Spectroscopy simulations of Polaritons

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Oral Exam location and time: Hutchison 118, 1 pm – 3 pm

Thesis advisory committee members:

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**Motivation:**

When molecules couple to the quantized radiation field inside an optical cavity, new hybrid light-matter states, called polaritons form. Due to this rich dynamical interplay among electronic and photonic degrees of freedom, one can control the electronic potential energy curvature and efficiently control chemical reactivity [1-5]. Recent experimentation has now demonstrated this collective coupling of large ensembles of molecules to an optical cavity, provides enhanced control over chemical reactions [8-10], and effectively decouples the system from its external bath (solvent) effects [9]. Understanding the spectroscopy of these polariton systems will pave the way toward unraveling the mysteries of polariton chemistry. In particular, 2D electronic spectroscopy (2DES) can reveal inherent intermolecular two-body couplings, where the broadening of peaks indicates the coupling of the bath to the system and the fluctuations of the intensity peaks give direct evidence of coherent mechanisms in the system. Thus, 2D spectroscopy is one of the best experimental techniques to explore polaritonic properties; however, there currently are no available software packages to simulate and predict these experimental results.

Theoretical investigations play an important role in understanding the fundamental and unexplored properties of polaritons due to their exotic and under-investigated nature. Despite several recent theoretical developments in polariton chemistry[11], accurately and efficiently simulating polaritonic dynamics and non-linear spectroscopy remains an open challenge in theoretical chemistry. Existing works often rely on perturbative treatments, and they often lack proper system-bath correlated dynamics and proper treatments of cavity loss.

**Theoretical background:**

1. **Linear Response Spectroscopy**
   1. If the light-matter interaction is very weak compared to the matter energy scales, it can be treated semiclassically as a perturbation to the matter Hamiltonian. With this treatment, we can effectively extract the system's dynamical properties by studying the system's evolution in the interaction picture. We can then expand the nth-order density matrix for an nth-order perturbation as,
2. **PLDM + Lindblad dynamics**
3. **Spectra simulations**

**Projects / Hypothesis:**

1. **Coherence Enhancement**
2. **Polaron Decoupling**
3. **Involvement of dark states**
4. **Polariton transport**

**Results:**

1. **Monomer in cavity**
2. **Dimer in cavity**
3. **N-molecules in cavity**

**Project Goals:**

1. **Short term goals**
2. **Long term goals**