On the electron transfer in Photosystem I and photoreactive chlorophyll clusters

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Abstract

Modern photovoltaic materials can be seen as biomimetics of photosynthesis. Photosystem I (PS1) has one of the highest conversion efficiencies of 88%

The challenge:

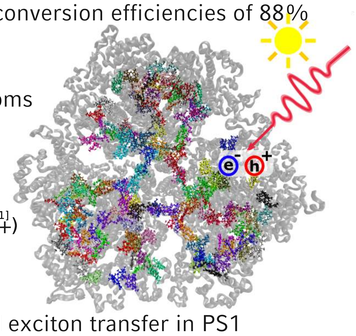
- What causes the efficiency of PS1
- How can we treat the vast amount of atoms accuratly enough

The approach:

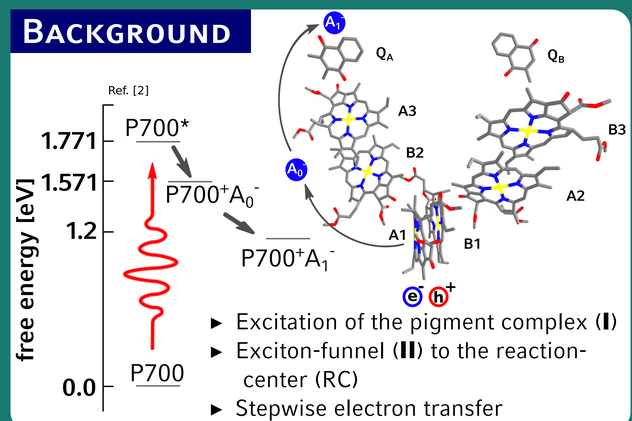
- Semi-empirical methods & validation
- Highly parallelized software (Fermions++)[Ref. 1]
- Dimensionality reduction (PCA)

What we present:

- General-purpose workflow, electron and exciton transfer in PS1



Background

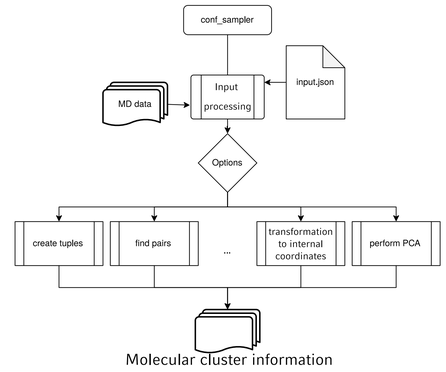


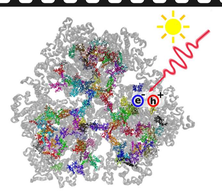
- Excitation of the pigment complex (**I**)
- Exciton-funnel (**II**) to the reaction-center (RC)
- Stepwise electron transfer

Methods

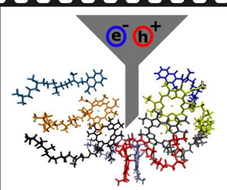
- Molecular dynamics simulation (MD) (see S. Reiter; Poster 41)
- Benchmarks
  - ZINDO/S (screening/ORCA5.0)[Ref. 3]
  - ωB97X-D3BJ (validation/Fermions++)
- Transition property analysis (in-house modified TheoDORE version)[Ref. 4]
- Dimensionality reduction workflow (internal coordinates, principal component analysis). In-house software developed for general-purpose application

Dimensionality Red.

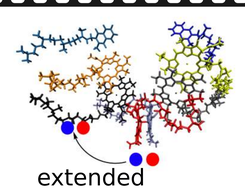




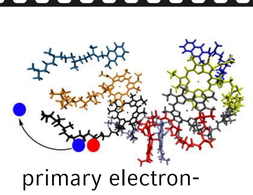
excitation **I**



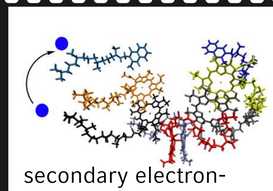
exciton-funnel **II**



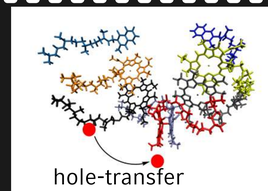
extended exciton-funnel **III**



primary electron-transfer to A3 **IV**



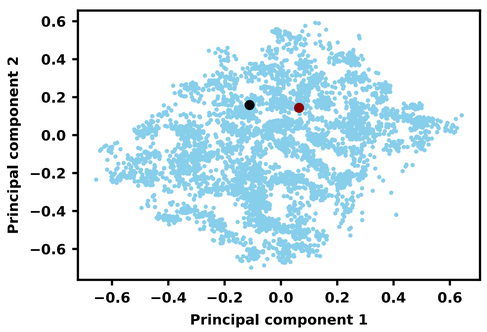
secondary electron-transfer to Q_A **V**



hole-transfer to the special pair **VI**

Antenna-complex

- Principal component analysis (PCA) for dimensionality reduction
- The antenna complex is modelled by chlorophyll pairs and their intermolecular coordinates (five snapshots)

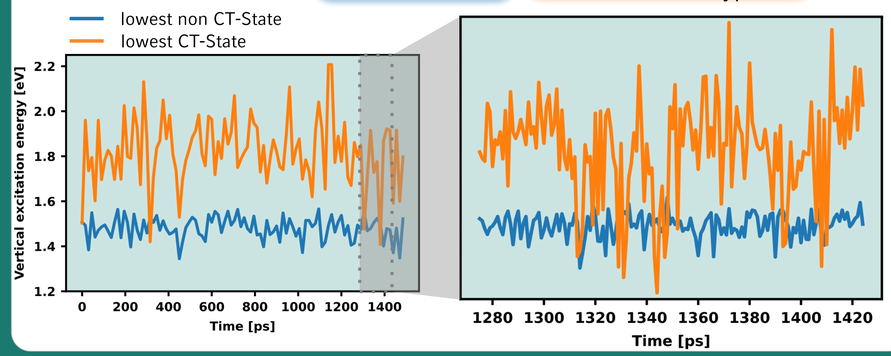


- Reduced dimensionality reveals clear cluster formation
- Clusters show networks for exciton transfer (**II**)
- Pairs A1B1 and B2A3 are directly connected

MD screening

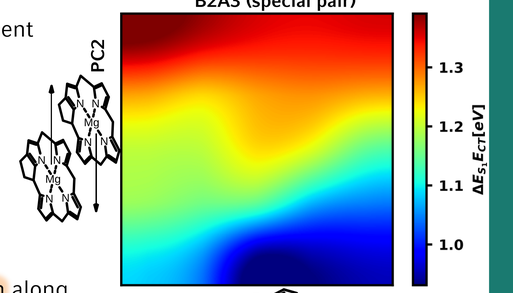
Full RC with QM/MM electrostatic-embedding

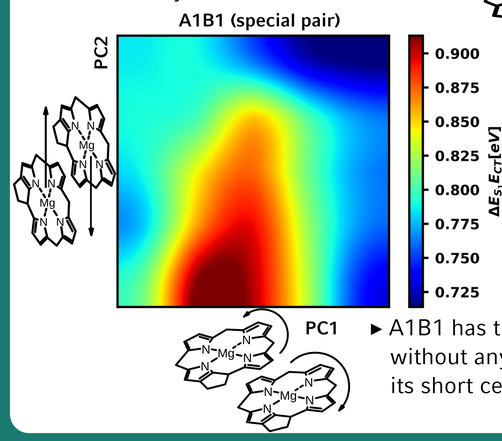
- Snapshots every 15ps of 1500ps MD
- Assignement of CT-states (CT-Number ω_{CT}>0.4)
- S1 CT-States are in reach of room temperature geometric fluctuations
- Additional exciton transfer to B2 needed (**III**); All CT-states are of type **IV**;



Pair PCA

- Partitioning in RC pigment pairs
- Analysis of major configurational change along the MD (without electronic-embedding)
- CT in B2A3 (**IV**) shows the highest stabilization along the 2D PCs by ~ 0.4 eV





- Center-to-center mode restriced in A1B1
- PC2 almost identically in both pairs
- Reduced and oxidized analogues (**V** and **VI**)
- A1B1 has the most stable CT-states without any enviroment due to its short center-to-center distance

Conclusion and Outlook

We were able to develop a workflow to efficiently investigate an excited state mechanism based on a MD-simulation. This additionally yielded new insights in the CT-events in the RC of PS1, questioning the current model of the electron transfer. With these preliminary results and the method described new opportunities and follow up studies arise.

In order to use the described methods to their full potential we plan to extend the pairwise calculations to the QM/MM scheme. Furthermore the processes **V** and **VI** need thorough validation. We plan to make the developed program accessible to the public, contributing to the available tools for MD-simulations.

References

[1] J. Kussmann, H. Laqua, C. Ochsenfeld, *J. Chem. Theory Comput.* **2021**, *17*, 1512-1521.

[2] K. Brettel, W. Leibl, *Biochimica et Biophysica Acta (BBA) - Bioenergetics* **2001**, *1507*, 100-114.

[3] F. Neese, *WIREs Computational Molecular Science* **2018**, *8*, e1327

[4] F. Plasser, *The Journal of Chemical Physics* **2020**, *152*, 084108.

e-conversion

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