(\underline{\underline{r}},\underline{\underline{R}},t\right)\;\nabla_\nu\Psi\left(\underline{\underline{r}},\underline{\underline{R}},t\right)\right\}/\left|\chi\left(\underline{\underline{R}},t\right)\right|^2-\nabla_\nu\theta\left(\underline{\underline{R}},t\right)$$

$$A_\nu\left(\underline{\underline{R}},t\right)=J_\nu\left(\underline{\underline{R}},t\right)/\left|\chi\left(\underline{\underline{R}},t\right)\right|^2-\nabla_\nu\theta\left(\underline{\underline{R}},t\right)$$

with the exact nuclear current density J_ν

Another way of reading this equation:

$$J_\nu\left(\underline{\underline{R}},t\right)=\left|\chi\left(\underline{\underline{R}},t\right)\right|^2\left\{A_\nu\left(\underline{\underline{R}},t\right)+\nabla_\nu\theta\left(\underline{\underline{R}},t\right)\right\}$$

Conclusion: The nuclear TD Schrödinger equation

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

yields both the exact nuclear N-body density and the exact nuclear N-body current density

A. Abedi, N.T. Maitra, E.K.U. Gross, JCP 137, 22A530 (2012)

Theorem III

The nuclear Schroedinger equation yields the true nuclear N-body density and the true nuclear N-body current density that one would also obtain from the full electron-nuclear wave function Ψ.

Consequence:

The gradient of the TDPES appearing in this Schrödinger equation is the only correct classical force on the nuclei, unique up to within an R-dependent gauge transformation.

Properties of the exact electronic EoM:

- Non-linear equation in $\phi_R(rt)$ because of $A[\phi]$
- Non-adiabatic terms are not operators in the electronic Hilbert space
- in BO-basis: non-Hermitian matrix, still the time-propagation conserves norm
- Electronic EoM depends on $\chi(Rt)$

Properties of the exact nuclear EoM:

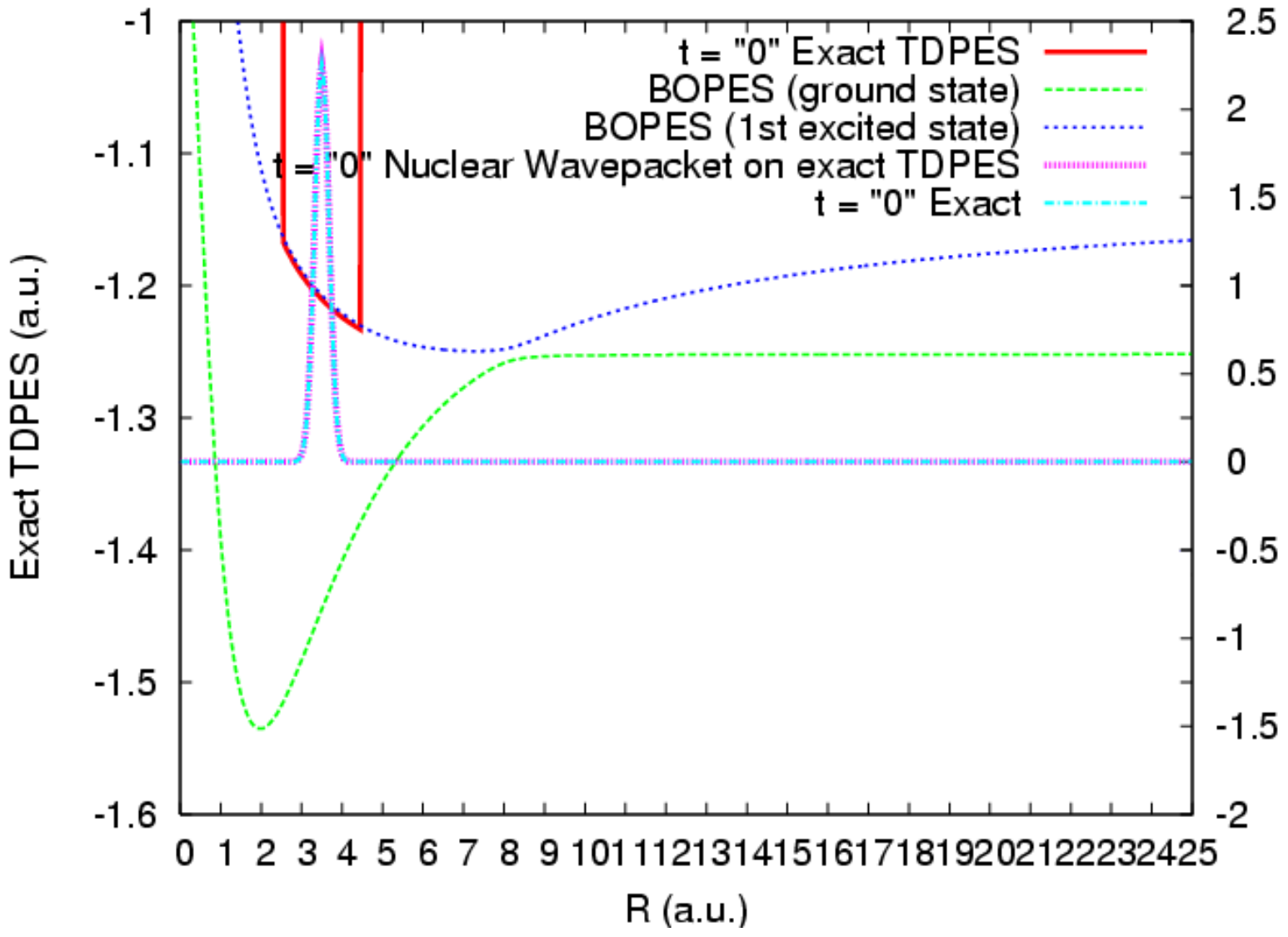
- Standard TDSE
- Scalar potential is N_n-body interaction
- Vector potential is N_n-body operator, i.e. 3D vector field depending on $\left(\vec{R}_1 \ldots \vec{R}_{N_n}\right)$

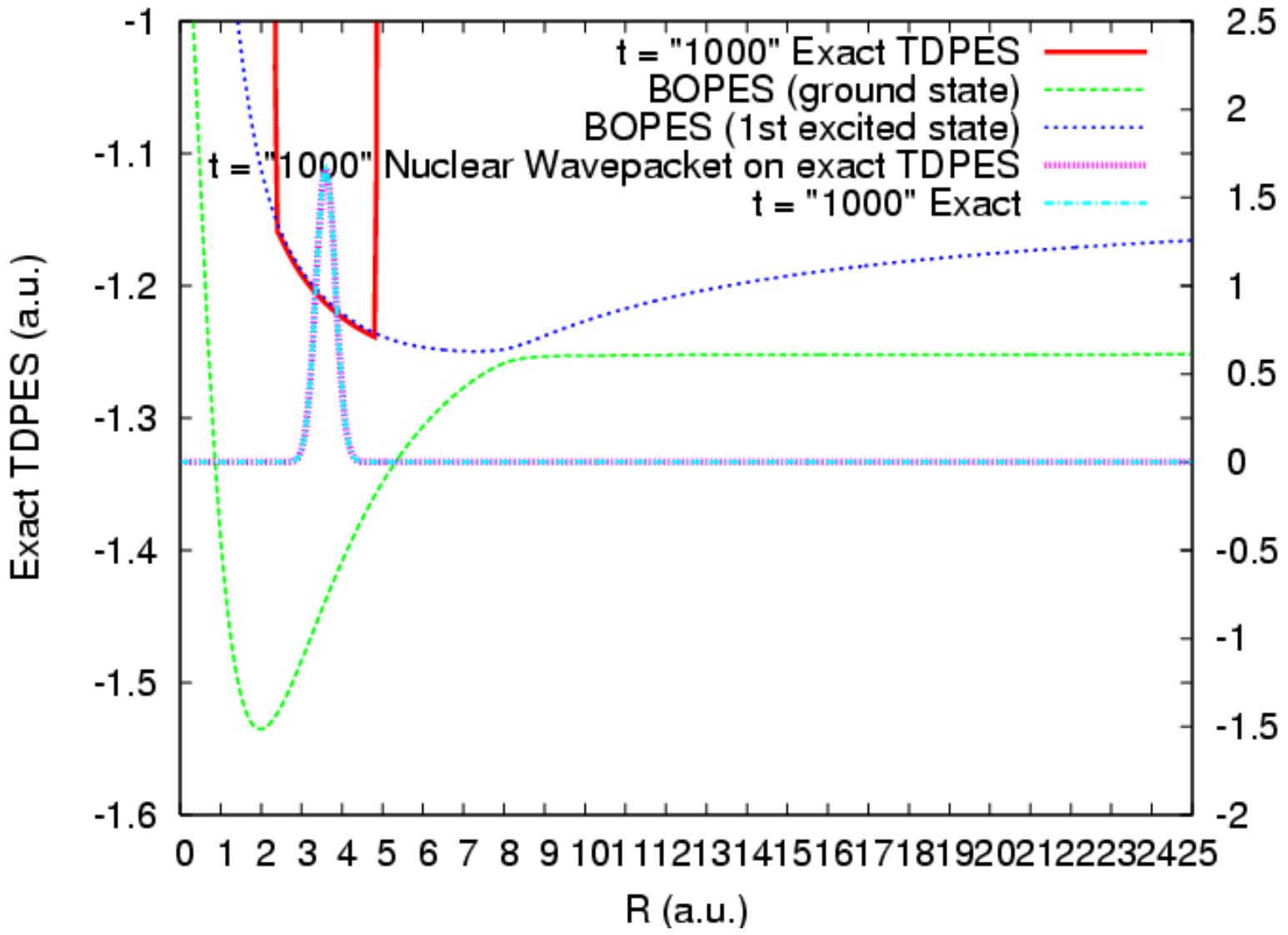
How does the exact time-dependent PES look like?

Example: Nuclear wave packet 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)


t = "0" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "0" Nuclear Wavepacket on exact TDPES
t = "0" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
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


t = "1000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "1000" Nuclear Wavepacket on exact TDPES
t = "1000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
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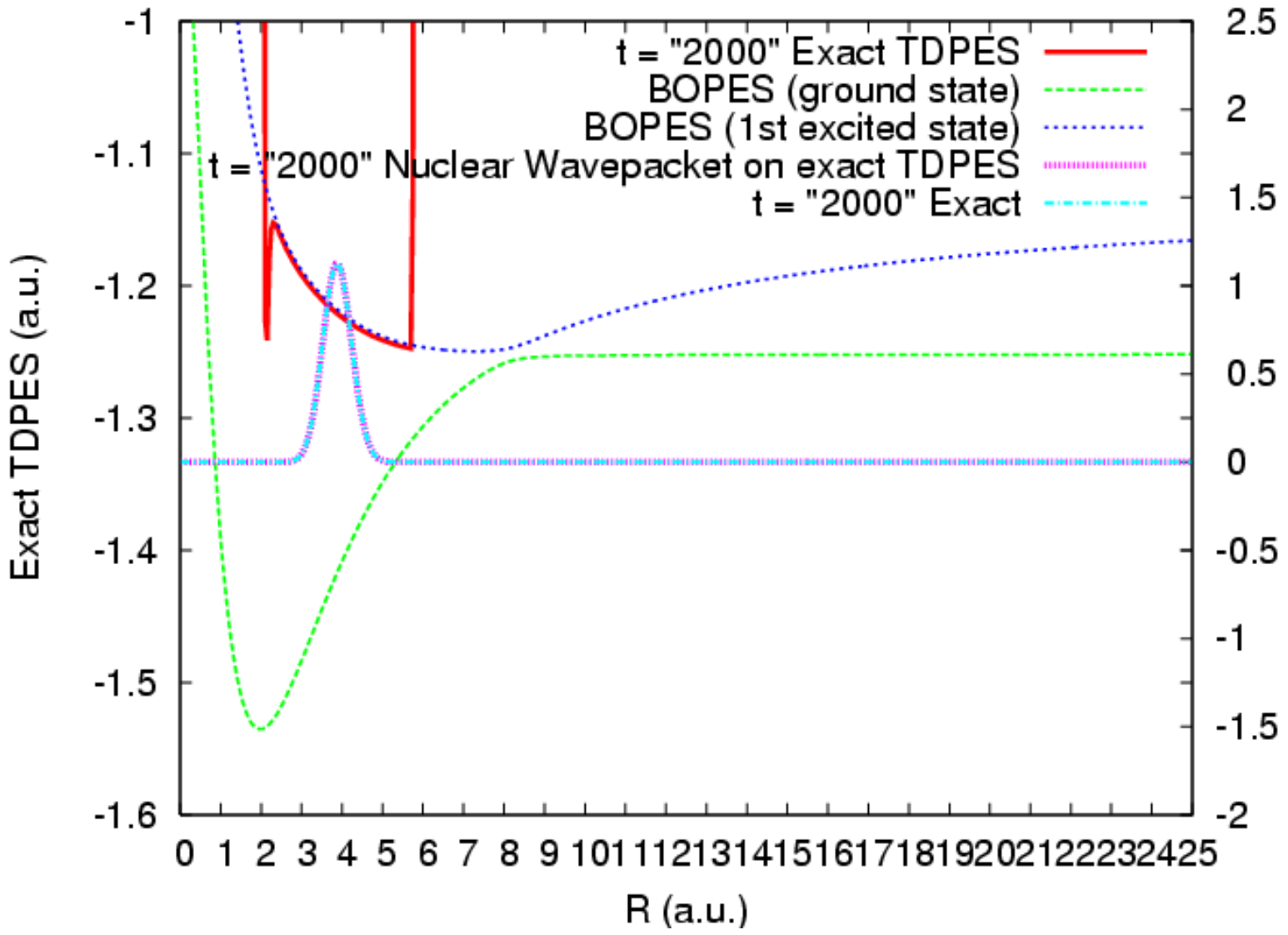
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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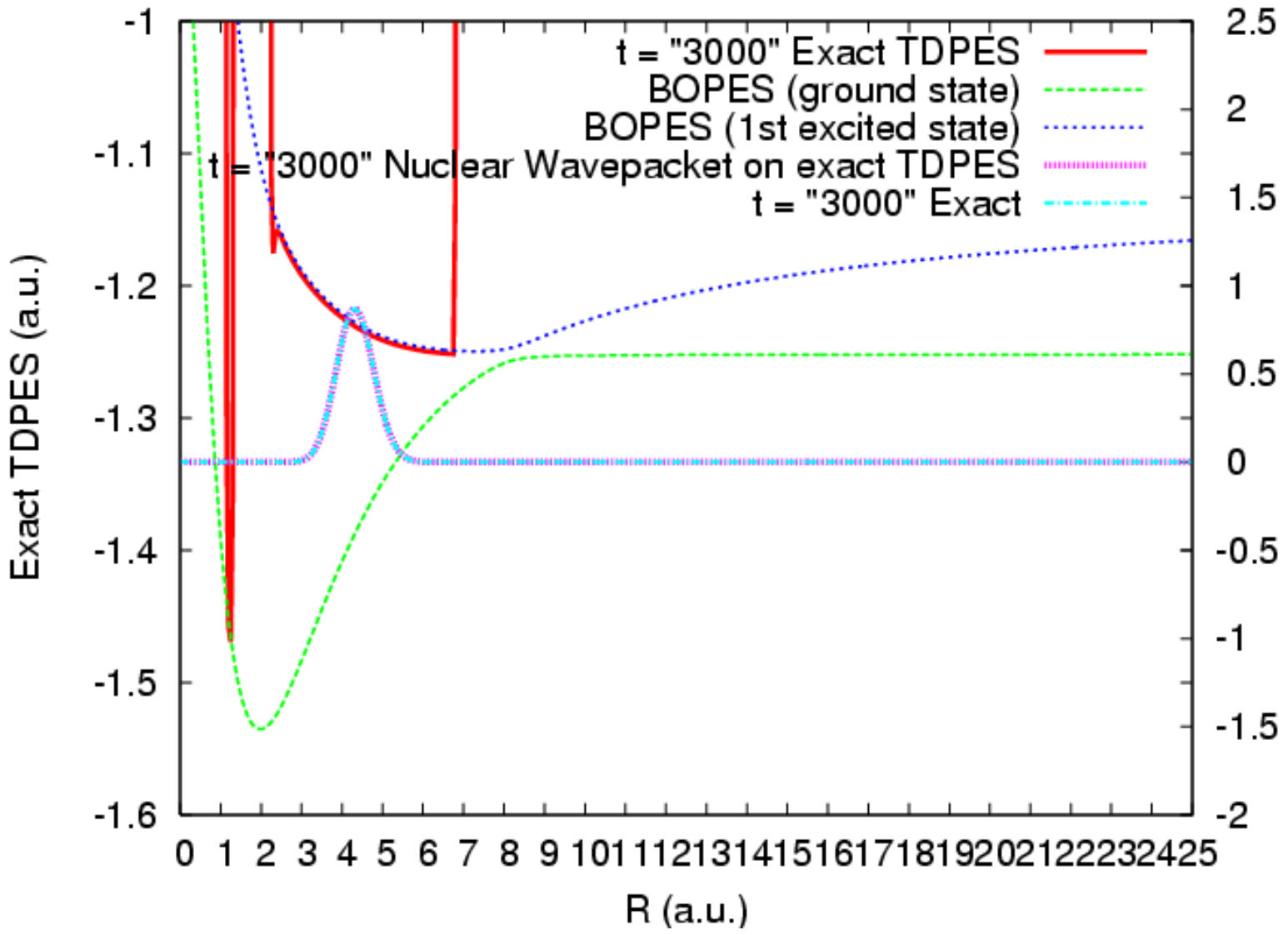
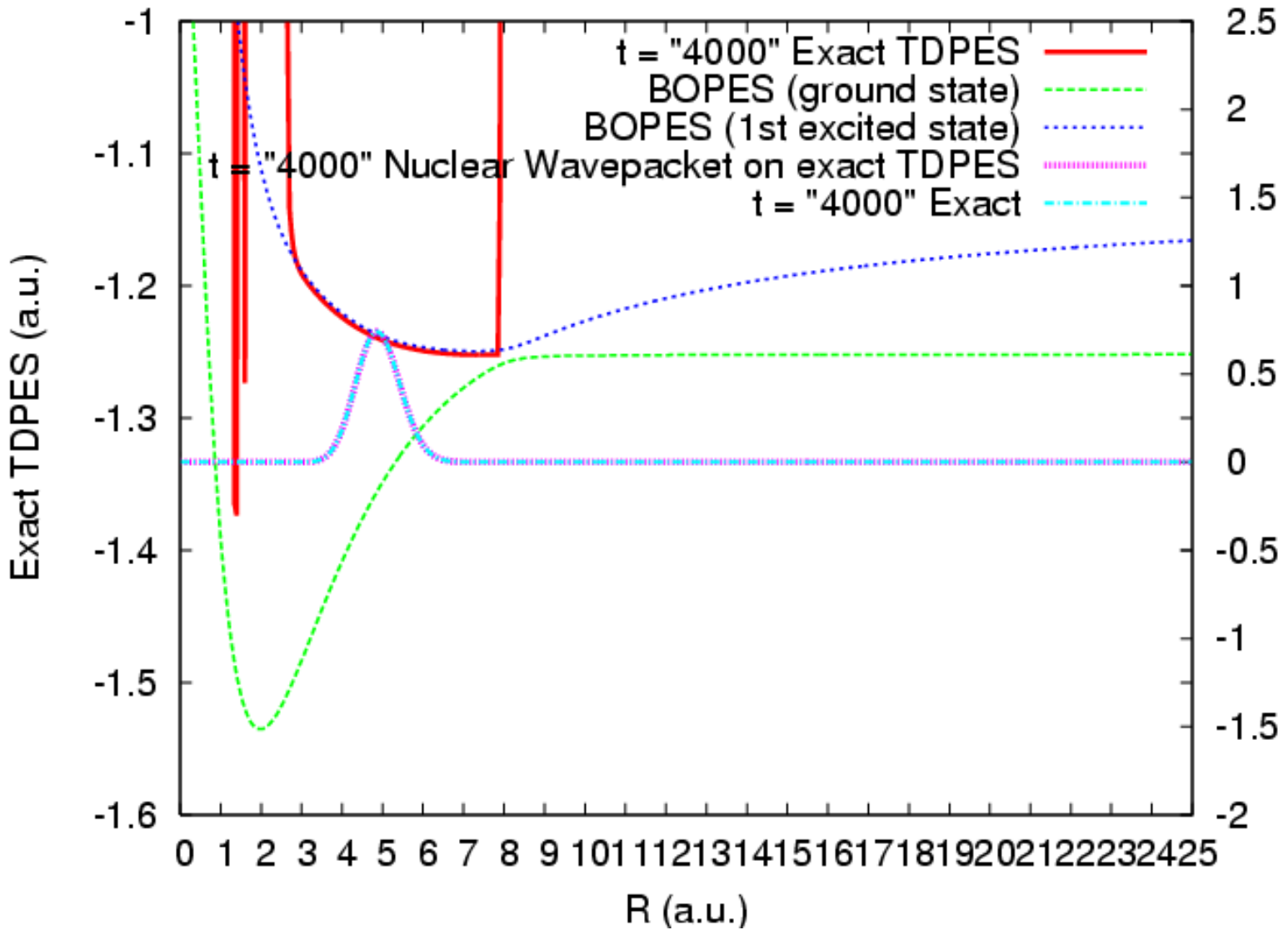
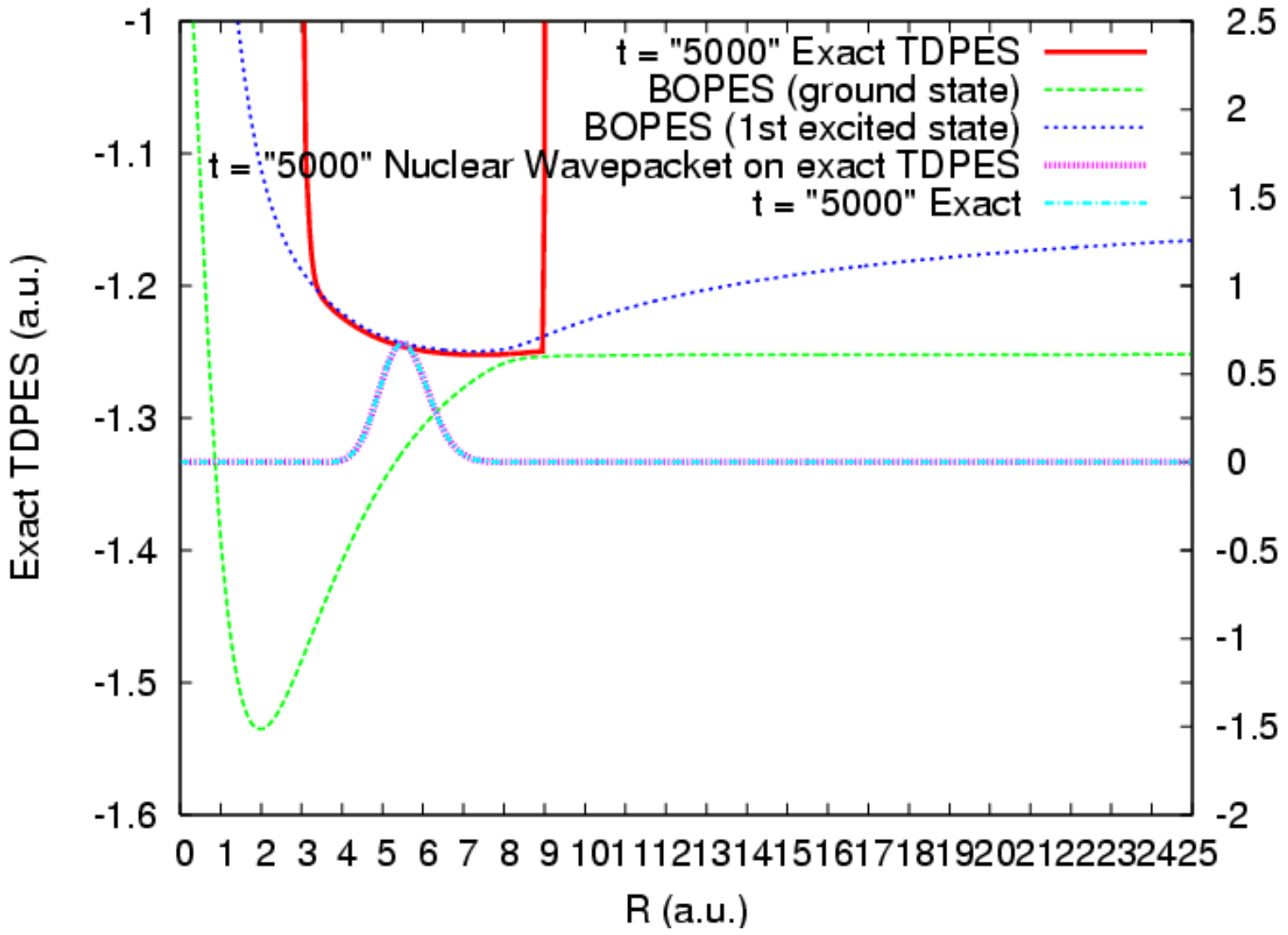
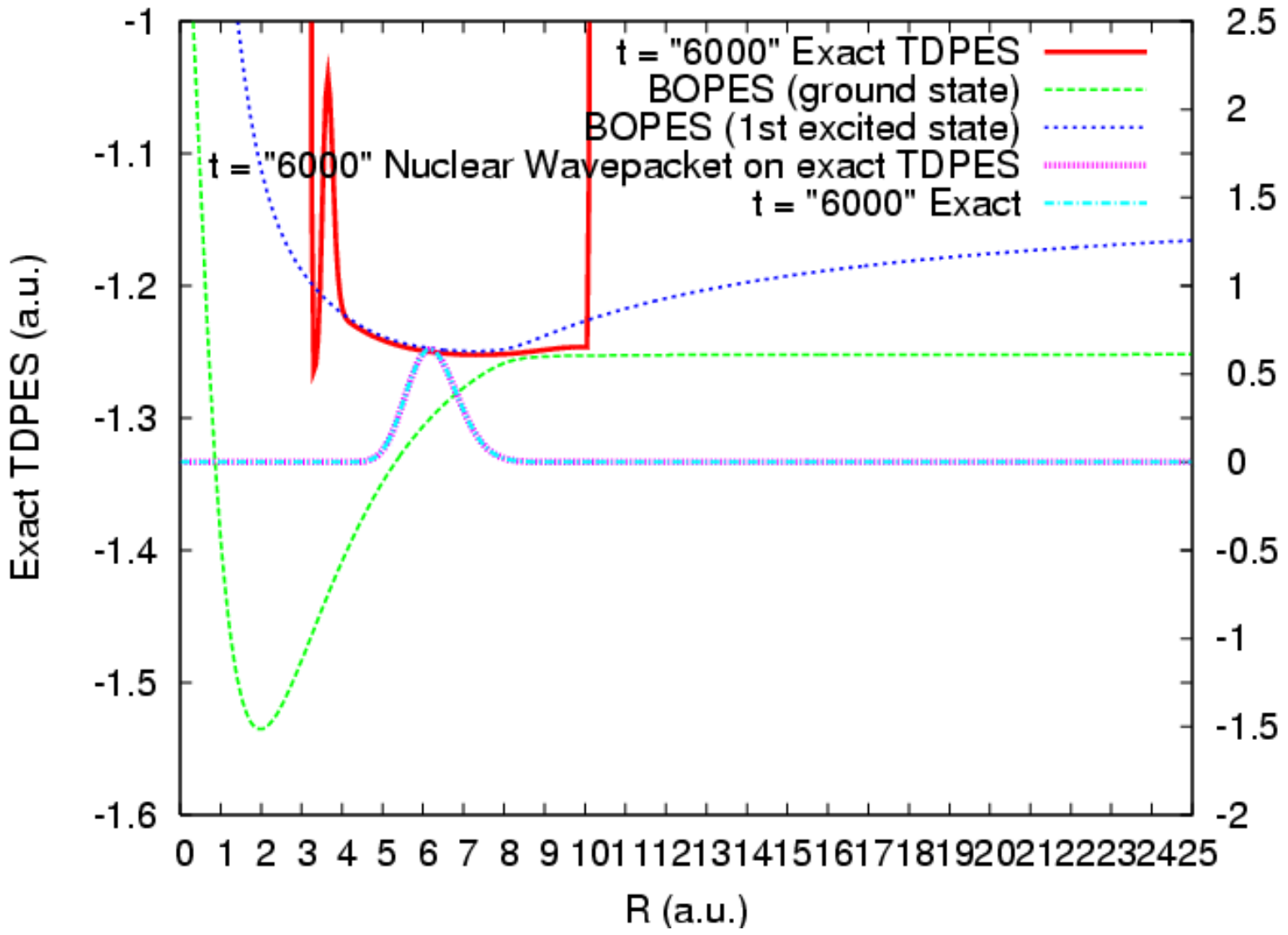
BOPES (ground state)
BOPES (1st excited state)
t = "2000" Nuclear Wavepacket on exact TDPES
t = "2000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "3000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "3000" Nuclear Wavepacket on exact TDPES
t = "3000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
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


t = "4000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "4000" Nuclear Wavepacket on exact TDPES
t = "4000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
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


t = "5000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "5000" Nuclear Wavepacket on exact TDPES
t = "5000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
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


t = "6000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "6000" Nuclear Wavepacket on exact TDPES
t = "6000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
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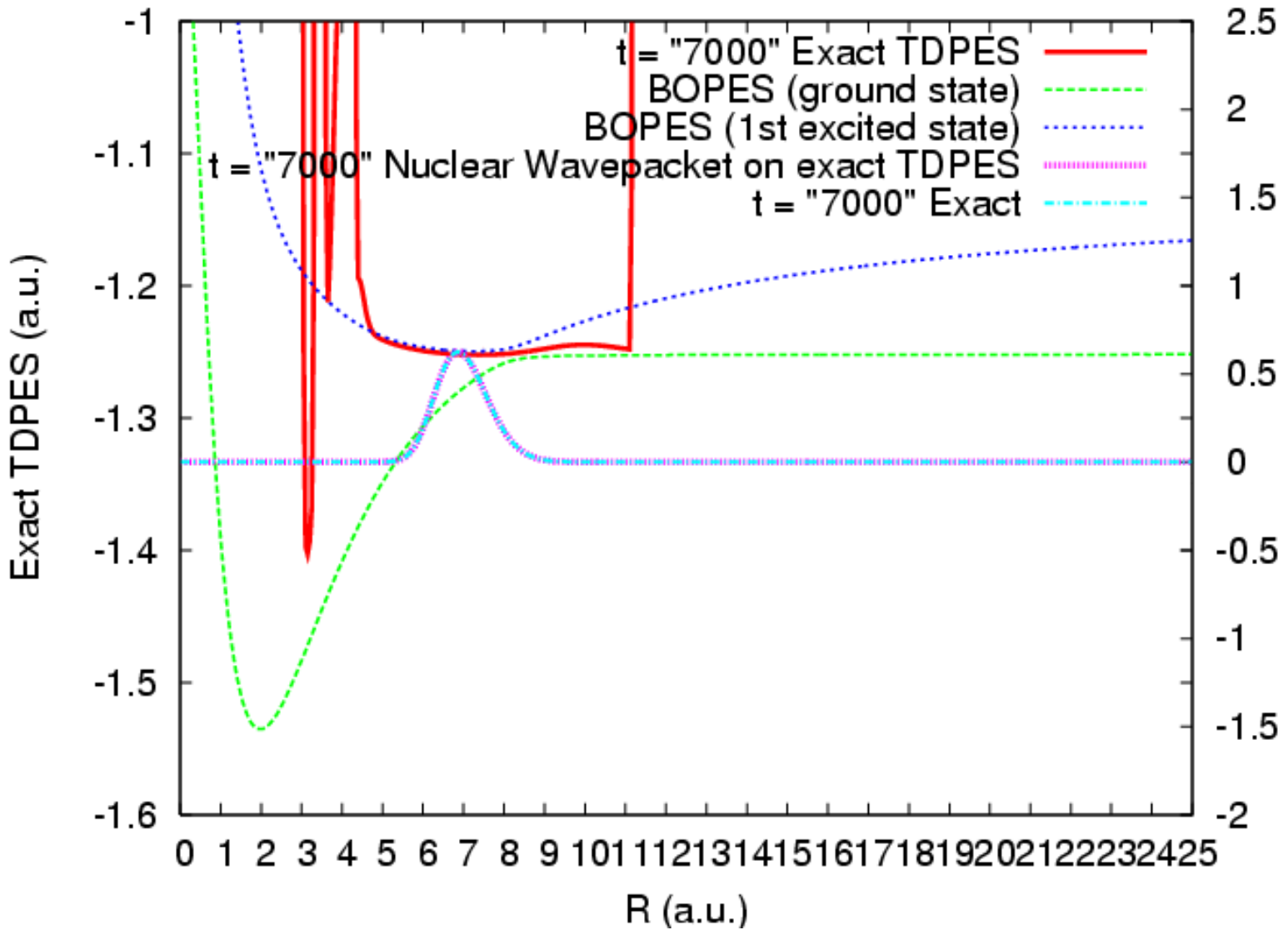
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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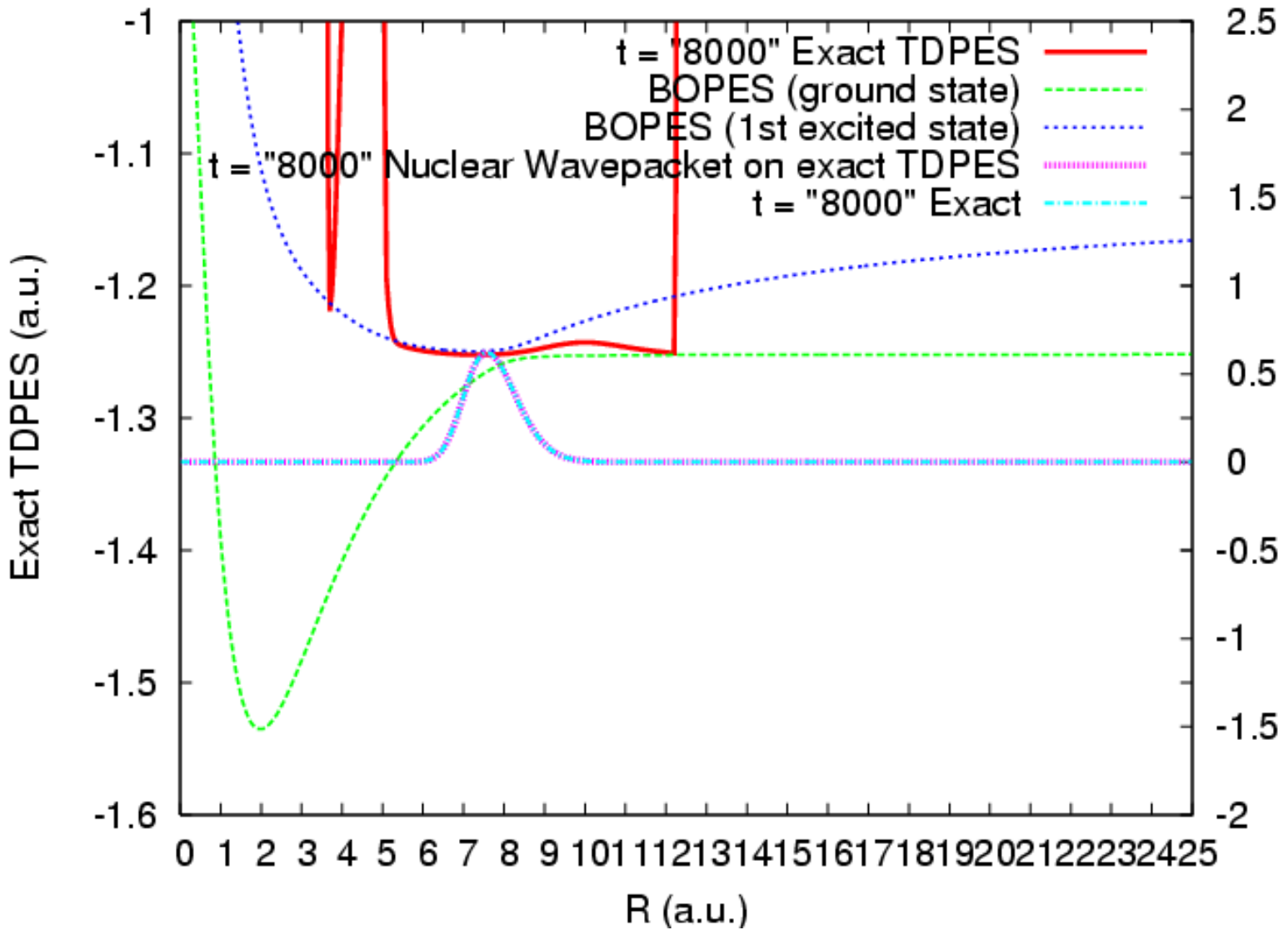
BOPES (ground state)
BOPES (1st excited state)
t = "7000" Nuclear Wavepacket on exact TDPES
t = "7000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "8000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "8000" Nuclear Wavepacket on exact TDPES
t = "8000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
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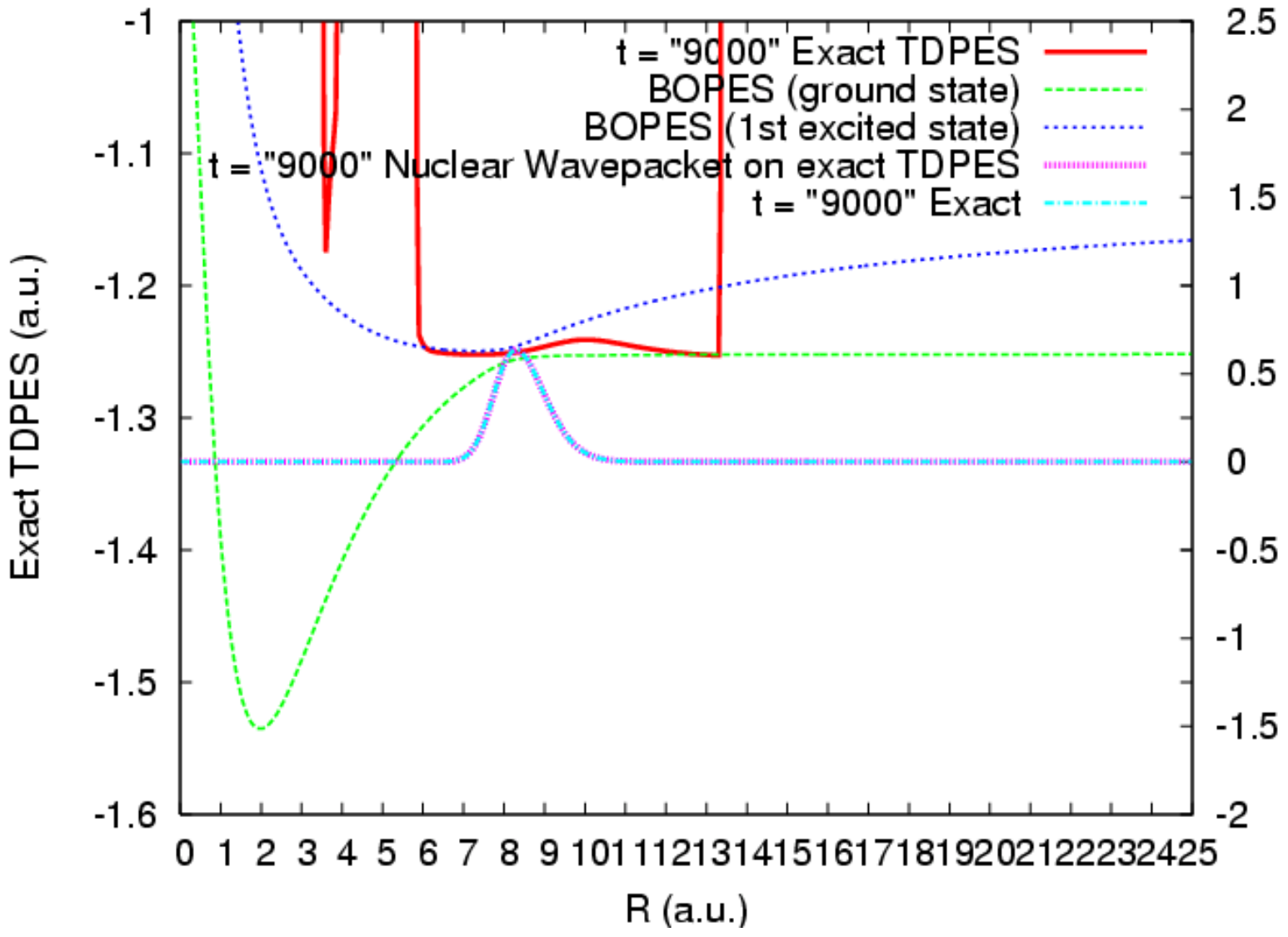
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "9000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "9000" Nuclear Wavepacket on exact TDPES
t = "9000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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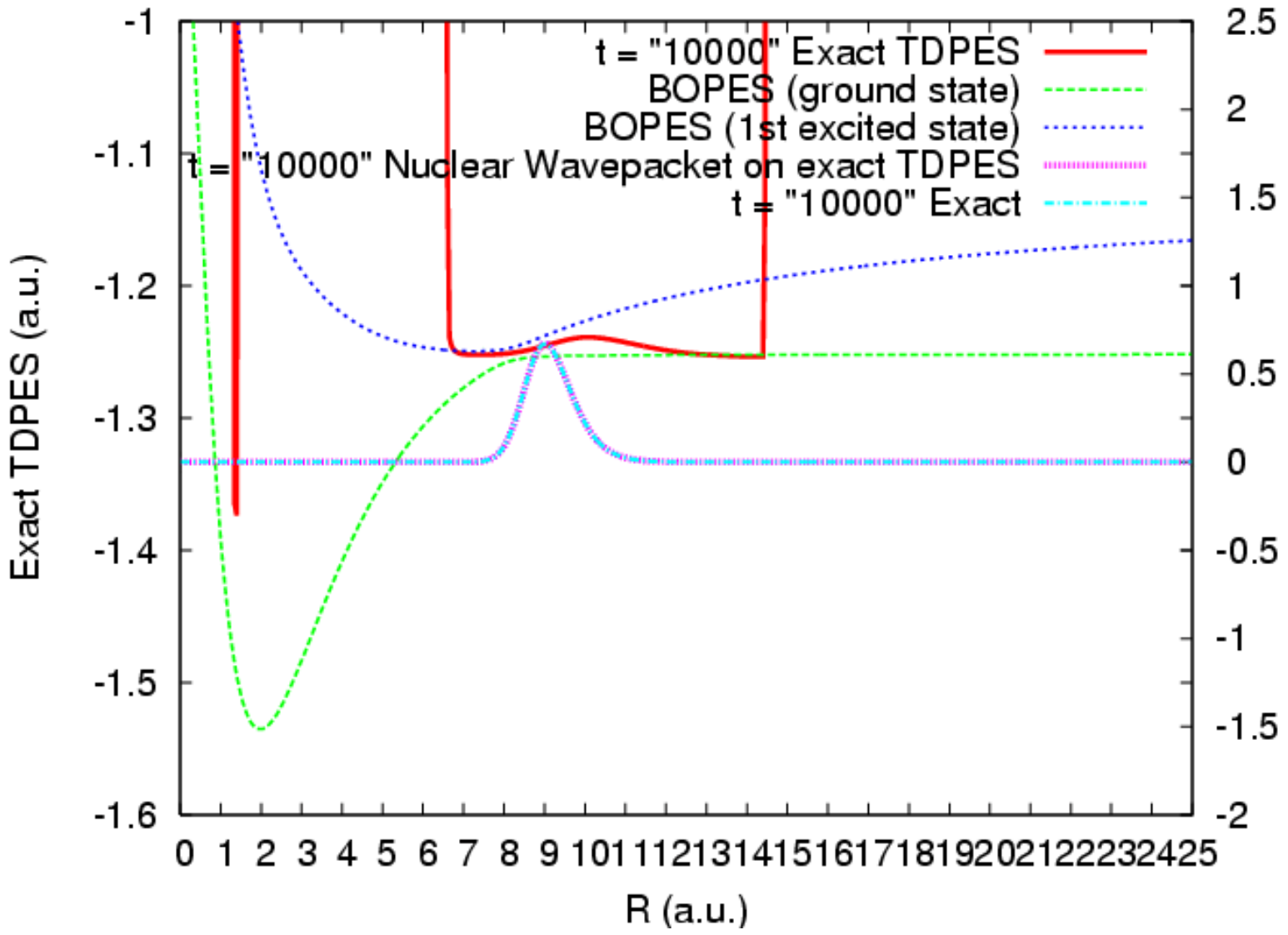
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "10000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "10000" Nuclear Wavepacket on exact TDPES
t = "10000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
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0
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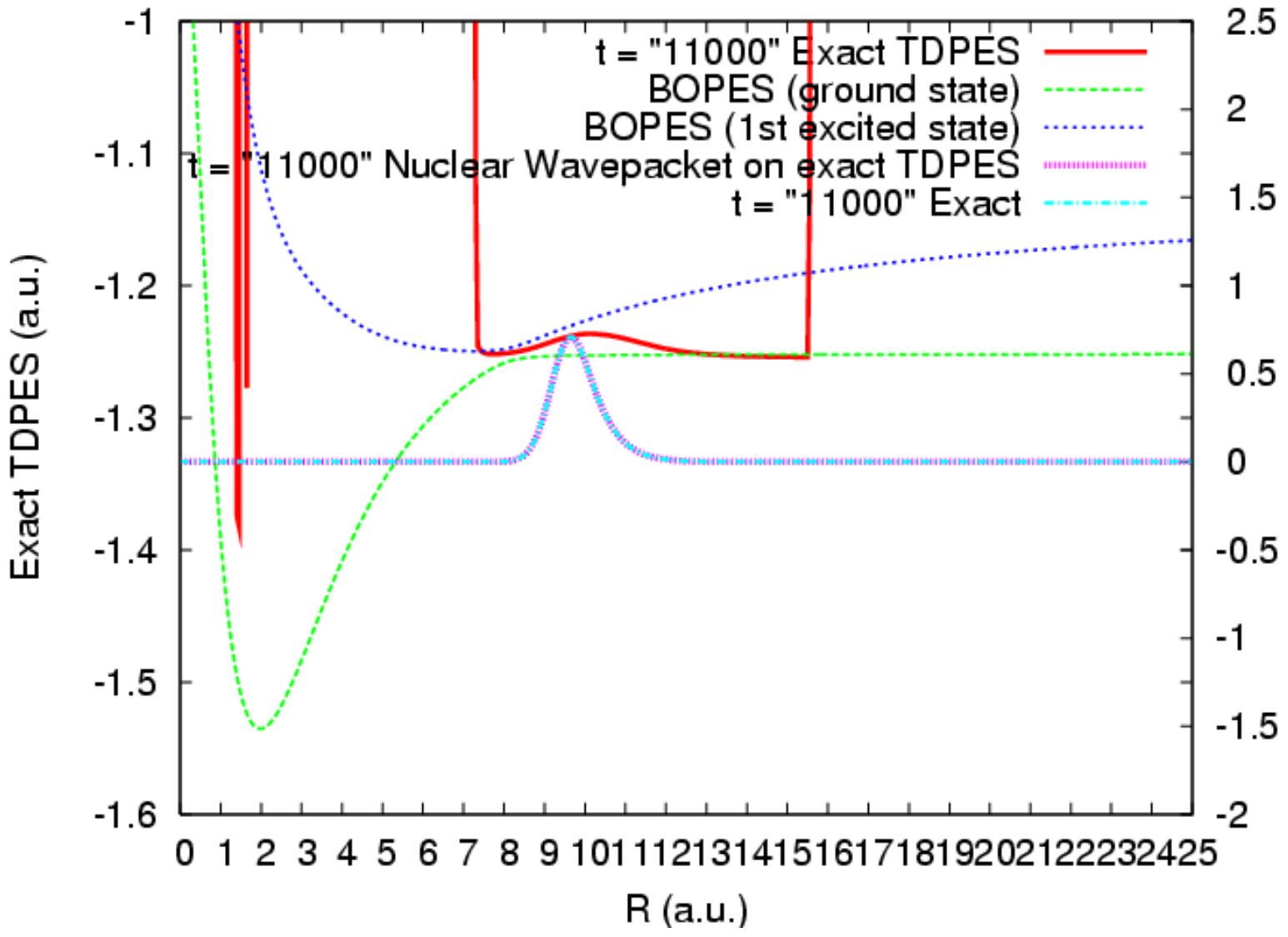
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "11000" Nuclear Wavepacket on exact TDPES
t = "11000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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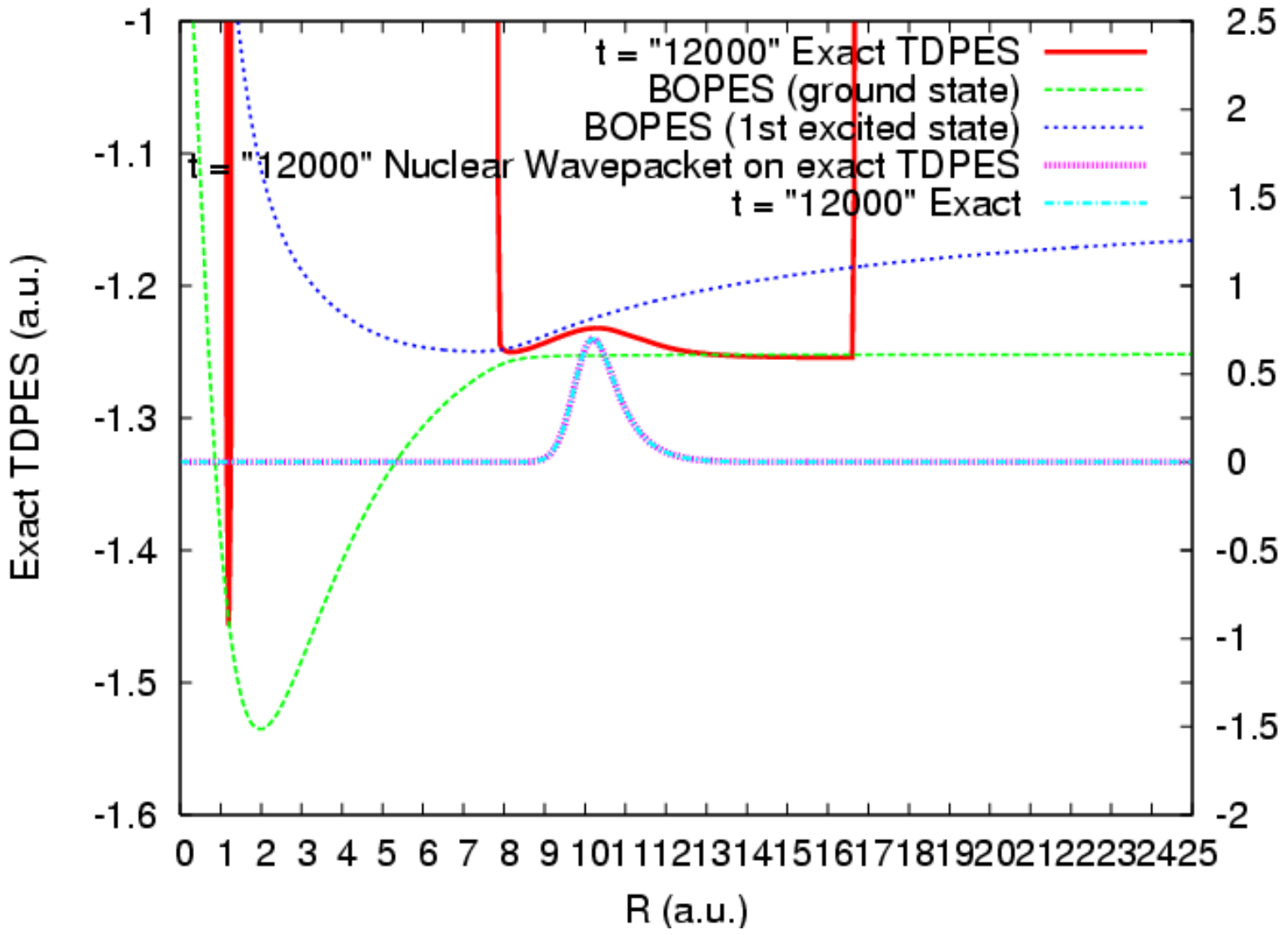
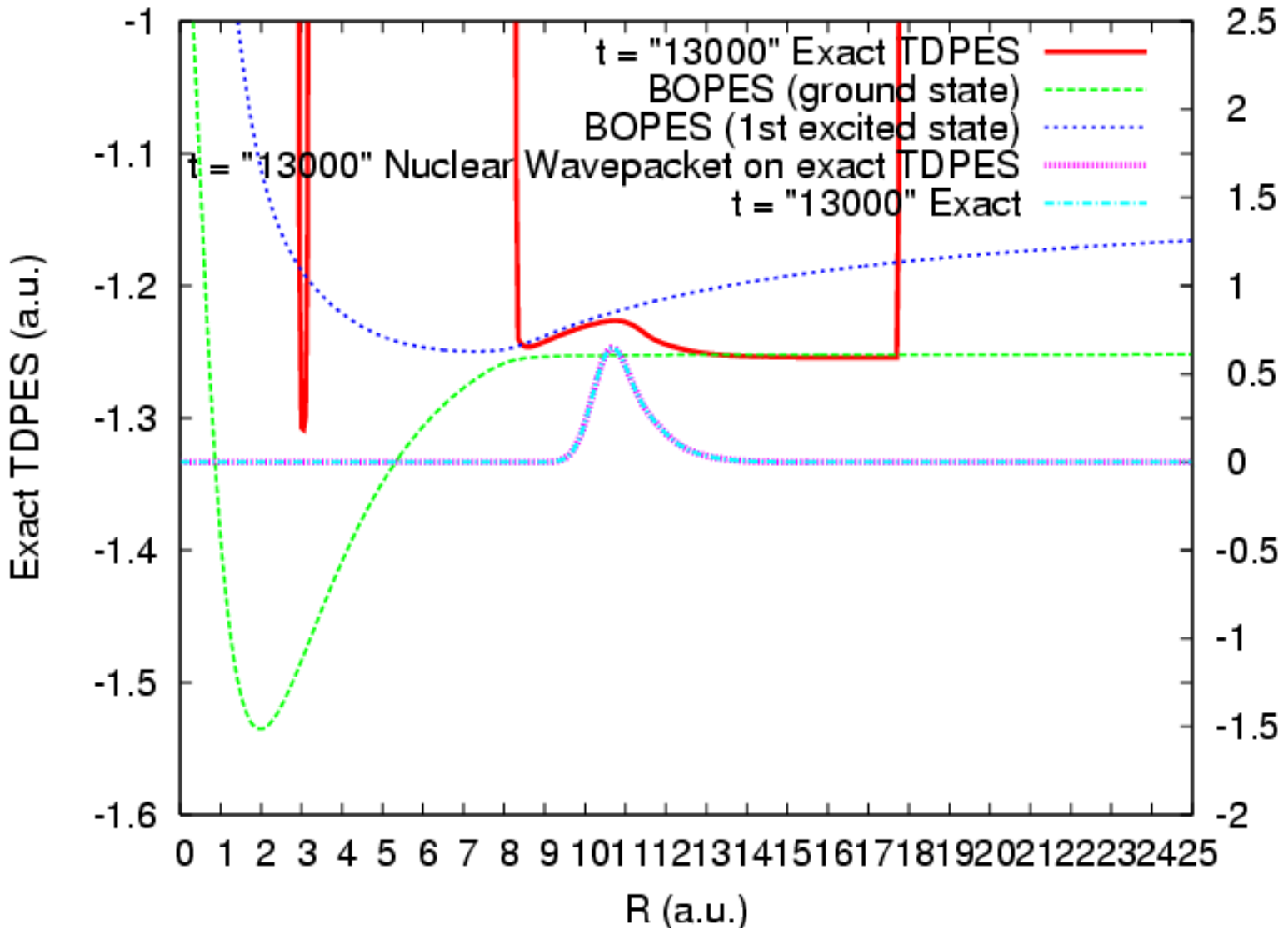
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "12000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "12000" Nuclear Wavepacket on exact TDPES
t = "12000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
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


t = "13000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "13000" Nuclear Wavepacket on exact TDPES
t = "13000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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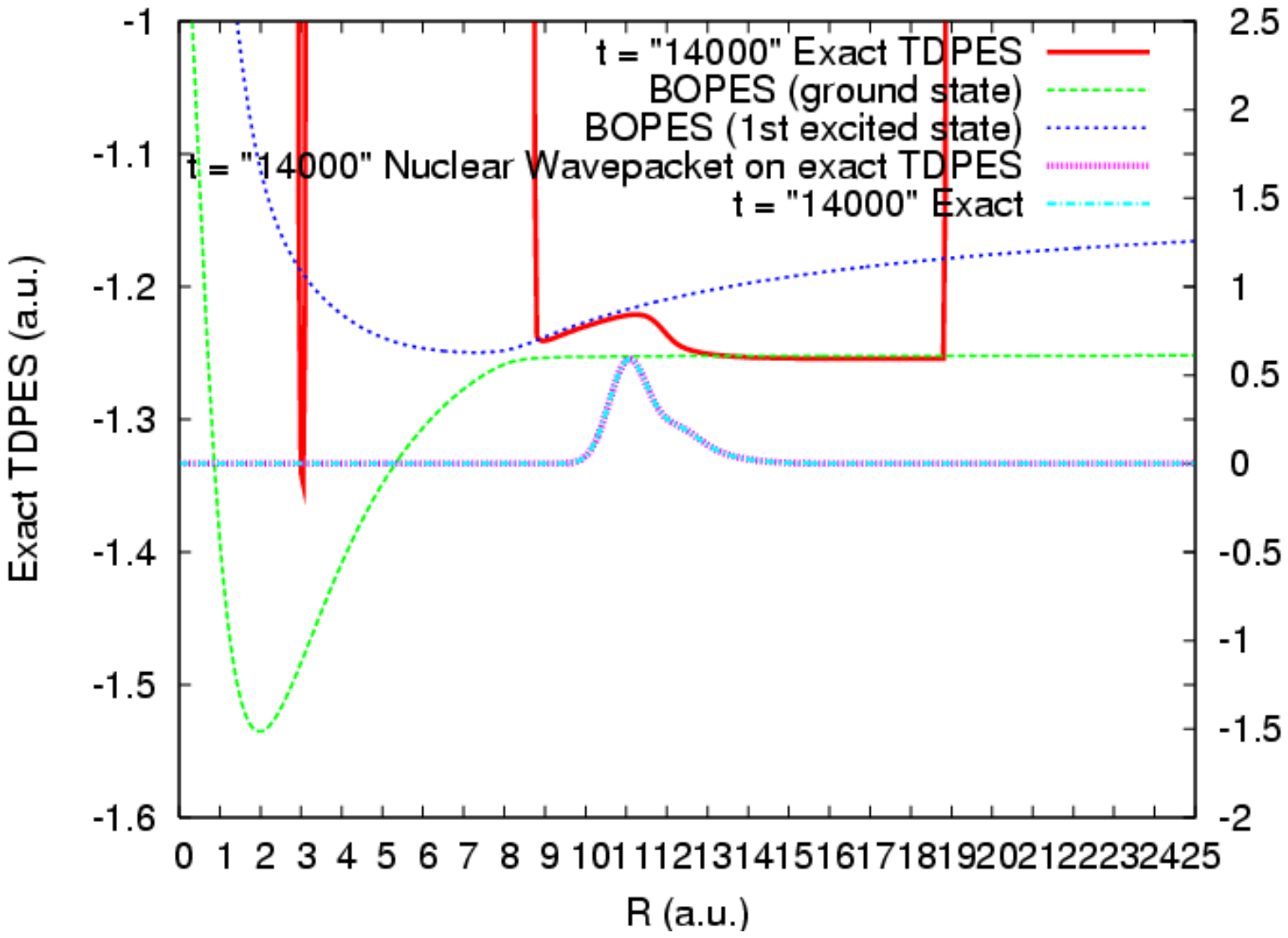
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "14000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "14000" Nuclear Wavepacket on exact TDPES
t = "14000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
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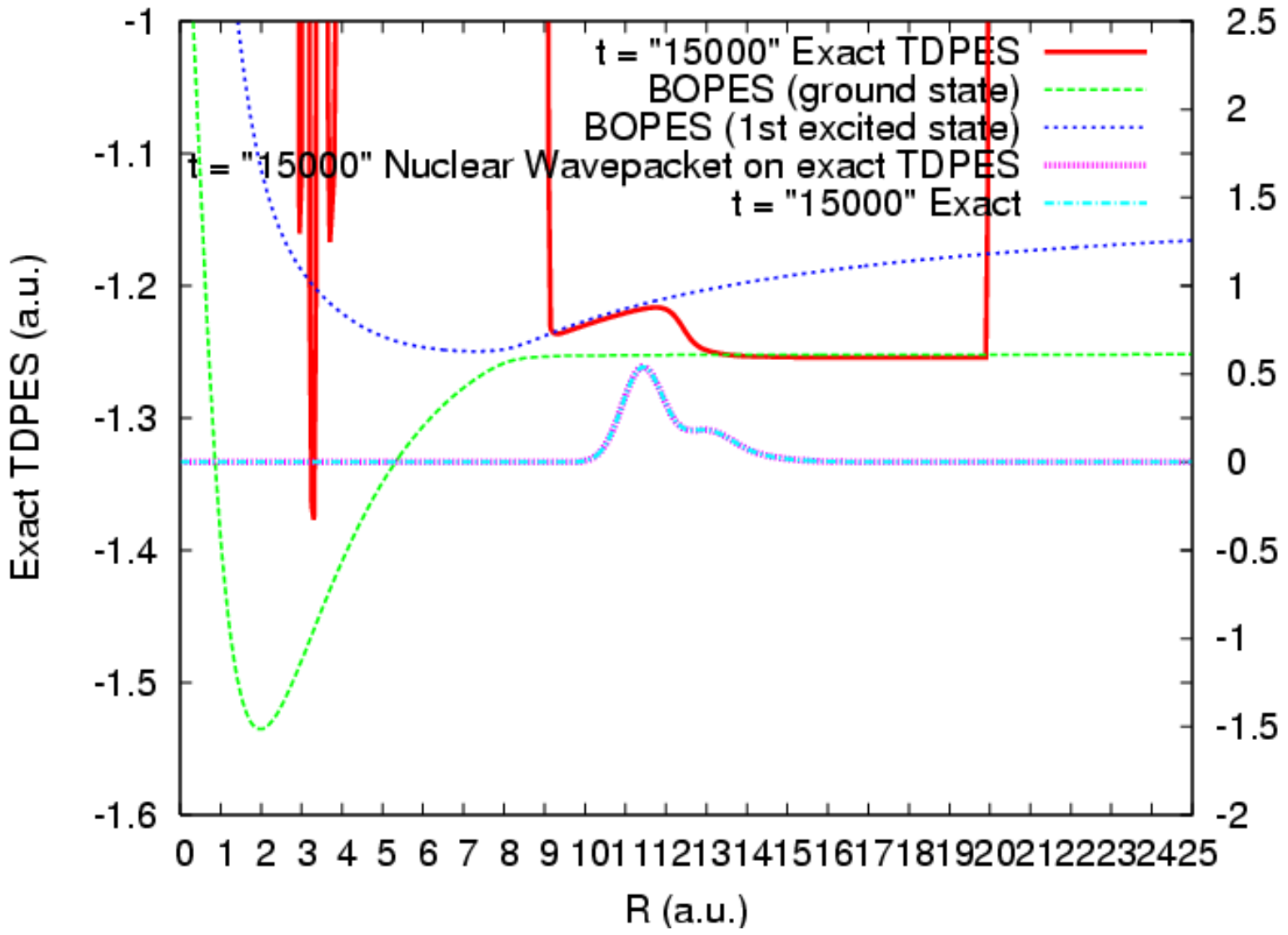
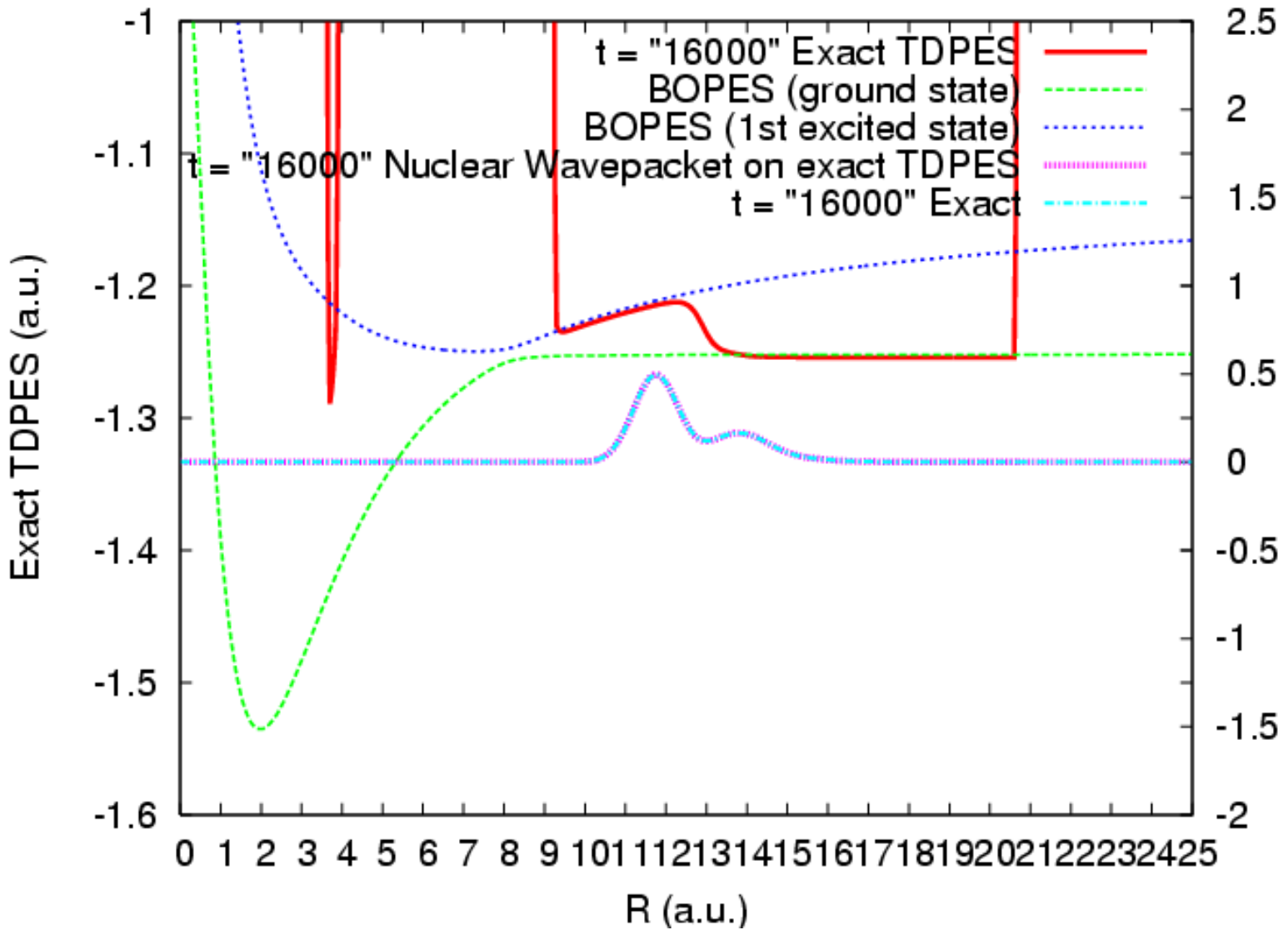
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "15000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "15000" Nuclear Wavepacket on exact TDPES
t = "15000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
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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BOPES (ground state)
BOPES (1st excited state)
t = "16000" Nuclear Wavepacket on exact TDPES
t = "16000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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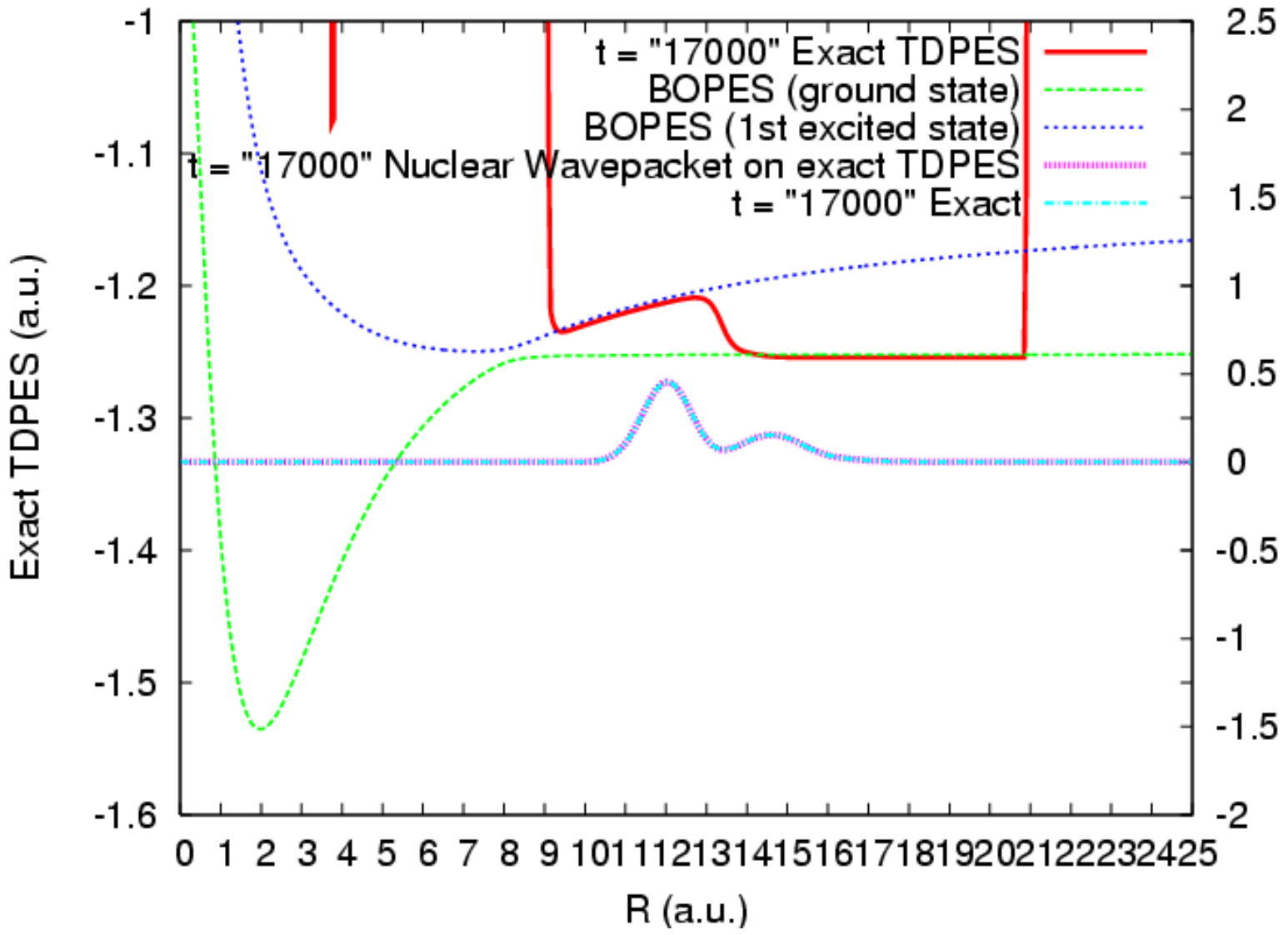
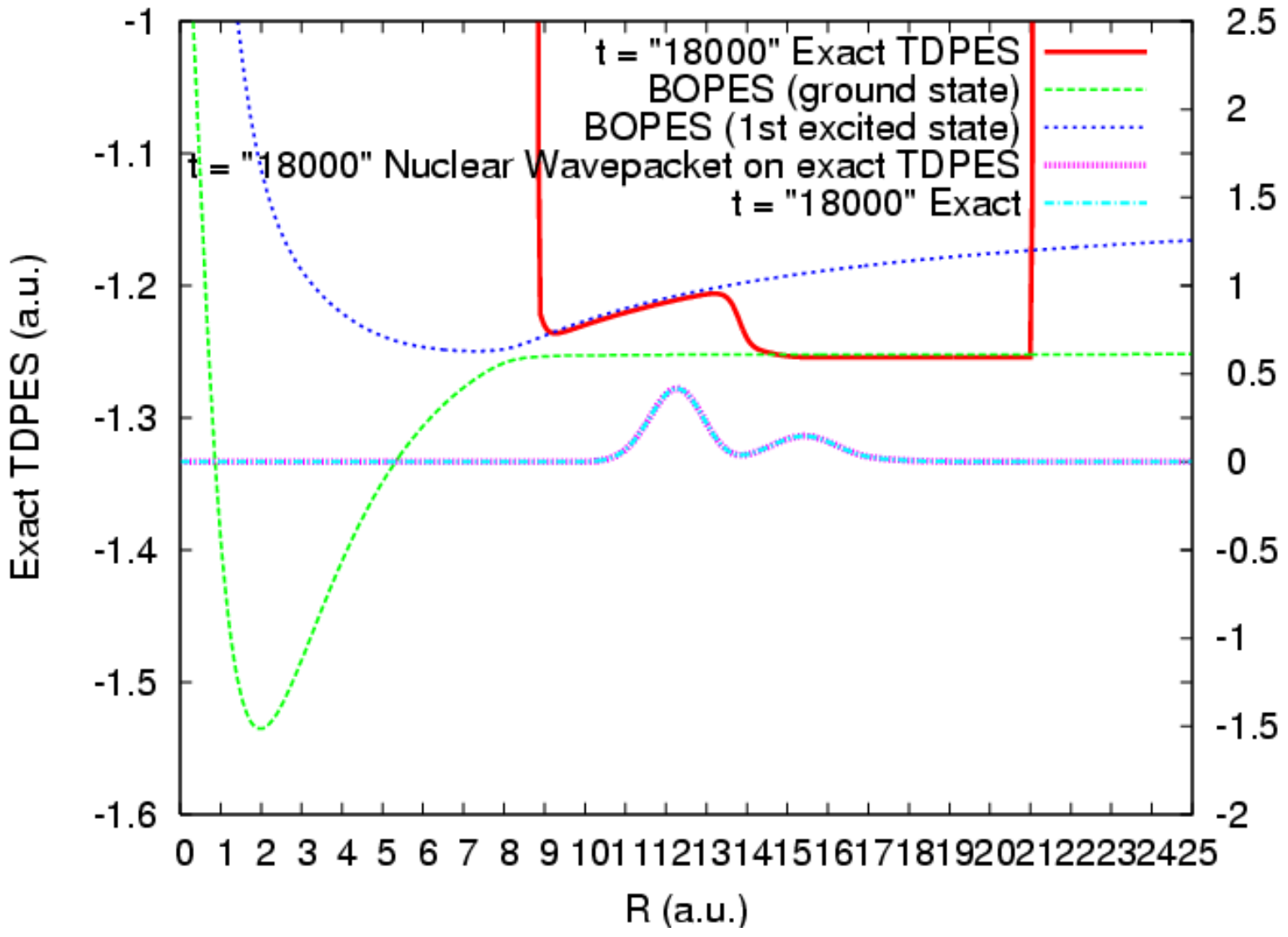
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "17000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "17000" Nuclear Wavepacket on exact TDPES
t = "17000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
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


t = "18000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "18000" Nuclear Wavepacket on exact TDPES
t = "18000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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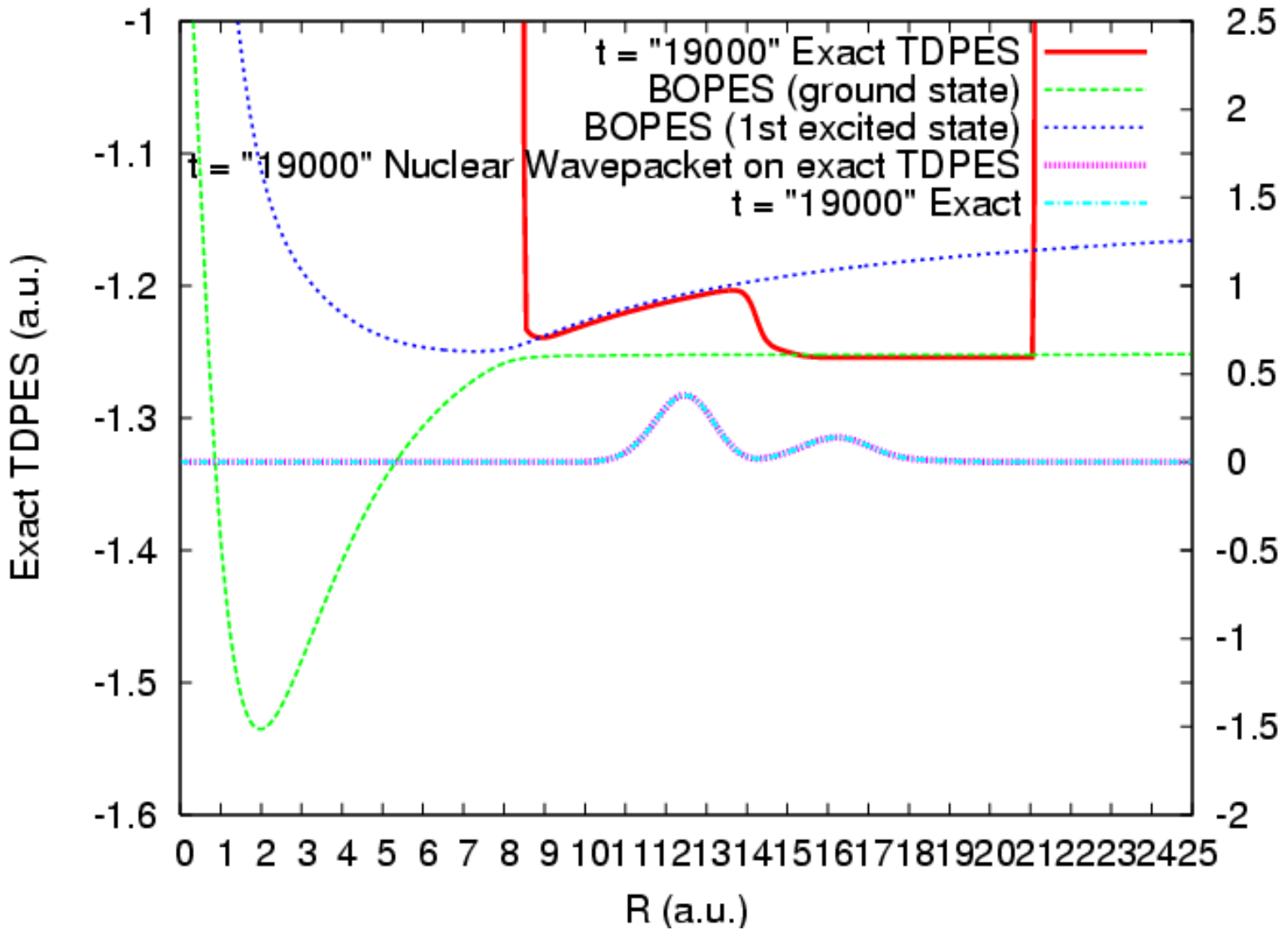
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "19000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "19000" Nuclear Wavepacket on exact TDPES
t = "19000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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0.5
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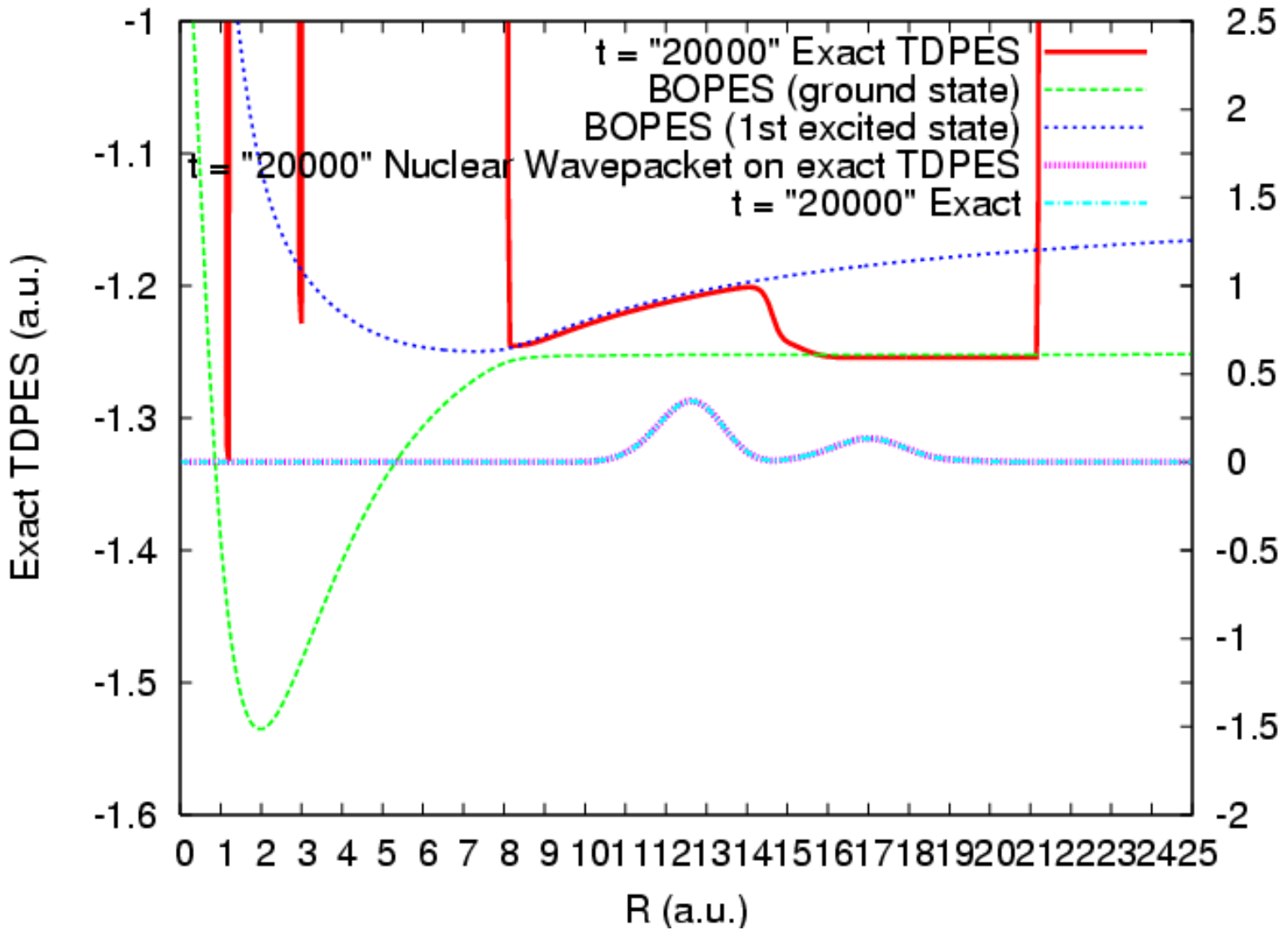
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "20000" Nuclear Wavepacket on exact TDPES
t = "20000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
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

On the exact level, the electronic and nuclear EoMs following from the factorization are equivalent to the full TDSE.

Crucial advantage:

Nuclei and electrons satisfy separate equations

$\Longrightarrow$ **Useful starting point to make approximations**

Use electronic EoM of exact factorization and treat the non-adiabatic terms in 1st-order perturbation theory

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

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

Allows the calculation of electronic flux densities very efficiently

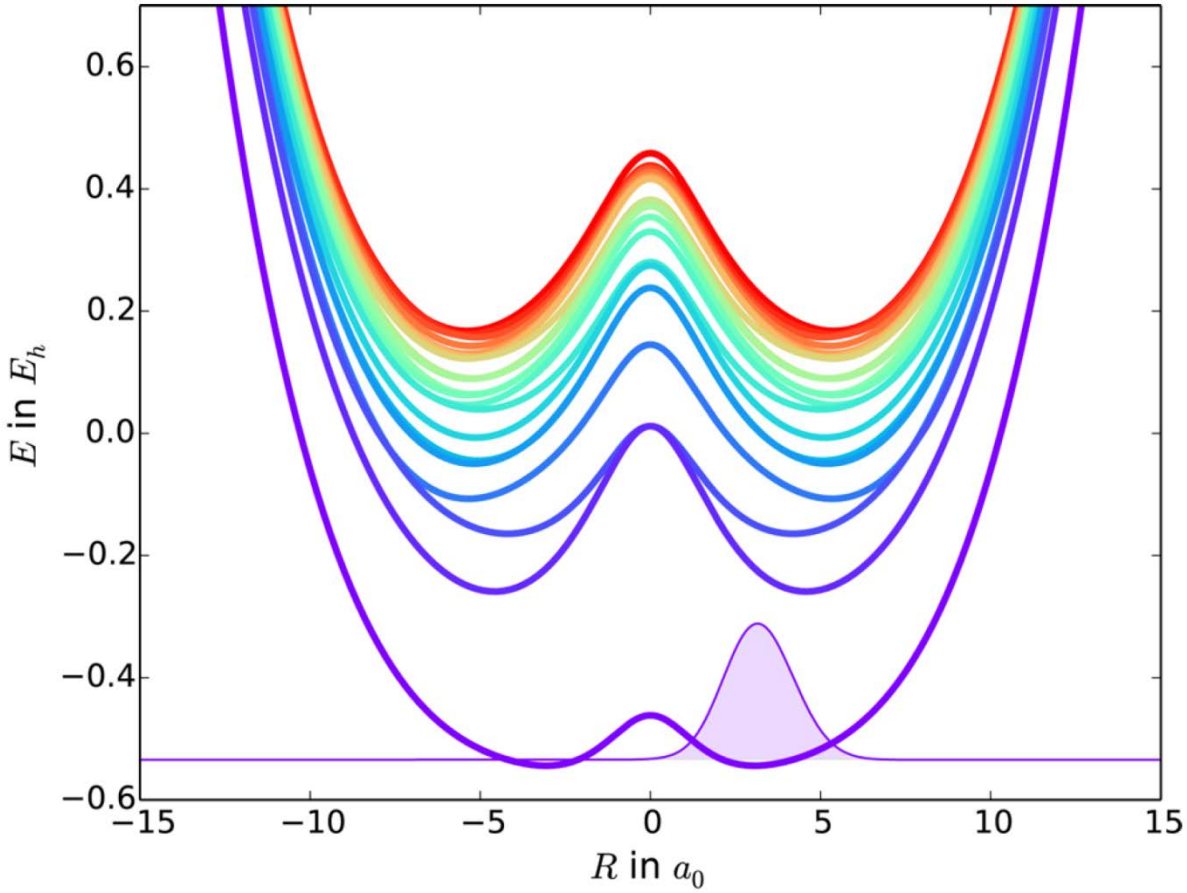
A. Schild, F. Agostini, EKUG., J. Phys. Chem. A 120, 3316 (2016)

A. Scherrer, F Agostini, D. Sebastiani, EKUG., R. Vuilleumier, JCP 143, 074106 (2015) , and PRX 7, 031035 (2017).

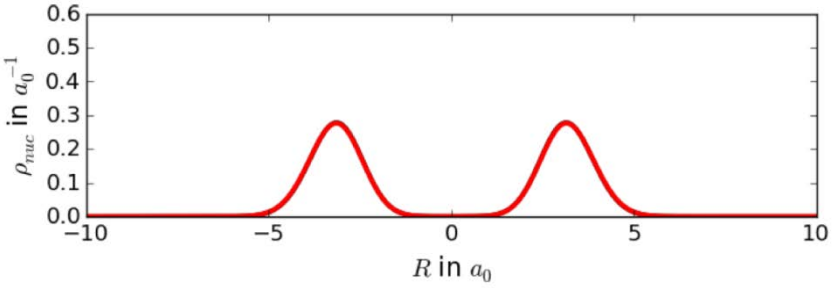
Model Study:

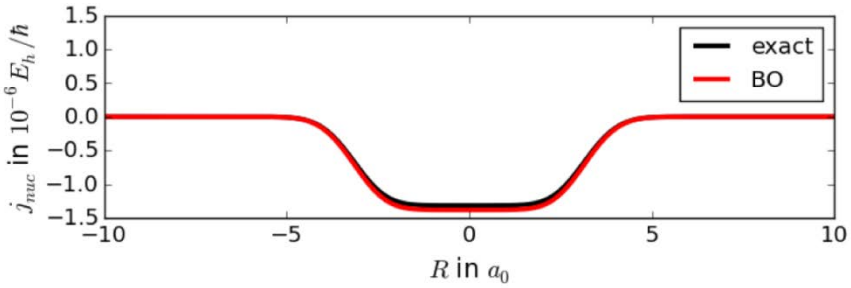
One electron in 2D (x,y), one nucleus in 1D (R), and another very heavy nucleus clamped at the origin, all interacting with soft Coulomb potentials

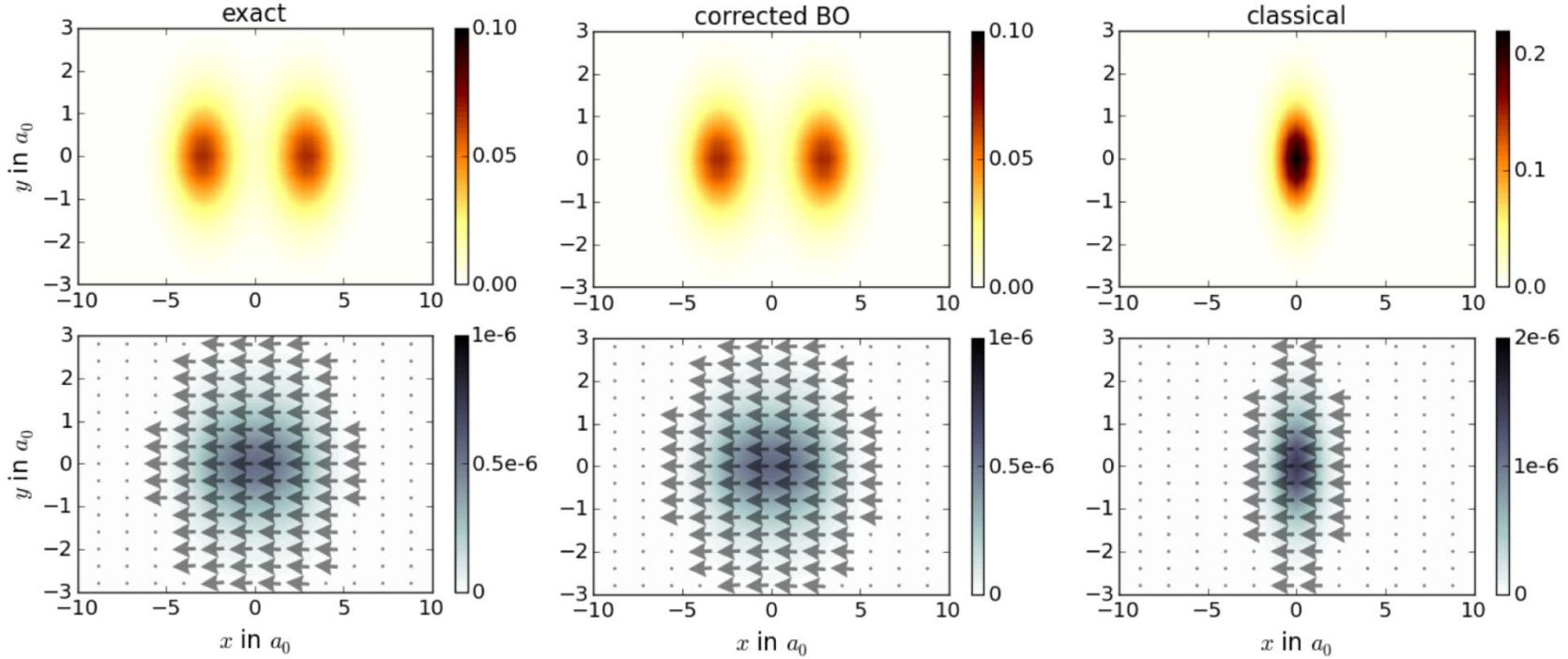
$$V = -\frac{1}{\sqrt{x^2 + y^2 + \alpha_2}} + \left(\frac{R}{R_0}\right)^4 + \frac{1}{\sqrt{R^2 + \beta}} - \frac{1}{\sqrt{(R - x)^2 + y^2 + \alpha_1}}$$



Lowest 20 Born−Oppenheimer potential energy surfaces and initial BO wave function.


ρ_{nuc} in a_0^{-1}
R in a_0


exact
BO
j_{nuc} in $10^{-6}\,E_h/\hbar$
R in a_0


exact
corrected BO
classical
y in a_0
x in a_0

Vibrational circular dichroism

Absorption difference between lefthanded and righthanded circularly polarized light:

$$\Delta \in (\omega) = 4 \frac{8\pi^3}{3Vhcn(\omega)} \sum_k R_k \omega \delta(\omega - \omega_k)$$

with harmonic vibrational frequencies ω_k and refractive index n(ω) and

Rotational strength: $$R_k = \frac{\partial \langle \hat{\boldsymbol{m}} \rangle}{\partial \dot{q}_k} \cdot \frac{\partial \langle \hat{\dot{\boldsymbol{\mu}}} \rangle}{\partial \dot{q}_k} \langle \dot{q}_k \rangle^2$$

$$\hat{\dot{\boldsymbol{\mu}}} = \hat{\dot{\boldsymbol{\mu}}}^e + \hat{\dot{\boldsymbol{\mu}}}^n = -\sum_{i=1}^{N_e} \frac{e}{m} \hat{\mathbf{p}}_i + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{M_\upsilon} \hat{\mathbf{P}}_\upsilon$$

$$\hat{\mathbf{m}} = \hat{\mathbf{m}}^e + \hat{\mathbf{m}}^n = -\sum_{i=1}^{N_e} \frac{e}{2mc} \hat{\mathbf{r}}_i \times \hat{\mathbf{p}}_i + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{2M_\upsilon c} \hat{\mathbf{R}}_\upsilon \times \hat{\mathbf{P}}_\upsilon$$

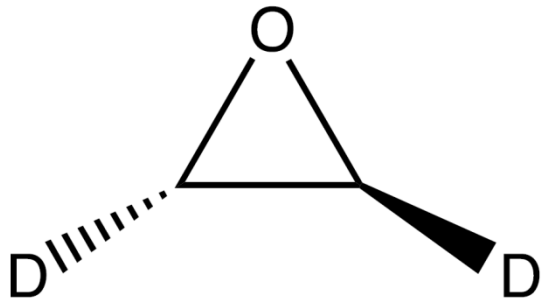
Electronic contributions to the electric current and to the magnetic dipole moment vanish identically in the adiabatic approximation.

Employ the exact factorization:

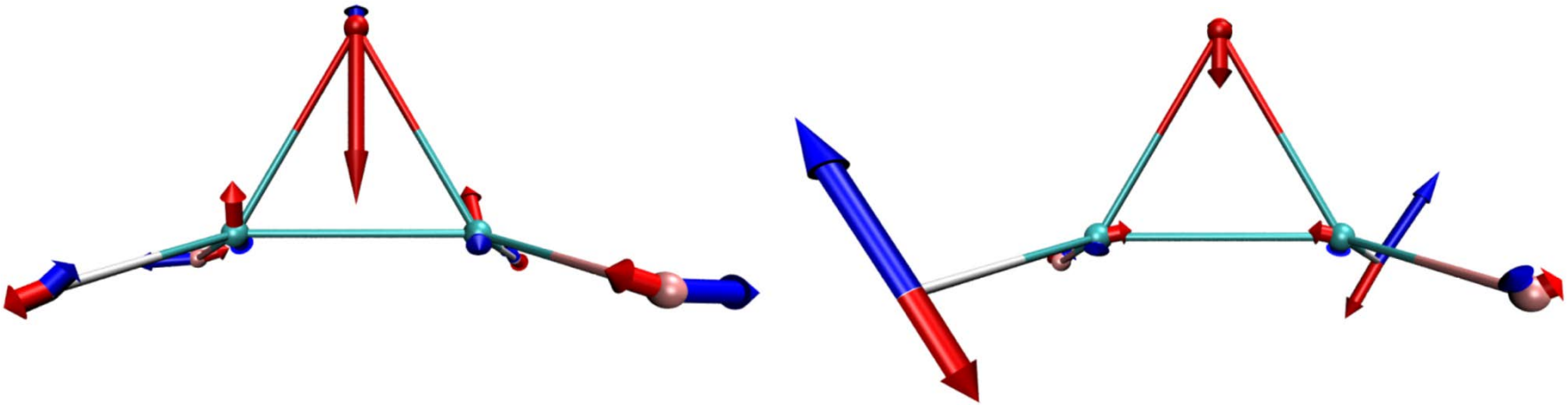
$$\left\langle \hat{\dot{\boldsymbol{\mu}}} \right\rangle_\Psi = \int d\mathbf{R} \chi^* (\mathbf{R},t) \left[\left\langle \Phi_{\mathbf{R}}(t) \middle| \hat{\dot{\boldsymbol{\mu}}}^e \middle| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}} + \hat{\dot{\boldsymbol{\mu}}}^n + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{M_\upsilon} \mathbf{A}_\upsilon (\mathbf{R},t) \right] \chi(\mathbf{R},t)$$

$$\left\langle \hat{\mathbf{m}} \right\rangle_\Psi = \int d\mathbf{R} \chi^* (\mathbf{R},t) \left[\left\langle \Phi_{\mathbf{R}}(t) \middle| \hat{\mathbf{m}}^e \middle| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}} + \hat{\mathbf{m}}^n + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{2M_\upsilon c} \hat{\mathbf{R}}_\upsilon \times \hat{\mathbf{A}}_\upsilon (\mathbf{R},t) \right] \chi(\mathbf{R},t)$$

and evaluate $\Phi_{\mathbf{R}}$ within first-order nuclear-velocity PT, employing DFT-PT



(S)-d2-oxirane



Vibrational modes at 896 cm^{-1} (left) and at 1089 cm^{-1} (right) for (S)-d_2-oxirane, with nuclear velocities indicated as blue arrows. The corresponding vector potential is shown as red arrows.

Normal modes, dipole and rotational strengths, for (S)-d_2-oxirane..

	D_{MFP}	D_{NVP}	R_{MFP}	R_{NVP}
$\tilde{\upsilon}(cm^{-1})$	$(10^{-44}\ esu^2\ cm^2)$		$(10^{-44}\ esu^2\ cm^2)$	
647.50	0.55	0.85	−0.35	−0.45
733.42	123.35	124.88	8.73	10.54
769.76	53.44	51.77	3.17	3.29
856.38	145.31	145.55	4.31	2.70
894.67	9.78	10.24	−3.37	−3.89
936.33	39.73	39.24	−19.14	−20.26
1088.21	3.79	4.44	6.95	8.34
1093.95	1.41	1.71	−3.98	−4.97
1210.44	26.26	26.09	9.56	10.45
1326.86	0.34	0.37	−0.91	−0.76
1377.38	11.65	10.78	−7.50	−8.17
2235.16	49.17	50.88	−22.60	−22.90
2244.19	12.63	12.81	16.80	16.78
3047.68	11.43	11.66	−32.80	−32.59
3054.15	58.64	60.16	46.63	47.04

A. Scherrer, F Agostini, D. Sebastiani, EKUG., R. Vuilleumier, JCP 143, 074106 (2015)

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, I. Tavernelli, E.K.U. Gross, JPCL 8, 3048 (2017)

Eq. ❶

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

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

Eq. ❷

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

Classical Newton equations for nuclear trajectories: Gradient (W_{nn}+ϵ) is the <u>unique</u> classical force. No need for Tully surface hopping and decoherence corrections

Eq. ❶

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

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

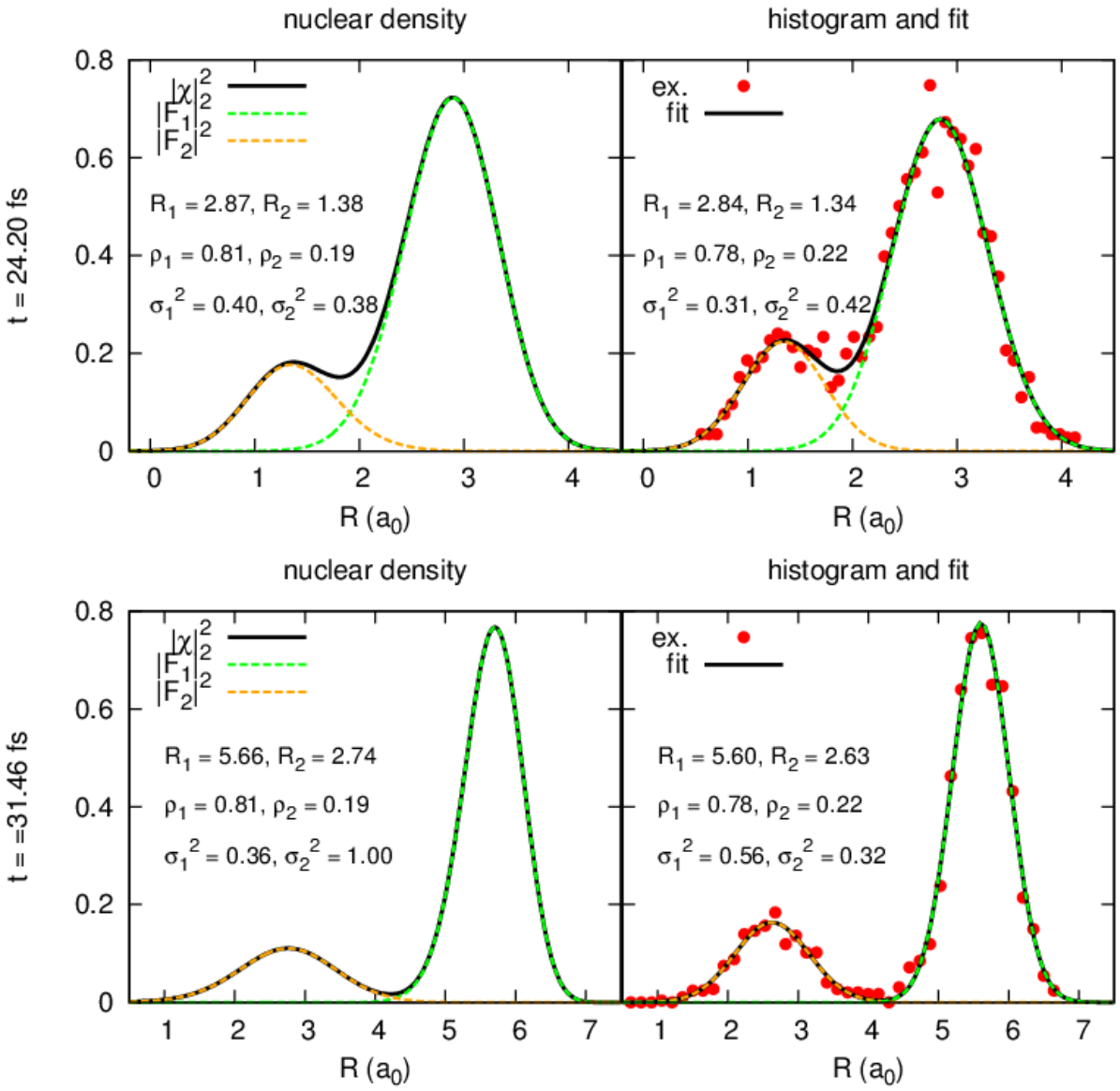
"Density-functionalize" this equation

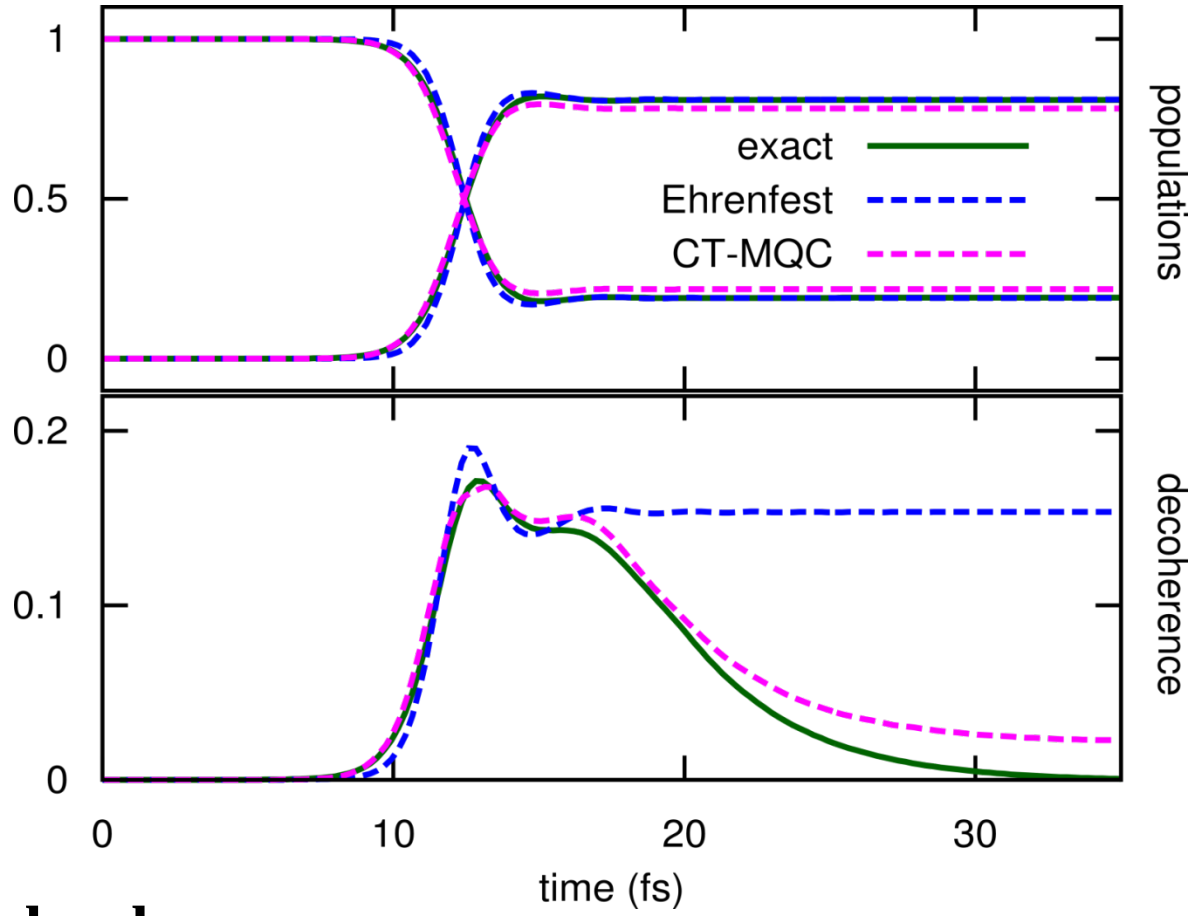
Eq. ❷

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

Classical Newton equations for nuclear trajectories: Gradient (W_{nn}+ϵ) is the <u>unique</u> classical force. No need for Tully surface hopping and decoherence corrections

Propagation of classical nuclei on exact TDPES (for Chin-Metiu model)



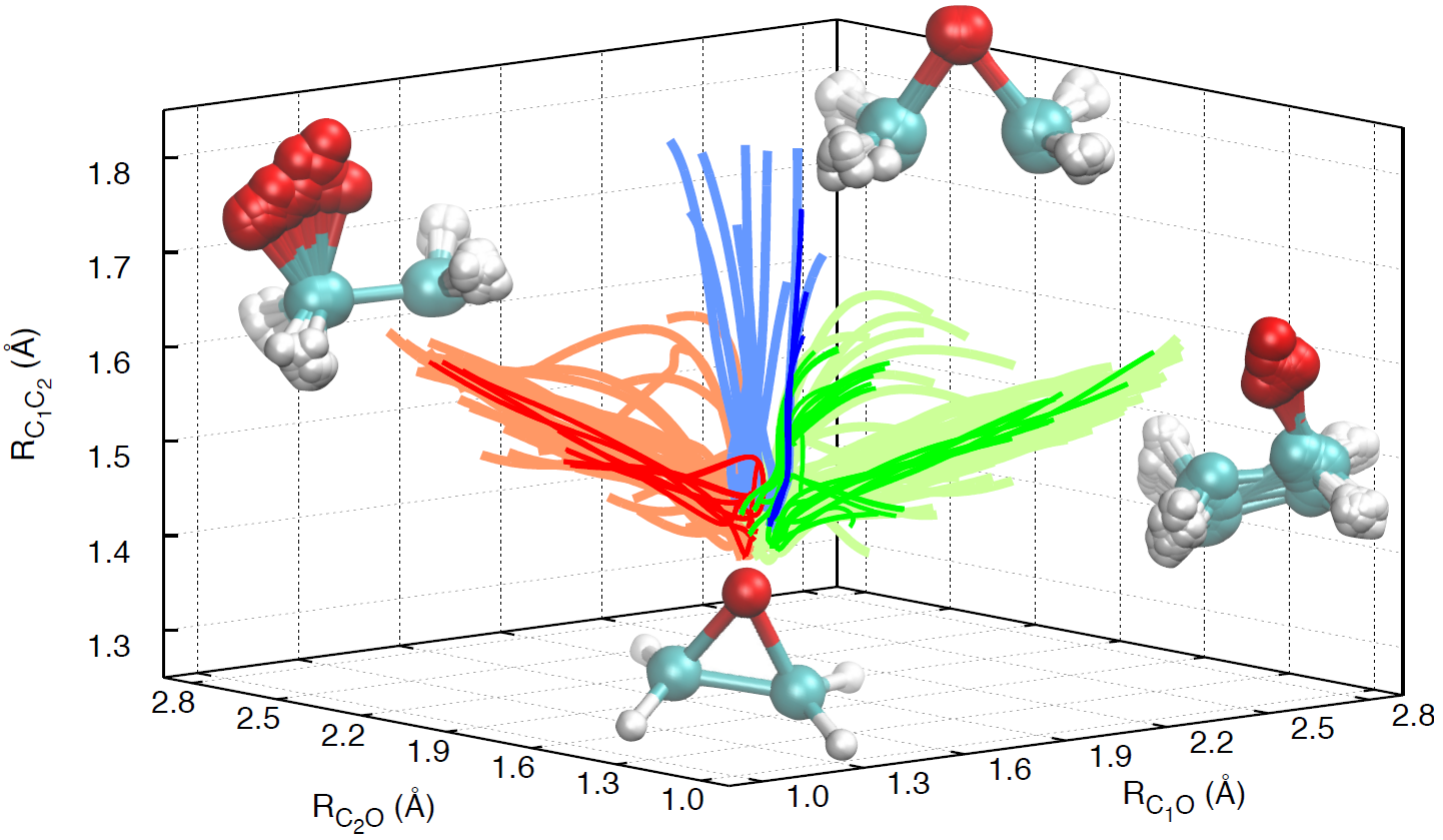


Measure of decoherence:

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

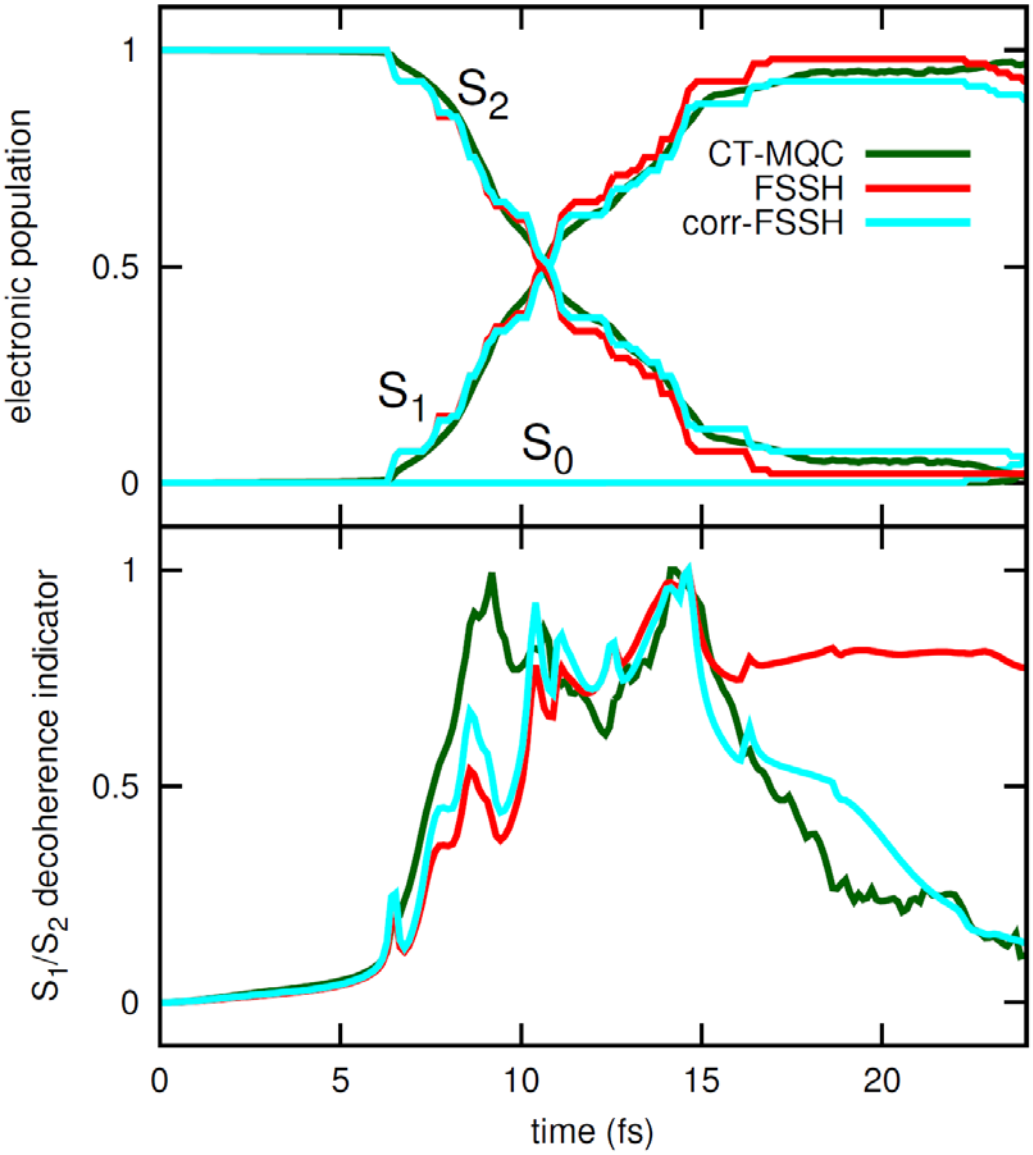
Photo-induced ring opening in Oxirane



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).

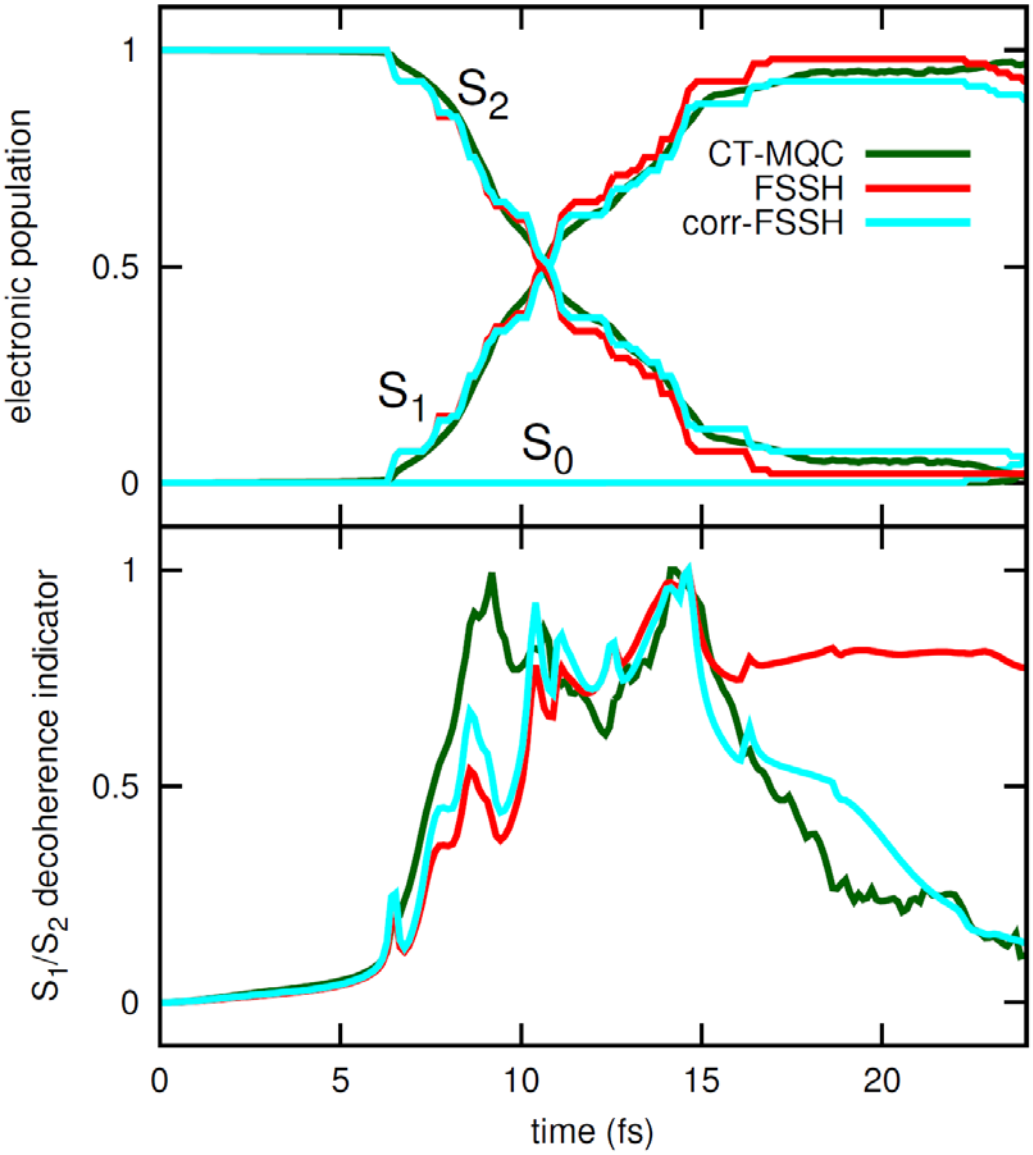
Result: Probability of ring-opening by oxygen motion is about 4 times larger than the C-C-bond stretch. Light colors identify CT-MQC trajectories and darker colors corr-FSSH trajectories.

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)



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).

Algorithm implemented in CPMD

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

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.**

Thanks !

SFB 450
SFB 685
SFB 762
SPP 1145