Independent Trajectory Mixed Quantum-Classical Approaches Based on Exact Factorization

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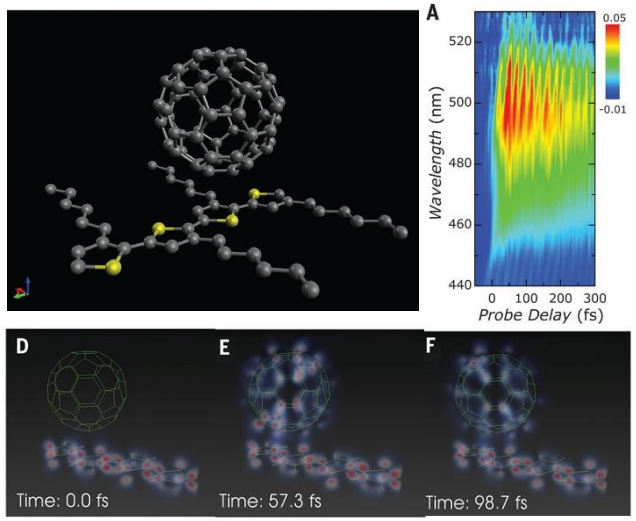
Outline

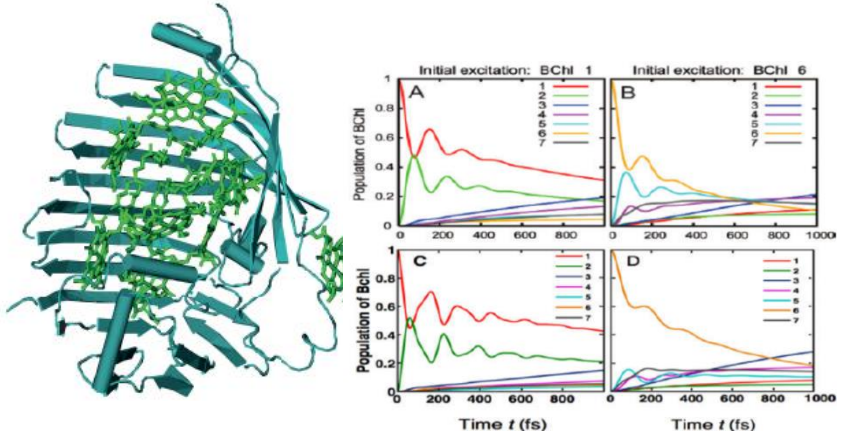
- Introduction – Excited state phenomena
- Electron-nuclear correlation from exact factorization
- Independent trajectory mixed quantum-classical approaches based on exact factorization : SHXF & EhXF
- PyUNIxMD program
- Summary

Excited state phenomena

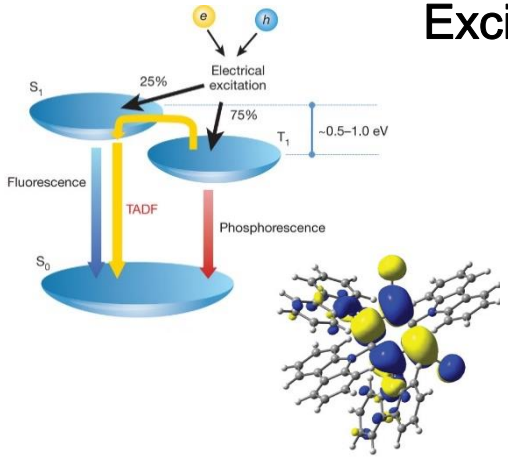


Science, 344, 1001 (2014)

Electron/hole transfers

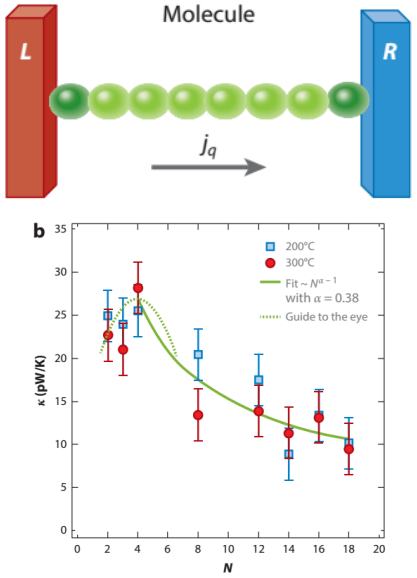


Exciton energy transfers



Nature, 492, 234 (2012)

Thermally activated delayed fluorescence

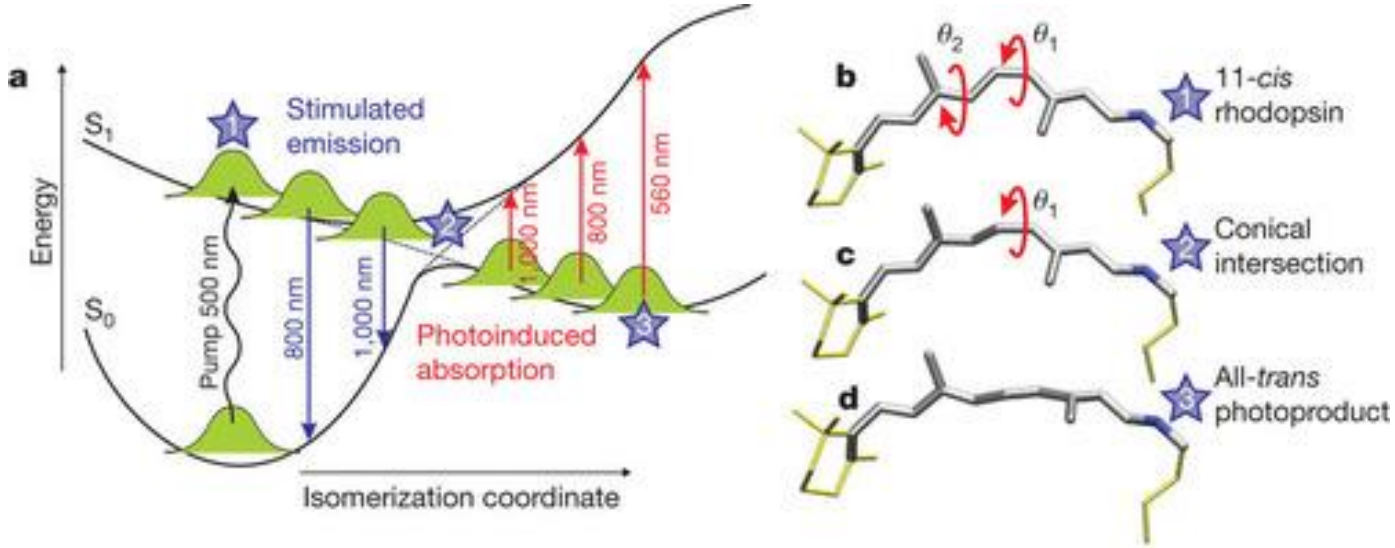


Phys. Rev. Lett., 113, 060801 (2014)

Nanoscale transport phenomena

Dynamics with electronic excited states

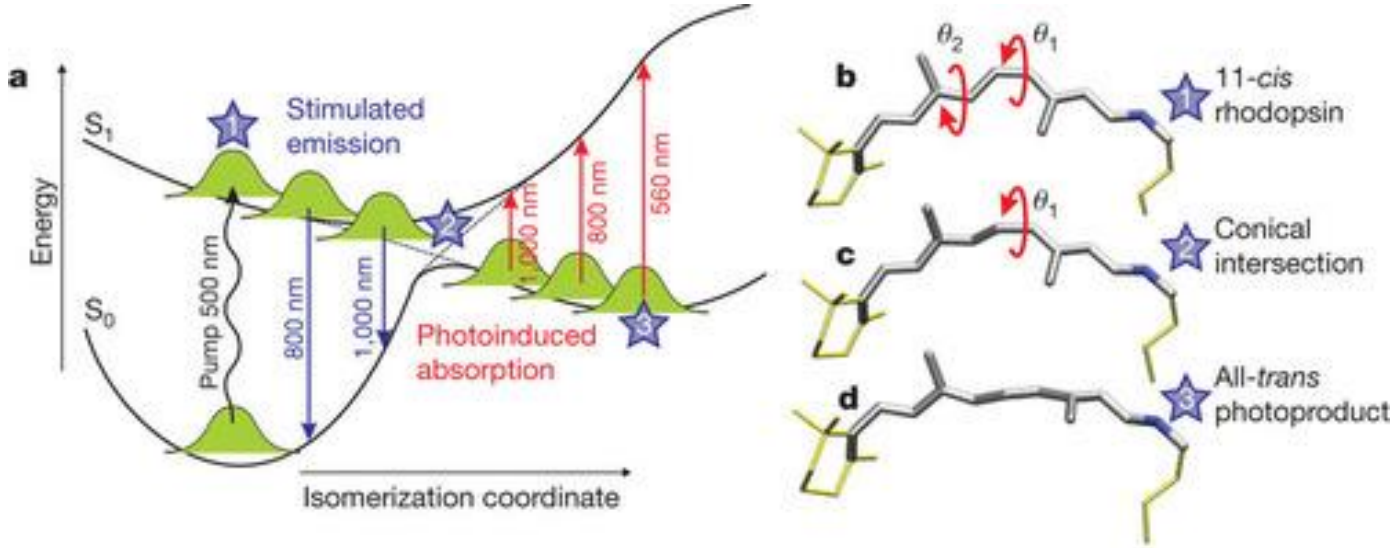
- Key ingredients



- Multiple Born-Oppenheimer potential energy surfaces (PESs)
- Nonadiabatic electronic transitions (internal conversion, …)
- Quantum nuclear dynamics (nuclear wave packet splitting)

Dynamics with electronic excited states

- Key ingredients



- Multiple Born-Oppenheimer potential energy surfaces (PESs)

  DFTB/SSR, ML/SSR

- Nonadiabatic electronic transitions (internal conversion, …)

- Quantum nuclear dynamics (nuclear wave packet splitting) CTMQC, SHXF, EhXF, PyUNIxMD

Beyond classical nuclei: exact factorization

- Molecular wave function as a single product

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

the solution of the full molecular TDSE

- Nuclear wave function χ → exact time-dependent nuclear density

- Nuclear EOM

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

- Electronic wave function Φ → a time-dep. (TD) PES ε, a TD vector potential *A*

$$\epsilon(\underline{\underline{\mathbf{R}}},t) = \left\langle \Phi_{\underline{\underline{\mathbf{R}}}}(t)\right| \hat{H}_{BO} + \hat{U}_{en}^{coup} - i\hbar\partial_t \left|\Phi_{\underline{\underline{\mathbf{R}}}}(t)\right\rangle_{\underline{\underline{\mathbf{r}}}} \qquad \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}},t) = \left\langle \Phi_{\underline{\underline{\mathbf{R}}}}(t)\right| - i\hbar\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}}(t)\right\rangle_{\underline{\underline{\mathbf{r}}}}$$

Phys. Rev. Lett., **105**, 123002 (2010), *J. Chem. Phys.*, **137**, 22A530 (2012)

Beyond classical nuclei: exact factorization

- Electronic equation of motion

$$i\hbar\partial_t \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t) = \left(\hat{H}_{BO}(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}}) + \hat{U}_{en}^{coup}[\Phi_{\underline{\underline{\mathbf{R}}}},\chi] - \epsilon(\underline{\underline{\mathbf{R}}},t)\right)\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}},t)$$

where the electron-nuclear correlation operator is

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

- Analysis of electron-nuclear correlation operator

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

generate a potential corresponding to diagonal BO correction (DBOC)

$$\frac{-i\hbar\nabla_\nu\chi}{\chi} + \mathbf{A}_\nu(\underline{\underline{\mathbf{R}}},t) = \mathbf{P}_{cl} - \frac{i\hbar\nabla_\nu|\chi|}{|\chi|}$$

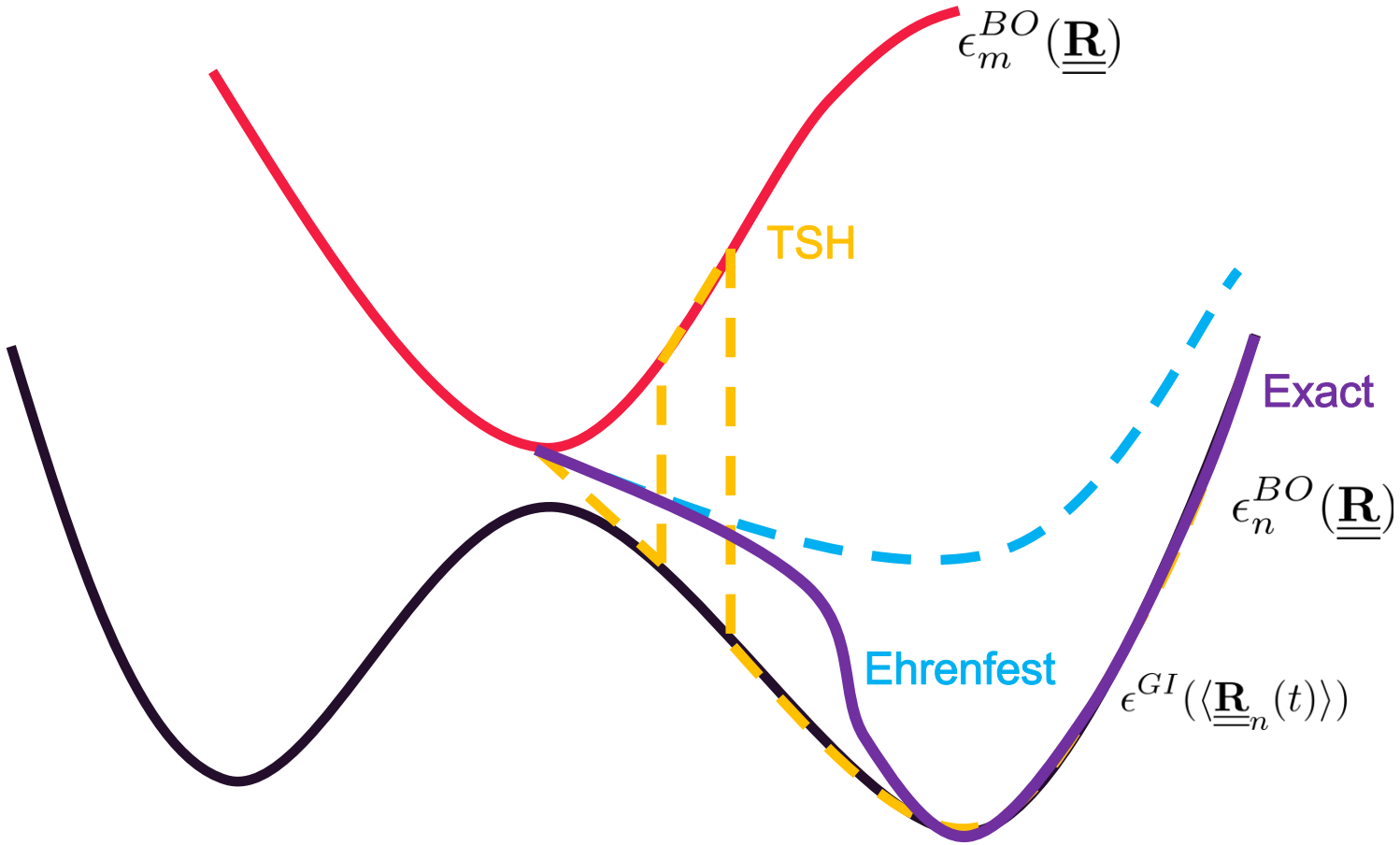
classical momentum provides Ehrenfest equation with trajectories

quantum momentum provides additional correlation toward quantum (de)coherence

Phys. Rev. Lett., **105**, 123002 (2010), *J. Chem. Phys.*, **137**, 22A530 (2012)

Effective potential energy surfaces

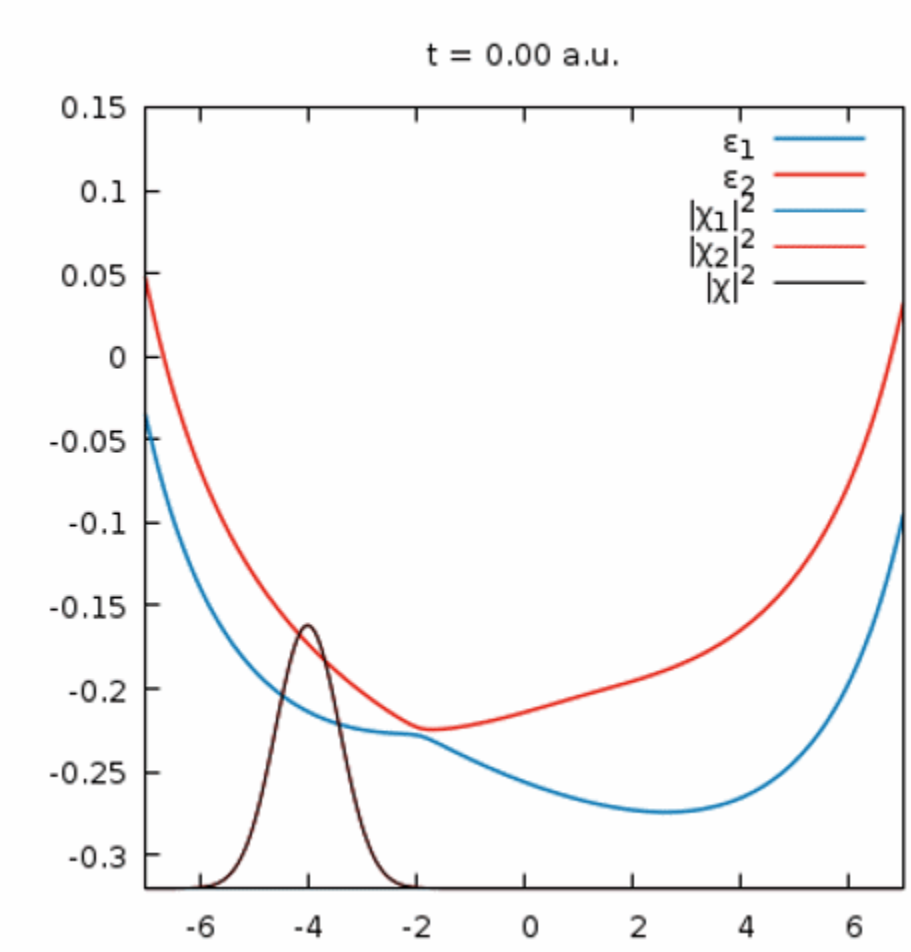
- Exact factorization can capture correct behavior in potential energy surfaces

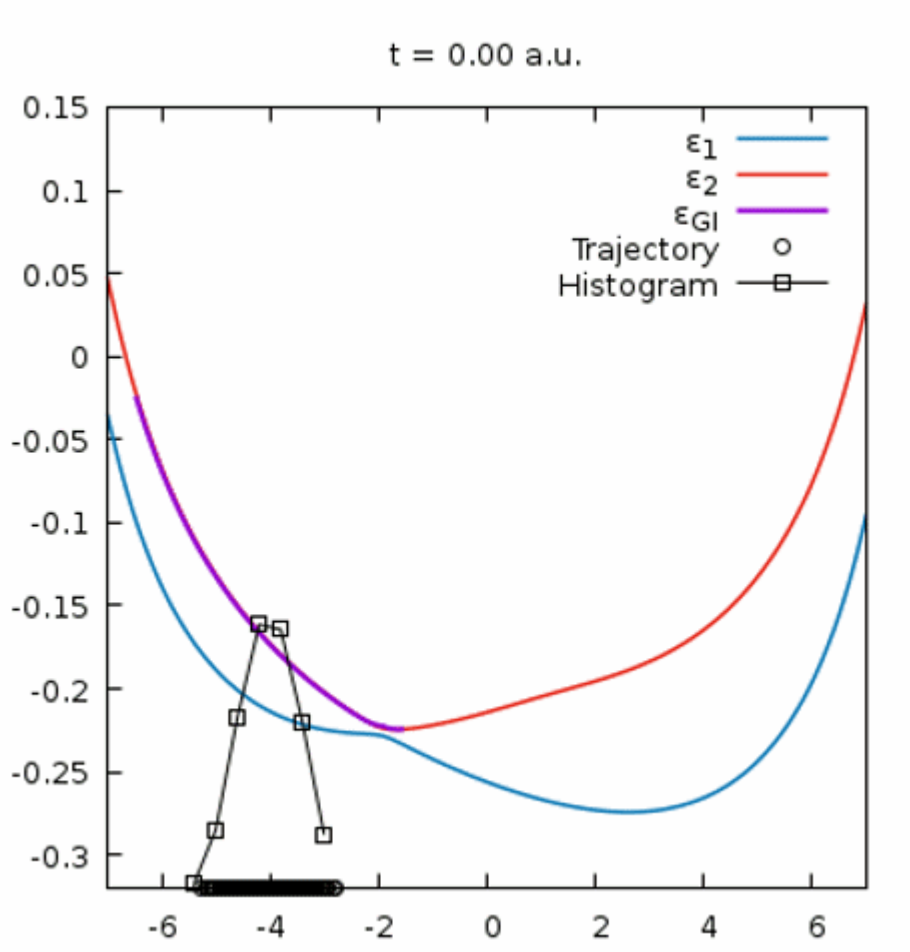


$$\langle\underline{\underline{\mathbf{R}}}_n(t)\rangle = \langle\chi_n(\underline{\underline{\mathbf{R}}},t)|\underline{\underline{\mathbf{R}}}|\chi_n(\underline{\underline{\mathbf{R}}},t)\rangle / \langle\chi_n(\underline{\underline{\mathbf{R}}},t)|\chi_n(\underline{\underline{\mathbf{R}}},t)\rangle$$

Toward mixed quantum-classical approach

Quantum dynamics vs. trajectories on potential from exact factorization





Trajectory-based equations of motion

- Electronic equation of motion

$$i\hbar\frac{d}{dt}\Phi_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(\underline{\mathbf{r}},t) = \hat{H}_{BO}(\underline{\mathbf{r}};\underline{\underline{\mathbf{R}}}^{(I)}(t))\Phi_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(\underline{\mathbf{r}},t) + i\hbar\sum_{\nu}^{N_n}\left.\frac{\nabla_\nu|\chi|}{|\chi|}\right|_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}\cdot\left(\mathbf{A}_\nu^{(I)}\Phi_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(\underline{\mathbf{r}},t) + i\hbar\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(\underline{\mathbf{r}},t)\right)$$

- Nuclear equation of motion

$$\dot{\mathbf{P}}_\nu = -\left\langle\Phi_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(t)\left|\nabla_\nu\hat{H}_{BO}\right|\Phi_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(t)\right\rangle_{\underline{\mathbf{r}}} + 2\sum_{\nu'}^{N_n}\frac{1}{M_{\nu'}}\left(\left.\frac{\nabla_{\nu'}|\chi|}{|\chi|}\right|_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}\cdot\mathbf{A}_{\nu'}^{(I)}(t)\right)\mathbf{A}_\nu^{(I)}(t) + 2\,\mathrm{Re}\int d\underline{\mathbf{r}}\left[\sum_{\nu'}^{N_n}\frac{1}{M_{\nu'}}\left.\frac{\nabla_{\nu'}|\chi|}{|\chi|}\right|_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}\cdot\left(-i\hbar\nabla_{\nu'}\Phi^*_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(\underline{\mathbf{r}},t)\right)\right]\left(-i\hbar\nabla_\nu\Phi_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(\underline{\mathbf{r}},t)\right)$$

Phys. Rev. Lett., **115**, 073001 (2015), *J. Chem. Theory Comput.*, **12**, 2127 (2016).

Trajectory-based equations of motion

- Electronic equation of motion

$$\Phi_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(\underline{\mathbf{r}},t) = \sum_{l=1}^{N_{st}} C_l(\underline{\underline{\mathbf{R}}}^{(I)}(t),t)\varphi^{(l)}_{\underline{\underline{\mathbf{R}}}^{(I)}(t)}(\underline{\mathbf{r}})$$

$$\dot{C}_l^{(I)}(t) = \frac{-i}{\hbar}\epsilon_{BO}^{(l)}\left(\underline{\underline{\mathbf{R}}}^{(I)}(t)\right)C_l^{(I)}(t) - \sum_{\nu=1}^{N_n}\mathbf{v}_\nu^{(I)}\cdot\sum_{k=1}^{N_{st}}C_k^{(I)}(t)\mathbf{d}^{(I)}_{\nu,lk}$$

$$+\sum_{\nu=1}^{N_n}\frac{1}{M_\nu}\frac{\nabla_\nu|\chi|}{|\chi|}\bigg|_{(I)}\cdot\Big(\sum_k \rho^{(I)}_{kk}(t)\mathbf{f}^{(I)}_{k,\nu}(t) - \mathbf{f}^{(I)}_{l,\nu}(t)\Big)C_l^{(I)}(t)$$

- Nuclear equation of motion

$$\dot{\tilde{P}}_\nu^{(I)}(t) = -\sum_k \rho^{(I)}_{kk}(t)\nabla_\nu\epsilon^{(k),(I)}_{BO} - \sum_{k,l}\rho^{(I)}_{lk}(t)\left(\epsilon^{(k),(I)}_{BO} - \epsilon^{(l),(I)}_{BO}\right)\mathbf{d}^{(I)}_{\nu,lk}$$

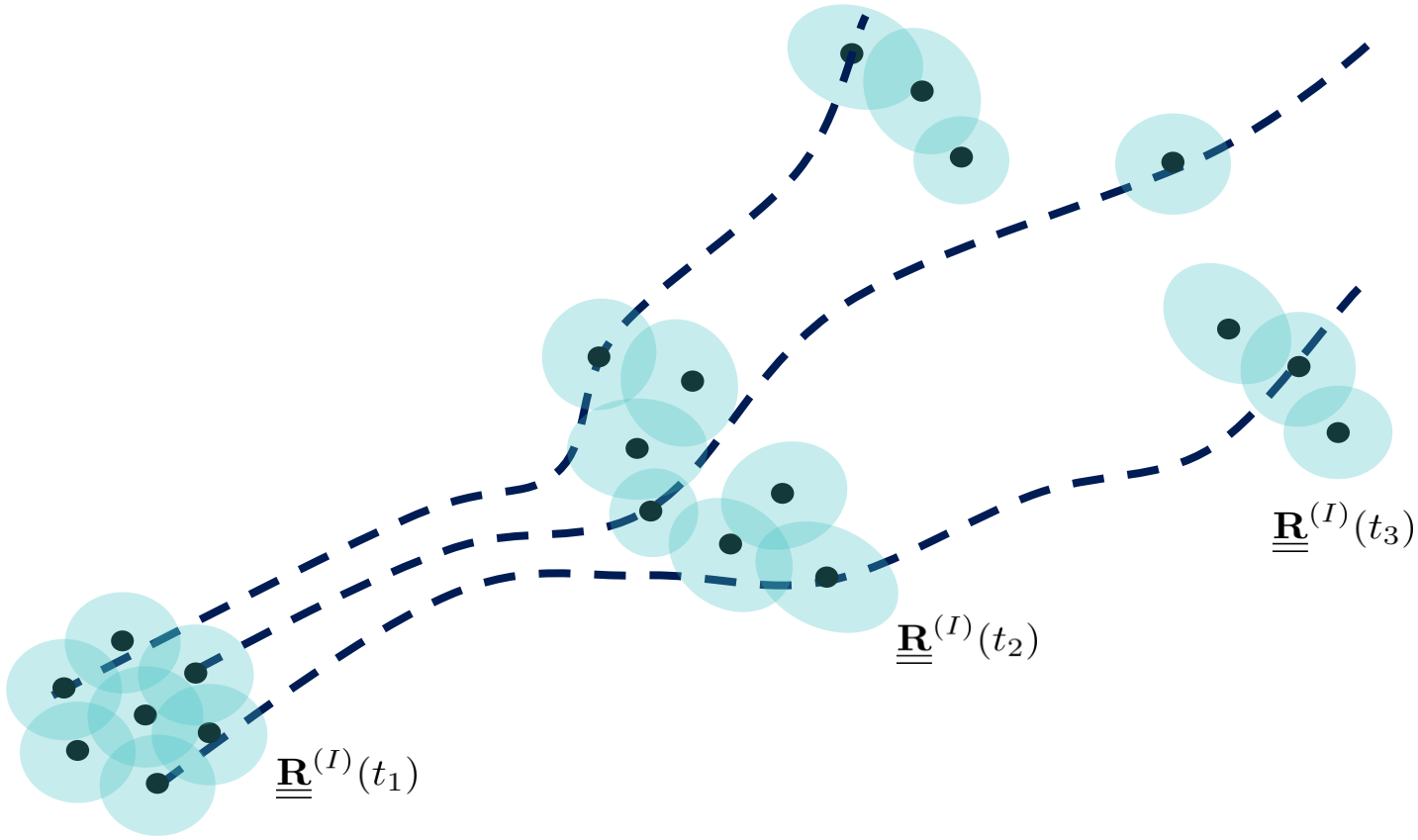
$$-\sum_l \rho^{(I)}_{ll}(t)\left(\sum_{\nu'=1}^{N_n}\frac{2\hbar}{M_{\nu'}}\frac{\nabla_\nu|\chi|}{|\chi|}\bigg|_{(I)}\cdot\mathbf{f}^{(I)}_{l,\nu'}(t)\right)\left[\sum_k \rho^{(I)}_{kk}(t)\mathbf{f}^{(I)}_{k,\nu}(t) - \mathbf{f}^{(I)}_{l,\nu}(t)\right]$$

$$\rho^{(I)}_{lk}(t) = C_l^{(I)*}(t)C_k^{(I)}(t) \qquad \mathbf{f}^{(I)}_{l,\nu}(t) = -\int_0^t dt'\nabla_\nu\epsilon^{(l)}_{BO}$$

Phys. Rev. Lett., **115**, 073001 (2015), *J. Chem. Theory Comput.*, **12**, 2127 (2016).

Coupled trajectory approach (CT-MQC)

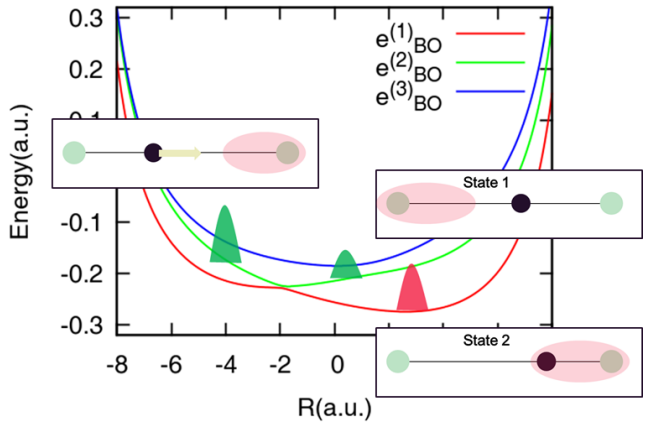
- Calculating quantum momentum from a nuclear density from multiple trajectories
  - Put Gaussians on all trajectories, and compute the quantum momentum

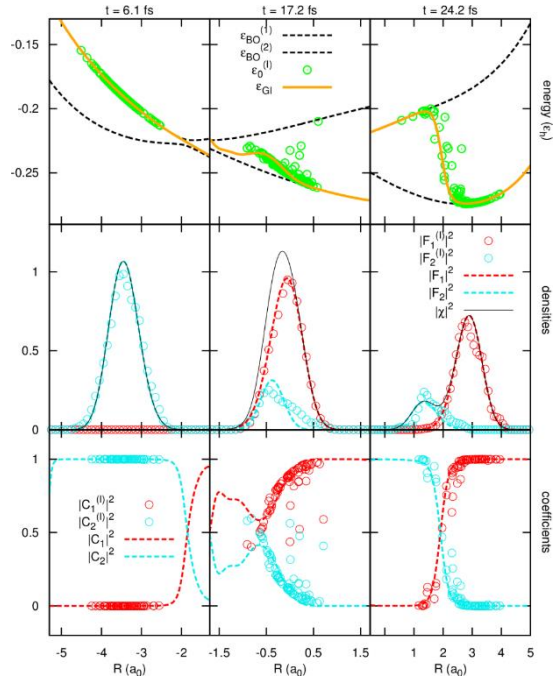


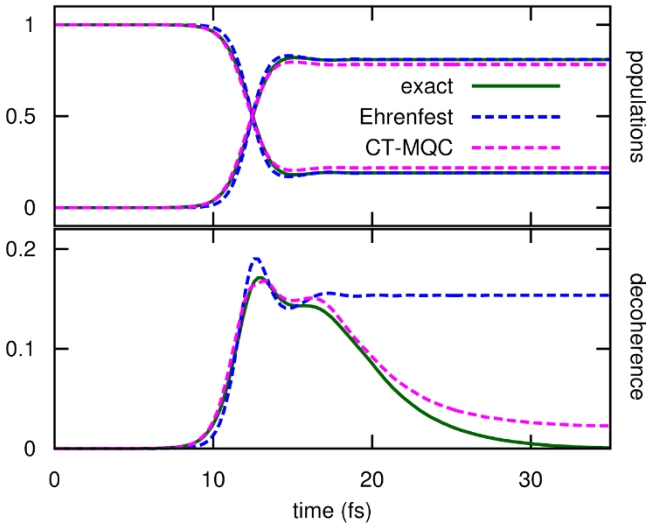
Phys. Rev. Lett., **115**, 073001 (2015), *J. Chem. Theory Comput.*, **12**, 2127 (2016).

Coupled trajectory approach (CT-MQC)

- Additional ingredients compared to Ehrenfest/Surface hopping dynamics
  - Positions of all trajectories to construct nuclear quantum momentum
  - Phase factors from all BO forces $\mathbf{f}_{l,\nu}^{(I)}(t) = -\int_0^t dt' \nabla_\nu \epsilon_{BO}^{(l)}$
  - All trajectories should be run simultaneously!





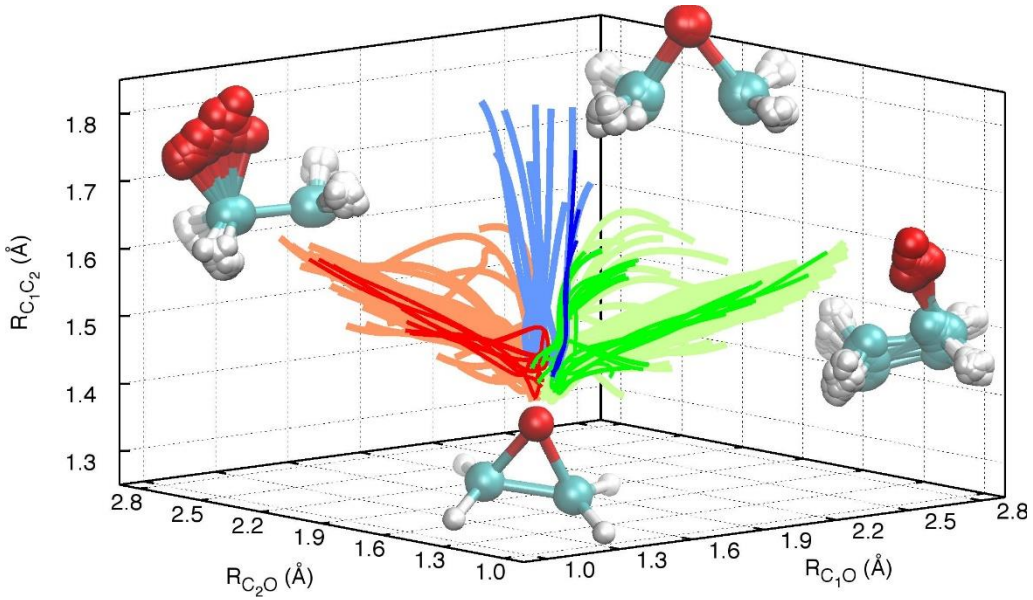


QM $\int dR |C_1(R,t)|^2 |C_2(R,t)|^2 |\chi(R,t)|^2$

CT $\sum_I |C_1^{(I)}(t)|^2 |C_2^{(I)}(t)|^2 / N_{traj}$

First principle-based implementation

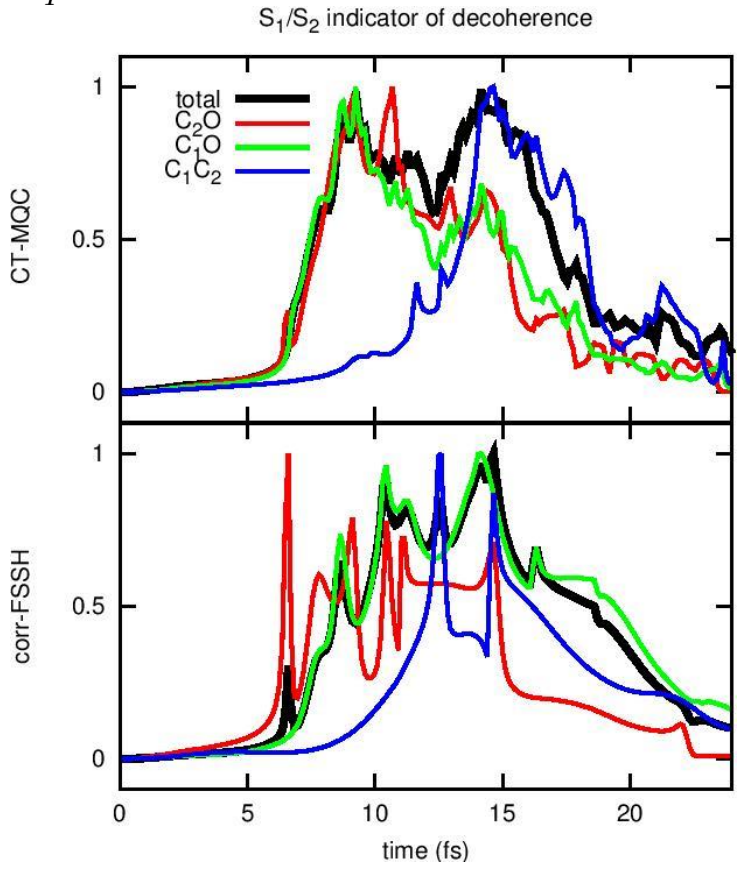
- Car-Parrinello Molecular Dynamics (CPMD) program
- Excited state calculation with LR-TDDFT
- Photodissociation dynamics of Oxirane ($S_2 \rightarrow S_1$)



100 trajectories
with initial Boltzmann distribution at 300K

Quantum-like trajectories for CT-MQC
(deep: (corr)-FSSH, pastel: CT-MQC)

$$\sum_I |C_1^{(I)}(t)|^2 |C_2^{(I)}(t)|^2 / N_{traj}$$



J. Phys. Chem. Lett., 8, 3048 (2017).

Independent (auxiliary)-trajectory method: Surface hopping based on exact factorization (SHXF)

J.K. Ha
(UNIST)

- Coupled-trajectory algorithm requires …
  - Nonadiabatic coupling vectors (NACVs) among all states
    c.f.) surface hopping : NACVs projected on velocities (NACME)
  - BO force for all electronic states
  - BO calculations should be stable for all trajectories
- Coupled-trajectory algorithm is efficient, but less efficient than the conventional surface hopping algorithm

Modified surface hopping algorithm based on exact factorization

➡ *Surface hopping based on exact factorization (SHXF)*

J. Phys. Chem. Lett., 9, 1097 (2018).

Independent (auxiliary)-trajectory method: Surface hopping based on exact factorization (SHXF)

- Nuclear equation: same as the conventional surface hopping,
  i.e. nuclear force from the running state or force state

- Electronic equation with the decoherence term

$$\dot{C}_l^{(I)}(t) = \frac{-i}{\hbar}\epsilon_{BO}^{(l)}\left(\underline{\underline{\mathbf{R}}}^{(I)}(t)\right)C_l^{(I)}(t) - \sum_{\nu=1}^{N_n}\mathbf{v}_\nu^{(I)}\cdot\sum_{k=1}^{N_{st}}C_k^{(I)}(t)\mathbf{d}_{\nu,lk}^{(I)}$$
$$+\sum_{\nu=1}^{N_n}\frac{1}{M_\nu}\frac{\nabla_\nu|\chi|}{|\chi|}\Bigg|_{(I)}\cdot\Big(\sum_k\rho_{kk}^{(I)}(t)\mathbf{f}_{k,\nu}(t) - \mathbf{f}_{l,\nu}^{(I)}(t)\Big)C_l^{(I)}(t)$$

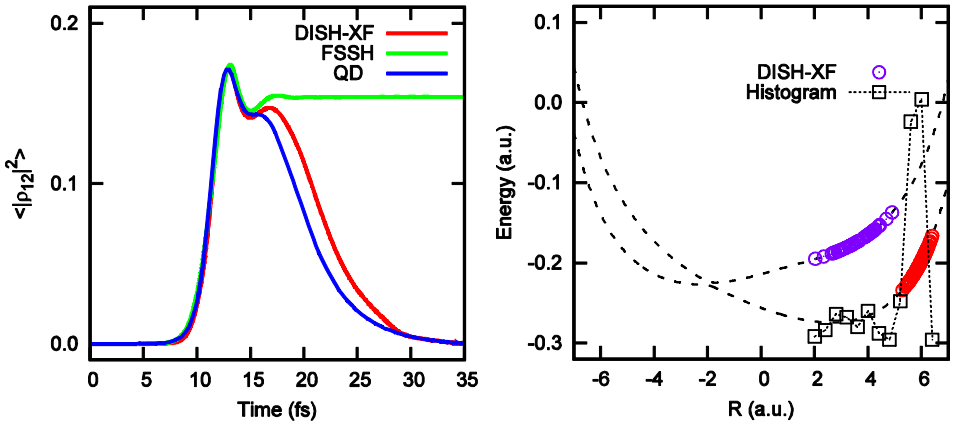
- Hopping probability: same as the conventional surface hopping

- Quantum momentum from auxiliary trajectories :
  put Gaussian wave packet when population exchange occurs

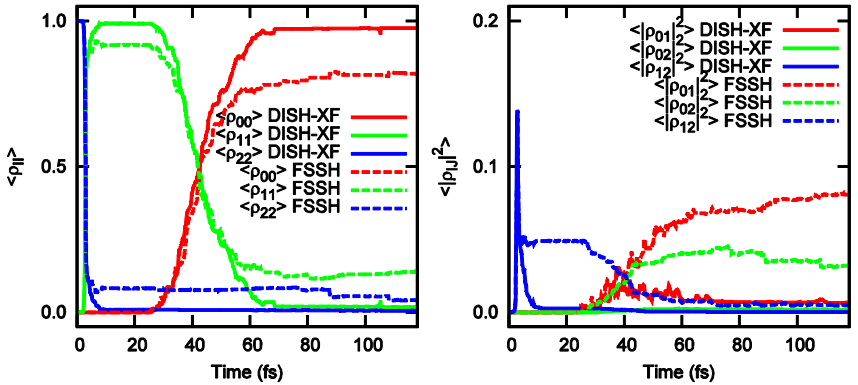
J. Phys. Chem. Lett., 9, 1097 (2018).

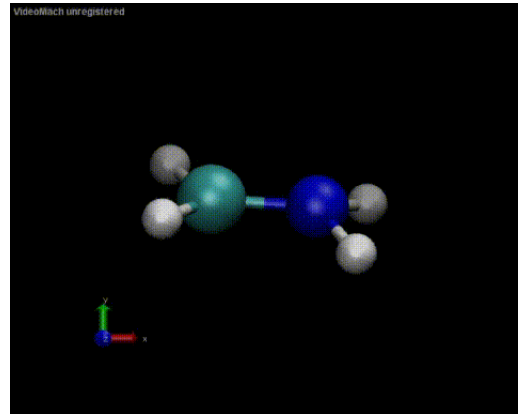
Applications of SHXF

- Shin-Metiu model (single crossing)

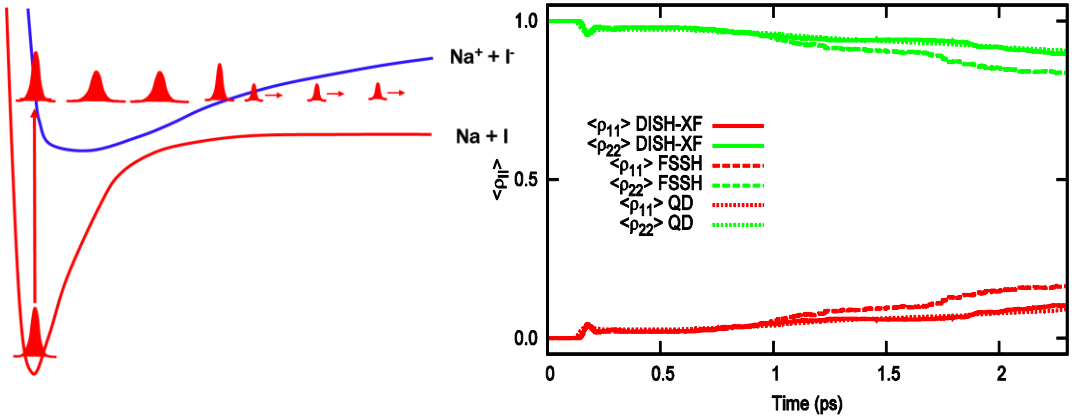


- $CH_2NH_2^+$: (multiple states)
  $S_2 \rightarrow (CI) \rightarrow S_1 \rightarrow (CI) \rightarrow S_0$





- NaI femtosecond pump-probe experiment (multiple crossing)



J. Phys. Chem. Lett., 9, 1097 (2018).

Role of the electron-nuclear correlation (ENC) term

- Population change in time

$$\frac{d}{dt}\rho_{ll}^{(I)}(t) = -2\sum_{k=1}^{N_{st}} \mathrm{Re}\left(\rho_{lk}^{(I)}(t)\sum_{\nu=1}^{N_n}\mathbf{v}_{\nu}^{(I)}\cdot\mathbf{d}_{\nu,lk}^{(I)}\right)$$
$$+\sum_{\nu=1}^{N_n}\frac{2}{M_\nu}\frac{\nabla_\nu|\chi|}{|\chi|}\bigg|_{(I)}\cdot\sum_{k=1}^{N_{st}}\left[\mathbf{f}_{k,\nu}^{(I)}-\mathbf{f}_{l,\nu}^{(I)}\right]\rho_{kk}^{(I)}(t)\rho_{ll}^{(I)}(t)$$

If $\mathbf{d}_{\nu,lk}^{(1)} = 0$,

$$\frac{d}{dt}\rho_{ll}^{(I)}(t) = \sum_{\nu=1}^{N_n}\frac{2}{M_\nu}\frac{\nabla_\nu|\chi|}{|\chi|}\bigg|_{(I)}\cdot\sum_{k=1}^{N_{st}}\left[\mathbf{f}_{k,\nu}^{(I)}-\mathbf{f}_{l,\nu}^{(I)}\right]\rho_{kk}^{(I)}(t)\rho_{ll}^{(I)}(t)$$
$$\neq 0 \text{ if } 0 < \rho_{ll}^{(I)} < 1$$
$$= 0 \text{ if } \rho_{ll}^{(I)} = 0 \text{ or } 1$$

Phys. Rev. Lett., **115**, 073001 (2015).

Role of the electron-nuclear correlation (ENC) term

- When we put Gaussian wave packets on surfaces, we obtain

$$\frac{d}{dt}\rho_{ll}^{(I)}(t) = \sum_{\nu=1}^{N_n} \left.\frac{2}{M_\nu}\frac{\nabla_\nu|\chi|}{|\chi|}\right|_{(I)} \cdot \sum_{k=1}^{N_{st}} \left[\mathbf{f}_{k,\nu}^{(I)} - \mathbf{f}_{l,\nu}^{(I)}\right] \rho_{kk}^{(I)}(t)\rho_{ll}^{(I)}(t)$$

$$= -\sum_{\nu=1}^{N_n} \frac{1}{M_\nu}\frac{1}{\sigma^2}\left(\mathbf{R}_\nu^{(I)} - \langle \mathbf{R}_\nu \rangle\right) \cdot \sum_{k=1}^{N_{st}} \left[\mathbf{f}_{k,\nu}^{(I)} - \mathbf{f}_{l,\nu}^{(I)}\right] \rho_{kk}^{(I)}(t)\rho_{ll}^{(I)}(t)$$

"Position" dependence — Averaged center of overall Gaussians

"Momentum" change — $\left(\mathbf{f}_{l,\nu}^{(I)}(t) = -\int_0^t dt' \nabla_\nu \epsilon_{BO}^{(l)}\right)$

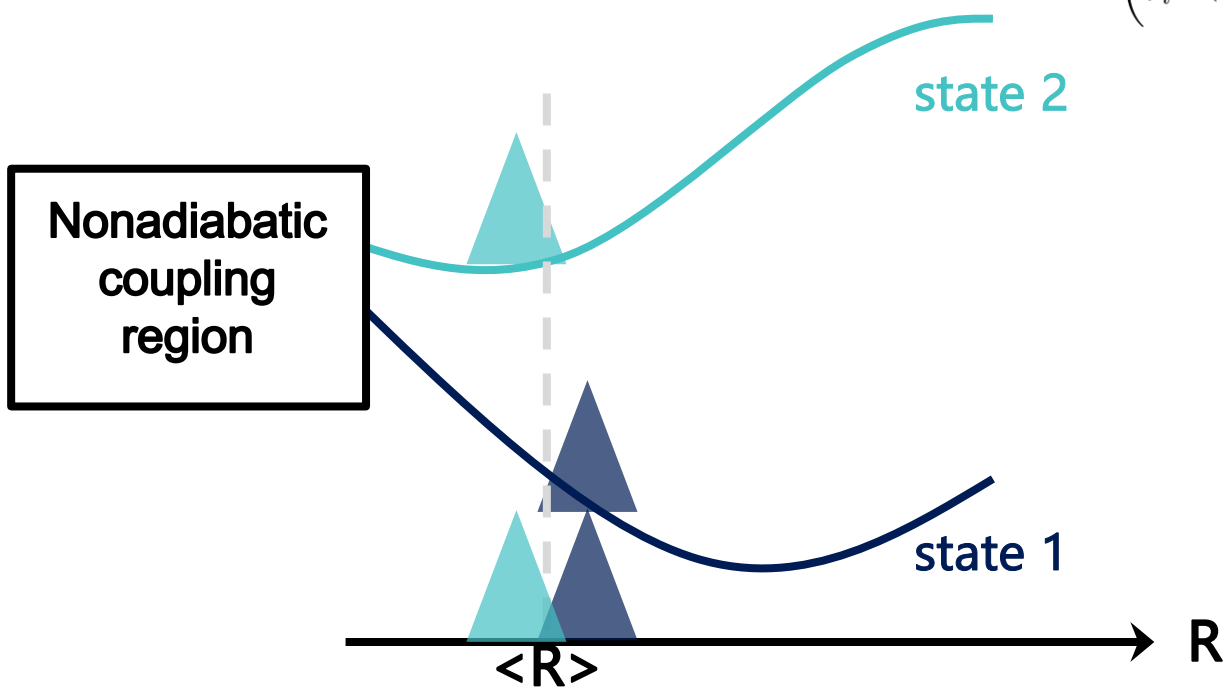
Role of the electron-nuclear correlation (ENC) term

- e.g. 1D 2-state problem

$$\frac{d}{dt}\rho_{11}^{(I)}(t) = -\frac{1}{M}\frac{1}{\sigma^2}\left(R^{(I)} - \langle R\rangle\right)\cdot\left[f_2^{(I)} - f_1^{(I)}\right]\rho_{22}^{(I)}(t)\rho_{11}^{(I)}(t)$$

$$\frac{d}{dt}\rho_{22}^{(I)}(t) = -\frac{1}{M}\frac{1}{\sigma^2}\left(R^{(I)} - \langle R\rangle\right)\cdot\left[f_1^{(I)} - f_2^{(I)}\right]\rho_{11}^{(I)}(t)\rho_{22}^{(I)}(t)$$

$$\left(f_l^{(I)}(t) = -\int_0^t dt'\partial_R\epsilon_{BO}^{(l)}\right)$$



Role of the electron-nuclear correlation (ENC) term

- e.g. 1D 2-state problem

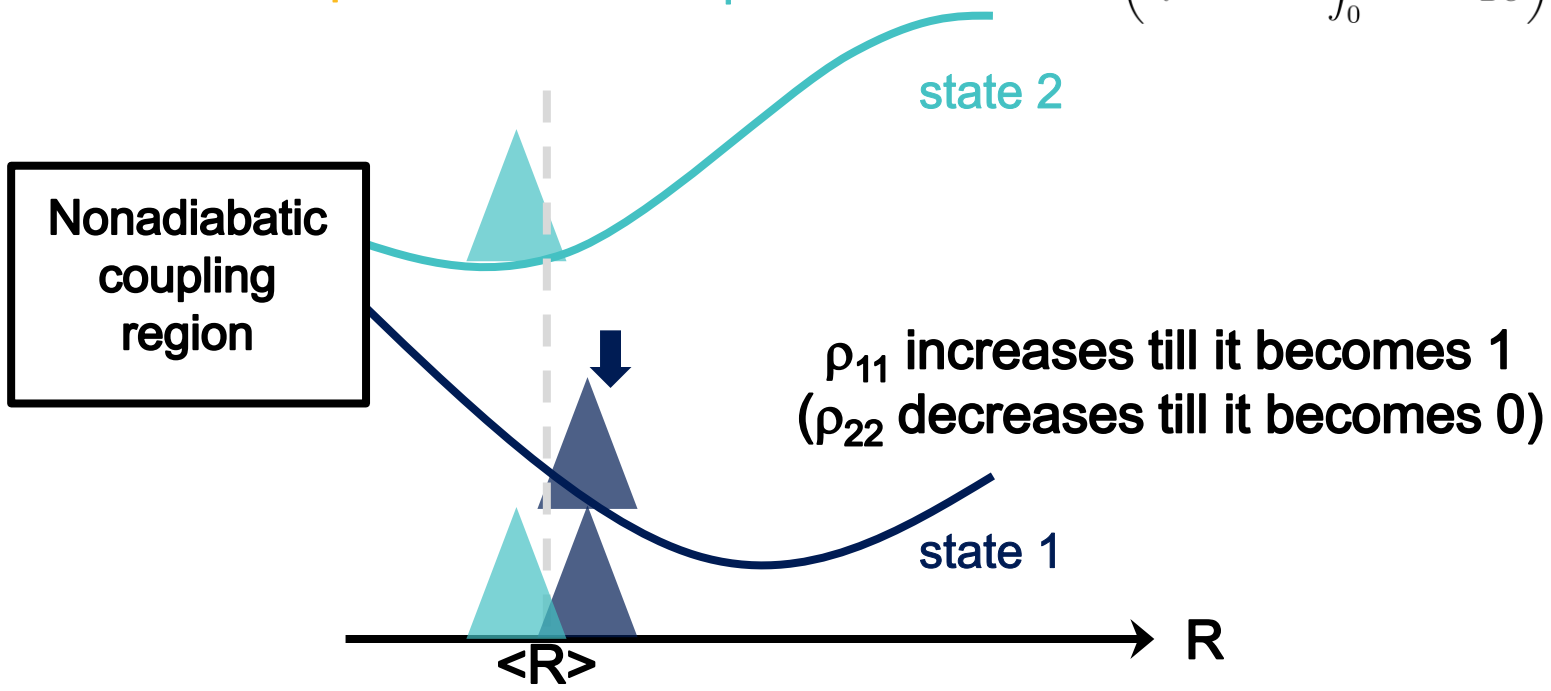
negative

$$\frac{d}{dt}\rho_{11}^{(I)}(t) = -\frac{1}{M}\frac{1}{\sigma^2}\left(R^{(I)} - \langle R\rangle\right)\cdot\left[f_2^{(I)} - f_1^{(I)}\right]\rho_{22}^{(I)}(t)\rho_{11}^{(I)}(t) \qquad > 0$$

$$\frac{d}{dt}\rho_{22}^{(I)}(t) = -\frac{1}{M}\frac{1}{\sigma^2}\left(R^{(I)} - \langle R\rangle\right)\cdot\left[f_1^{(I)} - f_2^{(I)}\right]\rho_{11}^{(I)}(t)\rho_{22}^{(I)}(t) \qquad < 0$$

positive positive

$$\left(f_l^{(I)}(t) = -\int_0^t dt' \partial_R \epsilon_{BO}^{(l)}\right)$$



Role of the electron-nuclear correlation (ENC) term

- e.g. 1D 2-state problem

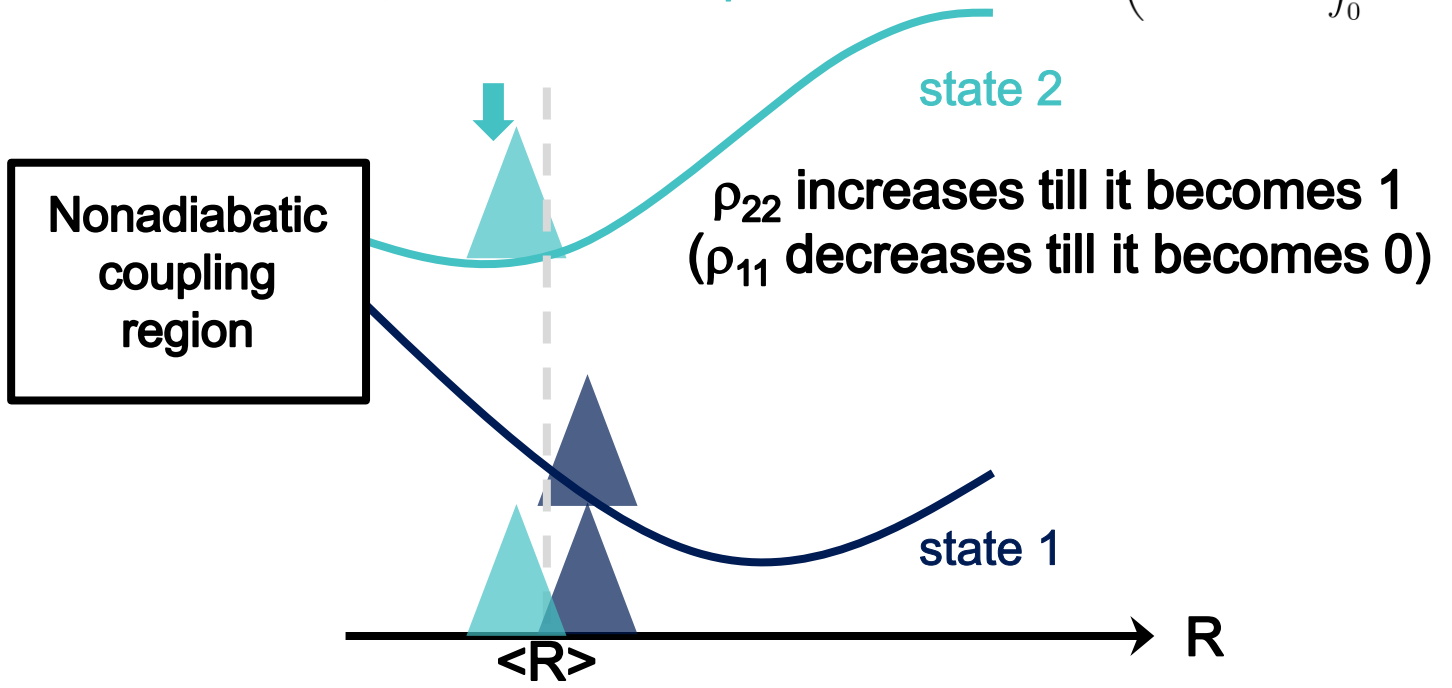
negative

$$\frac{d}{dt}\rho_{11}^{(I)}(t) = -\frac{1}{M}\frac{1}{\sigma^2}\left(R^{(I)} - \langle R\rangle\right)\cdot\left[f_2^{(I)} - f_1^{(I)}\right]\rho_{22}^{(I)}(t)\rho_{11}^{(I)}(t) \qquad < 0$$

$$\frac{d}{dt}\rho_{22}^{(I)}(t) = -\frac{1}{M}\frac{1}{\sigma^2}\left(R^{(I)} - \langle R\rangle\right)\cdot\left[f_1^{(I)} - f_2^{(I)}\right]\rho_{11}^{(I)}(t)\rho_{22}^{(I)}(t) \qquad > 0$$

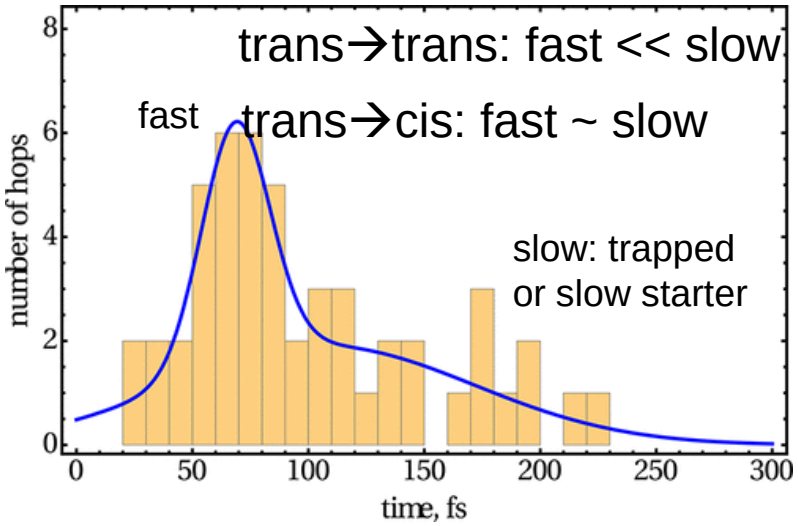
negative positive

$$\left(f_l^{(I)}(t) = -\int_0^t dt' \partial_R \epsilon_{BO}^{(l)}\right)$$

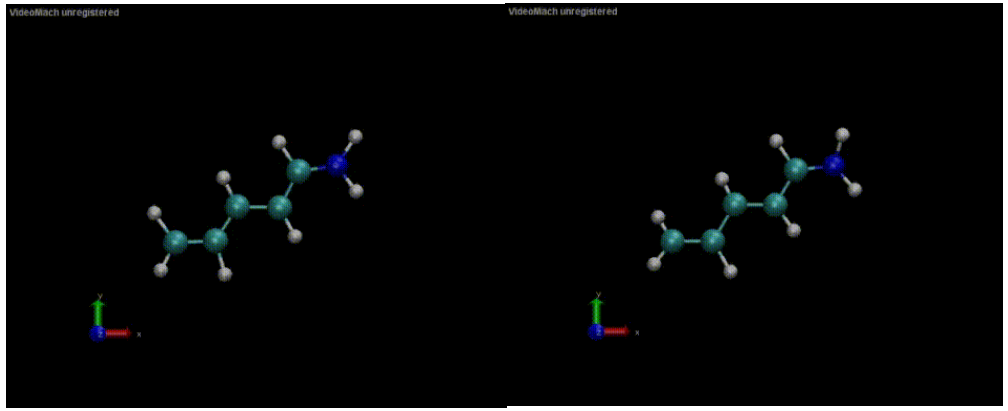


Applications of SHXF

- Dynamics of PSB3

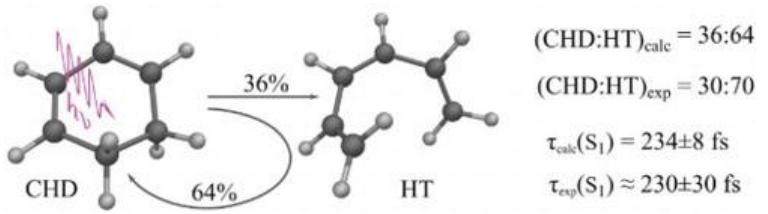


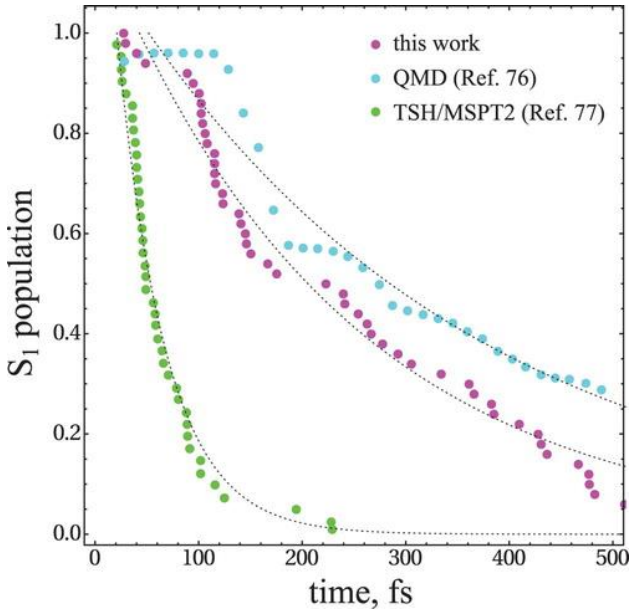
analysis of hop time



J. Chem. Theory Comput., 14, 4499 (2018).

- Ring opening dynamics of Cyclohexadiene

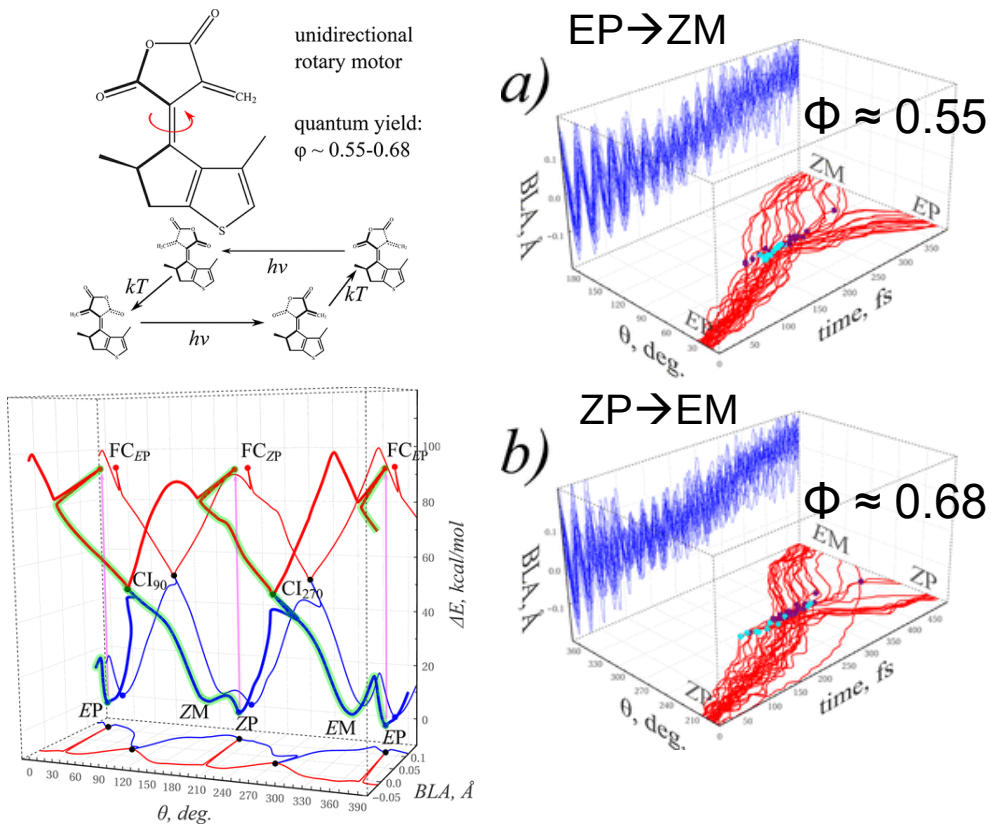




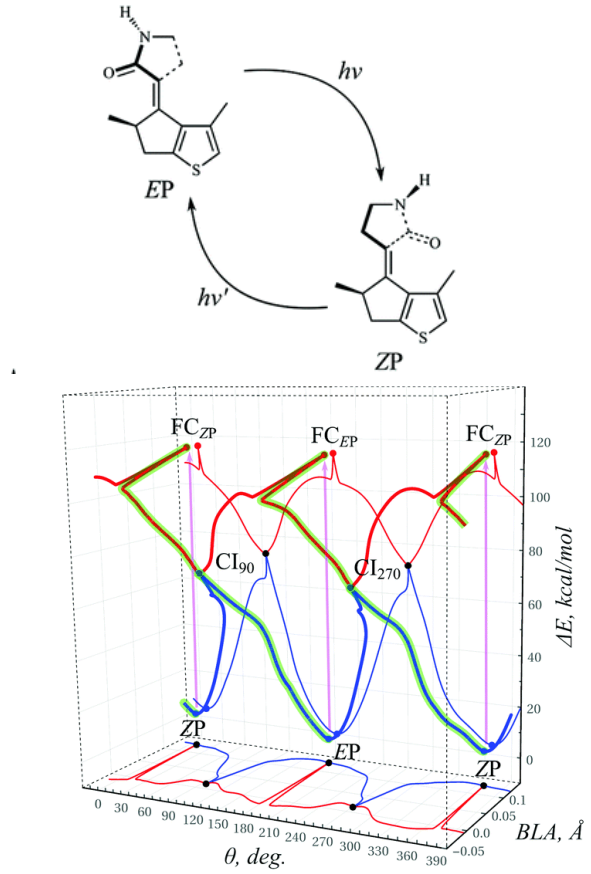
Mol. Phys. 117, 1128 (2019).

Applications of SHXF

- molecular rotary motors



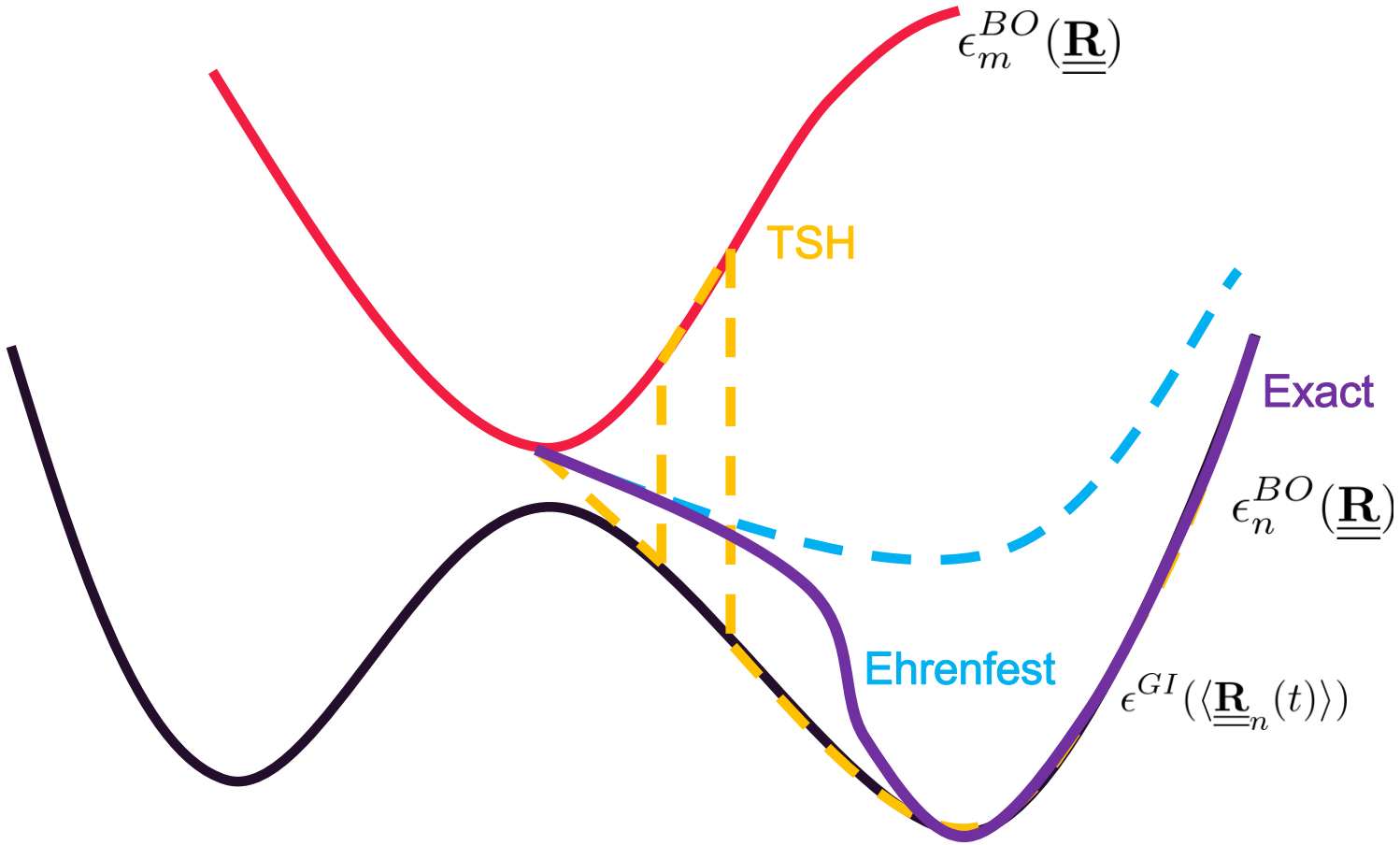
J. Phys. Chem. Lett., 9, 4995 (2018).



Chem. Comm., 55, 5247 (2019).

Ehrenfest + Exact factorization = EhXF

- Why not Ehrenfest?



$$\langle\underline{\underline{\mathbf{R}}}_n(t)\rangle = \langle\chi_n(\underline{\underline{\mathbf{R}}},t)|\underline{\underline{\mathbf{R}}}|\chi_n(\underline{\underline{\mathbf{R}}},t)\rangle / \langle\chi_n(\underline{\underline{\mathbf{R}}},t)|\chi_n(\underline{\underline{\mathbf{R}}},t)\rangle$$

Ehrenfest + Exact factorization = EhXF

- Ehrenfest dynamics + exact factorization (EhXF)

$$\mathbf{F}_\nu(t) = -\sum_l \rho_{ll}(t)\nabla_\nu E_l - \sum_{l,m}\rho_{ml}(t)\left(E_l - E_m\right)\mathbf{d}_{ml,\nu} - \sum_{l,m}\rho_{ll}(t)\rho_{mm}(t)\left[\sum_{\nu'}\frac{2\mathcal{P}_{\nu'}(t)}{\hbar M_{\nu'}}\cdot\left(\mathbf{f}_{m,\nu'}(t) - \mathbf{f}_{l,\nu'}(t)\right)\right]\mathbf{f}_{l,\nu}(t)$$

$$\dot{c}_l(t) = -\frac{i}{\hbar}E_l c_l(t) - \sum_m c_m(t)\sum_\nu \dot{\mathbf{R}}_\nu(t)\cdot\mathbf{d}_{lm,\nu} - \sum_m \rho_{mm}(t)\left[\sum_\nu \frac{\mathcal{P}_\nu(t)}{\hbar M_\nu}\cdot\left(\mathbf{f}_{m,\nu}(t) - \mathbf{f}_{l,\nu}(t)\right)\right]c_l(t)$$

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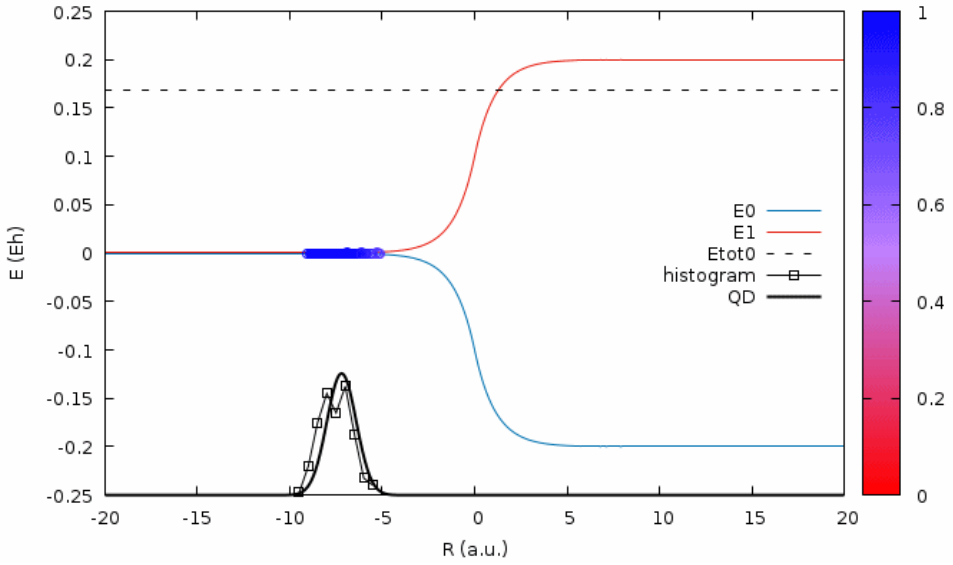
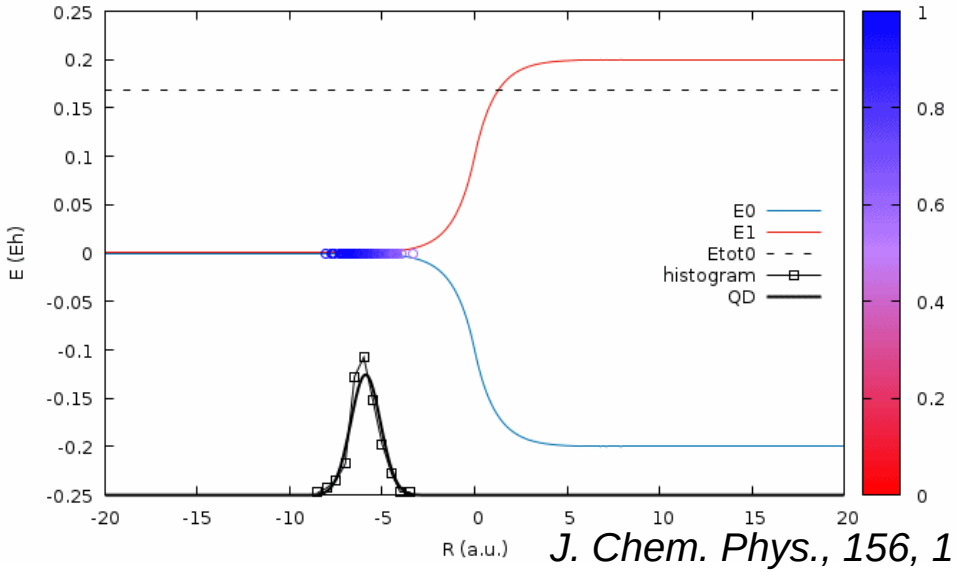
(UNIST)

- more accurate description to the exact potential energy surface

SHXF



EhXF

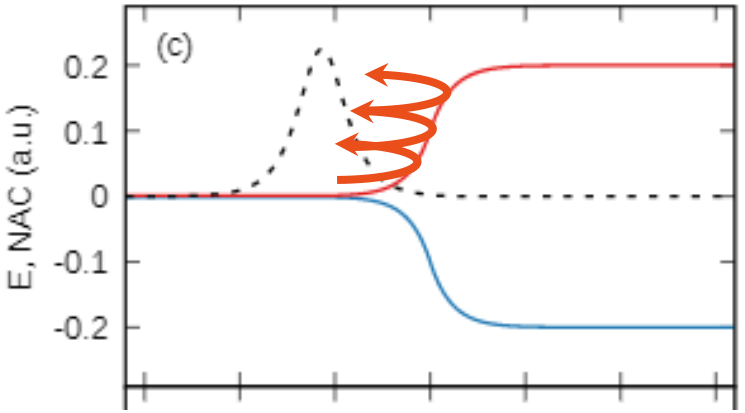


J. Chem. Phys., 156, 174109 (2022)

Energy conservation??

- Unlike SHXF, EhXF cannot enforce the energy conservation for the individual trajectory ← approximate ENC term calculations…

- Non-conserving total energy leads to the inaccurate description for classical turning points for Ehrenfest-like trajectories



- Energy conserving phase term

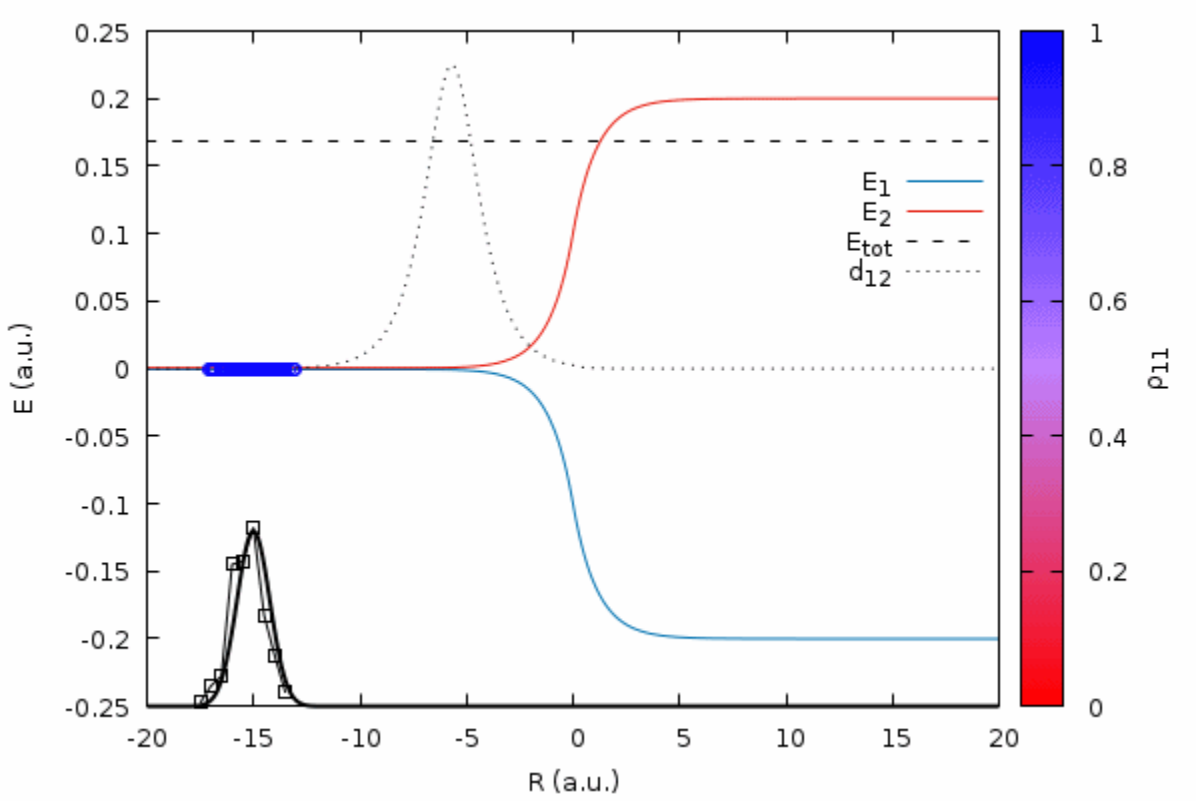
$$\dot{E}_{tot} = \sum_{l,m} \rho_{ll}\rho_{mm} \left[\sum_{\mu} \frac{\mathcal{P}_{\mu}}{\hbar M_{\mu}} \cdot (\mathbf{f}_{l,\mu} - \mathbf{f}_{m,\mu})\right] \left[E_l - E_m + \sum_{\nu}(\mathbf{f}_{l,\nu} - \mathbf{f}_{m,\nu}) \cdot \dot{\mathbf{R}}_{\nu}\right] = 0$$

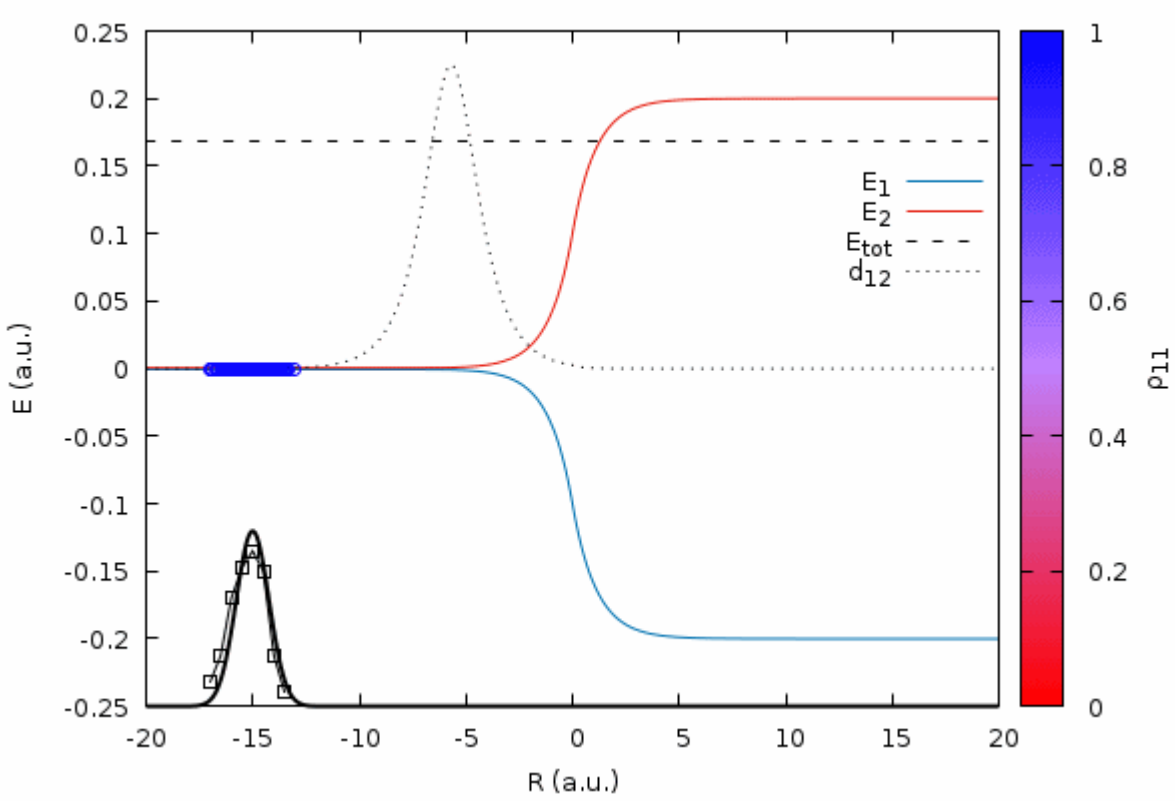
$$\Rightarrow \quad \mathbf{f}_{l,\nu} - \mathbf{f}_{m,\nu} = \beta_{lm}\mathbf{n}_{\nu} = -\frac{E_l - E_m}{\sum_{\nu} \mathbf{n}_{\nu} \cdot \dot{\mathbf{R}}_{\nu}} \mathbf{n}_{\nu}$$

J. Chem. Phys., 156, 174109 (2022)

Energy conservation??

- Normal phase vs. Energy conserving phase

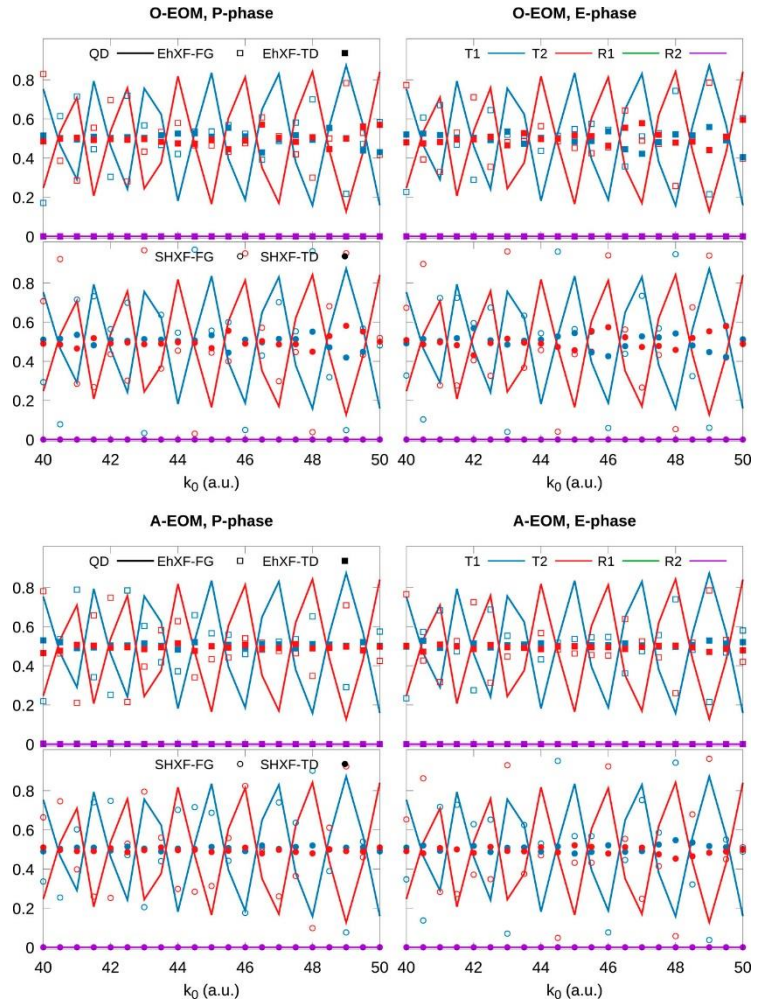


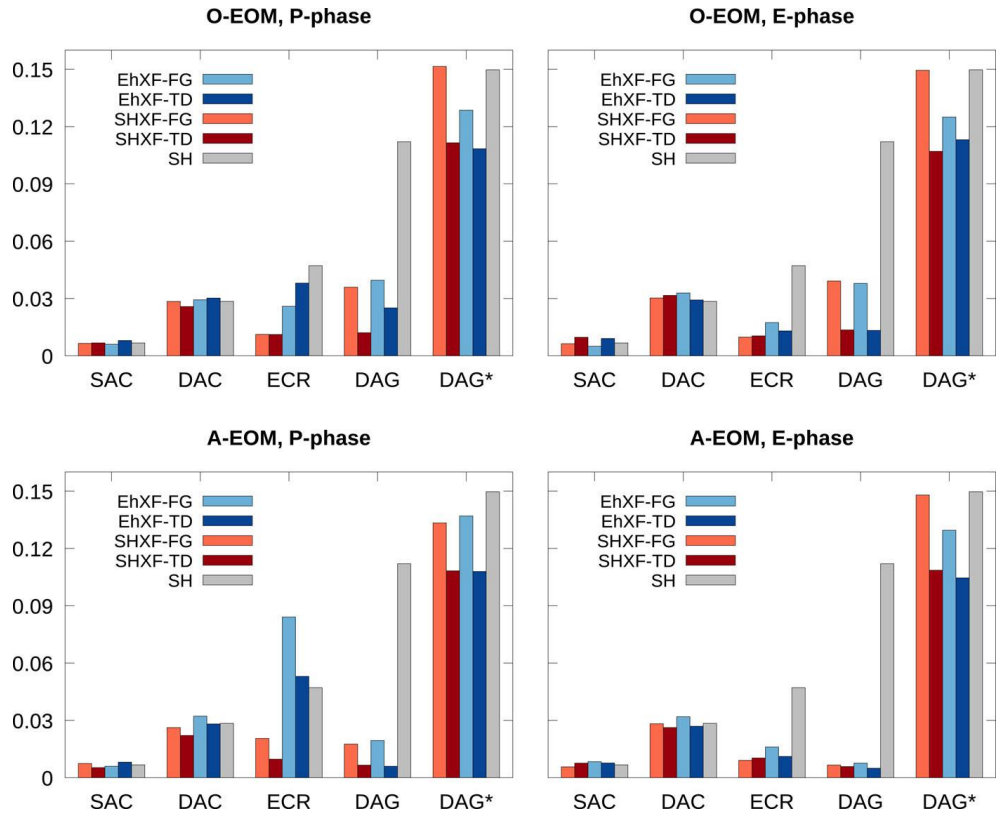


J. Chem. Phys., 156, 174109 (2022)

Failure of current approaches

- Dynamics with wider nuclear wave packets…
  → Stueckelberg oscillation in double-arch geometry





J. Chem. Phys., 156, 174109 (2022)

Python-based UNIversal eXcited-state Molecular Dynamics

- pyUNIxMD program
  - Python-based program suite for trajectory-based excited state molecular dynamics (BOMD, FSSH+α, Ehrenfest, CTMQC, SHXF, EhXF …)

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  - Interfaced with many quantum chemistry programs as:

COLUMBUS	TURBOMOLE	TeraChem	Molpro
Q-Chem	Gaussian16	DFTB+	Any home-made program

  - Public (https://github.com/skmin-lab/unixmd) with MIT license

Top. Cur. Chem., 380, 8 (2022).
J. Comput. Chem., 42, 1755 (2021).

Python-based UNIversal eXcited-state Molecular Dynamics

- pyUNIxMD program

Program	Method	BOMD	Ehrenfest	FSSH	DISH-XF	CTMQC
Columbus[69]	CASSCF	✓	✓	✓	✓	✓
	MRCI	✓	✓	✓	✓	✓
DFTB +[72]	TDDFTB	✓	–	✓	✓	–
	DFTB/SSR	✓	✓	✓	✓	✓
Gaussian 09[70]	TDDFT	✓	–	✓	✓	–
Molpro[33]	CASSCF	✓	✓	✓	✓	✓
Q-Chem[32]	TDDFT	✓	✓	✓	✓	✓
TeraChem[71]	SSR	✓	✓	✓	✓	✓

- Interfacing with any program is possible

Top. Cur. Chem., 380, 8 (2022).

J. Comput. Chem., 42, 1755 (2021).

Applications for material science

- Toward material calculations

D.H. Han
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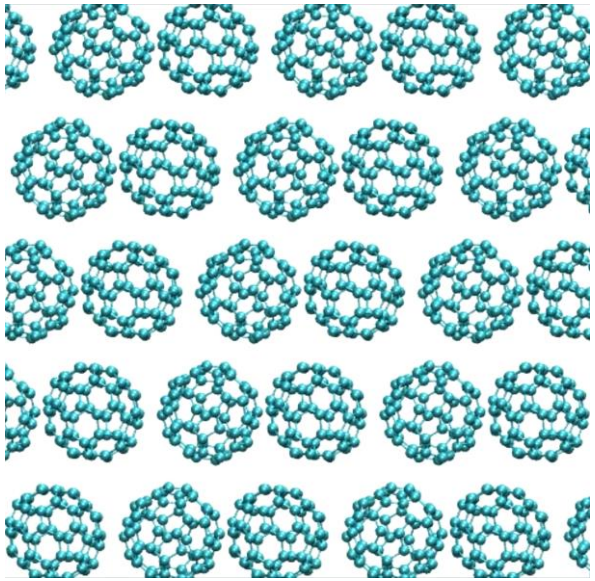
  - For a large-scale system, it is extremely difficult to calculate many-body electronic states
  - Instead of many-body states, we employ the concept of orbitals to simulate MQC dynamics
  - However, the previous equations for electron-nuclear correlation should be represented in terms of orbitals → NOT straightforward

ESMD within DFT frameworks
+ surface hopping based on the exact factorization

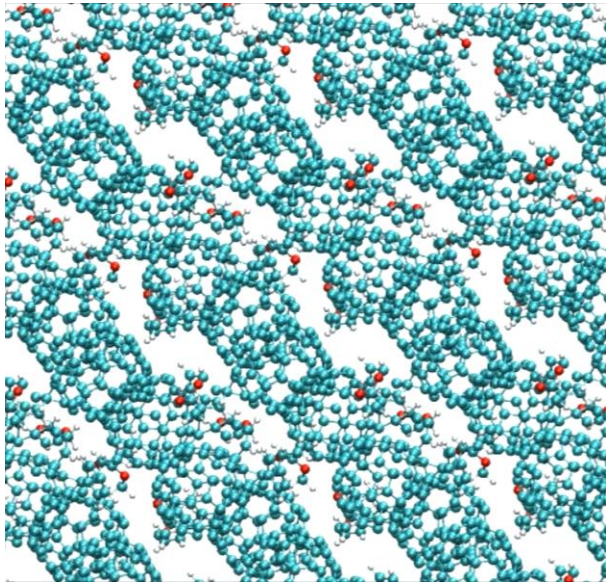
Orbital-based ESMD + α

- Toward material calculations

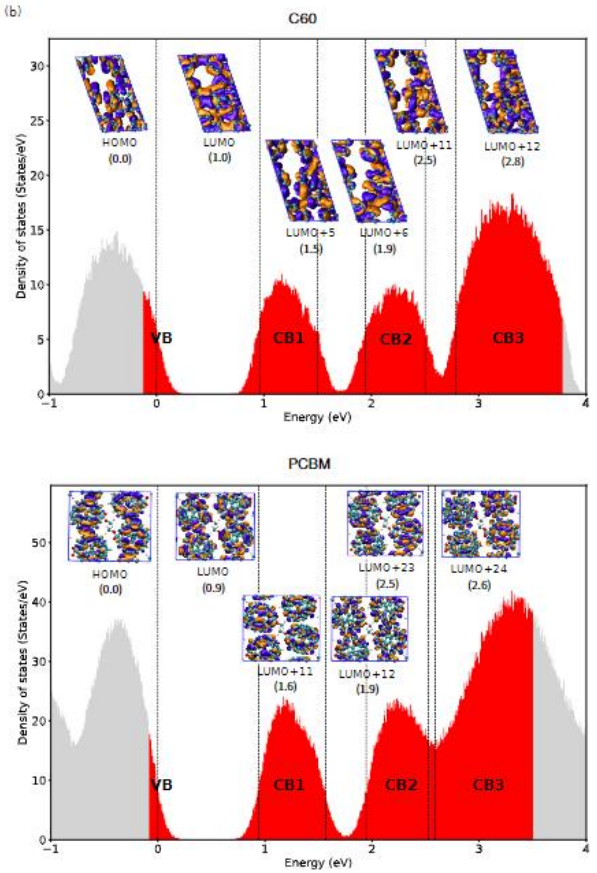
Dynamics of electron density coupled to nuclear motion
→ Charge transfer, exciton transfer, polaron dynamics, …



C_{60}



PCBM

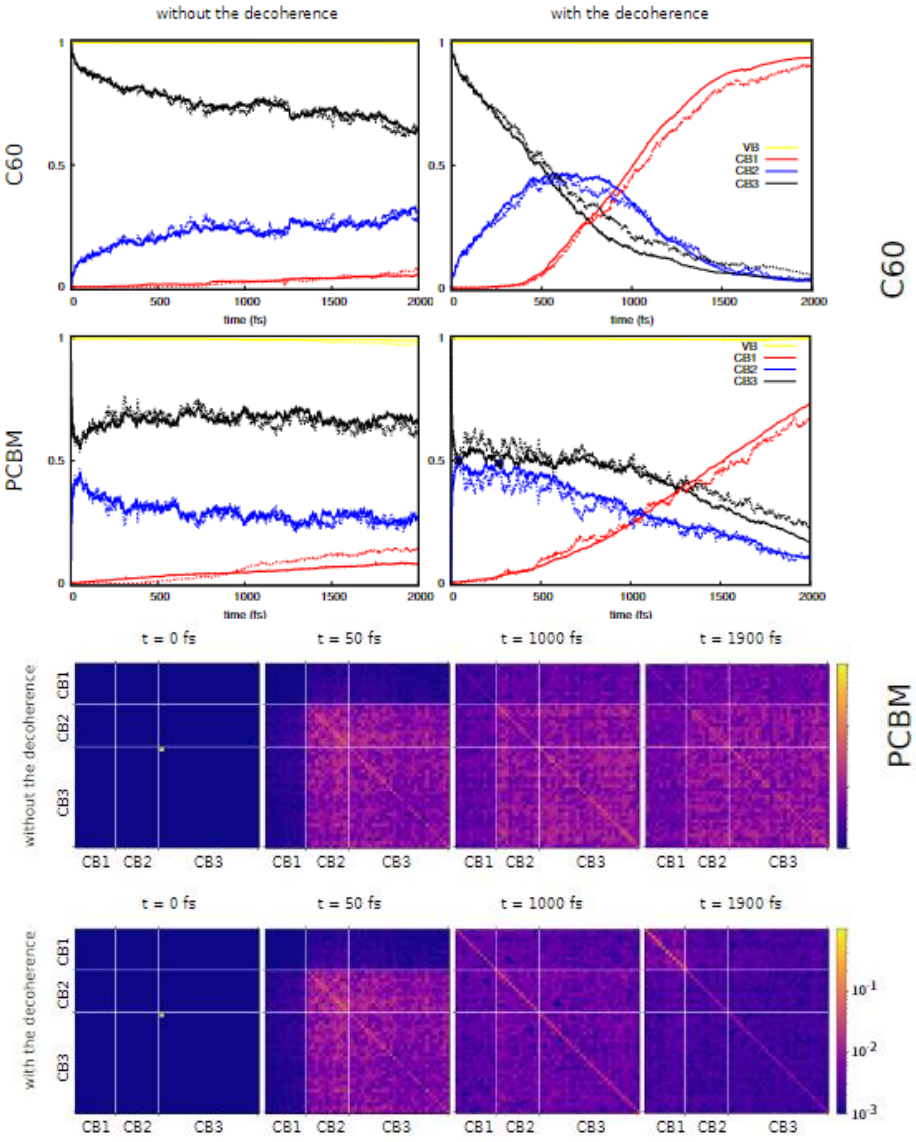


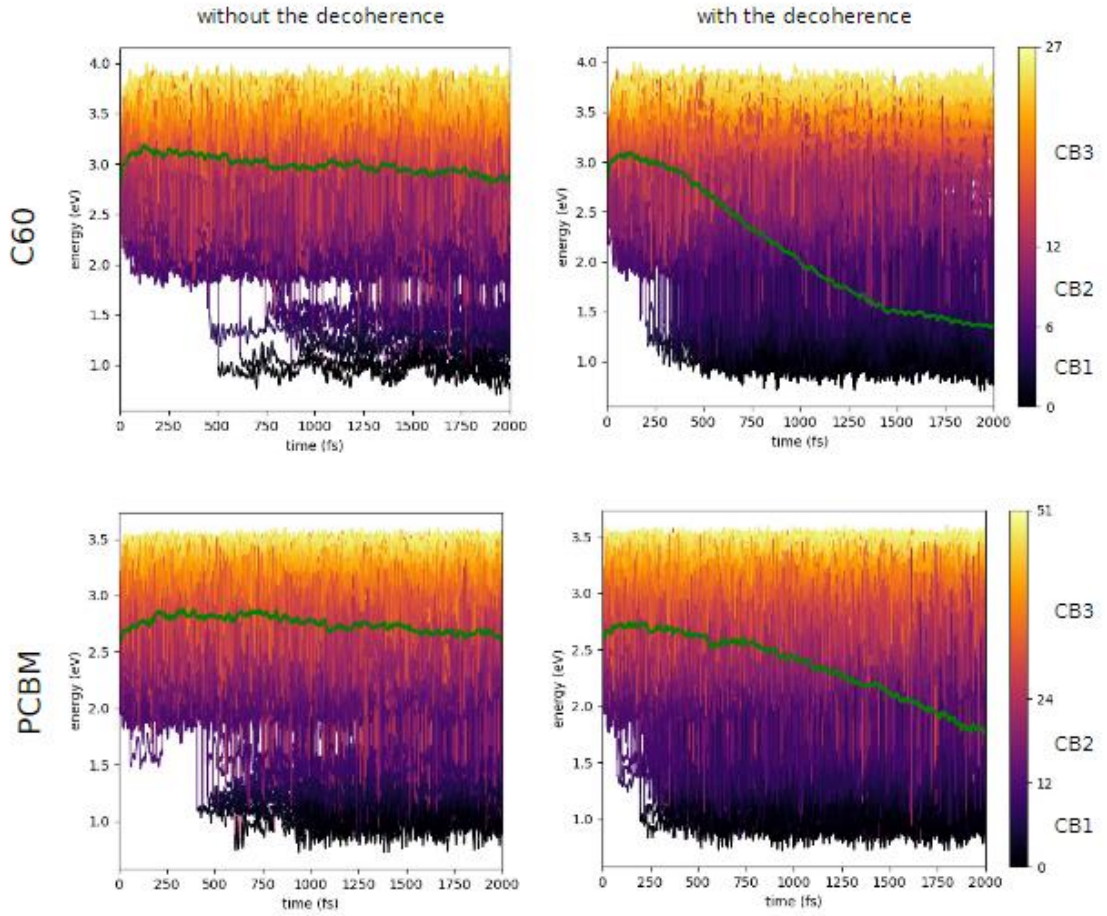
Density of states (DOS) from trajectories

Orbital-based ESMD + α

- Toward material calculations

population profile based on orbitals





Energy relaxation profile of electron transfer

Summary

- Development of excited state molecular dynamics approaches based on the exact factorization
- Electron-nuclear correlation term → Decoherence
- Dynamics : CTMQC, SHXF, EhXF, … (maybe SHXF is most efficient)
- Under construction: phase correction, orbital-based approaches, polariton dynamics, …
- pyUNIxMD program : Public (https://github.com/skmin-lab/unixmd)

Aknowledgements

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- $$$

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NRF

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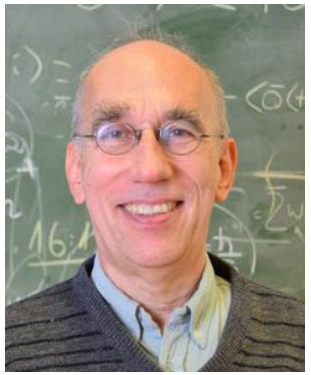

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THANK YOU