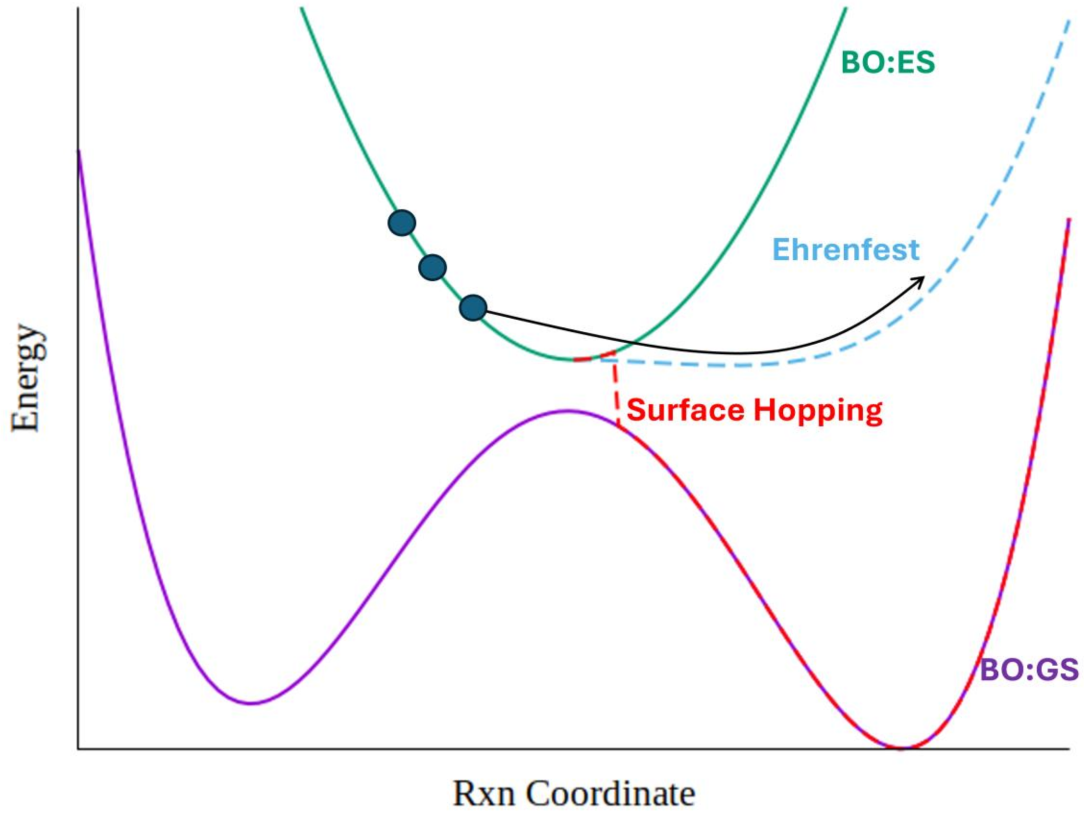
UNIVERSITY OF
South Carolina

Factorized Electron Nuclear Dynamics: Theory Development and Implementation

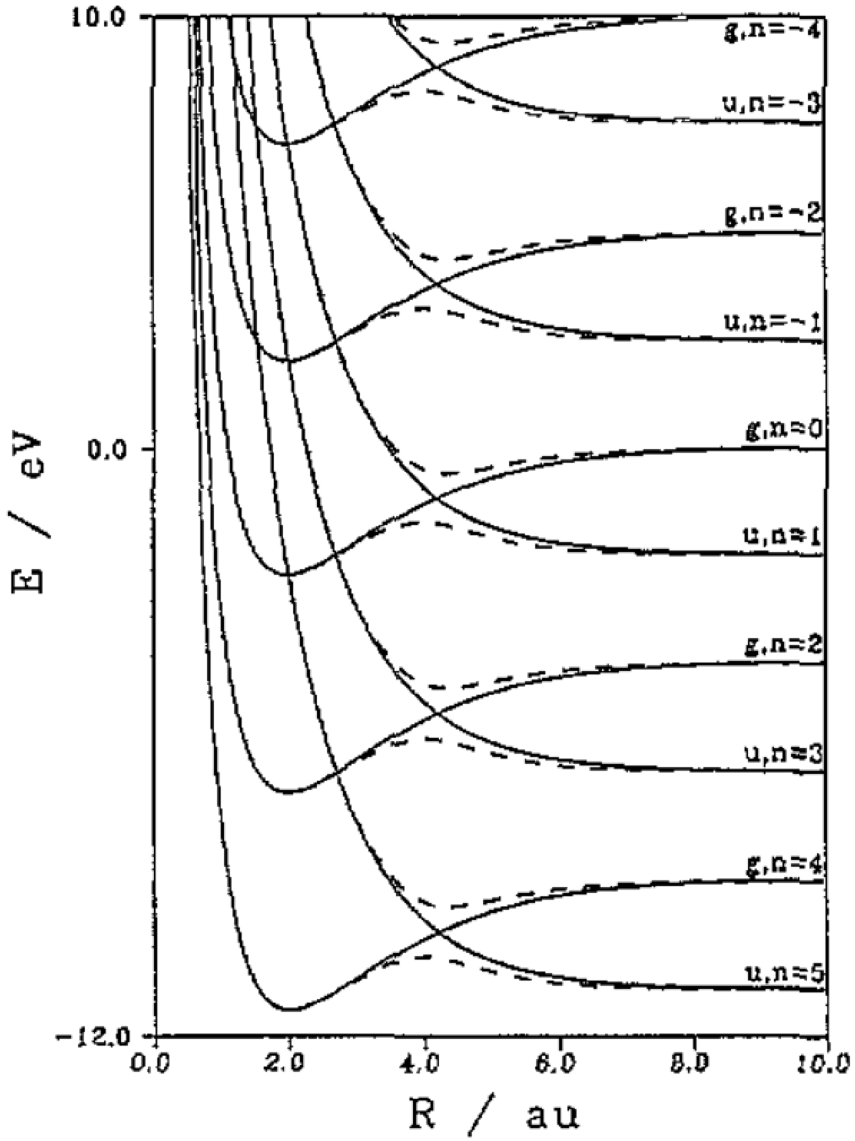
Julian Stetzler

Advisors: Vitaly Rassolov & Sophya Garashchuk

Non-adiabatic dynamics beyond Born-Huang

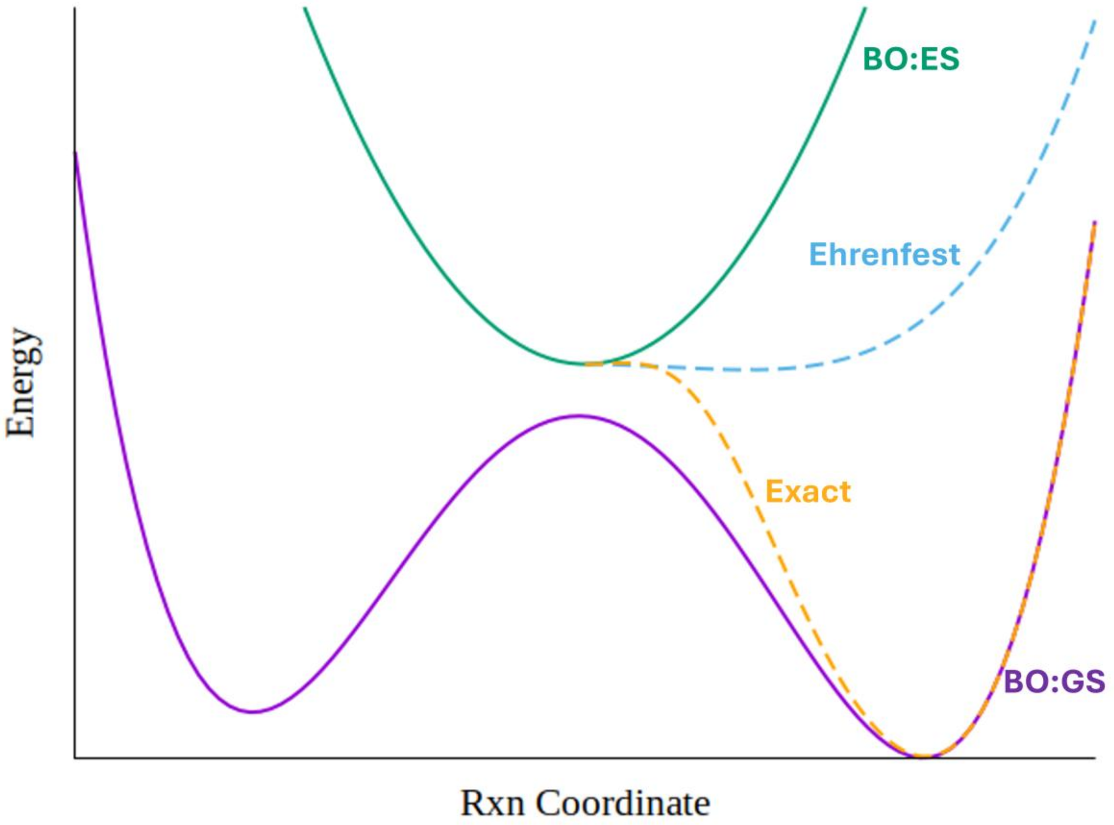


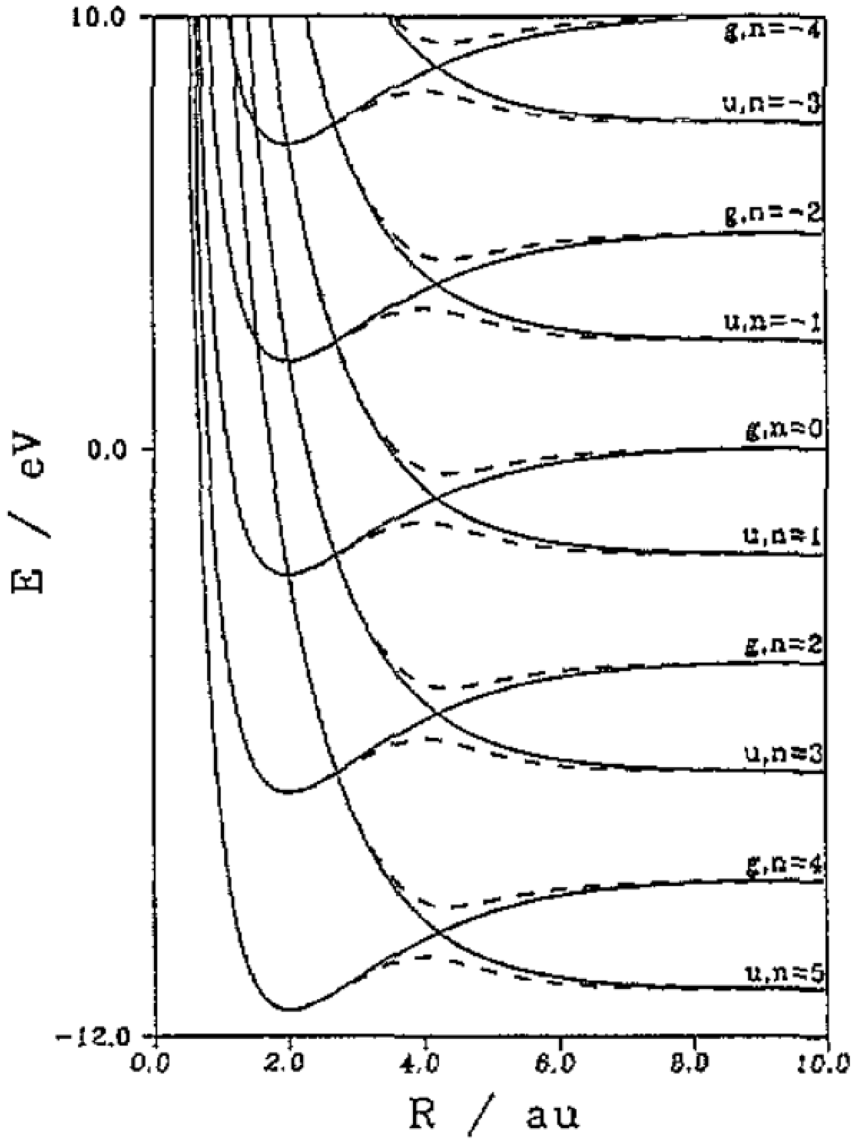
BH: $\Psi(x, y, t) = \sum_{i}^{\infty} \psi_i(y, t)\Phi_i(x; y)$



Giusti-Suzor, A, et al., B. Dynamics of H2+ in Intense Laser Fields. Journal of Physics B: Atomic, Molecular and Optical Physics 1995, 28, 309

Non-adiabatic dynamics beyond Born-Huang





XF: $\Psi(x,y,t) = \psi(y,t)\Phi(\mathrm{x},\mathrm{y},\mathrm{t})$

Giusti-Suzor, A, et al., B. Dynamics of H2+ in Intense Laser Fields. Journal of Physics B: Atomic, Molecular and Optical Physics 1995, 28, 309

Exact Factorization

- XF introduced by Abedi, Maitra, Gross:

$$\Psi(x,y,t) = \underbrace{\psi(y,t)}_{\substack{\text{Nuclear} \\ \text{y}}}\underbrace{\Phi(x,y,t)}_{\substack{\text{Electronic} \\ \text{x}}}$$

Partial Normalization Condition: $\langle \Phi | \Phi \rangle_x = 1$ for all y, t

- Numerically exact XF is a challenge:
  - Regions of low nuclear density $\left(\frac{\nabla|\psi|}{|\psi|}\right)$
  - Instabilities when propagating Φ
  - **Unstable after wavepacket splitting**

Abedi, A, et. al. *Phys. Rev. Lett.* **2010**, *105* (12), 123002.
Gossel, G. H., et. al. *J. Chem. Phys.* **2019**, *150* (15), 154112.

Factorized Electron-Nuclear Dynamics (FENDy): The Vision

Combine quantum trajectory description of nuclei with wave packet description of electrons for scalability to large systems

"optimal grid"

$$\psi(y,t) = |\psi| e^{iS(y,t)}$$

$$p = \nabla S(y,t)$$

$$\dot{y} = \frac{p}{M} \qquad \dot{p} = -\nabla(\mathrm{V} + \mathrm{U})$$

$$U = -\frac{\hbar^2}{2M}\frac{\nabla^2|\psi|}{|\psi|}$$

Electronic "wavepackets"

XF: $\Psi(x,y,t) = \psi(y,t)\Phi(\mathrm{x},\mathrm{y},\mathrm{t})$

BH: $\Psi(x,y,t) = \sum_i^{\infty} \psi_i(y,t)\Phi_i(x;y)$

Electronic functions "riding" nuclear trajectories

S. Garashchuk, **J. Stetzler**, and V. Rassolov. *J. Chem. Theory Comp.* **2023** *19* (5), 1393-1408

Factorized Electron-Nuclear Dynamics (FENDy) with a Complex Potential

XF ansatz:

$$\Psi(x,y,t) = \psi(y,t)\Phi(x,y,t)$$

FENDy with complex potential:

$$\hat{K}_y\psi + V_d(y,t)\psi = i\partial_t\psi$$

$$\hat{H}_{el}\Phi + \left(\hat{D}_2 + \hat{D}_1\right)\Phi - V_d(y,t)\Phi = i\partial_t\Phi$$

Definitions:

$$\hat{D}_2 = \hat{K}_y = -\frac{1}{2M}\nabla_y^2$$

$$\hat{D}_1 = -\frac{1}{M}\frac{\nabla_y\psi}{\psi}\nabla_y$$

$$\hat{H}_{el} = -\frac{1}{2}\nabla_x^2 + V(x,y)$$

$$\bar{p}_\Phi =< \Phi|\nabla_y \arg(\Phi)|\Phi >_x$$

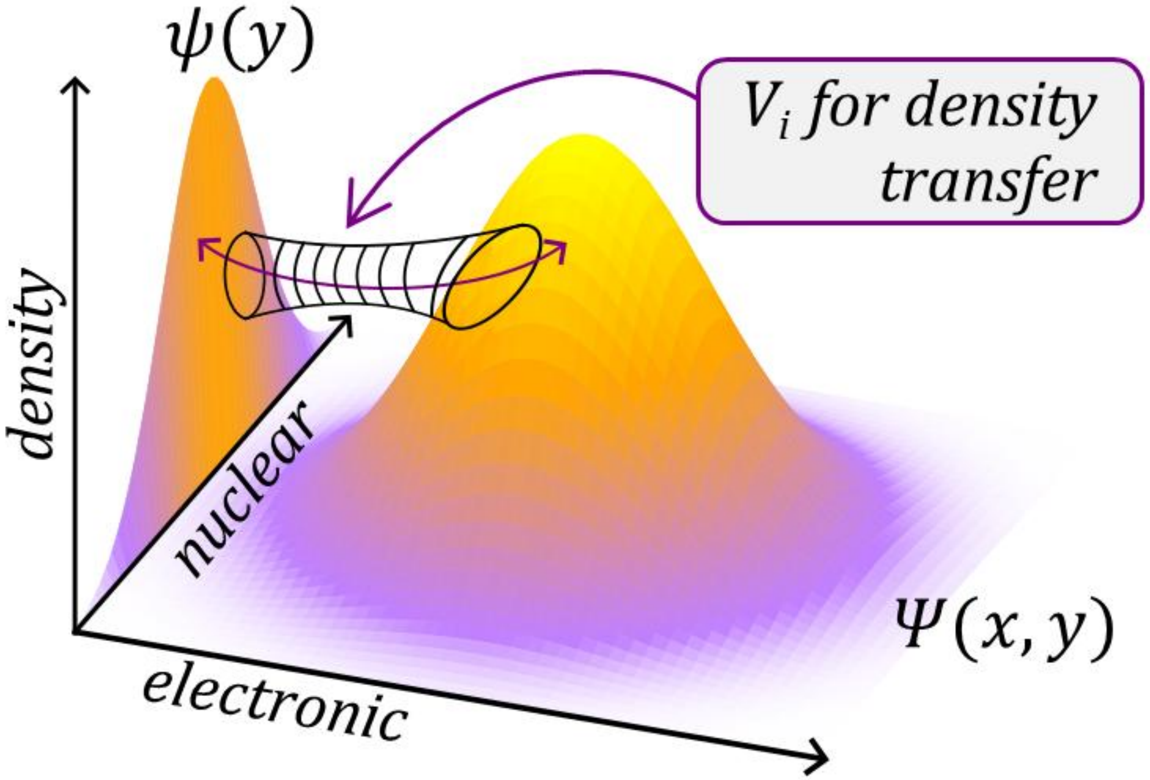
$$V_d = V_r + iV_i$$

S. Garashchuk, **J. Stetzler**, and V. Rassolov. Factorized Electron–Nuclear Dynamics with an Effective Complex Potential , *Journal of Chemical Theory and Computation* **2023** *19* (5), 1393-1408

Factorized Electron-Nuclear Dynamics (FENDy) with a Complex Potential

V_d…

- drives the dynamics
- captures average force from the electrons
- controls factorization of amplitude and phase

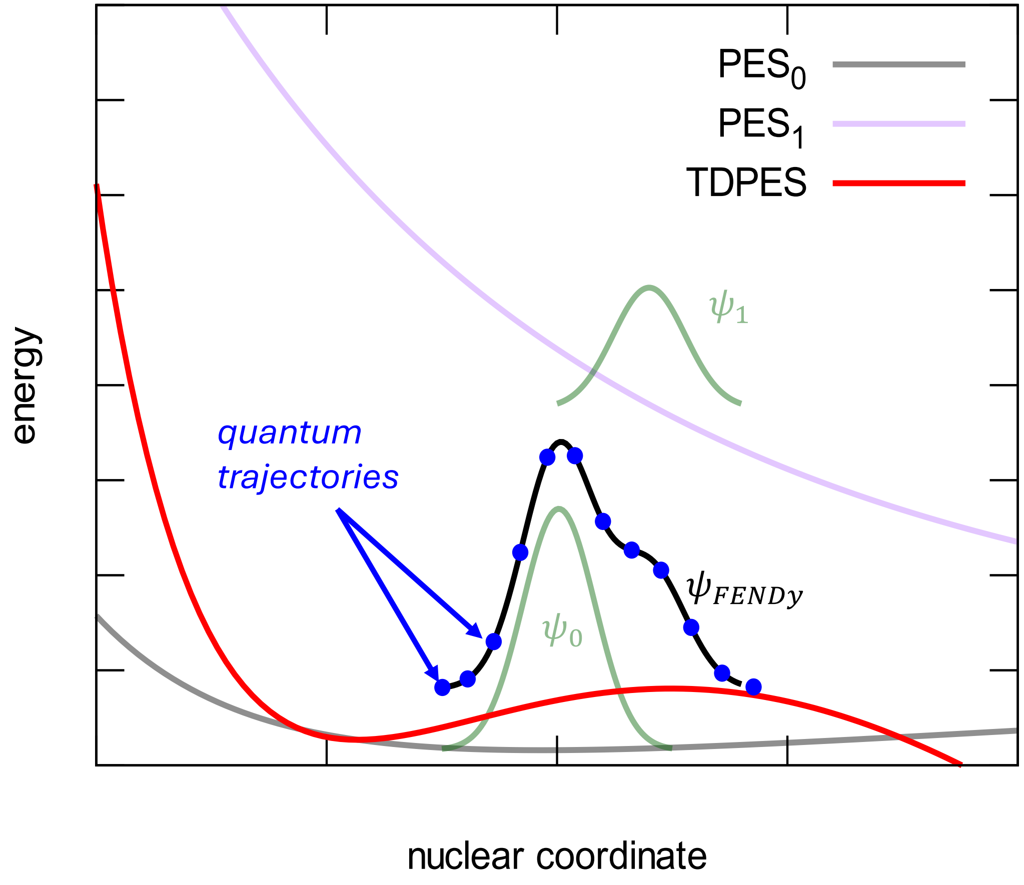


PNC: $\langle\Phi|\Phi\rangle_x = 1$ for all y, t

S. Garashchuk, **J. Stetzler**, and V. Rassolov. Factorized Electron−Nuclear Dynamics with an Effective Complex Potential , *Journal of Chemical Theory and Computation* **2023** *19* (5), 1393-1408

H_2^+ with FENDy

- Let's put a real electron and simulate photodissociation : H_2^+ w/ 6-31G basis
- **Problem:** Numerical implementation of FENDy
- Several unique conceptual challenges
  - Derivatives on unstructured grids
  - PNC
  - Propagation scheme



J. Stetzler, et. al. "Factorized electron-nuclear dynamics with effective complex potential: On-the-fly implementation for H2+ in a laser field" *Molecular Physics*. doi: 10.1080/00268976.2025.2611404.

FENDy Algorithm

FENDy algorithm

*/**Initialize basis sets***/

1: Initialize standard electronic structure basis set

*/**Read Parameters***/

2: QT parameters:

Number of quantum trajectories and span

3: Electronic projection basis parameters:

Number of Fourier functions and carrier frequency

4: Laser parameters:

Width, peak time, intensity and frequency of the laser (Table I)

*/**Initialize auxiliary bases***/

5: Define arrays for projections of p_ψ,r_ψ,V_d, and $\mathbf{C}$

*/**Initialize trajectories and electronic wavepackets***/

6: Compute electronic matrix elements in AO basis

7: Initialize trajectories on a uniform grid

8: Initialize interpolation scheme for electronic matrix elements

*/**Time loop***/

Time propagation algorithm

*/**Time loop***/

for n from 1 to N_{steps} *do*

*/**Self-consistent propagation***/

do

*/**Compute time-derivatives***/

9: Electronic matrix elements via interpolation

10: Project $\mathbf{C}$ into Fourier basis

11: Compute $(\hat{D}^{(1)} + \hat{D}^{(2)})|\Phi\rangle$

12: Compute $\overline{p_\Phi}$

13: Compute $\frac{d}{dt}\mathbf{C}$,$\langle\Phi|\mathbf{H}_D|\Phi\rangle_R$

14: Project V_d into $\boldsymbol{f}^{V_d}$

15: Project p_ψ into $\boldsymbol{f}^{p_\psi}$

16: Compute quantum force

17: Compute $\frac{d}{dt}p_\psi$ and $\frac{d}{dt}q_t$

18: Compute sum of squares change in $F(t+dt)$ from previous step

19: Compute average of $F(t+dt)$ and $F(t)$

20: Project r_ψ of average into f^{r_ψ}

until `error < threshold` *or* `iteration > max(iteration)`

*/**Low pass filter***/

21: Project $\mathbf{C}$, replace with $\tilde{\mathbf{C}}$ and re-normalize.

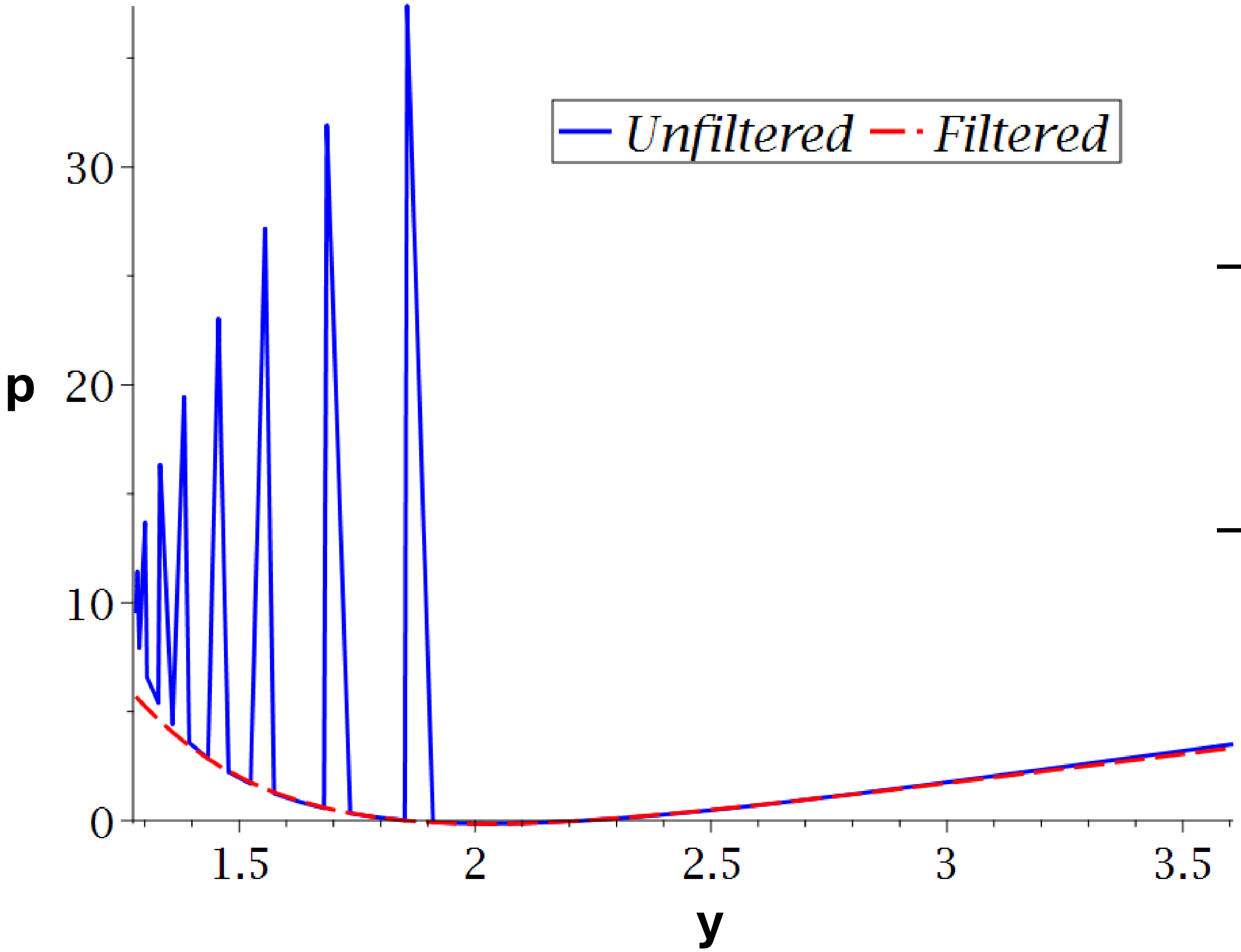
22: Project r_ψ and replace with $\tilde{r}_\psi$

23: Project p_ψ and replace with $\tilde{p}_\psi$

end do

J. Stetzler, et. al. "Factorized electron-nuclear dynamics with effective complex potential: On-the-fly implementation for H2+ in a laser field" *Molecular Physics*. doi: 10.1080/00268976.2025.2611404.

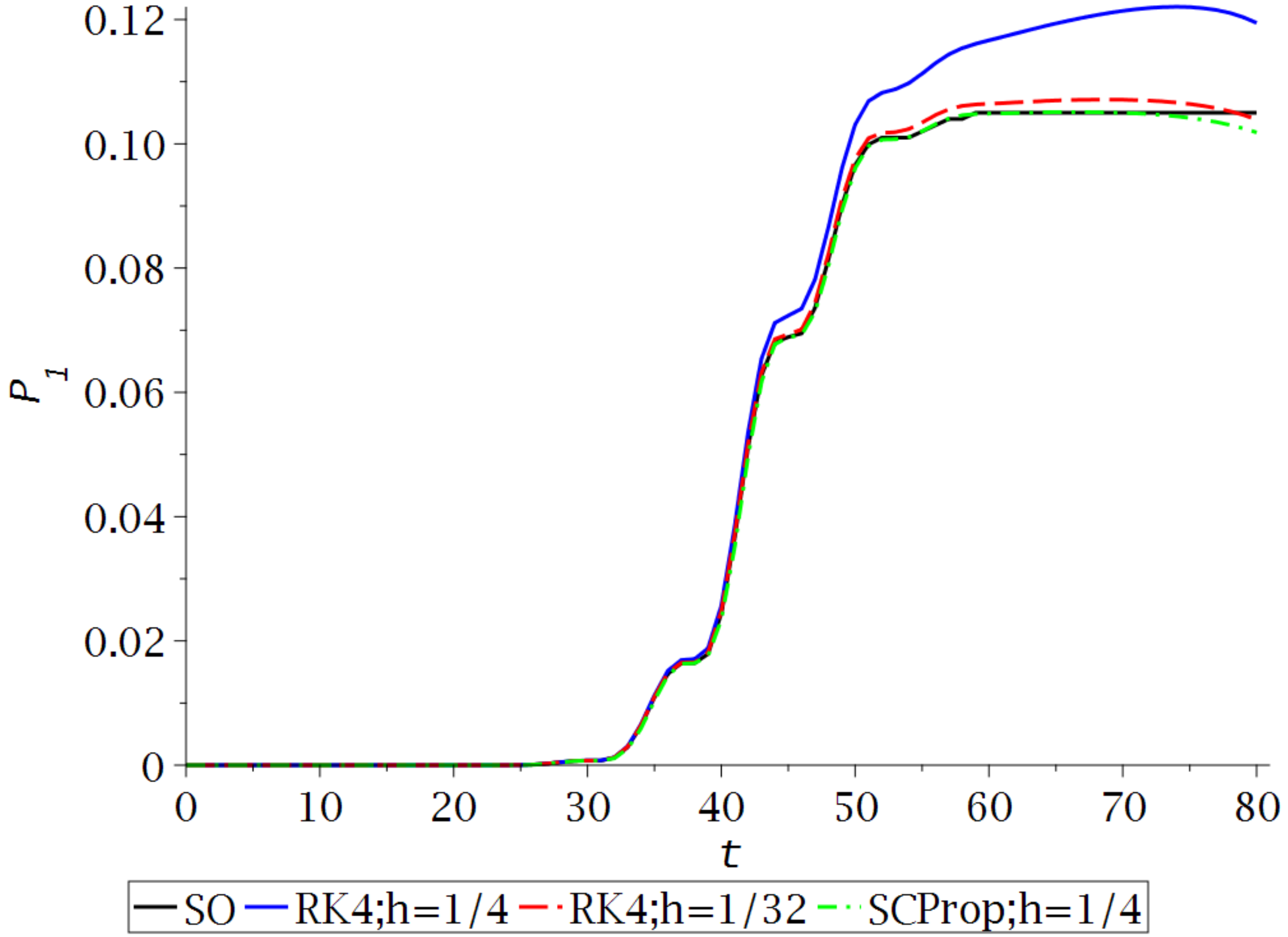
Suppressing noise via Low Pass Filter



- Projection into a basis reduces noise from unphysical crossing of trajectories
- Convenient way to obtain derivatives

J. Stetzler, et. al. *Molecular Physics* (2026)

Self-Consistent Prop

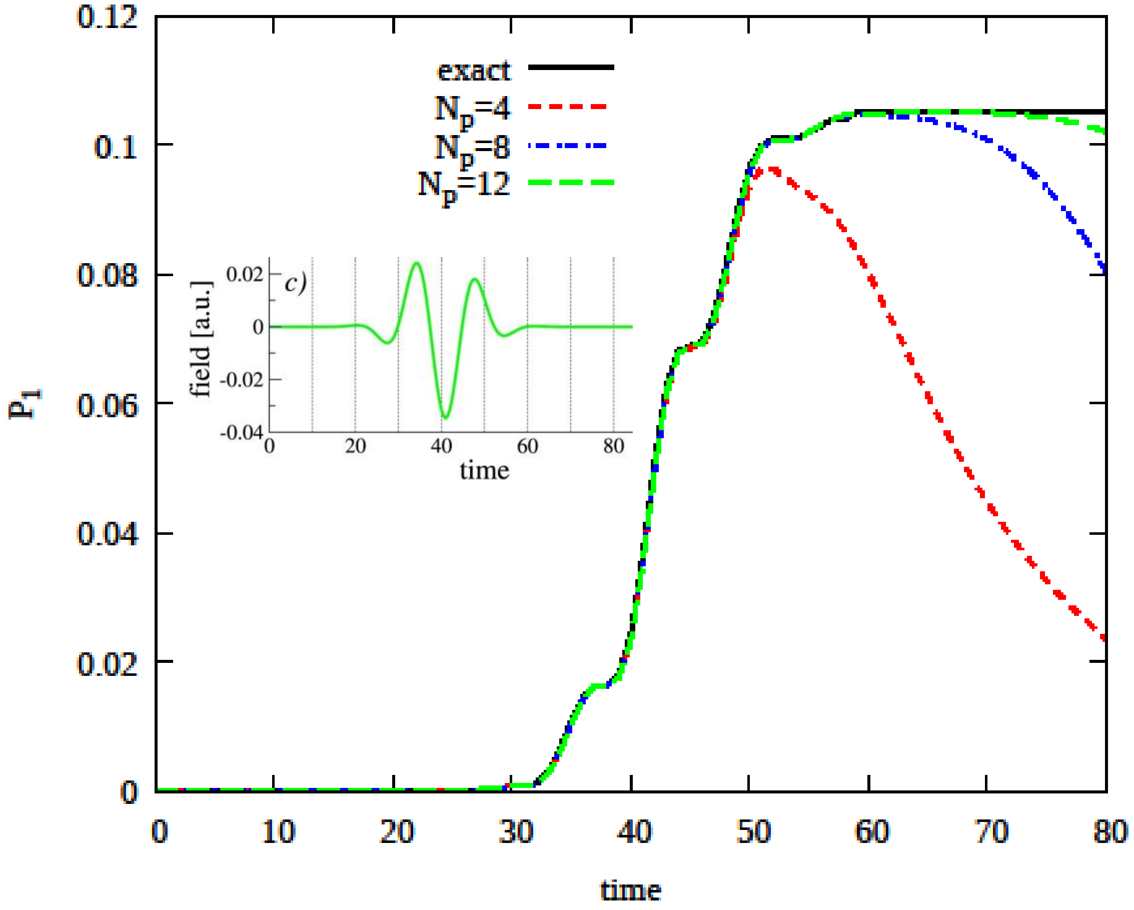


-RK4 was very slow to converge for this system

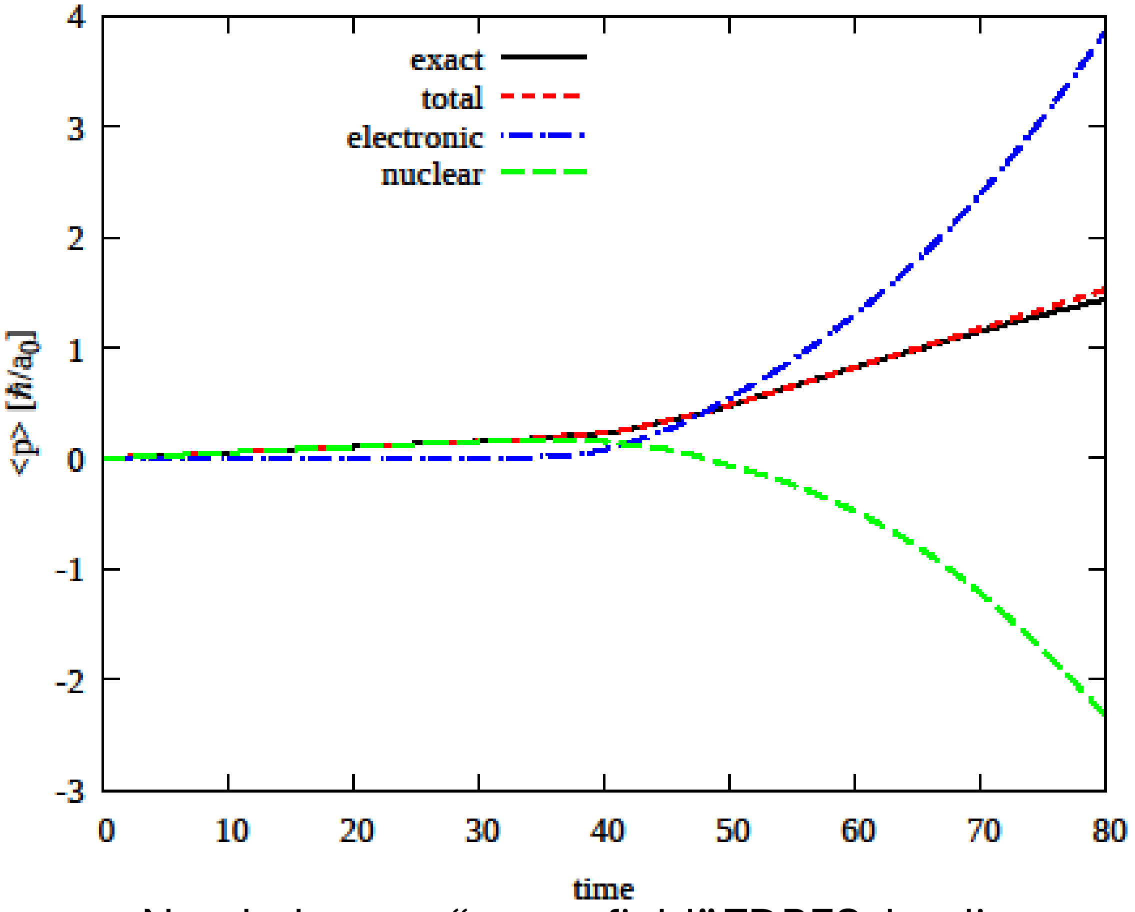
Idea adapted from:
J. Jakowski, et. al. , J. Chem. Theory Comput. **21** (3), 1322–1339 (2025). doi:10.1021/acs.jctc.4c01241.

J. Stetzler, et. al. "Factorized electron-nuclear dynamics with effective complex potential: On-the-fly implementation for H2+ in a laser field" *Molecular Physics*. doi: 10.1080/00268976.2025.2611404.

FENDy Applied to H_2^+



Convergence to exact results



Needed to use “mean-field” TDPES, leading to electronic momentum

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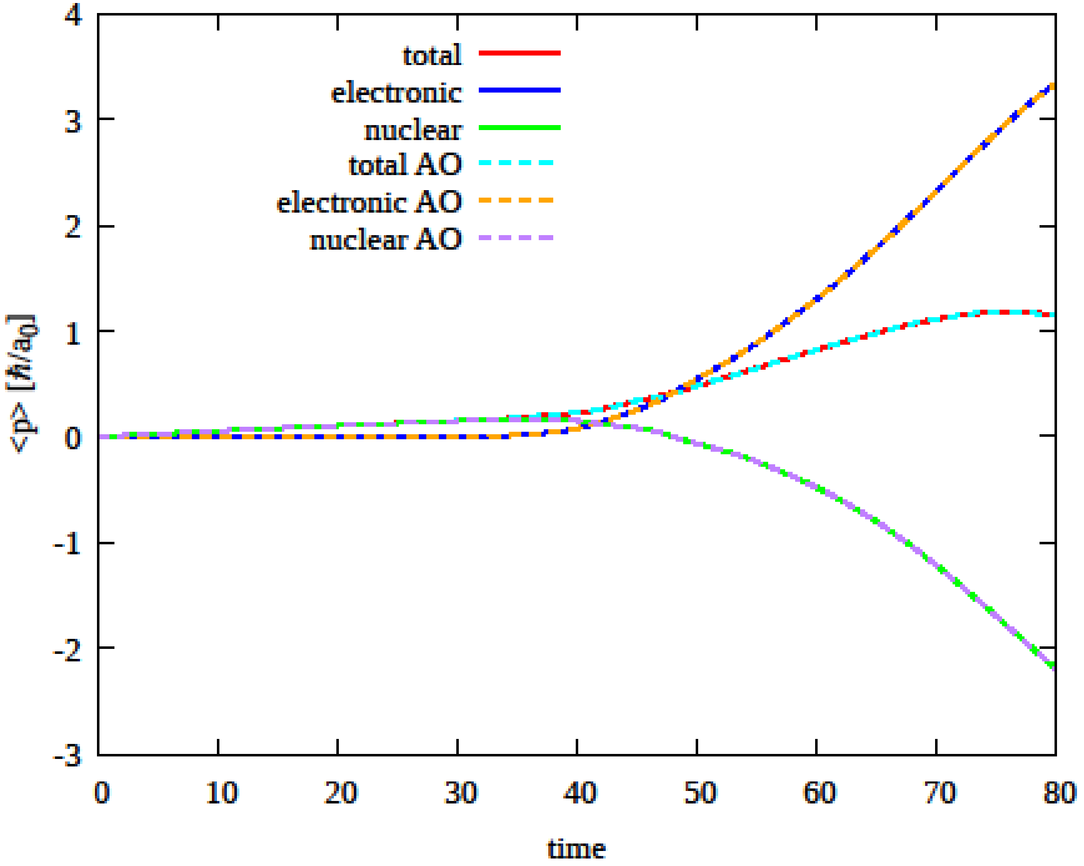
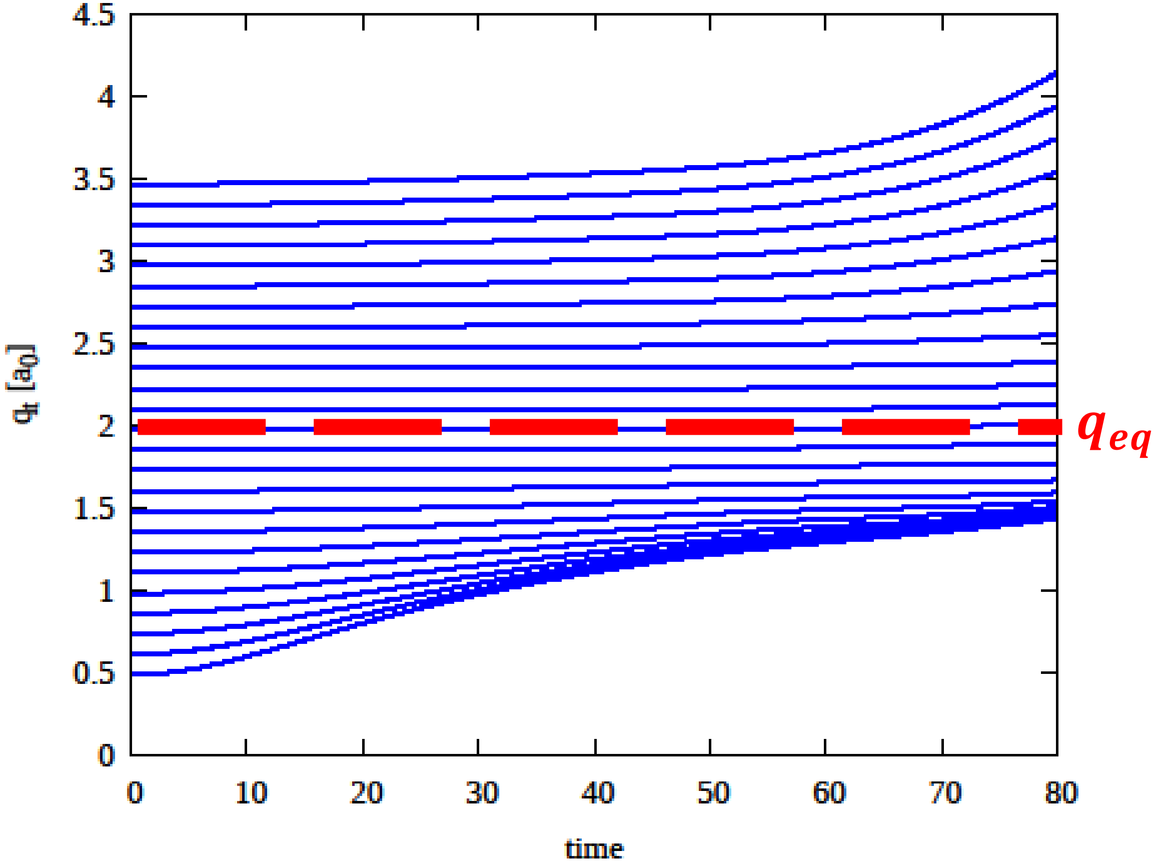
FENDy Success! For short times...

Avoid eigenfunction calculation and success with QT implementation





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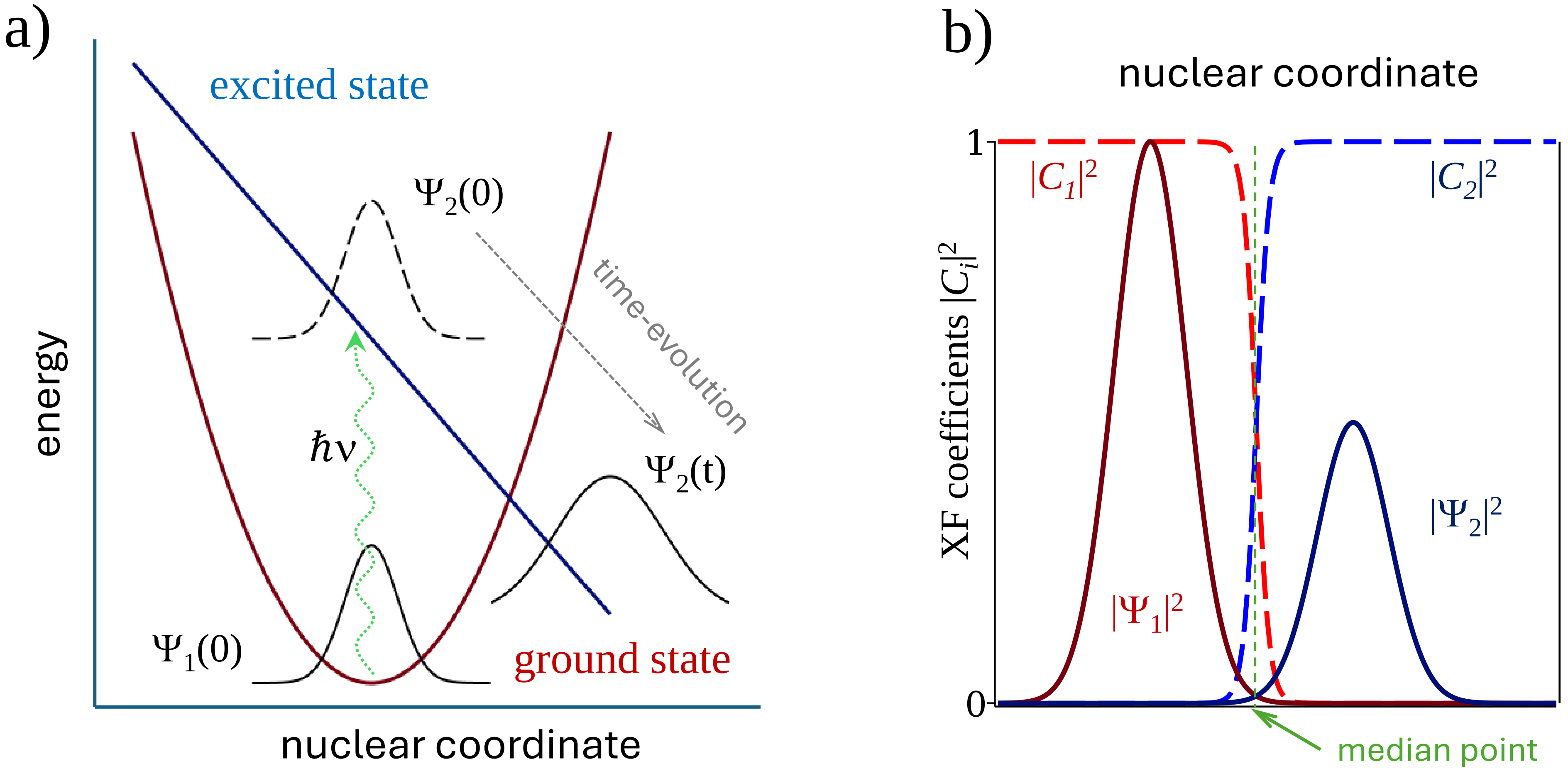
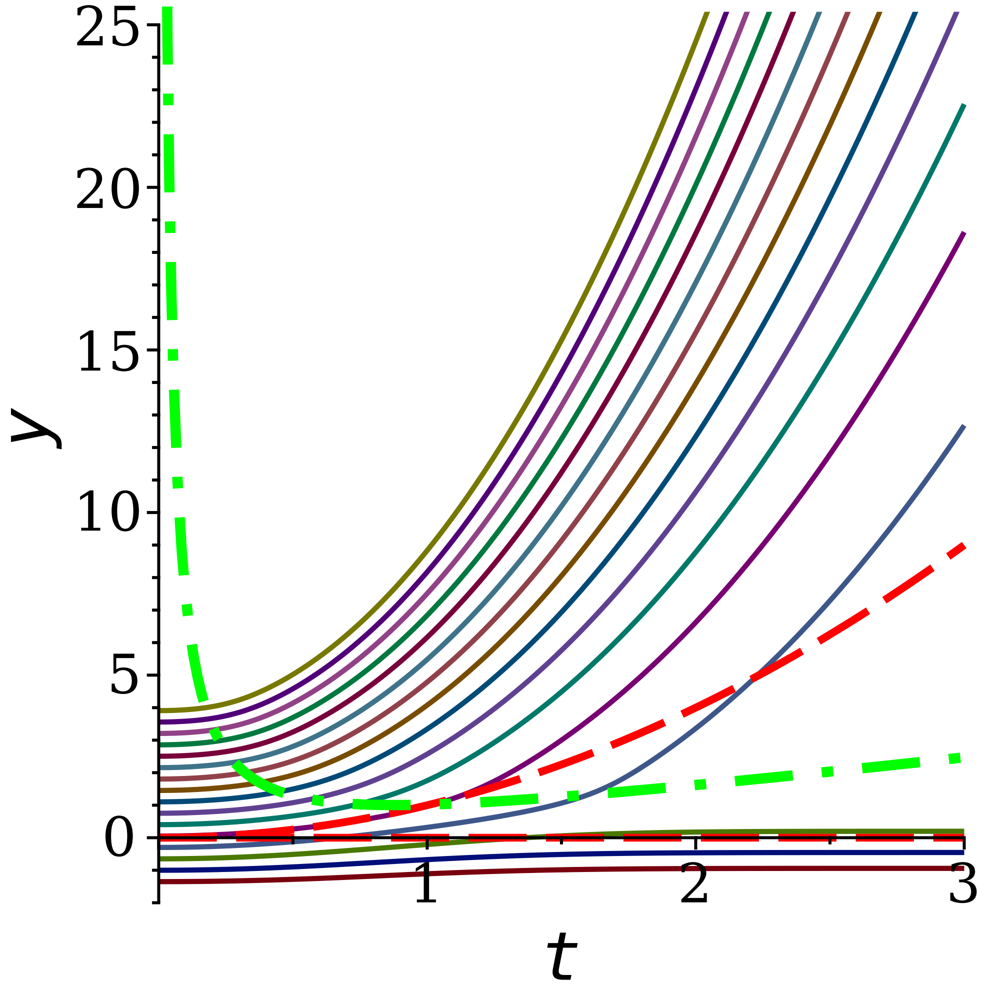
Dynamics of Bifurcating Factorized Wavefunctions

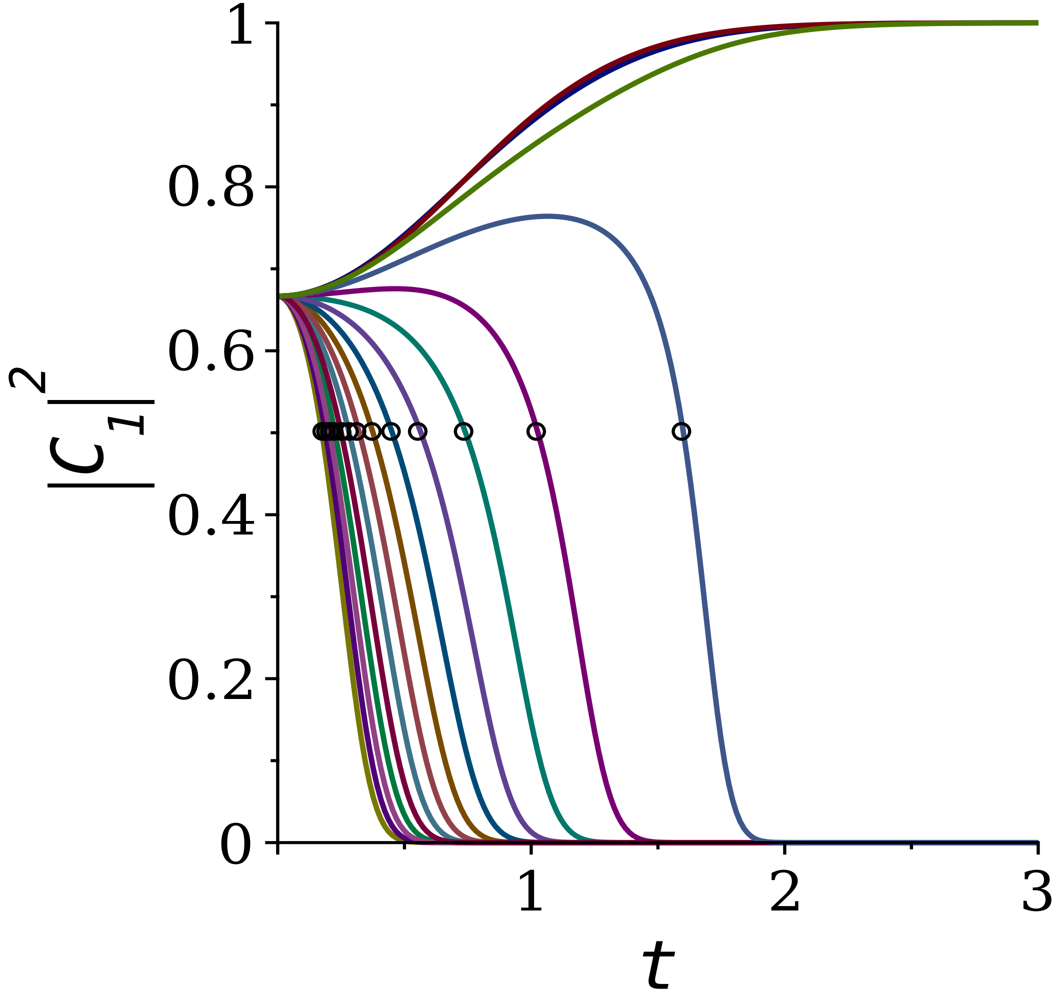


Size of derivative is $O(t^3)$

J. Stetzler, S. Garashchuk, V. A. Rassolov “Analysis of divergent dynamics of exactly factorized electron-nuclear wavefunctions” *Philosophical Magazine C: Quantum Matter, Theory and Phenomena* (2026), 1–20. doi: 10.1080/14786435.2026.2612828

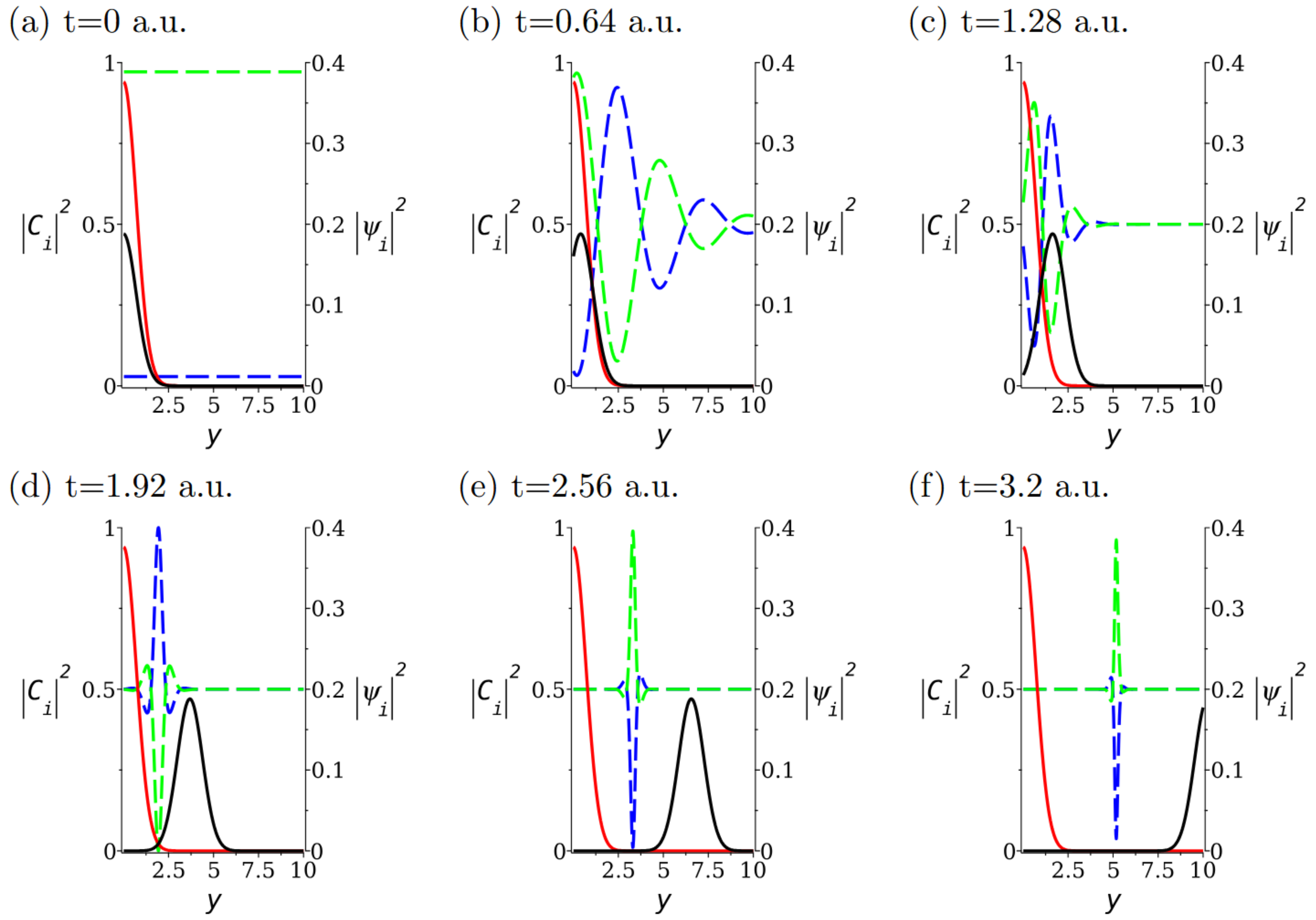
The problem of derivatives





J. Stetzler, S. Garashchuk, V. A. Rassolov “Analysis of divergent dynamics of exactly factorized electron-nuclear wavefunctions” *Philosophical Magazine C: Quantum Matter, Theory and Phenomena* (2026), 1–20. doi: 10.1080/14786435.2026.2612828

Localized Basis Diverging Wavepackets



J. Stetzler, et. al. *Philosophical Magazine C* (2026), 1–20

Summary

Built a numeric code from scratch for FENDy; and explored electron-nuclear dynamics in small systems

- Singularities limit simulation time
- Potential applications for obtaining initial conditions of NA-MD simulations
- Better definitions of V_r to minimize residual nuclear momentum
- Compatibility with real-time electronic structure

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https://doi.org/10.1080/00268976.2025.2611404
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Factorised electron-nuclear dynamics with effective complex potential: on-the-fly implementation for H_2^+ in a laser field

Julian Stetzler, Sophya Garashchuk and Vitaly Rassolov

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PHILOSOPHICAL MAGAZINE
https://doi.org/10.1080/14786435.2026.2612828
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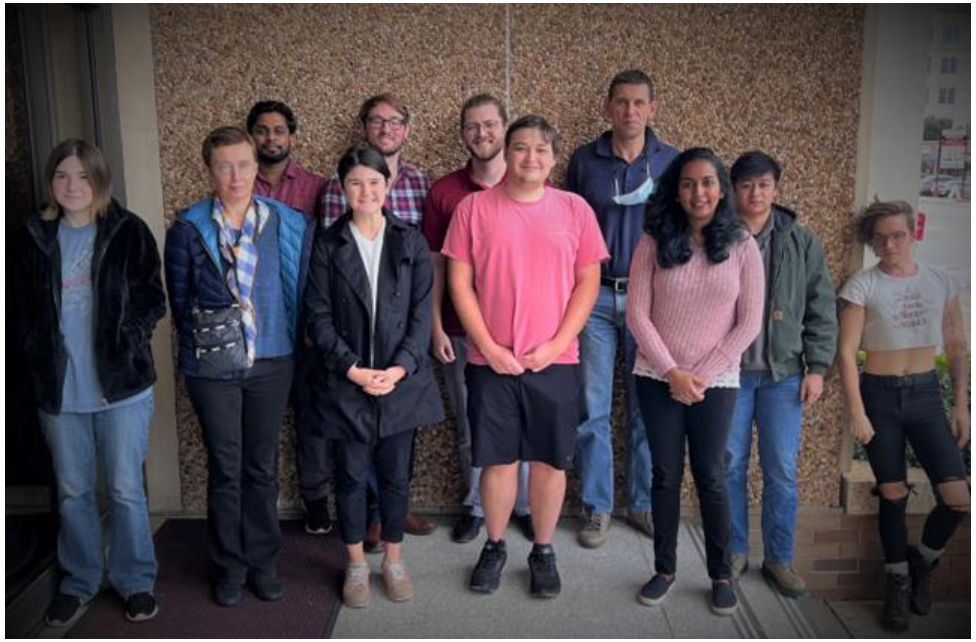
Analysis of divergent dynamics of exactly factorised electron-nuclear wavefunctions

Julian Stetzler, Sophya Garashchuk and Vitaly A. Rassolov

Department of Chemistry & Biochemistry, University of South Carolina, Columbia, SC, USA

Thank you!

Professor Vitaly Rassolov
Professor Sophya Garashchuk
Dr. Sachith Wickramasinghe
Dr. Shehani Wettasinghe
Dr. Matt Dutra
Dr. Giacomo Botti
Austin Hill
Chanikya Jayawardana
Michael Safo



The Imaginary Potential

- V_i will maintain normalization

$$\frac{d}{dt}\langle\Phi|\Phi\rangle_x = 0$$

Definitions:

$$\widehat{D}_2 = \widehat{K}_y = -\frac{1}{2M}\nabla_y^2$$

$$\widehat{D}_1 = -\frac{1}{M}\frac{\nabla_y\psi}{\psi}\nabla_y$$

$$\widehat{H}_{el} = -\frac{1}{2}\nabla_x^2 + V(x,y)$$

$$\bar{p}_\Phi =< \Phi|\nabla_y \arg(\Phi)|\Phi >_x$$

$$V_i = -\frac{1}{M}\left(\frac{\nabla_y|\psi|}{|\psi|} + \nabla_y\right)\bar{p}_\Phi$$

Exact in a complete basis

$$V_i = \Im(\langle\widehat{D}_1 + \widehat{D}_2\rangle_x)$$

Exact in a finite basis

Both proportional to $\bar{p}_\Phi$

S. Garashchuk, **J. Stetzler**, and V. Rassolov. *J. Chem. Theory Comp.* **2023** *19* (5), 1393-1408

J. Stetzler, et. al. “Factorized electron-nuclear dynamics with effective complex potential: On-the-fly implementation for H2+ in a laser field” *Molecular Physics*. doi: 10.1080/00268976.2025.2611404.

The Real Potential

- Ideal V_r defined to satisfy

$$\frac{d}{dt}\bar{p}_\Phi = 0$$

When satisfied $V_i = 0$

Definitions:

$$\hat{D}_2 = \hat{K}_y = -\frac{1}{2M}\nabla_y^2$$

$$\hat{D}_1 = -\frac{1}{M}\frac{\nabla_y \psi}{\psi}\nabla_y$$

$$\hat{H}_{el} = -\frac{1}{2}\nabla_x^2 + V(x,y)$$

$$\bar{p}_\Phi =< \Phi|\nabla_y \arg(\Phi)|\Phi >_x$$

$$\nabla_y V_r = \langle \nabla_y \hat{H}_{el} \rangle_x + \left(\frac{4\nabla_y|\psi|}{|\psi|} + 2\nabla_y\right)\langle \hat{\mathrm{D}}_2 \rangle_x$$

Exact in a complete basis and defined for 1D nucleus

$$V_r = \Re(\langle \hat{H}_{el} + \hat{D}_1 + \hat{D}_2 \rangle_x)$$

Numerically stable in a finite basis

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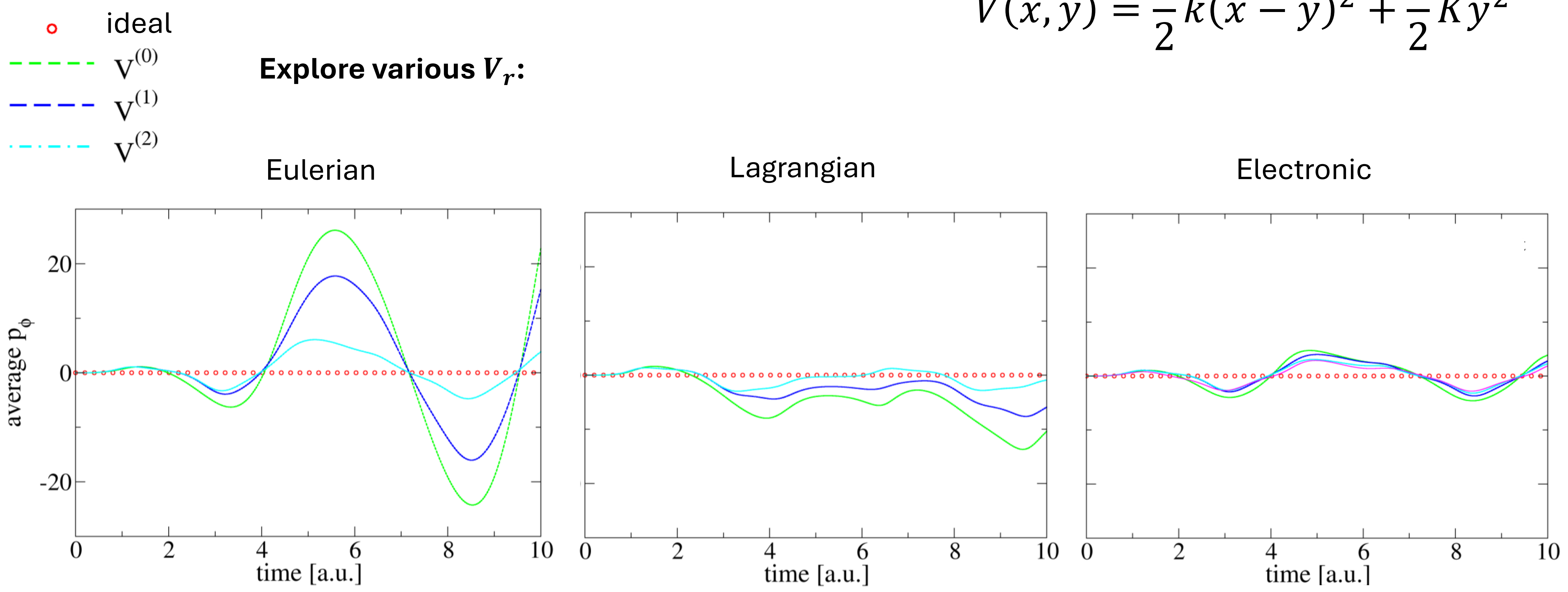
FENDy in a model system

Problem: V_i uniquely defined; V_r only for 1D nuclei

KST Model:

$$V(x,y) = \frac{1}{2}k(x-y)^2 + \frac{1}{2}Ky^2$$

Explore various V_r:



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More on Bohmian Dynamics

The quantum trajectory formulation offers some distinct advantages

$$\psi(y,t) = |\psi| e^{iS(y,t)}$$

$$p = \nabla_y S(y,t)$$

Continuity euation

$$\frac{d\rho_t}{dt} = -\frac{\rho_t}{M}\left(\nabla_y\,(\nabla_{\mathrm{y}} S)\right)\Big|_{y=yt}$$

Trajectory weight conservation:

$$w_t := w(y_t) = |\psi|^2 dy_t$$
$$w_t = w_0$$

Expectation values:

$$\langle \hat{O} \rangle = \int O(y)|\psi|^2 dy \approx \sum_i^{NTraj} O(y_t) w_t$$

S. Garashchuk, **J. Stetzler**, and V. Rassolov. *J. Chem. Theory Comp.* **2023** *19* (5), 1393-1408

Self-Consistent Propagation

Time propagation algorithm

*/**Time loop***/

for n from 1 to N_{steps} *do*

*/**Self-consistent propagation***/

do

*/**Compute time-derivatives***/

Electronic matrix elements via interpolation

Project $\mathbf{C}$ into Fourier basis

Compute $(\hat{D}^{(1)} + \hat{D}^{(2)})|\Phi\rangle$

Compute $\overline{p_\Phi}$

Compute $\frac{d}{dt}\mathbf{C}, \langle\Phi|\mathbf{H}_D|\Phi\rangle_{\mathbf{R}}$

Project V_d into $\boldsymbol{f}^{V_d}$

Project p_ψ into $\boldsymbol{f}^{p_\psi}$

Compute quantum force

Compute $\frac{d}{dt}p_\psi$ and $\frac{d}{dt}q_t$

Compute sum of squares change in $F(t+dt)$ from previous step

Compute average of $F(t+dt)$ and $F(t)$

Project r_ψ of average into f^{r_ψ}

until `error < threshold` *or* `iteration > max(iteration)`

*/**Low pass filter***/

Project $\mathbf{C}$, replace with $\tilde{\mathbf{C}}$ and re-normalize.

Project r_ψ and replace with $\tilde{r}_\psi$

Project p_ψ and replace with $\tilde{p}_\psi$

end do

Found to provide better convergence in larger (by number of parameters) systems

$$F(t) \coloneqq y(t), p(t), C(t)$$

Compute F(t+dt) self consistently using

$$F_{av} = \frac{F(t) + F(t+dt)}{2}$$

Error computed as:

$$\sum_i |\Delta y_i|^2 + |\Delta p_i|^2 + \sum_j |\Delta C_{ij}|^2$$

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Self-Consistent Propagation

Time propagation algorithm

***/Time loop*/**

for n from 1 to N_{steps} *do*

***/Self-consistent propagation*/**

do

***/Compute time-derivatives*/**

Electronic matrix elements via interpolation

Project **C** into Fourier basis

Compute $(\hat{D}^{(1)} + \hat{D}^{(2)})|\Phi\rangle$

Compute $\overline{p_\Phi}$

Compute $\frac{d}{dt}\mathbf{C}, \langle\Phi|\mathbf{H}_D|\Phi\rangle_{\boldsymbol{R}}$

Project V_d into $\boldsymbol{f}^{V_d}$

Project p_ψ into $\boldsymbol{f}^{p_\psi}$

Compute quantum force

Compute $\frac{d}{dt}p_\psi$ and $\frac{d}{dt}q_t$

Compute sum of squares change in $F(t+dt)$ from previous step

Compute average of $F(t+dt)$ and $F(t)$

Project r_ψ of average into f^{r_ψ}

until `error < threshold` *or* `iteration > max(iteration)`

***/Low pass filter*/**

Project **C**, replace with $\tilde{\mathbf{C}}$ and re-normalize.

Project r_ψ and replace with $\tilde{r}_\psi$

Project p_ψ and replace with $\tilde{p}_\psi$

end do

Found to provide better convergence in larger (by number of parameters) systems

$$F(t) \coloneqq y(t), p(t), C(t)$$

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Equations for V_r

$$V_r^{eul} = \overline{H}_{el} + \Re(\overline{D_2}) + \frac{\overline{p_\Phi} p_\psi}{M},$$

$$V_r^{lagr} = \overline{H}_{el} + \Re(\overline{D_2}) + \frac{\overline{p_\Phi} p_\psi}{M} - \frac{p_t}{M}\overline{p_\Phi}$$

$$V_r^{el} = \overline{H}_{el} + \Re(\overline{D_2}) + \frac{\overline{p_\Phi} p_\psi}{M} - \frac{\overline{p_\Phi}}{M}\overline{p_\Phi}$$

$$\nabla_y V_r = \langle \nabla_y V \rangle + \frac{1}{M}\left(2r_\psi + \nabla_y\right)\langle r_y^2 + p_\Phi^2 \rangle$$

LSF Eqs

$$I =< f(y) - \tilde{f}(y) | f(y) - \tilde{f}(y) >$$

$$\tilde{f} = \sum_i b_i \omega_i(y)$$

$$\vec{b} = \mathbf{S}^{-1}\,\vec{d}$$

$$\mathbf{S}_{\text{ij}} =< \omega_i \omega_j >$$
$$\vec{d}_i =< f\omega_i >$$

Variational Wavepackets

- **Motivation of the paper:** Modeling effects of molecular environments on a quantum subsystems using the TDSE

- My part was coding and analytically evaluating the error functionals for the simplest cases

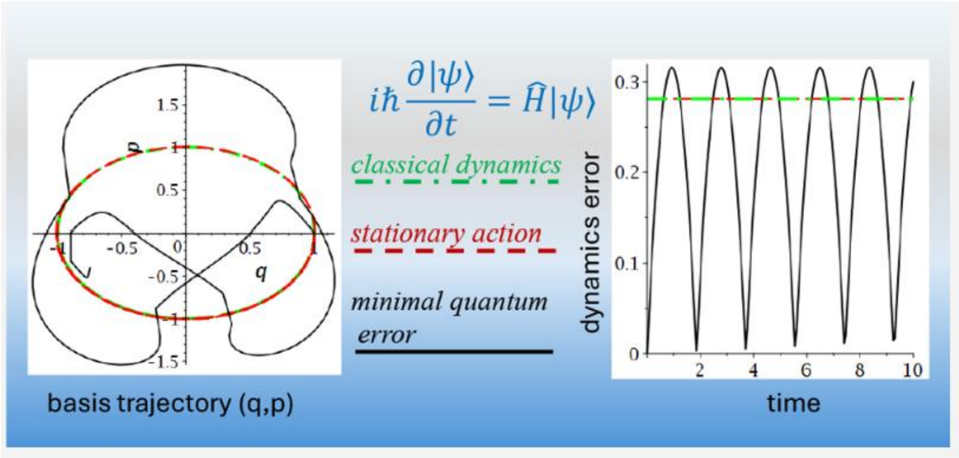
JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

Variational Dynamics of Multicomponent Wave Functions Represented in a Basis Driven by a Time-Dependent Gaussian Wavepacket

Sophya Garashchuk,* Julian Stetzler, Chanikya D. Jayawardana, Michael Anim Safo, and Vitaly A. Rassolov

Cite This: J. Chem. Theory Comput. 2025, 21, 7249–7266 Read Online



FIA Outliers

- Outliers were species with large negative charges far from the boron center or molecules with large substituents (t-butyl)
- Modelled steric by included surface area and volume of each molecule in the fit
- Also computed solvated FIA with SM6 (challenge was accuracy of Flouride ion)