Exact factorization of the electron-nuclear wave function and the concept of exact forces in MD

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OUTLINE

- Exact factorisation of electronic and nuclear degrees of freedom
- Exact time-dependent PES
- An alternative to Tully surface hopping

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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 $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{\mathbf{R}}}$, masses $M_1 \cdots M_{N_n}$ and charges $Z_1 \cdots Z_{N_n}$.

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

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

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

convention: **Greek indices → nuclei**
Latin indices → electrons

Full Schrödinger equation: $\hat{H}\Psi(\underline{r}, \underline{\underline{R}}) = E\Psi(\underline{r}, \underline{\underline{R}})$

Born-Oppenheimer approximation

solve

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

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

Make adiabatic ansatz for the complete molecular wave function:

$$\Psi^{BO}(\underline{r}, \underline{\underline{R}}) = \Phi_{\underline{\underline{R}}}^{BO}(\underline{r}) \cdot \chi^{BO}(\underline{\underline{R}})$$

and find best χ^{BO} by minimizing $\langle \Psi^{BO} | H | \Psi^{BO} \rangle$ w.r.t. χ^{BO} :

Nuclear equation

$$\left[\hat{T}_n(\underline{\underline{R}}) + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{V}_n^{ext}(\underline{\underline{R}}) + \sum_\upsilon \frac{1}{M_\upsilon} A_\upsilon^{BO}(\underline{\underline{R}})(-i\nabla_\upsilon) + \in^{BO}(\underline{\underline{R}}) \right.$$

$$\left. + \int \Phi_{\underline{\underline{R}}}^{BO\,*}(\underline{\underline{r}}) \hat{T}_n(\underline{\underline{R}}) \Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}}) d\underline{\underline{r}} \right] \chi^{BO}(\underline{\underline{R}}) = E\chi^{BO}(\underline{\underline{R}})$$

Berry connection

$$\mathbf{A_\upsilon^{BO}(\underline{\underline{R}}) = \int \Phi_{\underline{\underline{R}}}^{BO\,*}(\underline{\underline{r}})(-i\nabla_\upsilon)\Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}})d\underline{\underline{r}}}$$

$\gamma^{BO}(C) = \oint_C \vec{A}^{BO}(\underline{\underline{R}}) \cdot d\vec{R}$ **is a geometric phase**

In this context, potential energy surfaces $\in^{BO}(\underline{\underline{R}})$ **and the Berry potential** $\vec{A}^{BO}(\underline{\underline{R}})$ **are APPROXIMATE concepts, i.e. they follow from the BO approximation.**

Nuclear equation

$$\left[\hat{T}_n(\underline{\underline{R}}) + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{V}_n^{ext}(\underline{\underline{R}}) + \sum_\upsilon \frac{1}{M_\upsilon} A_\upsilon^{BO}(\underline{\underline{R}})(-i\nabla_\upsilon) + \in^{BO}(\underline{\underline{R}})\right.$$

$$\left. + \int \Phi_{\underline{\underline{R}}}^{BO\,*}(\underline{\underline{r}})\hat{T}_n(\underline{\underline{R}})\Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}})d\underline{\underline{r}}\right]\chi^{BO}(\underline{\underline{R}}) = E\chi^{BO}(\underline{\underline{R}})$$

Berry connection

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"Berry phases arise when the world is approximately separated into a system and its environment."

GOING BEYOND BORN-OPPENHEIMER

Standard procedure:

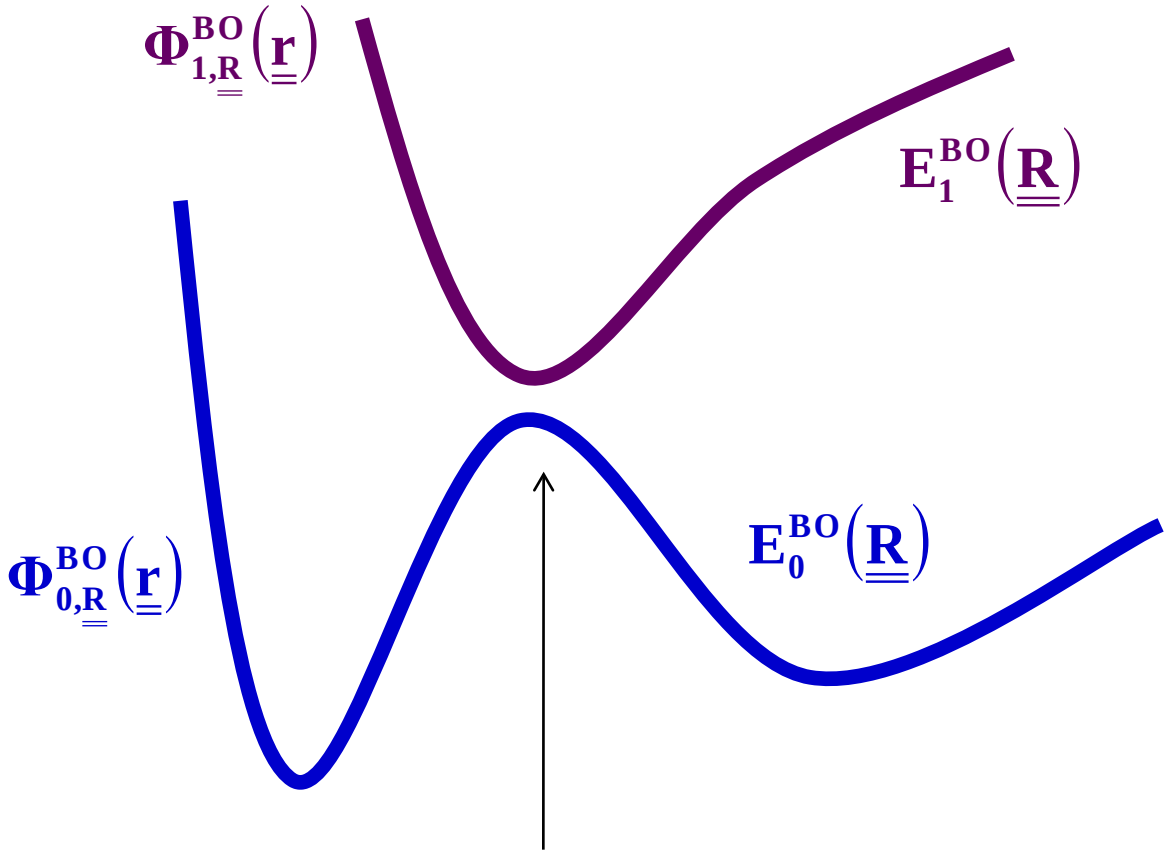
Expand full molecular wave function in complete set of BO states:

$$\Psi_K\left(\underline{\underline{r}},\underline{\underline{R}}\right)=\sum_J \Phi^{BO}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right)\cdot\chi_{K,J}\left(\underline{\underline{R}}\right)$$

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

Drawbacks:

- **$\chi_{J,K}$ depends on 2 indices: → looses nice interpretation as "nuclear wave function"**
- **In systems driven by a strong laser, many BO-PES can be coupled.**

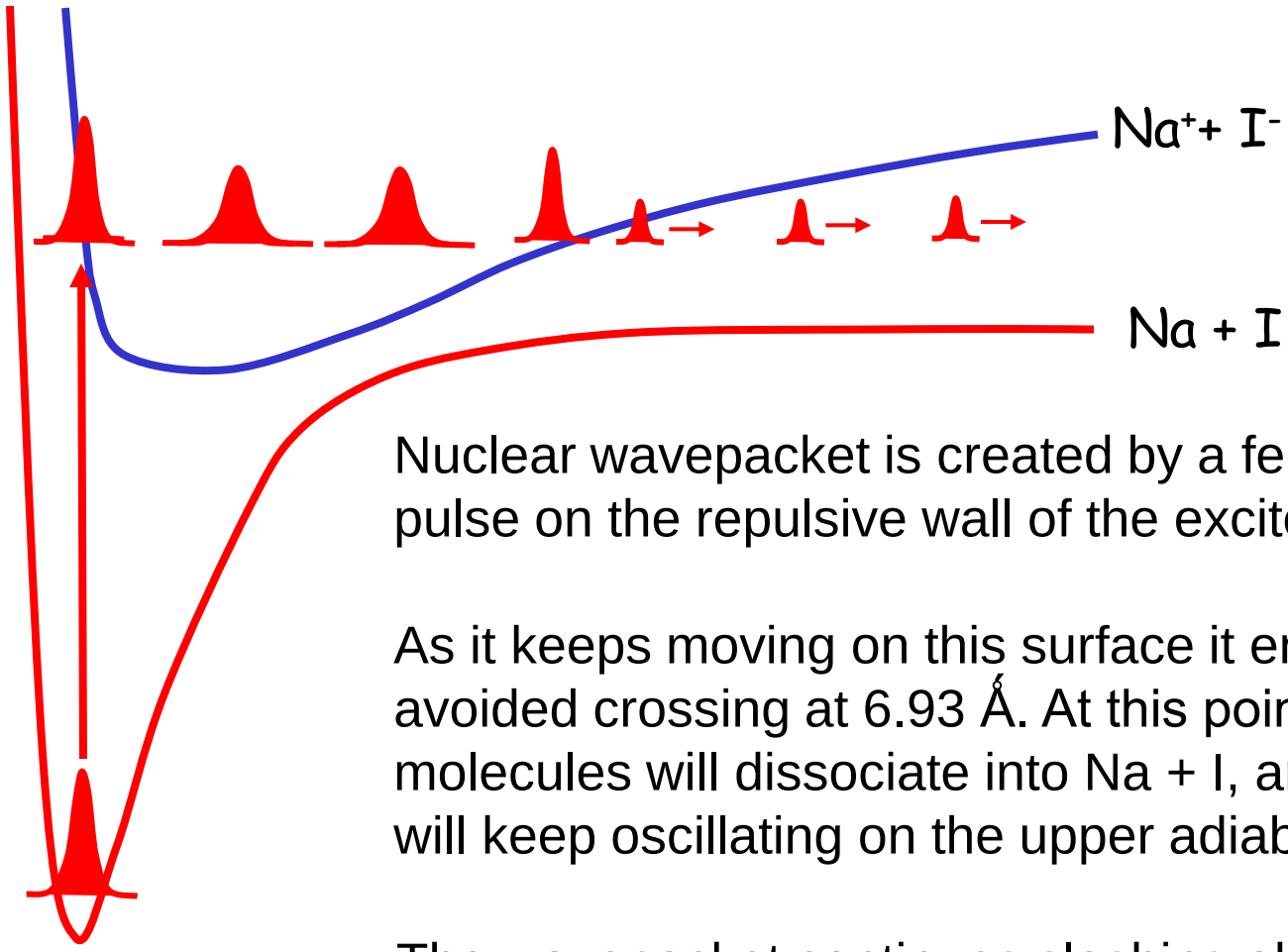


$$\Psi_0\left(\underline{\underline{r}},\underline{\underline{R}}\right) \approx \chi_{00}\left(\underline{\underline{R}}\right)\Phi^{BO}_{0,\underline{\underline{R}}}\left(\underline{\underline{r}}\right) + \chi_{01}\left(\underline{\underline{R}}\right)\Phi^{BO}_{1,\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

Potential energy surfaces are absolutely essential in our understanding of a molecule

.... and can be measured by femto-second pump-probe spectroscopy:
Zewail, *J. Phys. Chem.* **104**, 5660, (2000)

Example: NaI femtochemistry



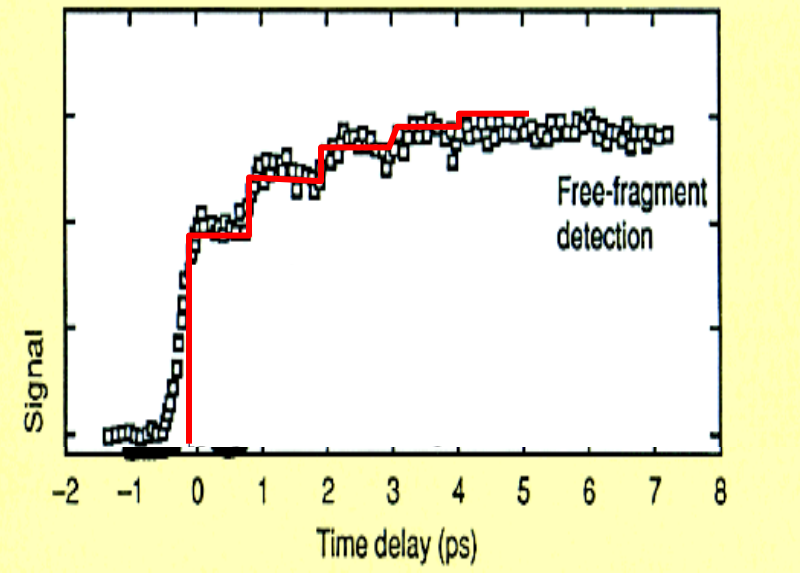
Nuclear wavepacket is created by a femto-second laser pulse on the repulsive wall of the excited surface.

As it keeps moving on this surface it encounters the avoided crossing at 6.93 Å. At this point some molecules will dissociate into Na + I, and some will keep oscillating on the upper adiabatic surface.

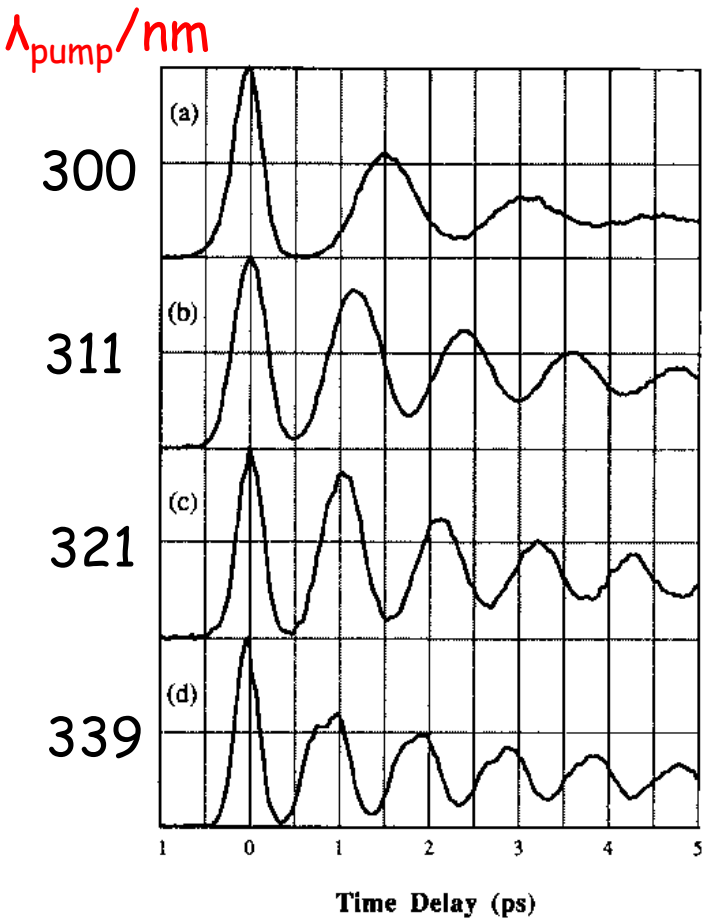
The wavepacket continues sloshing about on the excited surface with a small fraction leaking out each time the avoided crossing is encountered.

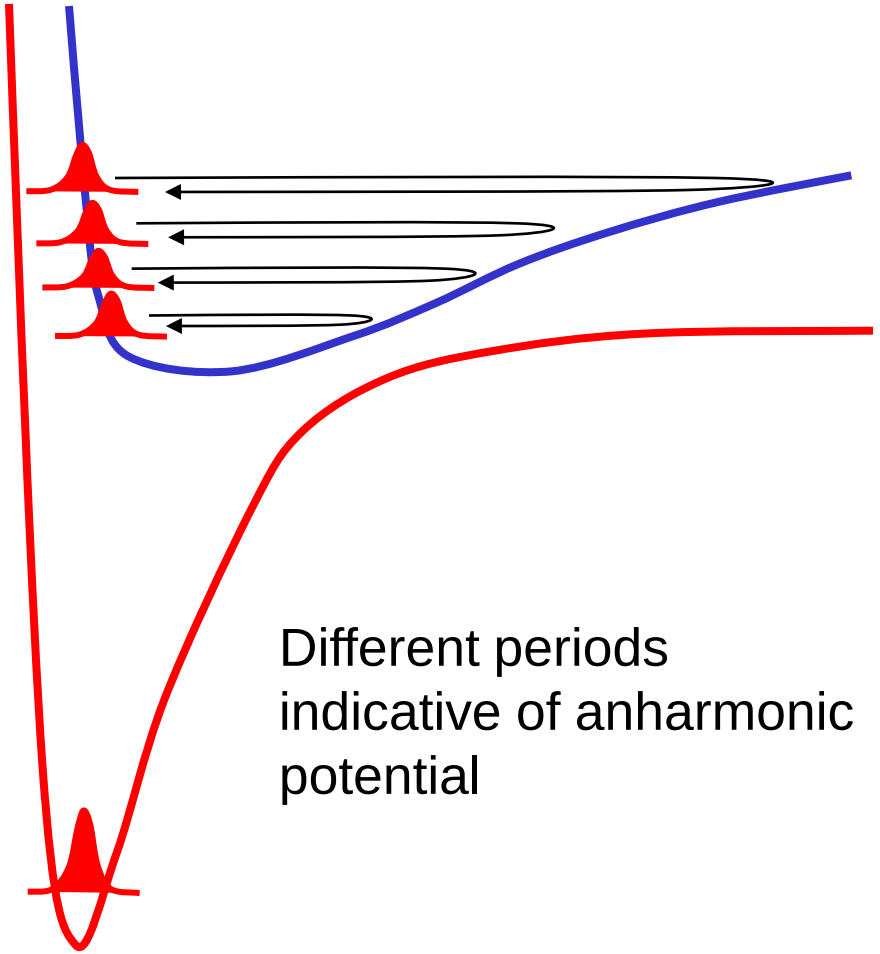
I. Probing Na atom products:

Steps in the production of Na as more of the wavepacket leaks out each vibration into the Na - I channel.



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)

<u>GOAL:</u> Show that $\Psi\left(\underline{\underline{r}}, \underline{\underline{\underline{R}}}\right) = \Phi_{\underline{\underline{\underline{R}}}}\left(\underline{\underline{r}}\right) \cdot \chi\left(\underline{\underline{\underline{R}}}\right)$ **can be made EXACT**

- **Concept of EXACT potential energy surfaces (both static and TD)**
- **Concept of EXACT Berry phase (both static and TD)**

Theorem I

The exact solutions of

$$\hat{H}\Psi\left(\underline{\underline{r}},\underline{\underline{\underline{R}}}\right)=E\Psi\left(\underline{\underline{r}},\underline{\underline{\underline{R}}}\right)$$

can be written in the form

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

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

First mentioned in: G. Hunter, Int. J.Q.C. 9, 237 (1975)

Immediate consequences of Theorem I:

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

proof: $$\Gamma(\underline{\underline{R}}) = \int d\underline{\underline{r}} \left|\Psi(\underline{\underline{r}}, \underline{\underline{R}})\right|^2 = \underbrace{\int d\underline{\underline{r}} \left|\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})\right|^2}_{1} |\chi(\mathbf{R})|^2 = |\chi(\underline{\underline{R}})|^2$$

$\Rightarrow$ in this sense, $\chi(\underline{\underline{R}})$ can be interpreted as a proper nuclear wavefunction.

2. **$\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})$ and $\chi(\underline{\underline{R}})$ are <u>unique</u> up to within the "gauge transformation"**

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

proof: Let $\phi \cdot \chi$ and $\tilde{\phi} \cdot \tilde{\chi}$ be two different representations of an exact eigenfunction Ψ i.e.

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

$$\Rightarrow \quad \frac{\tilde{\Phi}_{\underline{\underline{R}}}(\underline{\underline{r}})}{\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})} = \frac{\chi(\underline{\underline{R}})}{\tilde{\chi}(\underline{\underline{R}})} \equiv G(\underline{\underline{R}}) \qquad \Rightarrow \quad \tilde{\Phi}_{\underline{\underline{R}}}(\underline{\underline{r}}) = G(\underline{\underline{R}})\, \Phi_{\underline{\underline{R}}}(\underline{\underline{r}})$$

$$\Rightarrow \quad \underbrace{\int d\underline{\underline{r}} \left|\tilde{\Phi}_{\underline{\underline{R}}}(\underline{\underline{r}})\right|^2}_{1} = \left|G(\underline{\underline{R}})\right|^2 \underbrace{\int d\underline{\underline{r}} \left|\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})\right|^2}_{1}$$

$$\Rightarrow \quad \left|G(\underline{\underline{R}})\right| = 1 \qquad \Rightarrow G(\underline{\underline{R}}) = e^{i\theta(\underline{\underline{R}})}$$

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

Theorem II: $\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$ and $\chi\left(\underline{\underline{R}}\right)$ **satisfy the following equations:**

Eq. ❶

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

Eq. ❷

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

where

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

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

Eq. ❷

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

Exact PES

where

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

Exact Berry potential

OBSERVATIONS:

- **Eq. ❶ is a nonlinear equation in** $\Phi_{\underline{\underline{R}}}\left(\underline{r}\right)$
- **Eq. ❶ contains** $\chi\left(\underline{\underline{R}}\right)$ $\Rightarrow$ **selfconsistent solution of ❶ and ❷ required**

- **Neglecting the** $1/M_\nu$ **terms in ❶, BO is recovered**
- **There is an alternative, equally exact, representation** $\Psi = \Phi_{\underline{r}}\left(\underline{\underline{R}}\right)\chi\left(\underline{r}\right)$ **(electrons move on the nuclear energy surface)**

- **Eq. ❶ and ❷ are form-invariant under the "gauge" transformation**

$$\Phi \rightarrow \tilde{\Phi} = e^{i\theta\left(\underline{\underline{R}}\right)}\Phi$$

$$\chi \rightarrow \tilde{\chi} = e^{-i\theta\left(\underline{\underline{R}}\right)}\chi$$

$$A_\nu \rightarrow \tilde{A}_\nu = A_\nu + \nabla_\nu\theta\left(\underline{\underline{R}}\right)$$

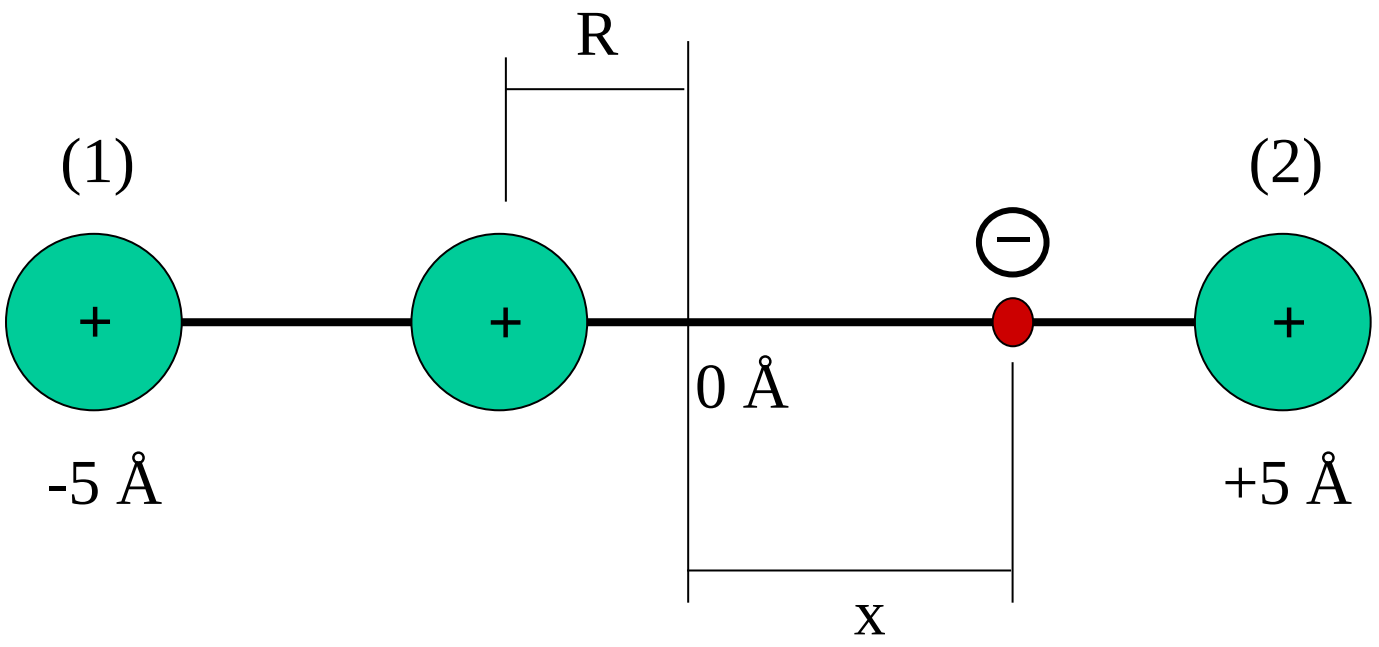
$$\in\left(\underline{\underline{R}}\right) \rightarrow \tilde{\in}\left(\underline{\underline{R}}\right) = \in\left(\underline{\underline{R}}\right)$$ **Exact potential energy surface is gauge invariant.**

- $\gamma(C) := \oint_C \vec{A}\cdot d\vec{R}$ **is a (gauge-invariant) geometric phase**
  the exact geometric phase

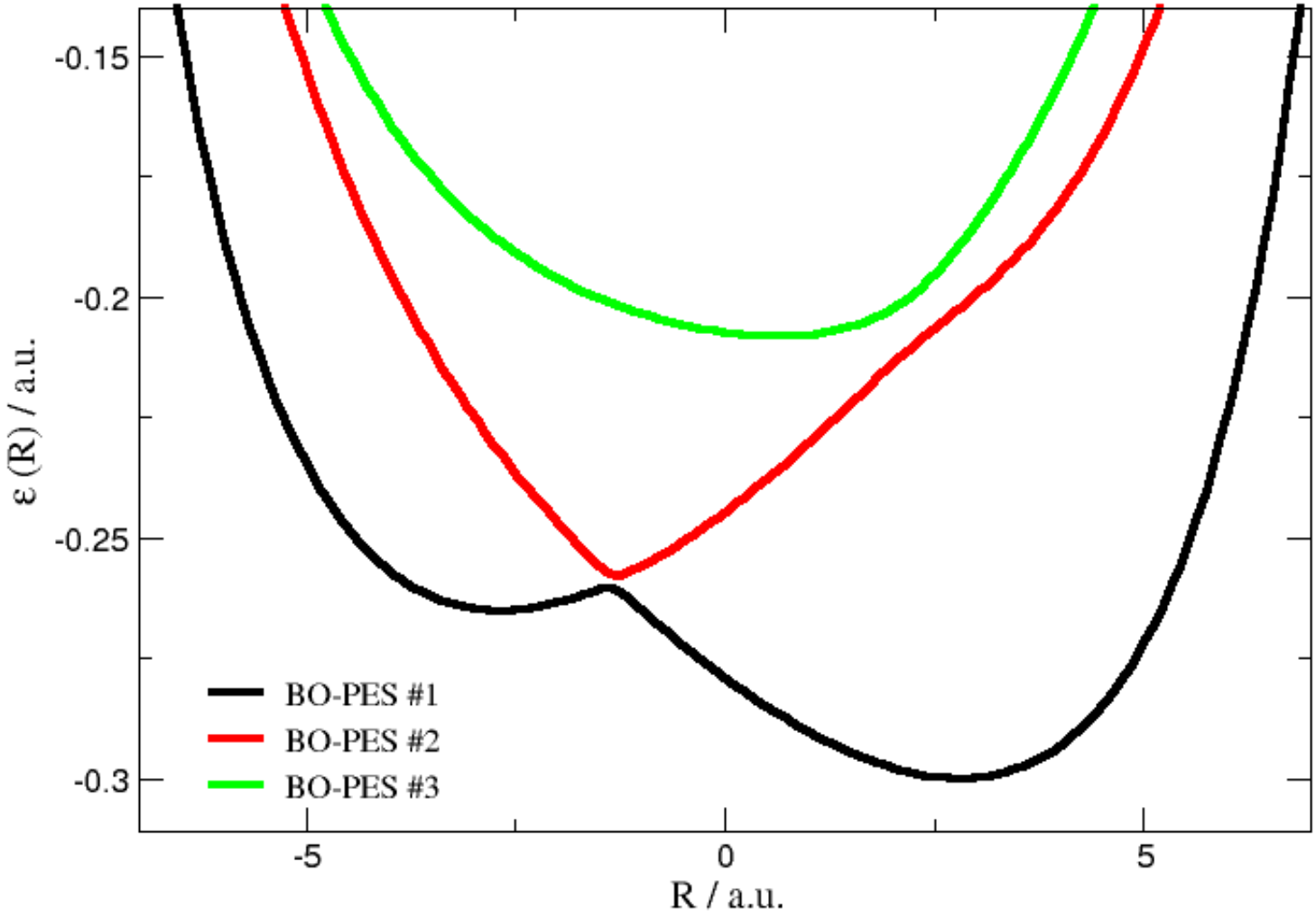
How do the exact PES look like?

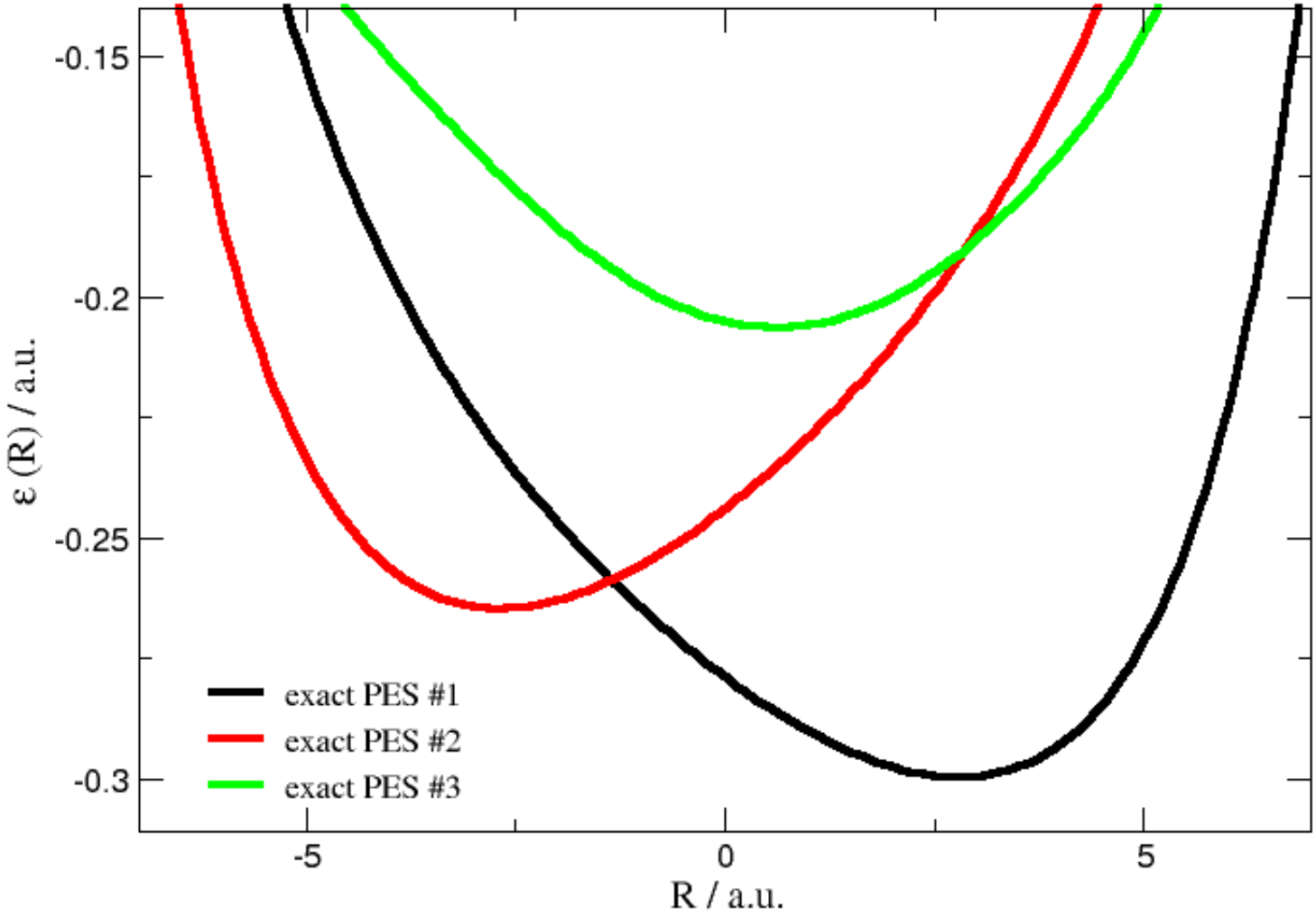
MODEL

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



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


-0.15
-0.2
-0.25
-0.3
ε (R) / a.u.
-5
0
5
R / a.u.
BO-PES #1
BO-PES #2
BO-PES #3


-0.15
-0.2
-0.25
-0.3
ε (R) / a.u.
-5
0
5
R / a.u.
exact PES #1
exact PES #2
exact PES #3

Exact Berry connection

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

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

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

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

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

with the exact nuclear current density J_ν

Time-dependent case

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 $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{R}}$, masses $M_1 \cdots M_{N_n}$ and charges $Z_1 \cdots Z_{N_n}$.

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

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

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

Time-dependent Schrödinger equation

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

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

Theorem T-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)

Theorem T-II

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

Eq. ❶

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

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)

$$\in\left(\underline{\underline{R}},t\right)=\int d\underline{\underline{r}}\,\Phi^{*}_{\underline{\underline{R}}}\left(\underline{\underline{r}},t\right)\left(H_{BO}(t)+\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu-A_\nu\left(\underline{\underline{R}},t\right)\right)^2-i\partial_t\right)\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}},t\right)$$

EXACT time-dependent potential energy surface

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

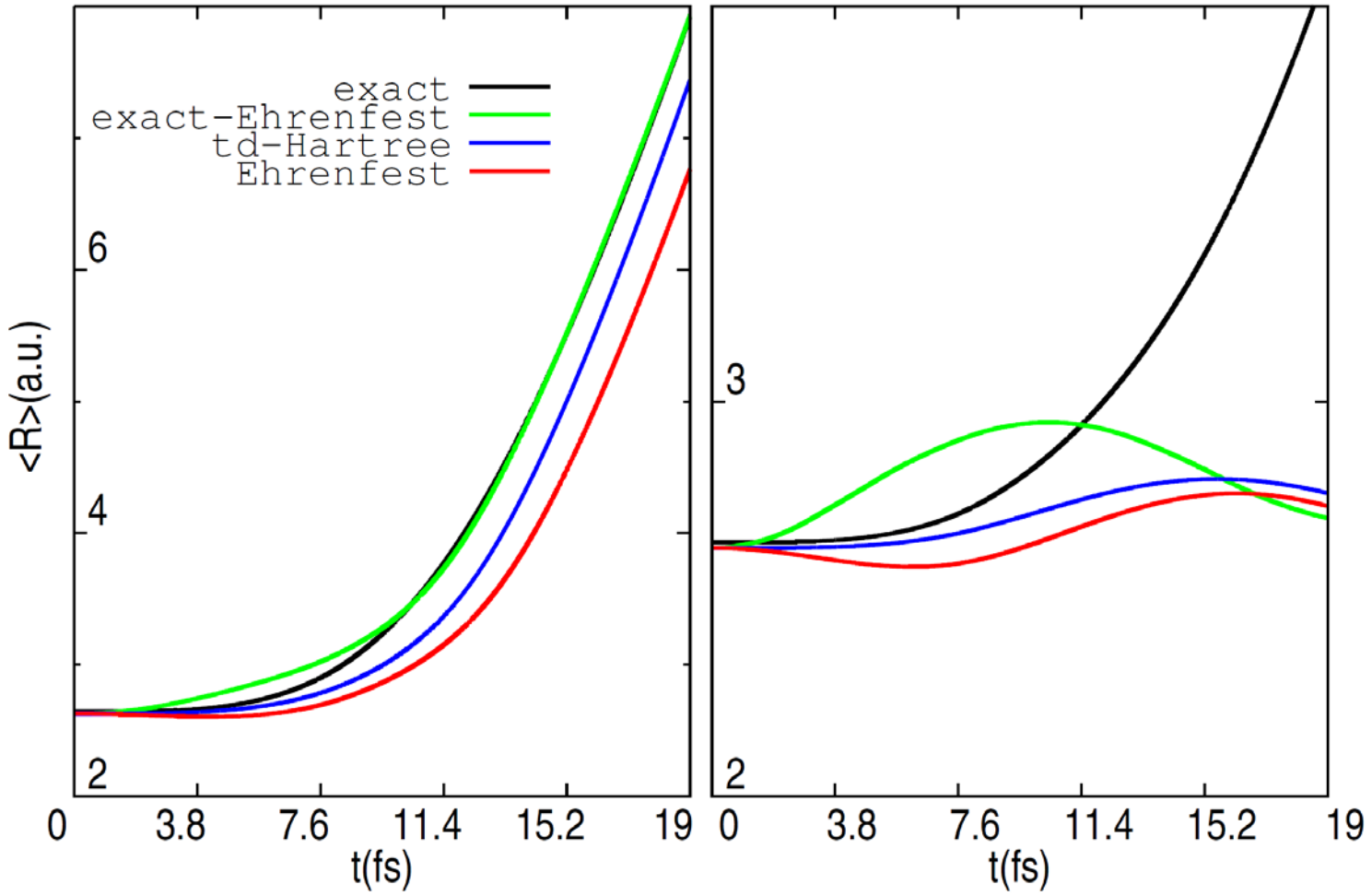
EXACT time-dependent Berry connection

Example: H_2^+ **in 1D in strong laser field**

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

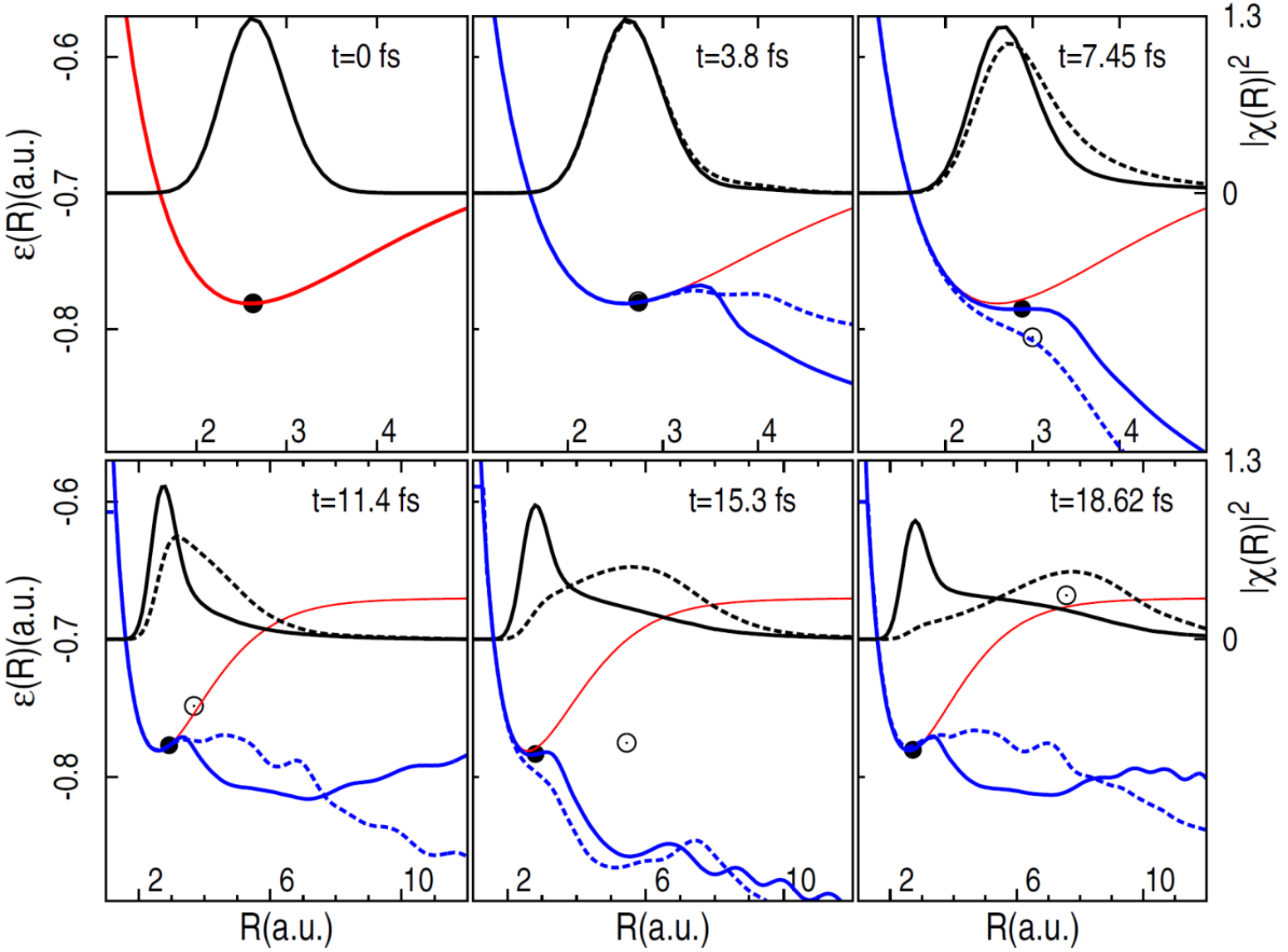
Compare with:

- Hartree approximation: $\Psi(r,R,t) = \chi(R,t)\cdot\varphi(r,t)$
- Standard Ehrenfest dynamics
- "Exact Ehrenfest dynamics" where the forces on the nuclei are calculated from the **exact** TD-PES



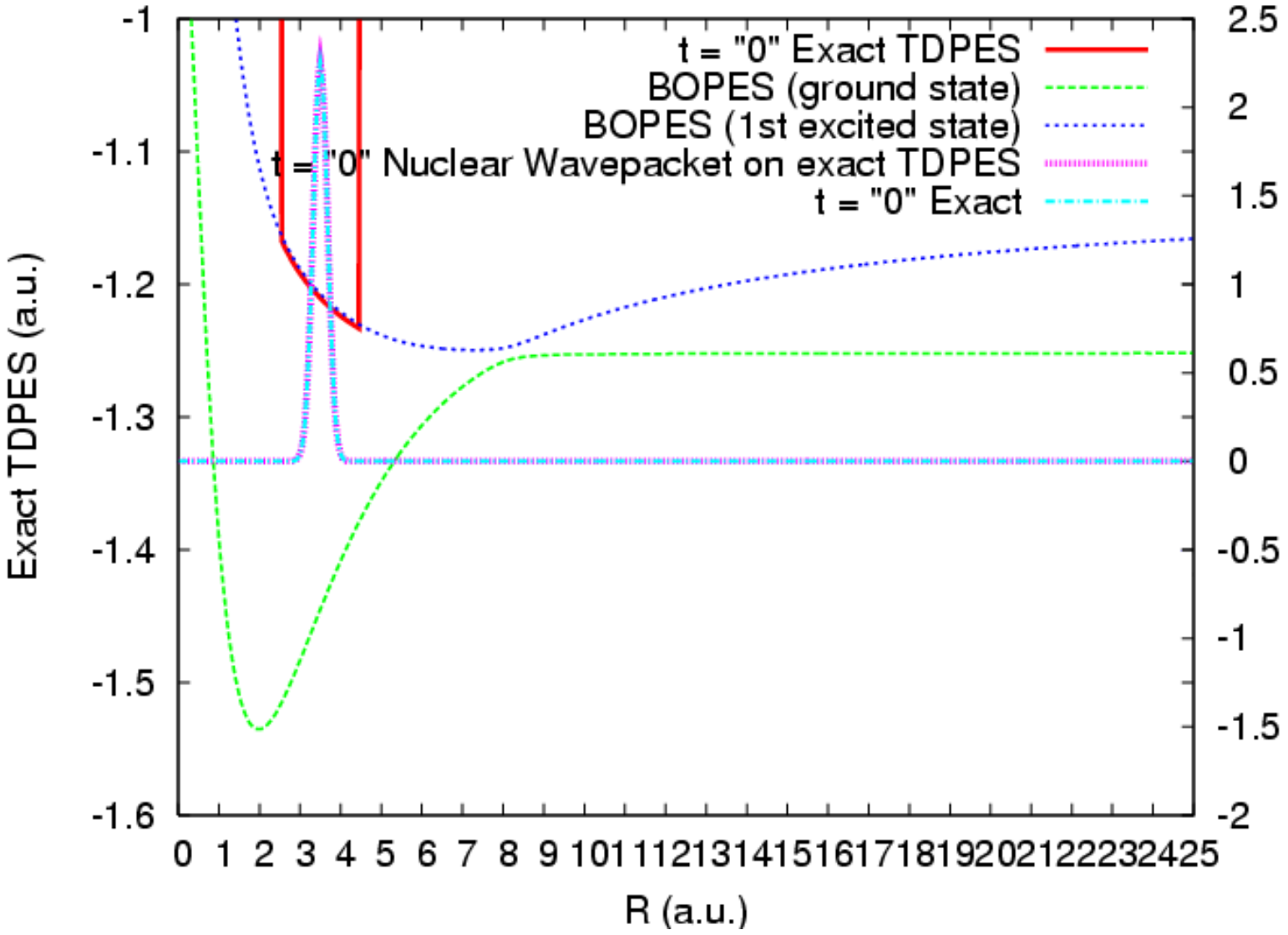
The internuclear separation < R>(t) for the intensities $I_1 = 10^{14}$W/cm^2 (left) and $I_2 = 2.5 \times 10^{13}$W/cm^2 (right)

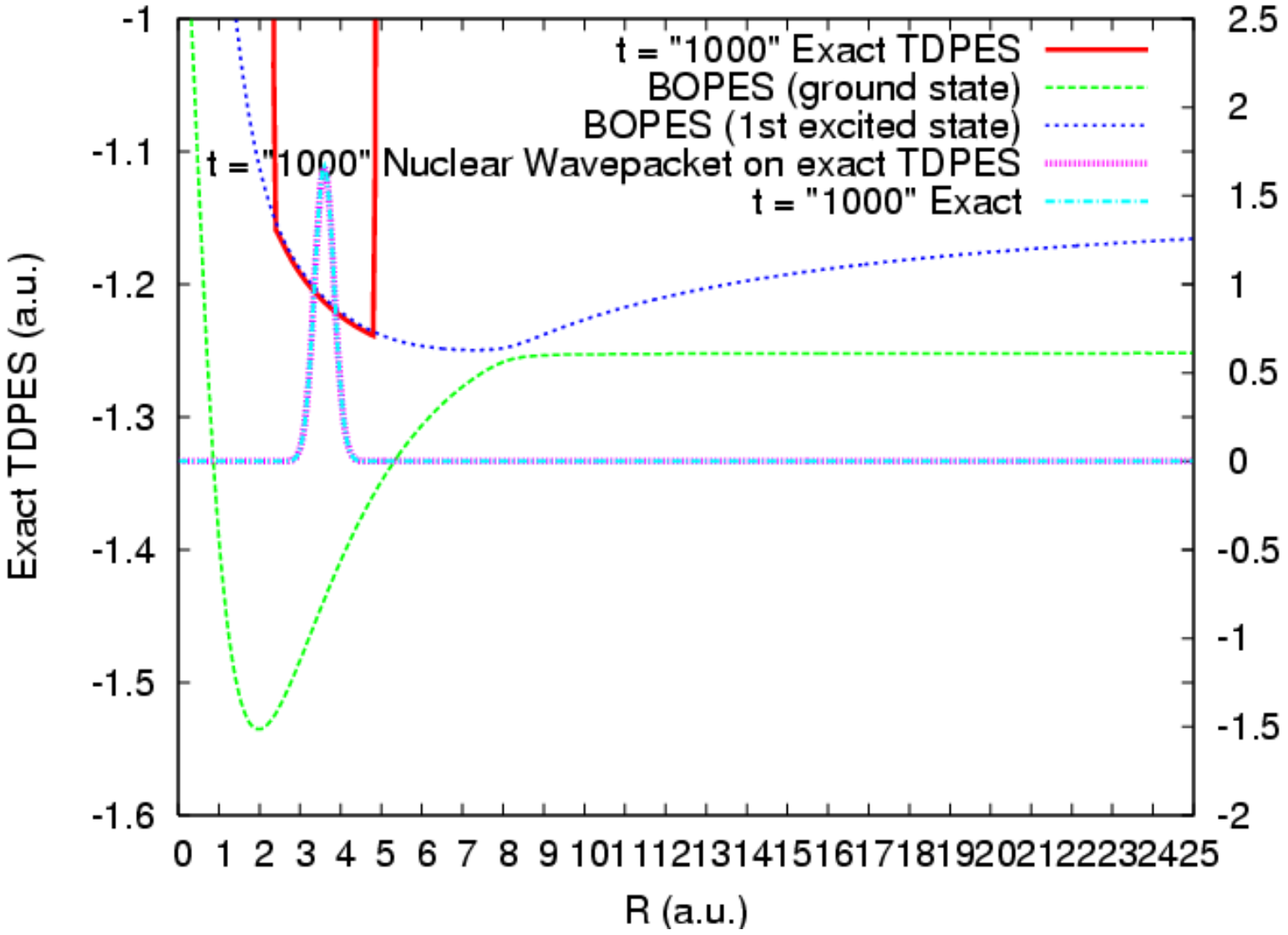
Exact time-dependent PES

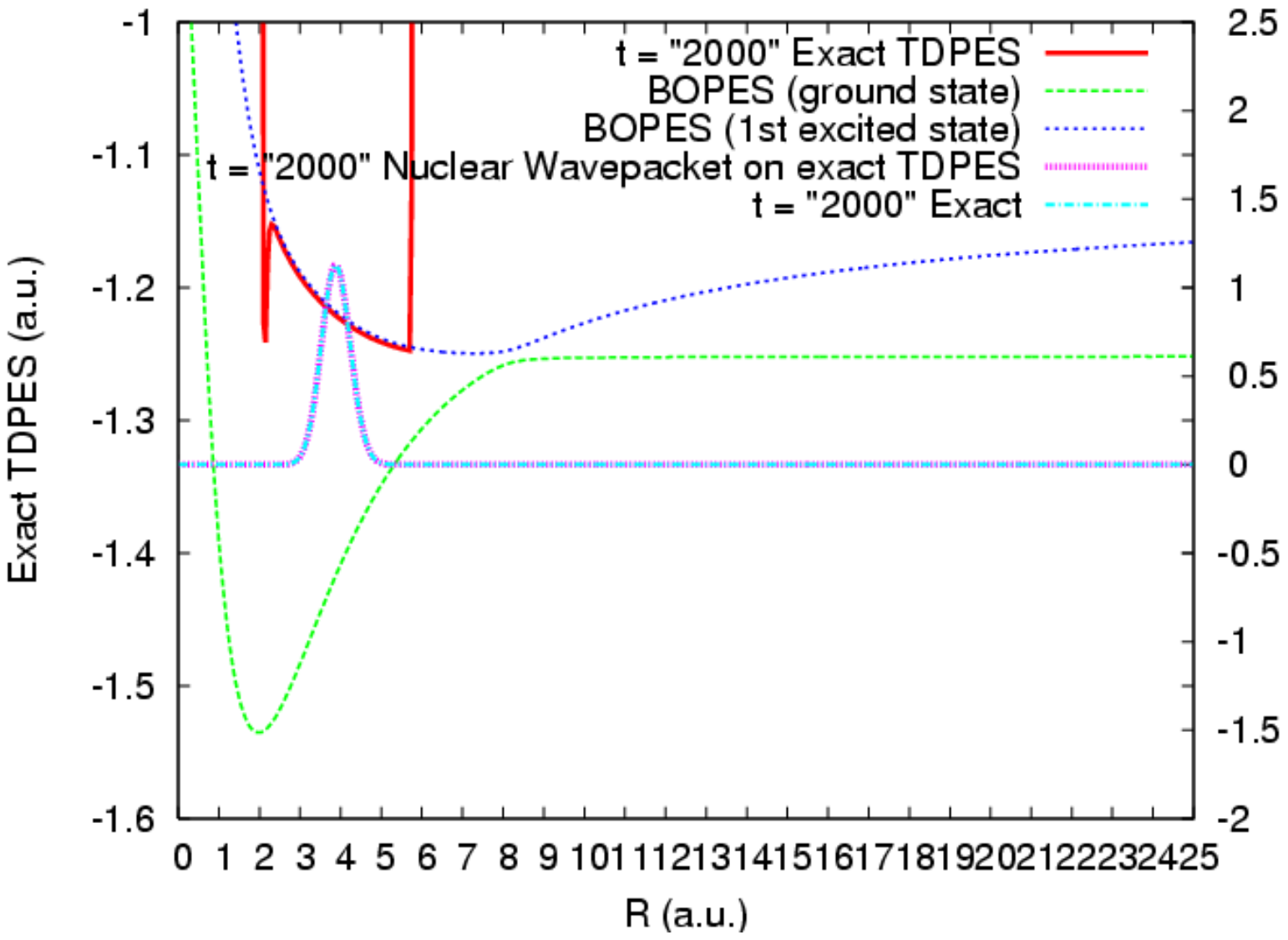


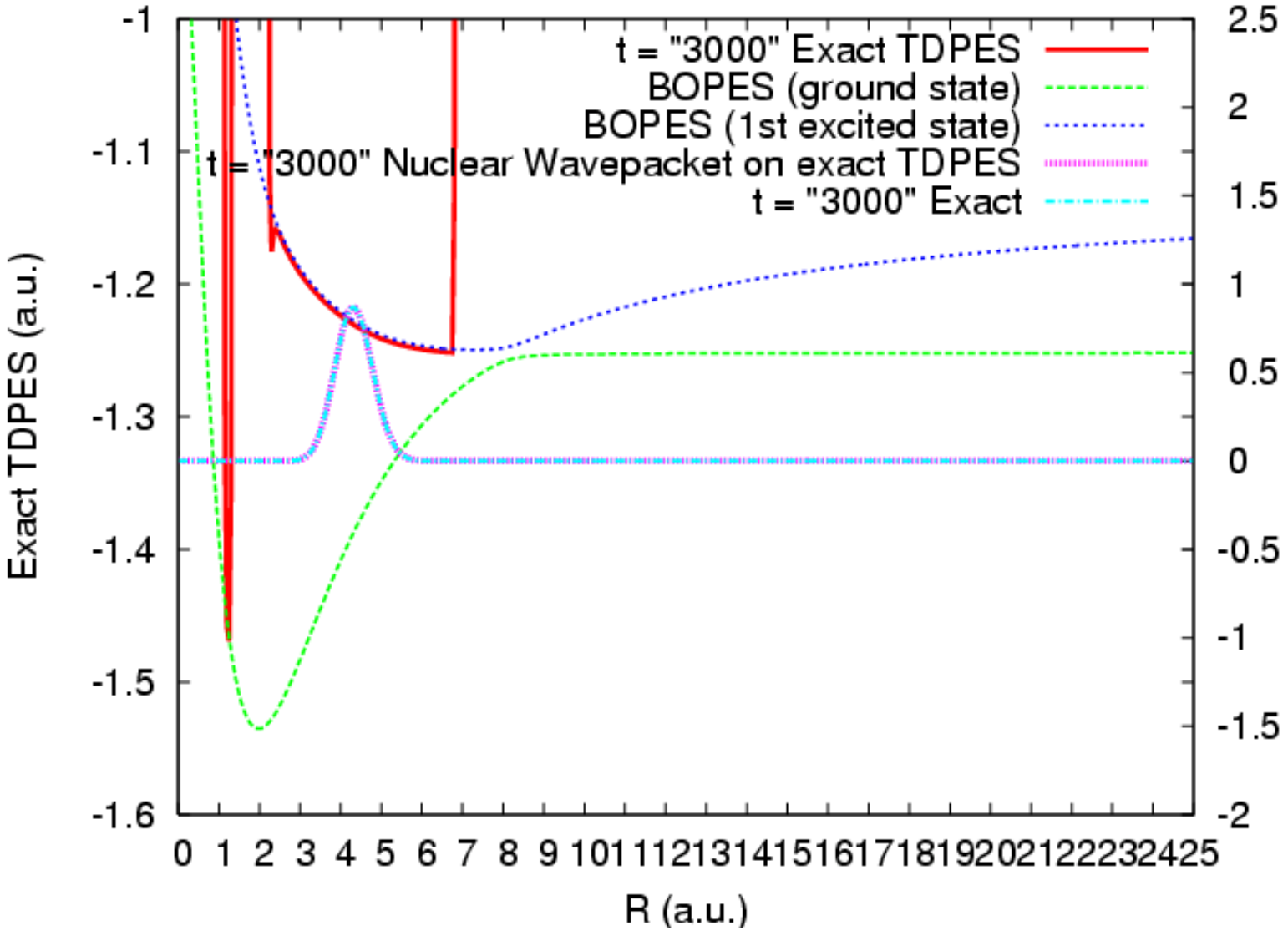
Dashed: $I_1 = 10^{14}$W/cm^2 ; solid: $I_2 = 2.5 \times 10^{13}$W/cm^2

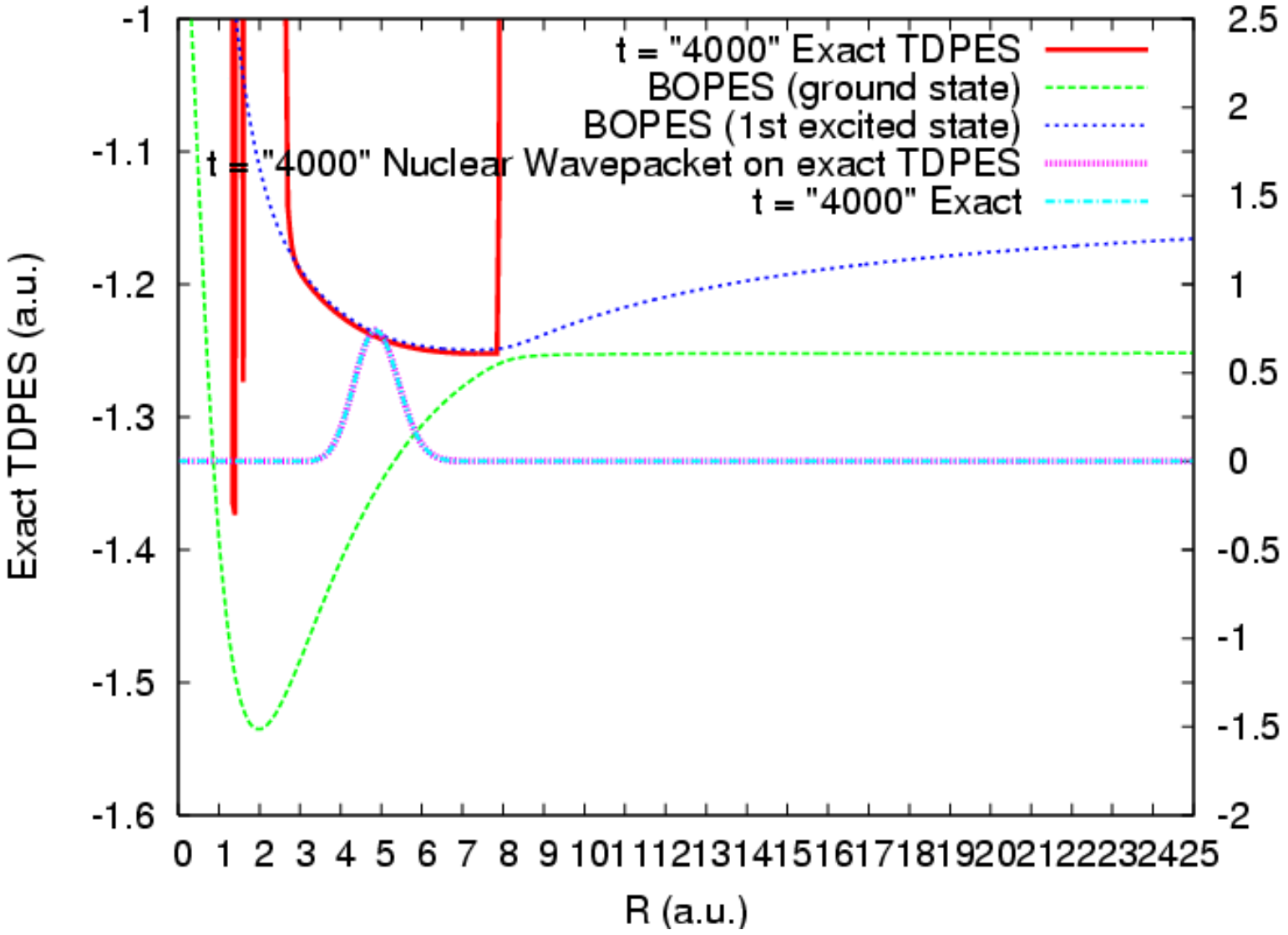
Second TD example: Molecular motion without laser, but initial state is a wavepacket (i.e. not an eigenstate)

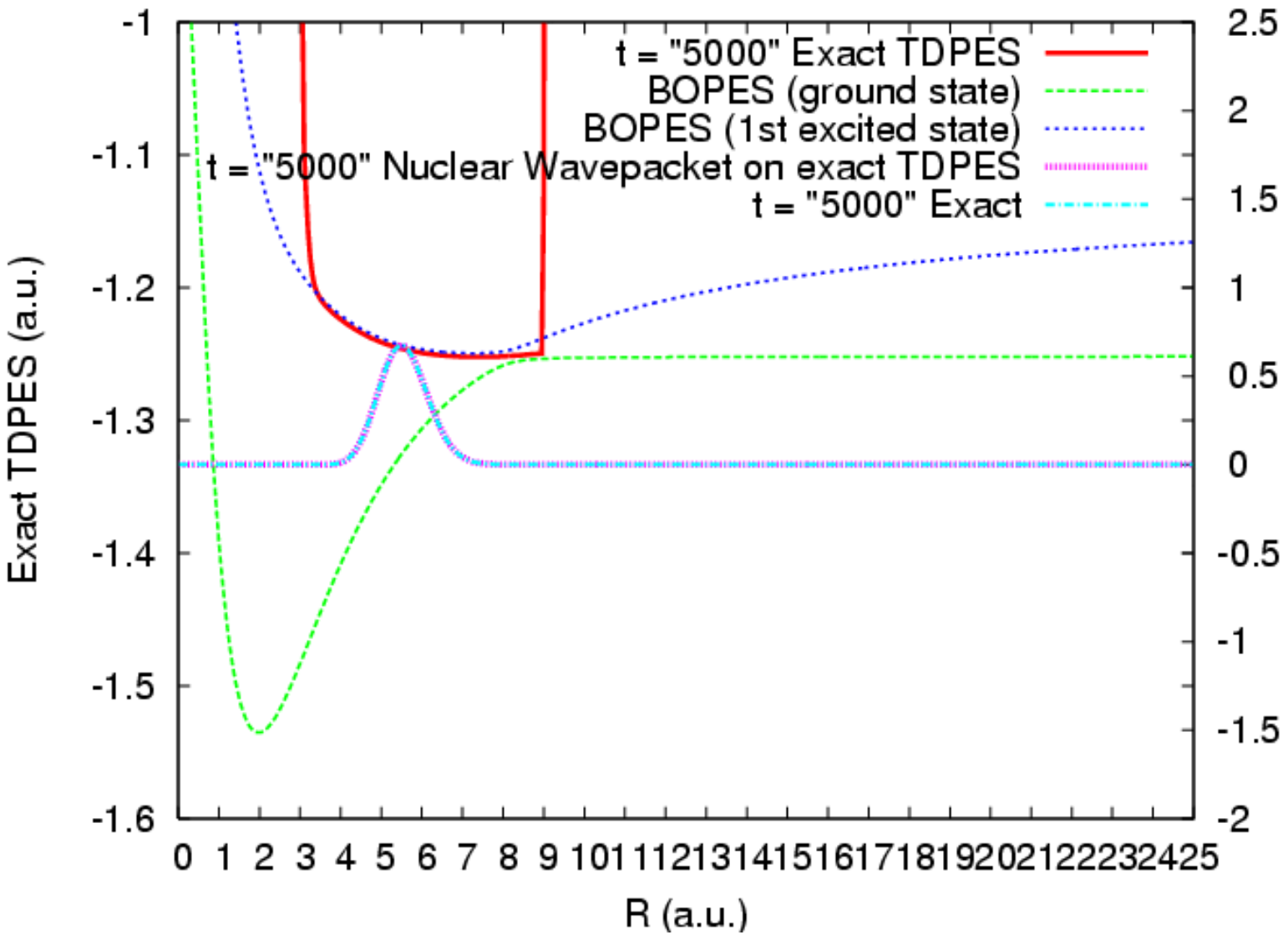

t = "0" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "0" Nuclear Wavepacket on exact TDPES
t = "0" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

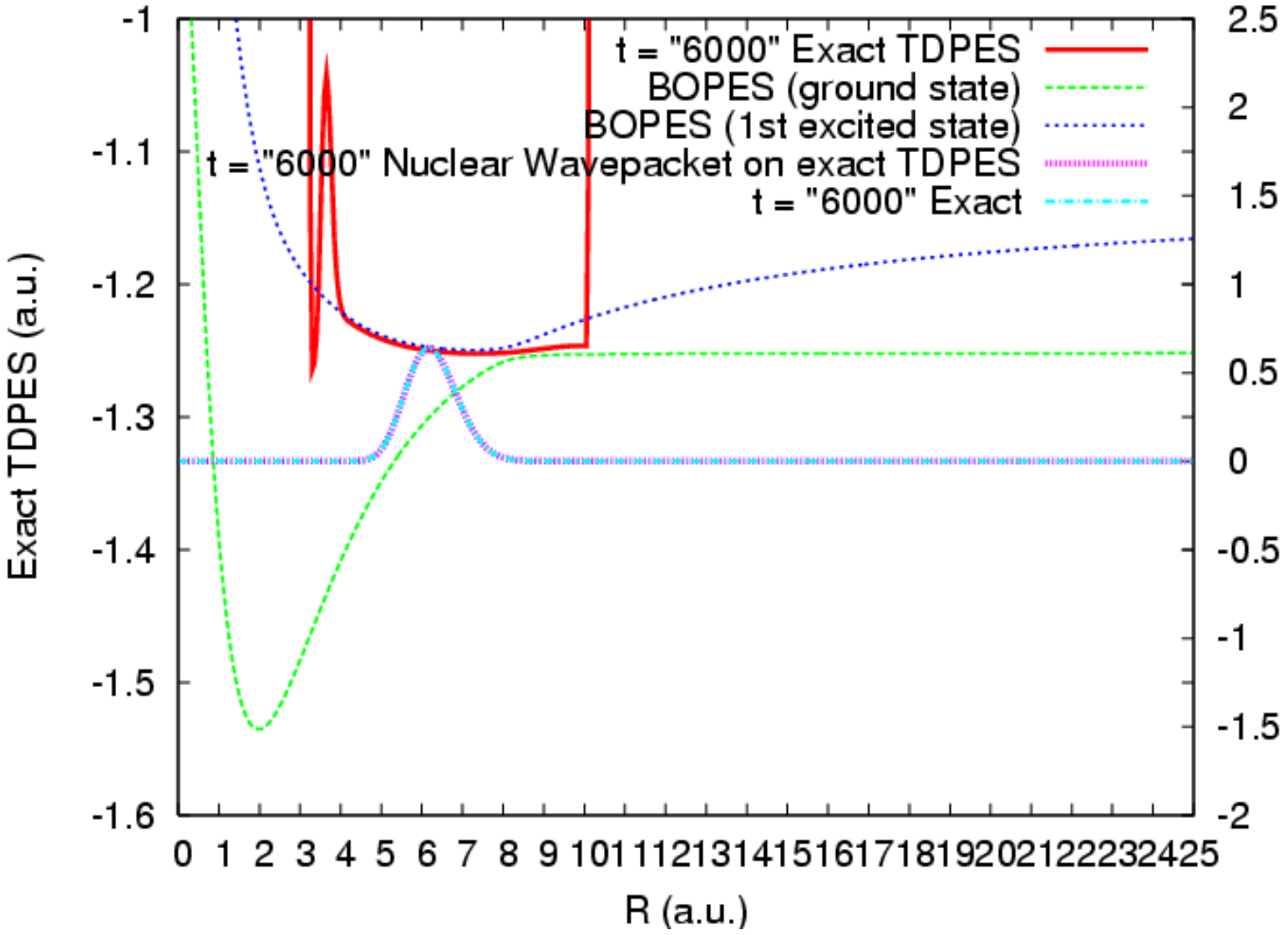

t = "1000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "1000" Nuclear Wavepacket on exact TDPES
t = "1000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

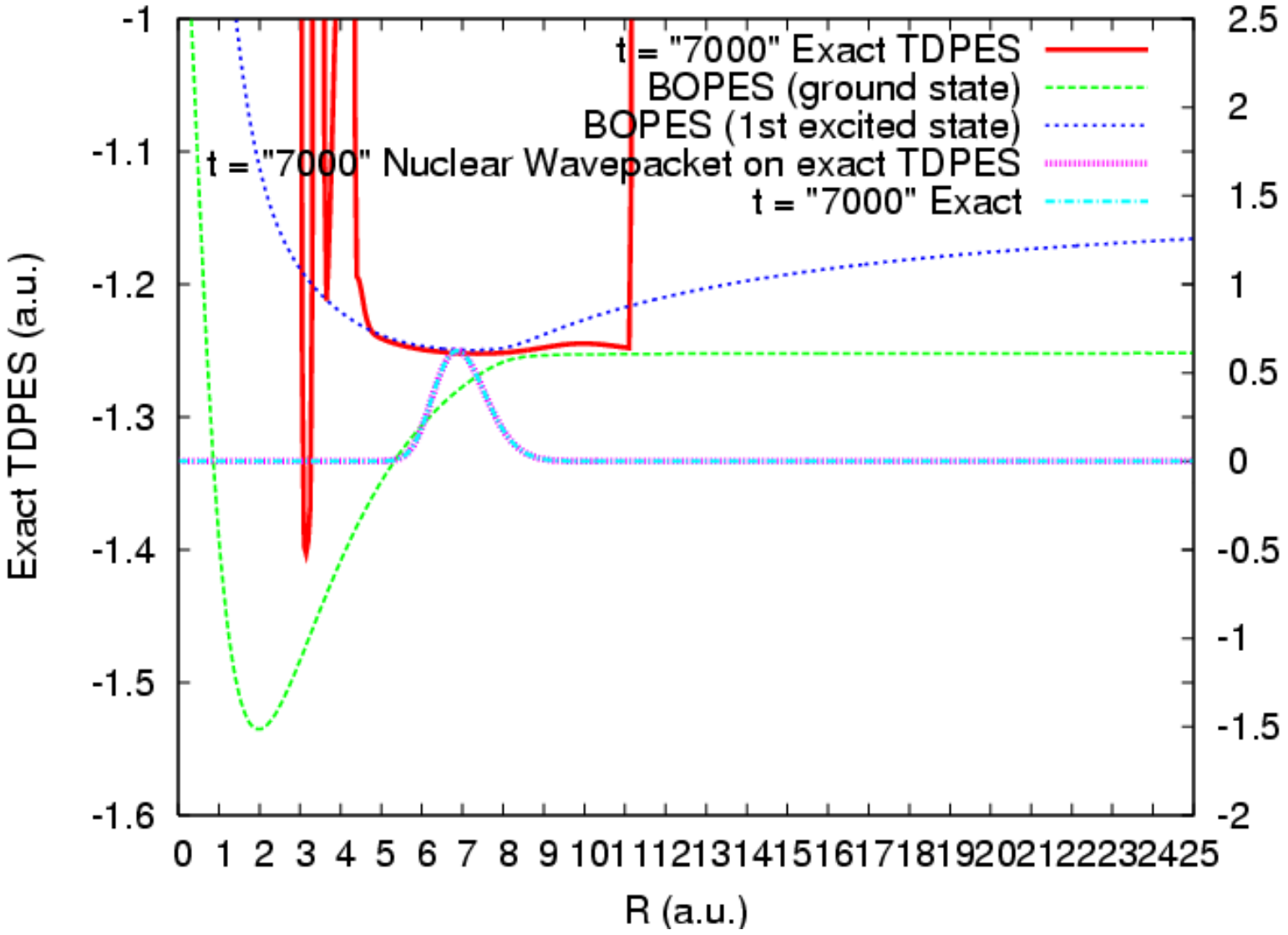

t = "2000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "2000" Nuclear Wavepacket on exact TDPES
t = "2000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

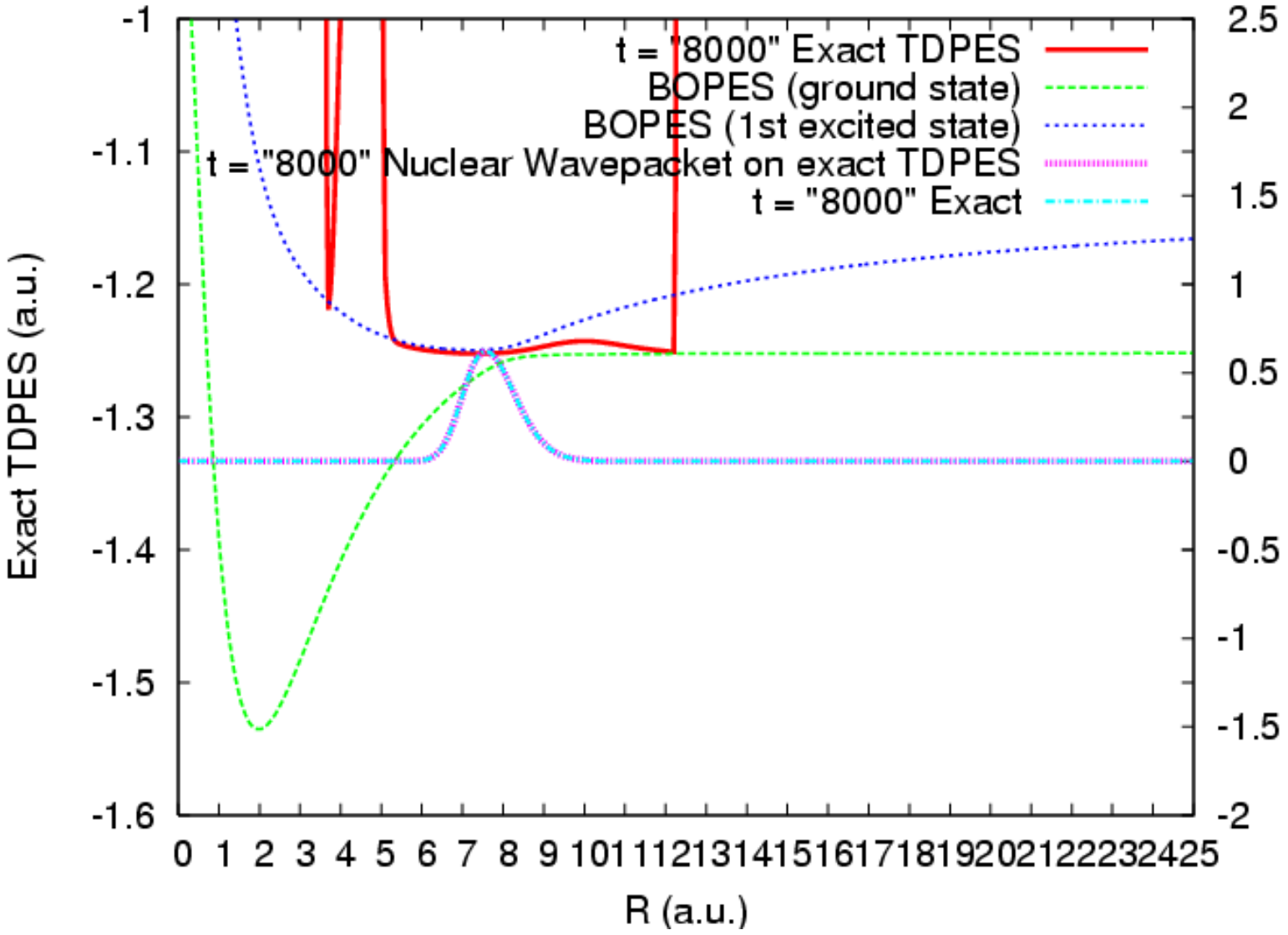

t = "3000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "3000" Nuclear Wavepacket on exact TDPES
t = "3000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

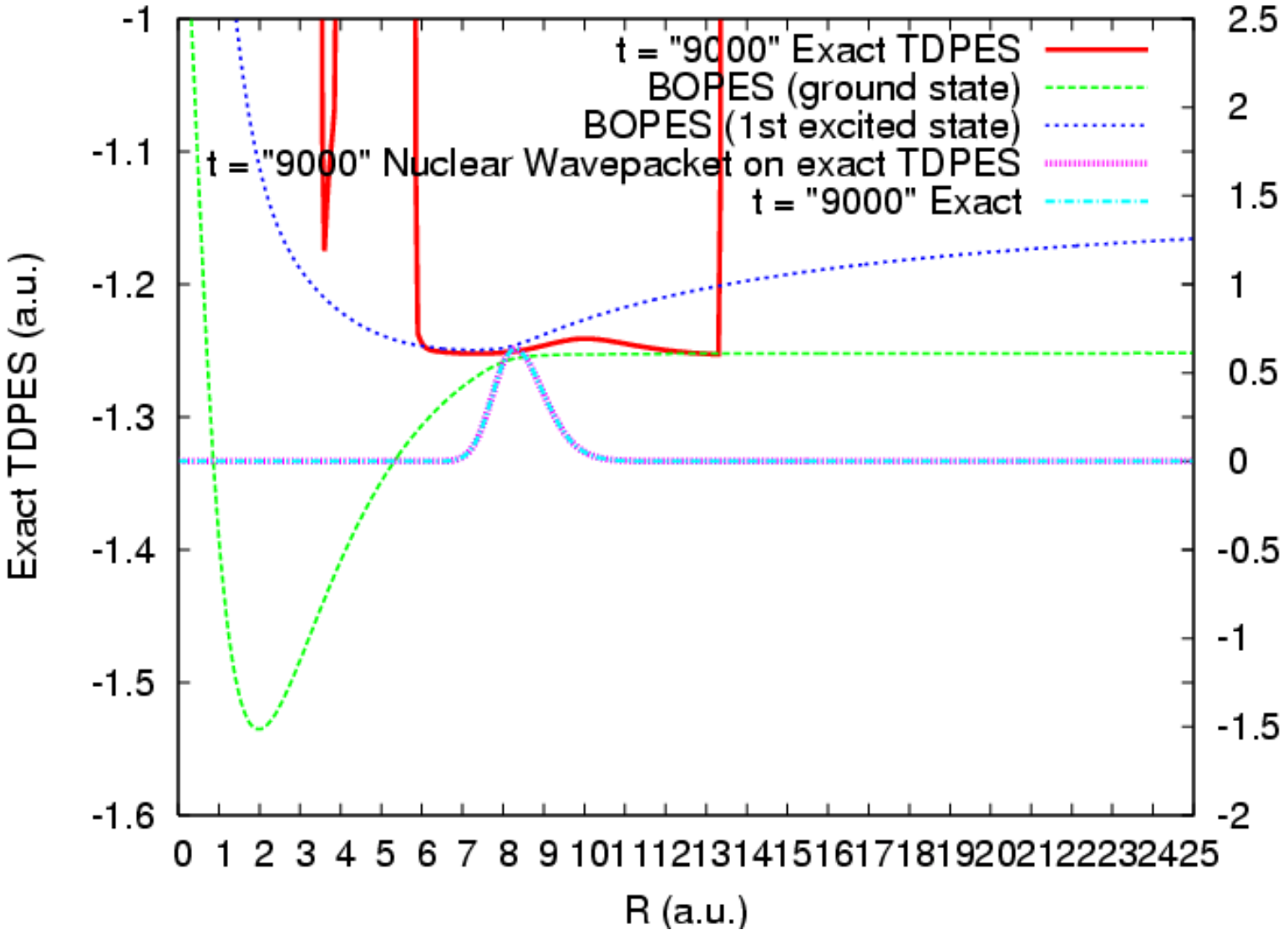

t = "4000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "4000" Nuclear Wavepacket on exact TDPES
t = "4000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

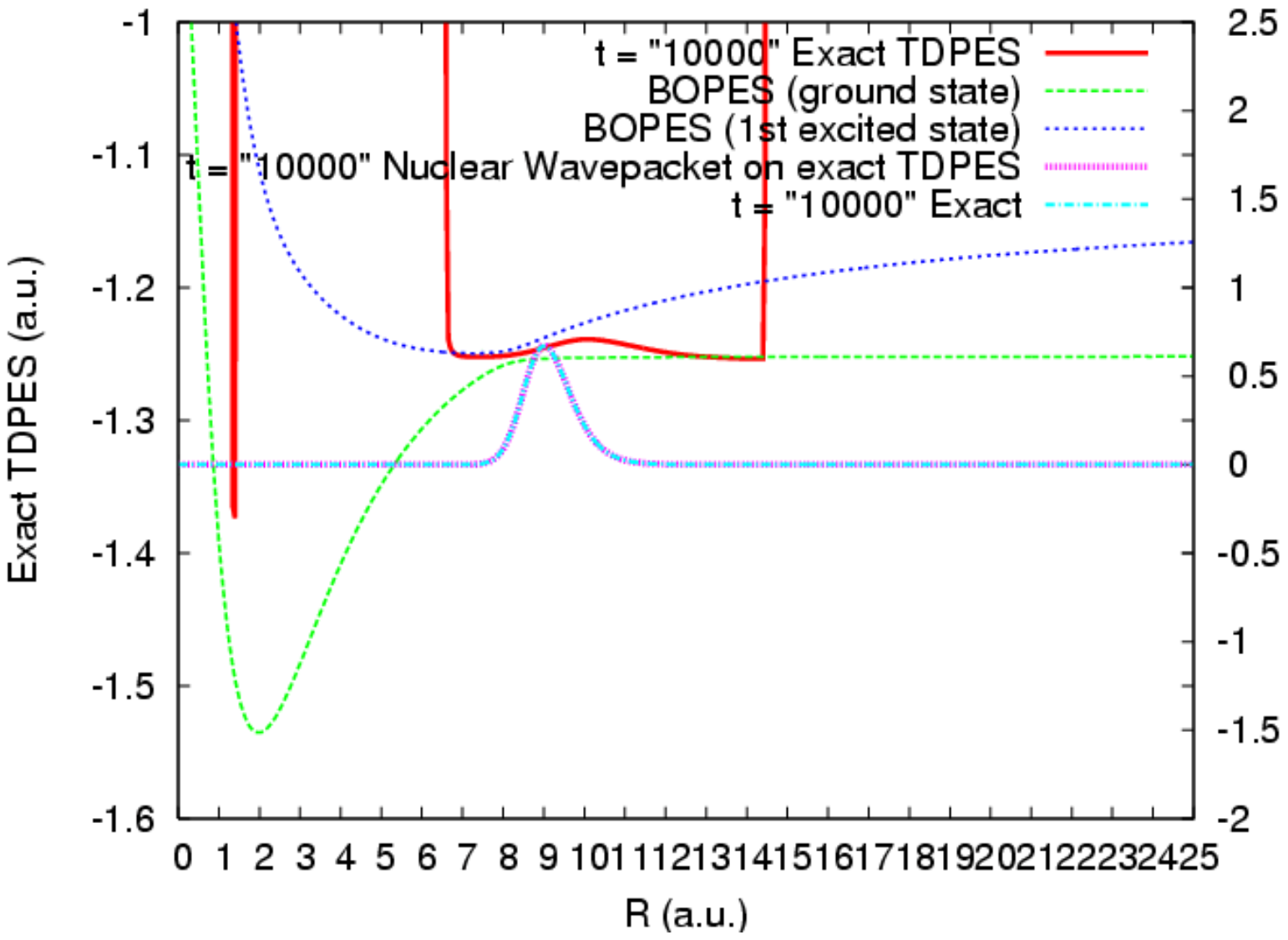

t = "5000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "5000" Nuclear Wavepacket on exact TDPES
t = "5000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

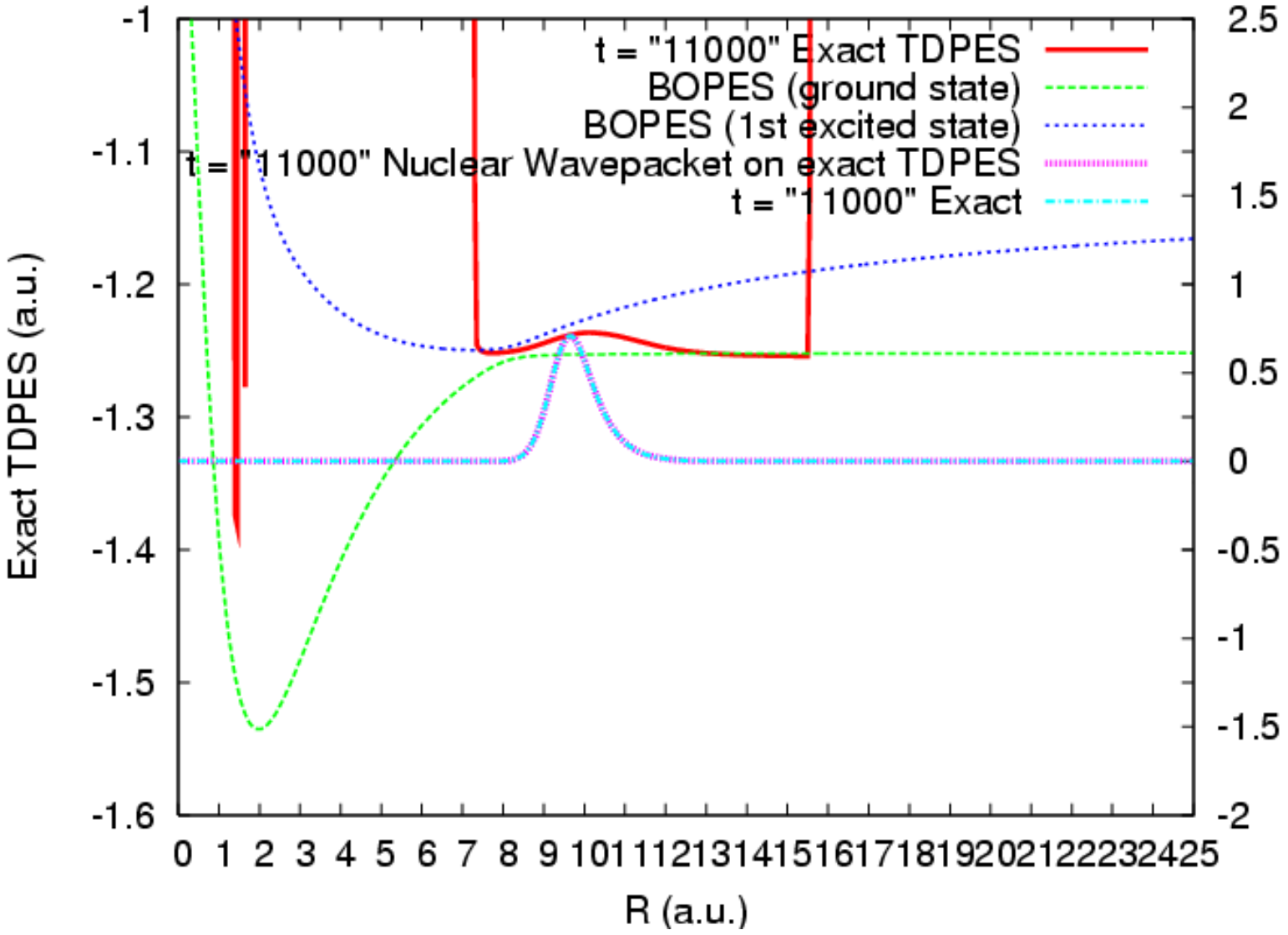

t = "6000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "6000" Nuclear Wavepacket on exact TDPES
t = "6000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

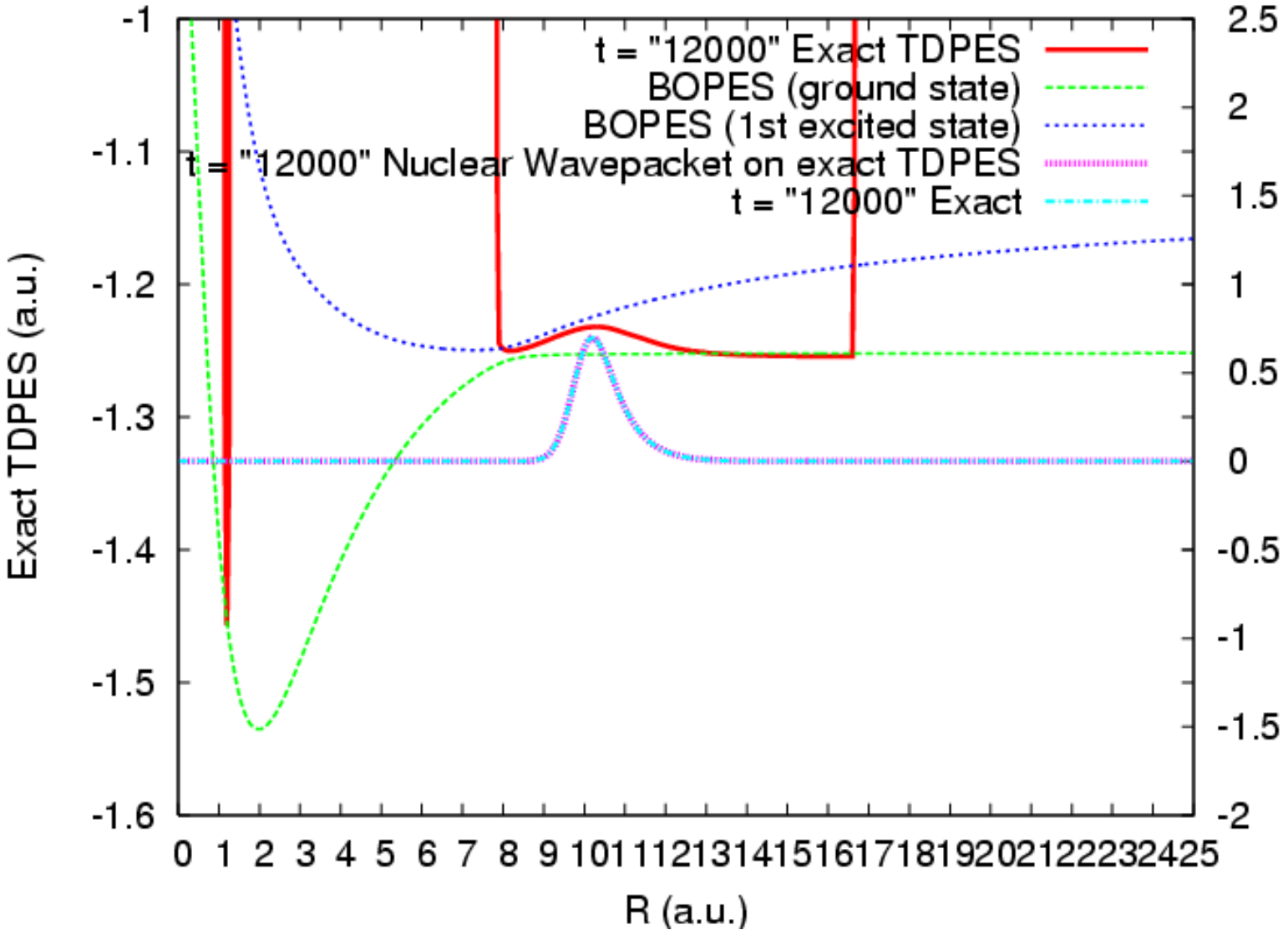

t = "7000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "7000" Nuclear Wavepacket on exact TDPES
t = "7000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

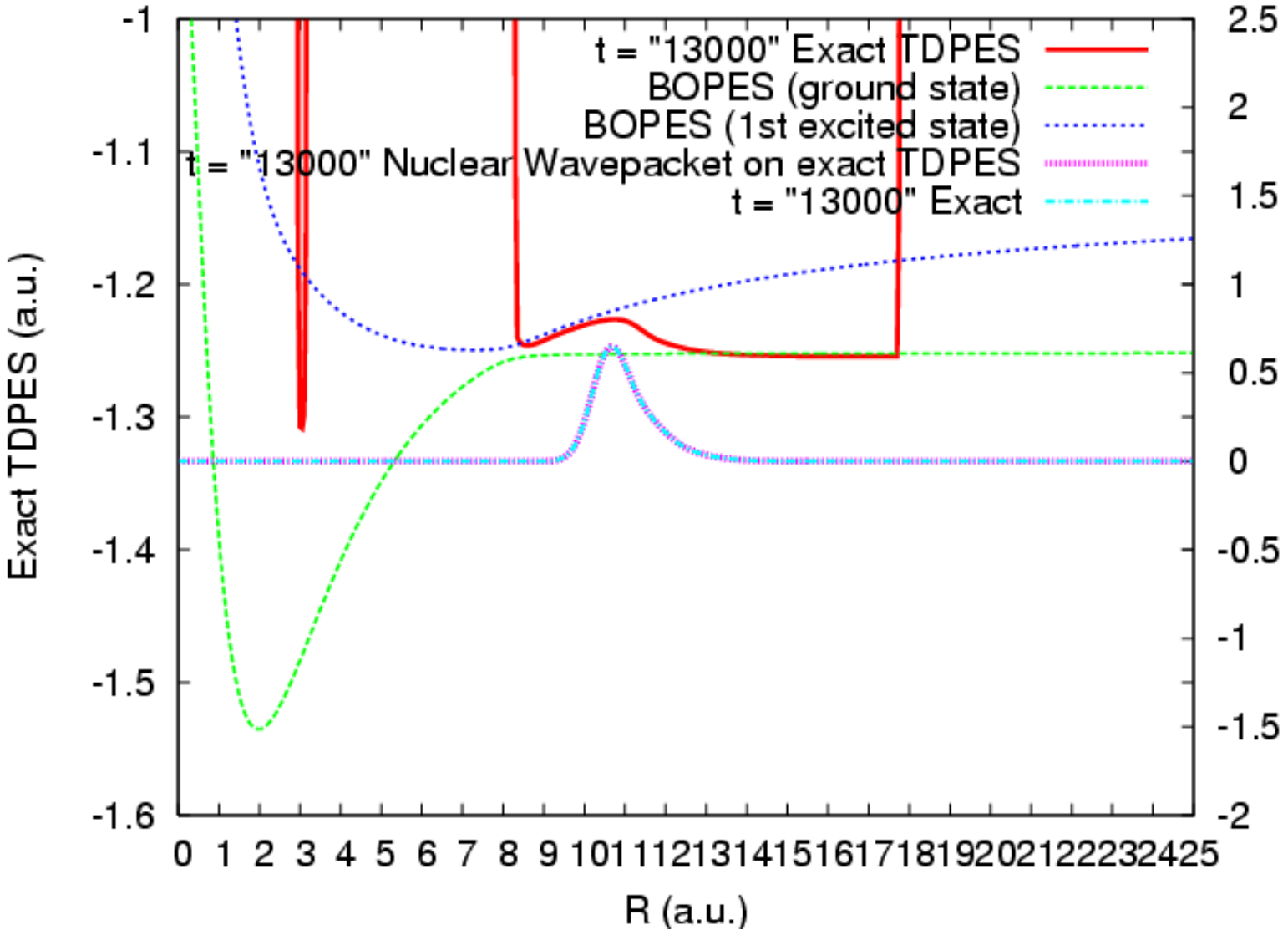

t = "8000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "8000" Nuclear Wavepacket on exact TDPES
t = "8000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

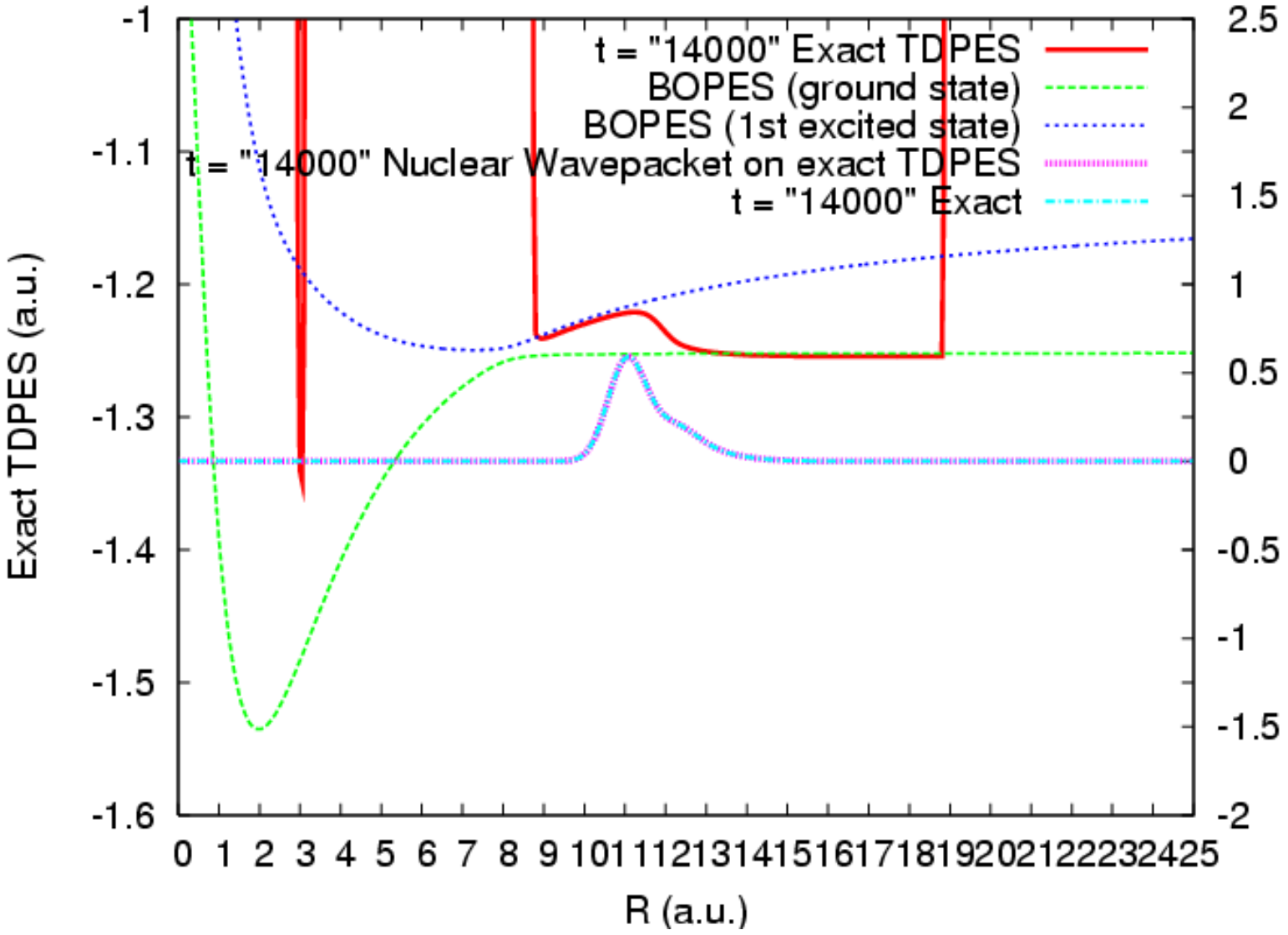

t = "9000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "9000" Nuclear Wavepacket on exact TDPES
t = "9000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

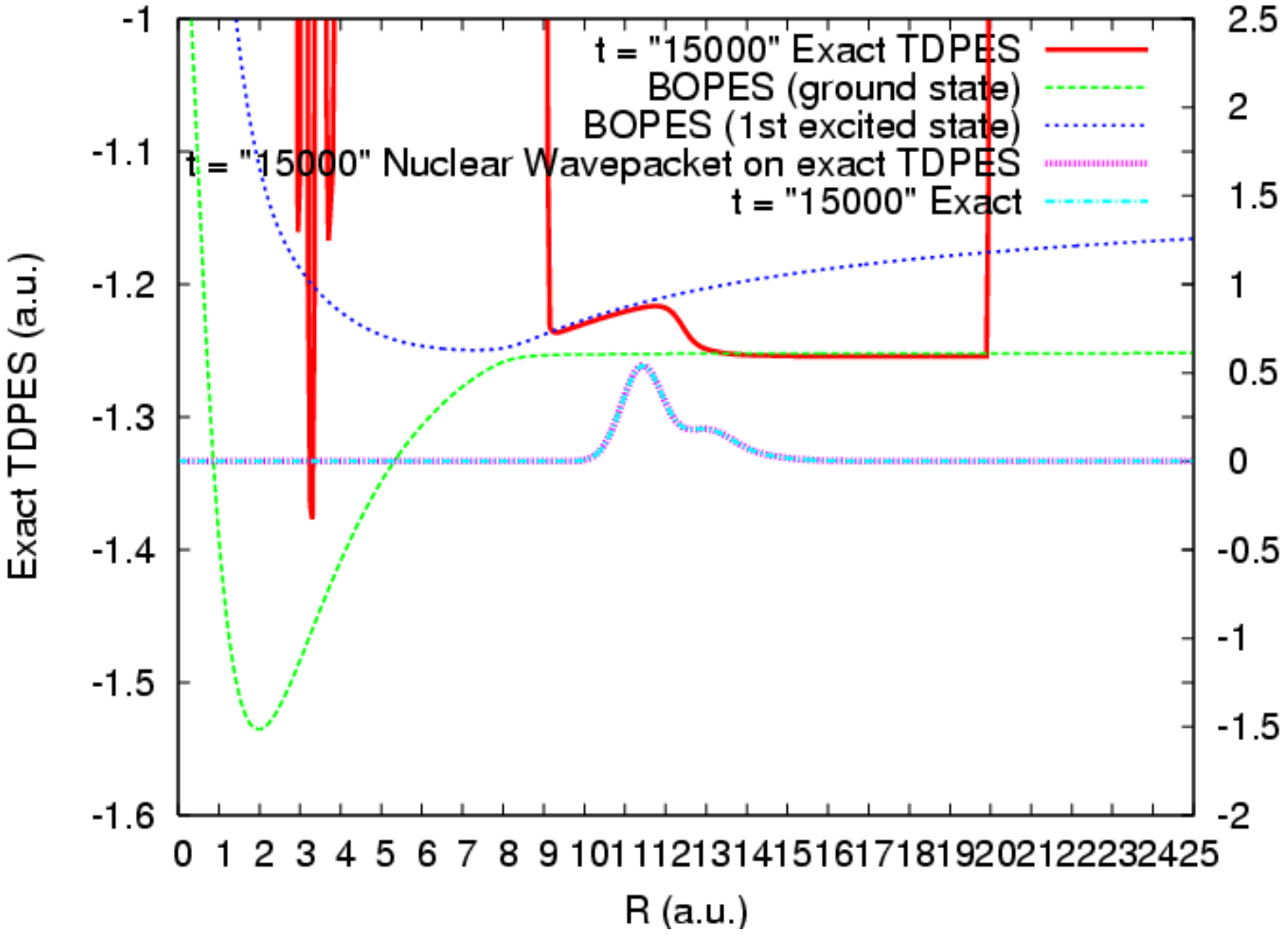

t = "10000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "10000" Nuclear Wavepacket on exact TDPES
t = "10000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

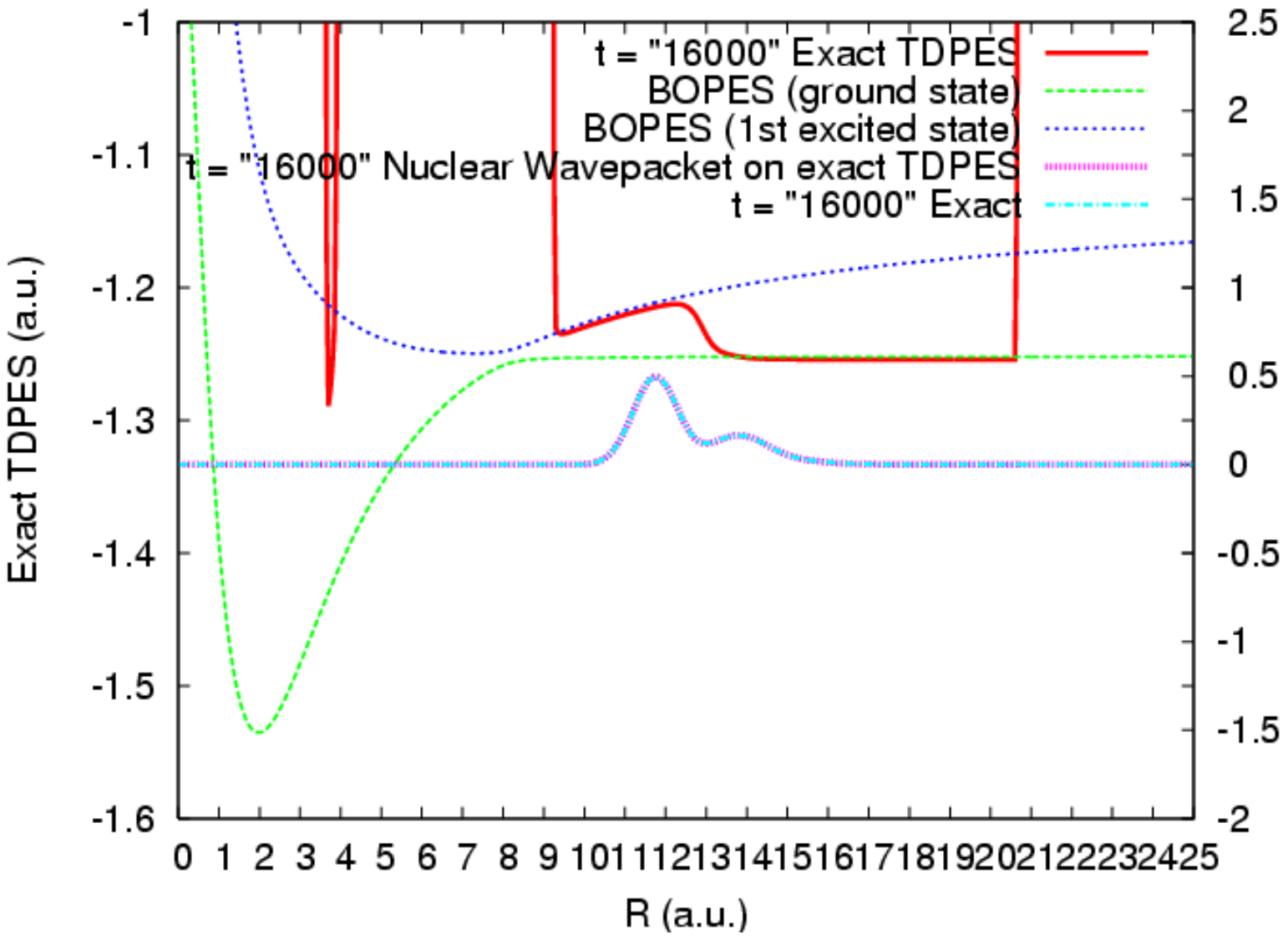

t = "11000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "11000" Nuclear Wavepacket on exact TDPES
t = "11000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

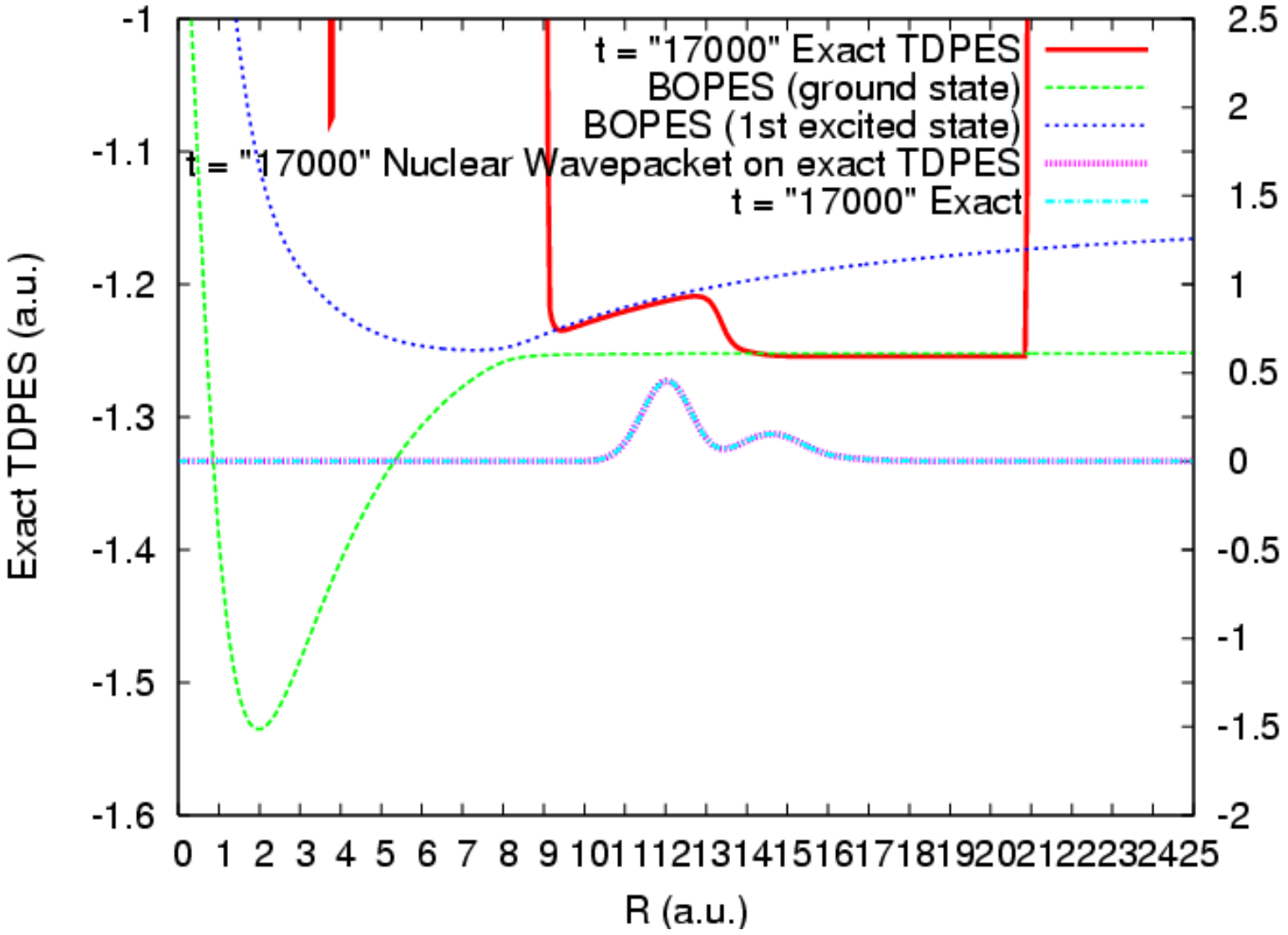

t = "12000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "12000" Nuclear Wavepacket on exact TDPES
t = "12000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

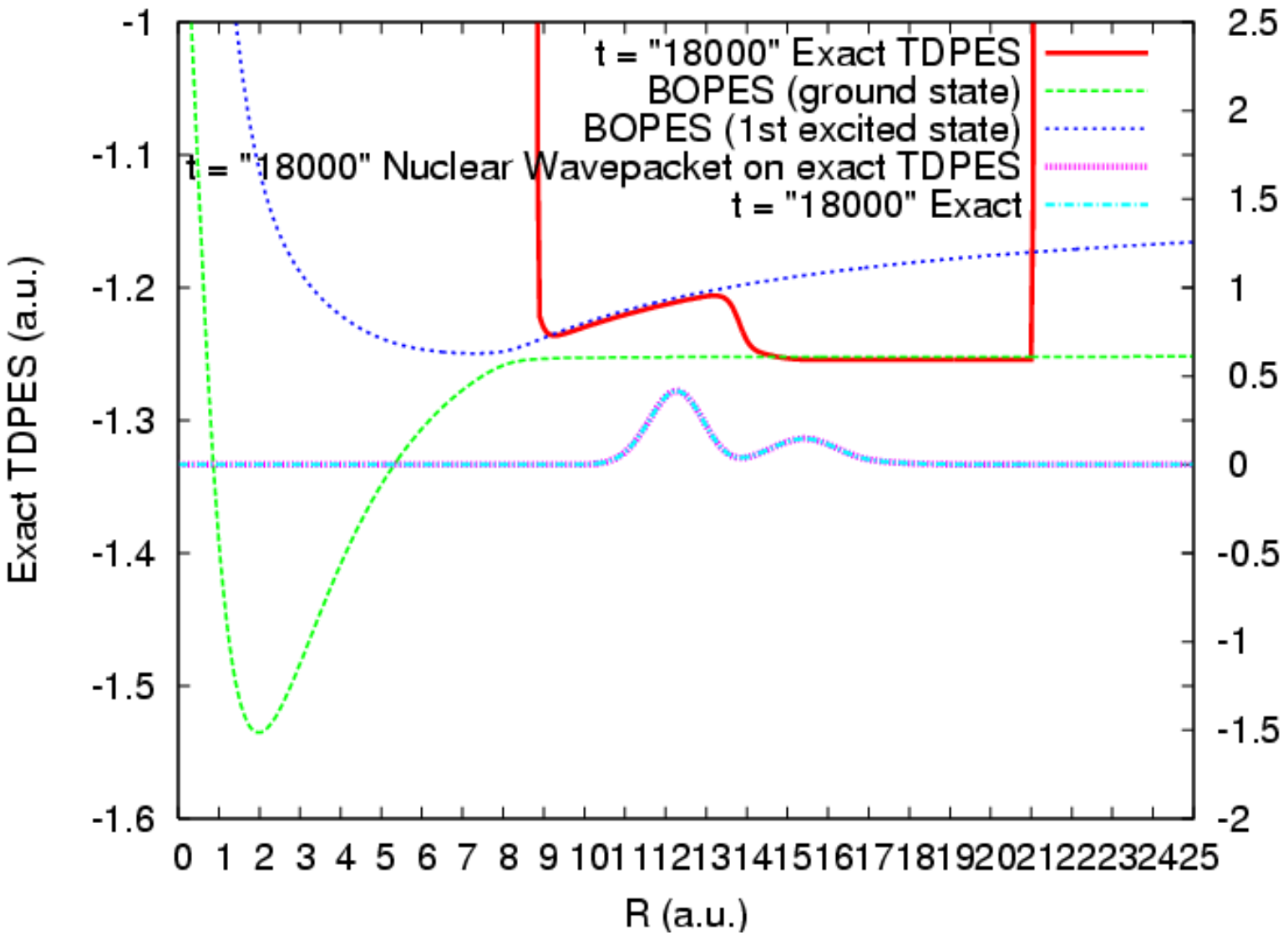

t = "13000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "13000" Nuclear Wavepacket on exact TDPES
t = "13000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

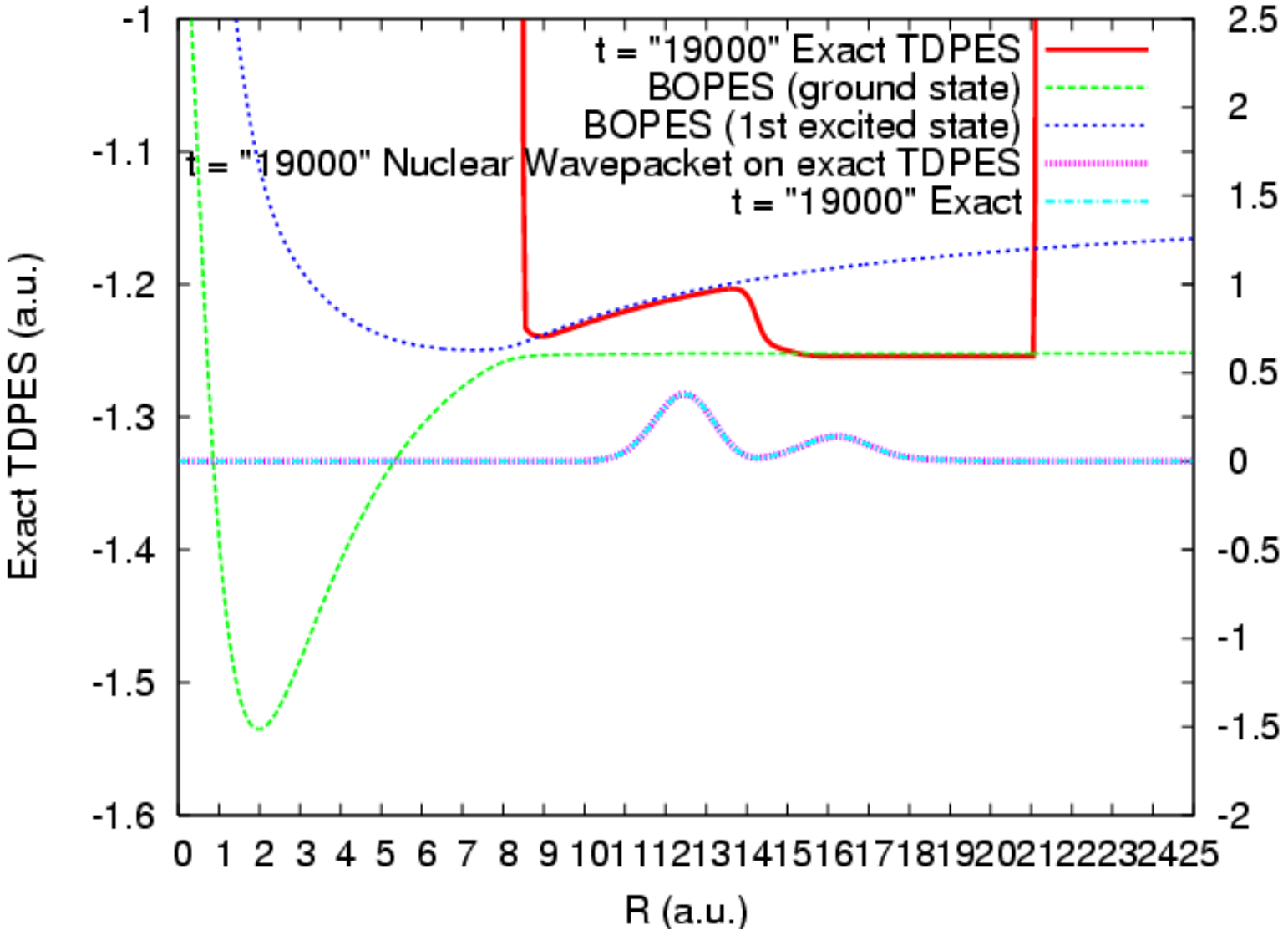

t = "14000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "14000" Nuclear Wavepacket on exact TDPES
t = "14000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

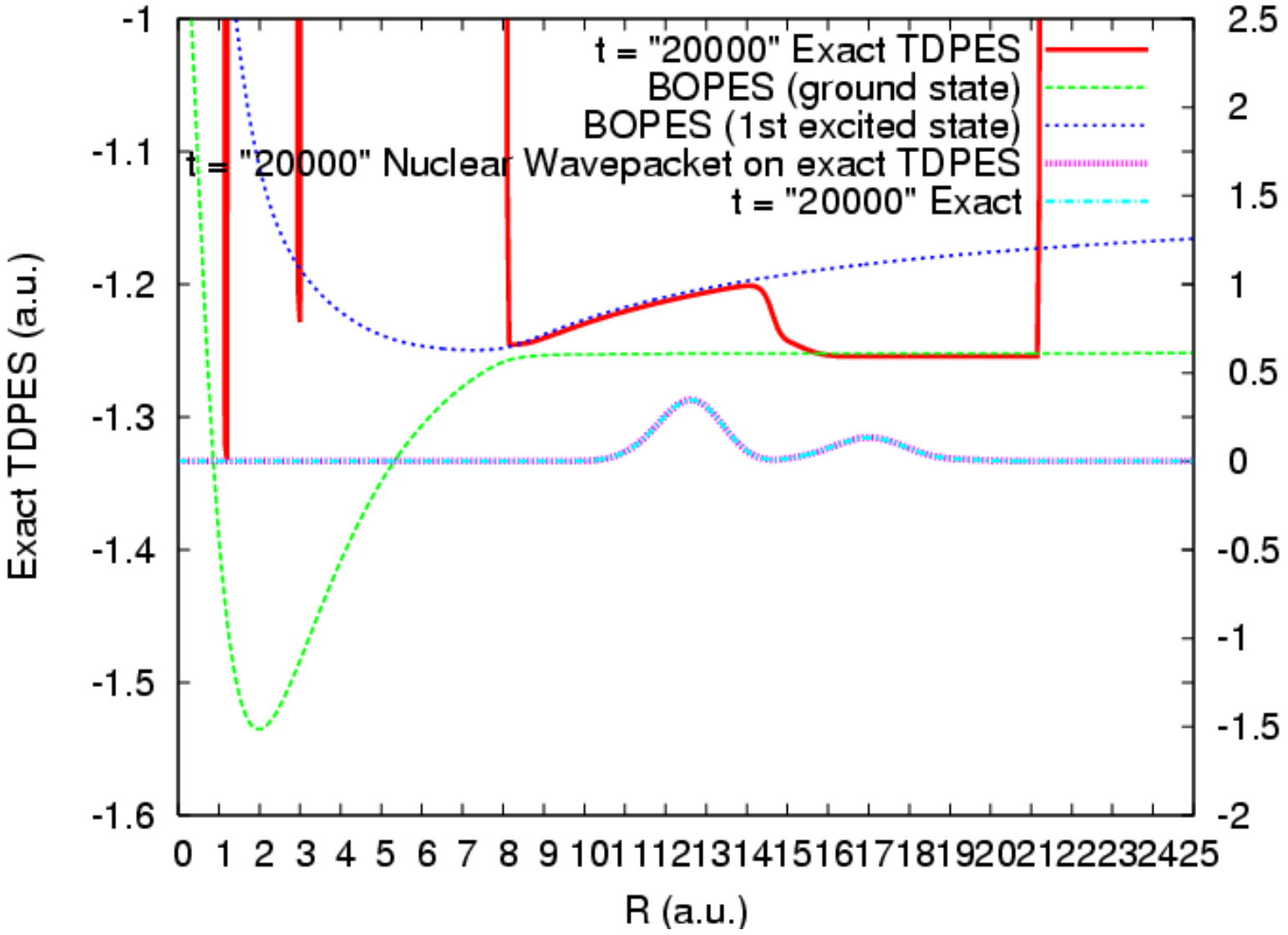

t = "15000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "15000" Nuclear Wavepacket on exact TDPES
t = "15000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

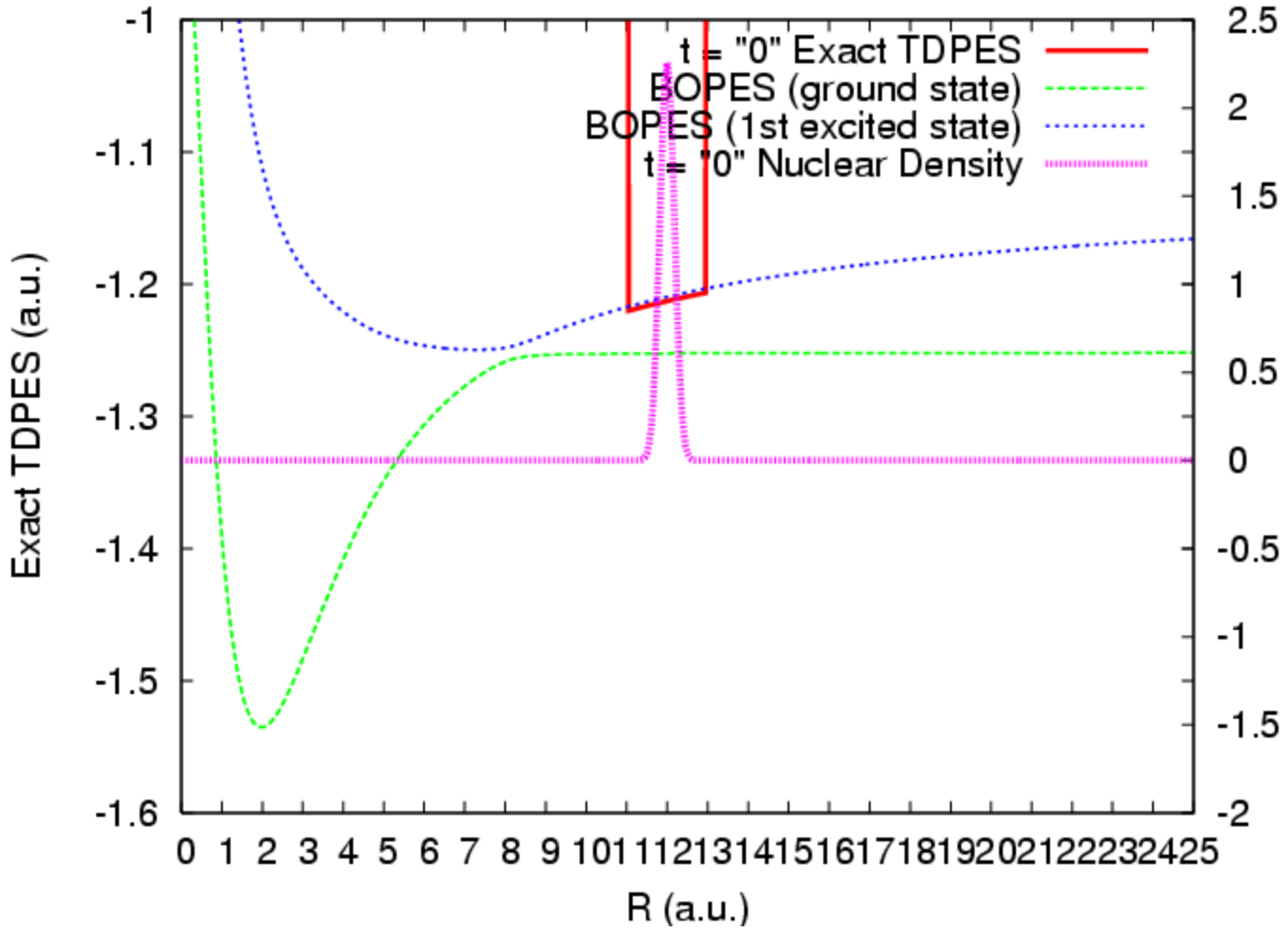

t = "16000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "16000" Nuclear Wavepacket on exact TDPES
t = "16000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "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

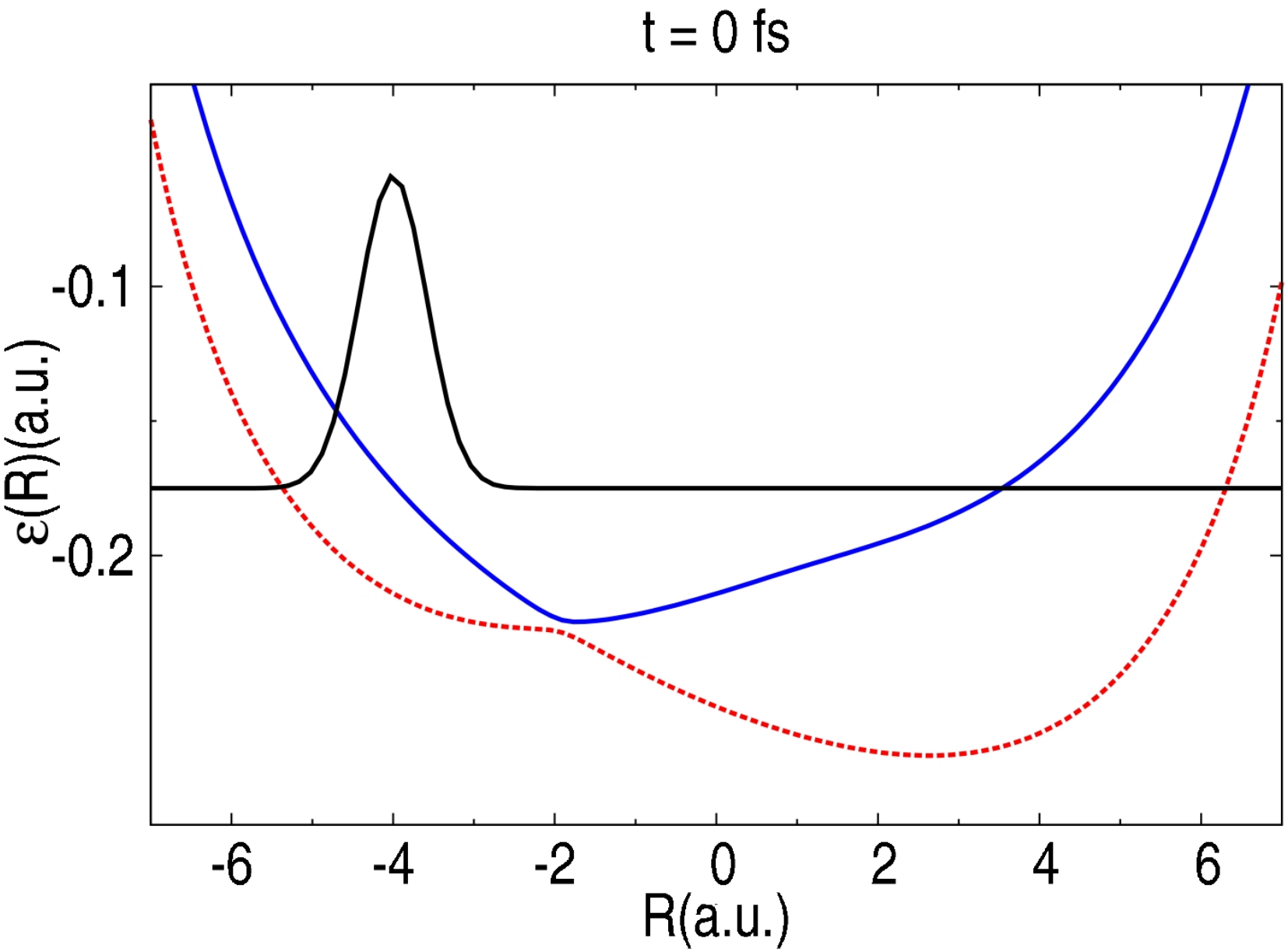

t = "18000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "18000" Nuclear Wavepacket on exact TDPES
t = "18000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

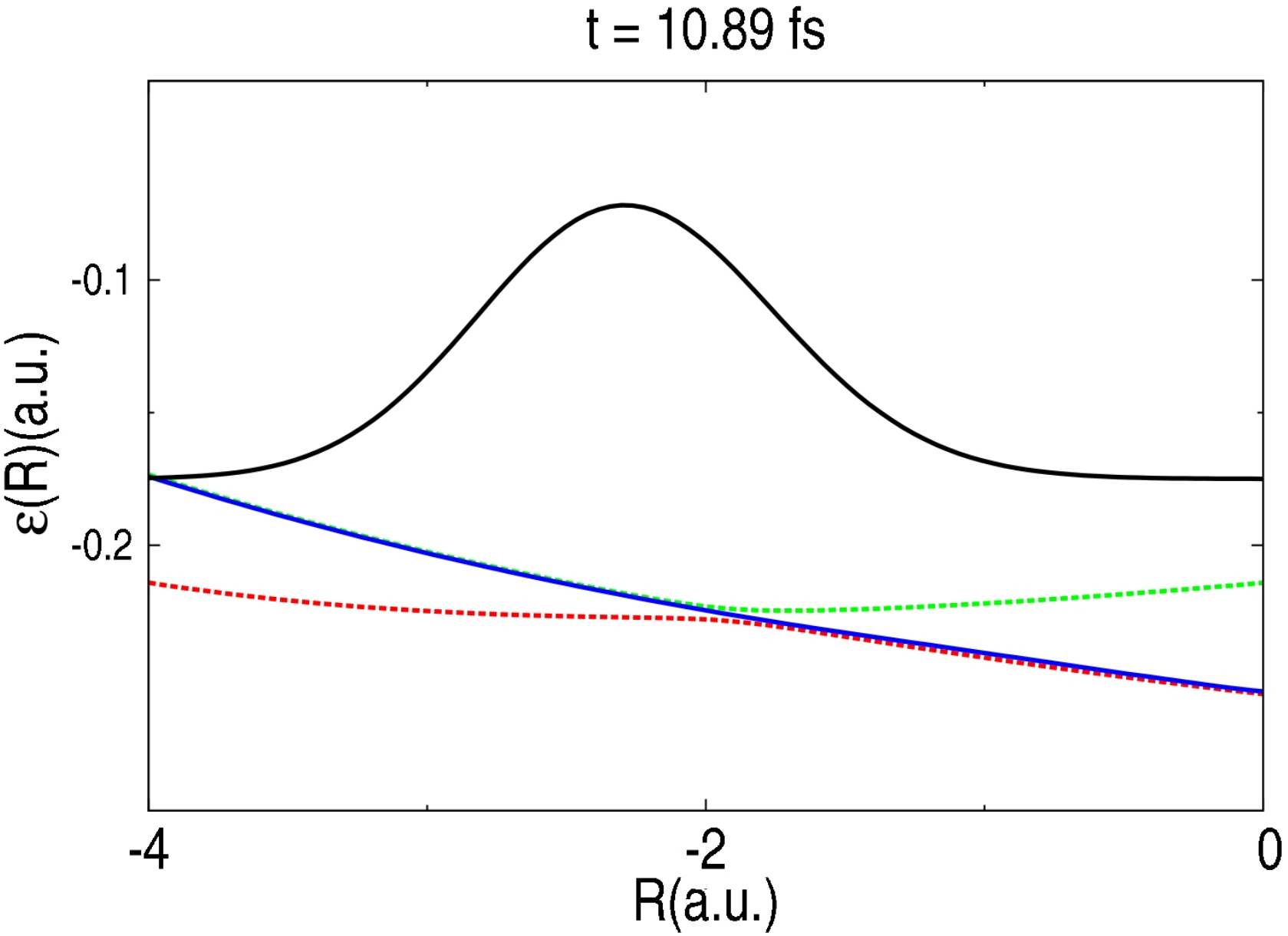

t = "19000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "19000" Nuclear Wavepacket on exact TDPES
t = "19000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

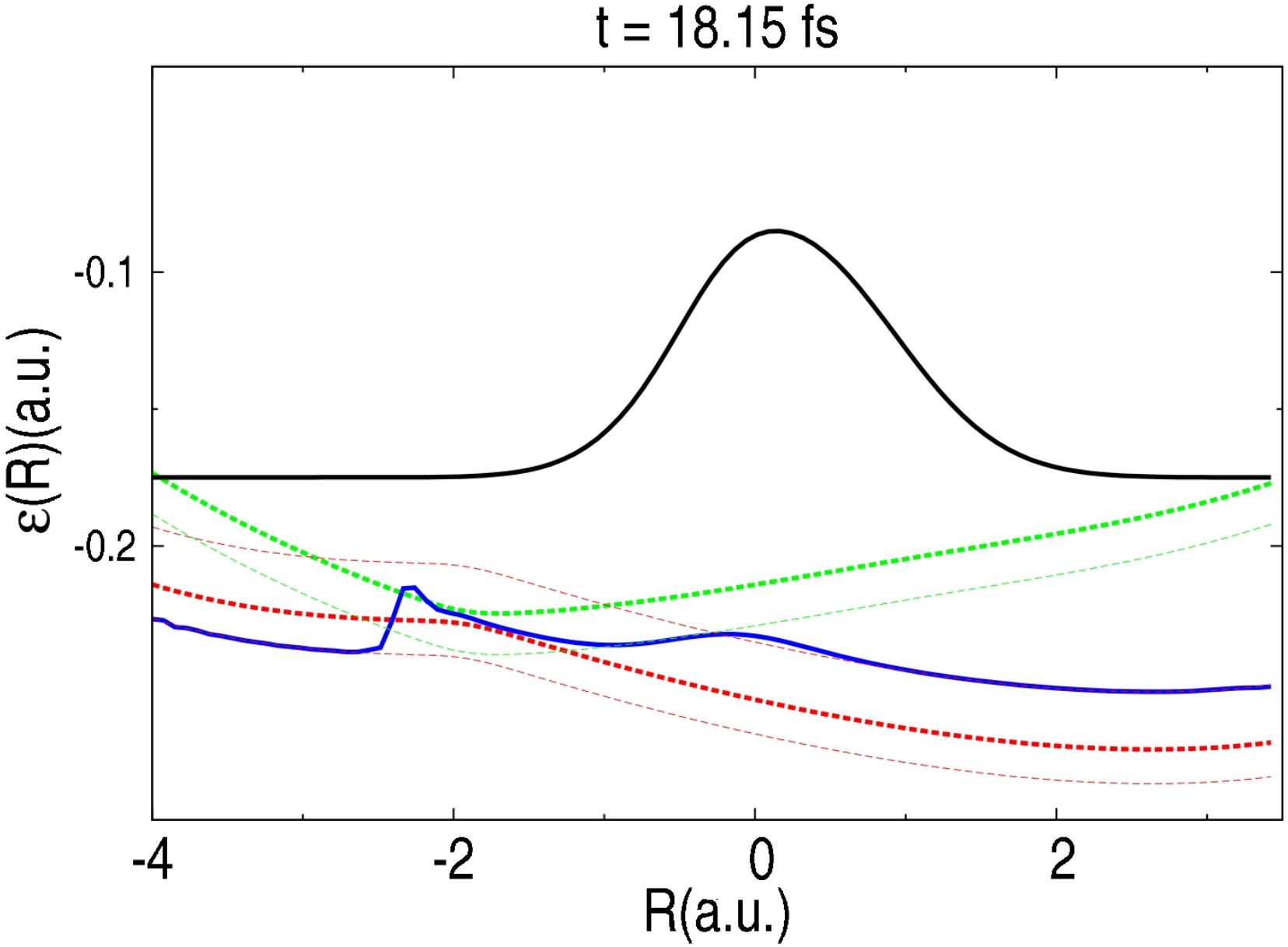

t = "20000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "20000" Nuclear Wavepacket on exact TDPES
t = "20000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "0" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "0" Nuclear Density
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

Shin-Metiu model




t = 10.89 fs
-0.1
-0.2
ε(R)(a.u.)
-4
-2
0
R(a.u.)


t = 18.15 fs
-0.1
-0.2
ε(R)(a.u.)
-4
-2
0
2
R(a.u.)

New MD scheme:

Perform classical limit of the nuclear equation, but retain the exact forces from the exact electronic equation

Nuclear wavefunction

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

Classical limit

$$\begin{cases} \left|\chi(R,t)\right|^2 \to \delta\left(R - R_c(t)\right) \\ \nabla_R S(R,t) \to P_c(t) \end{cases}$$

Hence

$$\frac{-i\hbar\nabla_R\chi}{\chi} \xrightarrow{\hbar\to 0} P_c(t)$$

Expand the exact electronic wave function in the adiabatic basis:

$$\Phi_R(r,t) = \sum_j c_j(R,t)\,\varphi^{BO}_{R,j}(r)$$

Insert this in the (exact) electronic equation of motion:

$$\dot{c}_j(R,t) = f_j\left(\{c_k(R,t)\},\{\nabla_R c_k(R,t)\},\{\nabla^2_R c_k(R,t)\}\right)$$

in the classical limit:

$$\nabla_R c_k(R,t),\ \nabla^2_R c_k(R,t) \to 0$$

i.e. in this limit the $c_k(R,t)$ become independent of R.

In practice we solve the following equations:

$$\dot{c}_j(t) = -\frac{i}{\hbar}\left[\varepsilon_{BO}^{(j)} - \left(V_{eff}^{(I)} + iV_{eff}^{(R)}\right)\right]c_j(t) - \sum_k c_k(t) D_{jk}$$

$$V_{eff}^{(I)} = \sum_j \left|c_j\right|^2 \varepsilon_{R,j}^{BO} + \frac{P \cdot A}{M} + \frac{\hbar^2}{M}\sum_{j<k} \Re\left[c_j^* c_k\right] d_{jk}^{(2)}$$

$$V_{eff}^{(R)} = -\frac{\hbar^2}{M}\sum_{j<k} \Im\left[c_j^* c_k\right] \nabla_R \cdot d_{jk}^{(1)}$$

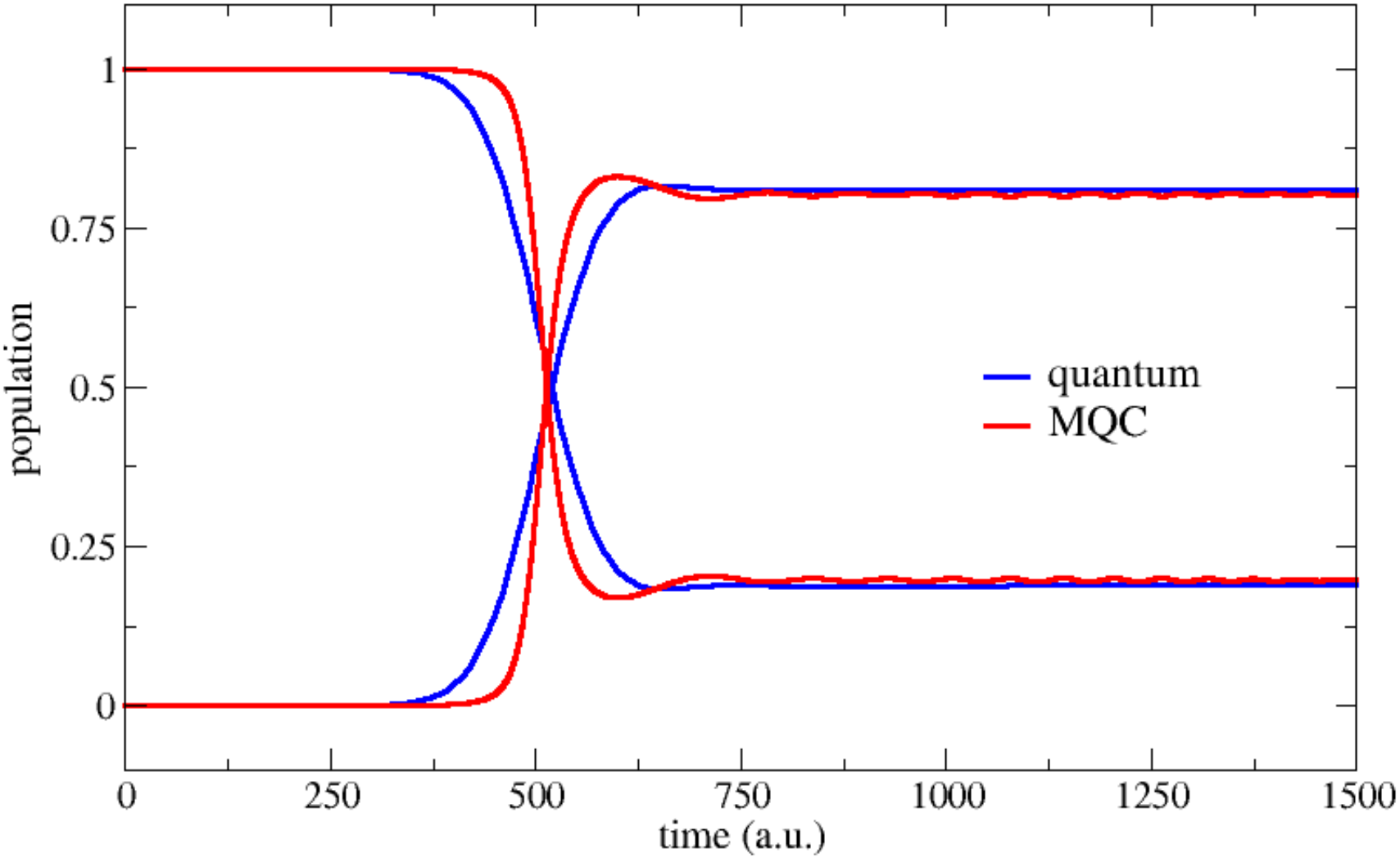
$$D_{jk} = \frac{P}{M} \cdot d_{jk}^{(1)} - \frac{i\hbar}{2M}\left(\nabla_R \cdot d_{jk}^{(1)} - d_{jk}^{(2)}\right)$$

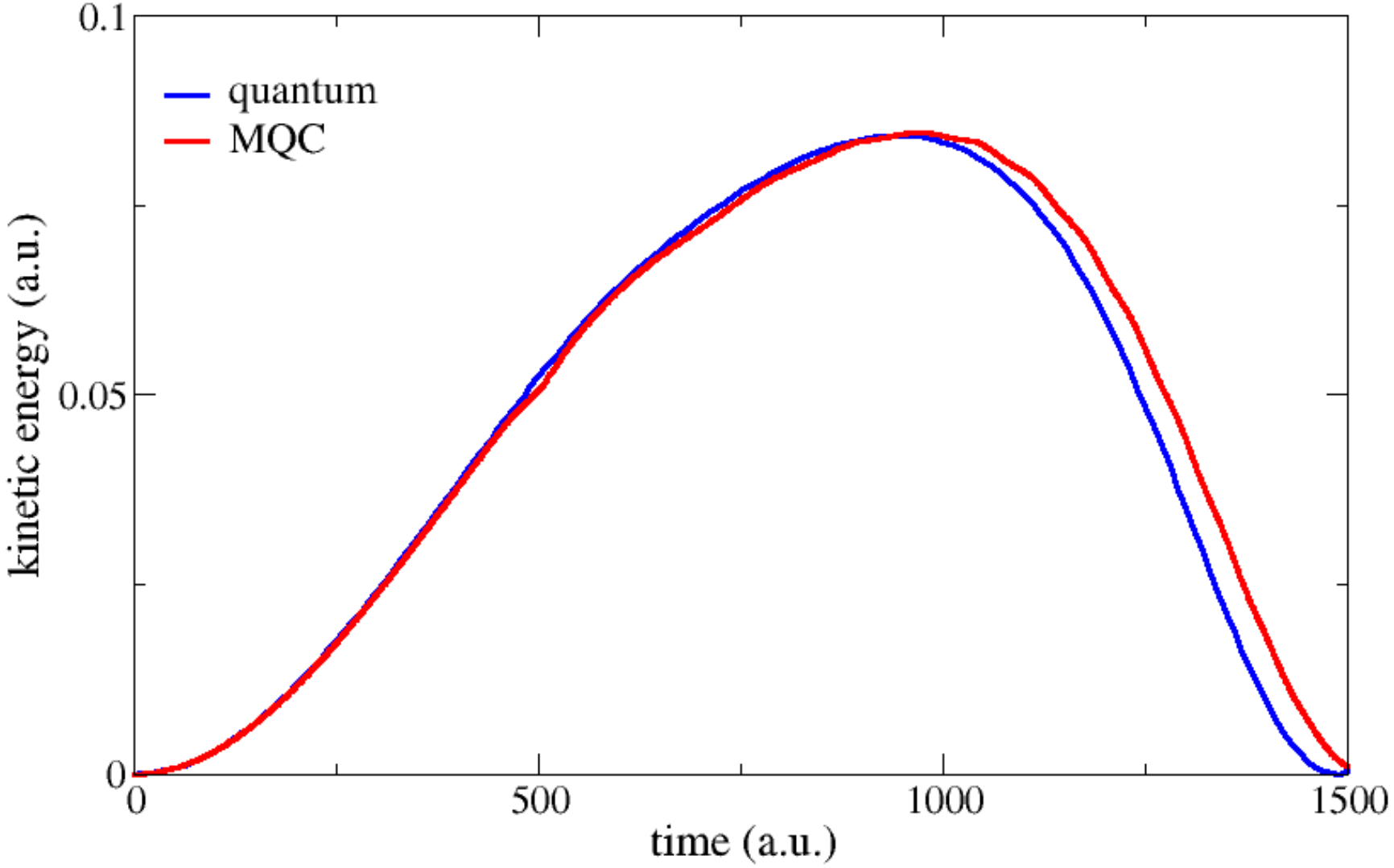
$$d_{jk}^{(1)}(R) = \left\langle \varphi_{R,j}^{BO} \middle| \nabla_R \varphi_{R,k}^{BO} \right\rangle \qquad d_{jk}^{(2)}(R) = \left\langle \nabla_R \varphi_{R,j}^{BO} \middle| \nabla_R \varphi_{R,k}^{BO} \right\rangle$$

and classical EoM for the nuclear Hamiltonian: $H_N = \frac{P^2}{2M} + V_{eff}^{(R)}$

Shin-Metiu model

populations of the BO states as functions of time




nuclear kinetic energy as a function of time
quantum
MQC
kinetic energy (a.u.)
0.1
0.05
0
0
500
1000
1500
time (a.u.)

Summary:

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

- **Eqs. of motion for** $\Phi_{\underline{\underline{\underline{R}}}}\left(\underline{\underline{r}}\right)$ and $\chi\left(\underline{\underline{\underline{R}}}\right)$ **lead to**

  --- exact potential energy surface
  --- exact Berry connection

  both in the static and the time-dependent case

- **TD-PES useful to interpret different dissociation meachanisms**

- **when few PES are involved: Jumps resembling surface hopping**

- **mixed quantum classical algorithm with “non-stochastic surface hopping”**

Thanks !

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