

# Exact Factorization Adventures for Electrons, Nuclei, and Photons

Patricia Vindel Zandbergen



Lionel Lacombe



Norah Hoffmann

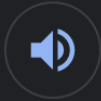


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vis·ta

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*noun*

a pleasing view, especially one seen through a long, narrow opening.

## Outline

- ❖ The exact factorization approach (in a nutshell)
- ❖ Exact-factorization-based surface hopping
  - first-principles decoherence correction
  - electronic transitions induced by the quantum momentum
- ❖ Extension to photons in polaritonic chemistry
  - cavity-modified time-dependent potential energy surfaces
  - understanding errors in classical trajectory methods for photons

*just so we are on the same starting page...*

## Exact molecular Hamiltonian

$$\hat{H} = \hat{H}_{\text{BO}} + V_{\text{ext}}^e(\underline{\mathbf{r}}, t) + \hat{T}_n(\underline{\mathbf{R}}) + V_{\text{ext}}^n(\underline{\mathbf{R}}, t)$$

All nuclear coordinates e.g. laser field

$$\hat{H}_{\text{BO}} = \hat{T}_e(\underline{\mathbf{r}}) + \hat{W}_{ee}(\underline{\mathbf{r}}) + V_{en}(\underline{\mathbf{r}}, \underline{\mathbf{R}}) + \hat{W}_{nn}(\underline{\mathbf{R}})$$

All electronic coordinates

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

## Exact Factorization (XF) Approach in a Nutshell

For electron-nuclear systems, *exact* solution to  $\hat{H}\Psi(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t) = i\partial_t\Psi(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t)$  is uniquely\* written as a *single* correlated product:

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

where  $\int d\underline{\mathbf{r}}|\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}, t)|^2 = 1$

**electronic wavefunction** (conditional):  
satisfies a more complicated eqn with coupling terms that depend on  $\chi$

**nuclear wavefunction** (marginal):  
satisfies a TDSE with potentials that depend on  $\Phi_{\mathbf{R}}$

In particular: time-dependent potential energy surface (**TD PES**) and TD Berry connection

\* up to an (R,t)-dependent phase transformation

*A. Abedi, N.T. Maitra, and E.K.U. Gross, PRL **105**, 123002 (2010); JCP **137**, 22A530 (2012)  
F. Agostini & E.K.U. Gross, Eur. Phys. J. B. **94**, 179 (2021)  
Hardy Gross Vista Talk! January 2021*

## Equations for the exact electronic and nuclear wavefunctions

$$\left\{ \begin{array}{l} (\hat{H}_{\text{el}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t) - \epsilon(\underline{\mathbf{R}}, t)) \Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}, t) = i \partial_t \Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}, t) \\ \left( \sum_{\nu=1}^{N_n} \frac{1}{2M_\nu} (-i \nabla_\nu + \mathbf{A}_\nu(\underline{\mathbf{R}}, t))^2 + \hat{V}_{\text{ext}}^n(\underline{\mathbf{R}}, t) + \epsilon(\underline{\mathbf{R}}, t) \right) \chi(\underline{\mathbf{R}}, t) = i \partial_t \chi(\underline{\mathbf{R}}, t) \end{array} \right.$$

$$\hat{H}_{\text{el}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t) = \hat{H}_{\text{BO}} + V_{\text{ext}}^e(\underline{\mathbf{r}}, t)$$

$$+ \sum_{\nu=1}^{N_n} \frac{1}{M_\nu} \left[ \frac{(-i \nabla_\nu - \mathbf{A}_\nu(\underline{\mathbf{R}}, t))^2}{2} + \left( \frac{-i \nabla_\nu \chi}{\chi} + \mathbf{A}_\nu(\underline{\mathbf{R}}, t) \right) (-i \nabla_\nu - \mathbf{A}_\nu(\underline{\mathbf{R}}, t)) \right]$$

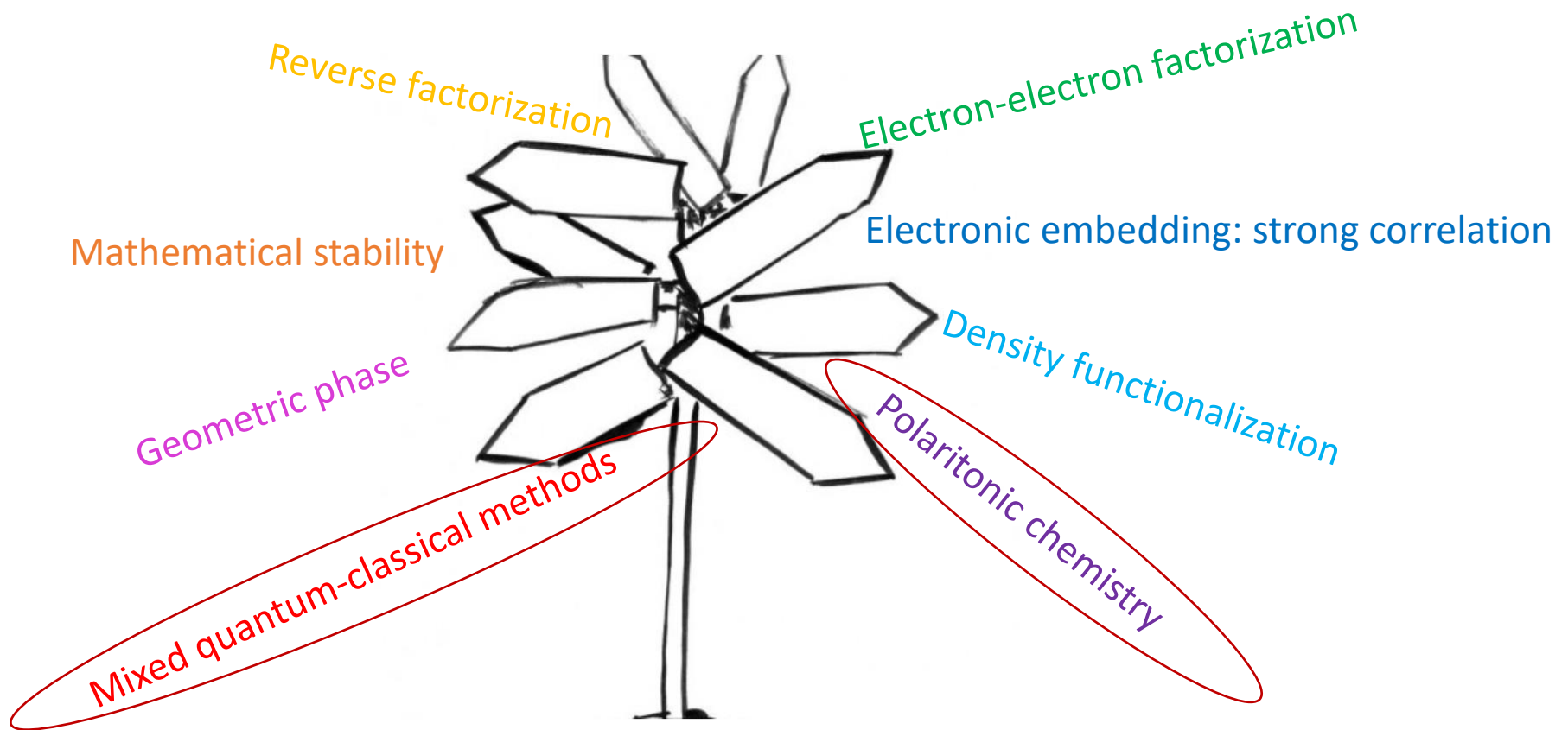
$$\epsilon(\underline{\mathbf{R}}, t) = \langle \Phi_{\underline{\mathbf{R}}}(t) | \hat{H}_{\text{el}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t) - i \partial_t | \Phi_{\underline{\mathbf{R}}}(t) \rangle_{\underline{\mathbf{r}}} \quad \text{exact TD PES}$$

$$\mathbf{A}_\nu(\underline{\mathbf{R}}, t) = \langle \Phi_{\underline{\mathbf{R}}}(t) | -i \nabla_\nu \Phi_{\underline{\mathbf{R}}}(t) \rangle_{\underline{\mathbf{r}}} \quad \text{exact TD Berry connection}$$

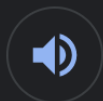
Eqns form-invariant under the gauge-like transformation:

$$\begin{array}{ll} \Phi \rightarrow \tilde{\Phi} = e^{i\theta(\underline{\mathbf{R}}, t)} \Phi & \mathbf{A}_\nu \rightarrow \tilde{\mathbf{A}} = \mathbf{A}_\nu + \nabla_\nu \theta(\underline{\mathbf{R}}) \\ \chi \rightarrow \tilde{\chi} = e^{-i\theta(\underline{\mathbf{R}}, t)} \chi & \epsilon(\underline{\mathbf{R}}) \rightarrow \tilde{\epsilon}(\underline{\mathbf{R}}) = \epsilon(\underline{\mathbf{R}}) + \partial_t \theta \end{array}$$

*Exact factorization has gone in all sorts of different directions...*



- Gaining insight into correlated dynamics of coupled quantum subsystems
- Practical tool – once we make some approximations!!



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*noun*

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# Mixed Quantum-Classical Approximations based on the XF

## ❖ Coupled-Trajectory MQC

Take classical limit of the nuclear equation, expand  $\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}, t) = \sum_l C_l(\underline{\mathbf{R}}, t) \varphi_{\underline{\mathbf{R}}}^{(l)}(\underline{\mathbf{r}})$ , & approximate some terms based on exact studies...

→ CTMQC = Ehrenfest + coupled-trajectory terms in both electronic and nuclear eqns.  
Unambiguous and well-defined terms yield wavepacket splitting and decoherence

*F. Agostini, S. K. Min, A. Abedi, and E. K. U. Gross, J. Chem. Theory Comput. **12**, 2127 (2016);  
S. K. Min, F. Agostini, I. Tavernelli, E. K. U. Gross, J. Phys. Chem. Lett. **8**, 3048 (2017).  
F. Agostini & E.K.U. Gross, Eur. Phys. J. B. **94**, 179 (2021)*

There are other possibilities for XF-based MQC methods (*e.g. for the impatient..*)

## ❖ XF-based surface hopping, SHXF (or, DISH-XF)

Nuclei: classical trajectory on one BO surface, hopping btn them via stochastic FSSH scheme

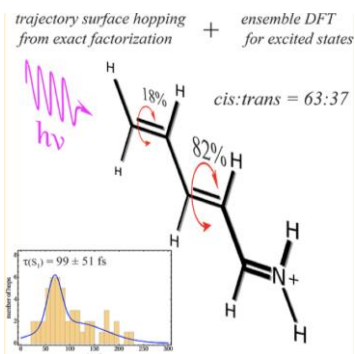
Electrons: follow the electronic eqn derived in CTMQC



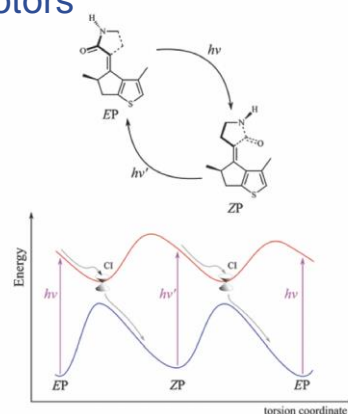
# SHXF: Exact-Factorization-Based Surface Hopping

Same electronic equation as in CT-MQC but used in an FSSH scheme

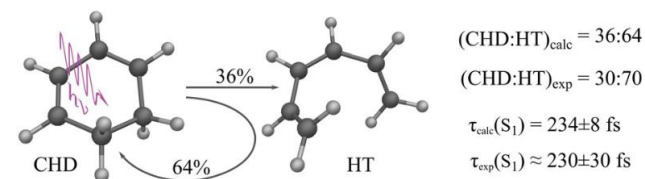
## Trans-Penta-2,4-dieniminium cation



## Light driven molecular rotary motors



## Ring opening in 1,3-cyclohexadiene



- M Filatov, SK Min, KS Kim, *J. Chem. Theo. Comp.* **14**, 4499-4512 (2019)  
M Filatov, SK Min, CH Choi, *Phys. Chem. Chem. Phys.* **1**, 2489 (2019)  
M Filatov, M Paolino, SK Min, CH Choi, *Chem. Commun.*, **55**, 5247 (2019)  
M Filatov, SK Min, KS Kim, *Mol. Phys.* **117**, 1128-1141 (2019)



**Seung-Kyu Min**  
UNIST, Korea

J.-K. Ha, I. S. Lee, S. K. Min, *J. Phys. Chem. Lett.* **9**, 1097 (2018)

PyUNIXMD: A Python-based excited state molecular dynamics package. *J. Comp. Chem.* **42**, 1755 (2021).



# SHXF: Exact-Factorization-Based Surface Hopping

Same electronic equation as in CT-MQC but used in an FSSH scheme

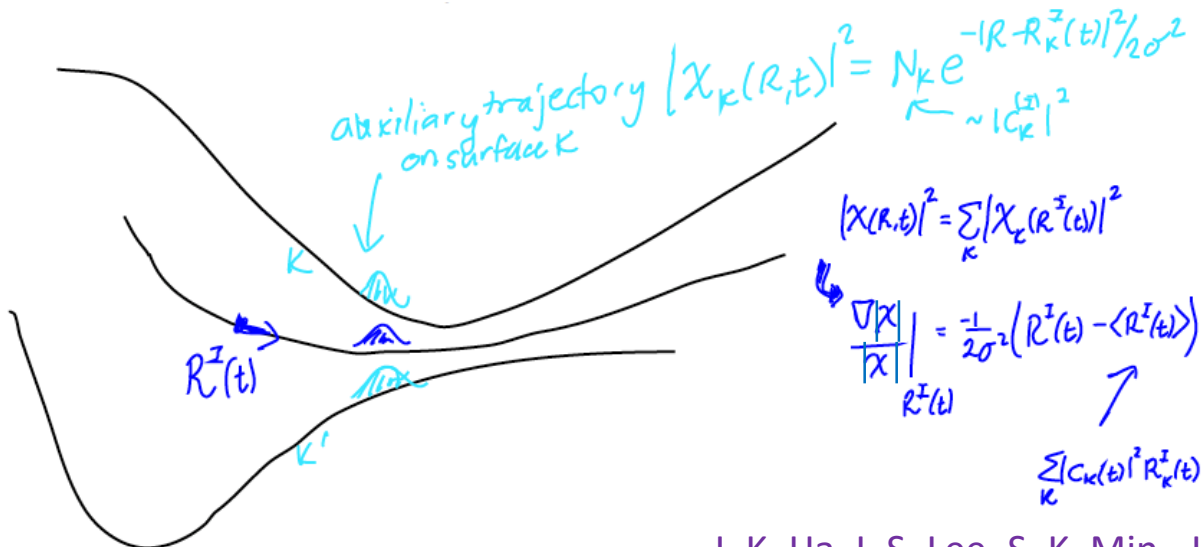
$$\dot{C}_n^{(J)} = -\frac{i}{\hbar} \epsilon_n^{(J)} C_n^{(J)} - \sum_k \sum_\nu d_{nk,\nu}^{(J)} \cdot \dot{\mathbf{R}}_\nu^{(J)} C_k^{(J)} \quad \leftarrow \text{usual electronic eqn}$$

$$+ \underbrace{\sum_k \sum_\nu \frac{1}{M_\nu} \frac{\nabla_\nu |\chi|}{|\chi|} \Big|_{\mathbf{R}^{(J)}(t)}}_{\text{correction derived from XF}} \cdot (f_{k,\nu}^{(J)} - f_{n,\nu}^{(J)}) |C_k^{(J)}|^2 C_n^{(J)}$$

$$\mathbf{f}_{k,\nu}^{(J)} = -\int^t \nabla_\nu \epsilon_{\text{BO},k}^{(J)}(t') dt'$$

To calculate the quantum momentum :

-- *auxiliary trajectories* coupled to each *independent trajectory*, launched on non-active states when the population becomes non-zero



# SHXF: Exact-Factorization-Based Surface Hopping

Same electronic equation as in CT-MQC but used in an FSSH scheme

$$\dot{C}_n^{(J)} = -\frac{i}{\hbar} \epsilon_n^{(J)} C_n^{(J)} - \sum_k \sum_\nu d_{nk,\nu}^{(J)} \cdot \dot{\mathbf{R}}_\nu^{(J)} C_k^{(J)} \quad \leftarrow \text{usual electronic eqn}$$

$$+ \underbrace{\sum_k \sum_\nu \frac{1}{M_\nu} \frac{\nabla_\nu |\chi|}{|\chi|} \Big|_{\mathbf{R}^{(J)}(t)} \cdot (f_{k,\nu}^{(J)} - f_{n,\nu}^{(J)}) |C_k^{(J)}|^2 C_n^{(J)}}_{\text{correction derived from XF}}$$

$$\mathbf{f}_{k,\nu}^{(J)} = -\int^t \nabla_\nu \bar{\epsilon}_{\text{BO},k}^{(J)}(t') dt'$$



Electronic transitions driven, not only by non-adiabatic couplings, but also by nuclear quantum momentum →

- (i) decoherence
- (ii) three-state intersections

## Comparison of XF decoherence with commonly used corrections:

$$\dot{C}_n^{(J)} = -\frac{i}{\hbar} \epsilon_n^{(J)} C_n^{(J)} - \sum_k \sum_\nu \mathbf{d}_{nk,\nu}^{(J)} \cdot \dot{\mathbf{R}}_\nu^{(J)} C_k^{(J)} + \xi_n^{(J)}$$

SHXF

$$\xi_n^{(J)} = \sum_k \sum_\nu \frac{1}{M_\nu} \frac{\nabla_\nu |\chi|}{|\chi|} \Big|_{\underline{\mathbf{R}}^{(J)}(t)} \cdot (\mathbf{f}_{k,\nu}^{(J)} - \mathbf{f}_{n,\nu}^{(J)}) |C_k^{(J)}|^2 C_n^{(J)}$$

SHEDC

$$\xi_{n \neq a}^{(J), \text{SHEDC}}(t) = -\frac{|\epsilon_{\text{BO},n}^{(J)} - \epsilon_{\text{BO},a}^{(J)}|}{\hbar} \left(1 + \frac{\alpha}{T}\right)^{-1} C_{n \neq a}^{(J)}$$

Granucci, Persico, Zocante, *J. Chem. Phys.* **133**, 134111 (2010)

Applied as an exp. damping of coefficients on inactive states

$T$  = kinetic energy: unphysical size-extensivity;  $\alpha$  parameter

AFSSH

$$\xi_{n \neq a}^{(J), \text{A-FSSH}} = -\frac{\delta \underline{\mathbf{F}}_n \cdot \delta \underline{\mathbf{R}}_n}{2\hbar} - \frac{2|\underline{\mathbf{d}}_{an} \cdot \dot{\underline{\mathbf{R}}}(\epsilon_{\text{BO},a} - \epsilon_{\text{BO},n}) \delta \underline{\mathbf{R}}_n \cdot \underline{\mathbf{R}}|}{\hbar |\dot{\underline{\mathbf{R}}}|^2} C_n^{(J)}$$

Jain, Alguire, Subotnik, *J. Chem. Theory and Comput.* **12**, 5256 (2016)

Decoherence rate is determined stochastically from this.

***These all look completely different from each other!!***

In particular, SHXF displays:

- Non-linearity
- $\xi_n$  couples to all  $k$ , not just active state

Note ~ DISH: Akimov, Prezhdo *JCTC* **10** 789 (2014); Jaeger, Fischer, Prezhdo *JCP* **137** 22A545 (2012)

*How does the XF-based surface hopping compare in practice with the traditional ones?*

Will study:

(i) small molecules where reference AIMS results are available

(ii) three-state intersection in uracil cation, where reference MCTDH available

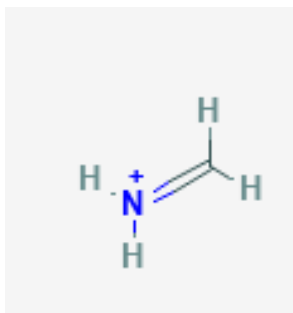
Use same initial conditions, same electronic structure method.

I'll just show a couple of results, in the interest of time.

(i) P. Vindel Zandbergen, L. Ibele, J.-K. Ha, S.-K. Min, B. E. Curchod, N. T. Maitra, *JCTC* **17**, 3852 (2021)

(ii) P. Vindel Zandbergen, S. Matsika, N. T. Maitra, in preparation (2021)

## Example: Methaniminium Cation



After photoexcitation to  $S_1$  → torsional motion  
→ begins to photoisomerize and transfer to  $S_0$   
→ recrosses back to  $S_1$  at a different nuclear configuration before slowly completing the transfer to  $S_0$

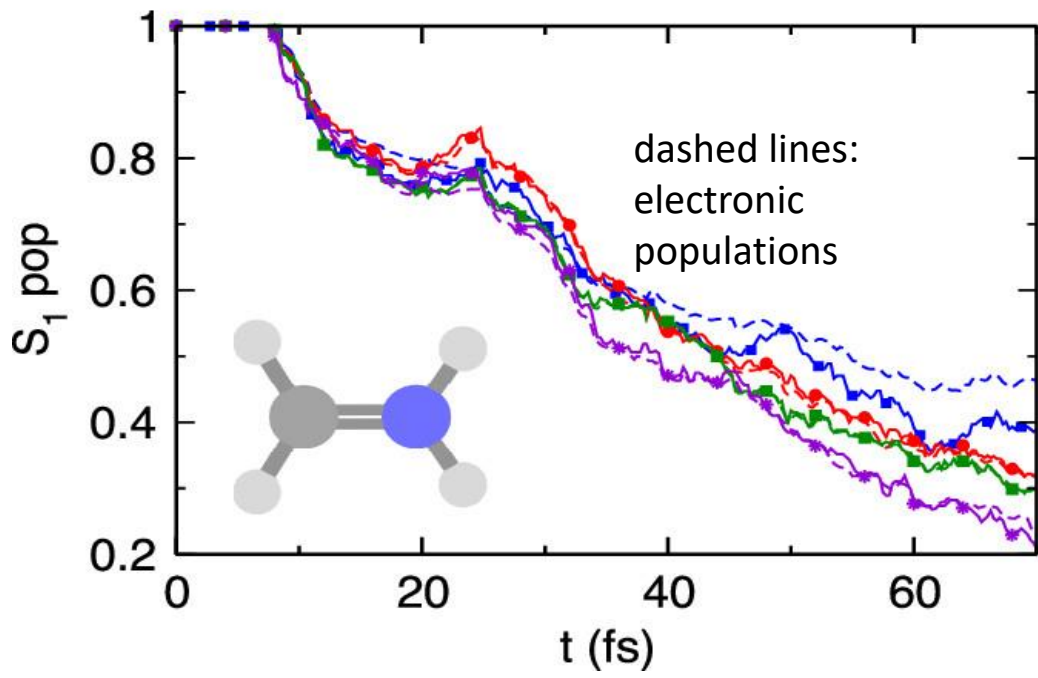
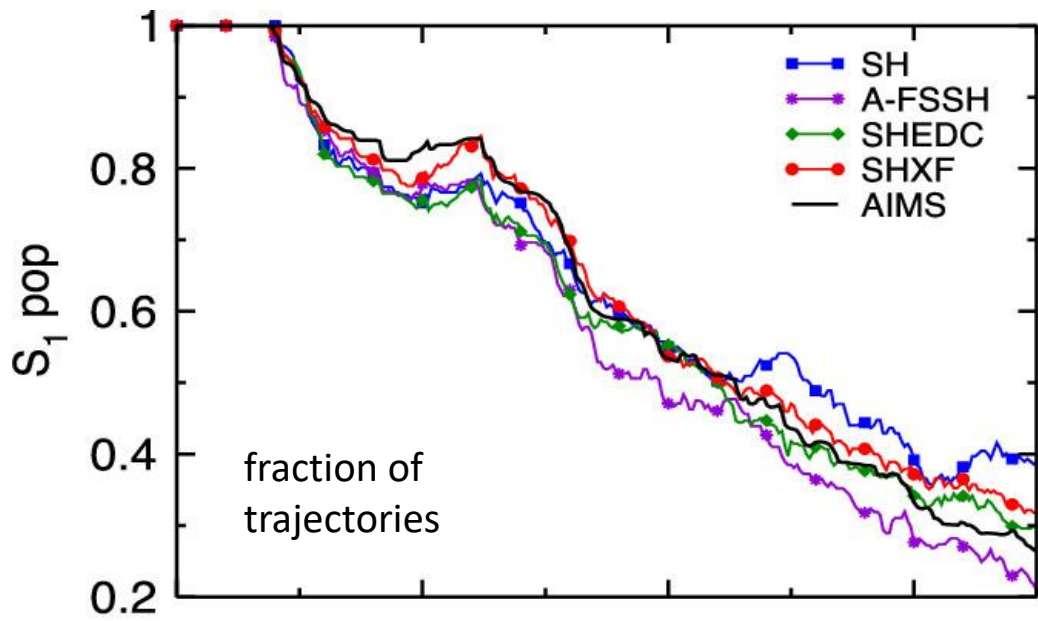
For all calculations:

SA(2)-CASSCF(6/5) in 6-31G\* basis set

70 initial conditions, each repeated 4 times for convergence (SH)

Time-step of  $dt = 0.25\text{fs}$  adequate for convergence.

SHXF  $\sigma = 0.056$  au determined from C=N distribution

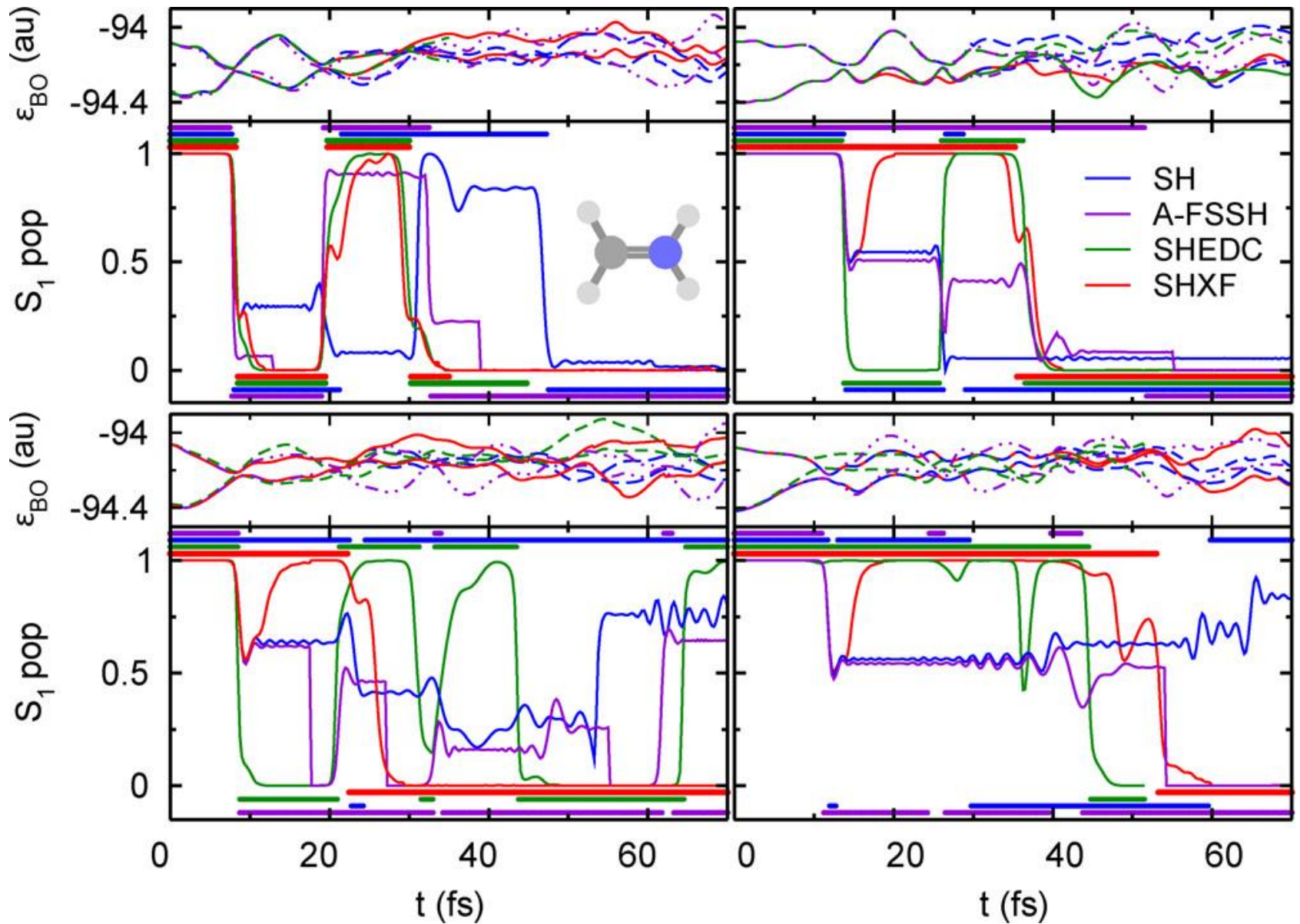


- The results are overall similar between the different methods.
- SHXF gives best overall agreement with AIMS (but they are all close), captures the back-transfer to  $S_1$  enthusiastically
- Poor internal consistency of SH evident, and is corrected by SHXF, SHEDDC, and A-FSSH methods.
- *Yet, the decoherence terms looked so different!*

Take a look at action on individual trajectories:



A sample of 4 trajectories:

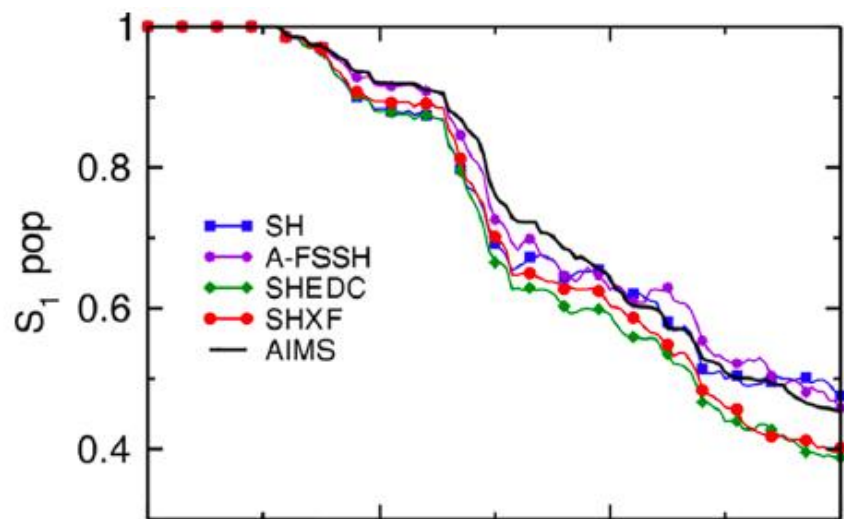


The decoherence mechanisms on an individual trajectory are indeed very different.

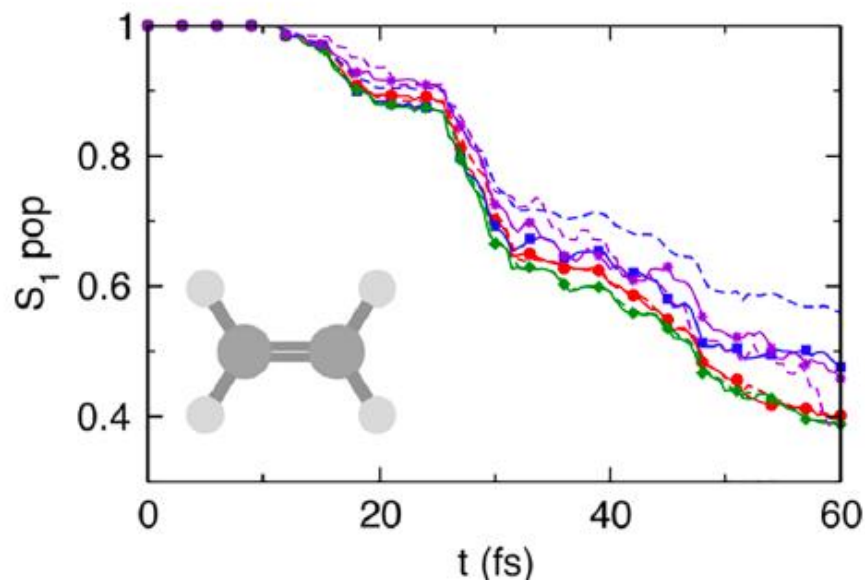


## Another Example: Ethylene dynamics after photoexcitation to $S_1$

SA(3)-CASSCF(2/2) (Molpro); (6-31G\*)/660 trajectories

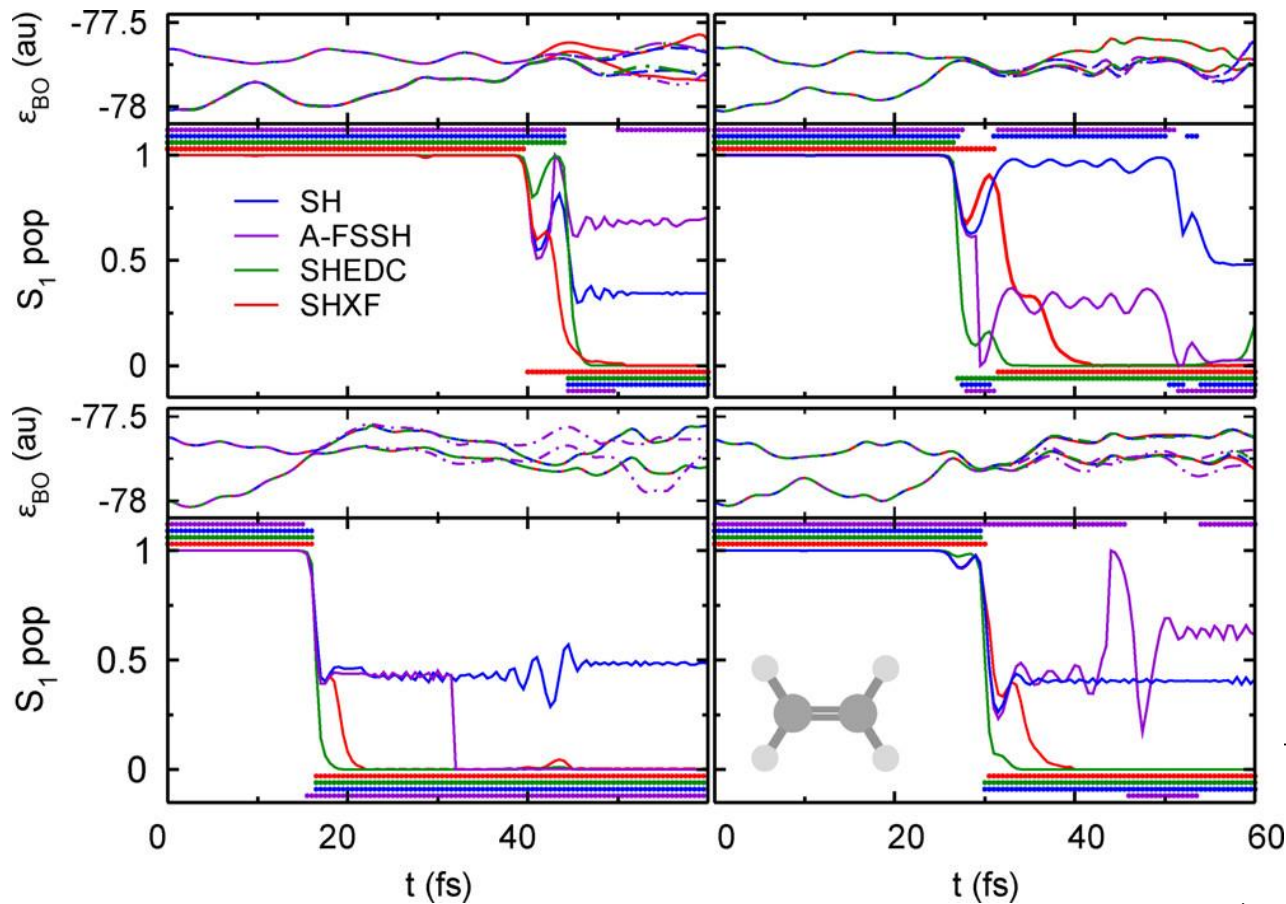


Fraction of trajectories



Dashed lines here: electronic populations

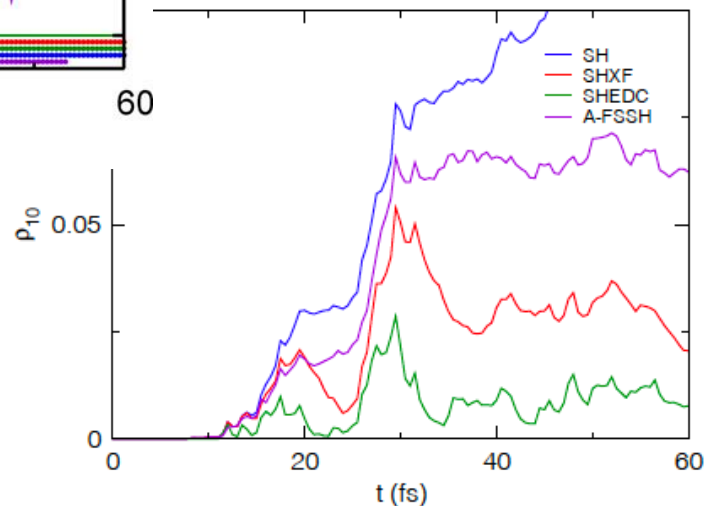
But again, on an individual trajectory level they act very differently:



XF decoherence is certainly not as simple as an expl decay

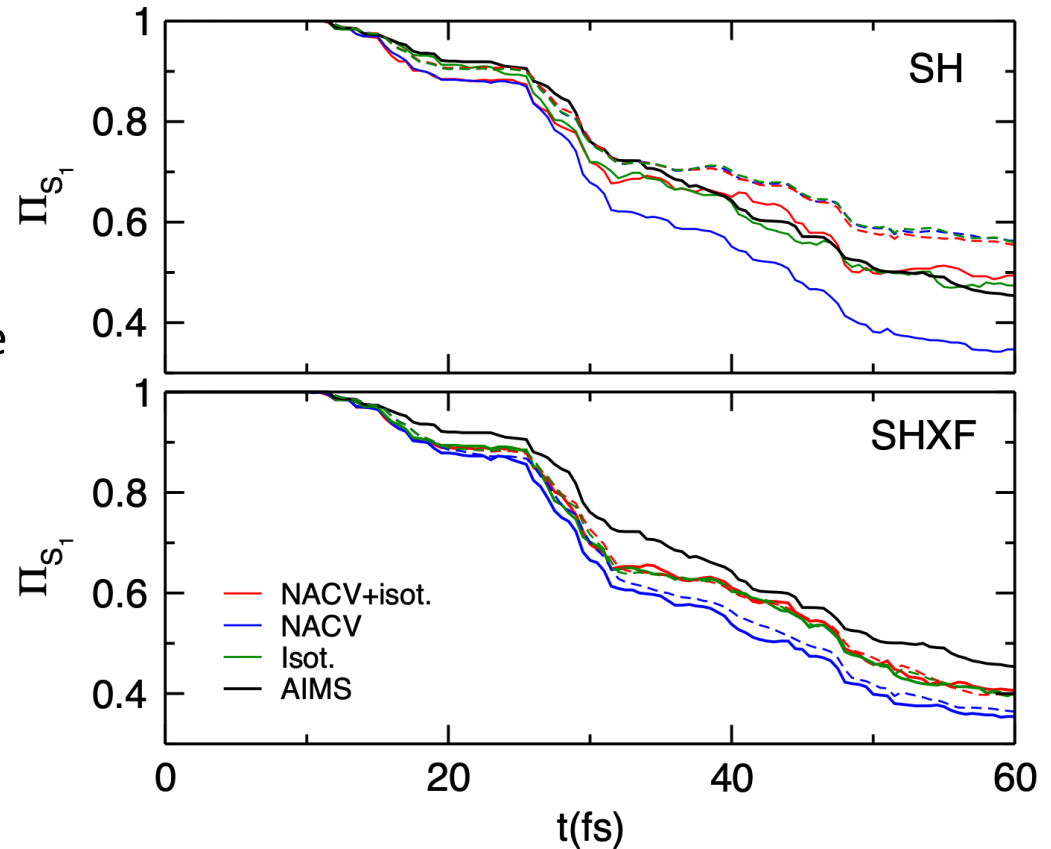
Reflected also in the “decoherence indicator”

$$\sum_J^{N_{\text{traj}}} |C_{S_1}^{(J)} C_{S_0}^{(J)}|^2 / N_{\text{traj}}$$



So, for these molecules, the SHXF and the different decoherence-corrected-SH approx's all gave about the same averaged results, despite different action on individual trajectories ...

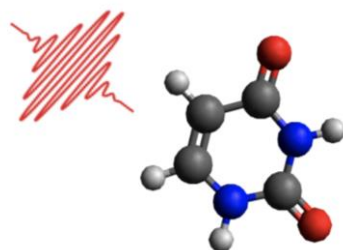
...and in fact, the choice of **momentum adjustment** can give differences similar to the differences in decoherence corrections:



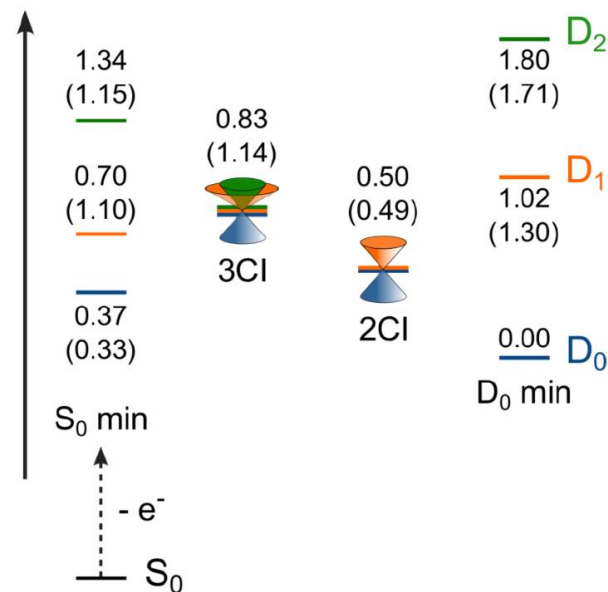
Is this always the case for some reason???

**No!!**

# Electronic transitions mediated by the quantum momentum: Dynamics through **three-state intersection** in uracil cation



Initial state: the adiabatic  $D_2$  excited state of the cation, at the geometry of the neutral.

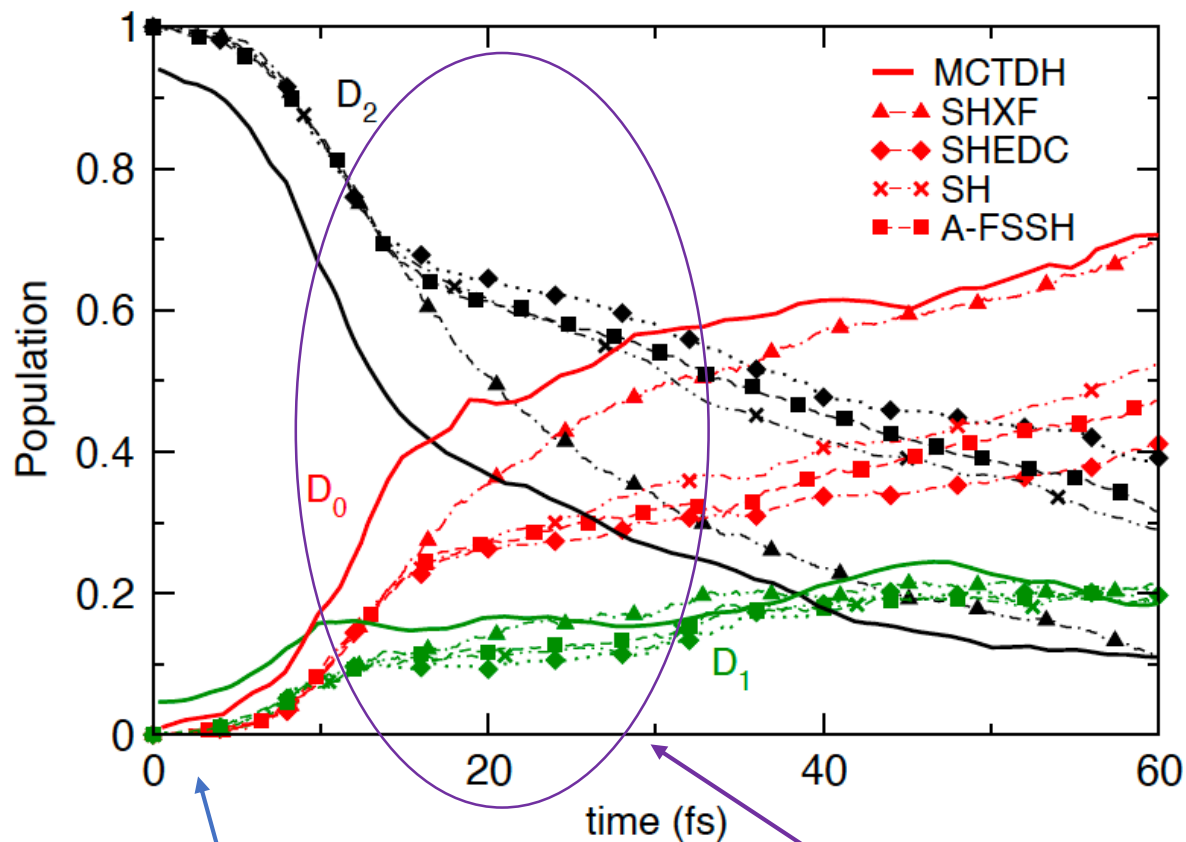


Vibronic coupling model fitted to EOM-IP-CCSD, with MCTDH calculations:

M. Assmann, H. Köppel, S. Matsika JPCA **119**, 866 (2015)

S. Matsika, Chem. Phys. **349**, 356 (2008)

# Dynamics through **three-state intersection** in uracil cation

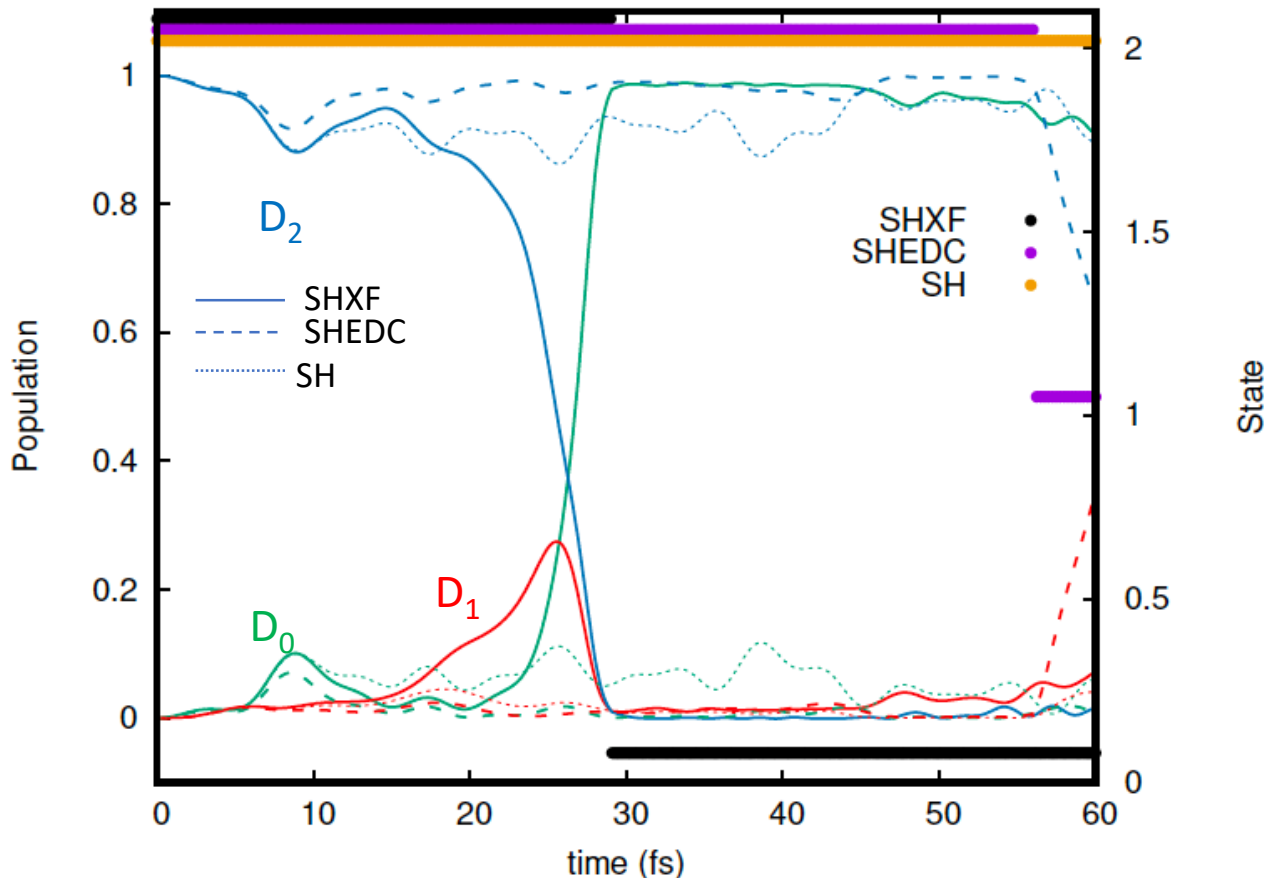


SHXF gives a significant improvement over the other SH methods!

Simultaneous rise of  $D_0$  and  $D_1 \rightarrow$  3-state CI

We find about twice as many  $D_2$ - $D_0$  hops in SHXF c.f. the others.

Taking a closer look at individual trajectories reveals why:



Hopping probability has same form for all methods ...

$$\max\left\{0, -\frac{2\text{Re}(\rho_{ak}^{(j)*} d_{ka,\nu}^{(j)} \cdot \dot{\mathbf{R}}_{\nu}^{(j)})}{\rho_{aa}^{(j)}} dt\right\}$$

...but the XF term leads to starkly different coefficients before any hop occurs!

SHEDC: states only coupled pairwise to the active state (same in A-FSSH)

SHXF: quantum momentum couples *all* states with non-zero population

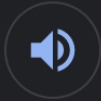
→ big differences when more than two states occupied at same time.

## Summary & Outlook so far..

- ❖ XF provides a useful, *derivable* correction to surface-hopping that yields decoherence ..and more!
- ❖ Mechanisms of decoherence on individual trajectory level are strikingly different
- ❖ Results for observables may be overall somewhat similar to traditional decoherence-corrected methods for two-state interactions, but SHXF captures dynamics with three-state interactions that the others fail to do accurately.
- ❖ But SH procedure has many *ad hoc* elements (e.g. velocity rescaling...), that can muddy the analysis of the effect of decoherence corrections...(*Apply XF to QTSH?* Martens, JPCA **123**, 1110 (2019))
- ❖ SH impractical when there are many surfaces, or laser fields... But XF is naturally suited in principle to that since it is based on a **single time-dependent surface** → develop other XF-based MQC methods?!

P. Vindel Zandbergen, L. Ibele, J.-K. Ha, S.-K. Min, B. E. Curchod, N. T. Maitra, JCTC **17**, 3852 (2021)

P. Vindel Zandbergen, S. Matsika, N. T. Maitra, in preparation (2021)



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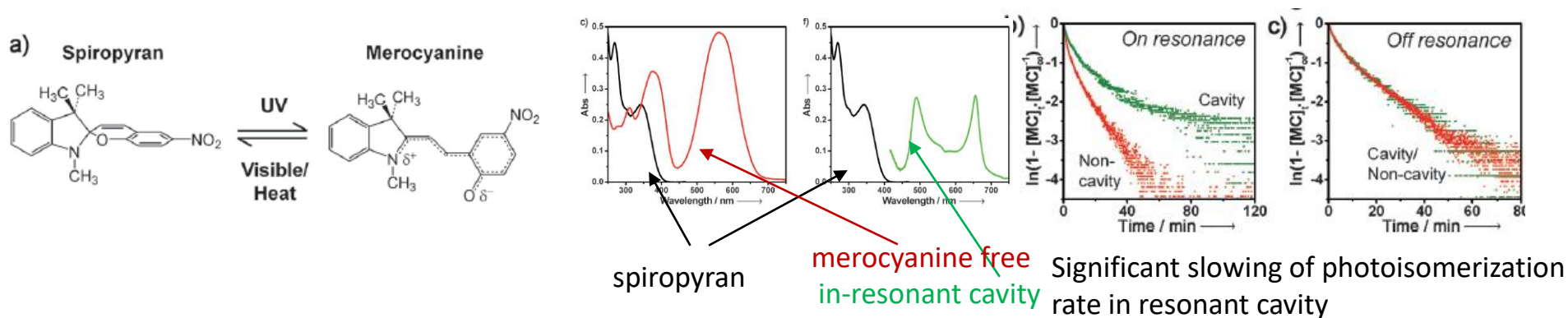
# Recent rekindling of interest in Cavity-QED

❖ Achieve strong light-matter coupling without using any external field!

-- manipulate matter via vacuum fluctuations of the radiation field

-- possibility of “cleaner” control at lower (no) input power, than with laser fields

*Hutchison, Schwartz, Genet, Devaux, Ebbesen, Angew. Chem. Int. Ed. 51, 1592 (2012).*



Many new phenomena:

e.g. enhanced conductivity, enhanced long-range excitation energy transfer, suppression of chemical reactions, superradiance...

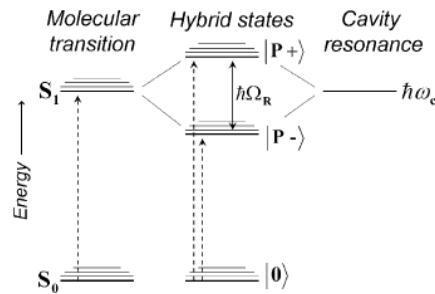


Joel Yuen-Zhou  
and Wei Xiong  
(UCSD)

# Recent rekindling of interest in Cavity-QED: Polaritonic Chemistry

Key concept: resonantly coupled quantum subsystems

## Hybrid light-matter states (polaritons)



How does this affect chemical reactions?

-- Molecule is resonant only at some nuclear configurations...

→ distorts the potential energy landscape

# Extension of EF to include photons

Possible factorizations of wavefunction of coupled electrons, nuclei, and photons:

$$\Psi(\underline{\mathbf{r}}, \underline{\mathbf{R}}, \underline{\mathbf{q}}, t) = \chi(\underline{\mathbf{q}}, t) \Phi_{\underline{\mathbf{q}}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t) = \chi(\underline{\mathbf{R}}, t) \Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}, \underline{\mathbf{q}}, t) = \chi(\underline{\mathbf{r}}, t) \Phi_{\underline{\mathbf{r}}}(\underline{\mathbf{q}}, \underline{\mathbf{R}}, t)$$

→ TDSE for the photonic system

N. Hoffmann, H. Appel, M. Rubio, N.T. Maitra, Eur. Phys. J. B **91**, 180 (2018)

→ TDSE for the nuclear system  
→ Exact potential driving the nuclei when coupled to electrons and photons

L. Lacombe, N. M. Hoffmann, N.T. Maitra, Phys. Rev. Lett. **123**, 083201 (2019).

Electron-photon factorization:

A. Abedi, E. Khosravi, I. Tokatly, Eur. Phys. J. B **91**, 194 (2018).

Unlike polaritonic surfaces, the exact TDPES from XF directly correlates with proton motion

# Simplest Hamiltonian for Systems of Correlated Nuclei, Electrons, and Photons

Non-relativistic, neglect spin-coupling, neglect any cavity-losses, dipole approximation in length gauge, no classical external fields →

$$\hat{H} = \hat{H}_m + \hat{H}_p + \hat{V}_{pm} + \hat{V}^{SP}$$

$$\hat{H}_m = \hat{T}_n + \hat{H}_{BO} = \hat{T}_n + \hat{T}_e + \hat{V}_m$$

$$\hat{H}_p = \frac{1}{2} \left( \sum_{\alpha=1}^{2N_p} \hat{p}_{\alpha}^2 + \omega_{\alpha}^2 \hat{q}_{\alpha}^2 \right) = \hat{T}_p + \hat{V}_p$$

displacement-field coordinate:

$$\hat{q}_{\alpha} = \sqrt{\frac{\hbar}{2\omega_{\alpha}}} (\hat{a}_{\alpha}^{\dagger} + \hat{a}_{\alpha})$$

$$\hat{V}_{pm} = \sum_{\alpha} \omega_{\alpha} \hat{q}_{\alpha} \vec{\lambda}_{\alpha} \cdot \left( \sum_I^{N_n} Z_I \hat{\mathbf{R}}_I - \sum_i^{N_e} \hat{\mathbf{r}}_i \right)$$

photon-matter coupling

$$\lambda_{\alpha} \sim 1/\sqrt{Vol}$$

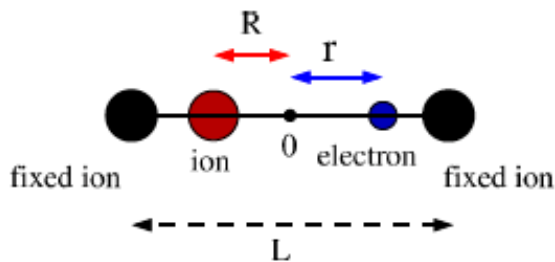
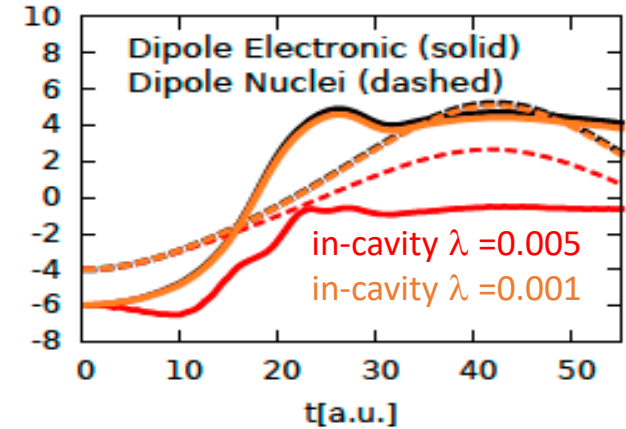
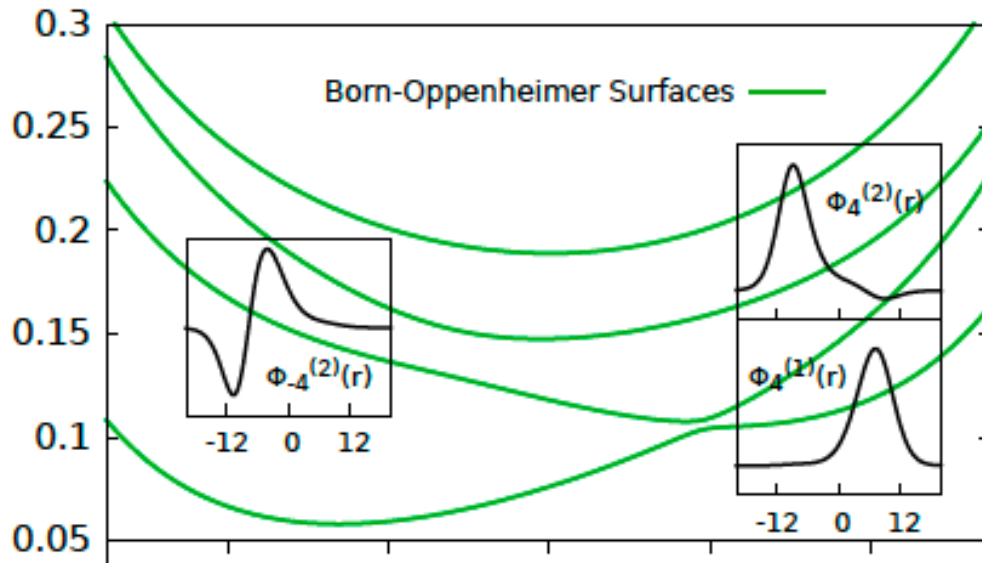
$$\hat{V}^{SP} = \frac{1}{2} \sum_{\alpha} \left( \vec{\lambda}_{\alpha} \cdot \left( \sum_I^{N_n} Z_I \hat{\mathbf{R}}_I - \sum_i^{N_e} \hat{\mathbf{r}}_i \right) \right)^2$$

e.g. 3D planar cavity:

$$\lambda_{\alpha} = \sqrt{\frac{2}{\epsilon_0 Vol.}} \sin(k_{\alpha} X)$$

A Motivation to choose the marginal as  $q$ :

Photonic parts of Hamiltonian are harmonic with bilinear coupling  $\rightarrow$  is classical dynamics of Wigner-sampled initial state for photons exact?



If we treated the photon dynamics with classical trajectories in  $q$ , is it accurate?

## A Motivation:

Photonic parts of Hamiltonian are harmonic with bilinear coupling  $\rightarrow$  is classical dynamics of Wigner-sampled initial state for photons exact?

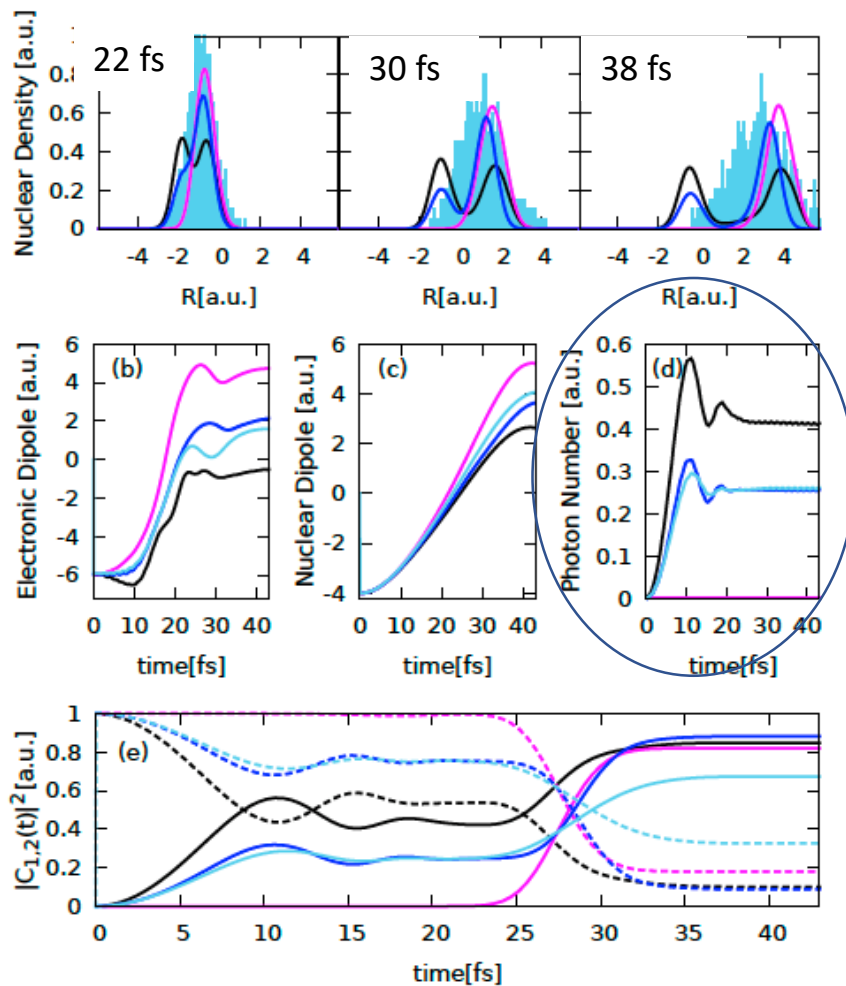
Exact

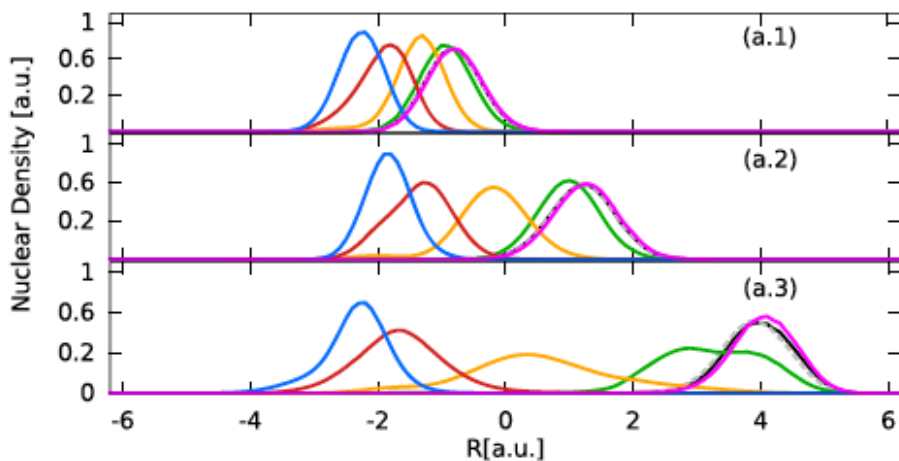
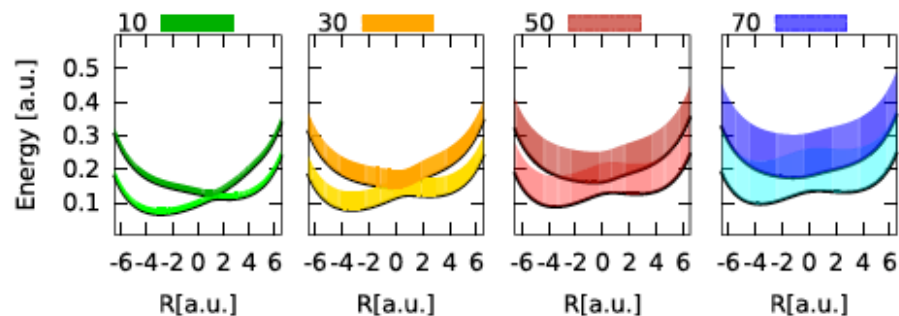
Multi-trajectory Ehrenfest-photons (MTE)

Multi-trajectory Ehrenfest-photons & nuclei

Cavity-free

underestimate of  
photon number

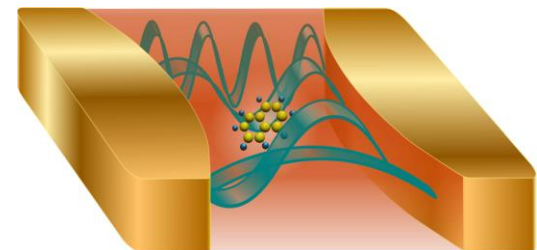




Underestimation also seen in 400-mode 2LS and 3LS studies of Hoffmann, Schäfer, Rubio, Appel, Kelly, PRA **99** (2019)

*Do we really care?!*

MTE for photons is a practical way to account for many modes in the cavity



.. As more cavity modes are accounted for, dramatic changes in the dynamics (self-polarization)

Also, recent analyses of vibrational strong coupling in real systems use classical trajectories on the BO surface...

Want a sense of the size of the error

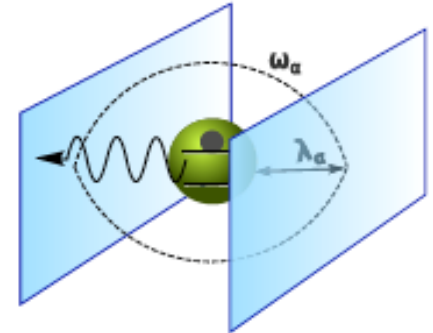
## Simplest example: Two-level system coupled to a single resonant cavity-mode

$$H_m = \epsilon_g |g\rangle\langle g| + \epsilon_e |e\rangle\langle e| + (\omega_c^2 q^2 - \partial^2 / \partial q^2) / 2$$

$$+ r_{eg} \lambda \omega_c q (|e\rangle\langle g| + |g\rangle\langle e|)$$

$$\omega_c = \epsilon_e - \epsilon_g \quad \text{coupling, } \lambda r_{eg} = 0.01$$

Initial state:  $|e\rangle$ , zero photons



Plan: Find the exact qTDPES from XF, choosing  $q$  as the marginal.  
Classically evolve on it & compare with MTE

$$|\Psi(q, t)\rangle = \chi(q, t) |\Phi_q(t)\rangle, \quad \text{with } \langle \Phi_q(t) | \Phi_q(t) \rangle_e = 1$$

$$\mathcal{E}^{\text{qTDPES}}(q, t) = \mathcal{E}^{\text{wBO}}(q, t) + \mathcal{E}^{\text{kin}}(q, t) + \mathcal{E}^{\text{GD}}(q, t)$$

$$\mathcal{E}^{\text{wBO}}(q, t) = \langle \Phi_q(t) | H^{\text{qBO}} | \Phi_q(t) \rangle \quad H^{\text{qBO}} = H - \partial_q^2 / 2$$

$$\mathcal{E}^{\text{kin}}(q, t) = |\langle \partial_q \Phi_q(t) | \partial_q \Phi_q(t) \rangle|^2 / 2$$

$$\mathcal{E}^{\text{GD}}(q, t) = \langle \Phi_q(t) | -i \partial_t \Phi_q(t) \rangle$$



# Simplest example: Two-level system coupled to a single resonant cavity-mode

Plan: Find the exact qTD PES from XF, choosing  $q$  as the marginal.

Classically evolve on qTD PES & compare with MTE

$$|\Psi(q, t)\rangle = \chi(q, t)|\Phi_q(t)\rangle, \text{ with } \langle\Phi_q(t)|\Phi_q(t)\rangle_e = 1$$

$$\mathcal{E}^{\text{qTD PES}}(q, t) = \mathcal{E}^{\text{wBO}}(q, t) + \mathcal{E}^{\text{kin}}(q, t) + \mathcal{E}^{\text{GD}}(q, t)$$

$$\mathcal{E}^{\text{wBO}}(q, t) = \langle\Phi_q(t)|H^{\text{qBO}}|\Phi_q(t)\rangle \quad H^{\text{qBO}} = H - \partial_q^2/2$$

$$\mathcal{E}^{\text{kin}}(q, t) = |\langle\partial_q\Phi_q(t)|\partial_q\Phi_q(t)\rangle|^2/2$$

$$\mathcal{E}^{\text{GD}}(q, t) = \langle\Phi_q(t)|-i\partial_t\Phi_q(t)\rangle$$

$$|\Phi_q(t)\rangle = C_g(q, t)|\Phi_{q,g}\rangle + C_e(q, t)|\Phi_{q,e}\rangle$$

$$\ddot{q}^{(I)}(t) = -\partial_q \mathcal{E}^{\text{qTD PES}}(q^{(I)}, t)$$

e.g.

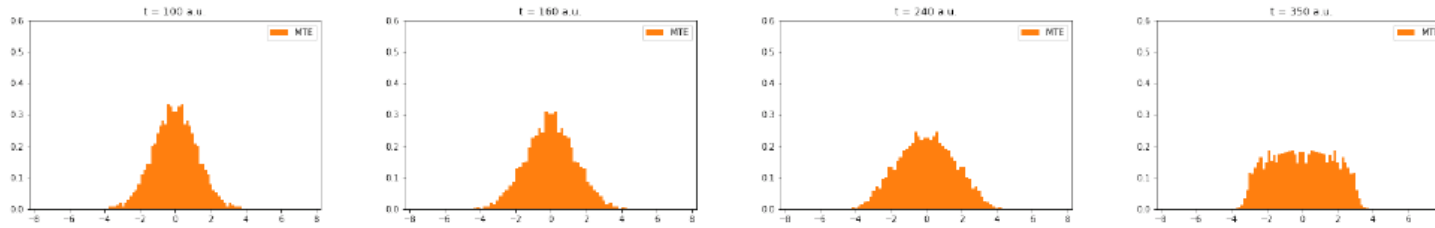
$$\begin{aligned} \ddot{q}^{(I), \text{wBO}}(t) &= -|C_g|^2 \partial_q \mathcal{E}_g^{\text{qBO}} - |C_e|^2 \partial_q \mathcal{E}_e^{\text{qBO}} \\ &\quad - ((\partial_q |C_g|^2) \mathcal{E}_g^{\text{qBO}} + (\partial_q |C_e|^2) \mathcal{E}_e^{\text{qBO}}) \end{aligned}$$

$$|\Phi^{(I)}(t)\rangle = C_g^{(I)}(t)|\Phi_{q,g}\rangle + C_e^{(I)}(t)|\Phi_{q,e}\rangle$$

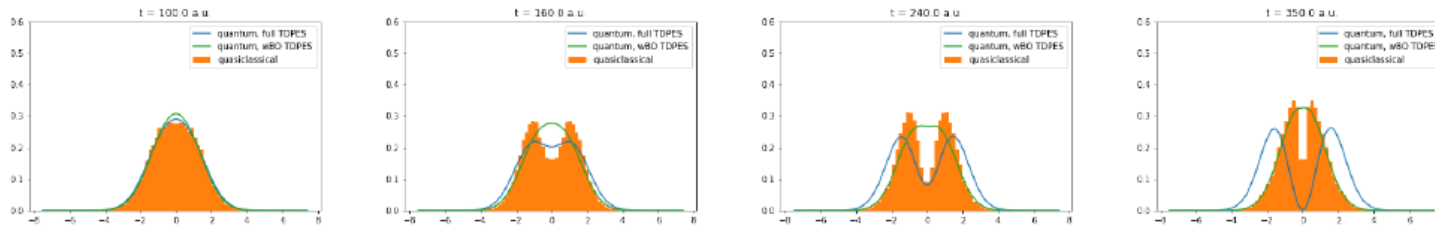
$$\ddot{q}^{(I)}(t) = - \sum_{i=g,e} |C_i|^2 \partial_q \mathcal{E}_i^{\text{qBO}} - C_g^* C_e (\mathcal{E}_e^{\text{qBO}} - \mathcal{E}_g^{\text{qBO}}) d_{eg}$$

$$\dot{C}_{g(e)}^{(I)}(t) = -i \mathcal{E}_{g(e)}^{\text{qBO}} C_{g(e)}^{(I)} - \dot{q}^{(I)} d_{eg} C_{e(g)}^{(I)}$$

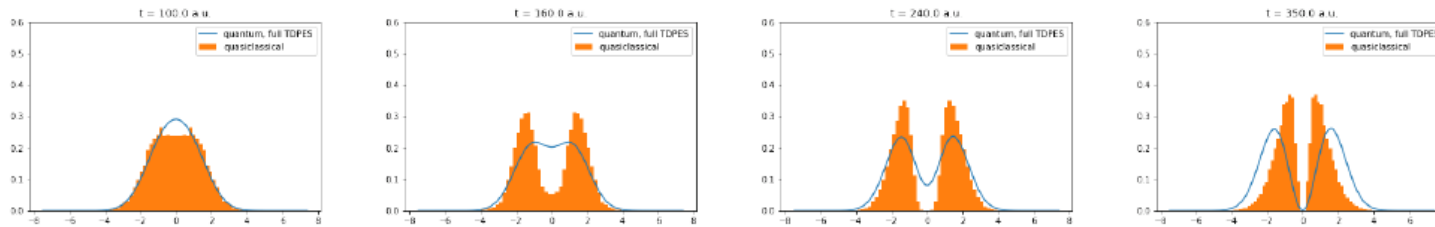
$$|\chi(q,t)|^2$$



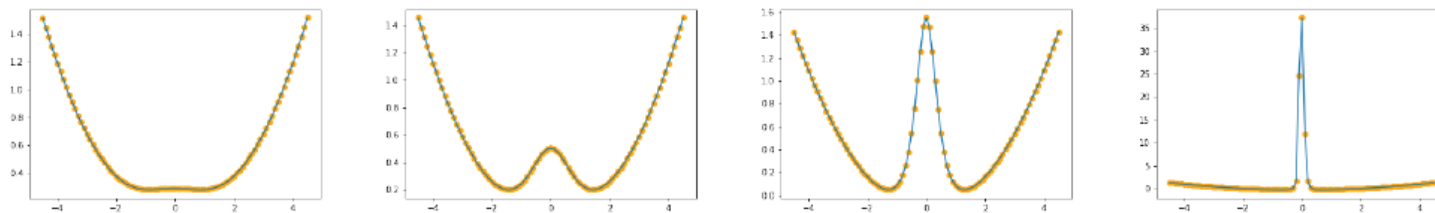
MTE



QC on wBO  
Exact  
QM on wBO



QC on qTDPEs  
Exact



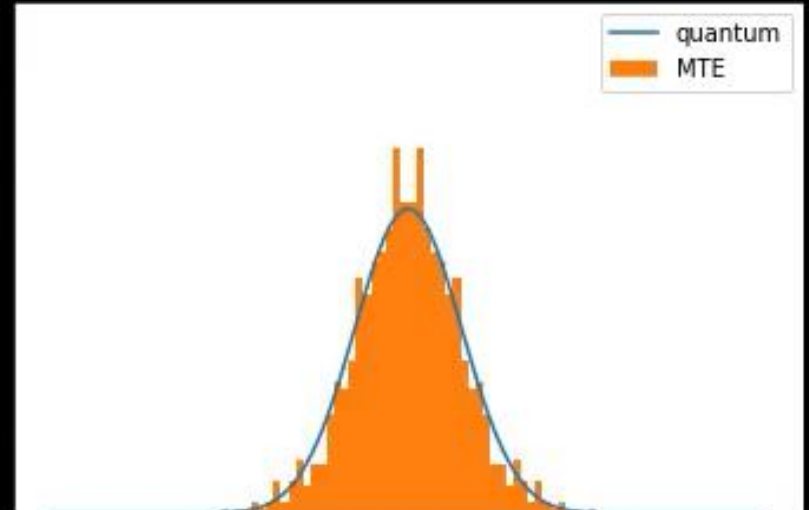
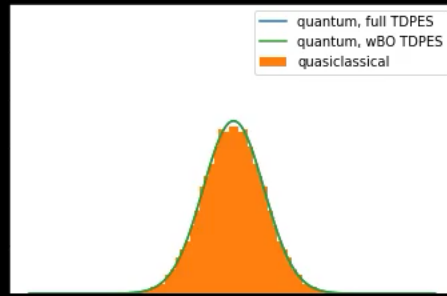
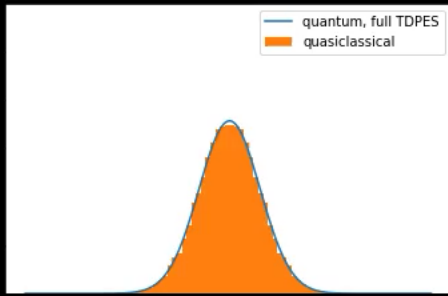
<-- exact qTDPEs

Deviations from harmonic!

MTE cannot generate the barrier → smaller photon-number observed

*B. Rosenzweig, N. M. Hoffmann, L. Lacombe, N.T. Maitra, in prep. (2021)*

# Movie



## Summary/Outlook of the 2<sup>nd</sup> Part

- ❖ A look at the exact potential driving photon dynamics reveals why quasiclassical propagation methods for photons tend to underestimate the photon number in stimulated emission phenomena
- ❖ Barrier in qTD PES localized at  $q = 0$  inherently associated with electron-photon correlation, completely missing in underlying force on MTE
- ❖ Implications for polaritonic chemistry modeling?

# Thanks to: Alexey, Sergei, Fede, and the VISTA team

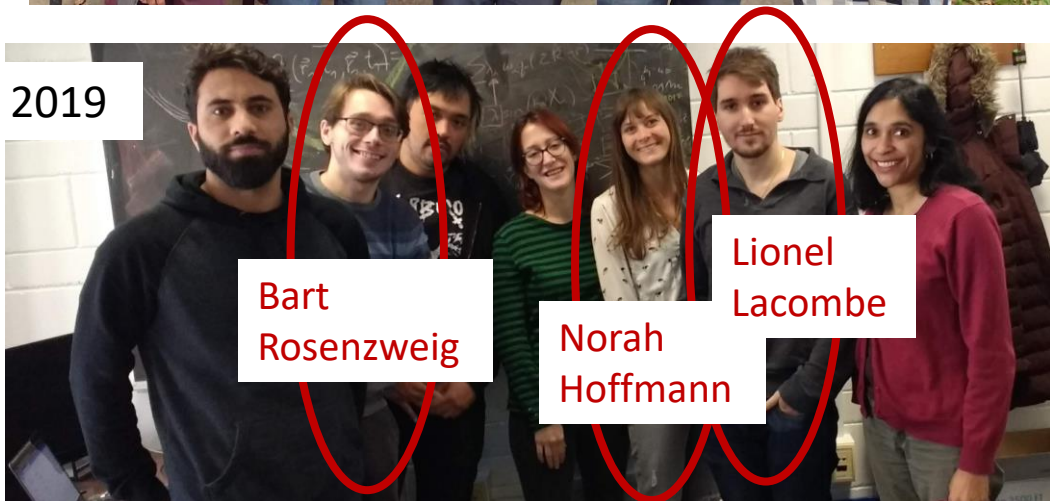
Fall 2021



Patricia Vindel  
Zandbergen



Fall 2019



Bart  
Rosenzweig

Norah  
Hoffmann

Lionel  
Lacombe



- Jong Kwon Ha & Seung-Kyu Min (UNIST, Korea)
- Lea Ibele & Basile Curchod (Durham, UK)
- Spiridoula Matsika (Temple University)

***And to you all for listening!***