

# Photochemistry of Proton Transfer with Tensor Networks

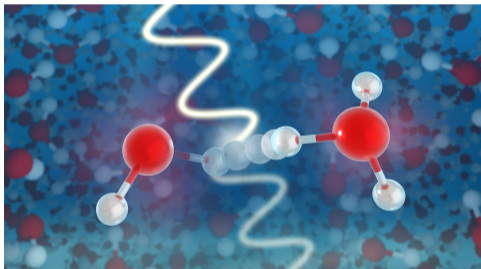


Figure: Proton transfer in biological medium  
(Image by Argonne National Laboratory)

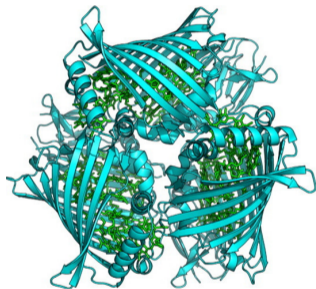
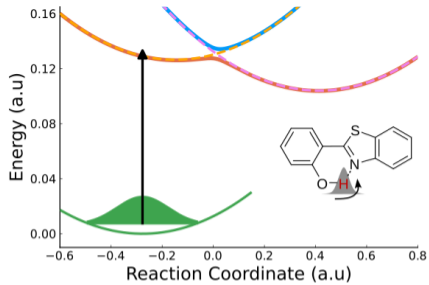
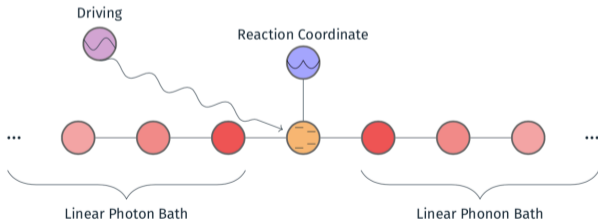
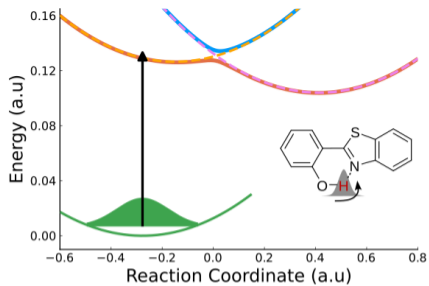
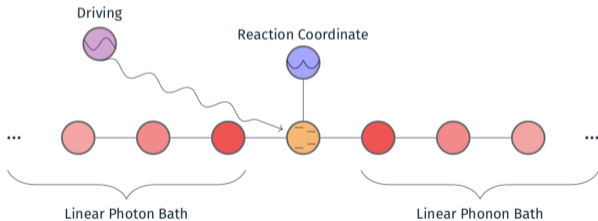
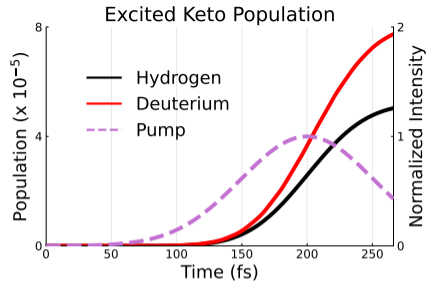
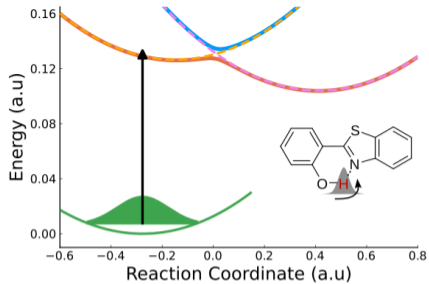
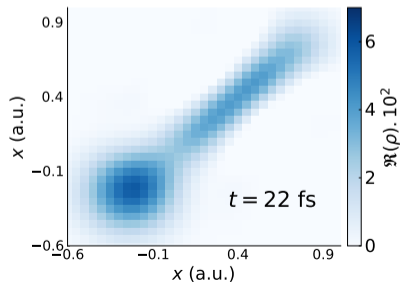
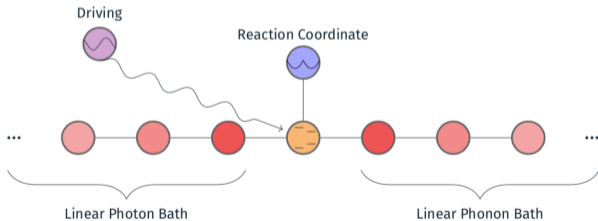
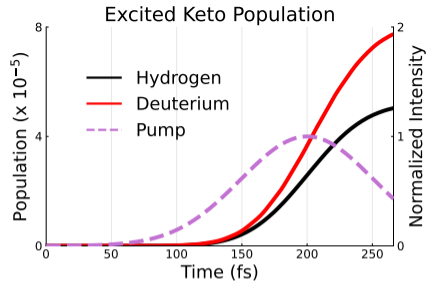
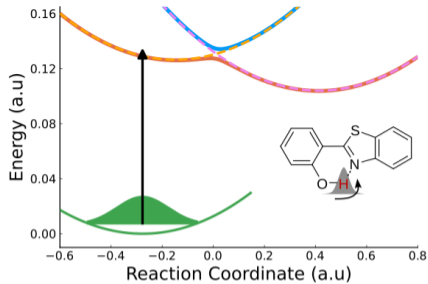


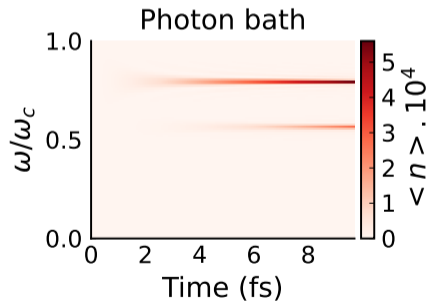
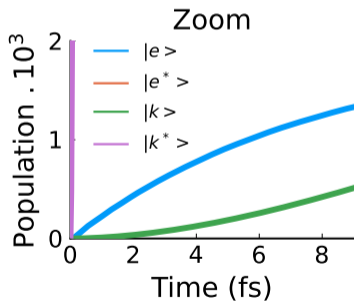
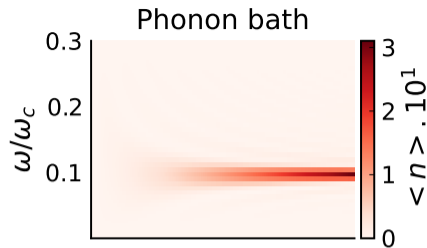
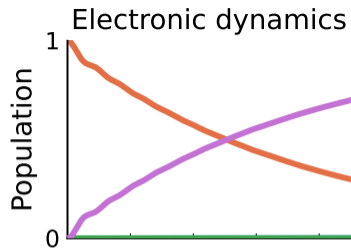
Figure: Crystal structure of an FMO pigment system, where proton transfer takes place









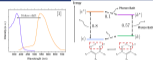


# Theory of Photoinduced Excited State Proton Transfer with Matrix Product States

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## An Ultrafast and Photoinduced Phenomenon



- The efficiency of the Photoinduced Excited State Proton Transfer is critical for light reactions of photosynthesis.
- It is characterized by an ultrafast response (up to a few tens of femtoseconds) and a large Stokes shift (2000 cm<sup>-1</sup> Stokes shift [1]).
- Out-of-equilibrium vibrational states are involved but are fully approached although it comes to be a ground state.
- We adapted the Julia package `TDVP/QuSpin` [2] on tensor networks to gain insight into the non-equilibrium dynamics of proton transfer.

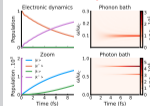
## Tensor decomposition

- Matrix Product States enable us to handle decomposing the general  $\rho(t) = \sum_{\alpha, \beta} C_{\alpha, \beta}(t) |\alpha\rangle\langle\beta|$  and the  $d^2$  dimension coefficient  $C_{\alpha, \beta}(t)$ .
- Time Dependent Variational Ansatz is a time evolution approach that makes use of the tensor with a change of  $d$  as bond dimension.
- The renormalization tensor is updated during the dynamics, leading to a renormalized MPO gate.

## Dual Fluorescence Dynamics

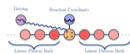
Bath is the only source of coupling between electronic states. Spectra are measured very accurately since information is retained from the bath.

$$\begin{aligned}
 P &= \langle \rho(t) | \rho(t) \rangle = \sum_{\alpha, \beta} \langle \alpha | \rho(t) | \beta \rangle \langle \beta | \rho(t) | \alpha \rangle \\
 &= \langle \rho(t) | \rho(t) \rangle = \sum_{\alpha, \beta} \langle \alpha | \rho(t) | \beta \rangle \langle \beta | \rho(t) | \alpha \rangle \\
 &= \langle \rho(t) | \rho(t) \rangle = \sum_{\alpha, \beta} \langle \alpha | \rho(t) | \beta \rangle \langle \beta | \rho(t) | \alpha \rangle
 \end{aligned}$$



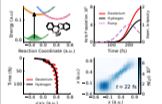
## Features on the Many-Body System

- The bath: molecular vibrations (phonons) and the electromagnetic coupling (photon).
- The Hamiltonian can be linear dependent (including a driving).
- A new tensor basis can be added to represent the proton reaction coordinate.



## Driven Doubtwell Description with Dissipation

The dynamics of a system upon excitation can be described in the very short term. The proton coordinate can be renormalized while maintaining it non-fermi-like.



## Conclusion

This study is tackling the general problem of electronic systems interacting with environments in the out-of-equilibrium regime. Bathes are treated very precisely thanks to the Matrix Product States technique, and many the system interaction, providing dual fluorescence spectra resolved in time. Moreover, this new framework allows to access the hydrogen reaction coordinate, approaching zero and many multiple nuclei.

## References

1. F. Baccin, A. Sore, et al. *Chem. Commun.* 17, 31, 5517-5522 (2017).
2. A. Dazzi, A. Chin, et al. *J. Chem. Phys.* 150(12) 124112 (2019).
3. S. Pauly et al. *Annals of Physics* 213 p. 30799 (2001)

Feel free to come to my poster :)



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