Real-Time Ehrenfest-TDDFT as a Tool to Understand Light-Harvesting

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Methodology

We use Ehrenfest-TDDFT to describe the coupled dynamics of electrons and nuclei in real time on a real-space grid:

- Electron dynamics: Kohn-Sham equations

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\varphi_i = \hat{h}_{\mathrm{KS}}\varphi_i$$

- Nuclear motion: Newton's second law

$$M_I\ddot{\vec{R}}_I = \vec{F}_I = -\nabla_{\vec{R}_I}E$$

Electrons and nuclei are propagated simultaneously.
Software: `BTDFT` [1]

Bacteriochlorophylls

Protein Environment

Amino acids

B850 Ring

Investigations for EET through ring so far were based on exciton models
→ Simulate fully coupled EET after Laser excitation with Ehrenfest at room temperature

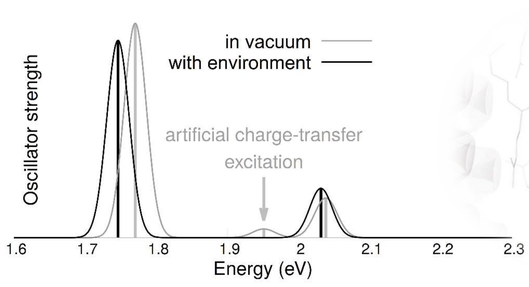
Further Methods

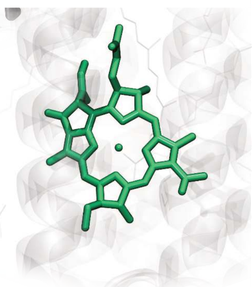
Pseudopotentials

- propagate only valence electrons using pseudopotentials
- Tafipolski-Schmid filtering [5]
  → grid spacing Δx = 0.3 bohr

Protein environment

- approximated as static electric field
- stabilizes Bacteriochlorophylls
- enables LDA as valid xc functional: fixes artificial CT excitation in spectrum [6]





Progress so far

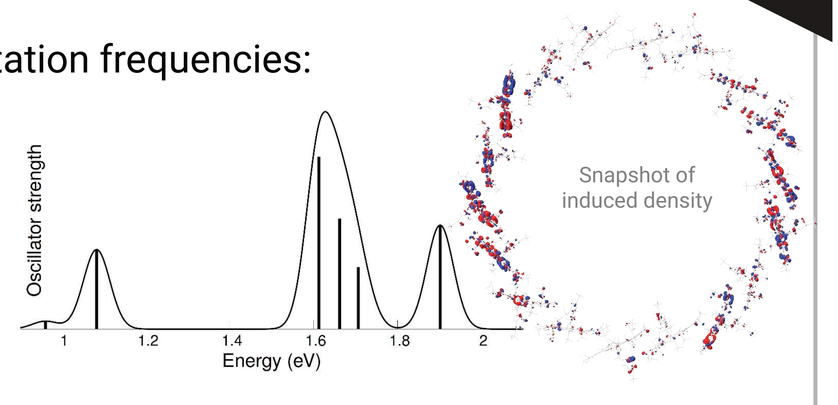
Thermalization

Experimental crystal structure → calculate electronic ground state → couple nuclei to Nosé-Hoover thermostat (T=298K) → propagate until thermalization (~250fs)

Excitation Frequencies

Calculate spectrum of B850 ring to get excitation frequencies:

- take snapshot of nuclear positions from thermalization
- calculate electronic ground state
- boost excitation ($\varphi_i(0) \to \exp(\mathrm{i}\vec{k}\cdot\vec{r})\varphi_i(0)$)
- Fourier transform dipole moment and evaluate according to ref. [1]



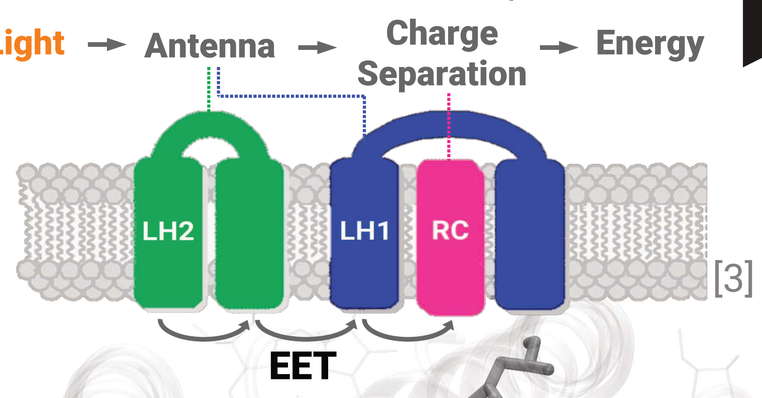
Next steps

- Excite thermalized B850 ring with laser and simulate coupled dynamics
- Track excitation energy with introduced energy measures

Aim

Quantify natural light-harvesting (LH) processes in purple bacteria with TDDFT.

Why? Remarkable quantum efficiency of excitation-energy transfer (EET) from antenna to reaction center at room temperature! [2]

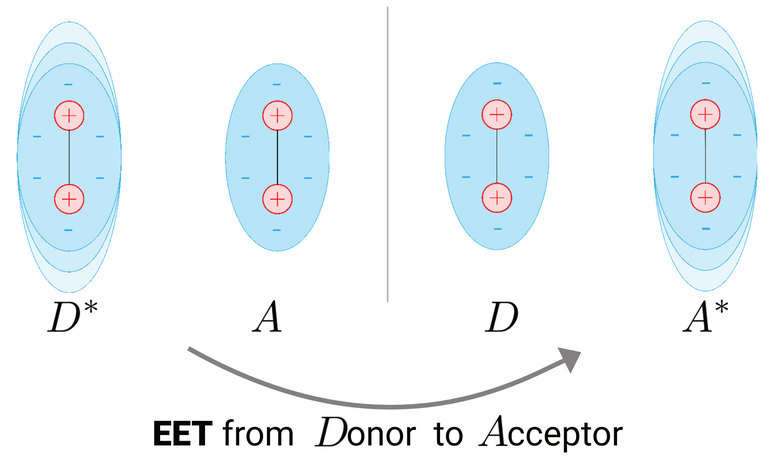


[3]

Excitation-Energy Transfer

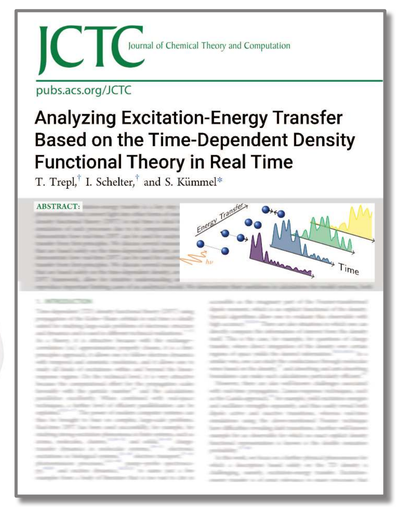
What is excitation-energy transfer?

- Transfer of energy without charge transport
- Conceptual idea: Density oscillation



How to quantify excitation-energy transfer?

Challenge with TDDFT
Time-dependent electron density is the only reliable observable



[4]

Concept
Measure local excitation energy via density-derived quantities:

- Induced dipole moment $d(t)$

$$\mathcal{E}_l^d \sim \overline{d_l^2} = \int_{V_l} \overline{(n(t)-n(0))^2}\vec{r}^{\,2}\mathrm{d}^3r$$

- Time-derivative of the density $\dot{n}(t)$

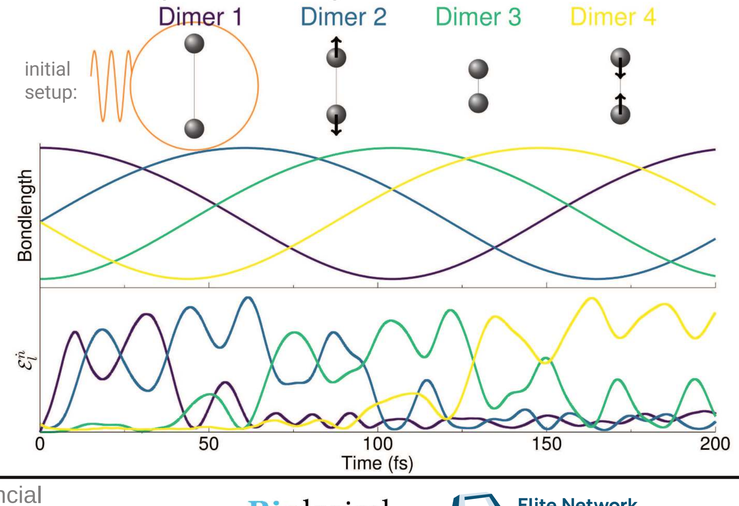
$$\mathcal{E}_l^{\dot{n}} \sim \int_{V_l}\varepsilon[\dot{n}]\mathrm{d}^3r = \int_{V_l}\overline{\dot{n}^2}\mathrm{d}^3r$$

V_l Molecule subspace
$\overline{\square}$ Time average

Energy measures agree analytically with excited state populations in an occupation-number model for the limiting case of 2 weakly coupled 2-level donor acceptor molecules.

Trial setup: EET through Sodium dimer chain

- Laser excitation of dimer 1
- Ehrenfest-TDDFT induces vibration of dimers
- Matching bondlengths enable EET



References & Acknowledgements

[1] I. Schelter, S. Kümmel, *Journal of Chemical Theory and Computation* 14.4 (2018): 1910-1927
[2] R. E. Blankenship, *John Wiley & Sons*, 2021
[3] J. Fiedor, et al., *Journal of Analytical Atomic Spectrometry* 31.10 (2016): 2078-2088
[4] T. Trepl, I. Schelter, S. Kümmel, *Journal of Chemical Theory and Computation* 18.11 (2022): 6577-6587
[5] M. Tafipolsky, R. Schmid, *The Journal of Chemical Physics*, 124.17 (2006): 174102
[6] I. Schelter, et a., *The Journal of Chemical Physics*, 151.13 (2019): 134114

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