Mixed Quantum–Classical Approaches to Ultrafast Excited-State Dynamics of Complex Systems

Dr. Hiroki Uratani

Excited-state dynamics of chemical species play important roles across many areas of chemistry, ranging from biological photosynthesis to organic solar cells. Because the microscopic and real-time details of such dynamics pose a formidable challenge for spectroscopic measurement techniques, computational simulations could play a key role in providing insights into phenomena at spatial and temporal resolutions otherwise inaccessible. However, their high computational cost has limited the target systems to medium-sized, i.e., composed of no more than dozens of atoms, model systems. Dr. Uratani has overcome these problems through his original theoretical approach, achieving world-record class computations including the excited-state dynamics of a 6000-atom system[*J. Chem. Theory Comput.* **17**, 7384 (2021)]. His achievements are summarized as follows; (i) He has extended excited-state molecular dynamics simulation techniques for application to nanoscale systems that are composed of thousands of atoms, which had been inaccessible by conventional techniques. Furthermore, (ii) he has elucidated excited-state dynamics of realistic systems through applications of his own methods, providing new physical insights.

For direction (i), he has developed a series of scalable excited-state molecular dynamics techniques by combining a semi-empirical quantum chemical calculation method, i.e., the density-functional tight binding (DFTB), and the spatial fragmentation approach called the divide and conquer (DC). By this approach he has greatly reduced the computational cost, enabling the simulations of systems composed of thousands of atoms. For example, this approach first enabled us to simulate excited-state dynamics of solute molecules in solution with explicit treatment of solvent molecules at the quantum-mechanical level[*J. Chem. Phys.* **152**, 224109 (2020)]. The method was also applied to condensed-phase photochemical reactions, i.e., *cis*-*trans* isomerization of azobenzene, successfully elucidating the solvent dependence of the photoisomerization dynamics[*J. Chem. Theory Comput.* **16**, 7299 (2020); *J. Chem. Theory Comput.* **17**, 1290 (2021)]. Recently, the method has further extended to incorporate spin-orbit coupling to enable treatment of intersystem crossing processes[*J. Phys. Chem. A* **128**, 5999 (2024)]. Moreover, through a similar approach, he realized an excited-state molecular dynamics method applicable to nanoscale delocalized excited states, which is a typical situation for semiconductor systems, and implemented it with an extensively parallelized manner[*J. Chem. Theory Comput.* **17**, 7384 (2021)]. The remaining obstacle for large-scale excited-state molecular dynamics is that large systems typically entail a high density of states that harms computational stability. Recently, he has developed an approach to tackle this problem by using a continuous representation of electronic states with respect to nuclear motion based on the real-time time-dependent density functional theory[*Theor. Chem. Acc.*, in press].

For direction (ii), he has elucidated the atomic-scale excited-state dynamics in diverse systems including perovskite solar cell materials[*Phys. Chem. Chem. Phys.* **22**, 97 (2020); *J. Phys. Chem. Lett.* **11**, 4448 (2020)], donor-acceptor interfaces in organic solar cells[*J. Phys. Chem. Lett.* **14**, 2292 (2023); *J. Chem. Phys.* **161**, 184710 (2024)], photoinduced phase transitions of an organic charge-transfer complex[*J. Chem. Phys.* **159**, 054101 (2023)], supramolecular assemblies incorporating metal complexes[*J. Chem. Phys.* **161**, 201101 (2024); *ChemPhotoChem* **10**, e202500343 (2025)], and water-splitting photocatalysts[*Phys. Chem. Chem. Phys.* **27**, 14748 (2025)]. For example, in [*J. Chem. Phys.* **161**, 184710 (2024)], he has revealed that the charge separation dynamics at donor–acceptor interfaces of organic solar cells strongly depend on the microscopic aggregation structures. This finding, which had been recognized neither experimentally nor theoretically, was achieved by his original computational approach that enables the use of sufficiently large structural models to explicitly incorporate the structural disorder of donor–acceptor interfaces.

Overall, his research activities, that have orders-of-magnitude extended the spatial scale of the target systems of excited-state dynamics simulations, open a new horizon for photochemistry providing the microscopic (atomic-scale) and real-time (attosecond) observation tool for complex molecular systems.