What’s the correct classical force on the nuclei

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What’s the correct classical force on the nuclei or: How to make the Born-Oppenheimer approximation exact

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Hamiltonian for the complete system of N_e electrons and N_n nuclei

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

with $\left(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}\right) \equiv \underline{\underline{\mathbf{r}}}$ $\left(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}\right) \equiv \underline{\underline{\mathbf{R}}}$

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

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

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

Born-Oppenheimer approximation

solve

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

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

Make adiabatic ansatz for the complete molecular wave function:

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

and find best χ^{BO} by minimizing $<\Psi^{BO} \mid H \mid \Psi^{BO}>$ w.r.t. χ^{BO} :

Nuclear equation

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

$$+ \int \Phi^{BO\,*}_{\underline{\underline{R}}}(\underline{\underline{r}})\,\hat{T}_n(\underline{\underline{R}})\,\Phi^{BO}_{\underline{\underline{R}}}(\underline{\underline{r}})\,d\underline{\underline{r}}\Big]\chi^{BO}(\underline{\underline{R}}) = E\chi^{BO}(\underline{\underline{R}})$$

Berry connection

$$\boxed{A^{BO}_{\upsilon}(\underline{\underline{R}}) = \int \Phi^{BO\,*}_{\underline{\underline{R}}}(\underline{\underline{r}})(-i\nabla_{\upsilon})\,\Phi^{BO}_{\underline{\underline{R}}}(\underline{\underline{r}})\,d\underline{\underline{r}}}$$

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

In this context, potential energy surfaces $\in^{BO}(\underline{\underline{R}})$ and the Berry potential $\vec{A}^{BO}(\underline{\underline{R}})$ follow from an APPROXIMATION (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

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

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

In this context, potential energy surfaces $\in^{BO}(\underline{\underline{R}})$ and the Berry potential $\vec{A}^{BO}(\underline{\underline{R}})$ follow from an APPROXIMATION (the BO approximation).

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

GOING BEYOND BORN-OPPENHEIMER

Standard procedure:

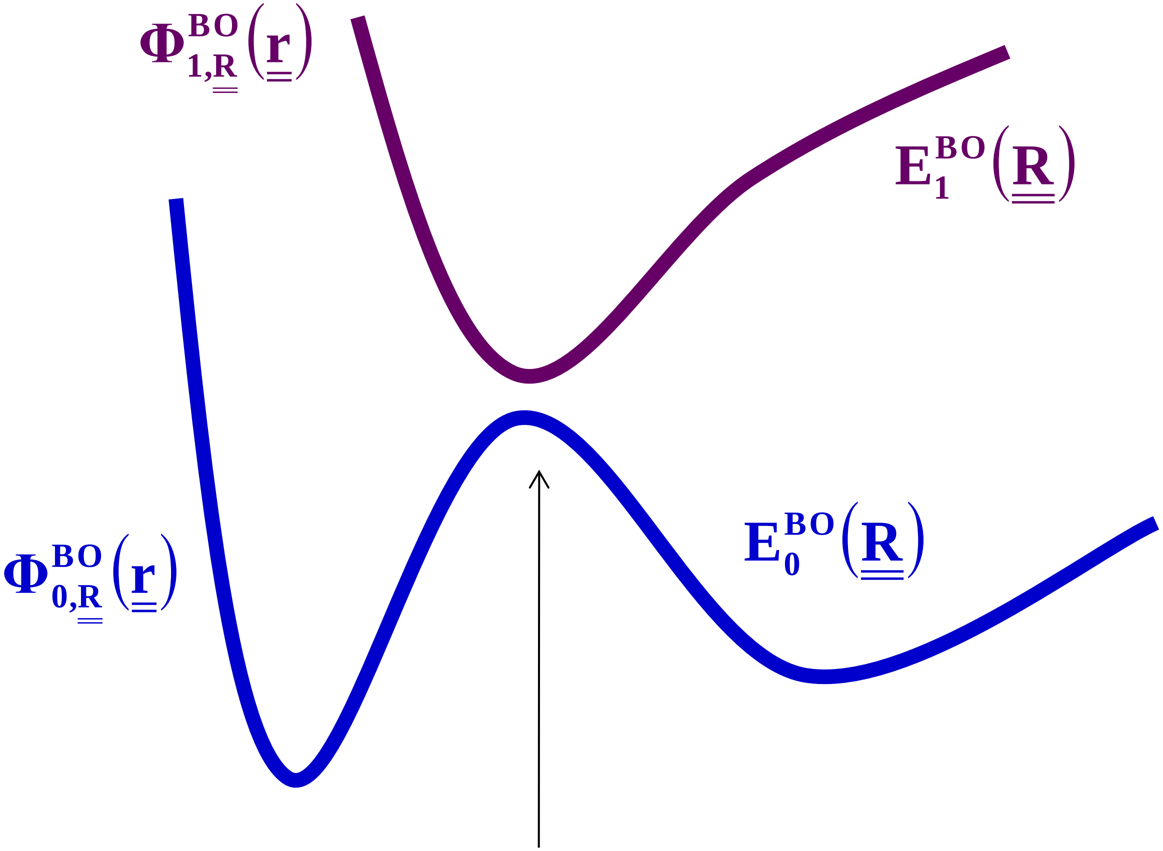
Expand full molecular wave function in complete set of BO states:

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

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.**

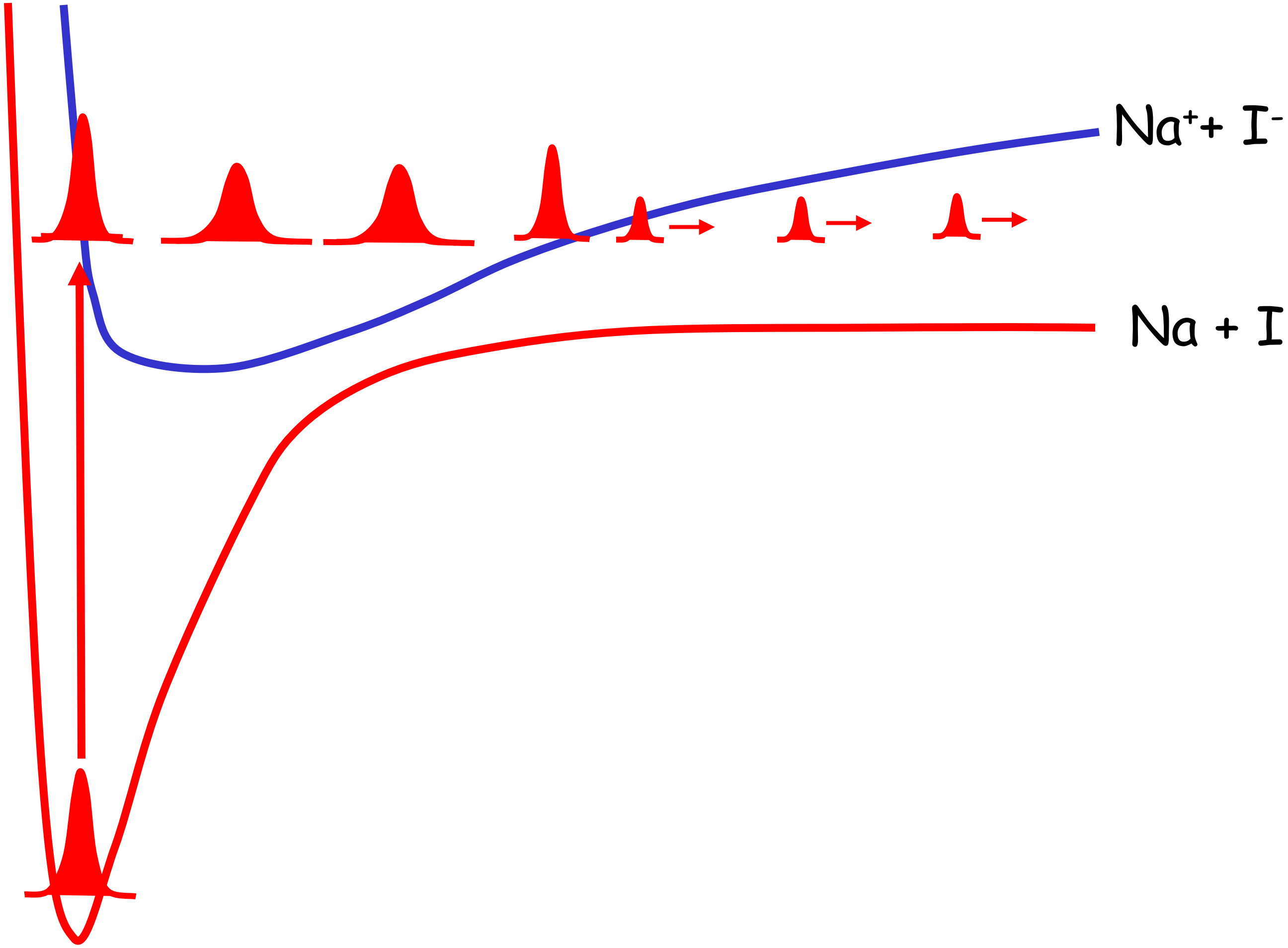


$$\Psi_0\left(\underline{\underline{r}},\underline{\underline{R}}\right) \approx \chi_{00}\left(\underline{\underline{R}}\right)\Phi^{BO}_{0,\underline{\underline{R}}}\left(\underline{\underline{r}}\right) + \chi_{01}\left(\underline{\underline{R}}\right)\Phi^{BO}_{1,\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

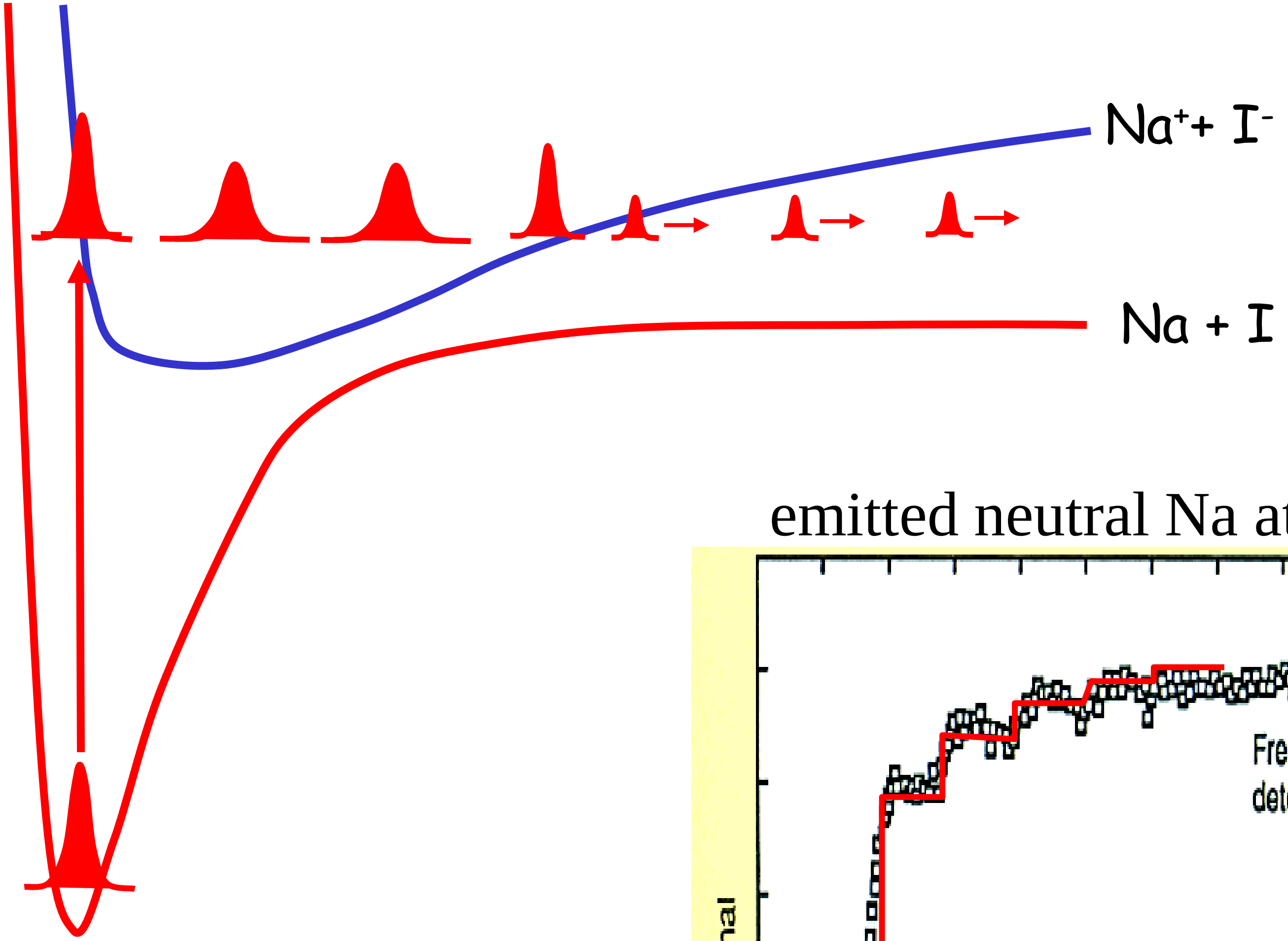
Potential energy surfaces are absolutely essential in our understanding of a molecule

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

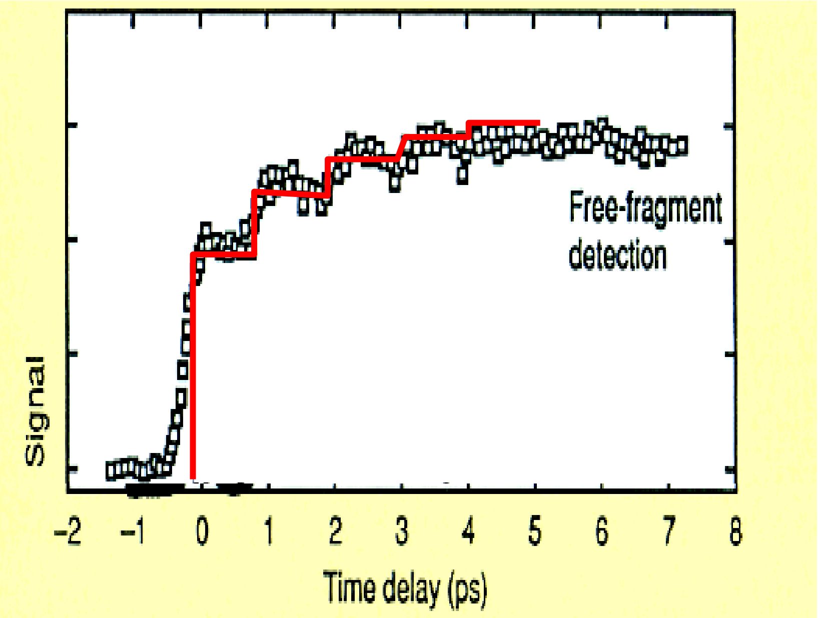
Example: NaI femtochemistry



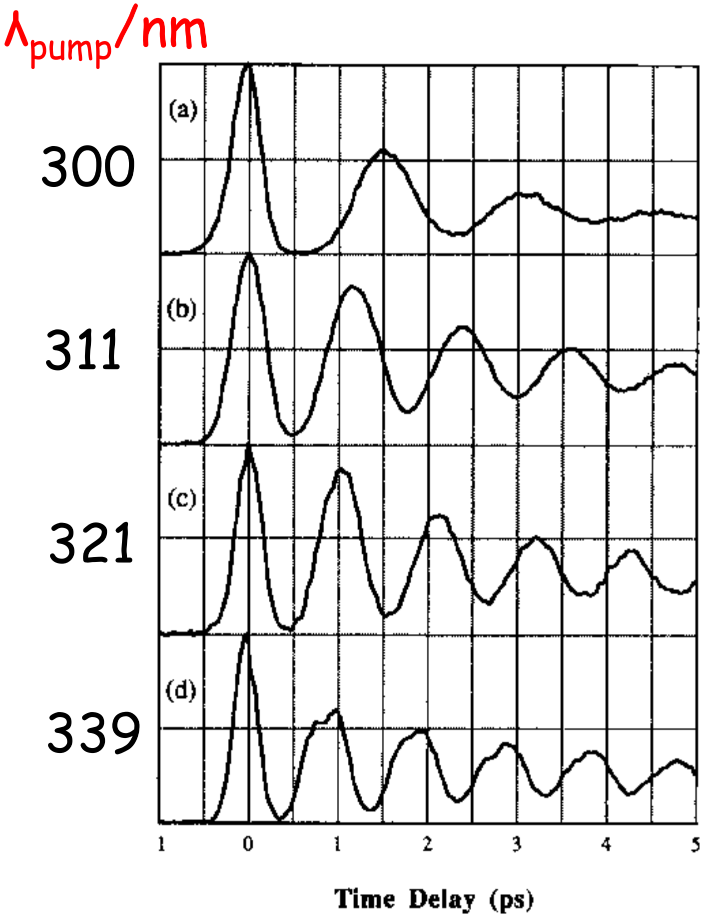
Example: NaI femtochemistry

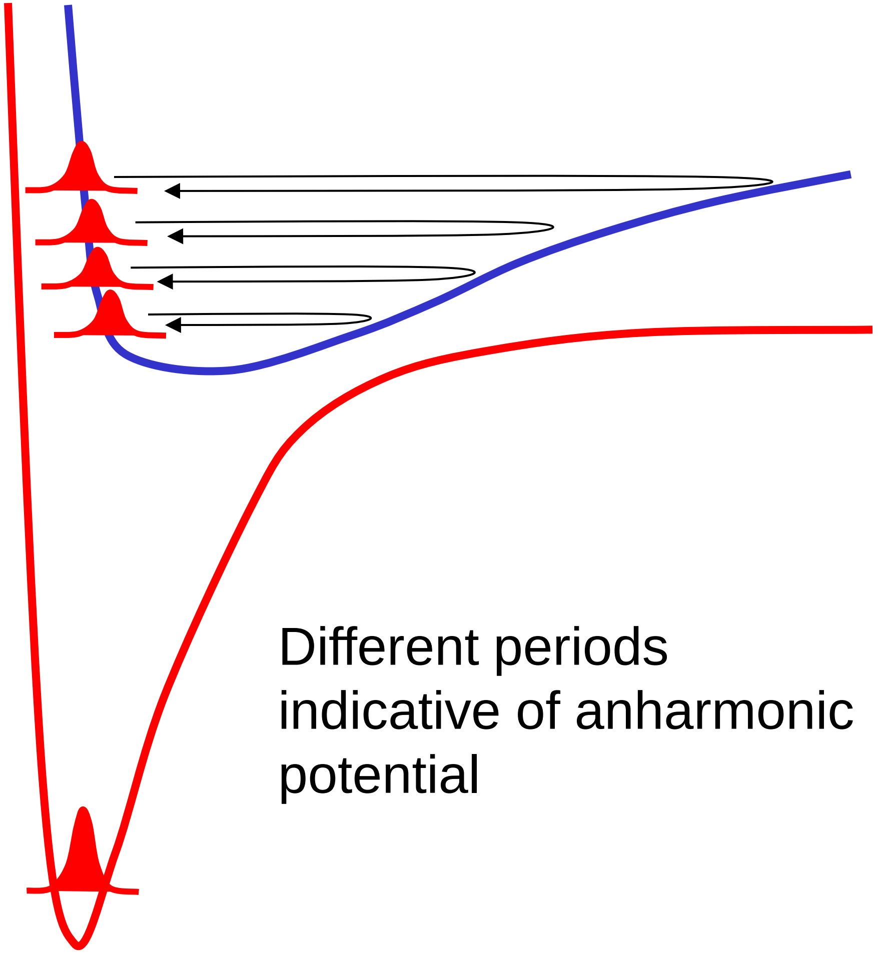


emitted neutral Na atoms



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)

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

OUTLINE

- **Show that the factorisation**

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

  can be made exact

- **Concept of exact PES and exact Berry phase**

- **Concept of time-dependent PES for nuclear motion**

- **Concept of time-dependent PES for electronic motion**

- **Mixed quantum-classical treatment**

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

can be made exact

- **Concept of exact PES and exact Berry phase**
- **Concept of time-dependent PES for nuclear motion**
- **Concept of time-dependent PES for electronic motion**
- **Mixed quantum-classical treatment**

Thanks

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Theorem I

The exact solutions of

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

can be written in the form

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

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

First mentioned in: G. Hunter, Int. J.Q.C. $\underline{9}$, 237 (1975)

Immediate consequences of Theorem I:

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

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

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

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

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

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

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

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

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

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

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

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

Eq. ❶

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

Eq. ❷

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

where

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

Proof in: N.I. Gidopoulos, EKUG, arXiv:cond-mat/0502433

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

Eq. ❶

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

Eq. ❷

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

where

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

<u>Exact</u> PES

<u>Exact</u> Berry connection

Proof in: N.I. Gidopoulos, EKUG, arXiv:cond-mat/0502433

OBSERVATIONS:

- Eq. ❶ is a nonlinear equation in $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{r}})$
- Eq. ❶ contains $\chi(\underline{\underline{R}})$ ⇒ 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 $\Psi = \Phi_{\underline{\underline{\mathbf{r}}}}(\underline{\underline{R}})\chi(\underline{\underline{r}})$
  (electrons move on the nuclear energy surface)

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

$$\Phi \to \tilde{\Phi} = e^{i\theta(\underline{\underline{\mathbf{R}}})}\Phi$$

$$\chi \to \tilde{\chi} = e^{-i\theta(\underline{\underline{\mathbf{R}}})}\chi$$

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

$$\in(\underline{\underline{R}}) \to \tilde{\in}(\underline{\underline{R}}) = \in(\underline{\underline{R}})$$

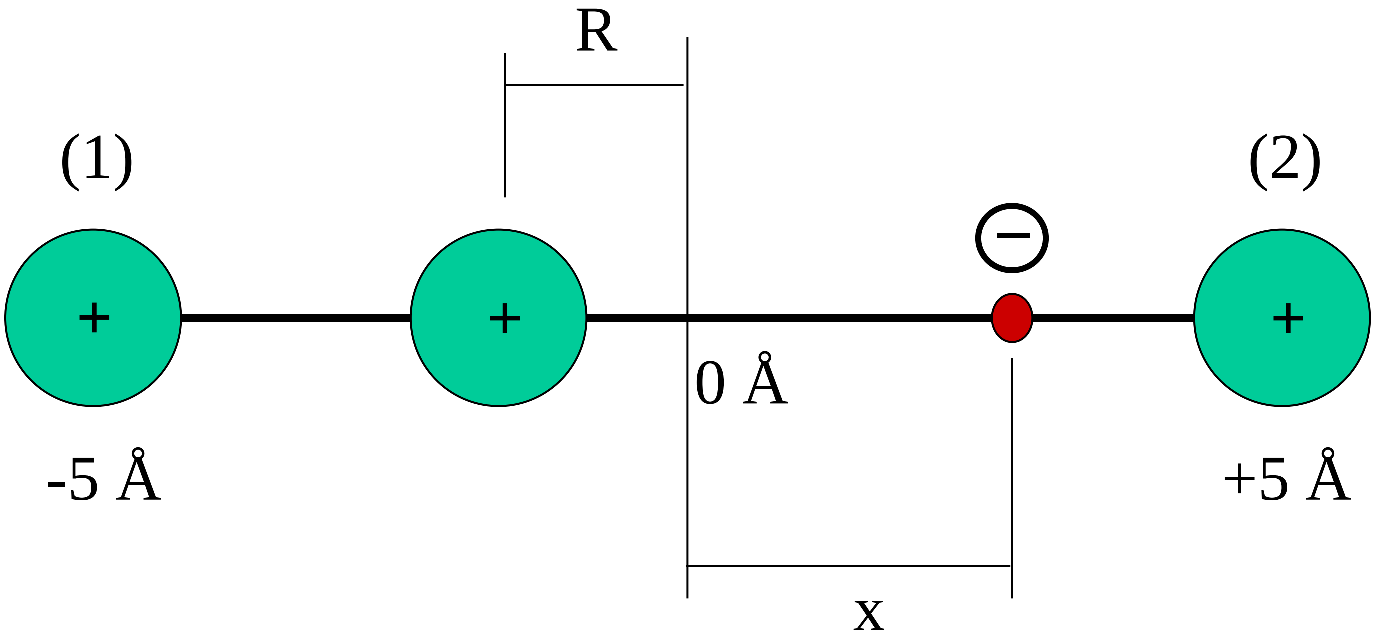
Exact potential energy surface is gauge invariant.

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

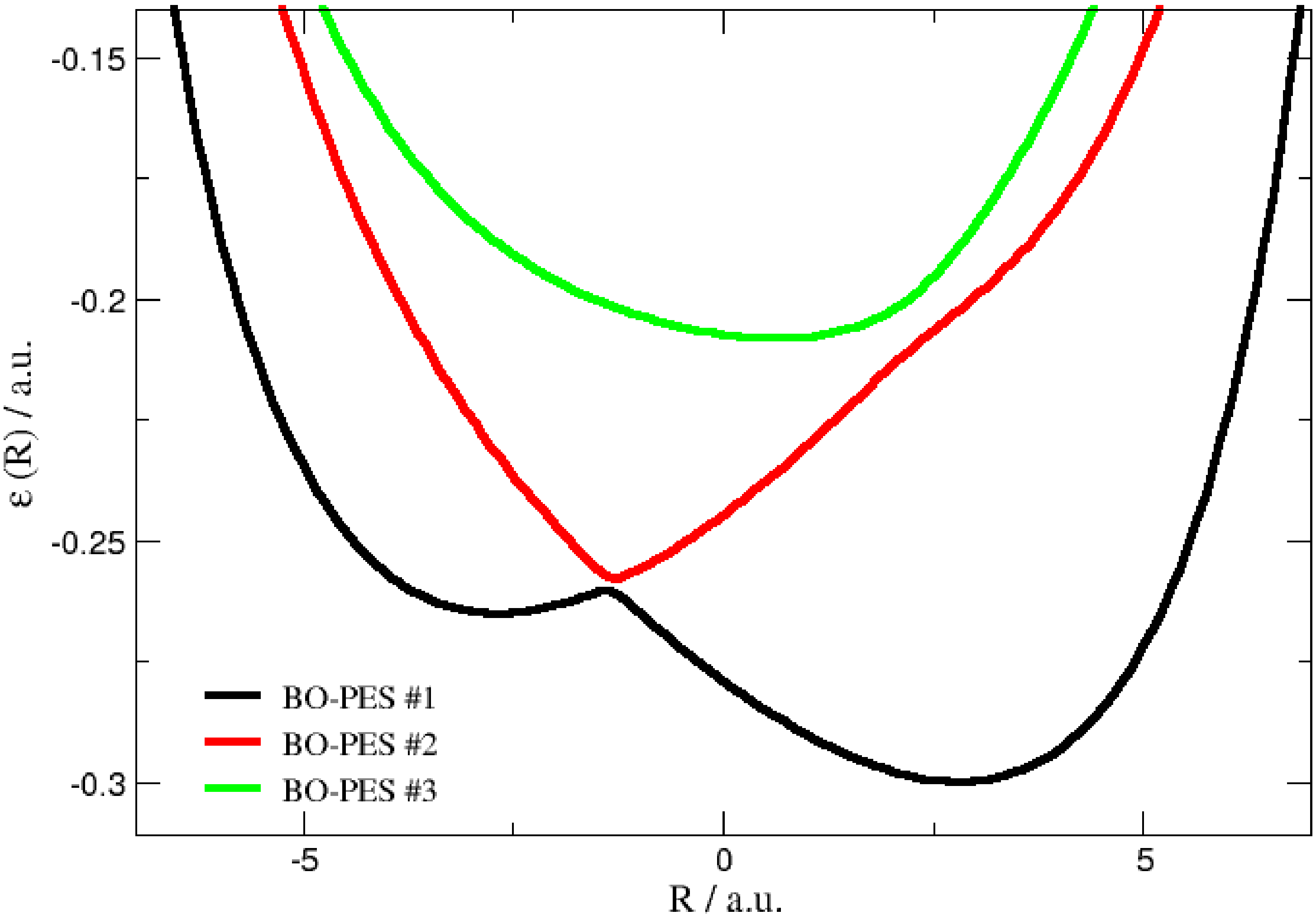
How do the exact PES look like?

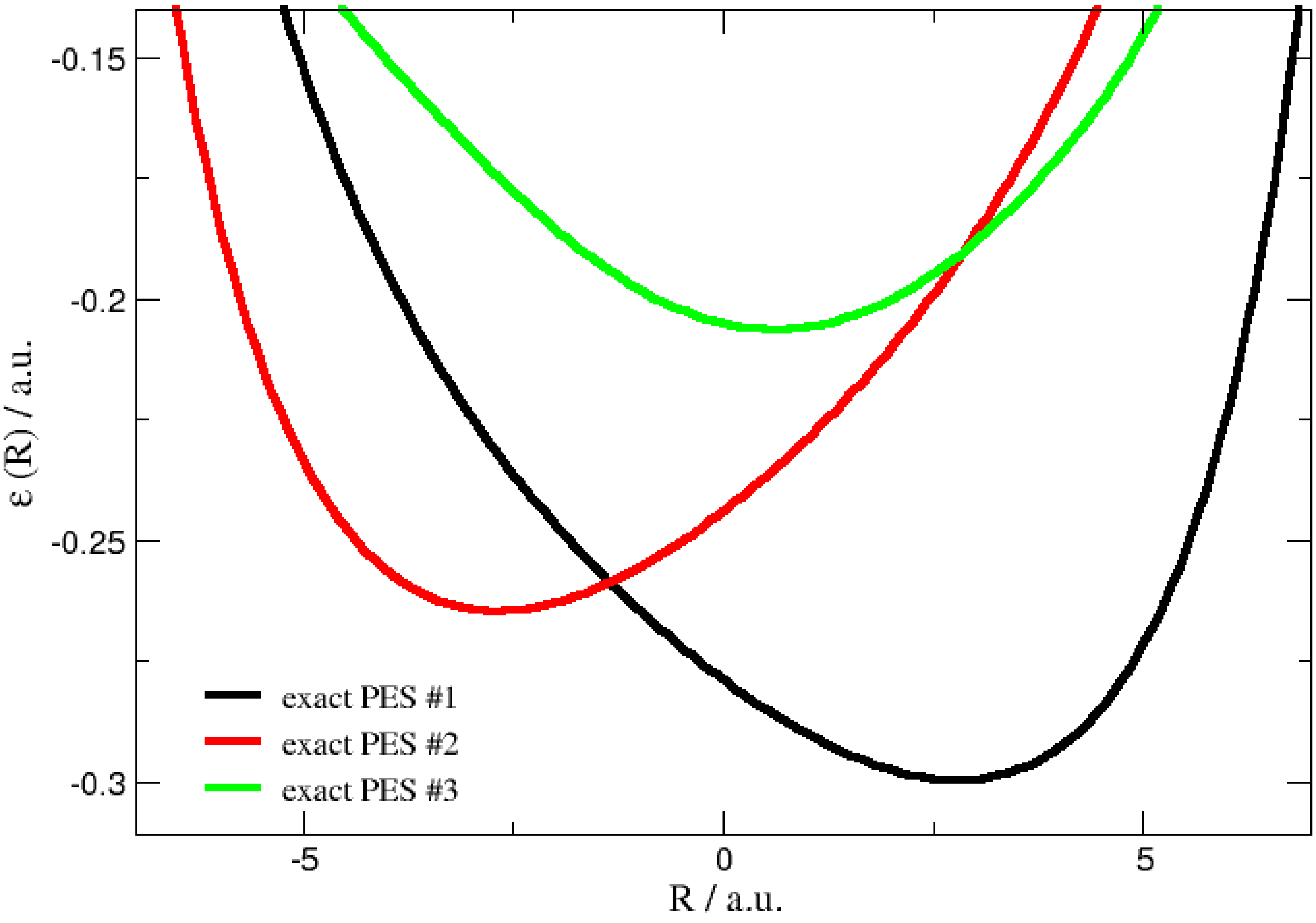
MODEL

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:

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

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

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

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

with the exact nuclear current density J_{ν}

Another way of reading this equation:

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

Conclusion: The nuclear Schrödinger equation

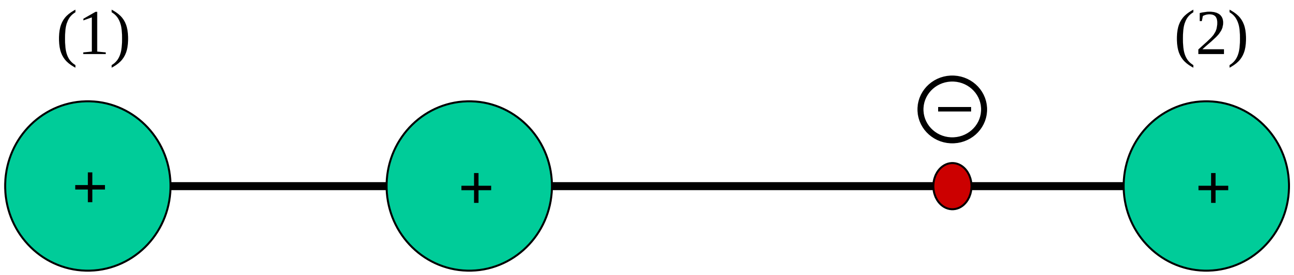
$$\boxed{\left(\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu+A_\nu\right)^2+\hat{W}_{nn}+\hat{V}_n^{ext}+\epsilon\left(\underline{\underline{R}}\right)\right)\chi\left(\underline{\underline{R}}\right)=E\chi\left(\underline{\underline{R}}\right)}$$

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

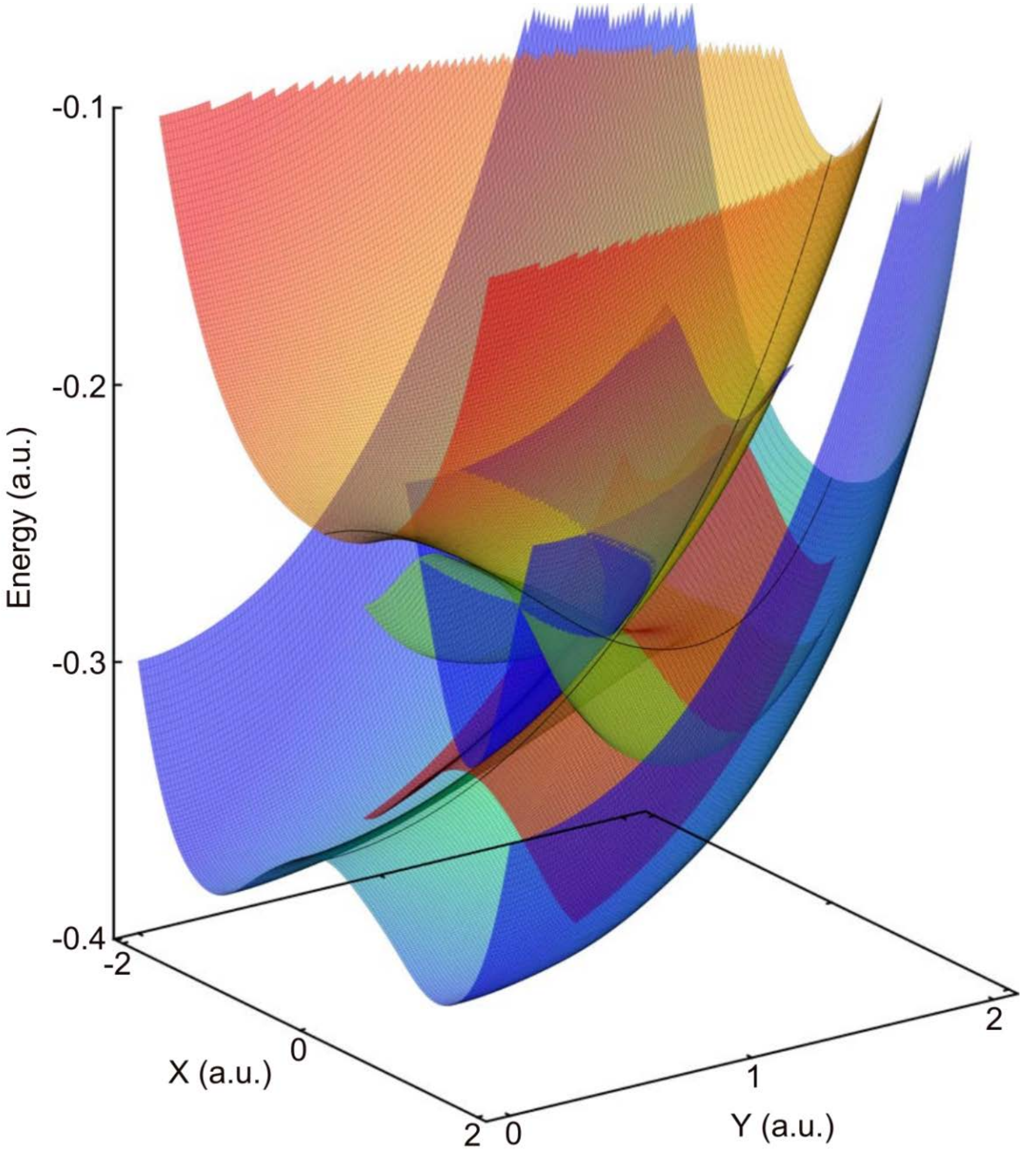
Question: Can the true vector potential be gauged away,
i.e. is the true Berry phase zero?

<u>Question</u>: Can the true vector potential be gauged away, i.e. is the true Berry phase zero?

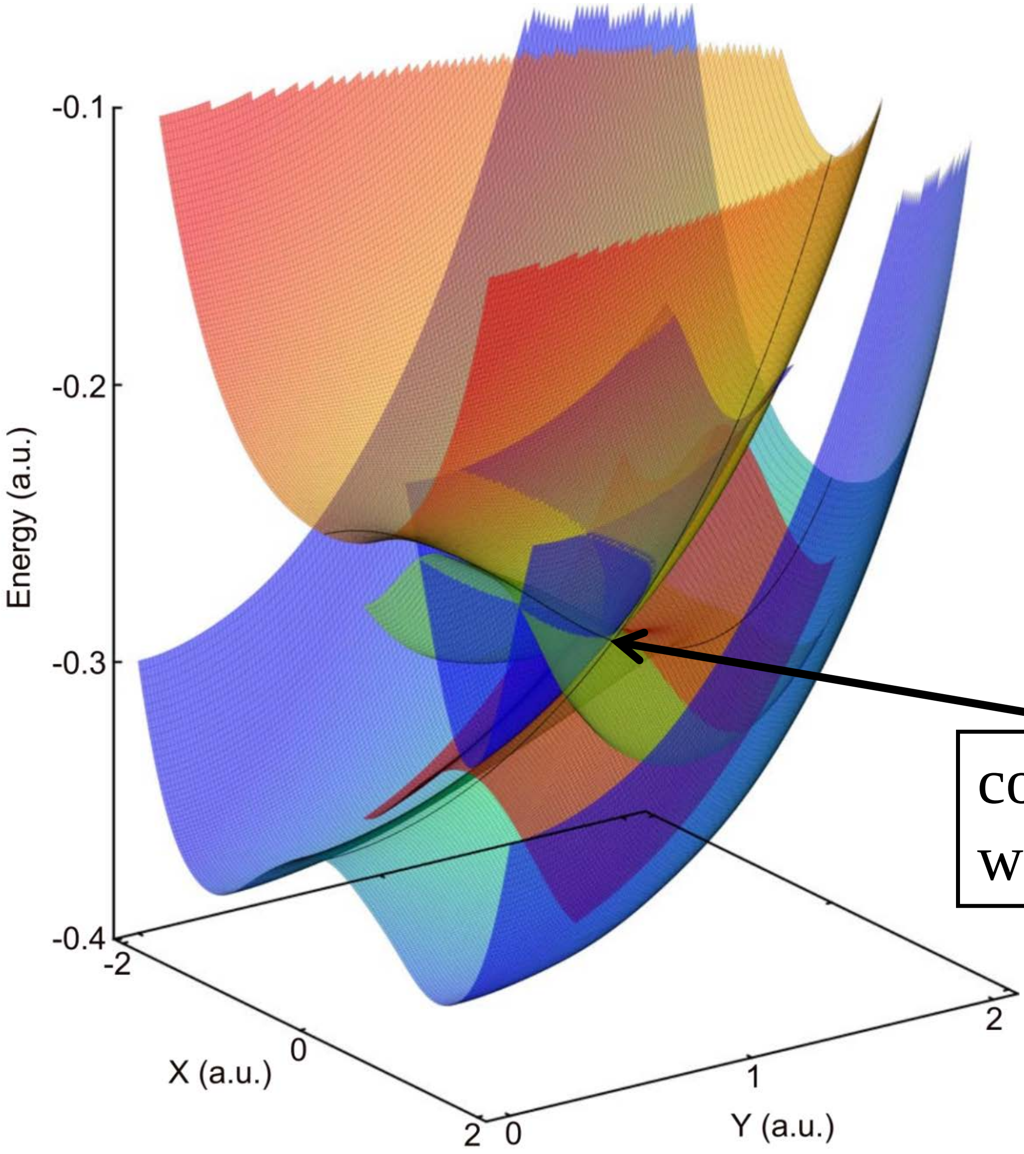
Look at Shin-Metiu model in 2D:



BO-PES of 2D Shin-Metiu model



BO-PES of 2D Shin-Metiu model



conical intersection
with Berry phase

- Non-vanishing Berry phase results from a non-analyticity in the electronic wave function $\Phi^{\mathrm{BO}}_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathrm{r}}}\right)$ as function of R.

- Such non-analyticity is found (for the 2D Shin-Metiu model) in the BO approximation.

- Non-vanishing Berry phase results from a non-analyticity in the electronic wave function $\Phi^{\mathrm{BO}}_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathrm{r}}}\right)$ as function of R.

- Such non-analyticity is found (for the 2D Shin-Metiu model) in the BO approximation.

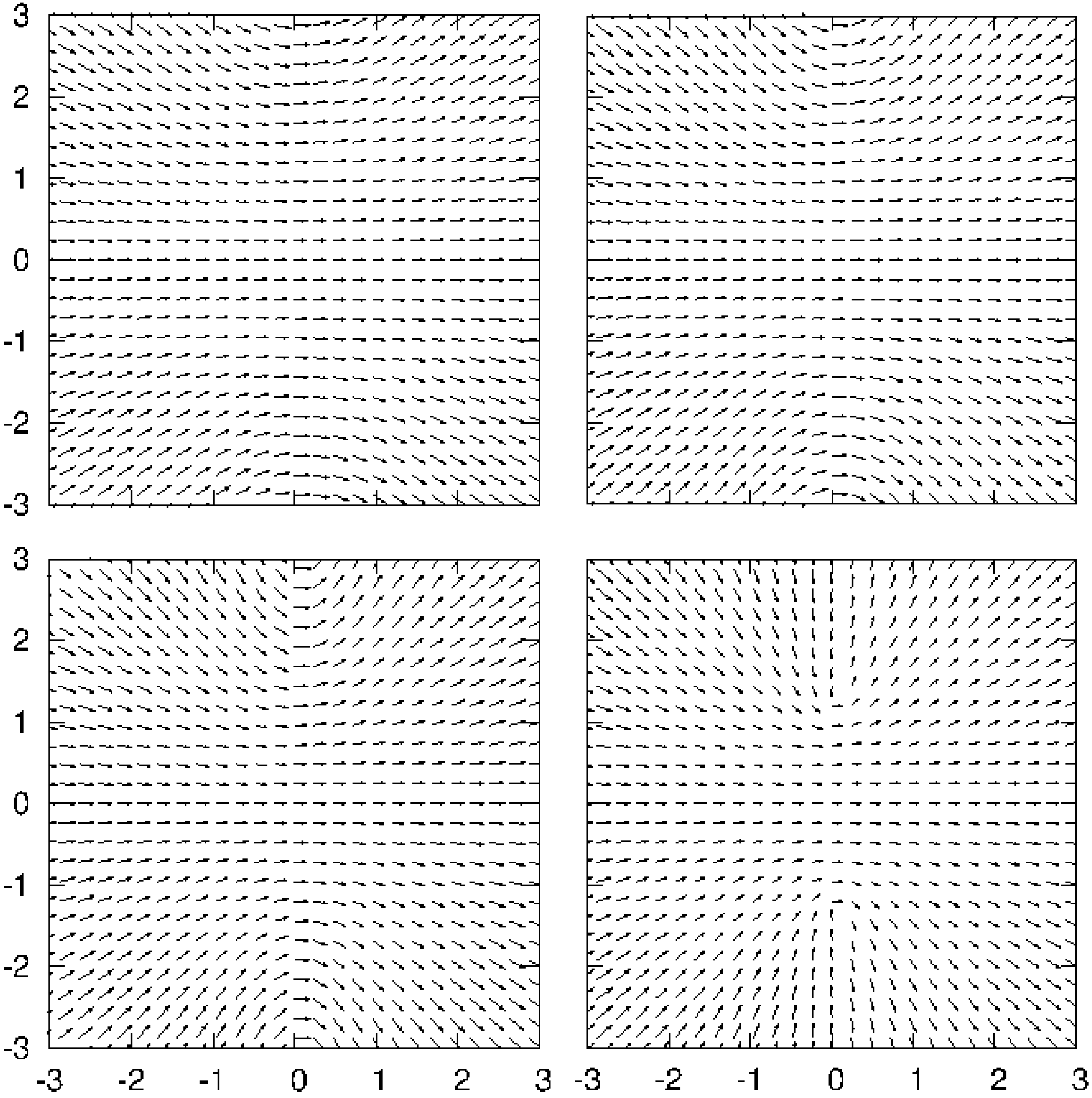
Does the exact electronic wave function show such non-analyticity as well (in 2D Shin-Metiu model)?

Look at

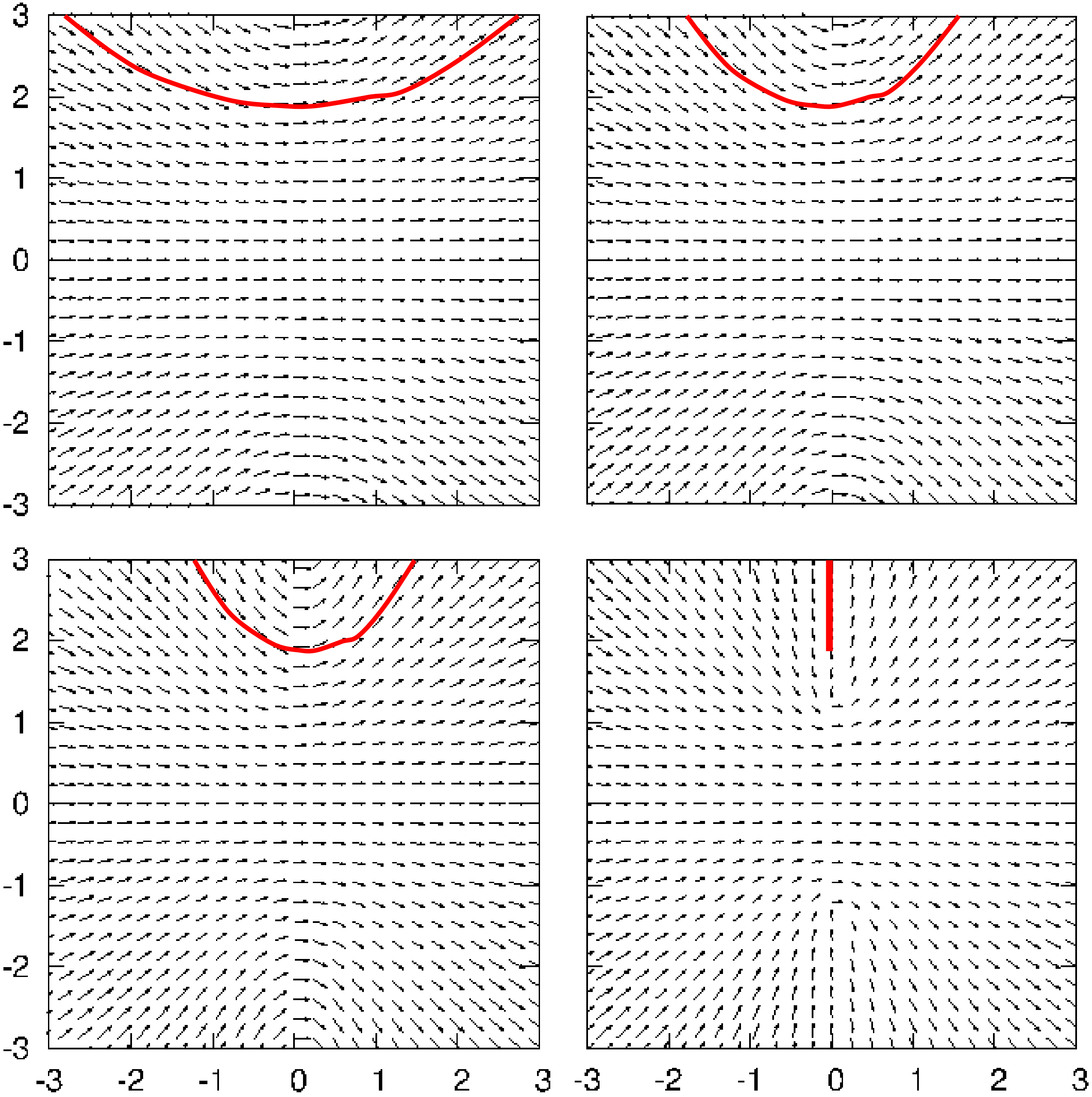
$$\mathrm{D}\left(\mathbf{R}\right) = \int \mathbf{r}\,\boldsymbol{\Phi}_{\mathbf{R}}\left(\mathbf{r}\right)d\mathbf{r}$$

as function of nuclear mass M.

D(R)



$M = \infty$



$\mathbf{M} = \infty$

QUESTION: Can one prove <u>in general</u> that the exact molecular Berry phase vanishes? Are there systems where the exact Berry phase does not vanish?

Time-dependent case

Hamiltonian for the complete system of N_e electrons with coordinates $\left(r_1 \cdots r_{N_e}\right) \equiv \underline{\underline{r}}$ and N_n nuclei with coordinates $\left(R_1 \cdots R_{N_n}\right) \equiv \underline{\underline{R}}$, masses $M_1 \cdots M_{N_n}$ and charges $Z_1 \cdots Z_{N_n}$.

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

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

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

Time-dependent Schrödinger equation

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

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

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)

JCP 137, 22A530 (2012)

Theorem T-II

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

Eq. ❶

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

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

Eq. ❷

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

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

Theorem T-II

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

Eq. ❶

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

Eq. ❷

Exact TD Berry connection

Exact TDPES

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

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

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

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

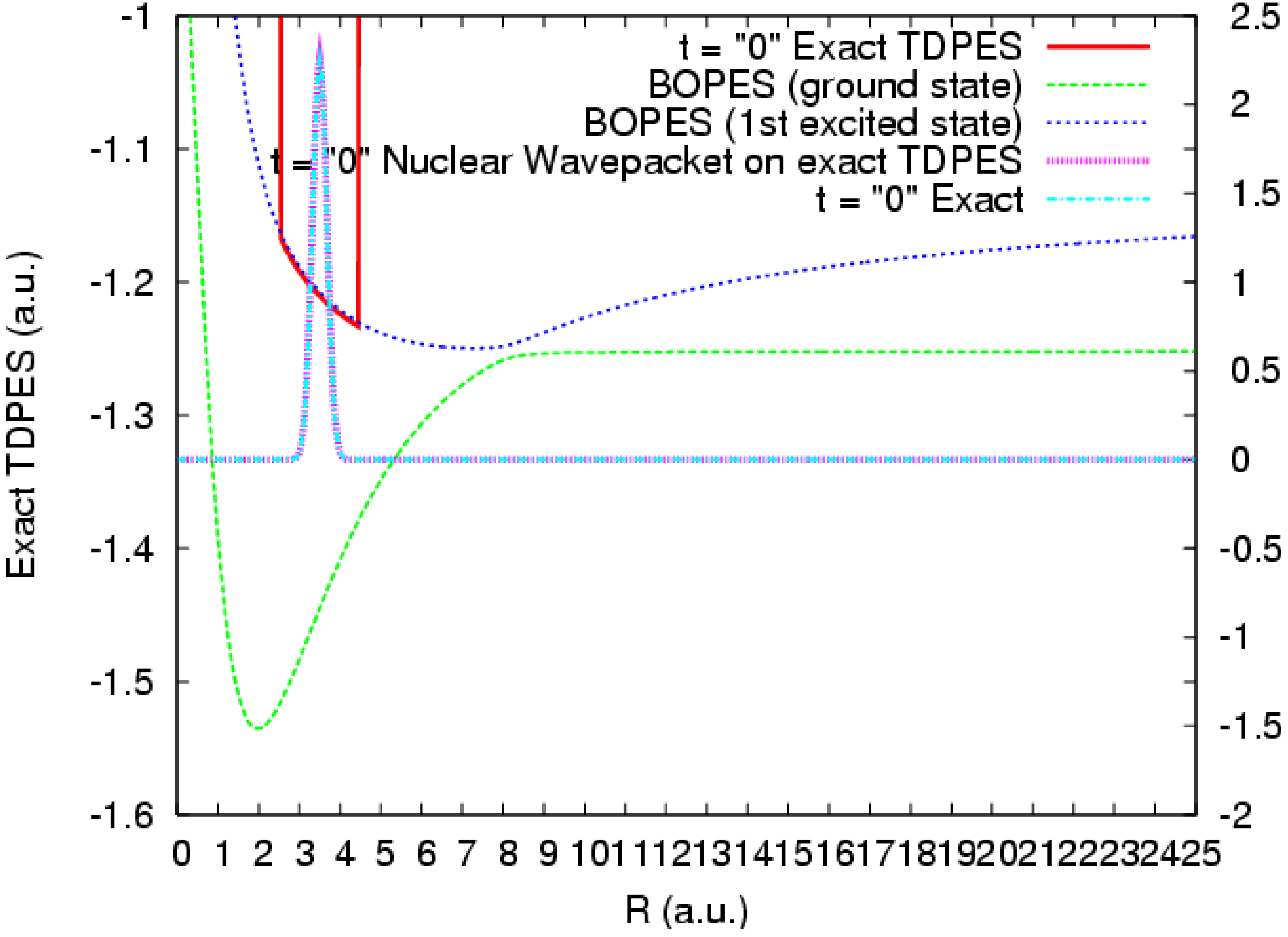
N-body version of Runge-Gross theorem guarantees that ϵ(R,t) and A(R,t) are UNIQUE (up to within a gauge transformation)

How does the exact time-dependent PES look like??

Example: Nuclear WP 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. (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
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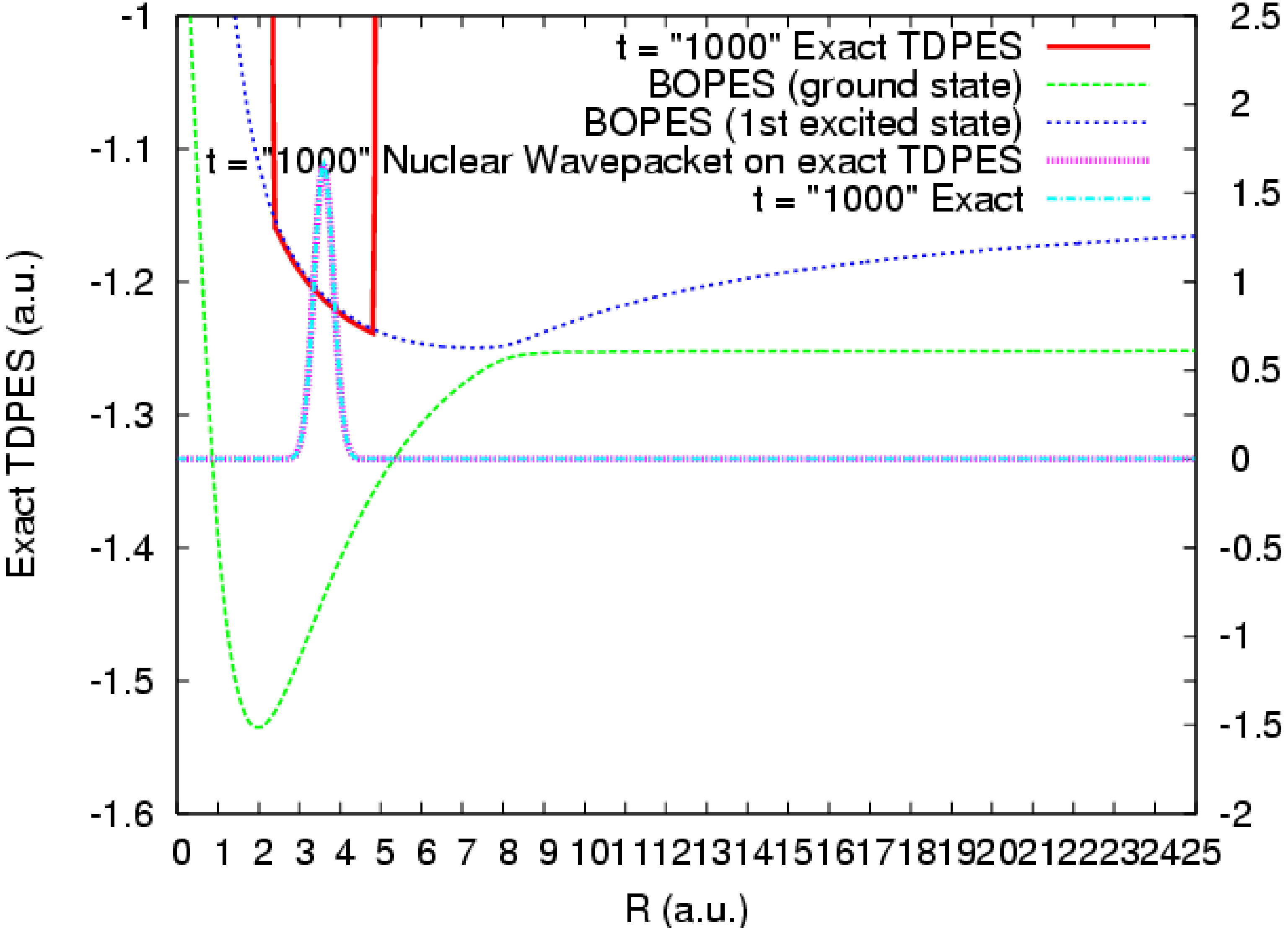
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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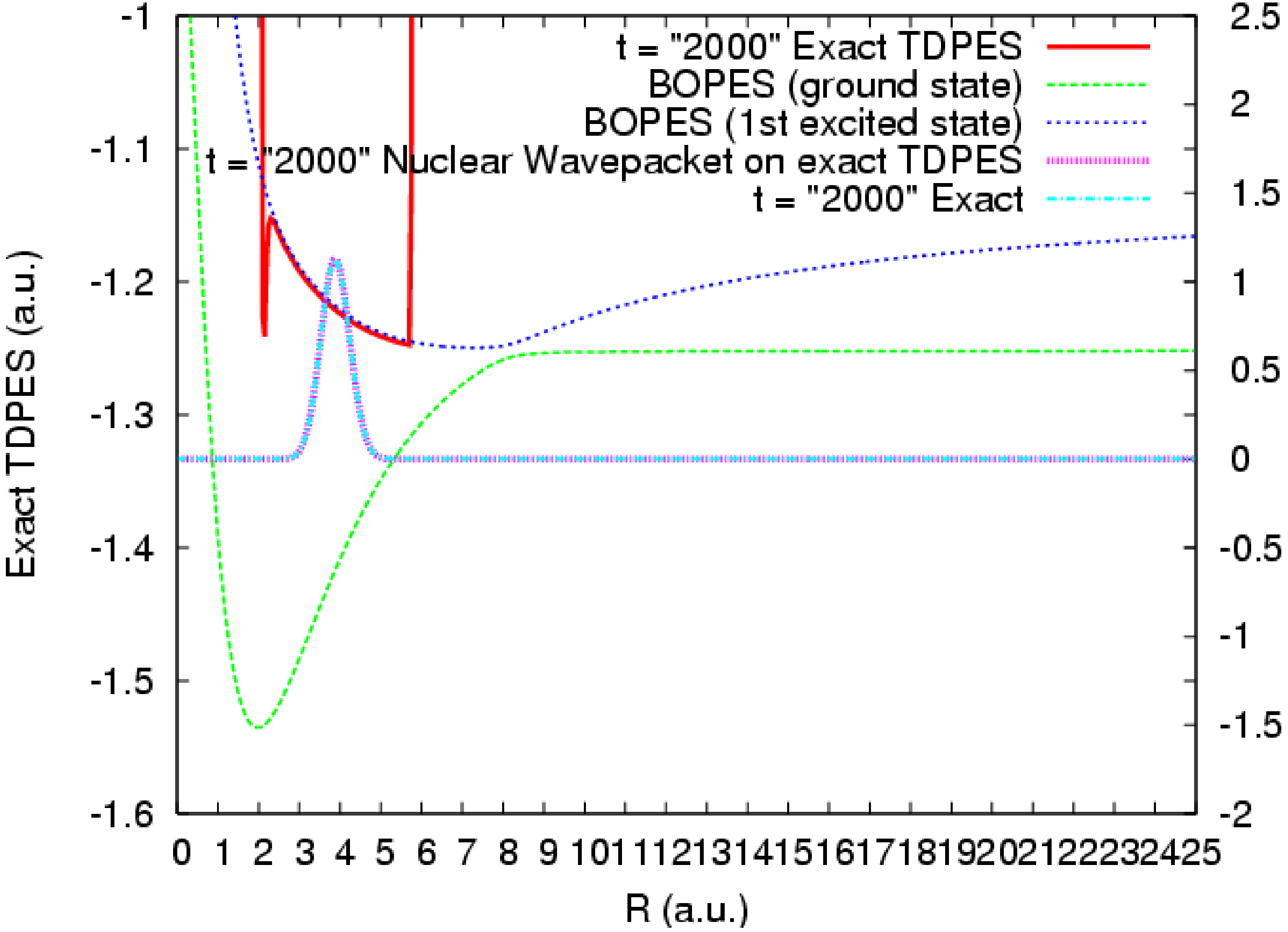
BOPES (ground state)
BOPES (1st excited state)
t = "1000" Nuclear Wavepacket on exact TDPES
t = "1000" Exact
Exact TDPES (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
R (a.u.)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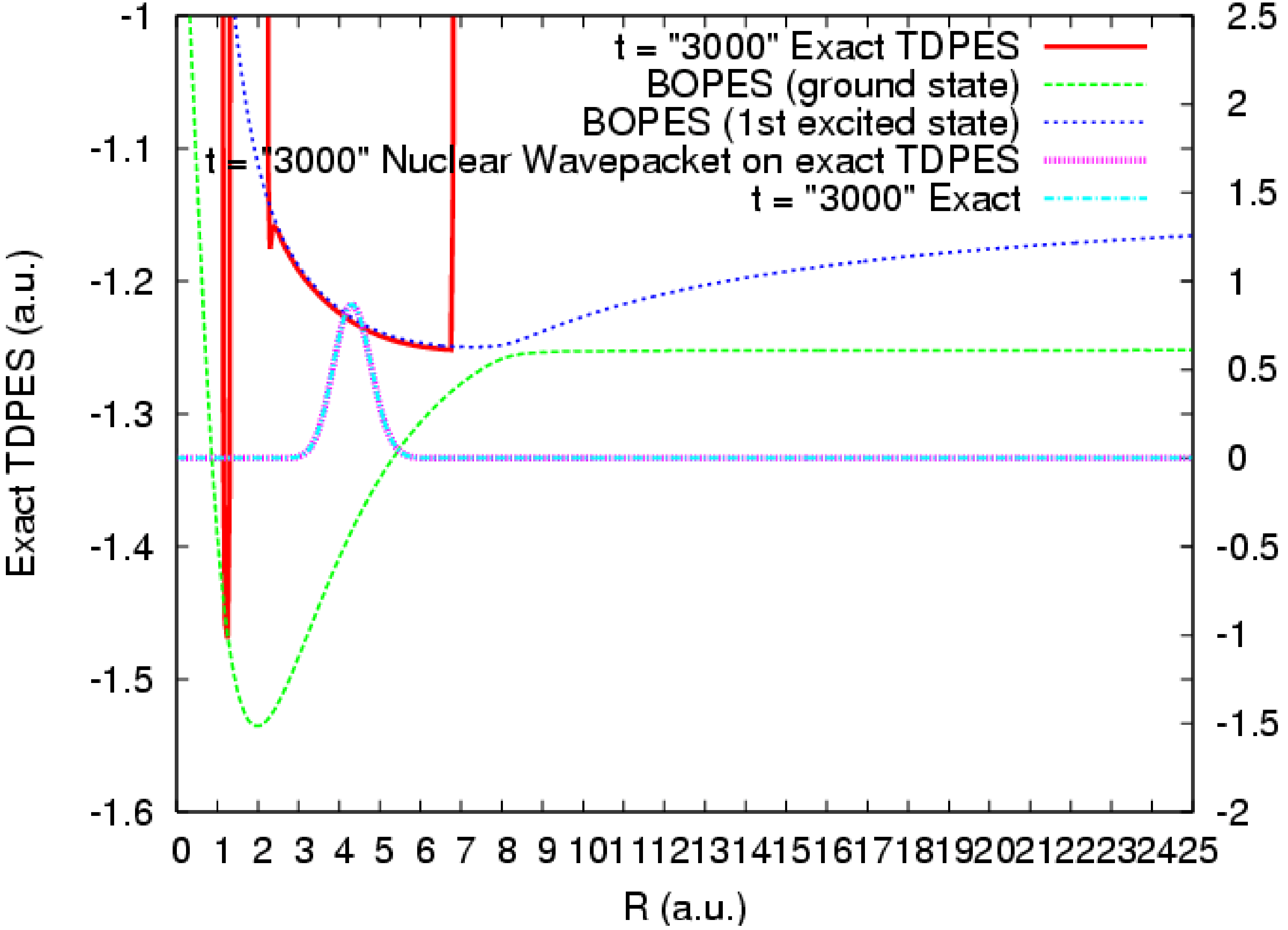
BOPES (ground state)
BOPES (1st excited state)
t = "2000" Nuclear Wavepacket on exact TDPES
t = "2000" Exact
Exact TDPES (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
R (a.u.)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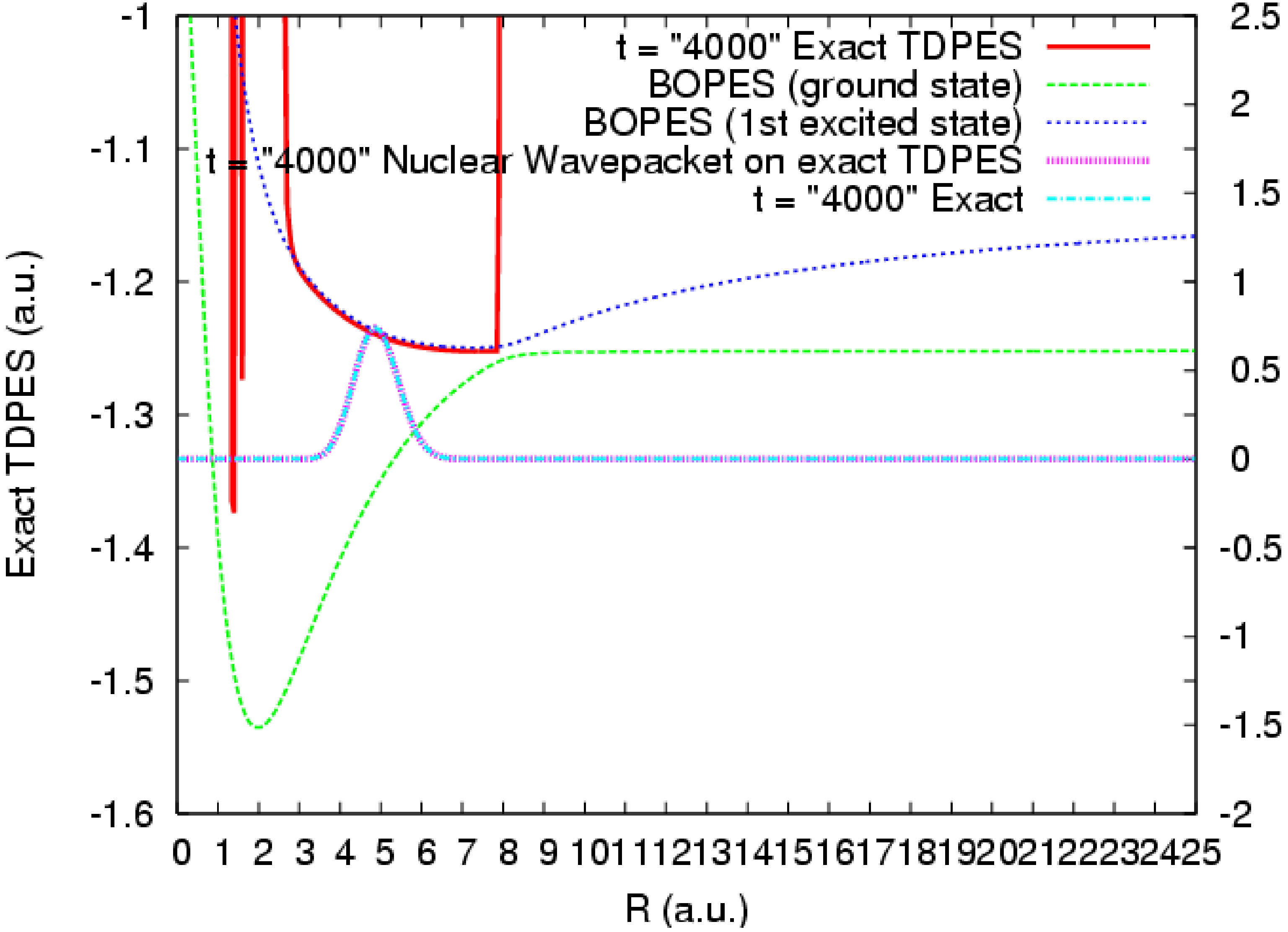
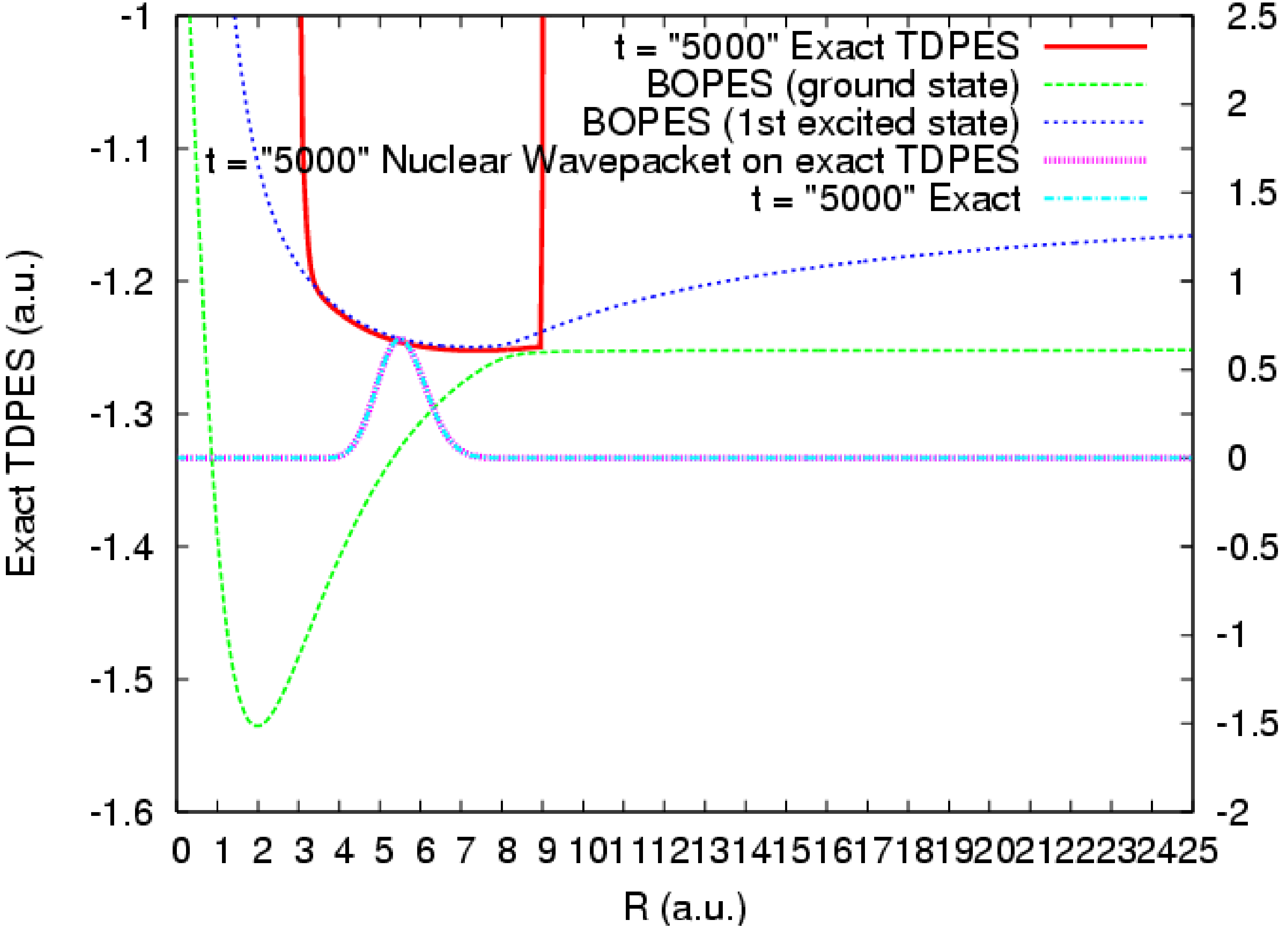
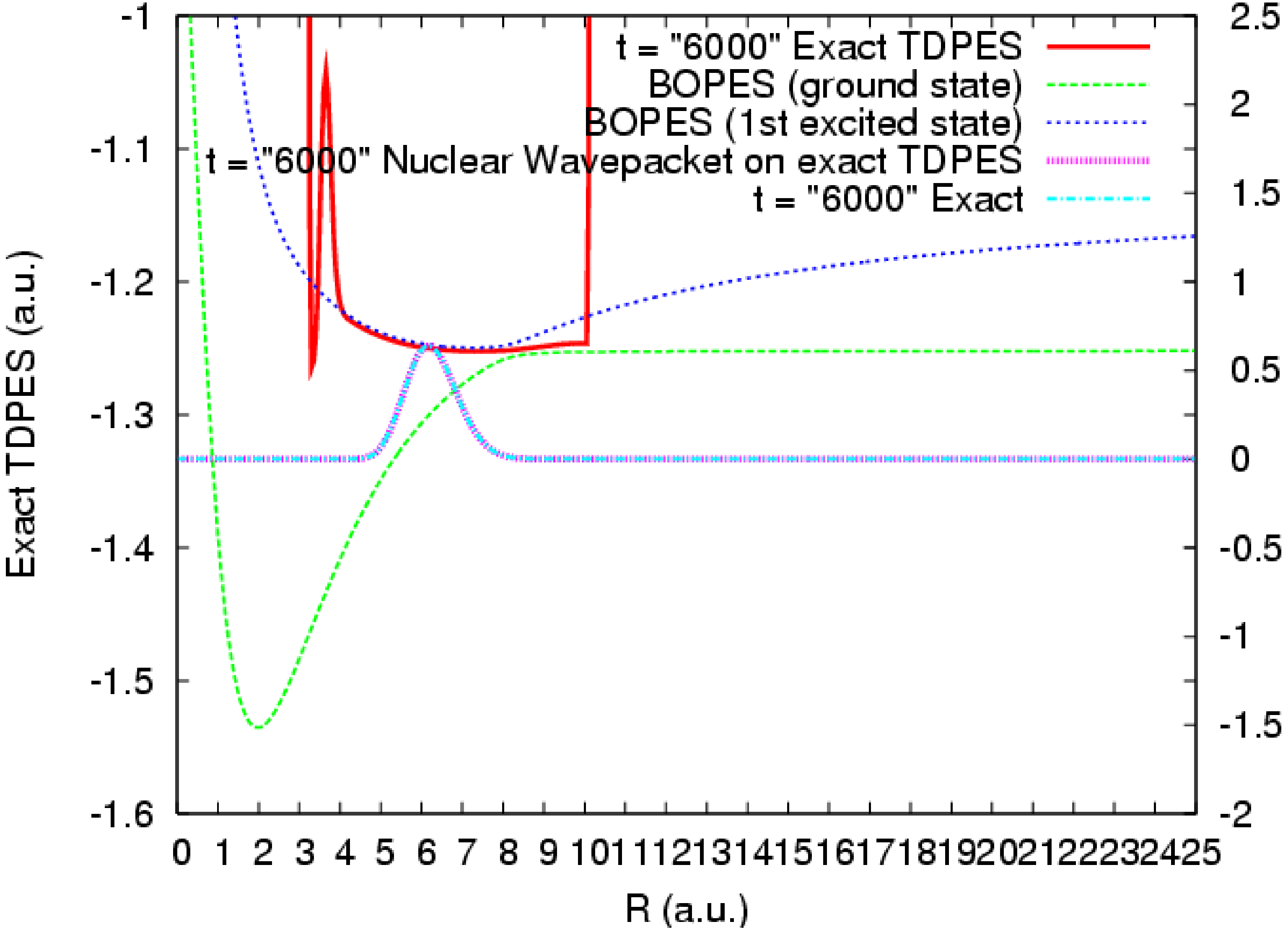
BOPES (ground state)
BOPES (1st excited state)
t = "3000" Nuclear Wavepacket on exact TDPES
t = "3000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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.)
-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
R (a.u.)



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.)
-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
R (a.u.)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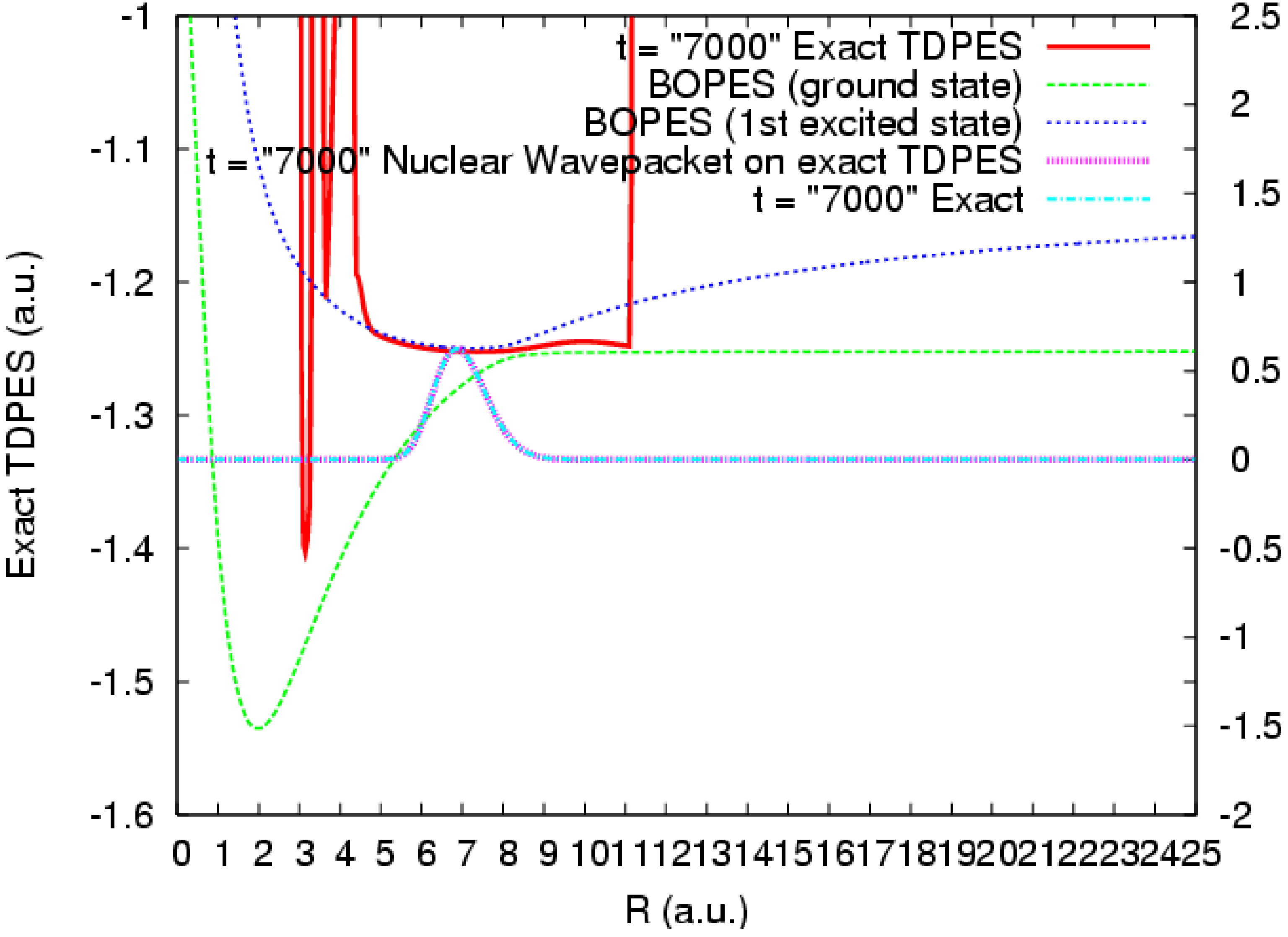
BOPES (ground state)
BOPES (1st excited state)
t = "6000" Nuclear Wavepacket on exact TDPES
t = "6000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (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
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-0.5
-1
-1.5
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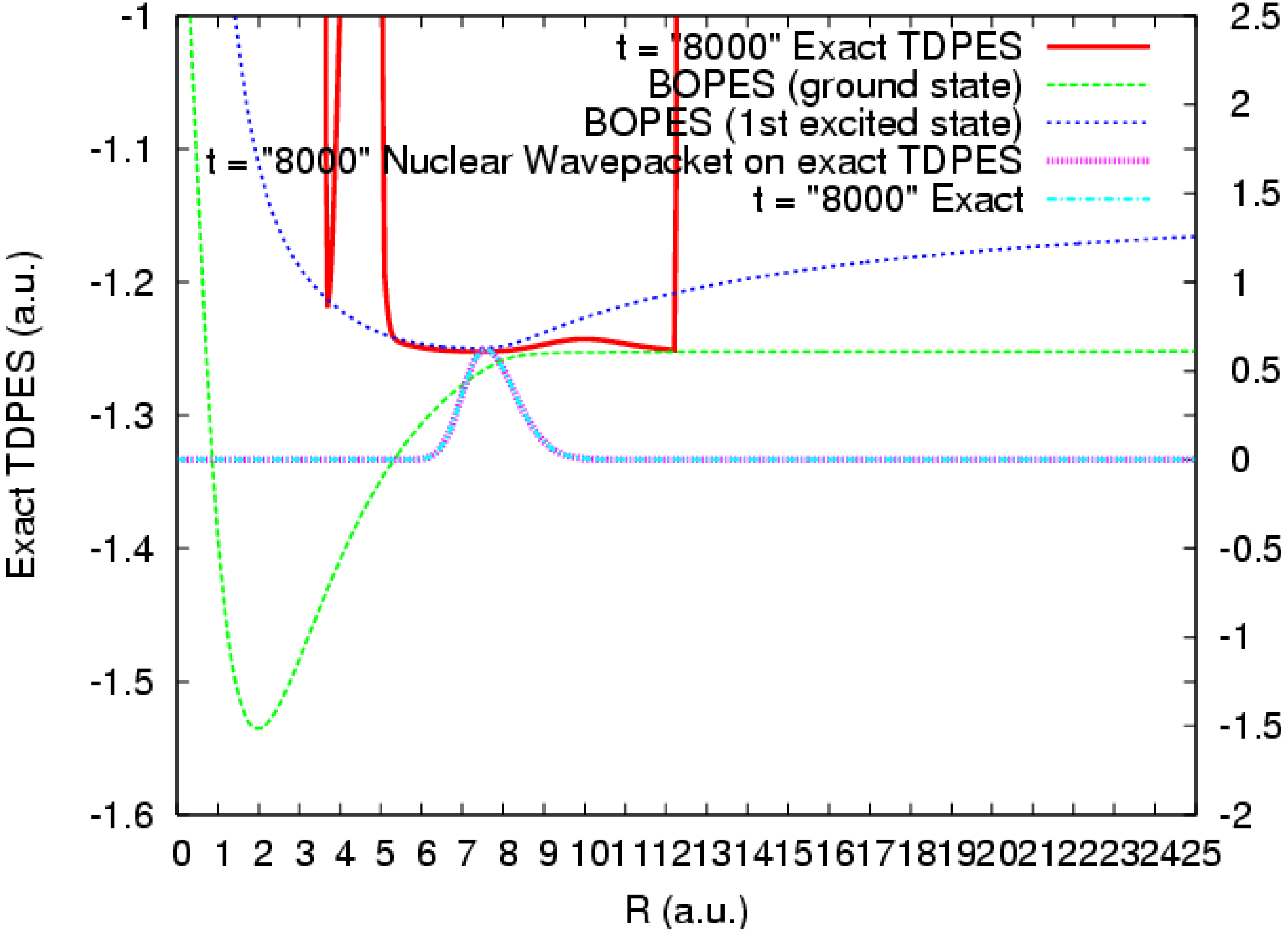
t = "8000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "8000" Nuclear Wavepacket on exact TDPES
t = "8000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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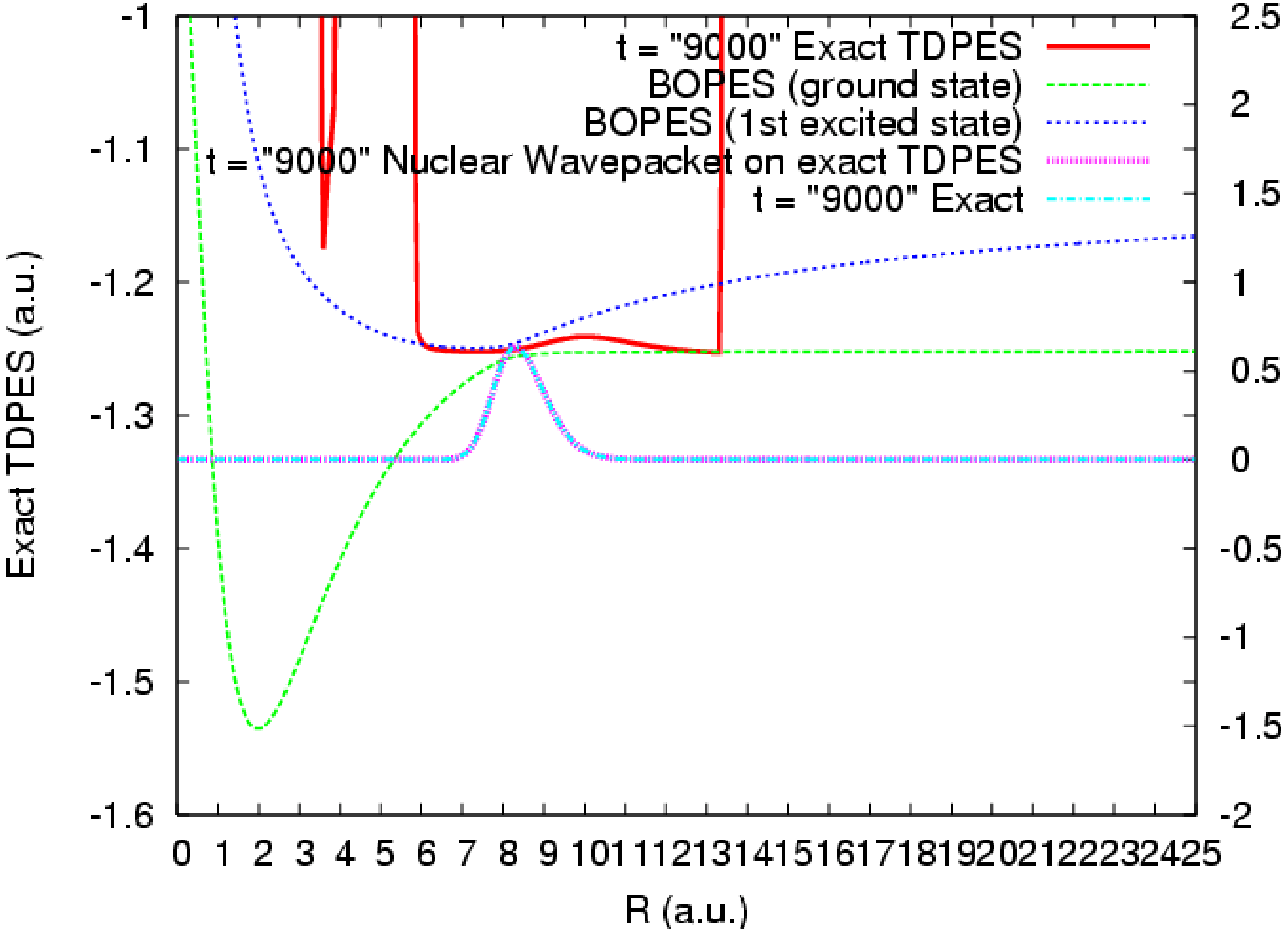
t = "9000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "9000" Nuclear Wavepacket on exact TDPES
t = "9000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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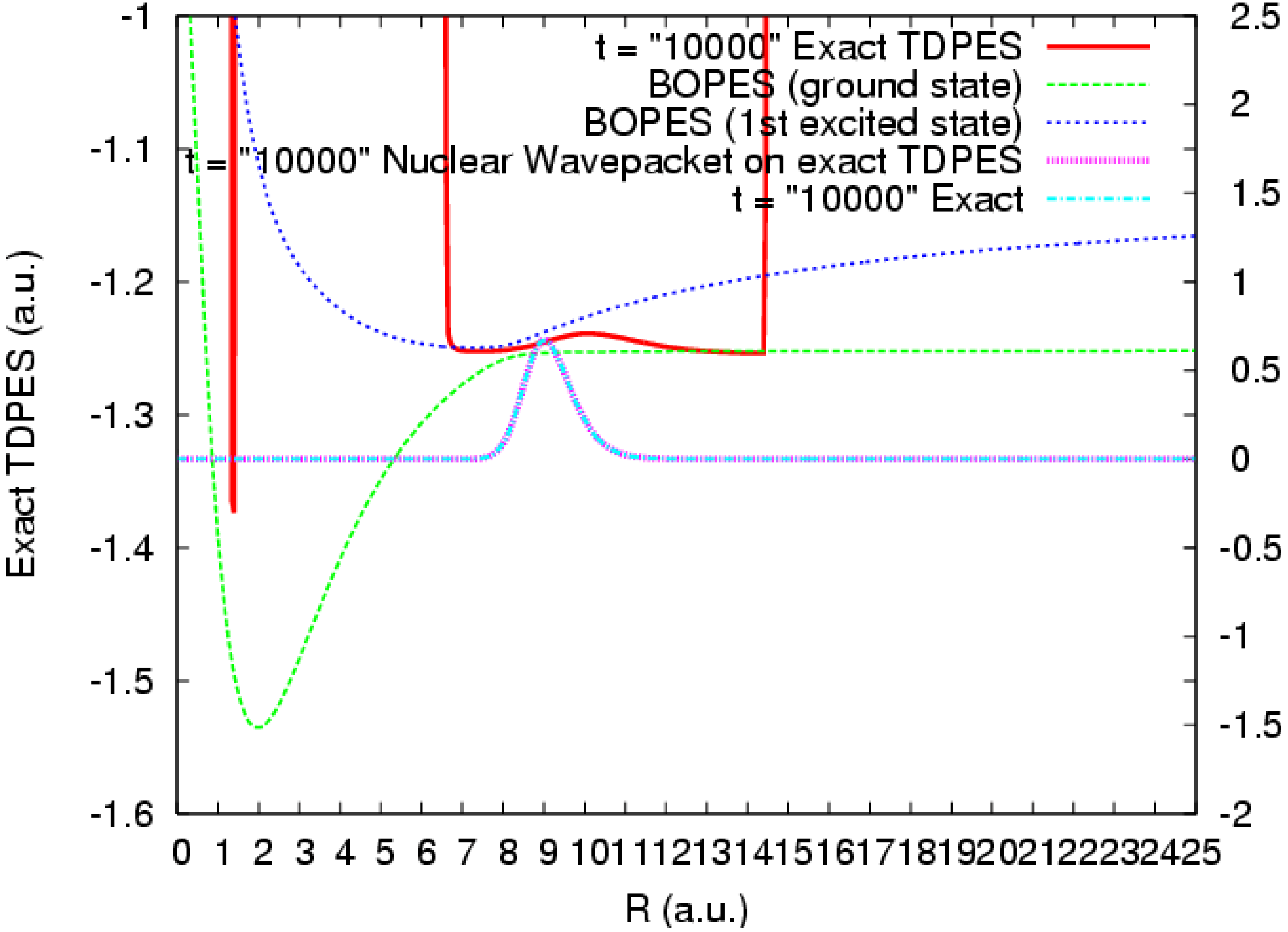
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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
0.5
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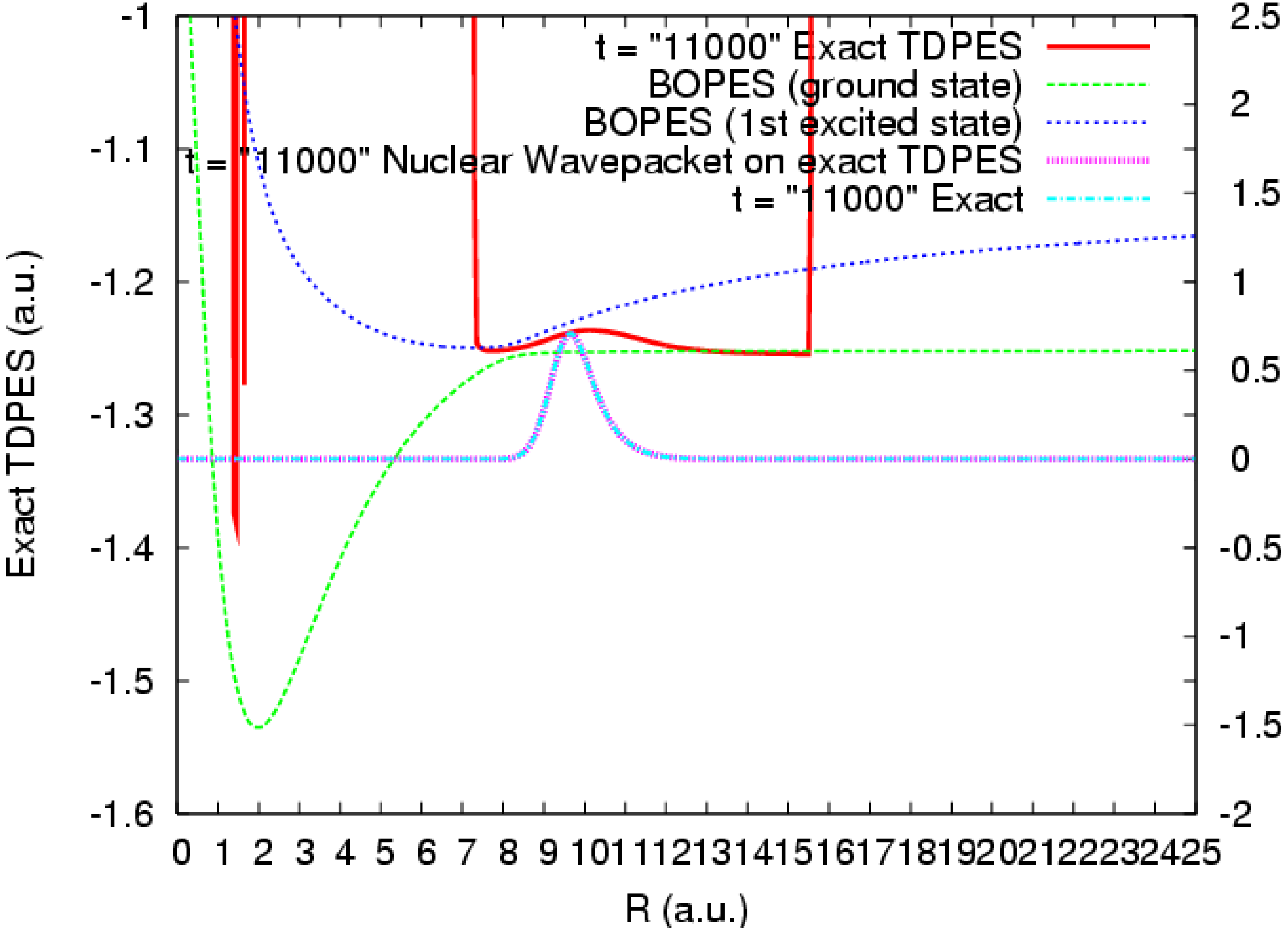
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "11000" Nuclear Wavepacket on exact TDPES
t = "11000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
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-1.5
-1.6
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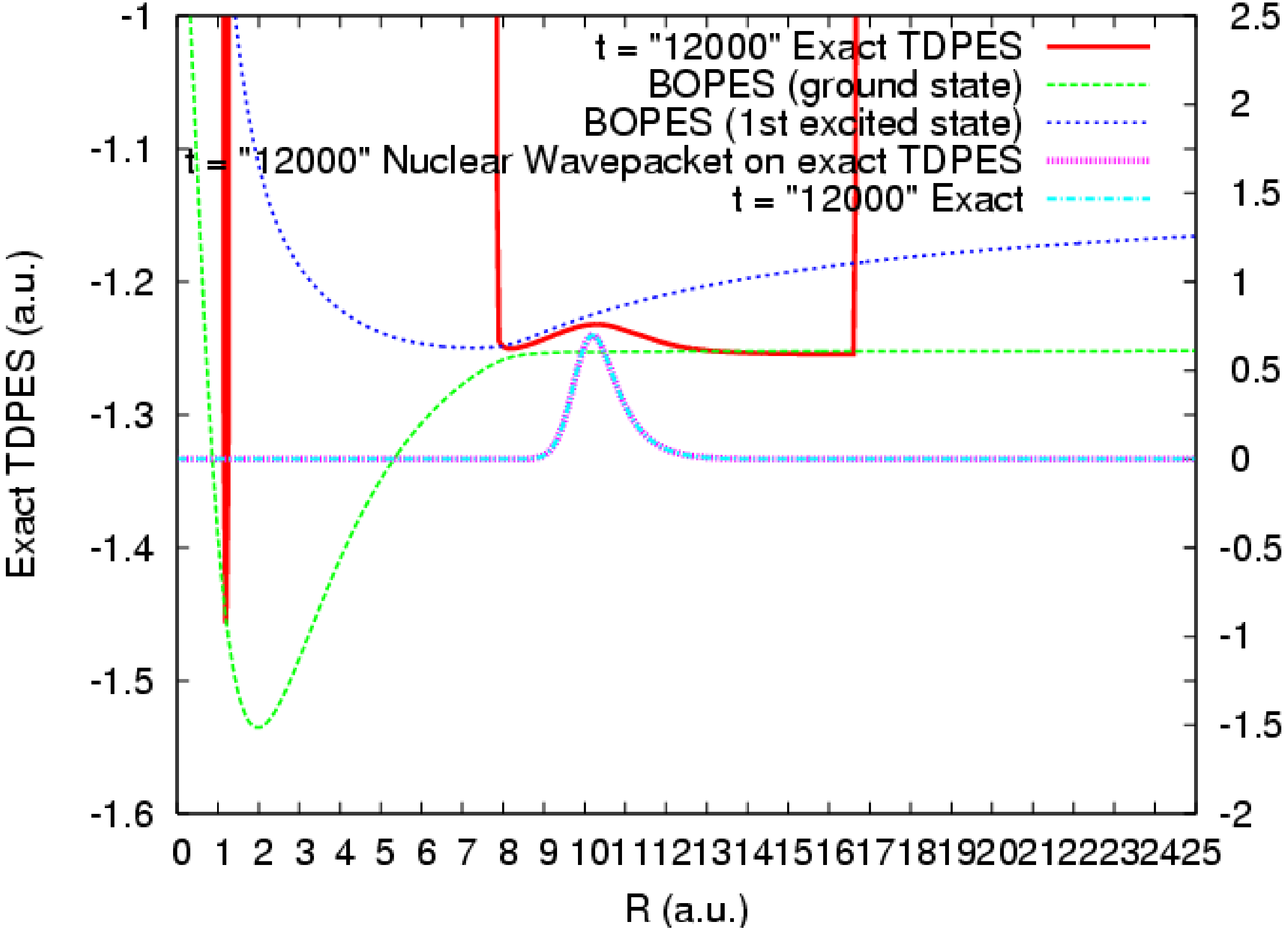
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BOPES (ground state)
BOPES (1st excited state)
t = "12000" Nuclear Wavepacket on exact TDPES
t = "12000" Exact
Exact TDPES (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
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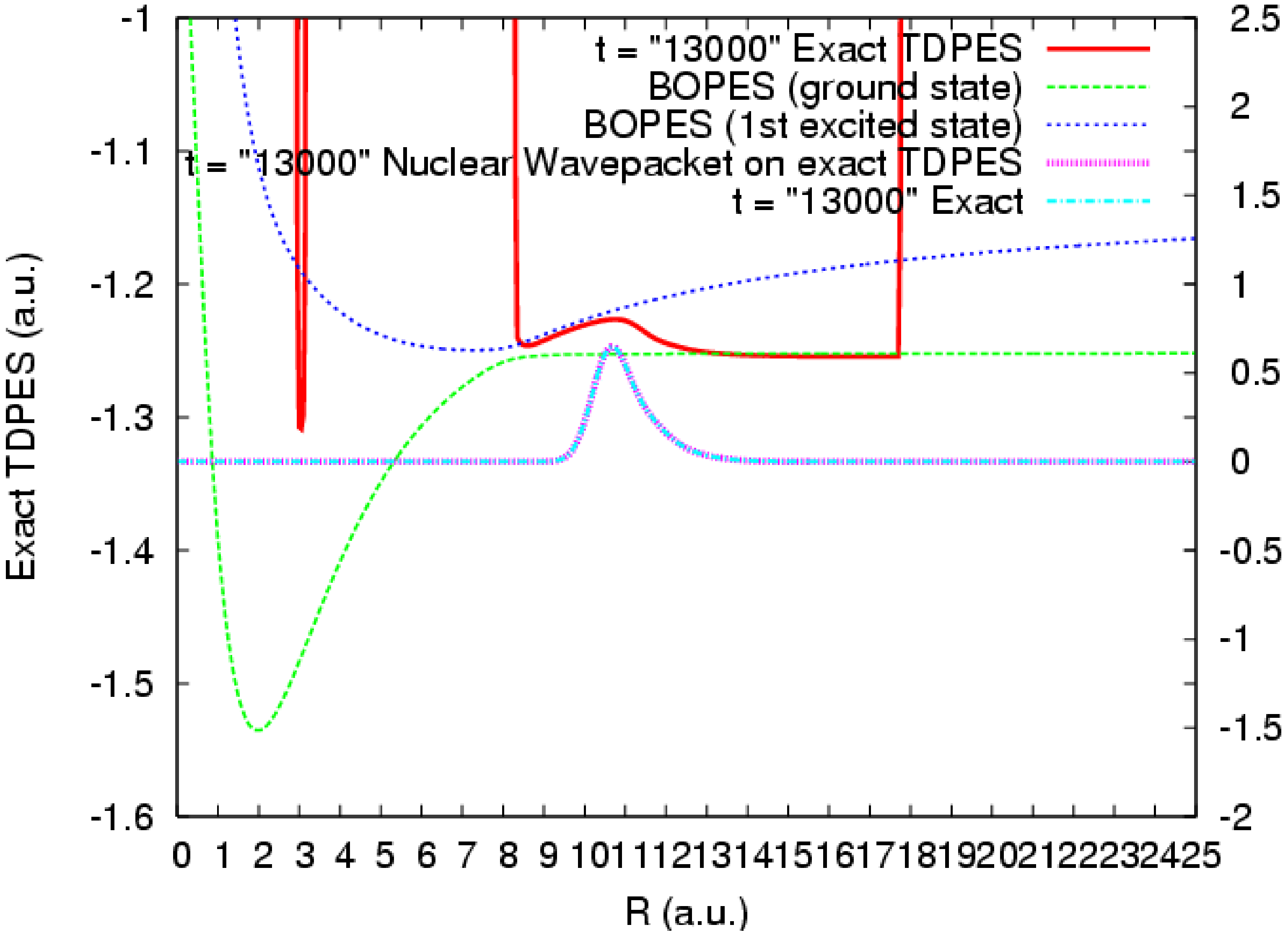
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
R (a.u.)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BOPES (ground state)
BOPES (1st excited state)
t = "13000" Nuclear Wavepacket on exact TDPES
t = "13000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
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-1.5
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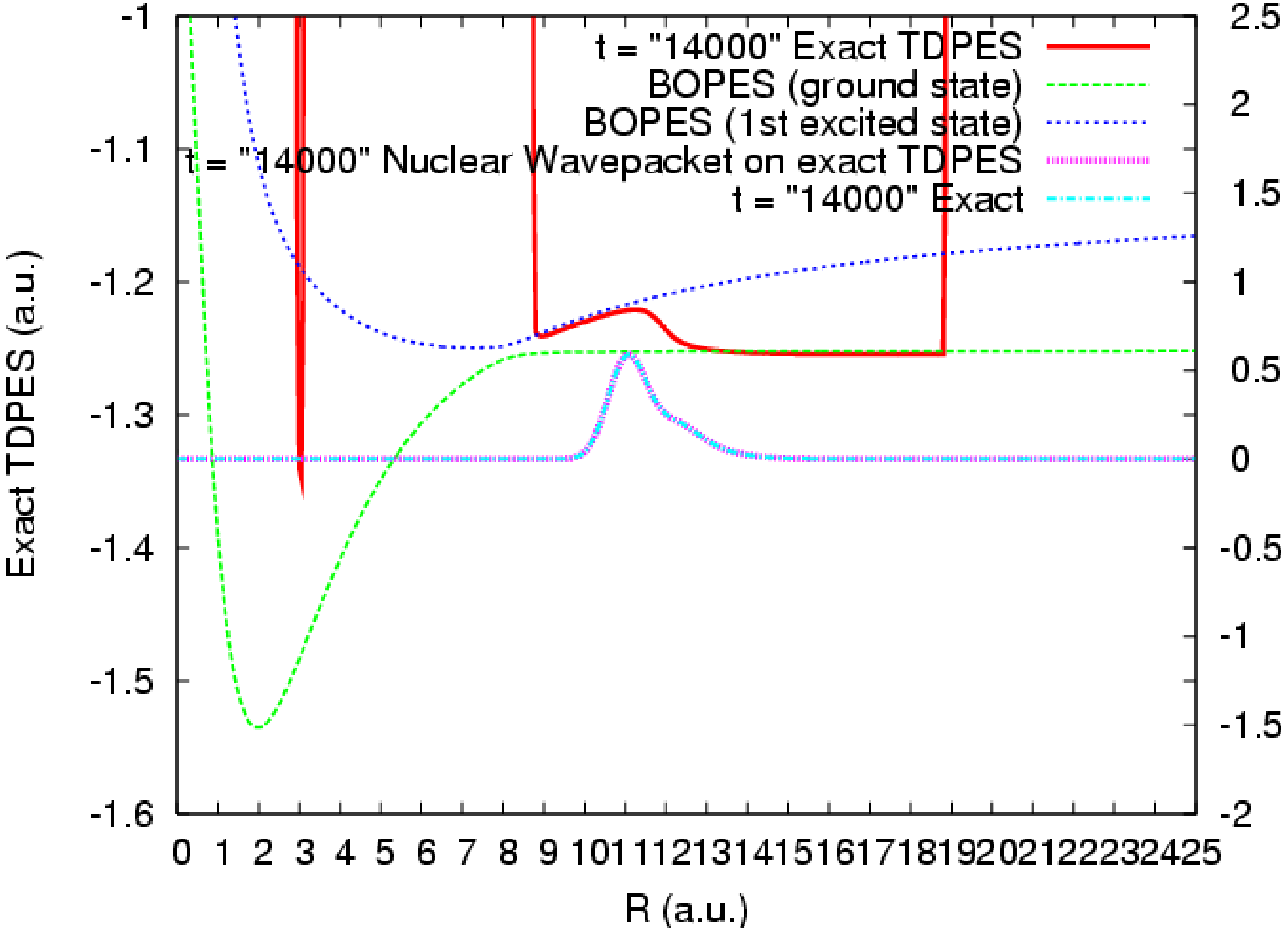
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BOPES (ground state)
BOPES (1st excited state)
t = "14000" Nuclear Wavepacket on exact TDPES
t = "14000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
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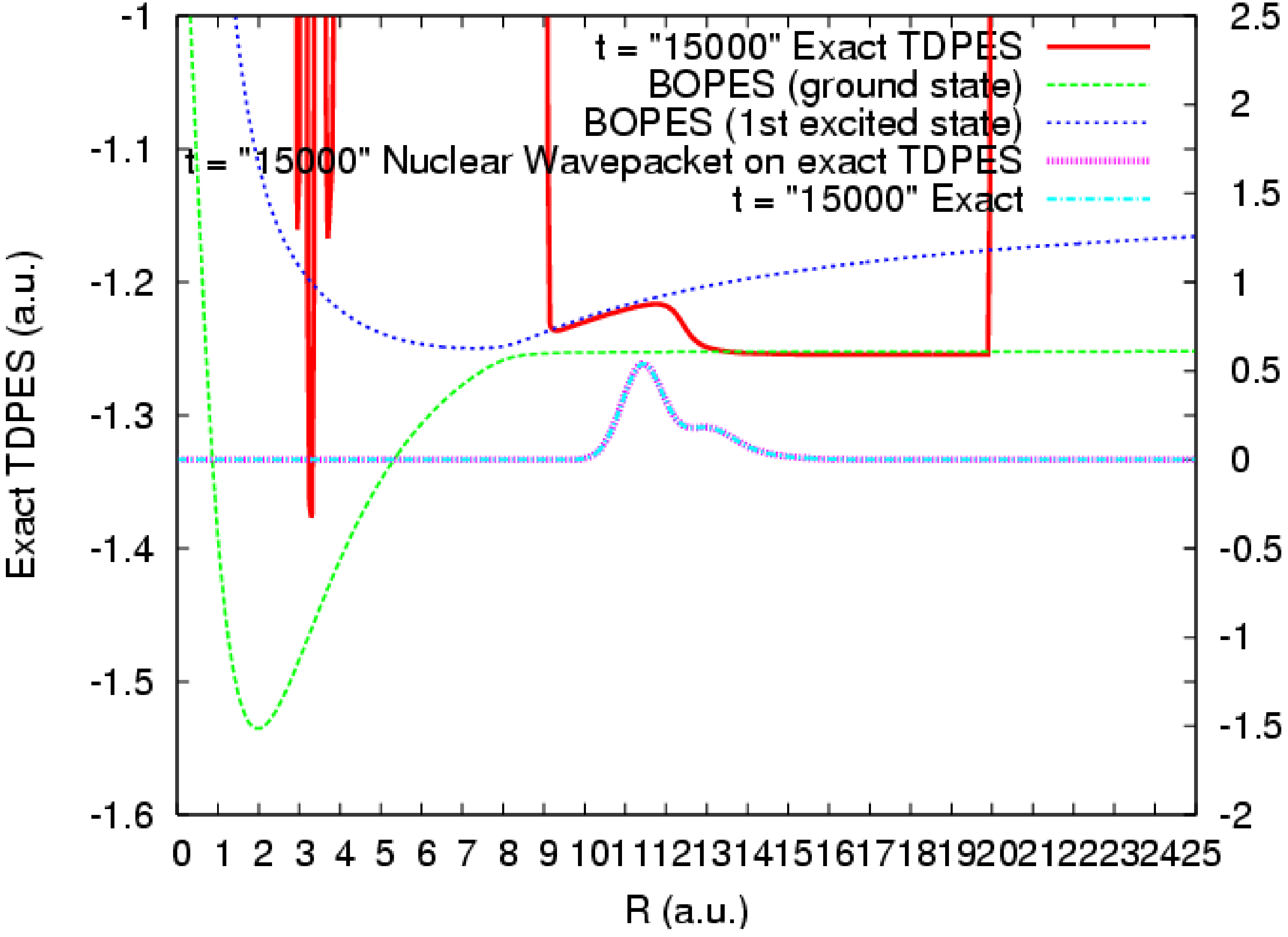
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "15000" Nuclear Wavepacket on exact TDPES
t = "15000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
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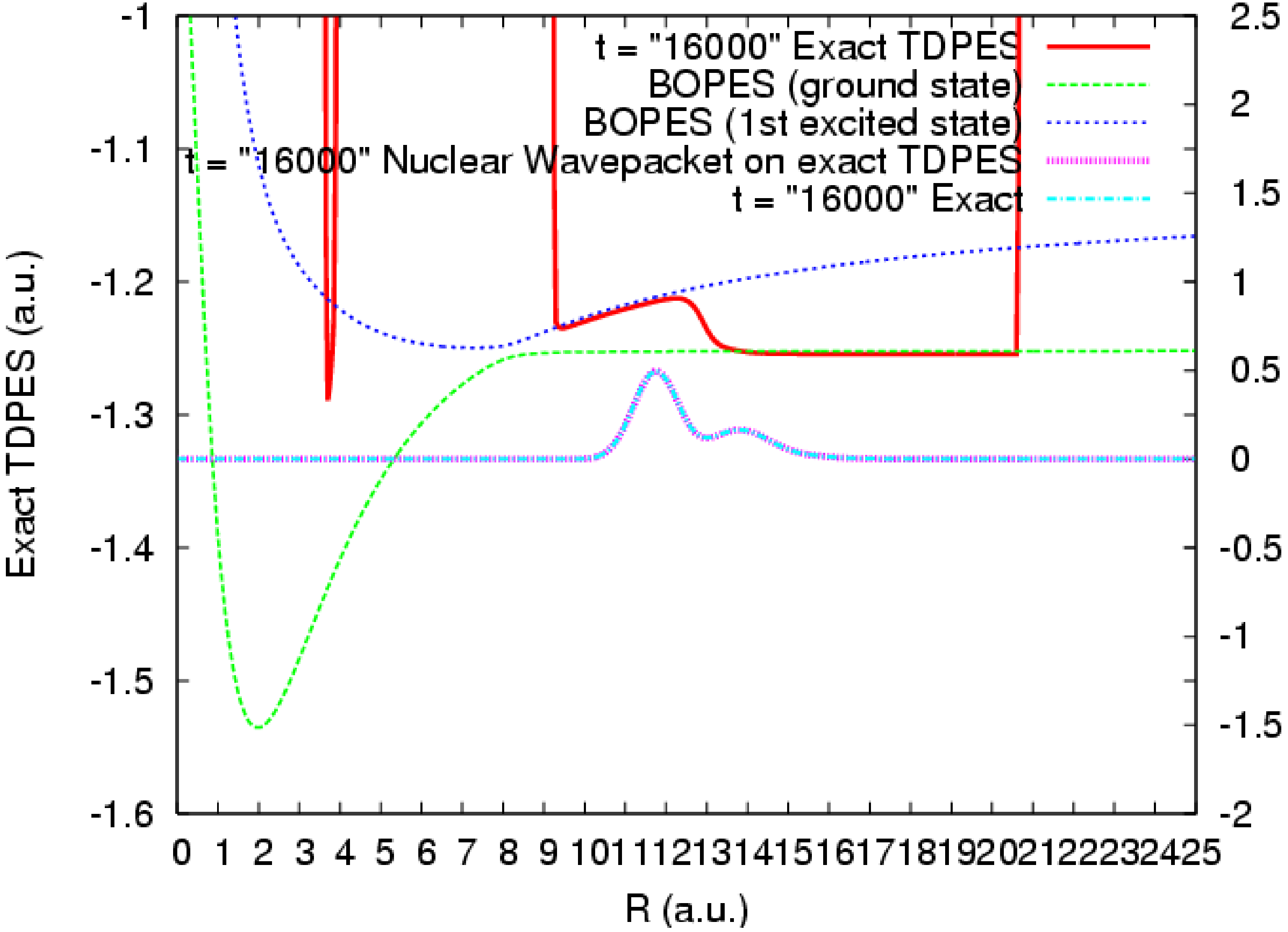
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "16000" Nuclear Wavepacket on exact TDPES
t = "16000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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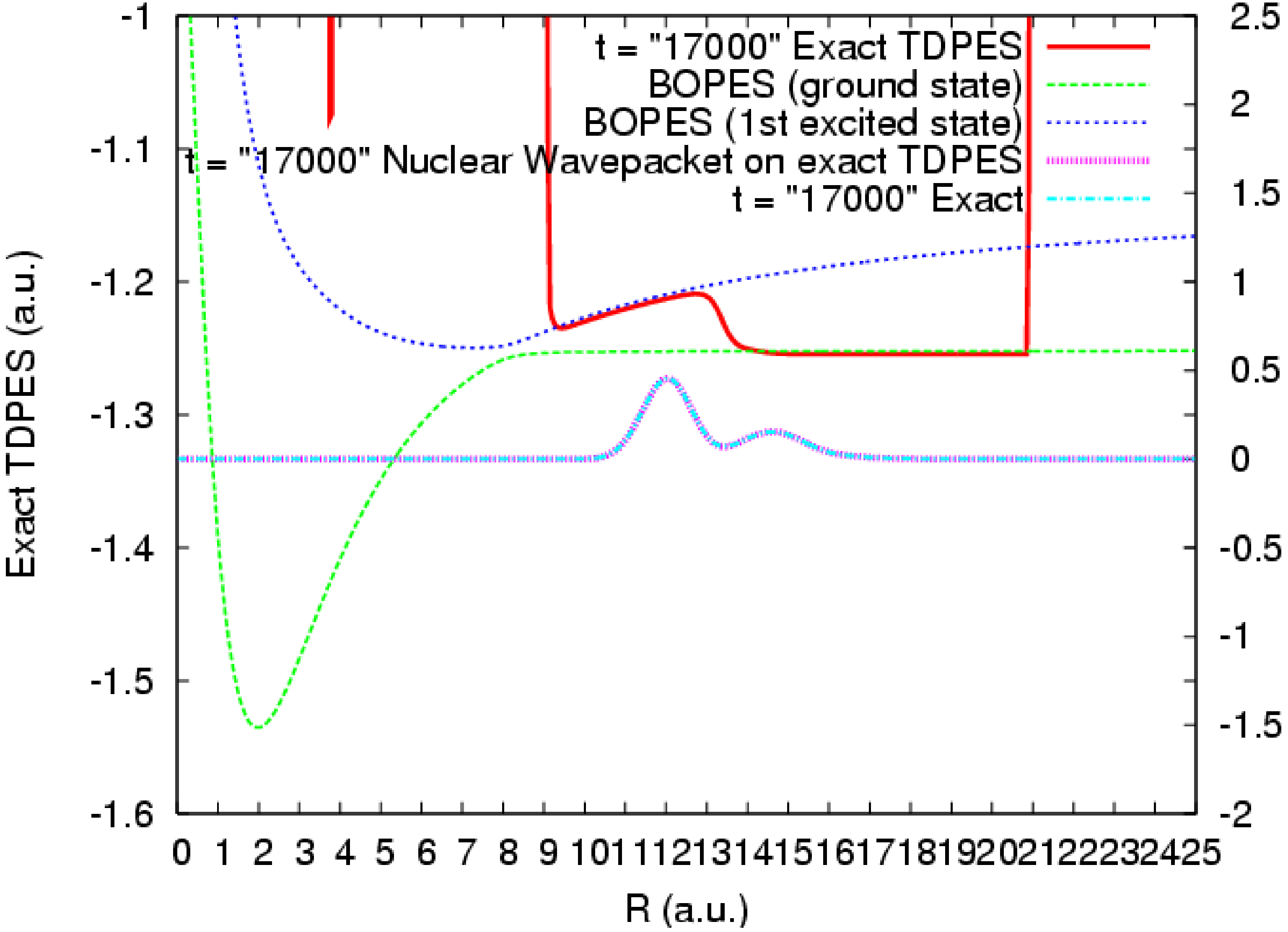
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BOPES (1st excited state)
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t = "17000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
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-1.3
-1.4
-1.5
-1.6
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-2
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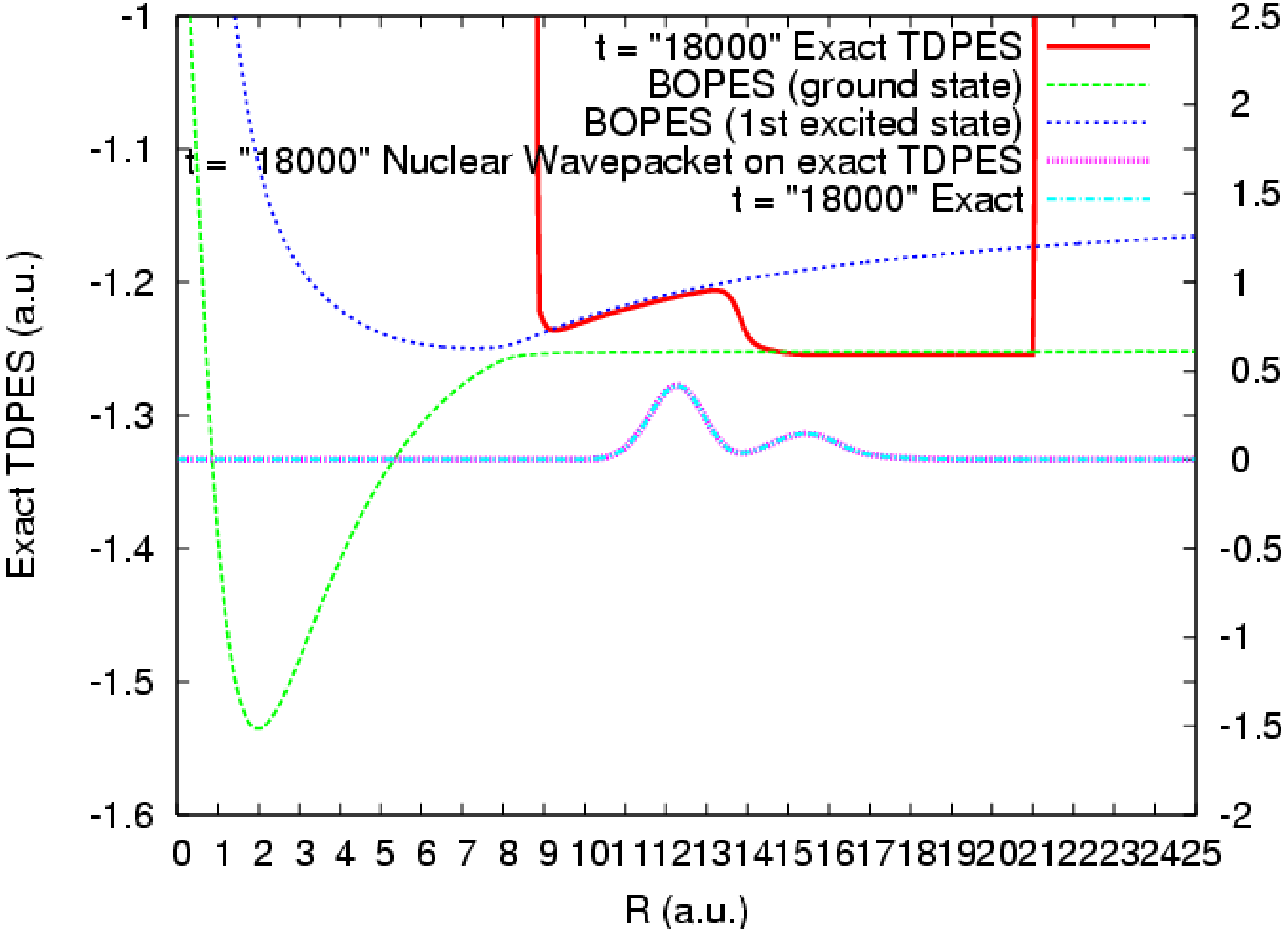
Exact TDPES (a.u.)
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-1.4
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-1.6
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1.5
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0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
R (a.u.)
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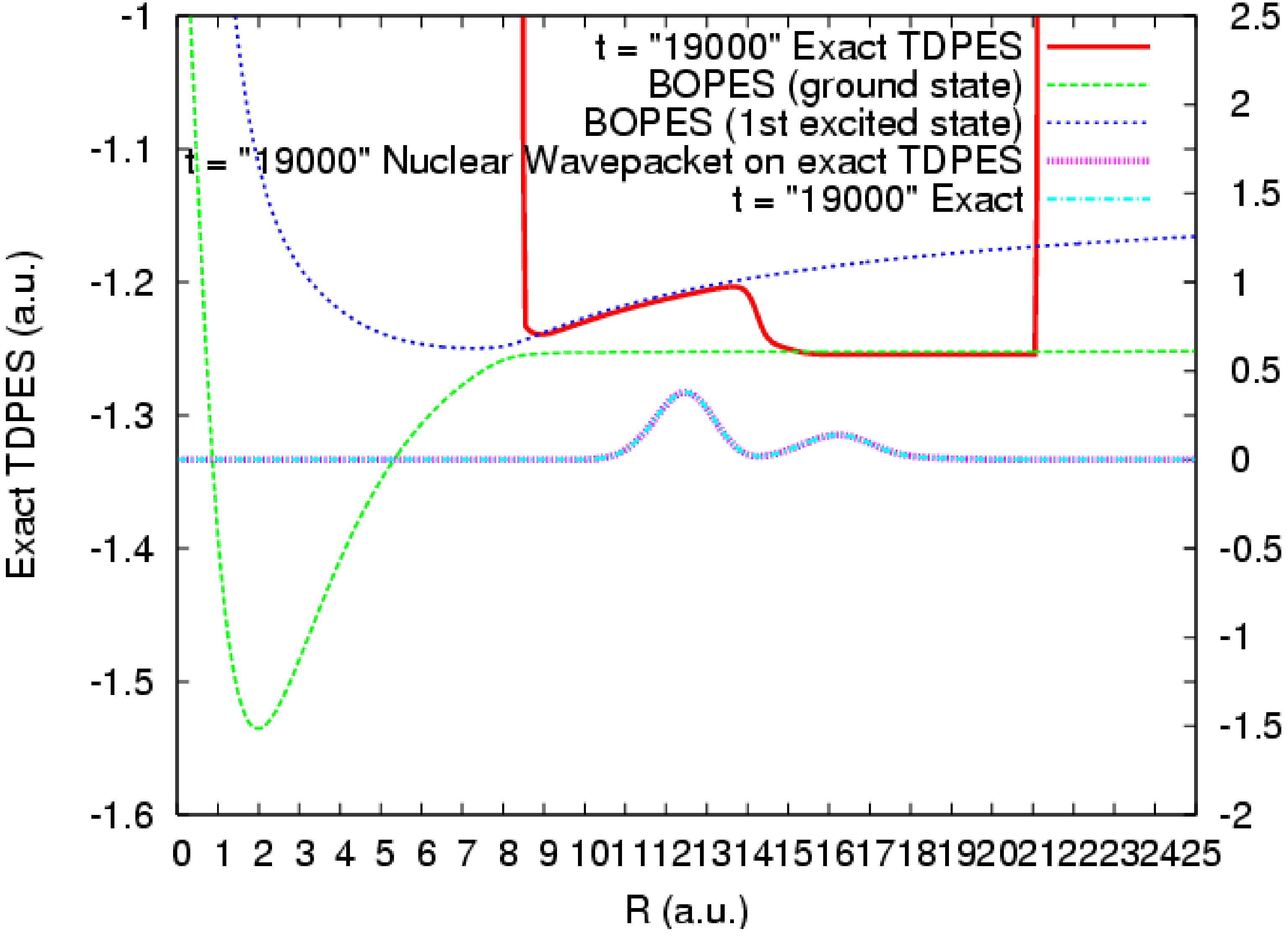
BOPES (1st excited state)
t = "18000" Nuclear Wavepacket on exact TDPES
t = "18000" Exact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BOPES (ground state)
BOPES (1st excited state)
t = "19000" Nuclear Wavepacket on exact TDPES
t = "19000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
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-1
-1.5
-2
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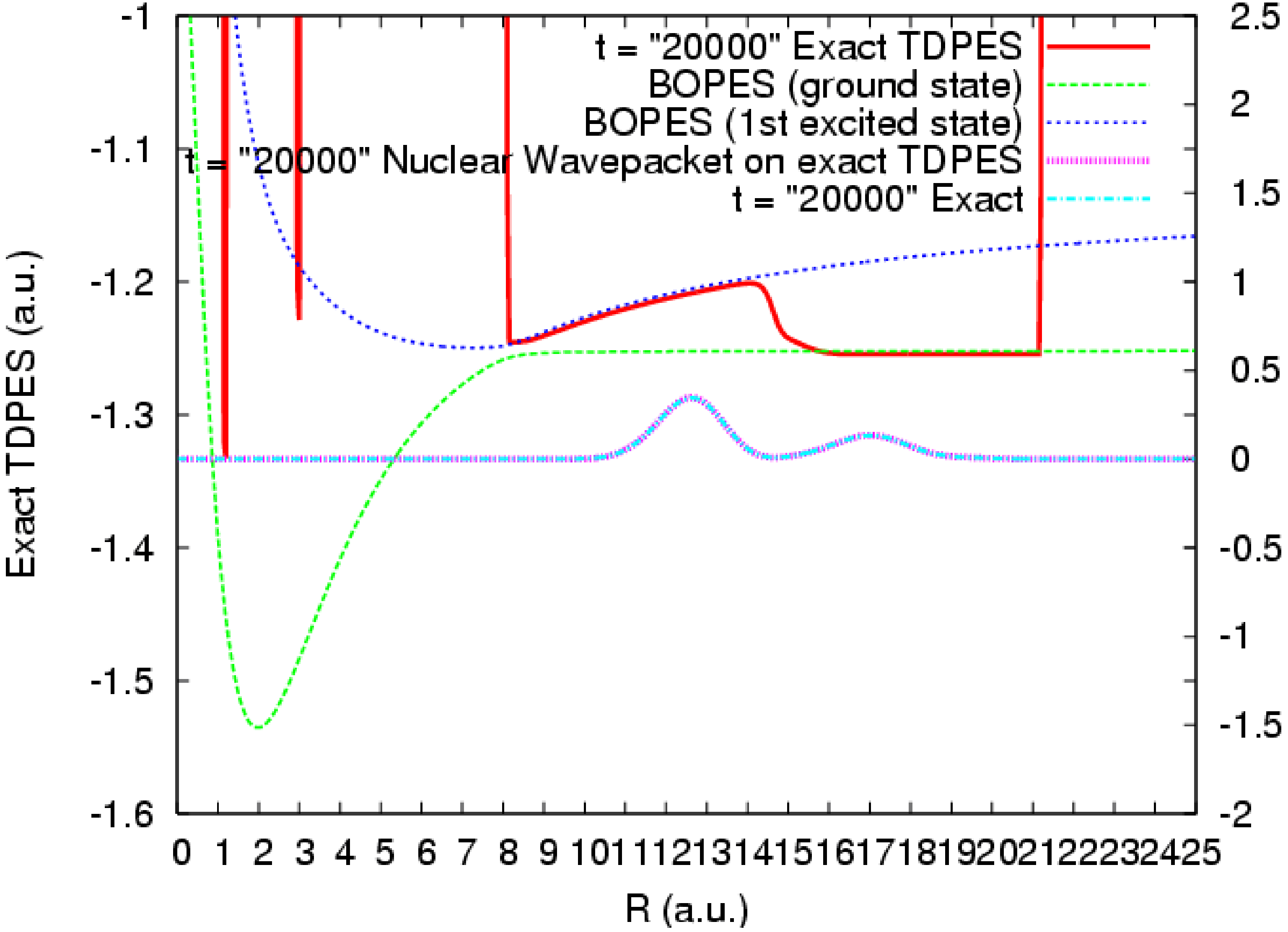
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BOPES (ground state)
BOPES (1st excited state)
t = "20000" Nuclear Wavepacket on exact TDPES
t = "20000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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-1
-1.5
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New MD scheme:

Perform classical limit of the nuclear equation, but retain the quantum treatment of the electronic degrees of freedom.

Nuclear wavefunction

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

Classical limit

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

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:

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

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:

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

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

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

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

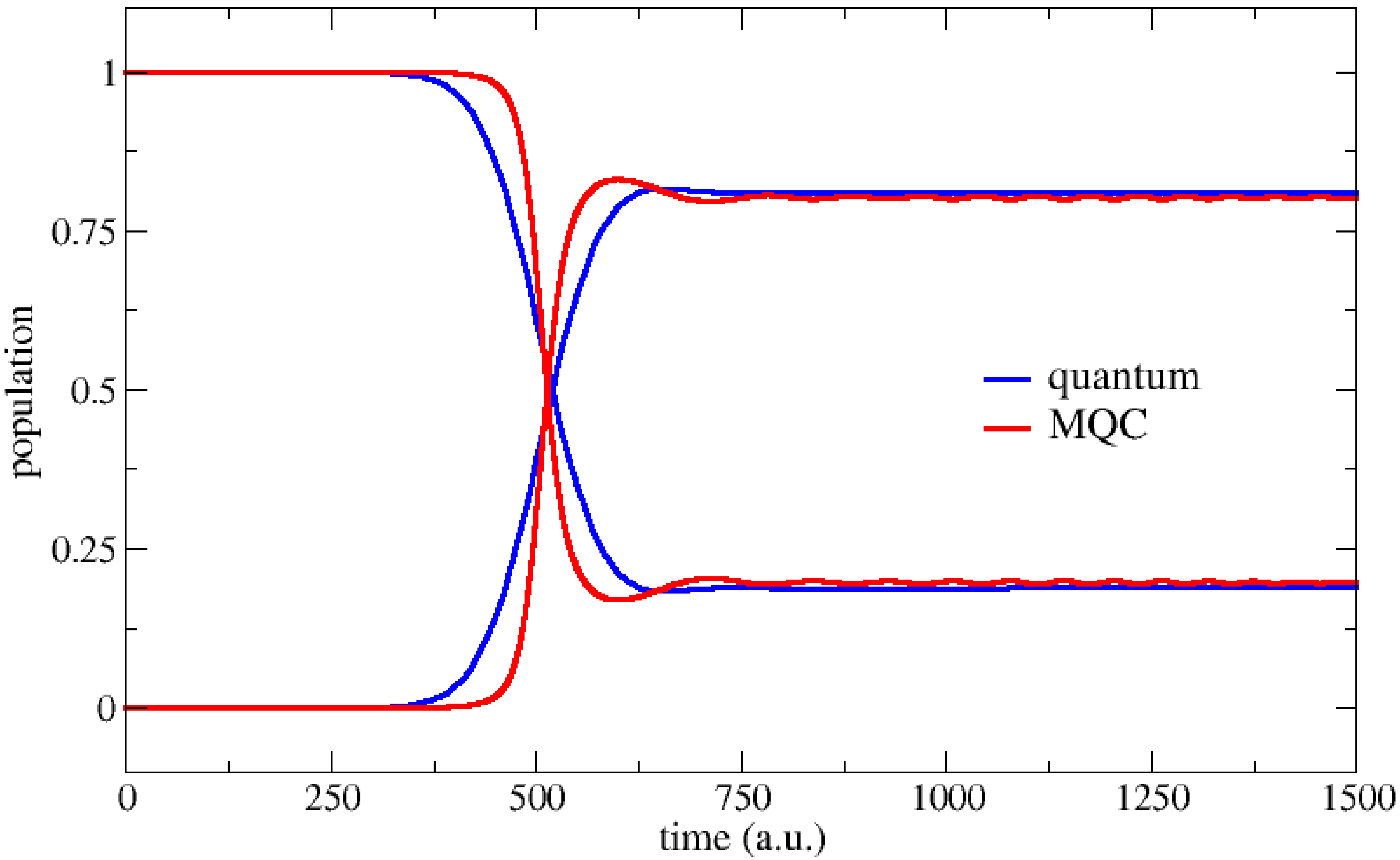
$$d_{jk}^{(1)}(R) = \left\langle \varphi_{R,j}^{BO} \middle| \nabla_R \varphi_{R,k}^{BO} \right\rangle \qquad d_{jk}^{(2)}(R) = \left\langle \nabla_R \varphi_{R,j}^{BO} \middle| \nabla_R \varphi_{R,k}^{BO} \right\rangle$$

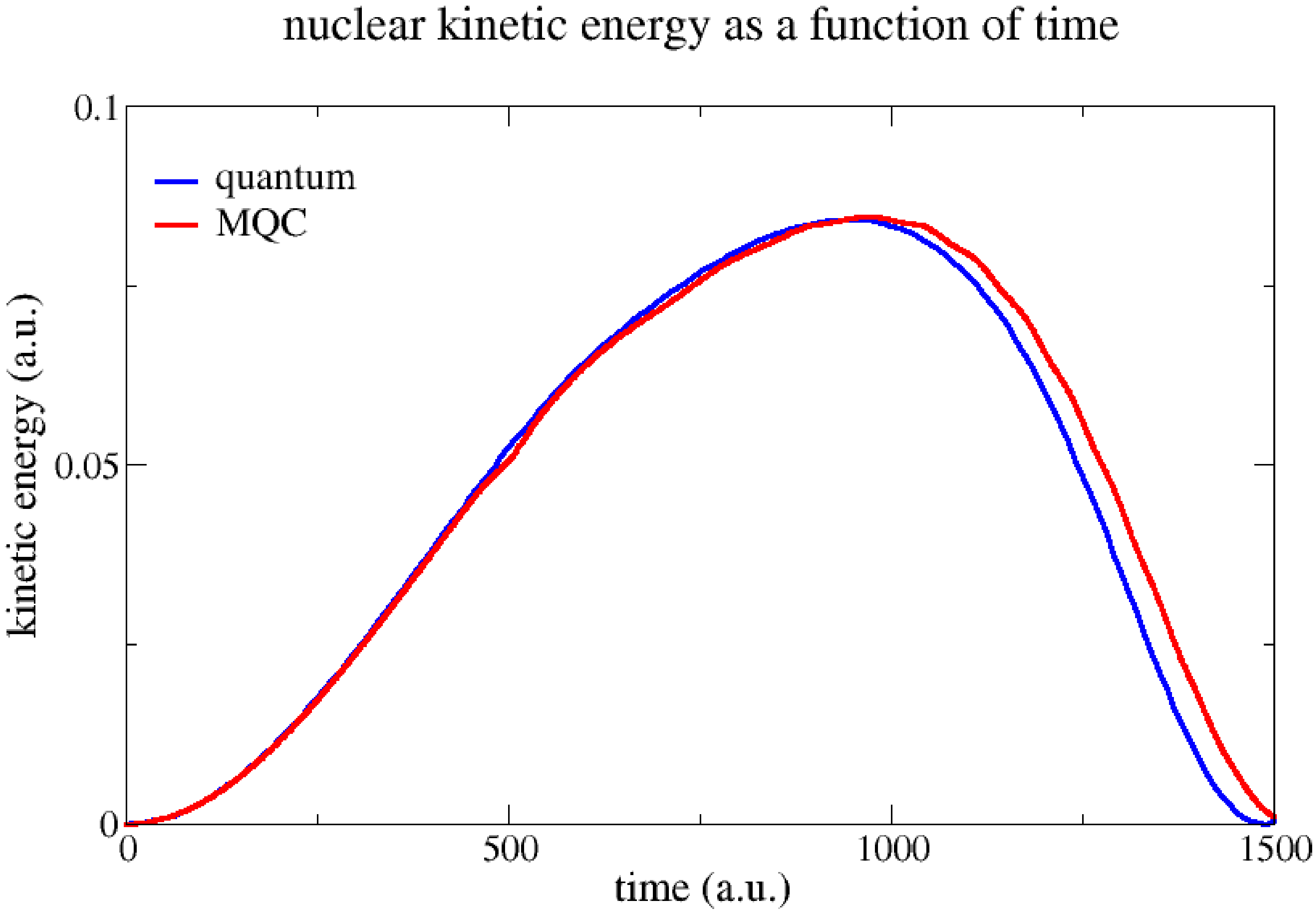
and classical EoM for the nuclear Hamiltonian:

$$H_N = \frac{P^2}{2M} + V_{eff}^{(R)}$$

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
time (a.u.)
0
500
1000
1500

Summary:

- $\Psi\left(\underline{\underline{r}}, \underline{\underline{R}}\right) = \Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) \cdot \chi\left(\underline{\underline{R}}\right)$ **is exact**
- **Eqs. of motion for** $\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$ and $\chi\left(\underline{\underline{R}}\right)$ **lead to**

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

  both in the static and the time-dependent case

- **Exact Berry phase may vanish when BO Berry phase ≠ 0**
- **TD-PES shows jumps resembling surface hopping**
- **mixed quantum classical algorithm**

Thanks !

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