Modeling the absorption spectra of light-harvesting antenna complexes

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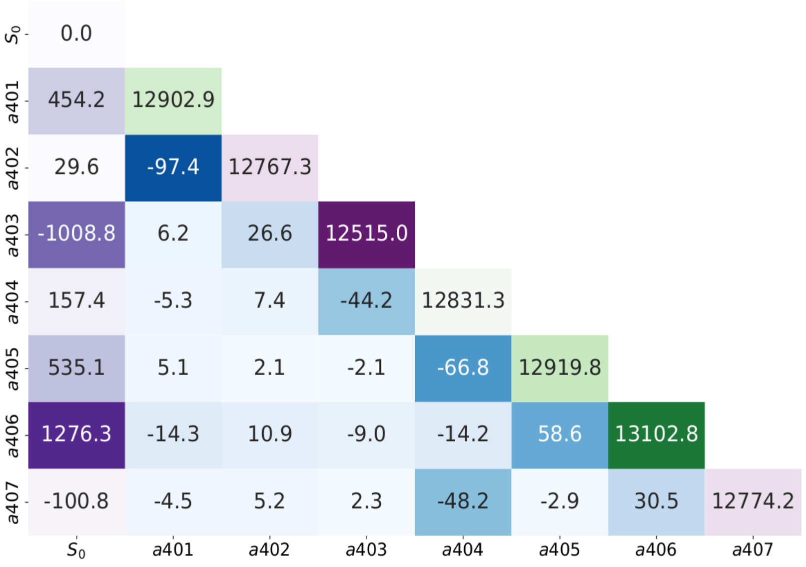
The process of photosynthesis was discovered back in the 17th century, but its molecular mechanisms still pose some questions related to the exciton energy landscape and its thermalization process. One of the core processes of photosynthesis is the “collection of light” through multi-pigment light-harvesting antenna complexes. A vast diversity of photosynthetic pigments and light-harvesting complexes has evolved, what adapted the process to occur both in water and on land, and it can be found in many bacteria, algae and plant species. In this work we construct the full exciton model stemming from pigment-pigment interactions and calculate absorption spectra and relaxation rates of three different light-harvesting complexes (Fenna-Matthews-Olson (FMO), light-harvesting 2 (LH2), fucoxanthin-chlorophyll binding protein (FCP)) using their protein structures. FCP, FMO and LH2 structures from the Protein Data Base were used. Ground state (S$_0$), first vertically excited (S$_{01}$) and equlibrated (S$_{11}$) excited states of chlorophyll *a*, *c*$_1$, *c*$_2$ and bacteriochlorophyll *a* were calculated with GAUSSIAN software[1] using the TD-DFT methodology with a CAM-B3LYP 6-31G(d) basis set. Then from the quantum mechanical calculation results, partial atomic charges were calculated using the CHELPG methodology with Multiwfn software[2]. Partial atomic charges of the protein backbone with PARSE and AMBER force fields were obtained via PDB2PQR[3]. We then model not only the Hamiltonian of the singly excited manifold, but also include the interactions with the S$_0$ state of the pigments. From these results via an in-house developed code, pigment-pigment excited state interactions, excitation frequencies, relaxation to ground state rates, and absorption spectra were calculated. Spectra of pigments *in vacuo*, in a protein environment with different force-fields and in a protein environment with the addition of ions in case of adiabatic and non-adiabatic (including the ground state of pigments) couplings were compared. The general trend tends to be that due to coupling to the ground state, pigment absorption spectra tend to shift to higher energies, some peak positions and shapes of the spectra change, and some details of the spectra’s fine structure can be seen. The results demonstrate that the coupling between the electronic ground and excited states of the molecular excitonic aggregates is necessary to include when considering various types of spectra.



	S_0	*a*401	*a*402	*a*403	*a*404	*a*405	*a*406	*a*407
S_0	0.0							
*a*401	454.2	12902.9						
*a*402	29.6	-97.4	12767.3					
*a*403	-1008.8	6.2	26.6	12515.0				
*a*404	157.4	-5.3	7.4	-44.2	12831.3			
*a*405	535.1	5.1	2.1	-2.1	-66.8	12919.8		
*a*406	1276.3	-14.3	10.9	-9.0	-14.2	58.6	13102.8	
*a*407	-100.8	-4.5	5.2	2.3	-48.2	-2.9	30.5	12774.2

Figure 1: Hamiltonian (in cm^{-1}) of FMO complex.

References
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