How to make the Born-Oppenheimer approximation exact: A fresh look at potential energy surfaces and Berry phases

E.K.U. Gross

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

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

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

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

Stationary Schrödinger equation

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

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Time-dependent Schrödinger equation

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

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

Born-Oppenheimer approximation

solve

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

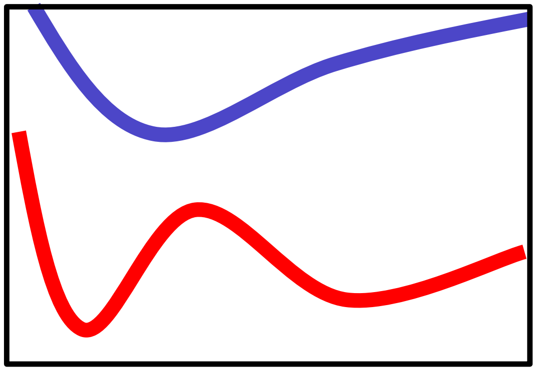
for each fixed nuclear configuration $\underline{\underline{R}}$.

Make adiabatic ansatz for the complete molecular wave function:

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

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

Born-Oppenheimer approximation



solve

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

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and find best χ^{BO} by minimizing $<\Psi^{BO} \,|\, H \,|\, \Psi^{BO}>$ 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

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

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

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

Nuclear equation

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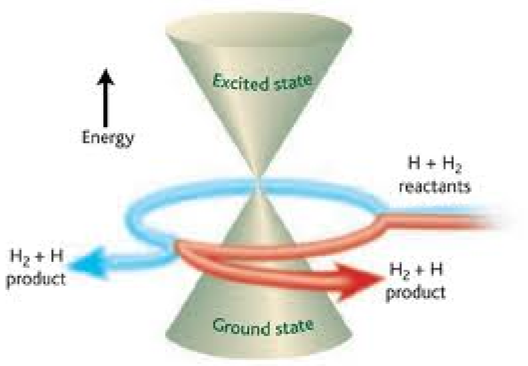

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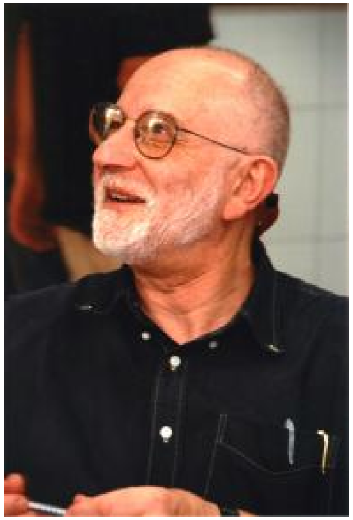
Geometric Phases

<u>Concept of geometric phase:</u>
Discovered by **S. Pancharatnam** (1956)
Proc. Indian Acad. Sci. A **44**: 247–262.



<u>In the context of quantum mechanics:</u>

Michael V. Berry (1984) *Proc. Royal Society* **392** (1802), 45–57.

Whenever the Hamiltonian of a quantum system depends on a vector of parameters, R, the Berry phase is defined as:

$$\gamma[C] = i \oint_C \langle \Phi_{\boldsymbol{R}} | \vec{\nabla}_R | \Phi_{\boldsymbol{R}} \rangle \, d\vec{R}$$

where the line integral is along a closed loop, C, in parameter space.

A non-vanishing value of γ only appears when C encircles some non-analyticity.

Standard representation of the full TD wave function

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

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

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

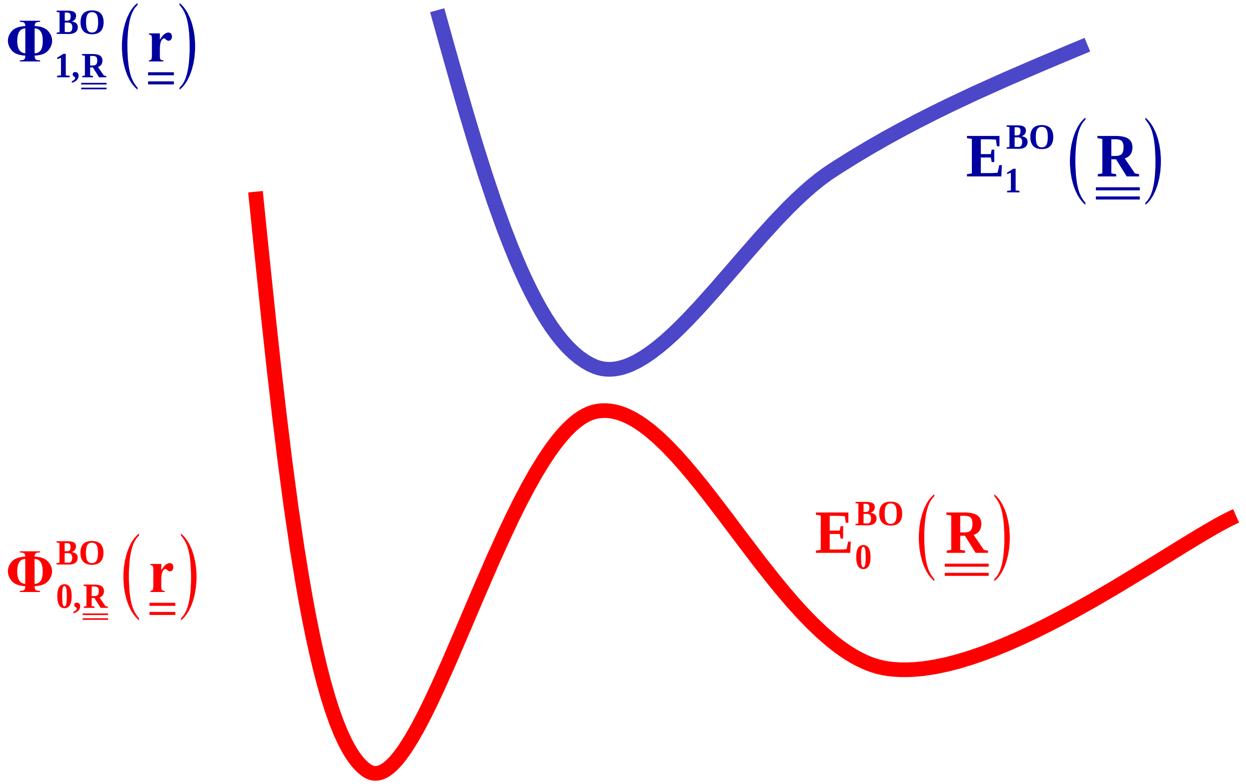
Plug Born-Huang expansion in full TDSE:

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

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

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

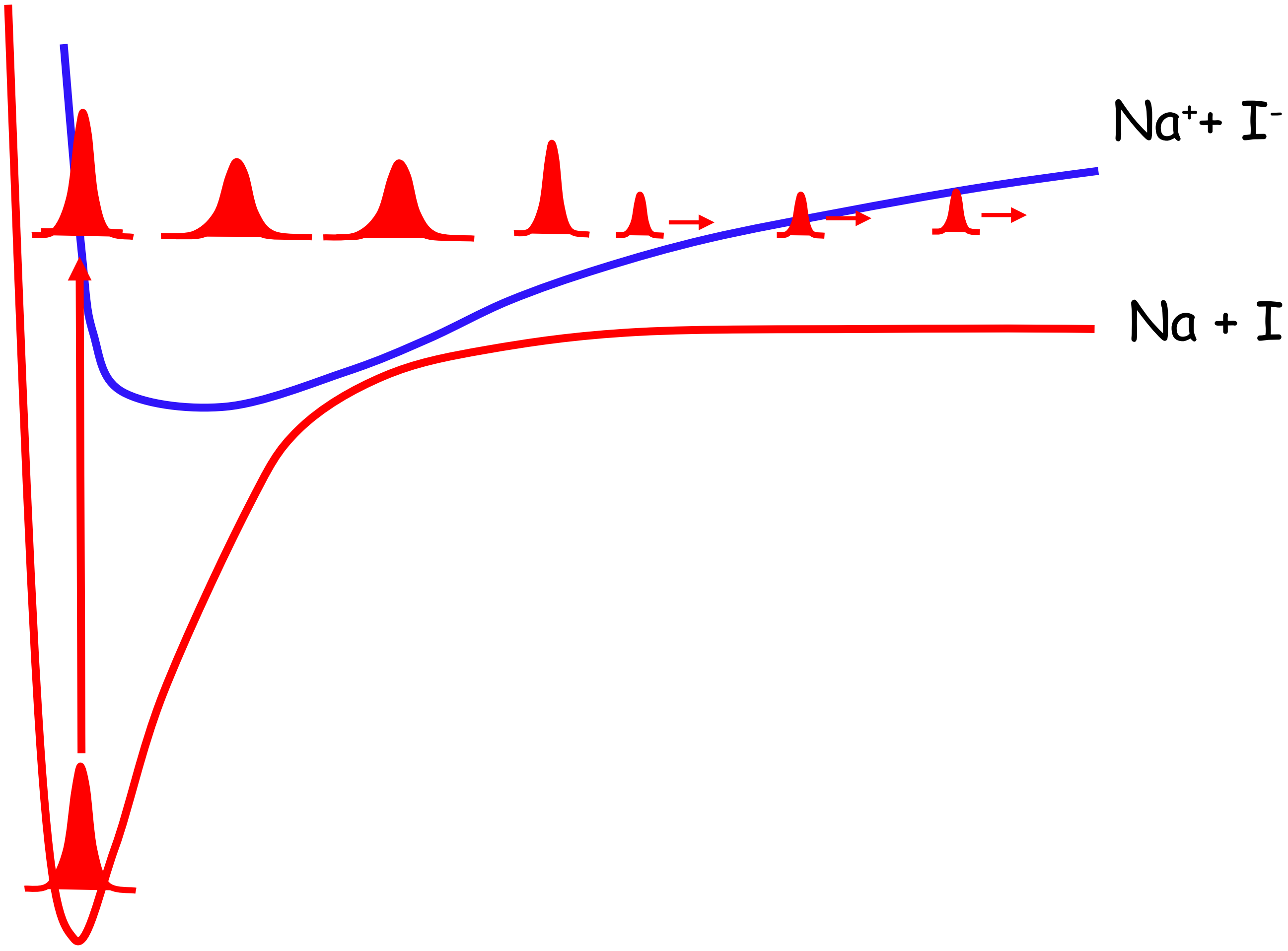
The dynamics is "non-adiabatic" when the NAC terms cannot be neglected



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

When only few BO-PES are important, the BO expansion gives a perfectly clear picture of the dynamics

Example: NaI femtochemistry



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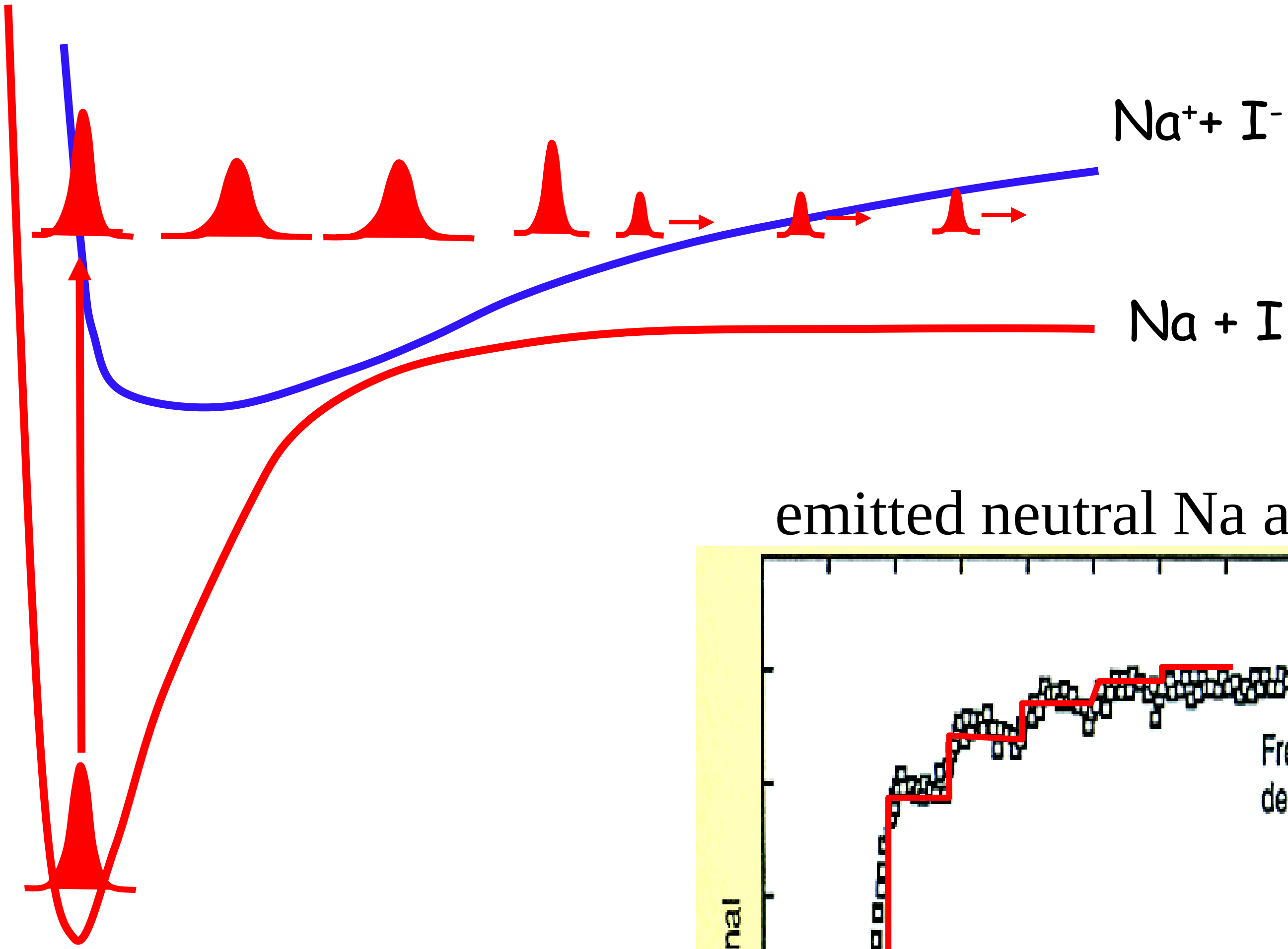
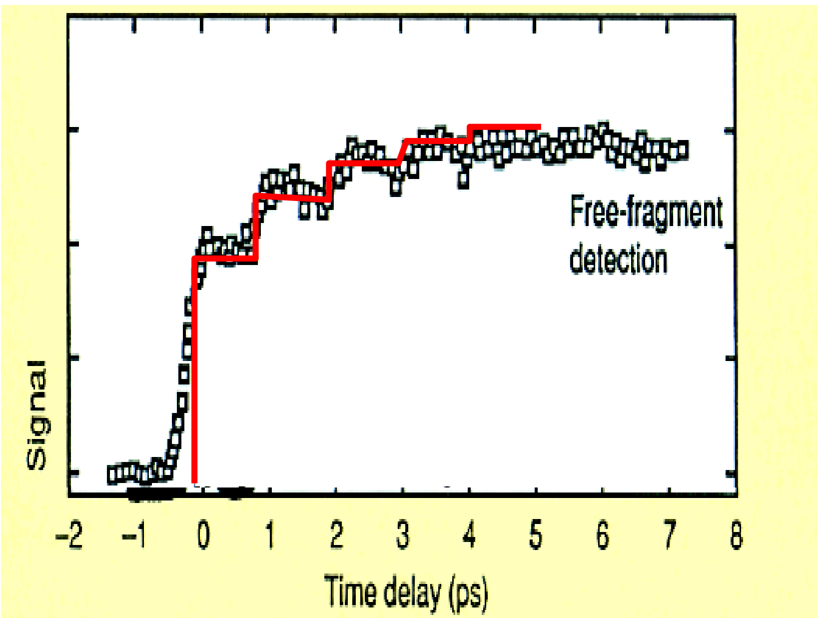
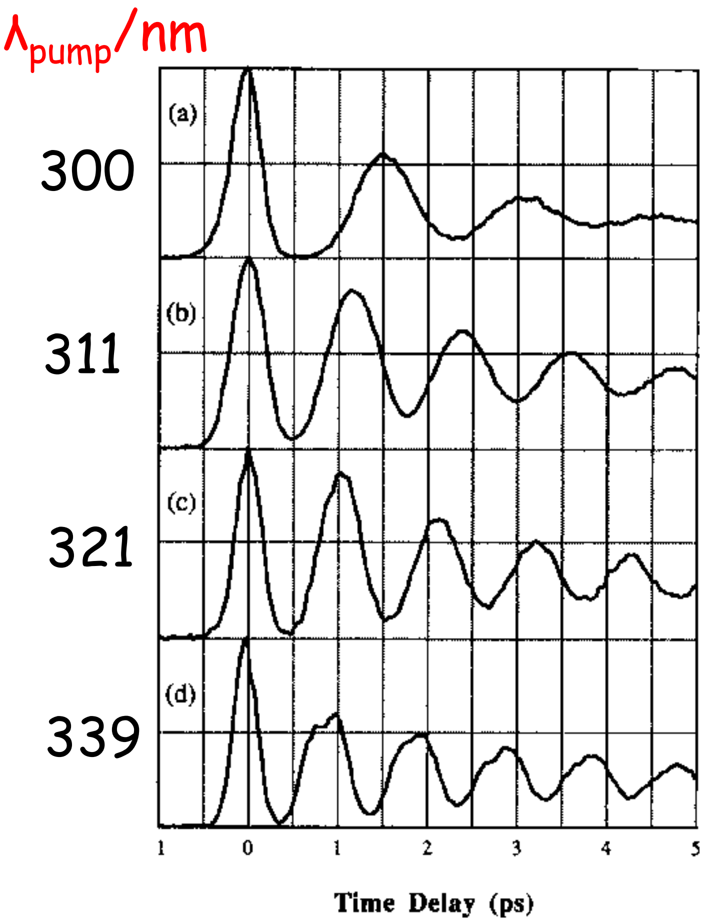
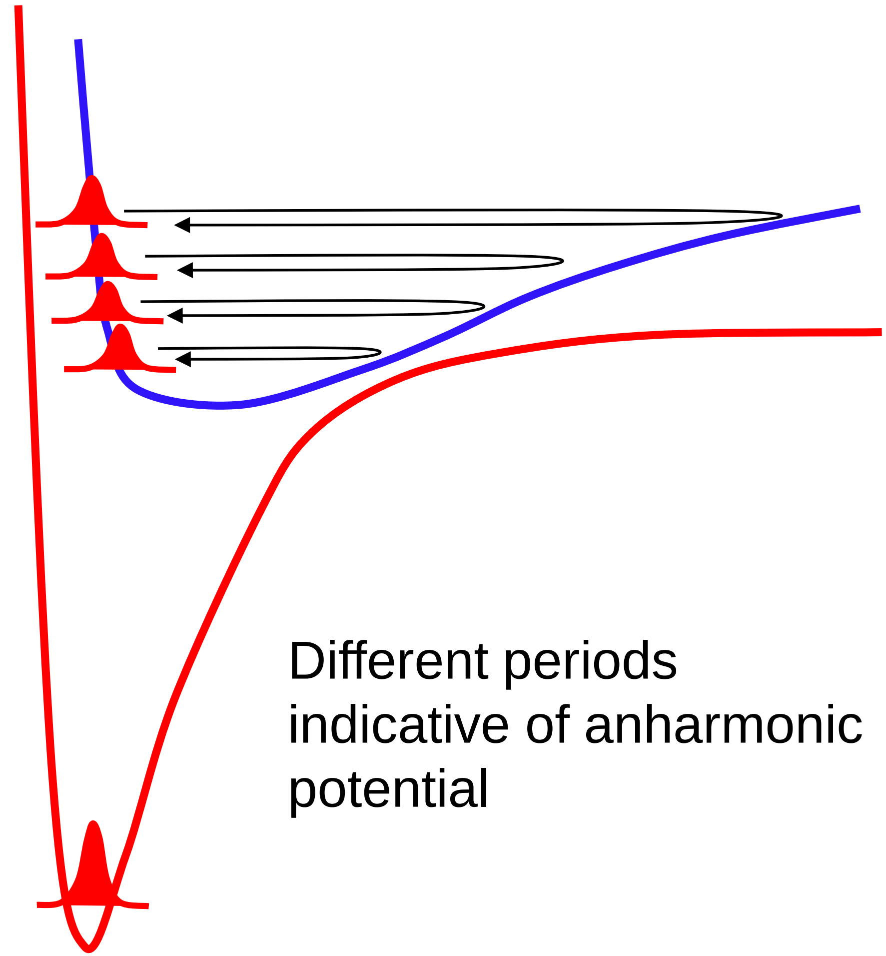


emitted neutral Na atoms



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



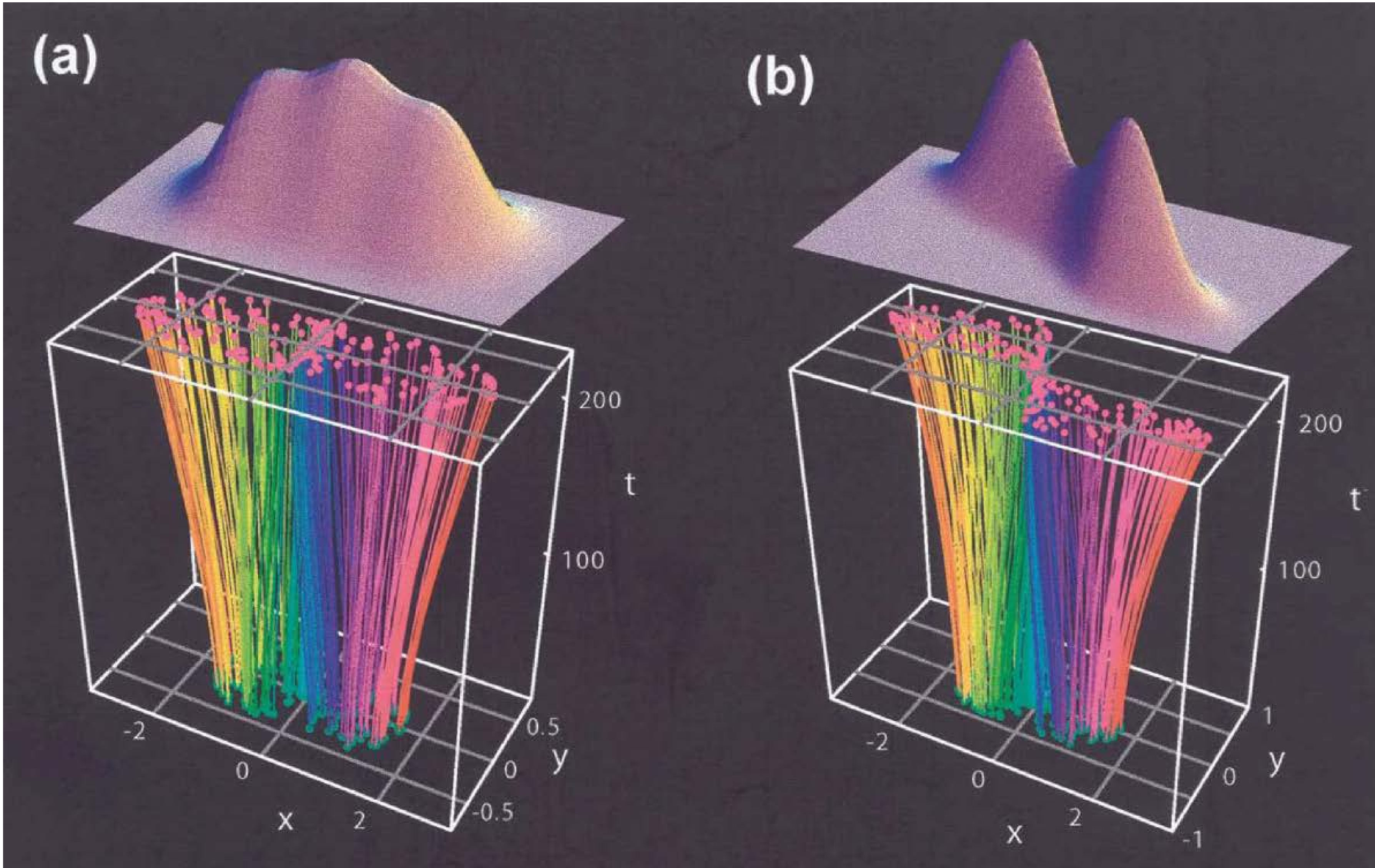


Different periods indicative of anharmonic potential

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

For larger systems one would like to (one has to) treat the nuclei classically.

Trajectory-based quantum dynamics



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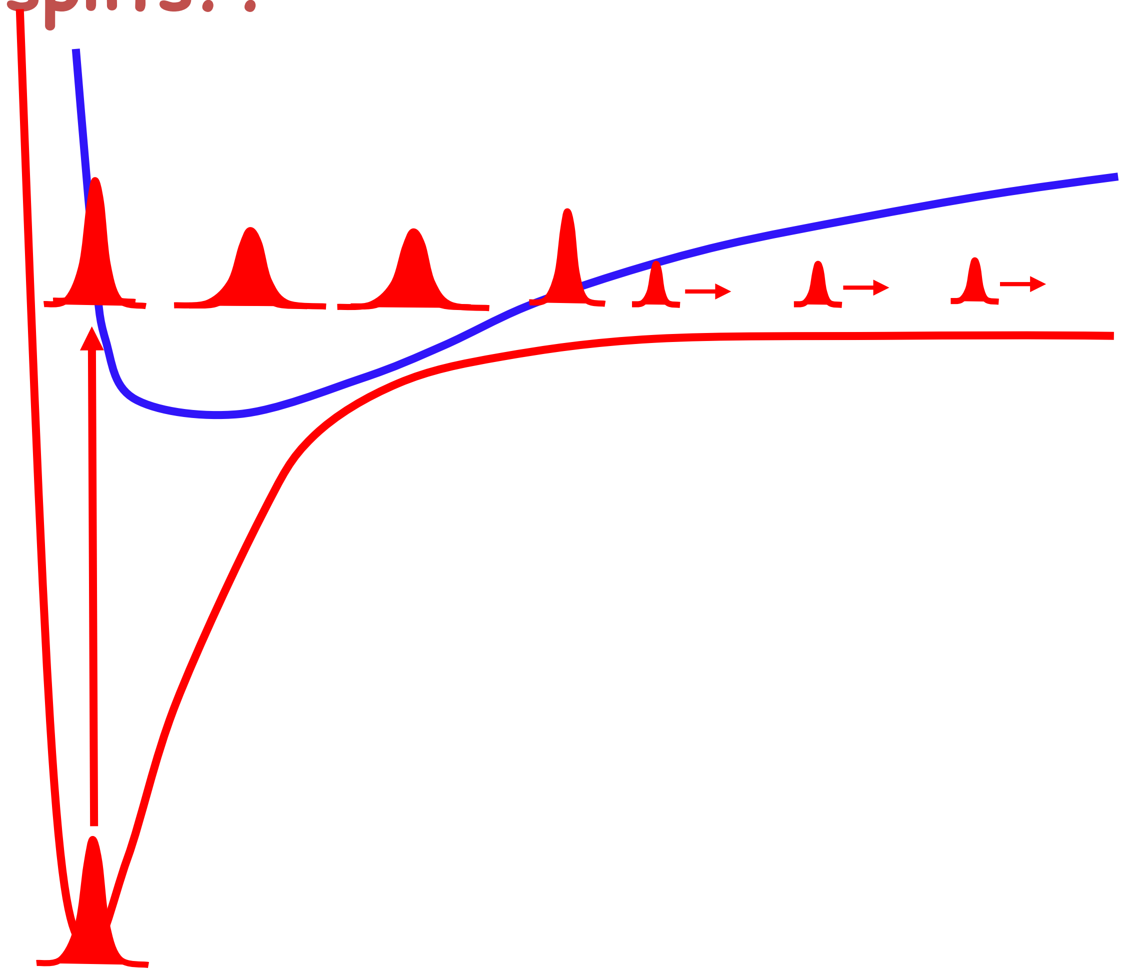

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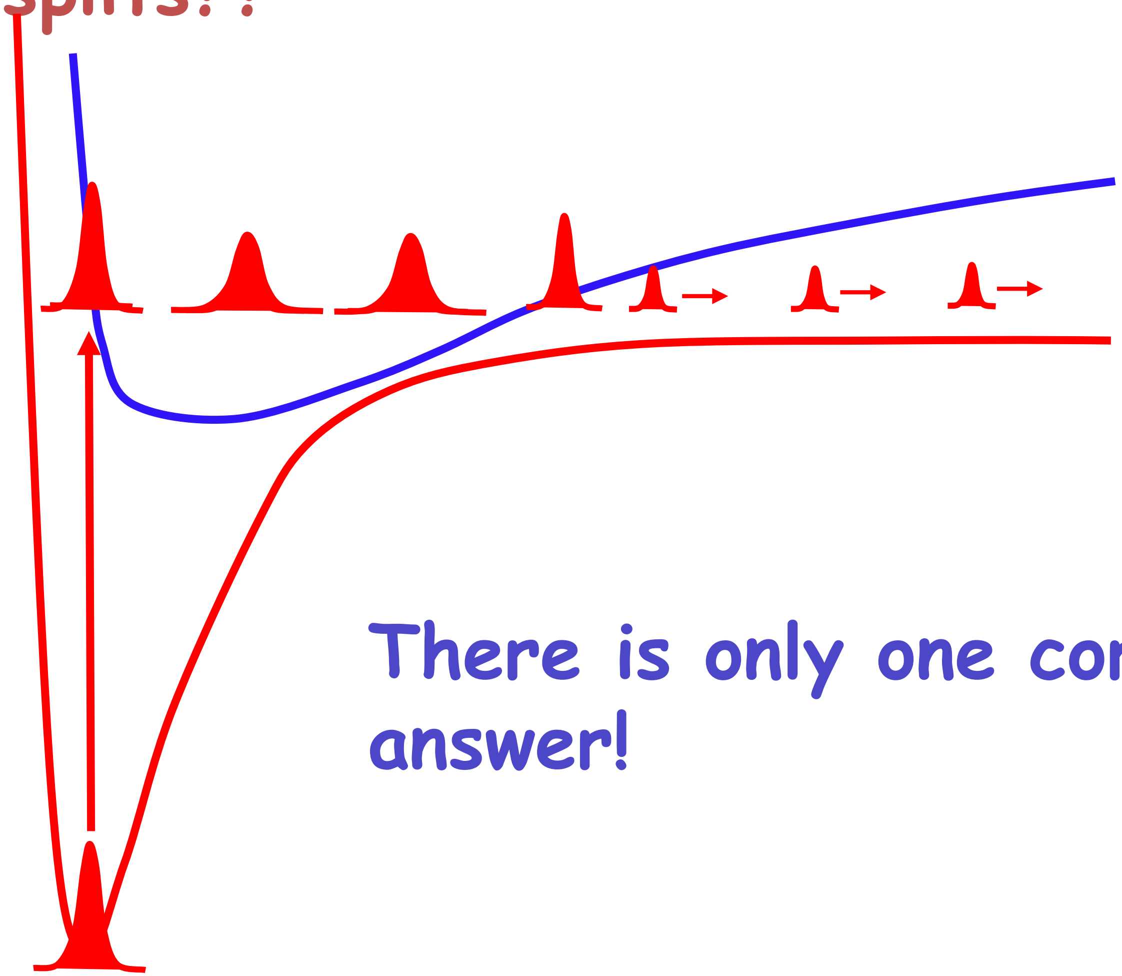


There is only one correct answer!

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 and unique time-dependent PES**

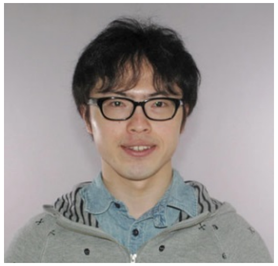
- **Mixed quantum-classical treatment**

THANKS

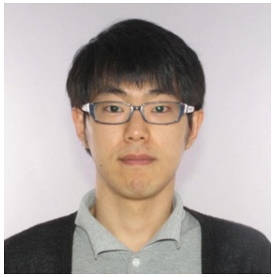
Ali Abedi

Axel Schild

Federica Agostini



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 (2005)

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

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

Note: If we want χ(R) to be smooth, S(R) may be discontinuous

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

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

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

Eq. ❶

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

Eq. ❷

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

where

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

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

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Exact PES

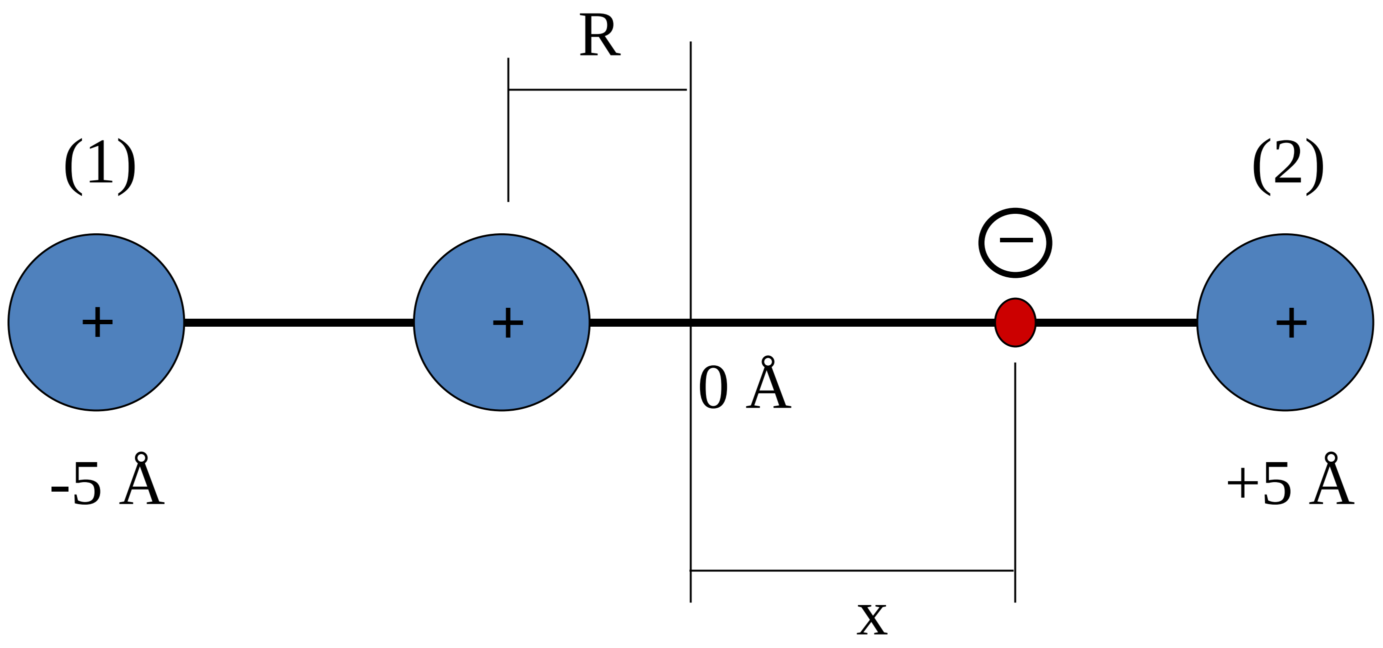
Exact Berry potential

N.I. Gidopoulos, E.K.U. Gross,
Phil. Trans. R. Soc. 372, 20130059 (2014), arXiv:cond-mat/0502433 (2005)

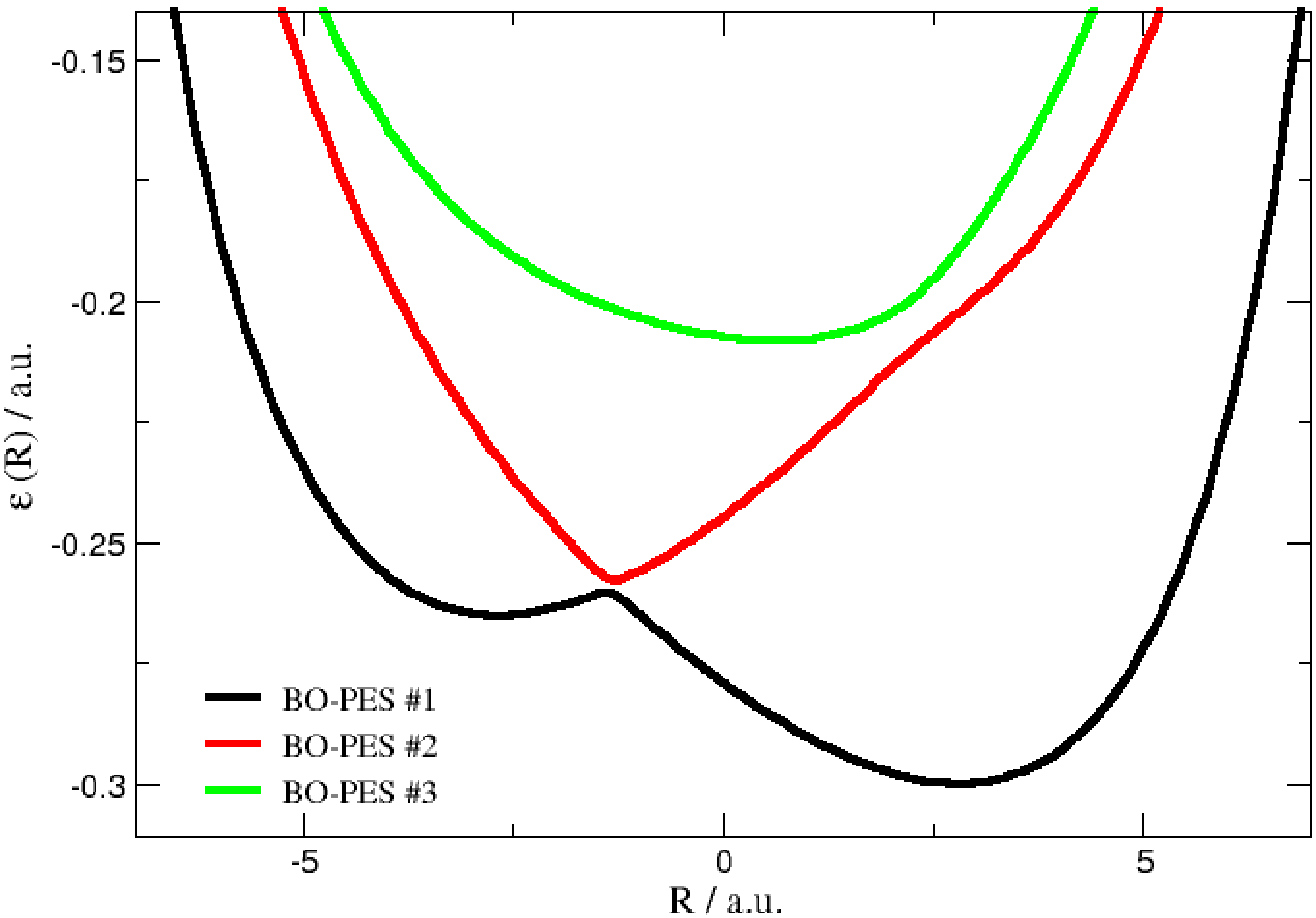
How do the exact PES look like?

MODEL

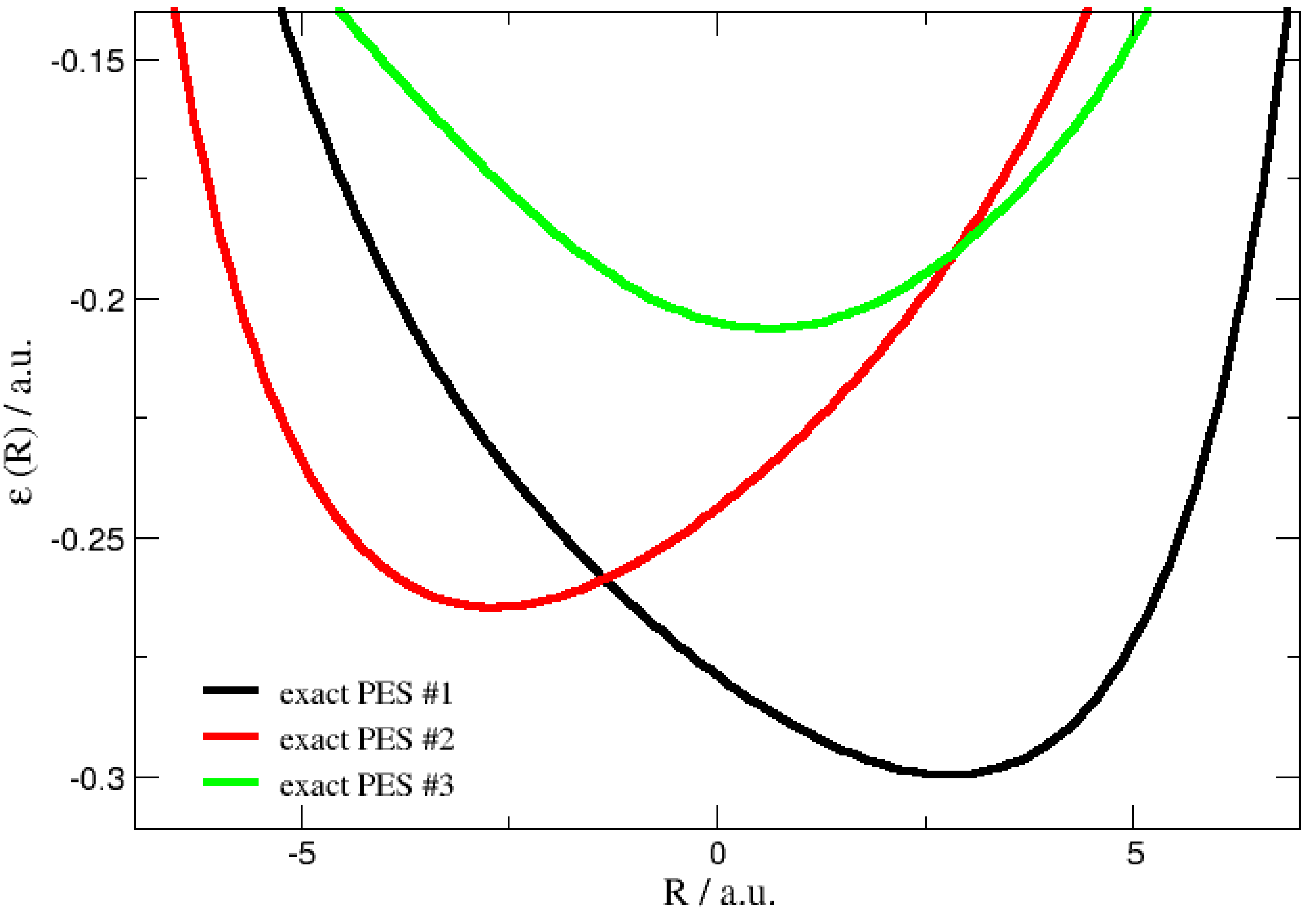
S. Shin, H. Metiu, JCP 102, 9285 (1995), JPC 100, 7867 (1996)



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



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

Exact Berry connection

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

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:

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

Conclusion: The nuclear Schrödinger equation

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

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)

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

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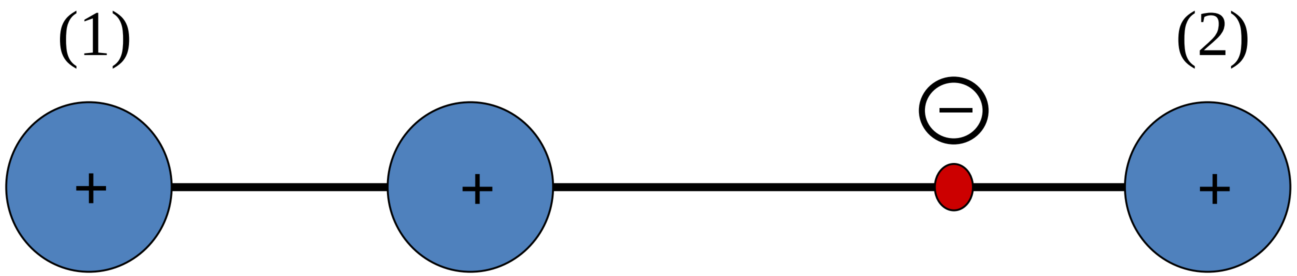
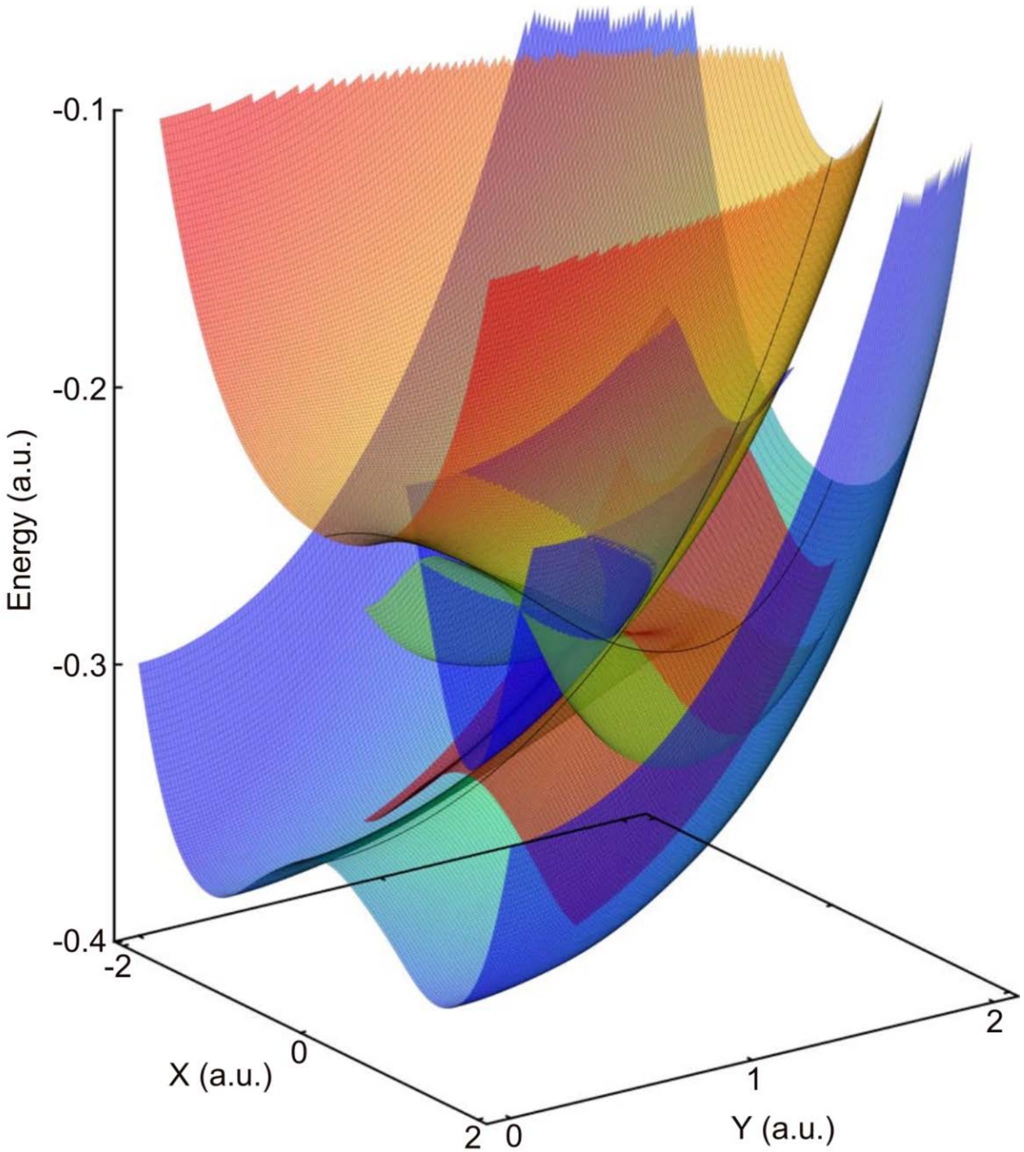
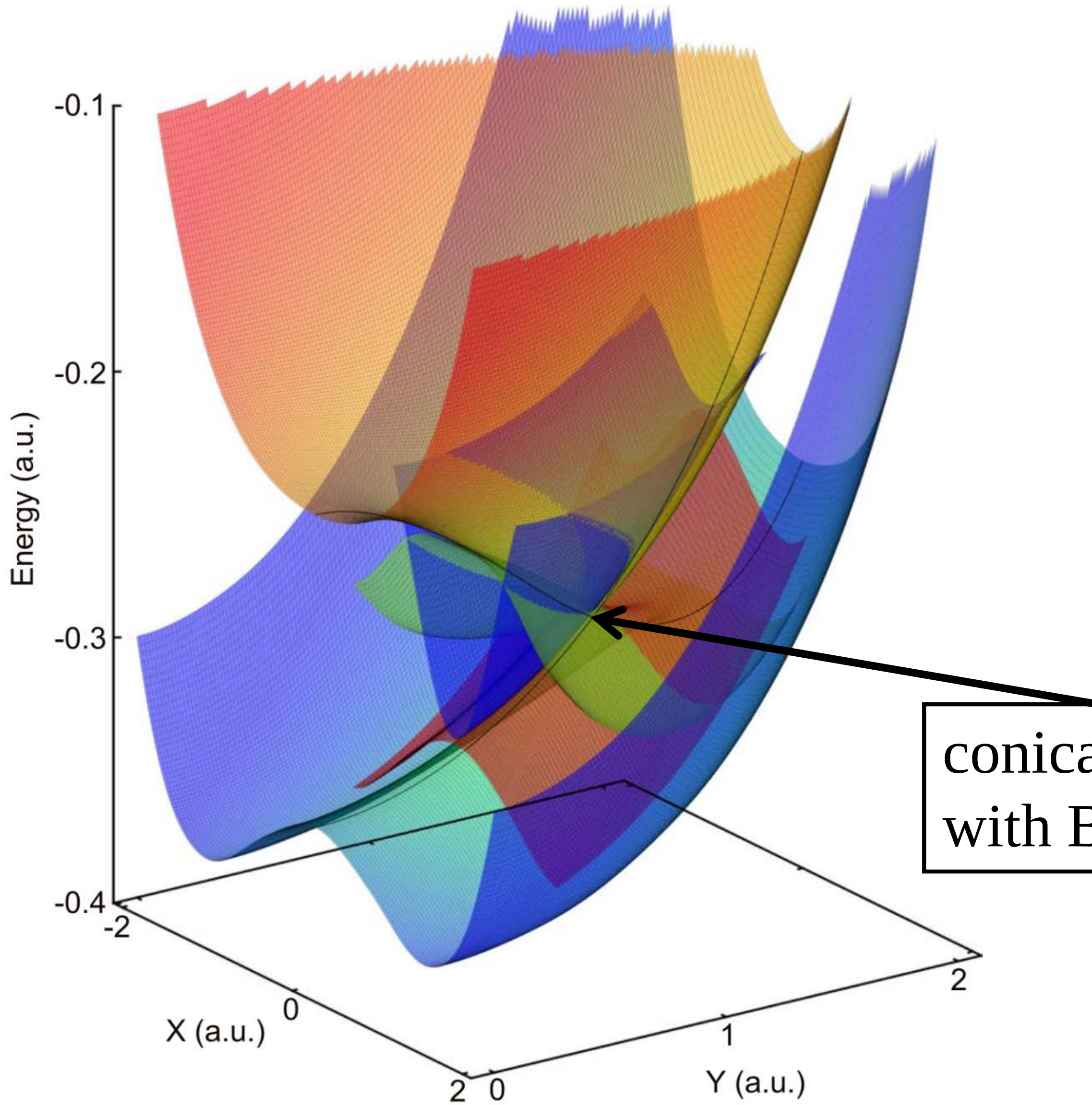
Look at Shin-Metiu model in 2D:



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.

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

- 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)?

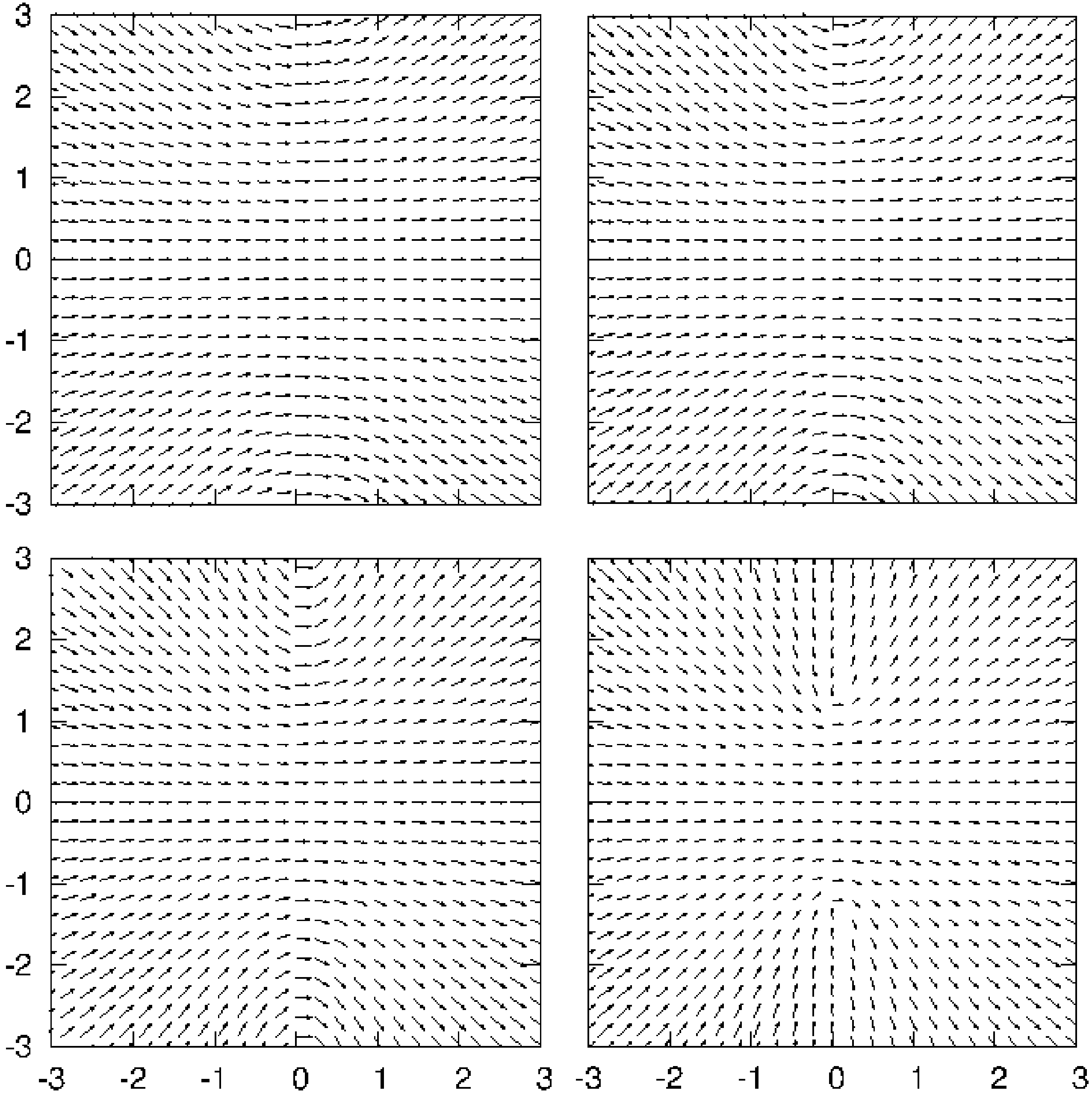
Look at

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

as function of nuclear mass M.

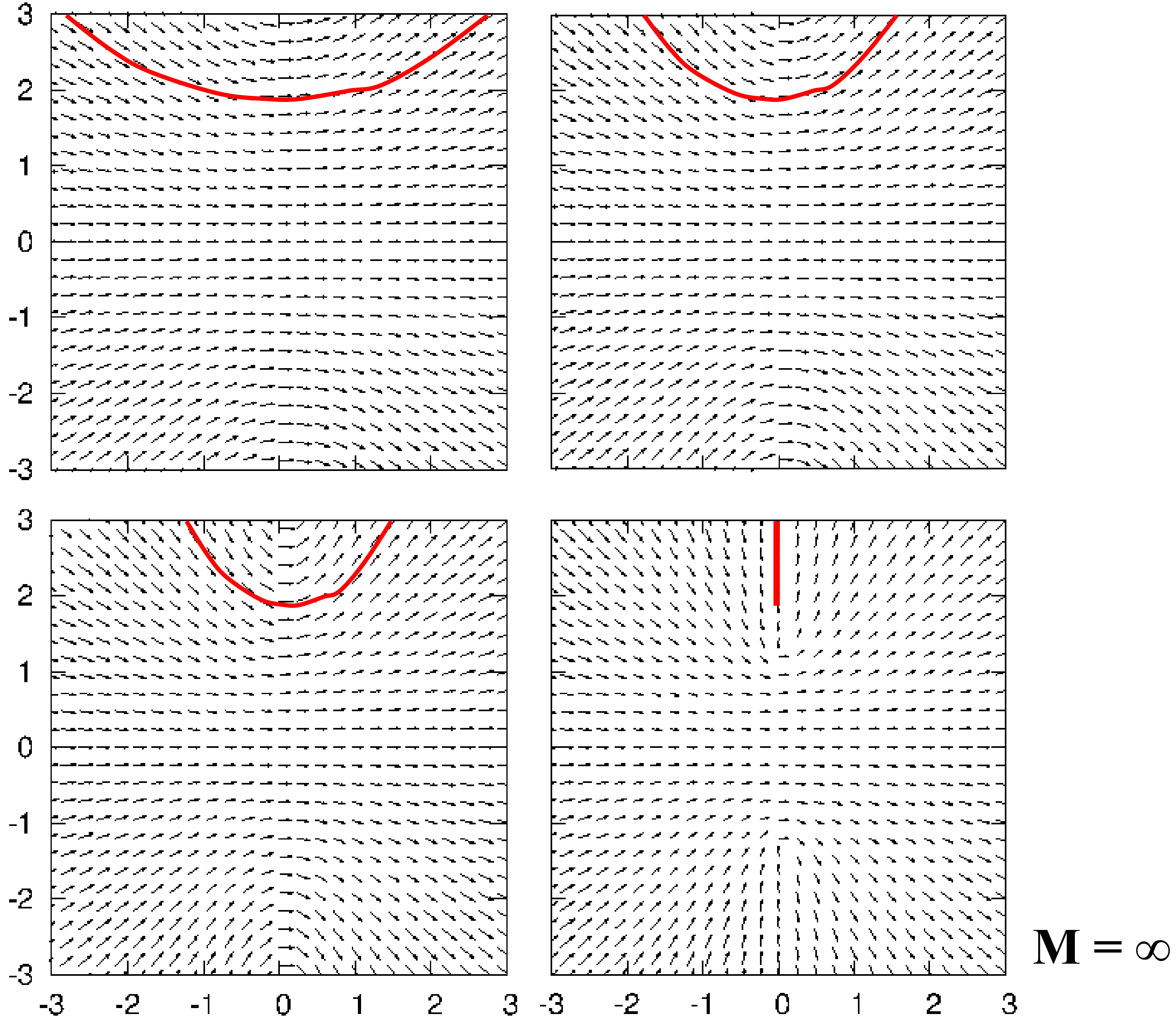
S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, PRL 113, 263004 (2014)

D(R)



M = ∞

D(R)



Question: Can one prove in general that the exact molecular Berry phase vanishes?

Question: Can one prove **in general** that the exact molecular Berry phase vanishes?

Answer: No! There are cases where a nontrivial Berry phase appears in the exact treatment.

R. Requist, F. Tandetzky, EKU Gross,
Phys. Rev. A 93, 042108 (2016).

Time-dependent case

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. ➊

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

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

Eq. ➋

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

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

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

Eq. ❷

Exact Berry potential

Exact TDPES

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

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

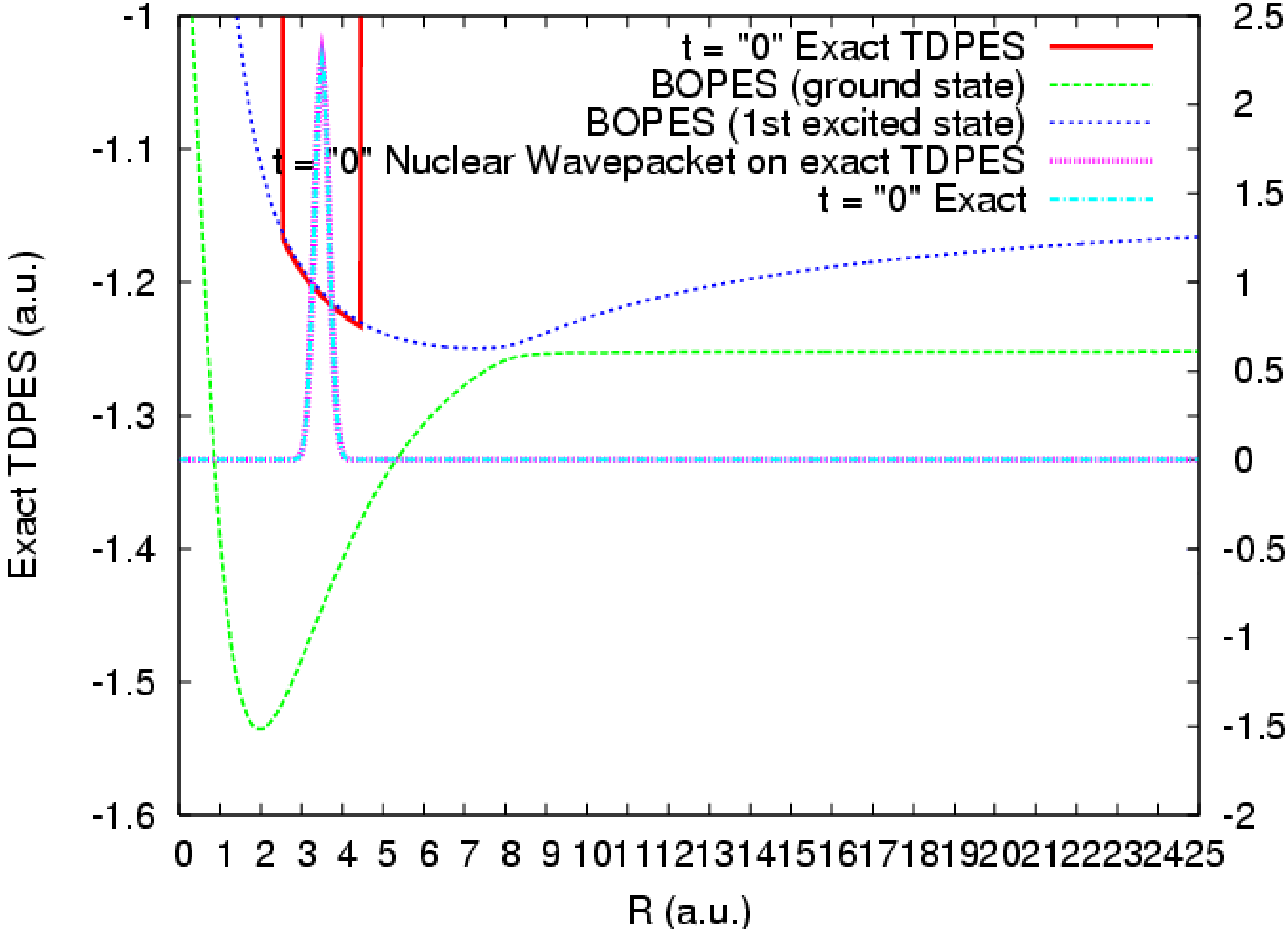
JCP <u>137</u>, 22A530 (2012)

How does the exact time-dependent PES look like?

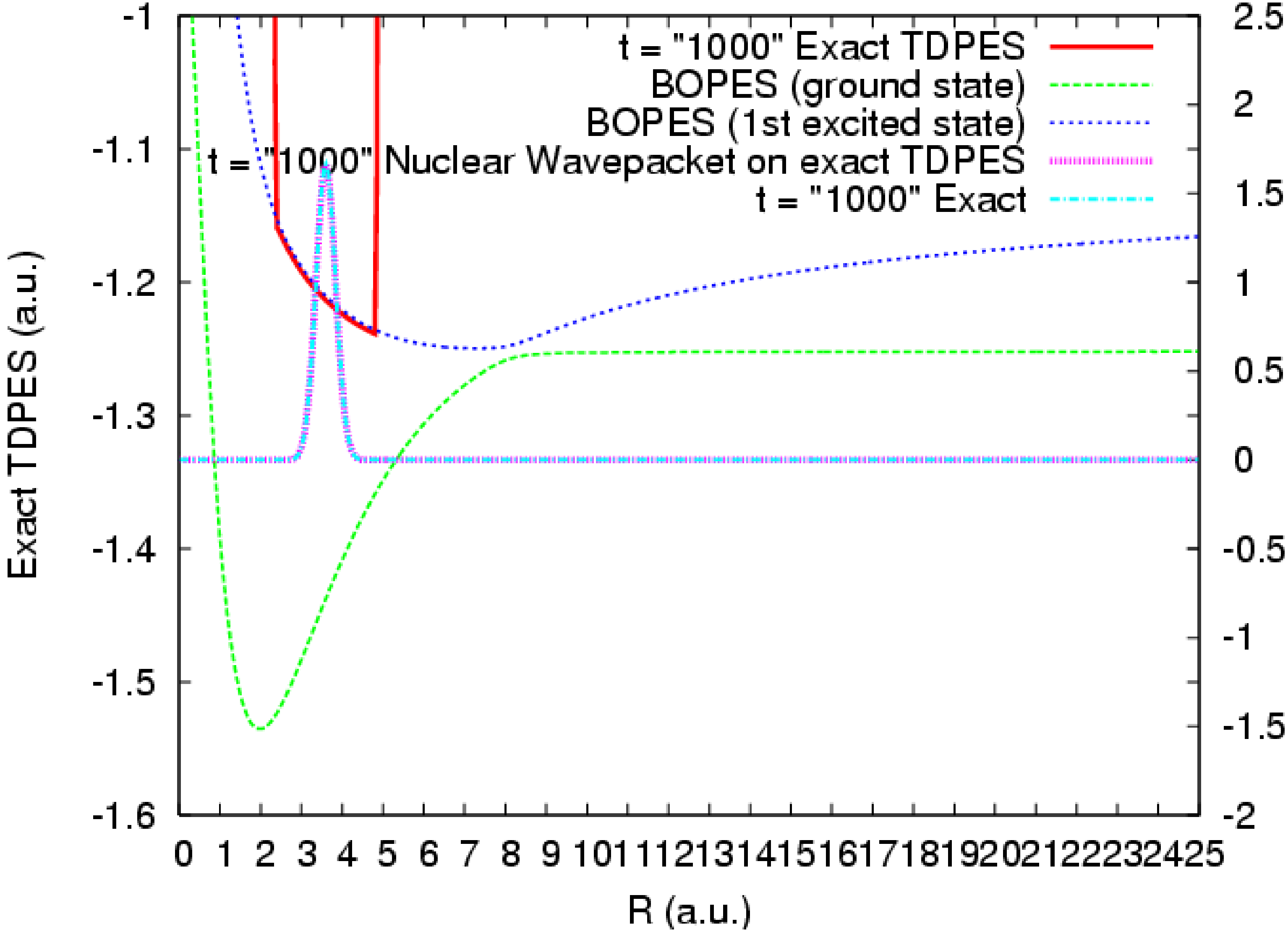
Example: Nuclear wave packet going through an avoided crossing (Zewail experiment)

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

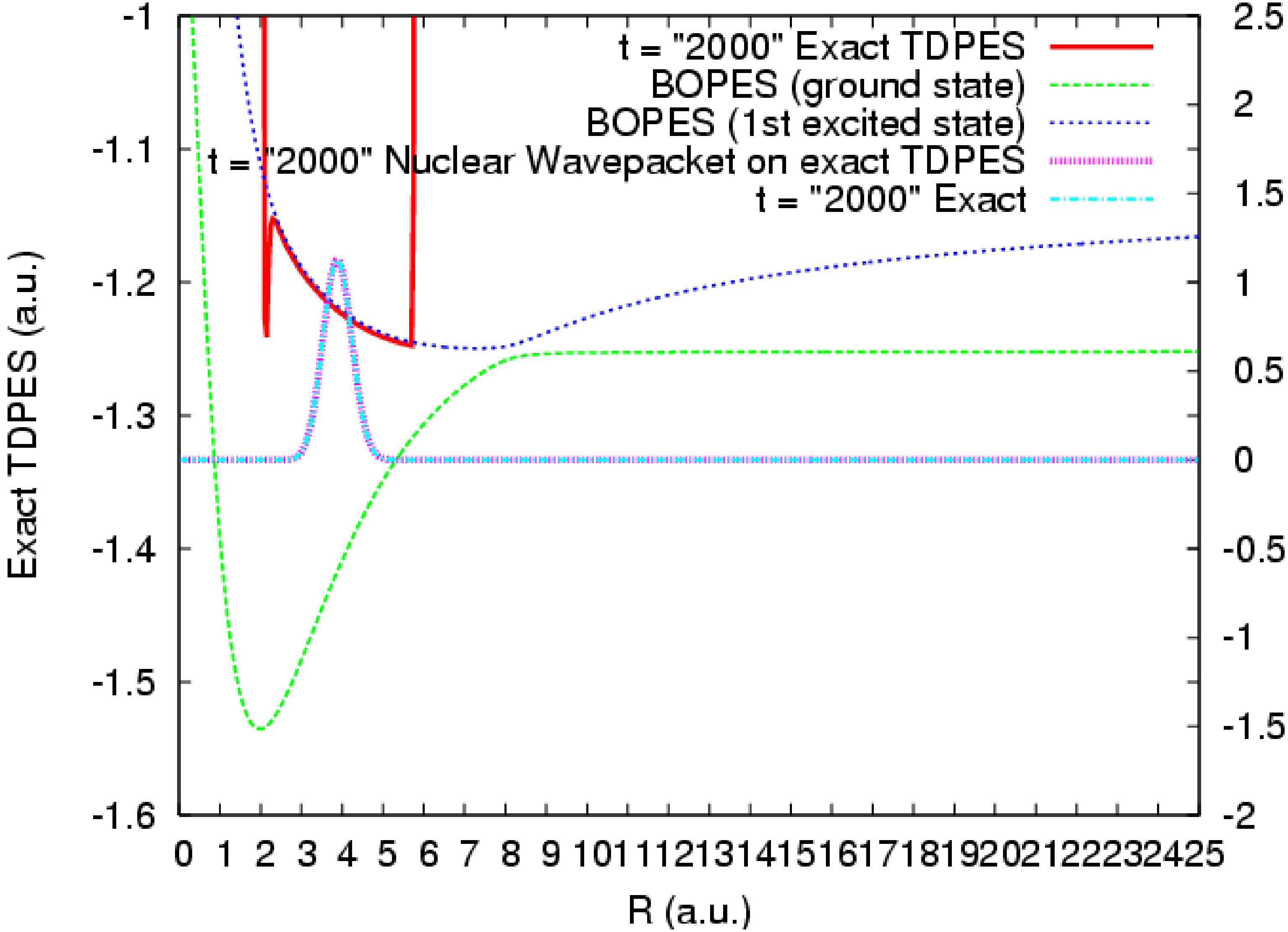
F. Agostini, A. Abedi, Y. Suzuki, E.K.U. Gross,
Mol. Phys. 111, 3625 (2013)



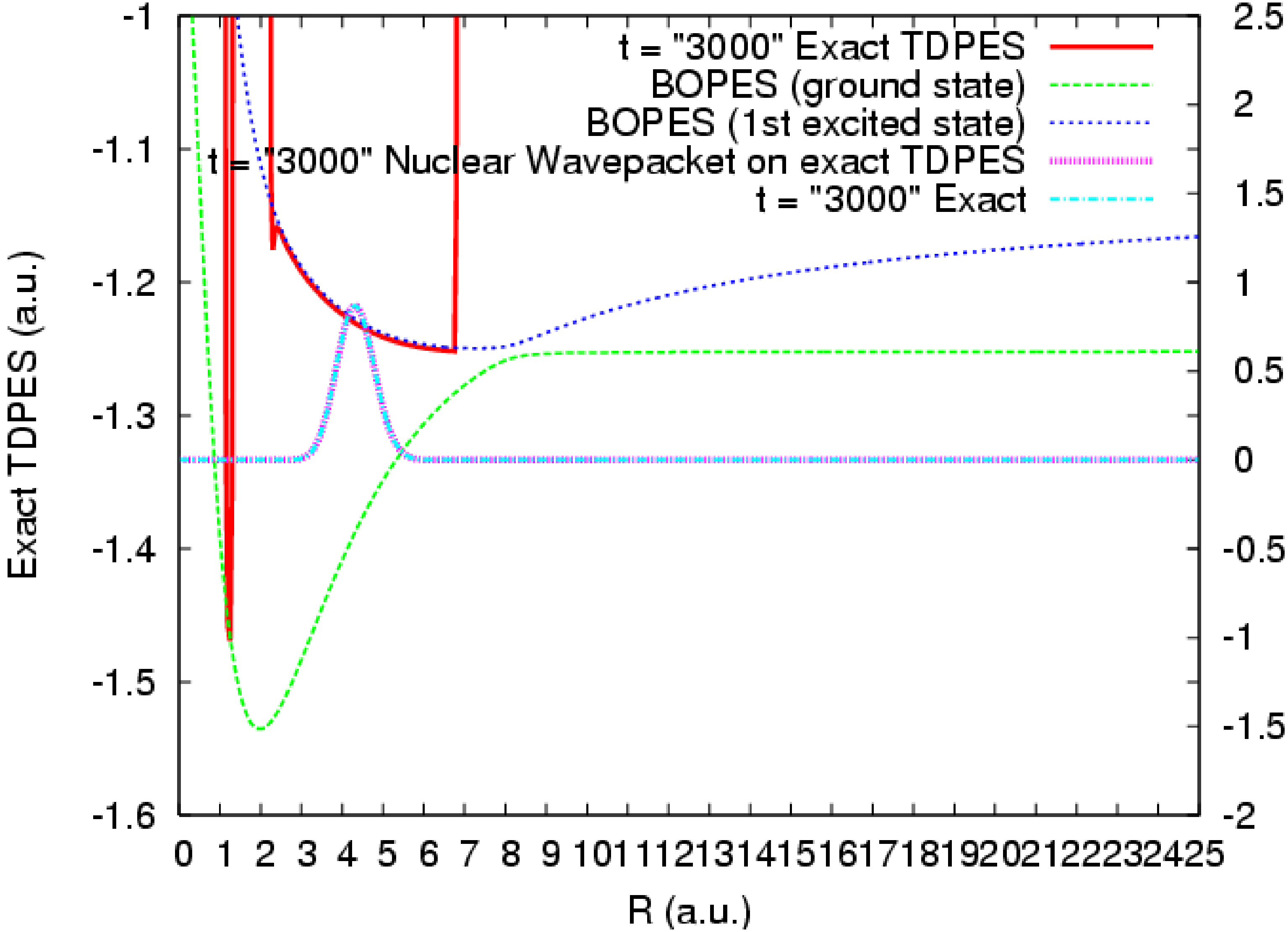
t = "0" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "0" Nuclear Wavepacket on exact TDPES
t = "0" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

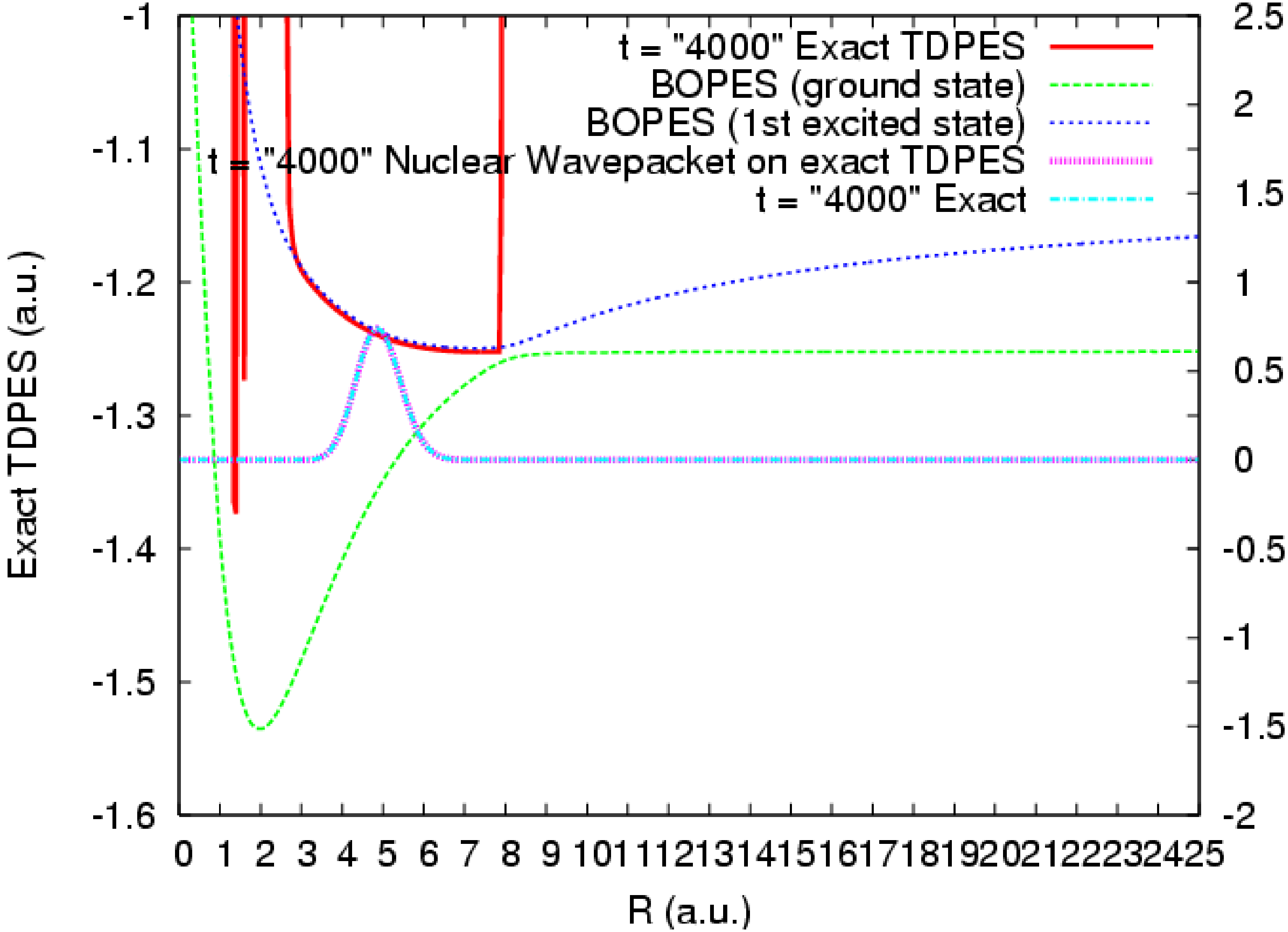


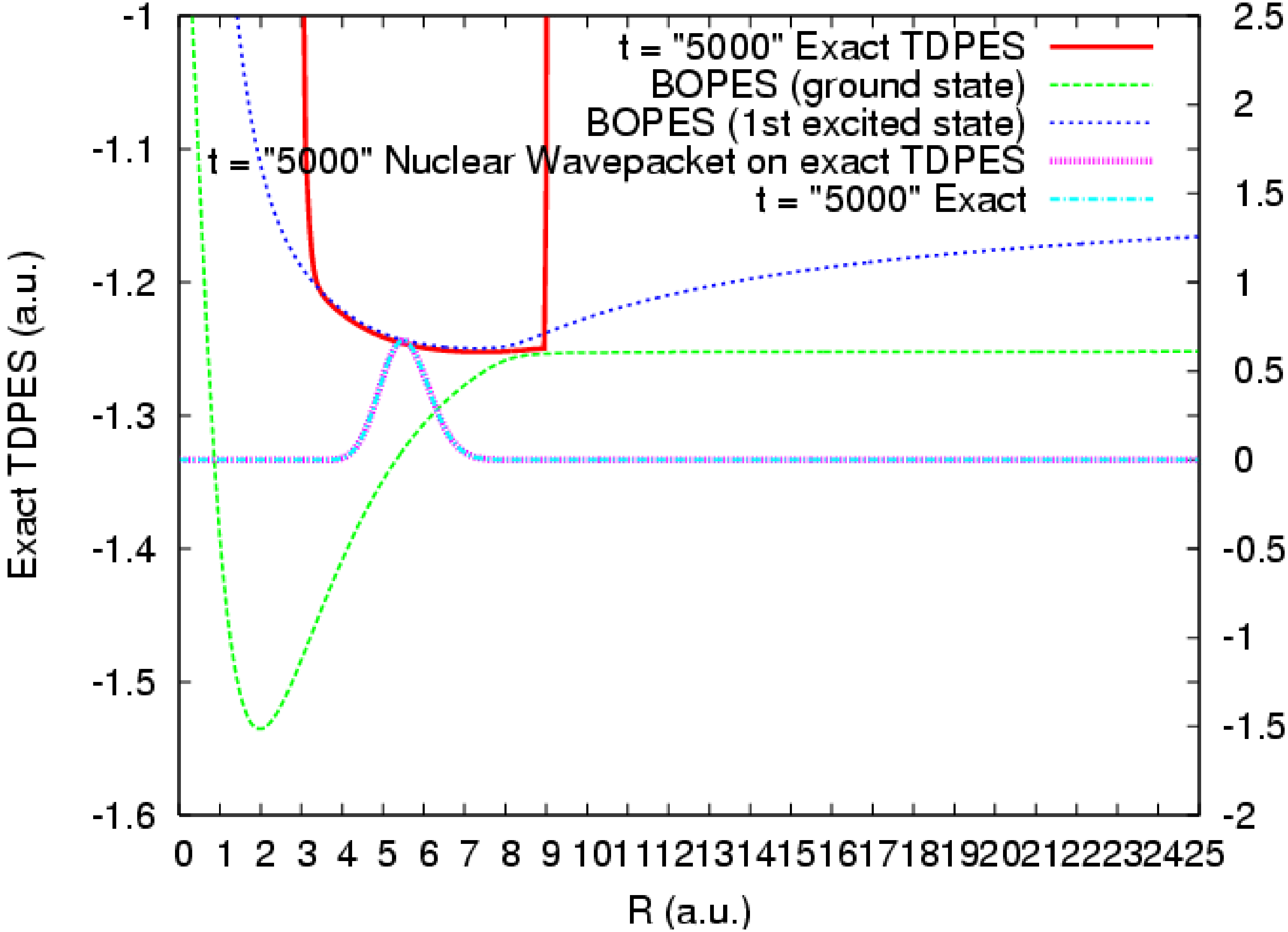
t = "1000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "1000" Nuclear Wavepacket on exact TDPES
t = "1000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

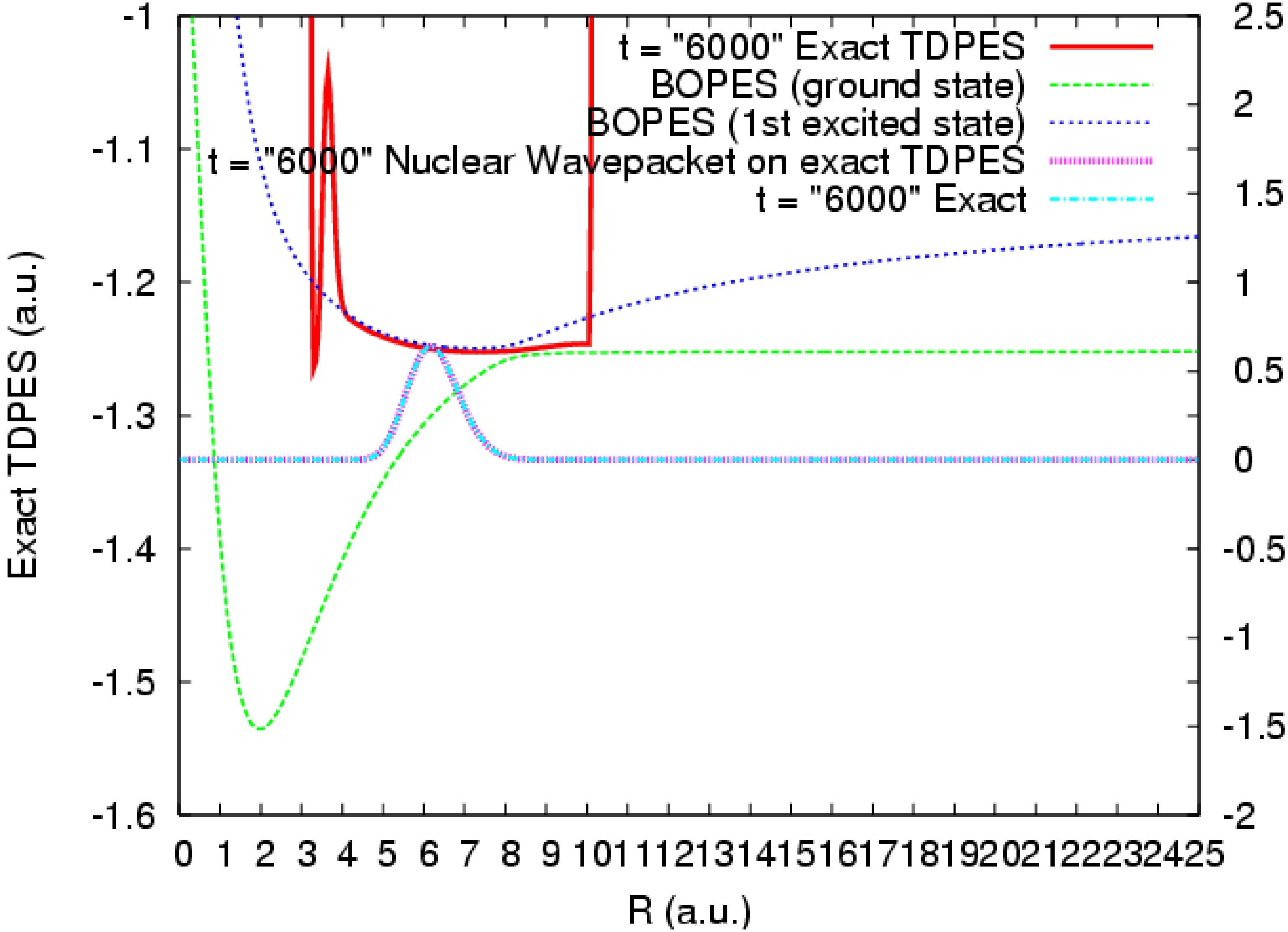


t = "2000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "2000" Nuclear Wavepacket on exact TDPES
t = "2000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

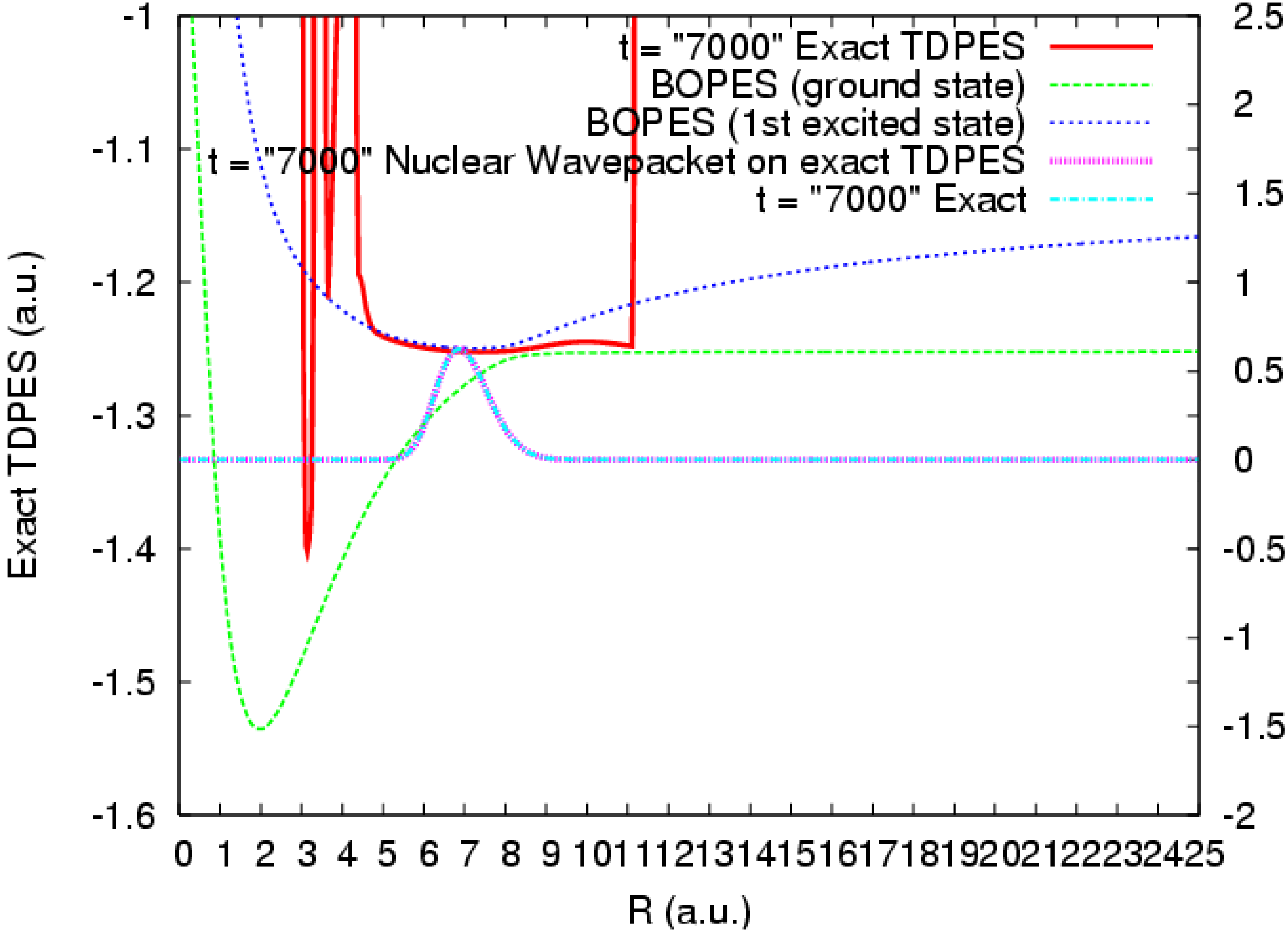

t = "3000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "3000" Nuclear Wavepacket on exact TDPES
t = "3000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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

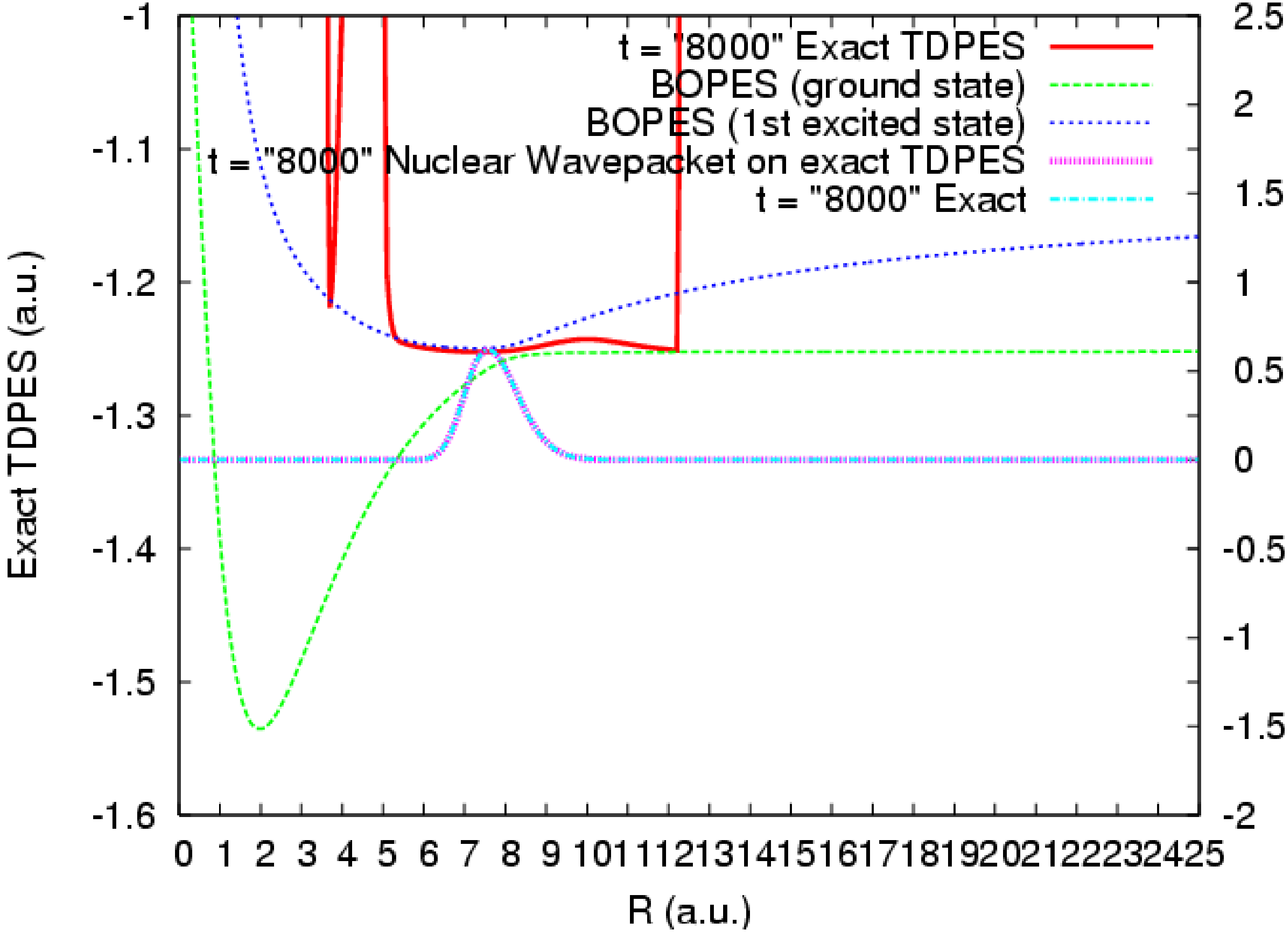

t = "5000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "5000" Nuclear Wavepacket on exact TDPES
t = "5000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



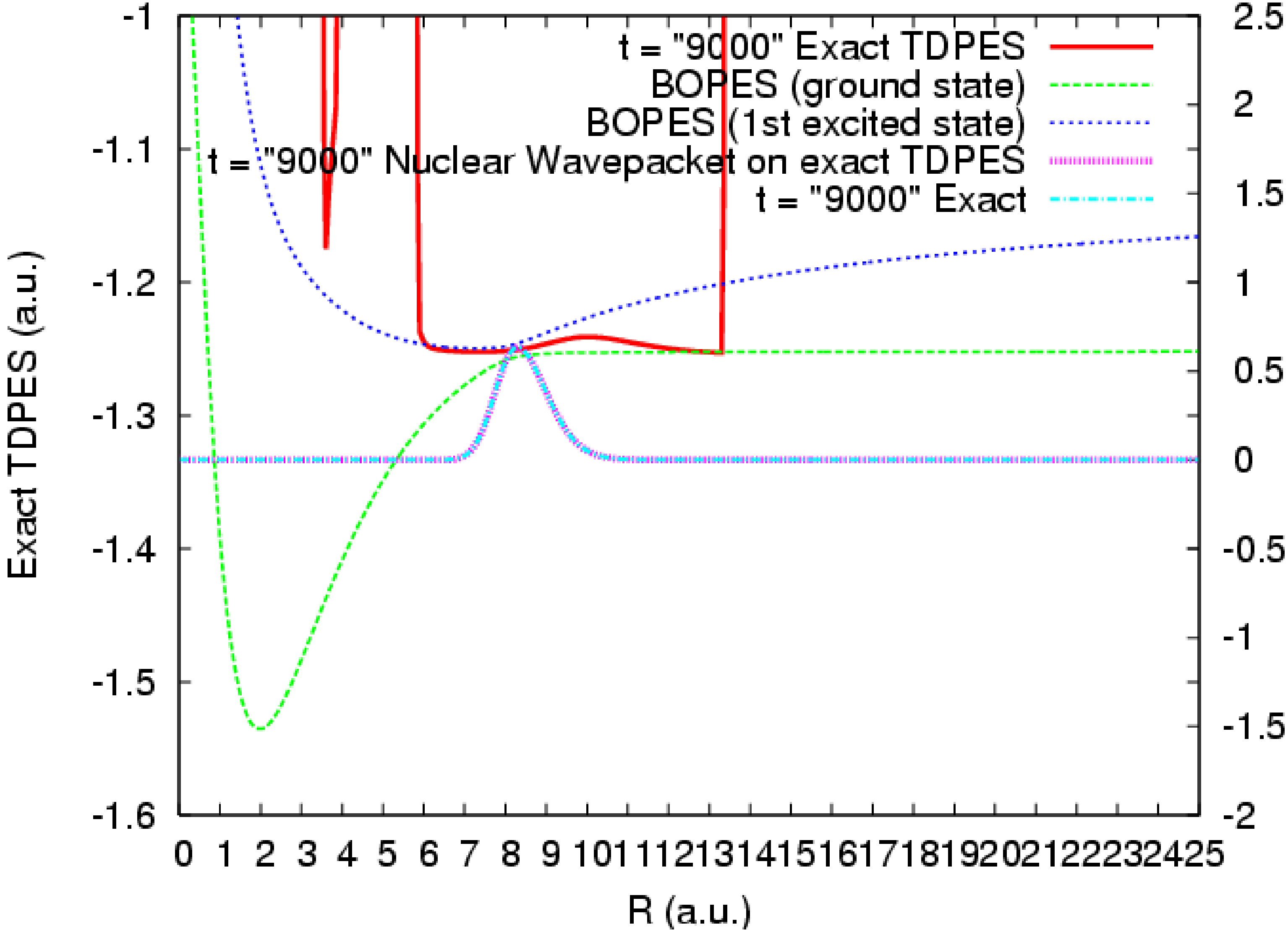
t = "6000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "6000" Nuclear Wavepacket on exact TDPES
t = "6000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



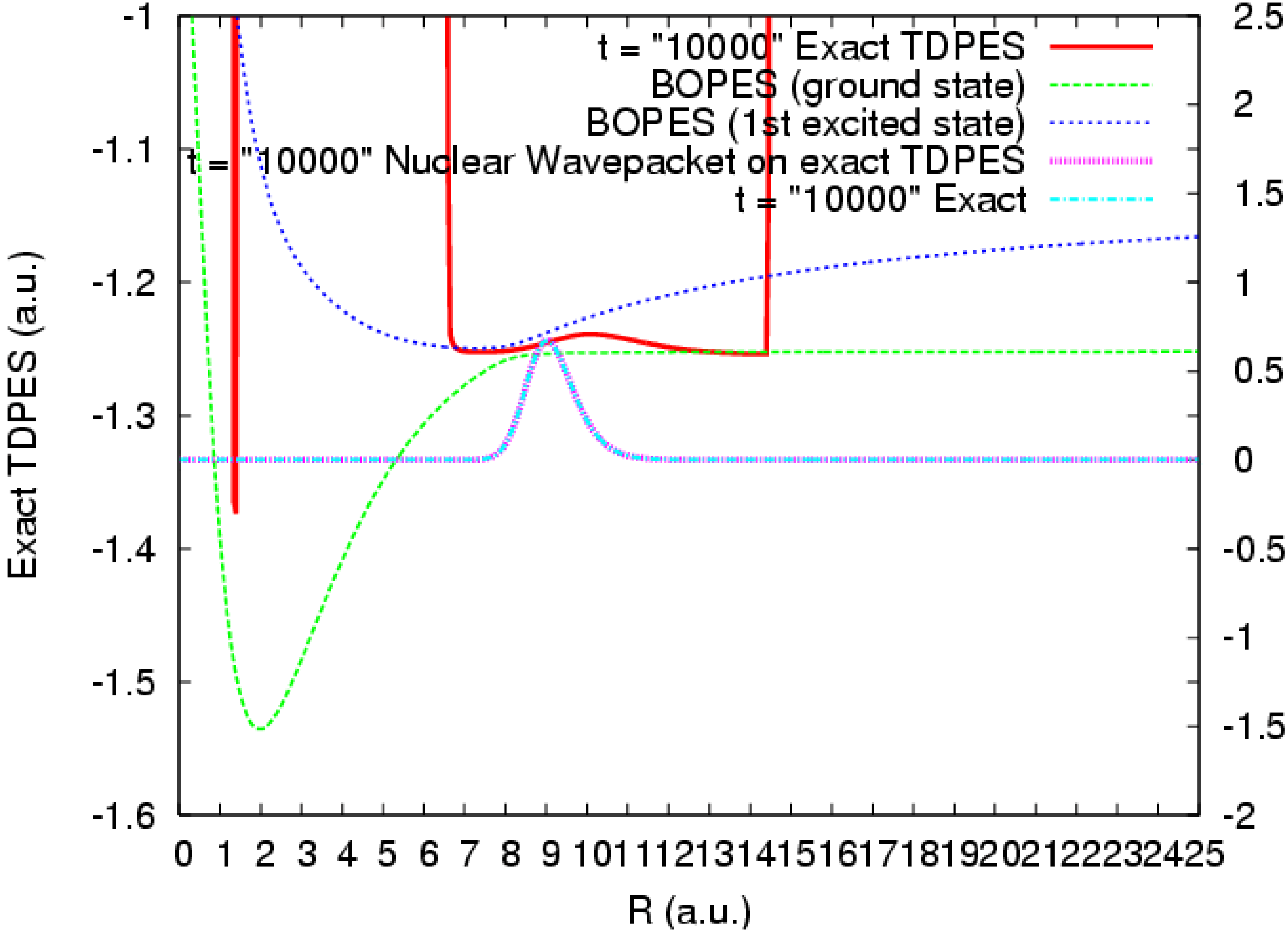
t = "7000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "7000" Nuclear Wavepacket on exact TDPES
t = "7000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



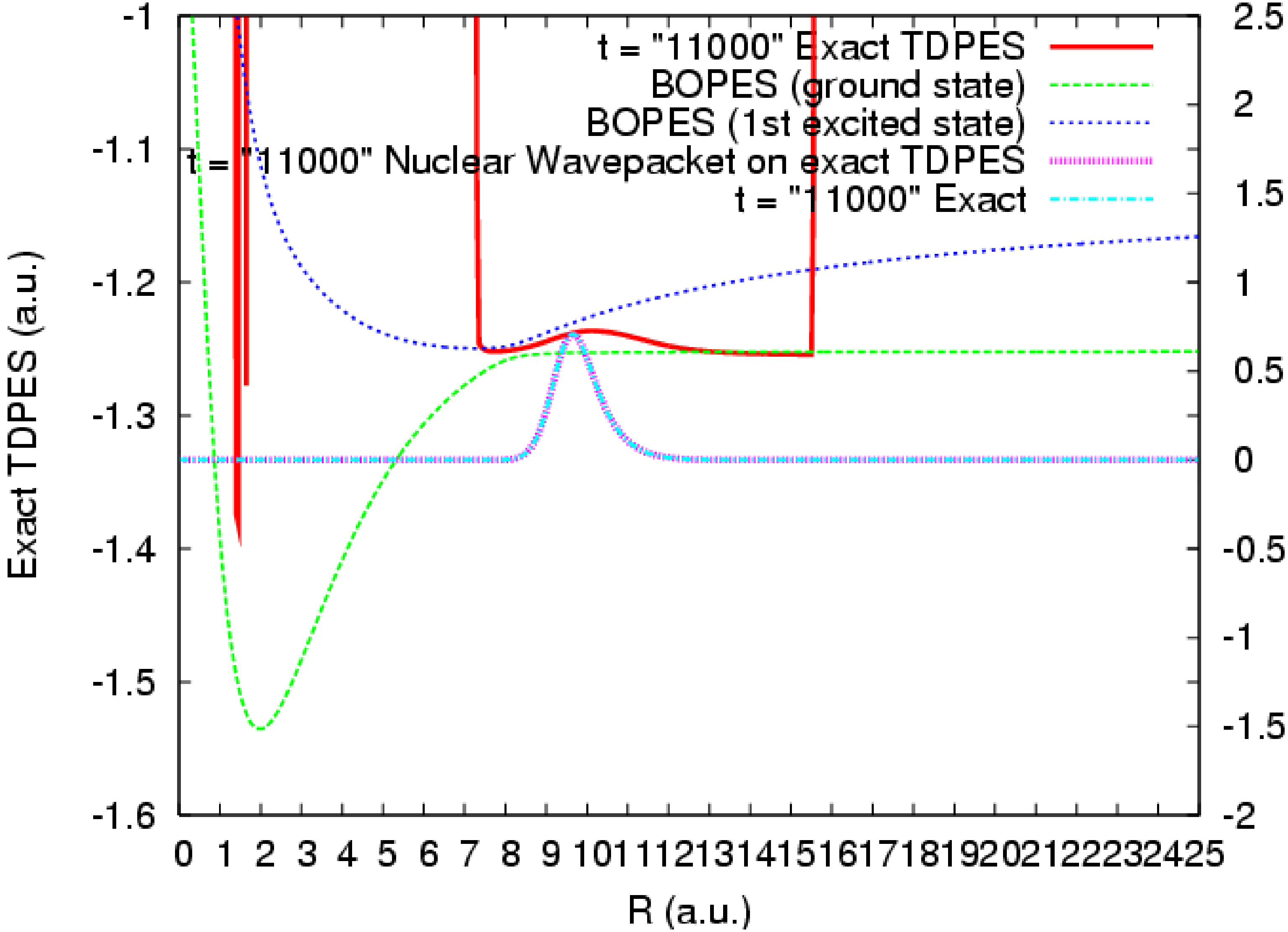
t = "8000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "8000" Nuclear Wavepacket on exact TDPES
t = "8000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



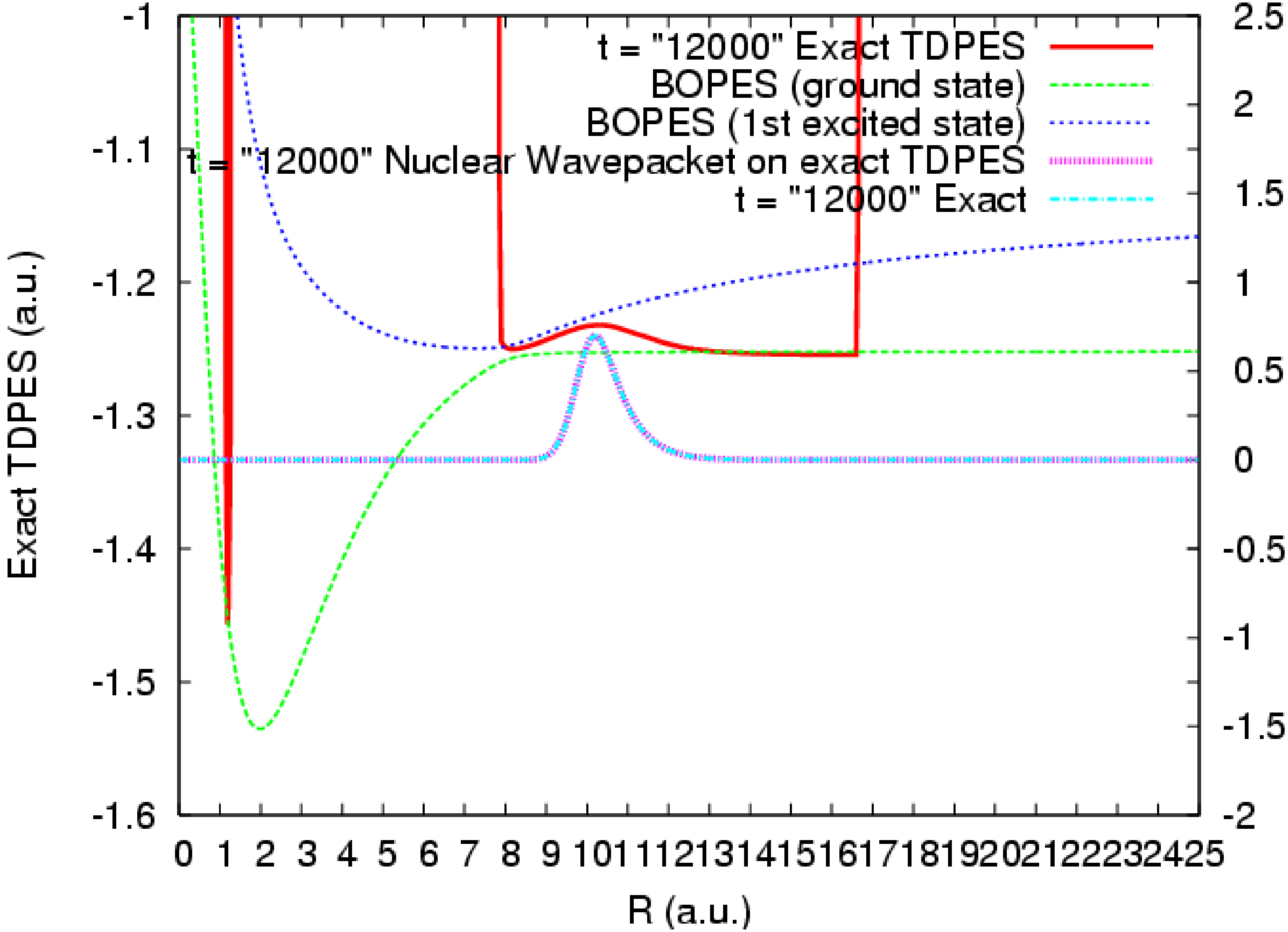
t = "9000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "9000" Nuclear Wavepacket on exact TDPES
t = "9000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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



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



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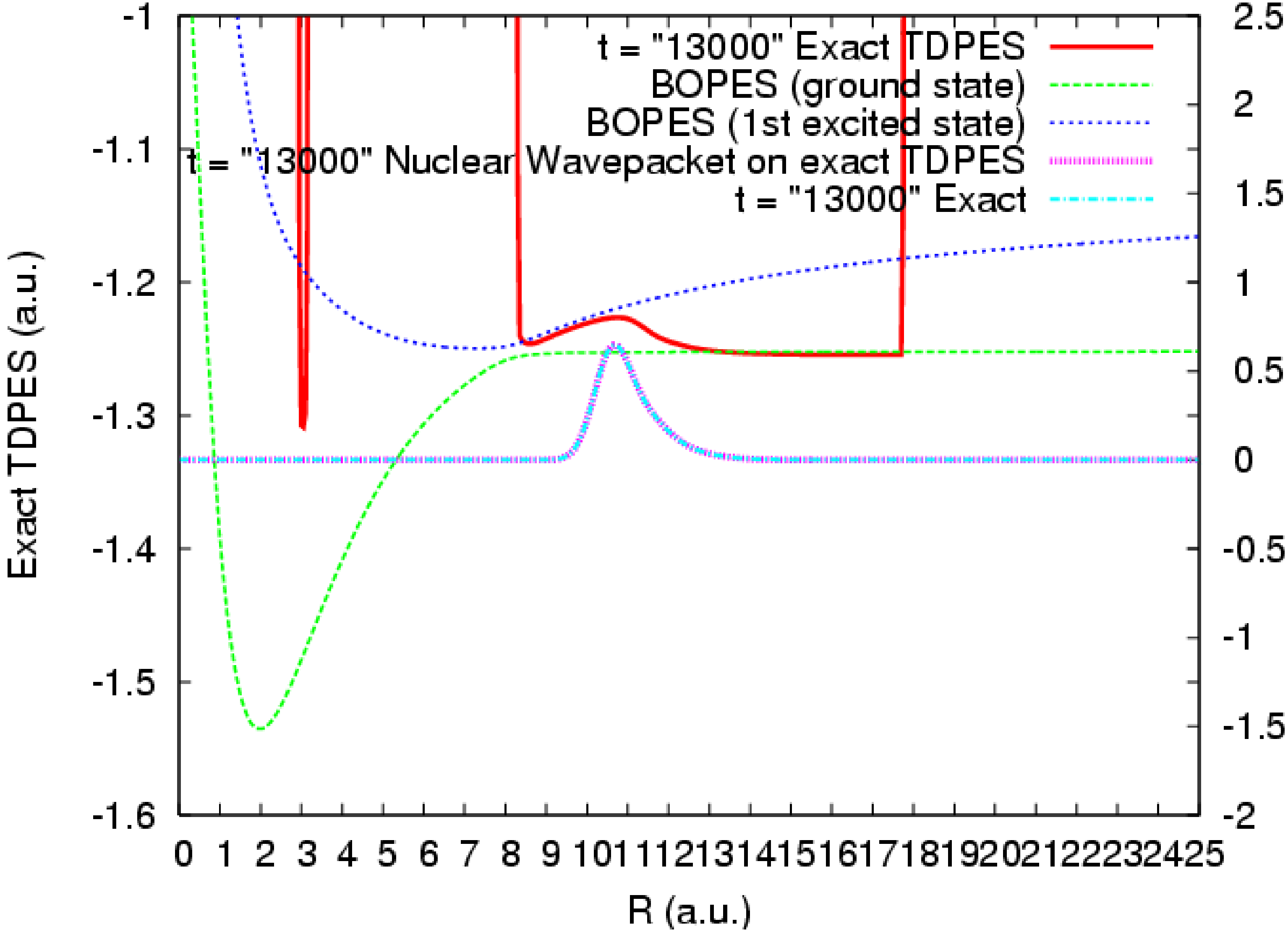
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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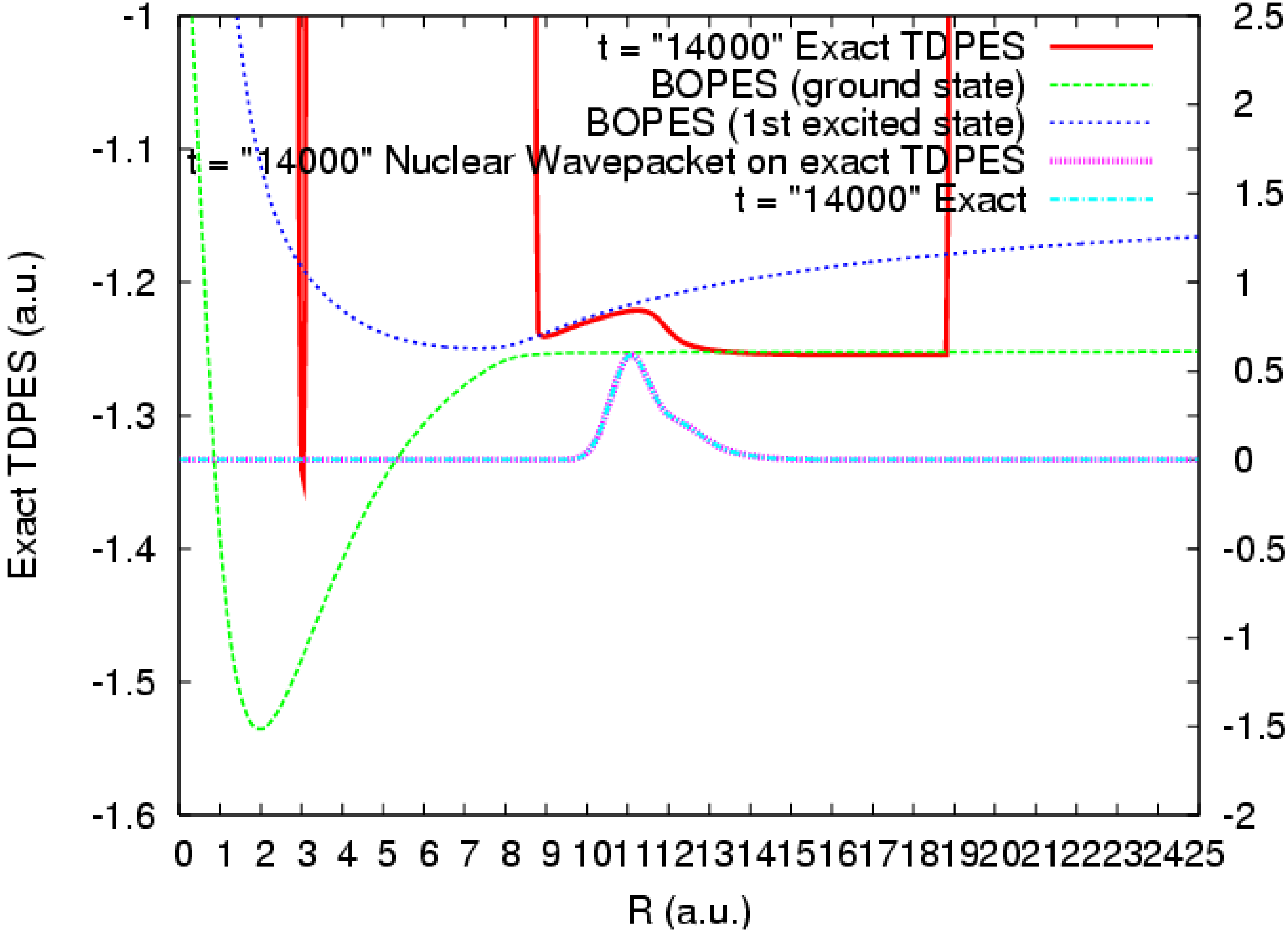
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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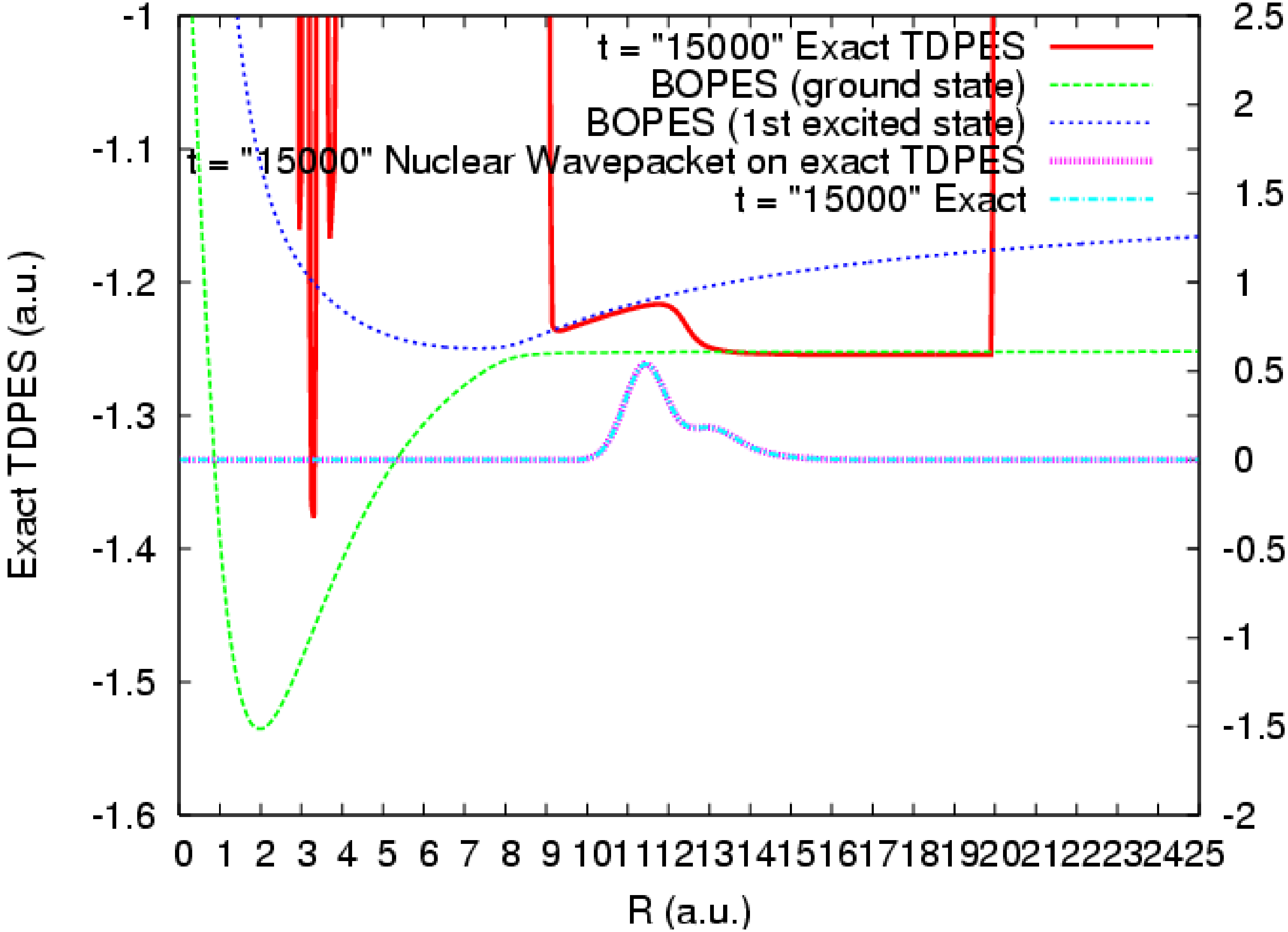
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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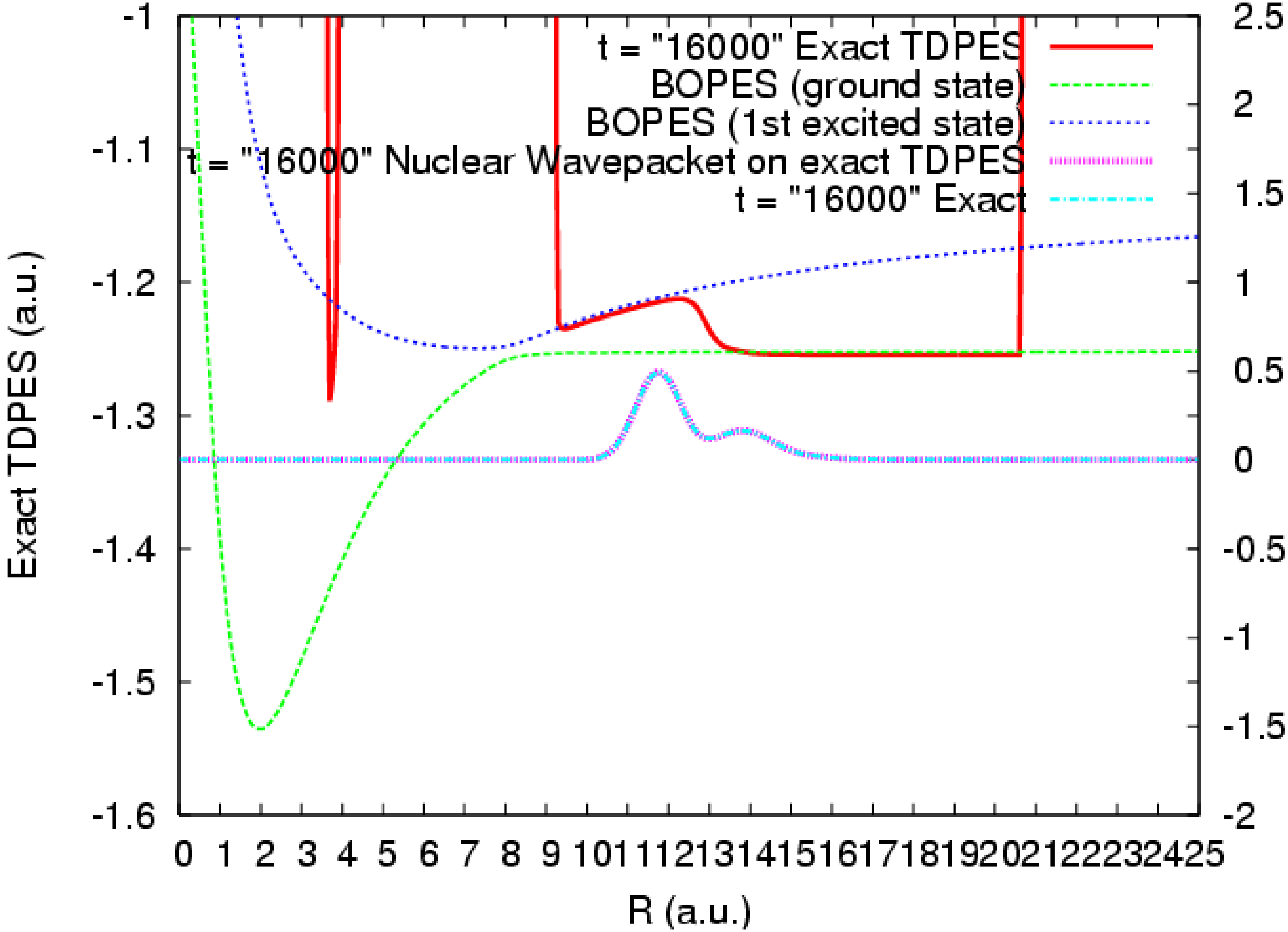
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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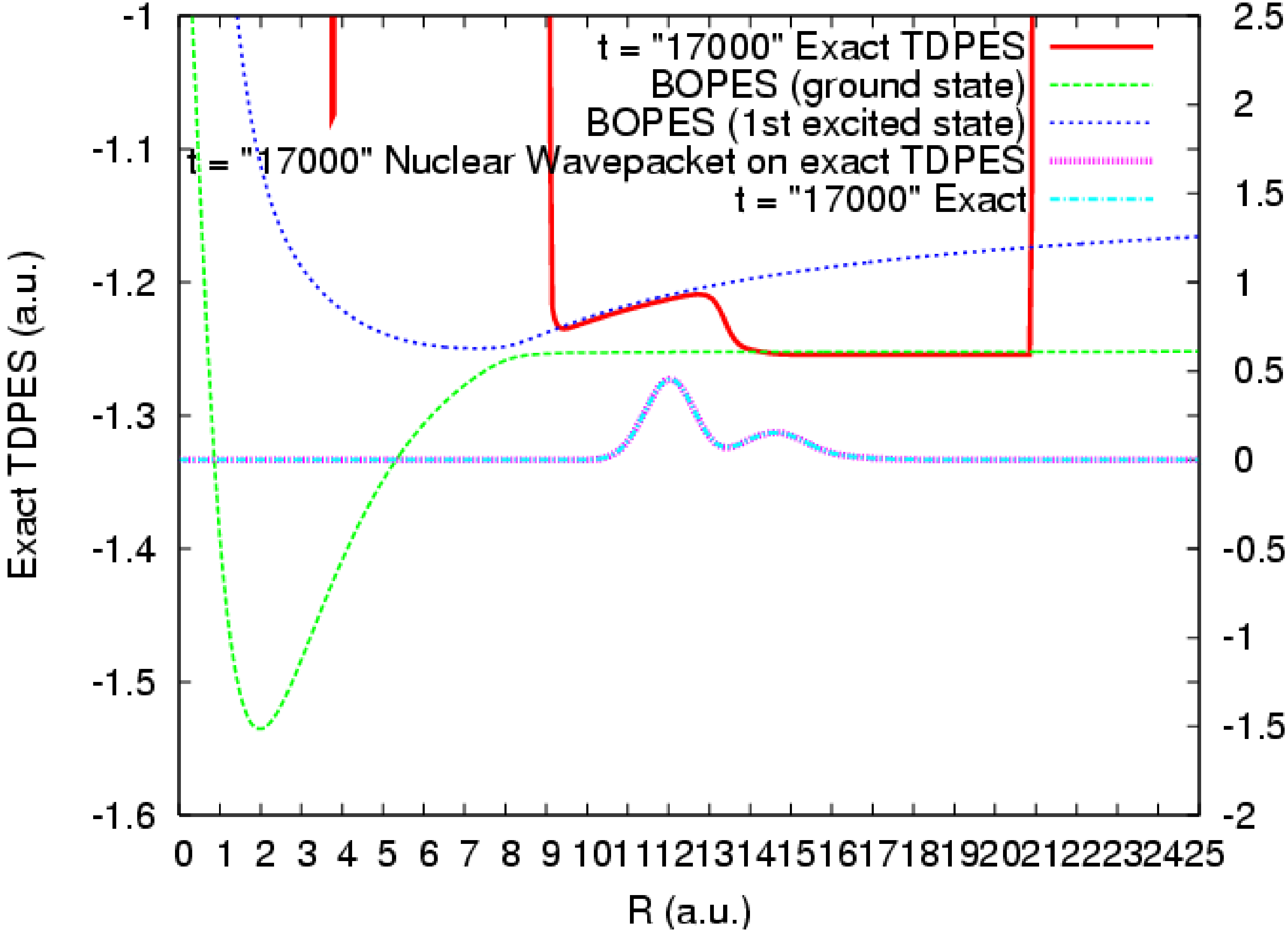
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



t = "17000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "17000" Nuclear Wavepacket on exact TDPES
t = "17000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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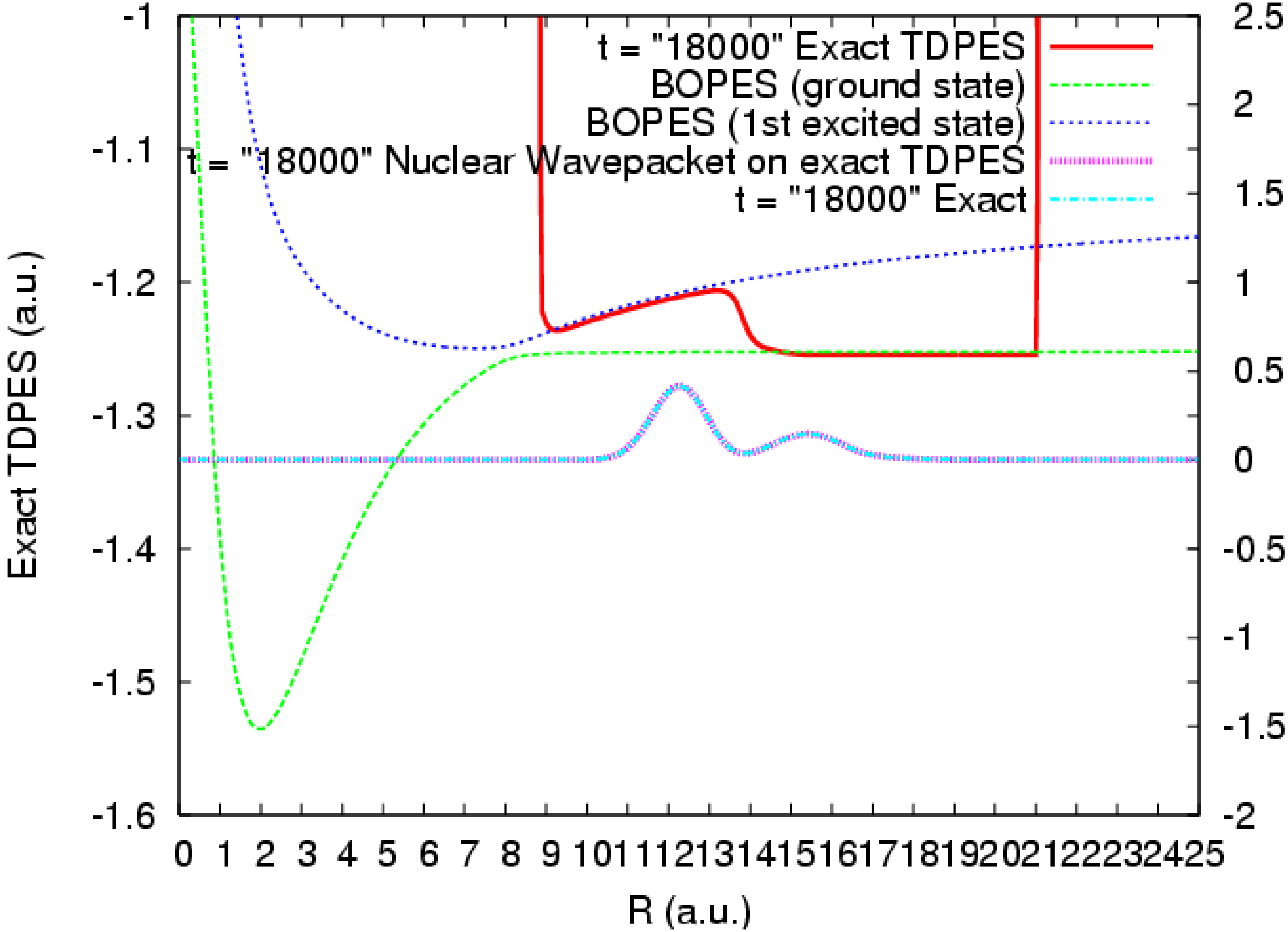
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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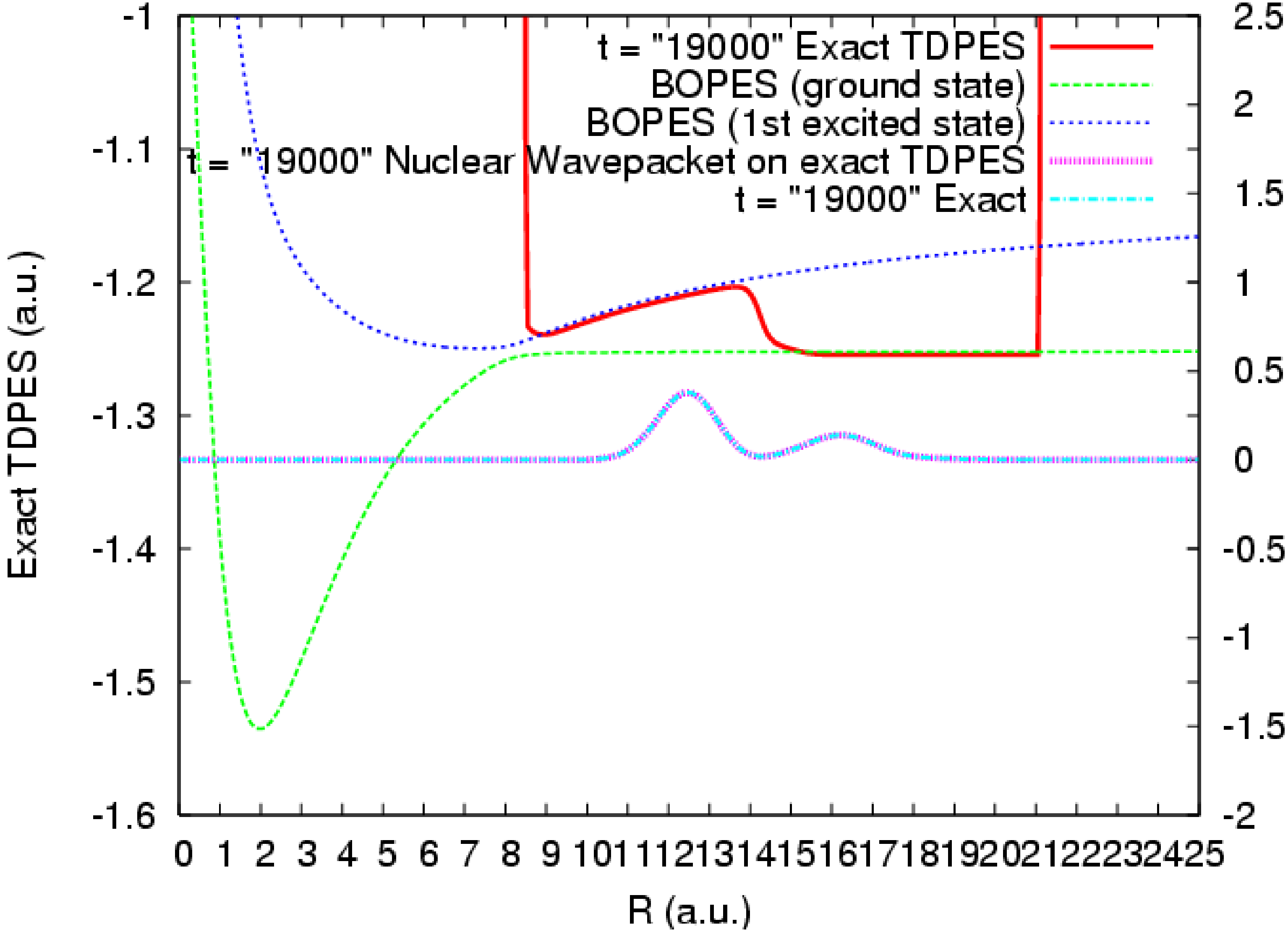
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



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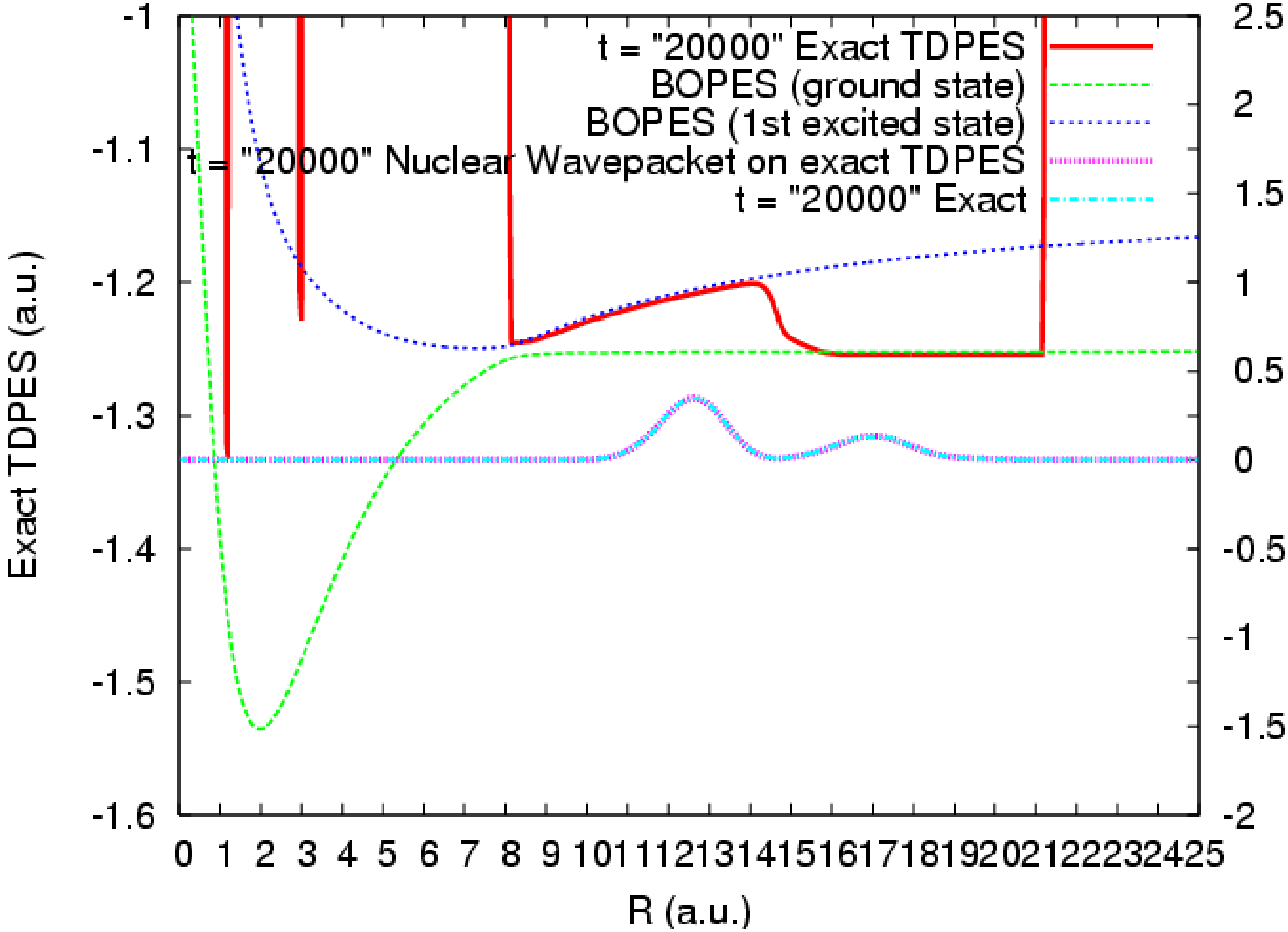
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



t = "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

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)

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

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

Theorem T-II

Eq. ➊

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

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

Eq. ➋

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

Theorem T-II

Eq. ❶

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

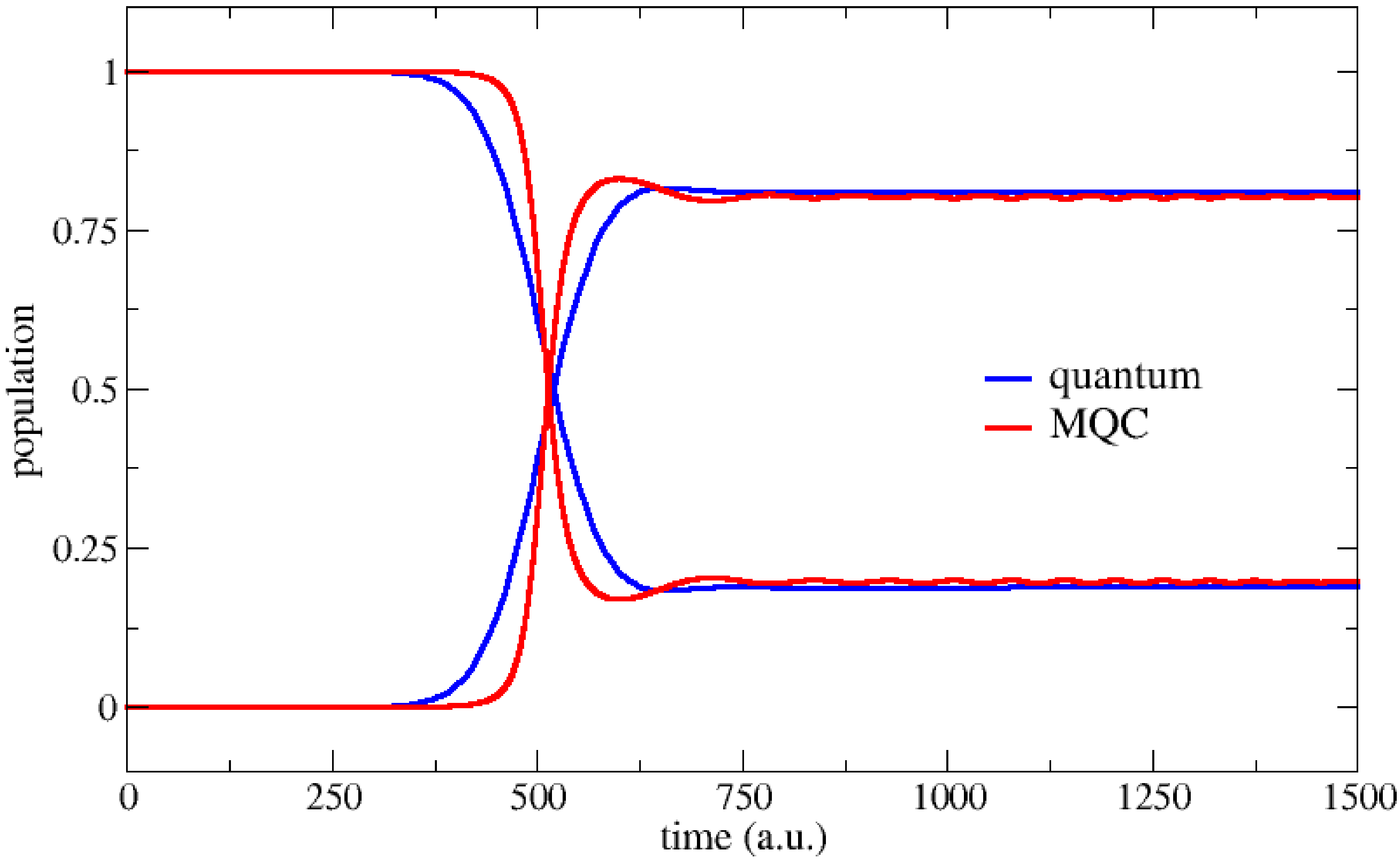
$$+ \sum_{\nu}^{N_n} \frac{1}{M_\nu}\left(\left(\frac{-i\nabla_\nu \chi\left(\underline{\underline{R}}, t\right)}{\chi\left(\underline{\underline{R}}, t\right)} + A_\nu\left(\underline{\underline{R}}, t\right)\right)\left(-i\nabla_\nu - A_\nu\right) - \in\left(\underline{\underline{R}}, t\right)\right)\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\un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

Eq. ❷

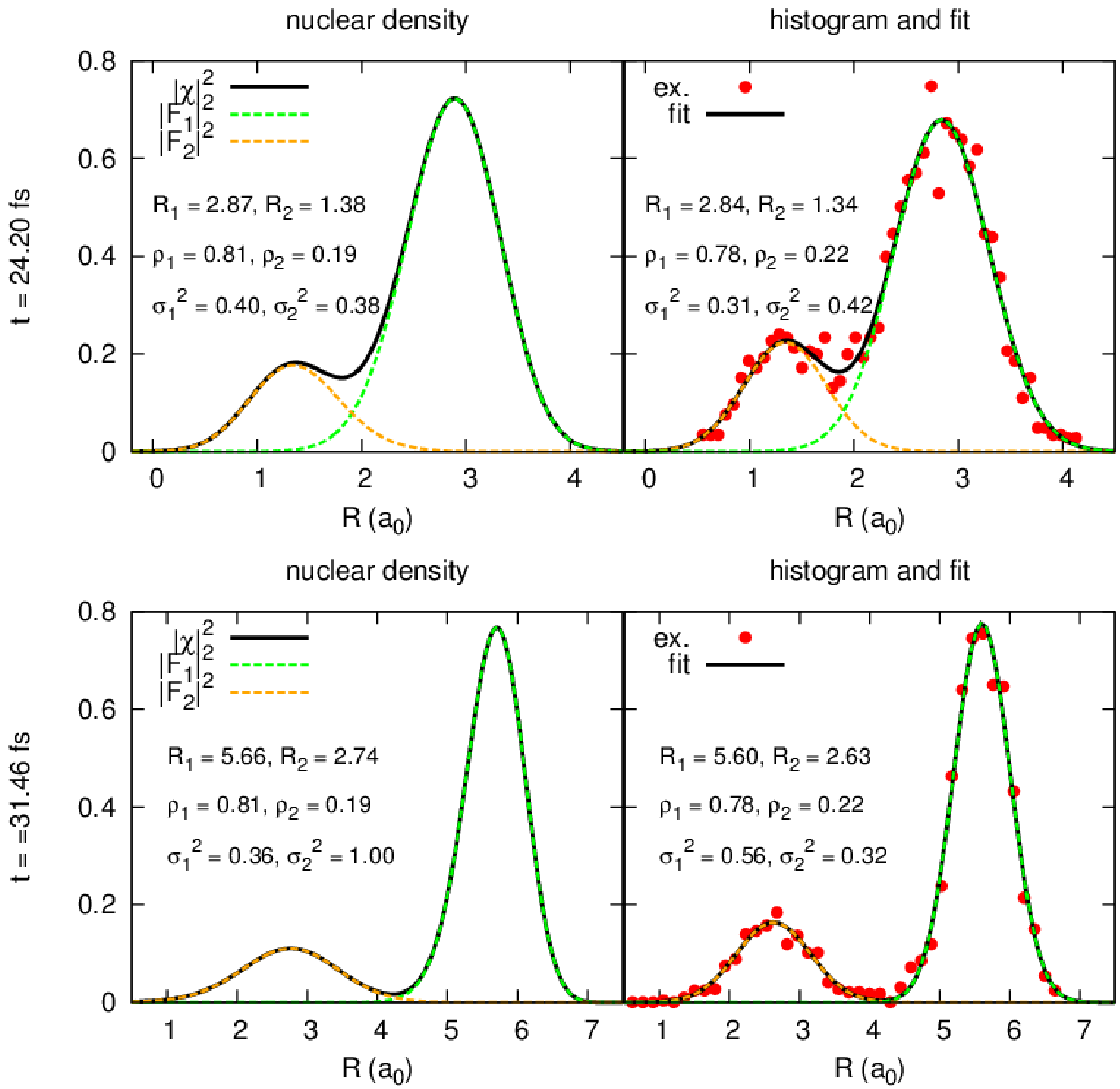
$$\left(\sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu\left(\underline{\underline{R}}, t\right)\right)^2 + \hat{W}_{nn}\left(\underline{\underline{R}}\right) + \hat{V}_n^{ext}\left(\underline{\underline{R}}, t\right) + \in\left(\underline{\underline{R}}, t\right)\right)\chi\left(\underline{\underline{R}},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

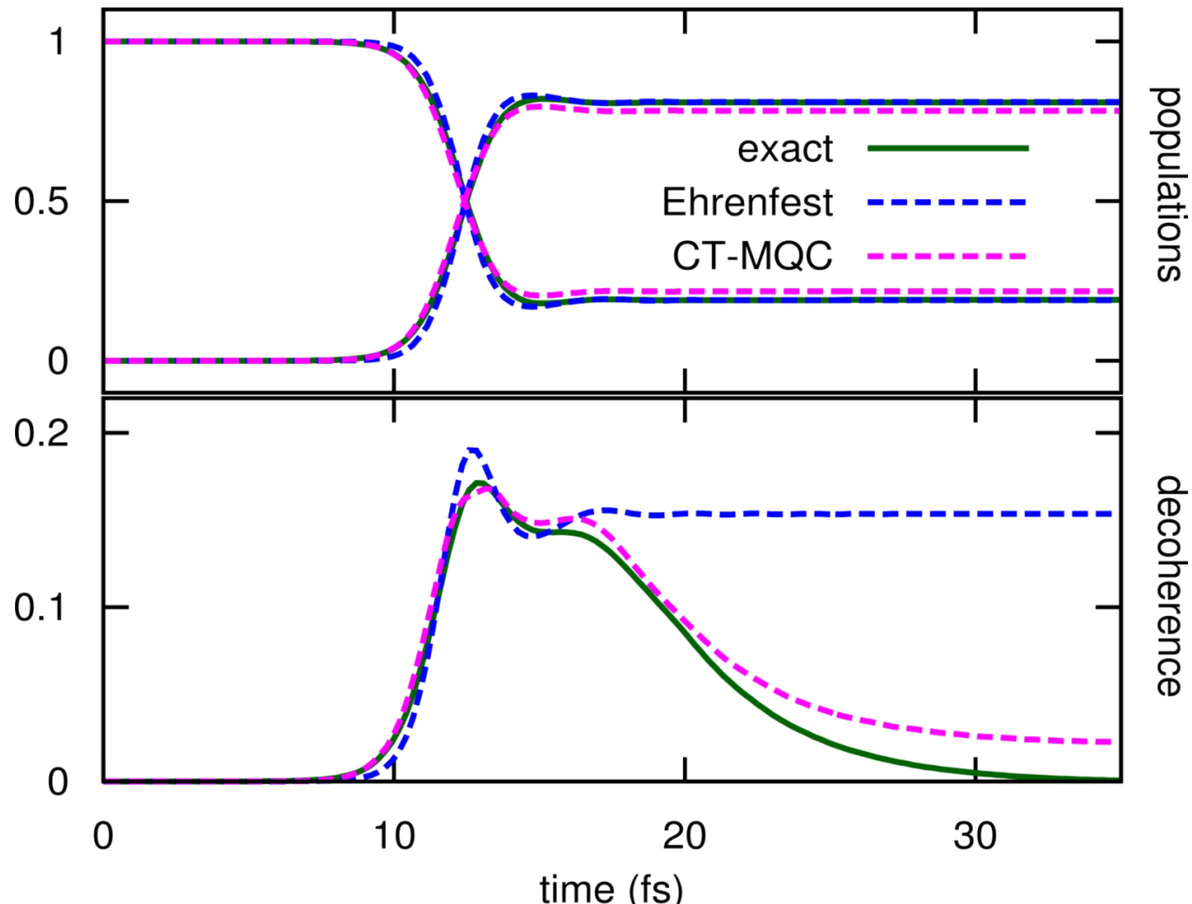
Shin-Metiu model

populations of the BO states as functions of time



Propagation of classical nuclei on exact TDPES





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

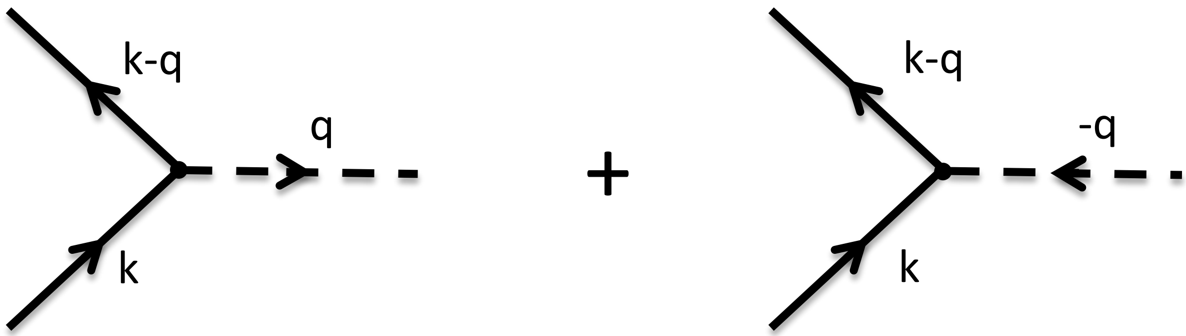
Algorithm implemented in:

CPMD

The "right" electron-phonon interaction

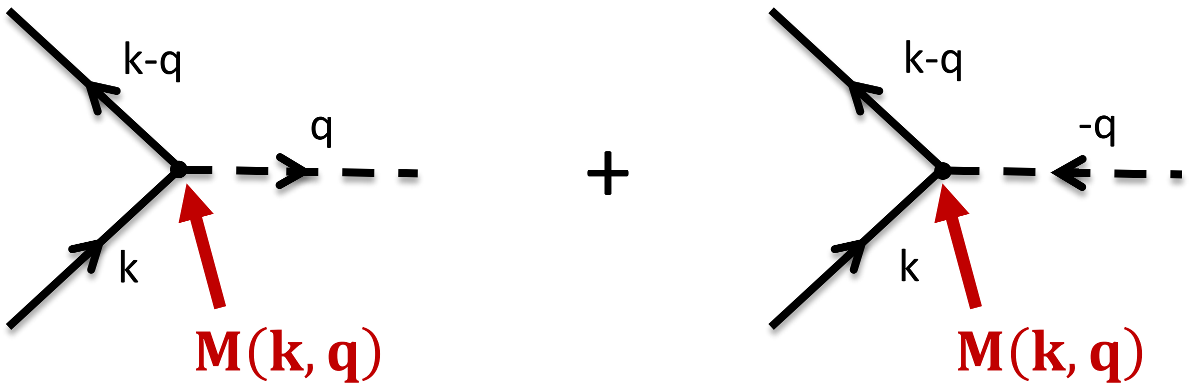
electron-phonon interaction

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



<u>electron-phonon interaction</u>

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



In a genuine ab-initio description, what is the exact coupling $\mathbf{M(k,q)}$?

LITERATURE on $\mathbf{M}(\mathbf{k},\mathbf{q})$:

- **What everybody uses:** $M_{\mathbf{q}\lambda}\left(n\mathbf{p}, n'\mathbf{p}'\right) = \delta_{g,\mathbf{p}'-\mathbf{p}+\mathbf{q}} \frac{\xi_{\mathbf{q}\lambda} \cdot \left\langle n\,\mathbf{p} \middle| \nabla_R V_{KS} \middle| n'\mathbf{p}' \right\rangle}{\left(2MN_c\omega_{\mathbf{q}\lambda}/\hbar\right)^{1/2}}$

- **Robert van Leeuwen, PRB 69, 115110 (2004):**

$$M_{\mathbf{q}\lambda}\left(\mathbf{r},\omega\right) = \left(2MN_c\omega_{\mathbf{q}\lambda}/\hbar\right)^{-1/2} \sum_{\alpha} \int d\mathbf{r}_1 \varepsilon_e^{-1}\left(\mathbf{r},\mathbf{r}_1;\omega\right) \xi_{\mathbf{q},\lambda} \cdot \nabla \frac{Z}{\left|\mathbf{r}_1 - \mathbf{R}_{0,\alpha}\right|} e^{i\mathbf{r}\cdot\mathbf{R}_{0,\alpha}}$$

Many textbooks neglect ϵ^{-1} completely (no screening).

- **Higher-order terms (Marini, Ponce, Gonze, PRB 91, 224310 (2015) (using DFPT):**

$$\hat{H}^{(2)}_{e-ph}\left(\mathbf{R}\right) = \sum_{\mathbf{k},\mathbf{q}\lambda,\mathbf{q}'\lambda'} \left[\theta_{\mathbf{q}\lambda,\mathbf{q}'\lambda'}(k)\hat{c}^{\dagger}_{k}\hat{c}_{\mathbf{k}-\mathbf{q}-\mathbf{q}'}\right]\left(\hat{b}^{\dagger}_{-\mathbf{q}\lambda} + \hat{b}_{\mathbf{q}\lambda}\right)\left(\hat{b}^{\dagger}_{-\mathbf{q}'\lambda'} + \hat{b}_{\mathbf{q}'\lambda'}\right)$$

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

Eq. ❶

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

Eq. ❷

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

Exact phonons

Expand $\epsilon(R)$ around equilibrium positions (to second order):

Eq. ❷ ➡

$$\hat{H}_{ph} = \sum_{q\lambda} \hbar\omega_{q\lambda}\left(k\right)\left(\hat{b}_{q\lambda}^{\dagger}\hat{b}_{q\lambda} + \frac{1}{2}\right)$$

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

Eq. ❶

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

Exact el-ph interaction

Eq. ❷

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

Exact phonons

Expand ϵ(R) around equilibrium positions (to second order):

Eq. ❷ ⇨

$$\hat{H}_{ph} = \sum_{q\lambda} \hbar\omega_{q\lambda}(k)\left(\hat{b}_{q\lambda}^{\dagger}\hat{b}_{q\lambda} + \frac{1}{2}\right)$$

$$M_{\mathbf{q}\lambda}\left(n\mathbf{p},n'\mathbf{p}'\right)=\delta_{g,\mathbf{p}'-\mathbf{p}+\mathbf{q}}\frac{\xi_{\mathbf{q}\lambda}\cdot\left\langle n\mathbf{p}\middle|\nabla_{u_\alpha}\hat{V}_{KS}\middle|n'\mathbf{p}'\right\rangle}{\left(2MN_n\omega_{\mathbf{q}\lambda}/\hbar\right)^{1/2}}\times\left(1+3\left\langle n\mathbf{p},n'\mathbf{p}'\middle|f_{HXC}\middle|n\mathbf{p},n'\mathbf{p}'\right\rangle\right)$$

Traditional term

Summary on exact factorisation

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

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

- **Exact Berry phase vanishes**

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

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

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

- **mixed quantum classical algorithms**

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

- **correct electron-phonon interaction shows new terms (in addition to standard DFT expression)**

Thanks !

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