Characterizing energy fluctuations in the FMO Complex on a DFT level potential: covering timescales from femto to sub-microseconds

Young Min Rhee

Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea

E-mail: ymrhee@kaist.ac.kr

Understanding how the environmental fluctuations affect exciton energies in a chromophore-embedded complex system is of utmost importance toward elucidating its spectroscopic and dynamic characters. Because exciton energies are determined by both ground and excited state energies of involved chromophores, a reliable and balanced description is conventionally required. At the same time, there are always low frequency motions in a complex system, whose treatment can only be accomplished by following the dynamics in the long timescale. In this talk, a method for handling both issues will be discussed with the specific example of the Fenna-Matthews-Olson complex. For describing realistic pigment vibrations, we have adopted an interpolated all-atom potential energy model based on DFT calculations and performed 100 ns long molecular dynamics simulations. This simulation timescale can encompass the effects of slow static disorder as well as fast dynamic disorder. With a simple argument, we demonstrate that the two disorders show clear timescale separation, with the slower one affecting fluctuations only beyond 1 ns. We then extract the spectral densities of the complex by considering both the site and the exciton bases and show that the one with the lowest exciton state at a low temperature condition well reproduces the experimentally observed one. Some results from non-equilibrium excited state trajectory simulations will also be discussed to demonstrate that the system lies well within the linear response regime after photo-absorption and that the pigments do not visit anharmonic regions of the potential surface to any significant extent. In its relation, the use of semi-classical non-adiabatic simulation scheme will also be touched. As concluding remarks, we will comment on the extensions of the methodology as well as the future prospects of their applications.