Macroscopic Simulations of Exciton-Polaritons with Single-Molecule Resolution: A Stochastic Chebyshev Approach to Spectroscopy

Braden M. Weight[1] and Pengfei Huo[2,3]

[1]*Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627, U.S.A*

[2]*Department of Chemistry, University of Rochester, Rochester, New York 14627, USA*

[3]*The Institute of Optics, Hajim School of Engineering, University of Rochester, Rochester, New York 14627, USA*

Polaritonic chemistry has become the leading direction to control a multitude of processes, such as charge transfer, selective bond breaking, and excited state dynamics. An exciton-polariton is an entangled state of light and matter in which the native excitonic and photonic degrees of freedom hybridize to form new states. These new states can be tuned in various ways to modify and produce unique properties, such as the potential energy landscape or the emission efficiency of materials. However, much is still unknown about how these new hybrid states can modify such chemical properties and subsequently their reactions. For example, collective effects – which arise from the coherent coupling of 10^5-10^{10} molecules to an optical cavity mode – are largely unexplored due to the size complexity of the Pauli-Fierz Hamiltonian. Using a stochastic resolution of the identity coupled with a Chebyshev expansion, it is possible compute various quantities of interest with a substantially reduced computational effort than would be needed for a direct diagonalization of the Hamiltonian. Such quantities of interest are the total density of states (*i.e.*, the eigenspectrum of the Hamiltonian) and the transmission spectrum of the photonic degrees of freedom, the latter of which is directly observable in experiment. In this work, we explore molecule-cavity systems with ~10^8 degrees of freedom, including the effects of static and dynamic disorder, exciton-exciton coupling, and cavity loss to shine light on recent experimental realizations of strongly coupled molecule-cavity systems.