Molecular Quantum Dynamics with Tensor Trains

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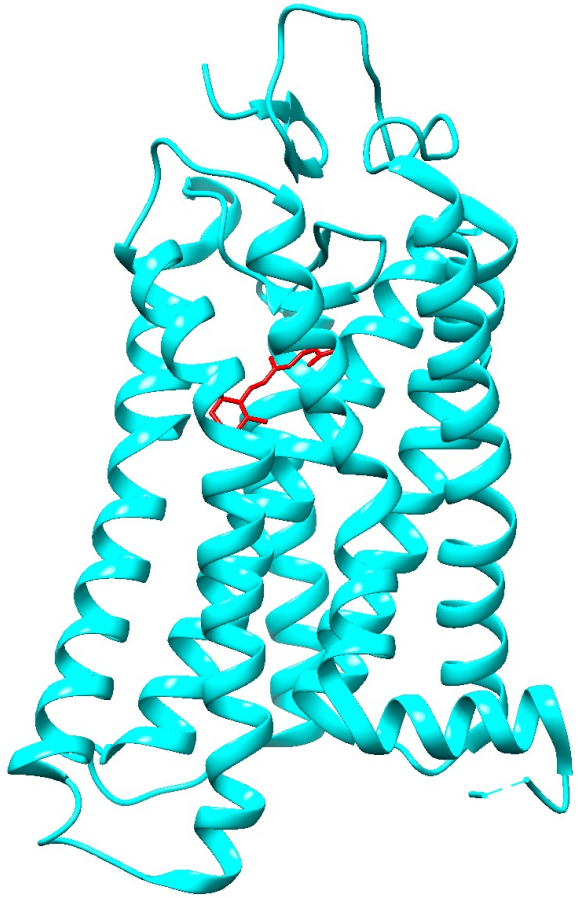
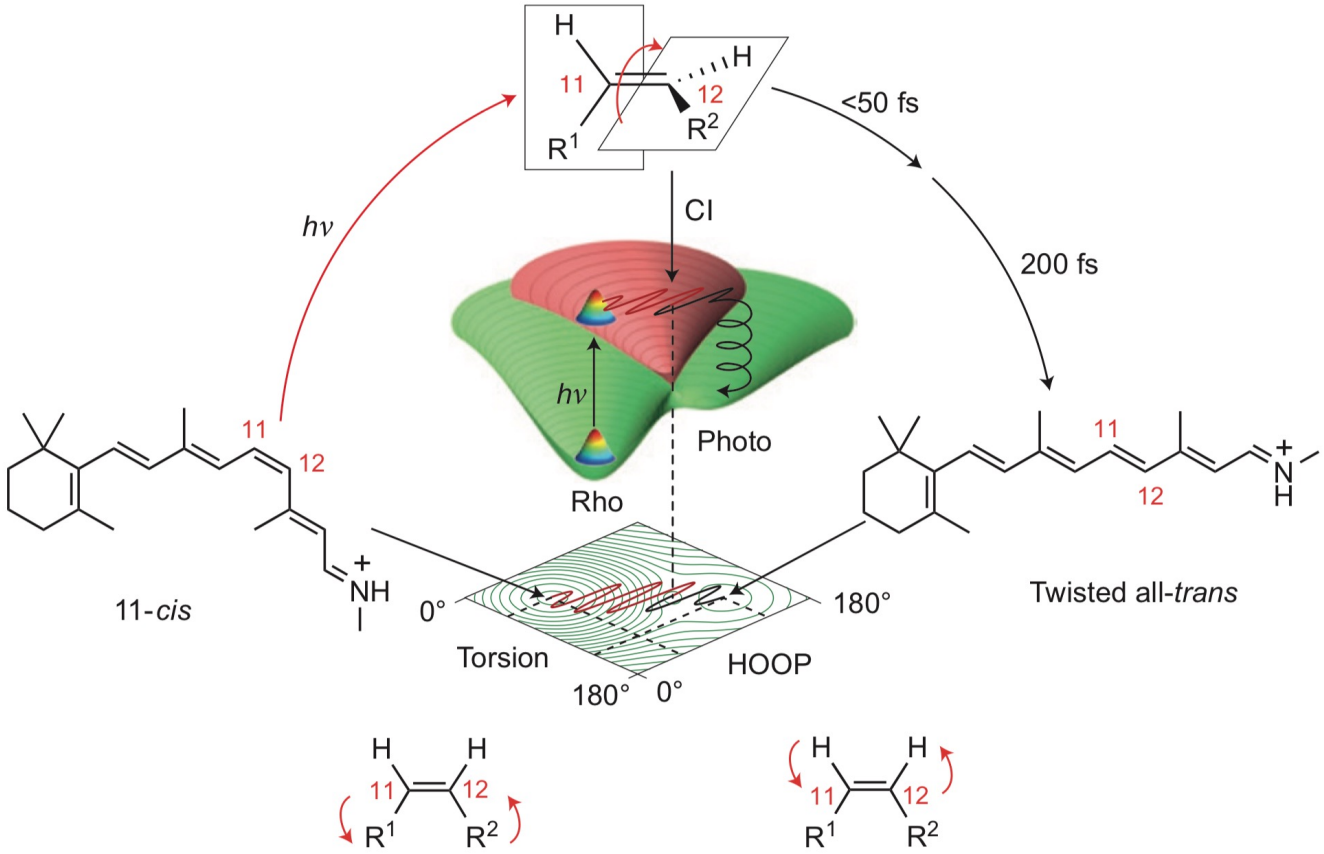
Retinal cis-trans isomerization as the first step of vision

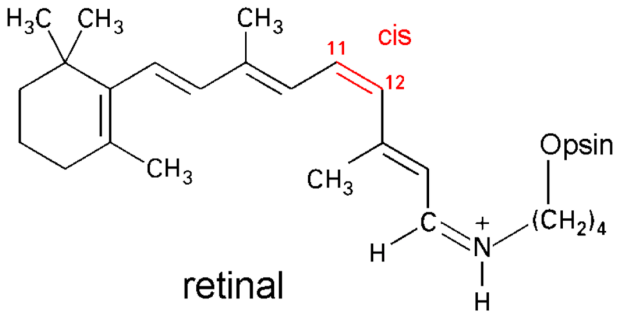


Crystal structure of Bovine Rhodopsin. Retinal chromophore in red. *Acta Cryst,* D64, 902–904 (PDB:3C9L).

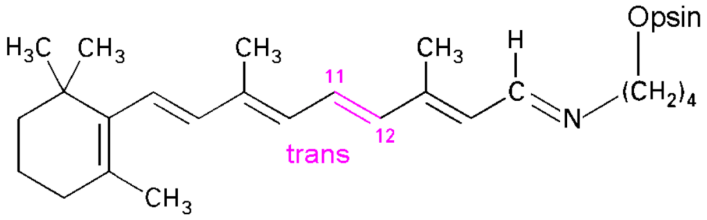


The primary photochemical step in vision. Adapted from *Nat. Chem.* 7, 975.

Overview: Wavepacket propagation of chemical processes



retinal



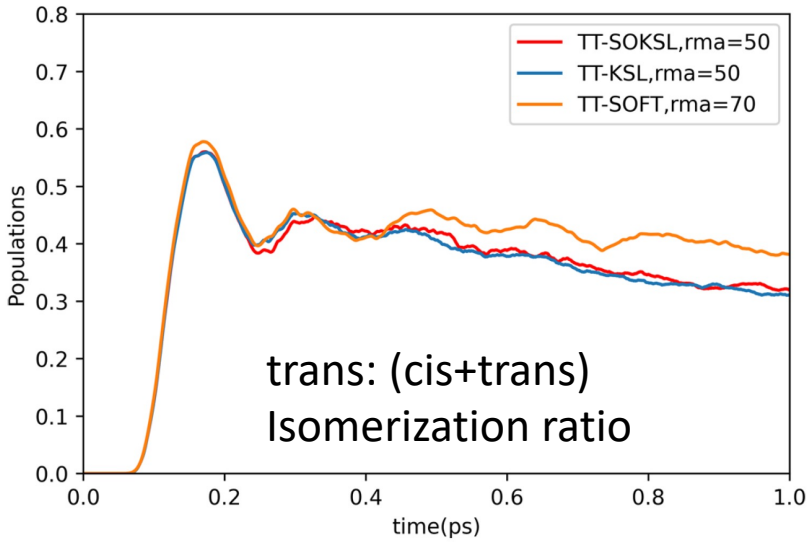
Molecular system, normal mode=3N-6, N=# of atoms

$\psi(x_1, x_2, \ldots, x_{3N-6}; t_0)$:
high-dimensional initial nuclear wavepacket

Quantum dynamics,
$\frac{\mathrm{d}}{\mathrm{dt}}|\psi(t)\rangle = -\frac{i\hat{H}}{\hbar}|\psi(t)\rangle$

$\psi(x_1, x_2, \ldots, x_{3N-6}; t)$

Extract physics from $|\psi(t)\rangle$



trans: (cis+trans)
Isomerization ratio

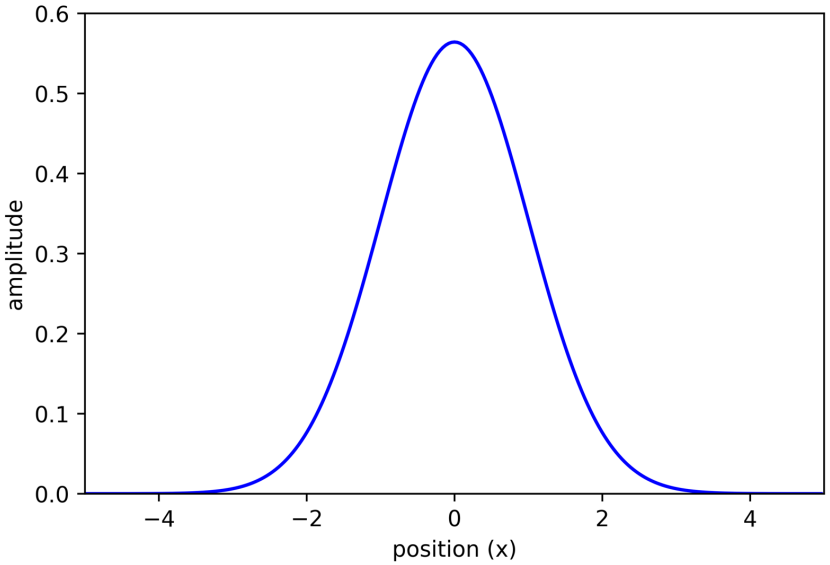
Molecular drawing adapted from "Photochemistry of Vision", https://theperspectiveinscience.wordpress.com/2015/03/01/photochemistry-of-vision/.

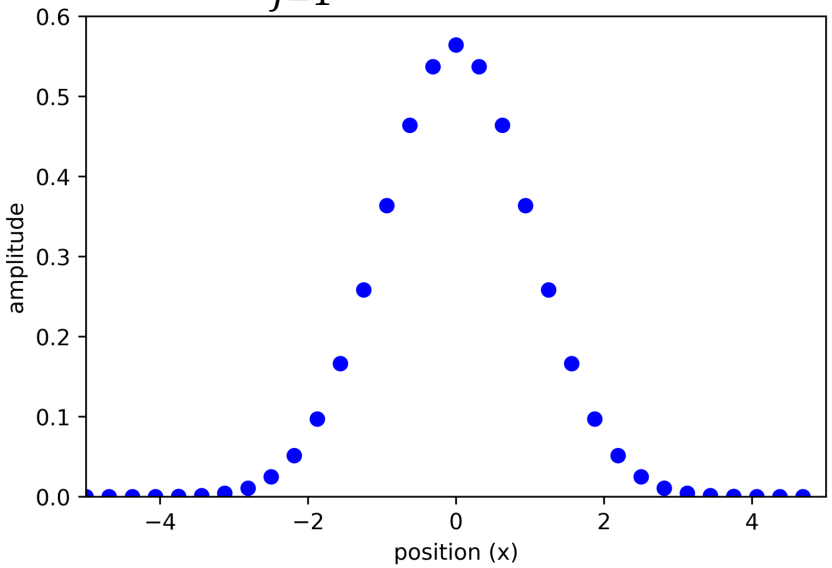
Challenge for theoretical chemists: 3N-6 DoF for molecules

1D Gaussian:

$$\psi(x) = \int dx' \delta_{xx'} \psi(x')$$

$$\psi(x) \approx \Delta \sum_{j=1}^{n} \psi(x_j) \delta_{xx_j}, \Delta = (x_{\max} - x_{\min})/(n-1)$$

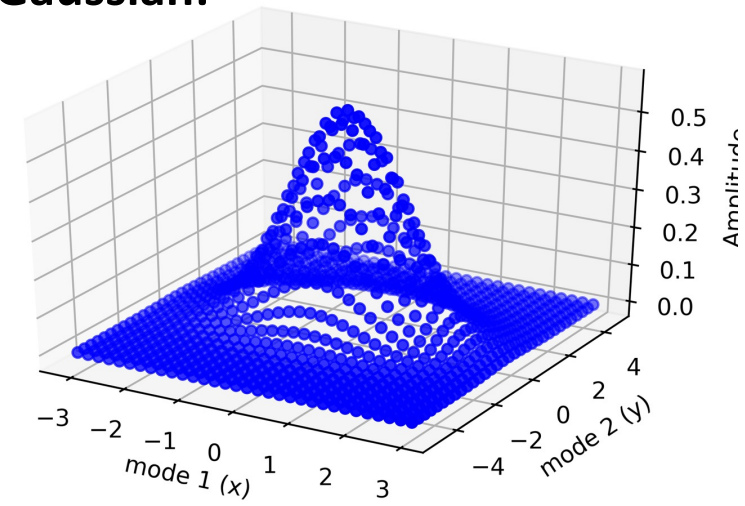




Array size: 32

Memory cost: 32*8B=256B
(8B for a float64 number)

2D Gaussian:



Array size: 32^2

Memory cost:
32^2 *8B=8192B=8K

25D Gaussian?

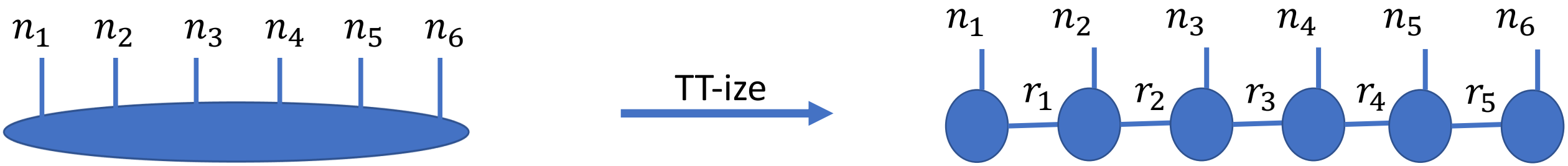
Array size: 32^{25}

Memory cost:
32^{25} *8B~$3.40*10^{38}$B=$3.40*10^{26}$TB

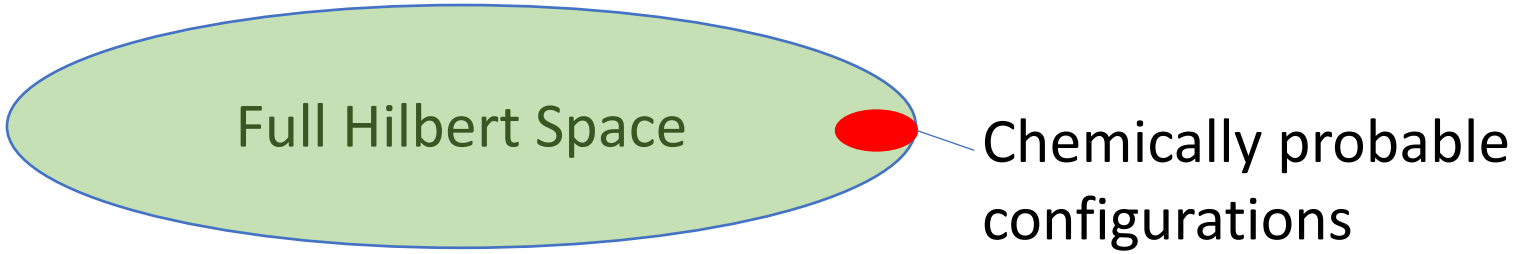
Curse of dimensionality makes molecular quantum dynamics extremely challenging!

Data compression via tensor train decomposition

- Stores information about each physical dimension in one individual array;
- Storage scales linearly with dimensionality ($\sim dnr^2$) as opposed to n^d of full array:



- Physically, we focus on one particular subset of all possible configurations:



- **Often, chemists need no more than a corner of the Hilbert space!**

TT-SOKSL methodology: efficient TT propagator

- Initialize $|\psi_x(t=0)\rangle$ in position representation as a tensor train array;

- Carry out split-operator Fourier Transform propagation with time-independent $\hat{H} = \hat{T} + \hat{V}$:

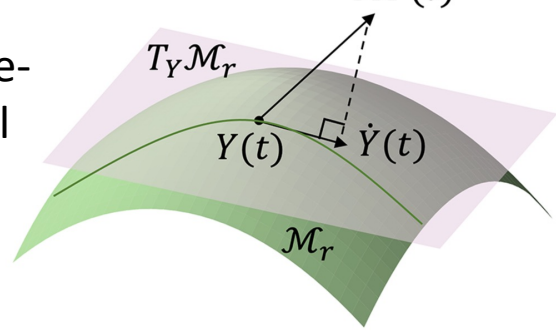
$$|\psi_x(t=\tau)\rangle = e^{-i(\hat{T}+\hat{V})\tau/\hbar}|\psi_x(0)\rangle \approx e^{-\frac{i\hat{V}\tau}{2\hbar}} e^{-\frac{i\hat{T}\tau}{\hbar}} e^{-\frac{i\hat{V}\tau}{2\hbar}} |\psi_x(0)\rangle = e^{-\frac{i\hat{V}\tau}{2\hbar}} \mathrm{FT}[e^{-\frac{i\hat{T}\tau}{\hbar}} \mathrm{IFT}[e^{-\frac{i\hat{V}\tau}{2\hbar}} |\psi_x(0)\rangle]].$$

- Instead of explicitly calculating the exponentials (as in TT-SOFT), their actions are evaluated by integrating equations as follows:

$$\frac{d}{dt}|\psi_1(t)\rangle = -\frac{i\hat{V}}{2\hbar}|\psi_1(t)\rangle, \text{ with } |\psi_1(0)\rangle = |\psi_x(0)\rangle \xrightarrow{integrating\ from\ 0\ to\ \tau} |\psi_1(\tau)\rangle = e^{-\frac{i\hat{V}\tau}{2\hbar}}|\psi_x(0)\rangle$$

which are performed with the TT-KSL integrator.

Illustration of the time-dependent variational principle (TDVP).



Greene, S.; Batista, V.S. *J. Chem. Theory Comput*. **2017**, 13, 4034-4042.
Lyu, N.; Soley, M. B.; Batista, V. S. *J. Chem. Theory Comput*. **2022**, 18, 3327-3346.

25 dimensional model of retinal isomerization

Two PESs coupled through conical intersection, each PES with one strongly anharmonic reaction coordinate (θ, $C_{11} = C_{12}$ dihedral angle), one polyene chain stretching coupling coordinate (q_c), and 23 harmonic bath coordinates with Raman active frequencies.

$$H = H_S + H_B$$

$$H_S = \sum_{n,m=0}^{1} |\psi_n^{el}\rangle (T_s \delta_{mn} + V_{mn}) \langle \psi_n^{el}|$$

Coupled two-surfaces problem

$$T_s = -\frac{\Omega_c}{2}\frac{\partial^2}{\partial q_c^2} - \frac{1}{2I}\frac{\partial^2}{\partial \theta^2}$$

$$V_{00} = \frac{W_0}{2}(1 - \cos\theta) + \frac{\Omega_c}{2} q_c^2$$

Strongly anharmonic surfaces

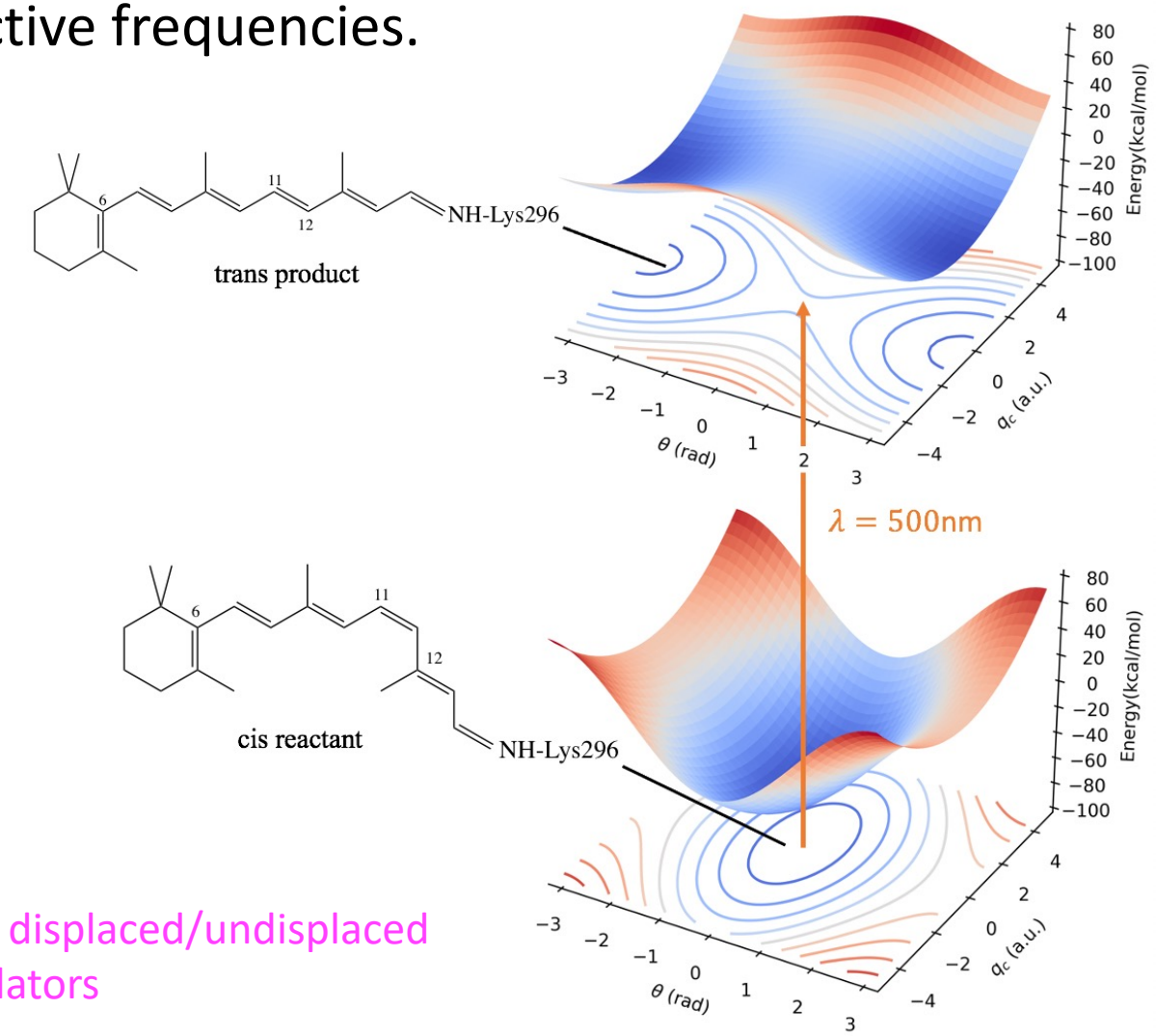
$$V_{11} = E_1 - \frac{W_1}{2}(1 - \cos\theta) + \frac{\Omega_c}{2} q_c^2 + \kappa q_c$$

$$V_{10} = V_{01} = \lambda q_c$$

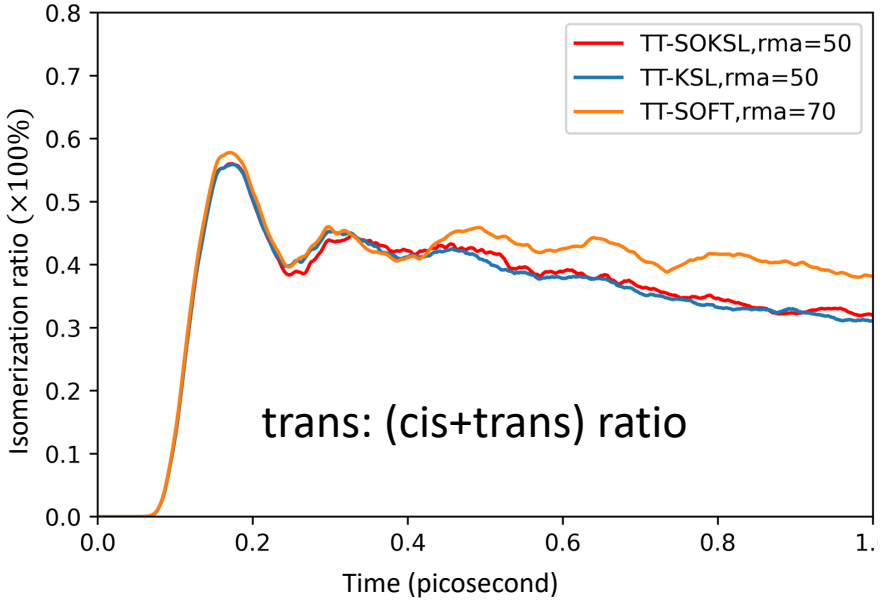
Linear vibronic coupling through the coupling coordinate

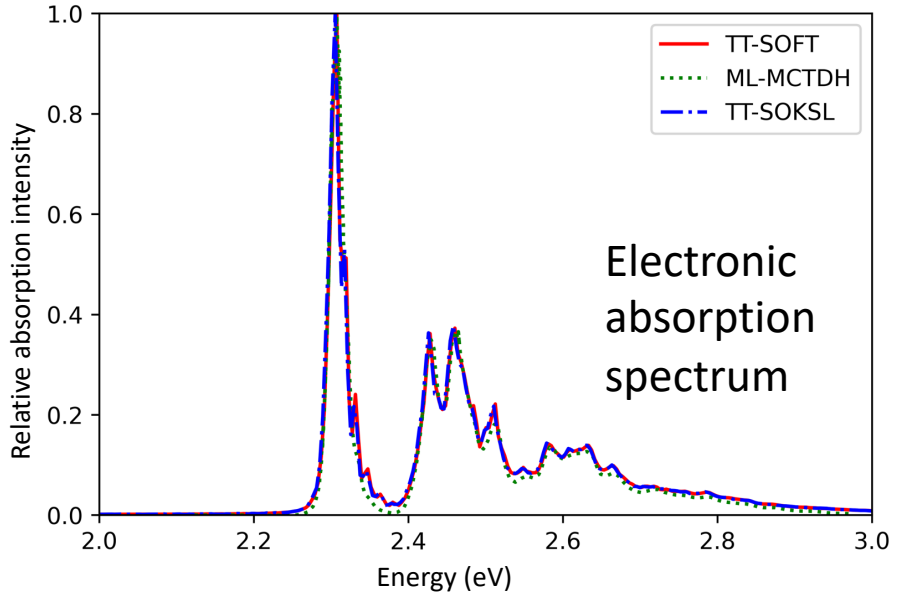
$$H_B = \sum_{n=0}^{1} \sum_{i=1}^{23} |\psi_n^{el}\rangle \left(\frac{\omega_i}{2}\left(\frac{\partial^2}{\partial q_c^2} + q_i^2 \right) + \kappa_i q_i \delta_{n1} \right) \langle \psi_n^{el}|$$

Bath modes as displaced/unddisplaced harmonic oscillators

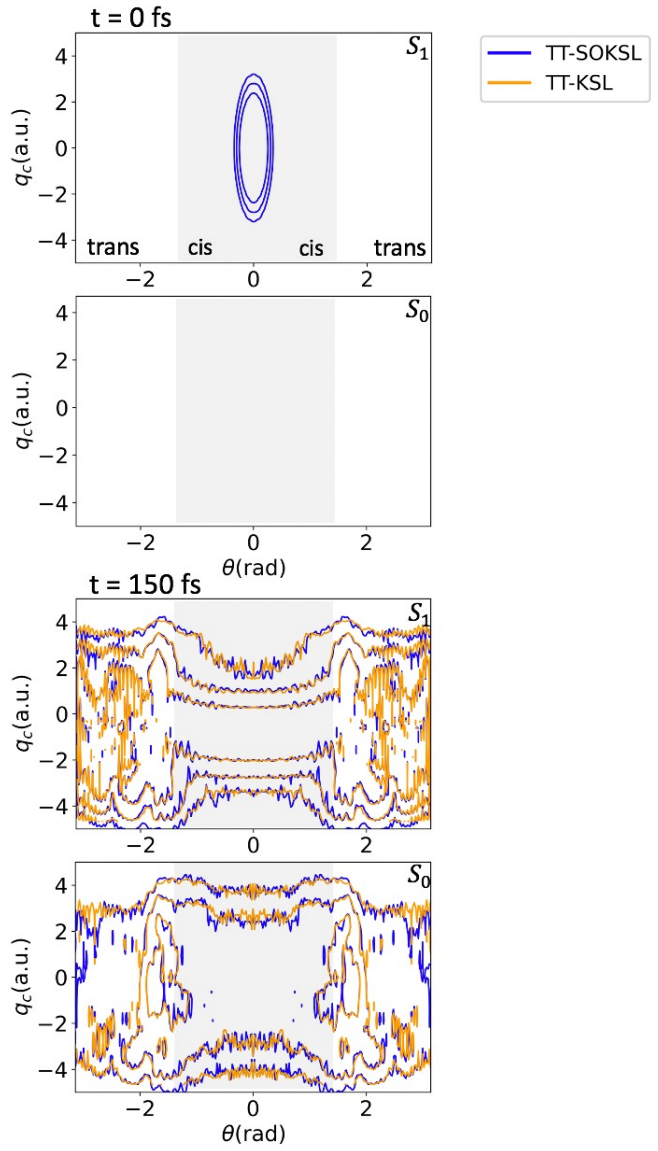


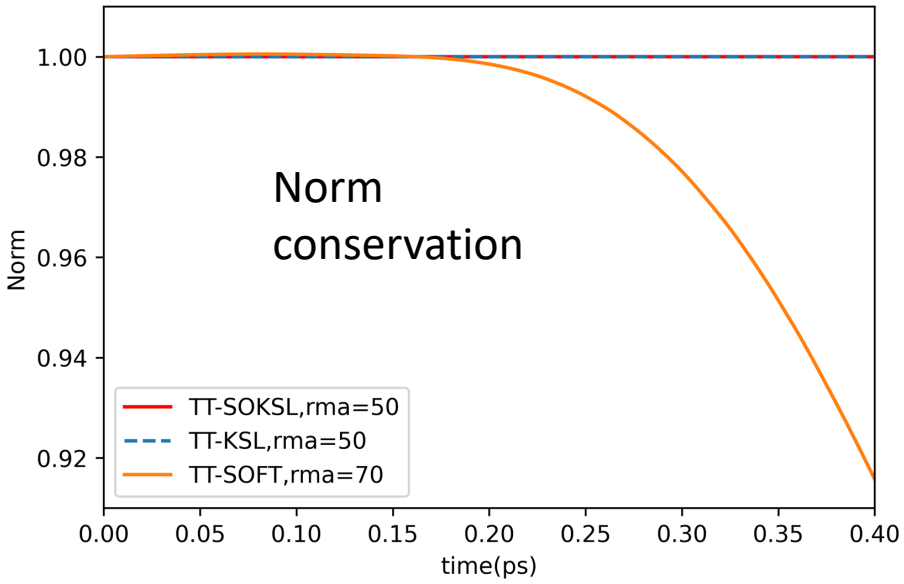
TT-SOKSL for the retinal model

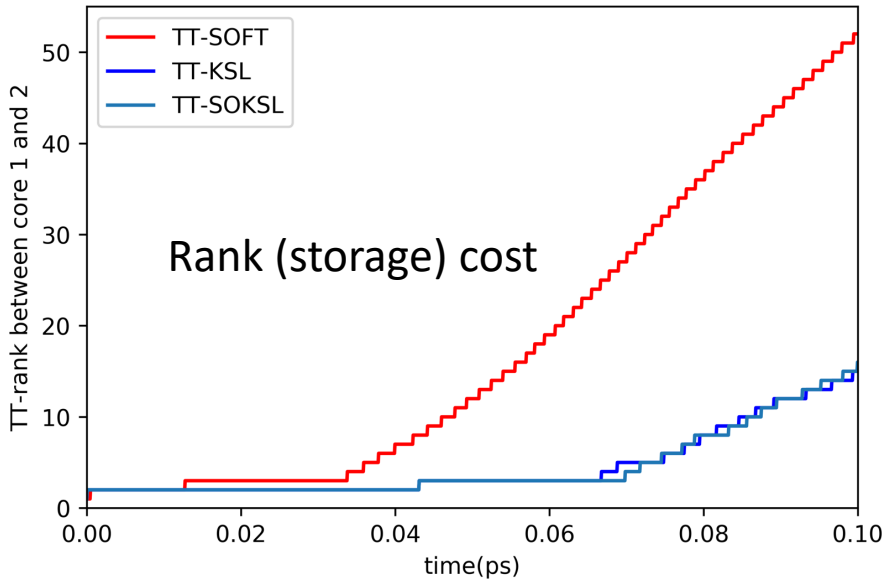




Reduced density plots







Lyu, N.; Soley, M. B.; Batista, V. S. *JCTC*, **2022**, 18, 3327-3346.

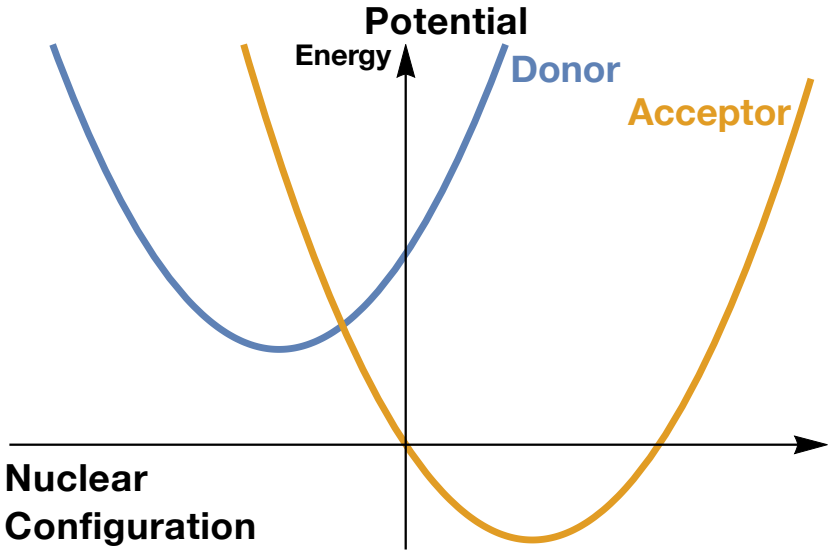
TT-Thermofield Dynamics: Finite temperature propagation

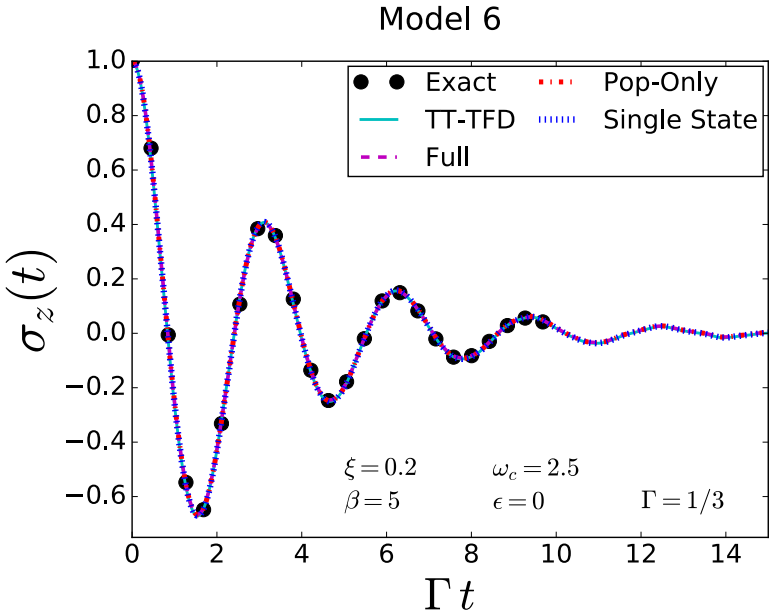
- Fixed temperature quantum system described as density matrix:

  e.g. thermal equilibrium initial density matrix $\rho(\beta, t=0) = e^{-\beta \hat{H}} / Z(\beta)$

- Dynamics of $\rho(\beta, t)$ described by quantum Liouville equation: $\dot{\rho}(t) = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}]$

- TT-TFD propagates $\rho(\beta, t)$ of high-dimensional systems by writing the d-dimensional density matrix as a $2d$-dimensional state vector in tensor train format.



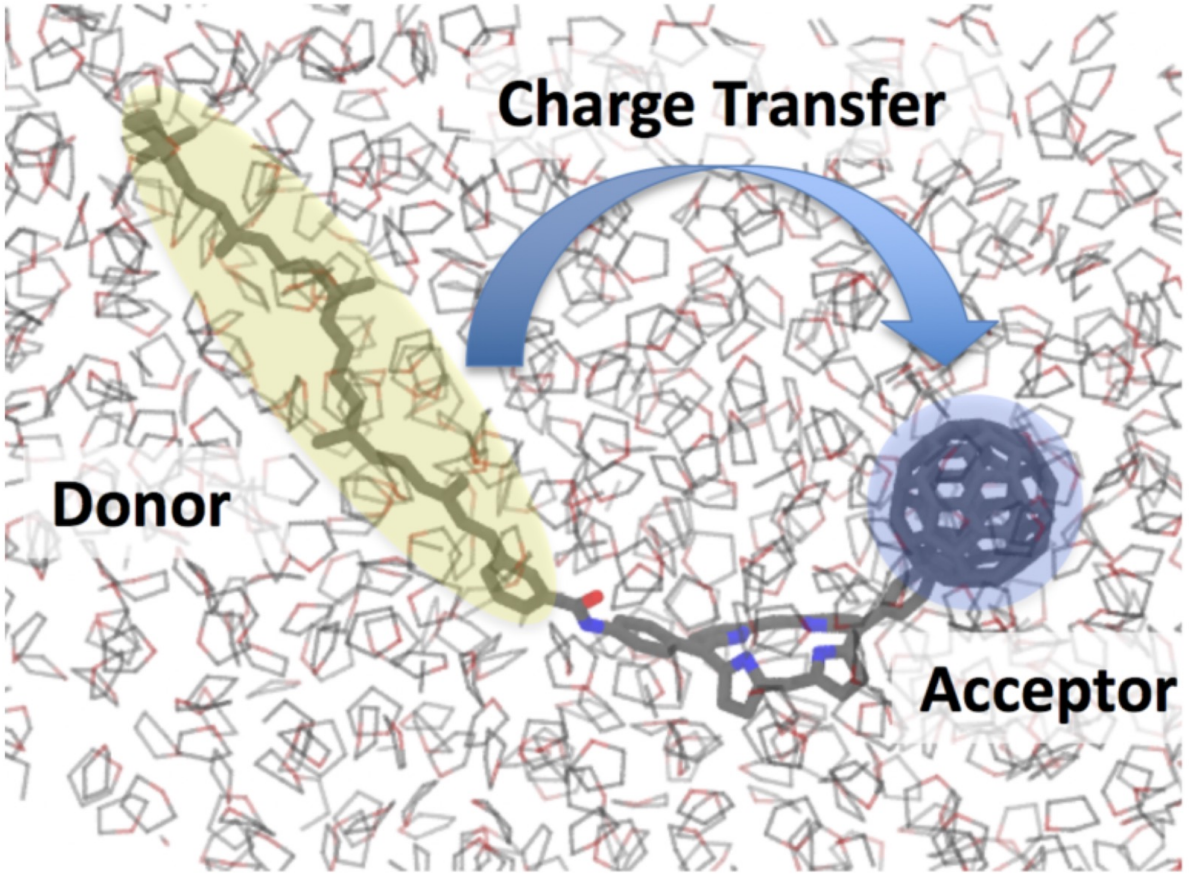


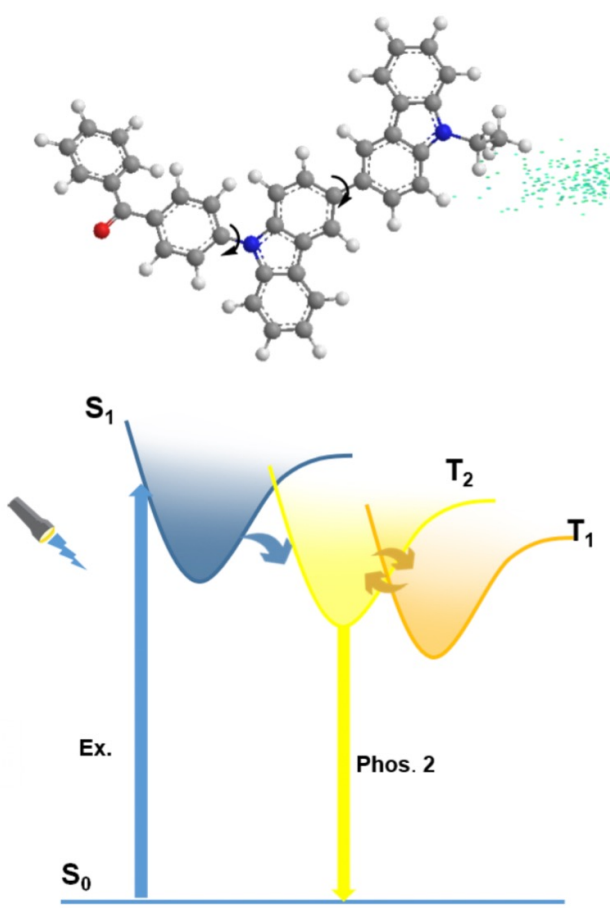
Borrelli, R.; Gelin, M.F. *J. Chem. Phys.* **2016**, 145, 224101.

Lyu, N.*; Mulvihill, E.*; Soley, M.B.; Geva, E.; V. S. Batista. Submitted. https://arxiv.org/pdf/2208.14273.pdf

TT-SOKSL and TT-TFD as benchmarks

- As numerically exact methods, TT-SOKSL and TT-TFD provide benchmarking results for reduced dynamics methods or methods with classical approximations.

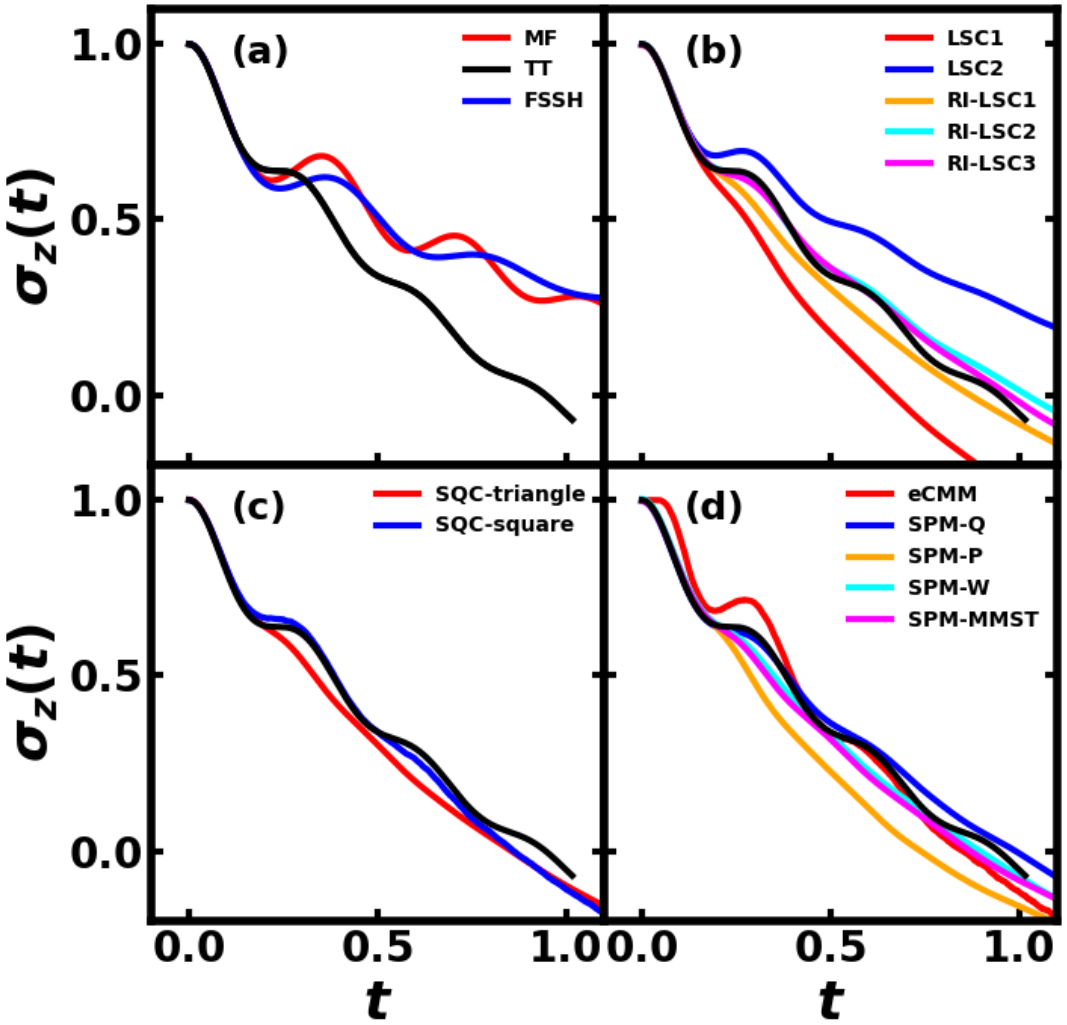


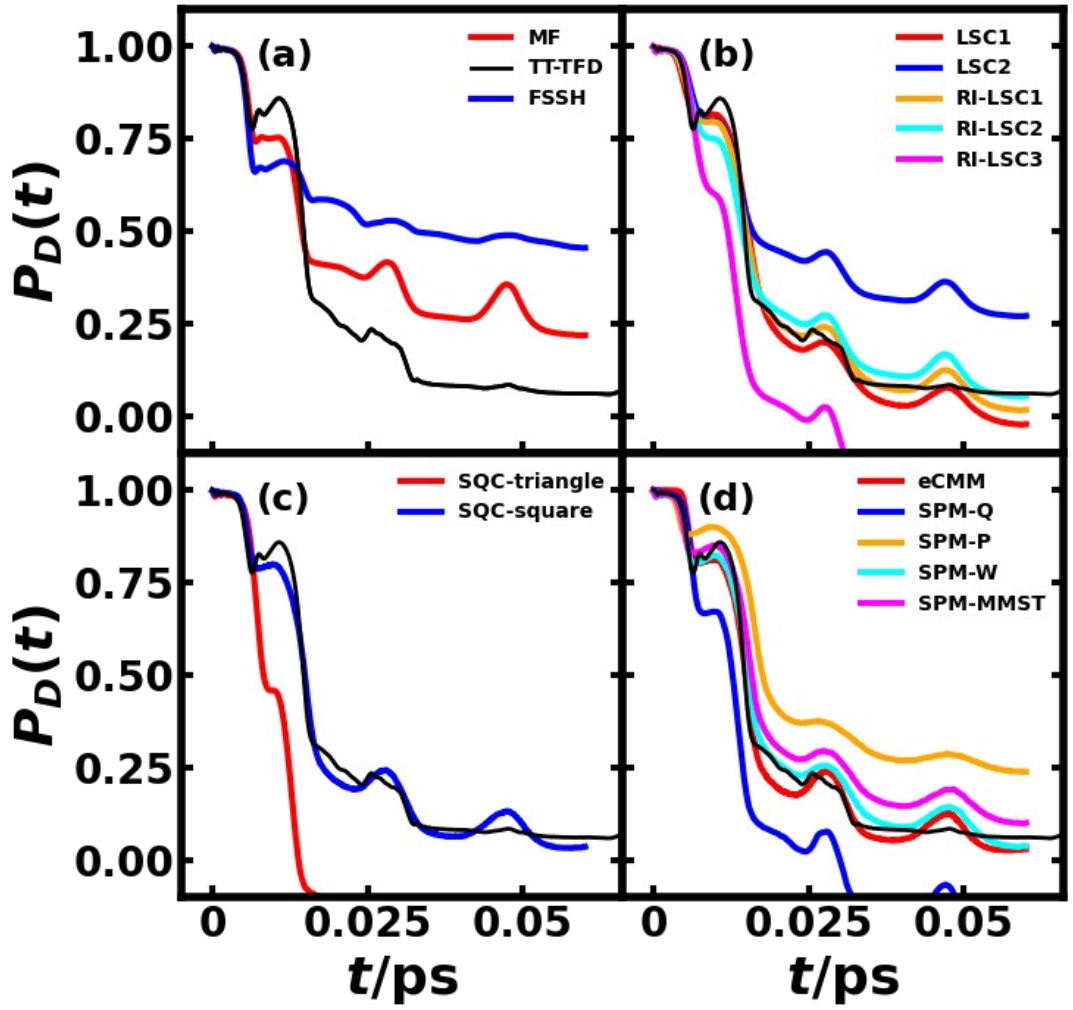


Figures from Prof. Xiang Sun's group website, https://wp.nyu.edu/xiangsun/research/

TT-TFD with approximate quantum dynamical methods

- Approximate methods: propagate the system classically when possible





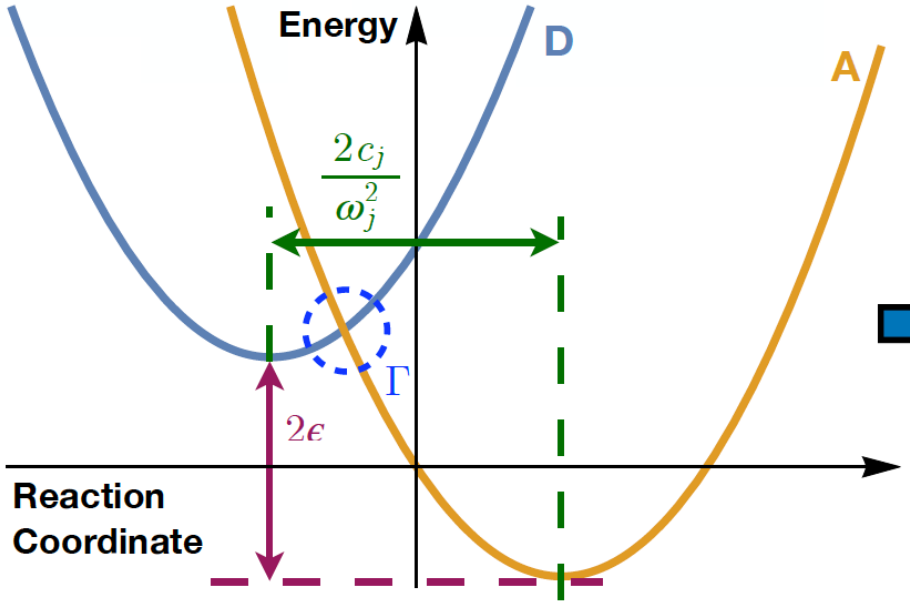
Liu, Z.*; Lyu, N.*; Hu, Z.; Batista, V.S.; Sun, X. In preparation.

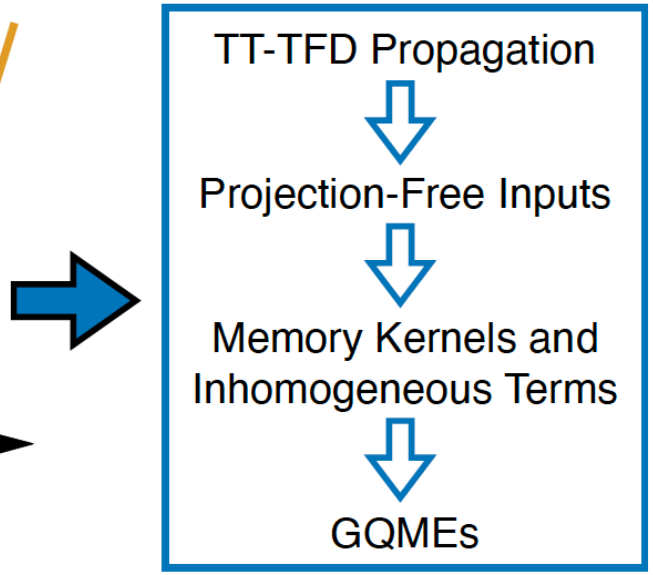
TT-TFD with Generalized Quantum Master Equations

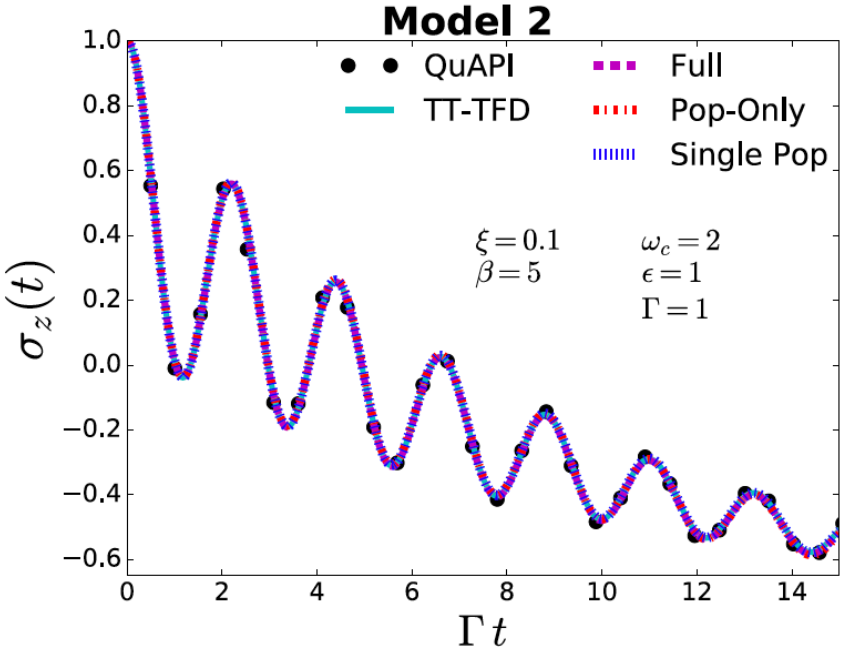
- GQME: compact equation of motion for a particularly interesting subset of system (i.e. electronic states in a vibronic system), while the rest of the system (i.e. vibrational DoF) only gets their influence on the subset evaluated:

$$\hat{\rho}(0) = \hat{\rho}_N(0) \otimes \hat{\sigma}(0)$$

$$\frac{d}{dt}\hat{\sigma}(t) = -\frac{i}{\hbar}\langle \mathbf{L} \rangle \hat{\sigma}(t) - \int_0^t d\tau \mathbf{K}^{\text{full}}(\tau)\hat{\sigma}(t-\tau)$$







Lyu, N.*; Mulvihill, E.*; Soley, M.B.; Geva, E.; V. S. Batista. Submitted.

Summary

- We developed new, accurate large-scale molecular wavepacket propagation schemes based on tensor train decomposition, which helped to solve the very challenging retinal cis-trans isomerization problem;

- We carried out zero temperature and finite temperature tensor train propagations that 1) established reduced GQME as a numerically exact method and 2) explored the accuracy and suitability of semiclassical and mixed quantum-classical method with various models.

Thank you for your attention!