# Factorized electron-nuclear dynamics with an effective complex potential

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# Outline

1. Motivation and background
2. Nuclear subspace-factorized wavefunctions
3. Vibrationally non-adiabatic model
4. Summary

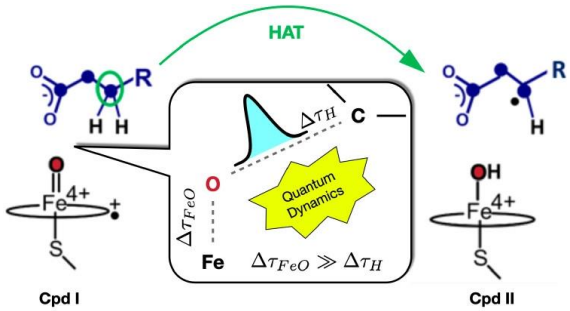
# Nuclear quantum effects (NQE)

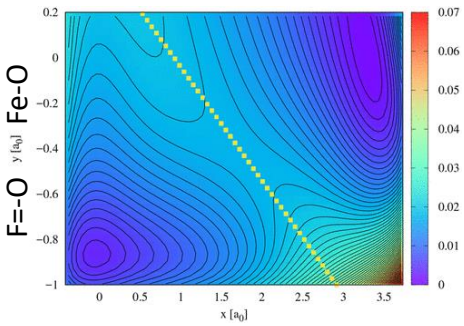
*hard NQE: tunneling*

Kinetic Isotope Effect in Cytochrome P450 Decarboxylase OleT

Experiments at T=[4,21]C at transient step:
KIE ~8–16; $E_a$=16/32 kJ/mol

[moderate tunneling; tunneling-ready state]

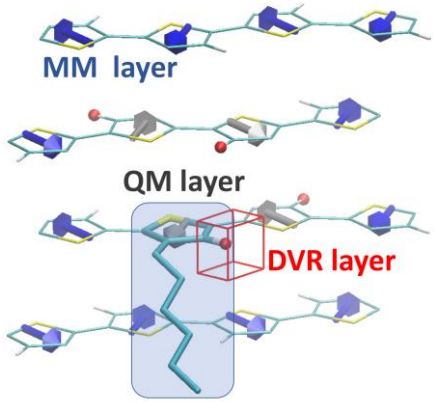



Dutra, Amaya, McElhenney, OManley, Makris, Rassolov, SG
*J. Phys. Chem. B* 126 (2022); *J. Phys. Chem. A* 126 (2022)

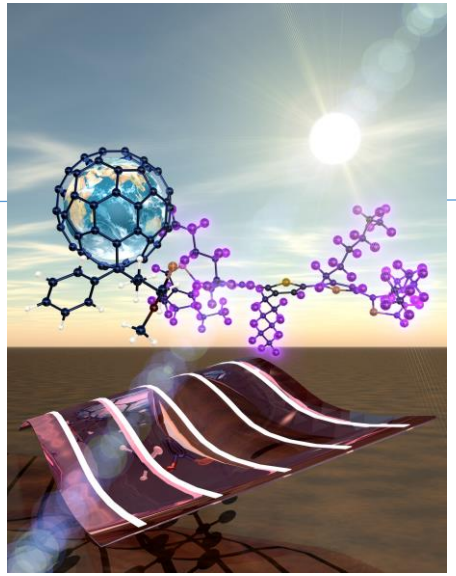
H/D substitution reduces polymer crystallinity of P3HT when D on main chain, but not on side chain

[ΔΔZPE crystal vs chain & NQE on dipoles, interchain correlation]




Jakowski, Huang, SG, Hong, Keum, Bobby Sumpter JPCL 2017

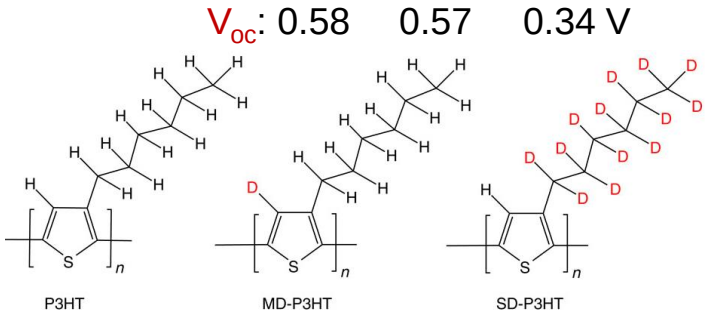
*soft NQE: ZPE, anharmonicity*



*electronic excitations + NQE*

H/D isotope effect on the optoelectronic properties of P3HT/PCBM

[fluctuations in HOMO-LUMO gaps]




https://www.ornl.gov/news/solar-surprise
Nature Comm. 5, 4180 (2013) doi:10.1038/ncomms4180
JCTC 12 (2016) Wang, Jakowski, SG, Sumpter

# coherence@photocatalysis

**Using coherence to enhance function in chemical and biophysical systems**

Scholes, G., Fleming, G., Chen, L. *et al.*. *Nature* **543**, 647–656 (2017).

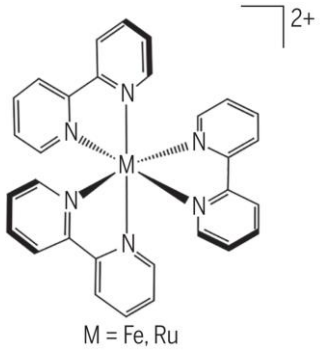
- high yield
- long-lived electronic excitations
- earth-abundant metals in chromopohores
- reversibility, favorable redox energetics
- property and functionality control

**On the use of vibronic coherence to identify reaction coordinates for ultrafast excited-state dynamics of transition metal-based chromophores**

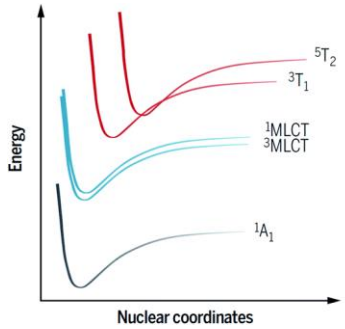
Paulus, McCusker *Faraday Discussions* 237, 274 (2022).

**Leveraging excited-state coherence for synthetic control of ultrafast dynamics**

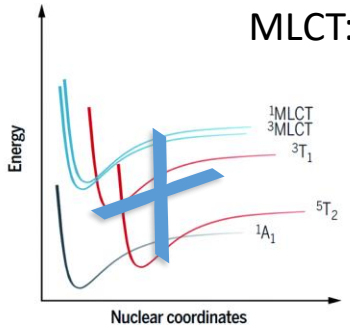
Paulus, B.C., Adelman, S.L., Jamula, L. *et al. Nature* **582**, 214–218 (2020).




***Ru ~100 ns***



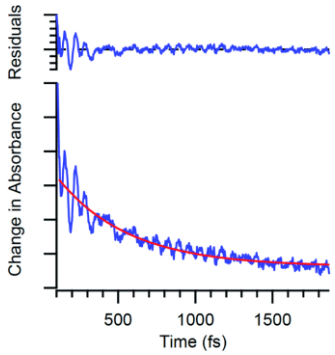

***Fe ~ 100 fs***

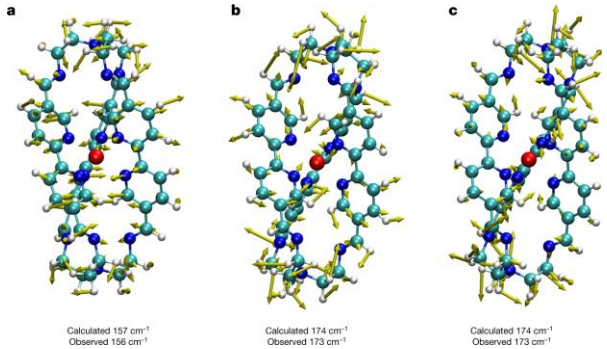



Photoinduced electron transfer

MLCT: metal-to-ligand charge transfer

identify DOFs coupled to MLCT→T evolution




chemical perturbation: 100-fold increase of MLCT lifetime

# quantum dynamics ~ quantum nuclei

$$H(t)|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

- NQEs and time-dependent Hamiltonians + exponential scaling of complexity
- take advantage of mass, energy and time-scale separation
- time-dependent bases, multilayer representations, trajectories

# established approaches for electrons + nuclei

- Born-Oppenheimer approx. → PES
- Classical trajectories for the nuclei
- Multiple electronic PES
- Ehrenfest trajectory dynamics; surface hopping
- Kinetic (non-adiabatic) vs potential (diabatic) formulation

Derivatives of PES w/r to nuclear positions are zeros

Backreaction from nuclear to electronic DOFs

PESs cross; Berry phase

Not exact, non-unique

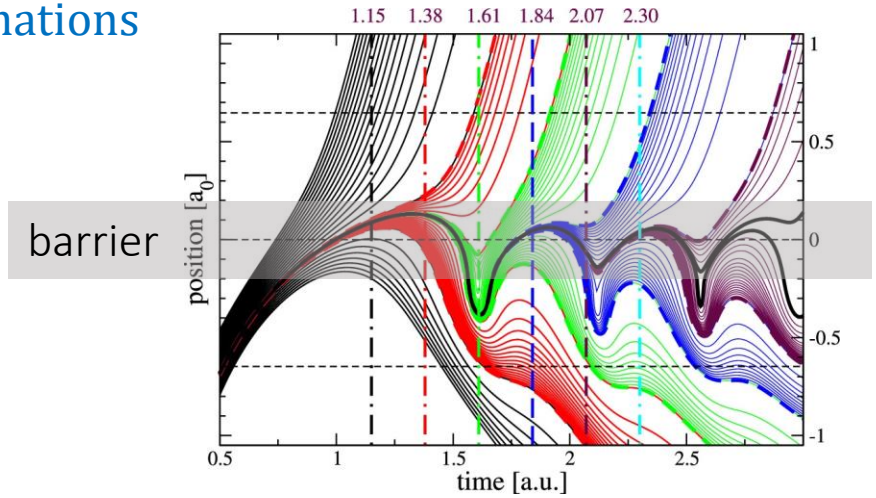
want to include the **dominant NQEs** within a trajectory frame for controllable approximations

Exact quantum trajectories (***q, p***)

$$\frac{d\boldsymbol{q}}{dt} = \frac{\boldsymbol{p}}{m} \qquad \boldsymbol{p} = \nabla(\arg\psi)|_{\boldsymbol{x}=\boldsymbol{q}}$$

trajectory 'weight' conservation

**Tunneling via WF coherence**




solve for the nuclei and electrons together

hard

- Nuclear-electronic orbital (NEO) method
- Electron-nuclear dynamics (END); multi-configuration END
- Exact factorization (XF), TDPES, conditional WF
- Nuclear subspace factorized END with effective complex potential


Deumens and Öhrn "Electron-nuclear dynamics with diabatic and adiabatic wave packets," J. Phys. Chem. 92, 3181–3189 (1988)

Wang et al Multi-configuration electron–nuclear dynamics: An open-shell approach J. Chem. Phys. 155, 154103 (2021)D

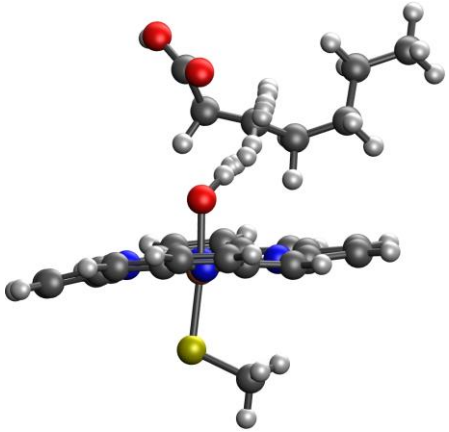
SG, Stetzler, Rassolov "Factorized Electron-Nuclear Dynamics with an Effective Complex Potential" JCTC (2023)

# XF- and QT- inspired fast/slow factorization

light: m, x  heavy: M, y

$$\Psi(x,y,t) = \underbrace{\Phi(x,y,t)}_{electronic}\underbrace{\psi(y,t)}_{nuclear}$$

$$\psi(y,t) = \sqrt{\rho(y,t)}e^{\imath s(y,t)} \qquad \dot{y}_t = \frac{p_t}{M}$$



**requirements**

(i) light DOF  norm conservation

(ii) continuity eq for heavy DOF along

or trajectory weight conservation

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separate TDSEs  via a complex potential

$$V_d := V_r(y,t) + \imath V_i(y,t)$$

$$\Phi \underbrace{\left[(\hat{K_y} + V_d)\psi - \imath\partial_t\psi\right]}_{=0,\ nuclear\ TDSE} + \psi \underbrace{\left[(\hat{K_x} + \hat{K_y} - \frac{1}{M}\frac{\nabla_y\psi}{\psi}\nabla_y + V - V_d)\Phi - \imath\partial_t\Phi\right]}_{=0,\ electronic\ TDSE} = 0$$

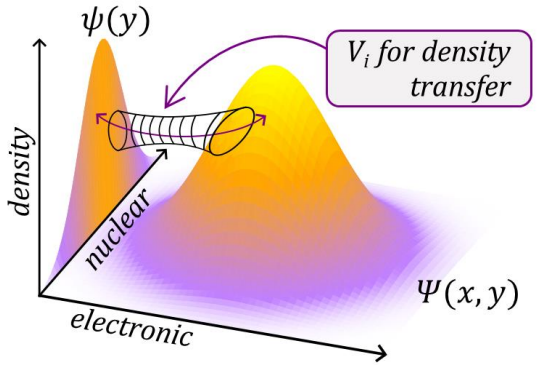
$$\psi(y,t) = \sqrt{\rho(y,t)}e^{\imath s(y,t)}$$

## conditions

$$\partial_t N(y) = -\imath(\langle\Phi|(\hat{D}_1 + \hat{D}_2)\Phi\rangle_x - \langle(\hat{D}_2 + \hat{D}_1)\Phi|\Phi\rangle_x - 2V_i N(y)$$

$$\partial_t \rho + \frac{\nabla_y s}{M}\nabla\rho + \frac{\nabla_y^2 s}{M}\rho - 2V_i\rho = 0$$

derivation …




## results

trajectory follows the average momentum in *y*
(normalized by the electronic density at y)

$$p_t = \nabla_y s + \overline{p_\Phi}$$

$$p_\Phi := \nabla_y(\arg\Phi)$$

imaginary potential

$$V_i = \Im(\langle\Phi(\hat{D}_2 + \hat{D}_1)\Phi\rangle) = -\frac{\nabla_y\overline{p_\Phi}}{2M} - \frac{\overline{p_\Phi}}{M}\frac{\nabla_y|\psi|}{|\psi|}$$

# real potential driving dynamics

$$\Phi \underbrace{\left[(\hat{K}_y + V_d)\psi - \imath\partial_t\psi\right]}_{=0,\ nuclear\ TDSE} + \psi \underbrace{\left[(\hat{K}_x + \hat{K}_y - \frac{1}{M}\frac{\nabla_y\psi}{\psi}\nabla_y + V - V_d)\Phi - \imath\partial_t\Phi\right]}_{=0,\ electronic\ TDSE} = 0$$

*try to 'minimize' change in S (energy)*

$$\langle \partial_t S \rangle_x = 0 \text{ or } \langle dS/dt \rangle_x = 0 \qquad S = \arg\Phi$$

does not track y-motion

$$V_r = \underbrace{\overbrace{\bar{H}_{el} + \Re(\bar{D}_2) + \frac{\overline{p_\Phi}\nabla_y(\arg\psi)}{M}}^{Eulerian} - \frac{p_t}{M}\overline{p_\Phi}}_{Lagrangian}$$

removes 1st derivative coupling

*minimize the nuclear momentum of electronic WF:* set to zero $\dfrac{d\overline{p_\Phi}}{dt}$

$$V_r^{(e)} = \overline{H_{el}} + \overline{U_\Phi} + \frac{\overline{p_\phi^2}}{2M} + \frac{\overline{p_\Phi}p_\psi}{M} - \frac{(\overline{p_\Phi})^2}{M}$$

*Intermediate 'electronic' frame works best (model)*

## initialize the nuclear WF

so that electronic WF has zero nuclear momentum

$$z(y,0) = \frac{\int \Psi^*(x,y,0)\nabla_y \Psi(x,y,0)dx}{\int |\Psi(x,y,0)|^2 dx}$$

$$\psi(y,0) = N_\psi \exp\left(\int_{-\infty}^{y} z(y',0)dy'\right)$$

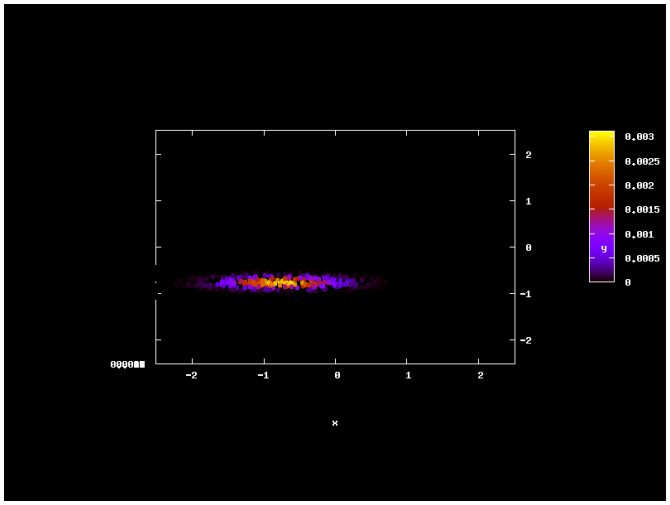
$\overline{p_\Phi} = 0$

- uniform electronic norm
- exact in one nuclear DOF
- can be done at all times
- ideal or 'exact'

## KST model

## two-dimensional Gaussian dynamics

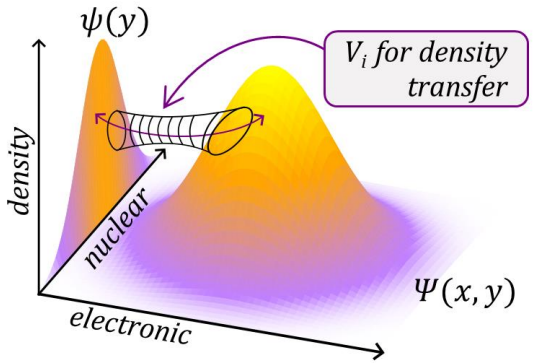
$$V = \frac{k(x-y)^2}{2} + \frac{Ky^2}{2}$$



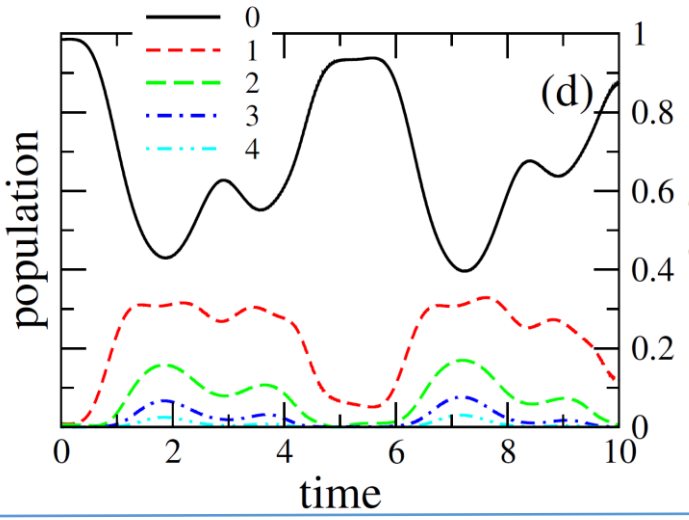

$$\psi(\boldsymbol{x},t) = N_0 \exp\left(-(\boldsymbol{x}-\overline{\boldsymbol{x}}_t)\mathbf{A}_t(\boldsymbol{x}-\overline{\boldsymbol{x}}_t)/2 + \imath\overline{\boldsymbol{p}}_t(\boldsymbol{x}-\overline{\boldsymbol{x}}_t) + \imath s_t + \gamma_t\right)$$

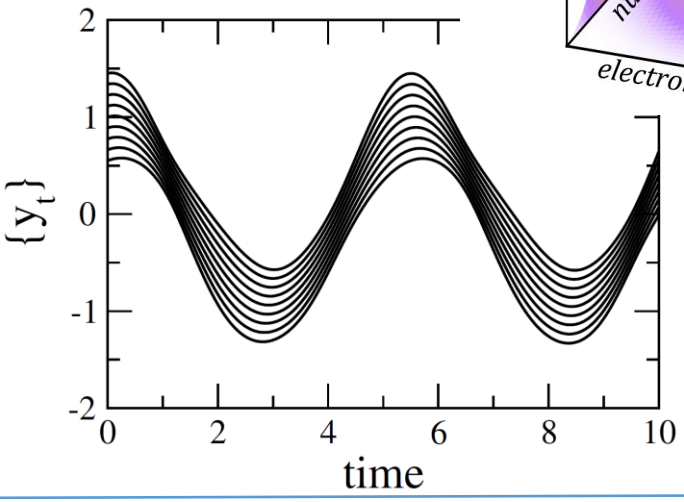
# vibrationally nonadiabatic dynamics

IC: complex correlated 2D wavepacket



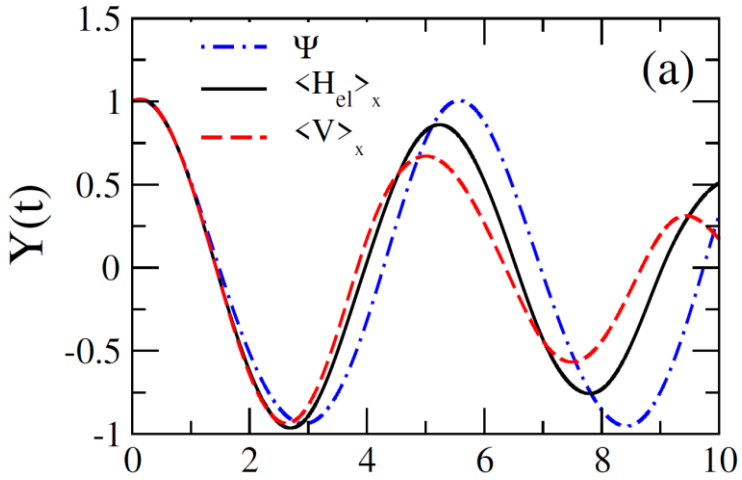

**'electronic' state populations**



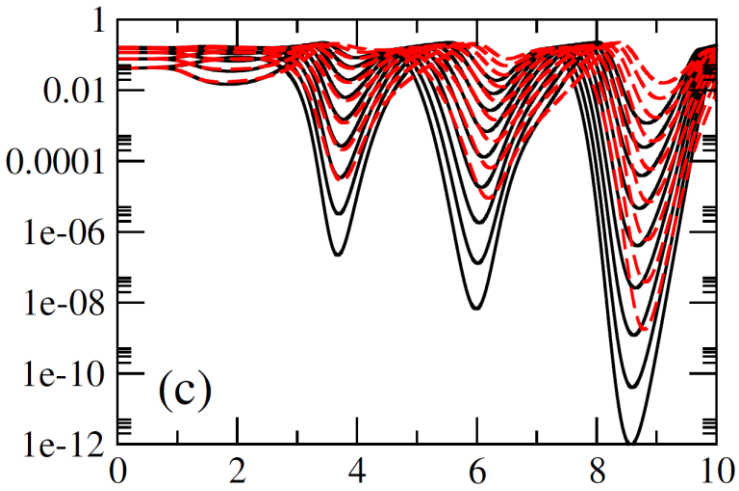




**nuclear subspace trajectories**

***$V_r$:=mean-field  $V_i$:=0***



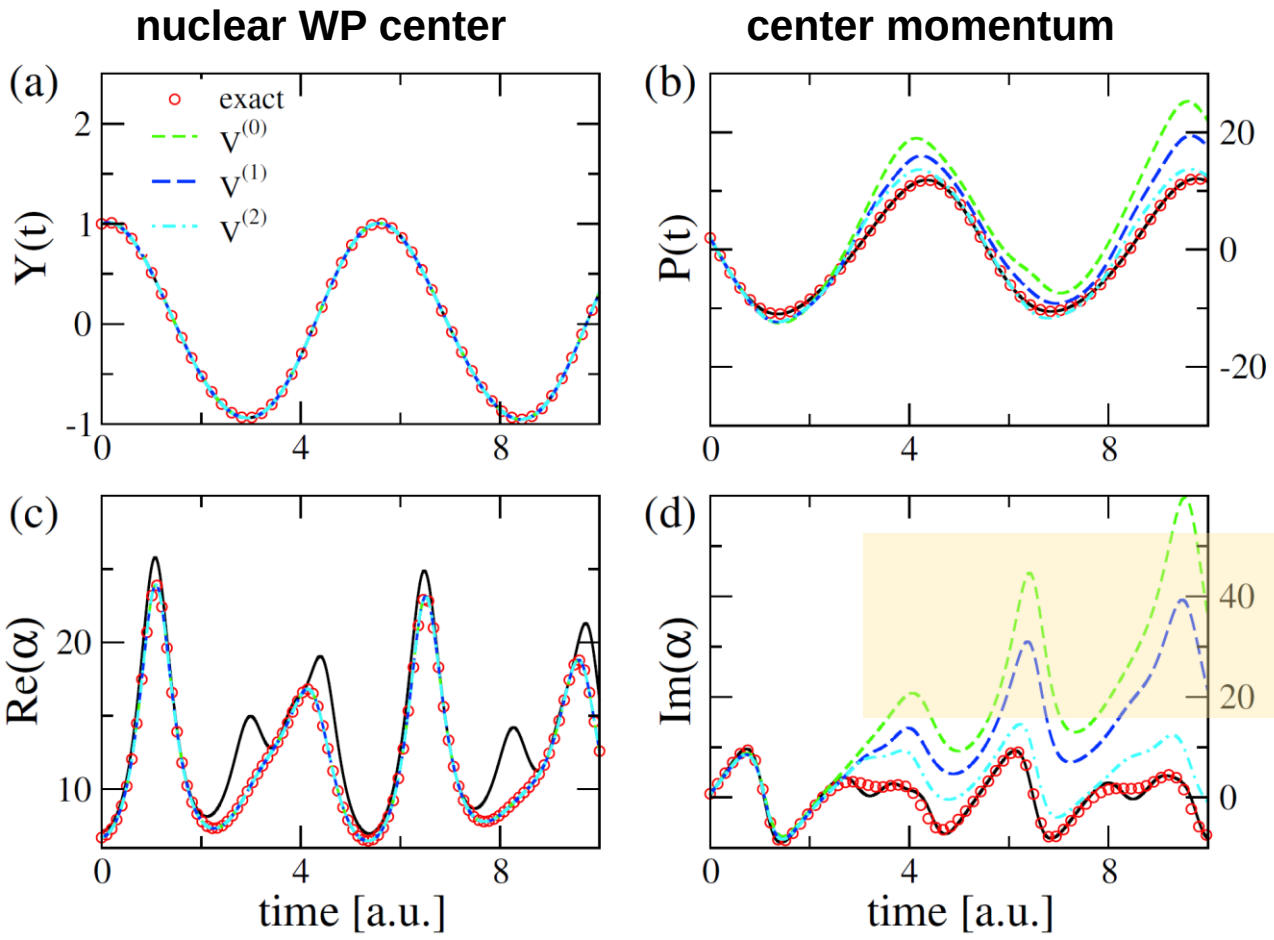

**nuclear WP center**




**inverse electronic norm**

# complex effective potential

Lagrangian frame; exact: = ideally factorized; $V^{(0,1,2)}$:= kinetic energy in $V_r$




correlates with large imaginary potential ☹

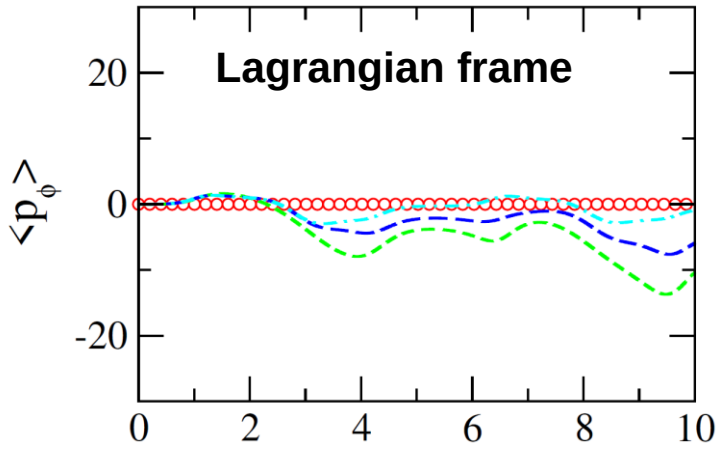
**can we have purely real potential?**

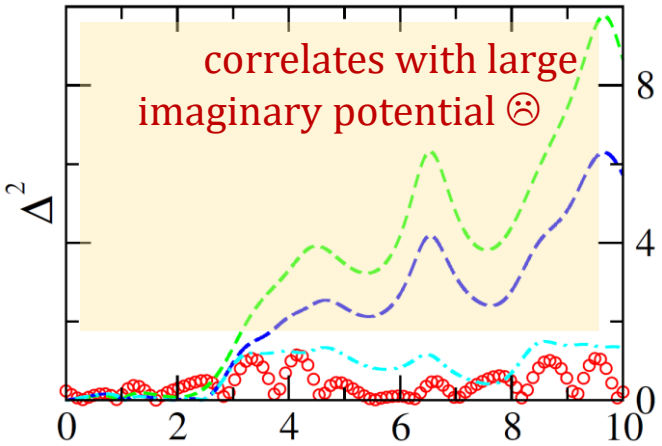
# ‘exact’ corresponds to zero imaginary potential (1 DOF)

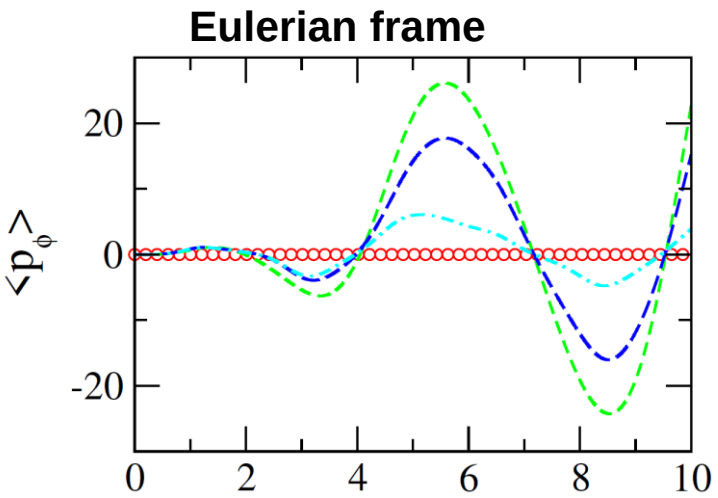
$$\nabla_y V_r = \langle \nabla_y V \rangle_x + \frac{1}{M} (2 r_\psi + \nabla_y) \langle r_\Phi^2 + p_\Phi^2 \rangle_x$$

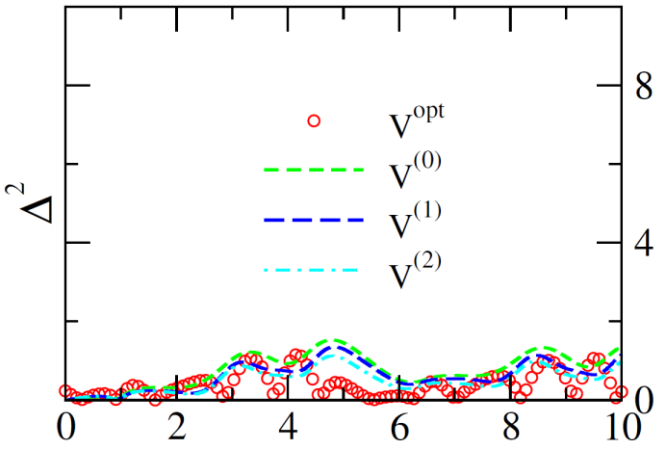
condition on $V_r$
frame-independent

$p_\phi$, nuclear momentum of electronic function and its dispersion are good measures of efficient factorization



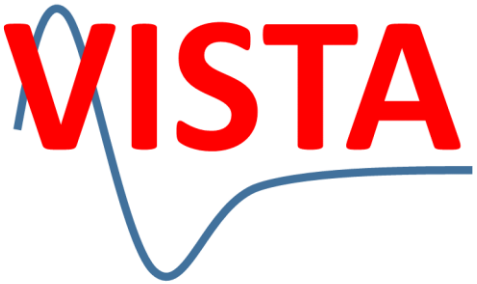



## Summary:

- QT -- momentum from phase -- define compact WF representations for the 'BO-and-beyond' exact, approximate, mixed quantum dynamics
- Conservation properties at the expense of complex effective nuclear potential
- Imaginary potential is frame-independent; depends on nuclear momentum of electronic wavefunction
- Frame of reference affects $V_i$ amplitude and dynamics stability
- There is (for 1D) an ideally factorized dynamics with zero $V_i$ and frame-independent $V_r$
- Beyond 1D: intermediate frame, dropping the kinetic energy terms in $V_r$ work the best

## Future:

- The role of the residual nuclear phase in the electronic wavefunction; simplifications
- The role of the kinetic energy, including the quantum potential terms
- Test systems and chemical models




**Thank you VISTA organizers and participants!**

**Questions?**

## *Propagation scheme for exact implementation*

0. *initialize nuclear WF*
1. *define Vd*
2. *update by **dt** the nuclear SE with complex potential*
3. *update by **dt** the full WF exactly*
4. *define the electronic WF at **dt** as (full WF)/(nuclear WF)*
5. *go to 1 and repeat until final time is reached*

### *Gaussian wavepacket*

$$\psi(\boldsymbol{x},t) = N_0 \exp\left(-(\boldsymbol{x}-\overline{\boldsymbol{x}}_t)\mathbf{A}_t(\boldsymbol{x}-\overline{\boldsymbol{x}}_t)/2 + \imath\overline{\boldsymbol{p}}_t(\boldsymbol{x}-\overline{\boldsymbol{x}}_t) + \imath s_t + \gamma_t\right)$$