PHD PROJECT DESCRIPTION

(4000 characters max., including the aims and work plan to de published online)

Project title:

Nonadiabatic Dynamics of Molecular Polaritons: Relaxation Pathways under Strong Light-Matter Coupling

1.1. Project goals

The primary objective of this project is to elucidate the fundamental mechanisms governing polaritonic relaxation in molecular systems under strong light–matter coupling using nonadiabatic molecular dynamics. In such hybrid systems, the formation of polaritonic states modifies potential energy landscapes and opens novel relaxation pathways that are not accessible in purely molecular or photonic regimes. While recent studies have explored polaritonic potential energy surfaces, a consistent nonadiabatic dynamical treatment of relaxation processes remains underdeveloped. Despite increasing experimental interest, a detailed mechanistic understanding of how energy redistributes among electronic, nuclear, and photonic degrees of freedom is still lacking. This project aims to address this gap by developing a rigorous theoretical and computational framework capable of capturing these coupled processes beyond the Born–Oppenheimer approximation.
A central goal is the development and validation of nonadiabatic molecular dynamics methodologies adapted to polaritonic systems, followed by their application to realistic molecular models using first-principles electronic structure methods. We hypothesize that strong light–matter coupling can alter the topology and strength of nonadiabatic couplings near molecular avoided crossings and conical intersections, thereby opening cavity-controlled relaxation pathways between polaritonic states. By systematically progressing from model Hamiltonians to ab initio descriptions, the project will identify key factors controlling relaxation dynamics, such as light–matter coupling strength, cavity mode characteristics, and vibronic interactions, and will quantify relaxation pathways through population dynamics, branching ratios, and energy transfer timescales. Ultimately, the work seeks to establish predictive insight into polaritonic relaxation mechanisms and enable rational control of excited-state dynamics and photochemical reactivity in strongly coupled systems.

1.2. Outline

The project will proceed in two main stages. First, a theoretical and computational framework for nonadiabatic dynamics in polaritonic systems will be developed and tested using model Hamiltonians (simplified molecular–cavity systems). In the second stage, the methodology will be extended to ab initio simulations of realistic molecular systems strongly coupled to quantized photon modes, enabling the investigation of polaritonic relaxation mechanisms under chemically relevant conditions. The results from both stages will be integrated to provide a consistent mechanistic picture across different levels of theory.

1.3. Work plan

The project will begin with the formulation of a polaritonic Hamiltonian incorporating electronic, nuclear, and photonic degrees of freedom within a cavity quantum electrodynamics (QED) framework. This will involve constructing model systems where light–matter coupling can be systematically tuned and where nonadiabatic couplings between polaritonic states can be explicitly analyzed. A trajectory-based nonadiabatic dynamics scheme will be extended to operate in the polaritonic basis, including appropriate treatment of decoherence effects and population transfer between hybrid states.

In the second phase, the developed methodology will be interfaced with ab initio electronic structure methods to generate on-the-fly potential energy surfaces and couplings in the presence of cavity modes. Simulations will be performed to investigate relaxation pathways, population dynamics, and energy redistribution mechanisms in representative molecular systems. Particular attention will be given to the role of vibronic coupling, cavity frequency, and coupling strength in shaping relaxation dynamics. The computational results will be analyzed to extract mechanistic insights and, where possible, compared with available experimental observations or simplified theoretical models.

1.4. Literature (max. 7 listed as a suggestion for a PhD candidate preliminary study)

1. M. Ruggenthaler, D. Sidler, A. Rubio. Understanding Polaritonic Chemistry from Ab Initio Quantum Electrodynamics. *Chem Rev.* (2023) **123**, 11191-11229. https://doi.org/10.1021/acs.chemrev.2c00788
2. B. M. Weight, P. Huo. Ab Initio Approaches to Simulate Molecular Polaritons and Quantum Dynamics. *Wiley Interdisciplinary Reviews: Computational Molecular Science*. (2025) **15**, e70039. https://doi.org/10.1111/wcms.70039
3. A. Mandal, M. A. D. Taylor, B. M. Weight, E. R. Koessler, X. Li, P. Huo. Theoretical Advances in Polariton Chemistry and Molecular Cavity Quantum Electrodynamics. *Chem. Rev.* (2023) **123**, 9786-9879. https://doi.org/10.1021/acs.chemrev.2c00855
4. G. Groenhof, C. Climenti, J. Feist, D. Morozov, J. J. Toppari. Tracking Polariton Relaxation with Multiscale Molecular Dynamics Simulations. *J. Phys. Chem. Lett.* (2019) **10**, 5476-5483. https://doi.org/10.1021/acs.jpclett.9b02192
5. R. H. Tichauer, J. Feist, G. Groenhof. Multi-scale dynamics simulations of molecular polaritons: The effect of multiple cavity modes on polariton relaxation. *J. Chem. Phys.* (2021) **154**, 104112. https://doi.org/10.1063/5.0037868
6. J. B. Pérez-Sánchez, J. Yuen-Zhou. Polariton Assisted Down-Conversion of Photons via Nonadiabatic Molecular Dynamics: A Molecular Dynamical Casimir Effect. *J. Phys. Chem. Lett.* (2020) **11**, 152-159. https://doi.org/10.1021/acs.jpclett.9b02870

1.5. Required initial knowledge and skills of the PhD candidate

The candidate should have a solid background in chemical physics, with particular emphasis on methods for the description of excited electronic states. Prior experience with theoretical models of light-matter coupling is advantageous. Proficiency in Python programming is required, along with the ability to work with scientific computing environments. The candidate is expected to demonstrate strong communication skills in English, both written and spoken, as well as a high level of motivation and the ability to work effectively both independently and as part of a research team.

1.6. Expected development of the PhD candidate's knowledge and skills

The proposed PhD project will provide comprehensive and interdisciplinary training at the interface of theoretical chemistry, chemical physics, and computational modeling of light-matter interactions, equipping the candidate with advanced competencies relevant to both academic research and innovation-driven industry.

During the course of the project, the candidate will:

- Acquire advanced knowledge of excited-state processes, nonadiabatic molecular dynamics, and polaritonic phenomena in strongly coupled light–matter systems.
- Gain a solid understanding of cavity quantum electrodynamics (QED) in molecular systems, including the construction and analysis of polaritonic potential energy surfaces.
- Learn to bridge model Hamiltonian approaches and first-principles electronic structure methods, enabling multiscale investigation of complex dynamical processes.
- Strengthen skills in scientific programming (Python), numerical modeling, and high-performance computational workflows relevant to modern theoretical chemistry.

In parallel, the candidate will develop key transferable skills by:

- Enhancing scientific communication through presentations at group meetings, doctoral training events, and international conferences.
- Developing high-level scientific writing skills through the preparation of publications in peer-reviewed journals.
- Building independence in research planning, problem-solving, and critical analysis of complex theoretical models and simulation data.
- Gaining experience in project organization, reproducibility, and data management, aligned with best practices in computational research.

The training provided within this project will prepare the candidate for a versatile career path, offering strong prospects in academia as well as in industry sectors requiring advanced computational expertise, including pharmaceutical research, materials science, photonics, and emerging quantum technologies.