Quantum and Classical Dynamics of Energy Transfer and Storage Systems: From Photosynthesis to Lithium Batteries

Sohang Kundu, Postdoctoral Research Scientist, Columbia University

In this talk I will discuss recent work that investigates the impact of nuclear motion on chemical processes relevant for energy transfer and storage. The talk consists of two sections:

In Section I, I will explore how nuclear vibrations influence the dynamics of inter-molecular excitation energy transfer (EET), which has key bearings on our understanding of photosynthetic light harvesting, and on the design of energy-efficient materials. I will mainly recount the development [1,2] and use [3] of real time path integral methods to perform the first all-state, all-mode simulation of the bacterial LH2 complex at room temperature. From this simulation, we discovered that the remarkable (~90%) efficiency and (~1 ps) timescale of EET that have been observed experimentally are enabled by the two-ring arrangement of chromophores and quantum effects associated with nuclear vibrations. I will briefly browse through some other consequences of strong electron-vibration couplings – e.g., on the scrambling of information [4] by chemical reactions, and on the breakdown of the Franck-Condon approximation [5] in metalloporphyrins.

Section 2 will focus on the chemical dynamics of battery systems. Aside from the complexities of nuclear motion in the electrolyte solution and at the electrode-electrolyte interface, the dynamics of such systems are riddled by the external electric field and potentially non-adiabatic electron transfer at the electrodes. I will briefly describe our recent theory [6] of reaction rates for electric field catalysis in polar solvents. I will also discuss a new approximate method [7] to compute charge-transfer excitations and non-adiabatic couplings using ground state force fields that allow dynamic fluctuations of atomic charges. Finally, and if time permits, I will share ongoing progress towards uncovering the role of nuclear dynamics in forming the solid-electrolyte interphase (SEI) of lithium-based batteries. Using first-principles electronic structure and molecular dynamics calculations, we developed neural network potentials that allow us to compute accurate free energies and exact (classical) rates for electrolyte decomposition on the lithium surface [8].

Selected Publications (for the full list, visit webpage)

[1] **S. Kundu** and N. Makri, "Modular Path Integral for Finite-Temperature Dynamics of Extended Systems with Intramolecular Vibrations", Journal of Chemical Physics **153**, 044124 (2020)

[2] **S. Kundu** and N. Makri, "Small Matrix Quantum Classical Path Integral", Journal of Physical Chemistry Letters, **13**, 3492-3498 (2022)

[3] **S. Kundu**, R. Dani and N. Makri, "Tight Inner Ring Architecture and Quantum Motion of Nuclei Enable Efficient Energy Transfer in Bacterial Light Harvesting", Science Advances, **8**, eadd0023 (2022)

[4] C. Zhang#, **S. Kundu#,** N. Makri, M. Gruebele, and P. Wolynes, "Quantum Information Scrambling and Chemical Reactions", Proceedings of the National Academy of Sciences, **121** (15) e2321668121 (2024). # denotes authors contributed equally.

[5] **S. Kundu**, P. P. Roy, G. R. Fleming and N. Makri, "Franck-Condon and Herzberg-Teller signatures in molecular absorption and emission spectra", Journal of Physical Chemistry B, **126**, 15, 2899–2911 (2022).

[6] **S. Kundu** and T.C. Berkelbach, "Reaction Rate Theory for Electric Field Catalysis in Solution", Journal of the American Chemical Society **146**, 38, 26041–26047 (2024)

[7] **S. Kundu***, H.-Z. Ye, and T.C. Berkelbach*, "Charge-Transfer Excitations from Fluctuating Charge Force Fields", (2024) (*in preparation*). * denotes corresponding author.

[8]. **S. Kundu***, D. Chamaki, H.-Z. Ye, and T.C. Berkelbach*, "Reaction dynamics and rates for the decomposition of ethylene carbonate on lithium using fine-tuned machine learning potentials", (2024) (*in preparation*).