

# Investigating Molecular Exciton-Polaritons using Ab Initio Cavity Quantum Electrodynamics

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Coupling molecules to the quantized radiation field inside an optical cavity creates a set of new photon-matter hybrid states called polariton states.

In this talk, I will present our recent progress on developing ab-initio simulation approaches to investigate molecular polariton properties. First, I'll discuss a recent ab-initio QED approach we developed, which we refer to as the "parametrized QED" approach [1]. We combine electronic structure theory with quantum electrodynamics (QED) to investigate molecular polaritons using ab initio simulations. This framework joins unperturbed electronic adiabatic states with the Fock state basis to compute the eigenstates of the QED Hamiltonian. The key feature of this "parametrized QED" approach is that it provides the exact molecule-cavity interactions, limited by only approximations made in the electronic structure. Using time dependent density functional theory, we demonstrated comparable accuracy with QED coupled cluster benchmark results for predicting potential energy surfaces in the ground and excited states and showed selected applications to light-harvesting and light-emitting materials. We anticipate that this framework will provide a set of general and powerful tools that enable direct ab initio simulation of exciton polaritons in molecule-cavity hybrid systems.

Second, I will present a mixed quantum-classical simulation of polariton dynamics for molecule-cavity hybrid systems [2]. In particular, we treat the coupled electronic-photonic degrees of freedom (DOFs) as the quantum subsystem and the nuclear DOFs as the classical subsystem.

and use the trajectory surface hopping approach to simulate non-adiabatic dynamics among the polariton states due to the coupled motion of nuclei. We use the accurate nuclear gradient expression derived from the Pauli-Fierz quantum electrodynamics Hamiltonian without making further approximations. The energies, gradients, and derivative couplings of the molecular systems are obtained from the on-the-fly simulations at the level of complete active space self-consistent field (CASSCF), which are used to compute the polariton energies and nuclear gradients. The cavity loss process is modeled with the Lindblad jump super operator on the reduced density of the electronic-photonic quantum subsystem. We investigate the azomethane molecule and its photoinduced isomerization dynamics inside the cavity. Our polariton dynamics results demonstrate the isomerization reaction of azomethane can be effectively tuned by coupling to an optical cavity and by changing the light-matter coupling strength and the cavity loss rate.

[1] Investigating Molecular Exciton-Polaritons using Ab Initio Cavity Quantum Electrodynamics B. M. Weight, T.D. Krauss, P. Huo, J. Phys. Chem. Lett. 25, 5901-5913 (2023).

[2] Ab Initio Molecular Cavity Quantum Electrodynamics Simulations Using Machine Learning Models, D. Hu, P. Huo, J. Chem. Theory Comput. 8, 2353-2368 (2023)