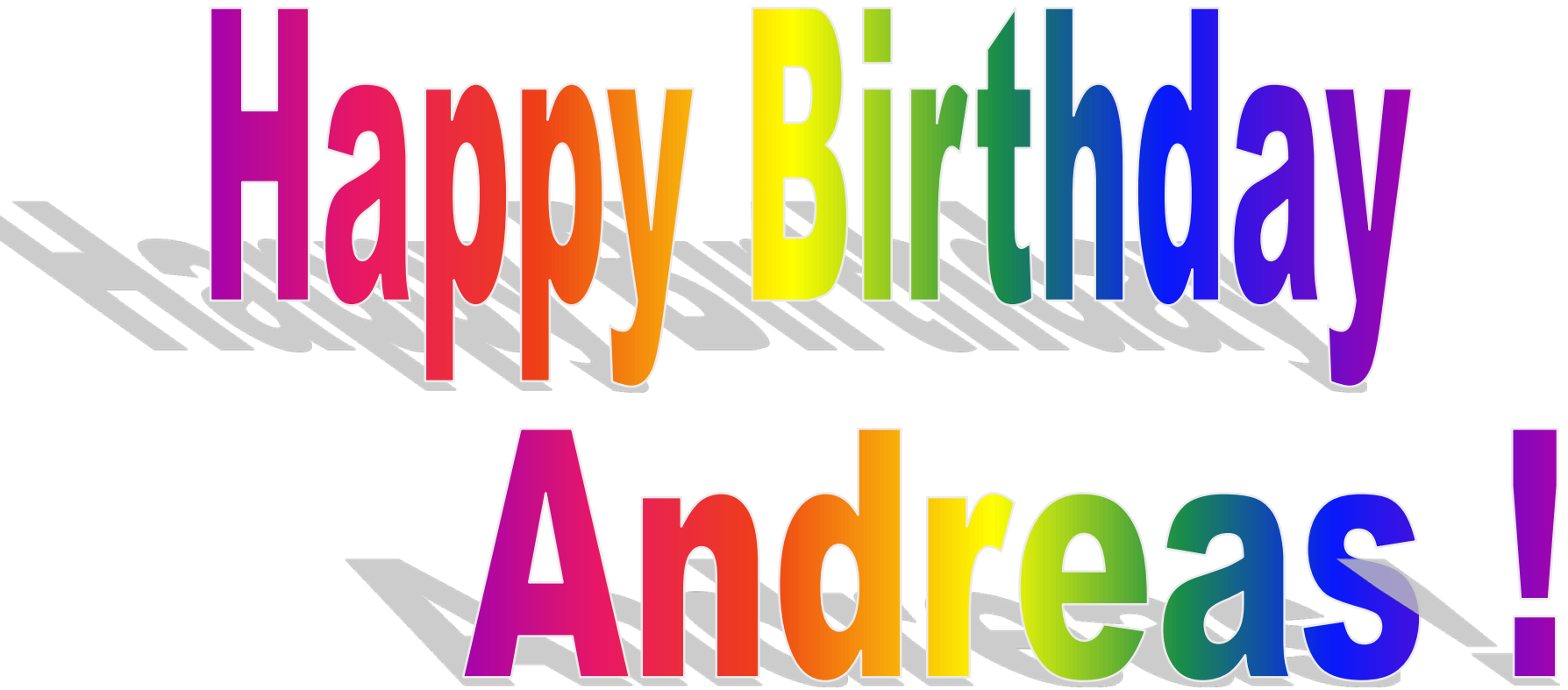
Conditional probability amplitudes for electrons and nuclei

E.K.U. Gross

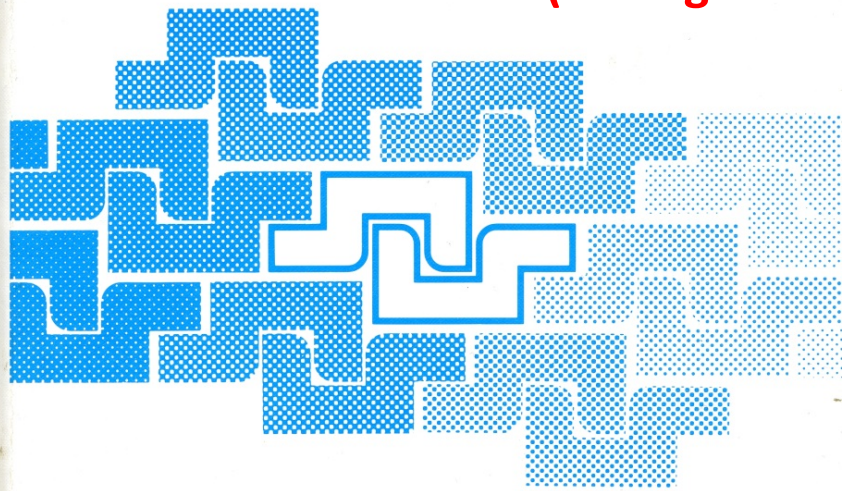
Max-Planck Institute of Microstructure Physics Halle (Saale)


Happy Birthday
Andreas !

Andreas Savin…….

Andreas Savin……. **A truly independent mind**

NATO School
(Portugal 1983)



Density Functional Methods in Physics

Edited by

Reiner M. Dreizler

and

João da Providencia

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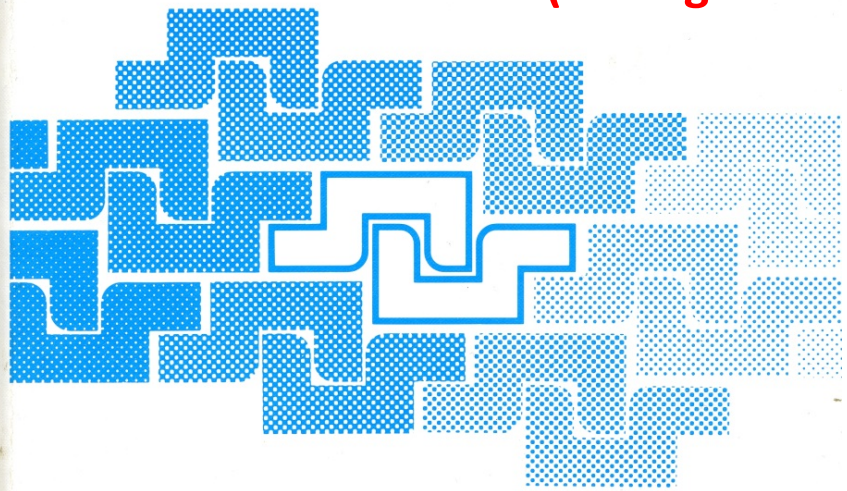
NATO School
(Portugal 1983)



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DENSITY FUNCTIONALS FOR CORRELATION ENERGIES OF ATOMS AND MOLECULES

Hermann Stoll and Andreas Savin

Institut für Theoretische Chemie
Universität Stuttgart
D-7000 Stuttgart 80, West Germany

I. INTRODUCTION

The correlation energy, E_c, is usually defined as the difference of the exact (non-relativistic) energy, E, and the Hartree-Fock (HF) energy, E_{HF}.[1] E_c is a very small part of E only (1.4% for the He atom, 0.3% for Ne, 0.1% for Ar), but it is non-negligible in absolute value: for valence-shell removal, ΔE_c is 1.1 eV for He, 9.5 eV for Ne, and 9.3 eV for Ar. Inclusion of E_c is important in cases where the number of (strongly interacting) electron pairs is changed, for dissociation energies (D_e), ionization potentials and excitation energies, e.g.. Correlation is responsible for 23% of D_e in the case of H_2, and for 84% of D_e in the case of Li_2; Na_2 and K_2 are unbound at the HF level.

There is a number of methods for calculating E_c, among which are configuration interaction (CI), many-body perturbation theory (MBPT), and the density-functional (DF) method. Before concentrating on DF, a few remarks seem to be in order with regard to CI, the method which is most widely used in quantum chemistry nowadays.[2] In the CI wave-function, excited configurations are admixed to the HF wave-function, Φ_o, and the expansion coefficients are determined by energy minimization. The expansion is usually restricted to single and double substitutions (CI-SD). CI-SD is not size-consistent ($E_c \sim \sqrt{N}$ for a system of N non-interacting two-electron atoms), but unlinked-cluster effects can be introduced into CI-SD in a simple and efficient (although non-variational) way.[3] Already with few terms in the CI expansion, a substantial portion of the correlation contribution to dissociation energies can be obtained (70% for F_2, e.g., with two determinants, Φ_o and $\Phi(\sigma_g^2 \rightarrow \sigma_u^2)$, if orbitals are optimized[4]), but the convergence is extremely slow eventually;

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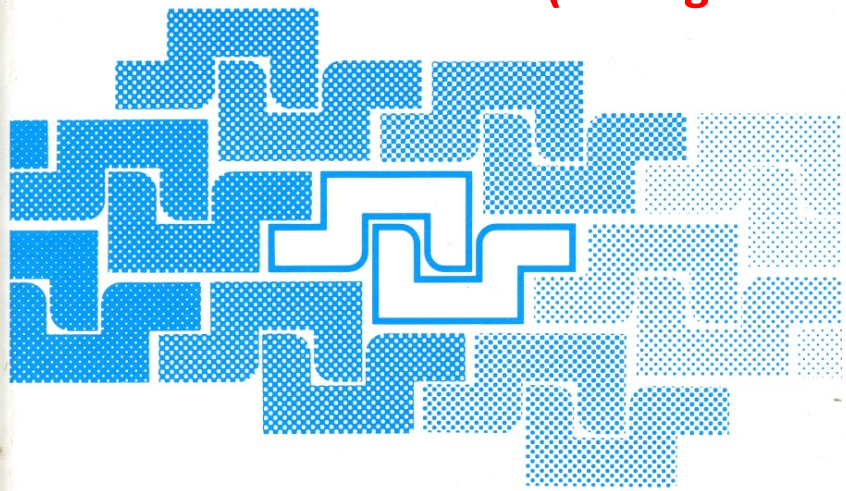

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Concept of range-separated hybrids outlined in this article

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Andreas Savin (Portugal 1983)

Hardy Gross (1983)

Conditional probability amplitudes for electrons and nuclei

Born-Oppenheimer approximation

solve

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

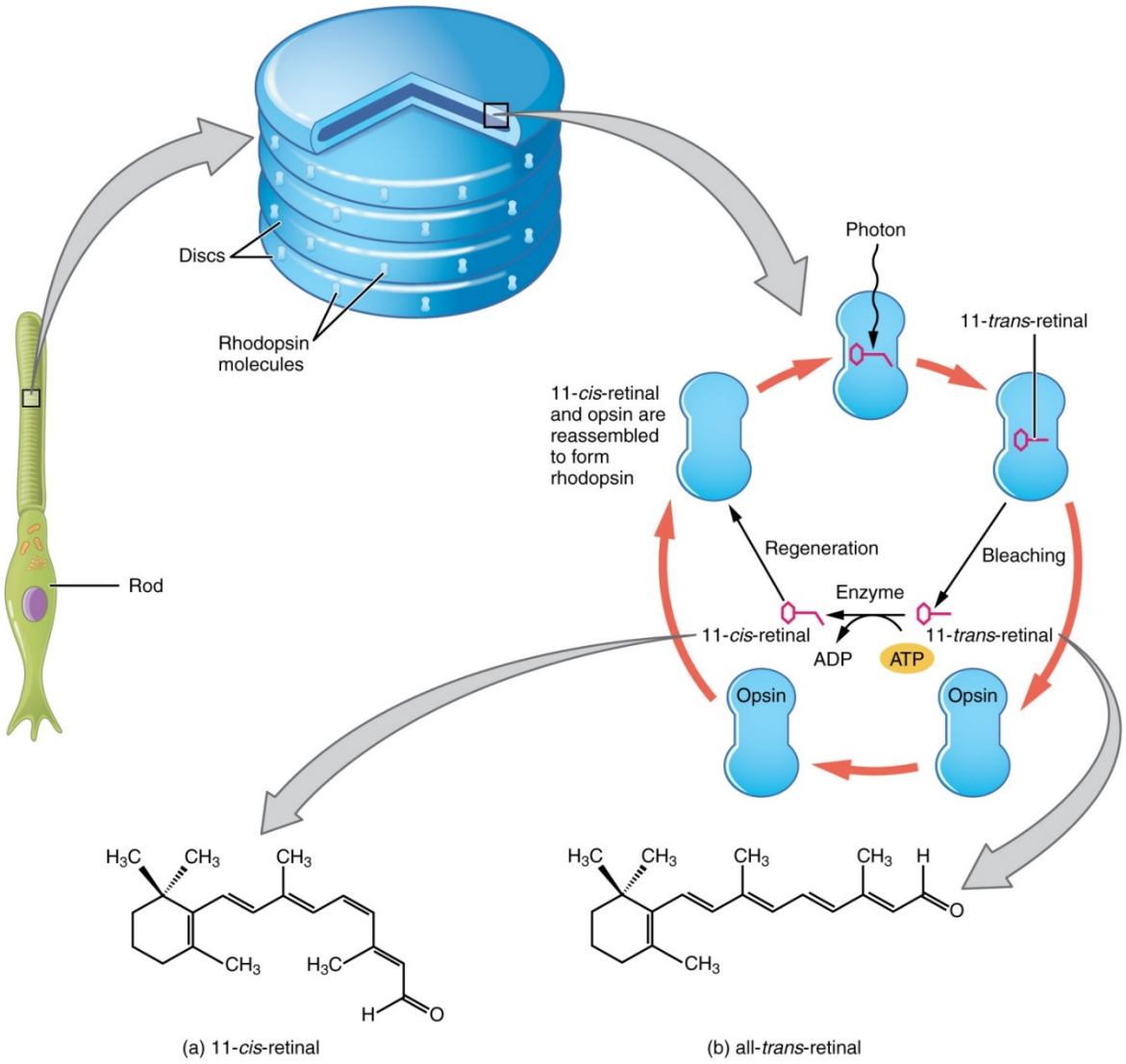
for fixed nuclear configuration $\underline{\underline{R}} \equiv \left(R_1 .... R_{N_n}\right)$ **and normalize:**

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

Physical meaning of $\left|\Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}})\right|^2$**:**

Conditional probability of finding the electrons at $\left(r_1 \cdots r_{N_e}\right) \equiv \underline{\underline{r}}$
if we know for sure that the nuclear configuration is $\underline{\underline{R}}$ **.**

Process of vision



Light-induced isomeriztion

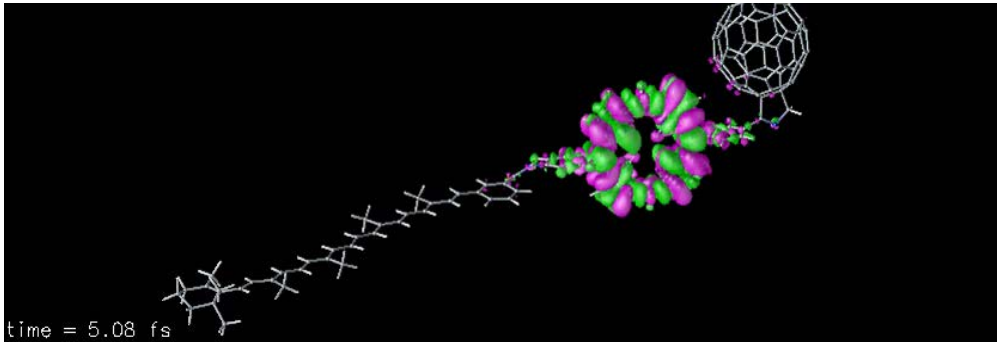
"Triad molecule": Candidate for photovoltaic applications

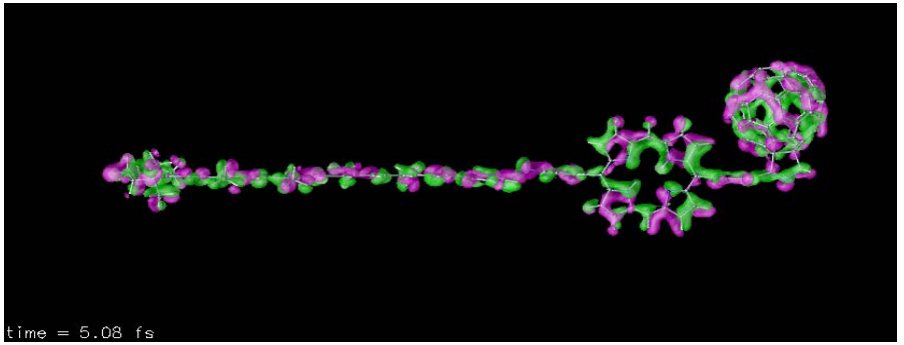
C.A. Rozzi et al, Nature Communications 4, 1602 (2013)

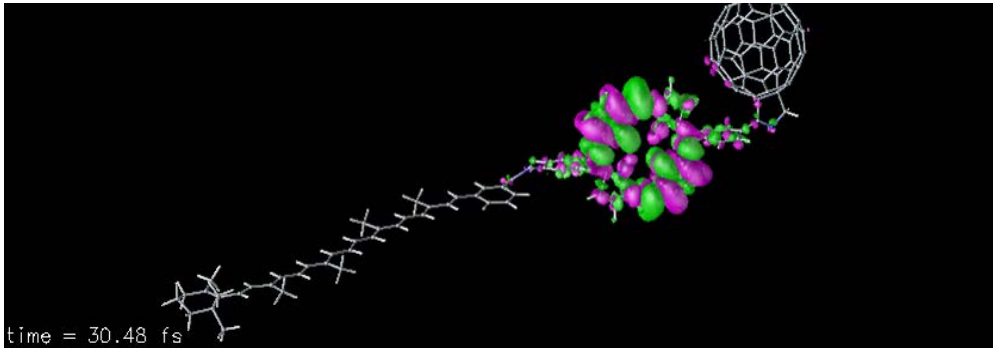
S.M. Falke et al, Science 344, 1001 (2014)

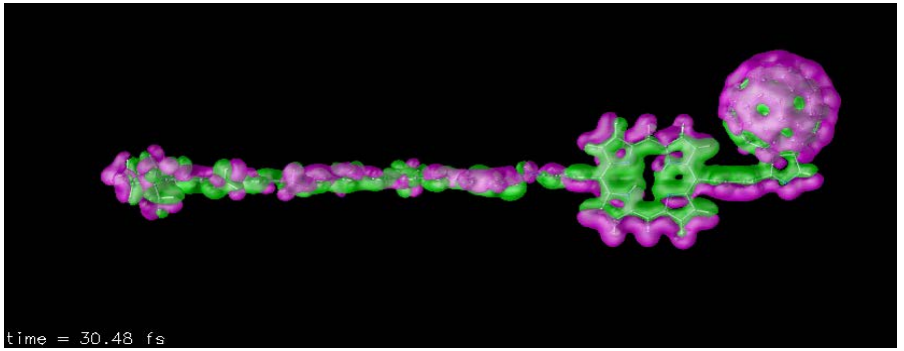
Without e-n coupling

With e-n coupling









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

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

with

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

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

Stationary Schrödinger equation

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

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

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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

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

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

Make adiabatic ansatz for the complete molecular wave function:

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

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

Nuclear equation

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

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

Berry connection

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

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

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

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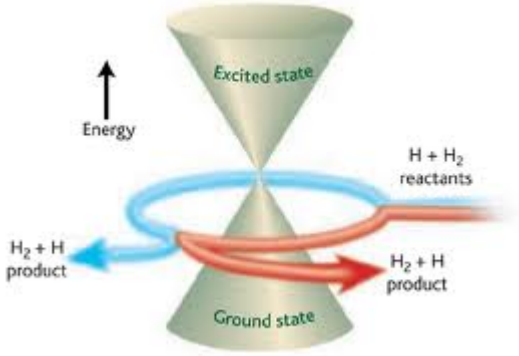

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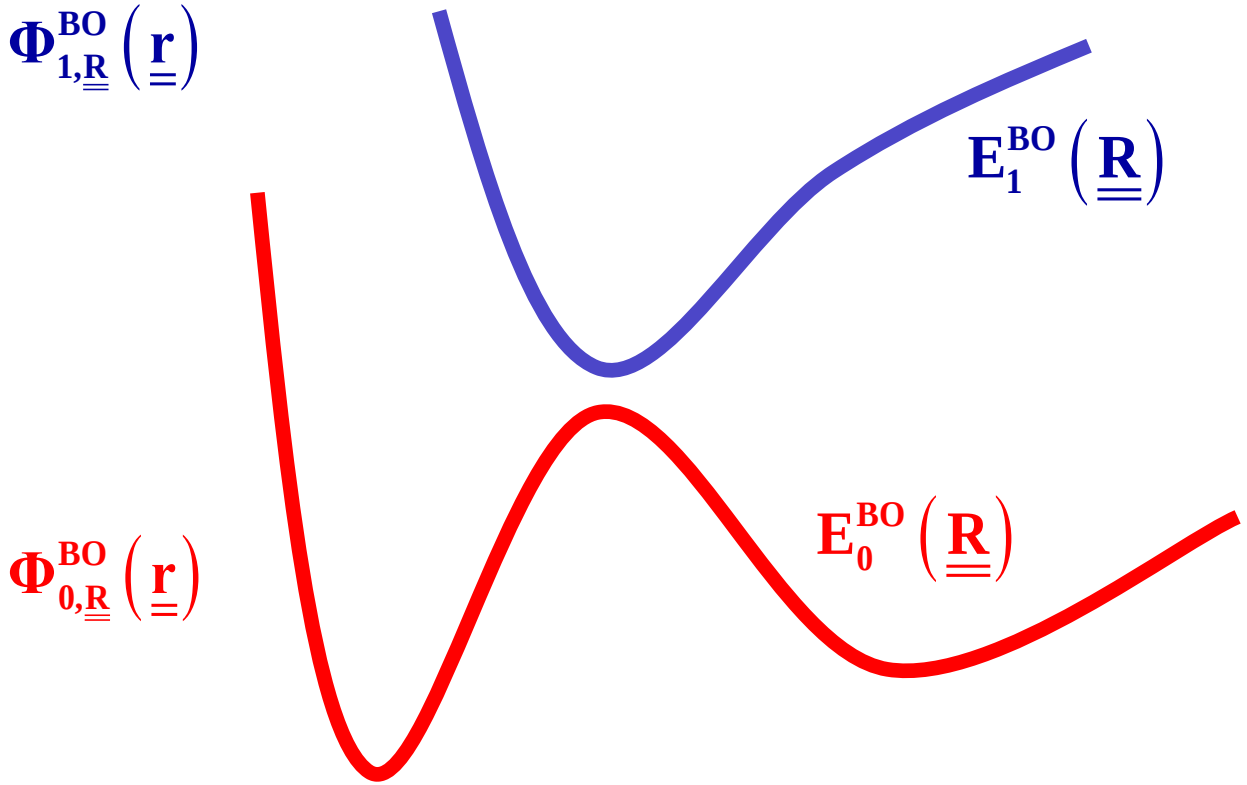
In this context, potential energy surfaces $\in^{BO}(\underline{\underline{R}})$ **and the vector potential** $\vec{A}^{BO}(\underline{\underline{R}})$ **follow from an APPROXIMATION (the BO approximation).**

Standard representation of the full TD wave function

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

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

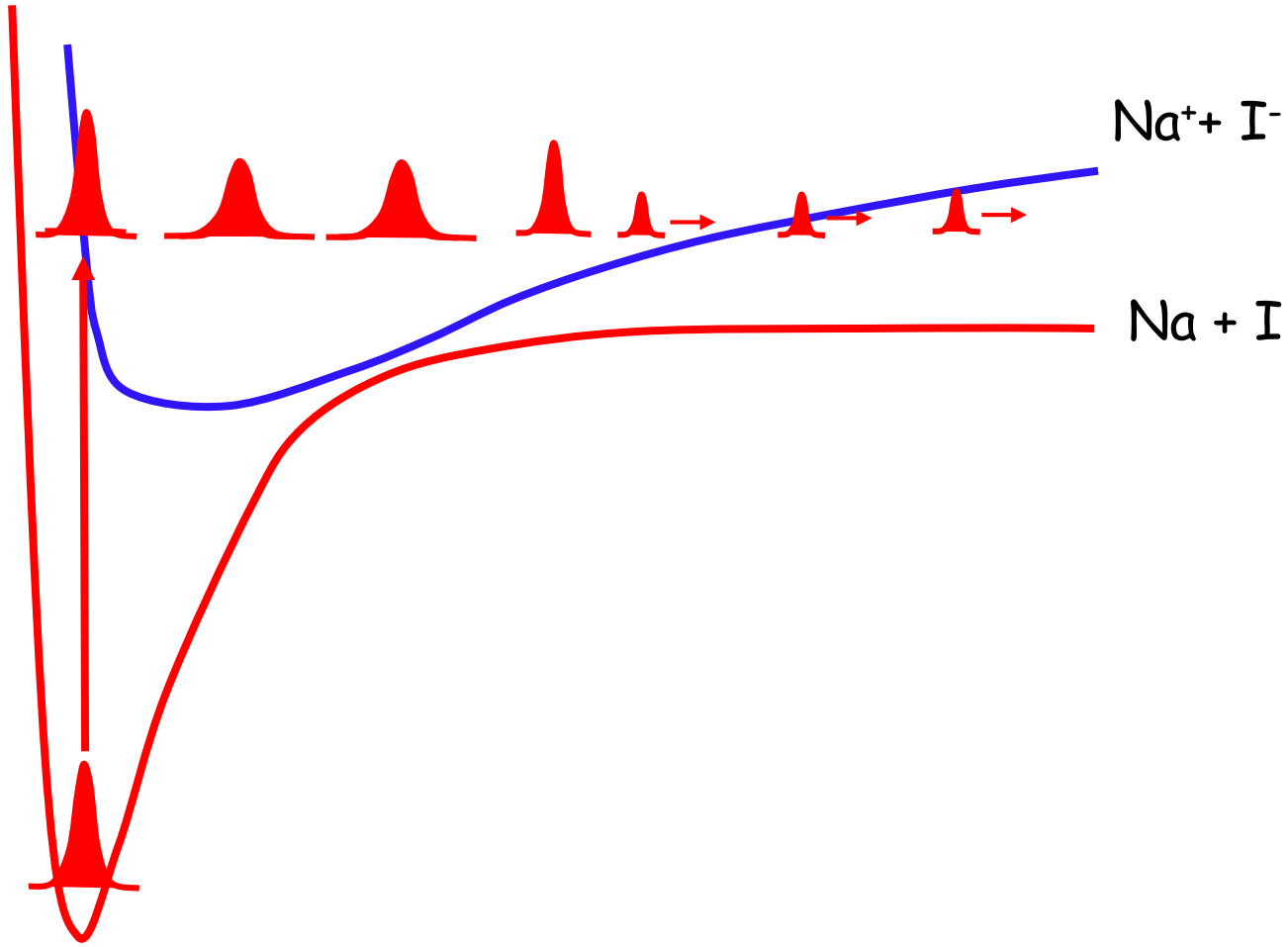
and insert expansion in the full Schrödinger equation → standard non-adiabatic coupling terms from T_n acting on $\Phi^{BO}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right)$.



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

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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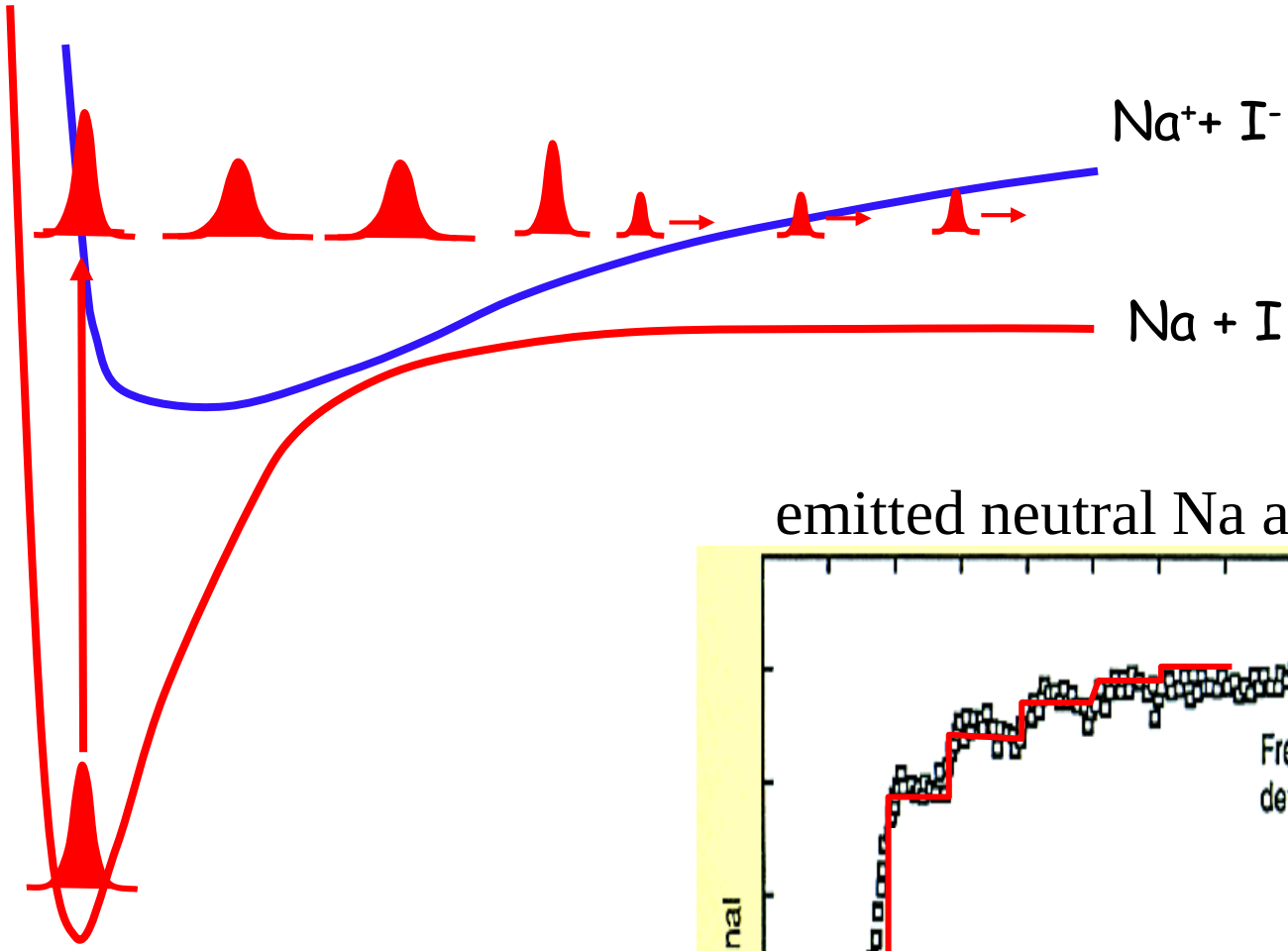
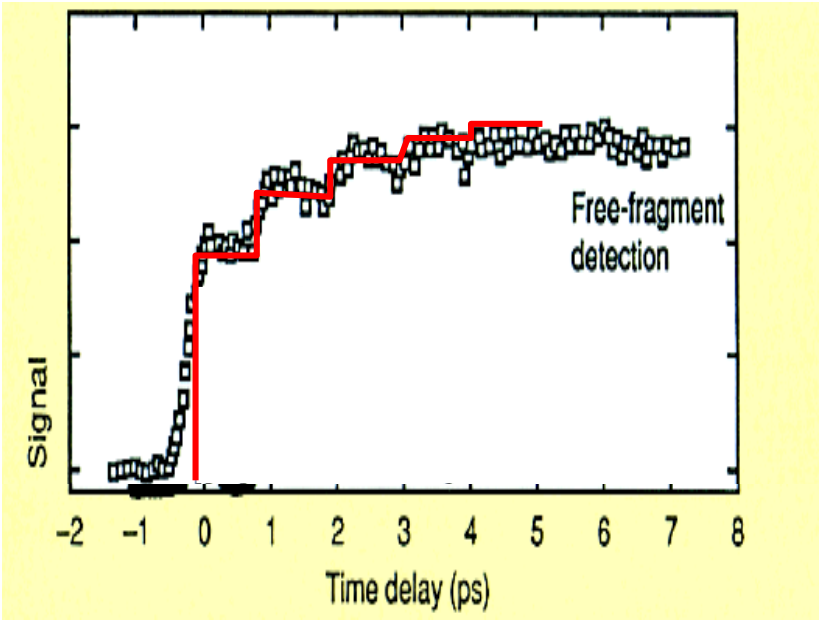
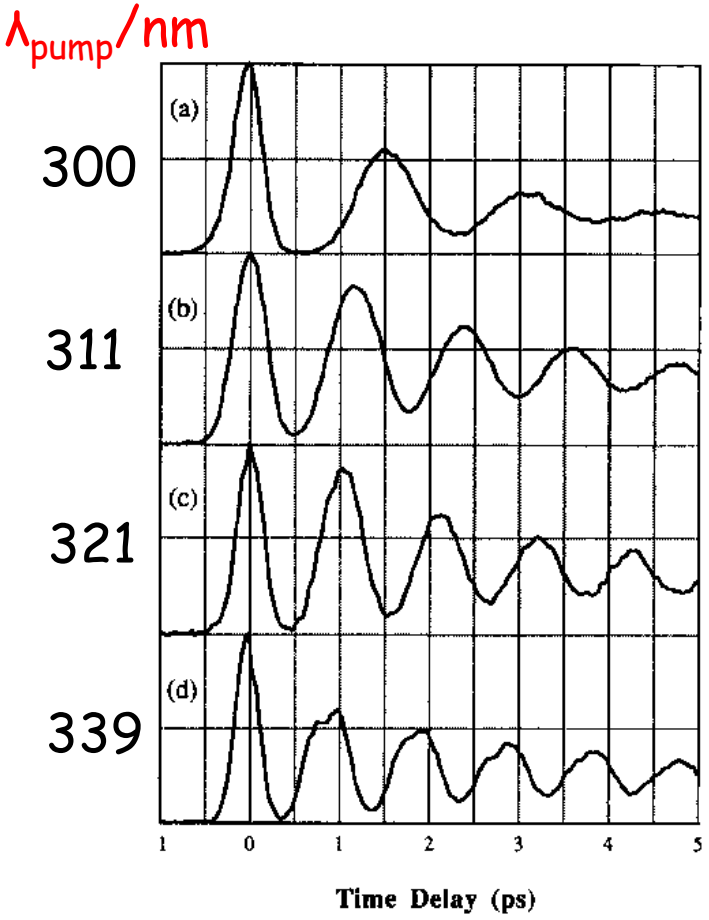
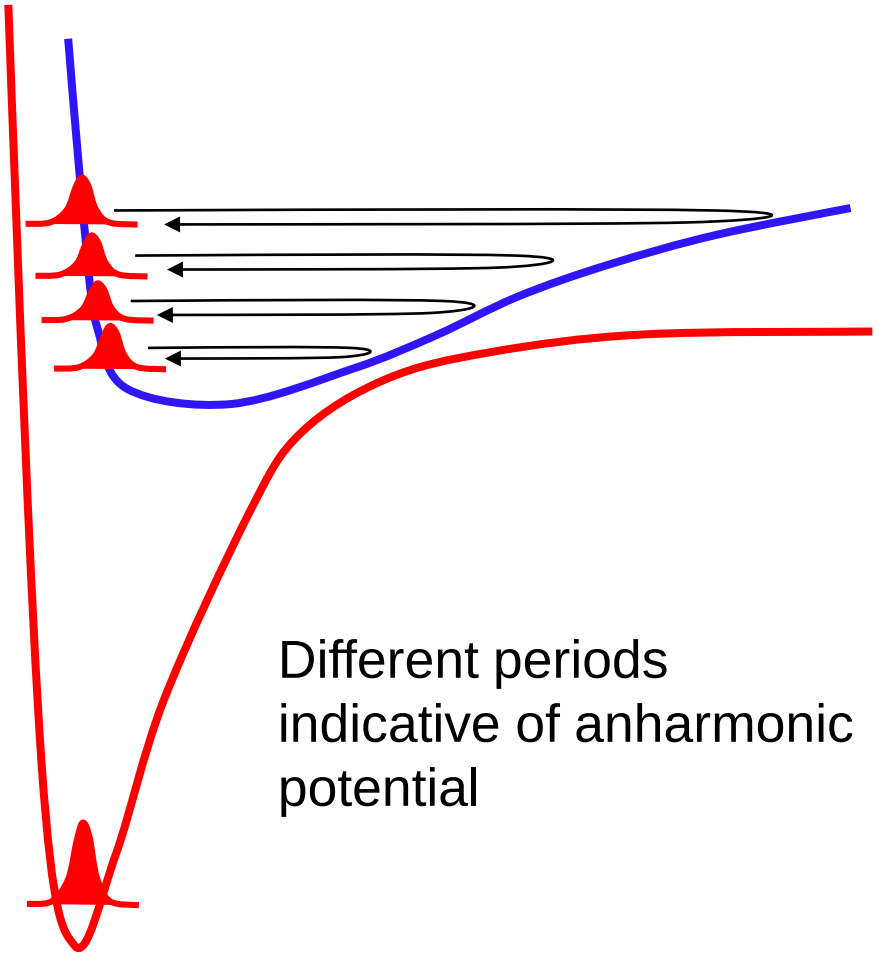


emitted neutral Na atoms



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.

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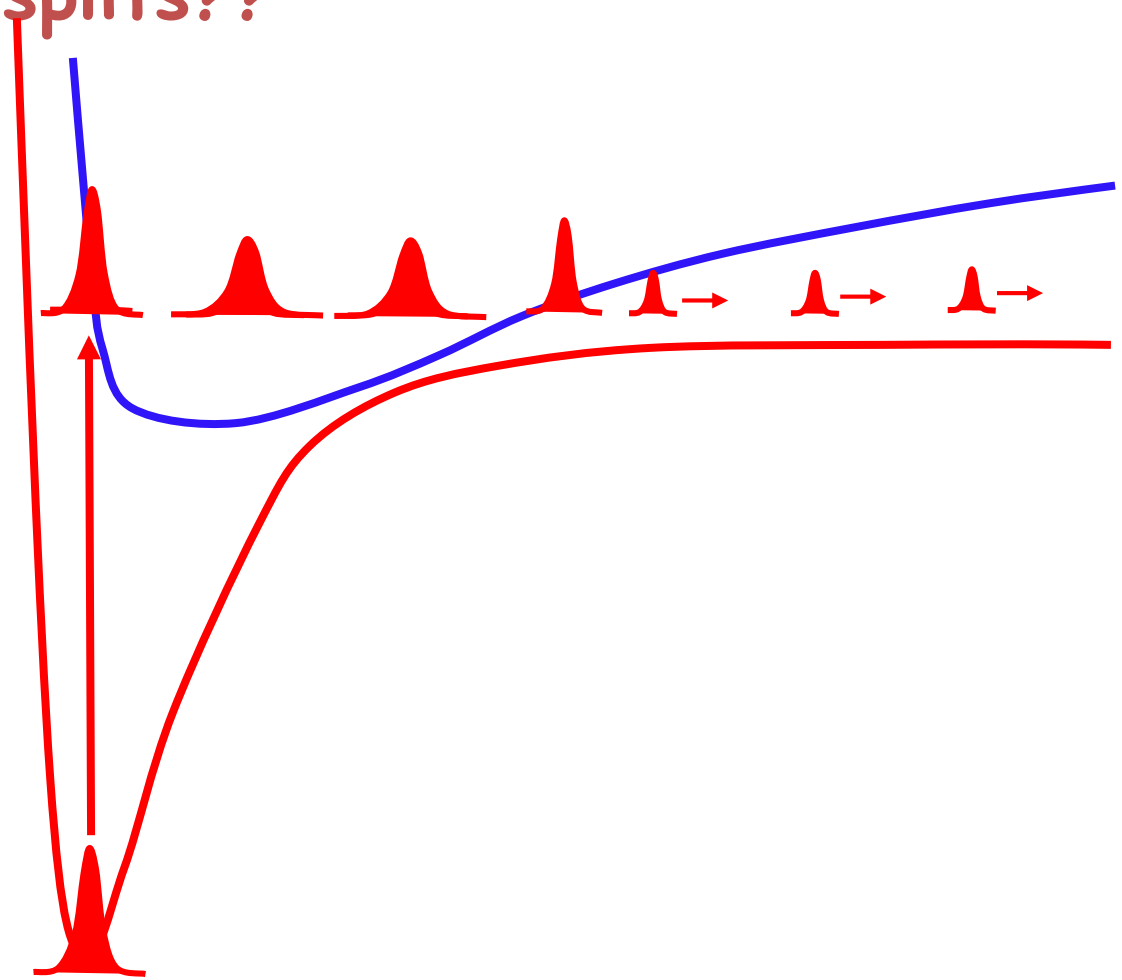

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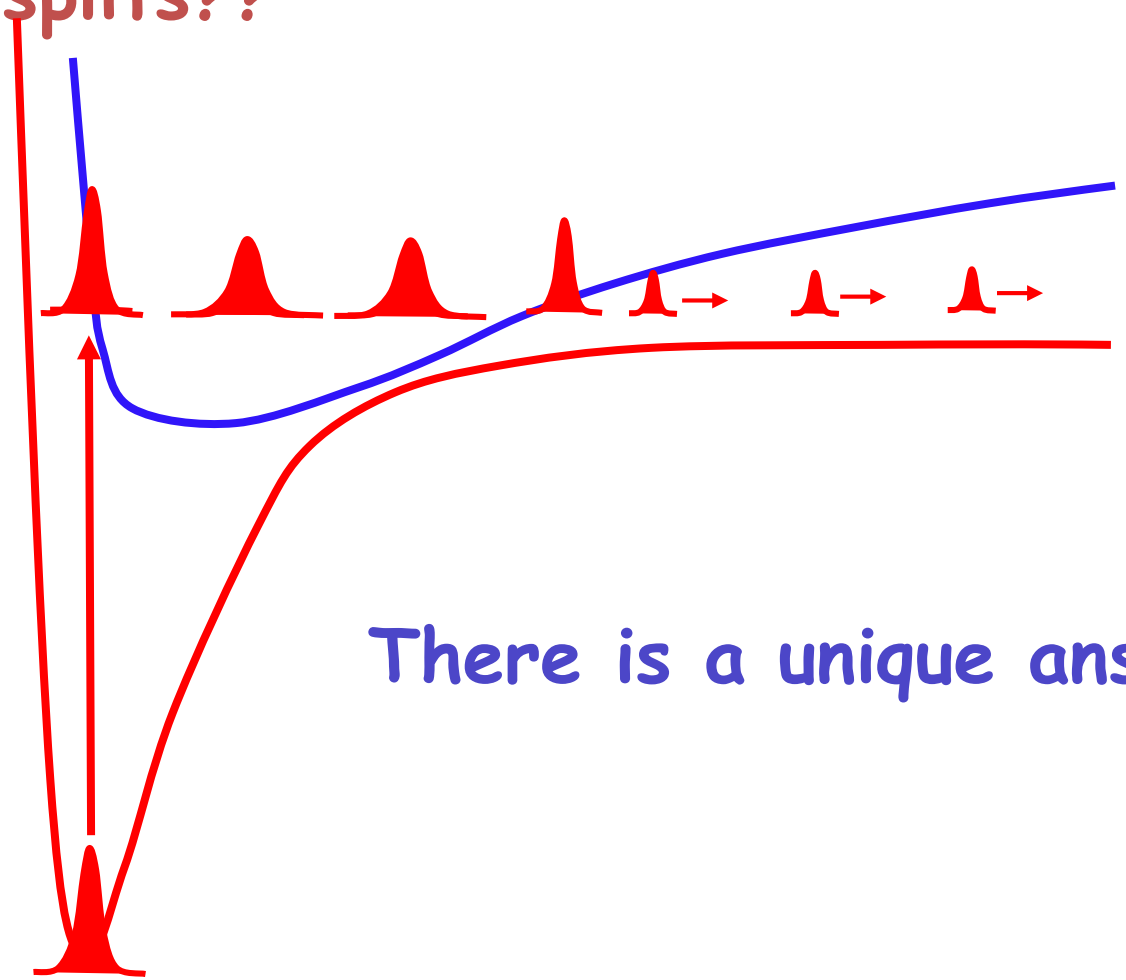


There is a unique answer!

Outline

- **Show that the factorisation**

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

  can be made exact

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

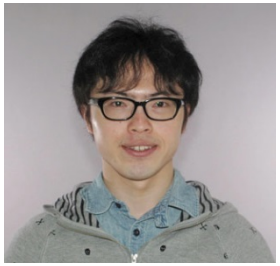
- **Concept of exact time-dependent PES**

- **Mixed quantum-classical treatment**

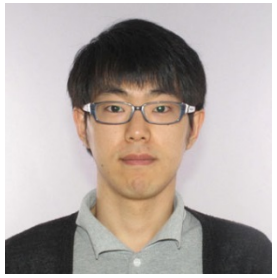
THANKS

Ali Abedi

Federica Agostini



Yasumitsu Suzuki



Seung Kyu Min

Neepa Maitra (Hunter College, CUNY)

Nikitas Gidopoulos
(Durham University, UK)

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

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

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

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

Proof of Theorem I:

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

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

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

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

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

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

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

Immediate consequences of Theorem I:

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

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

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

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

Eq. ❶

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

Eq. ❷

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

where

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

N.I. Gidopoulos, E.K.U. Gross,
Phil. Trans. R. Soc. 372, 20130059 (2014)

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

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

Exact PES

where

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

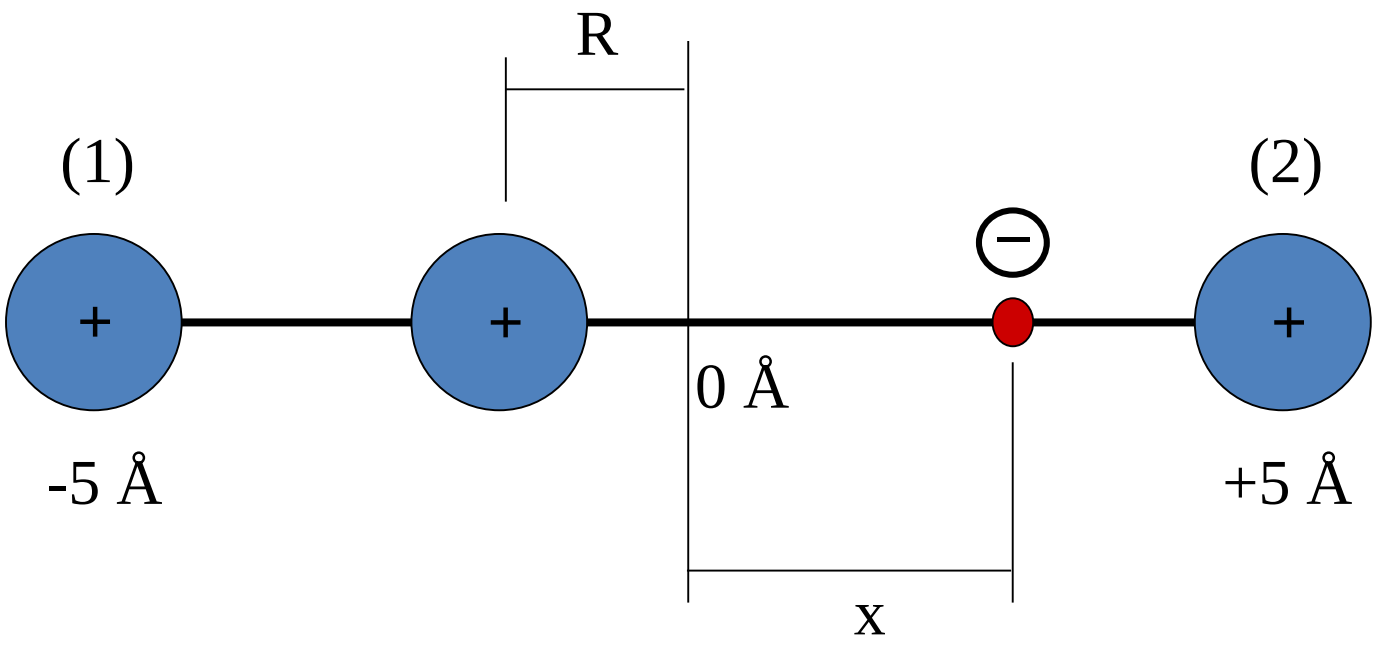
Exact Berry potential

N.I. Gidopoulos, E.K.U. Gross,
Phil. Trans. R. Soc. 372, 20130059 (2014)

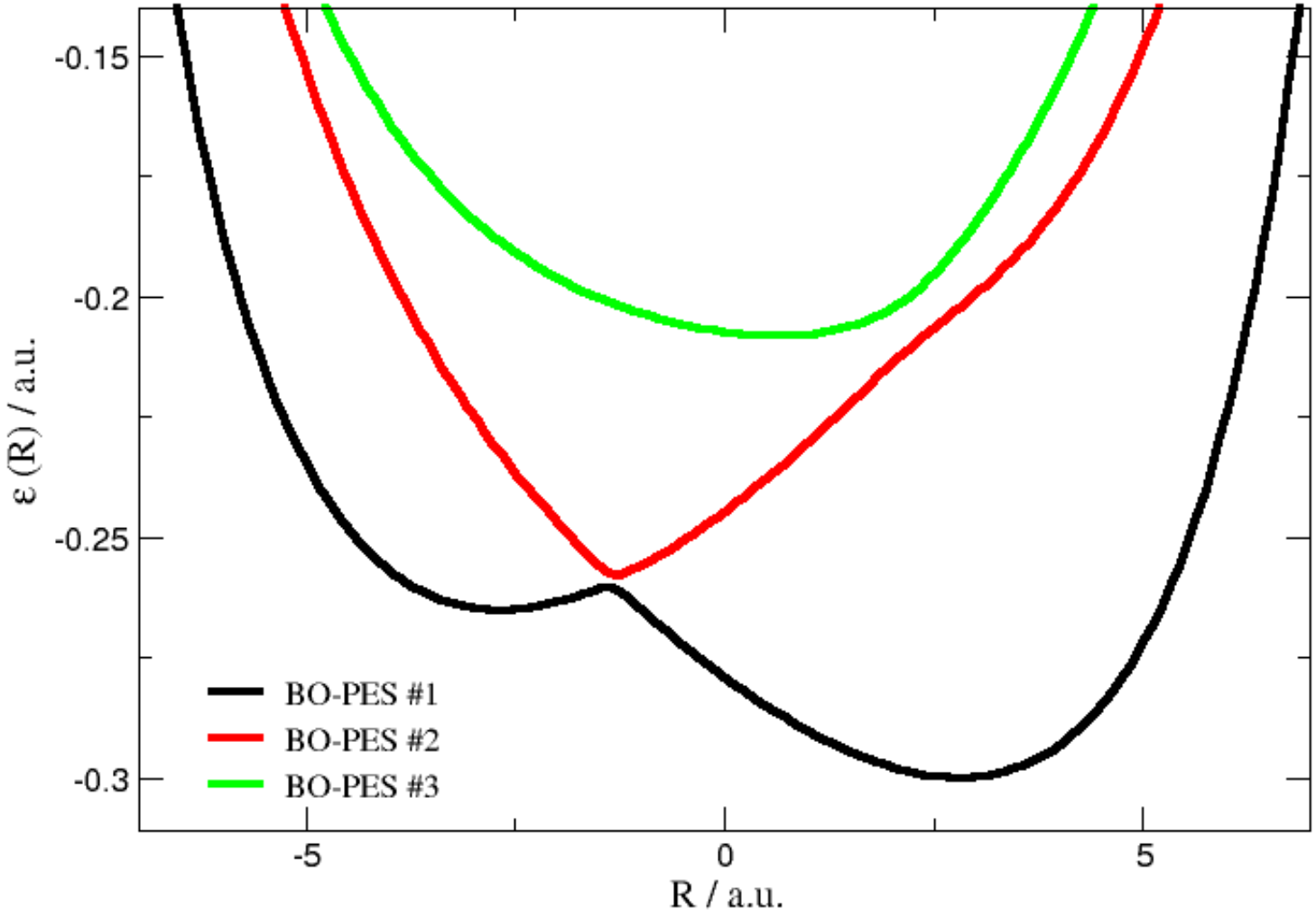
How do the exact PES look like?

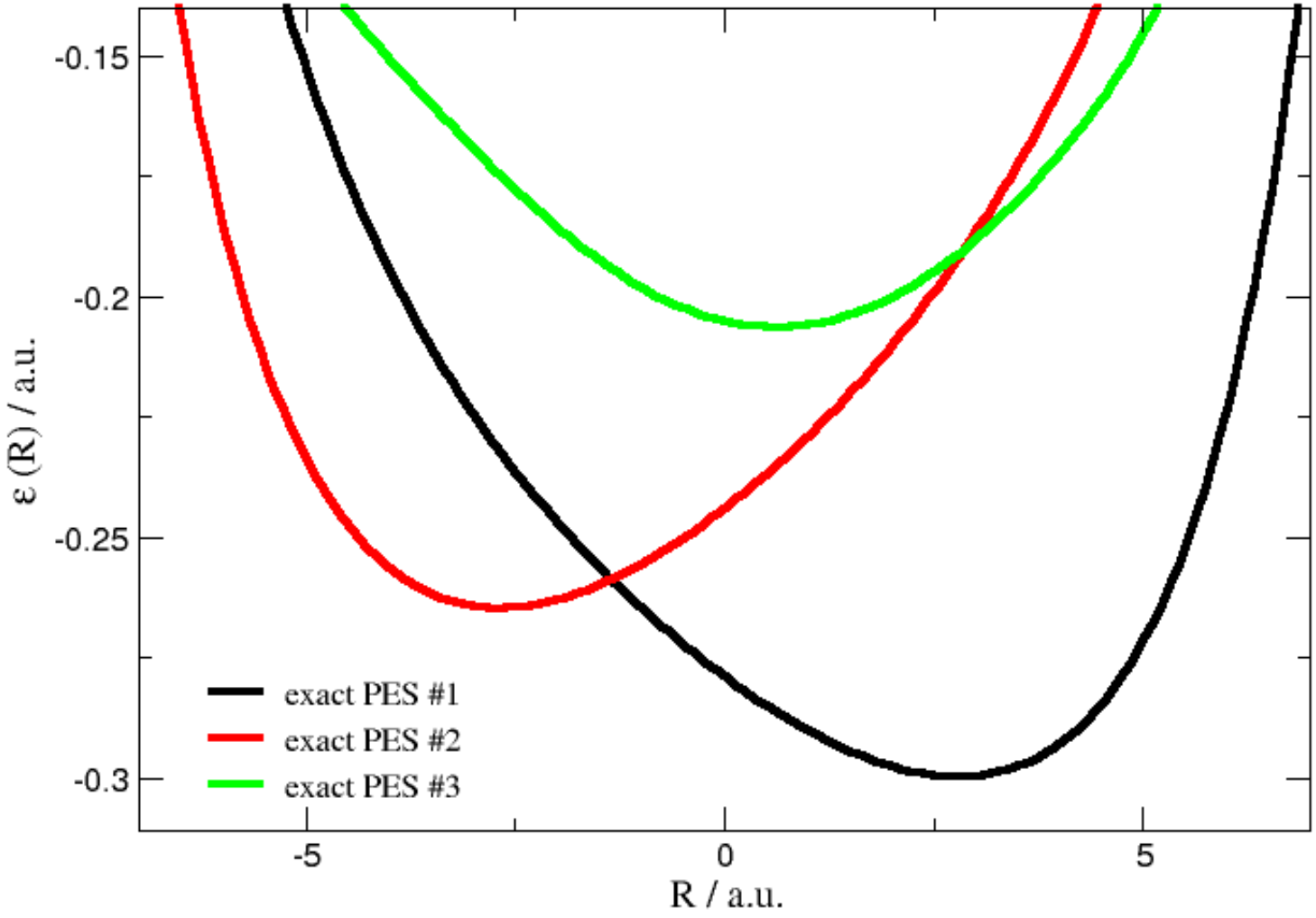
MODEL

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



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


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


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

Exact Berry connection

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

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

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

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

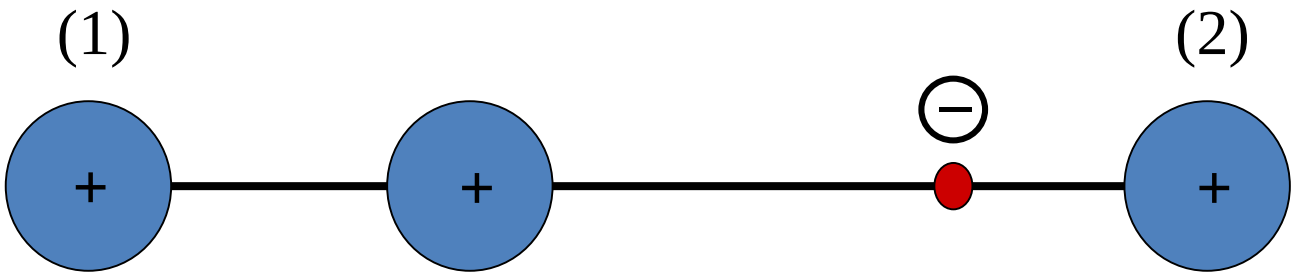
$$\boxed{A_\nu\left(\underline{\underline{R}}\right) = J_\nu\left(\underline{\underline{R}}\right) / \left|\chi\left(\underline{\underline{R}}\right)\right|^2 - \nabla_\nu \theta\left(\underline{\underline{R}}\right)}$$

with the exact nuclear current density J_ν

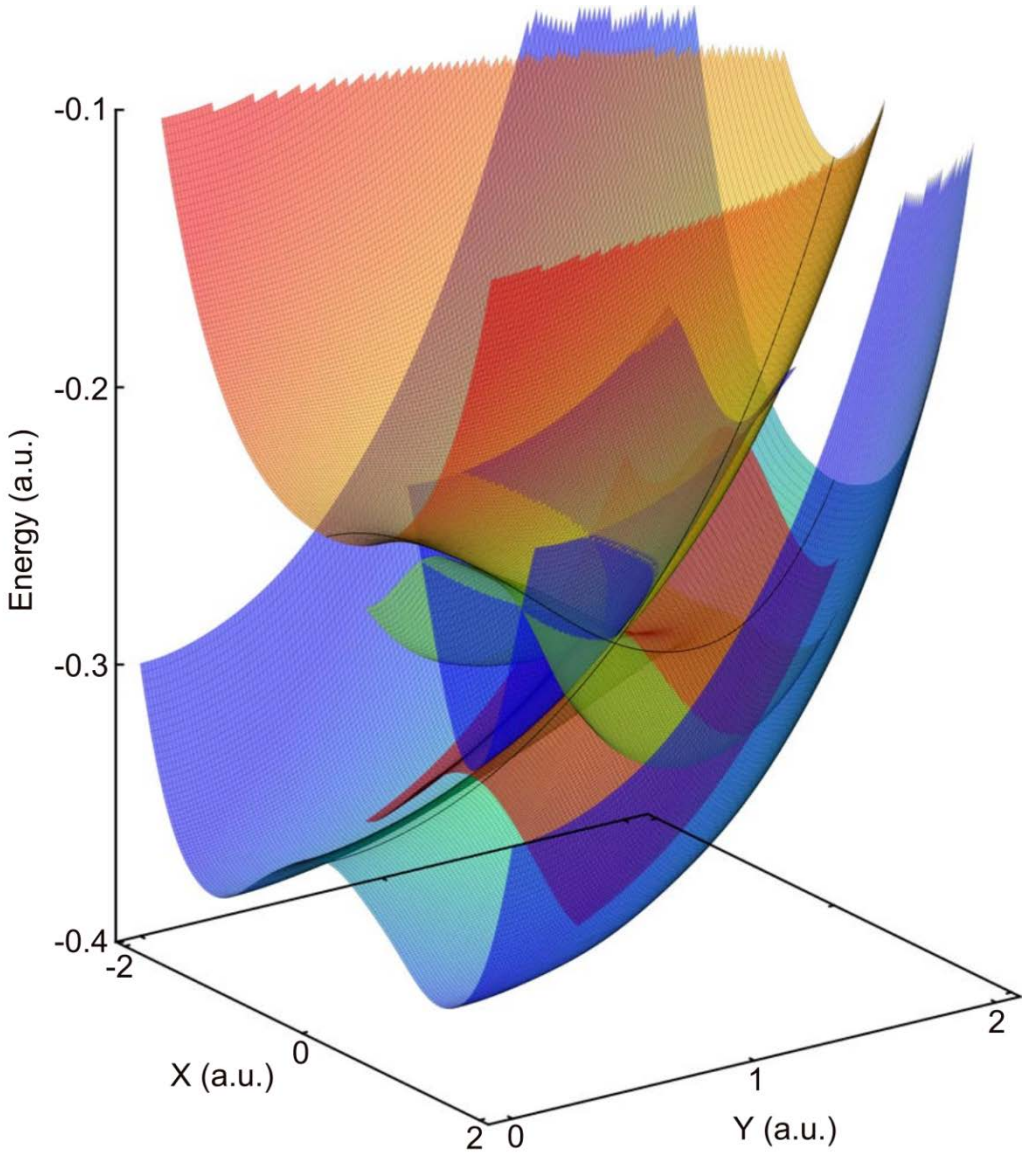
Question: Can the true vector potential be gauged away, i.e. is the true Berry phase zero?

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

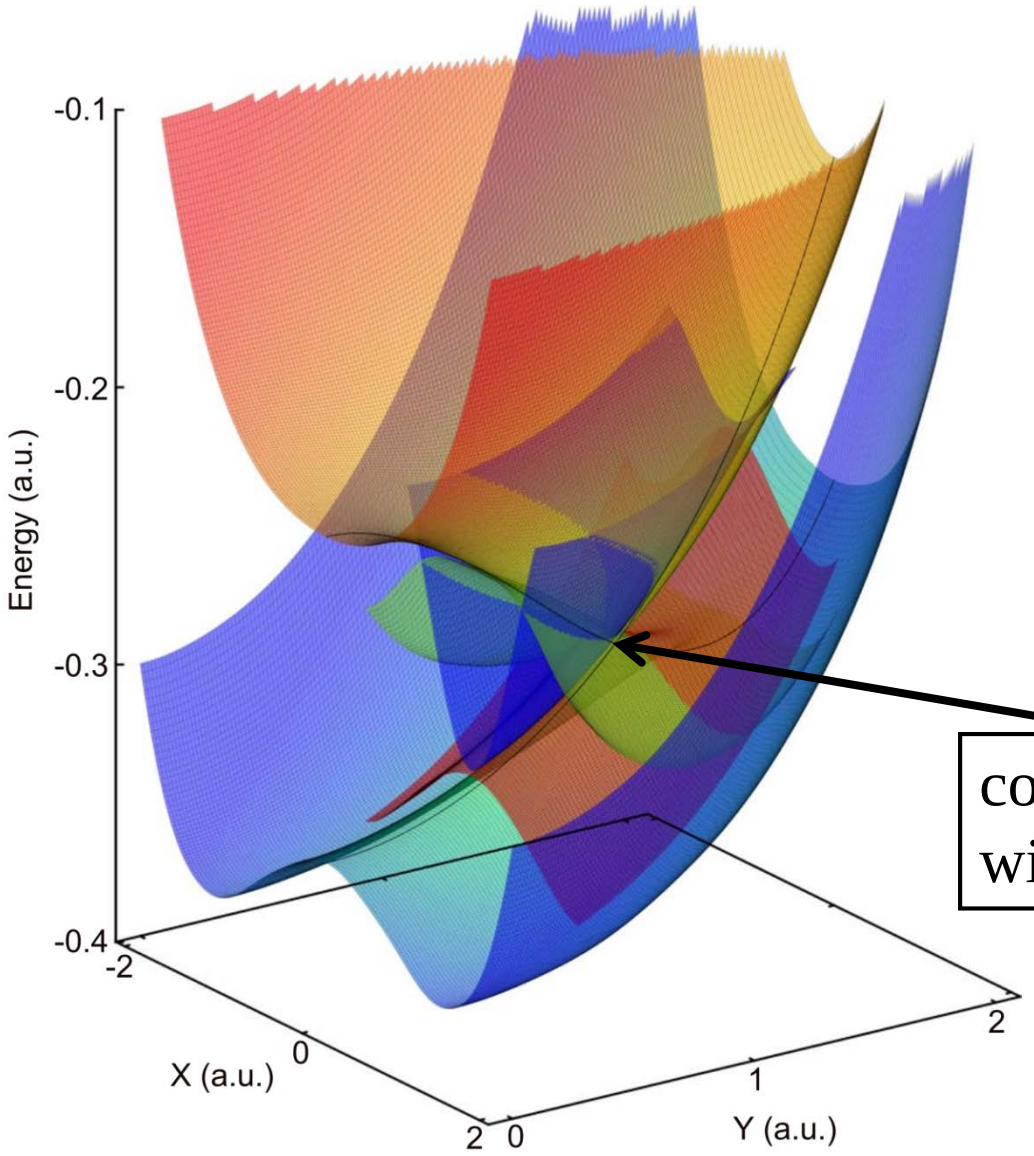
Look at Shin-Metiu model in 2D:



BO-PES of 2D Shin-Metiu model



BO-PES of 2D Shin-Metiu model



conical intersection with Berry phase

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

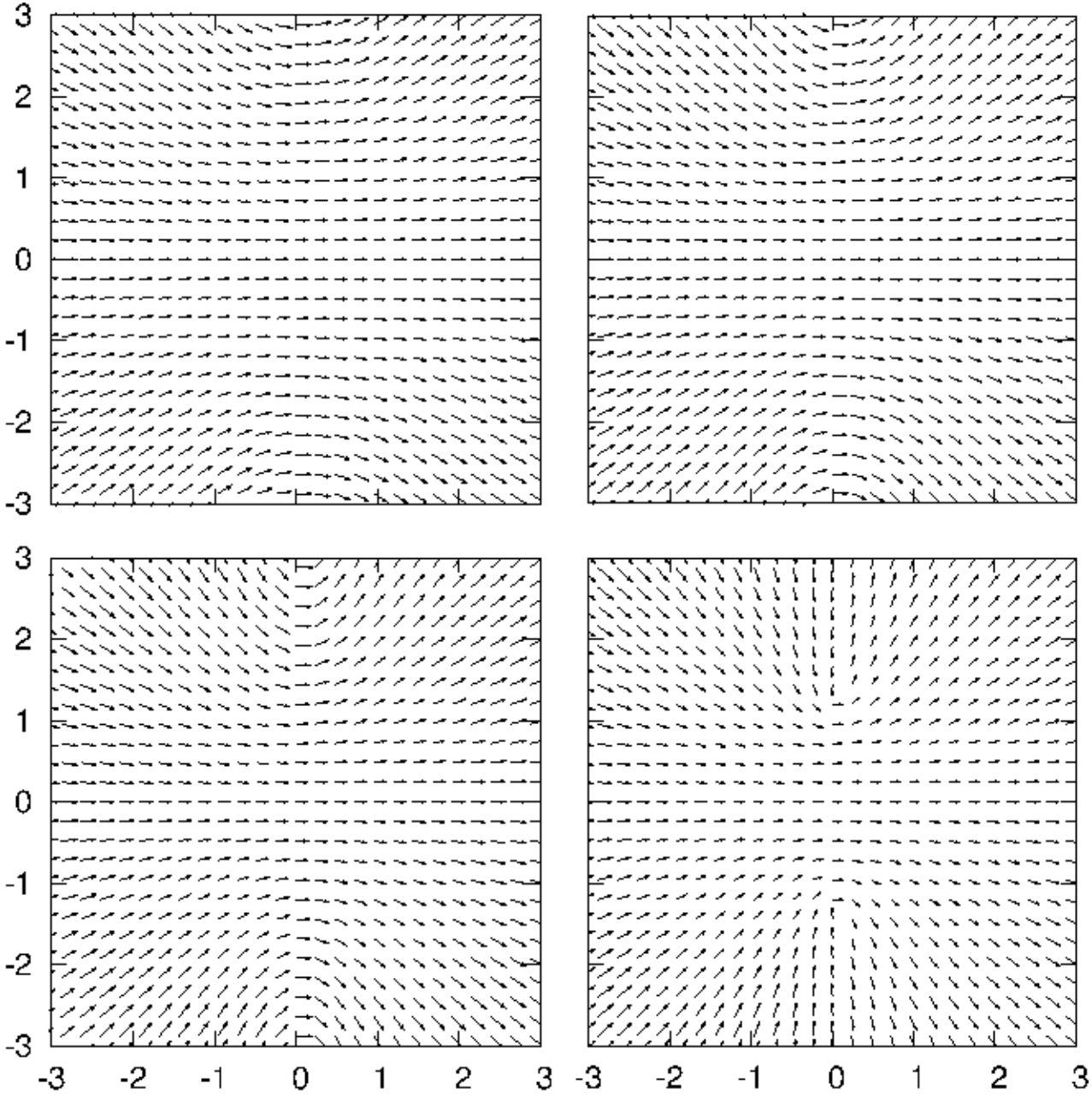
Does the exact electronic wave function show such non-analyticity as well (in 2D Shin-Metiu model)?

Look at $$D(\mathbf{R}) = \int \mathbf{r}\,\Phi_{\mathbf{R}}(\mathbf{r})\,d\mathbf{r}$$

as function of nuclear mass M.

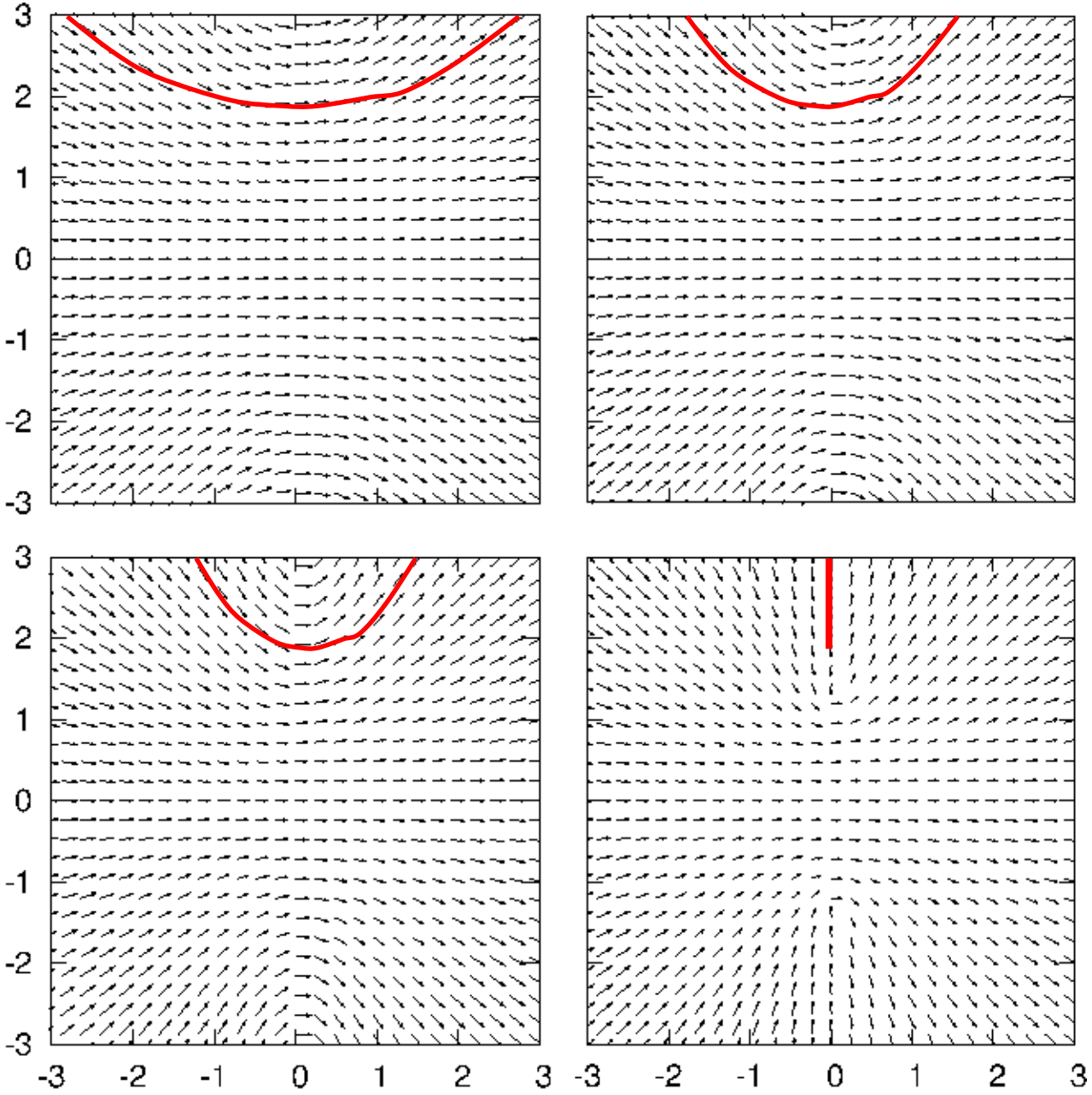
S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, PRL 113, 263004 (2014)

D(R)



$\mathbf{M = \infty}$

D(R)



$\mathbf{M = \infty}$

Open Question: Can one prove in general 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

Theorem T-I

The exact solution of

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

can be written in the form

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

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

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

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

Eq. ❷

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

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

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

Exact Berry potential

Exact TDPES

Eq. ❷

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

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

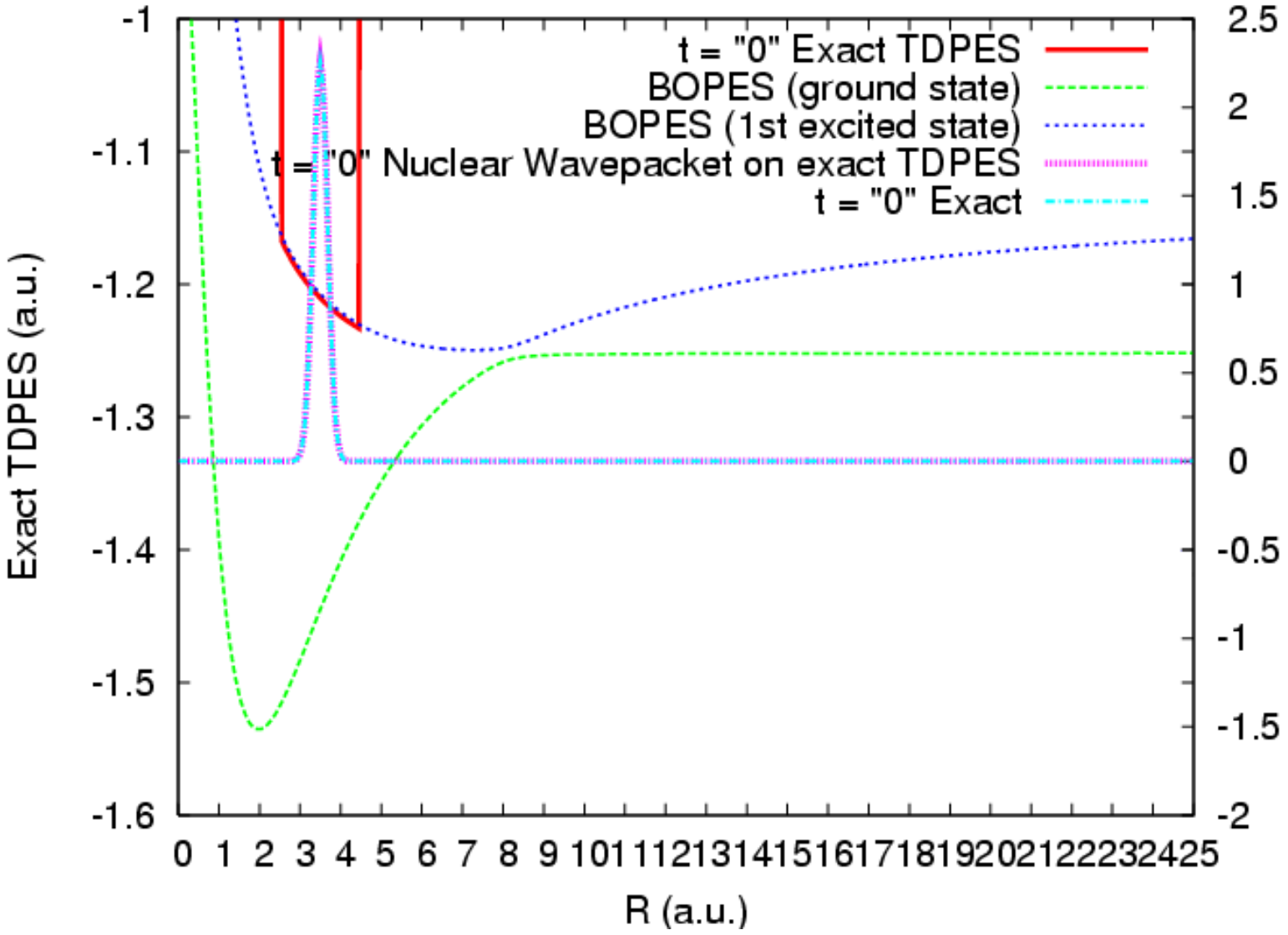
JCP 137, 22A530 (2012)

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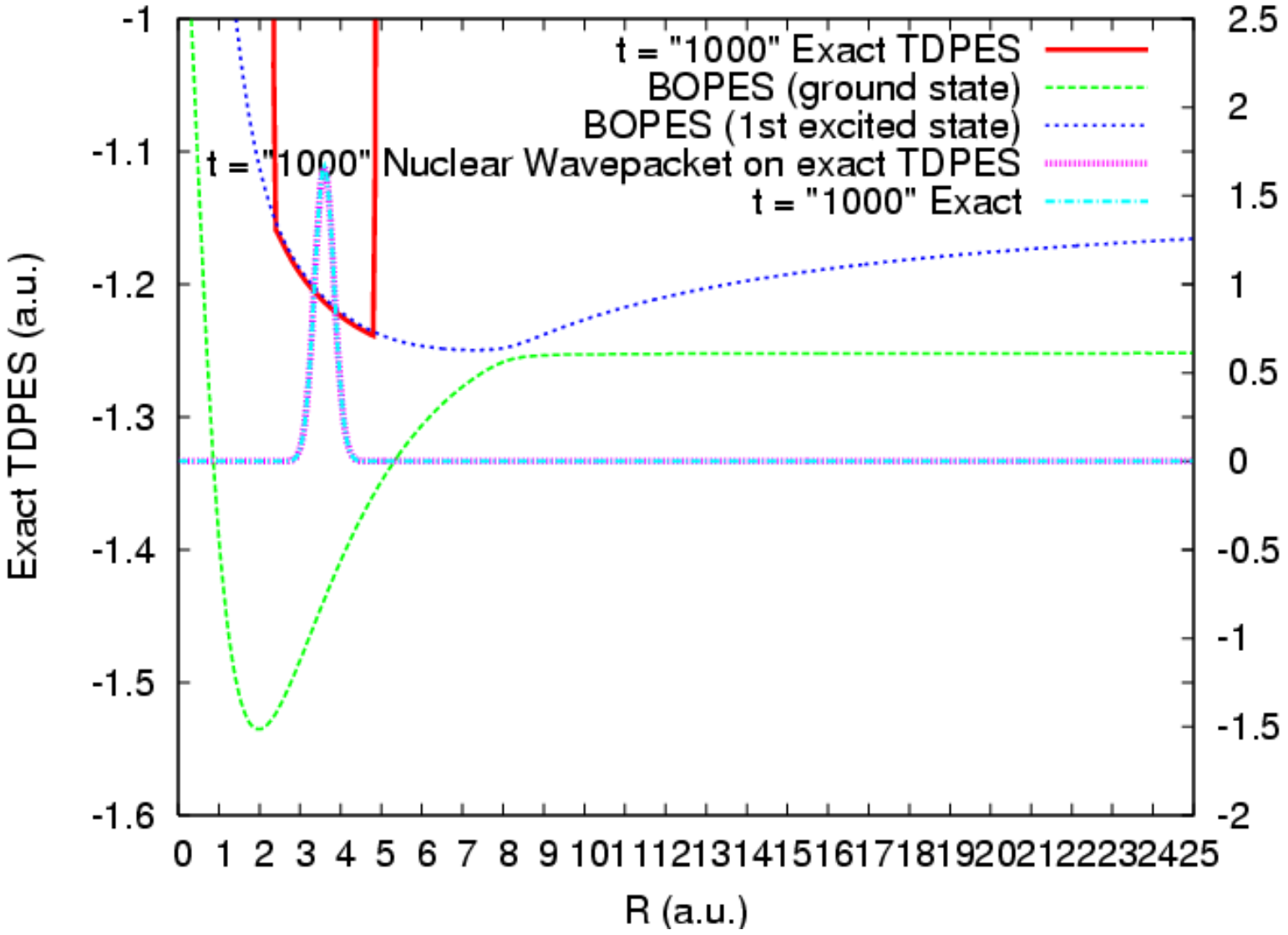
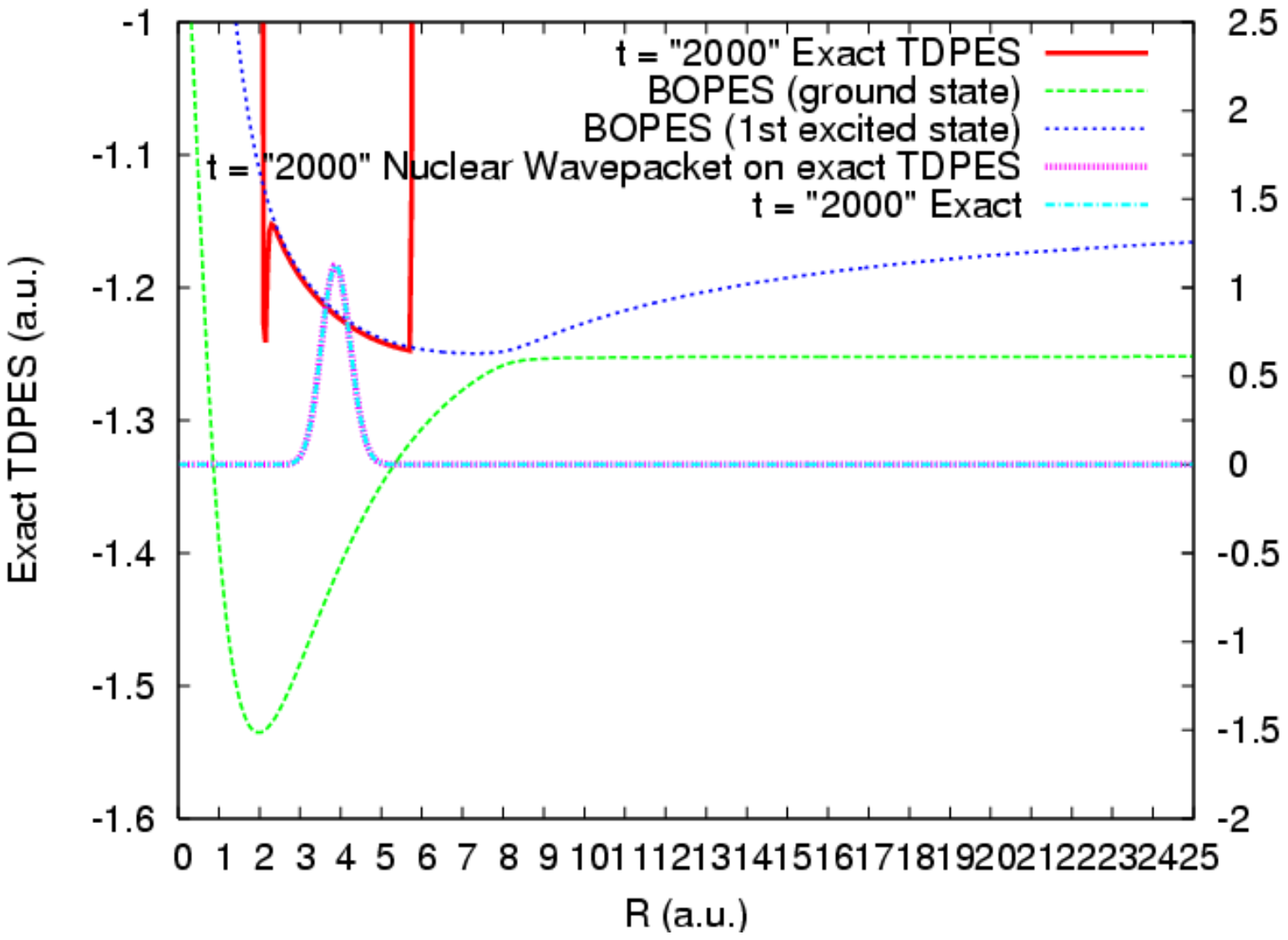
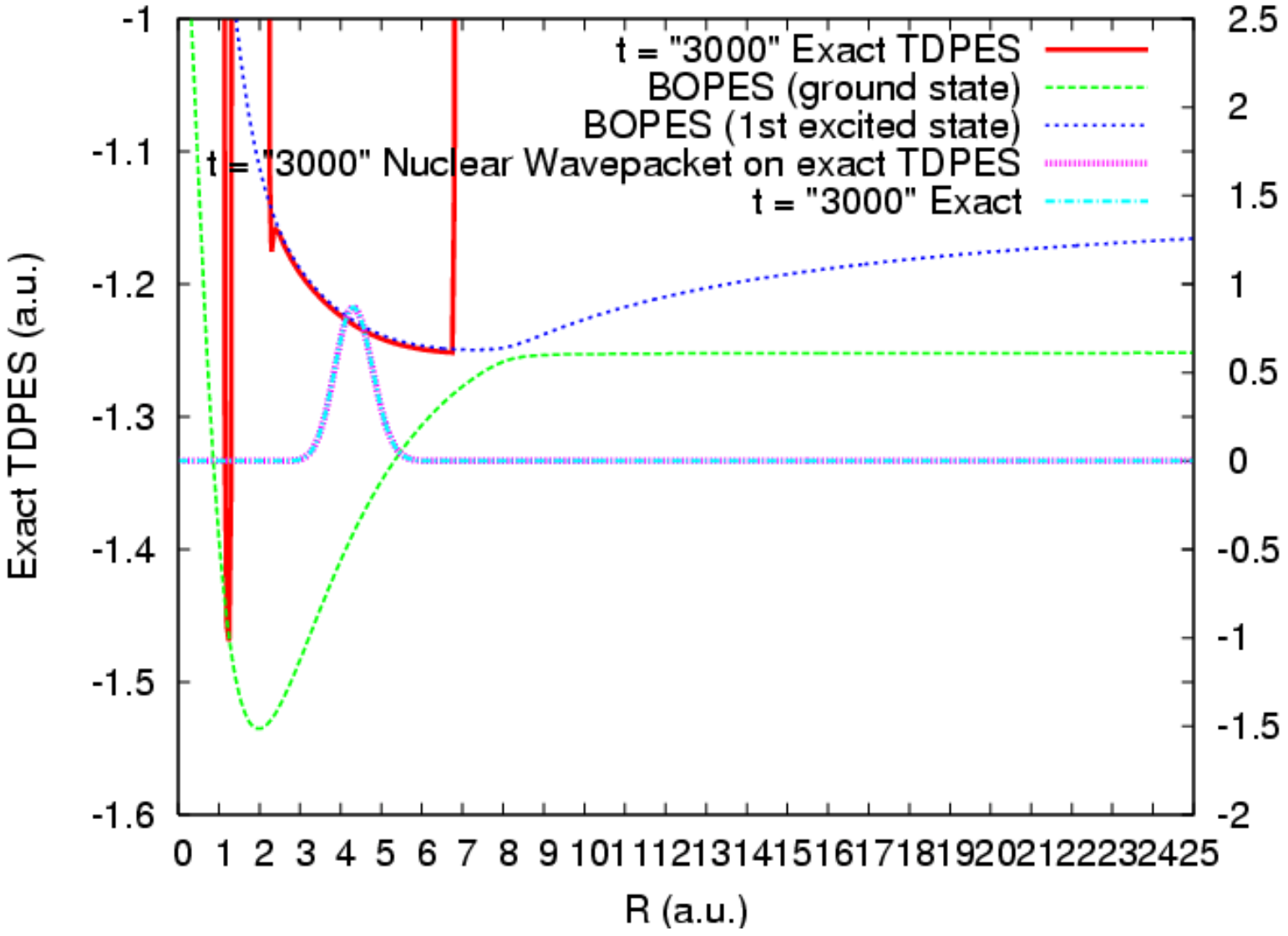
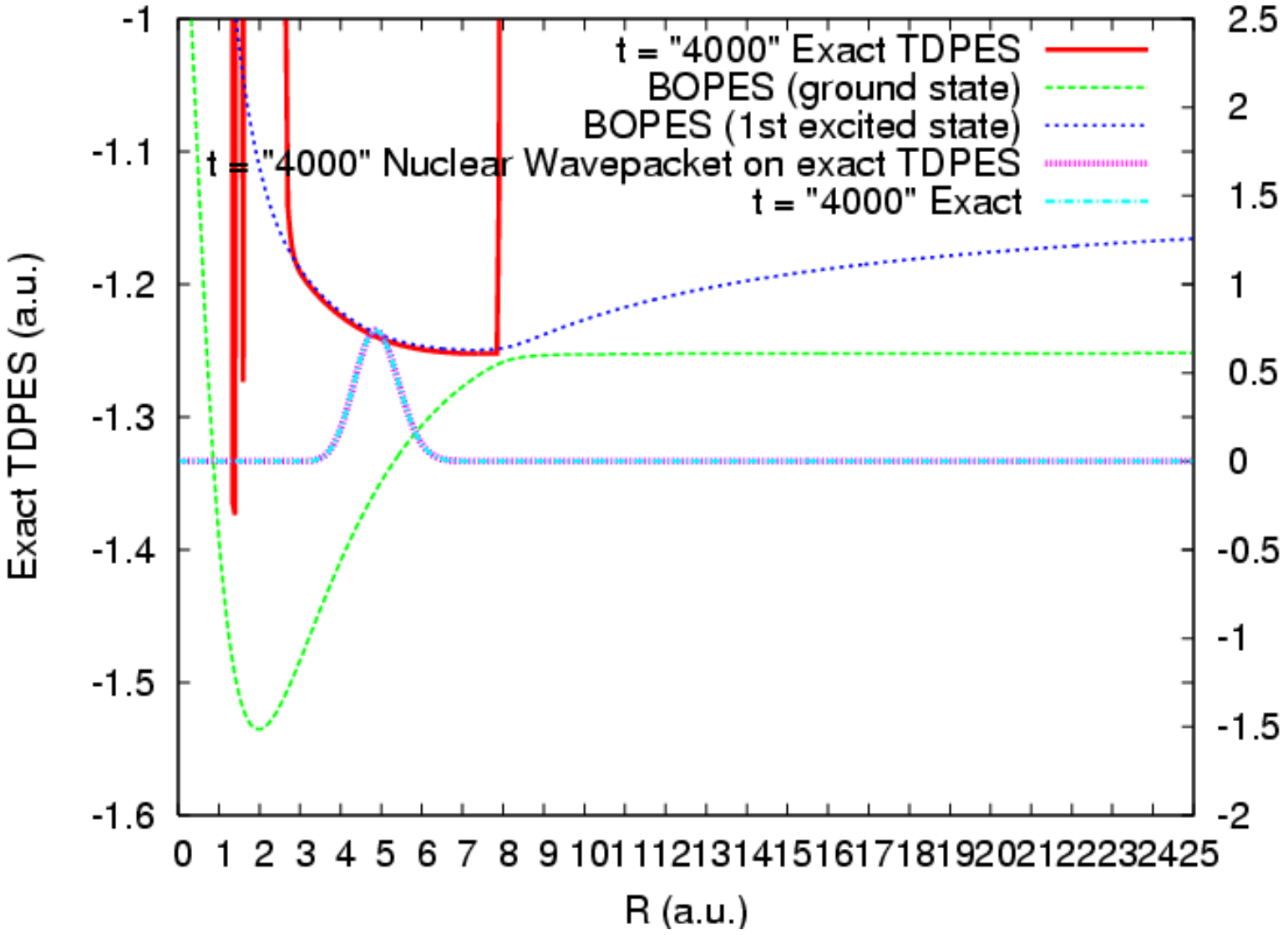
BOPES (ground state)
BOPES (1st excited state)
t = "0" Nuclear Wavepacket on exact TDPES
t = "0" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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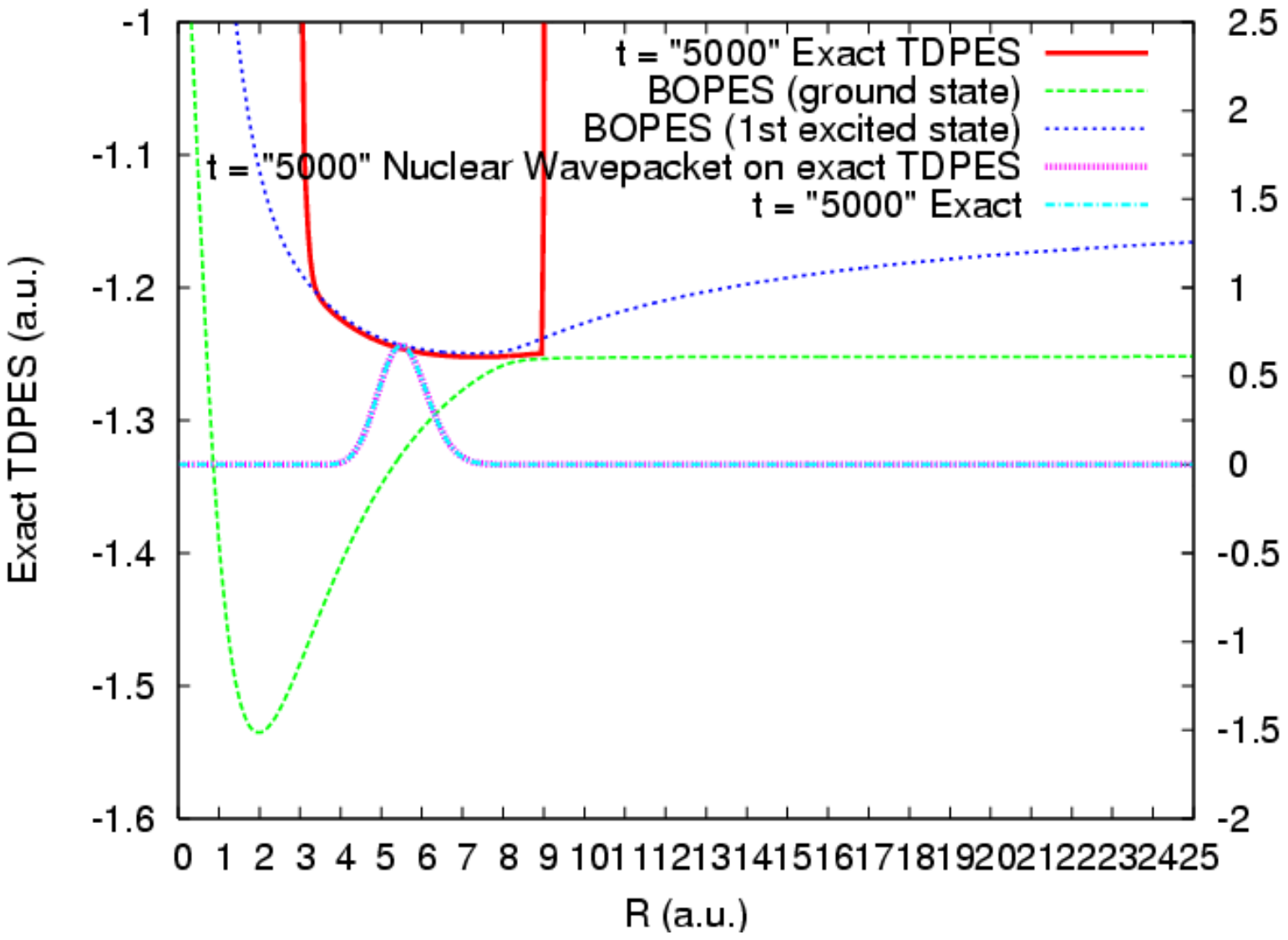
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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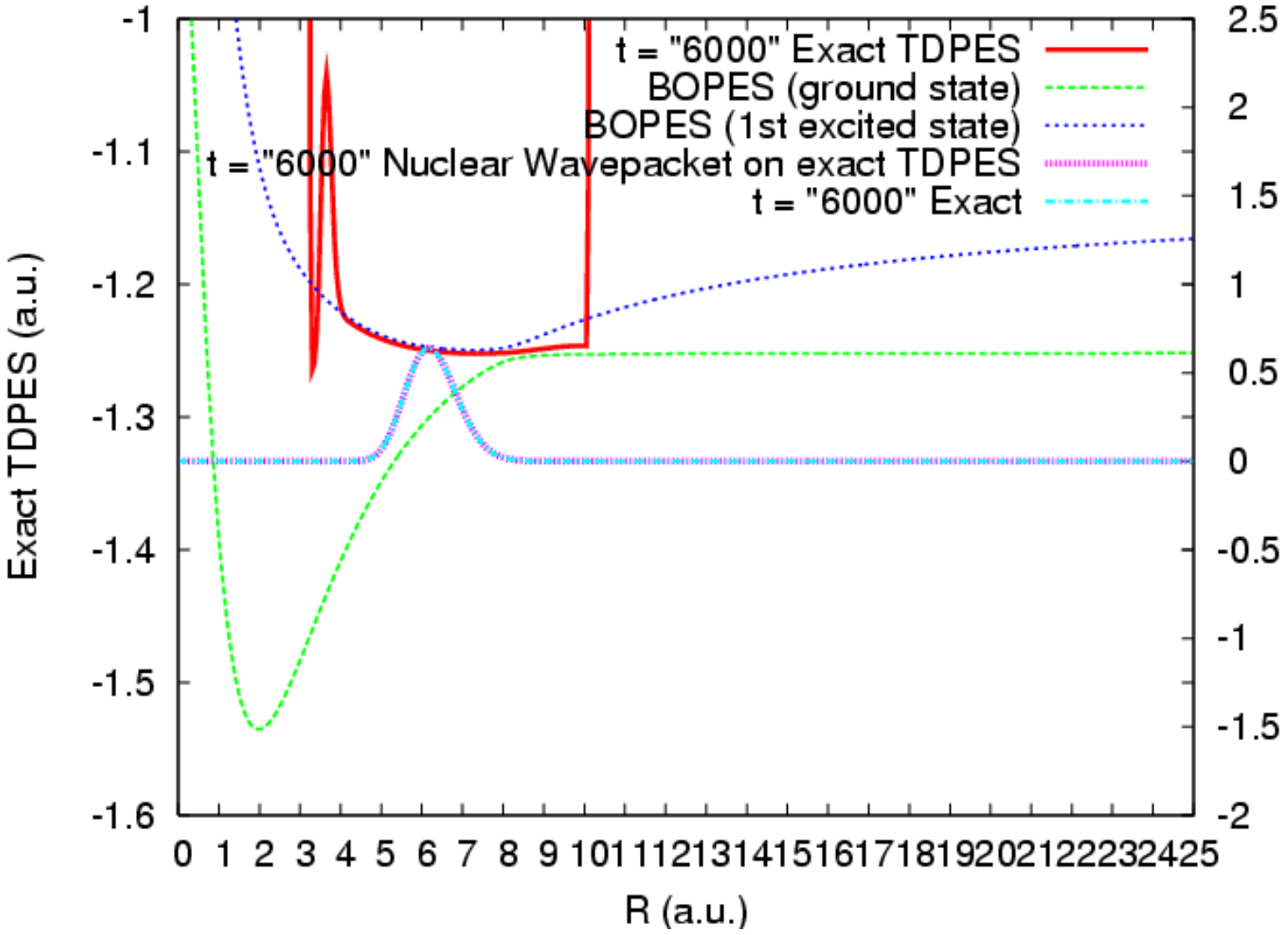
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "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
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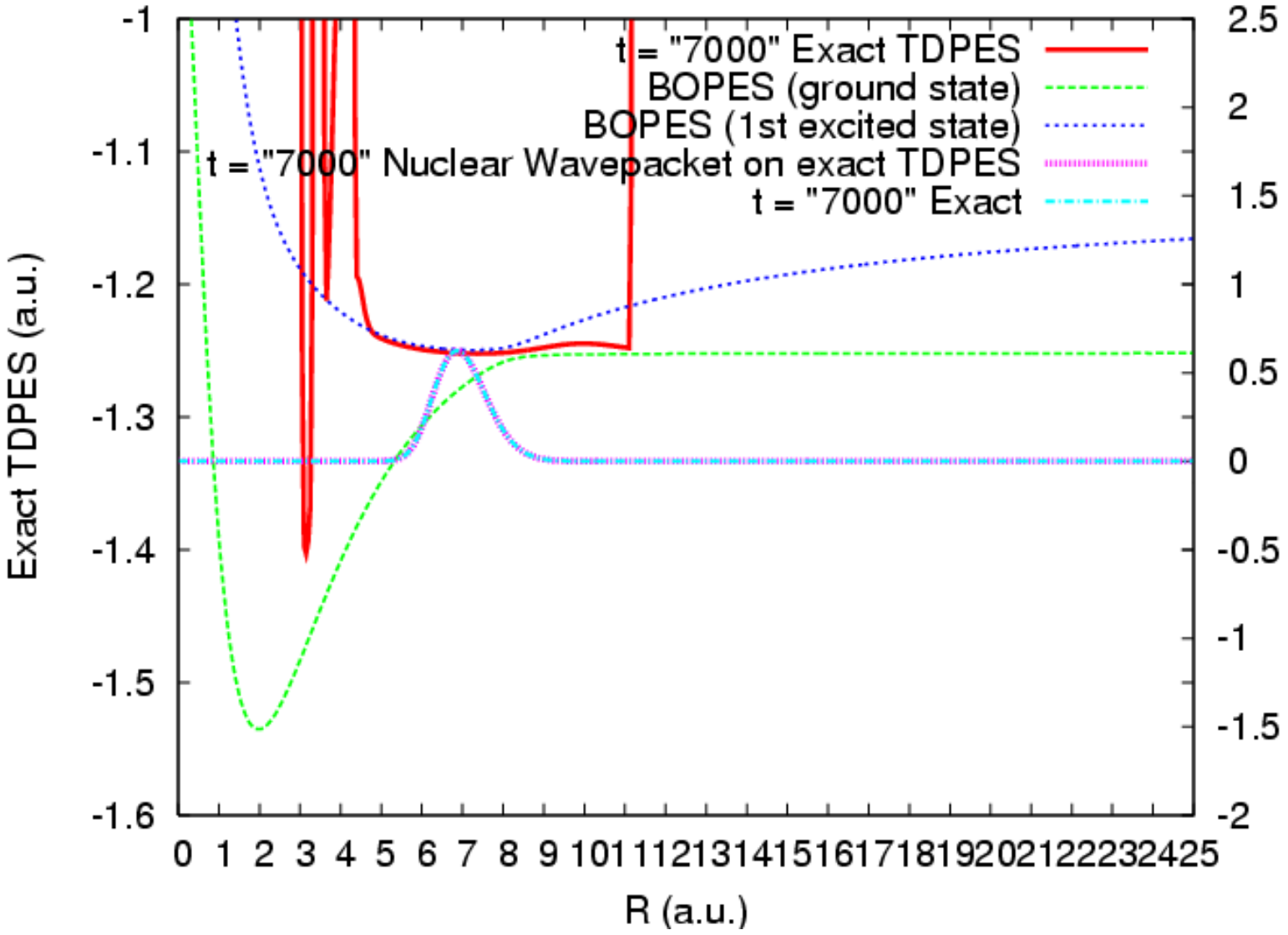
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "7000" Nuclear Wavepacket on exact TDPES
t = "7000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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0.5
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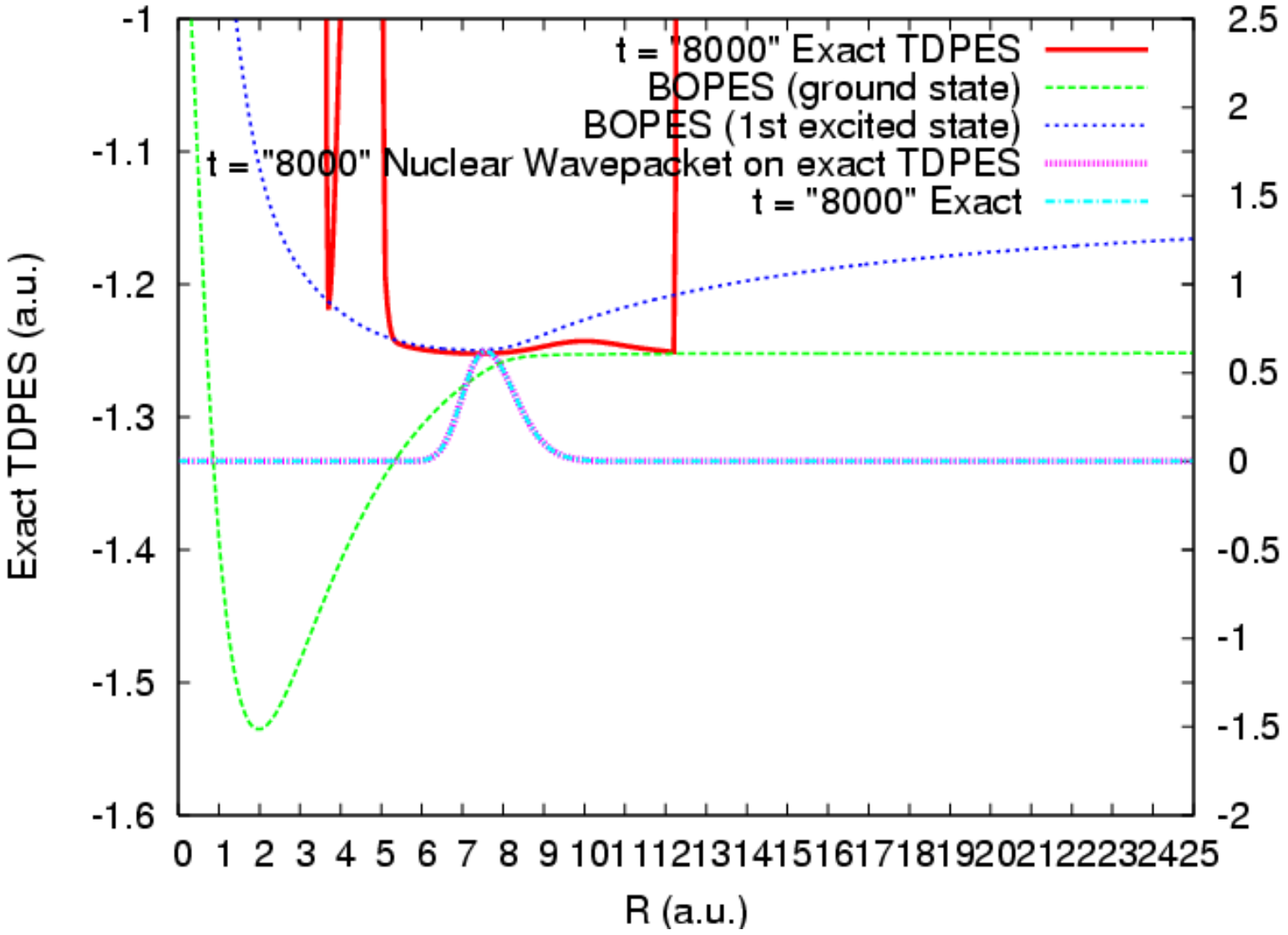
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "8000" Nuclear Wavepacket on exact TDPES
t = "8000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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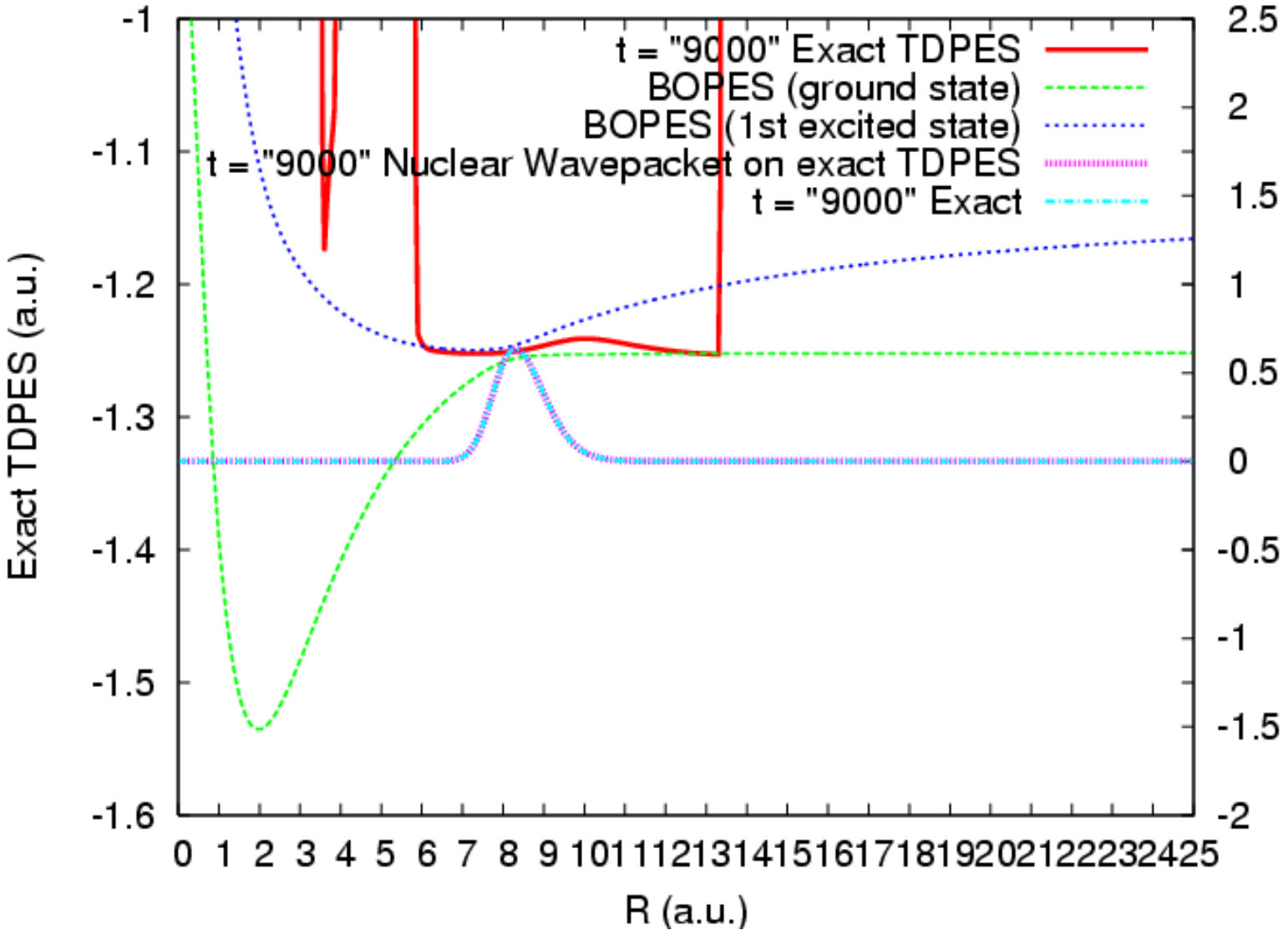
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "9000" Nuclear Wavepacket on exact TDPES
t = "9000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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1.5
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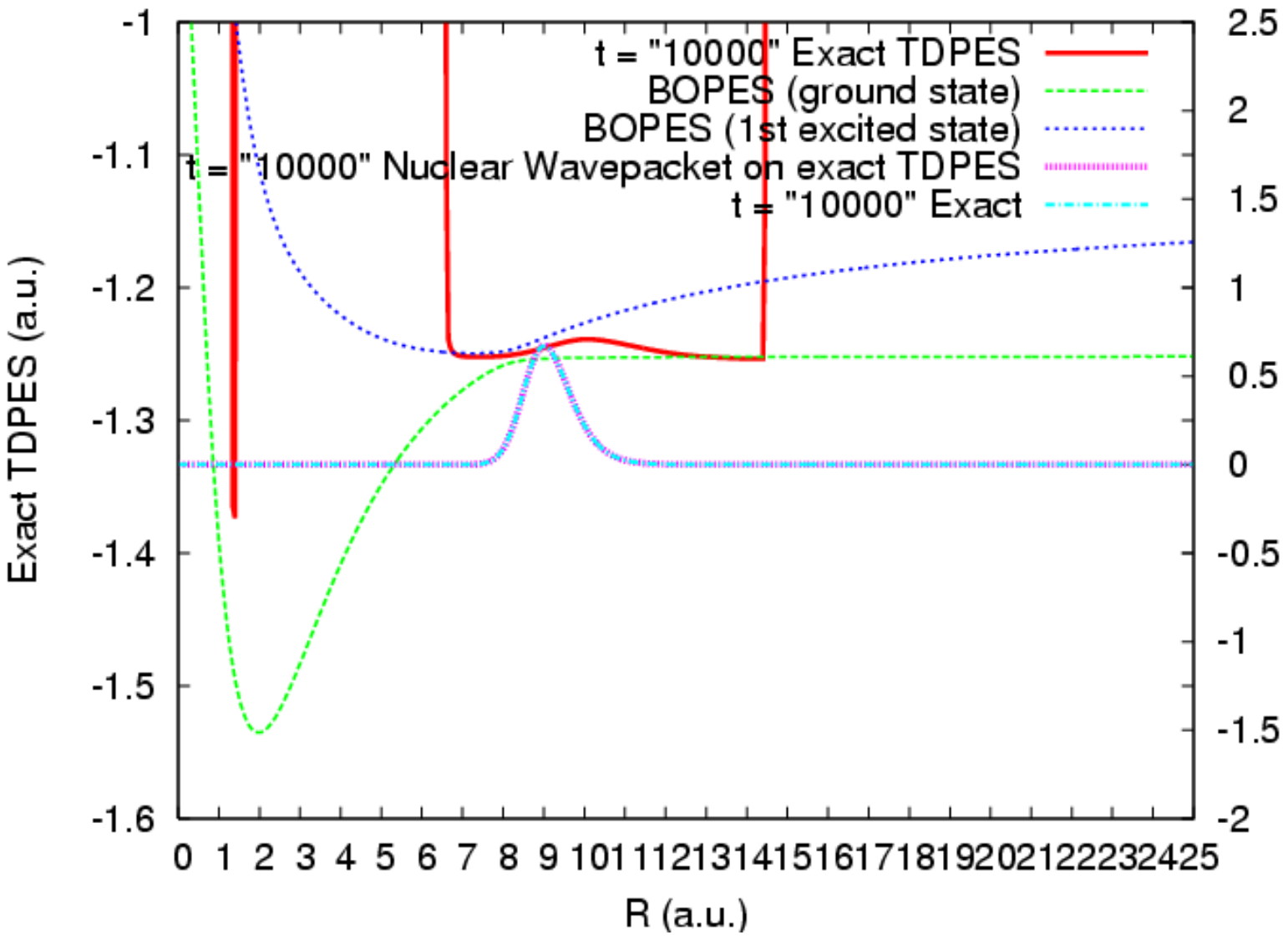
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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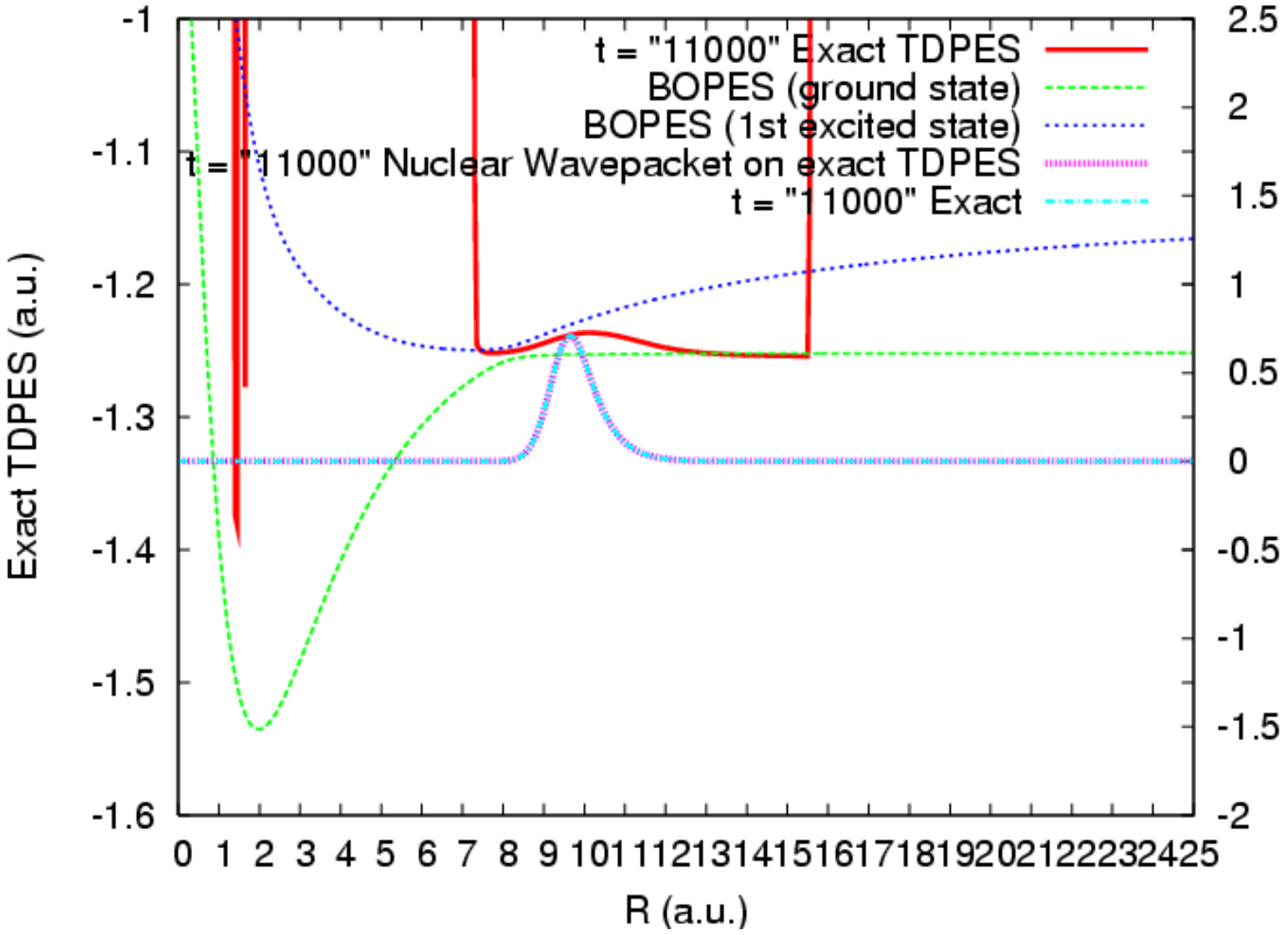
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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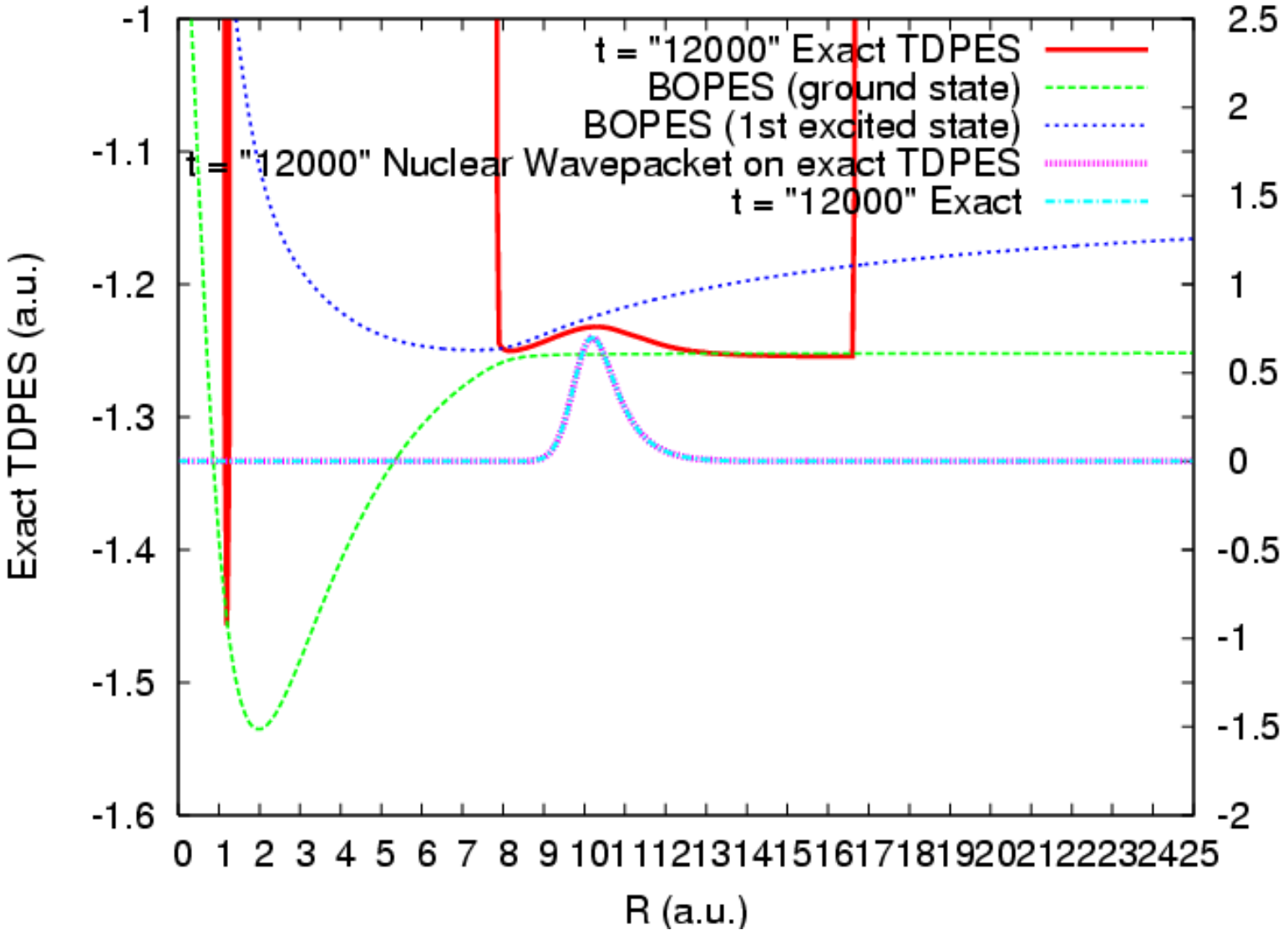
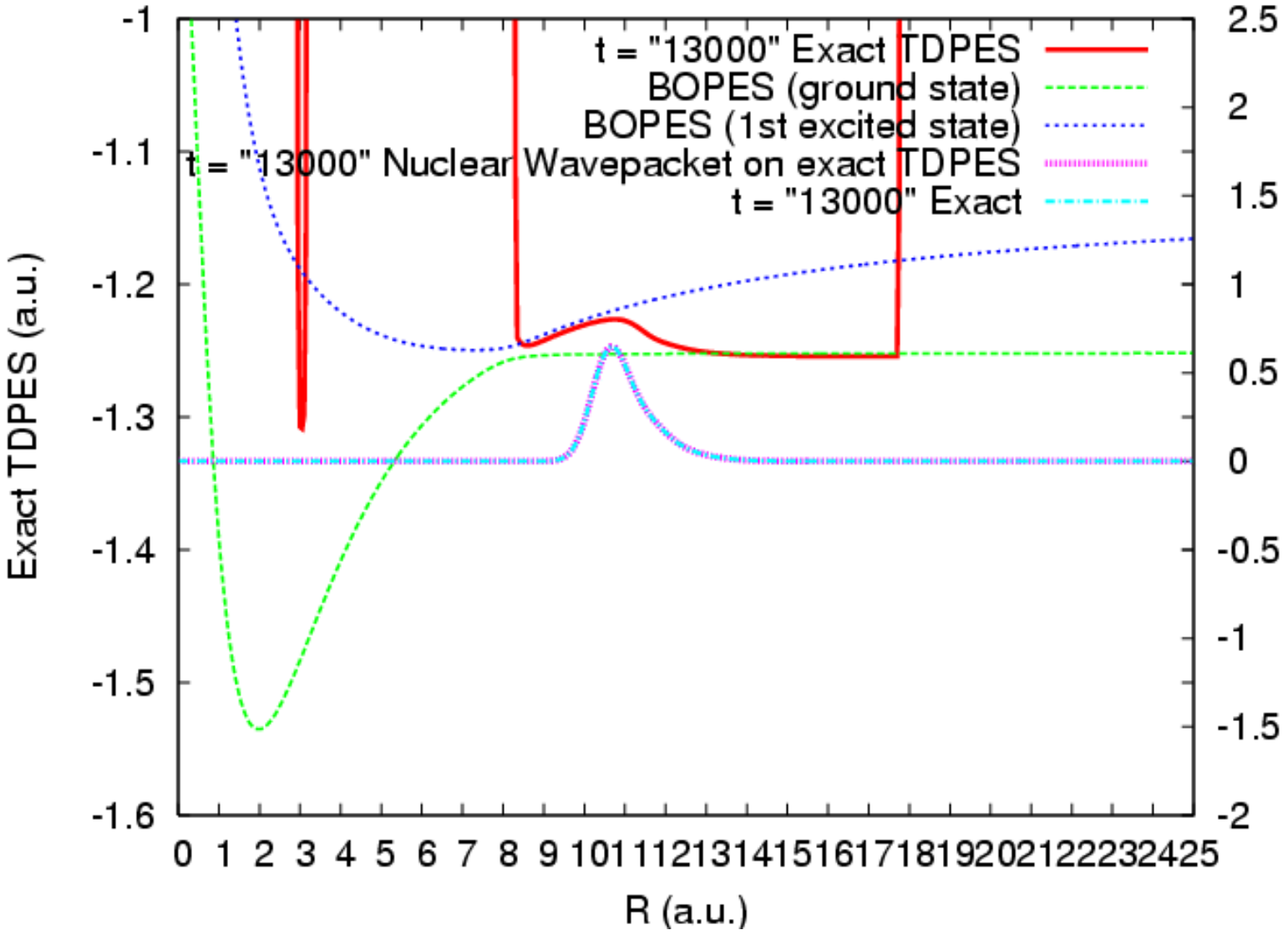
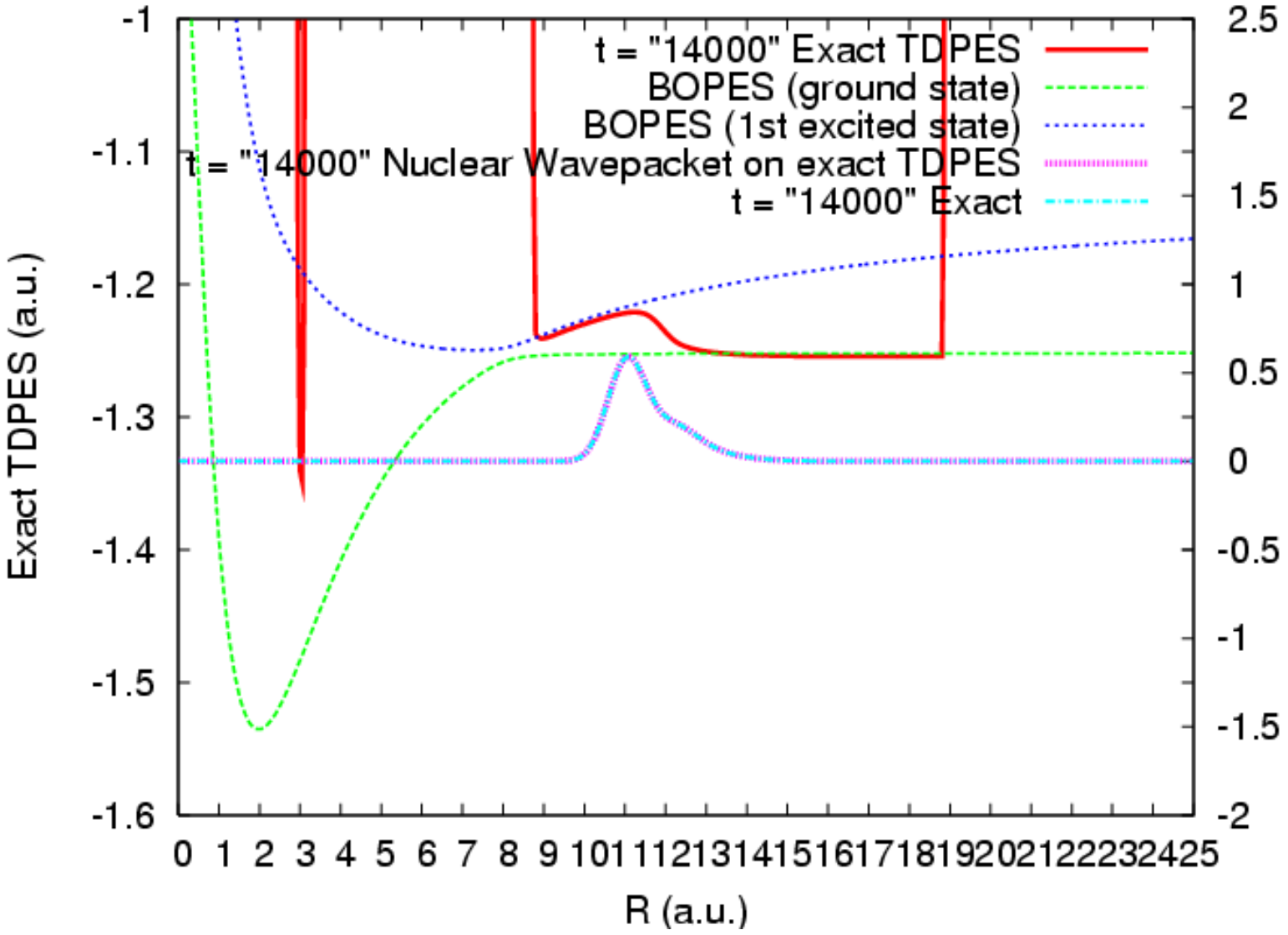
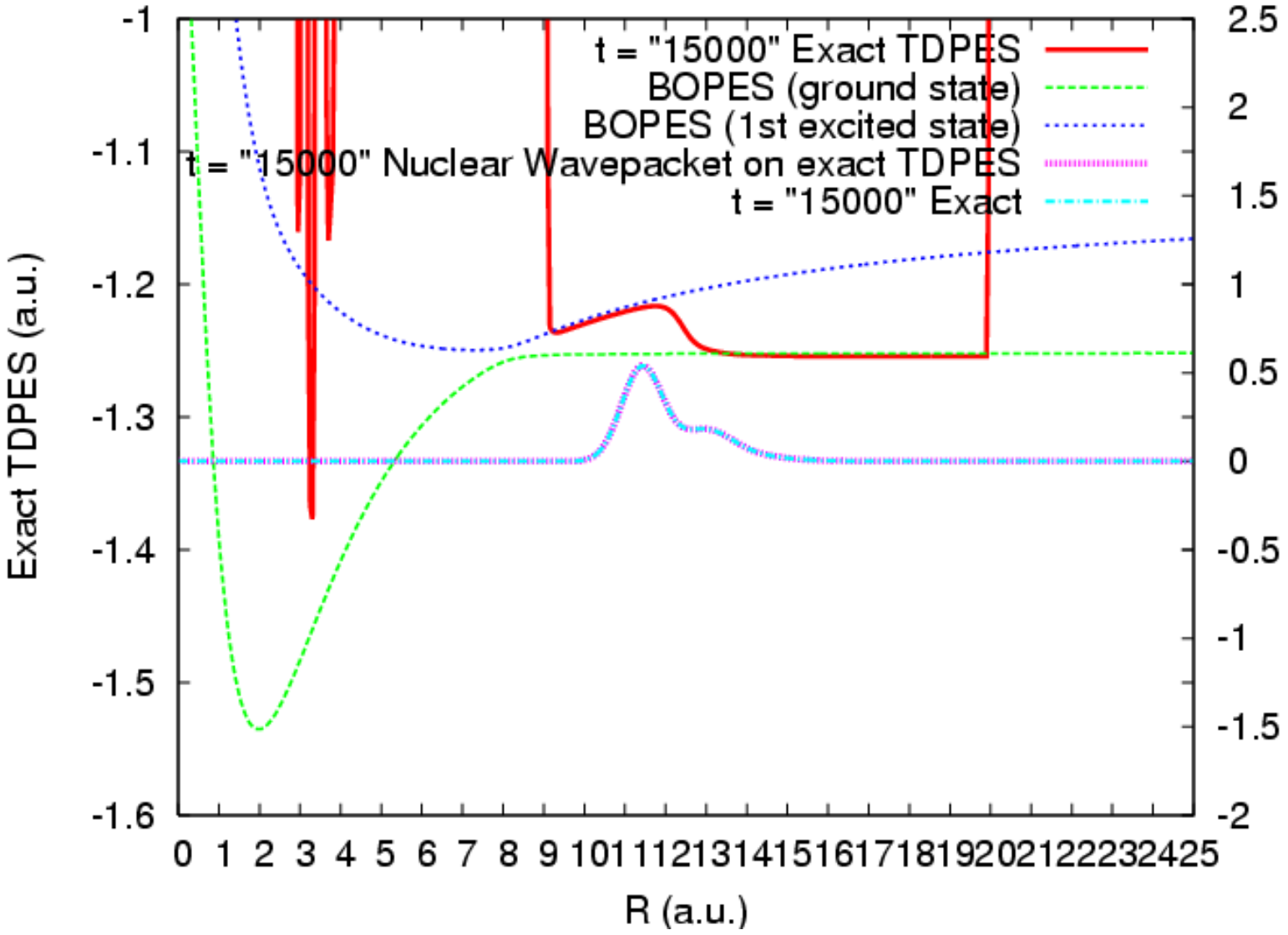
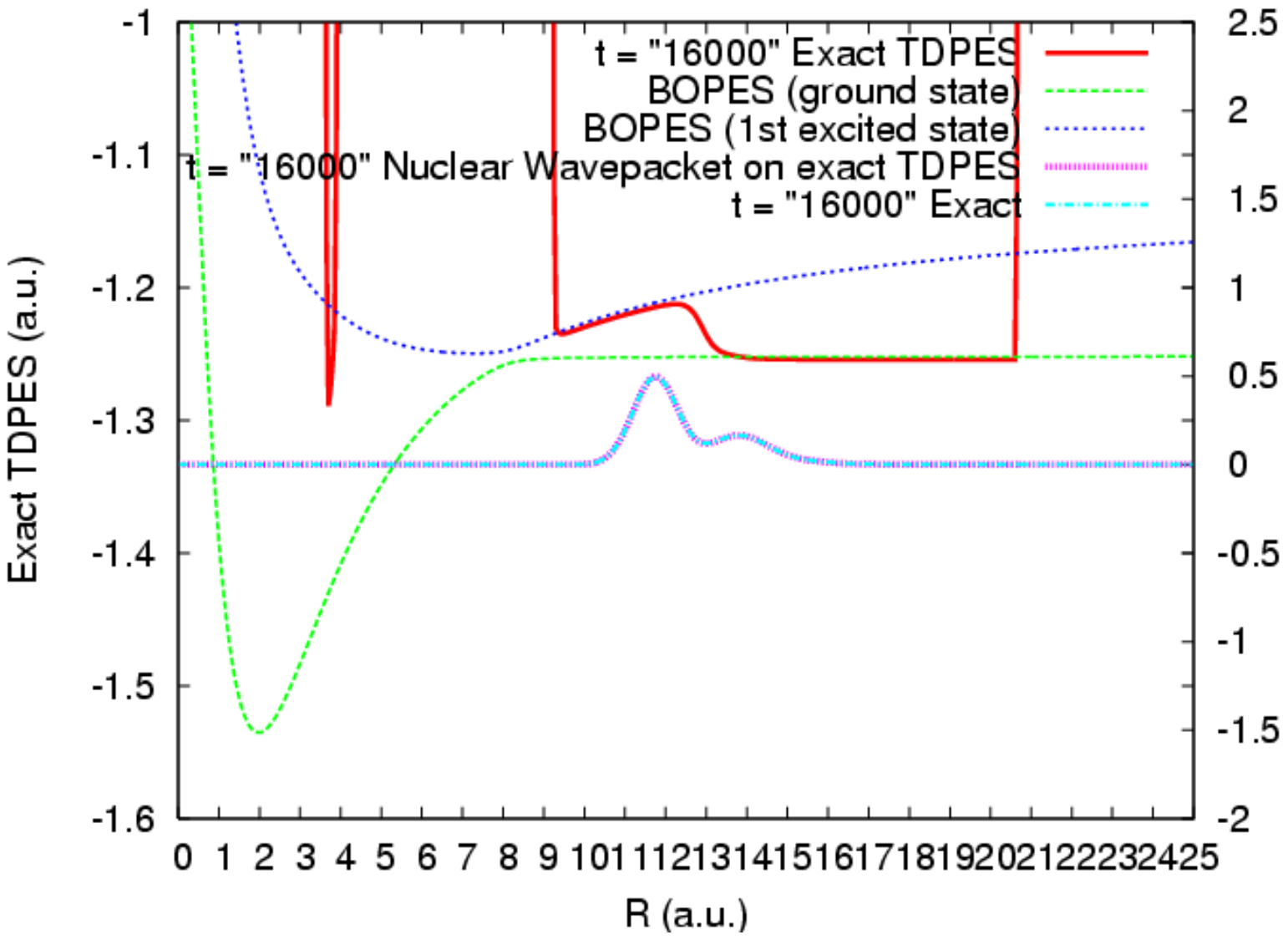
BOPES (ground state)
BOPES (1st excited state)
t = "11000" Nuclear Wavepacket on exact TDPES
t = "11000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

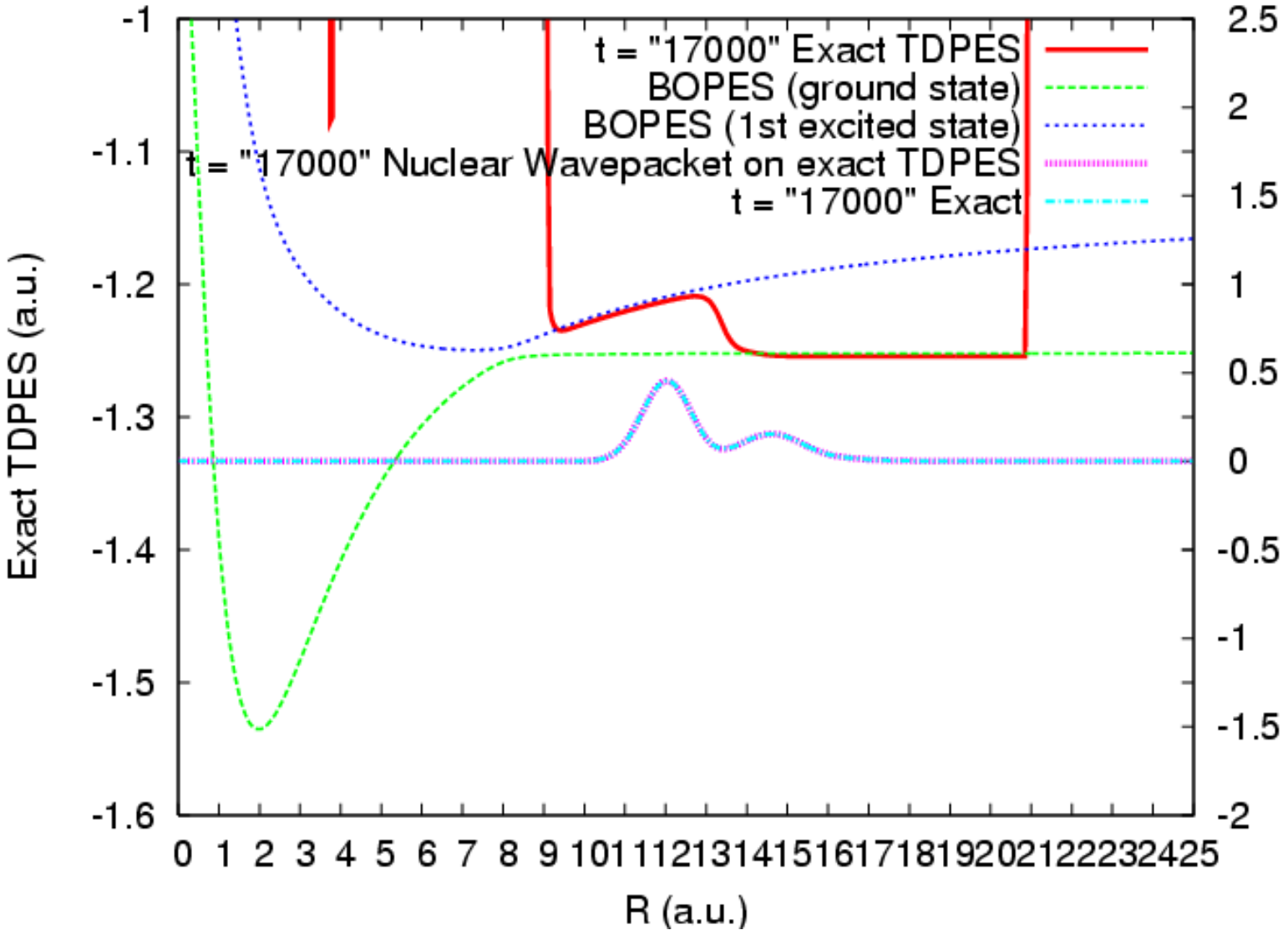

t = "12000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "12000" Nuclear Wavepacket on exact TDPES
t = "12000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

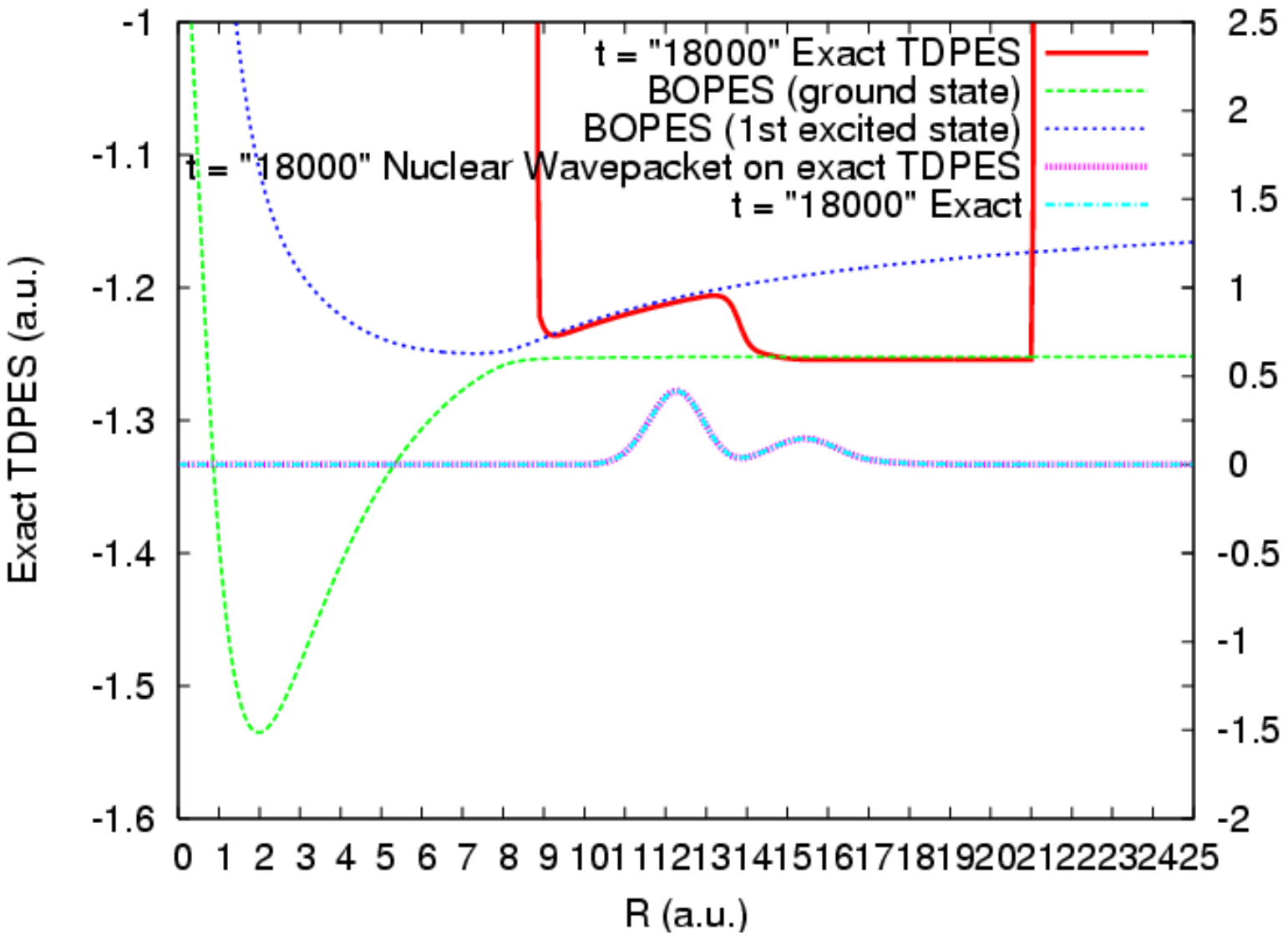

t = "13000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "13000" Nuclear Wavepacket on exact TDPES
t = "13000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

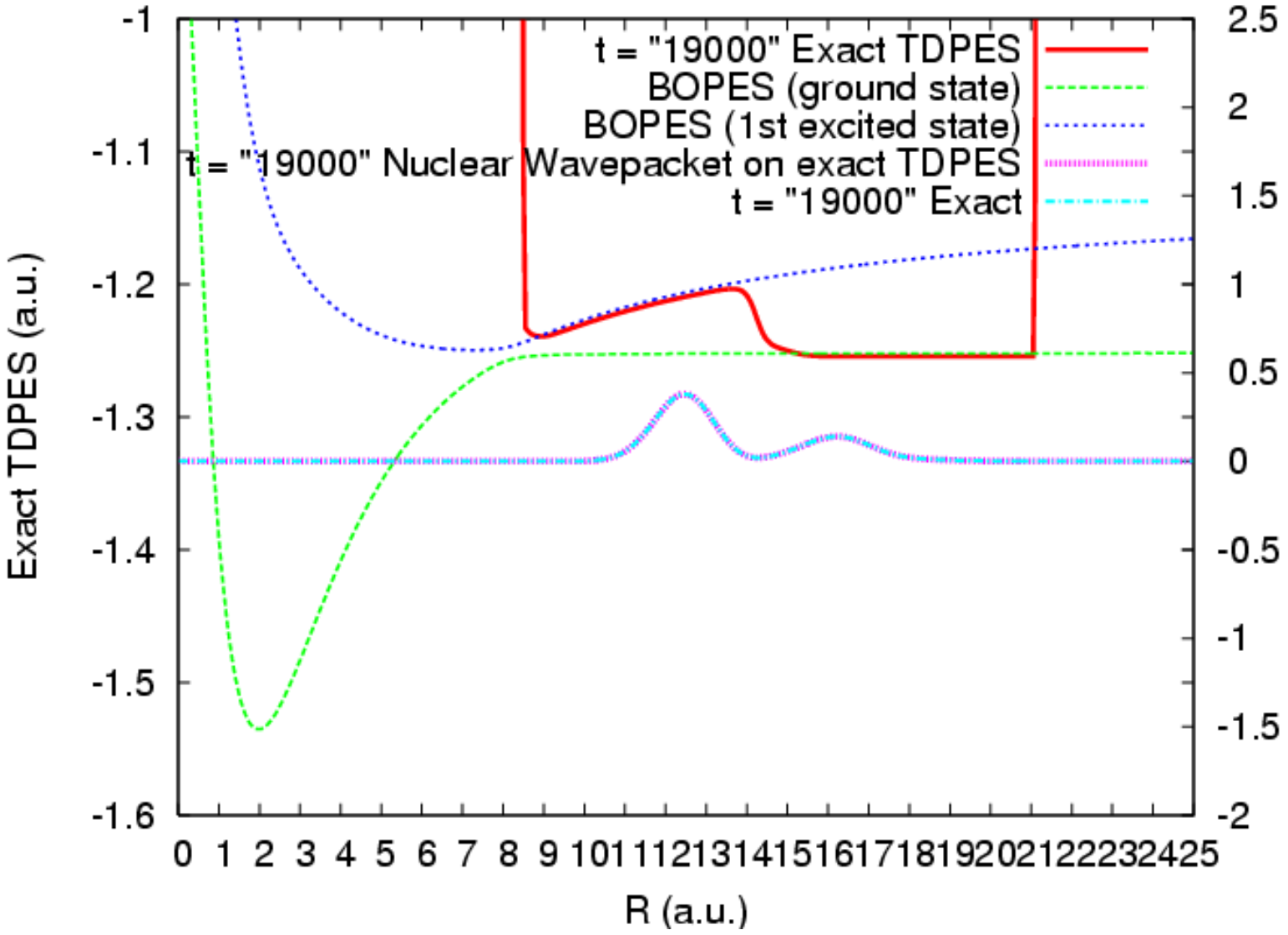

t = "14000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "14000" Nuclear Wavepacket on exact TDPES
t = "14000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

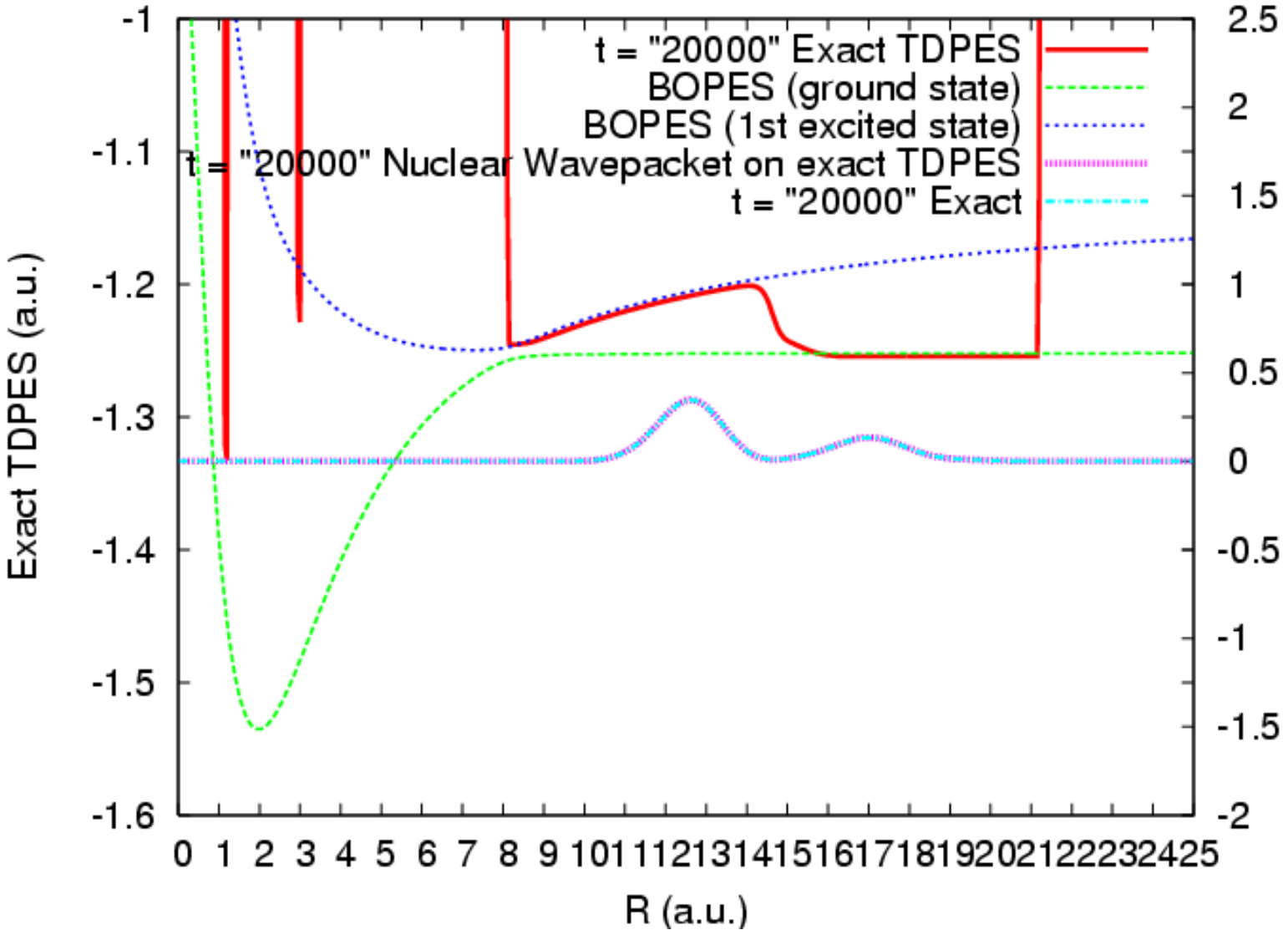

t = "15000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "15000" Nuclear Wavepacket on exact TDPES
t = "15000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


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


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


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


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


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

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

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

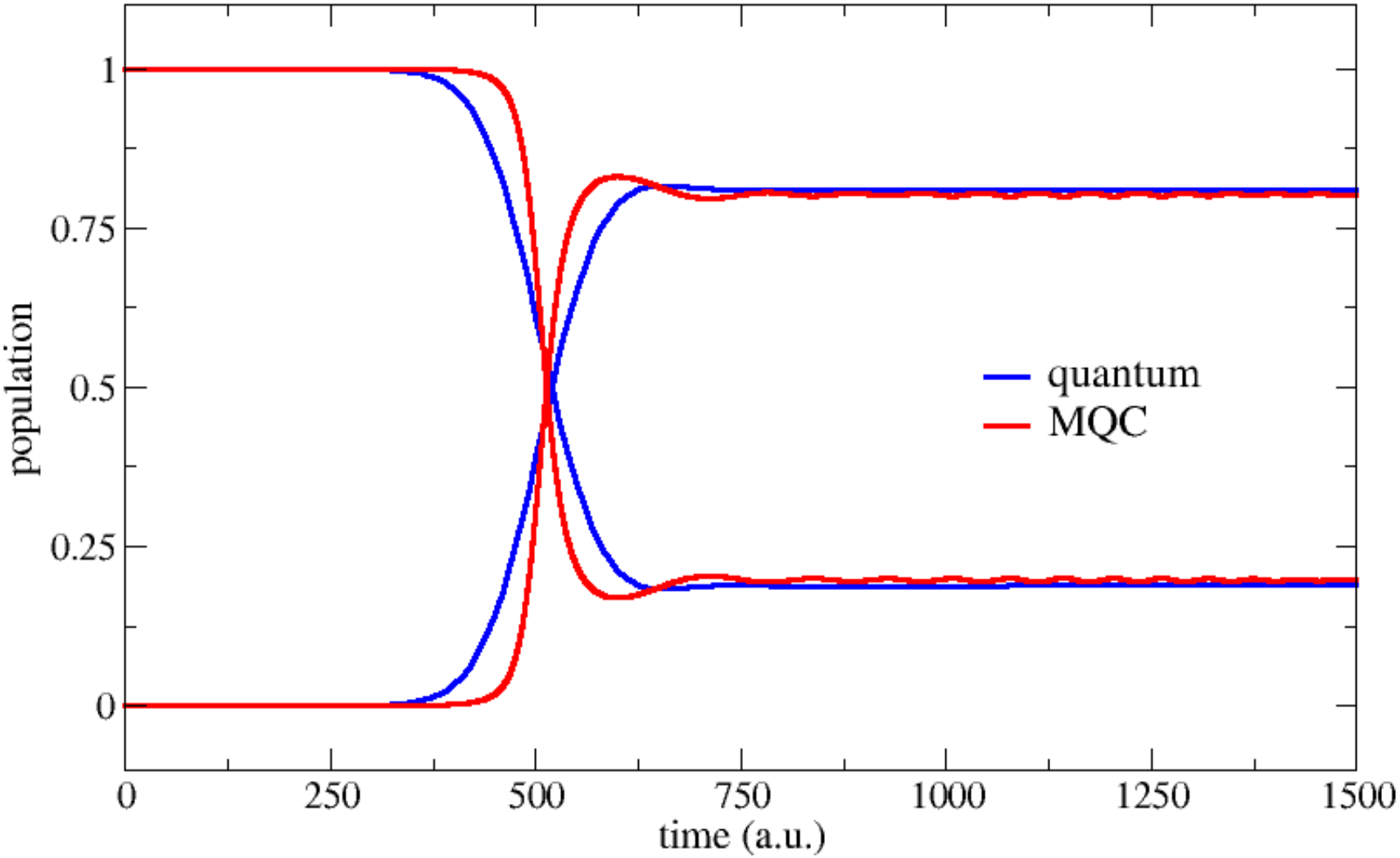
$$+\sum_{\nu}^{N_n}\frac{1}{M_\nu}\left(\frac{-i\nabla_\nu\chi\left(\underline{\underline{R}},t\right)}{\chi\left(\underline{\underline{R}},t\right)} + A_\nu\left(\underline{\underline{R}},t\right)\right)\left(-i\nabla_\nu - A_\nu\right) - \in\left(\underline{\underline{R}},t\right)\Bigg)\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\ri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

Eq. ❷

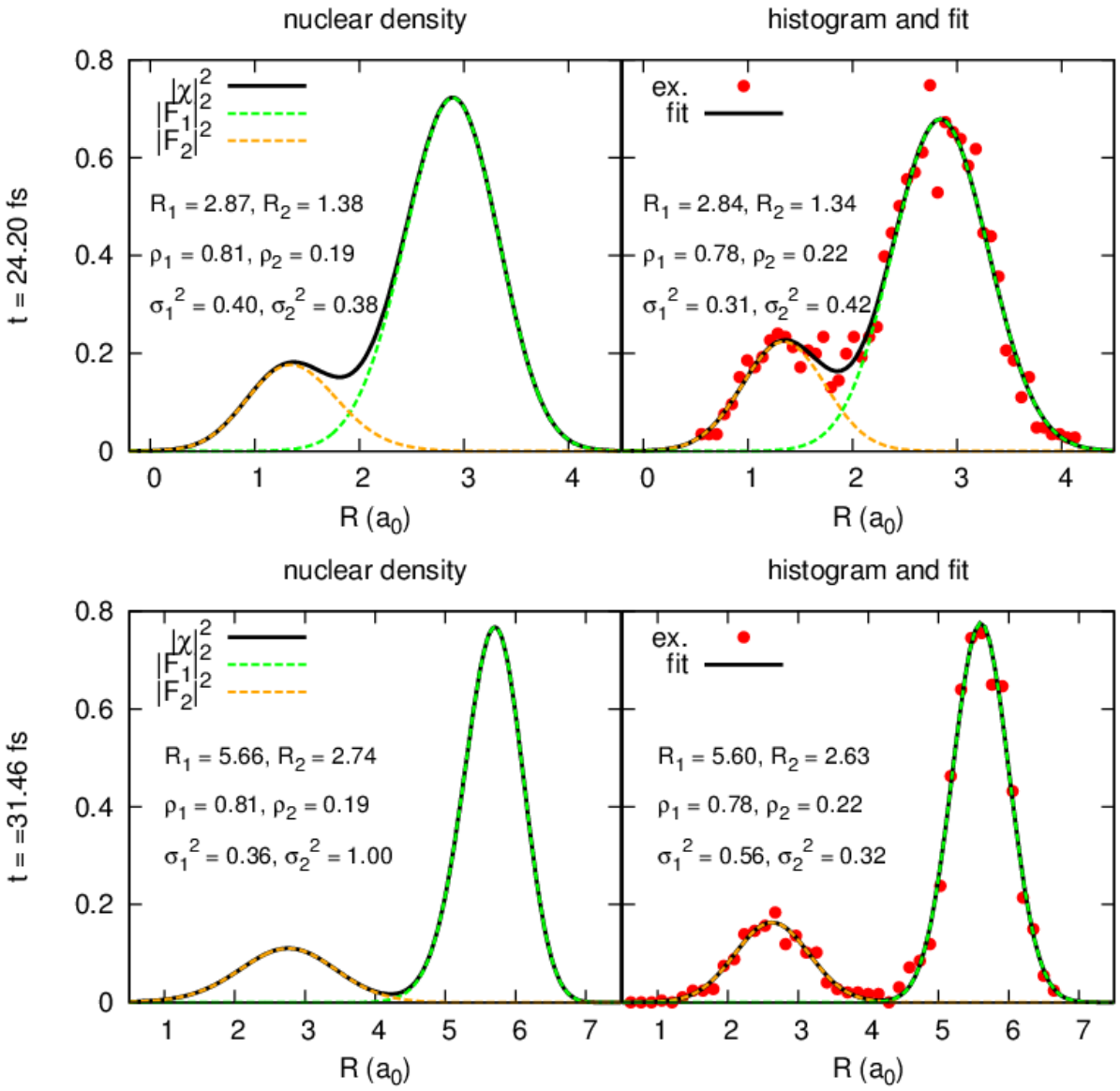
$$\left(\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu\left(\underline{\underline{R}},t\right)\right)^2 + \hat{W}_{nn}\left(\underline{\underline{R}}\right) + \hat{V}_n^{ext}\left(\underline{\underline{R}},t\right) + \in\left(\underline{\underline{R}},t\right)\right)\chi\left(\underline{\underline{R}},t\right)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

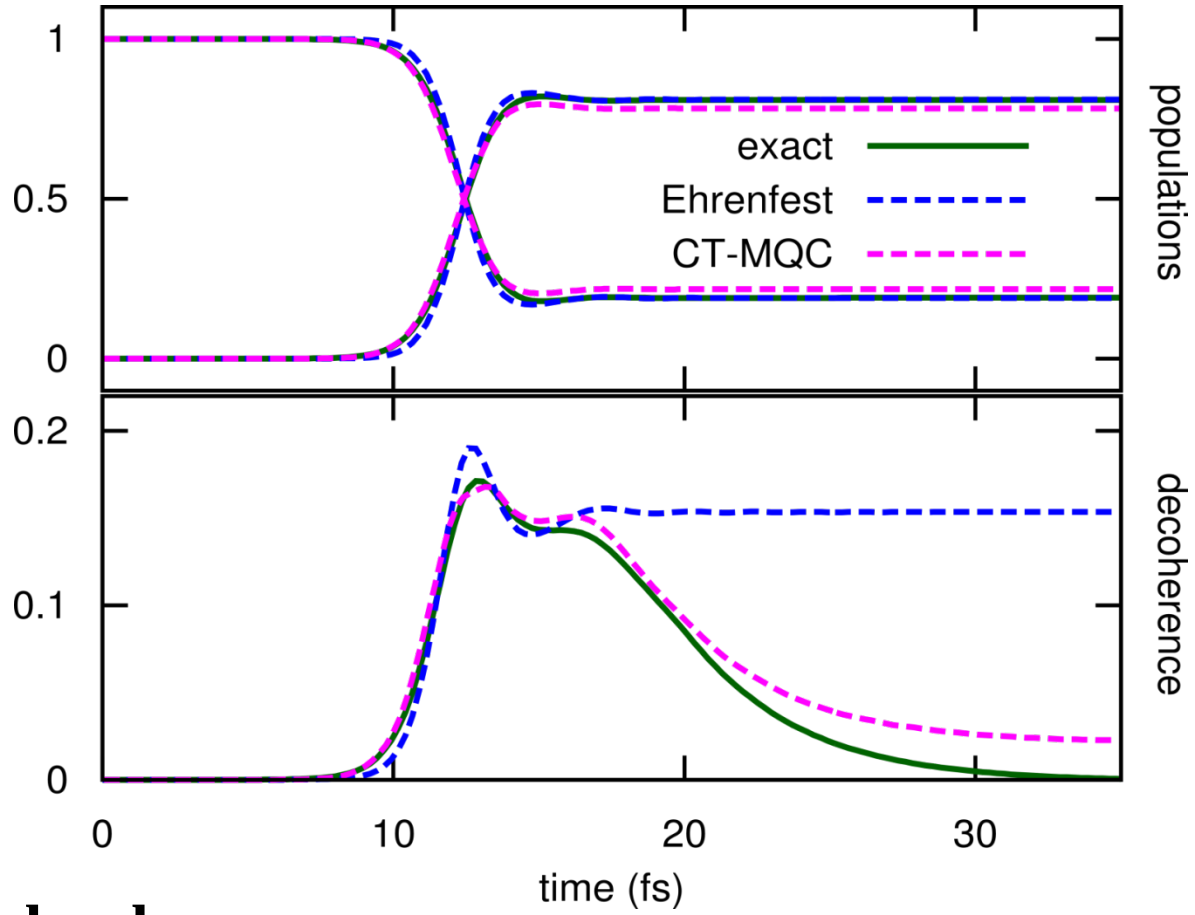
Shin-Metiu model

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

Summary:

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

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

  both in the static and the time-dependent case

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

Thanks !

SFB 450
SFB 685
SFB 762
SPP 1145