# DFT beyond the Born-Oppenheimer approximation

**Hamiltonian for the complete system of $N_e$ electrons with coordinates $(r_1 \cdots r_{N_e}) \equiv \underline{r}$ and $N_n$ nuclei with coordinates $(R_1 \cdots R_{N_n}) \equiv \underline{\underline{R}}$**

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

**with**

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

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

## Time-dependent Schrödinger equation

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

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

# Standard approach: Adiabatic approximation

$$\Psi^{\text{adiab}}(\underline{\underline{r}},\underline{\underline{R}},t) = \chi(\underline{\underline{R}},t)\,\Phi^{\mathbf{BO}}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

$$\left(\hat{T}_{\mathbf{e}}(\underline{\underline{r}}) + \hat{W}_{\mathbf{ee}}(\underline{\underline{r}}) + \hat{W}_{\text{nn}}(\underline{\underline{R}}) + \hat{V}_{\mathbf{en}}(\underline{\underline{r}},\underline{\underline{R}})\right)\Phi^{\mathbf{BO}}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right) = \in^{\text{BO}}_{J}\left(\underline{\underline{R}}\right)\Phi^{\mathbf{BO}}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right)$$

$$i\partial_t\,\chi\left(\underline{\underline{R}},t\right) = \left(T_n + \in^{\text{BO}}_{J}\left(\underline{\underline{R}}\right)\right)\chi\left(\underline{\underline{R}},t\right)$$

- **achieves approximate separation of electronic and nuclear degrees of freedom, making calculations possible**

# Standard approach: Adiabatic approximation

$$\Psi^{\text{adiab}}(\underline{\underline{r}},\underline{\underline{R}},t) = \chi(\underline{\underline{R}},t)\,\Phi^{\mathbf{BO}}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

One of the BO eigenstates (ground state in DFT context)

$$\left(\hat{T}_{\mathbf{e}}(\underline{\underline{r}}) + \hat{W}_{\mathbf{ee}}(\underline{\underline{r}}) + \hat{W}_{\mathrm{nn}}(\underline{\underline{R}}) + \hat{V}_{\mathbf{en}}(\underline{\underline{r}},\underline{\underline{R}})\right)\Phi^{\mathbf{BO}}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right) = \in^{\mathrm{BO}}_{J}\left(\underline{\underline{R}}\right)\Phi^{\mathbf{BO}}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right)$$

$$i\partial_t \chi\left(\underline{\underline{R}},t\right) = \left(T_n + \in^{\mathrm{BO}}_{J}\left(\underline{\underline{R}}\right)\right)\chi\left(\underline{\underline{R}},t\right)$$

- **achieves approximate separation of electronic and nuclear degrees of freedom, making calculations possible**

# The "variationally best" adiabatic approximation

**Plug the ansatz**

$$\tilde{\Psi}^{\text{adiab}}(\underline{\underline{r}},\underline{\underline{R}},t) = \tilde{\chi}(\underline{\underline{R}},t)\,\Phi^{\text{BO}}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

**into the TD variational principle and determine the "best" nuclear wave function by making the QM action stationary:**

$$i\partial_t \tilde{\chi}\left(\underline{\underline{R}},t\right) = \left(\tilde{T}_n + \tilde{\epsilon}\left(\underline{\underline{R}}\right)\right)\tilde{\chi}\left(\underline{\underline{R}},t\right)$$

$$\tilde{T}_n = \sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu\left(\underline{\underline{R}}\right)\right)^2$$

$$A_\nu\left(\underline{\underline{R}}\right) = \int d\underline{\underline{r}}\;\Phi^{\text{BO}}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)^*\left(-i\nabla_{R_\nu}\right)\Phi^{\text{BO}}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) = \left\langle \Phi^{\text{BO}}_{\underline{\underline{R}}} \middle| -i\nabla_{R_\nu}\Phi^{\text{BO}}_{\underline{\underline{R}}}\right\rangle$$

**Berry connection**

$$\tilde{\epsilon}\left(\underline{\underline{R}}\right) = \epsilon^{\text{BO}}\left(\underline{\underline{R}}\right) + \sum_{\nu}^{N_n}\left\{\left\langle \nabla_\nu \Phi^{\text{BO}}_{\underline{\underline{R}}} \middle| \nabla_\nu \Phi^{\text{BO}}_{\underline{\underline{R}}}\right\rangle - A_\nu\left(\underline{\underline{R}}\right)^2\right\}/2M_\nu$$

**"Diagonal correction"**

# Effects not captured in the adiabatic approximation

- **Decoherence (quantumness of the electronic many-body wave function disappears through interaction with other degrees of freedom)**
- **Electronic currents associated with nuclear motion are zero in the adiabatic approximation (probed in vibrational circular dichroism)**
- **Photo-chemistry (splitting of the nuclear wave packet)**
- **Laser-induced structural phase transitions in solids**
- **Thermalization of extended systems after excitation**

## Where does the adiabatic approximation come from? What is neglected?

**Expand full electron-nuclear wave function in complete set of BO States (Born-Huang expansion) to get formally exact representation:**

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

**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:**

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

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

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

**Plug Born-Huang expansion in full TDSE:**

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

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

NAC-1

NAC-2

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

**Setting all NACs ≡ 0 is the simple adiabatic approximation.**

**Setting only the off-diagonal NACs ≡ 0 yields the variationally best one.**

**Keeping only the diagonal NACs in the Born-Huang expansion:**

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

vector potential (Berry connection)

$$+\cancel{\sum_j} \sum_\alpha \left(\frac{\hbar^2}{M_\alpha}\right) \left\langle \phi^{BO}_{\underline{\underline{R}},k} \middle| -i\nabla_{\underline{\underline{R}}_\alpha} \middle| \phi^{BO}_{\underline{\underline{R}},k} \right\rangle \left(-i\nabla_{\underline{\underline{R}}_\alpha} \chi_k\left(\underline{\underline{R}},t\right)\right)$$

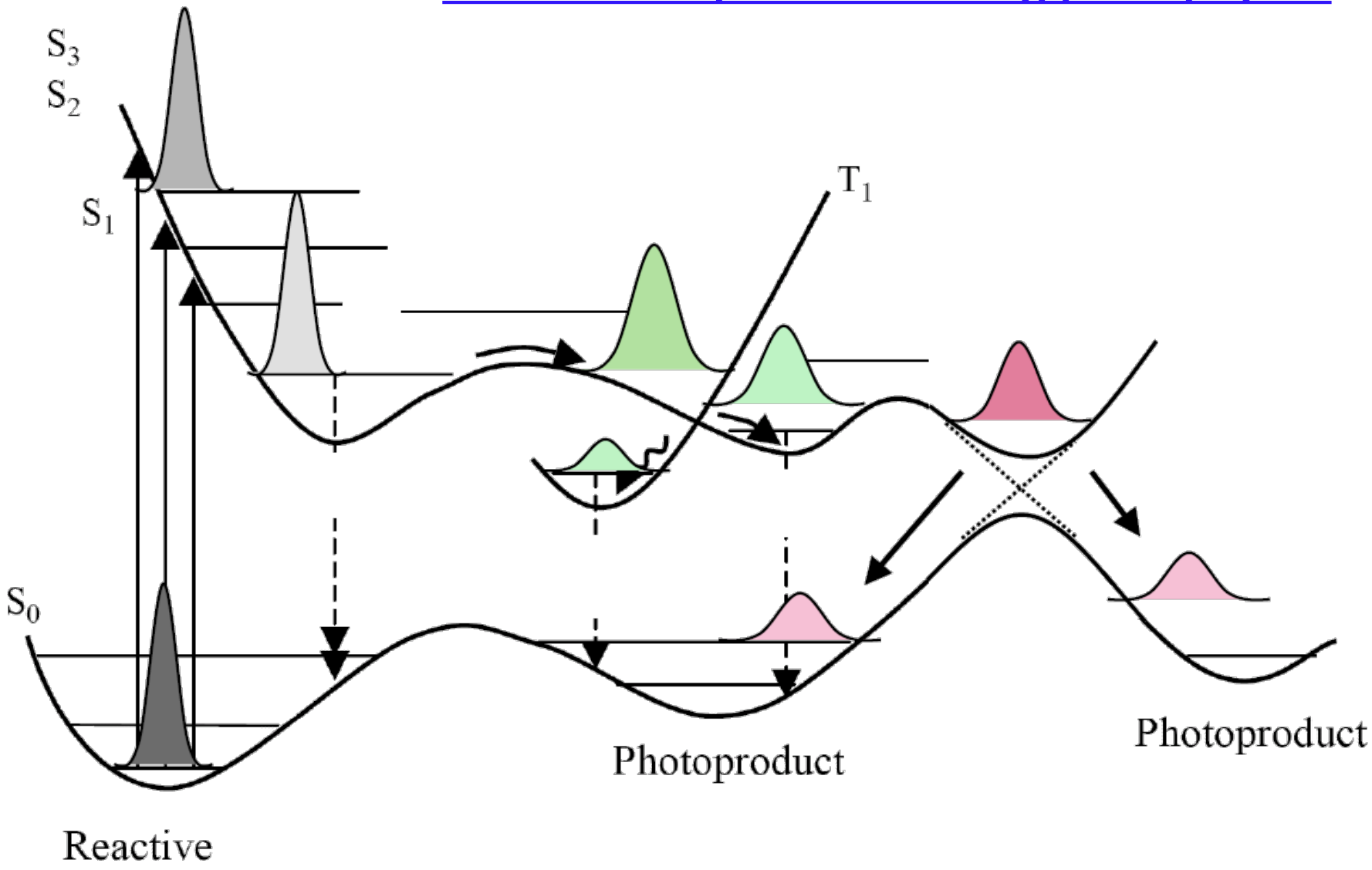
NAC-1

$$+\cancel{\sum_j} \sum_\alpha \left(-\frac{\hbar^2}{2M_\alpha}\right) \left\langle \phi^{BO}_{\underline{\underline{R}},k} \middle| \nabla^2_{\underline{\underline{R}}_\alpha} \middle| \phi^{BO}_{\underline{\underline{R}},k} \right\rangle \chi_k\left(\underline{\underline{R}},t\right)$$

NAC-2

**When does the adiabatic approximation fail?**

# The world of photochemistry/photophysics




From Ivano Tavernelli, Benasque TDDFT School 2012

## Another, very different, failure of the adiabatic approximation: Electronic flux density associated with nuclear motion vanishes

**Adiabatic approximation (dynamics on a single BO-PES)**

$$\Psi^{\text{adiab}}\left(\mathbf{R},\mathbf{r},t\right)=\chi\left(\mathbf{R},t\right)\Phi^{\text{BO}}\left(\mathbf{r}\middle|\mathbf{R}\right)$$

with non-degenerate, real-valued BO state $\Phi^{\text{BO}}\left(\mathbf{r}\middle|\mathbf{R}\right)$

**Time-dependent electronic (N-body, or one-body) density:**

$$\rho^{\text{adiab}}\left(r,t\right)=\int\left|\chi\left(R,t\right)\right|^2\left|\Phi^{\text{BO}}\left(r\middle|R\right)\right|^2 dR$$

**very close to true TD density**

$$\mathbf{j}^{\text{adiab}}\left(\mathbf{r},t\right)=\int \text{Im}\left(\left[\Psi^{\text{adiab}}\right]^{*}\partial_{\mathbf{r}}\Psi^{\text{adiab}}\right)d\mathbf{R}=\int\left|\chi\left(\mathbf{R},t\right)\right|^2\text{Im}\left(\Phi^{\text{BO}*}\partial_{\mathbf{r}}\Phi^{\text{BO}}\right)d\mathbf{R}=0$$

**completely wrong!! Dramatic failure of adiabatic approximation**

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**completely wrong!! Dramatic failure of adiabatic approximation**

**Hard problem: Many terms of Born-Huang expansion required**

**When the adiabatic approximation fails one has to go back to the Born-Huang expansion.**

**Problem: Born-Huang expansion numerically not feasible when very many terms are necessary, e.g. for**

- **local electronic flux density**
- **systems with dense set of BO PES (solids)**
- **strong initial excitation of many BO PES**

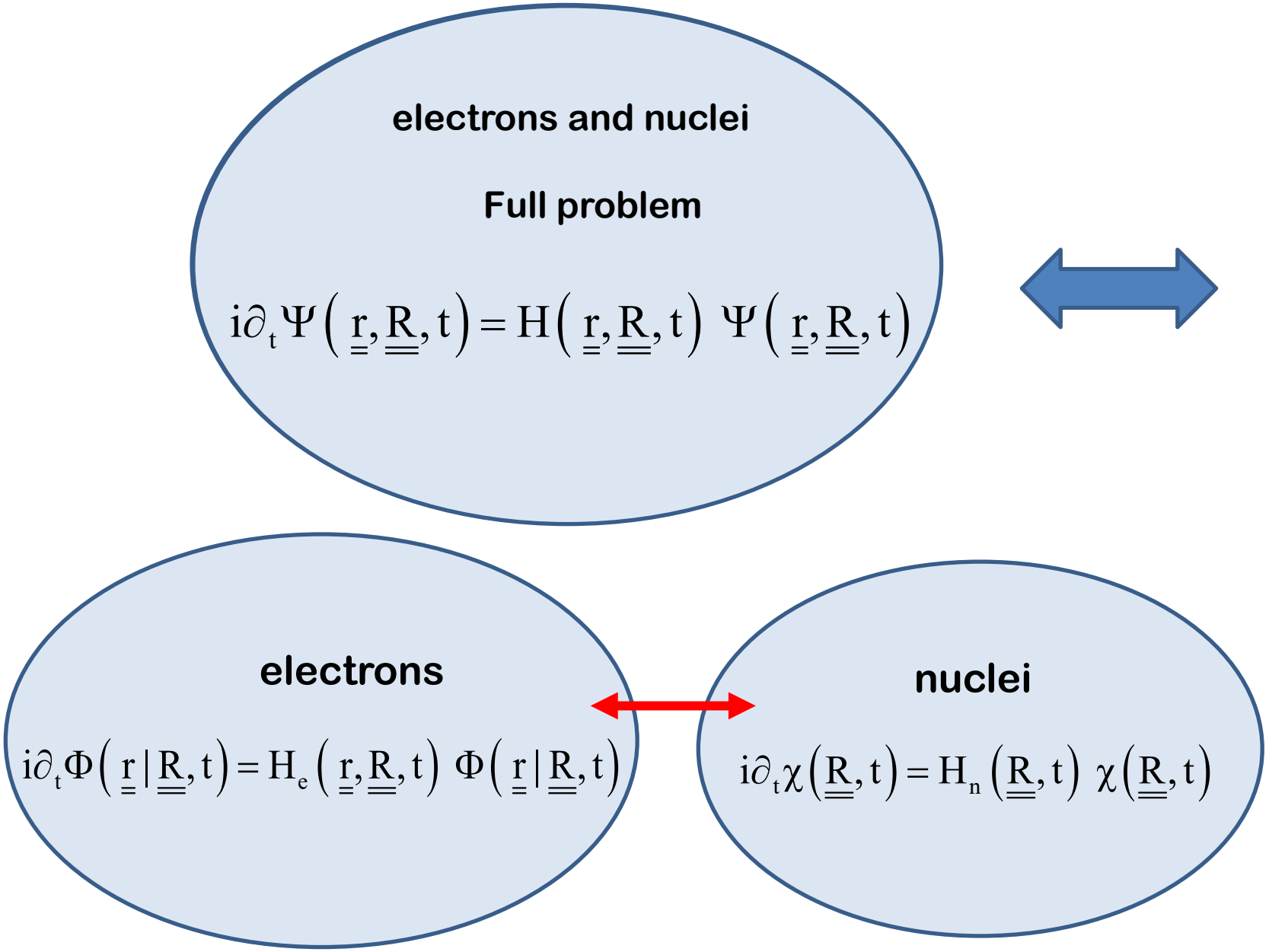
# The exact factorization

# The exact factorization

**"Exactification"** $\Psi^{\text{exact}}\left(\underline{\underline{r}},\underline{\underline{R}},t\right)=\Phi\left(\underline{\underline{r}}\,|\,\underline{\underline{R}},t\right)\cdot\chi\left(\underline{\underline{R}},t\right)$

**of the adiabatic approximation**

$$\Psi^{\text{adiab}}\left(\underline{\underline{r}},\underline{\underline{R}},t\right)=\Phi^{\text{BO}}_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right)\cdot\chi\left(\underline{\underline{R}},t\right)$$


electrons and nuclei
Full problem
$i\partial_t \Psi\left(\underline{r},\underline{\underline{R}},t\right) = H\left(\underline{r},\underline{\underline{R}},t\right)\ \Psi\left(\underline{r},\underline{\underline{R}},t\right)$
electrons
$i\partial_t \Phi\left(\underline{r}\,|\,\underline{\underline{R}},t\right) = H_e\left(\underline{r},\underline{\underline{R}},t\right)\ \Phi\left(\underline{r}\,|\,\underline{\underline{R}},t\right)$
nuclei
$i\partial_t \chi\left(\underline{\underline{R}},t\right) = H_n\left(\underline{\underline{R}},t\right)\ \chi\left(\underline{\underline{R}},t\right)$

# Theorem I

**The exact solution of**

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

**can be written in the form**

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

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

**A. Abedi, N.T. Maitra, E.K.U.G., PRL 105, 123002 (2010), JCP 137, 22A530 (2012).**
**Static case:**
**N. Gidopoulos, E.K.U.G. arXiv 0502433, Phil. Trans. R. Soc. A372, 20130059 (2014).**

## History

**1927 John von Neumann: Formulation of Quantum Mechanics in terms of conditional probabilities**

"Wahrscheinlichkeitstheoretischer Aufbau der Quantenmechanik."
Göttingen Nachrichten(1927)

**1975 Geoffrey Hunter Conditional probability amplitudes in wave mechanics.**

Int. J. Quant. Chem. **9**, 237 (1975) ….

No equations of motion were deduced for the conditional and marginal amplitudes

# Theorem II

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

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

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

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

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

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

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

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

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

$$\left(\mu\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\big(-i\nabla_\nu+A_\nu(\underline{\underline{R}},t)\big)^2+\in(\underline{\underline{R}},t)\right)\chi(\underline{\underline{R}},t)=i\partial_t\chi(\underline{\underline{R}},t)$$

**Measure energies in a.u. and nuclear masses in multiples of a reference mass $M_p$, (e.g. proton mass), a small dimensionless parameter appears: $\mu = m_e/M_p$**

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

$$\in\left(\underline{\underline{R}},t\right)=\left\langle\Phi_{\underline{\underline{R}}}(t)\middle|H^{BO}\middle|\Phi_{\underline{\underline{R}}}(t)\right\rangle+\sum_\nu^{N_n}\left\{\left\langle\nabla_\nu\Phi_{\underline{\underline{R}}}(t)\middle|\nabla_\nu\Phi_{\underline{\underline{R}}}(t)\right\rangle-A_\nu\left(\underline{\underline{R}},t\right)^2\right\}/2M_\nu+\left\langle\Phi_{\underline{\underline{R}}}(t)\middle|-i\partial_t\middle|\Phi_{\underline{\underline{R}}}(t)\right\rangle$$

## Properties of the exact electronic EoM:

- Non-linear equation in $\phi_R(rt)$ because of $A[\phi]$
- Non-adiabatic terms are not operators in the electronic Hilbert space
- in BO-basis: non-Hermitian matrix, still the time-propagation conserves norm
- Electronic EoM depends on $\chi(Rt)$

## Properties of the exact nuclear EoM:

- Standard TDSE
- Scalar potential is $N_n$-body interaction
- Vector potential is $N_n$-body operator, i.e. 3D vector field depending on

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

$$\in\left(\underline{\underline{R}},t\right)=\left\langle\Phi_{\underline{\underline{R}}}(t)\middle|H^{BO}\middle|\Phi_{\underline{\underline{R}}}(t)\right\rangle+\sum_\nu^{N_n}\left\{\left\langle\nabla_\nu\Phi_{\underline{\underline{R}}}(t)\middle|\nabla_\nu\Phi_{\underline{\underline{R}}}(t)\right\rangle-A_\nu\left(\underline{\underline{R}},t\right)^2\right\}/2M_\nu+\left\langle\Phi_{\underline{\underline{R}}}(t)\middle|-i\partial_t\middle|\Phi_{\underline{\underline{R}}}(t)\right\rangle$$

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**essential for decoherence**

## Properties of the exact nuclear EoM:

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**On the exact level, the electronic and nuclear EoMs following from the factorization are equivalent to the full TDSE.**

**Crucial advantage:**

**Nuclei and electrons satisfy separate equations**
**$\Rightarrow$ Useful starting point to make approximations**

**Which approximations?**

- **Perturbation theory for non-adiabatic terms in electronic EoM**
- **Electronic-structure methods for electronic EOM, e.g. TDDFT**
- **classical EOM for nuclei, single trajectory vs swarm of trajectories**

## Use electronic EoM of exact factorization and treat the non-adiabatic terms in 1st-order perturbation theory to determine the electronic flux density

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

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

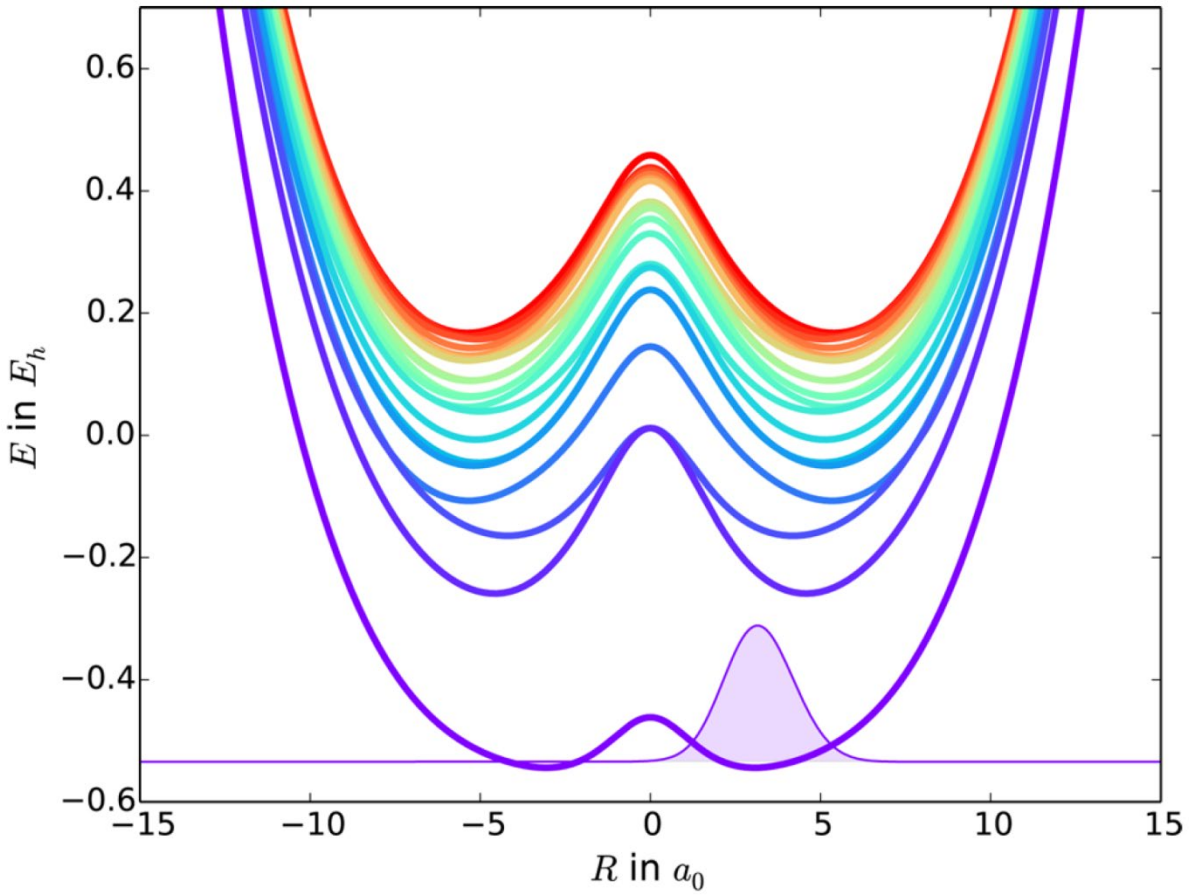
A. Schild, F. Agostini, EKUG., J. Phys. Chem. A 120, 3316 (2016)

A. Scherrer, F Agostini, D. Sebastiani, EKUG., R. Vuilleumier, JCP 143, 074106 (2015) , and PRX 7, 031035 (2017).

**Model Study:**

One electron in 2D (x,y), one nucleus in 1D (R), and another very heavy nucleus clamped at the origin, all interacting with soft Coulomb potentials

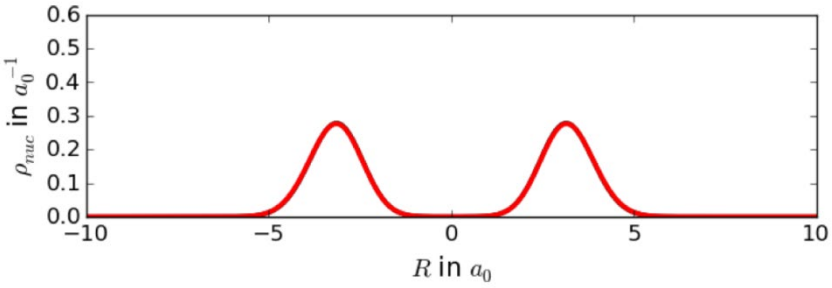
$$V = -\frac{1}{\sqrt{x^2 + y^2 + \alpha_2}} + \left(\frac{R}{R_0}\right)^4 + \frac{1}{\sqrt{R^2 + \beta}} - \frac{1}{\sqrt{(R - x)^2 + y^2 + \alpha_1}}$$

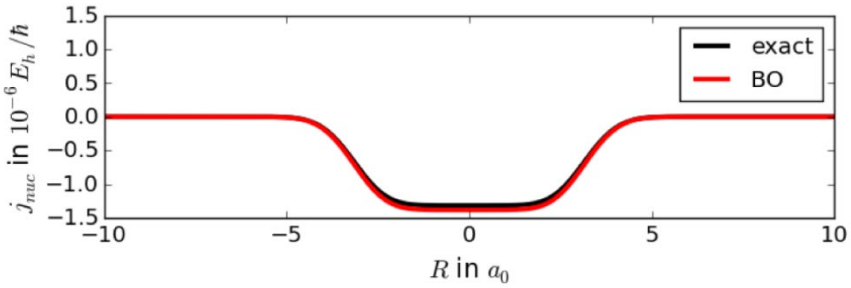


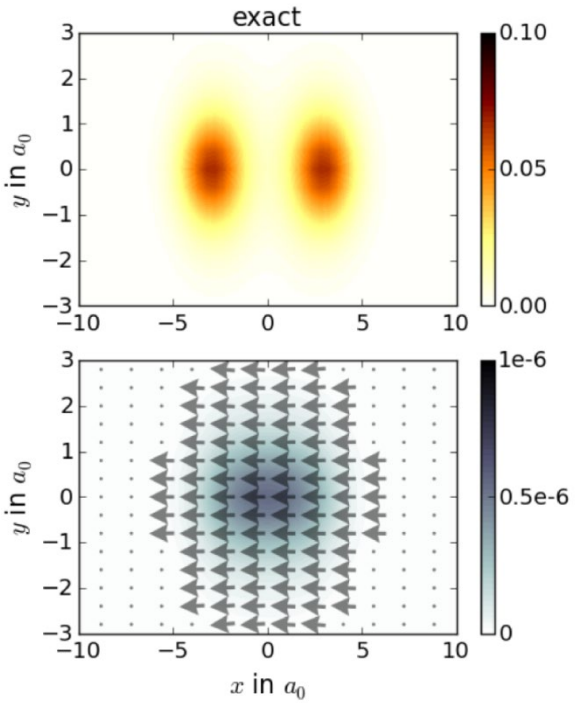

**Axel Schild**

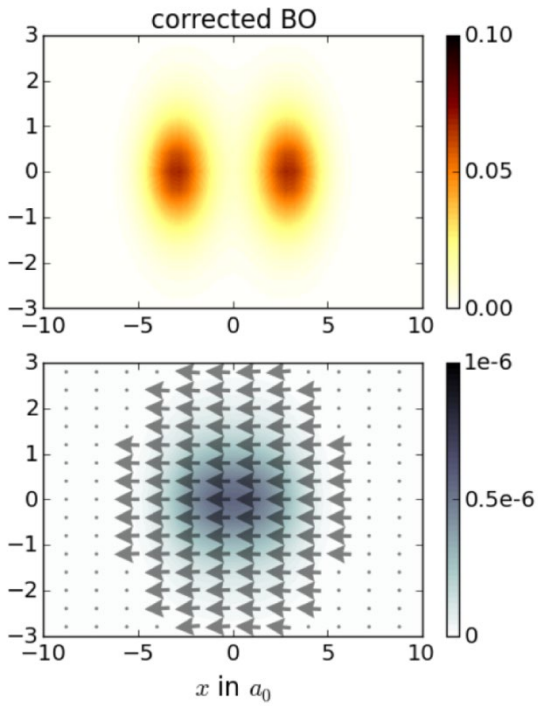
**Federica Agostini**

Lowest 20 Born–Oppenheimer potential energy surfaces and initial BO wave function.


$\rho_{nuc}$ in $a_0^{-1}$
$R$ in $a_0$


exact
BO
$j_{nuc}$ in $10^{-6}\,E_h/\hbar$
$R$ in $a_0$


exact
$y$ in $a_0$
$x$ in $a_0$


corrected BO
$x$ in $a_0$

# Vibrational circular dichroism

**Absorption difference between lefthanded and righthanded circularly polarized light:**

$$\Delta \in (\omega) = 4\frac{8\pi^3}{3Vhcn(\omega)}\sum_k R_k \omega \delta(\omega - \omega_k)$$

with harmonic vibrational frequencies $\omega_k$ and

**Rotational strength:** $$R_k = \frac{\partial \langle \hat{\boldsymbol{m}} \rangle}{\partial \dot{q}_k} \cdot \frac{\partial \langle \hat{\dot{\boldsymbol{\mu}}} \rangle}{\partial \dot{q}_k} \langle \dot{q}_k \rangle^2$$

Daniel Sebastiani

Rodolphe Vuilleumier

Federica Agostini

$$\hat{\dot{\boldsymbol{\mu}}} = \hat{\dot{\boldsymbol{\mu}}}^e + \hat{\dot{\boldsymbol{\mu}}}^n = -\sum_{i=1}^{N_e} \frac{e}{m} \hat{\boldsymbol{p}}_i + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{M_\upsilon} \hat{\boldsymbol{P}}_\upsilon$$

$$\hat{\boldsymbol{m}} = \hat{\boldsymbol{m}}^e + \hat{\boldsymbol{m}}^n = -\sum_{i=1}^{N_e} \frac{e}{2mc} \hat{\boldsymbol{r}}_i \times \hat{\boldsymbol{p}}_i + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{2M_\upsilon c} \hat{\boldsymbol{R}}_\upsilon \times \hat{\boldsymbol{P}}_\upsilon$$

**Electronic contributions to the electric current and to the magnetic dipole moment vanish identically in the adiabatic approximation.**

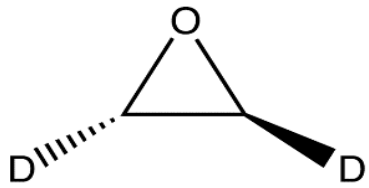
**Employ the exact factorization:**

$$\left\langle \hat{\dot{\boldsymbol{\mu}}} \right\rangle_\Psi = \int d\mathbf{R} \chi^* (\mathbf{R},t) \left[ \left\langle \Phi_{\mathbf{R}}(t) \middle| \hat{\dot{\boldsymbol{\mu}}}^e \middle| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}} + \hat{\dot{\boldsymbol{\mu}}}^n + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{M_\upsilon} \boldsymbol{A}_\upsilon (\mathbf{R},t) \right] \chi(\mathbf{R},t)$$

$$\left\langle \hat{\boldsymbol{m}} \right\rangle_\Psi = \int d\mathbf{R} \chi^* (\mathbf{R},t) \left[ \left\langle \Phi_{\mathbf{R}}(t) \middle| \hat{\boldsymbol{m}}^e \middle| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}} + \hat{\boldsymbol{m}}^n + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{2M_\upsilon c} \hat{\mathbf{R}}_\upsilon \times \hat{\mathbf{A}}_\upsilon (\mathbf{R},t) \right] \chi(\mathbf{R},t)$$

**and evaluate $\Phi_{\mathbf{R}}$ within first-order PT, employing DFT-PT**

**Normal modes, dipole and rotational strengths, for (S)-$d_2$-oxirane.**

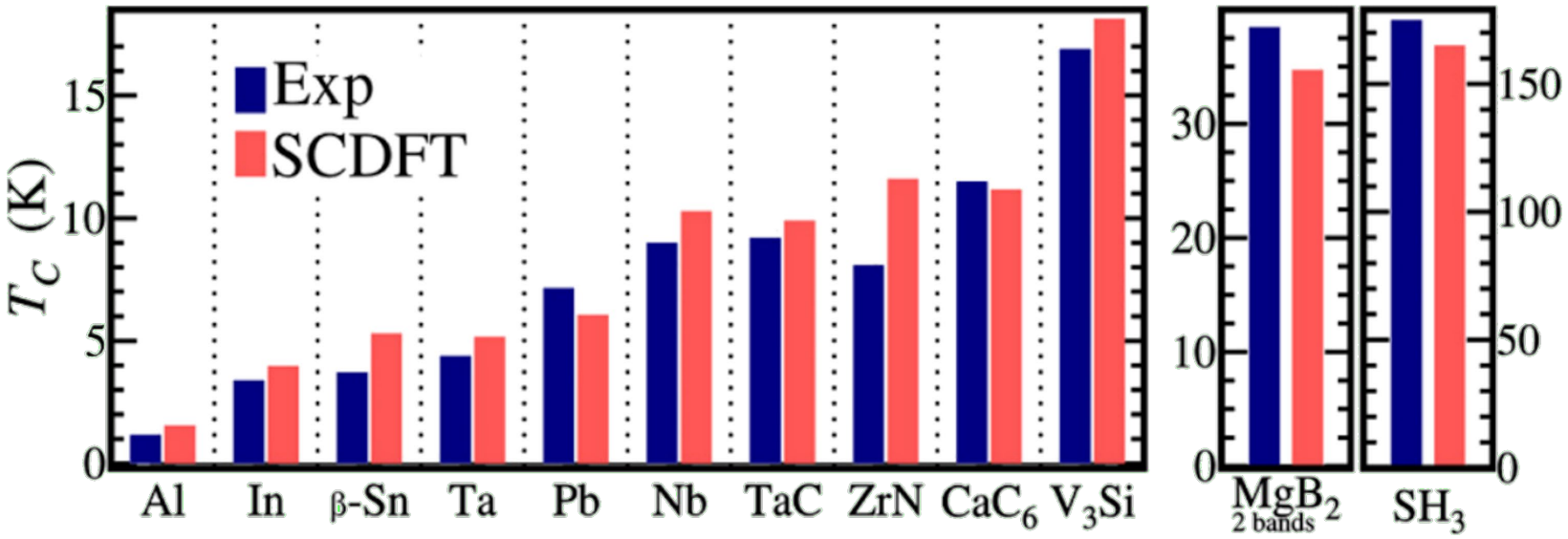



| | $D_{MFP}$ | $D_{NVP}$ | $R_{MFP}$ | $R_{NVP}$ |
|---|---|---|---|---|
| $\tilde{\upsilon}(cm^{-1})$ | $(10^{-44}\ esu^2\ cm^2)$ | | $(10^{-44}\ esu^2\ cm^2)$ | |
| 647.50 | 0.55 | 0.85 | −0.35 | −0.45 |
| 733.42 | 123.35 | 124.88 | 8.73 | 10.54 |
| 769.76 | 53.44 | 51.77 | 3.17 | 3.29 |
| 856.38 | 145.31 | 145.55 | 4.31 | 2.70 |
| 894.67 | 9.78 | 10.24 | −3.37 | −3.89 |
| 936.33 | 39.73 | 39.24 | −19.14 | −20.26 |
| 1088.21 | 3.79 | 4.44 | 6.95 | 8.34 |
| 1093.95 | 1.41 | 1.71 | −3.98 | −4.97 |
| 1210.44 | 26.26 | 26.09 | 9.56 | 10.45 |
| 1326.86 | 0.34 | 0.37 | −0.91 | −0.76 |
| 1377.38 | 11.65 | 10.78 | −7.50 | −8.17 |
| 2235.16 | 49.17 | 50.88 | −22.60 | −22.90 |
| 2244.19 | 12.63 | 12.81 | 16.80 | 16.78 |
| 3047.68 | 11.43 | 11.66 | −32.80 | −32.59 |
| 3054.15 | 58.64 | 60.16 | 46.63 | 47.04 |

**A. Scherrer, F Agostini, D. Sebastiani, EKUG, R. Vuilleumier, JCP 143, 074106 (2015)**
**MFP values from P. J. Stephens, J. Phys. Chem. 89, 748 (1985).**

# Phonon-mediated superconductivity

**The same strategy (lowest order PT in μ) is employed in the ab-initio theory of phonon-mediated superconductivity**




Camilla Pellegrini

Antonio Sanna

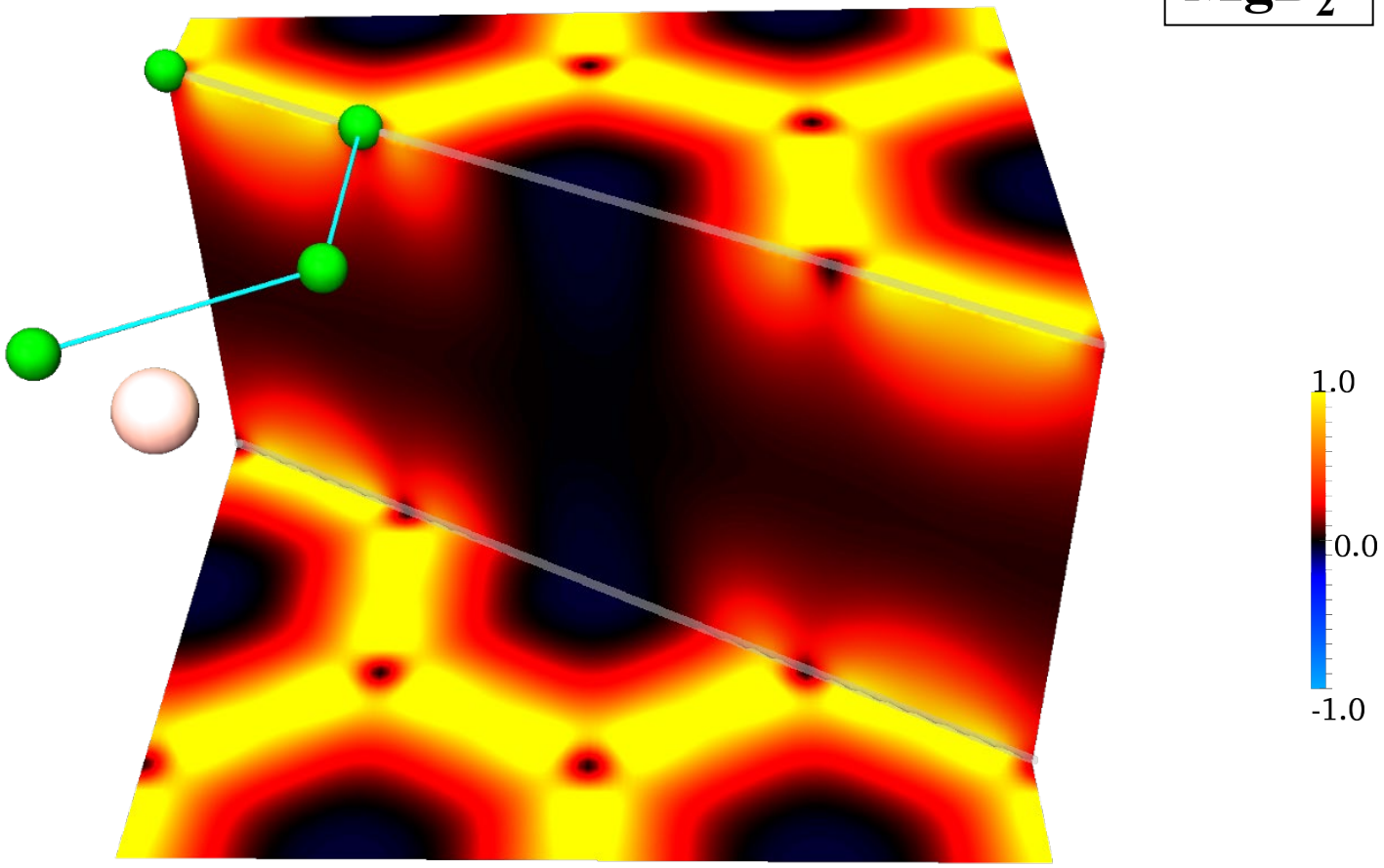
A Sanna, C Pellegrini, EKUG, PRL 125, 057001 (2020).

## Order parameter of superconductivity in real space is an output of the theory:

$$\chi\left(r,r'\right)=\left\langle \hat{\psi}_{\uparrow}(r)\hat{\psi}_{\downarrow}(r')\right\rangle =\sum_{nk}\chi_{nk}\varphi_{nk}\left(r\right)\varphi_{nk}^{*}\left(r'\right)$$

# $\chi(r,r)$ as function of r

$MgB_2$




A. Linscheid, A. Sanna, A. Floris, E. K. U. Gross,
Phys. Rev. Lett. 115, 097002 (2015).

**The superconducting OP $\chi(r,r)$ "lives" in the chemical bonds**

# Non-adiabaticity in nuclear motion

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

# Non-adiabaticity in nuclear motion

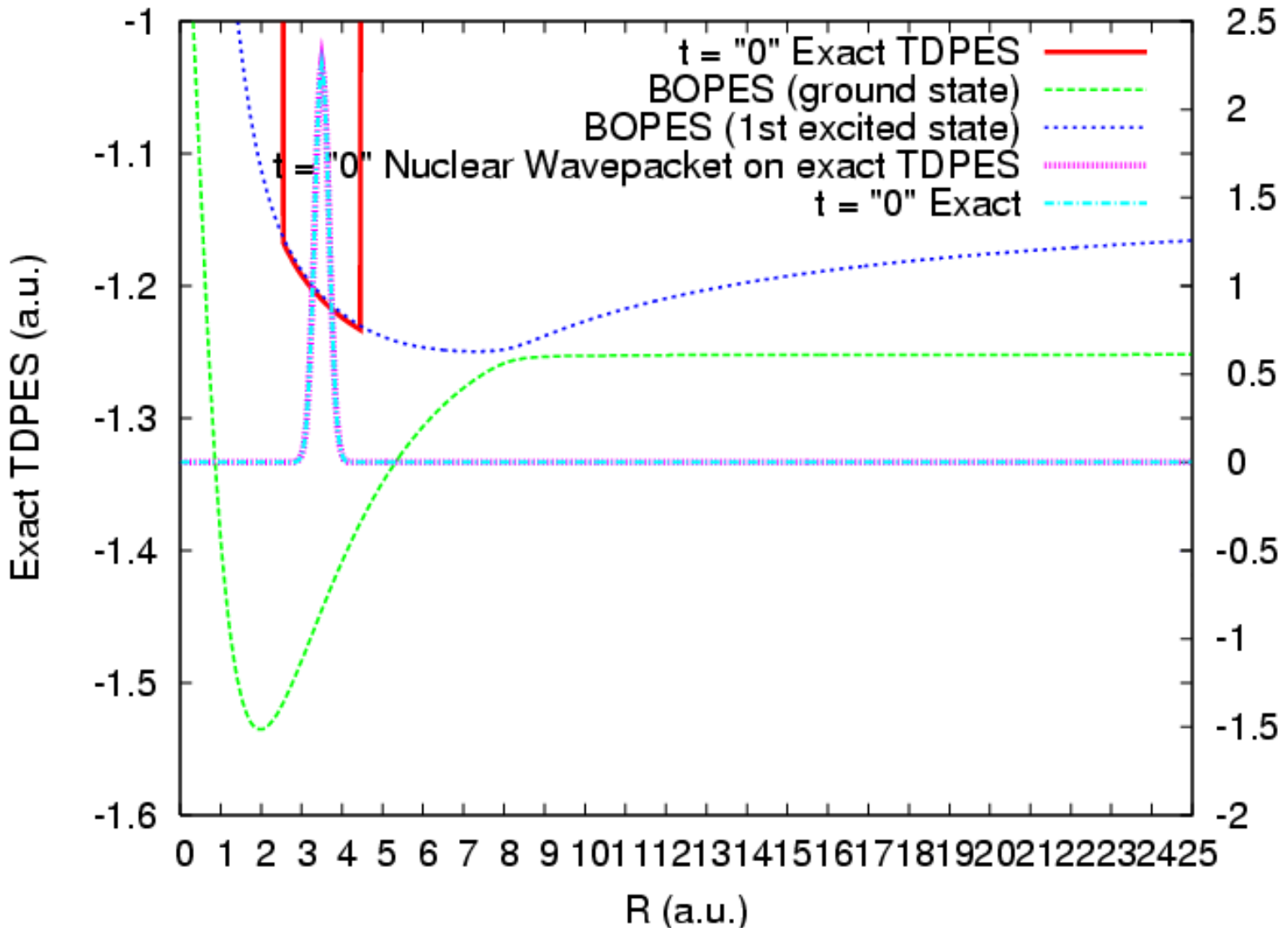
$$\left(\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu+A_\nu\left(\underline{\underline{R}},t\right)\right)^2+\in\left(\underline{\underline{R}}\,t\right)\right)\chi\left(\underline{\underline{R}},t\right)=i\partial_t\chi\left(\underline{\underline{R}},t\right)$$

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

# Example: Nuclear wave packet going through an avoided crossing, using 1D model Hamiltonian with soft Coulomb potentials

**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
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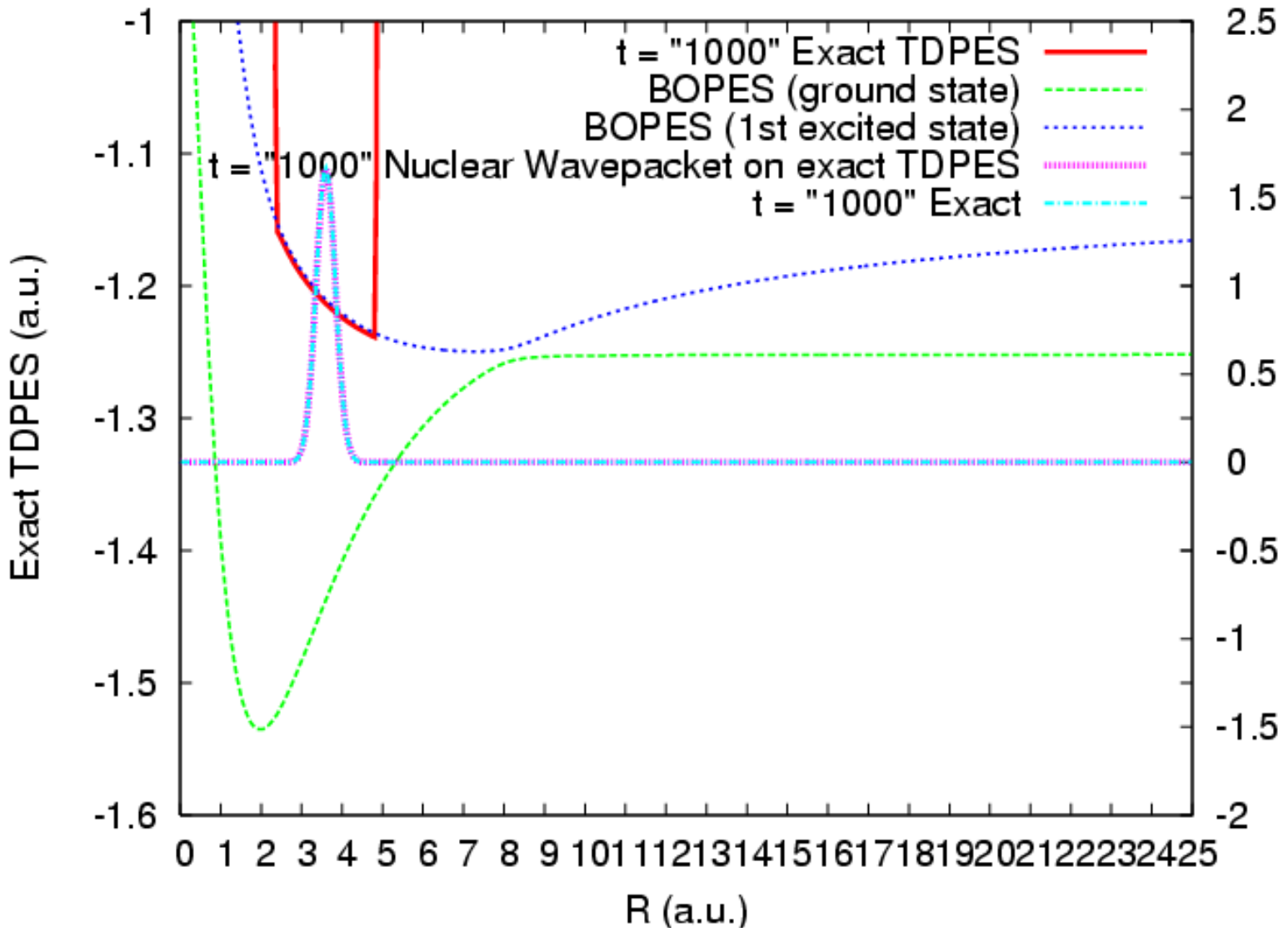
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (1st excited state)
t = "1000" Nuclear Wavepacket on exact TDPES
t = "1000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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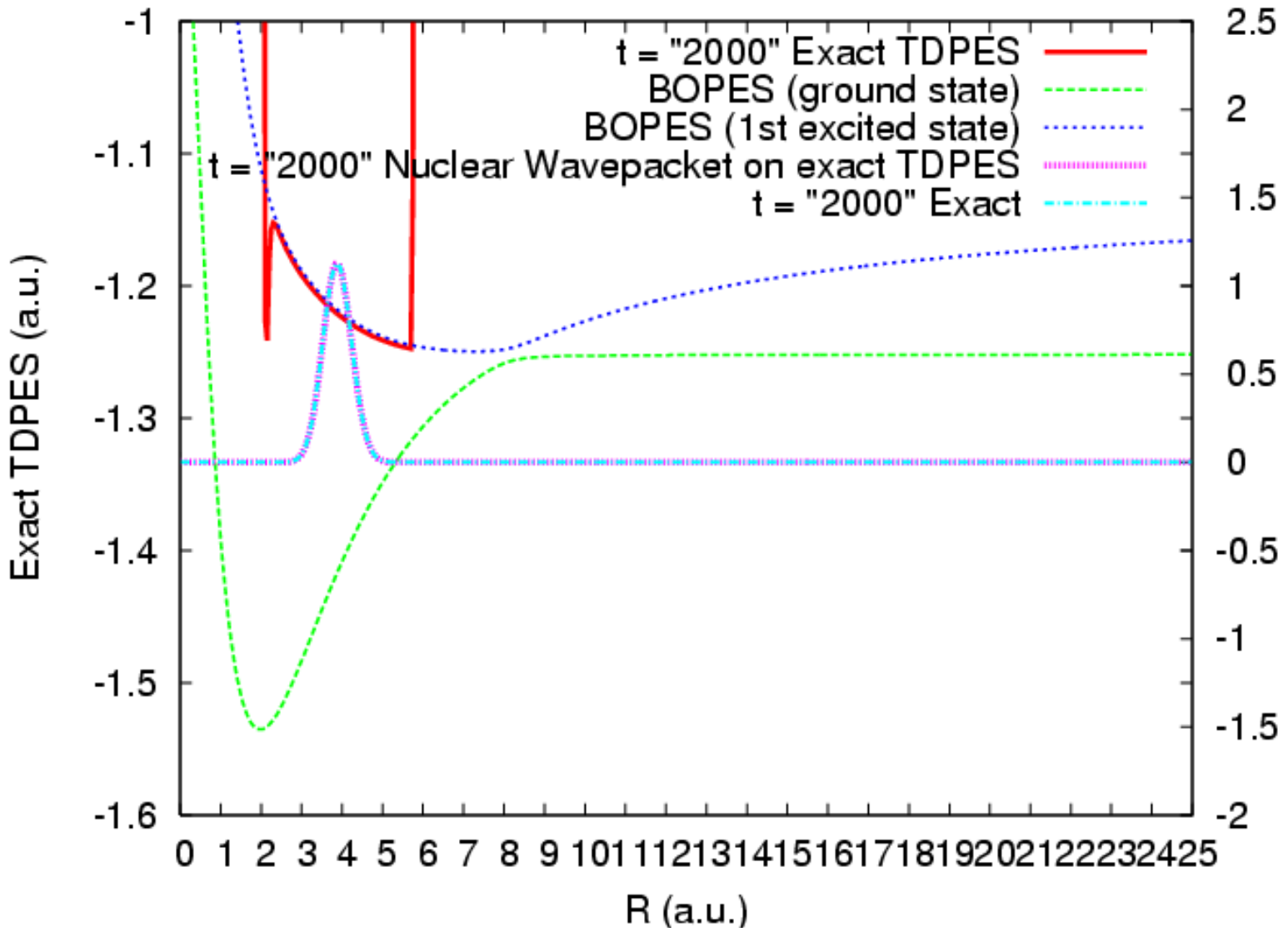
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
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t = "2000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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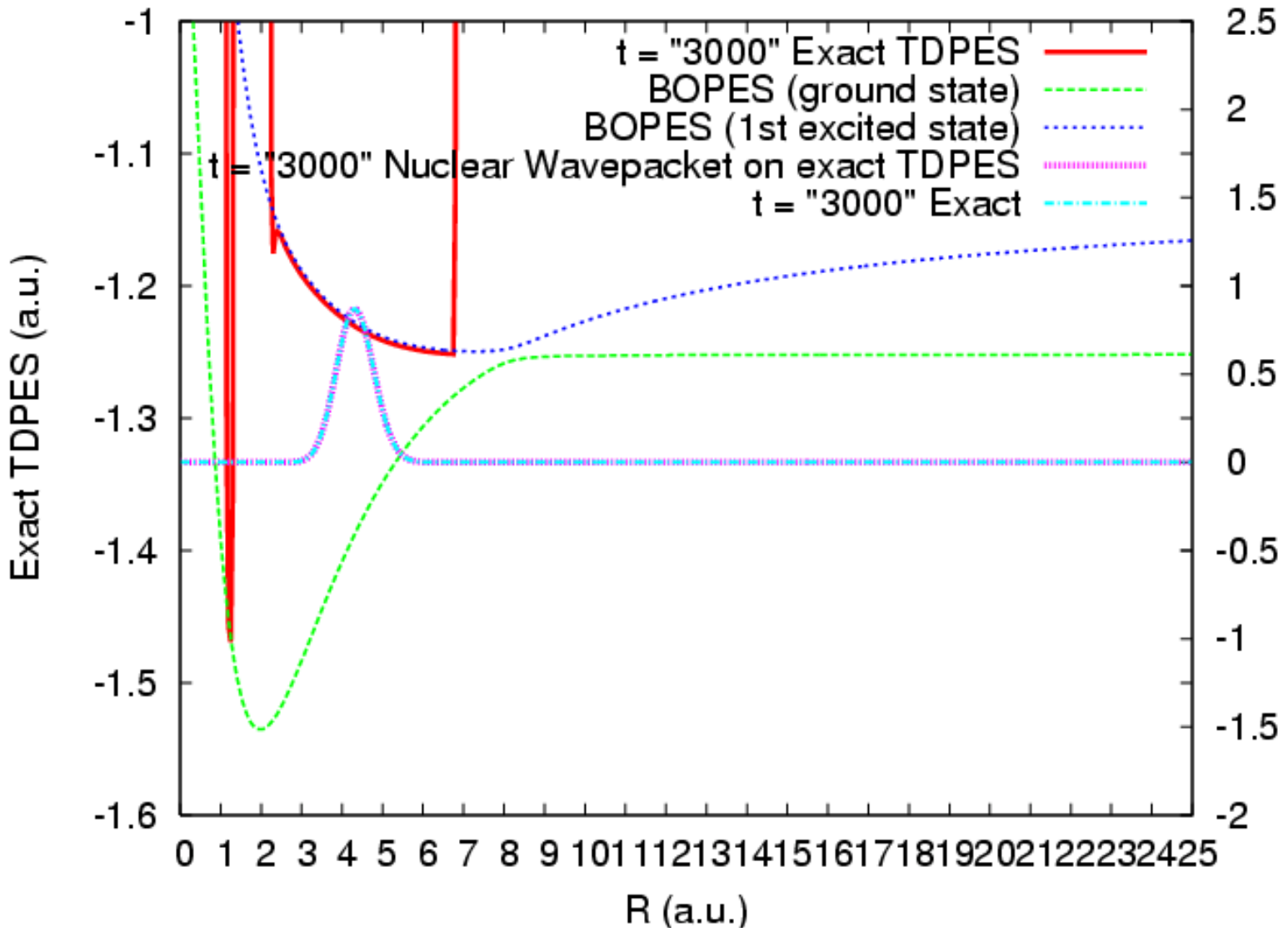
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "3000" Nuclear Wavepacket on exact TDPES
t = "3000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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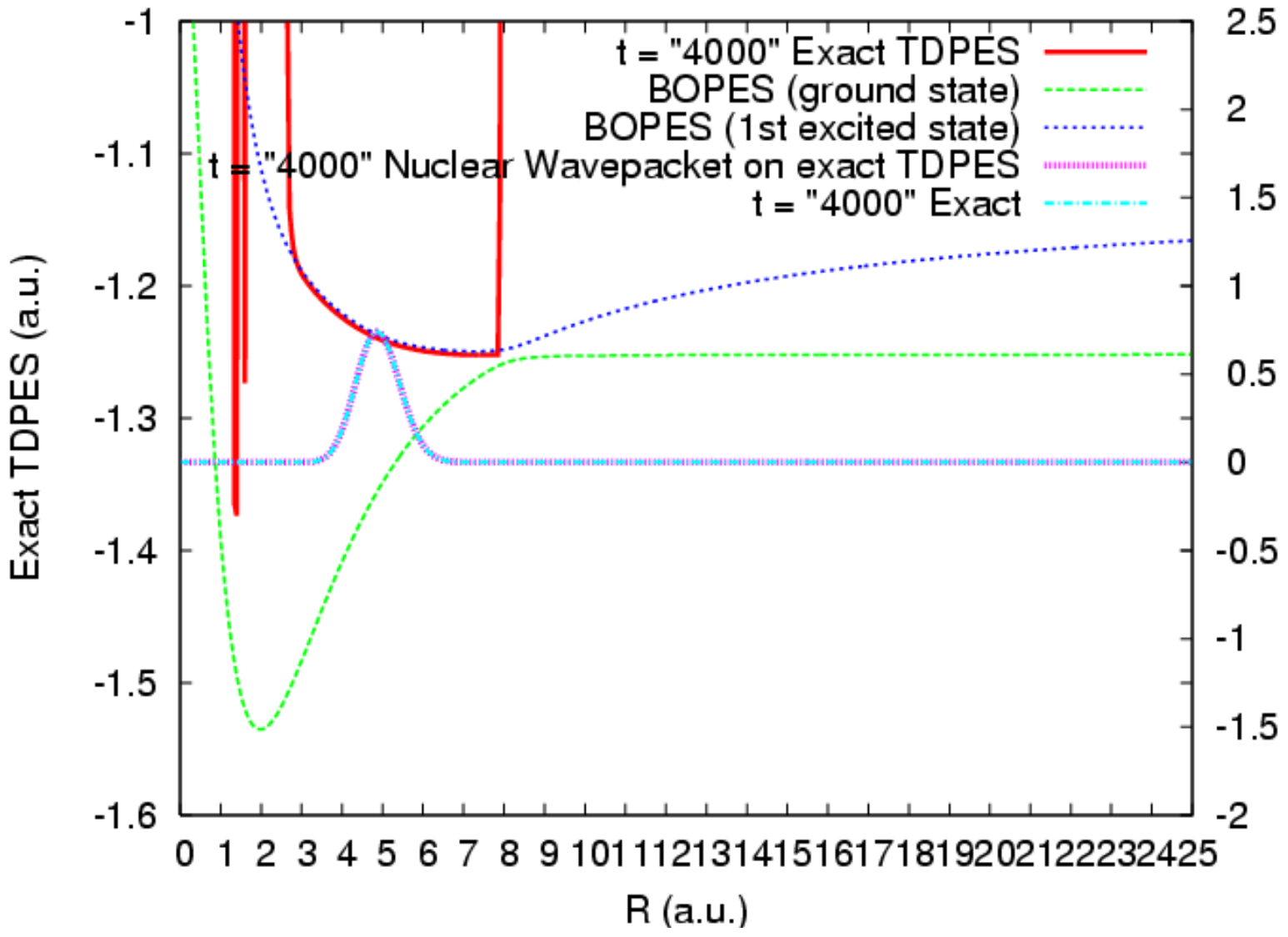
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "4000" Nuclear Wavepacket on exact TDPES
t = "4000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
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-1.6
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1.5
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-1.5
-2
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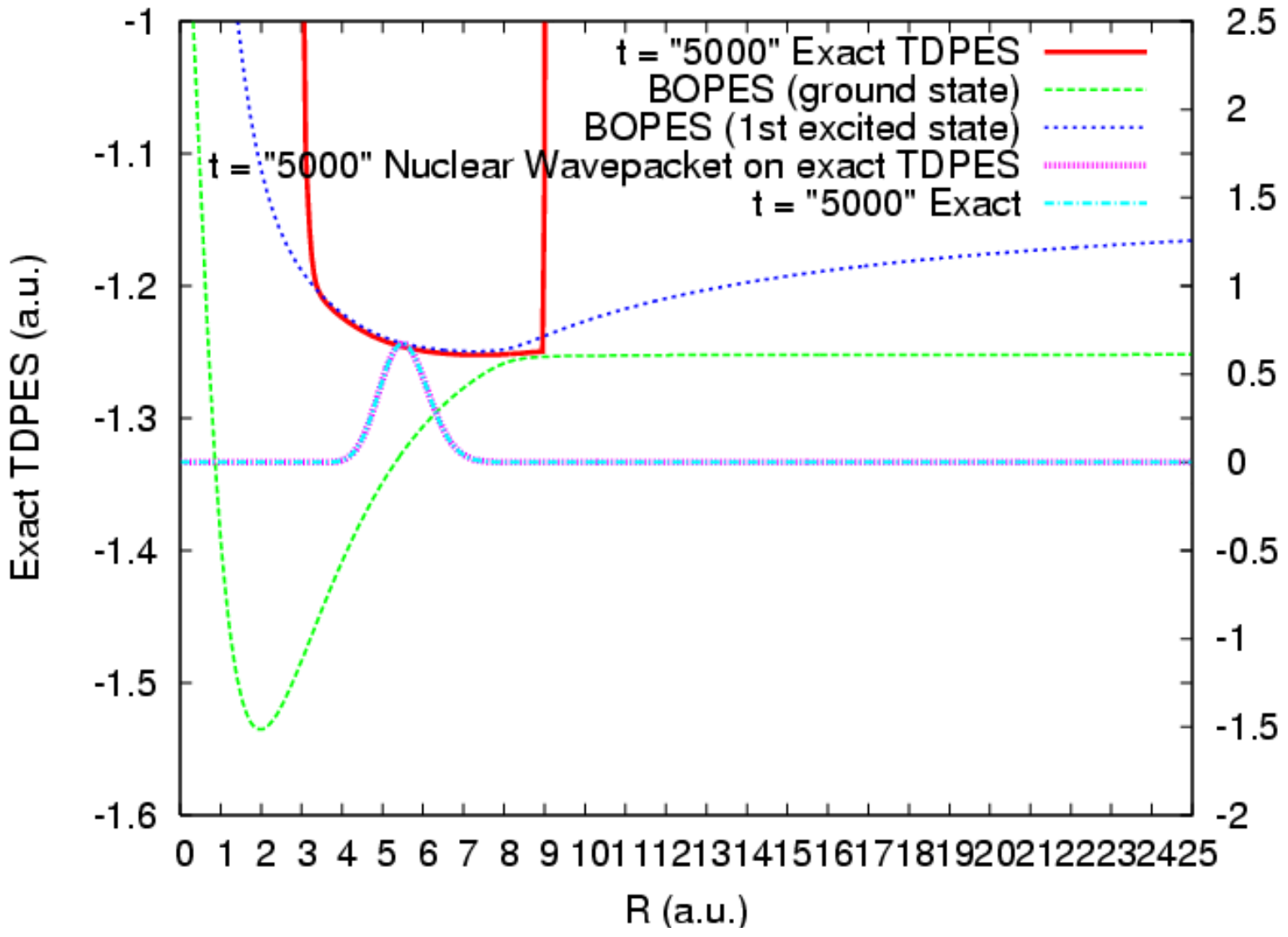
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BOPES (1st excited state)
t = "5000" Nuclear Wavepacket on exact TDPES
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Exact TDPES (a.u.)
R (a.u.)
-1
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-1.2
-1.3
-1.4
-1.5
-1.6
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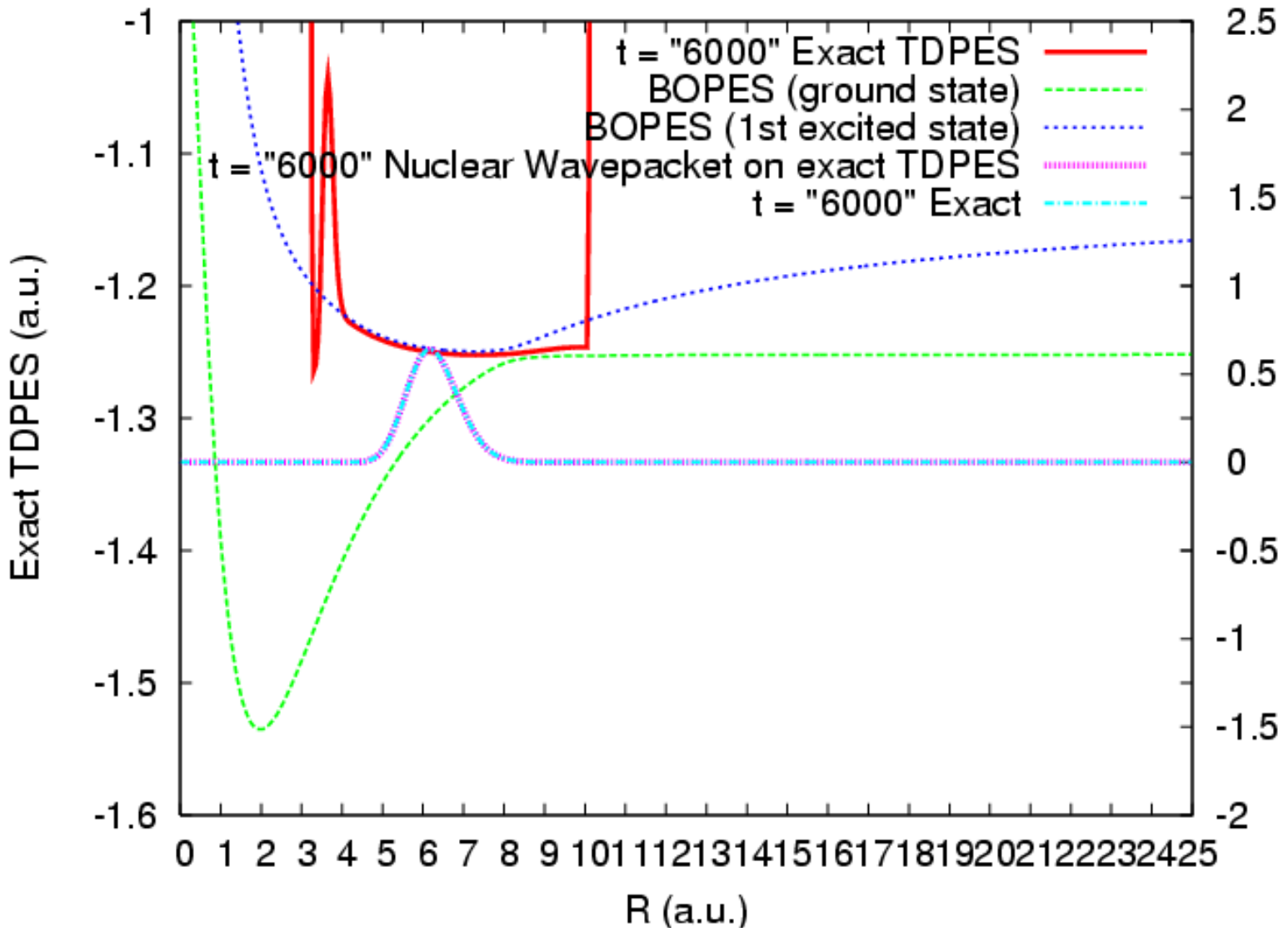
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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R (a.u.)
-1
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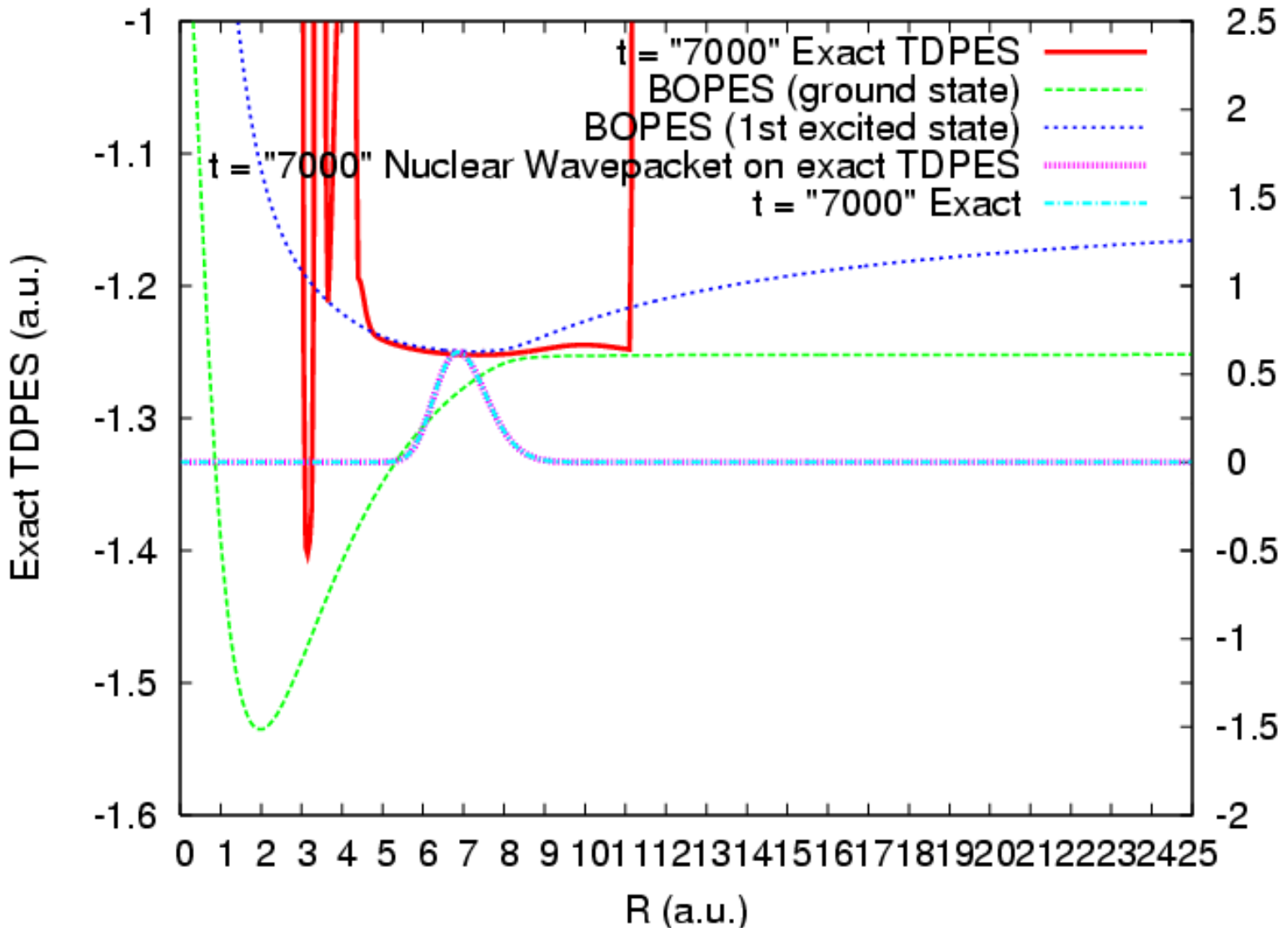
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BOPES (1st excited state)
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R (a.u.)
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-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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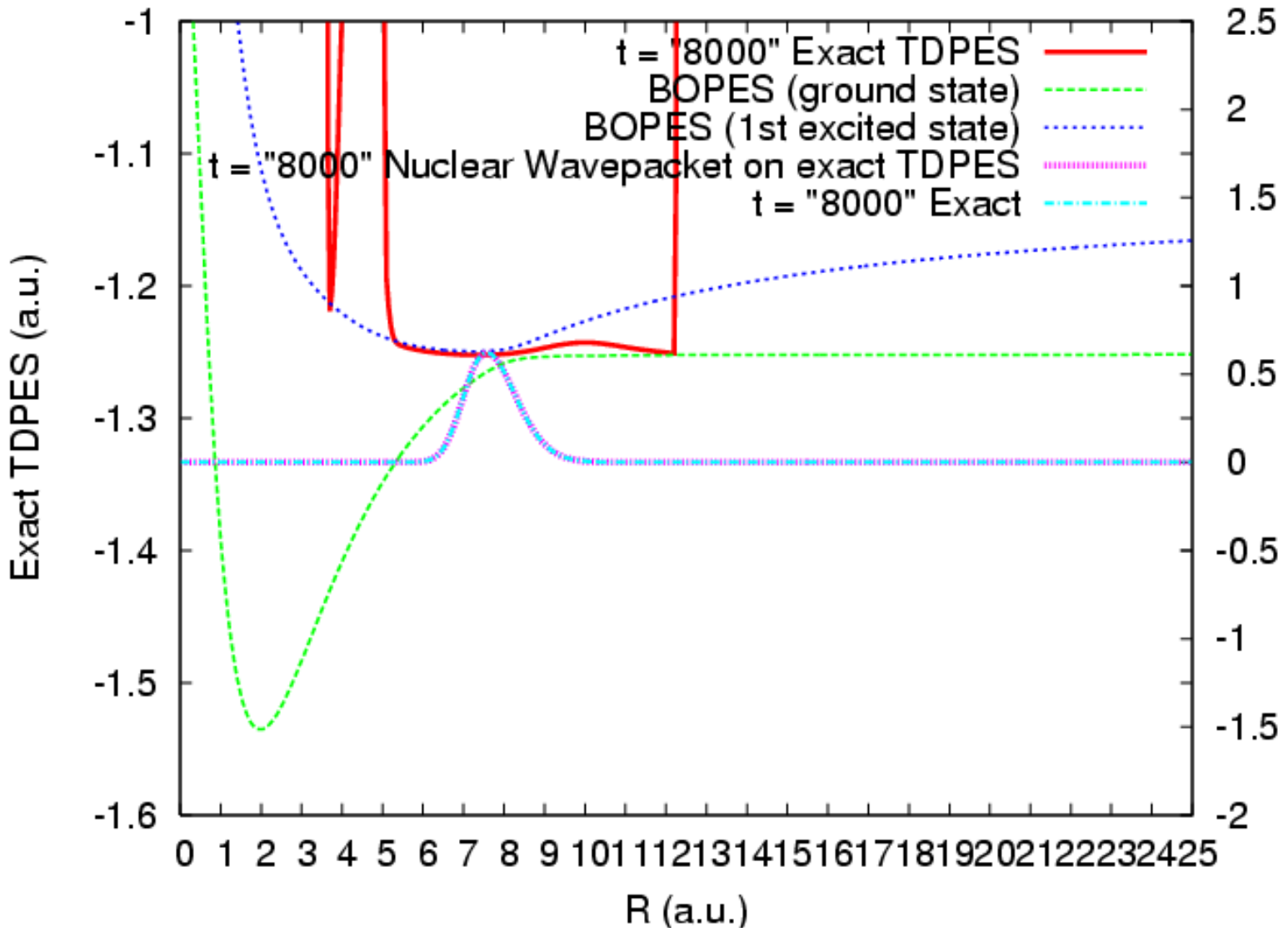
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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R (a.u.)
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-1.2
-1.3
-1.4
-1.5
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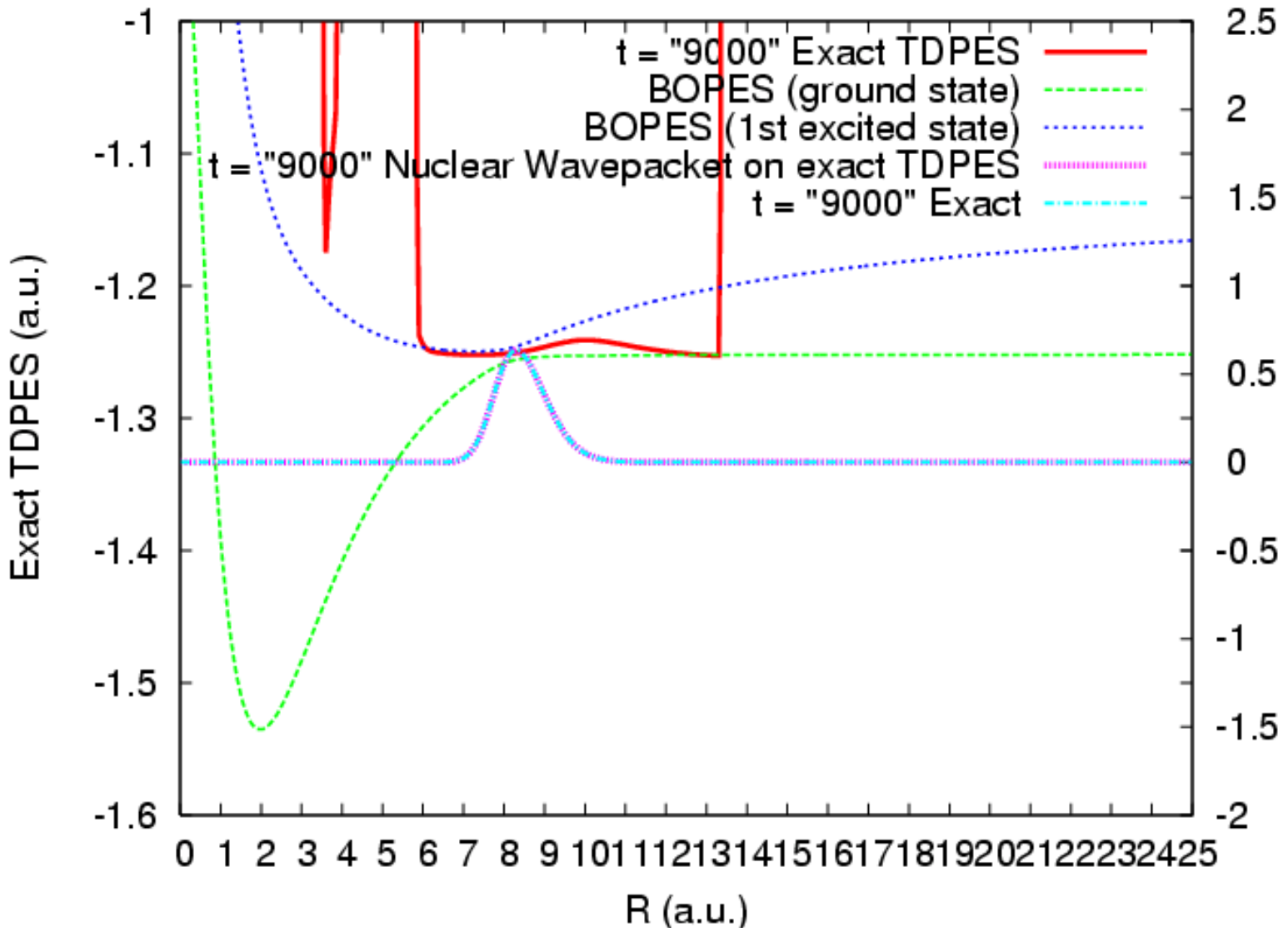
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R (a.u.)
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-1.2
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-1.5
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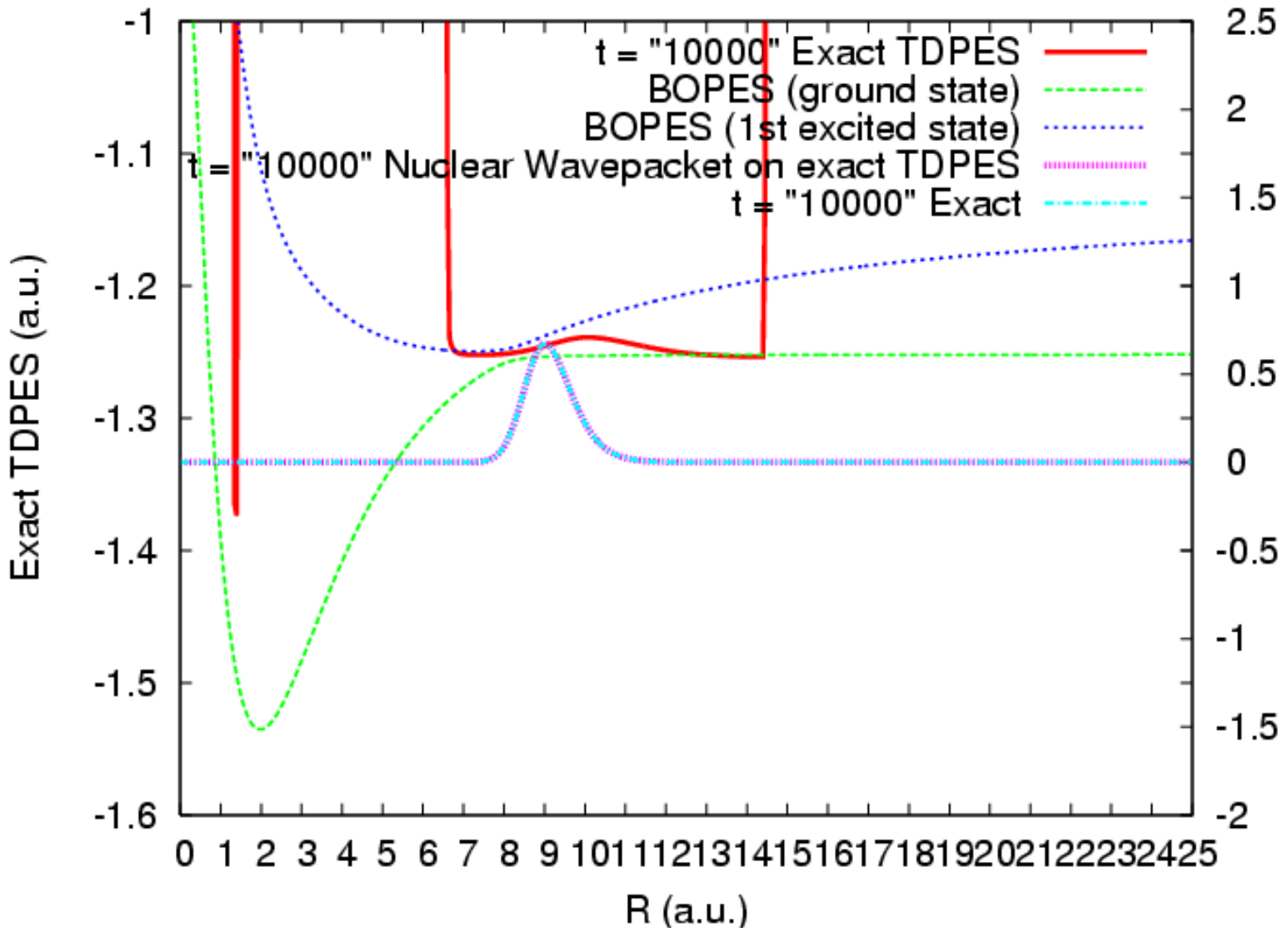
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R (a.u.)
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-1.5
-1.6
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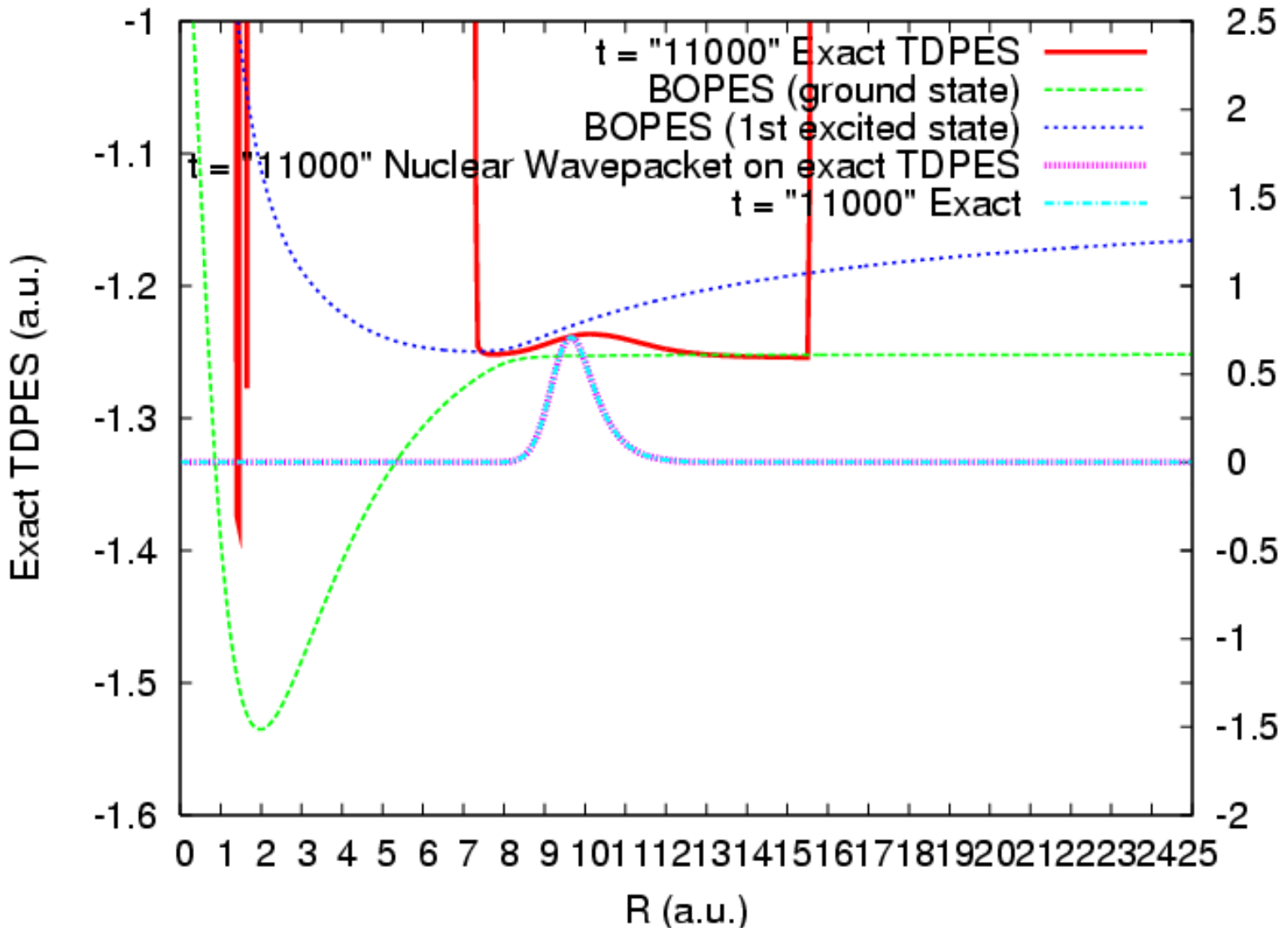
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BOPES (1st excited state)
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R (a.u.)
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-1.2
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-1.4
-1.5
-1.6
2.5
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-1.5
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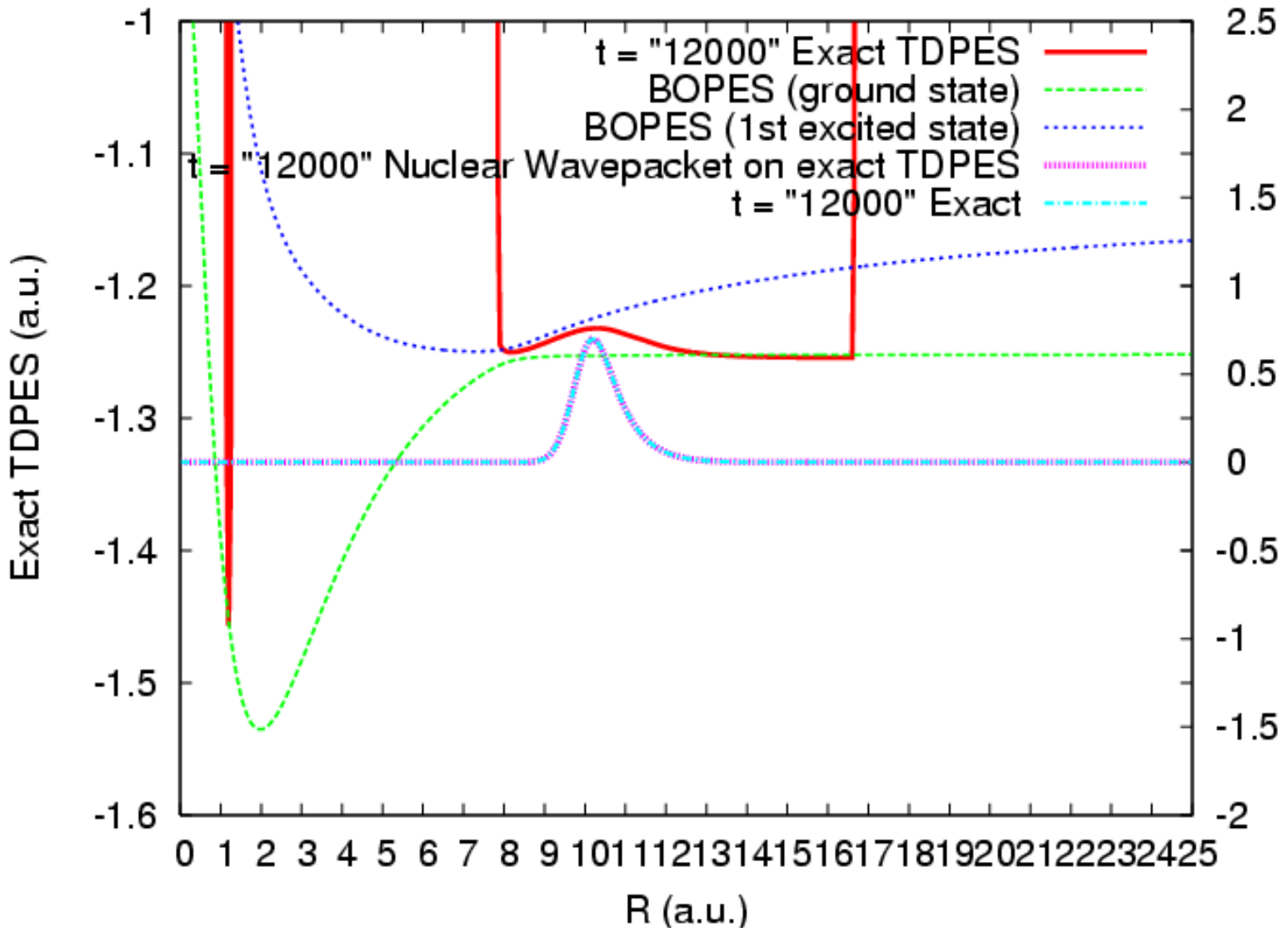
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BOPES (1st excited state)
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t = "12000" Exact
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R (a.u.)
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-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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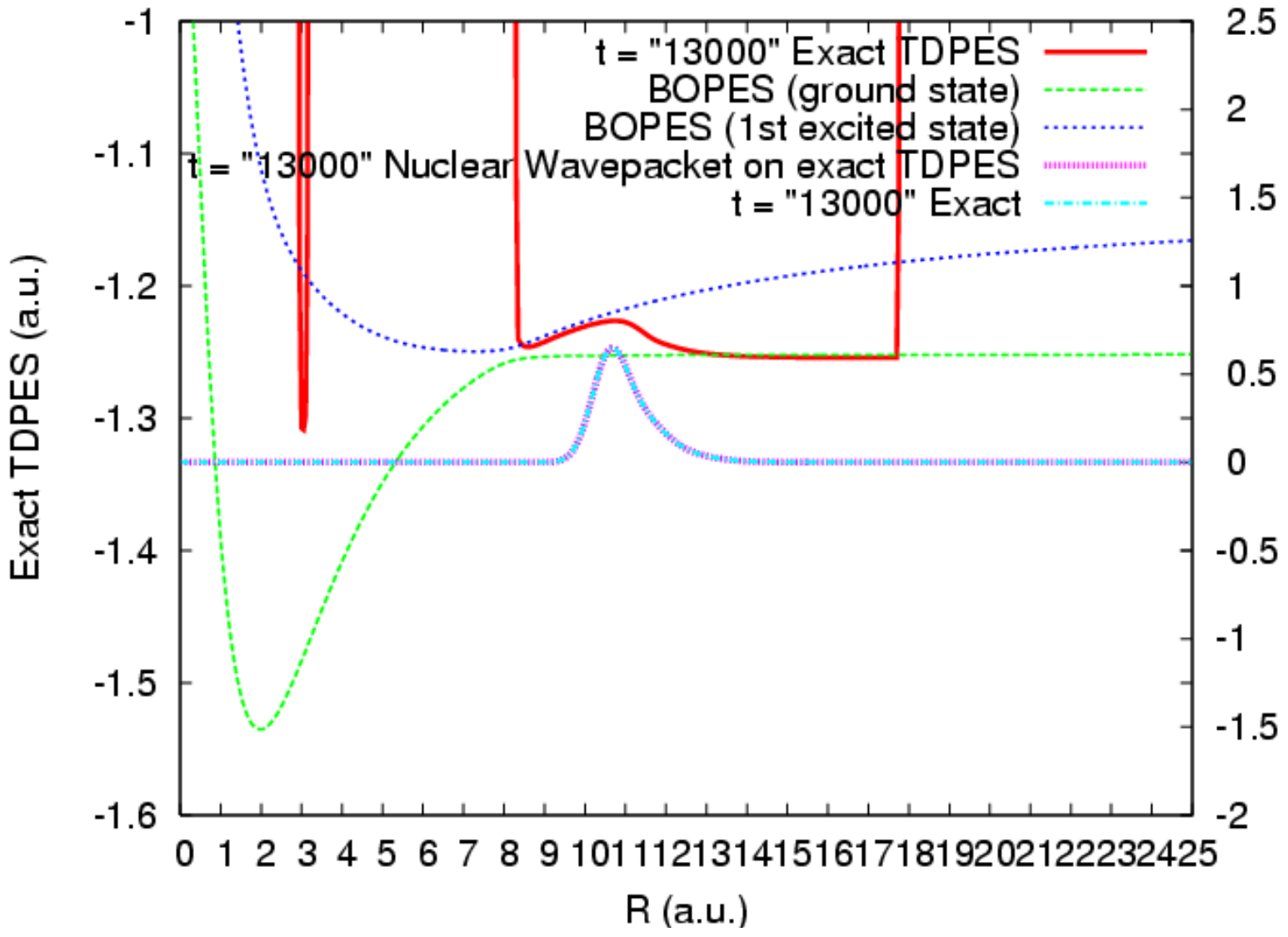
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "13000" Nuclear Wavepacket on exact TDPES
t = "13000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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-1
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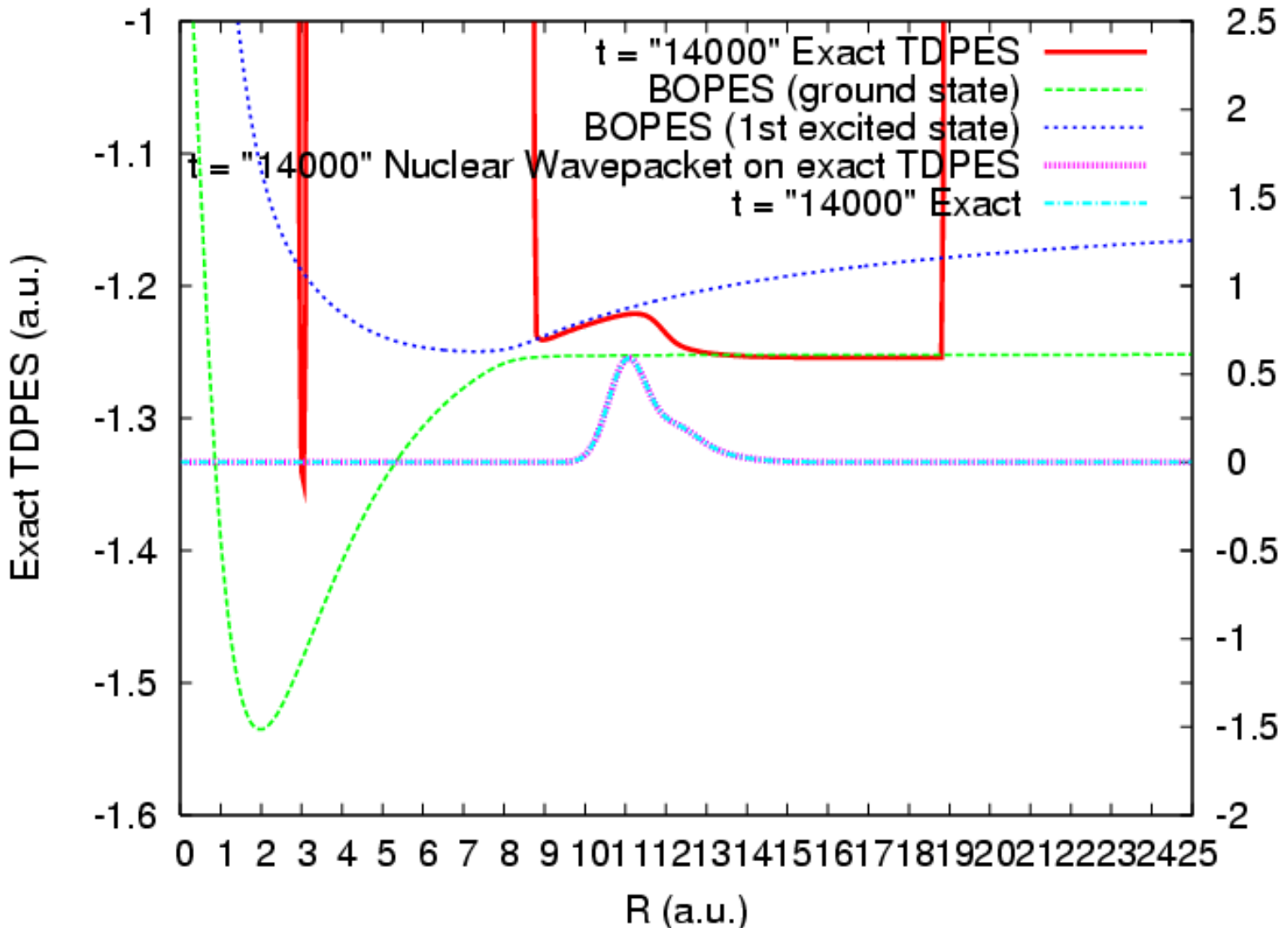
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t = "14000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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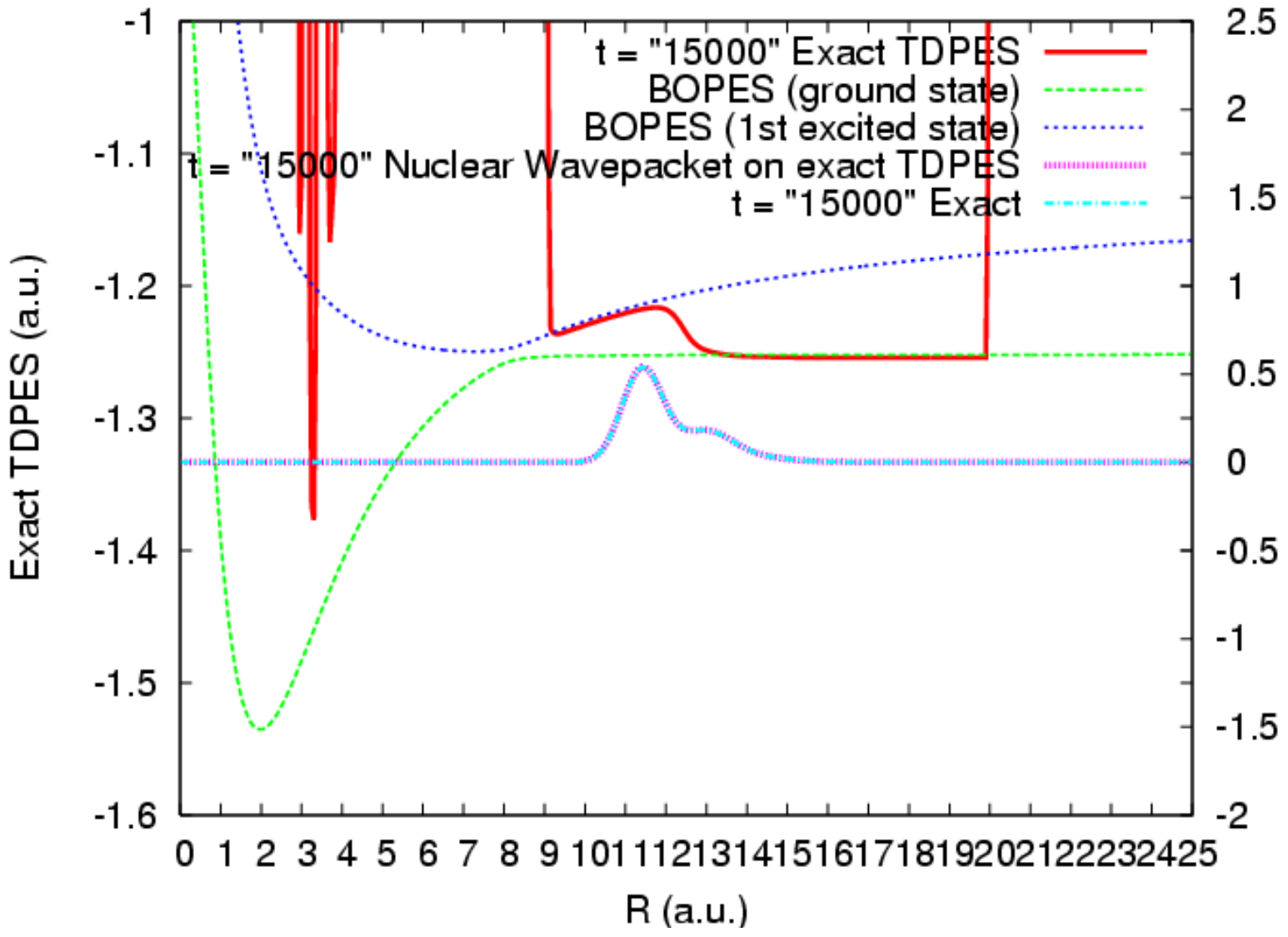
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "15000" Nuclear Wavepacket on exact TDPES
t = "15000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
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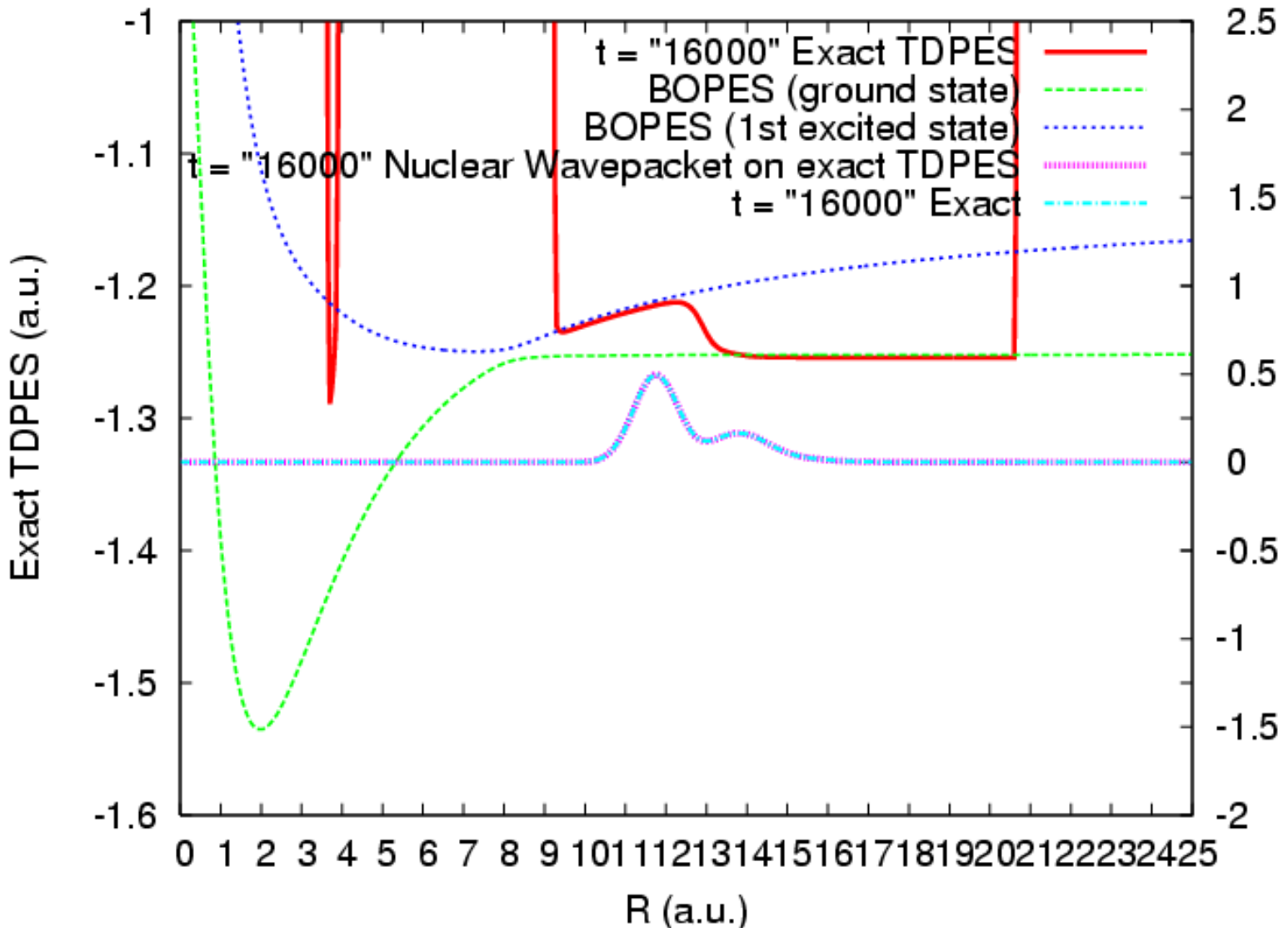
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
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Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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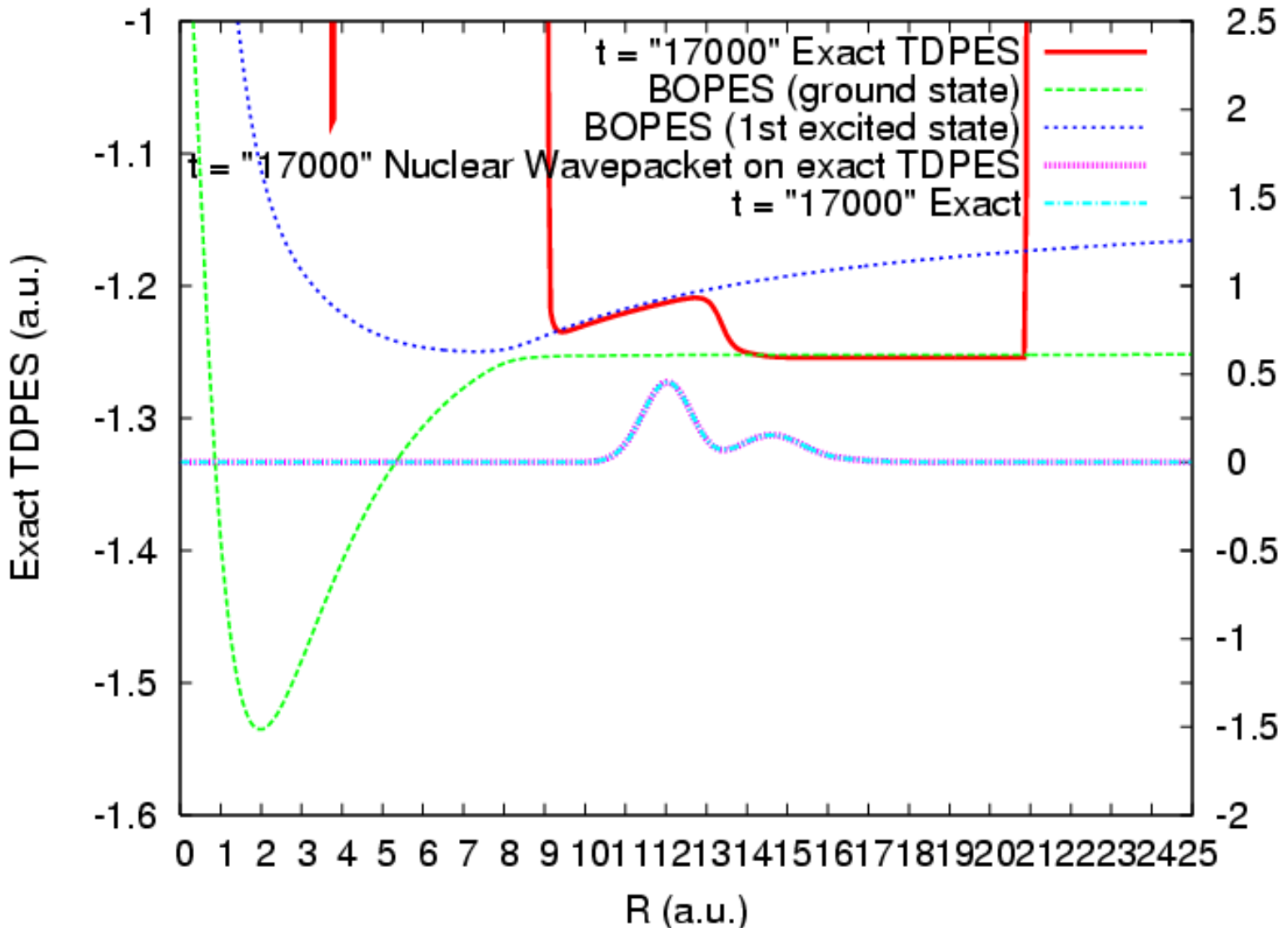
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BOPES (ground state)
BOPES (1st excited state)
t = "17000" Nuclear Wavepacket on exact TDPES
t = "17000" Exact
Exact TDPES (a.u.)
R (a.u.)
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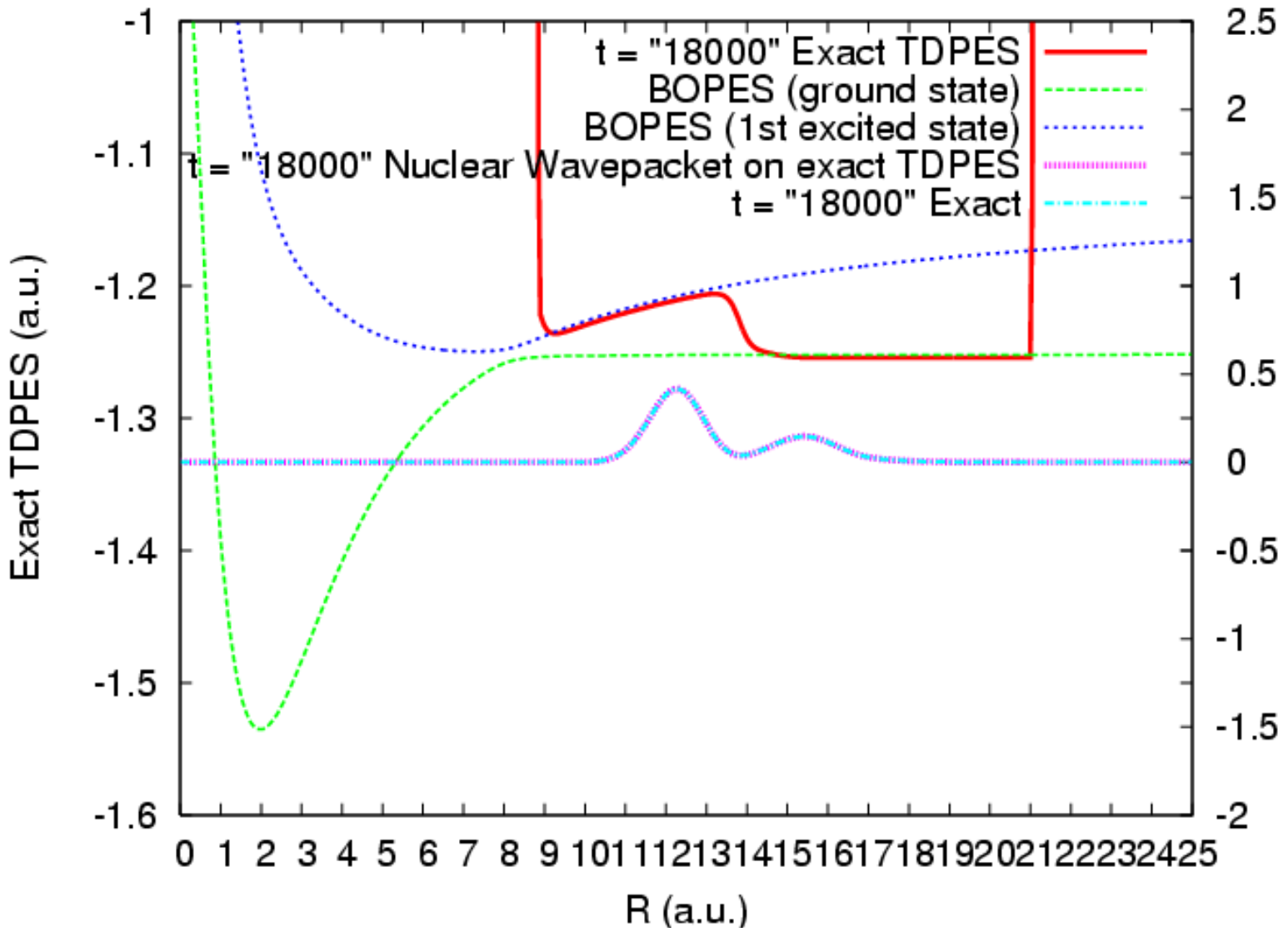
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BOPES (ground state)
BOPES (1st excited state)
t = "18000" Nuclear Wavepacket on exact TDPES
t = "18000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
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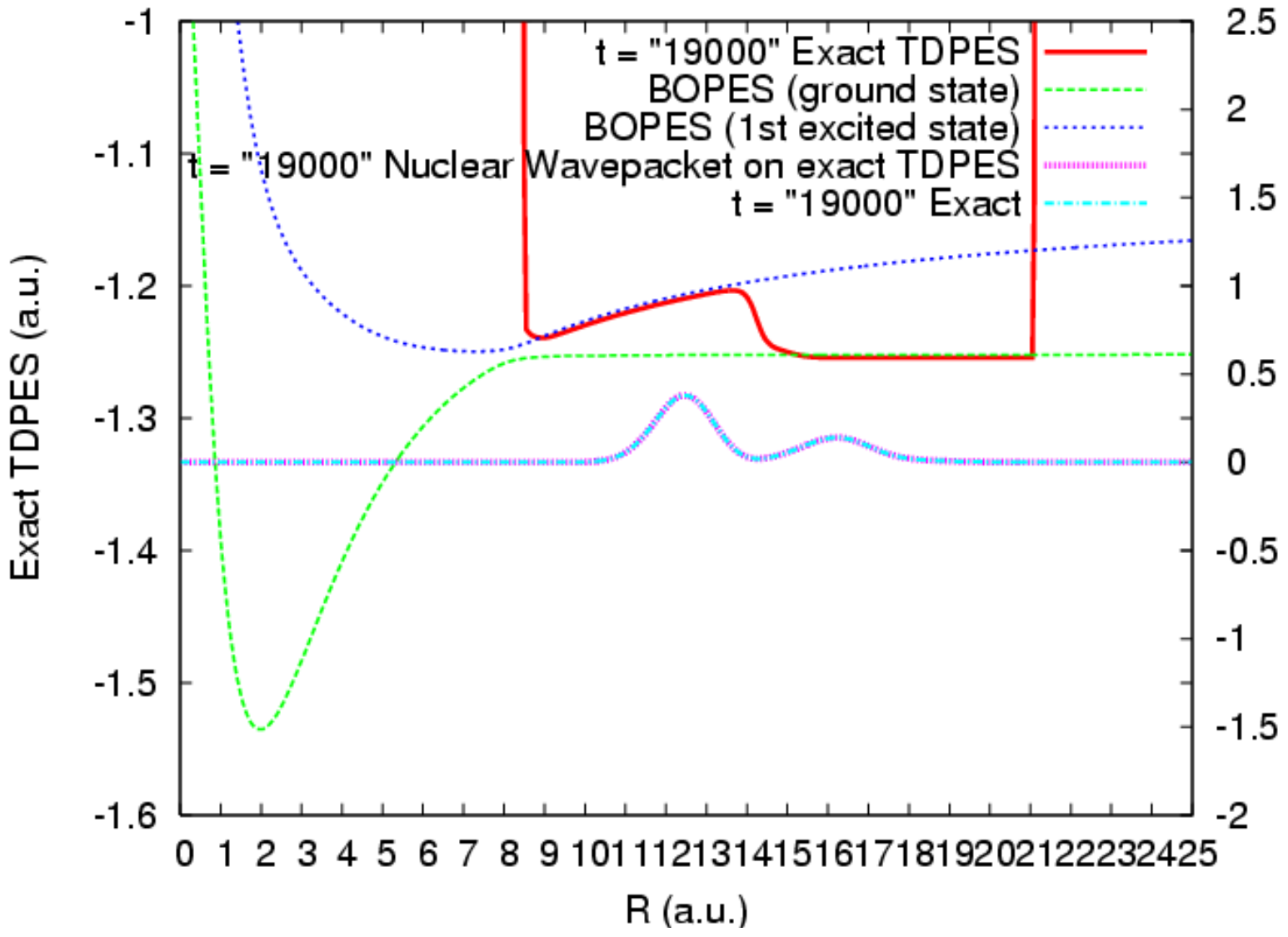
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (1st excited state)
t = "19000" Nuclear Wavepacket on exact TDPES
t = "19000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
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-1.3
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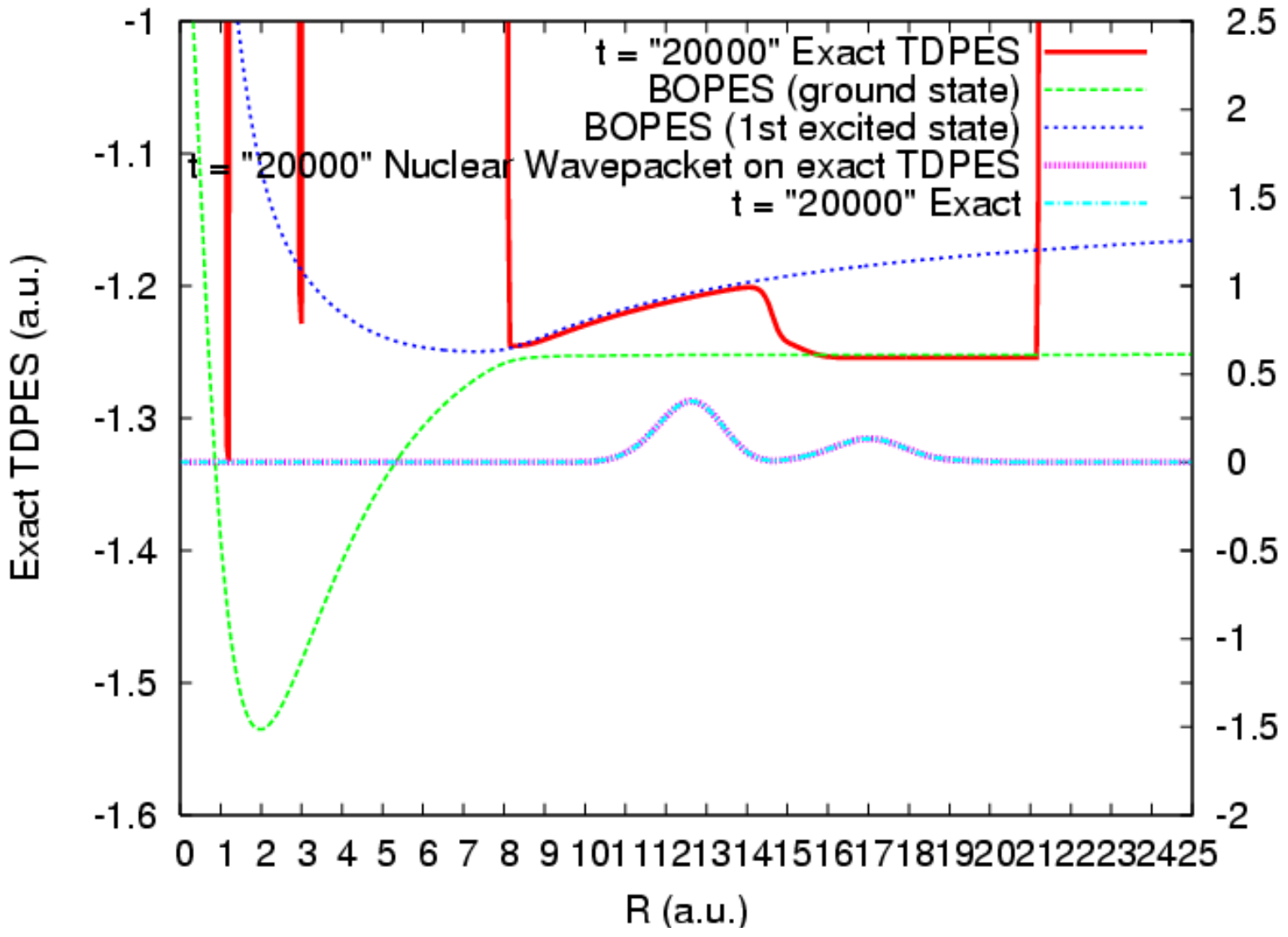
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BOPES (ground state)
BOPES (1st excited state)
t = "20000" Nuclear Wavepacket on exact TDPES
t = "20000" Exact
Exact TDPES (a.u.)
R (a.u.)
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-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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-0.5
-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

# Non-adiabaticity in nuclear motion

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

## Theorem III:

$$\boldsymbol{P}_n = \left\langle \Psi \left| \sum_{\mu=1}^{N_n} -i\nabla_{\boldsymbol{R}_\mu} \right| \Psi \right\rangle_{\underline{\underline{r\boldsymbol{R}}}}$$

**true momentum of nuclear subsystem**

$$\boldsymbol{L}_n = \left\langle \Psi \left| \sum_{\mu=1}^{N_n} \boldsymbol{R}_\mu \times \left( -i\nabla_{\boldsymbol{R}_\mu} \right) \right| \Psi \right\rangle_{\underline{\underline{r\boldsymbol{R}}}}$$

**true angular momentum of nuclear subsystem**

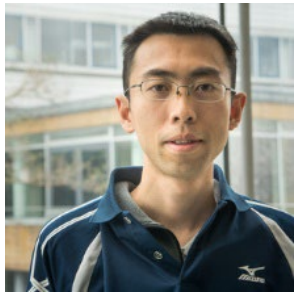
**can be calculated from the nuclear wave function alone as:**

$$\boldsymbol{P}_n = \left\langle \chi \left| \sum_{\mu=1}^{N_n} \left( -i\nabla_{\boldsymbol{R}_\mu} + \boldsymbol{A}_\mu \right) \right| \chi \right\rangle_{\underline{\underline{\boldsymbol{R}}}}$$

$$\boldsymbol{L}_n = \left\langle \chi \left| \sum_{\mu=1}^{N_n} \boldsymbol{R}_\mu \times \left( -i\nabla_{\boldsymbol{R}_\mu} + \boldsymbol{A}_\mu \right) \right| \chi \right\rangle_{\underline{\underline{\boldsymbol{R}}}}$$

# Theorem IV: Subsystem Ehrenfest equations:

$$\frac{d\boldsymbol{P}_\mu}{dt} = \mathrm{Re}\left\langle \chi \middle| \hat{\boldsymbol{\mathcal{F}}}_\mu \middle| \chi \right\rangle_{\underline{\underline{\boldsymbol{R}}}} \qquad \frac{d\boldsymbol{L}_\mu}{dt} = \mathrm{Re}\left\langle \chi \middle| \boldsymbol{R}_\mu \times \hat{\boldsymbol{\mathcal{F}}}_\mu \middle| \chi \right\rangle_{\underline{\underline{\boldsymbol{R}}}}$$



Chen Li

$$\hat{\boldsymbol{\mathcal{F}}}_\mu = \hat{\boldsymbol{F}}_\mu + \hat{\boldsymbol{D}}_\mu$$

$$\hat{\boldsymbol{F}}_\mu = \boldsymbol{E}_\mu + \boldsymbol{B}_\mu \times \hat{v}_\mu$$

"Electric-like" and "Lorentz-like" force

with $\boldsymbol{E}_\mu = \dot{\boldsymbol{A}}_\mu - \nabla_{R_\mu} \varepsilon$

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

$$\hat{v}_\mu = \left(-i\nabla_{R_\mu} + \boldsymbol{A}_\mu\right) / M_\mu$$

$$\boldsymbol{B}_\mu = \nabla_{R_\mu} \times \boldsymbol{A}_\mu$$

Berry curvature

$$\hat{D}_\mu = \sum_{\nu \neq \mu, G'} \left(\partial_{G'_\nu} A_{G_\mu} - \partial_{G_\mu} A_{G'_\nu}\right) \hat{v}_{G'_\nu}$$

with $G_\alpha \in (X_\alpha, Y_\alpha, Z_\alpha)$

Lorentz-like force, but with internuclear Berry curvature

## These forces appear:

- **in the subsystem Ehrenfest equations**

  Chen Li, R. Requist, EKU Gross, PRL 128, 113001 (2022)

- **in the classical limit of the nuclear TDSE**

  F. Agostini, A. Abedi, EKU Gross, JCP 141, 214101 (2014)
  A. Abedi, F. Agostini, EKU Gross, EPL 106, 33001 (2014)

- **in the mixed-quantum-classical algorithm**

  S.K. Min, F. Agostini, E.K.U. Gross, Phys. Rev. Lett. 115, 073001 (2015)
  F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, JPCL 8, 3048 (2017)

**Note:**

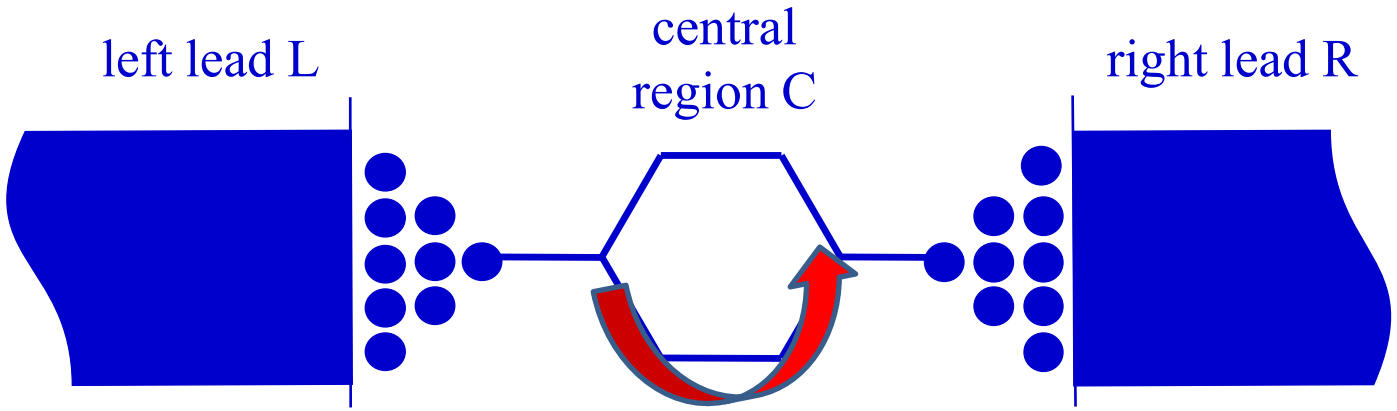
- **These forces are the "right" forces. There are no other choices!**

- **These forces appear in any two-component system (not just for electrons and nuclei)**

## Are the Lorentz-like forces important?

- **For a neutral atom moving in a constant external magnetic field, the magnetic field associated with the Berry connection cancels the external magnetic field exactly (making the atom move on a straight line).**

- **Current-induced forces in molecular junctions can be cast into the form of a Berry-connection vector potential. The internuclear Lorentz force, D, plays an important role in the "water wheel"**




**-- atomic waterwheels (Dundas, McEniry, Todorov, Nature nanotechnology 4, 99 (2009))**

**Coupled-Trajectory Mixed Quantum-Classical Algorithm**

Treat the nuclear motion with classical trajectories, but retain the quantum treatment of the electronic degrees of freedom.


**S.K. Min, F. Agostini, E.K.U. Gross, Phys. Rev. Lett. 115, 073001 (2015)**

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

**F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, JPCL 8, 3048 (2017)**

## Electronic EoM

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

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

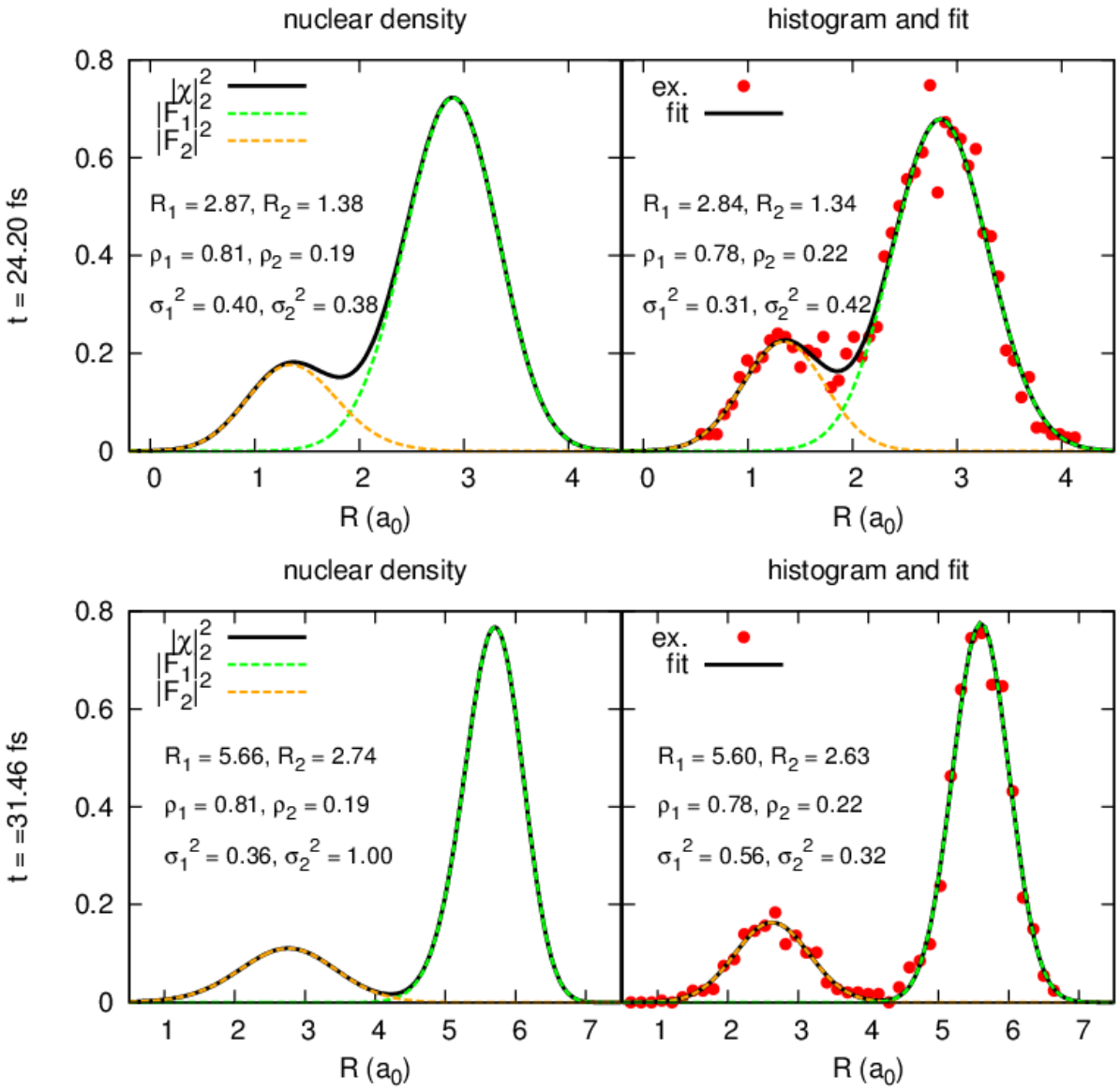
**"TD-Density-functionalize" this equation**

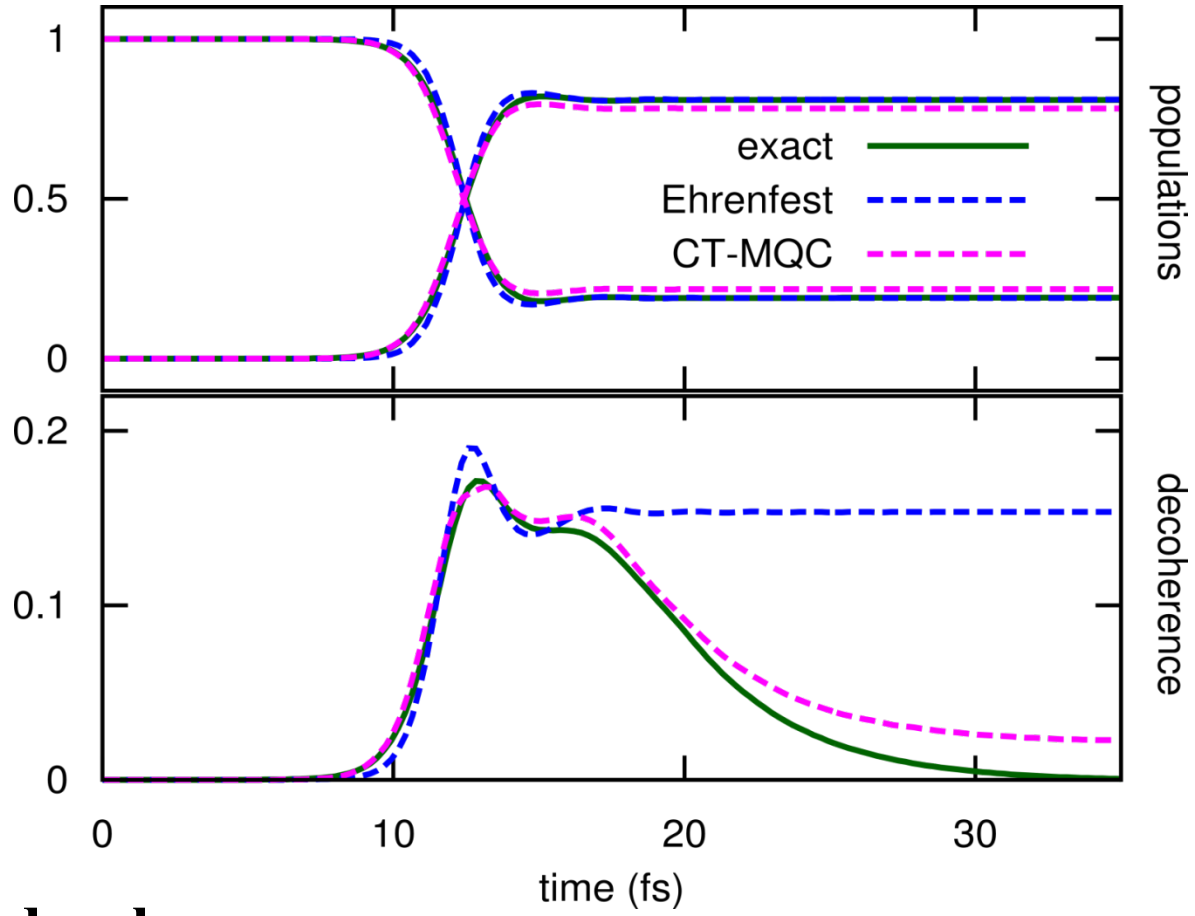
## Nuclear EoM

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

**Represent χ(R,t) by swarm of classical trajectories (method of charactristics). Classical forces are unique. No need for Tully surface hopping and decoherence corrections.**

# Propagation of classical nuclei on exact TDPES (for Chin-Metiu model)



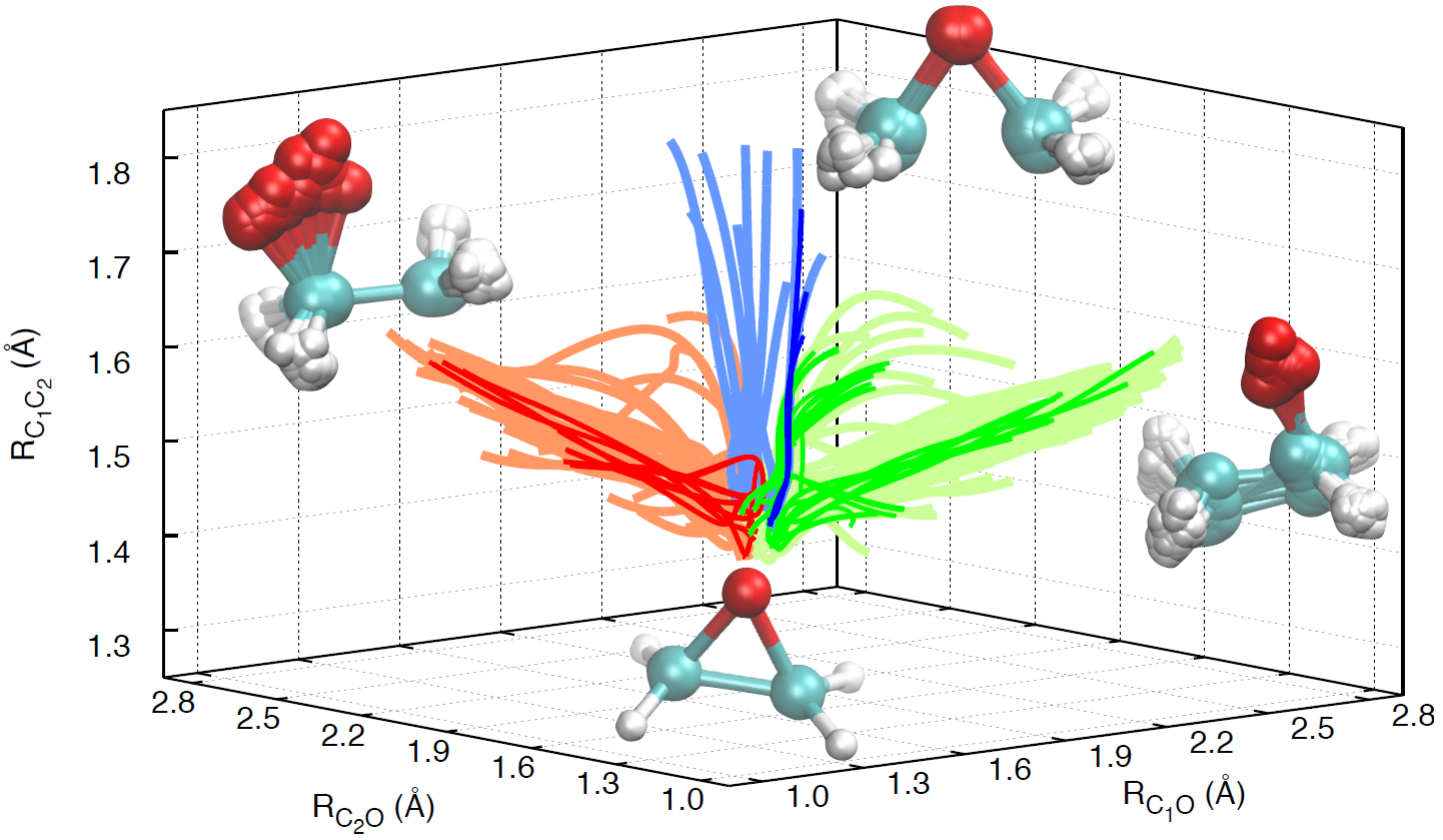



## Measure of decoherence:

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

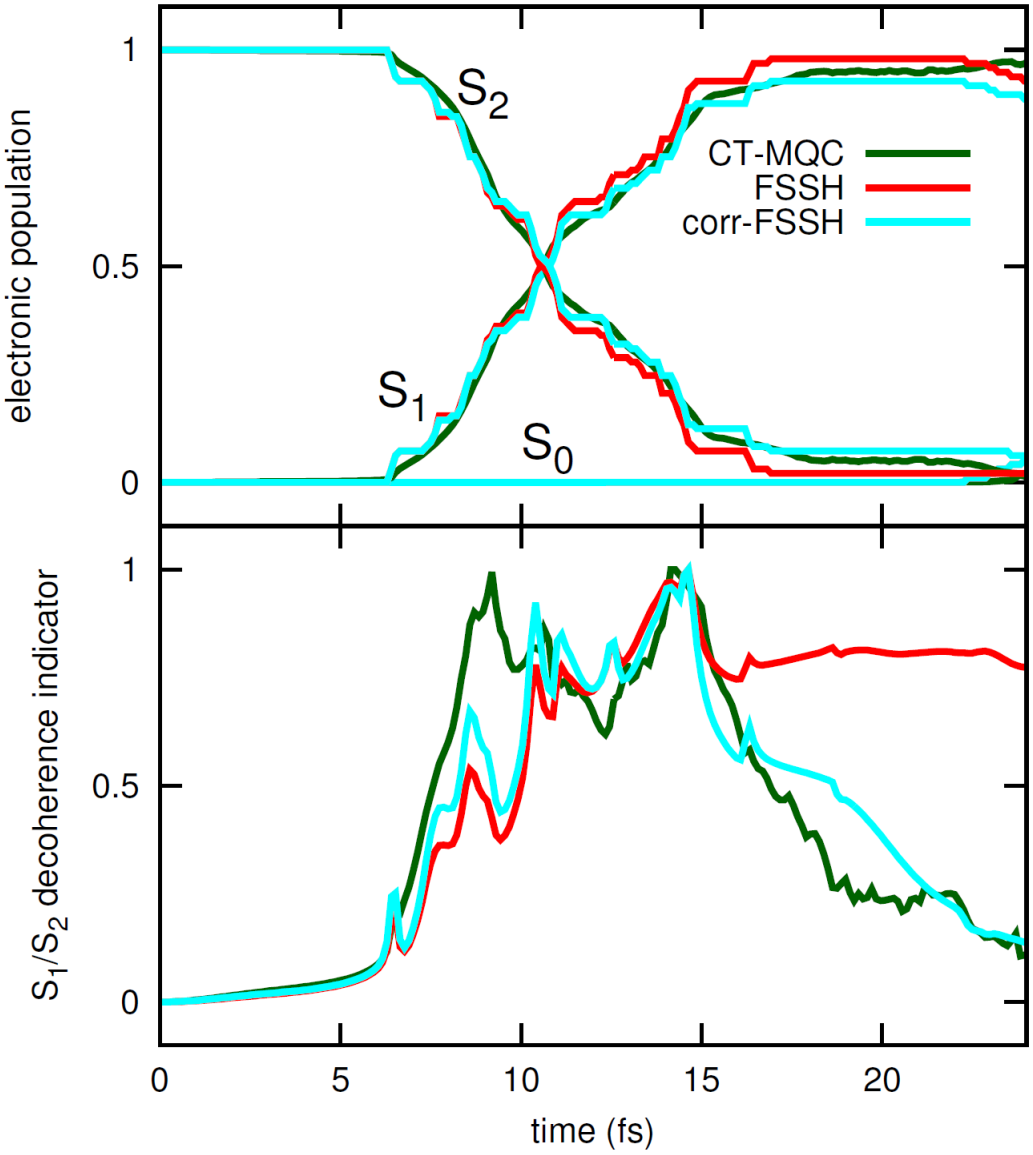
# Photo-induced ring opening in Oxirane




Identification of the three groups of trajectories that, starting from the initial geometries, yield right-open (red) or left-open (green) ring structures and CC-extended bond geometry (blue).

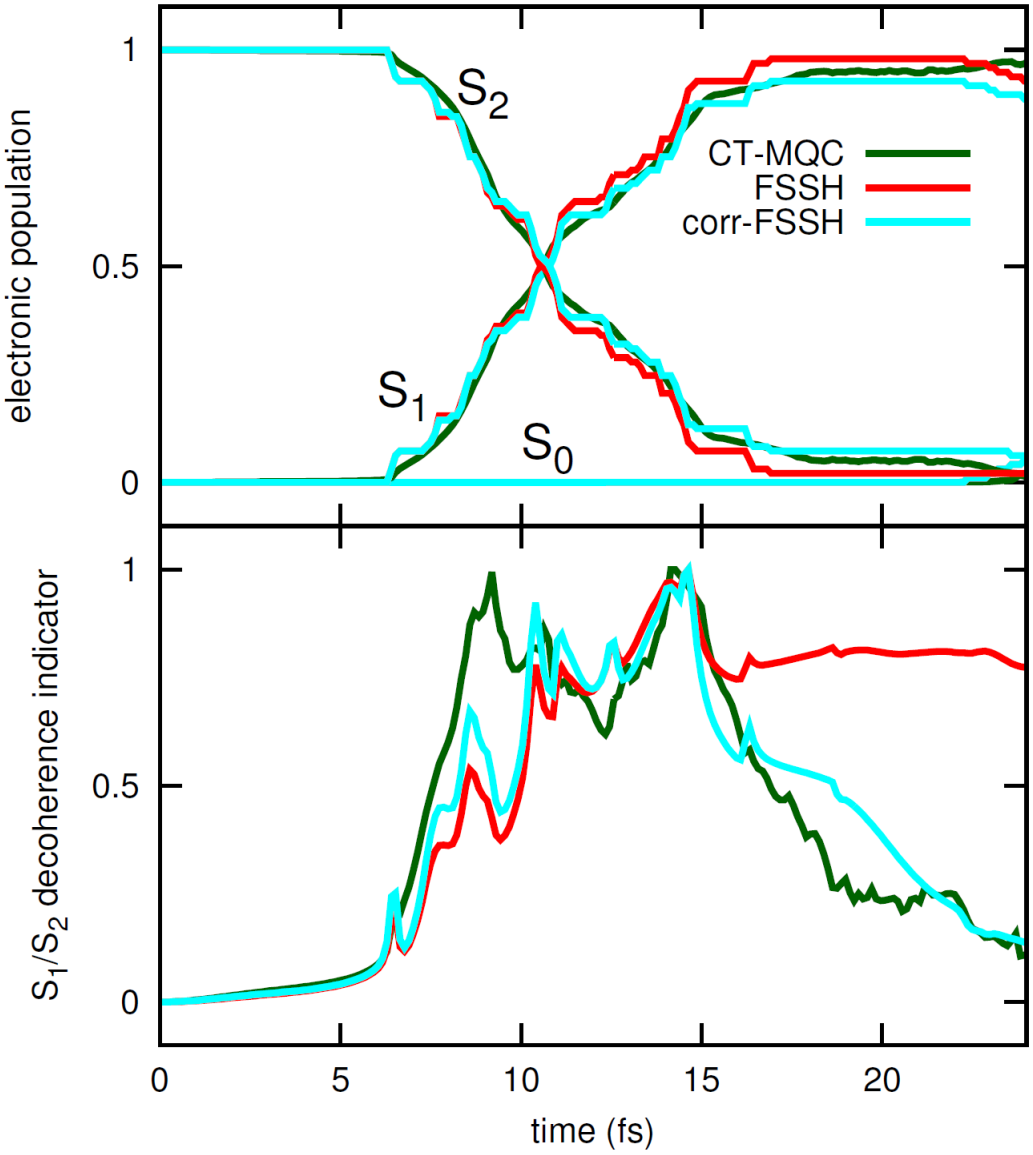
Result: Probability of ring-opening by oxygen motion is about 4 times larger than the C-C-bond stretch. Light colors identify CT-MQC trajectories and darker colors corr-FSSH trajectories.

**F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, J.Phys.Chem. Lett. 8, 3048 (2017)**




Upper panel: electronic populations of S0, S1 and S2 as functions of time. Lower panel: indicator of decoherence for the element S1=S2. Three sets of results are compared, based on the CT-MQC algorithm (dark-green lines), FSSH (red lines) and corr-FSSH (cyan lines).

**F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, J.Phys.Chem. Lett. 8, 3048 (2017)**




Upper panel: electronic populations of S0, S1 and S2 as functions of time. Lower panel: indicator of decoherence for the element S1=S2. Three sets of results are compared, based on the CT-MQC algorithm (dark-green lines), FSSH (red lines) and corr-FSSH (cyan lines).

**Algorithm implemented in CPMD**

F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, J.Phys.Chem. Lett. 8, 3048 (2017)

## How can we capture decoherence mathematically?

Let $\Psi(r,R,t) = \langle r,R|\Psi(t)\rangle$ be the full solution of the electron-nuclear TDSE.

**We look at the reduced density matrix of the electronic subsystem:**

$$\hat{\rho}^{e}(t) = \mathrm{Tr}_{R}\left|\Psi(t)\right\rangle\left\langle\Psi(t)\right| = \int d^{N}R \left\langle R\middle|\Psi(t)\right\rangle\left\langle\Psi(t)\middle|R\right\rangle$$

**One speaks of decoherence when**

$$\rho^{e}_{jk}(t) \longrightarrow 0 \quad \text{for } j \neq k \quad \text{and large } t$$

**(marking the transition from a pure-state DM to an ensemble DM)**

**One speaks of thermalization when**

$$\rho^{e}_{jk}(t) \longrightarrow \delta_{jk}\, \rho^{e}_{\text{thermal}}(E_k) \quad \text{for large } t$$

**(marking the transition from a pure-state DM to the DM of a thermal ensemble)**

**A basis-independent measure:** **Purity:** $P^{e}(t) = \mathrm{Tr}\ [\rho^{e}(t)^{2}]$

**Reduced DM of the electronic subsystem is**

$$\hat{\rho}^{e}(t) = \mathrm{Tr}_{R}\left|\Psi(t)><\Psi(t)\right| = \int d^{N}R \left\langle R\middle|\Psi(t)\right\rangle\left\langle\Psi(t)\middle|R\right\rangle$$

Inserting the exact factorization $\Psi(r,R,t) = \chi(R,t)\,\Phi\left(r\middle|R,t\right)$ yields

$$\hat{\rho}^{e}(t) = \int d^{N}R \left|\chi(R,t)\right|^{2}\,\hat{\rho}^{e}_{\mathrm{cond}}(R,t)$$

with the conditional reduced DM $\hat{\rho}^{e}_{\mathrm{cond}}(R,t) = \left|\Phi(R,t)\right\rangle\left\langle\Phi(R,t)\right|$

**Reduced DM of the electronic subsystem is**

$$\hat{\rho}^{e}(t) = \mathrm{Tr}_{R}\left|\Psi(t)><\Psi(t)\right| = \int d^{N}R \left\langle R\middle|\Psi(t)\right\rangle\left\langle\Psi(t)\middle|R\right\rangle$$

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$$\hat{\rho}^{e}(t) = \int d^{N}R \left|\chi(R,t)\right|^{2}\,\hat{P}^{e}_{\mathrm{cond}}(R,t)$$

with the conditional reduced DM $\hat{P}^{e}_{\mathrm{cond}}(R,t) = \left|\Phi(R,t)\right\rangle\left\langle\Phi(R,t)\right|$

**For a single trajectory:** $\left|\chi(R,t)\right|^{2} = \delta(R-R^{c}(t))$

$$\hat{\rho}^{e}(t) = \left|\Phi(R^{c}(t),t)\right\rangle\left\langle\Phi(R^{c}(t),t)\right|$$

**Pure-state RDM!!**

**Is decoherence lost, as consequence of having only one single trajectory?**

**<u>Remember</u>: Single-trajectory Ehrenfest Dynamics gives no decoherence!**

**"Common wisdom": One needs ensemble of trajectories to describe decoherence.**

**Reduced DM of the electronic subsystem is**

$$\hat{\rho}^e(t) = \mathrm{Tr}_R \left|\Psi(t)><\Psi(t)\right| = \int d^N R \left\langle R \middle| \Psi(t) \right\rangle \left\langle \Psi(t) \middle| R \right\rangle$$

Inserting the exact factorization $\Psi(r,R,t) = \chi(R,t)\, \Phi\left(r \middle| R,t\right)$ yields

$$\hat{\rho}^e(t) = \int d^N R \left|\chi(R,t)\right|^2 \hat{P}^e_{\mathrm{cond}}(R,t)$$

with the conditional reduced DM $\hat{P}^e_{\mathrm{cond}}(R,t) = \left|\Phi(R,t)\right\rangle\left\langle\Phi(R,t)\right|$

**For a single trajectory:** $\left|\chi(R,t)\right|^2 = \delta(R - R^c(t))$

$$\hat{\rho}^e(t) = \left|\Phi(R^c(t),t)\right\rangle\left\langle\Phi(R^c(t),t)\right|$$

**Pure-state RDM!!**

**Is decoherence lost, as consequence of having only one single trajectory?**

**Remember: Single-trajectory Ehrenfest Dynamics gives no decoherence!**

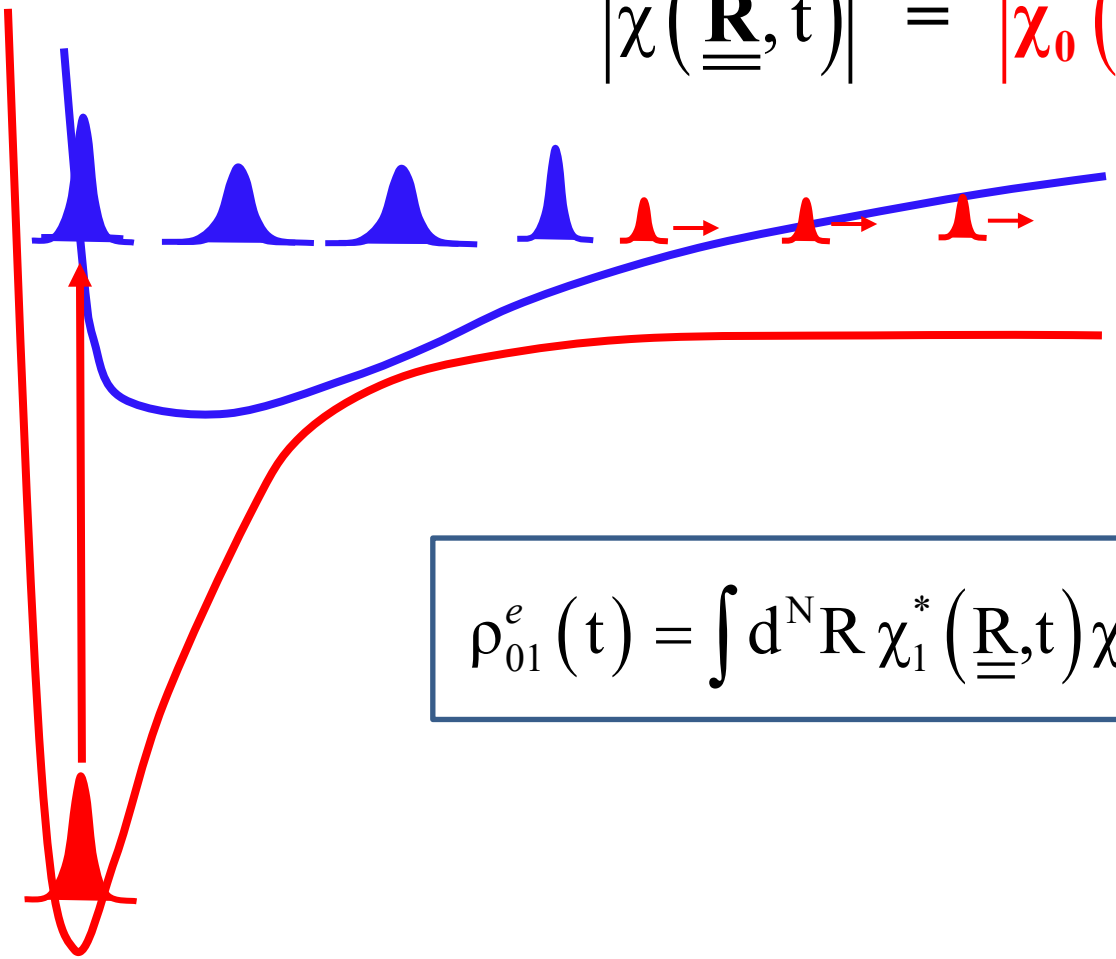
**"Common wisdom": One needs ensemble of trajectories to describe decoherence.**

**Our single trajectory gives decoherence because Φ follows a non-unitary evolution!**

## Example: Splitting of nuclear wave packet at an avoided crossing

$$\Psi\left(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}},t\right) \approx \chi_0\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{0,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right) + \chi_1\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{1,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right)$$

$$\left|\chi\left(\underline{\underline{\mathbf{R}}},t\right)\right|^2 = \left|\chi_0\left(\underline{\underline{\mathbf{R}}},t\right)\right|^2 + \left|\chi_1\left(\underline{\underline{\mathbf{R}}},t\right)\right|^2$$



$$\rho^e_{01}(t) = \int d^N R\, \chi_1^*\left(\underline{\underline{\mathbf{R}}},t\right)\chi_0\left(\underline{\underline{\mathbf{R}}},t\right) = \left\langle \chi_1(t)\middle|\chi_0(t)\right\rangle$$

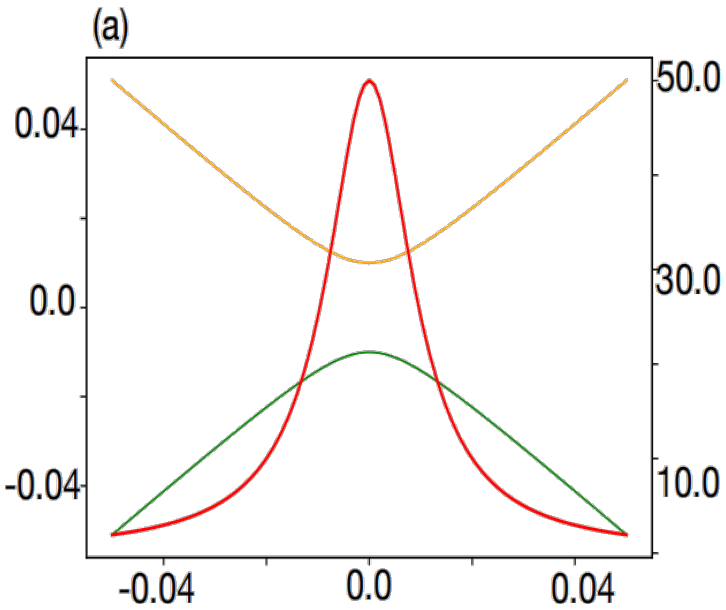
## Test calculation for a 2-state model for $H^{BO}$

(Matisse Tu, EKUG, arXiv: 2502.08247)

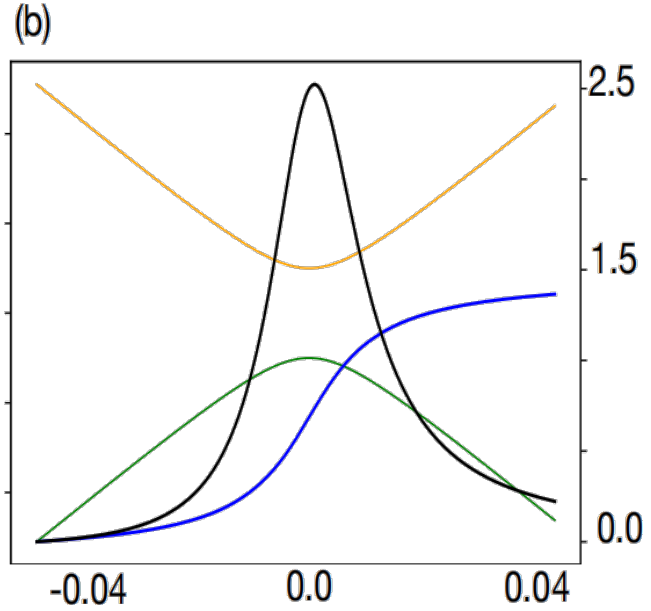
**Step 1:** Do time-propagation with $H^{BO}$

**Step 2:** Evaluate conditional electronic WF in 1st-order PT w.r.t. $\mu$ along the classical trajectory $R^c(t)$

**Step 3:** Calculate $\rho_{01}(t)$




BO-PES and NAC as function of R of model $H^{BO}$




$\rho_{01}(R^c)$: Ehrenfest dynamics

$\rho_{01}(R^c)$: Non-unitary (EF) dynamics

# DFT of the combined system of electrons and phonons, based on the exact factorization

R Requist, EKU Gross, Phys. Rev. Lett. 117, 193001 (2016).
Chen Li, R Requist, EKU Gross, JCP 148, 084110 (2018).
R Requist, C Proetto, EKU Gross, Phys. Rev. B 99, 165136 (2019)

## Basic densities

**Electrons:** $n(r|R)$ conditional probability of finding an electron at r, given the nuclei are at R.
follows directly from the exact electronic conditional wave function $\Phi(r_1, \ldots r_N |R)$

**Nuclei:** $\Gamma(R_1, \ldots, R_N) = |\chi(R_1, \ldots, R_N)|^2$ nuclear N-body density as it follows from exact factorization

## Electronic Kohn-Sham equation:

$$\left[\frac{\boldsymbol{p}^2}{2m} + v_{en}\left(\boldsymbol{r},\boldsymbol{R}\right) + v_{Hxc}^{EF}\left(\boldsymbol{r},\boldsymbol{R}\right)\right]\psi_i\left(\boldsymbol{r}\,|\,\boldsymbol{R}\right) = \varepsilon_i(\boldsymbol{R})\psi_i\left(\boldsymbol{r}\,|\,\boldsymbol{R}\right)$$

$$v_{en}\left(\boldsymbol{r},\boldsymbol{R}\right) = -\sum_{\mu}\frac{Z_\mu e^2}{4\pi \in_0 \left|\boldsymbol{r}-\boldsymbol{R}_\mu\right|}$$

$v_{Hxc}^{EF}\left(\boldsymbol{r},\boldsymbol{R}\right)$ **is a functional of n(*r*|*R*): need approximations**

**Nuclear "Kohn-Sham" equation:**

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

**identical with the nuclear equation from the exact factorization**

**In practice: Expand all functions w.r.t. their R-dependence around equilibrium positions** ⟹ **exact phonons**

$$\boldsymbol{R}_{l\kappa}^{(0)} = \boldsymbol{R}_l^{(0)} + \tau_\kappa \qquad \boldsymbol{R}_l^{(0)} = l_1\boldsymbol{a}_1 + l_2\boldsymbol{a}_2 + l_3\boldsymbol{a}_3 \qquad \boldsymbol{u}_{l\kappa} = \boldsymbol{R}_{l\kappa} - \boldsymbol{R}_{l\kappa}^{(0)}$$

**Take expansion to 2nd order in the displacements** $\boldsymbol{u}_{l\kappa} = \boldsymbol{R}_{l\kappa} - \boldsymbol{R}_{l\kappa}^{(0)}$

**Makc transformation to collective coordinates**

$$\hat{U}_{\boldsymbol{q}\lambda} = \sqrt{\frac{M_\kappa}{NM_0}} \sum_\kappa \boldsymbol{u}_{l\kappa} \cdot \boldsymbol{e}_\kappa^* \left(\boldsymbol{q}\lambda\right) e^{-i\boldsymbol{q}\cdot\boldsymbol{R}_l^{(0)}}$$

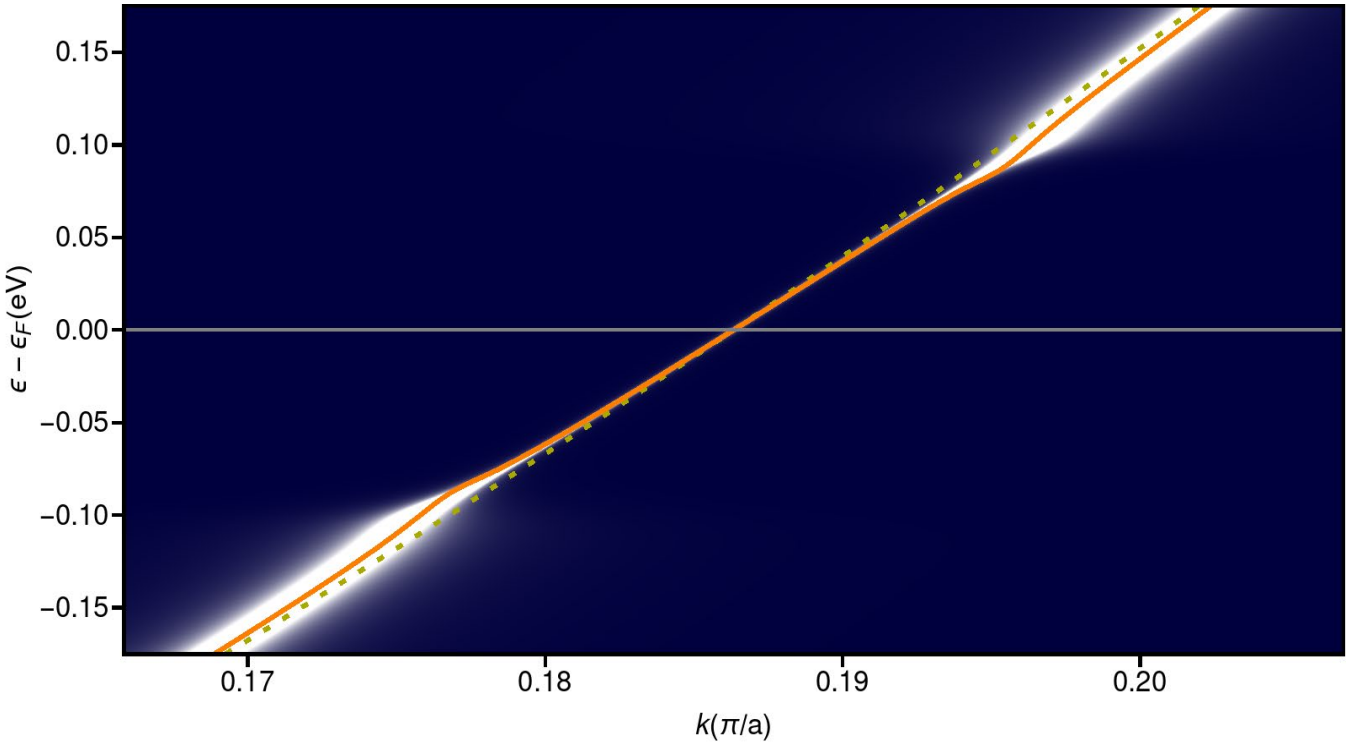
**(and analogously for the conjugate momenta)**

$$\hat{H}_{nucl}^{(2)} = \sum_{\boldsymbol{q}\lambda} \left[ \frac{1}{2\mathcal{M}_{\boldsymbol{q}\lambda}} \hat{P}_{-\boldsymbol{q}\lambda} \hat{P}_{\boldsymbol{q}\lambda} + \frac{\mathcal{M}_{\boldsymbol{q}\lambda} \Omega_{\boldsymbol{q}\lambda}^2}{2} \hat{U}_{-\boldsymbol{q}\lambda} \hat{U}_{\boldsymbol{q}\lambda} \right]$$

$$b^{\dagger}_{q\lambda} = \sqrt{\frac{\mathcal{M}_{q\lambda}\Omega_{q\lambda}}{2\hbar}}\hat{U}_{-q\lambda} - \frac{i}{\sqrt{2\hbar\mathcal{M}_{q\lambda}\Omega_{q\lambda}}}\hat{P}_{q\lambda}$$

$$b_{q\lambda} = \sqrt{\frac{\mathcal{M}_{q\lambda}\Omega_{q\lambda}}{2\hbar}}\hat{U}_{q\lambda} - \frac{i}{\sqrt{2\hbar\mathcal{M}_{q\lambda}\Omega_{q\lambda}}}\hat{P}_{-q\lambda}$$

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




The Kohn-Sham band structure (orange) in exact factorization-based DFT captures the phonon-induced wiggle in the electronic spectral function

# Other applications

- **Inverse factorisation**: $\Psi\left(\underline{r},\underline{\underline{R}},t\right)=\Phi_{\underline{r}}\left(\underline{\underline{R}},t\right)\cdot\chi\left(\underline{r},t\right)$ **and electronic PES**

  **Y. Suzuki, A. Abedi, N. Maitra, K. Yamashita, E.K.U. Gross, Phys. Rev. A 89, 040501(R) (2014)**

- **Factorisation for electrons only: Processes involving "fast" (core) electrons and "slow" (ionizing, or HHG producing) electrons. Concept of an exact PES on which the slow electrons move**

  **A. Schild, E.K.U. Gross, PRL 118, 163202 (2017)**

- **Factorisation for electrons only, but in Fock space : Strongly correlated electrons vs weakly correlated electrons (embedding allowing for long-range correlations)**

  **R. Requist, E.K.U. Gross, PRL 127, 116401 (2021)**

  **inspired by: X. Gonze, S. Zhou, L. Reining, EPJ B 91, 224 (2018).**

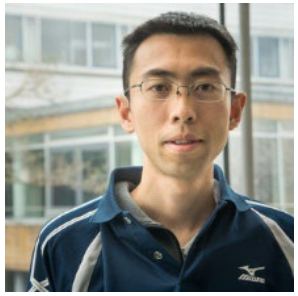
- **Exact TD-PES of systems driven by CW lasers are piecewise identical with Floquet surfaces with steps in between. Surface hopping algorithms should hop between Floquet surfaces. T. Fiedlschuster, J. Handt, E.K.U. Gross, R. Schmidt, Phys Rev A 95, 063424 (2017)**

- **Non-adiabaticity in nuclar motion (vector potential). Compare adiabatic Berry phase with the exact one. S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, PRL 113, 263004 (2014)**

# Thanks !



# THANKS!



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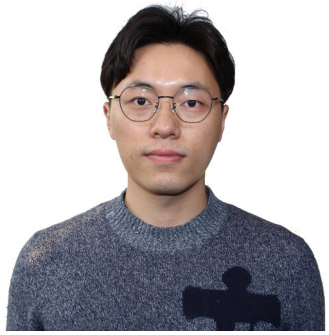

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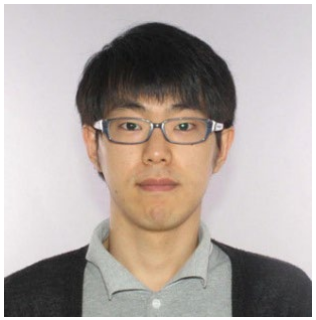

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# Take-home messages

**Exact factorization useful to settle conceptual issues**

- **Identification of the correct forces on the nuclei**
- **Identification of the exact (non-adiabatic) molecular Berry phase**

**Exact factorization useful to develop practical algorithms**

- **Starting from the right Schrödinger equation for the nuclei (the one that comes from the exact factorization), the resulting mixed quantum-classical algorithm correctly describes wave packet splitting and decoherence.**
  **No need for surface hopping nor decoherence corrections.**

- **Treating the non-adiabatic terms in the exact electronic EoM by 1$^{st}$-order perturbation theory provides an accurate and numerically efficient way to calculate**
  **--electronic flux densities and vibrational circular dichroism**
  **--measures of decoherence in an ab-initio fashion**