First Principles Model Hamiltonian Ensembles and Quantum Dynamics for Photosynthetic Light Harvesting

D.F. Coker and M.K. Lee

Department of Chemistry, Boston University, 590 Commonwealth Avenue, Boston, MA, 02215, U.S.A.

coker@bu.edu

Abstract:

Nonadiabatic excited state energy transfer dynamics plays a key role in enabling the high quantum efficiency of photosynthetic light harvesting pigment-protein complexes. Accurate simulation methods are crucial to understanding the mechanisms of these processes. In this talk we present an overview of ab initio quantum chemistry methods that are used to generate ensembles of model Hamiltonians that include fluctuations in chromophore excitation energies, electronic couplings, electronic – intramolecular vibrational couplings, and long-range chromophore - intermolecular environmental interactions. [1-2] The reliability of these first principles model Hamiltonian ensembles is demonstrated by comparing predictions of absorption and CD spectra with experiments. Density matrix based quantum dynamics methods are then used to explore the dissipation and decoherence dynamics that occur on competing timescales with the excitation energy transfer. [3] The different roles of higher frequency chromophore vibrations that can be resonant with differences in chromophore excitation energies and low frequency vibrational motions will be explored.

References:

[1] “Modeling electronic-nuclear interactions for excitation energy transfer processes in light-harvesting complexes”, M.K. Lee and D.F. Coker, *J. Phys. Chem. Lett.*, **7** 3171-3178 (2016).

[2] “Semiclassical path integral dynamics: Photosynthetic energy transfer with realistic environment interactions”, M.K. Lee, P. Huo and D.F. Coker, *Ann. Rev. Phys. Chem.*, **67** 639-668 (2016).

[3] “Consistent schemes for non-adiabatic dynamics derived from partial linearized density matrix propagation”, P. Huo and D.F. Coker, *J. Chem. Phys.*, **137** 22A535 (2012).