NICOLAUS COPERNICUS
UNIVERSITY
IN TORUŃ
Doctoral Schools

Doctoral School of Exact and Natural Sciences

PHD PROJECT DESCRIPTION

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

Project title: PhotoInter

1. Project goals

The primary objective of this project is to develop a rigorous perturbation-theory-based framework for describing intermolecular interactions in the presence of photons — both in electronically excited states and under strong light–matter coupling conditions relevant to polaritonic chemistry. Modelling the dynamics of photoexcited systems is of extreme importance in many areas of physics and chemistry, including photosynthesis, the design of OLED materials, and understanding the photostability of organic and biochemically relevant molecules under UV light. In many of these applications, the interaction between the photoactive site and its environment — a solvent, an amorphous matrix, or a structured surface — plays a decisive role. While excited-state methods such as TDDFT, ADC(2), and CC2 can provide total interaction energies via supermolecular calculations, a physically transparent decomposition of intermolecular interactions involving excited-state species into electrostatic, exchange, induction, and dispersion components remains largely unavailable. This project aims to fill this gap by extending Symmetry-Adapted Perturbation Theory (SAPT) to excited-state complexes and, subsequently, to the polaritonic regime.

A central goal is the development and implementation of excited-state SAPT capable of describing how electronic excitation modifies each fundamental component of the intermolecular interaction. We hypothesize that excitation-induced changes in molecular charge distributions and polarizabilities will lead to qualitatively different balances of interaction energy components, providing insight inaccessible to supermolecular approaches alone. In the second part of the project, the SAPT formalism will be further generalized to incorporate quantized photon modes within a cavity quantum electrodynamics framework. This polaritonic SAPT will allow us to answer the fundamental question of how optical nanocavities can alter and control interactions between molecules. By systematically progressing from excited-state dimers to cavity-coupled systems, the project will identify how light–matter coupling strength, cavity mode frequency, and molecular electronic structure jointly shape the individual components of the intermolecular interaction, ultimately establishing a new theoretical toolbox for rational design in polaritonic chemistry.

There are two papers on the subject of the thesis. In Pernal group the SAPT(MC) theory was developed recently but theory does not apply for cases near the conical intersections and cannot work efficiently for large systems due to MCSCF limitations. Secondly, the topic molecular interactions in cavity in two papers from Koch's group so far, but the field is merely emerging.

2. Outline and Plan of the Work

The project will proceed in two interconnected stages, both built upon pythonic quantum chemistry codes (Psi4 and PyBeSt) and leveraging automatic code generation for the derivation and implementation of working equations.
In the first stage, we will develop SAPT for intermolecular interactions involving electronically excited monomers. The starting point will be a CIS description of the excited monomer, for which the SAPT expressions will be derived and implemented. The formalism will then be extended to TDDFT-based monomer descriptions, and, if time permits, to ADC(2) wavefunctions. The resulting interaction energy decompositions will be benchmarked against SAPT(MC) based on CASSCF references — a more demanding approach due to the strong orbital dependence of multiconfigurational wavefunctions. A particular focus will be placed on conical intersection and avoided crossing regions, where the standard single-state SAPT breaks down and a degenerate formulation is required. We have recently developed the

necessary degenerate SAPT framework, which will be extended and applied to excited-state complexes in these critical regions of the potential energy surface.

In the second stage, we will formulate polaritonic SAPT by introducing a quantized bosonic photon field into the intermolecular perturbation theory framework. The plan minimum is the derivation and implementation of the dispersion (van der Waals) interaction component in the presence of cavity photon modes. This approach parallels recent developments by the Koch and Rubio groups, who incorporated quantized photon fields into coupled-cluster (CCSD) and equation-of-motion (EOM-CCSD) theories within the cavity QED framework. We will adapt a similar strategy to the SAPT formalism, deriving how the photonic degrees of freedom modify the long-range intermolecular interaction and exploring how cavity parameters can be used to tune dispersion forces between molecules. The computational results from both stages will be analyzed to extract physical insights into photon-modified intermolecular interactions and their implications for polaritonic chemistry.

Milestones: M1: Implementation of SAPT(CIS) M2: Test of SAPT(CIS) for excited states of selected molecules; M3: Development of polaritonic SAPT in the first order M4: Development of dispersion interaction theory in the polaritonic regime

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

M. Hapka, M. Przybytek, and K. Pernal, "Symmetry-Adapted Perturbation Theory Based on Multiconfigurational Wave Function Description of Monomers," J. Chem. Theory Comput. 17(9), 5538–5555 (2021). doi: 10.1021/acs.jctc.1c00344.

B. Tyrcha, F. Brzęk, and P. S. Żuchowski, "Second quantization-based symmetry-adapted perturbation theory: Generalizing exchange beyond single electron pair approximation," J. Chem. Phys. 160(4), 044118 (2024). doi: 10.1063/5.0184750.

T. S. Haugland, C. Schäfer, E. Ronca, A. Rubio, and H. Koch, "Intermolecular Interactions in Optical Cavities: An ab Initio QED Study," J. Chem. Phys. 154, 094113 (2021). doi: 10.1063/5.0039256

T. S. Haugland, E. Ronca, E. F. Kjønstad, A. Rubio, and H. Koch, "Coupled Cluster Theory for Molecular Polaritons: Changing Ground and Excited States," *Phys. Rev. X* 10, 041043 (2020). doi:10.1103/PhysRevX.10.041043.

J. P. Philbin, T. S. Haugland, T. K. Ghosh, E. Ronca, M. Chen, P. Narang, and H. Koch, "Molecular van der Waals Fluids in Cavity Quantum Electrodynamics," J. Phys. Chem. Lett. 14(40), 8988–8993 (2023). doi: 10.1021/acs.jpclett.3c01790.

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

4. Required initial knowledge and skills of the PhD candidate

The candidate should have a background in chemical physics, with particular emphasis on methods for the description of many-body quantum systems. Second quantisation theory is another important piece. The knowledge of light-matter coupling. Experience 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.

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

The proposed PhD project will provide interdisciplinary training at the interface of theoretical chemistry, quantum physics, and computational modeling, equipping the candidate with competencies relevant to both academic research and industry. During the course of the project, the candidate will:
a) Acquire advanced knowledge of intermolecular interaction theory, symmetry-adapted perturbation theory, and excited-state electronic structure methods.
b) Gain a solid understanding of cavity quantum electrodynamics (QED) and the theory of light-matter interactions
c) Learn to bridge perturbative approaches with first-principles electronic structure methods (TDDFT, ADC(2), EOM-CCSD) for the description of complex molecular systems.
d) Strengthen skills in scientific programming (Python), automatic code generation for many-body theories, and high-performance computational workflows.

The training will prepare the candidate for a career in academia as well as in industry sectors requiring advanced computational expertise in machine learning, materials science, photonics, and quantum technologies.