Coupled electron-nuclear dynamics beyond Born-Oppenheimer: A fresh look at potential energy surfaces and Berry phases in the time domain

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

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

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

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

Born-Oppenheimer approximation

solve

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

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 $\langle\Psi^{BO} | H | \Psi^{BO}\rangle$ w.r.t. χ^{BO}:

Nuclear equation

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

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

Berry connection

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

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

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

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 $\Phi^{BO}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right)$.

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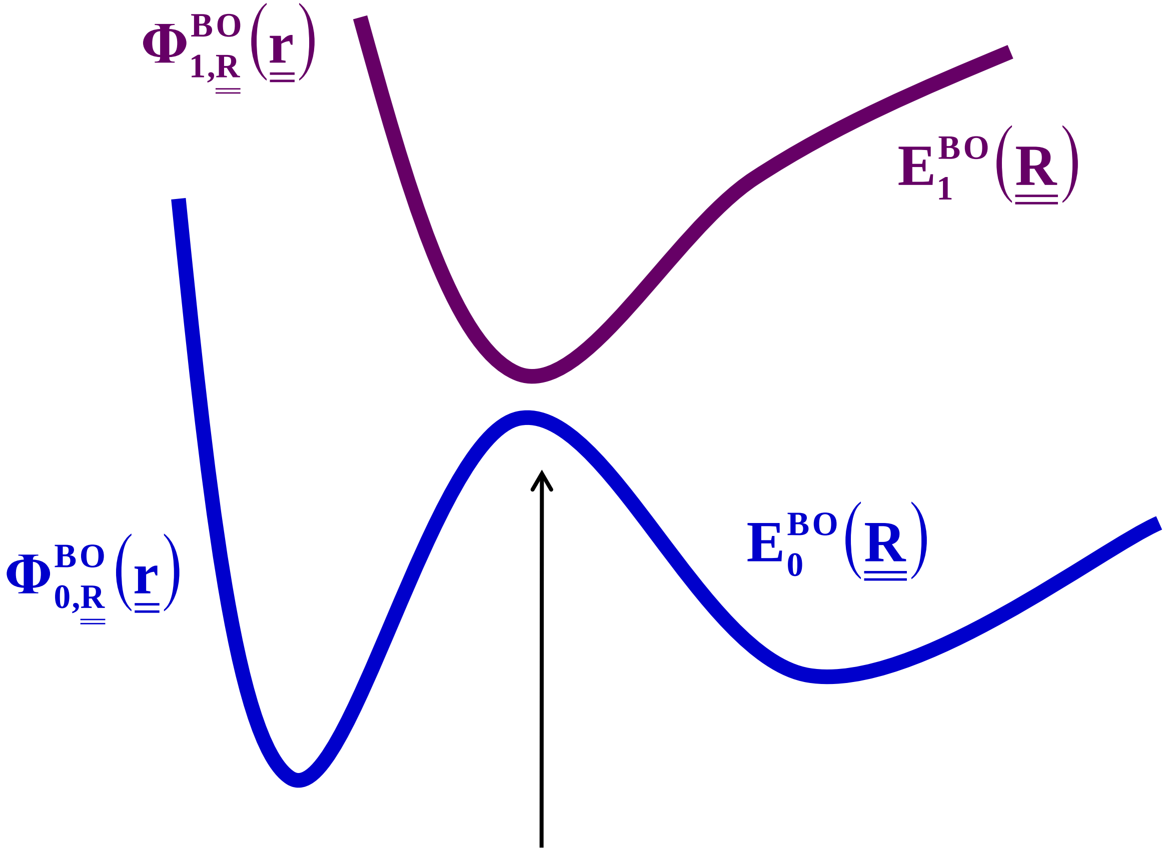
Drawbacks:

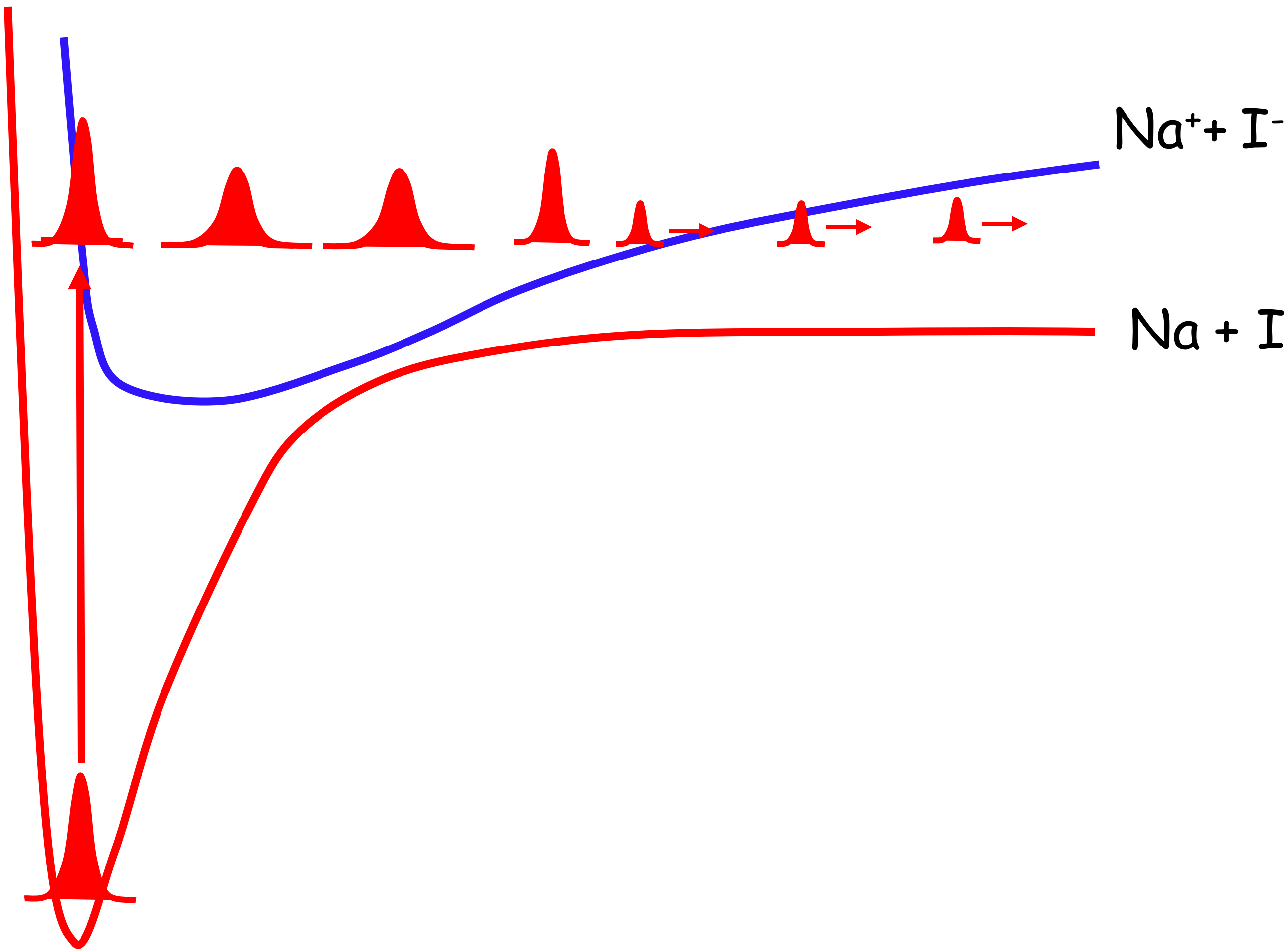
- **$\chi_{J,K}$ depends on 2 indices: → looses nice interpretation as "nuclear wave function"**
- **In systems driven by a strong laser, many BO-PES can be coupled.**



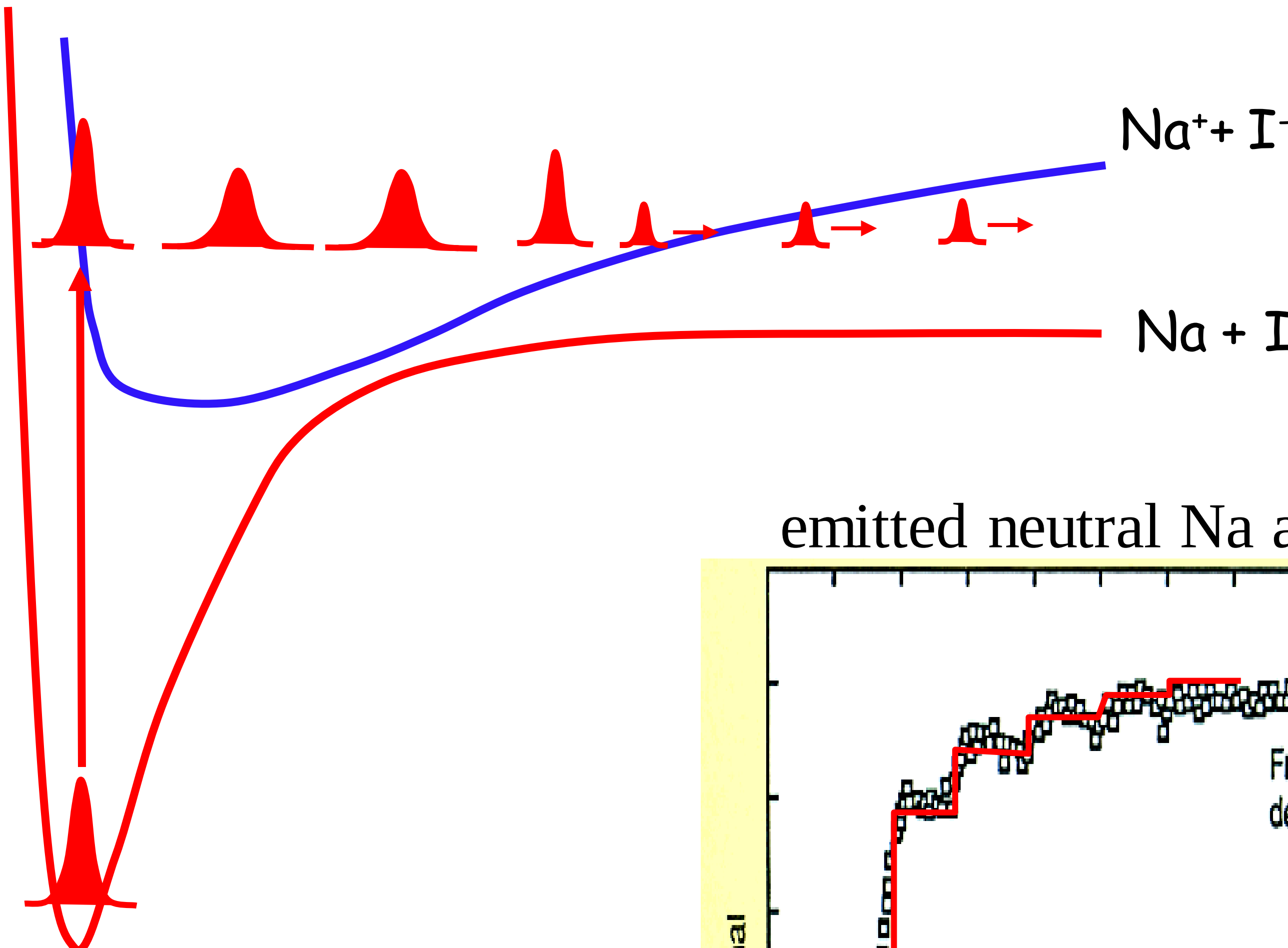
$$\mathbf{\Psi}_{\mathbf{0}}(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}}) \approx \chi_{\mathbf{00}}(\underline{\underline{\mathbf{R}}})\mathbf{\Phi}^{\mathbf{BO}}_{\mathbf{0},\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}) + \chi_{\mathbf{01}}(\underline{\underline{\mathbf{R}}})\mathbf{\Phi}^{\mathbf{BO}}_{\math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

For few degrees of freedom, BO PES provide essential insight in the dynamics of molecules, and can even be measured by femto-second pump-probe spectroscopy: *A. Zewail*, *J. Phys. Chem.* 104, 5660, (2000)

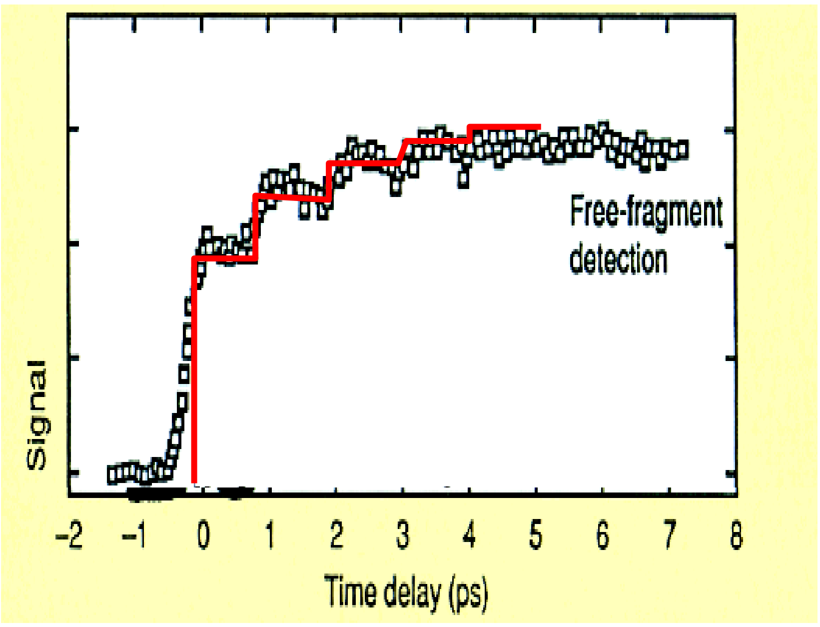
Example: NaI femtochemistry



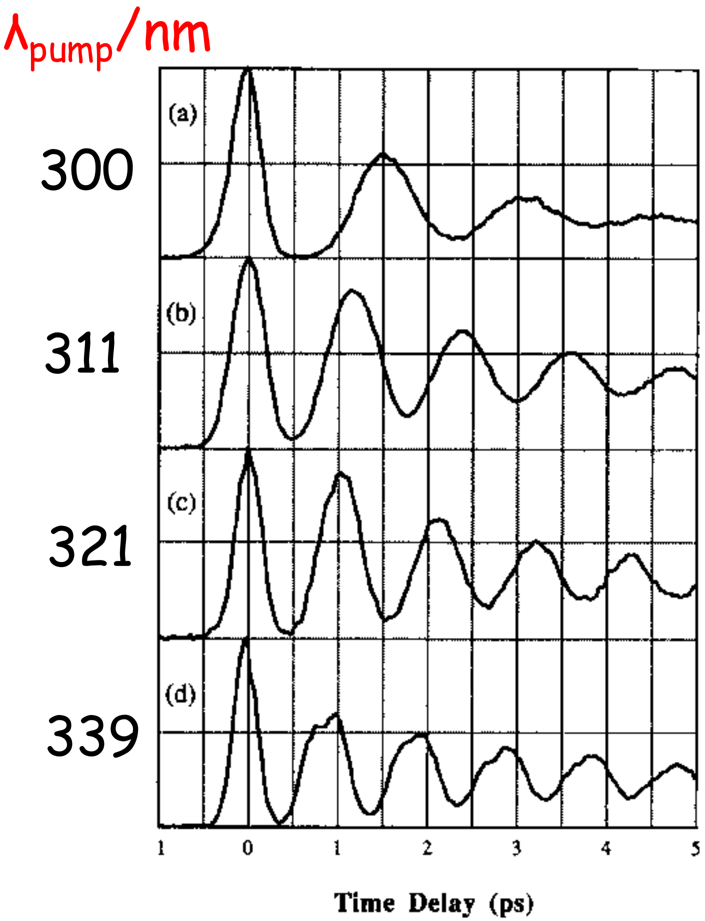
Example: NaI femtochemistry

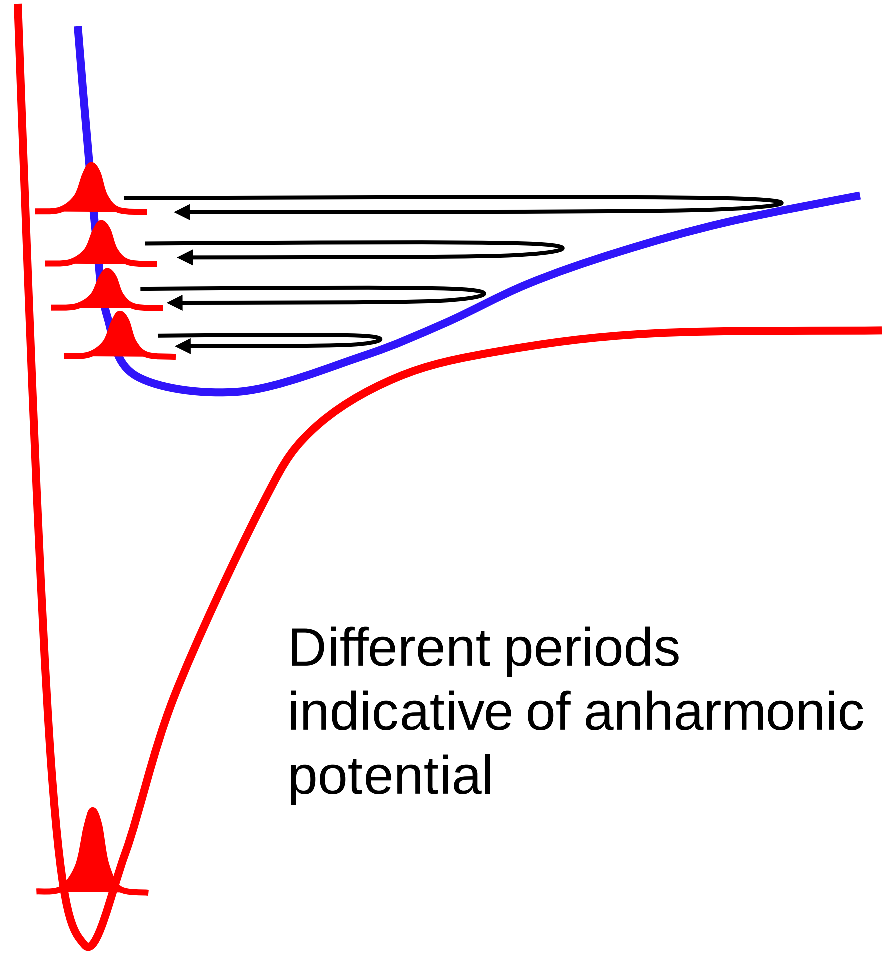


emitted neutral Na atoms



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





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

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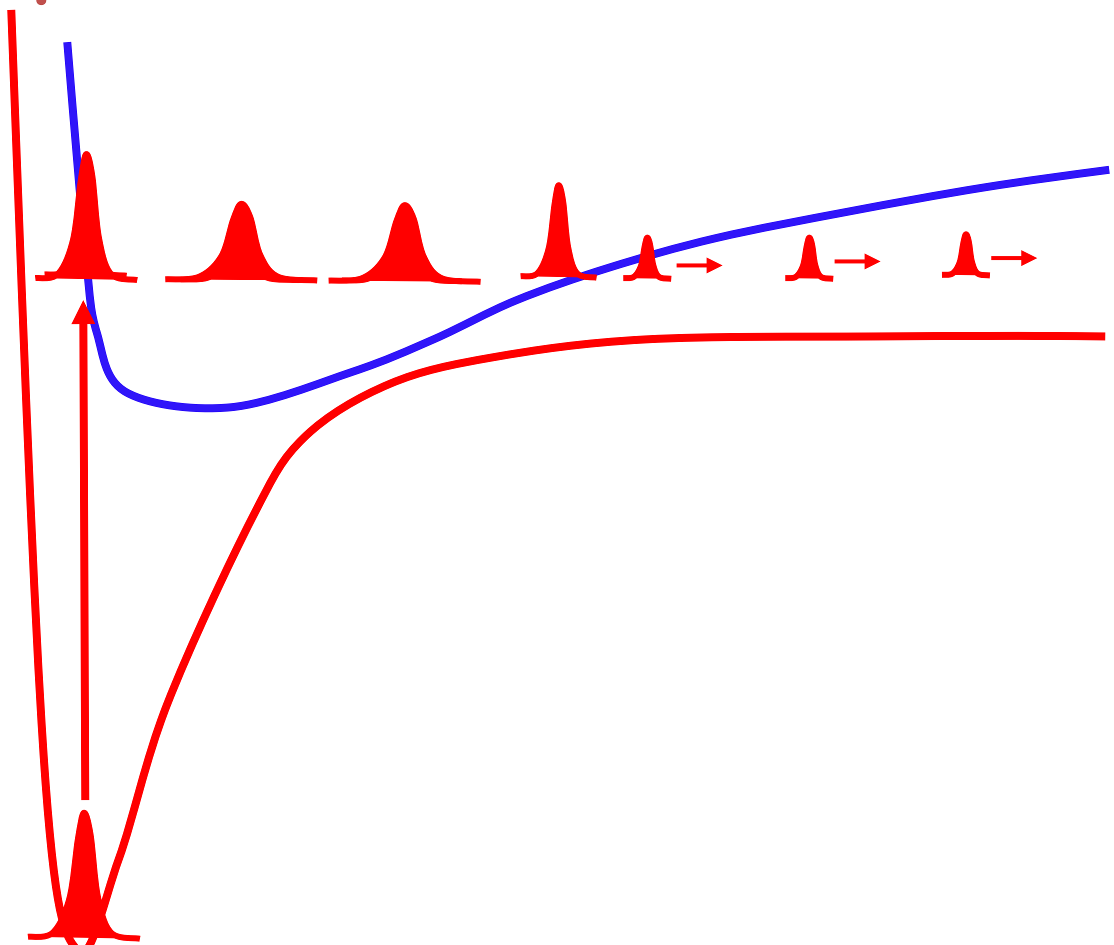

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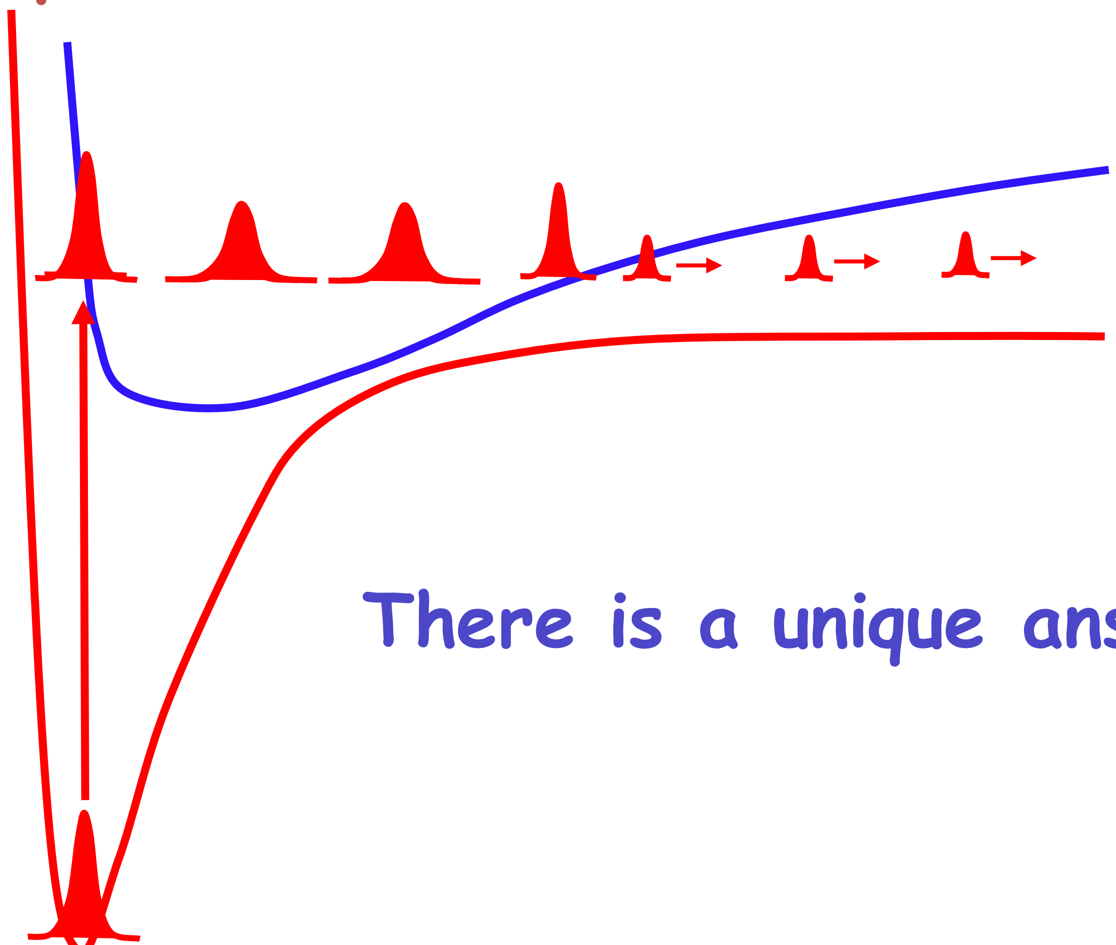

There is a unique answer!

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 exact time-dependent PES**

- **Mixed quantum-classical treatment**

- **Concept of time-dependent PES acting on the electrons**

THANKS

Ali Abedi

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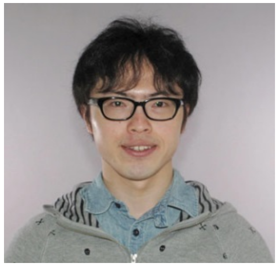
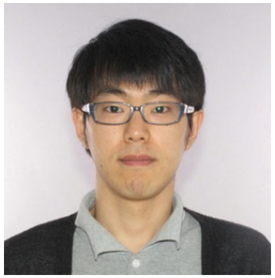


Yasumitsu Suzuki



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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** $\underline{\underline{\mathbf{R}}}$**.**

N.I. Gidopoulos, E.K.U. Gross,
Phil. Trans. R. Soc. 372, 20130059 (2014); arXiv cond-mat/0502433

Proof of Theorem I:

Given the exact electron-nuclear wavefuncion $\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)$

Choose: $$\chi\left(\underline{\underline{R}}\right) := e^{iS\left(\underline{\underline{R}}\right)}\sqrt{\int d\underline{\underline{r}}\left|\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)\right|^2}$$

with some real-valued funcion $S\left(\underline{\underline{R}}\right)$

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

Then, by construction, $\int d\underline{\underline{r}}\left|\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\right|^2 = 1$

N.I. Gidopoulos, E.K.U. Gross,
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Immediate consequences of Theorem I:

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

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

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

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

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

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

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

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

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

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

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

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

Eq. ❶

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

Eq. ❷

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

where

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

N.I. Gidopoulos, E.K.U. Gross,
Phil. Trans. R. Soc. 372, 20130059 (2014); arXiv cond-mat/0502433

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Eq. ❶

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

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

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

Exact PES

Exact Berry potential

N.I. Gidopoulos, E.K.U. Gross,
Phil. Trans. R. Soc. 372, 20130059 (2014); arXiv cond-mat/0502433

Proof of theorem II (basic idea)

Find the variationally best $\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})$ and $\chi(\underline{\underline{R}})$ by making stationary the total energy under the subsidiary condition that $\int d\underline{\underline{r}} \left|\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})\right|^2 = 1$. This gives two Euler equations:

Eq. ❶

$$\frac{\delta}{\delta\Phi^*_{\underline{\underline{R}}}(\underline{\underline{r}})}\left(\frac{\langle\Phi\chi|\hat{H}|\Phi\chi\rangle}{\langle\Phi\chi|\Phi\chi\rangle} - \int d\underline{\underline{R}}\,\Lambda(\underline{\underline{R}})\int d\underline{\underline{r}}\left|\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})\right|^2\right) = 0$$

Eq. ❷

$$\frac{\delta}{\delta\chi(\underline{\underline{R}})}\left(\frac{\langle\Phi\chi|\hat{H}|\Phi\chi\rangle}{\langle\Phi\chi|\Phi\chi\rangle}\right) = 0$$

OBSERVATIONS:

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

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

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

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

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

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

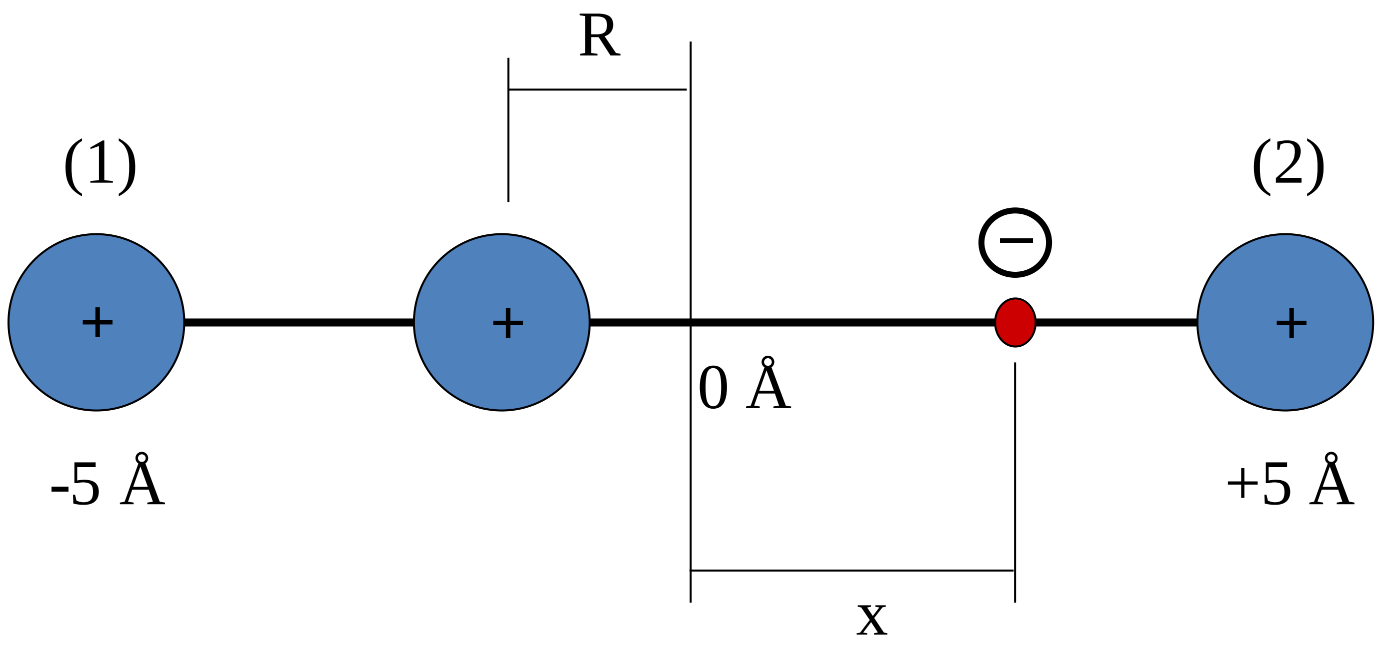
$$\in\left(\underline{\underline{R}}\right) \rightarrow \tilde{\in}\left(\underline{\underline{R}}\right) = \in\left(\underline{\underline{R}}\right)$$ Exact potential energy surface is gauge invariant.

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

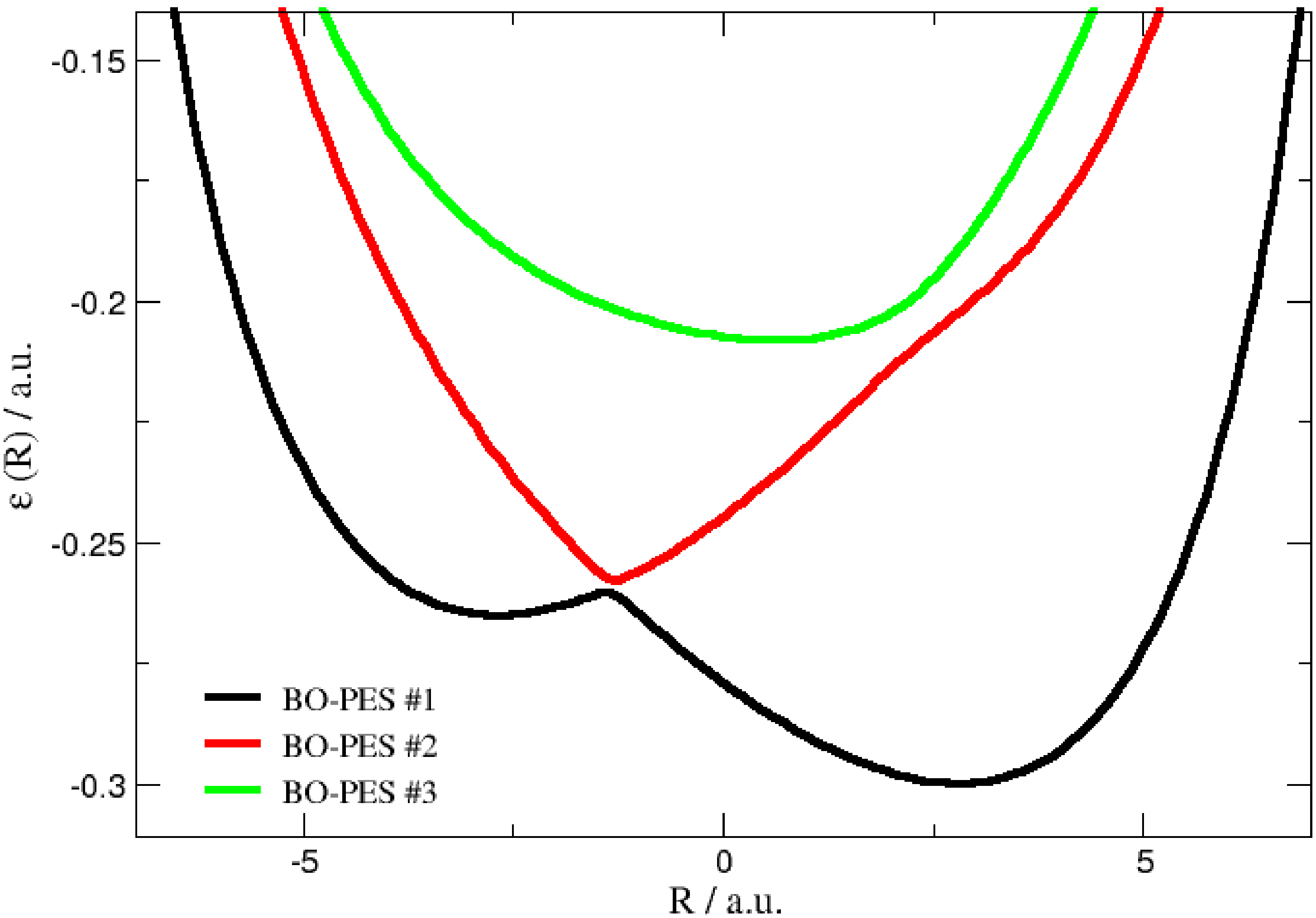
How do the exact PES look like?

MODEL

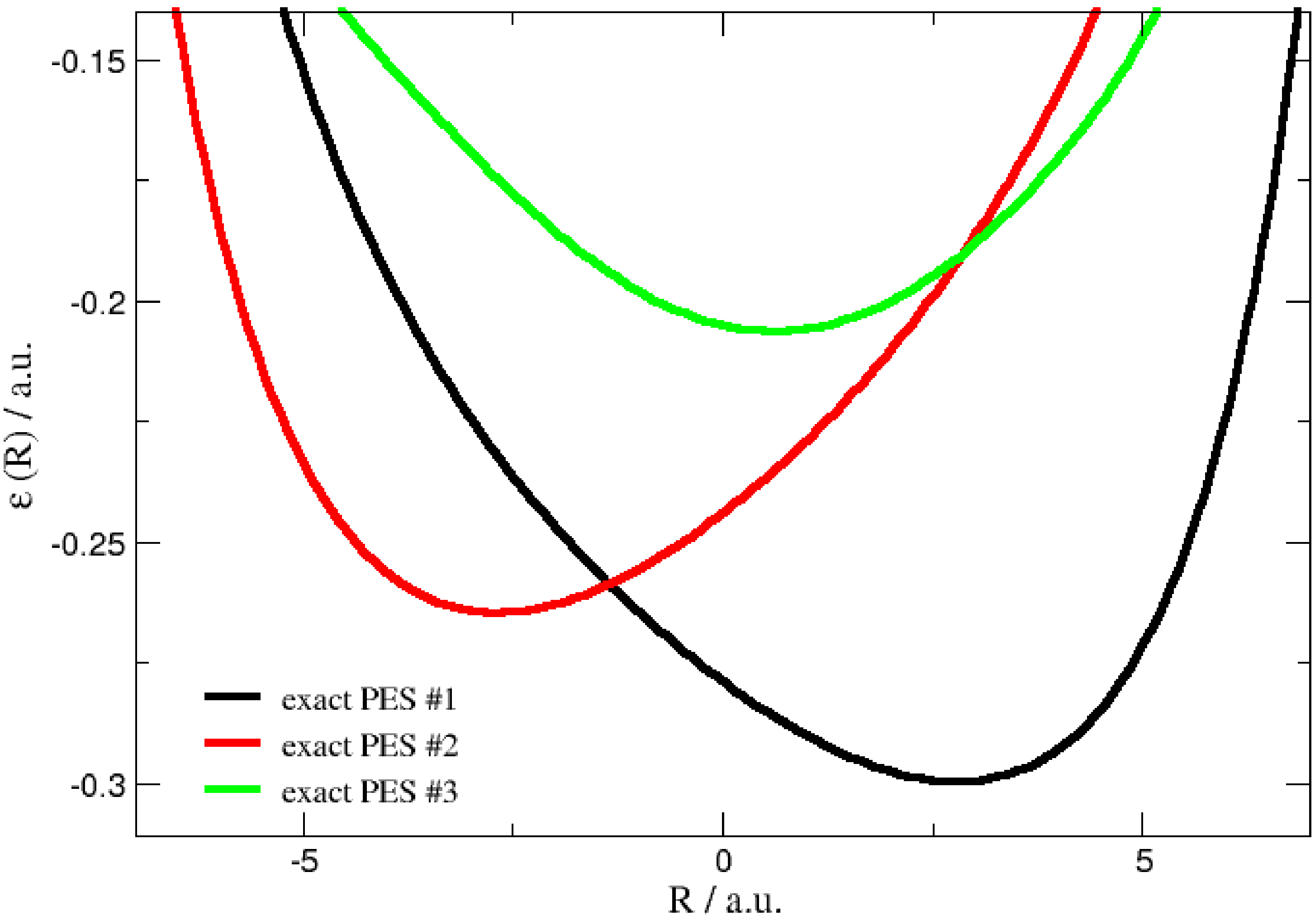
S. Shin, H. Metiu, JCP 102, 9285 (1995), JPC 100, 7867 (1996)



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
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exact PES #1
exact PES #2
exact PES #3

Exact Berry connection

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

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

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

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

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

with the exact nuclear current density J_ν

Another way of reading this equation:

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

Conclusion: The nuclear Schrödinger equation

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

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

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

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

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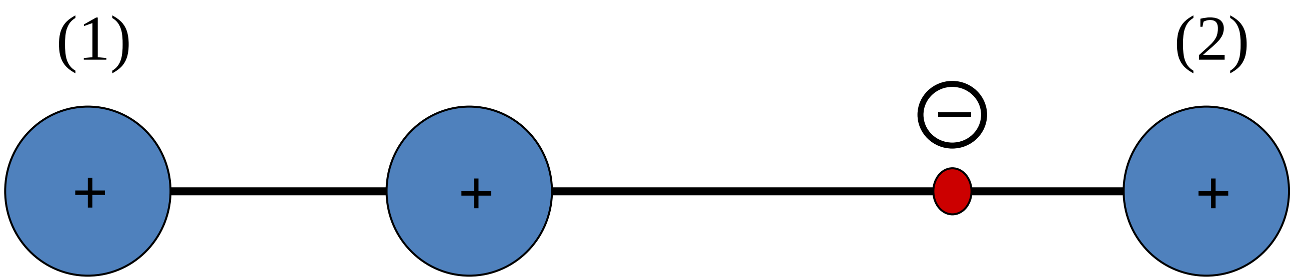
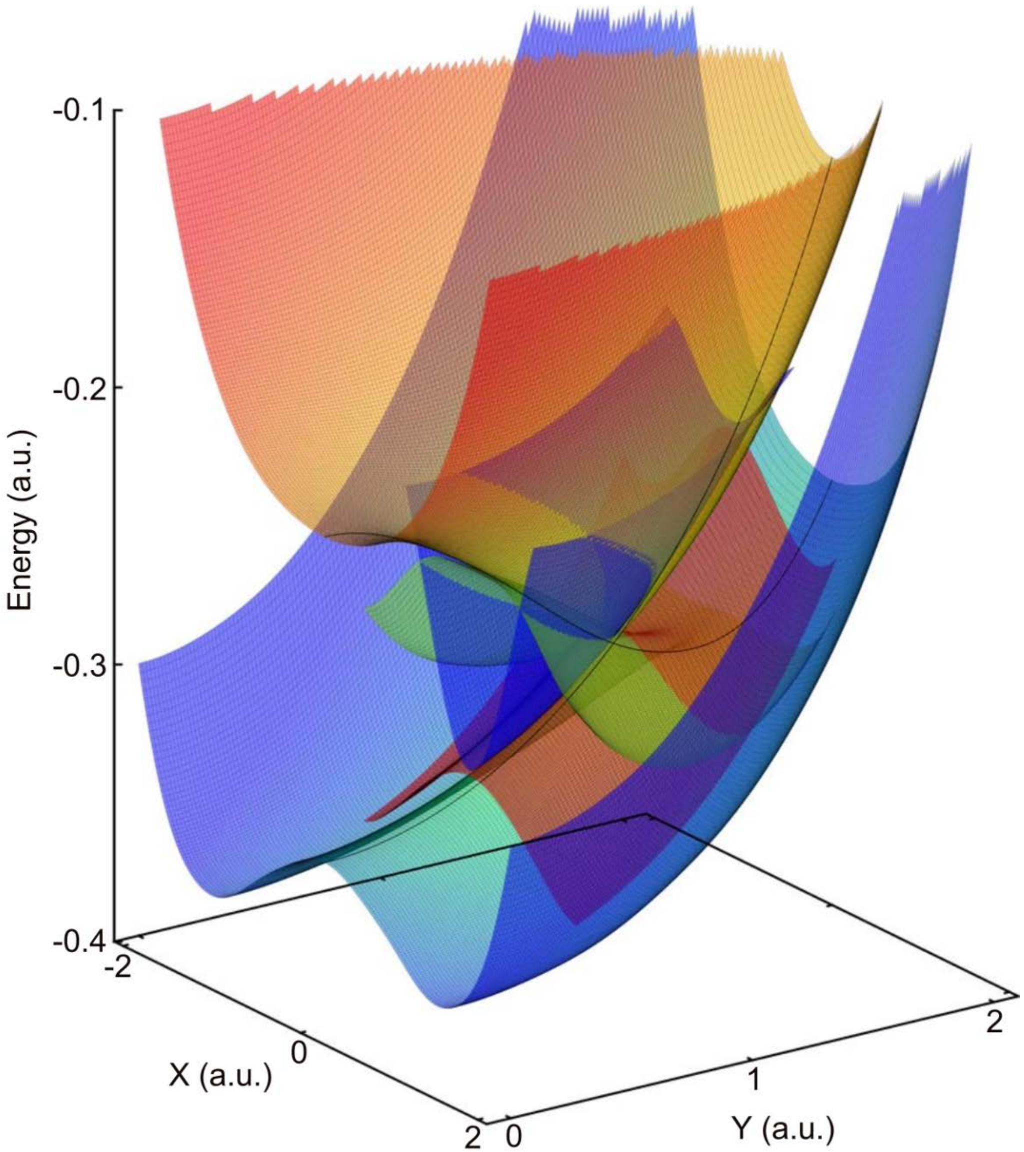
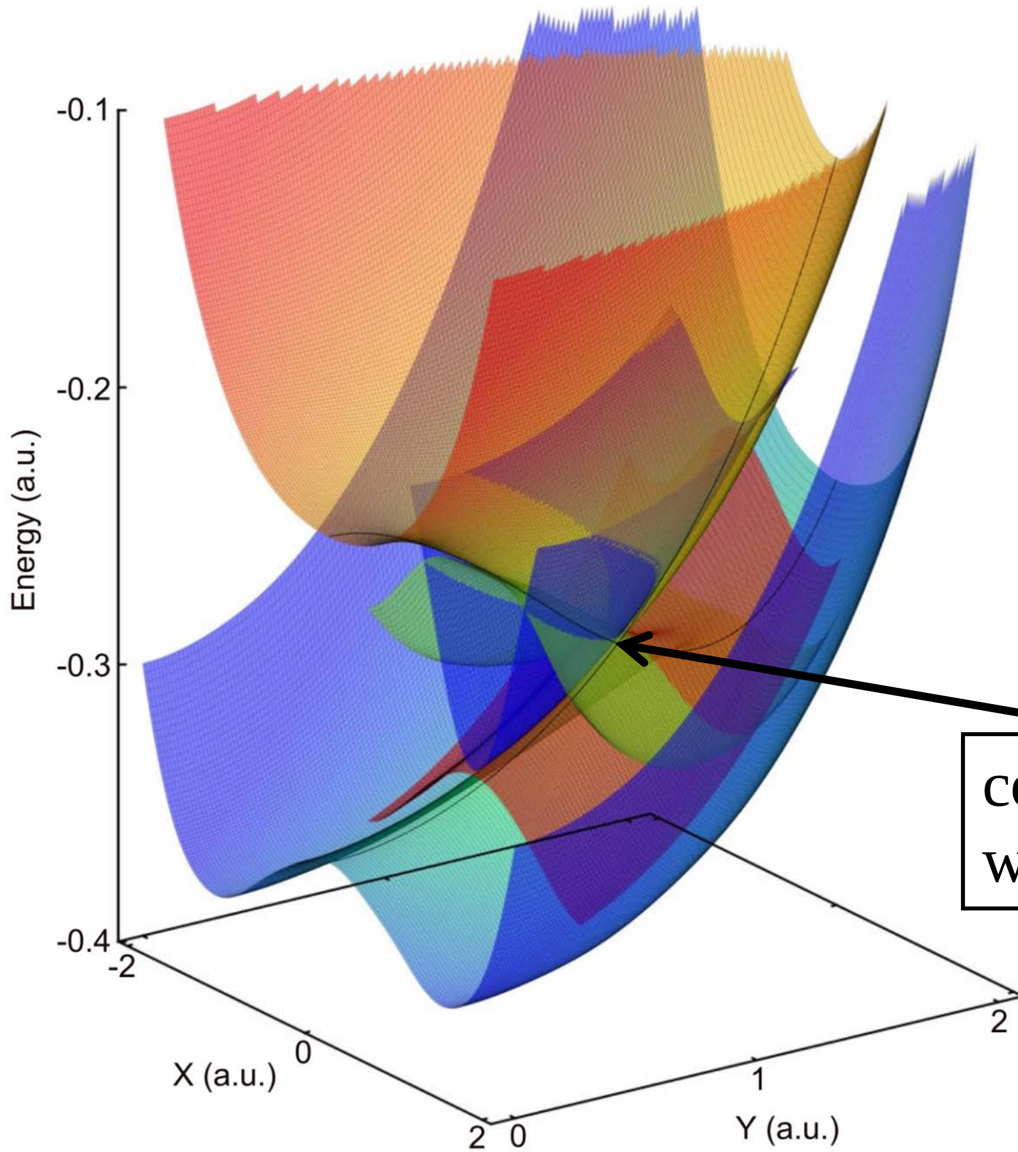
Look at Shin-Metiu model in 2D:



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 $\Phi^{BO}_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right)$ as function of R.

- Such non-analyticity is found in BO approximation.

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- Such non-analyticity is found in BO approximation.

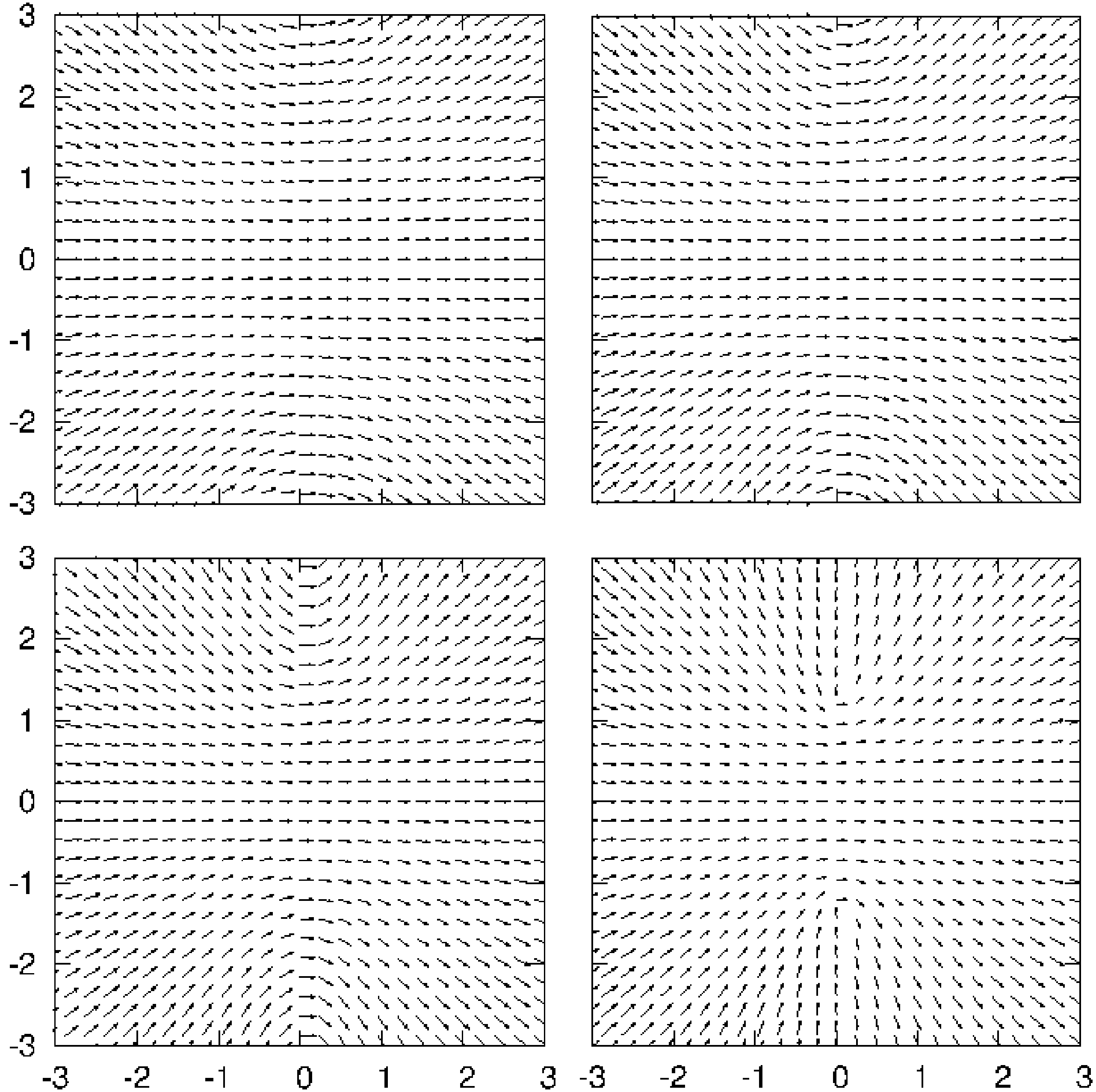
Does the exact electronic wave function show such non-analyticity as well (in 2D Shin-Metiu model)?

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

as function of nuclear mass M.

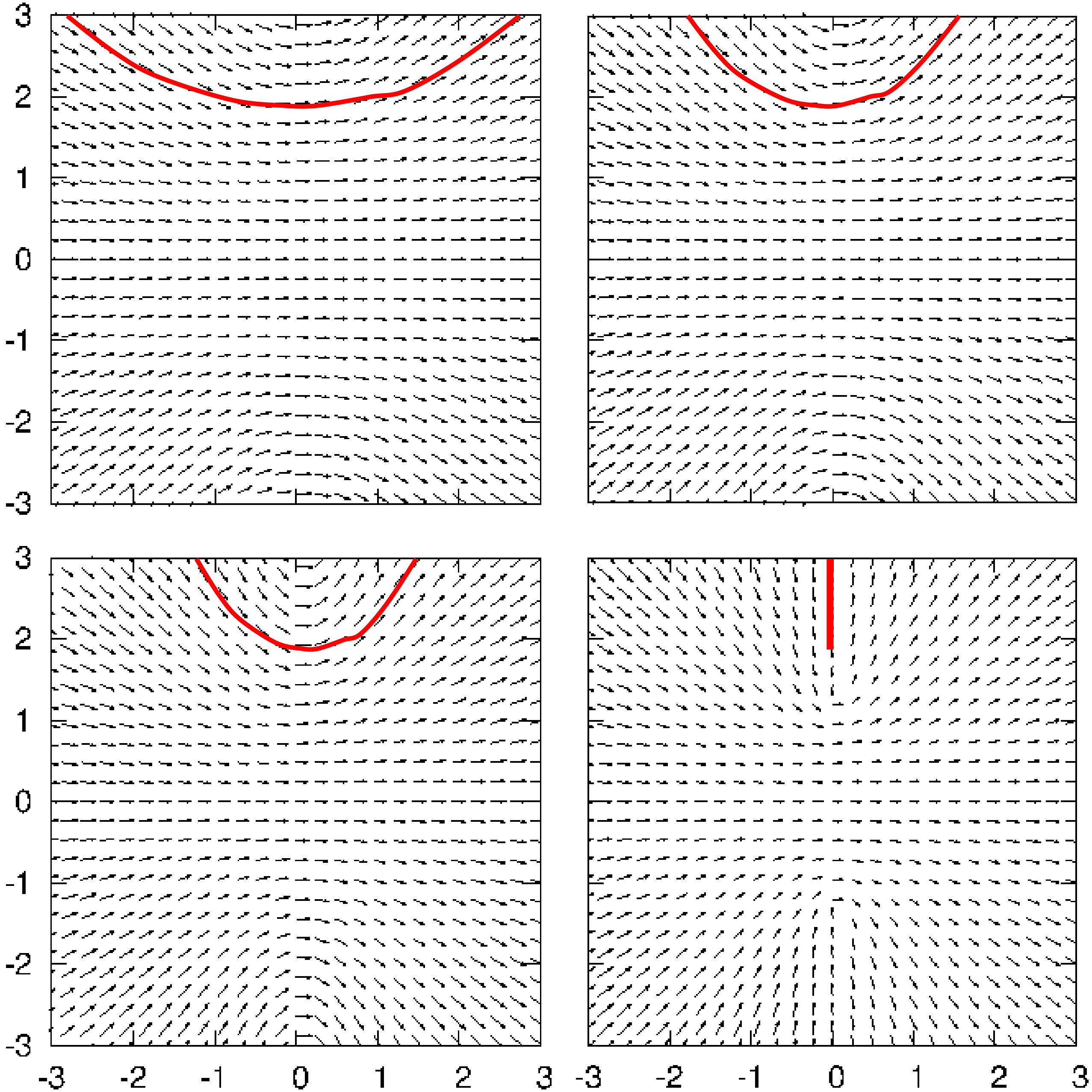
S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, arXiv: 1402.0227 (2014)

D(R)



M = ∞

D(R)



M = ∞

<u>Open Question</u>: Can one prove <u>in general</u> that the exact molecular Berry phase vanishes? Are there systems where the non-analyticity associated with the molecular Berry phase survives as true feature of nature.

Time-dependent case

Hamiltonian for the complete system of N_e electrons with coordinates $(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) \equiv \underline{\mathbf{r}}$ 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 $\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla_\nu^2}{2M_\nu}$ $\quad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m}$ $\quad \hat{W}_{nn} = \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$

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

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

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

can be written in the form

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

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

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

Eq. ❷

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

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

Theorem T-II

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

Eq. ❶

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

Eq. ❷

Exact Berry potential

Exact TDPES

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

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

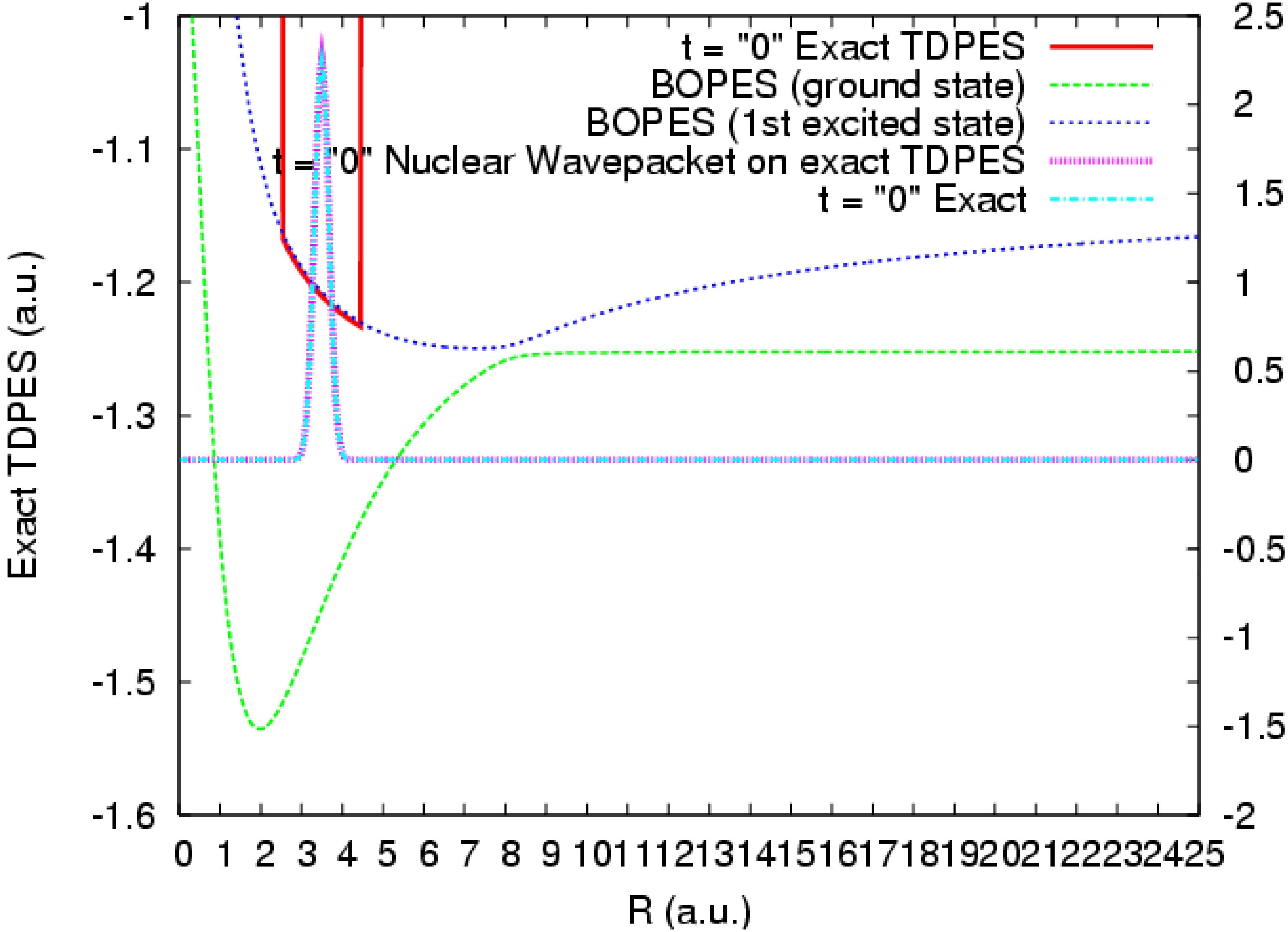
N-body version of Runge-Gross theorem guarantees that ϵ(R,t) and A(R,t) are UNIQUE (up to within a gauge transformation)

How does the exact time-dependent PES look like?

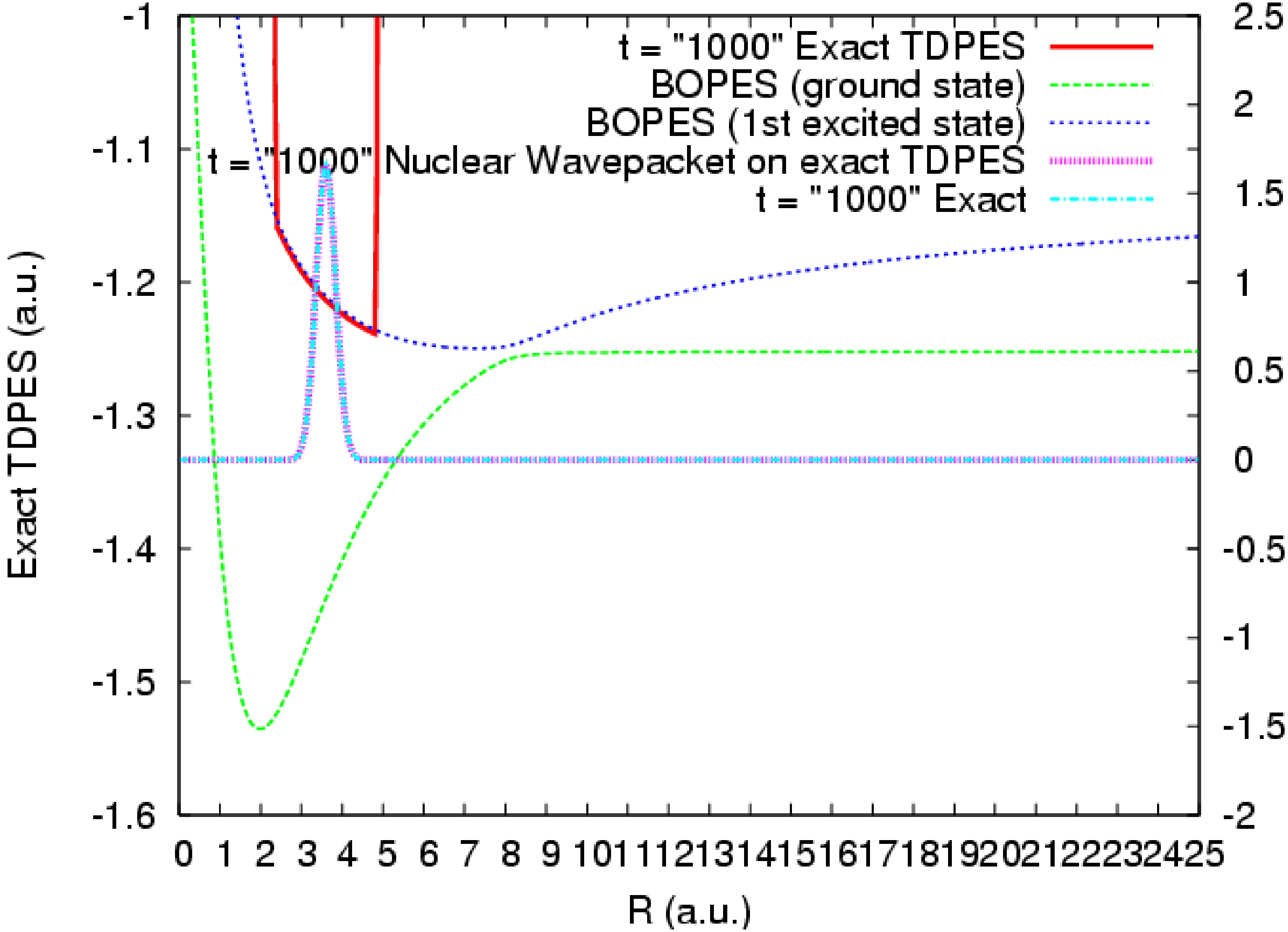
Example: Nuclear wave packet going through an avoided crossing (Zewail experiment)

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

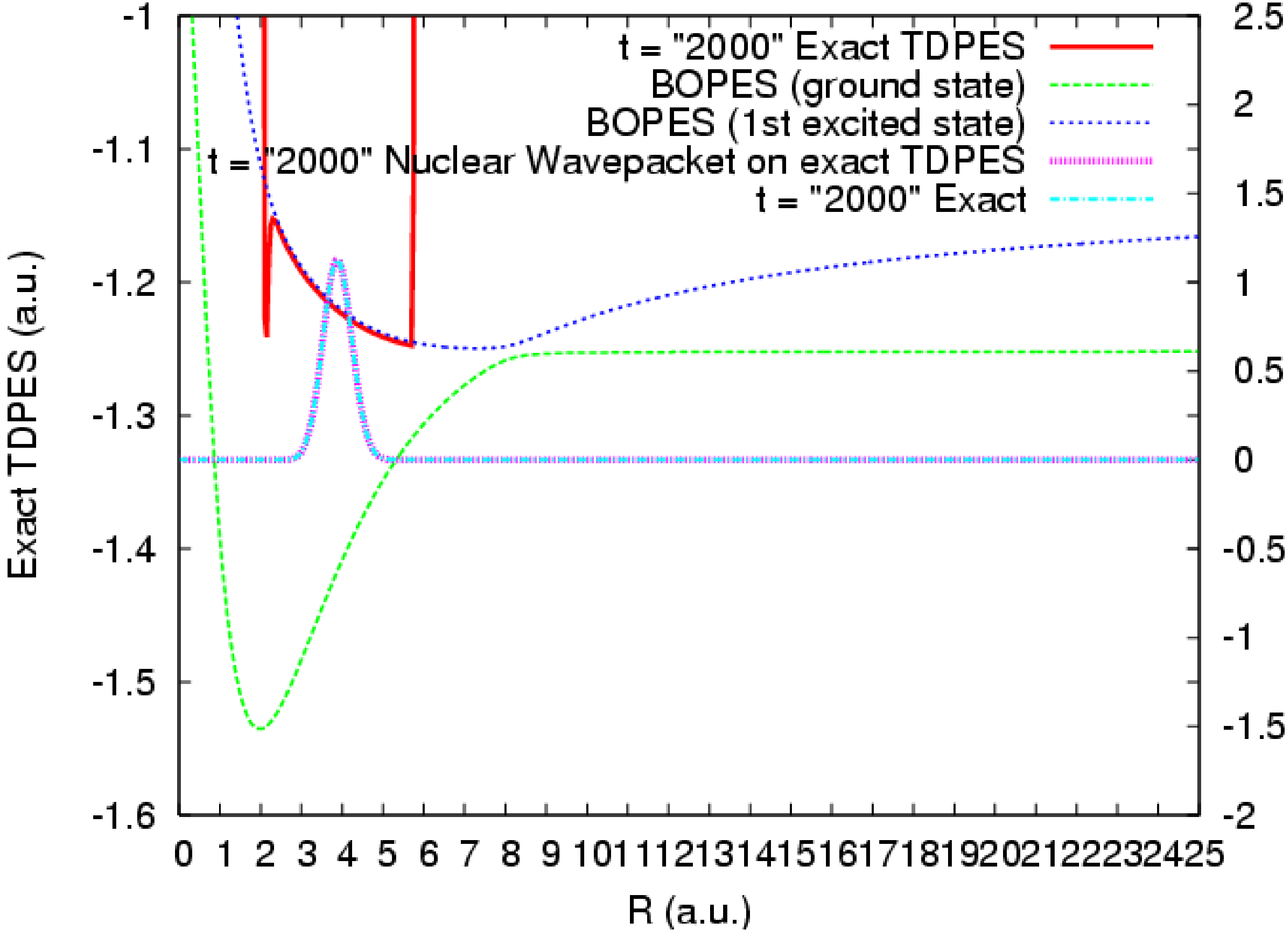
F. Agostini, A. Abedi, Y. Suzuki, E.K.U. Gross,
Mol. Phys. 111, 3625 (2013)



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
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
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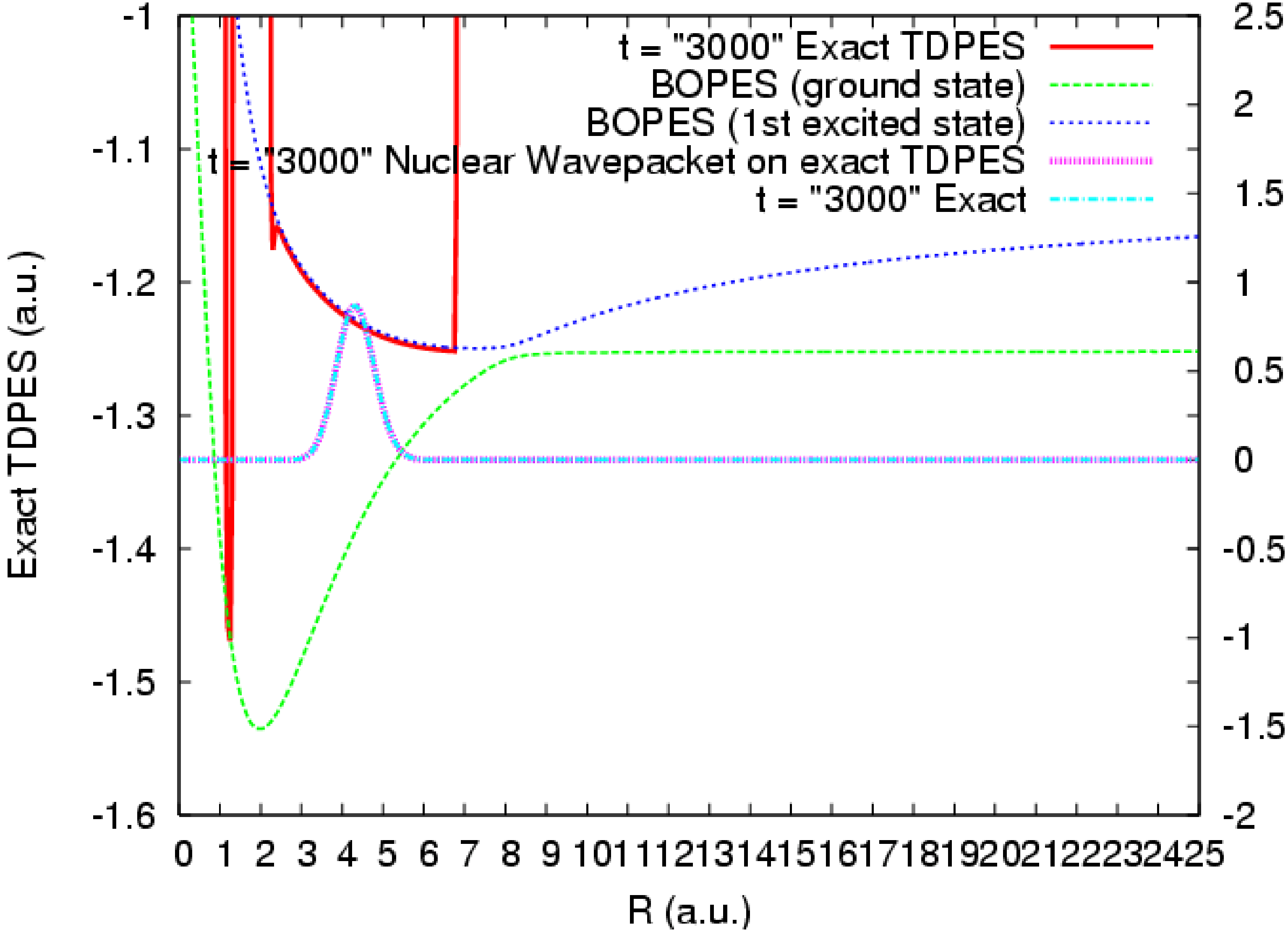
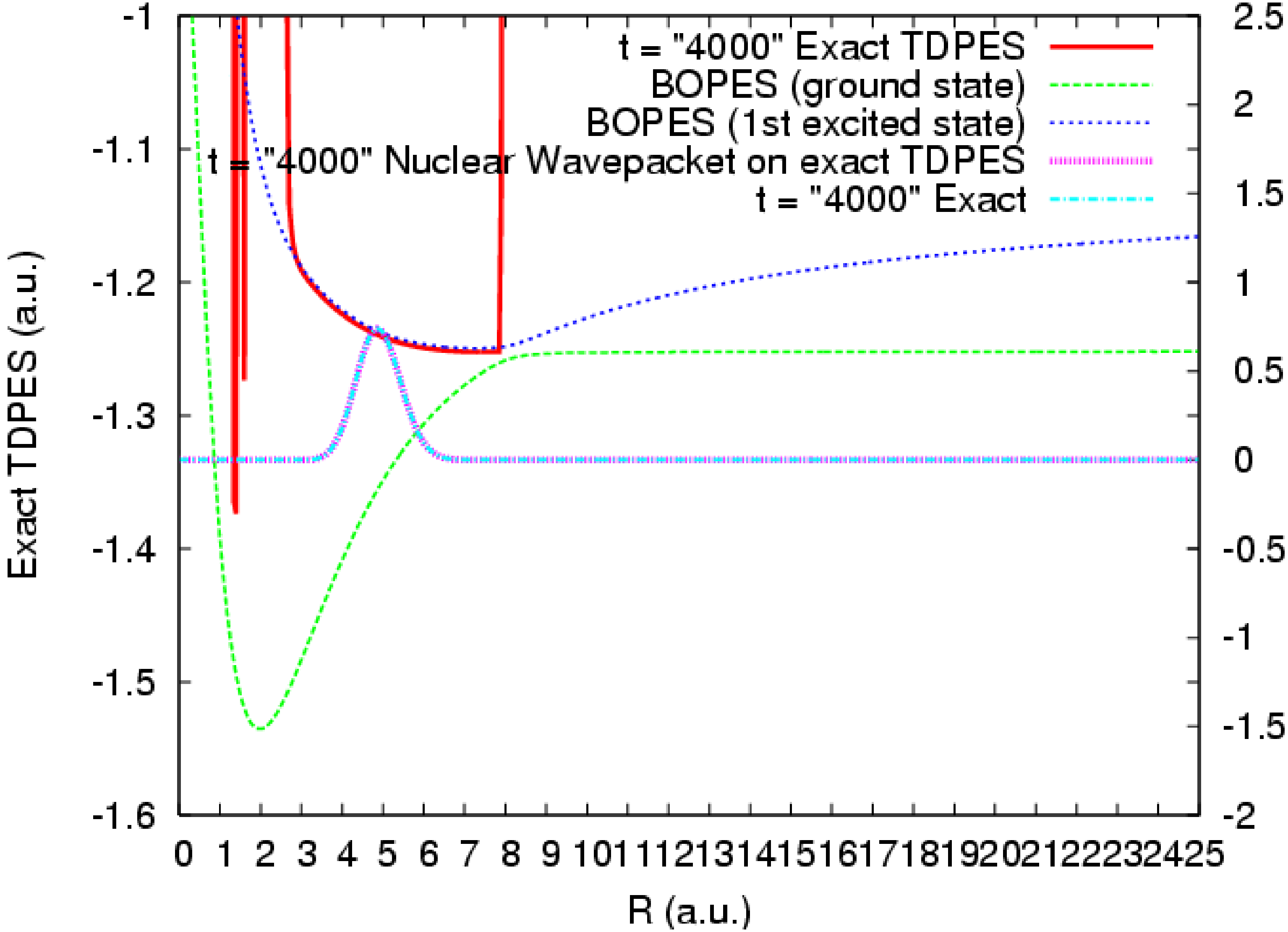
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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
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1.5
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0.5
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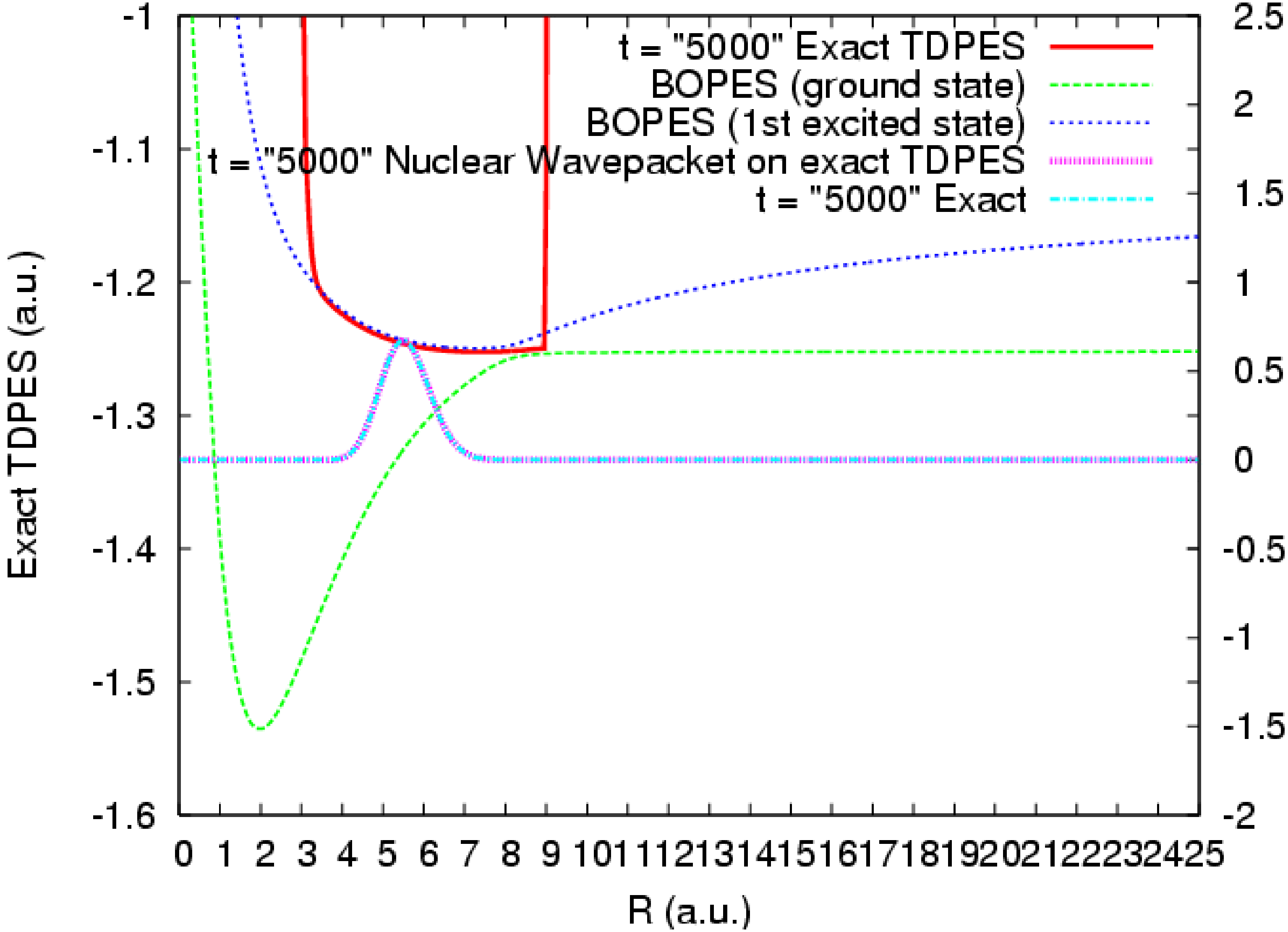
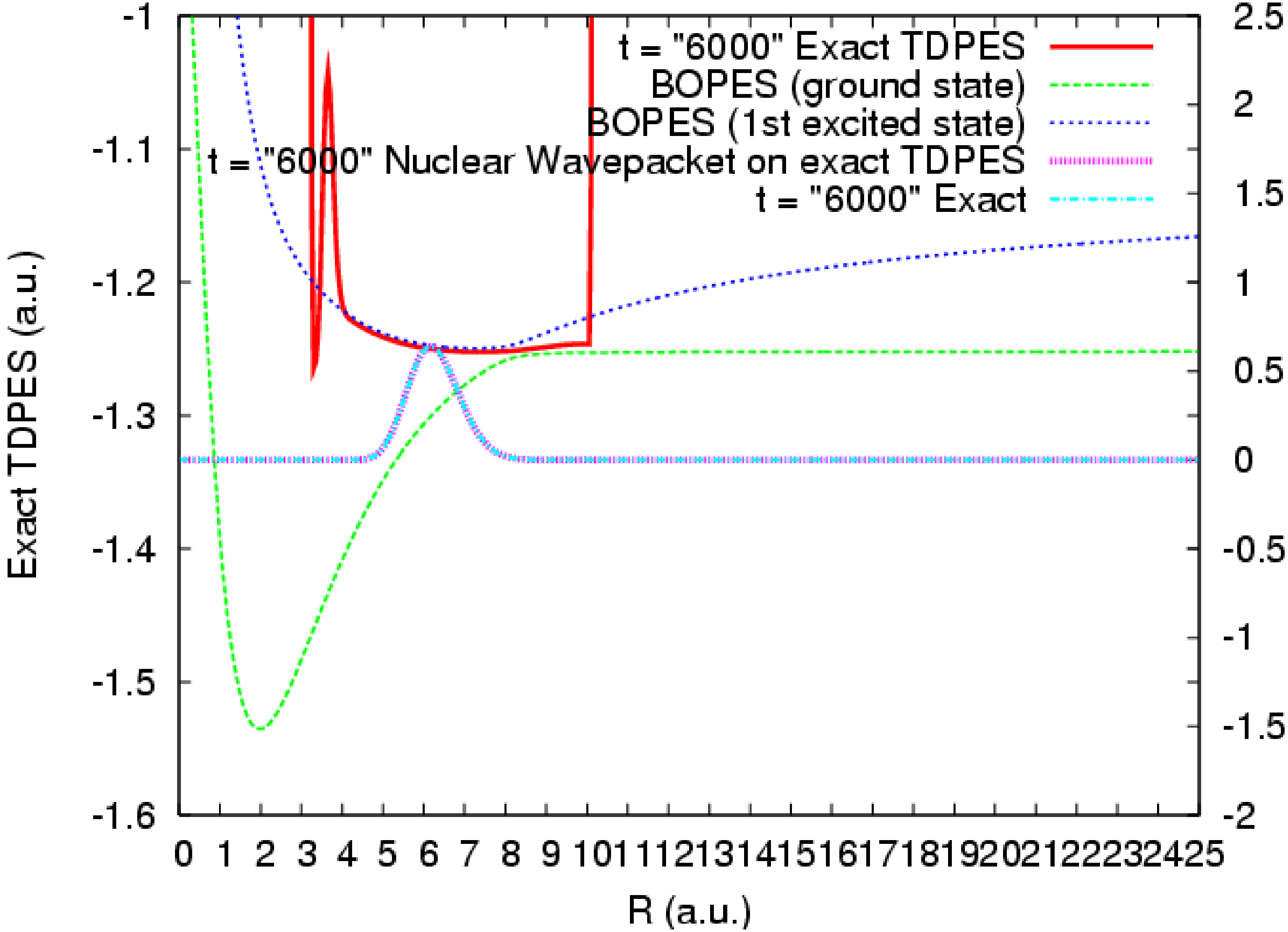
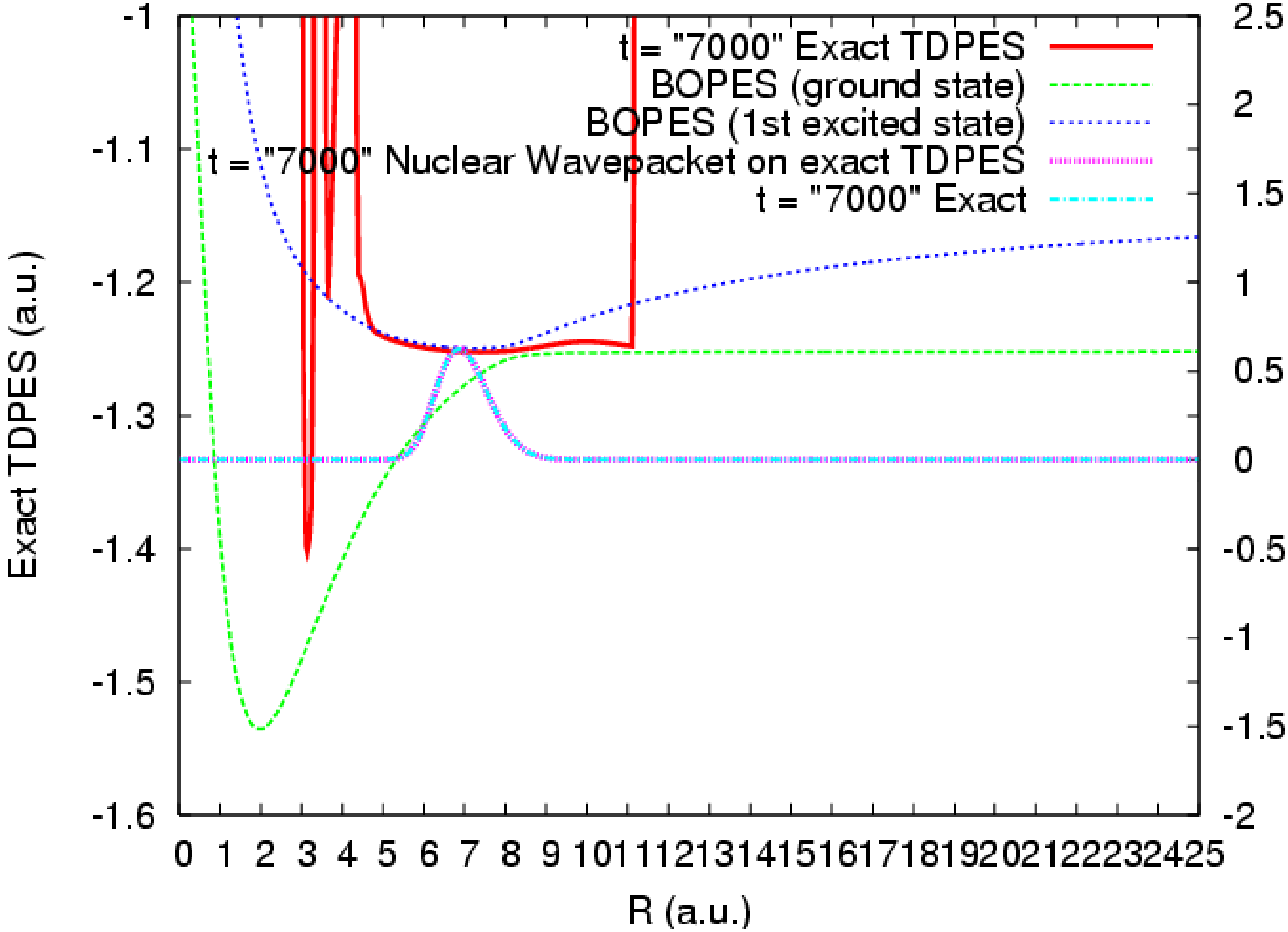
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



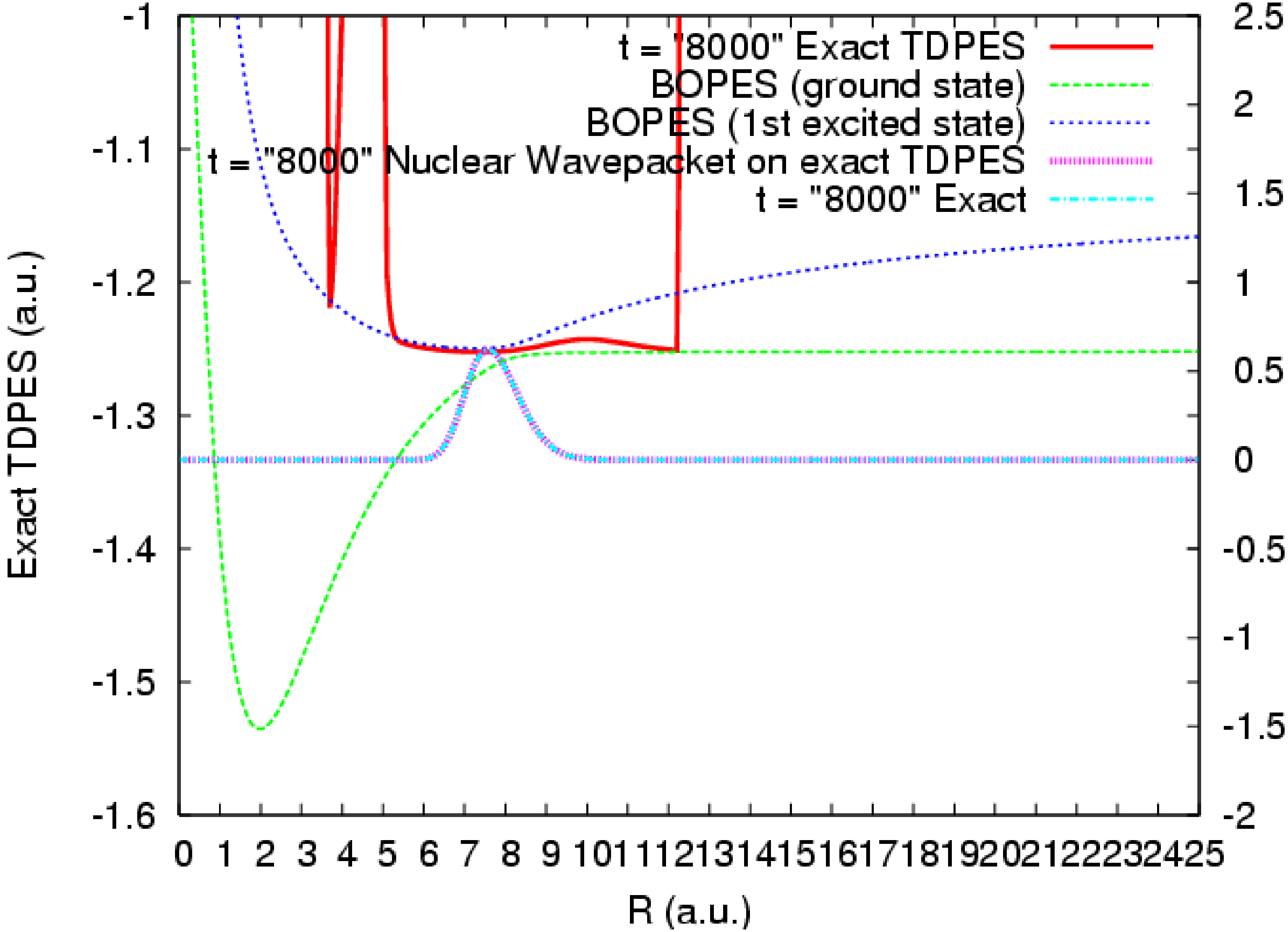
t = "5000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "5000" Nuclear Wavepacket on exact TDPES
t = "5000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



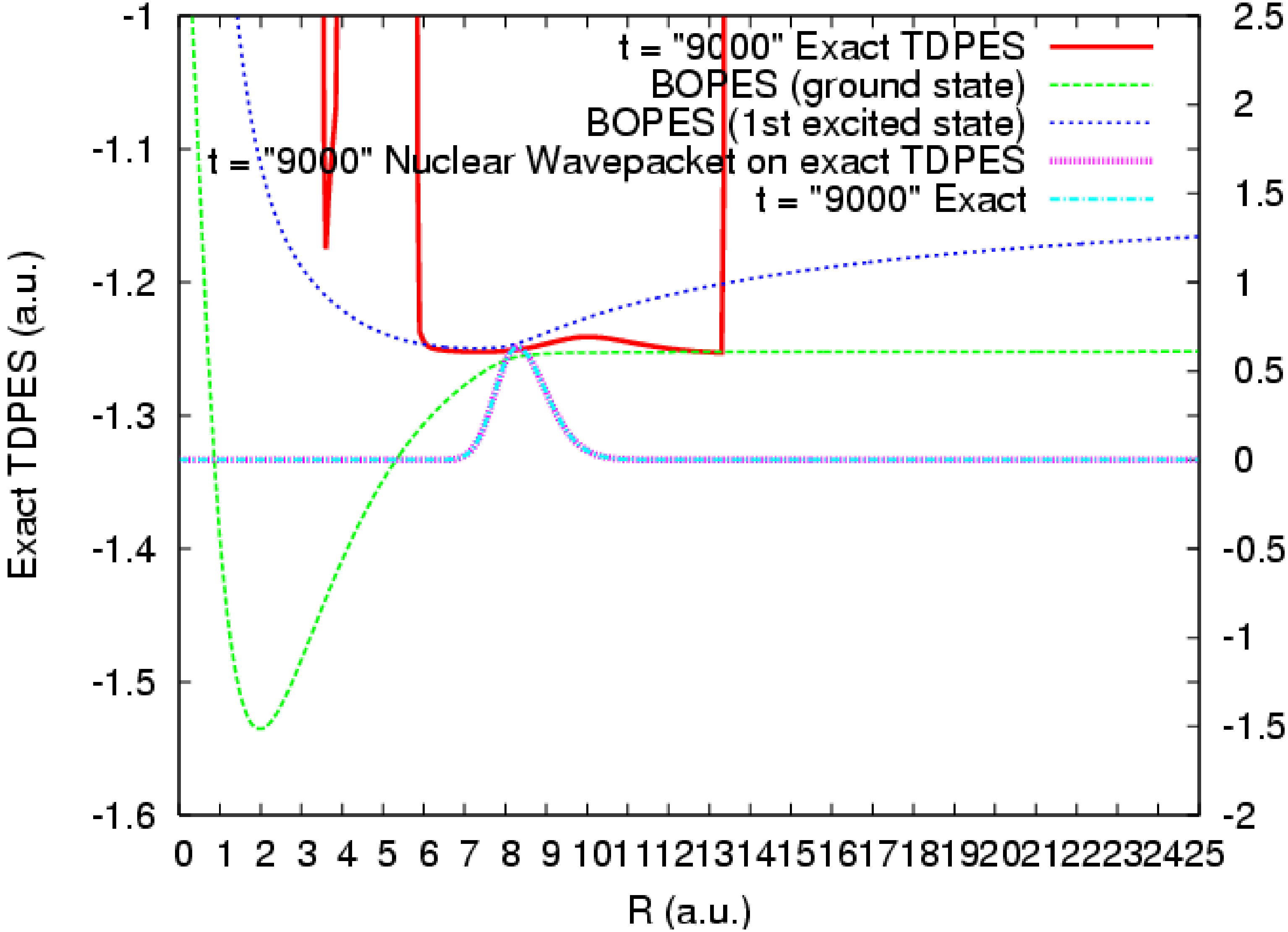
t = "6000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "6000" Nuclear Wavepacket on exact TDPES
t = "6000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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
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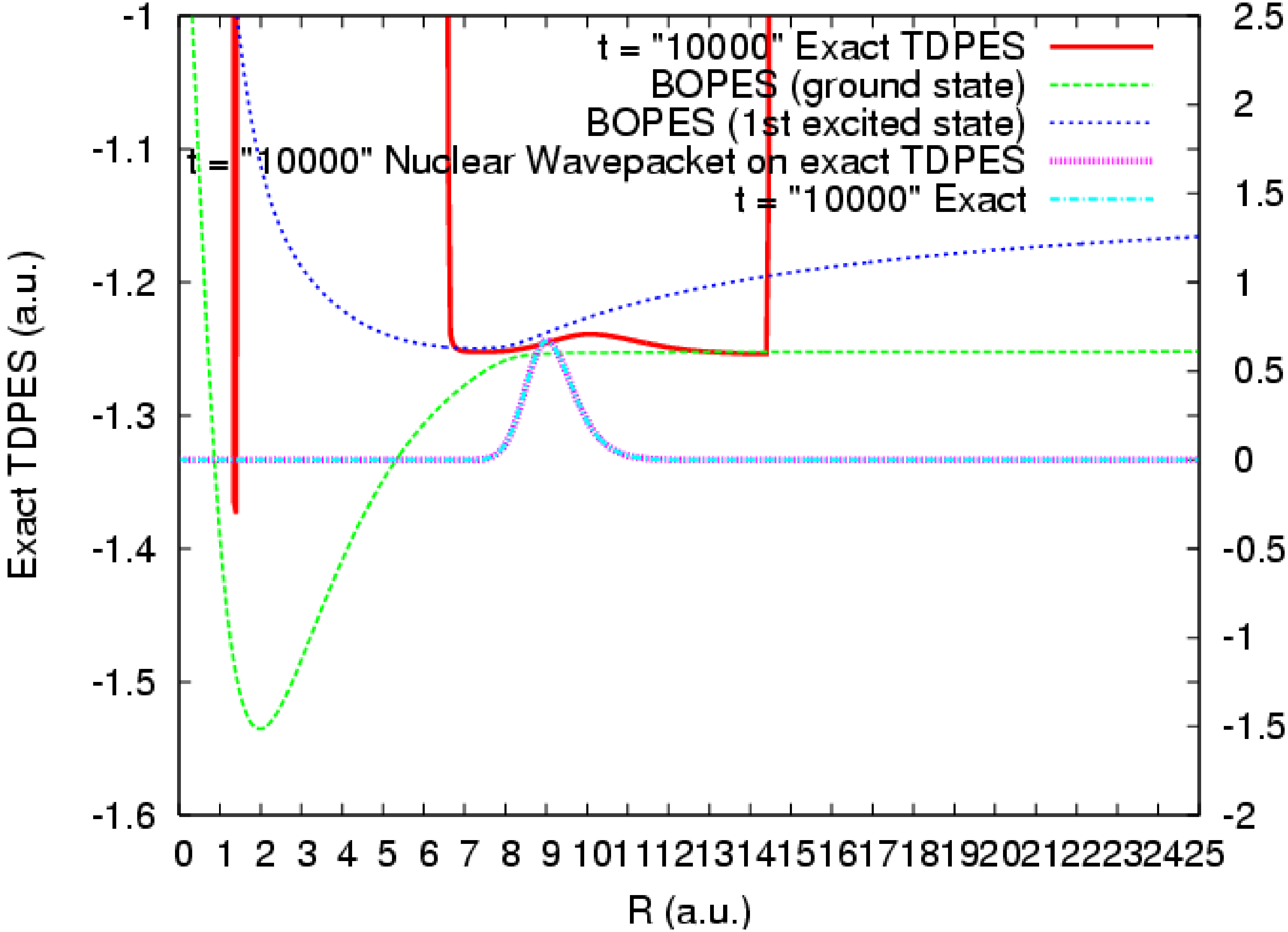
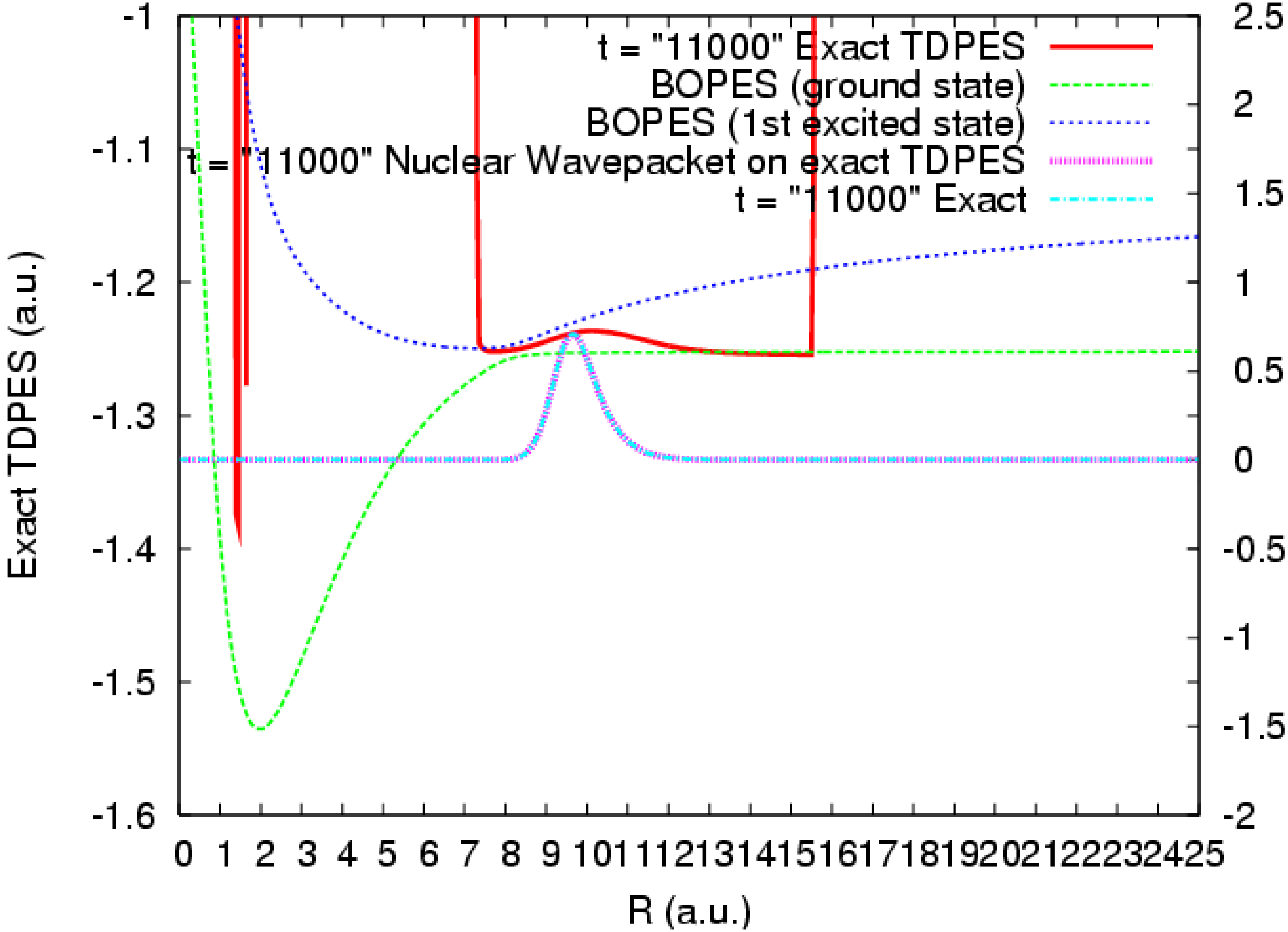
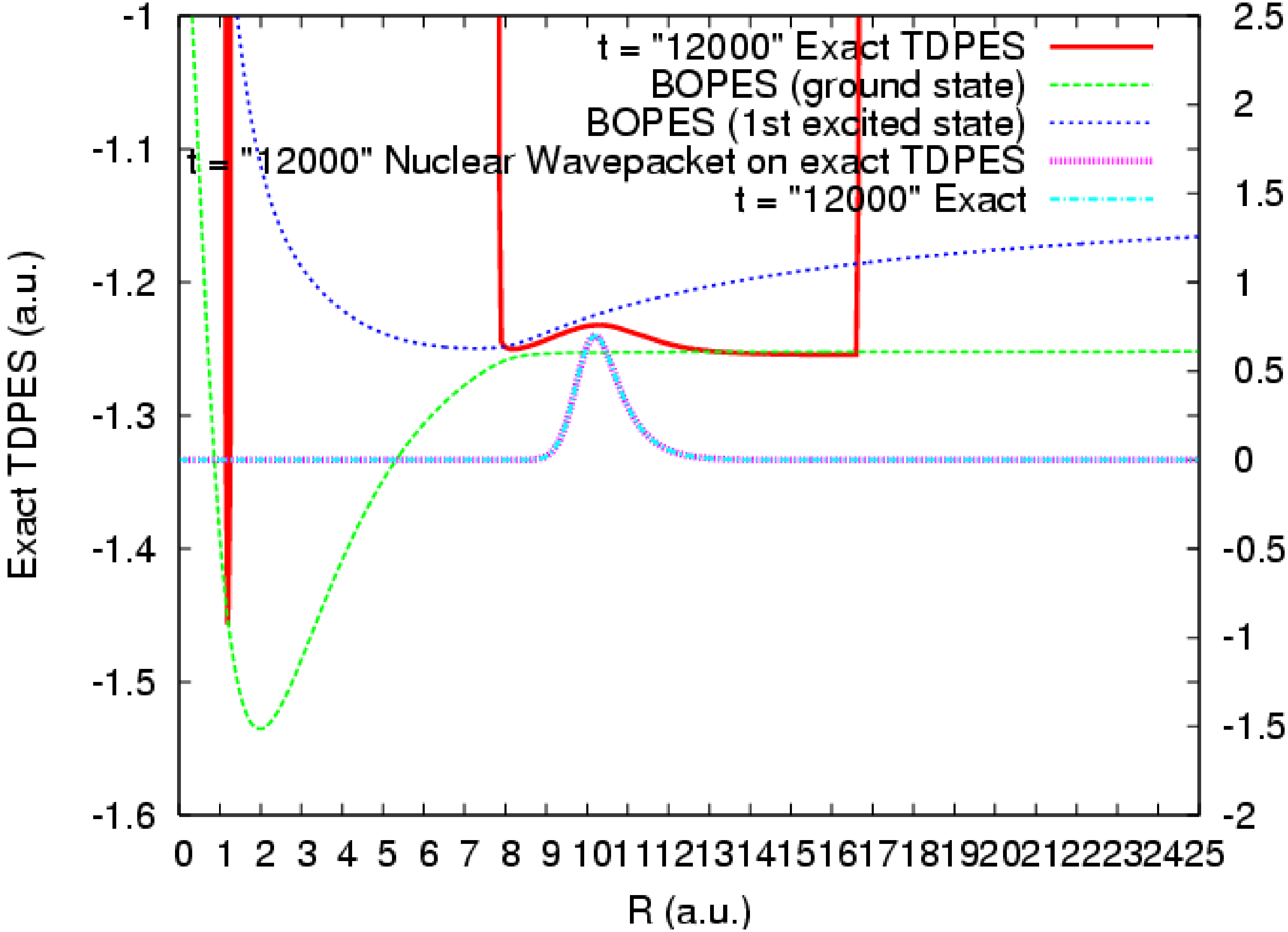
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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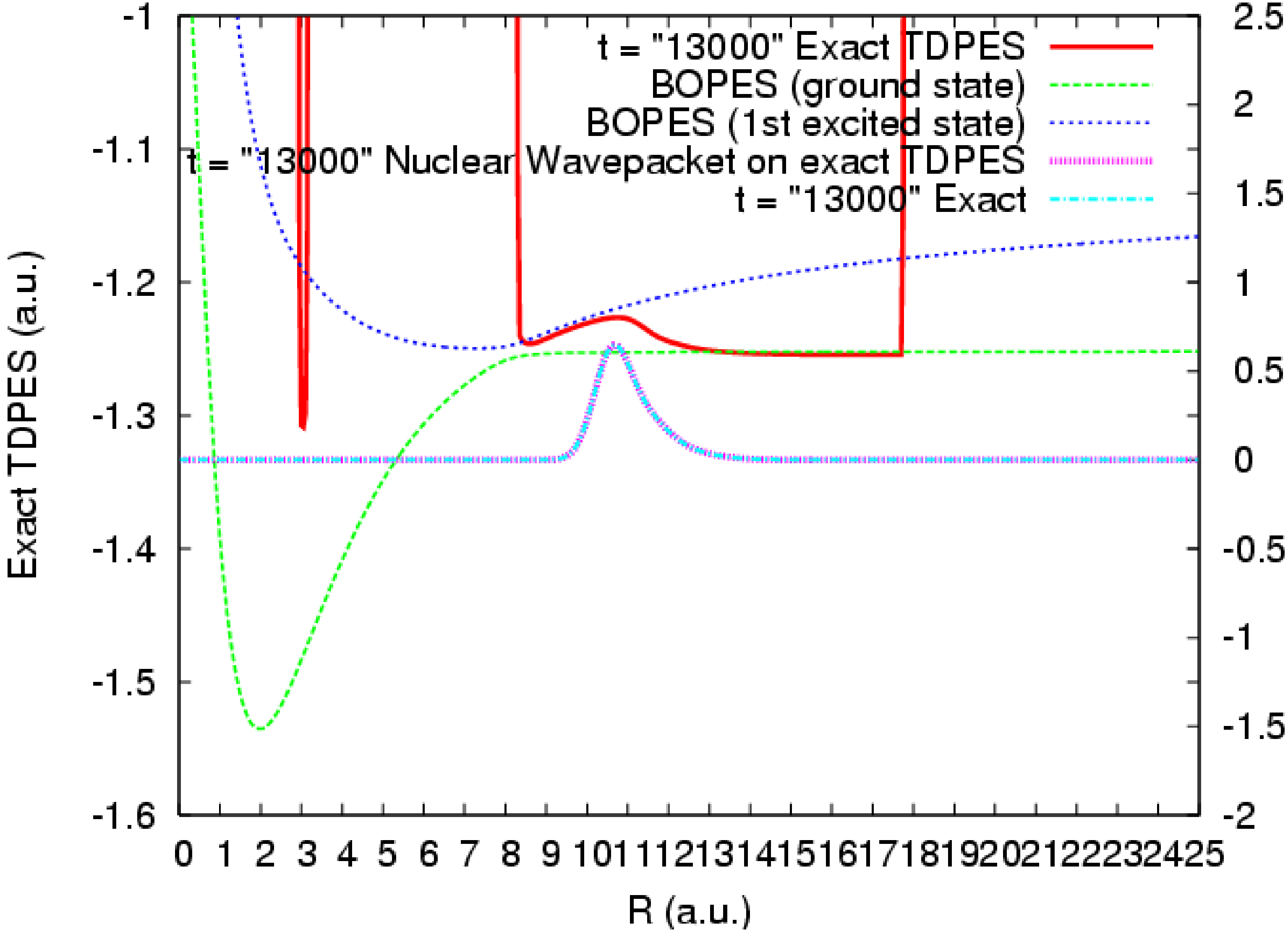
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "13000" Nuclear Wavepacket on exact TDPES
t = "13000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2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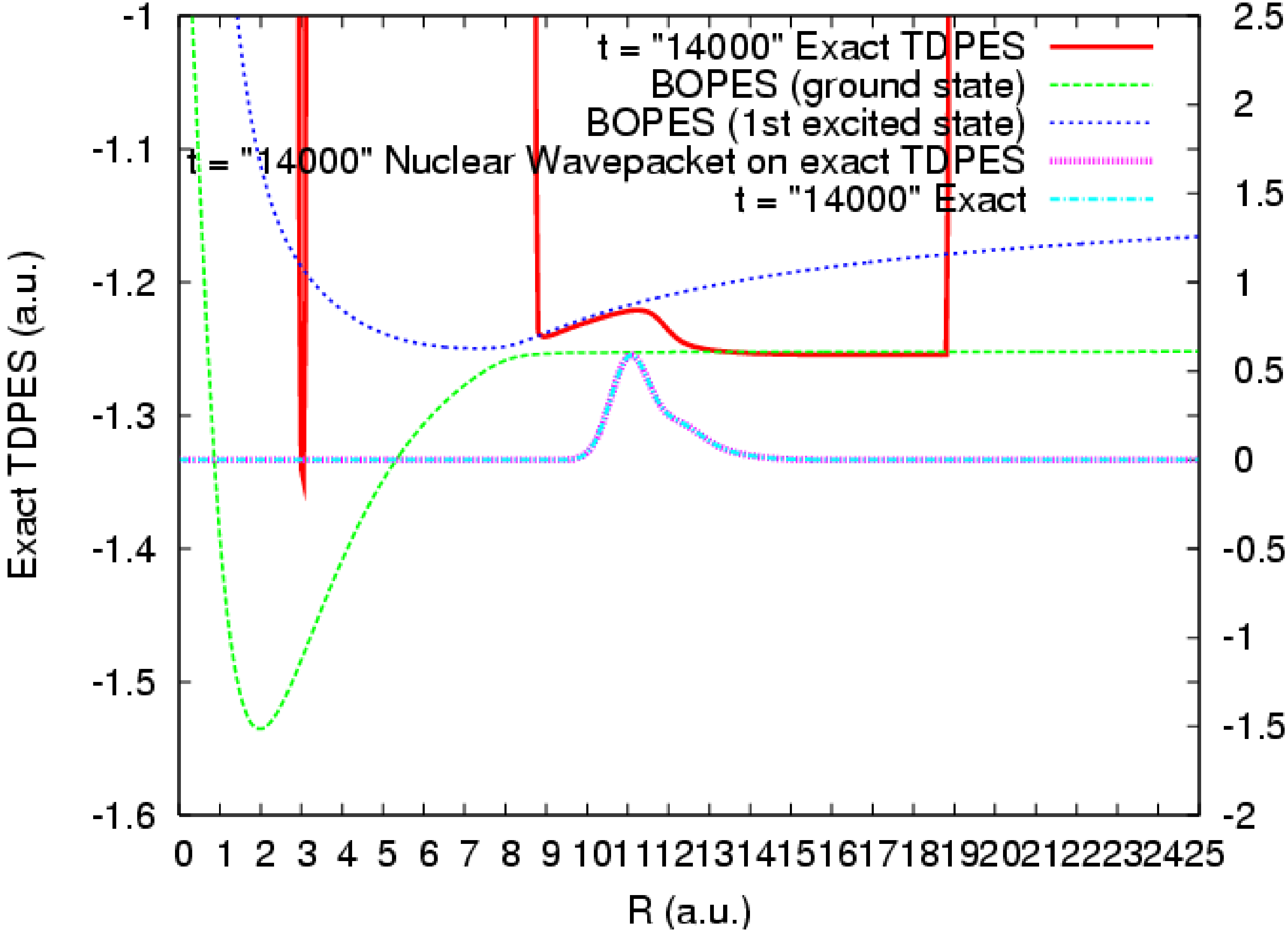
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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
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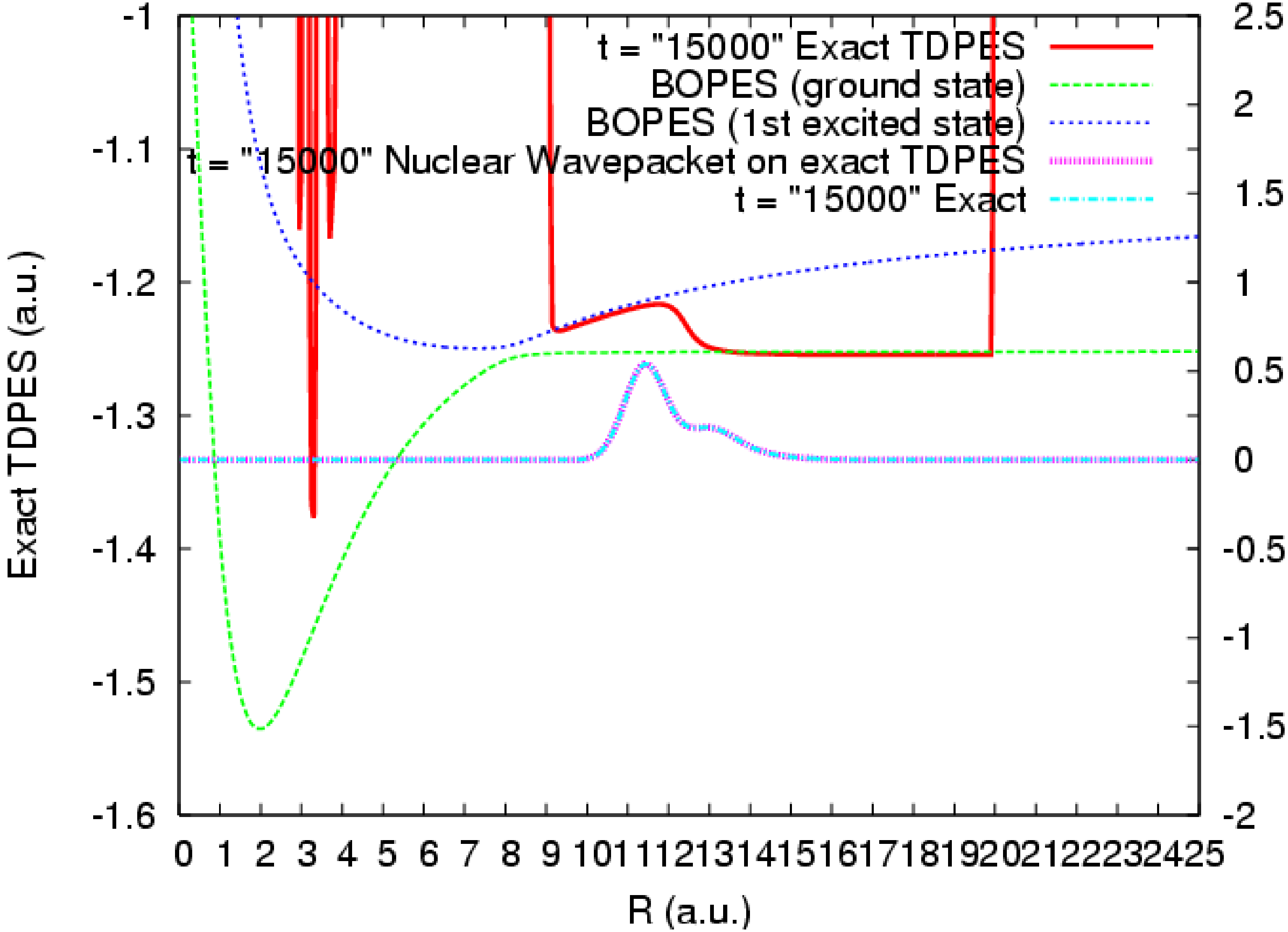
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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
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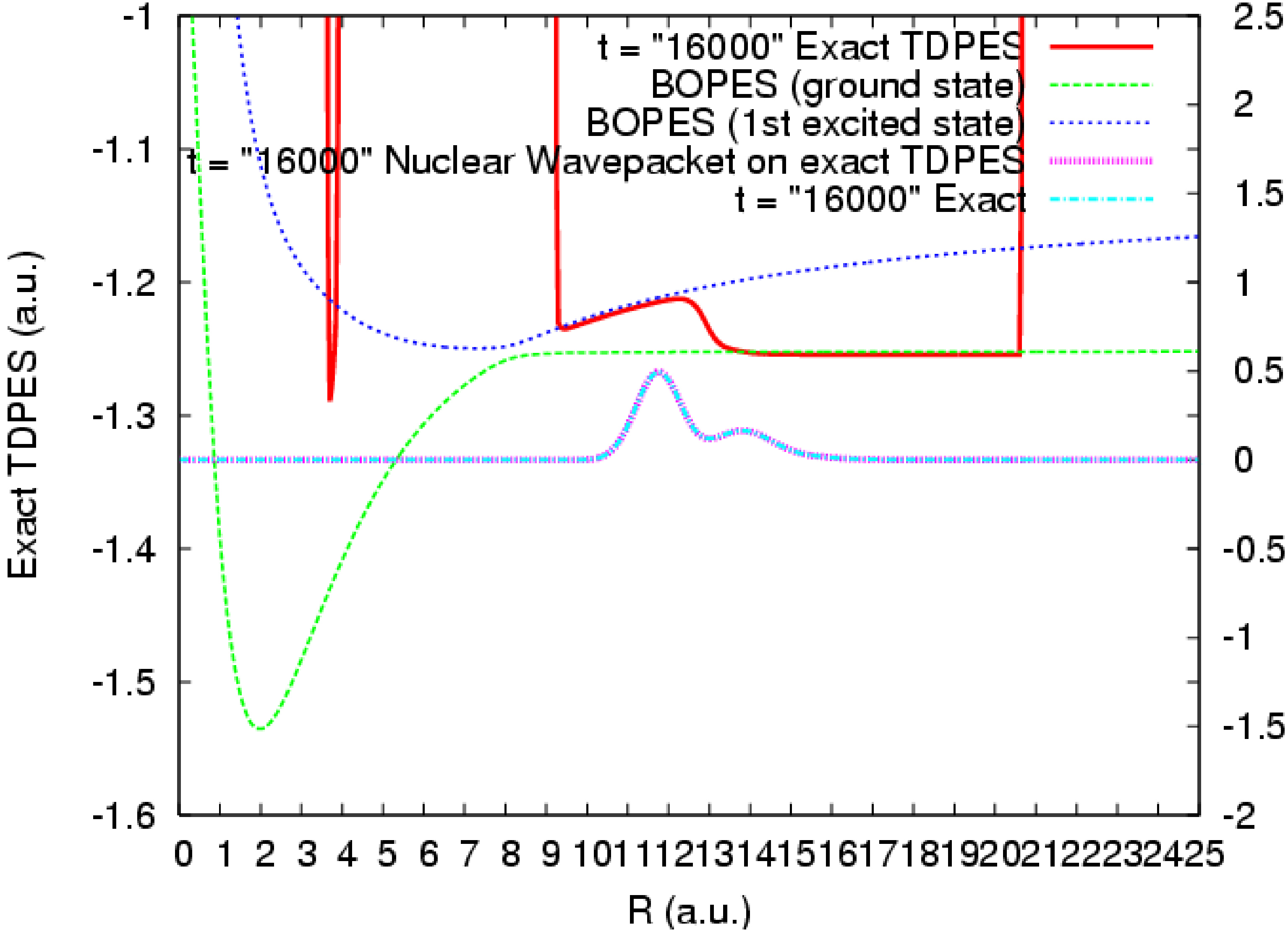
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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BOPES (ground state)
BOPES (1st excited state)
t = "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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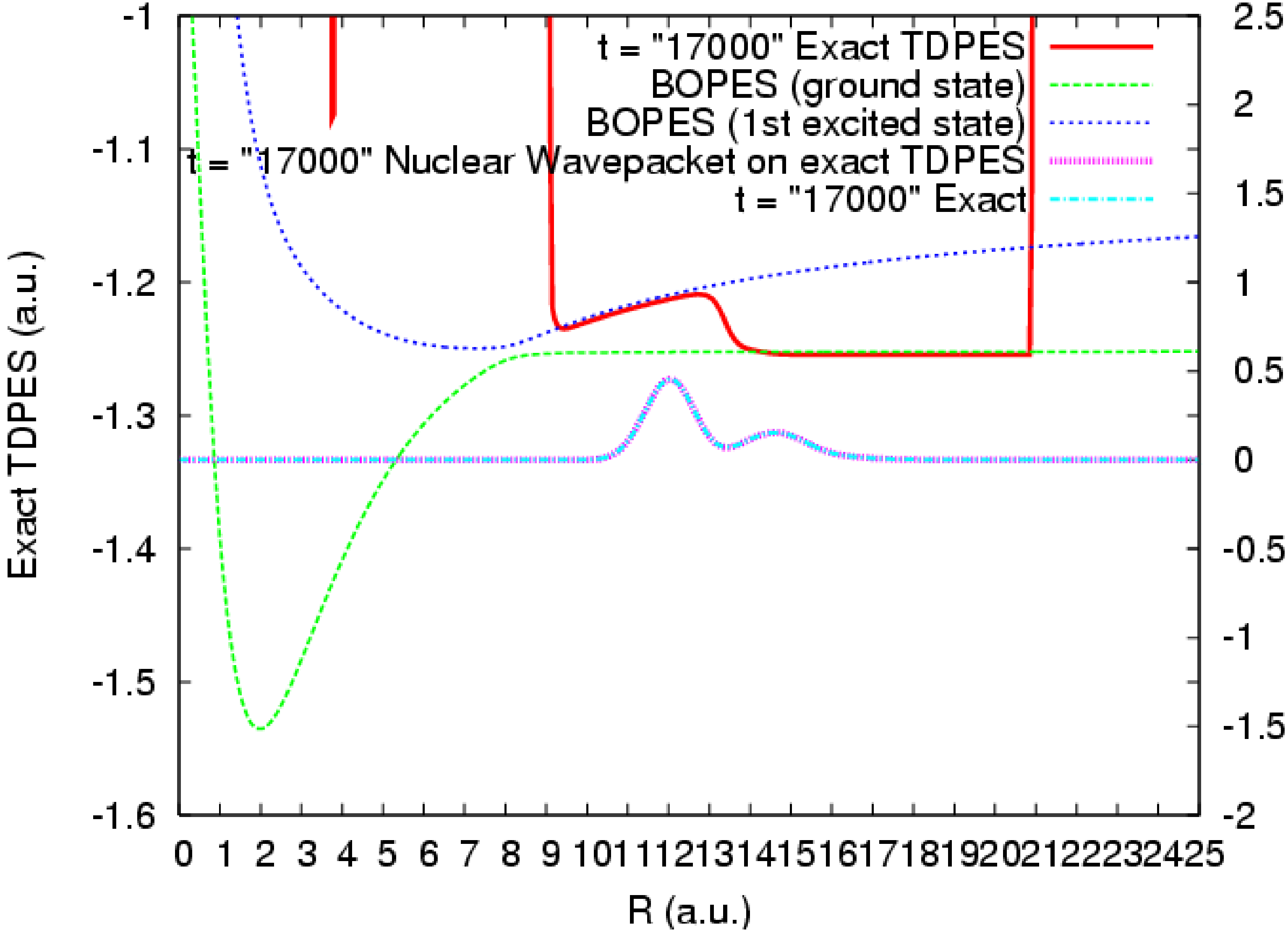
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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
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-1
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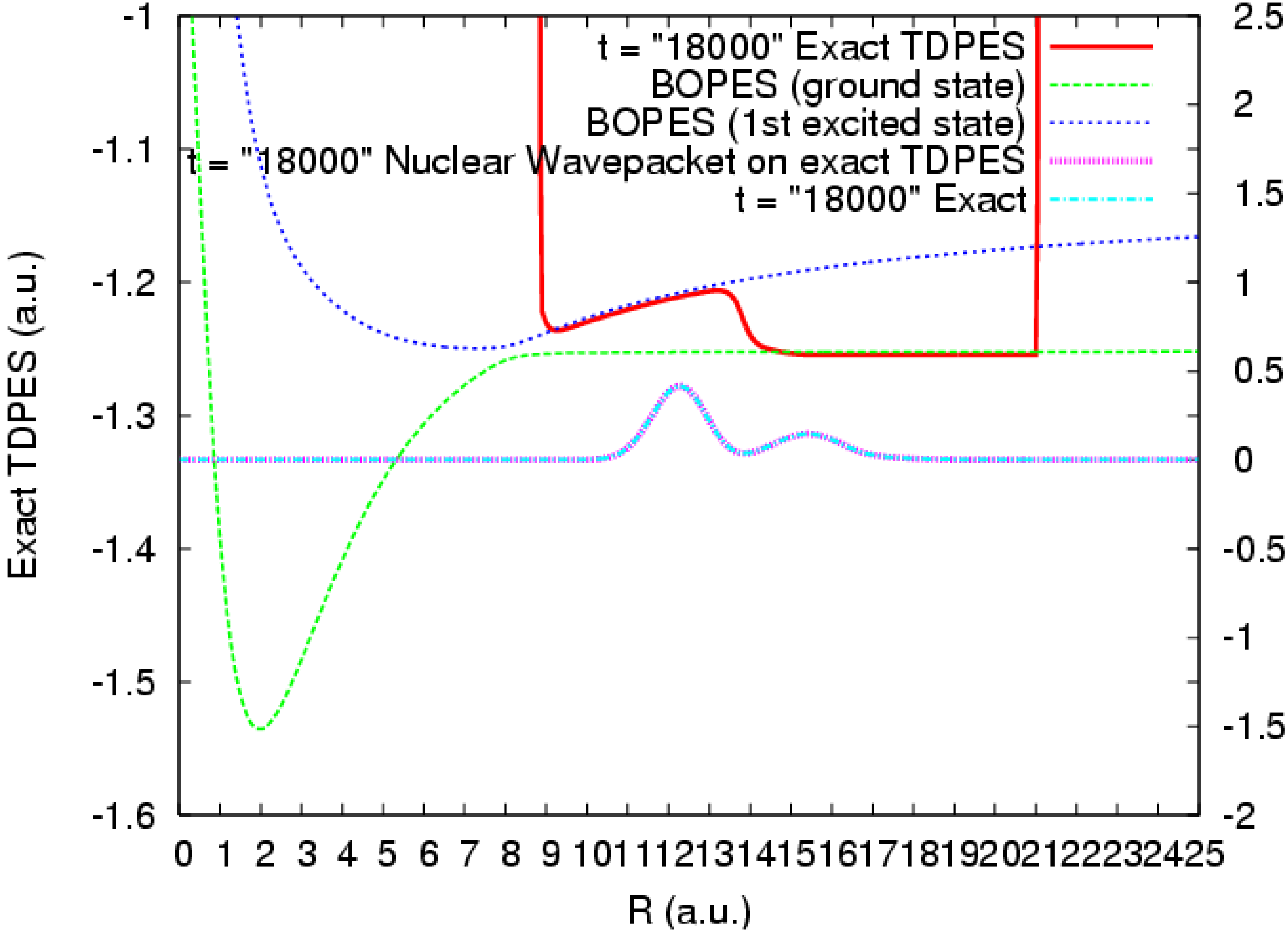
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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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-1.5
-2
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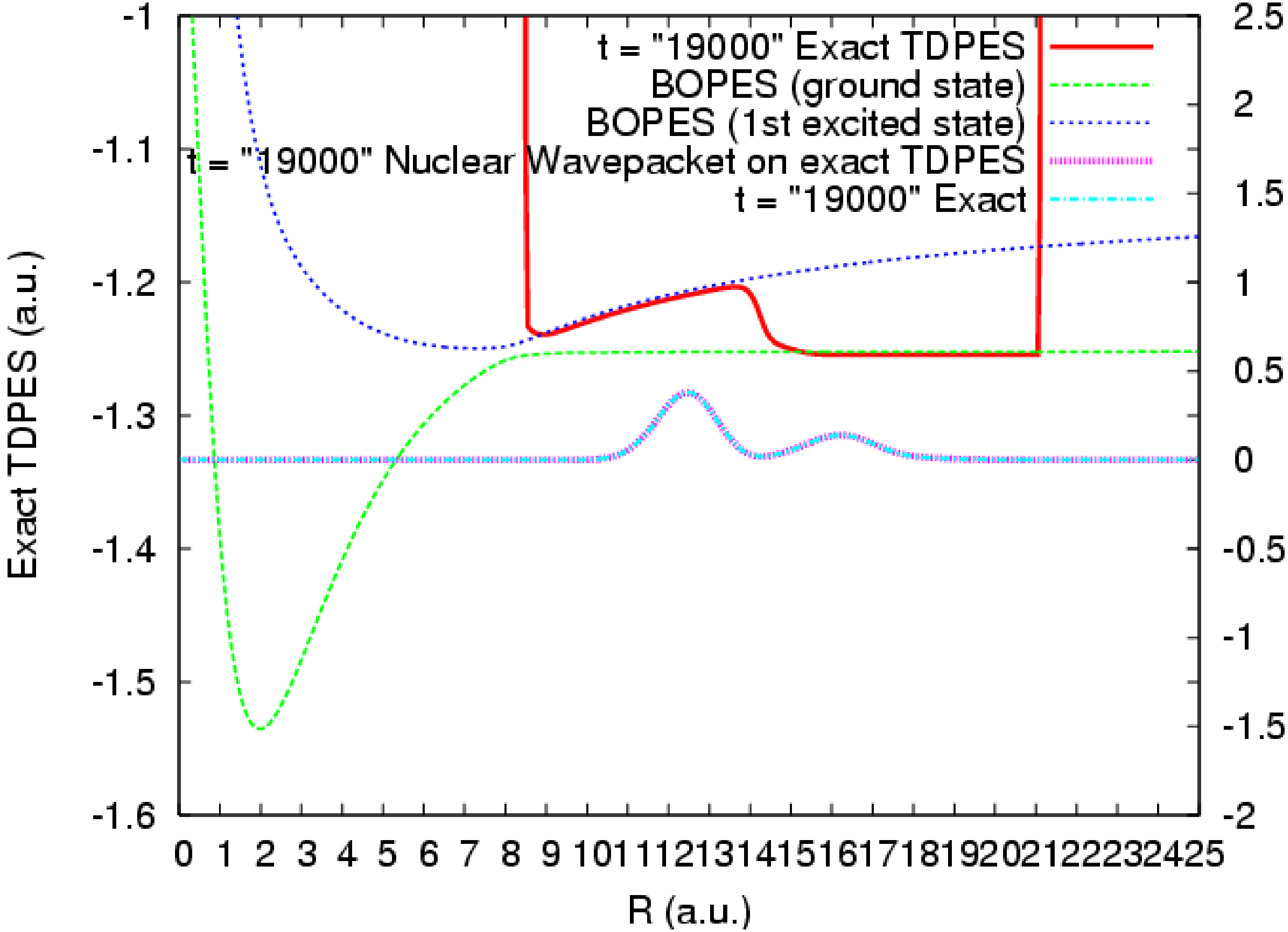
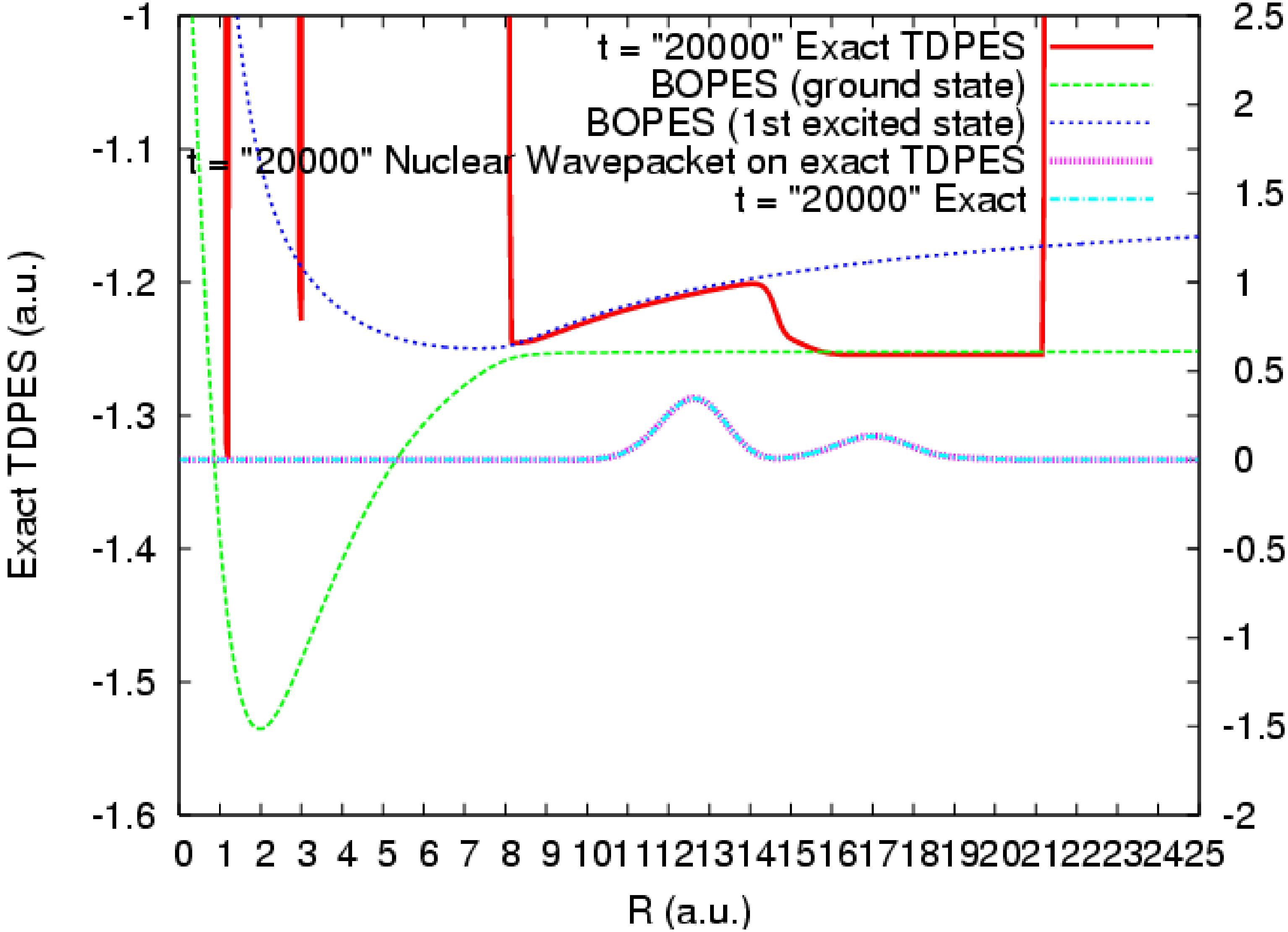


t = "19000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "19000" Nuclear Wavepacket on exact TDPES
t = "19000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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

Potential Energy Surfaces for electronic motion (ePES)

Traditionally: Electrons provide a soup that modifies the interactions between bare nuclei leading to the BO (or exact) potential energy surface.

Whenever the nuclei move as fast as electrons or faster, nuclei provide a soup that modifies the potential the electrons are exposed to.

Question:

Can one write down a purely electronic Hamiltonian with a suitable PES such that the resulting many-electron wave function yields the true N-electron density and current density (that one would get from the full electron-nuclear wave function $\Psi(R,r)$)?

Theorem

The exact solution of

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

can be written in the form

$$\Psi(\underline{\underline{r}}, \underline{\underline{R}}, t) = \Phi(\underline{\underline{r}}, t)\ \chi_{\underline{\underline{r}}}(\underline{\underline{R}}, t)$$

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

Y. Suzuki, A. Abedi, N.T. Maitra, K. Yamashita, E.K.U.Gross, Phys. Rev. A 89, R040501 (2014) exact TDPES for electrons

$$\left(\sum_{j}^{N_e}\frac{1}{2}\left(-i\nabla_j - \tilde{A}_j(\underline{\underline{r}},t)\right)^2 + \hat{W}_{ee}(\underline{\underline{r}}) + \tilde{\epsilon}(\underline{\underline{r}},t)\right)\Phi(\underline{\underline{r}},t) = i\partial_t\Phi(\underline{\underline{r}},t)$$

$$\tilde{\epsilon}(\underline{\underline{r}},t) = \int d\underline{\underline{R}}\,\chi^*_{\underline{\underline{r}}}(\underline{\underline{R}},t)\left(H_{nuc}[\Phi](\underline{\underline{R}},\underline{\underline{r}},t) - i\partial_{\mathbf{t}}\right)\chi_{\underline{\underline{r}}}(\underline{\underline{R}},t)$$

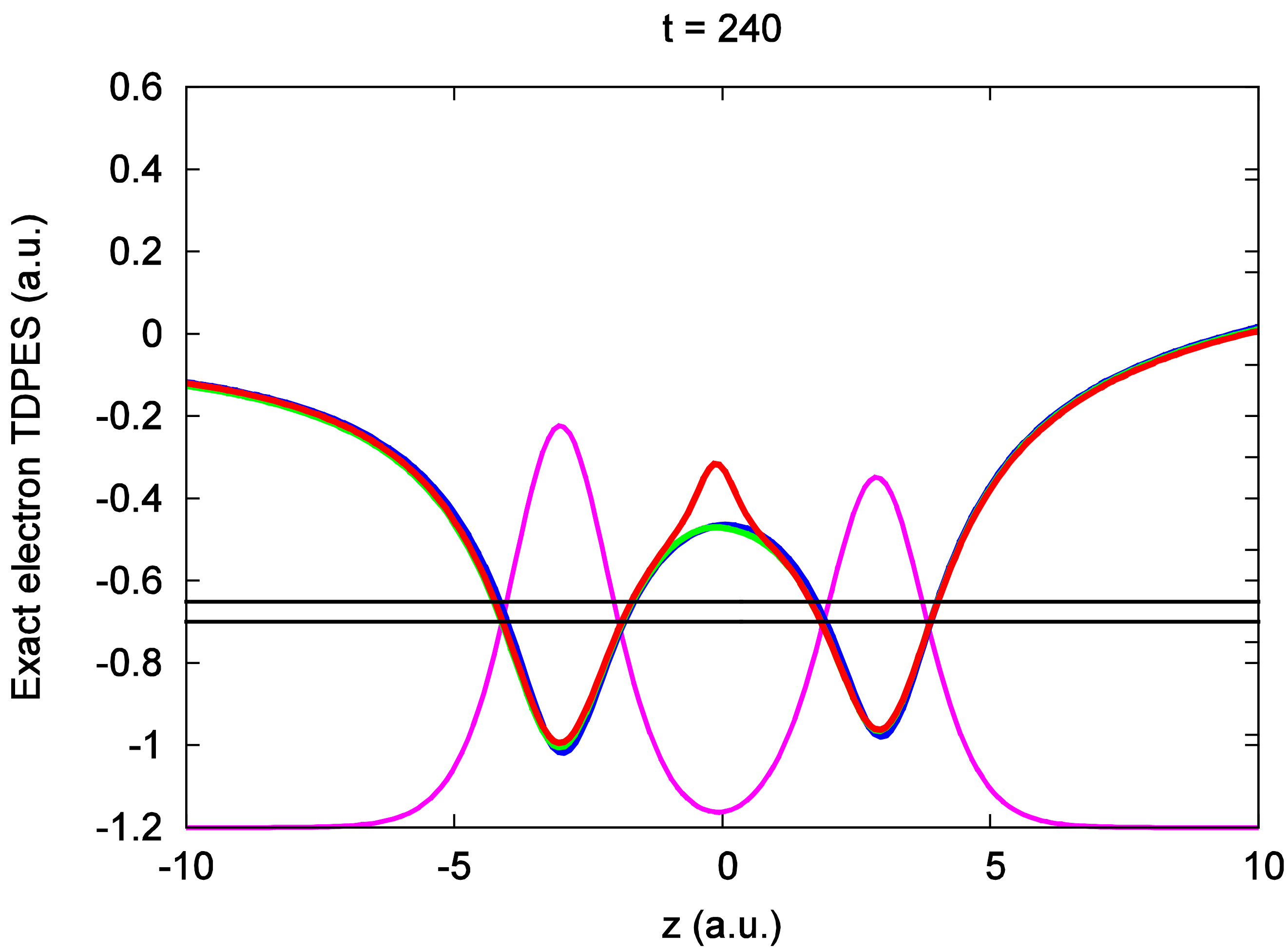
EXACT <u>electronic</u> potential energy surface

$$\tilde{A}_j(\underline{\underline{r}},t) = -i\int \chi^*_{\underline{\underline{r}}}(\underline{\underline{R}},t)\nabla_j\chi_{\underline{\underline{r}}}(\underline{\underline{R}},t)\,d\underline{\underline{R}}$$

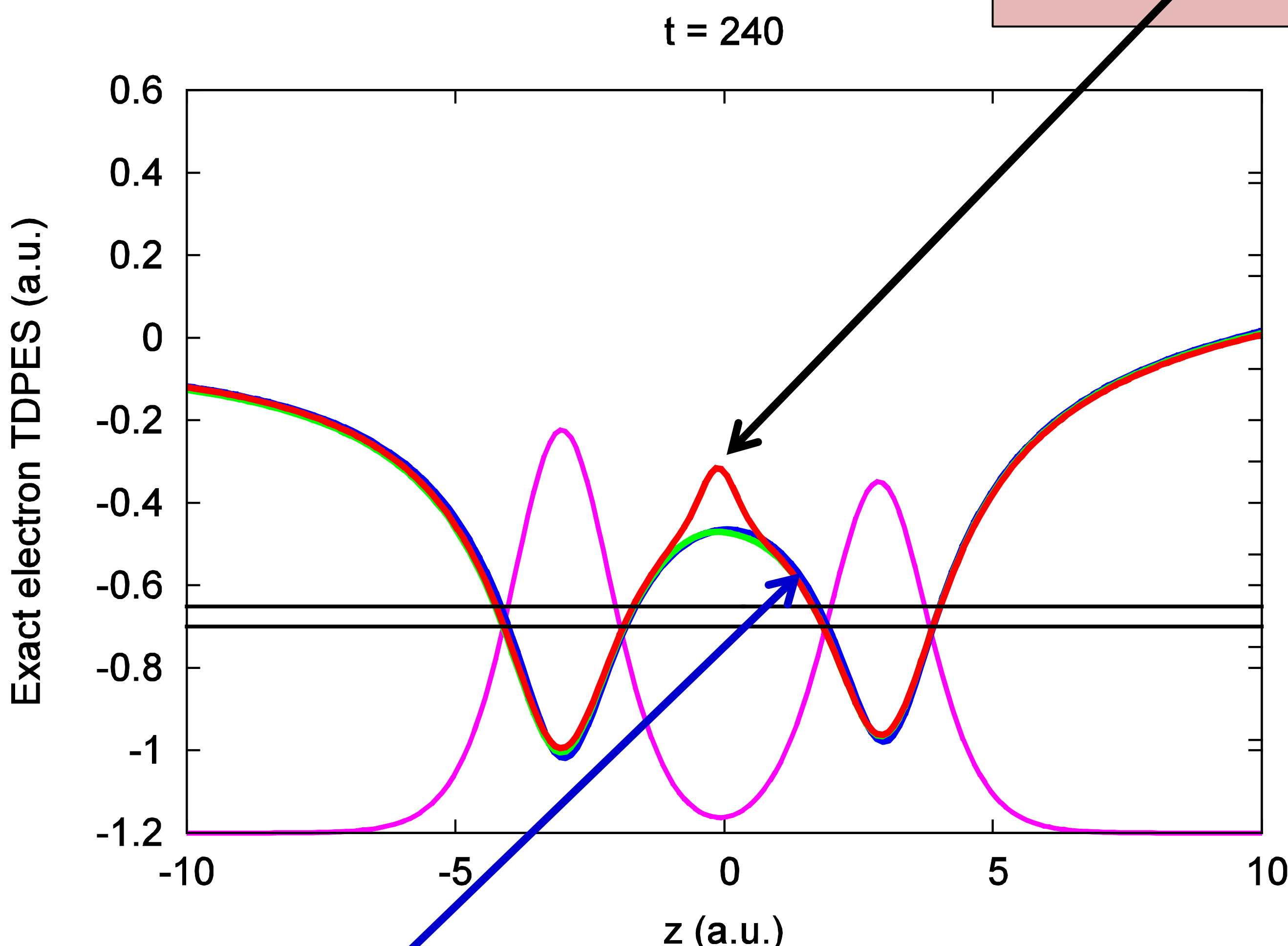
EXACT e<u>lectronic</u> Berry connection

Study electron localization in the dissociation of H_2^+ in suitably shaped laser pulse <u>using exact electronic surface.</u>

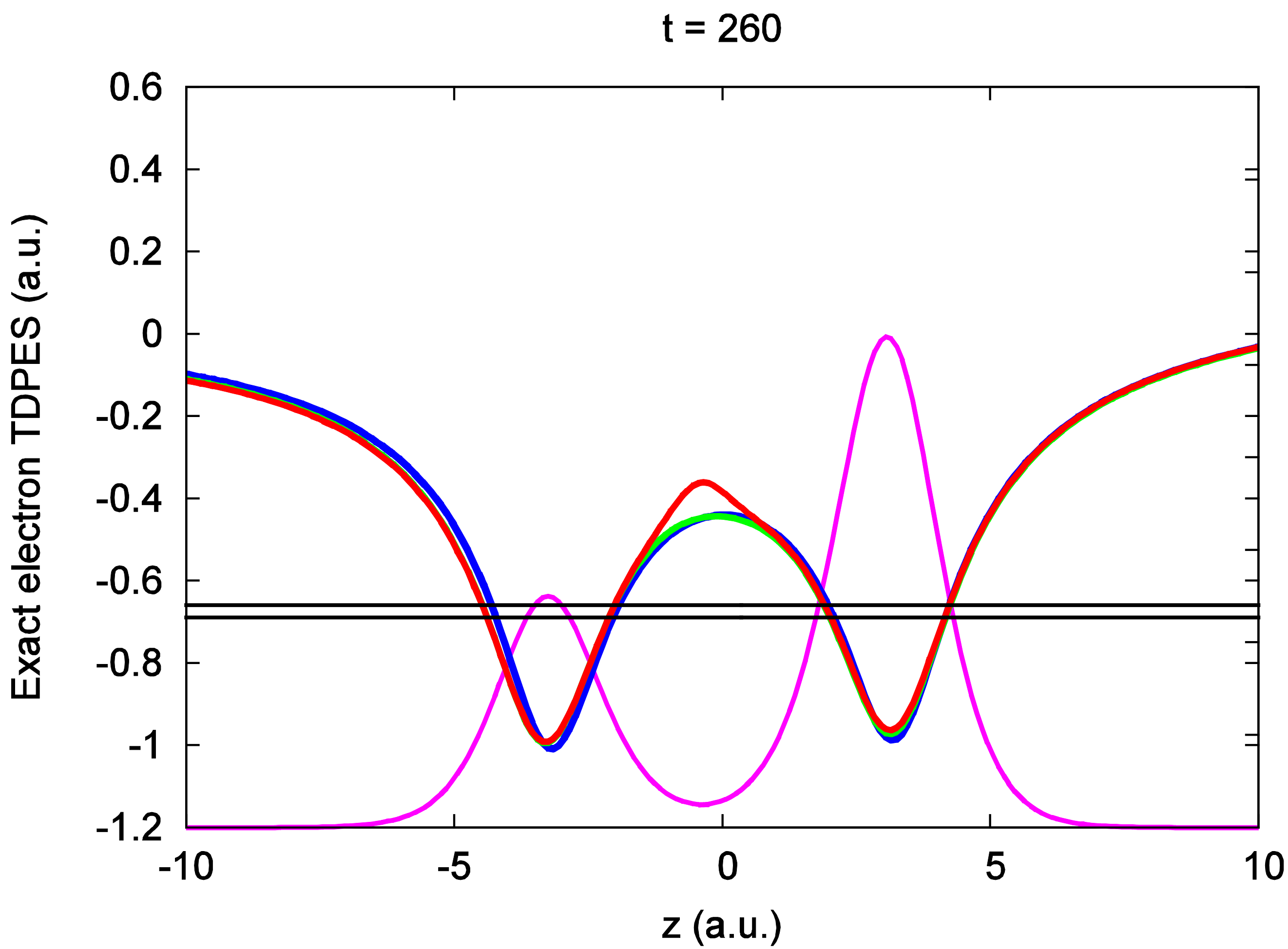
Experiments by M. Vrakking (Max Born Institute, Berlin)


t = 240
Exact electron TDPES (a.u.)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-10
-5
0
5
10
z (a.u.)

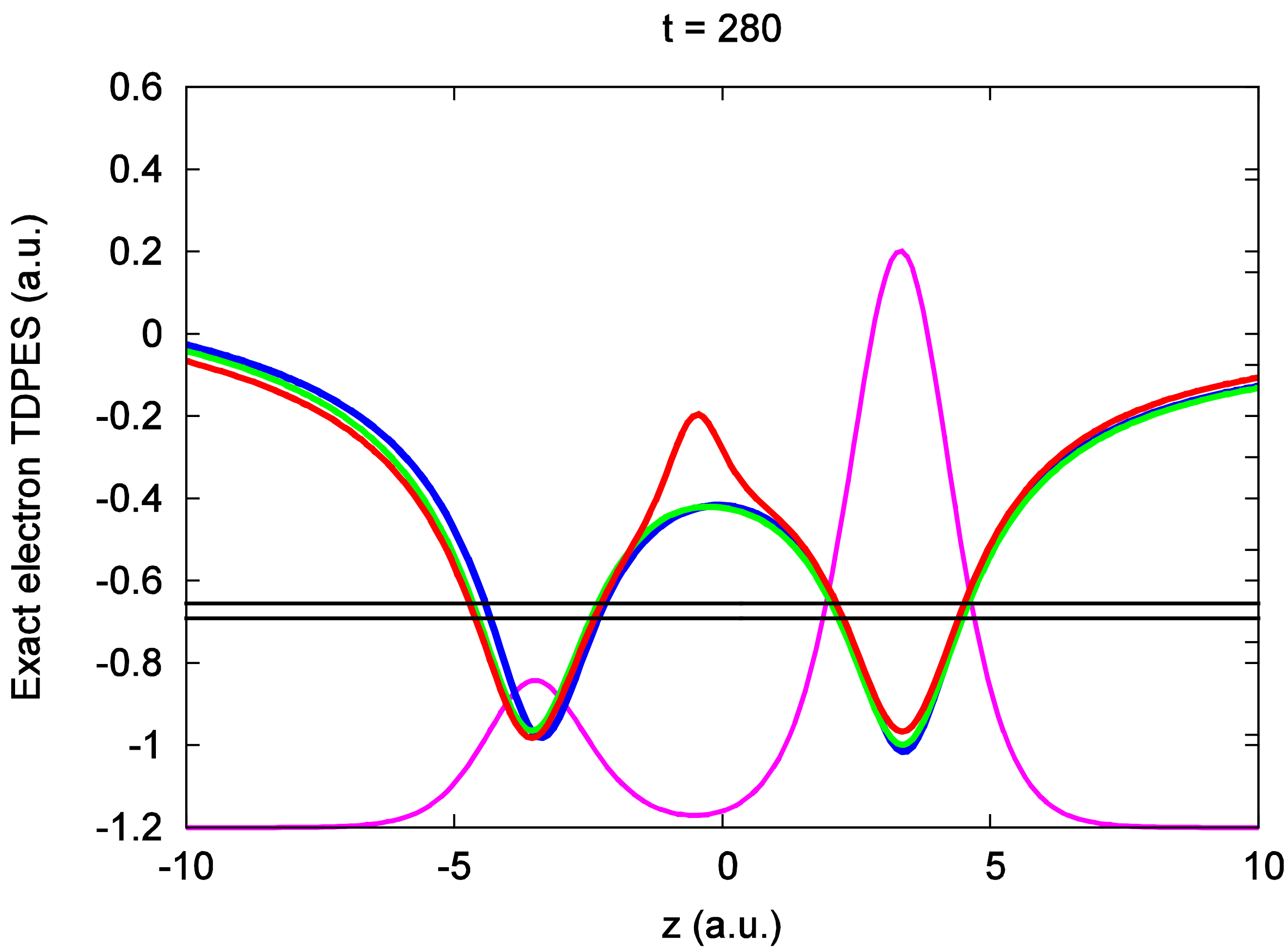
Exact electronic TDPES

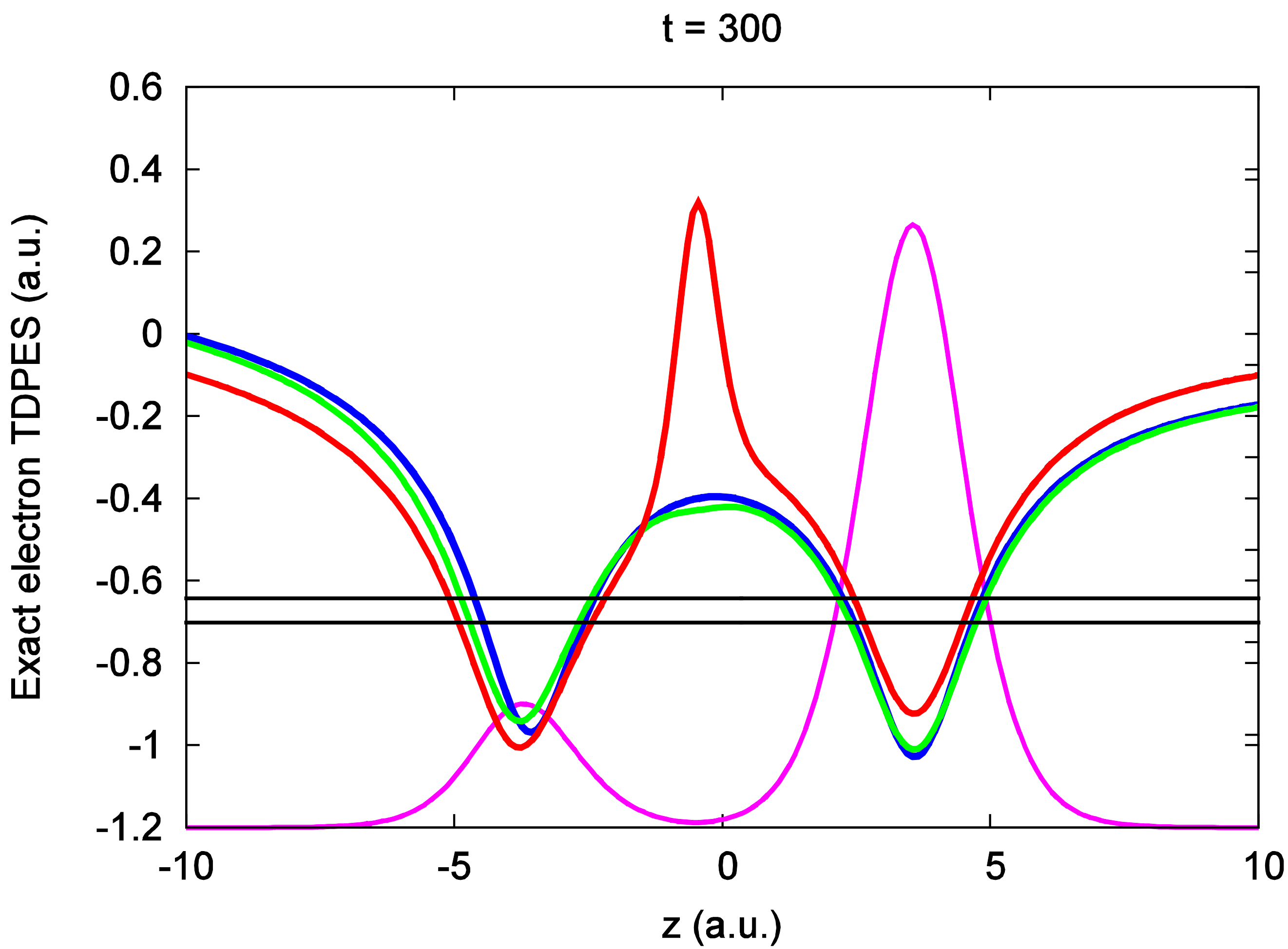


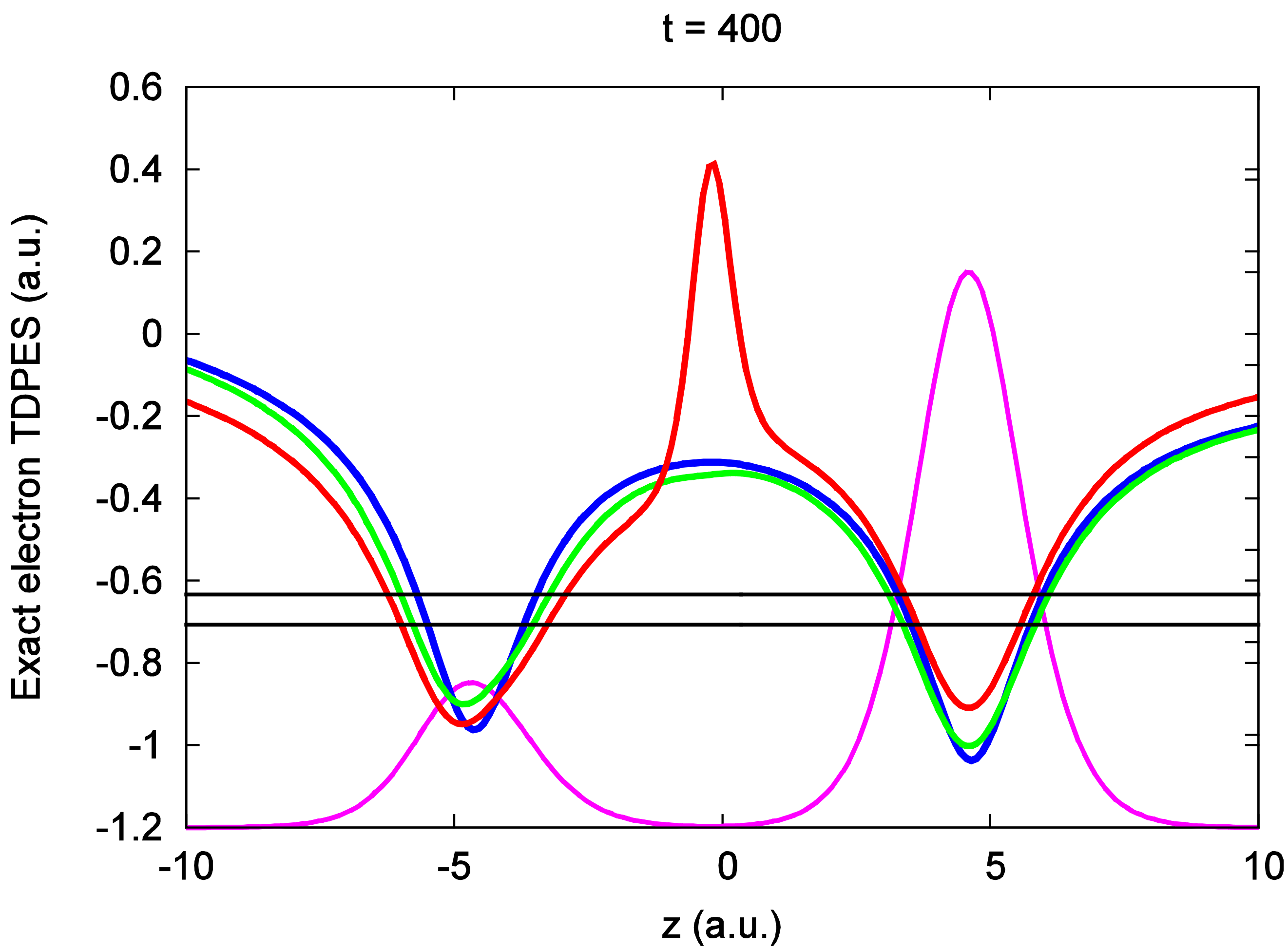
electrostatic potential produced by nuclear density



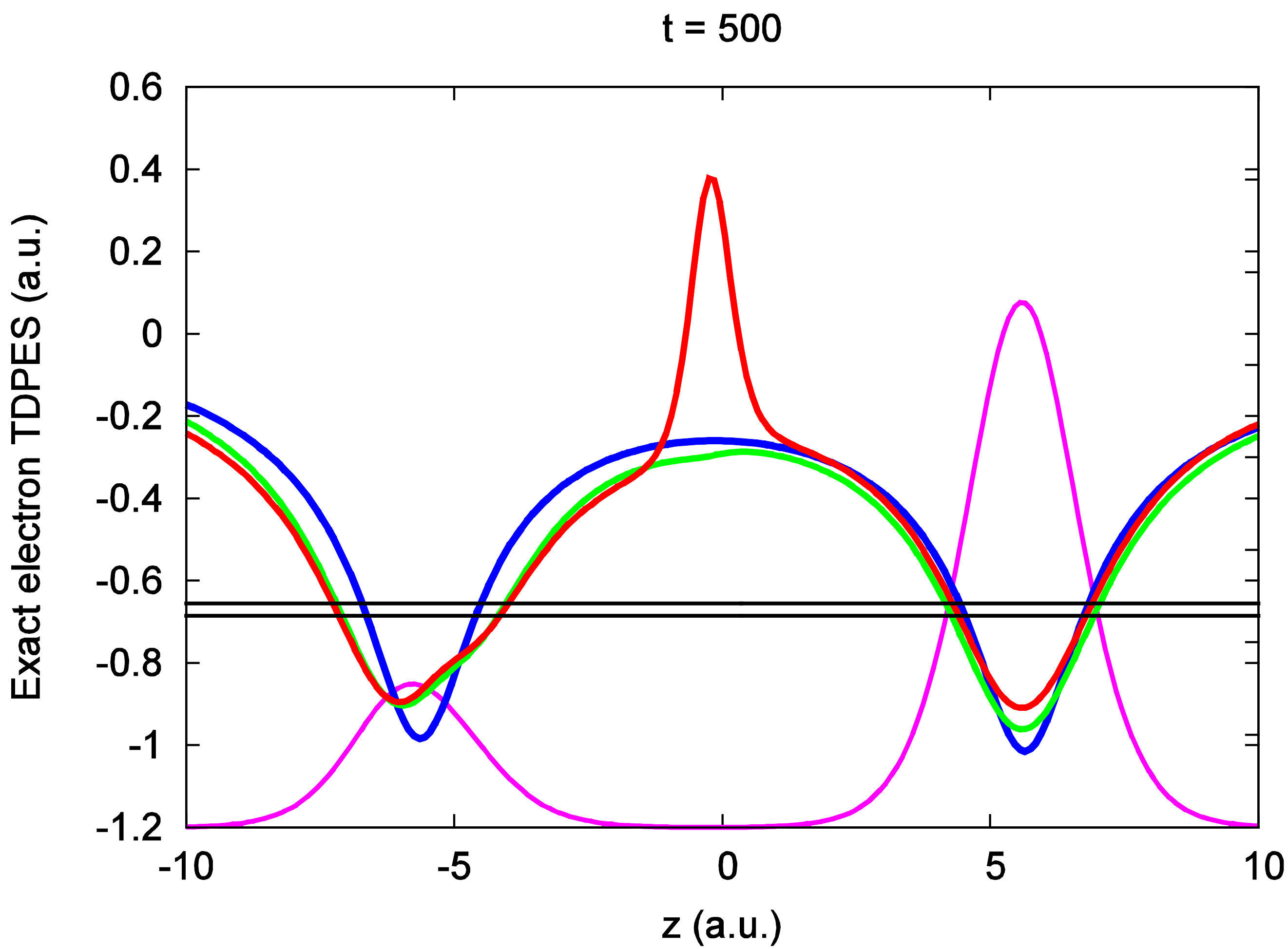
t = 260
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-10
-5
0
5
10
Exact electron TDPES (a.u.)
z (a.u.)

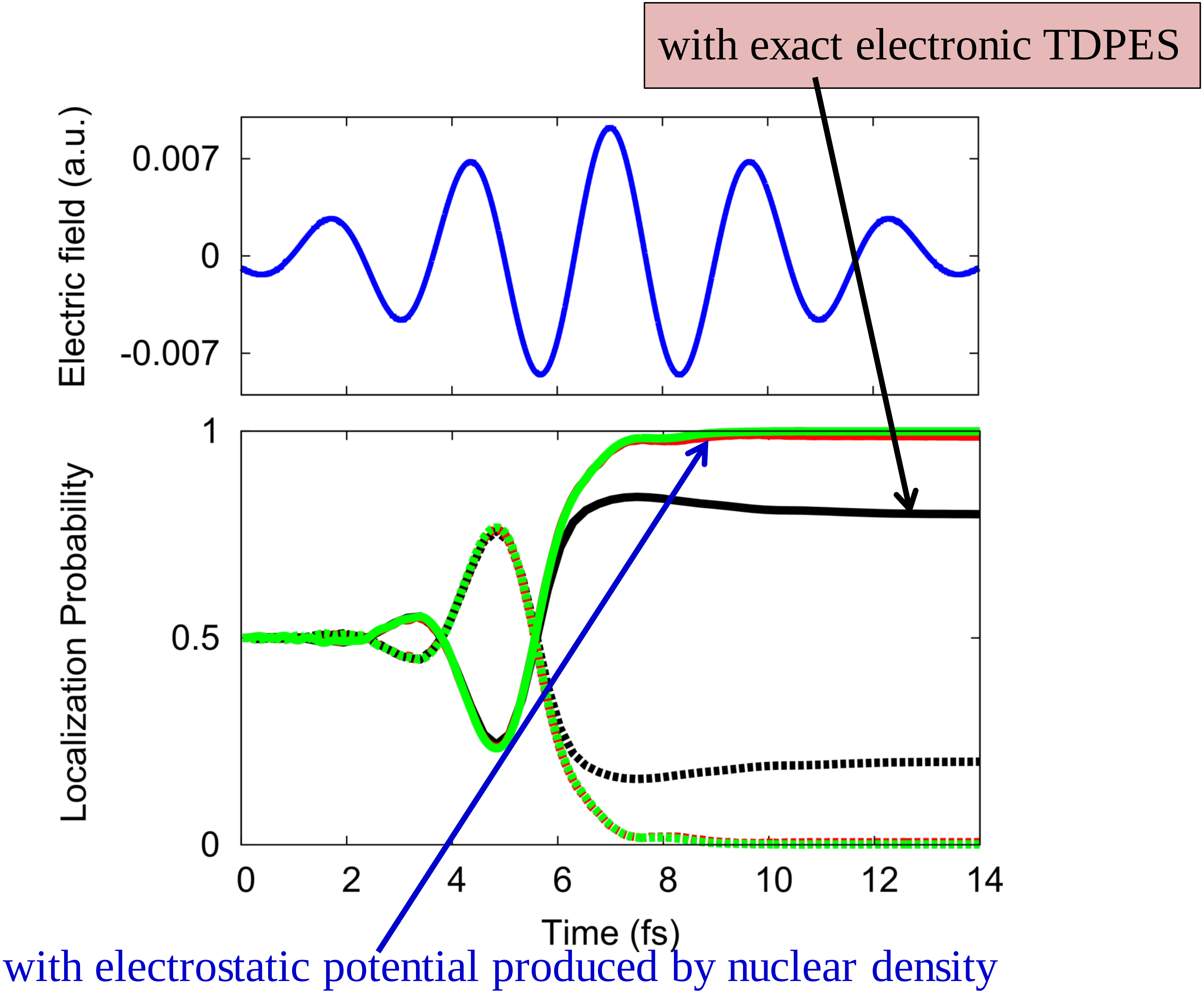

t = 280
Exact electron TDPES (a.u.)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-10
-5
0
5
10
z (a.u.)


t = 300
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
Exact electron TDPES (a.u.)
-10
-5
0
5
10
z (a.u.)



t = 400
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
Exact electron TDPES (a.u.)
-10
-5
0
5
10
z (a.u.)


t = 500
Exact electron TDPES (a.u.)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-10
-5
0
5
10
z (a.u.)



with exact electronic TDPES
Electric field (a.u.)
0.007
0
-0.007
Localization Probability
1
0.5
0
0
2
4
6
8
10
12
14
Time (fs)
with electrostatic potential produced by nuclear density

New MD scheme:

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

A. Abedi, F. Agostini, E.K.U.Gross, EPL 106, 33001 (2014)

Theorem T-II

Eq. ❶

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

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

Eq. ❷

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

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

$$\begin{cases}\left|\chi\left(R,t\right)\right|^{2}\rightarrow\delta\left(R-R_{c}\left(t\right)\right)\\ \nabla_{R}S\left(R,t\right)\rightarrow P_{c}(t)\end{cases}$$

Hence

$$\frac{-i\hbar\nabla_{R}\chi}{\chi}\xrightarrow{\hbar\rightarrow 0}P_{c}(t)$$

Expand the exact electronic wave function in the adiabatic basis:

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

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

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

in the classical limit:

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

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

In practice we solve the following equations:

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

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

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

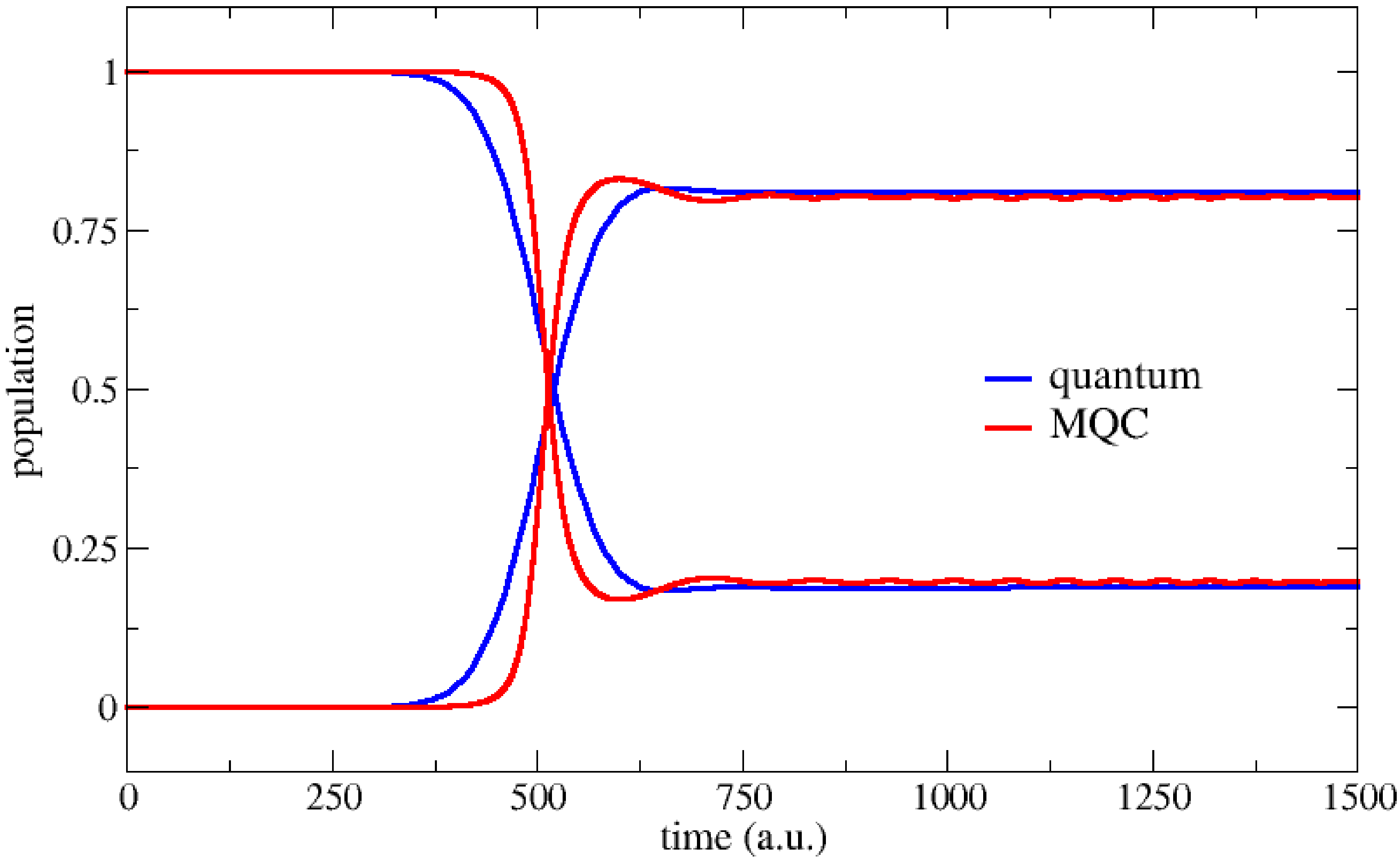
$$D_{jk} = \frac{P}{M}\cdot d_{jk}^{(1)} - \frac{i\hbar}{2M}\left(\nabla_R \cdot d_{jk}^{(1)} - d_{jk}^{(2)}\right)$$

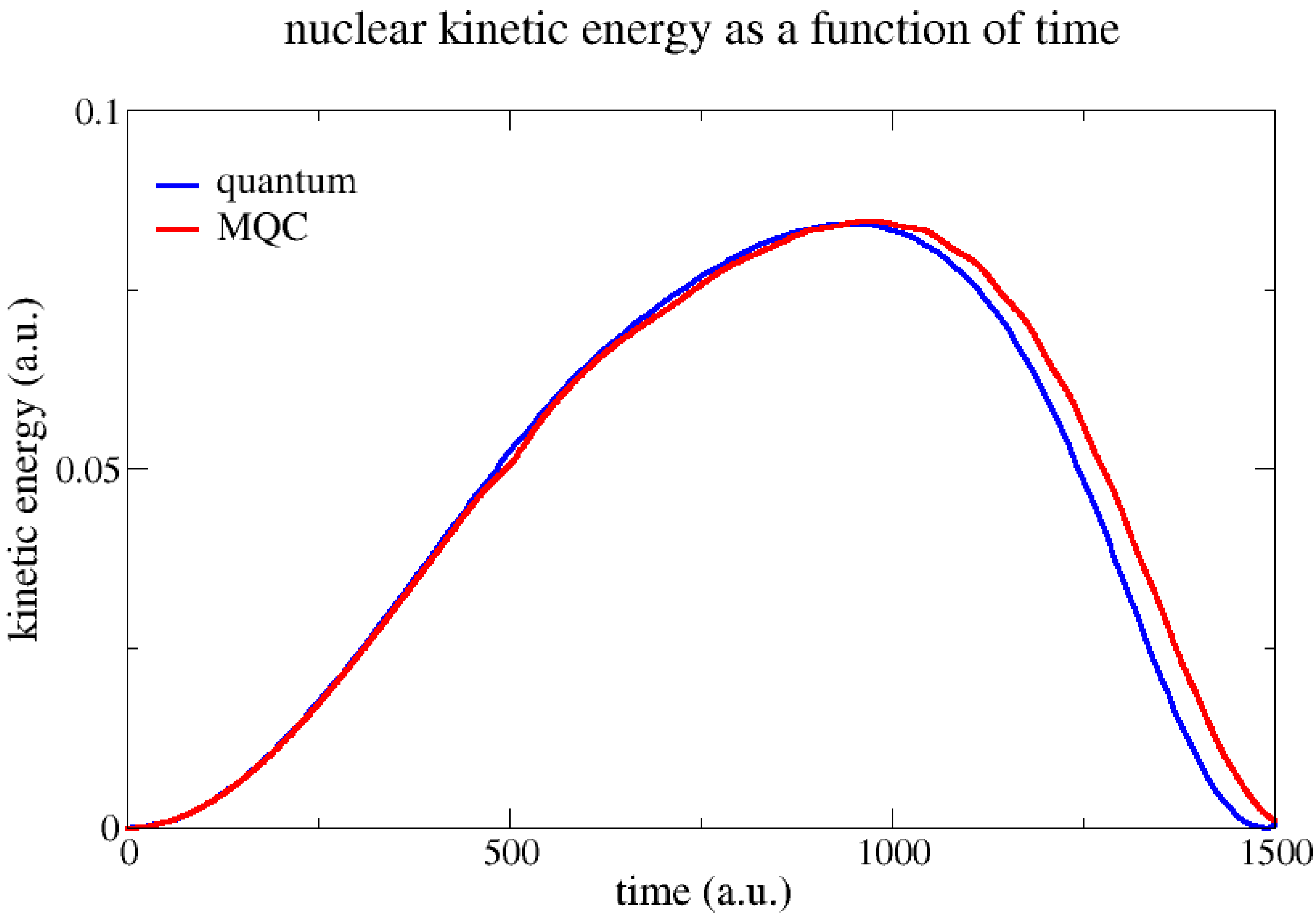
$$d_{jk}^{(1)}(R) = \left\langle \varphi_{R,j}^{BO} \middle| \nabla_R\, \varphi_{R,k}^{BO} \right\rangle \qquad d_{jk}^{(2)}(R) = \left\langle \nabla_R\, \varphi_{R,j}^{BO} \middle| \nabla_R\, \varphi_{R,k}^{BO} \right\rangle$$

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

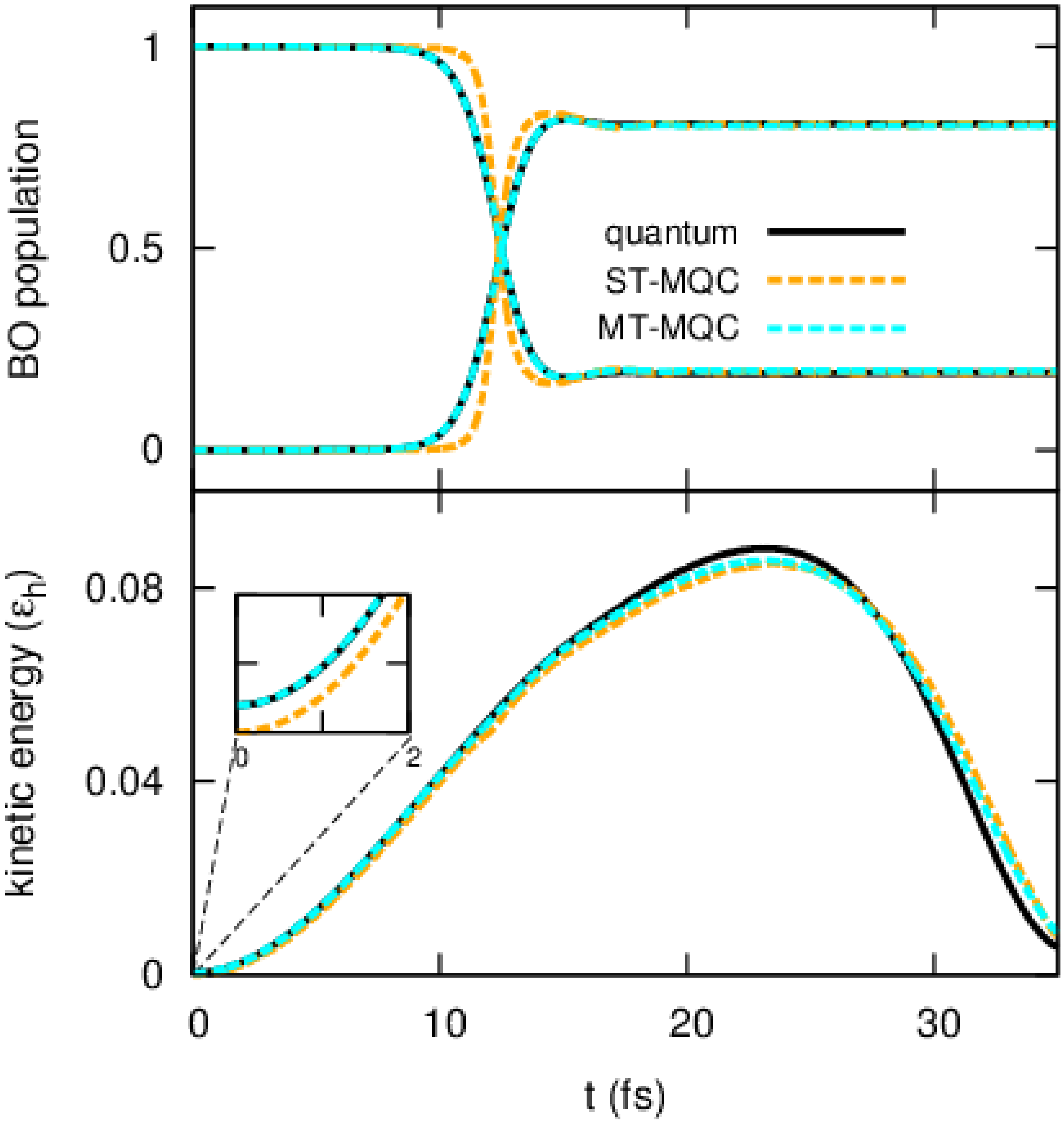
Shin-Metiu model

populations of the BO states as functions of time



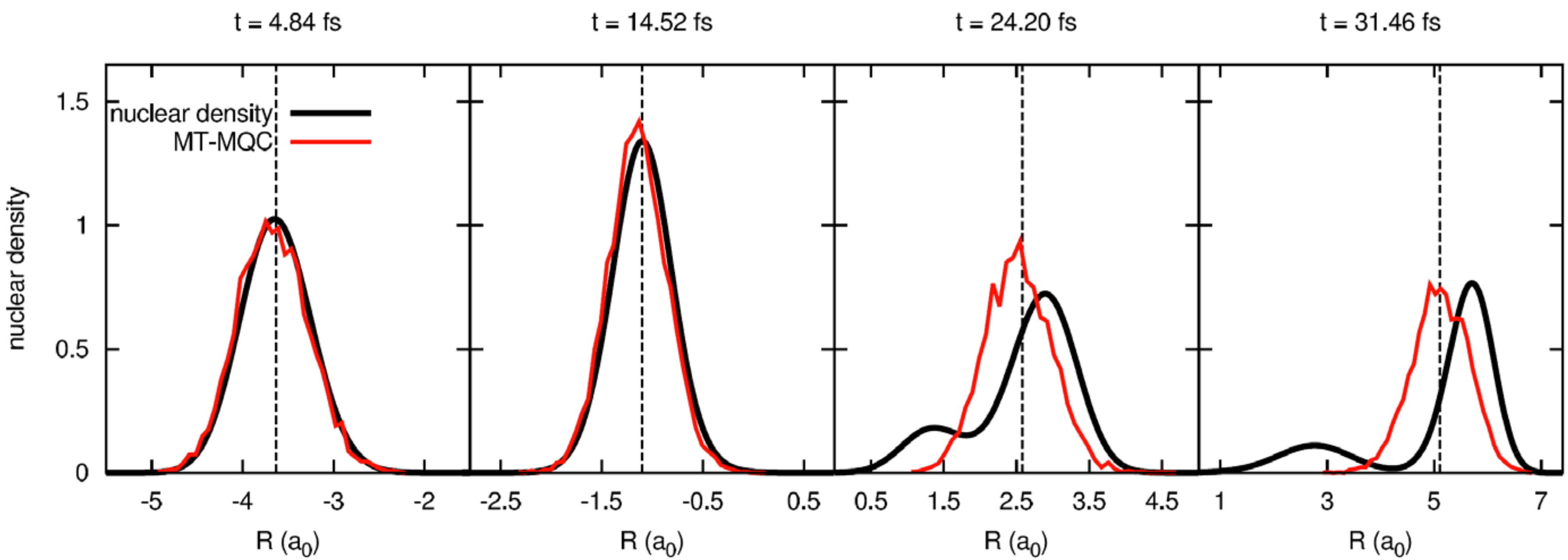


nuclear kinetic energy as a function of time
0.1
0.05
0
kinetic energy (a.u.)
quantum
MQC
0
500
1000
1500
time (a.u.)

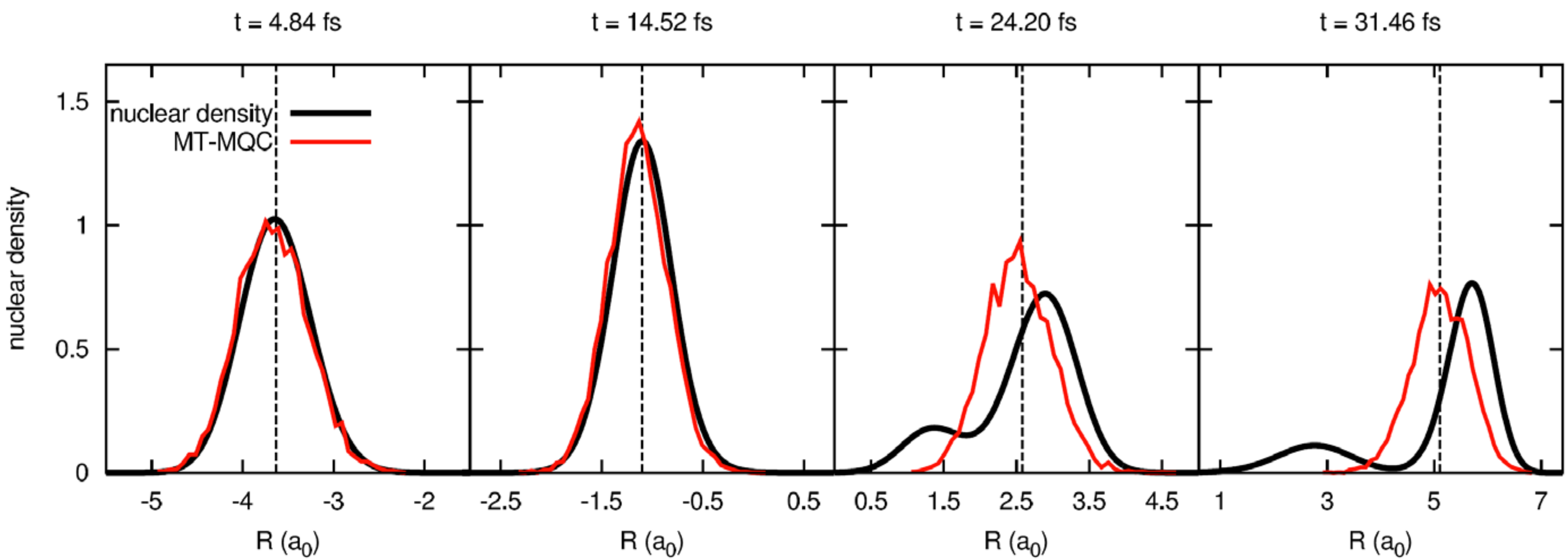


BO population
1
0.5
0
quantum
ST-MQC
MT-MQC
kinetic energy (ϵ_h)
0.08
0.04
0
0
2
0
10
20
30
t (fs)

Exact nuclear density vs. histogram constructed from distribution of classical nuclear positions

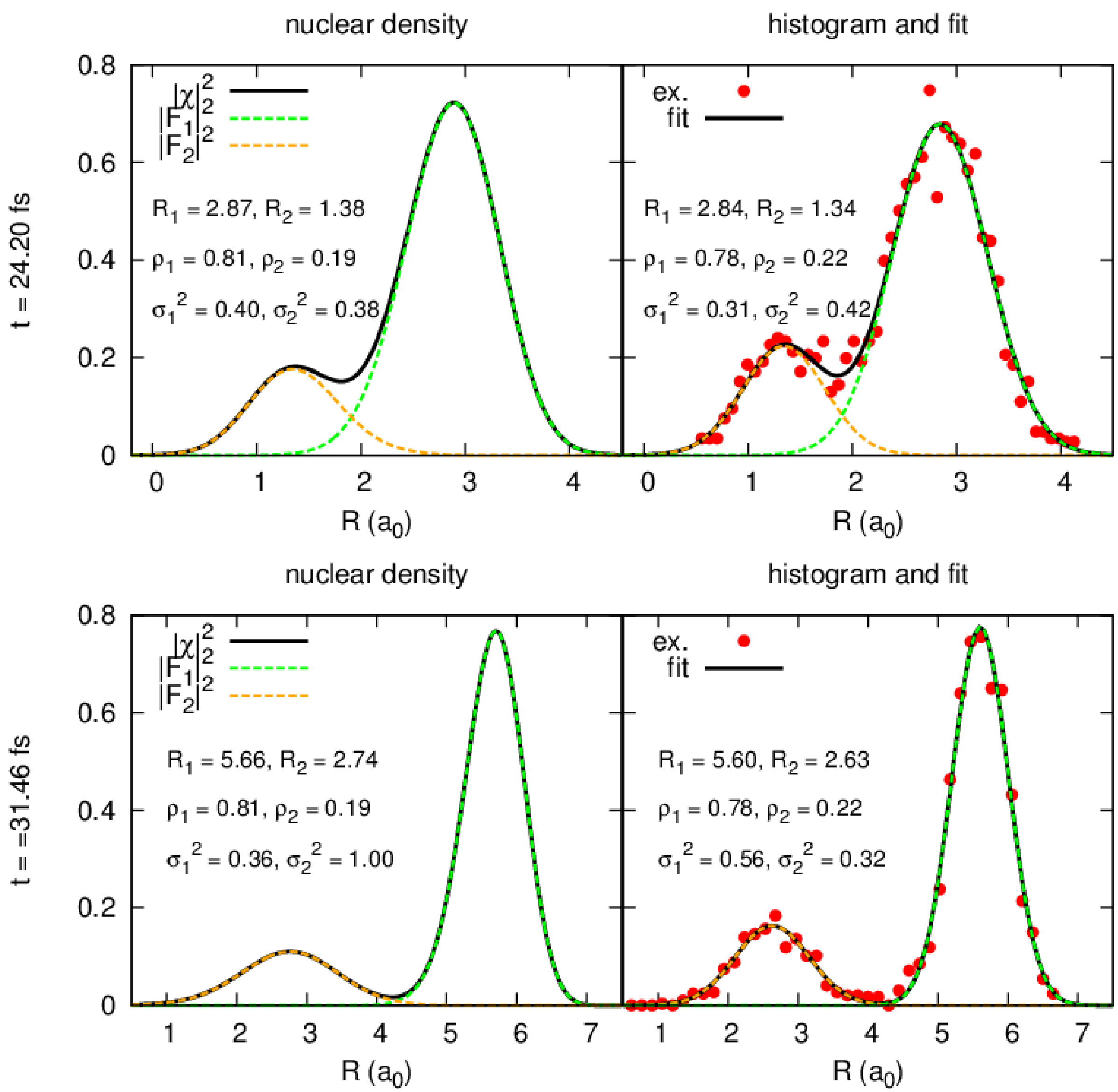


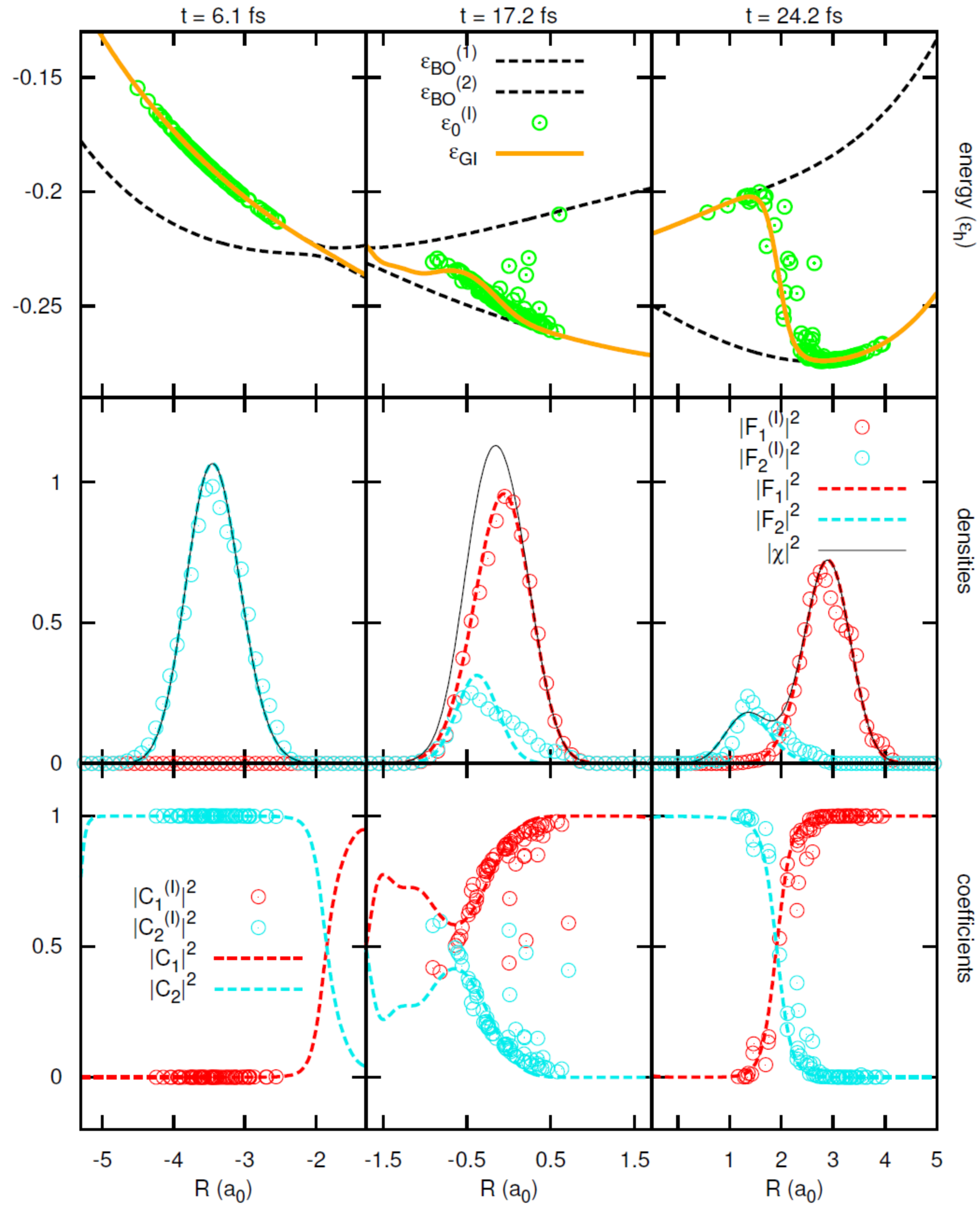
Exact nuclear density vs. histogram constructed from distribution of classical nuclear positions



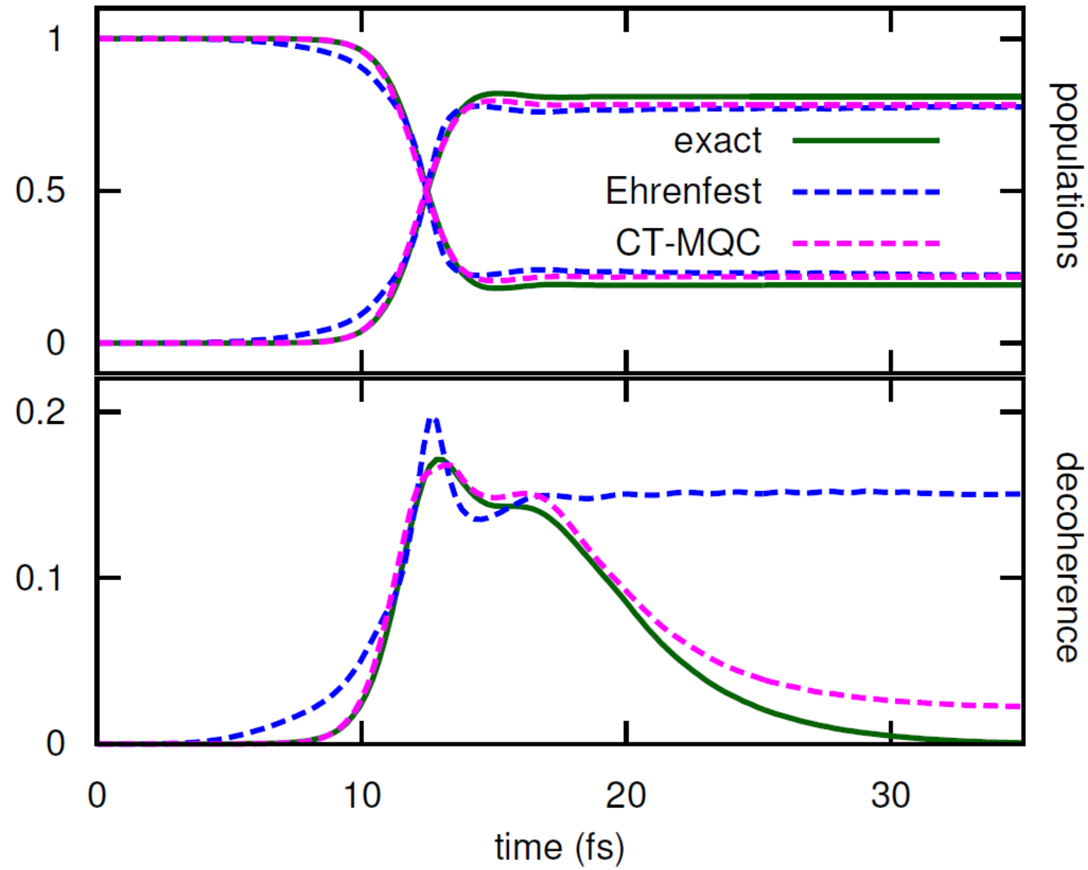
Algorithm not good enough to reproduce splitting of nuclear density!

Propagation of classical nuclei on exact TDPES





t = 6.1 fs
t = 17.2 fs
t = 24.2 fs
-0.15
-0.2
-0.25
$\varepsilon_{BO}^{(1)}$
$\varepsilon_{BO}^{(2)}$
$\varepsilon_0^{(I)}$
ε_{GI}
energy (ε_h)
1
0.5
0
$|F_1^{(I)}|^2$
$|F_2^{(I)}|^2$
$|F_1|^2$
$|F_2|^2$
$|\chi|^2$
densities
1
0.5
0
$|C_1^{(I)}|^2$
$|C_2^{(I)}|^2$
$|C_1|^2$
$|C_2|^2$
coefficients
-5
-4
-3
-2
-1.5
-0.5
0.5
1.5
1
2
3
4
5
R (a_0)
R (a_0)
R (a_0)



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

Summary:

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

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

  --- <u>exact</u> potential energy surface
  --- <u>exact</u> 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**

- **reverse the role of electrons and nuclei: <u>Electronic</u> TDPES**

- **mixed quantum classical algorithms**

Thanks !

SFB 450
SFB 685
SFB 762
SPP 1145