

Q 7: Polaritonic Effects in Molecular Systems I (joint session MO/Q)

Time: Monday 11:00–13:00

Location: HS XV

Q 7.1 Mon 11:00 HS XV

Changes in excimer properties under collective strong coupling — ●MATTEO CASTAGNOLA, MARCUS TAKVAM LEXANDER, and HENRIK KOCH — Department of Chemistry, Norwegian University of Science and Technology, 7491 Trondheim, Norway

The interplay between the local molecular dynamics and the collective polaritonic excitation is a fundamental but challenging aspect of polaritonic chemistry. While light-matter strong coupling has been proven to affect chemical properties, the underlying mechanism is still unclear. We employ a recently developed electronic-structure method for collective strong coupling to study the argon excimer, providing a simple prototype for a more general discussion on excimer properties. The computed potential energy surface exhibits a region where electronic, nuclear, and photonic degrees of freedom are strongly intertwined, and we analyze their coupling. Collective strong coupling produces an abrupt transition in the excited state's vibrational landscape, causing the higher vibrational levels to behave similarly to the ground state vibrations. We thus find that collective strong coupling inhibits the formation of the excimer once the collective coupling exceeds a critical value. We propose this is a general feature of excimers under collective strong coupling, which could be investigated by recording absorption and emission spectra, offering an additional facet of polaritonic chemistry.

Q 7.2 Mon 11:15 HS XV

Quantized embedding approaches for collective strong coupling – and what about Coulomb? — FRIEDER LINDEL^{1,2}, DOMINIK LENTRODT², STEFAN BUHMANN³, and ●CHRISTIAN SCHÄFER⁴ — ¹Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain — ²Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Hermann-Herder-Straße 3, D-79104 Freiburg, Germany — ³Institut für Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany — ⁴Department of Physics, Chalmers University of Technology, 41296 Göteborg, Sweden

Collective light-matter interactions have been used to control chemistry and energy transfer, yet accessible approaches that combine ab initio methodology with large many-body quantum optical systems are missing due to the fast increase in computational cost for explicit simulations. We introduce such an accessible ab initio quantum embedding concept for many-body quantum optical systems that allows us to treat the collective coupling of molecular many-body systems effectively in the spirit of macroscopic quantum electrodynamics while keeping the rigor of ab initio quantum chemistry for the molecular structure [1]. We illustrate the underlying assumptions by comparison to the Tavis-Cummings model and highlight the importance of Coulombic interactions between emitter and solvent molecules, as well as their potential interplay in collective strong coupling [2].

[1] J. Chem. Phys. 161, 154111 (2024). [2] J. Phys. Chem. Lett. 2024, 15, 1428-1434.

Q 7.3 Mon 11:30 HS XV

Simulation of polaritons in real cavities through a semiclassical approach — ●CARLOS BUSTAMANTE¹, FRANCO BONAFÉ¹, MICHAEL RUGGENTHALER¹, MAXIM SUKHAREV², ABRAHAM NITZAN³, and ANGEL RUBIO¹ — ¹Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany — ²Department of Physics, Arizona State University, Tempe, Arizona, USA — ³Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, USA

The strong coupling between light and matter reached within optical cavities has opened a new path to modify material properties and chemical reactions. For chemical effects, this strong coupling condition may be achieved when the photonic modes of the cavity resonate with molecular vibrations or electronic transitions, leading to vibrational strong coupling (VSC) and electronic strong coupling (ESC) respectively, creating a hybrid state between light and matter called polaritons. Although this research area is rapidly expanding, the simulation of a realistic experimental setup, capturing all relevant factors, remains a challenge. Our study proposes a semiclassical approach involving the propagation of Maxwell equations on a grid, while incorporating tens to hundreds of molecules using the quantum mechanical simulation

software DFTB+. By modelling the mirrors with the Drude permittivity, we can integrate them into the setup to emulate a Fabry-Perot cavity. Our results demonstrate that our setup can accurately represent various experimental observations, including Rabi-splitting and collective effects.

Q 7.4 Mon 11:45 HS XV

Analytic model reveals local molecular polarizability changes induced by collective VSC — ●JACOB HORAK^{1,2}, DOMINIK SIDLER^{1,2,3}, THOMAS SCHNAPPINGER⁴, MICHAEL RUGGENTHALER^{1,2}, and ANGEL RUBIO^{1,2,5} — ¹Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany — ²The Hamburg Center for Ultrafast Imaging, Hamburg, Germany — ³Paul Scherrer Institut, Villigen, Switzerland — ⁴Stockholm University, Stockholm, Sweden — ⁵The Flatiron Institute, New York, USA

Despite recent numerical evidence, one of the fundamental theoretical mysteries of polaritonic chemistry is how and if collective strong coupling can induce local changes of the electronic structure to modify chemical properties. Here we present non-perturbative analytic results for a model system consisting of an ensemble of N harmonic molecules under vibrational strong coupling (VSC) that alters our present understanding of this fundamental question. We discover that the electronic molecular polarizabilities are modified even in the case of vanishingly small single-molecule couplings. Consequently, this non-perturbative local polarization mechanism persists even in the large- N limit. In contrast, a perturbative calculation of the polarizabilities leads to a qualitatively erroneous scaling behavior with vanishing effects in the large- N limit. Our fundamental theoretical observations demonstrate that hitherto existing collective-scaling arguments are insufficient for polaritonic chemistry / physics.

Q 7.5 Mon 12:00 HS XV

Polaritonic Molecular Orbitals — ●YASSIR EL MOUTAOUKAL — Norwegian University of Science and Technology, 7491 Trondheim, Norway

A comprehensive understanding of electron-photon correlation is essential for describing the reshaping of molecular orbitals in quantum electrodynamics (QED) environments.

The strong coupling QED Hartree-Fock (SC-QED-HF) theory tackles these aspects by providing consistent molecular orbitals in the strong coupling regime. The previous implementation, however, displays significant convergence issues.

In this talk I present how these limitations can be overcome by capturing the coupling between the electron-photon dressing parameters, enhancing the modeling of large molecular systems coupled to electromagnetic vacuum fluctuations.

The development of more correlated methods and response theory using the SC-QED-HF reference wavefunction are now possible and currently in development, as well as the extension to a multi-mode Hamiltonian and chiral cavities.

Q 7.6 Mon 12:15 HS XV

Higher excitations manifolds in the Tavis-Cummings model for multi-level systems — ●LUCAS BORGES, THOMAS SCHNAPPINGER, and MARKUS KOWALEWSKI — Department of Physics, Stockholm University, Stockholm, Sweden

The Tavis-Cummings model describes the interaction of multiple quantum emitters, such as atoms or molecules, with the quantized electromagnetic field modes of an optical cavity, leading to the emergence of polariton states (eigenstates of the coupled system). Most studies focus on the first excitation manifold, which includes states with a single excitation (one photon or one excited atom). The polariton states within this manifold are well separated into bright and dark states.

However, molecular ensembles in a cavity may carry multiple excitations, thus requiring the inclusion of higher excitation manifolds. We present a study of a system of N three-level systems coupled to a single lossy cavity mode, truncating the Hamiltonian to the N th excitation manifold. The system models a molecular ensemble, where two levels are directly coupled to the cavity, while the third level is weakly coupled to the second energy level. We show that when a fraction of the system's excitations initially reside in these third levels, the cavity mediates its decay to the ground state, revealing a new pathway

influenced by the cavity dynamics.

Q 7.7 Mon 12:30 HS XV

Relativistic quantum electrodynamical density functional theory beyond ideal cavities — •LUKAS KONECNY¹, MARK KAMPER SVENDSEN^{2,3}, VALERIA KOSHELEVA³, MICHAEL RUGGENTHALER³, and ANGEL RUBIO³ — ¹Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, UiT The Arctic University of Norway, Tromsø, Norway — ²NNF Quantum Computing Programme, Niels Bohr Institute, Copenhagen, Denmark — ³Max Planck Institute for the Structure and Dynamics of Matter, Center for Free Electron Laser Science, Hamburg, Germany

Quantum electrodynamical density functional theory (QEDFT) is one of the computational methods that combine quantum chemical treatment of matter with quantized description of light. This allows to describe the effect of strong coupling of matter to photonic modes while preserving the accuracy necessary for chemical and spectroscopic applications together with the favourable computational cost associated with density functional theory. Building on recently introduced relativistic QEDFT based on the four-component Dirac–Coulomb Hamiltonian we extend the methodology beyond idealized single-mode Fabry–Pérot cavities to the interaction with a quasi continuum of photonic modes that enables the description of realistic cavities as well as radiative decay via the coupling to vacuum modes while the relativistic approach to electronic structure enables accurate treatment of heavy elements and effects of spin–orbit coupling

such as singlet–triplet transitions. Thus we expand the applicability of QEDFT into new domains.

Q 7.8 Mon 12:45 HS XV

Impact of dipole self-energy on cavity-induced nonadiabatic dynamics — CSABA FÁBRI^{1,2}, GÁBOR J. HALÁSZ³, LORENZ S. CEDERBAUM⁴, and •ÁGNES VIBÓK¹ — ¹HUN-REN-ELTE Complex Chemical Systems Research Group, Budapest, Hungary — ²Department of Theoretical Physics, Debrecen University, Debrecen, Hungary — ³Institute of Informatics, Debrecen University, Debrecen, Hungary — ⁴Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Heidelberg, Germany

The coupling of matter to the quantized electromagnetic field of a plasmonic or optical cavity can be harnessed to modify and control the chemical and physical properties of molecules. In optical cavities, a term known as the dipole self-energy (DSE) appears in the Hamiltonian to assure gauge invariance.

We study the impact of the DSE on cavity-induced nonadiabatic dynamics in a realistic system. For that purpose, various matrix elements of the DSE are computed as functions of the nuclear coordinates and the dynamics of the system after laser excitation is investigated. The cavity is known to induce conical intersections between polaritons, which gives rise to substantial nonadiabatic effects. The DSE is shown to slightly affect these light-induced conical intersections and, in particular, break their symmetry.