Simulations Of Photochemistry Inside An Optical Resonator

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Photochemistry has opened the door to new materials and new fabrication processes. For example, laser chemical vapor deposition can be used to manufacture high purity materials at the micro scale. Photofragmentation and photopolymerization offer a tailored degree of control in metal-organic ligands and frameworks. Photovoltaic and photoluminescent systems provide many useful means of converting energy between electricity and light. Exciton-polaritons have unique properties that may be key to next-generation materials. However, accurate descriptions of the underlying photophysical properties and mechanisms of these systems are necessary to systematically improve designs and fabrication processes. Providing such theoretical descriptions remains an open challange. These photophysical properties and mechanisms inherently arise from the simultaneous coupling of quantized nuclear, electronic, and photonic degrees of freedom (DoF). Treating this properly would involve highly complicated systems of coupled differential equations within many-body problems, which is analytically infeasible except in the simplest of cases.

The goal of this project is to create a publicly available computational tool that can perform molecular dynamics (MD) within a Fabry- Pérot cavity while coupling the quantized electronic and photonic DoF. The light-matter Hamiltonian is used perturbatively under the electric dipole approximation to capture this coupling within the framework of density functional theory. This allows for electronic transitions to occur "on-the-fly" during MD trajectories. The first model tested is H_2^+ with fixed nuclear positions. This was chosen to replicate, as closely as possible, a two-level electronic system. This allows for comparison of state populations with time-dependent perturbation theory and Rabi oscillations. The model has already shown some promising signs, such as a consistent quadratic growth in population of the excited state across ~ 1 fs trajectories and oscillatory behavior across longer trajectories. Preliminary data of a HF molecule may also be provided. This system introduces asymmetry and far greater electronic complexity without moving beyond a diatomic molecule, and the plethora of data on HF will allow for the expansion of characteristics to be validated.