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On the interface of quantum electrodynamics and electronic structure theory: Cavity QED

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List of Publications (as introduced)

P1 Christian Schäfer, Michael Ruggenthaler, Vasilis Rokaj, and Angel Rubio,
Relevance of the quadratic diamagnetic and self-polarization terms in cavity quantum electrodynamics, [1],
ACS Photonics 2020, 7(4), 975-990.

P2 Christian Schäfer, Michael Ruggenthaler, and Angel Rubio,
Ab initio nonrelativistic quantum electrodynamics: Bridging quantum chemistry and quantum optics from weak to strong coupling, [2],
PHYSICAL REVIEW A 98, 043801 (2018).

P3 Christian Schäfer, Michael Ruggenthaler, Heiko Appel, and Angel Rubio,
Modification of excitation and charge transfer in cavity quantum-electrodynamical chemistry, [3],
PNAS March 12, 2019 116 (11) 4883-4892.

P4 Johannes Flick, Christian Schäfer, Michael Ruggenthaler, Heiko Appel, and Angel Rubio,
Ab Initio Optimized Effective Potentials for Real Molecules in Optical Cavities: Photon Contributions to the Molecular Ground State, [4],
ACS Photonics 2018, 5, 992-1005.

P5 Soeren Ersbak Band Nielsen, Christian Schäfer, Michael Ruggenthaler, and Angel Rubio,
Dressed-Orbital Approach to Cavity Quantum Electrodynamics and Beyond, [5],
arXiv:1810.00388. Under restructuring after reports from PRL.

P6 Norah M. Hoffmann, Christian Schäfer, Angel Rubio, Aaron Kelly, and Heiko Appel,
Capturing vacuum fluctuations and photon correlations in cavity quantum electrodynamics with multitrajectory Ehrenfest dynamics, [6],
PHYSICAL REVIEW A 99, 063819 (2019).

P7 Norah M. Hoffmann[†], Christian Schäfer[†], Niko Säkkinen, Angel Rubio, Heiko Appel, and Aaron Kelly,
Benchmarking semiclassical and perturbative methods for real-time simulations of cavity-bound emission and interference, [7],
J. Chem. Phys. 151, 244113 (2019).

[†] Those authors contributed equally.

Not part of this cumulative thesis but noteworthy:

P8 Nicolas Tancogne-Dejean, Micael J. T. Oliveira, Xavier Andrade, et al.
Octopus, a computational framework for exploring light-driven phenomena and quantum dynamics in extended and finite systems, [8],
J. Chem. Phys. 152 (12), 124119 (2020).

Contribution to publications

P1 With the investigations around [9], P4, and P2, the relevance of the different quadratic contributions for the stability of the light-matter coupled system manifested. The vibrant exchange with a broad community consisting of quantum opticians, mathematicians and quantum chemists, lead to the realization among A. Rubio, C. Schäfer, and M. Ruggenthaler that a clear derivation of the physical meaning and impact of the quadratic components was demanded. C. Schäfer and M. Ruggenthaler shaped in close exchange with V. Rokaj and A. Rubio the didactic storyline, consisting of analytic and numerical arguments. C. Schäfer and M. Ruggenthaler prepared a first draft, all authors edited the manuscript.

P2 Driven by curiosity, C. Schäfer investigated extensions of the Born-Huang expansion into the strongly correlated domain. In various discussions with A. Rubio and M. Ruggenthaler, the precise direction and form of the publication was shaped. C. Schäfer wrote the first draft, all authors edited the manuscript.

P3 Recent experimental progress showed that energy transfer (charge and excitation energy) could be altered in cavity environments. In an attempt to complement previous model-system calculations, we aimed to investigate those processes (possible physical mechanisms, their maximum efficiency, the role of correlation and intermolecular distance) from a real-space perspective. The conceptual approach was designed dominantly by C. Schäfer and A. Rubio. C. Schäfer, M. Ruggenthaler, H. Appel, and A. Rubio contributed to the interpretation of the collected data and edited the manuscript. C. Schäfer wrote the first draft.

P4 The numerical limitations of the photonic OEP equation [10] demanded a clever reduction of computational complexity for realistic applications. J. Flick and C. Schäfer investigated various approaches that arose within discussions between J. Flick and C. Schäfer, M. Ruggenthaler, H. Appel, and A. Rubio. Interpretation and conclusion of encountered obstacles and obtained results were discussed among all authors. J. Flick and C. Schäfer wrote the first draft, all authors edited the manuscript.

P5 Quantum electrodynamic density-functional theory (QEDFT) demands a cleverly designed local potential that is, as historically proven, nontrivial to obtain, especially when strong correlation plays a role. Taking inspiration in the conception behind quasiparticles, foremost A. Rubio and M. Ruggenthaler triggered the investigation of the possibility to define a functional approach based on dressed orbitals. SEB Nielsen, C. Schäfer and M. Ruggenthaler tackled the encountering obstacles analytically and numerically. All authors proved essential during various discussions. SEB Nielsen, C. Schäfer and M. Ruggenthaler prepared a first draft, all authors edited the manuscript.

P6 The obvious similarity of phononic and bosonic modes lead to discussions among N. Hoffmann, C. Schäfer, A. Kelly, A. Rubio, and H. Appel how one would redesign common semiclassical methods to describe the light-matter interaction, especially from the point of view of the photonic field. Encountered obstacles, such as the normal ordering, and the interpretation of data were discussed among all authors. N. Hoffmann and C. Schäfer prepared a first draft, all authors edited the manuscript.

P7 Motivated by the good performance of the MTEF ansatz of P6, N. Hoffmann, C. Schäfer, A. Kelly, A. Rubio, and H. Appel decided to extend the previous investigations and look into the realm of quantum correlation from a semiclassical but also quantum perspective. N. Hoffmann, C. Schäfer, N. Säkkinen and A. Kelly utilized the various employed methodologies with the goal to benchmark and characterize the capability of each method. During this extended time frame, constant communication between N. Hoffmann, C. Schäfer, N. Säkkinen, A. Rubio, H. Appel, and A. Kelly influenced the scientific progress on all levels and culminated in the final manuscript. N. Hoffmann and C. Schäfer prepared a first draft, all authors edited the manuscript.

P8 The numerical methods employed in P4 were implemented into the massively parallelized real-space code OCTOPUS. This implementation is part of the invited comprehensive paper addressing novel features in OCTOPUS. J. Flick and C. Schäfer prepared a first draft of the specific subsection, N. Tancogne-Dejean, M. Oliveira, and A. Rubio designed the paper and environment around the specific sections. All authors edited the manuscript.

Contents

1 Deutsche Zusammenfassung

Wenn Licht durch Spiegel auf kleinem Raum, als Kavität bezeichnet, eingesperrt und kontrolliert wird kann die Interaktion mit Materie so signifikant werden, dass sogar neue ‚Teilchen', die polaritonischen Quasiteilchen, erzeugt werden. Polaritonen, weder ganz Licht noch ganz Materie, teilen essentielle Eigenschaften mit beiden Spezies. So verfügen sie über die Flinkheit des Lichts, welche uns die unvergleichlich schnelle Übermittlung von Informationen und Energie ermöglicht, und die Robustheit und Widerstandsfähigkeit von Materie, uns schaffend und von uns geschaffen. Kontrolle über die Polaritonen hält gewaltige technologische Möglichkeiten bereit, sei es durch die Manipulation der Regeln der Chemie oder die Eigenschaften von Materie. Innerhalb dieser Dissertation werde ich den bahnbrechenden Fortschritt der aktuellen Forschung sowie meinen Anteil daran beleuchten. Letzterer zeichnet sich zu allererst dadurch aus, dass er die Forschungsgemeinschaft mit der unvoreingenommenen Perspektive ausstattet, die Notwendig ist, um die im neuen Kontext unzutreffenden theoretischen Paradigmen zu überwinden.

Unsere Reise beginnt mit einer kurzen Einführung (Kapitel 3) in das neue Forschungsgebiet um die starke Wechselwirkung eingeschlossener Felder mit Materie, auch bezeichnet als Kavitäts-Quanten-Elektrodynamik (QED) oder QED Chemie. Von dort aus werden wir Schritt für Schritt das notwendigste Wissen gewinnen um QED zu verstehen (Kapitel 4), wie die zentrale nicht-relativistische Gleichung der QED, die Pauli-Fierz Gleichung, üblicherweise bearbeitet wird, und, dass es nicht trivial ist übliche Herangehensweisen mit dem neuen Bereich zu verknüpfen. Letzteres ergibt sich aus der Tatsache, dass übliche Schritte, wie zum Beispiel die Einschränkung auf nur wenige Zustände, die Drehwellennäherung und die Vernachlässigung von quadratischen Anteilen in der Wechselwirkung hinterfragt werden müssen wenn wir anstreben selbstkonsistent das korrelierte System ohne vorherige Annahmen zu beschreiben. Dieser Prozess wird die Publikationen P1, P2 und Teile von P3 einführen, welche in ihrem vollen Umfang in Kapitel 8 zu finden sind. Das darauf folgende Kapitel 5 beinhaltet eine Einführung zu der (nicht-)Gleichgewichtsstruktur der Materie und insbesondere hierzu entsprechende Methoden die zu ihrer Beschreibung konzipiert wurden. Dies wird ebenfalls die quantumelektrodynamische Dichtefunktionaltheorie (QEDFT) beinhalten, welche eine Erweiterung der Dichtefunktionaltheorie (DFT) durch das Einbeziehen der photonischen Freiheitsgrade ist, sowie erste Schritte die in den Publikationen P4 und P5 unternommen wurden. Ausgestattet mit einem Werkzeug um realistische System zu beschreiben, dennoch eingeschränkt in ihrer Größe, setzen wir in Kapitel 5.2 unsere Reise zu (semi)klassischen und perturbativen Ansätzen fort. Diese Methoden könnten uns erlauben größere Systeme zu beschreiben als zuvor. Dabei werden wir beobachten wie Ehrenfestmethoden angewendet werden können um photonische Felder zu beschreiben sofern die Phaseninformation letzterer weniger relevant ist (Publikation P6) und wie fortgeschrittene Ansätze diese teilweise wiederherstellen (Publikation P7). Durch ausgiebige Vergleiche mit exakten und perturbativen Ansätzen, welche der reduzierten Dichtematrixhierarchie (BBGKY) folgen, gewinnen wir Einsichten, welchem dieser Wege in Zukunft besonderes Interesse entgegengebracht werden sollte.

Methodik ohne den Gewinn physikalischer Einsichten ist brotlose Kunst und so sammelt Kapitel 6 einige der aussichtsreichsten Anwendungen von Kavitäts-QED. Darin ist mitunter enthalten wie Verschränkung, Ladung, und ihr Transfer zwischen Bestandteilen durch die starke Licht-Materie Wechselwirkung modifiziert werden können (Publikationen P3, P4 und P2). Die Kontrolle chemischer Reaktionen mittels vibronischer starker Kopplung (VSC), die Manipulation von Materie durch chirales, kohärentes Treiben oder der Konstruktion von Kavitäten, sowie kollektive ultrastarke Licht-Materie Wechselwirkung bieten vielversprechende Aussichten. Kapitel 7 wird sich letztlich in aller Kürze mit Studien beschäftigen die aus dieser Arbeit resultieren und sich bereits im Prozess der Ausarbeitung befinden.

2 Abstract

When light is confined and controlled in a restricting geometry, referred to as cavity, the way how light and matter affect each other reaches such significant levels that even novel species, the polaritonic quasiparticles, are created. They inherit the swiftness of light, incomparable speed of information and energy transfer, and the tenacity of matter, shaping and being shaped by our existence. Control over the polaritonic quasiparticles holds great technological promises, e.g. by altering the rules on which chemistry evolves and materials are characterized. Within this work, I will highlight the breathtaking progress of state-of-the-art research as well as my contribution. The latter foremost provides the community with the highly demanded untainted perspective as many previous theoretical paradigms render obsolete on the interface of quantum chemistry and optics.

The journey will start with a brief introduction (Sec. 3) into the novel field of research around the strong interaction of confined fields with matter, often referred to as cavity quantum electrodynamics (QED) or QED chemistry. From there on, we will little by little attain the necessary knowledge to understand QED (Sec. 4), how the central equation of non-relativistic QED, the Pauli-Fierz equation, is commonly approached and that interfacing the most common approaches is entirely nontrivial. The latter arises from the fact that common steps, such as the few-level approximation, the rotating-wave approximation and neglecting quadratic interaction terms have to be scrutinized when we attempt to self-consistently describe the correlated system from first principles. This will introduce the publications P1, P2 and parts of P3 that the reader can find in their full extent in Section 8. In the following Section 5, we introduce the reader to the (non)equilibrium structure of matter and especially the methodologies we design to enable their description. This will include quantum electrodynamics density-functional theory (QEDFT), the extension of density-functional theory (DFT) to include the photonic degrees of freedom, and the first steps that this method is undertaking in publications P4 and P5. Equipped with a tool to describe realistic systems, that we yet have to limit in size, we move our attention in Subsection 5.2 to semiclassical and perturbative methods. Those might enable us to scale the size of systems that we will be able to describe. We will see that Ehrenfest methods can be applied to describe the photonic fields when phase-information is of less relevance (publication P6) and how parts of this information can be restored by advanced semiclassical methods (publication P7). By benchmarking those semiclassical methods against exact and perturbative approaches, that follow the reduced density matrix (BBGKY) hierarchy, we are able to highlight which path might be most promising for future steps. Methodology without physical gain is fruitless science and Section 6 collects a set of the most promising applications of cavity QED. This includes how entanglement, energy, charge and their transfer among constituents can be modified by the strong light-matter interaction (publication P3, P4 and P2). The control of chemical reactions via vibrational strong coupling (VSC), the manipulation of matter via chiral, coherent driving or cavity design and collective ultra-strong light-matter interaction provide exciting perspectives. Section 7 briefly illustrates on-going studies originating from this work.

3 The emerging relevance of cavity quantum electrodynamics

IMAGINE a world electrified with renewable energy from highly efficient photo voltaic installations. Light and efficient energy storage and a novel age of virtuous microstructure creation enabled by the pinpoint control of energy flow and the structure of matter itself. A novel age of computation and communication, enabled by quantum information, entanglement and topology. Delivering those desperately demanded tools into the right hands, mankind would be equipped to tackle so many of the pressing issues holding back this world. Understanding and controlling the interaction between light and matter will turn imagination into reality, unfortunately an entirely nontrivial problem.

As fundamental theory of the electromagnetic interaction, quantum electrodynamics (QED) is essential to describe and understand the interaction of charged particles. Its gauge boson, mediator of the electromagnetic interaction, is the photon. QED is a relatively simple gauge theory with U1 symmetry, i.e. it conserves charge. During its long existence, QED proved to be exceptionally accurate and the best tested theoretical description of physics by predicting e.g. the anomalous magnetic dipole moment of the electron to breathtaking precision (e.g. [11]). While part of its beauty is the covariant, i.e. relativistic, compatibility of Dirac's equation and Maxwell's equations, within this work we will focus on the non-relativistic limit of the corresponding quantized theory. This limit is justified as bound molecular systems and field frequencies discussed in this work posses vanishingly small relativistic features. We therefore approximate the description of matter with the Schödinger equation and the photonic gauge field will give rise to interactions among the non-relativistic particles (see P1).

A variety of different approaches (gauges) are available to precisely characterize the occurring photonic gauge field, the vector-potential $\hat{\mathbf{A}}(\mathbf{r}_i)$ [12]. Fixing a gauge is necessary to restrict redundant degrees of freedom that arise from an invariance under here local transformations. The probably most prominent choice in non-relativistic physics is the Coulomb gauge $\nabla \cdot \mathbf{A}(\mathbf{r}t) = 0$ which is disentangling longitudinal and transversal components. As already implied by its name, it gives rise to the longitudinal and instantaneous Coulomb interaction in addition to retarded transversal fields which are able to prolong into free space. The corresponding Pauli-Fierz Hamiltonian [13, 14] describing the coupled system of light and non-relativistic matter without consideration of spin reads

$$\begin{aligned}
\hat{H}_C = \frac{1}{2}\sum_{i=1}^{N_e} \frac{1}{m_e}\left(-i\hbar\nabla_i - (-e)\hat{\mathbf{A}}(\mathbf{r}_i)\right)^2 &+ \frac{1}{8\pi\varepsilon_0}\sum_{i,j\neq i}^{N_e} \frac{(-e)(-e)}{|\mathbf{r}_i - \mathbf{r}_j|} \\
+ \frac{1}{2}\sum_{i=1}^{N_n} \frac{1}{M_i}\left(-i\hbar\nabla_i - (eZ_i)\hat{\mathbf{A}}(\mathbf{R}_i)\right)^2 &+ \frac{1}{8\pi\varepsilon_0}\sum_{i,j\neq i}^{N_n} \frac{(eZ_i)(eZ_j)}{|\mathbf{R}_i - \mathbf{R}_j|} \\
+ \frac{\varepsilon_0}{2}\int dr^3 \left(|\hat{\mathbf{E}}_\perp(\mathbf{r})|^2 + c^2|\hat{\mathbf{B}}(\mathbf{r})|^2\right) &+ \frac{1}{4\pi\varepsilon_0}\sum_{i,j}^{N_e,N_n} \frac{(-e)(eZ_j)}{|\mathbf{r}_i - \mathbf{R}_j|} \,.
\end{aligned} \tag{1}$$

The matter system is represented by N_e electrons with positions $\mathbf{r}_i$ interacting among each other with the bare mass m_e, the charge $-e$ and furthermore interacting with the N_n nuclei with mass M_i, positions $\mathbf{R}_i$ and charge eZ_i. The vacuum permittivity ε_0 can be seen as the conductance of the vacuum and relates together with the vacuum permeability μ_0 to the speed of light in vacuum $c = 1/\sqrt{\varepsilon_0\mu_0}$. The electric field $\mathbf{E}(\mathbf{r}t)$, with transversal $\perp$ and longitudinal $\|$ component, and the transverse magnetic field $\mathbf{B}(\mathbf{r}t)$ satisfy the microscopic Maxwell equations

$$\begin{aligned} \varepsilon_0\nabla\cdot\mathbf{E}(\mathbf{r}t) &= \rho(\mathbf{r}t) & \nabla\cdot\mathbf{B}(\mathbf{r}t) &= 0 \\ \nabla\times\mathbf{E}(\mathbf{r}t) &= -\partial_t\mathbf{B}(\mathbf{r}t) & \nabla\times\mathbf{B}(\mathbf{r}t) &= \mu_0\left[\mathbf{j}(\mathbf{r}t)+\varepsilon_0\partial_t\mathbf{E}(\mathbf{r}t)\right] \end{aligned} \tag{2}$$

with the charge

$$\rho(\mathbf{r}t) = \sum_{i=1}^{N_e}(-e)\delta(\mathbf{r}-\mathbf{r}_i(t)) + \sum_{i=1}^{N_n}(eZ_i)\delta(\mathbf{r}-\mathbf{r}_i(t))$$

and current

$$\mathbf{j}(\mathbf{r}t) = \sum_{i=1}^{N_e}(-e)\dot{\mathbf{r}}_i(t)\delta(\mathbf{r}-\mathbf{r}_i(t)) + \sum_{i=1}^{N_n}(eZ_i)\dot{\mathbf{r}}_i(t)\delta(\mathbf{r}-\mathbf{r}_i(t))$$

densities. Furthermore the fields relate to the, in Coulomb gauge purely transversal $\mathbf{A} = \mathbf{A}_\perp$, vector-potential $\mathbf{A}(\mathbf{r}t)$ via [1]

$$\begin{aligned} \mathbf{E}(\mathbf{r}t) &= \mathbf{E}_{\|}(\mathbf{r}t) + \mathbf{E}_\perp(\mathbf{r}t) = -\nabla\frac{1}{4\pi\varepsilon_0}\int d^3r'\,\frac{\rho(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} - \partial_t\mathbf{A}(\mathbf{r}t) \\ \mathbf{B}(\mathbf{r}t) &= \mathbf{B}_\perp(\mathbf{r}t) = \nabla\times\mathbf{A}(\mathbf{r}t)\ . \end{aligned} \tag{3}$$

Sec. 4.1 will introduce the process of quantization $\mathbf{A}(\mathbf{r}t) \rightarrow \hat{\mathbf{A}}(\mathbf{r})$. The instantaneous Coulomb interaction, last terms in all lines of (1), is of uttermost importance for the electronic structure and thus at the very heart of chemistry. It is the essential building block to describe molecular reactions, the structure of condensed matter and biology. The transversal field on the other hand was considered in chemistry, up until the very recent predecessors of this work, dominantly as classical perturbation to the electronic structure. While quantum optics, and nowadays quantum information, investigated the quantum character of light in conjunction with matter, those considerations focused historically on clean atomic systems. They gave rise to impressive technological possibilities rewarded with the Nobelprize for Haroche and Wineland in 2012 [15, 16]. While the scattering of transversal light with matter gives rise to such fundamental features as spontaneous and stimulated emission, for low intensity and coupling strength this can be often adequately described by perturbation theory. Increasing

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[1] Or correspondingly their quantum-equivalence utilizing the Heisenberg equation of motion $i\hbar\frac{d}{dt}\hat{O}_H(t) = [\hat{O}_H(t), \hat{H}]_- + i\hbar\partial_t\hat{O}(t)|_H$. Notice the slight difference of $\mathbf{A} \leftrightarrow \frac{1}{c}\mathbf{A}$ in relation to P1. We assume here full $\mathbb{R}^3$ without boundary conditions (in contrast to a confining geometry) such that the longitudinal potential $\phi(\mathbf{r}t)$ solving the Poisson equation $\varepsilon_0\nabla\cdot(-\nabla\phi(\mathbf{r}t)) = n(\mathbf{r}t)$ is given by the common Coulomb interaction.

the field strength or coupling, as they became available with the development of compact strong laser sources, opened up non-perturbative regimes of light-matter interaction, utilized e.g. in high-harmonic generation.

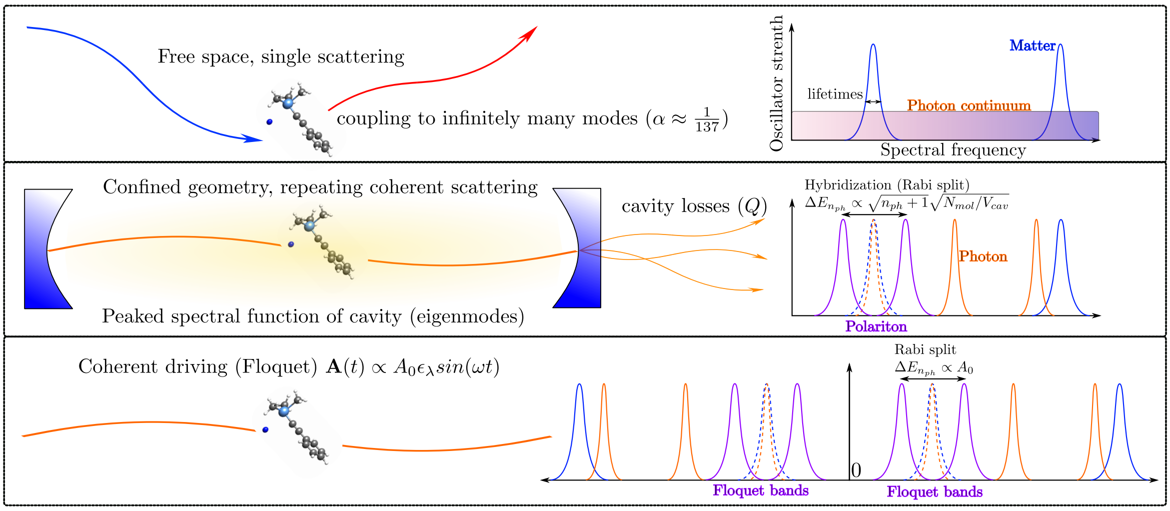

Figure 1: Light-matter coupling in a nutshell. Illustrated are the three distinct and most relevant situations for light-matter interplay. In free space infinitely many photon modes scatter with matter, leading to lifetimes and physical masses. The cavity restricts the photonic spectrum to a set of allowed eigenmodes with enhanced individual coupling. The coherent and resonant exchange between modes and matter result in a hybridization of eigenstates and introduces new quasiparticles, the polaritons, that are of mixed character. Losses (Q) and decoherences determine the width of resonances and define the cross-over between strong coupling (polaritons can be resolved) and purely perturbative coupling (Purcell effect, enhanced spontaneous emission). The strength of hybridization scales with the number of photons (the vacuum fluctuations $n_{ph} = 0$ lead to nonzero splitting), the number of coherently participating molecules/polarization N_{mol} (see Sec. 5.2) and the inverse of the cavity (quantization) volume V_{cav}. The coherent driving of matter (e.g. via an external laser) leads to novel equilibrium (Floquet) states in which the matter excitations are dressed and hybridized via the oscillating field. The major difference to the quantized cavity interaction is the negative spectrum and that the Floquet hybridization is not anharmonic (no $\sqrt{n_{ph}+1}$).

Let us focus back on low field intensities but this time confine the light-field in a restricting geometry, a cavity, as illustrated in Fig. 1. In its simplest case this cavity can consist of parallel plane mirrors, reflecting a light ray into itself. With each reflection, the transversal field can scatter with the matter system of interest inside the cavity. How often this process takes place, i.e. the quality of the cavity at hand, is given by the quality (Q) factor $Q = \omega/\Delta\omega$ which is defined by the ratio between frequency and full width at half maximum (FWHM) of the resonance. If the interaction of the material inside the cavity and the light-field becomes significant, they build a new quasiparticle, the polariton, of mixed light-matter character. The higher the decoherence of matter excitations or loss of photons from the cavity, the stronger dephasing effects will conceal the polaritonic features (for more details see Sec. 5.1.2). In the extreme limit where the loss-rates dominate we will merely retain the enhanced spontaneous emission of a material close to a surface, the so called Purcell-effect [17]. State of the art high-Q cavities vary depending on their design in mode-volume and quality-factor and can reach Q-values of thousands up to tens of millions (see e.g. [18–28] and references therein). How strong a single photon-scattering can interact with matter is given under those confined conditions by the quantization volume of the cavity mode $\lambda = 1/\sqrt{\varepsilon_0 V}$ and the inducible current or dipole moment of the matter at hand. Strong interaction between an individual particle and the field thus demands a small cavity volume, where the minimal possible volume should be naively restricted by half the wavelength of the smallest frequency (for more details see Sec. 4). While conventional high-Q cavities are thus typically restricted to very small coupling values, effective sub-wavelength confined fields in form of e.g. nanoplasmonic devices can posses extraordinary small mode volumes of less than a nanometer [20, 29]. So far nanoplasmonic cavities, in which the distinction between longitudinal and transversal modes vanishes, suffer from high leakage and therefore low Q-values ($\sim \mathcal{O}(10^2)$). It is now important to realize that the photonic field is indeed quantized and thus features vacuum fluctuations. It becomes apparent that we expect to observe polaritonic features even if we do not pump the cavity, photons will be *virtually* present due to the basic principles of quantum mechanics.

A manifold of different realizations for cavity environments arose within the past decades. Some of them utilize microwave cavities, excitonic solid state and quantum dot excitations, and even superconducting qubits [25, 30], to name a few. Besides reducing the mode-volume to increase the coupling strength itself, a further point of interest is to increase the currents, thus dipole-moments, of the involved excitations and thus maximize the effective coupling strength to the cavity. This idea is especially prominent in the domain of circuit quantum electrodynamics, where not actual transversal fields couple to a material but rather a circuit of capacity and inductance mimics the transversal photonic field. The corresponding coordinates current and voltage couple to an artificial atom (qubit), represented by a mesoscopic device, e.g. a superconducting island. The associated large dipoles, due to the significant number of collectively moving charges, result in massive 'light'-matter couplings on the order of the matter excitation itself and posses even relatively high quality factors [31, 32]. It can be expected that the impressive light-matter coupling will further increase and without a doubt non-perturbative features of light-matter-(like) interactions will become an essential pillar of modern science. This marvelously quick development represents a great opportunity for a variety of different physical and chemical processes. So is the high coherence and long-range correlation (or entanglement) between different constituents, investigated in P3 and Section 6, a promising route for quantum chemistry experimentally [20, 33–52], theoretically (P3,[3, 53–55, 55–57]) and also for quantum information [19, 30, 58].
Those novel considerations that come hand in hand with non-perturbative features will give rise to a demand for non-perturbative theoretical methods and it is precisely the goal of this thesis to present a perspective on considerations that arise with this problem. Common practices, developed many decades ago for clean atomic systems interacting with the transversal field, have to be revisited. We will elaborate on this problem in Section 4 and Publications

P1, P2, P3 and P4.

In our previous considerations, we dominantly referred to effects that can be assigned to a single matter-excitation, e.g. an atomic, molecular or excitonic excitation. The larger the mode volume, the more constituents could potentially enter and participate. Indeed, considering an ensemble of N identical constituents will lead to two states with collective and aligned excitations coupling to the light with an effective dipole amplified by $\sqrt{N}$, so called superradiant or bright states. In addition N-1 states exist that will feature anti-symmetric combinations and decouple from the cavity, called subradiant or dark states, all just valid in a perturbative sense. It becomes apparent that this limit is especially relevant in chemical considerations where a macroscopic number of various molecules seemingly magically result in a large variety of desired or not desired products. This specific sub-section of cavity quantum electrodynamics is often called polaritonic or QED chemistry [33, 53, 59–61], P2 and gained recent interest due to experimental realizations that catalyze and steer chemical reactions, solely by the presence of the cavity [43, 49–51]. Those exciting observations suggest that future chemical reactions will be tunable by a completely non-intrusive knob, the surrounding cavity parameters, without the need to provide external energy as e.g. via an external laser-field. It can be however shown that the continuous driving with an external laser is structurally very similar to the cavity QED environment, illustrated in Publications P2, Fig. 1 and Sec. 7. This will allow us to use the elaborated computational methodology of Floquet physics in this novel subject and vice versa provides the possibility to create physics similar to Floquet physics without the need to drive and therefore heat the system.

Such a twist for chemical perspectives, where the transversal fields are typically expected to be classical, will without doubt call for a reconsideration of successful quantum chemical methods in the context of cavity QED. Two important and successful *ab initio* quantum chemical methodologies are (time dependent) density-functional theory [62] and semiclassical statistical methods such as surface hopping [63]. Further essential representatives are wavefunction based methods such as configuration interaction (CI) [64, 65] and coupled cluster [66]. While wavefunction based approaches are considered to be very accurate yet computationally expensive, density-functional theory avoids the utilization of a many-body wavefunction and instead describes observables in terms of the electronic density, resulting in a massive computational simplification. Semiclassical methods on the other hand utilize the results that those previous methods present for the electronic structure to predict the nuclear dynamics, i.e. how chemical reactions evolve in time. In Section 5 and accordingly Publications P2, P3, P4, P5, P6 and P7, we present how each of these methods can be projected onto the QED setting and we furthermore not just provide various considerations but also first realistic calculations, conclusions and future perspectives.

This thesis is structured such that it introduces and relates fundamental considerations that appear in the novel domain of research (Sec. 4, P1 and P2). Following is a short introduction into the methodology developed and applied within this thesis, briefly illustrated in the context of alternative approaches and applications (Sec. 5, foremost the contributions P2, P3, P4, P5, P6 and P7). Section 6 (and especially P3, P4, P2) emphasizes a selected set of the most important physical features that arise with cavity QED, presenting a brief introduction into scientific literature and the therein obtained results. A short perspective on work that is still in progress and originated from this thesis (Sec. 7) finalizes the introductory component before the scientific contributions (Sec. 8) and subsequent conclusions (Sec. 9) are presented.

4 Perspectives on Quantum electrodynamics

QED in different limits

ALTHOUGH one manages to write down the equations that define the minimal coupling between light and matter, we will quickly realize that their solution is yet an entirely intractable problem without the help of decades of active research. Performing small steps, we will start with the quantization of the field degrees of freedom, then briefly introduce the most prominent perspectives for the QED problem and lastly clarify that hell breaks loose when we attempt to combine QED and electronic structure theory without very careful scrutinizing every involved step. It will become clear how the so commonly applied models, dominating this field of research, have to be reconsidered when we attempt to unify the long history of quantum optics and quantum chemistry within one consistent approach, the goal of this work.

4.1 Crash course on cavity QED

Before starting further investigations we have to specify what quantized fields are and how the minimal coupling is transformed into more convenient formulations. We will give a very short introduction disregarding most details and suggest the reader to investigate P1, P2 and especially the various mentioned textbooks for further details. The question how to quantize longitudinal and transversal fields is a rather extensive task, involving a manifold of very fundamental problems such as mass-renormalization, cut-offs to avoid divergences for high frequencies, various gauges suited for different situations and many more [12, 67]. Let us at the start assume that we treat the photonic field in absence of any restricting geometry and material. We can derive from Maxwell's equations (2) together with the electromagnetic fields (3), the differential equation

$$\nabla \times \nabla \times \mathbf{A}(\mathbf{r}t) = \nabla(\nabla \cdot \mathbf{A}(\mathbf{r}t)) - \nabla^2 \mathbf{A}(\mathbf{r}t) = -\mu_0 \varepsilon_0 \partial_t^2 \mathbf{A}(\mathbf{r}t) \ .$$

We choose to remain in Coulomb gauge such that the transversality of the vector potential simplifies the above equation to the wave or d'Alembert equation

$$\left[\nabla^2 - \frac{1}{c^2}\partial_t^2\right] \mathbf{A}(\mathbf{r}t) = \Box \mathbf{A}(\mathbf{r}t) = 0.$$

Solving this equation, e.g. by a separation of variables, lets us express the vector potential in eigenmodes of the corresponding Helmholtz-operator $\nabla^2 + \mathbf{k}^2$

$$\mathbf{A}(\mathbf{r}t) = \frac{1}{\sqrt{\varepsilon_0 V}} \sum_{\mathbf{k},\xi} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}}}} \left[\boldsymbol{\epsilon}_{\mathbf{k}\xi} a_{\mathbf{k}\xi}(t) e^{i\mathbf{k}\cdot\mathbf{r}} + \boldsymbol{\epsilon}^*_{\mathbf{k}\xi} a^*_{\mathbf{k}\xi}(t) e^{-i\mathbf{k}\cdot\mathbf{r}}\right] \ .$$

The transversality condition allows for two linearly independent solutions per $\mathbf{k}$ with polarization $\xi \in \{1, 2\}$ represented by the polarization vector $\boldsymbol{\epsilon}_{\mathbf{k}\xi}$ satisfying $\boldsymbol{\epsilon}_{\mathbf{k}\xi} \cdot \mathbf{k} = 0$ defined on the quantization volume V.[2] The linear expansion coefficient $a_{\mathbf{k}\xi}(t)$ satisfies the harmonic oscillator differential equation $\left[\partial_t^2 + \omega_{\mathbf{k}}^2\right] a_{\mathbf{k}\xi}(t) = 0$ with $\omega_{\mathbf{k}} = c|\mathbf{k}|$ such that $a_{\mathbf{k}\xi}(t) = a_{\mathbf{k}\xi}e^{-i\omega_{\mathbf{k}}t}$. The set of plane waves $e^{i\mathbf{k}\cdot\mathbf{r}}$ manifests the spatial mode functions, eigenmodes of the Helmholtz operator, and the time-dependent coefficients describe harmonic oscillations in time with the frequency ω corresponding to mode $\mathbf{k}$. If the photonic fields are driven by a current, i.e. coupled to a polarizable material or they feel an external current, the harmonic equation becomes inhomogeneous according to Maxwell's equations (2). A driving that is 'classically' coupled by expectation values gives rise to a coherent displacement. The quantum eigenstates describing coherently displaced harmonic oscillators are referred to as generalized coherent states. The displaced ground or coherent state possesses the same minimal uncertainty and Gaussian structure as the quantum ground state and represent the classical limit of a quantized field. One could now follow the elaborate second quantization procedure by identification of conjugate coordinates [67–69]. In Coulomb gauge they will turn out as vector potential $\mathbf{A}(\mathbf{r}t)$ and conjugate momentum $\mathbf{\Pi}(\mathbf{r}t) = -\varepsilon_0\mathbf{E}_\perp(\mathbf{r}t)$, proportional to the electric field, together with the classical Poisson bracket to quantum commutator promotion $\{\mathbf{A}(\mathbf{r}t), \mathbf{\Pi}(\mathbf{r}t)\} \rightarrow -i/\hbar[\hat{\mathbf{A}}(\mathbf{r}), \hat{\mathbf{\Pi}}(\mathbf{r})]_- = \delta_\perp(\mathbf{r}-\mathbf{r}')$. Important is here to realize the transversal character, i.e. the polarization components satisfy $\sum_\xi \epsilon_{\mathbf{k}\xi,i}\epsilon^*_{\mathbf{k}\xi,j} = \delta_{ij} - k_ik_j/|\mathbf{k}||\mathbf{k}|$ and define the transversal delta-function $\delta^{ij}_\perp(\mathbf{r}) = \delta_{ij}\delta(\mathbf{r}) - \delta^{ij}_\parallel(\mathbf{r})$. Instead of following the full quantization procedure, the harmonic structure might motivate us to simply assign the creation and annihilation operator algebra $[\hat{a}_{\mathbf{k}\xi}, \hat{a}^\dagger_{\mathbf{k}'\xi'}]_- = \delta_{\mathbf{k}\xi,\mathbf{k}'\xi'}$ to the complex time-dependent coefficients such that we arrive at the quantized equivalent

$$\hat{\mathbf{A}}(\mathbf{r}) = \frac{1}{\sqrt{\varepsilon_0 V}} \sum_{\mathbf{k},\xi} \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}}}} \left[\boldsymbol{\epsilon}_{\mathbf{k}\xi}\hat{a}_{\mathbf{k}\xi}e^{i\mathbf{k}\cdot\mathbf{r}} + \boldsymbol{\epsilon}^*_{\mathbf{k}\xi}\hat{a}^\dagger_{\mathbf{k}\xi}e^{-i\mathbf{k}\cdot\mathbf{r}}\right] \,. \tag{4}$$

Plugging (4) into the field energy expression of (1) leads to the well known simplified result

$$\hat{H}^\perp_{em} = \frac{\varepsilon_0}{2}\int dr^3 \left(|\hat{\mathbf{E}}_\perp(\mathbf{r})|^2 + c^2|\hat{\mathbf{B}}(\mathbf{r})|^2\right) = \sum_{\mathbf{k},\xi}\hbar\omega_{\mathbf{k}}\left(\hat{a}^\dagger_{\mathbf{k}\xi}\hat{a}_{\mathbf{k}\xi} + \frac{1}{2}\right) \,. \tag{5}$$

If now an arbitrary confining geometry restricts the allowed eigenmodes, it will promote the simple plane wave expansion to an arbitrarily complicated mode structure where the transversality is a non-trivial condition. The QED $U(1)$ symmetry is restricted to a discrete $Z(n)$ symmetry as only discrete translations/group operations, e.g. $i\mathbf{k}\cdot\mathbf{r} \rightarrow i\mathbf{k}\cdot\mathbf{r} + i2\pi n$, $n \in \mathbb{Z}$, will retain the consistency among eigenmodes and boundary conditions.[3] Modern nanofabricated resonantors can be of rather complicated structure and embody the possibility to

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[2] The appearance of the mode volume V, which is the domain on which the spatial eigenmodes are defined, might be slightly concerning. The plane waves are not $\mathbb{L}^2$ functions but a rather special basis for which the limit to free space $\int_V dr^3 e^{+i\mathbf{k}\cdot\mathbf{r}}e^{-i\mathbf{k}\cdot\mathbf{r}} = V \rightarrow \infty$ for $V \rightarrow \infty$ is only defined when sending the number of eigenmodes $\{\mathbf{k}\}$ equivalently to infinity $1/V\sum_{\mathbf{k}} \rightarrow \int 1/(2\pi)^3 dk^3$. As one might expect, this will lead to subtle questions such as how to take a sensible limit, when to cut off $\{\mathbf{k}_1, ..., \mathbf{k}_M\}$ and indeed the selection of this cutoff will describe what we consider as physical mass of a particle. For more details we refer the reader to various excellent textbooks e.g. [12, 14, 67–69].

[3] While it seems trivial at first glance, this realization drags with it a non-negligible amount of mathematical subtleties, e.g. that the spectral basis-representation of scalar ∇^2 and vectorial $\nabla \times \nabla$ kinetic operators

support modes with more obscure features such as orbital angular momentum in combination with various polarizations, see e.g. Sec 7 or the recent progress in the field of twisted light [71].[4] Most common in cavity QED is the simplified assumption of a single dimension of relevance, e.g. $\{\mathbf{k}\} = \{k\mathbf{e}_z\}$, motivated by idealized parallel plane-mirror Fabry-Perot type resonators[5], clearly a rather crude approximation to realistic cavities. Often we will assume that the matter-system of interest extends spatially very little around its center $\mathbf{r}_0$ such that e.g. $e^{\pm i\mathbf{k}\cdot\mathbf{r}} \approx e^{\pm i\mathbf{k}\cdot\mathbf{r}_0}$, $\mathbf{k}\cdot\mathbf{r} \ll 1$, referred to as long-wavelength approximation. In conjunction with the restriction to linearly polarized light $\boldsymbol{\epsilon}_{\mathbf{k}\xi} = \boldsymbol{\epsilon}^*_{\mathbf{k}\xi}$ and the introduction of canonical harmonic variables

$$q_{\mathbf{k}\xi} = \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}}}}(\hat{a}_{\mathbf{k}\xi} + \hat{a}^\dagger_{\mathbf{k}\xi}),\ p_{\mathbf{k}\xi} = -i\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2}}(\hat{a}_{\mathbf{k}\xi} - \hat{a}^\dagger_{\mathbf{k}\xi});\ \text{with } [\hat{q}_{\mathbf{k}\xi}, \hat{p}_{\mathbf{k}'\xi'}]_- = i\hbar\delta_{\mathbf{k}\xi,\mathbf{k}'\xi'}$$

we can remarkably simplify equation (4) to

$$\hat{\mathbf{A}} = \sum_{\mathbf{k},\xi} \boldsymbol{\lambda}_{\mathbf{k}\xi}\hat{q}_{\mathbf{k}\xi}\ , \qquad \boldsymbol{\lambda}_{\mathbf{k}\xi} = \frac{1}{\sqrt{\varepsilon_0 V}}\boldsymbol{\epsilon}_{\mathbf{k}\xi}S_{\mathbf{k}}(\mathbf{r}_0)\ . \tag{6}$$

The mode function $S_{\mathbf{k}}(\mathbf{r}_0)$, e.g. $S_{\mathbf{k}}(\mathbf{r}_0) = e^{i\mathbf{k}\cdot\mathbf{r}_0}$, incorporates the geometry of our cavity and the respective position of our matter-system, for more details see footnote 5 and P1. One should consider that Eq. (6) lost all spatial character and with it the possibility to transfer momentum. The introduced dipole-field should be thought of as approximation to the coupling components after all transformations and integrations for Eq. (5) are performed. It should be noticed now that substituting this highly approximated $\hat{\mathbf{A}}$ into the minimally coupled Hamiltonian (1) leads to bilinear coupling terms and quadratic components proportional to $\hat{\mathbf{A}}\cdot\hat{\mathbf{A}}$. The latter ones are, although they seem awkward at first glance [75], very fundamental and e.g. represent a diamagnetic shift of the mode frequency thus regularizing the low frequency limit $\omega_{\mathbf{k}} \to 0$. The high-frequency limit is still not well defined and typically we restrict ourself to a sensible set of most relevant modes inside the cavity. The large quantity

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do not have the same eigenfunctions and hence combining them becomes non-trivial. Often enough, we will brush over those fundamental mathematical non-trivialities, which can indeed matter [70], to obtain a 'physically driven' solution. This is well motivated by the fact that the boundary conditions themselves are simplified representations of a real (reflective) material which will feature a finite penetration depth.

[4] Where a distinction between transversal and longitudinal (mirror-charges) modes becomes non-trivial, a solution in terms of Green's functions might become beneficial. Macroscopic QED utilized such a construction to describe quantized fields under effect of various linear or non-linear media, see e.g. [72, 73]. Reconsidering the following work in this context will be surely non-trivial but similarly beneficial to extend the present insight and machinery towards truly realistic predictions in various state-of-the art topics.

[5] The corresponding zero-boundary conditions then imply sine-type eigenmodes instead of plane-waves. In a three-dimensional setup, special attention should be devoted to fulfill the transversality condition $\nabla\cdot\hat{\mathbf{A}}(\mathbf{r})$ in conjunction with the boundary conditions. Each mode-expansion should present a complete set of orthonormal eigenmodes $\frac{1}{V}\int dr^3 S_{\mathbf{k}}(\mathbf{r})S_{\mathbf{k}'}(\mathbf{r}) = \delta_{\mathbf{k},\mathbf{k}'}$, e.g. $e^{i\mathbf{k}\cdot\mathbf{r}}$ for periodic boundaries in full space would transfer into $\sqrt{2}\sin(k_z z)$ for one-dimensional idealized plane parallel mirrors located at 0 and $L = \pi/k_z$. When our resonator itself is not stationary but subject to modulations in time, e.g. an oscillatory driving that might be selected to precisely steer a chemical reaction, the above transversal basis is just a single instantaneous realization and its time-dependent adjustment should be considered (see for instance [74]).

of modes that are merely weakly affecting the matter-system of interest are then subsumed into its effective mass, as common practice in quantum chemistry and physics, see also P1 and P2. [6]

For a large set of interesting matter-systems, such as e.g. molecules within chemical reactions, it would be much more preferable to handle an operator that is well localized in space. The dipole operator $\hat{\mathbf{R}} = -e\sum_{j=1}^{N_e}\hat{\mathbf{r}}_j + \sum_{j=1}^{N_n} eZ_j\hat{\mathbf{R}}_n^j$, who's expectation value is easier to observe experimentally than the non-local momentum operator, manifests as reasonable choice. Furthermore would it be beneficial if the gauge dependence of the vector potential could be avoided and we would be able to express our theory in terms of manifestly gauge invariant quantities. From those considerations, a very elegant yet non-trivial and easily misunderstood reformulation developed, the unitary Power-Zienau-Wooley (PZW) transformation [68, 77–79]. How this transformation $\hat{U} = e^{-i\sum_{\mathbf{k},\xi}\boldsymbol{\lambda}_{\mathbf{k}\xi}\cdot\hat{\mathbf{R}}\hat{q}_{\mathbf{k}\xi}}$ is designed, how it is connected to a gauge transformation, what subtleties make it non-trivial and how we precisely arrive at the following dipole approximated Hamiltonian (7), is in length and on alternative paths elaborated in Publication P1, P2 and [9, 80]. [7]

$$
\begin{aligned}
\hat{H}_D = \frac{1}{2}\sum_{i=1}^{N_e}\frac{-\hbar^2}{m_e}\nabla_i^2 + \frac{1}{8\pi\varepsilon_0}\sum_{i,j\neq i}^{N_e}\frac{(-e)(-e)}{|\mathbf{r}_i-\mathbf{r}_j|} + \frac{1}{2}\sum_{i=1}^{N_n}\frac{-\hbar^2}{M_i}\nabla_i^2 + \frac{1}{8\pi\varepsilon_0}\sum_{i,j\neq i}^{N_n}\frac{(eZ_i)(eZ_j)}{|\mathbf{R}_i-\mathbf{R}_j|} \\
+ \frac{1}{2}\sum_{\mathbf{k},\xi}^{M,2}\left[\hat{p}_{\mathbf{k}\xi}^2 + \omega_{\mathbf{k}}^2\left(\hat{q}_{\mathbf{k}\xi} - \frac{\boldsymbol{\lambda}_{\mathbf{k}\xi}}{\omega_{\mathbf{k}}}\cdot\hat{\mathbf{R}}\right)^2\right] + \frac{1}{4\pi\varepsilon_0}\sum_{i,j}^{N_e,N_n}\frac{(-e)(eZ_j)}{|\mathbf{r}_i-\mathbf{R}_j|}
\end{aligned}
\tag{7}
$$

Of special interest is the fact that the interaction between light and matter is now completely absorbed into an effective photonic-like component $\left(\hat{q}_{\mathbf{k}\xi} - \frac{\boldsymbol{\lambda}_{\mathbf{k}\xi}}{\omega_{\mathbf{k}}}\cdot\hat{\mathbf{R}}\right)$ which relates to the transversal electric field. The canonical operator $\hat{q}$ in turn is now related to the displacement field $\hat{\mathbf{D}}_\perp(\mathbf{r}) = \varepsilon_0\hat{\mathbf{E}}_\perp(\mathbf{r}) + \hat{\mathbf{P}}_\perp(\mathbf{r}) = \varepsilon_0\sum_{\mathbf{k}\xi}\omega_{\mathbf{k}}\boldsymbol{\lambda}_{\mathbf{k}\xi}\hat{q}_{\mathbf{k}\xi}$. Interaction is therefore mediated through the projected transversal polarization $\hat{\mathbf{P}}_\perp(\mathbf{r})$ of the matter system and our novel field quantities are transformed in accordance with the macroscopic Maxwell equations.

The bilinear coupling $-\omega_{\mathbf{k}}\hat{q}_{\mathbf{k}\xi}\boldsymbol{\lambda}_{\mathbf{k}\xi}\cdot\hat{\mathbf{R}} = -\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2}}(\hat{a}_{\mathbf{k}\xi} + \hat{a}_{\mathbf{k}\xi}^\dagger)\boldsymbol{\lambda}_{\mathbf{k}\xi}\cdot\hat{\mathbf{R}}$ gives rise to matter excitation and deexcitation processes in combination with the creation $\hat{a}^\dagger$ and annihilation $\hat{a}$ of photons. Let us express the dipole operator in a restricted 2-level basis of excitation and deexcitation operators such that $\hat{\mathbf{R}} = \sum_{i,j=1}^{2}|i\rangle\langle i|\hat{\mathbf{R}}|j\rangle\langle j| = R_{01}|0\rangle\langle 1| + R_{01}^*|1\rangle\langle 0|$, if $R_{00} = R_{11} = 0$. We then assume a resonant interaction $\varepsilon_1 - \varepsilon_0 = \omega$ with a single cavity mode ω. This simplification is known as the Rabi model, illustrated in Fig. 2, and its spectrum can be analytically obtained [81]. We notice that terms with an excitation and the

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[6] When investigating transfer on the length scales of the wavelength, the set of modes should be expanded as otherwise unphysical superluminal transfer appears [76]. The spatial resolution encoded into the eigenmodes $S_{\mathbf{k}}(\mathbf{r})$ guarantees that the speed of light remains the upper limit for information transfer.

[7] When we closely inspect the different publications in this field, for instance even P1 and P2, we will notice that the sign of the bilinear coupling fluctuates. Changing from $\left(\hat{q}_{\mathbf{k}\xi} - \frac{\boldsymbol{\lambda}_{\mathbf{k}\xi}}{\omega_{\mathbf{k}}}\cdot\hat{\mathbf{R}}\right)$ to $\left(\hat{q}_{\mathbf{k}\xi} + \frac{\boldsymbol{\lambda}_{\mathbf{k}\xi}}{\omega_{\mathbf{k}}}\cdot\hat{\mathbf{R}}\right)$ does however not change any presented result. Instead it merely flips the sign of $\hat{q}_{\mathbf{k}\xi}$ as the photonic Hamiltonian is symmetric under inversion. The here presented convention is consistent with P1 and we suggest the reader to follow this formulation.

absorption of a photon are paired $|1\rangle\langle 0|\hat{a}$ (vice versa the reversed process) but furthermore terms appear in which an excitation takes place and a photon is created $|1\rangle\langle 0|\hat{a}^\dagger$. While the first components seem very intuitive as each scattering event would conserve energy, the latter seem unintuitive, would they demand that the system somehow compensates for the large demand of energy to excite photons and matter at the same time. Considering the free evolution of those components (interacting frame), the excitation processes attain a phase $e^{i\omega t}$ while deexcitations obtain the reverse $e^{-i\omega t}$. The counter-intuitive components, called counter-rotating, such as $|1\rangle\langle 0|e^{i(\varepsilon_1-\varepsilon_0)t}\hat{a}^\dagger e^{i\omega t}$ superimpose then to a very fast oscillating phase $e^{\pm i2\omega}$ that will barely be able to affect the coupled system. A prototypical approximation in quantum optics is now to ignore those counter-rotating components and thus enter the 'secular' or 'rotating wave approximation' (RWA) which reduces the Rabi to the Jaynes-Cummings (JC) model. This decouples each excitation from subsequent ones which leads to a rather easy analytic solution. For not too large light-matter coupling, this RWA provides often satisfying results. We should note however, that for larger couplings, stronger detuning (not on resonance) or multi-photon processes, the RWA will break down.[8] Notice further that the ground state is affected just by the counter-rotating components, i.e. any theory that aims to deliver a real-space and consistent treatment of electronic, nuclear and photonic structure should consider them. The JC model is *the* prototypical model shaping the perception of strong light-matter coupling in cavity QED. It will become apparent within this work how greatly beneficial, yet limited this model is, and how we can design an approach to solve the correlated light-matter system without the need for such drastic limitations. Another common approximation is to omit and reabsorb the term $\frac{1}{2}(\boldsymbol{\lambda}_{\mathbf{k}\xi}\cdot\hat{\mathbf{R}})^2$, named here self-polarization, into an adjusted physical mass of the particles [69, 79]. It turns out however, that any self-consistent calculation, as desirable for chemical and non-perturbative regards, will necessarily demand this component. We illustrate in Publications P1, P2 and P3 how over-simplification in terms of restricted Hilbert spaces or unbalanced approximations will inevitably result in unphysical predictions. Table 1 collects

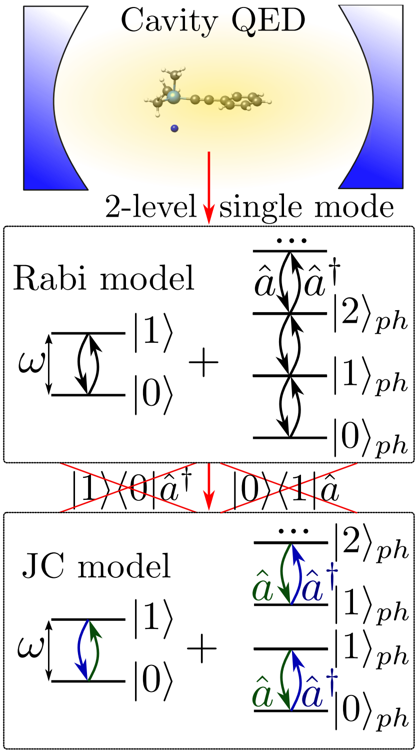

Figure 2: Schematic illustration of the connection between full cavity QED, the Rabi model featuring 2-levels approximating the structure of matter and a single photonic mode, as well as the Jaynes-Cummings (JC) model that originates from the Rabi model with subsequent RWA (see also table 1). Performing the RWA decouples the excitations of photons into blocks that can be easily analytically solved.

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[8] Improved versions inspired by the adiabatic elimination can partially compensate for some of those failures, e.g. account for a rescaling of energetic spacings. The interested reader is referred to [82–84] and references therein.

Approximation	Model	Coupling	Valid if
Long-wavelength	el. dipole QED	$\omega_{\mathbf{k}}^2 \left(\hat{q}_{\mathbf{k}\xi} - \frac{\boldsymbol{\lambda}_{\mathbf{k}\xi}}{\omega_{\mathbf{k}}} \cdot \hat{\mathbf{R}} \right)^2$	$S(\mathbf{r}) \approx S(\mathbf{r}_0)$
No $\mathbf{R}^2$	perturbative QED	$-\omega_{\mathbf{k}} \hat{q}_{\mathbf{k}\xi} \lambda_{\mathbf{k}\xi} \cdot \hat{\mathbf{R}}$	$\lambda_{\mathbf{k}\xi}^2 / 4\varepsilon_i^2 \ll 1$
2-level + 1 mode (many 2-level)	Rabi (Dicke)	$-\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2}} \lambda_{\mathbf{k}\xi} R_{01} (\hat{a}_{\mathbf{k}\xi} + \hat{a}_{\mathbf{k}\xi}^\dagger)(\|0\rangle\langle 1\| + \|1\rangle\langle 0\|)$	$\varepsilon_1 - \varepsilon_0 - \omega_{\mathbf{k}} \approx 0$ and $\sqrt{\frac{1}{2\hbar\omega_{\mathbf{k}}}} \lambda_{\mathbf{k}\xi} \|R_{01}\| < 1$
Rabi + RWA (many 2-level)	Jaynes-Cummings (Tavis-Cummings)	$-\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2}} \lambda_{\mathbf{k}\xi} R_{01} (\hat{a}_{\mathbf{k}\xi} \|1\rangle\langle 0\| + \hat{a}_{\mathbf{k}\xi}^\dagger \|0\rangle\langle 1\|)$	$\sqrt{\frac{1}{2\hbar\omega_{\mathbf{k}}}} \lambda_{\mathbf{k}\xi} \|R_{01}\| \ll 1$

Table 1: Jacob's ladder of light-matter interaction starting from the long-wavelength approximation. The ideal description would feature the full (relativistic) minimal coupling. Indicated are subsequent approximations, their respective models, light-matter coupling and validity. It is common to assume $R_{01} = R_{10} = 1$. If coupling or frequency of the photonic field allow to reach higher excited states, a 2-level description is no longer valid (P3). Satisfactorily describing real-space observables will largely prohibit any approximation beyond the electric dipole approximation (P1, P2).

the here illustrated steps and models. A highly convenient feature of the PZW transformed Hamiltonian is that mirror-charges can be avoided for perfect conductor boundary conditions [85]. The transverse fields merely have to obey the boundary conditions $\mathbf{n}_{\partial V} \times \hat{\mathbf{E}}_\perp(\mathbf{r}) = 0$ with the surface normal vector $\mathbf{n}_{\partial V}$. The eigenmodes $\boldsymbol{\epsilon}_{\mathbf{k}\xi} S_{\mathbf{k}}(\mathbf{r})$ remain as only reference to the boundary geometry. Let us turn our intention in the following to the question how we theoretically predict something from here on.

4.2 Solving the Schrödinger equation

With the help of the Hamiltonian (7), we could now straightforwardly solve the corresponding Schrödinger equation

$$i\hbar\partial_t \Psi(\mathbf{r}_1, ..., \mathbf{r}_{N_e}, \mathbf{R}_1, ..., \mathbf{R}_{N_n}, q_{\mathbf{k}_1\xi_1}, ..., q_{\mathbf{k}_M\xi_2}, t) = \hat{H}_C \Psi(\mathbf{r}_1, ..., \mathbf{r}_{N_e}, \mathbf{R}_1, ..., \mathbf{R}_{N_n}, q_{\mathbf{k}_1\xi_1}, ..., q_{\mathbf{k}_M\xi_2}, t)$$

to determine the (non)-equilibrium structure of the correlated nuclei-electron-photon problem. Unfortunately, the exponentially increasing number of dimensions for the configuration space $3^{N_e} \times 3^{N_n} \times (2 \times M)$ indicate a subtle issue, namely, that it is hopeless to expect the exact solution for anything of realistic size, might it be with or without the transversal fields. This issue is known in electronic structure theory as the exponential wall problem [62]. How fast and large our computer might be, the cost is increasing so quickly that everything beyond a handful of dimensions and therefore particles is out of scope.

Now the question arises, is all of this huge Hilbert space illustrated in Fig. 3 relevant and do we actually need the full wavefunction? In the vast majority of physical and chemical

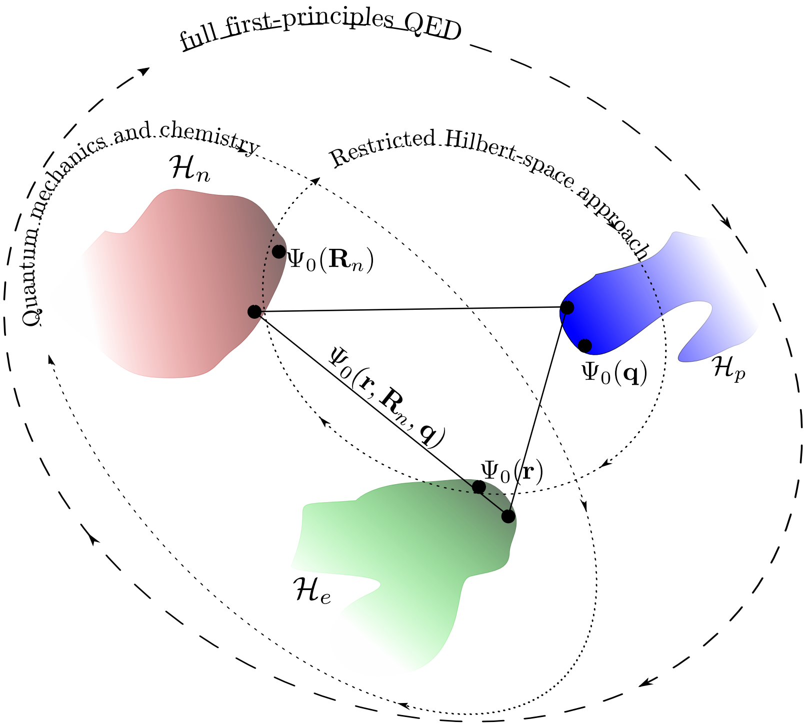

Figure 3: Simplified illustration of conceptually different approaches to describe the coupled set of electronic, nuclear and photonic Hilbert space $\mathcal{H}$ and the according ground-state solution Ψ_0. The combined ground state for interacting systems is usually not a product of the individual ground states but rather a correlated combination of eigenstates. Depending on how essential or interesting we deem a specific subspace, we might want to explicitly consider it, may it be fully quantum or in a simplified limit (see Sec. 4.2.2 and 4.3), or subsume its effect into an effective bath that weakly affects the remaining system of interest (see Sec. 4.2.1 and 5.1.2).

problems, the answer to this question is a confident no. Often, just a very specific subspace might be of interest, e.g. the nuclear arrangement during a chemical reaction, and we might attempt to subsume or even simplify the remaining degrees of freedom as efficiently as possible. We might now take different paths to benefit from this knowledge according to Fig. 3, each with individual advantages and limitations. Representing more than 60 years of research, we will only motivate the main ideas to provide a fundamental context and set the stage for further steps. The applicability of each method will highly depend on the problem of interest, the degree of accuracy that we demand and how intricate the involved interactions play out. An especially promising approach to describe many degrees of freedom is designed around the density of the system rather than its wavefunction, implying its name density-functional theory (DFT). This leads to an interpretation of electronic structure as a nonlinear quantum fluid characterized by its density $n(\mathbf{r}t)$ rather than the linear Schrödinger equation.[9] Rephrasing our problem in terms of reduced quantities will enable us to climb the exponential wall and we merely have to find the right tool for the precise problem at hand, a not always trivial problem as elaborated in Sec. 5.1.1 and P4, P5.

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[9] After inspecting the following sections, the interested reader is encouraged to investigate the close conceptual similarity between fluid dynamics, density-functional theory and general relativity [86, 87]. Geometric stresses originate for the electronic fluid as a consequence of their quantum mechanical interaction. This realization allows to derive TDDFT in a Lagrangian rather than the Eulerian frame. While the Lagrangian frame, co-moving with the electrons, holds great opportunities to derive non-adiabatic exchange-correlation potentials [86, 87], the associated geometric equations are computationally demanding.

4.2.1 System-Bath approach

Historically quantum optics focused on atomic systems under the influence of external fields. The electronic structure can be satisfyingly calculated and its interaction with external fields gives rise to rather clean excitations from one atomic state to another. Due to the high energetic separations on the order of electron volts, processes of absorption and emission can be assigned to few eigenstates and the evolution of population can be conveniently solved when restricted to two levels. For molecular or extended systems, the high incoherence due to electronic and nuclear scatterings calls for adjustments. The variable toolset of open quantum systems, based on the density matrix

$$\hat{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)| = \sum_{ij} c_i(t)c_j^*(t)|\Psi_i\rangle\langle\Psi_j|$$

defined on the full Hilbert space via the many-body equilibrium wavefunctions Ψ_j and occupations $c_i(t) = \langle\Psi_i|\Psi(t)\rangle$, was designed to take dephasing and dissipating effects into account (see Sec. 5.1 and 5.1.2). Starting from the Liouville (or von Neumann) equation for the density matrix [10]

$$i\hbar\partial_t\hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)]_- \ ,$$

it is convenient to define projection operators $\mathcal{P}\hat{\rho} = (1-\mathcal{Q})\hat{\rho} = tr_B(\hat{\rho}) \otimes \hat{\rho}_B$ which, according to their name, project the correlated matrix into subspaces. Those components are defined on a system $\hat{\rho}_S$, commonly the electronic system, and a bath $\hat{\rho}_B$, e.g. the eigenstates of the nuclear vibrations or the photonic free-space modes [88]. Projecting the density matrix into a subspace of the full Hilbert space will render it no longer pure, i.e. it can not be represented by a single wavefunction such that $tr_x(\hat{\rho}_x^2) < 1$, if the states do not factorize (are correlated) $\hat{\rho} = \hat{\rho}_S \otimes \hat{\rho}_B + \hat{\rho}_{corr}$, $\hat{\rho}_{corr} \neq 0$. Assuming the bath to start in thermal equilibrium, a convenient shift in energy of the subsystem, and most importantly assuming the initial state to be uncorrelated $\hat{\rho}(t=0) = \hat{\rho}_S(t=0) \otimes \hat{\rho}_B(t=0)$, the Nakajima–Zwanzig equation (8) [88–90] for the adjusted density matrix in interaction picture $\hat{\rho}'(t)$ is

$$\partial_t\mathcal{P}\hat{\rho}'(t) = \int_0^t dt'\mathcal{K}(t,t')\mathcal{P}\hat{\rho}'(t') \ . \tag{8}$$

The memory-kernel $\mathcal{K}(t,t')$ in this integro-differential equation stems from propagating effects inside the bath, i.e. the system will be driven by retarded interactions with itself via the bath degrees of freedom. This implies that solving for $t = T$, we have to retain the full information of the correlated movement starting from time $t = 0$. When this kernel becomes singular, i.e. when the memory of the bath vanishes and it merely adjusts adiabatically, the evolution is referred to as Markovian. Limiting to a given order in perturbation theory, performing the Markovian limit and the RWA, one arrives at the highly used Lindblad master equation [88].

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[10] Notice the opposite sign in relation to the Heisenberg equation of motion $i\hbar\frac{d}{dt}\hat{O}_H(t) = [\hat{O}_H(t), \hat{H}]_- + \partial_t\hat{O}(t)|_H$.

How quick information is exchanged between system and bath, i.e. how strong the bath affects the system, depends on the spectral overlap and energy of the involved physical species. In many situations a qualitative consideration of the bath degrees of freedom might be sufficient when the dynamics of system and bath can be well distinguished (see Sec. 5.1.2 for an extended discussion). Solving the (simplified) equations for the density matrix is unfortunately just in a very restricted limit possible as the exponential wall problem prohibits us from accessing the complete density matrix. It is thus common practice to consider a small number of eigenstates to represent the system, e.g. we assume a molecule to posses a ground and a single excited electronic state (2-level approximation). The possibility to conveniently solve the 2-level system, representing it as spin/Bloch equations via Pauli matrices, in combination with its intuitive interpretation and valuable insight in many situations renders this strong limitation of the electronic Hilbert space the most common application. Many dynamical features that give rise to a strong interaction between system and bath, such as strong light-matter coupling in cavity QED, will question the representability of the infinite electronic Hilbert space by just two states. We show in P3 that excitations into higher excited states can even dominate the dynamics and it is part of the scientific responsibility of a theoretician that the physical prediction and interpretation concluding from his research should not depend on this number of states. By simplifying the system towards few states, we furthermore loose a substantial amount of information as real-space observables are typically far less accurately represented if at all, see P2 and Sec. 6. Special care has to be taken with the fact that the highly limited Hilbert space introduces very fundamental issues if not considered with great caution. Examples include breaking translational invariance, gauge independence, and the interpretation of observables as illustrated in Section 4.3, P1, P2 and other recent publications [91, 92].

4.2.2 Quantum chemical approach

Chemical processes involve the correlated dynamics of various interacting electrons under the influence of nuclear evolution. The small but essential energetic changes in the meV range decide which path a reaction will take and smallest geometric distortions of the molecule can have a sizeable influence. So will the reorientation of methyl groups lead to energetic changes on the order of eV, essential for the current research mentioned in Sec. 7. This gave rise to a large set of accurate wavefunction techniques, such as configuration interaction [64, 65] and coupled cluster theory [66], most of them based on the explicitly antisymmetric Slater-Determinants

$$\Phi_{SD}(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_{N_e}\sigma_{N_e}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1\sigma_1) & ... & \phi_{N_e}(\mathbf{r}_1\sigma_1) \\ \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_{N_e}\sigma_{N_e}) & ... & \phi_{N_e}(\mathbf{r}_{N_e}\sigma_{N_e}) \end{vmatrix}_- .$$

Slater-Determinants (SD) allow to represent an antisymmetric many-body wavefunction in terms of single particle orbitals, i.e. $\phi_i(\mathbf{r}_j\sigma_j)$ describe the spatial plus spin dependent wavefunction of a single indistinguishable electron. In general, a single SD is not sufficient to describe interacting electrons due to correlation, which demands a superposition of multiple such SDs. If we restrict ourself to a single SD, we arrive at the Hartree-Fock approximation, or in different contexts often referred to as exchange only or mean-field approximation. In the light-matter context we will use the terminology mean-field as equivalent to solving Maxwell's equations of motion. One should distinguish two fundamentally different origins of electronic correlation, namely dynamic and static correlation. The former is of collective nature and represents that two electrons do not feel just each other but always also the surrounding electrons which effectively screen the interaction. Various approaches are tailored for this problem ranging between perturbative extension on Hartree-Fock, most famous Møller–Plesset (MP) [93, 94], exchange correlation kernels in density-functional theory [95], up to self-consistent Green's functions [96] and Quasi-particle corrections [97]. Static correlation on the other hand can be reduced to the dissociation limit of molecules (see e.g. P3). To visualize static correlation assume H_2, initial very close and well approximated by a single SD, the more we pull the hydrogens apart, the more the electrons will localize on atom 1 and 2 until their Coulomb interaction vanishes but the many-body wavefunction will then be precisely one SD per atom. With a few exceptions, such as multi-reference extensions [98] or reduced density matrix theory [99], static correlation and therefore bond-breaking is very cumbersome to describe for any method based on a single SD. Providing a sufficiently accurate and computationally inexpensive method is still an active domain of research.

In conjunction with techniques to describe the nuclei, e.g. the Born-Oppenheimer approximation (Section 4.3), Ehrenfests equation of motion or semiclassical techniques such as fewest-switches surface-hopping (Section 5.2.1), a methodology focused on the accurate solution of 'small' molecules arose. By embedding the calculation of small most relevant domains with advanced techniques into a surrounding environment predicted with inexpensive, sometimes even classical (QM/MM [100]), techniques, it was possible to expand the 'small' system limit up to biomolecules. Sometimes however, the electronic interaction might be so strong that correlation effects become non-perturbative. In those situations slightly improving a single SD will not be sufficient and strong correlation methods are more desirable. One famous wavefunction based representative is the density-matrix renormalization group (DMRG) [101] which gained increasing interest with the investigation of Hubbard-type models for low-dimensional highly correlated applications. The multiconfiguration time-dependent Hartree (MCTDH) [102, 103] method on the other hand is designed to capture correlated dynamics by a variationally optimal set of single-particle wavefunctions. Both explicitly utilize the knowledge that a small subset of the Hilbert space is physically relevant, resulting in separating wavefunctions (and operators) such that they stay within their according subsets. So far, those techniques are, however, limited by the scaling of correlation (the area law [101]). DMRG is mostly used in one-dimensional calculations, e.g. chains of simplified atoms, and MCTDH utilized for around 10 degrees of freedom of the wavefunction, where extensions such as multilayer MCTDH might extend those limits.

As we are actually interested in observables and not the wavefunction, why not design a theory phrased in terms of a more minimalistic object? This realization leads into various directions, two of them are part of this work, namely (time-dependent) density-functional theory (TDDFT) and many-body perturbation theory (MBPT). We present a short introduction into both methods in Section 5.1.1. The main difference to our previous considerations is that instead of directly solving the exponentially scaling linear Schrödinger equation, we attempt to solve equivalent low-dimensional but nonlinear equations. The very low cost of handling e.g. the electronic density $n(\mathbf{r},t) = N_e \int dr_2...dr_{N_e} |\Psi(\mathbf{r},...,\mathbf{r}_{N_e},t)|^2$ and single particle orbitals $\phi(\mathbf{r},t)$, in contrast to the high-dimensional wavefunction $\Psi(\mathbf{r}_1,...,\mathbf{r}_{N_e},t)$, lead to the success of TDDFT in quantum chemistry and solid-state physics. The multicomponent formulation of DFT can be conceptually easily extended to include photonic degrees of freedom as discussed in Sec. 5.1.1 and thus renders itself as a promising approach to tackle the correlated nuclei, electron, photon system.

It is apparent that quantum optics and quantum chemistry, although described by the very same Hamiltonian (1), developed over the years in their methodological toolset and their perspective on nature in far opposite directions. The novel interest in the modification of materials and chemical reactions by quantum light, however, calls now for a combined and consistent treatment. As a first step, we illustrate in Section 4.3 that an oversimplified attempt to merge light and matter is doomed to deliver unphysical predictions. In Section 5 we present then different perspectives and tools connected to this work, all designed to tackle different arising issues in the demanding field of *ab initio* cavity QED.

4.3 Treating light and matter on equal footing and what can go wrong

By stressing the need for a theory that is able to consistently treat the electronic structure to great detail and especially spatially resolved, we open our self for a fair share of concerns. Fundamental considerations such as the relevance of the self-polarization or qualitative changes when restricting the basis after unitary transformations demand special care. The success of few-level systems is based on its simplicity, accurate predictions for spectral features and especially very intuitive application and interpretation. It however embodies always the demand to test if the limited set of eigenstates considered is sufficient, thus converged. This concept is often neglected and subsuming all but the lowest eigenstates by adiabatic elimination or projection will only be applicable if the higher excited states are never truly of importance.

When aiming to merge quantum chemistry with quantum optics it is convenient to work in a basis that is common in chemistry. We provided above a glimpse into possibilities how the electronic problem can be solved, e.g. based on SDs and single particle orbitals. The Hamiltonian (7) and its multi-dimensional wavefunction involve furthermore nuclear and photonic degrees of freedom. It is common practice to separate the wavefunction into electrons and nuclei via the Born-Huang expansion [104] and we present in publication P2 how this

ansatz can be extended to include photonic coordinates as an additional species.
Our starting point is the realization that we can exploit the unitarity of our Hamiltonian to expand any wavefunction into a basis of eigenstates with a parametric dependence such that

$$\begin{aligned}\Psi_i(\mathbf{R}_n,\mathbf{r},\mathbf{q}) &= \sum_{\mu=0}^{\infty}\chi_i^{\mu}(\mathbf{R}_n)\tilde{\Psi}_{\mu}(\{\mathbf{R}_n\},\mathbf{r},\mathbf{q})\\ &= \sum_{\mu,k=0}^{\infty}\chi_i^{\mu}(\mathbf{R}_n)\psi_{\mu}^{k}(\mathbf{r},\{\mathbf{R}_n\})\Phi_k(\mathbf{q},\{\mathbf{R}\})\ ,\end{aligned}$$

where $\mathbf{R}_n=\{\mathbf{R}_n^1,...,\mathbf{R}_n^{N_n}\}$, $\mathbf{r}$ and $\mathbf{q}$ represent the full list of nuclear, electronic and photonic coordinates and $\mathbf{R}$ the total matter dipole. The indexation $\psi_{\mu}^{k}(\mathbf{r},\{\mathbf{R}_n\})$ indicates that the electronic many-body wavefunction depends parametrically on the nuclear configuration and each eigenstate μ is associated with the full set of photonic excitations k. This expansion is defined in conjunction with the normalization condition

$$\begin{aligned}\langle\Psi_i|\Psi_i\rangle &= \sum_{\mu',k'=0}^{\infty}\sum_{\mu,k=0}^{\infty}\langle\chi_i^{\mu'}|\chi_i^{\mu}\rangle_n\langle\psi_{\mu'}^{k'}|\psi_{\mu}^{k}\rangle_e\langle\Phi_{k'}|\Phi_k\rangle_p\\ &= \sum_{\mu,\mu'=0}^{\infty}\langle\chi_i^{\mu'}|\chi_i^{\mu}\rangle_n\sum_{k=0}^{\infty}\langle\psi_{\mu'}^{k}|\psi_{\mu}^{k}\rangle_e = \sum_{\mu=0}^{\infty}\langle\chi_i^{\mu}|\chi_i^{\mu}\rangle_n = 1\ .\end{aligned} \tag{9}$$

This is an exact expansion, while certainly infinite basis functions are computationally out of scope and thus a converged limitation will be demanded. How well we can restrict this set of eigenfunctions very much depends on the problem at hand and how suitable the basis is to address this problem. From this separation of the wavefunction, a separation of the Schrödinger equation into interacting sub-equations results naturally by applying the Hamiltonian (see P2), i.e. the electronic equation reads in atomic units

$$\begin{aligned}&\hat{H}_{BO}^{l}(\mathbf{r},\{\mathbf{R}_n\})\psi_{\mu}^{l}(\mathbf{r},\{\mathbf{R}_n\}) - \frac{1}{2}\sum_{k=0}^{\infty}\left[2\nabla^{lk}\cdot\sum_{j=1}^{N_e}\nabla_{\mathbf{r}_j} + N_e\Delta^{lk}\right]\psi_{\mu}^{k}(\mathbf{r},\{\mathbf{R}_n\})\\ &= E_{\mu}(\{\mathbf{R}_n\})\psi_{\mu}^{l}(\mathbf{r},\{\mathbf{R}_n\})\ .\end{aligned} \tag{10}$$

When utilizing this procedure we should consider that carrying out the integration over the nuclear coordinates demands the completeness of the photonic and subsequently the electronic eigenstates. For example the full electronic density would demand to integrate out the parametric nuclear dependence

$$\begin{aligned}n_i(\mathbf{r}_1) &= \int d\mathbf{R}_n\int d\mathbf{r}_2...d\mathbf{r}_{N_e}\int d\mathbf{q}\Psi_i(\mathbf{R}_n,\mathbf{r},\mathbf{q})\Psi_i^*(\mathbf{R}_n,\mathbf{r},\mathbf{q})\\ &= \sum_{\mu,\nu,k=0}^{\infty}\int d\mathbf{R}_n\int d\mathbf{r}_2...d\mathbf{r}_{N_e}\chi_i^{\mu}(\mathbf{R}_n)\chi_i^{\nu,*}(\mathbf{R}_n)\psi_{\mu}^{k}(\mathbf{r},\{\mathbf{R}_n\})\psi_{\nu}^{k,*}(\mathbf{r},\{\mathbf{R}_n\})\\ &\neq \sum_{\mu,k=0}^{\infty}\int d\mathbf{r}_2...d\mathbf{r}_{N_e}|\psi_{\mu}^{k}(\mathbf{r},\{\mathbf{R}_n\})|^2\int d\mathbf{R}_n|\chi_i^{\mu}(\mathbf{R}_n)|^2\ ,\end{aligned}$$

from which follows that the parametric dependence has to be respected if we want to get the 'true' electronic average density which will include a nuclear average. Commonly this is ignored such that the electronic density is considered to be parametrically depending on the nuclear configuration, i.e. the nuclear ensemble is encoded in the parametric dependence of the observable. In this sense the above braket-notation of Eq. (9) can be misleading when this fact is forgotten, i.e. this short-hand form implies the stepwise integration from the right towards the left.

Equation (10) is structurally very similar to the Floquet picture where a matter system is coherently driven by an external field such that a time-periodic ansatz provides a quasistatic solution. Floquet physics comprises a manifold of possibilities which are based on the concept of stabilizing the system in an eigenstate with peculiar features, e.g. topological switching of conical intersections [105]. The disadvantage is that the system is constantly subject to strong illumination. This implies heating, strong decoherence and a demand for constant supply of energy. The cavity on the other hand enables a path with very similar features yet without the demand of pumping and subsequent drawbacks. Similarities, differences and possible proposals to exploit the cavity for material design are elaborated in publication P2 and Sec. 7.

The second-order differential structure of the non-relativistic Schrödinger equation ($\propto \nabla_{\mathbf{r}}^2, \nabla_{\mathbf{R}}^2, \hat{p}^2$) results in components that mix different eigenstates μ whenever the so called non-adiabatic elements ∇^{lk} are non-zero, very similar to the hybridization of atomic orbitals in molecules. If we assume that all $\nabla^{lk} = 0$, we enter the famous Born-Oppenheimer approximation.[11] In this sense, the non-adiabatic couplings lead to novel eigenstates that carry light, nuclei and electron character, representing the quantum interaction among the different species. Those dressed eigenstates are the previously introduced polaritons, illustrated in Fig. 4, quasiparticle states of mixed character. In addition to the linear couplings ∇^{lk}, we notice that quadratic couplings Δ^{lk} arise in the expansion. Those components represent how the curvature of subsystem-states $\Delta\Phi_k$ affect the combined system. This clearly emphasizes that the Schrödinger equation has to give rise to non-linear components, as a basic consequence of the fact that it includes second order differentials. Those terms, as is illustrated in P2 and P1, precisely reproduce the quadratic $\hat{\mathbf{A}}^2$ term but furthermore lead to the so called Debye-Waller contribution [111, 112]. Both effectively rescale the excitations according to the involved nuclear/electronic displacements. Those rescalings are not just manifestly rendering a quantum-system stable, i.e. preventing the bilinear coupling that favors a large displacement from resulting in an ever increasing charge-separation, but furthermore are es-

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[11] It is indeed in principle possible to obtain a set of equations for which $\nabla^{lk} = 0$ and that exactly solve the Schrödinger equation. The frame and corresponding transformations are referred to as diabatic [106]. Within this frame, coupling between surfaces will persist through energetic couplings (off-diagonals in the photonic/electronic eigenvalues). Within the photonic context of P2, the diabatic transformations are related to unitary transformations between Coulomb and PZW-gauge. The interested reader is suggested to furthermore relate this to [107]. The interested reader might also refer to the exact factorization ansatz [108], which explicitly enforces an exact factorization of components. Recently this ansatz was applied to light-matter correlated systems [109, 110].

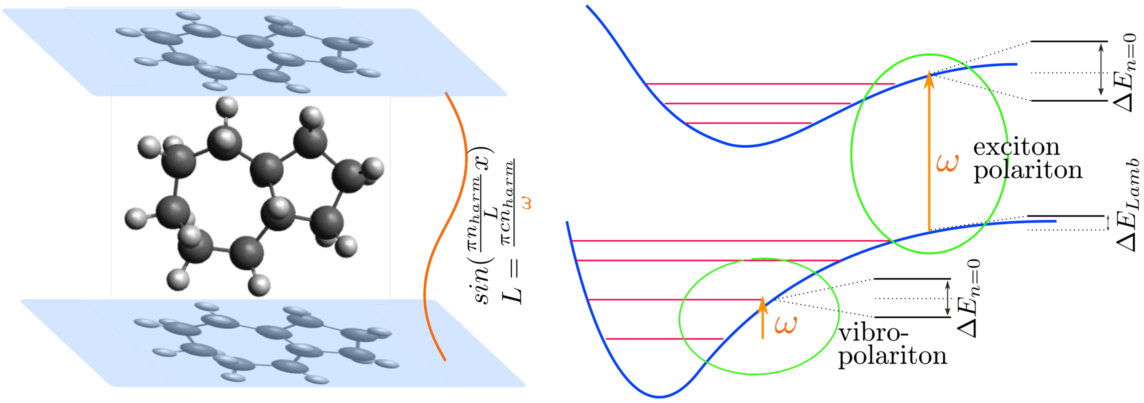

Figure 4: Schematic of strong light-matter interaction giving rise to light-matter correlated eigenstates. The strength of interaction can be characterized by the hybridization/splitting $\Delta E_{n=0}$, often referred to as the Rabi splitting (providing the beating frequency). In principle every state connected by non-adiabatic coupling elements will be affected by the light-matter interaction, including vibrational and electronic excitations. For sufficient energy separation, just one of the species (nuclei or electrons) will be dominantly affected and we can define vibro- and exciton-polaritons. Notice that this distinction might be questionable around avoided crossings and conical intersections of the electron-nuclei system.

sential to guarantee fundamental physical concepts such as translational invariance, gauge independence and non-radiating eigenstates (see P1). Let us stress once more, *any* Hamiltonian that includes purely bilinear couplings between e.g. nuclei and electrons and/or photon is manifestly limited to perturbative treatments, demands a restriction to a finite basis or an underlying squeezing transformations with adaptive parameters (see e.g. [91, 113]). This is clearly a contradiction to our goal of *ab initio* self-consistent calculations.

All complexity is merely rephrased in a hierarchy of coupled eigenvalue equations instead of solving directly the Schrödinger equation, which nevertheless allows for convenient further simplifications and interpretation of the various contributions as described above. The photons are now of special character as they do not interact among themselves but merely via a polarizable material (and the $\hat{\mathbf{A}}^2$ which is subsumed into the matter equations). We can therefore solve the photonic sub-system equation analytically and all the complexity of the light-matter interaction enters then in the aforementioned (non)-adiabatic couplings, known also analytically (for details please refer to P2). The beauty of this approach is that the matter eigenstate can be expressed and calculated with typical quantum chemical methods, e.g. in an CI sense expanded in SDs, while the coupling elements are mixing those eigenstates. Following this concept in P2, one is then able to elegantly connect to few-level representations.

Solving the photonic equation analytically by introducing generalized coherent states corresponds amusingly to the unitary transformation that transfers the PZW gauge back into the Coulomb gauge. The translation of photonic coordinates switches between the two most common expressions of light-matter interaction and they are merely equivalent when the full Hilbert space is considered (see Sec. 4.3.1 and especially P1). It furthermore illustrates the connection of quadratic $\hat{\mathbf{A}}^2$ and $\hat{\mathbf{R}}^2$ components, i.e. while they both effectively confine the

coupled system and rescale excitations (light or matter), they are not equivalent. For spatially well localized (finite) systems, the PZW gauge is typically converging faster with the number of eigenstates (P2,[91, 114]) and therefore seems preferential when a reduced description is envisioned. However, the PZW gauge is accompanied with the demand to treat $\hat{\mathbf{R}}^2$ self-consistently within the matter subspace and therefore gives rise to additional long range matter-matter interactions. To be precise, it scales for larger distances identical to the Coulomb interaction which leads to a cancellation of the two components (see P1 and [13, 69]). So far just very few theoretical approaches such as QEDFT P4, photon adopted reduced density-matrix functional-theory (RDMFT) [99] and coupled-cluster theory [115, 116], present feasible solutions for realistic systems.
Let us highlight at this point that we could have decided to merely perform the common separation of 'fast' electrons from the 'slow' nuclei and consider similarly the photons as 'slow'. Then, we would need to solve the common electronic problem with parametric nuclear and photonic coordinates in addition to the $\hat{\mathbf{R}}^2$ term. This cavity Born-Oppenheimer (cBO) ansatz [107] therefore implies that the photonic and nuclear excitation energies are on comparable scale and well separated from the electronic excitations. Assuming we solve the electronic problem under those conditions, the photon-nuclear problem can be diagonalized which gives rise to well approximated 'vibro-polaritons', i.e. the photon-nuclei quasiparticles moving on adiabatic electronic surfaces. Describing the electron-photon hybridization would however demand considering an expanded basis according to our description above. Nevertheless, for situations where dominantly nuclei and photons couple, this might present a very effective approach, once functional solutions to $\hat{\mathbf{R}}^2$ are designed. It provides furthermore a very illustrative tool to visualize the influence of the cavity onto molecular systems.

4.3.1 Limitations of few-level systems and the ambiguity of physical conclusions

The energy splitting between the two 'bright' polaritons of the Tavis-Cummings model (recall Tab. 1), with N identical 2-level emitters, scales as

$$\Delta E^{TC}_{n=0} = \sqrt{\delta^2 + (2\sqrt{N}g)^2},\ g = \sqrt{\frac{\omega}{2}}\lambda.$$

Here $n = 0$ indicates that the cavity is in the vacuum state and $\delta = \omega - \varepsilon_1 - \varepsilon_0$ is the detuning between electronic and photonic excitation (recall Sec. 3, 4.1 and see 5.2). The above framework however clarifies that the reduced model originating from Eq. (10) (see P2) and the Tavis-Cumming model are not quite consistent for two reasons. First, the coupling elements (dipole moments and non-adiabatic couplings) deviate from each other by a component $\propto \delta/\omega$ such that they merely coincide in the case of resonant coupling, and second, even in the 2-level restricted setup the adiabatic couplings Δ^{ll} will give rise to rescaling of excitations. To include this into the Tavis-Cummings splitting above, the detuning has to know about the rescaling of energy levels. This naturally appears through an adjusted detuning $\tilde{\delta} = \delta + \mathcal{L}$ with the collective Lamb-shift $\mathcal{L} = \left[\sqrt{N}\frac{\lambda}{\sqrt{2\omega}}\right]^2$. How impactful those differences turn out

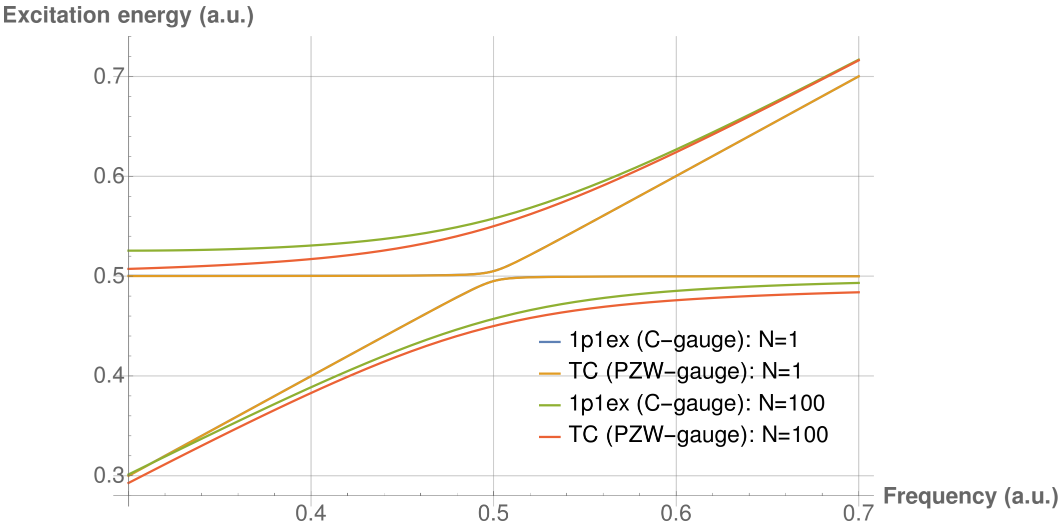

Figure 5: Excitation energies vs cavity frequency for N 2-level systems ($\varepsilon_1 - \varepsilon_0 = 0.5,\ R_{01} = 1$) coupled to one cavity mode $\lambda = 0.01$. Plotted is the single-photon single-excitation limit of Eq. (10) in Coulomb gauge (1p1ex) (Sec. IV(B) of P2) and the Tavis-Cummings solution in PZW gauge for $N = 1$ and $N = 100$. The Rabi splitting for very small coupling and very few 2-level systems is in close agreement between the two alternative formulations. The deviations in the matrix elements $\propto \delta/\omega$ and the collective shift $\mathcal{L}$ are of minor influence as offside the resonance cavity and matter hybridize just weakly. Increasing the number of 2-level systems amplifies the hybridization of the bright states and illustrates the deviating behavior especially for $\delta \neq 0$. The diamagnetic contribution that manifests here via $\mathcal{L}$ slightly shifts the resonance and off-set of the excitations. The ground state of the TC model is constant.

depends foremost on the effective coupling between cavity and matter and is illustrated in Fig. 5. While the Tavis-Cummings model provides often very valuable intuition, the fact that even in this extremely fringe and simplified setup our approach indicates inconsistencies signalizes that it might easily lead to tainted conclusions.

We have seen that the precious gauge invariance is lost once the Hilbert space is restricted. Clearly, any approach that connects light and matter in a rather *ad hoc* fashion [117–121] will need to verify that their predictions are not tainted or jeopardized by the underlying approximations that lead to this description. Omitting the self-polarization component, by restricting the basis or the Hamiltonian itself, will for instance suggest that the permanent dipole plays a crucial role for the equilibrium structure of molecules [120, 122] which is in strict contrast to observations when the $\mathbf{R}^2$ part is considered (see P1). Similar ambiguities appear in the ultra-strong coupling limit in which a phase-transition into a superradiant ground state is suggested by some models. Depending on factors such as the underlying gauge, the inclusion of quadratic components or Coulomb interaction, the size of the restricted basis and the application of the RWA, many different predictions can be obtained (see P2 and [91, 123–130]). While individual investigations (see P2 and [91, 114]) suggest that the PZW-gauge performs superior when the matter basis is restricted, it is unclear to which extend this will be universally true and if certain subsequent modifications might not change this observations. In addition, converging the coupled light-matter system will not always monotonically improve observables. We have shown in P2, that certain observables are resembled worse when the basis for matter and photon excitations are not consistently improved. This can lead to the point that qualitatively contradictory predictions are obtained for the electronic density and mode occupation. Lastly but especially important, P2 illustrated that the amount of bare matter eigenstates can become overwhelming for very strong interaction to the point that convergence renders as a cumbersome task. Given the fact that typically just very few many-body eigenstates can be obtained with reasonable effort, such a convergence scheme in bare eigenstates will be unfeasible in many interesting situations in which substantial differences can be observed. It becomes apparent that the future development of cavity QED will greatly benefit from those conclusions (P1, P2, P3) and the development of *ab initio* techniques such as P4, P5, P7 and P6. Let us emphasize here that this does not imply that common models should be abandoned. In contrast, they will remain a substantial component to obtain physical intuition in a broad range of situations. It merely illustrates that they should be considered as the approximate models that they are, limited to a perturbative treatment and not suited for true *ab initio* self-consistent calculations.

Our considerations so far have been dominantly focused on equilibrium eigenstates but we extended this point of view in publication P3. In Fig. 6 of P3, we show that for rather small coupling values the effect of the self-polarization contribution will accumulate over time, leading to small quantitative deviations for short times. However, when amplifying the coupling by a factor of 10 to a relative strength of $g/\hbar\omega \approx 5.8\%$, commonly still considered as strong coupling, this picture completely changes and lacking the self-polarization will result in a qualitatively different energy transfer. This qualitative change originates from the fact that without self-polarization, charge transfer suddenly dominates the excitation transfer as large (permanent) dipoles become energetically favorable. In combination with P1, P2 and recent experimental observations which indicate that quadratic couplings give rise to enhanced superconductivity [131], we consider it sufficiently proven that quadratic contributions are by no means unphysical. On the contrary, they are essential to guarantee fundamental physical concepts and are often of non-negligible importance, especially when we aim to build a self-consistent machinery, subject to following sections. The 'extension criterion' $\lambda^2/4\varepsilon_i^2$ with i'th energetic eigenvalue ε_i defined in P1, allows to estimate the influence of quadratic components and thus delivers very accessible yet essential insight for theoretical predictions. The community, on both theoretical [91, 92] and experimental [131] side, increasingly realizes the limitations of few-level systems and the impact of quadratic components with continuing development towards an *ab initio* treatment.

4.3.2 Gauge invariance in restricted Hilbert spaces

Let us face the fact that not always an *ab initio* technique might be available or suitable to cover a problem, e.g. the strongly correlated limit of electron-electron interactions. If we restrict thus the applicable Hilbert space, we have seen in Sec. 4.3.1, P1 and P2, that this will break fundamental physical rules and the gauge invariance of the light-matter coupled system. Attempts to understand this problem in the 2-level context illustrated that restricting the dimensionality relates to an adjustment of the unitary transformations that connect the Coulomb and PZW gauge [92]. Now the question still remains which of our gauges is suited best, which basis converges quicker to the correct result and which fulfills the previously mentioned conditions best (translational/origin invariance, stability, radiation less eigenstates, gauge invariance and consistency among observables)? Clearly, this will depend on the problem at hand and the form of dimensional restriction, e.g. a smart basis might capture much more of the physics and converge quicker. Imagine for example we try to describe a system with a permanent dipole in the PZW gauge. This in turn implies a coherent shift of the canonical displacement $q = \frac{\lambda}{\omega} \cdot \mathbf{R}_{perm}$ and thus a large basis of states $(\hat{a}^{\dagger})^n|0\rangle$ would be needed to converge the results as a lot of photons have to be excited to capture a coherent displacement (classical shift of the harmonic potential '$n \rightarrow \infty$'). On the other hand, a basis with generalized coherent states, such as the Born-Huang basis in P2, will capture the coherent shift trivially and merely the fluctuations around it have to be approximated. Similarly, a specific basis that intrinsically accounts for gauge invariance and e.g. the conservation of dipole moments, the Thomas-Reiche-Kuhn sum-rule, will be superior over others. While the gauge theory at hand (QED) is actually rather simple with a single gauge field, being abelian and usually coupling perturbatively to matter ($\alpha \sim 1/137$), Quantum chromodynamics, the gauge theory for the interaction of quarks and gluons, features coupling strengths around unity and a manifold of gauge bosons. The lattice gauge theory is nowadays the method at hand to tackle non-perturbatively and intrinsically gauge invariant the challenges that define quantum chromodynamics. The basic idea of lattice gauge theory is to represent the system by a lattice consisting of small plaquettes which are all intrinsically gauge invariant by construction as they allow for a closed loop (the Wilson loop $e^{iq\oint_C A_\mu(x)dx^\mu}$) of the vector potential [132–135]. The action of those loops cancel when in contact to other loops around them such that the connection of plaquetes allow a gauge invariant formulation of any restricted space and the full action is given always correctly as a closed loop around its surface. This conceptional approach was already in its early steps exemplified by applying it to QED and scrutinizing it in the novel context might deliver the demanded method to go beyond the dipole approximation, beyond a perturbative treatment and remain intrinsically gauge invariant.

We have seen that by no means a clear and unambiguous description in terms of simplified models is always common or available. With increasing coupling strength, the design of non-conventional cavities (plasmonic, circuit QED, ...) and their interplay with molecular rather than atomic systems, fundamental concerns appeared that call for a careful reflection on common methodologies. The beauty of QEDFT is now that it allows a spatially resolved first principles description which circumvents many of the previously mentioned issues. All our problems culminate in the construction of a local potential that will mimic quantum interactions that appear within the potpourri of electrons, nuclei and photons. The design of possible approaches as well as their application is one of the focus points of this thesis. The following Sec. 5 will introduce the ideas and efforts that associate QEDFT and related methods with this work.

5 Quantum chemistry in cavities

Theoretical approaches and promising steps for an untainted perspective

After we set the physical framework and the according correct equations, let us briefly review a set of options that arise to describe cavity QED from first-principles. Specific details can be obtained from the corresponding publications. In this sense, this section will provide merely a methodological motivation, introduction as well as highlighting strength and weaknesses in the big picture. Let us start with the ground state, extend to equilibrium eigenstates, debate the role of decoherence and finally provide a perspective how large systems could be described. We use atomic units in the following.

5.1 (Non)Equilibrium features of the light-matter correlated system

Solving the full light-matter problem with a finite number of modes, thus treating all possible degrees of freedom as part of the Hamiltonian and system, will always allow us to identify static quantities. The corresponding ground and excited states characterize the complete Hilbert space (see Fig. 6). Any (time-dependent) state $\Psi(t)$ can be expressed in terms of the known equilibrium states (spectrum) and associated energies $\Psi(t) = \sum_i c_i \psi_i e^{-i\varepsilon_i(t-t_0)}$ with expansion coefficients c_i, $\sum_i |c_i|^2 = 1$. Weakly perturbing the set of eigenstates in the form of a linear response measurement allows to deduce all equilibrium features. Precise knowledge of equilibrium quantities and their perturbative response covers therefore often a substantial part of physics. The ideal cavity would feature cleanly separated eigenstates and the correlated system would posses polaritonic states with infinite lifetime. The fact however that no cavity is truly perfect leads to a finite width (recall the Q-value $Q = \Delta\omega/\omega$) such that in reality every excited state will posses a finite lifetime. For instance, imagine that we start in an initial 'pure' state, e.g. the ground state, for which $\hat{\rho}(t) = c_0(t)c_0^*(t)|\Psi_0\rangle\langle\Psi_0|$. An external drive will lead to non-vanishing transition matrix elements $\langle\Psi_0|\hat{H}(t)|\Psi_j\rangle \neq 0$ in the state-basis, disturbing the system out of equilibrium. In turn, the evolution will feature coherent oscillations between the various participating states Ψ_j, referred to as polarization. The more states participate in this process, the more different oscillation periods are present and the longer it takes until the initial configuration reappears (revival). If j becomes very large or even tends towards a continuum of states, every small excitation will couple to a vast number of states, all with different associated oscillations. If we now project (in the sense of Sec. 4.2.1) into one specific subsection of interest $\mathcal{P}$, e.g. the dynamic of the electronic system instead of the full photon-matter system, the remaining degrees of freedom $\mathcal{Q}$ will still influence the subspace and render the hole system still unitary if no approximations are employed. Each subsystem individually evolves however non-unitary and experiences decoherence. The electronic system might for instance undergo spontaneous emission, i.e. initial occupation is turned into polarization and relaxes towards the electronic ground state (see e.g. P6). For a finite number of photonic modes, the spontaneously emitted photon will after some time bounce back from the boundaries of the quantization box and return to the

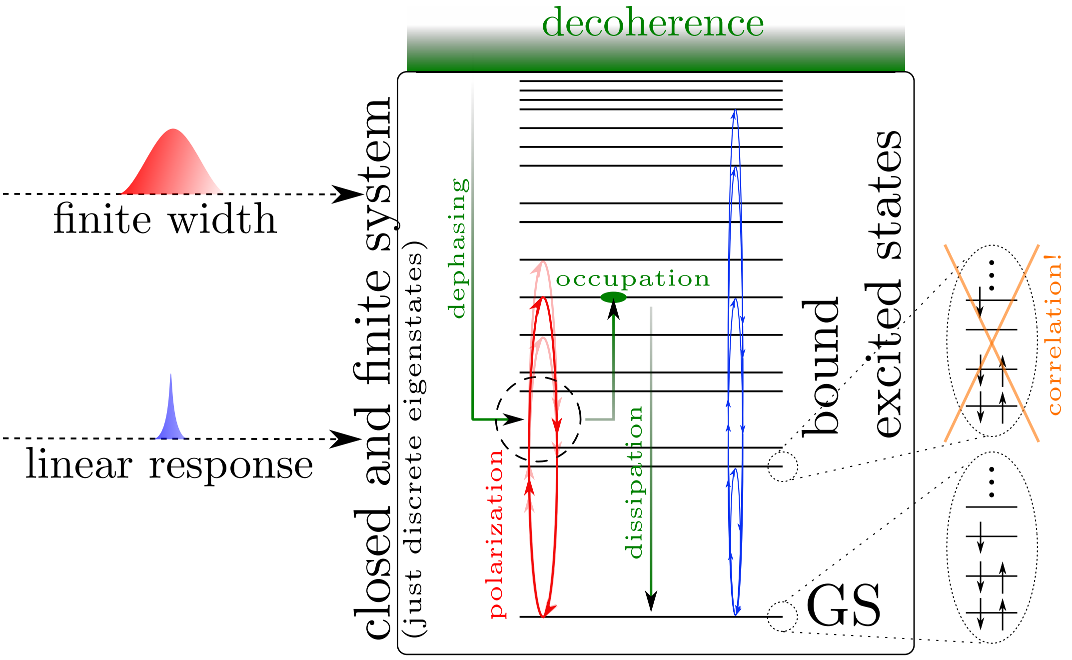

Figure 6: Schematic of a quantum system subject to external driving. Any closed quantum system with finitely many degrees of freedom has a set of discrete eigenstates which are the solutions to the Schrödinger equation with employed boundary conditions. Note that the correlation among e.g. the fermions lead to excitations that are not just single-particle excitations but instead of correlated nature, e.g. removing one electron does also relax all other single-particle eigenvalues. This 'closed' system is in constant interplay with other degrees of freedom, e.g. a continuum of states, that represent channels for decoherence. A pulse of finite width will excite coherent oscillations within a small energy-window. A $\delta(t)$ linear response kick instead will excite towards all non-forbidden eigenstates as the sharp pulse includes all frequencies. Occupation is the result of decoherence disturbing the polarization, where 'effective' decoherence via many channels can in practice also result from the large Hilbert space of correlated particles. External perturbations or absorbing boundaries [136] transform $\delta(\omega)$-like spectral peaks, characterizing the closed system eigenstates, into resonances with finite lifetime and therefore introduce concepts such as spontaneous emission or vibrational relaxation.

electronic system, which is the concept behind strong light-matter coupling in cavities. If we instead send the box to infinity [14, 137], define absorbing boundaries [136] or assume that the photonic system acts merely as an energy accommodating bath, the electronic system will have been permanently relaxed to the ground state. In general, spectral features and the anharmonicity of the bath define how quickly polarization dephases into occupation which in turn decays via dissipation as a consequence of energy or particle transfer between the specific subsystem of interest and the surrounding system. Therefore describing a large Hilbert space does not always demand the inclusion of external decoherence to effectively thermalize a state, motivated in P3 and illustrated by the spontaneous emission process in P6 and P7. It is much more the consequence of focusing our attention on a subset of the system, may it be via theoretical projection or selective measurement. The feature of thermalization in closed systems is known as many-body thermalization and prethermalization, i.e. the system can be (partially) characterized by thermodynamic quantities such that the dependence on the initial state is seemingly erased [138]. Exclusions are situations were many-body localization appears which effectively permits thermalization.

5.1.1 Quantum electrodynamic density-functional theory (QEDFT)

Density-functional theory is nowadays an essential tool in the set of methods to capture ground and excited state features for molecules and extended systems. The basic idea is to describe the interacting system, usually subject to the high-dimensional wavefunction $\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, ...)$, in terms of a strongly reduced quantity (see Fig. 7), the density $n(\mathbf{r})$. This would render the latter approach tremendously less expensive. And indeed, Hohenberg an Kohn [139] found that a unique bijective mapping between the electronic ground-state density $n(\mathbf{r})$ and the many-body electronic wavefunction $\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, ...)$ exists. Let us briefly illustrate this elementary concept before we extend it to include the photonic degrees of freedom. This and following [140–142] proofs are based on two assumptions that have to be fulfilled. The first is the *N-representability* which ensures that always an antisymmetric normalizable N-electron wavefunction as solution to the Schrödinger equation exists that leads to the density $n = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$. Our second condition, the *v-representability*, has to guarantee that there exists an external potential (e.g. the nuclear potential binding the electrons) for which we obtain exactly this density. While fringe cases exist where those situations are not met, mostly due to specific boundary problems, for most physically relevant examples the bijectivity conditions are fulfilled such that

$$E\Psi = (\hat{T} + v(\mathbf{r}) + \frac{1}{2}\sum_{i \neq j} \tfrac{1}{|\mathbf{r}_i - \mathbf{r}_j|})\Psi \text{ with } v \leftrightarrow \Psi$$

$$\Psi \leftrightarrow n(\mathbf{r}) = N \int d\mathbf{r}_2 ... d\mathbf{r}_N \Psi^*(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N)\Psi(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N) \ .$$

We can therefore express the wavefunction uniquely in terms of its density $\Psi[n]$ for a given v, where v is unique up to a constant. This by itself is quite amazing but the true beauty of this approach manifests once we realize that at no point during this proof the Coulomb interaction among electrons $\frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$ played any role. So a system with a different local potential, lets call it Kohn-Sham potential v_{KS}, but without electronic Coulomb interaction will be able to reproduce the same density, thus the same wavefunction $\Psi[n]$ and all observables, if we just know what the difference between the local potentials $v_{Hxc} = v_{KS} - v$ is. This difference is called Hartree-exchange-correlation potential (Hxc) and it should intuitively somehow mimic the effect that the electronic Coulomb interaction had for the interacting system v for the non-interaction (Kohn-Sham) system with v_{KS}. If we succeed, we can solve a non-interacting system, a rather trivial task, instead of the exponentially complex interacting system. The Hartree-component is indeed trivial $v_H(\mathbf{r}) = \int d\mathbf{r}_2 \frac{n(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|}$ and we quickly realize that it boils down to the question if we can find the exchange-correlation component v_{xc}. In practice, obtaining the exact v_{xc} is of similar complexity as exactly solving the Schrödinger equation and any practical v_{xc} will be of approximative nature. Most commonly, this approximation

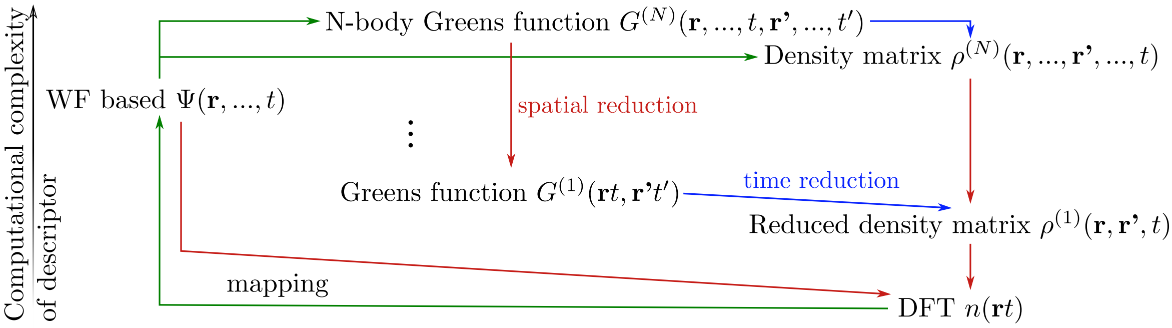

Figure 7: Computational complexity of various common descriptors (describing the system). Despite its simplicity and therefore computationally convenient handling, the density uniquely reproduces the wavefunction (up to a global phase). The same is not true for the other descriptors as their mapping is not surjective without further conditions (see e.g. RDMFT theory).

manifests as an abstraction of the solution of the (homogeneous) electron gases to our system of interest (see also Sec. 7). This approach brings with it various flavors (a vast amount of different v_{xc} derivations, ensemble, multicomponent and various other DFTs), subtleties (degeneracies, convergence, ...) and decades of active research and we therefore refer the reader to [95, 141, 143] and references therein. Similar proofs for the time-dependent situation based on most commonly a Taylor expansion [141, 144] allow us to similarly define a time-dependent density-functional theory (TDDFT). Let us note here that the non-interacting Kohn-Sham system is just one special and convenient choice. The auxiliary system could also feature an arbitrarily adjusted interaction, e.g. we could assume a system with weak kinetic energy (Coulomb dominating) and the above proofs would remain valid. Following this direction one can approach the problem of static correlation with DFT, a rather small but active domain of research (see e.g. [145] and references therein) that could similarly proof interesting for the following QEDFT. Note that the wavefunctions and eigenvalues of the auxiliary (e.g. Kohn-Sham) system are not identical with the interacting solutions even if we would have had the exact v_{xc}. The Kohn-Sham eigenvalues for instance represent the effective single-particle energies (bands in solids) but their energy difference is not providing us with the excitation energy of the correlated system (band gap of a solid). Nevertheless is it possible to obtain the correct values (see derivative continuity and adiabatic connection [141]), gain physical insight (the ionization potential is for example given by the Kohn-Sham eigenvalue of the highest occupied orbital) and utilize the Kohn-Sham solutions as perturbative ansatz if we do not know how to express an observable in terms of a functional of the density. This fact causes an immense amount of confusion about the applicability of DFT.

The photonic system attributes now an additional dimension to this problem and again one can proof as before the bijectivity of the system. QEDFT was initially designed for the time-dependent and relativistic situation [146, 147], received subsequent improvements [9, 80] and a ground-state proof similar to the Hohenberg-Kohn theorem was presented by M. Ruggenthaler [148]. The bijective mapping describes a unique relation between external potentials $(\mathbf{j}_{ext}, \mathbf{A}_{ext})$ and internal variables $(\mathbf{A}, \mathbf{j})$ of any system. Again, we can get the

same internal variables by solving a (non-interacting system) with the effective Kohn-Sham potentials $(\mathbf{j}_{KS}, \mathbf{A}_{KS})$ such that $(\mathbf{j}_{ext}, \mathbf{A}_{ext}) \leftrightarrow (\mathbf{A}, \mathbf{j}) \leftrightarrow (\mathbf{j}_{KS}, \mathbf{A}_{KS})$. It becomes apparent that QED is a theory of *vector* potentials and *currents*, therefore extends into the domain of current density-functional theory [141, 149]. Taking the non-relativistic limit and in addition the long-wavelength approximation, we end up however in the same DFT framework as before $(\mathbf{j}_{ext}, v_{ext}) \leftrightarrow (q, n) \leftrightarrow (\mathbf{j}_{KS} \propto \int d\mathbf{r}\mathbf{r}n(\mathbf{r}), v_{KS})$ with a density to potential map. The mode displacements q are trivially known as solution to Maxwell's equations with the system plus external current $\mathbf{j}_{KS}$ (coherent states) [9, 80].
Consequentially, the non-relativistic cavity QEDFT problem can be solved once we obtain the exchange-correlation potential v_{xc}, as the Hartree, now mean-field or Maxwell $v_{Hxc} \to v_{Mxc}$, contribution is known analytically in the mode-expanded form (P4,[10, 80]). The photonic xc-potential v^{p}_{xc} thus mimics the effect of interactions among charged particles via the transversal fields which manifests via (virtual) photon excitations $\hat{q}\hat{\mathbf{R}}$ and direct interactions $(\boldsymbol{\lambda} \cdot \hat{\mathbf{R}})^2 \propto r_i^2 + r_i r_{j\neq i}$. The Coulombic xc-potential does the same for the longitudinal fields. The xc-potential (of longitudinal and transversal origin) is as usual the non-trivial hurdle to take as it behaves highly non-linear and has to fulfill a given set of exact conditions [150]. First attempts to obtain a photonic xc-potential v^{p}_{xc} followed the optimized effective potential (OEP) approach [96, 151] on an exact exchange level [10] (see following section for more details). The OEP emerges from a response equality equation that determines v_{xc} self-consistently depending on a self-energy $\Sigma_{xc}(\mathbf{r}t, \mathbf{r}'t')$ that encapsulates a given order of perturbation theory (for more details see P4 and [10, 152]). We improved in Publication P4 the algorithm to a point that it enables for the first time real-space *ab initio* calculations for realistic molecules. This represent the first results that demonstrate how the ground-state electronic density, and thus chemistry, is altered inside the cavity. Sec. 5.1.2 and P5 will furthermore highlight a Kohn-Sham construction that is based on the polaritonic quasiparticles rather than the bare matter and photonic components. QEDFT developed within the last few years into a highly beneficial approach for QED chemistry due to our recent contributions. As presented in Sec. 7, the current perspective to develop an xc-potential based on the homogeneous electron gas and the direct application of QEDFT to the experimental setting of [43] will illustrate the potential that QEDFT inhibits. For systems with substantial static correlation, e.g. stretched molecules (see P3), the high amount of correlation will be non-trivial to capture with any Kohn-Sham based QEDFT ansatz. In this regime, a multi-reference ansatz or the Quantum Electrodynamic Reduced Density Matrix Functional Theory [99] might deliver more satisfying results with the drawback of increased computational cost.
Let us clarify at this point why the following Sec. 5.1.2 addresses aspects of uttermost importance. Ground-state QEDFT allows us to capture polarization dependent changes in the density that originate from the influence of the cavity as presented in P4. The interest in strong light-matter interaction is however dominantly driven by the design of the excited and correlated polaritonic states. To obtain the latter, a time-dependent DFT framework similar to [153, 154] or P5 is demanded. The in P4 applied OEP can be similarly phrased as time-dependent theory [10] but is in its current form computationally intractable for re-

alistic systems, even if numerical instabilities would be covered [155], and foremost lacks the polaritonic nature without further additions that we present in Sec. 5.1.2 and App. 10.1. The quantum description of light-matter interaction by means of QEDFT will therefore fundamentally depend on the clever design of functionals that allow a time-dependent evaluation. Our conclusions illustrated in Sec. 5.1.2, App. 10.1 as well as the polaritonic approach in P5 manifest the first satisfying realizations that address this demand.

5.1.2 Spectral information and tilting out-of equilibrium

Obtaining the characteristics of excited states demands in many quantum chemical frameworks, e.g. DFT, coupled cluster, statistical approaches, a formulation which is intrinsically time-dependent. In density-functional theory, two major approaches are used, the explicit propagation of the system with subsequent Fourier analysis and the Casida linear response framework. Explicit propagation in time has the major advantage that it is general in the sense that we can describe also systems out-of-equilibrium and subject to losses (e.g. via loss of electrons that are emitted from the simulation box). The drawback is that it is typically computationally more involved than the Casida approach for small systems which will deliver the excited states of the system in equilibrium [95].

Both approaches have been realized in the classical limit, i.e. the explicit Maxwell-Kohn-Sham solver was developed by Jestädt et al. [153] which is conceptually similar to the classical Casida approach by Flick et al. [154]. A mode reduced description of Maxwell's equations allowed to furthermore consider the classical component of vibrational interaction [156]. In the classical (Maxwell) limit, the first ($n = 0$) polariton will be qualitatively captured for moderate coupling strengths [154]. Stronger coupling or higher lying polaritonic states demand however a quantum description (see e.g. P5 or [115, 154]). So far, all those approaches suffer from the lack of suitable exchange-correlation potentials and the for response constructions demanded xc-kernels, i.e. the latter connects between the response of the Kohn-Sham and many-particle system (see e.g. [141, 154]). One specific construction might however provide a very interesting and apparently well performing approach to tackle the lack of potentials in QEDFT, the dressed Kohn-Sham construction presented in P5 and illustrated in Fig. 8. This approach, in contrast to the QEDFT Kohn-Sham ansatz, does not assume that light and matter are uncorrelated in the auxiliary system. It takes the set of N-fermionic and M-photonic modes and rephrases the system in terms of quasiparticle orbitals where each electron is dressed by M artificial photonic modes such that $\phi(\mathbf{r}, q_1, ..., q_M, t)$ describes a polaritonic orbital of the auxiliary Kohn-Sham system (for a more detailed explanation please see P5). The neat idea behind this is that the strong light-matter interaction is then already part of the Kohn-Sham orbitals. The local exchange-correlation potential does then merely take care of the 'polariton-polariton' interaction, thus the interactions between the dressed particles. The simplest (exchange-only) approximation does already improve over its competitors TDOEP and the non-dressed QEDFT construction. Conceptually the usage of dressed particles is by no means novel (see e.g. the extensive literature on quasiparticles and

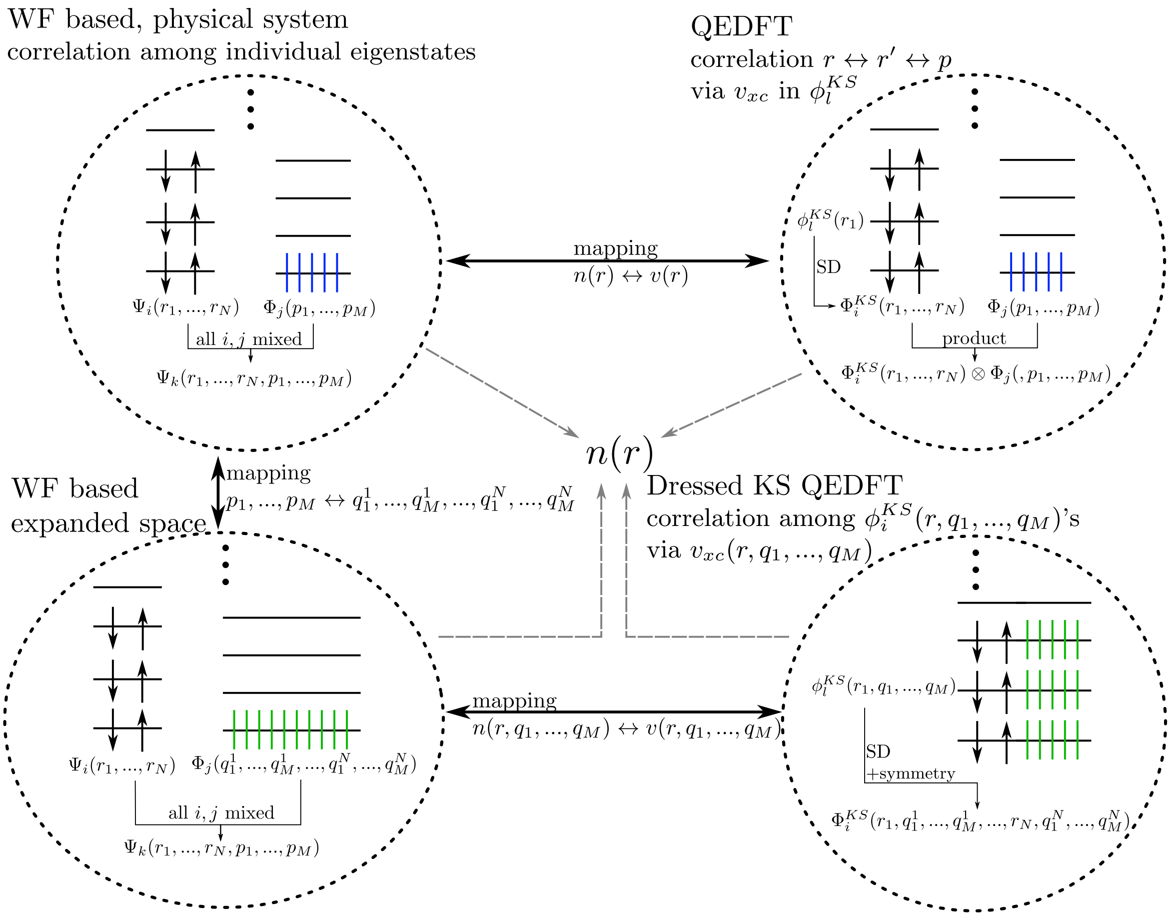

Figure 8: Schematic of the dressed Kohn-Sham construction. Standard Kohn-Sham QEDFT is based on the factorization of fermionic and bosonic components, correlation appears though v_{xc} in adjusted single-particle orbitals $\phi_l^{KS}(r_1)$. By expanding the space of the physical wavefunction, i.e. mapping from physical modes p to auxiliary modes q, and subsequent DFT mapping, a dressed Kohn-Sham construction is build in which dressed (polaritonic) single-particle orbitals represent the basis. This does however enforce special constrains for the symmetry to enforce physical solutions.

the polaritonic operators of macroscopic QED [72, 73]) and yet their application for strongly light-matter correlated systems, such as transmons in the quantum circuit and quantum information community, could represent the most beneficial path. The non-perturbative character of the light-matter treatment (merely the 'polariton-polariton' interactions have to be approximated) is especially interesting when extremely strong couplings of order $g/\omega = \lambda/\sqrt{2\omega} \sim 1$ are reached [32].

Patchwork approaches that utilize the by first-principles methods solved electronic and nuclear structure and use those parameters as input into a limited basis or quantum optical models [118, 119, 157] allow a quick investigation with the help of decades of quantum chemical methods. As suggested in section 4.3 and P2, this will however remain intrinsically perturbative and furthermore demands special caution as features such as coherent shifts, gauge and translational invariance can be easily missed and might provide a tainted or wrong conclusion. Other first-principles techniques not based on density-functional theory, such as the equation-of-motion coupled cluster for electron-photon correlated systems [115, 116] provide promising alternatives that will complement the highly efficient time-dependent QEDFT calculations.[12] The relatively well controlled perturbative order of coupled cluster and many-body perturbation theory will prove very beneficial as the advantage and on the same hand disadvantage of DFT is the rather non-perturbative and non-linear design of approximations. The TDOEP equation on the other hand is a special case and exclusion from that rule. In the following, we want to use it to illustrate how perturbative constructions should be designed to capture the essentials of correlated light-matter dynamics.

Many-body perturbation theory and spectral features in the TDOEP framework Many-body perturbation theory (MBPT) is an instructive and extremely successful tool that often allowed to tackle existing problems, e.g. the band-gap problem in DFT for extended systems, due to its clear yet by no means trivial way of construction and solution. For a detailed introduction we refer the reader to [96, 160, 161] and references therein.[13] Two very similar constructions are of special interest to us, the first is based on the equation of motion for the one-body reduced density matrix, known as the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierachy, and the second builds on the one-body reduced Green's function, known as Martin-Schwinger hierarchy.[14] As a consequence of the structure of the Heisenberg equation of motion, each order of the given descriptors couples to the next higher order and is

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[12] Please notice that the cluster excitation operator ansatz $e^{\hat{T}_e+\sum_{i,j,\dots} c_{i,j,\dots}\hat{a}_i^\dagger\hat{a}_j^\dagger\cdots}$ suggested in P2 can only produce uncorrelated eigenstates as we can separate the exponential in light and matter excitations, thus explicit coupling terms in the exponential are necessary. The harmonic oscillator basis becomes indeed problematic for $\mathcal{O}((\hat{a}^\dagger)^3)$ [158]. Using the above form would produce the optimal mean-field solution (allowing for displacement and squeezing of photonic modes) that might be interesting in the thermodynamic limits (see e.g. [130]) but will lack the so interesting quantum correlation effects. Another beneficial aspect of coupled cluster is size-extensivity, i.e. the feature that doubling the system without introduction of interaction (a far more specific condition in the cavity P3) leads merely to double the energy (conveniently enforced by the exponential ansatz). Density-functional theory is sharing the same size-extensivity when, as commonly done, constructed from localized single-particle orbitals [159], in contrast to a restricted CI expansion.

[13] The concept of dynamical mean-field theory (DMFT) (structurally similar to MBPT) in which an impurity problem is solved to describe strong local interactions can be found in [162] and investigations using this technique are currently perceived by the community.

[14] The major difference between both is, that BBGKY remains time-local, thus scales much more favorable than the time non-local Kadanov-Baym equations, a clear advantage for longer propagations. This is related to the fact that the Green's function gains an advantage in spatial dimensionality as it absorbs information into memory terms leading to the highly unfavorable scaling in time. This problem can be diminished by the Generalized Kadanov-Baym approximation (GKBA) [163]. However, applying the GKBA effectively reduces the spectral information during propagation to a single Hartree-Fock SD and thus limits this ansatz quite substantially in its predictability. The Kadanov-Baym equations demand merely the handling of spatial one-body objects (two-dimensional matrices such as $G(\mathbf{r}_1t_1, \mathbf{r}_2, t_2)$ and $\Sigma(\mathbf{r}_1t_1, \mathbf{r}_2, t_2)$) instead the BBGKY hierarchy implies a quick increase in spatial dimensionality $\rho(\mathbf{r}_1, \mathbf{r}_2, t), \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, t), \dots$ up to the limit of factorization. It is indeed possible to show that BBGKY and GKBA in a given level of approximation are of similar form [164, 165].

thus subject to a hierarchy that extends to order N when N particles are present. This is now intuitively even more expensive than solving the Schrödinger equation and an applicable theory is merely created if we somehow limit the number of higher-order correlators. For example, we could decide to propagate only one- and two-body reduced density matrices and factorize any higher order to express it perturbatively as one- and two-body correlators. This gives rise to various different levels of approximations, some conserve physical restrictions, such as the most trivial Hartree-Fock/exact-exchange approximation, and others do not [96]. How the BBGKY hierarchy can be applied to the light-matter problem is illustrated in P7 and references therein while the Martin-Schwinger hierarchy was fundamental in the construction of the OEP [10], P4 and P5 and both have a long standing history in QED. Indeed, their close relation to the system-bath approach (density-matrix descriptor) provides a convenient framework to connect the mentioned unitary methodologies in the context of an open system as mentioned in Section 4.2.1, efforts in this direction are under development.

One essential aspect that distinguishes the pure electronic structure evaluation from the problem at hand is that the photonic correlators (the photonic one-body reduced Green's function $D_{\mathbf{k}\xi\mathbf{k}'\xi'}(t,t')$) have to be considered in addition to the pure matter correlators (the electronic and/or nuclear propagator $G(\mathbf{r}t,\mathbf{r}'t')$). This gives rise to a coupled set of integro-differential equations, the Kadanov-Baym equations, for Green's functions and the coupled set of differential equations for the different correlators and cumulants in the BBGKY hierachy. The TDOEP ([10], P4) now features the lowest possible ansatz to this problem, the exact exchange solution, where the photon propagator is not 'updated' by the light-matter coupling. The fluctuations of the photonic field are thus assumed completely unaffected in time. It is instructive to investigate when this approximation breaks down to understand why a proper consideration of the photonic fields becomes essential for the most interesting situations and why the second Born approximation in P7 performs superior. To do this, we will perform here a simple trick. We can keep the structure of the TDOEP equations[15], and thus to a large extent their computational complexity, if we would already know how the correct $D(t,t')$ should look like instead of the bare $D_0(t,t')$. For the investigated 2-level ([10], P5) system at hand, we can utilize the RWA to obtain a good estimate for the correlated wave function and can then trivially obtain $D(t,t')$ (see Appendix 10.1). The given correlator is then included in the TDOEP exact-exchange equation which approximately promotes it to the full GW or self-consistent Born solution (here named GW_{RWA}). This level of diagrammatic expansion is indeed consistent with the RWA as shown in [167]. Figures 9, 10 and Fig. 1 of P5 clearly illustrate now that on-resonance, the exact exchange approximation GW_0 of the TDOEP equation introduces artificial beatings while the GW_{RWA} solution very accurately reproduces the dynamics, even for longer times and stronger coupling. The reason is simply that the

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[15] This can be motivated by the resummation of topologically unique diagrams arising from Wicks theorem [96] into many-body propagators $G_0 \rightarrow G$. Performing the same procedure for the interaction potential, the response function or polarization, the vertex correction and the self-energy leads to Hedin's pentagon and the famous GW approximation [96, 160, 166].

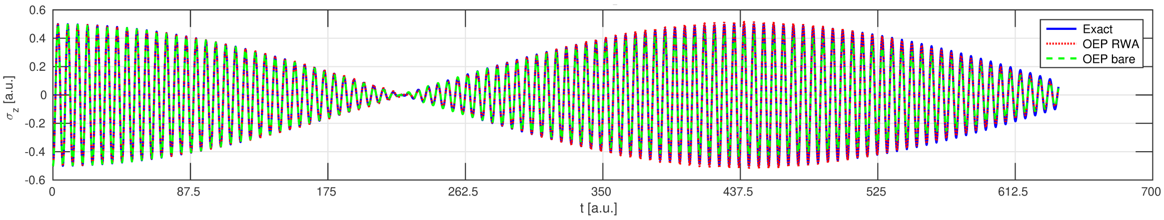

Figure 9: Weak coupling on-resonant performance of bare (GW_0) and RWA dressed (GW_{RWA}) TDOEP equation in relation to the exact solution for the relative occupation of a 2-level system with $t = 0.5, \omega = 1$ in atomic units and a sudden quench of the light-matter coupling $\lambda(t) = 0.01\theta(t-0^+)$. The wrong beating of the bare TDOEP, which is getting increasingly worse for longer times, see also Fig. 1 of P5, is almost completely cured by the GW_{RWA}.

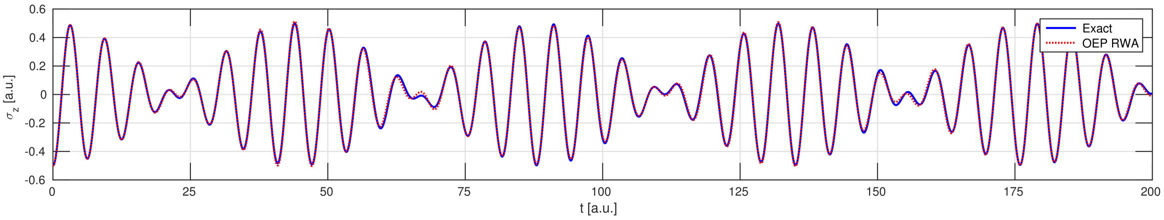

Figure 10: Strong coupling on-resonant performance of the RWA dressed (GW_{RWA}) TDOEP equation in relation to the exact solution for the relative occupation of a 2-level system with $t = 0.5, \omega = 1$ in atomic units and a sudden quench of the light-matter coupling $\lambda(t) = 0.1\theta(t-0^+)$. Even for stronger interaction the RWA dressed TDOEP performs excellent. Numerical comparison with full GW calculations performed by Niko Säkkinen showed very high consistency.

photon fluctuations are now (approximately) adjusted in time according to the polaritonic eigenstates. It becomes apparent that strong (but not ultra-strong) light-matter correlation might be satisfyingly captured by the GW (or even the second Born P7) approximation. When extending into even stronger coupling, the concept of dressing the basic single-particle orbitals (as in the dressed Kohn-Sham framework or implied in [168]) could be used, following the conceptual idea behind strongly correlated methods such as the Gutzwiller wave function ansatz [169]. One should however be conscious that the employed approximation might break energy and momentum conservation if not derived consistently (e.g. variationally). The derivation of accurate self-energies that remain conserving is a non-trivial problem [96, 170]. The most common diagrams Hartree-Fock, second Born, and GW are conserving. The according conditions in the photonic context have been recently investigated [170]. It was shown that the photonic GW_0 TDOEP, and even the here presented GW_{RWA}, obey the form $\mathcal{W}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = W(\mathbf{r}_1 - \mathbf{r}_2)\delta(t_1 - t_2) + r_1^i D^{ij}(t_1, t_2) r_2^j$ and therefore fulfill energy and momentum conservation as well as the zero-force theorem. The latter states that internal interactions should not emit a physical force on the full system. This opens a manifold of direct improvements over the bare TDOEP [10] as any dressed photon propagator just dependent on time will be similarly conserving as the bare propagator. Specifically, we can use as above the polaritonic eigenstates by e.g. using QEDFT Casida on mean-field level [154] to construct an approximately dressed photon-propagator $D(t_1, t_2)$ and subsequently solve the OEP equation with this dressed propagator. This will approximately shift the excitation poles $D(\omega) = \frac{1}{D_0^{-1}(\omega)-\Pi(\omega)}$ by the full polarization $\Pi(\omega)$ such that excitations appear at the poles of the quasiparticles (polaritons). Simplifying on the other hand the TDOEP equation itself towards the time-dependent Krieger-Li-Iafrate (TDKLI) approximation [171] is rather unattractive. The TDKLI equations feature large artificial self-interactions and such violations of the zero-force theorem [172]. As the light-matter interaction is mediated via local polarizations, the flaw of the KLI approximation for exactly those local polarizations [152] is disqualifying time-dependent propagations and massively limits the performance of KLI for light-matter correlated systems.

The role of decoherence and loss in cavity QED In our attempt to solve the Schrödinger, or more precise Pauli-Fierz, equation for the correlated setup composed of nuclei, electrons and photons, we naturally remain within a unitary system. Every physical system of interest (smaller than the universe) is however subject to ambient conditions such as exchange of particles and energy. The very same is true for the cavity where photons scatter into free-space modes, the lower the Q-value the quicker the loss. Observed from another perspective, the cavity and its included matter system will modify any external photon that is put into the cavity and the output of the cavity includes precious information about the correlated system at hand. The description and utilization of this perspective is known as input-output theory [173–176] and can be similarly beneficial for spectroscopy, photonic devices and information theory. A very illustrative example is the photon blockade effect [177] in which a single photon inside a cavity is blocking the entrance of the next photon. This appears as a consequence of the anharmonic energetic spacing of the polaritonic state consisting of an atom and the cavity.

Within this work we focus however on the dynamics of the matter-system inside the cavity. As mentioned in Sec. 3, nanoplasmonic devices feature so far rather small Q-values ($Q < 10^2$) and therefore lifetimes on femtosecond scale. Extremely high-Q optical cavities ($Q > 10^8$) with (typically) much weaker coupling, e.g. the whispering gallery modes of microresonators, can on the other hand even exceed nanoseconds [19, 20, 27, 28, 178]. The very same effects appear if we consider theoretically merely a subset of the system, e.g. a limited domain of the electronic Hilbert space. Vibrational, rotational and other degrees of freedom will then act as external bath that can accommodate energy and phase-information. In this sense, everything of the universe that is not considered explicitly is then effectively projected (in the sense of Sec. 4.2.1 and 5.1) into a bath. Theoretically, dissipation (e.g. the occupation of photonic modes) could be considered via absorbing boundaries or quenched trajectories. The exterior affecting the subsystem signalizes that even a lossy cavity will always feature the possibility to host a photon and first theoretical investigations showed that this will merely quantitatively change our conclusions [180]. Dephasing and the related thermalization are active and intricate subjects of research and their consideration vary strongly depending on the system of interest and the theoretical perspective. The simplest, yet often applicable, approach is to consider unitary dynamics within an effective lifetime τ that will be defined by the loss of

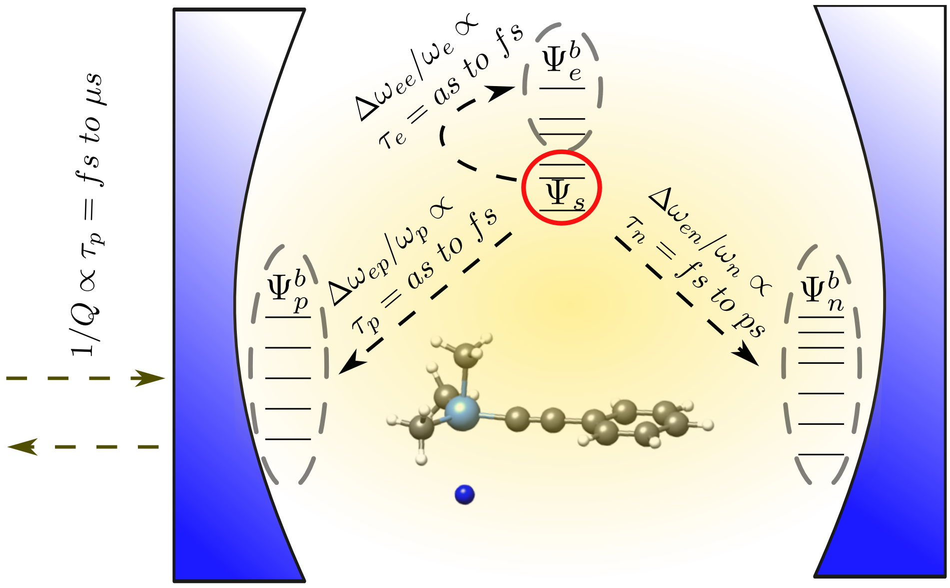

Figure 11: Illustration of common decoherence times for an electronic subspace that we consider as our system of interest Ψ_s. In the absence of conical intersections, the nuclear system is typically strongly detuned from the electronic system due to the mass-ratio m_e/M_p (Born-Oppenheimer approximation). The rate of interaction scales with the spectral overlap (minimal detuning $\Delta\omega_{xy} = \omega_x - \omega_y$) and the speed of oscillations. The cavity itself is partially transmitting (in and out) according to the Q-value. Isolated exchange among few states, e.g. a resonant photon-matter interaction with a single mode, can remain largely coherent. The interested reader can find an extended yet introductory discussion in Sec. 8.2 of [179].

coherence. Figure 11 illustrates common interactions and their according decoherence times. This approach was chosen in P3 to debate how decoherence would affect energy transfer inside the cavity and we obtained indeed quite similar conclusions as predicted from Markovian rate-equations [57]. We utilized time-scales of $15 - 200\ fs$, motivated dominantly by the decoherence via nuclear vibrations but similar considerations can happen for the photonic lifetimes. This approach, while extremely simplified and phenomenological, can be applied widely and is not restricted to our method of choice. We might find however situations where the decoherence is essential, e.g. they compete with the timescales of reactions, or the bath itself is of interest. Under those conditions various possibilities arise based on Sec. 4.2.1. To which extent memory can be omitted is characterized by the bath-bath correlation function which indicates if the bath itself dilutes information quickly, instantaneously in the Markovian approximation, or in contrast might posses a highly peaked spectral structure implying a coherent exchange between system and bath (for details see e.g. [88, 175, 179]). Methods that build around a density-matrix or Green's function technique can be extended relatively easy to consider decoherence (see e.g. [55, 181]). In addition, similar constructions for QEDFT can be designed starting from the OEP equation by coupling to a Caldeira-Leggett bath (proposed in [80]), following for example a stochastic approach [182] or utilizing the connection to density matrix formulations [183]. In this sense, while state-of-the-art QEDFT is applied to purely unitary systems, the generalization will be merely a matter of time. Recall also that a large Hilbert space will to a large extent mimic the thermalization/decoherence of a specific (measured) subsystem state. The present realization of QEDFT is capable to describe the full correlated motion of electrons, nuclei and photons for finite but realistic systems (see e.g. [153]). 'Opening' QEDFT is therefore much more tailored to account for degrees of freedom that might be hard to explicitly describe, such as for example the vibrations of a solvent.

5.2 Collectivity in ensemble light-matter interaction

So far we have focused our attention on a single instance of a system, e.g. a single molecule undergoing a reaction. Some experimental realizations describe indeed strong light-matter coupling between a single molecule and the cavity while others couple a dilute gas or fluid to the cavity. Fig. 12 illustrates the coupling of such an ensemble of approximately identical and isolated molecules to the cavity. The latter leads to an effective amplification of light-matter coupling and appears to drive the presently existing cavity reactivity experiments that provide an exciting perspective on chemical reaction steering. The collective interaction does not just scale the polaritonic splitting and introduces dark states, it furthermore also results in modified nonequilibrium features such as the burst-like coherent emission of photons (superradiance) [184]. In Section 4.1 and 4.3 we briefly mentioned how the Born-Huang expansion relates to the dominantly applied Tavis-Cummings models, in which the Dicke model is approximated by the RWA. Those models drive the current perception of the dynamic of a weakly concentrated set of emitters in gaseous, liquid and solid-state systems. This resulted in the recent years in first crossovers between quantum chemistry and quantum optics (e.g. [118, 119, 130, 157] and many more). As emphasized in Sec. 4.3.1, P1and P2, the intrinsic assumptions to those models should be considered with caution when applied outside of the regime of e.g. dilute gases of atoms as the number of coherently participating

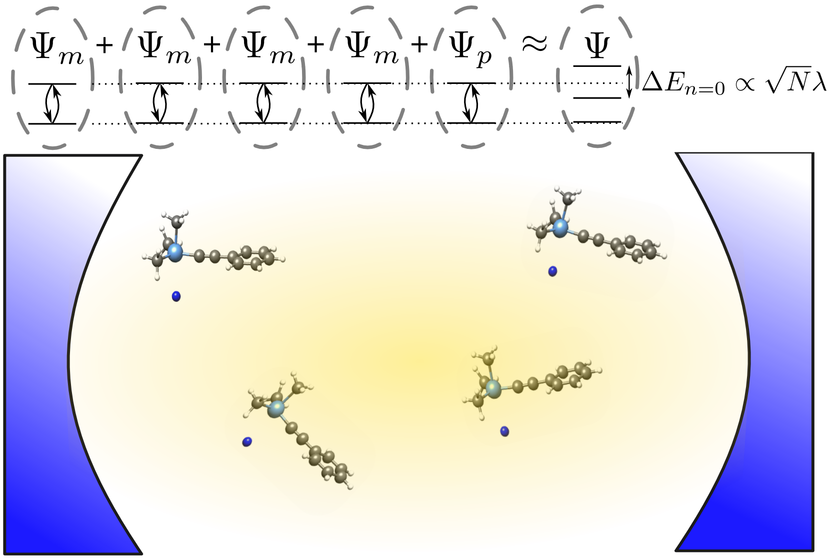

Figure 12: Schematic of collective light-matter coupling of a dilute ensemble (no Coulomb molecule-molecule interaction). The Tavis-Cummings model with N molecules features a manifold of $N-1$ dark states which are of antisymmetric character in the transition-dipole and decouple from the mode, i.e. they do not hybridize. In addition, two bright polariton branches (also referred to as superradiant) exist which obey a hybridization splitting $\propto \sqrt{N}\lambda$.

molecules might then be much smaller [185]. In an attempt to nevertheless accurately describe an ensemble without deviating from our first-principles conception, we investigated possible approaches utilizing the quantum-classical correspondence. This approach has a long history in quantum optics but especially molecular dynamics and features an excellent scaling in terms of system size. In recent efforts the here introduced concepts have been applied to ensembles of molecules [186] (superradiance already appears within a mean-field description) and the here envisioned approaches have already seen partial realization.

5.2.1 The Quantum-Classical Correspondence
A toolbox tailored to tear down the scalability problem?

Although we often speak of quantum and classical electrodynamics as distinct domains of physics, the latter seen as the limit of light-matter interactions described by Maxwell's equations, in practice this separation is often non-trivial and can be misleading. Indeed a wide range of mixed quantum classical, from here on referred to as semiclassical, approaches originated from quantum optics [187] and proved to be an essential pillar of electron-nuclei dynamics in the past 50 years (see e.g. semiclassical, mapping and surface-hopping methods [63, 188]). Let us briefly introduce the conceptual idea behind those and connect to the corresponding application in P6 and P7.

They are based on the idea of mapping all operators belonging to a given Hilbert space onto classical phase-space functions $\hat{f} \leftrightarrow f(\chi)$, thus creating an isomorphism between Hilbert space and phase space. It can be shown [187, 188] that this bijectivity can be established under restricted conditions.[16] One approach is the so called Weyl quantization which establishes a correspondence by introducing a quantization kernel $\hat{w}(q_1, ..., q_N, p_1, ..., p_N)$ such that

$$\hat{f} = \int \frac{dq_1}{\sqrt{2\pi}} ... \frac{dq_N}{\sqrt{2\pi}} \frac{dp_1}{\sqrt{2\pi}} ... \frac{dp_N}{\sqrt{2\pi}} \hat{w}(q_1, ..., q_N, p_1, ..., p_N) f(q_1, ..., q_N, p_1, ..., p_N) \ .$$

Often the set of coordinates $q_1, ..., q_N$ is represented in short in a collective notation Q. Different choices for $\hat{w}$ are possible, given they fulfill a set of conditions (e.g. hermiticity, see [187, 188]), as different selections of operator orderings are valid. One especially important choice is the Wigner-transformation as quantization kernel, being self-dual [187], such that expectation values can be calculated in a straight-forward manner

$$tr(\hat{f}\hat{\rho}) = \int \frac{dQ}{\sqrt{2\pi}^N} \frac{dP}{\sqrt{2\pi}^N} f_W(Q, P) \rho_W(Q, P) \ .$$

In the given context, we are interested in light-matter coupled systems, such that the density matrix $\hat{\rho}$ and the corresponding Liouville or von Neumann equation $i\hbar\partial_t\hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)]$ includes electronic(-nuclear) and photonic variables. A manifold of possibilities open up now

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[16] This approach can be rendered sometimes more convenient by switching basis to a set of new operators that can be easily associated with classical phase-space variables, e.g. the harmonic displacement operators. This procedure will give rise to the LSC and FBTS procedure in P7.

how we could tackle this problem within the given Quantum-Classical context and with it different limitations and drawbacks of our approach. So far, no separation of the Hilbert space and the associated Liouville space in which $\hat{\rho}$ is represented has been done. As the fermionic subspace is somewhat different in nature (mass, energy-scale, symmetry, dissipation time-scale), it could be beneficial to handle fermionic and bosonic components differently.

In the following, we investigate two different strategies, 1) we try to explicitly separate the fermionic and bosonic dynamics, yet retaining them interacting, and perform the above correspondence in just the bosonic subspace (partial Wigner transformation). And on the other hand, 2) include the fermionic quantities into the correspondence by mapping their discrete eigenstates (hard to express in terms of classical phase-space variables) onto discrete excitations of a set of harmonic oscillators $|n\rangle \rightarrow |0_0, ..., 0_{n-1}, 1_n, 0_{n+1}, ...\rangle$ (clear relation between excitations and phase-space variables) in combination with a subsequent phase-space mapping.
In practice, the starting point for both is a partial Wigner-transformation of the N bosonic modes with $X = (Q, P)$ [17]

$$\hat{\rho}_W(X) = \int \frac{dZ}{\sqrt{2\pi\hbar}^N} e^{iP\cdot Z} \langle Q - \frac{Z}{2}|\hat{\rho}|Q + \frac{Z}{2}\rangle; \quad tr_{\text{bosonic}}(\hat{\rho}_{\text{bosonic}}) = \int \frac{dX}{\sqrt{2\pi\hbar}^N} \rho_W(X) \ .$$

We therefore express the density matrix as quantum operator in the fermionic subspace which also depends on classical phase-space coordinates $\hat{\rho} \rightarrow \hat{\rho}_W(P_{\text{bosonic}}, Q_{\text{bosonic}}) = \hat{\rho}_W(X)$. The evolution of this object in time is then described by the Quantum Classical Liouville Equation (QCLE) exactly if the interaction between fermionic and bosonic subsystem is purely bilinear [189].[18] The QCLE reads

$$\partial_t \hat{\rho}_W(X, t) = -i\hat{\mathcal{L}}\hat{\rho}_W(X, t); \qquad -i\hat{\mathcal{L}}\cdot = -\frac{i}{\hbar}[\hat{H}_W, \cdot] + \frac{1}{2}(\{\hat{H}_W, \cdot\} - \{\cdot, \hat{H}_W\}) \tag{11}$$

with the partial Wigner transformed Hamiltonian $\hat{H}_W(X)$ and the Poisson bracket $\{.,.\}$. This is of rather little advantage without further restrictions as our equations of motion posses in the Liouville space an even larger level of complexity than the Schrödinger equation itself. If we compare our investigations in this section with the concepts elaborated in Sec. 4.2.1, we notice how closely related both approaches and subsequent derivations are.[19]
Following option 1), we could continue performing the mean-field ansatz

$$\hat{\rho}(t) \approx \hat{\rho}_{\text{fermion}} \otimes \hat{\rho}_{\text{boson}} \rightarrow \hat{\rho}_W(X, t) \approx \hat{\rho}_{\text{fermion}}(t)\rho_{W,\text{boson}}(X, t) \tag{12}$$

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[17] Note that the here selected normalization is symmetric, in contrast to P6 and P7.

[18] For nonlinear couplings (e.g. $\hat{q}^2\hat{R}$, a squeezing type of coupling) the operator $e^{-\frac{i\hbar}{2}(\overleftarrow{\nabla}_Q\overrightarrow{\nabla}_P - \overleftarrow{\nabla}_P\overrightarrow{\nabla}_Q)}$, appearing in between operators when partially Wigner-transformed $(\hat{A}\hat{B})_W = \hat{A}_W e^{-\frac{i\hbar}{2}(\overleftarrow{\nabla}_Q\overrightarrow{\nabla}_P - \overleftarrow{\nabla}_P\overrightarrow{\nabla}_Q)} \hat{B}_W$, will lead to higher order terms changing the structure of (11). Alternatively the QCLE can be derived in a classical limit procedure [189].

[19] We suggest the interested reader to embrace the extensive literature that debates subsequent derivations, e.g. the connection to the Fokker–Planck equations (see for instance [190]).

which tremendously simplifies the full algorithm as our equations of motion are then solely coupled by expectation values (traces separate). We therefore have to solve a von Neumann equation for the fermionic system coupled to the expectation values of the field variables. The equation of motion of the latter in turn is represented by a classical-type phase-space equation for the bosonic subsystem coupled to the expectation values of the fermionic system (see publication P6 for further details). The consequential simplicity comes, as usual, with substantial drawbacks that we elucidate in P6. Those are the loss of phase-relations and subsequently interferences between bosonic and fermionic system as well as an incomplete emission and absorption. The time needed for this incomplete decay to appear (simplified $N_e(t) - N_e^{t\to\infty} \approx (N_e^{t=0} - N_e^{t\to\infty})e^{-t/\tau}$) is however in close agreement with the exact solution such that one can expect a good prediction of line widths and lifetimes τ, consistent with the observation for the linear response of a purely Maxwell coupled light-matter system [154]. For practical purposes an uncorrelated initial state (as e.g. present in our spontaneous emission setup) should be chosen. A (semi)classical approach seems indeed promising as long as the number of molecules heavily out-competes the number of photons participating, i.e. single photon excitations dominate, or the number of photons tends towards the coherent (infinite) limit. If strong photonic fluctuations affect each molecule significantly, the anharmonic quantum effects deviate from a classical description (recall Fig. 1). Nevertheless including strongly correlated bosonic modes into the subsystem, effectively defining a polaritonic subsystem similar to our approach in P5 or the QEDFT method in general, and treating the remaining bosonic modes as before might still recover many of the strongly correlated features.[20] This separation of degrees of freedom is conceptually similar to the correlated systems + dissipative bath ideology of (non-)Markovian dynamics [194] and might be promising for future developments yet will be computationally and conceptually more demanding. We suggest and plan to investigate those intersections of QEDFT (e.g. P5) and P6 in the future, e.g. separating resonant from off-resonant bosonic modes.

When we solve a classical phase-space equation starting from an initial $\rho_W(X, t = 0)$, we may very well also represent this initial function in terms of independent trajectories [189] which we define as the Multi-Trajectory Ehrenfest dynamics (MTEF) approach. The idea is therefore that we sample a combination $X = (Q, P)$ randomly from the initial $\rho_W(X, t = 0)$ and then evolve a large amount of those trajectories. Observables are then calculated by averaging over the set of trajectories $\rho_W(X, t) = \frac{1}{N_{\text{traj}}} \sum_{j=1}^{N_{\text{traj}}} \delta(X_j - X(t))$. It becomes apparent that the outcome heavily depends on how dense the phase-space is represented by the number of trajectories and with increasing phase-space, the necessary number of trajectories tends to increase quickly. We thus have to ensure that observables of interest are densely represented which may very well lead to hundreds of thousands of trajectories, strongly depending on the order $\mathcal{O}(\hat{q}^N, \hat{p}^M)$ of operators involved in the observable of interest. The larger the effective phase-space of a given observable the stronger will the initial ensemble of trajectories

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[20] This could also go well in line with conditional dynamics, e.g. to generate a weighted probability distribution to enforce specific physical effects [191, 192], or we can even exclude classical trajectories of less interest to reach Fokker-Planck type of dynamics [193].

be diluted and the higher the amount of trajectories necessary to achieve a reliable prediction. How demanding this criteria can be is well represented by e.g. the $G^{(2)}$ function in publication P6. Other more advanced methods which are based on coupled trajectories (such as e.g. [195–197]) need commonly fewer trajectories, with the drawback of a much higher computational cost for each trajectory itself.

Publication P6 presents how this method is constructed and practically applied. Within this context, we discuss the relevance of normal-ordering which is of fundamental physical relevance and demands some additional consideration when constructing observables in the classical phase-space. How the initial conditions affect the equation of motion and how they define the spontaneous emission can be very illustratively seen when considering the explicit solution of the mode-displacement $q_\alpha,\ \alpha = \mathbf{k}\xi$ in dipole approximation. As a consequence of the mode-resolved Heisenberg equations of motion (and corresponding Maxwell's equation)

$$\partial_t^2 \hat{q}_\alpha(t) + \omega_\alpha^2 \hat{q}_\alpha(t) = \omega_\alpha \boldsymbol{\lambda}_\alpha \cdot \hat{\mathbf{R}}(t)$$

originating from the Hamiltonian (7) with the full (electronic plus nuclear) dipole $\mathbf{R}(t) = -\int dr^3 \mathbf{r} n(\mathbf{r},t) + \int dR_n^3 \mathbf{R}_n n_n(\mathbf{R}_n, t)$, $n(\mathbf{r},t)$ being the electronic density, we get via the classical Green's function the solution

$$q_\alpha(t) = \int_{t_0}^{t} dt' \frac{\sin[\omega_\alpha(t-t')]}{\omega_\alpha} \omega_\alpha \boldsymbol{\lambda}_\alpha \cdot \mathbf{R}(t) + q_\alpha(t_0)\cos[\omega_\alpha(t-t_0)] + \partial_t q_\alpha(t_0) \frac{\sin[\omega_\alpha(t-t_0)]}{\omega_\alpha} \ .$$

Within the mean-field approximation (12), the matter system is purely driven by the local potential $-\sum_\alpha \omega_\alpha q_\alpha(t) \boldsymbol{\lambda}_\alpha \cdot \hat{\mathbf{R}}$. Clearly, if the matter system is resting in an eigenstate with $\mathbf{R}(t_0) = 0$ [21] and the photonic modes start with zero momentum and displacement, then light and matter completely decouple in the mean-field limit. No spontaneous emission can take place as some form of light-matter quantum effects have to be considered. The exact solution would feature now two components, (1) that the photonic wavefunction corresponds to the solution of the quantum harmonic oscillator (represented by a Gaussian in its ground state) and thus has a probability for nonzero displacements and (2) that this quantum distribution couples to the dipole operator $\langle \hat{q}_\alpha \hat{\mathbf{R}} \rangle$ and therefore the probability for polarization. The MTEF approach now repairs point (1) but disregards (2). This way, we allow each trajectory to posses a set of nonzero $q_\alpha(t_0)$, $\partial_t q_\alpha(t_0)$ which in turn leads to a non-vanishing $q_\alpha(t)$ and consequentially will enact a force on the matter system stimulating spontaneous emission. Notice that the rate of spontaneous emission will not be exact as we are lacking (2). Further details are elaborated in P6.

From the different observables presented in this publication and the fact that we disregard (2), it becomes apparent that the mean-field limit inevitably leads to the loss of phase-relations such that no interference effects can be captured. Nevertheless, the rate of spontaneous decay will not be a constant but features small oscillations that emerge from the Rabi oscillations

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[21] To be precise, the self-polarization part contributes an additional component that precisely cancels any generated local MF potential for $\mathbf{R}(t_0) \neq 0$ if the combined system is in equilibrium, see e.g. P1.

and the discrete cavity spectral function (see [67] page 201 ff). Although we lost interference effects, repairing component (1) allows us to extend classical light-matter descriptions to a semiclassical treatment in a straight-forward manner that is highly compatible with available Maxwell-matter implementations based on QEDFT [153, 156] (see Sec. 7).

Let us now come back to the second option, i.e. we rephrase not just the bosonic system in a classical phase-space but similarly the fermionic system and treat both on equal footing. This way we hope that we can not just repair (1) but also approximate (2) in a satisfying fashion. The very convenient Meyer-Miller-Stock-Thoss mapping [198, 199] will render this procedure much more applicable. Here, the fermionic many-body subsystem eigenstates, precisely the projector of states, are mapped onto a set of harmonic oscillators, each harmonic excitation representing one specific eigenstate $|\Psi_k^e(\mathbf{r}_1, \mathbf{r}_2, ...)\rangle \rightarrow |0_1, ..., 1_k, 0_{k+1}, ...\rangle$. We can directly see that this will in principle demand the knowledge of the k'th excited many-body fermionic eigenstate, something rather rarely available due to the exponential wall of electronic structure theory. In reality, the wavefunction that we map will be an approximated object, unless the fermionic subspace is very limited such as in P7.[22] Depending on how we specify this mapping, e.g. forward and backward propagation treated differently and how we approximate consecutively generated phase-space equations of motion, we can build a hierarchy of approximations. In P7, we focus on the linearized semiclassical dynamics (LSC) and forward-backward trajectory solution (FBTS) (for further details we refer the reader to P7 and the citations therein).[23] The propagated classical equations of motion in phase space quite consistently reproduce the spontaneous emission process and are even capable to capture interference features, although limited to qualitative agreement. Interestingly they give rise to a rather large overestimation of beyond RWA features, illustrated by the bound photon-peak in P7. While this approach provides overall a more desirable performance, its application to realistic systems might be far more demanding than performing the similar, rather comprehensible step, in the MTEF approach.

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[22] When handling this approximated wavefunction, we have to consider the fact that available standards come hand in hand with a set of implications. Configuration interaction provides a wavefunction that can be used as normal but with rather high computational effort in relation to its accuracy, it is further not size-consistent. Coupled cluster, the 'gold-standard' of quantum chemistry, provides a rather accurate wavefunction with the drawback that Hilbert space and corresponding dual-space are no longer trivially connected by hermitian conjugates but represents a bi-orthonormal system with $|\Psi^e_{cc,k}\rangle = \hat{\mathcal{R}}_k e^{\hat{T}}|\Psi^e_{SD,0}\rangle$, $\langle\Psi^e_{cc,k}| = \langle\Psi^e_{SD,0}|e^{-\hat{T}}\hat{\mathcal{L}}_k$ where $\hat{\mathcal{L}}_k$, $\hat{\mathcal{R}}_k$ are left and right excitation operators and $\exp(\hat{T})$ is the excitation operator that transfers the uncorrelated SD $\Psi^e_{SD,0}$ into a correlated ground state [200]. A (TD)DFT wavefunction on the other hand is an uncorrelated SD of optimized single particle orbitals. Excitations are thus uncorrelated single particle excitations.

[23] The Wigner-function can attain negative values for excited states which should be considered during the sampling (see e.g. Fig. 16 in [15]). Alternative quantum-classical phase-space mappings, which are then not self-dual, exist with their individual strengths and weaknesses. For example the Husimi function is strictly positive and possesses the Glauber transformation as its dual [187, 188]. In the given publication (common in the LCS approach), the excited electronic state was sampled from the ground-state Gaussian of the mapping variables $\phi(Q,P) = \frac{2^{N_e+1}}{\hbar} e^{-\frac{1}{\hbar}\sum_\alpha^{N_e}(q_\alpha^2+p_\alpha^2)}$ and subsequently weighted to obtain the electronic occupation operators in the Wigner-transformed mapping basis $|\alpha\rangle\langle\alpha|^W_{Q,P} = \phi(Q,P)(q_\alpha^2 + p_\alpha^2 - \frac{\hbar}{2})$ [201].

We mentioned previously that the tremendous effort in the domain of fermion-nuclei interaction resulted in a flourishing field of possible approaches, each comprising opportunities and drawbacks. A staple of this regime is Tully-surface hopping [63], which allows a trajectory to jump between potential energy surfaces (PES) corresponding to an empirically motivated hopping rate. While it is not obvious at first glance how to develop this technique for the photonic interaction, it can be indeed derived by following the cBO approach (see Sec. 4.3 and [107]). The electronic system is considered to adjust instantaneously such that we can solve the electronic system with a parametric dependence on the nuclear coordinates $\hat{\mathbf{R}}_n \rightarrow \{\mathbf{R}_n\}$ and the photonic displacements $\hat{q}_\alpha \rightarrow \{q\}$. The PES's depend now on both coordinates $\varepsilon_l(\mathbf{R}_n, q)$ with an electronic wavefunction $\Psi_l^e(\mathbf{r}, \{\mathbf{R}_n\}, \{q\})$. Photonic and nuclear coordinates move then within the cBO approximation adiabatically on this surface

$$E_{k,l}\Phi_{k,l}(\mathbf{R}_n, q) = \big[-\frac{1}{2}\sum_i \nabla^2_{\mathbf{R}_i} + \frac{1}{2}\sum_\alpha \partial^2_{q_\alpha} + \varepsilon_l(\mathbf{R}_{n,i}, q)\big]\,\Phi_{k,l}(\mathbf{R}_n, q)\ .$$

It is thus trivial to extend the common surface hopping approach to the light-matter interaction as displayed in P7. Although often well performing for the electron-nuclear interaction, this approach seems to fail to properly capture the light-matter dynamics. The reason might be that the cBO describes well the renormalization of the bare states, i.e. captures Lamb-physics, but it fails for the hallmark of strong light-matter interaction, the polaritons (motivated in P2). The combination of good performance and perfect compatibility of MTEF method (and possible extensions) with the efficient Maxwell implementation renders the surface hopping thus relatively unattractive and we resigned from further progress in this direction for the moment. It might be nevertheless interesting to inspect the cBO from the point of view of entangled classical trajectories as suggestions by Donoso and Martens [202]. Here, the classical equation of motion for the momentum is extended by higher order nonlinearities of the PES $\dot{p} = -\partial_q\varepsilon(q) + \frac{\hbar^2}{24}\partial_q^3\varepsilon(q)\frac{1}{\rho(q,p,t)}\partial_p^2\rho(q,p,t) + ...$ where our distribution function $\rho(q,p,t) = \frac{1}{N_{traj}}\sum_{j=1}^{N_{traj}} \delta(q - q_j(t))\delta(p - p_j(t))$ is again represented by an ensemble of classical trajectories. It becomes apparent that this approach is notoriously unstable as we divide by a distribution represented by singular values, a problem that it shares with various other attempts such as exact factorization or conditional wavefunctions [108, 203]. It could be however that various analytic insights could assist curing those issues [204].

We certainly cannot claim that we presented a complete evaluation of semiclassical and perturbative methods for light-matter interaction in P6 and P7 or that our conclusions can be directly transfered to realistic systems due to the necessary simplicity of the matter system. We nevertheless provided a route for extensions, benchmarked the performance for a sizable selection of approaches, gathered interesting insights regarding interference, strong coupling, and finite size features, and shined light on the non-trivial question which methods might be worth it to explore further. To which extent those conclusions can be extrapolated to realistic materials is of course a different question and it is indeed possible that the self-polarization component omitted here might improve the performance as it provides an additional classical self-correlation channel (see also [154]). The simplicity of the few-level system investigated leads to a small set of resonances, it represents thus an extraordinarily demanding benchmark for a method to preserve phase-information and it could easily be that for realistic systems the failures of semiclassical methods become less influential. Due to the structural similarity between the harmonic representation of photonic modes and the approximatively harmonic nuclear vibrations many other methods could get beneficially extended. For instance ring-polymer molecular dynamics, a path-integral representation of the imaginary propagation, typically improves MTEF in situations of passing non-adiabatic coupling-points [205–207]. However, the failure of the cBO in resonant situations should be considered such that the right tools are applied to their correspondingly suited problems.

Our approach is directly applicable for realistic systems with the help of the Maxwell-Kohn-Sham implementation by Jestädt et al. [153] and thus provides us on the spot with the demanded first-principles predictability to describe recent experimental realizations. Already in [153], the feasibility to describe the dynamics of nanoparticles from *ab initio* allows us to tackle systems that are usually hard to describe with a high degree of detail, e.g. nanotubes in microcavities [208, 209]. It furthermore allows us to investigate nanoplasmonic cavities, including their associated scattered light, completely untainted. It therefore extends previous investigations [153, 210, 211], allowing even for the investigation of possible electron emission or charge transfer, all subject to longitudinal and transversal quantum field effects. The full propagation of quantum fields which allows for near and far-field measurements as in experiments in combination with the semiclassical representation provides us with a theoretical toolset that is incomparably close to experiments and possesses the full predictive power of time-dependent density-functional theory.

The following section briefly elucidates some of the fascinating effects that arise from the interplay of light with matter. We focus here on the extensive work of this thesis, setting it in relation to recent experimental and theoretical developments in the field.

6 Progress in cavity QED

Setting some spotlights

The publications within this work have to be considered in the wider context of the efforts to understand, predict and utilize strong light-matter interaction for chemical, physical and quantum informational purposes and selected aspects are illustrated in Fig. 13. We included already in the previous sections many side remarks related to the state-of-the-art research. This section will provide a short, not comprehensive, list of effects that comprise to a large extend cavity QED research.

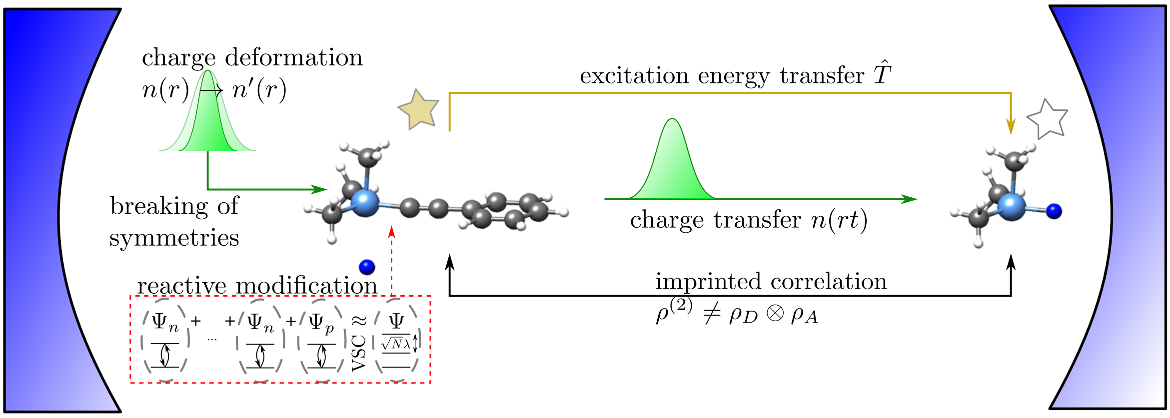

Figure 13: Schematic illustration of the various effects of strong light-matter coupling on physical and chemical features as highlighted below.

Excitation energy transfer Most intuitively, the photo-excitation of a molecular system is connected to photons, i.e. especially the preparation of an excited state is often performed by illumination. This subject, known as photo-chemistry, renders itself therefore as natural starting point for investigations if we want to shape the chemical process with the help of a cavity environment. Based on many previous investigations (e.g. [212]) not further named here, recent attempts started in J-aggregates [33, 36, 39, 40] and proved quickly that strong light-matter interaction was able to significantly shape the energetic structure by creating strong polaritonic branches. Obtained spectra showed furthermore a domination of emission from the lower polariton, dissipation channels via e.g. vibrations seemed therefore important to quantitatively characterize the dynamics of the molecular ensemble. Still considering J-aggregates, Zhong et al. [44, 213] observed energy transfer over scales of $\geq 100\ nm$ under strong coupling, remaining effectively distance independent as long as the light-matter coupling strength was preserved. This extends far beyond the common scales that could appear following the Förster resonant energy-transfer (FRET) mechanism in which Coulombic (longitudinal photon exchange) dipole-dipole coupling quickly diminishes with $\propto 1/R^6$. Illustrated in Fig. 5 of P3 is the crossover between Coulombic and photonic driven regime. Here, the photonic interaction opened a very efficient energy transfer channel under strong coupling. Other investigations based on 2-level systems came to similar conclusions regarding high exciton conductance [54, 214], efficient energy transfer [57] and furthermore suggest that the middle polariton, dark states and the vibrational reservoir play a crucial role [56, 215]. In this context, one should remember that photons couple to polarization (coherence). To move occupation permanently, i.e. non reversible, multiple interactions (multi photon) or decoherence have to be present.

Driving a chemical reaction by illumination is our daily experience, may it be the synthetization of vitamin D or the deterioration of a chemical complex as part of our cuisine. And indeed this subject represents the forefront of current research when utilizing large-scale quantum chemistry approaches. This can vary between a single molecule coupled in a restricted (one-)photon basis [157] and the many-particle limit where up to 100 molecules are coupled by the Tavis-Cummings model. The real-time electronic excitations undergo then a photochemical reaction featuring coherence and localization effects [118, 119]. The close similarity between cavity and Floquet should be naturally interesting to control chemical reactions that are based on photonic excitations (see Sec. 7 and P2).

Charge transfer The transfer of charge seems more intricate in the cavity context. It has been shown experimentally however that strong light-matter coupling can also enhance the conductivity of a molecular extended structure [38]. Considering a tight-binding 2-level chain, theoretical investigations [167, 216] suggested that the cavity effectively populates the conduction band, thus opens an additional channel in the valence band, and therefore increases the conductivity. A theoretical estimation to which extend charge transfer and subsequent chemical reactivity could be enhanced inside the cavity was first provided by Herrera and Spano [59] for a molecular ensemble characterized by few-level systems. We decided to shift in P3 the focus away from the few-level ensemble description towards a single but accurately described molecule with the goal to understand the interplay of the competing contributions that manifest in excitation and charge transfer as well as involved correlations. Fig. 4 of P3 illustrates the conclusion that the hybridization of charge-transfer and polaritonic states, tunable by the cavity, opens an efficient channel to transfer charge between Donor and Acceptor. Most remarkably, this does not merely improve the transfer from Donor to Acceptor but it can completely flip the direction of transfer, thus rendering the transfer from Acceptor to Donor suddenly favorable and consequently inverting the role of Donor and Acceptor. Relevant for this flip is the varying contribution of Donor and Acceptor in the middle polariton, i.e. depending on from which side we approach the middle polariton, the character will change and thus the preferred direction of charge-flow. The high coherence imprinted by the avoided crossing is visible in sub-figure (D) of Fig. 4 of P3. This conclusion could be efficiently used to steer charge transfer and electronic correlation in functional materials.

For example MoS_2WS_2 heterostructures exhibit ultrafast electron transfer between the MoS_2 and WS_2 layer around $50fs$ [217] and by steering distance and light-matter coupling, a similar effect should be observed. This would not only provide experimental evidence but further delivers an additional knob for optoelectronic and light-harvesting devices. Integrated devices on the nanoscale, featuring a plasmonic antenna [218], could furthermore investigate single particle effects and provide valuable insight for the design of models describing plasmonic cavity interaction (see P1).

Describing chemical reactivity usually demands the consideration of reorganization of the molecules due to vibrations and solvent effects. Marcus theory [219, 220], and extensions such as the Marcus-Levich-Jortner theory that account for vibrational excitation, describe the reaction in an elegant fashion. At the heart of this approach is the idea that energy-conservation has to be guaranteed. Reactant and product feature in this model parabolic free-energy curves with a curvature provided by vibrational and solvation effects. A transfer of charge demands then enough free energy to overcome the crossing point of both parabola. If the product possesses a much smaller free energy than the reactant, the rate does not reduce monotonically but takes the opposite trend in the so called inverted region. Two independent publications utilized this model with modifications by the cavity and restricted to a kinetic discussion. In the limit of resonant interaction with the vibrations [221], a catalytic behavior was proposed when the product is coupled to the cavity. Off-resonant, a reshaping of the reaction barrier (via renormalization of the curvature or via introducing replica in the inverted region) was suggested [222].

Vibrational strong coupling (VSC) One of the most exciting applications of strong light-matter interaction builds around reshaping the vibrational landscape with the cavity. In this field, recent experiments showed impressive results that suggest that under the cavity influence the rate of a reaction can be substantially decreased [43], steered as demanded [50], or even accelerated [49, 223]. This suggests a completely novel pathway to synthesize chemical components with the help of a cavity. The precise microscopic explanation of this effect, for example what decides if the reaction experiences acceleration or deacceleration, has been not delivered so far. First theoretical investigations suggest a change of the reactive barrier, thus reshaping the (free-)energy landscape [120, 221], but either do not show full qualitative agreement with experimental observation as resonant effects are absent or lack a mechanism when the reactant is coupled. The quick extension of the given field of research into the chemical community and the progress in QED-based quantum chemical methods, such as QEDFT (P4, P5, [9]), cavity extended Born-Huang expansions (P2, [107]) or semiclassical approaches (P6, P7, [153]), may allow us to overcome the yet existing hurdles (see also Sec. 7).

Shaping of electronic density and breaking of symmetries The large extent of theoretical investigations describing the restructuring of matter inside the cavity assume a bare basis of matter excitations. While this is in principle exact, the lack of possibility to obtain the full matter Hilbert space sets an intriguing limit to this approach (see e.g. P2). When the interaction becomes so strong that for instance the electronic structure itself will be reshaped by the cavity, a different approach that explicitly obtains the correlated density, such as QEDFT, might provide further insight. A fascinating yet very intuitive feature that can be

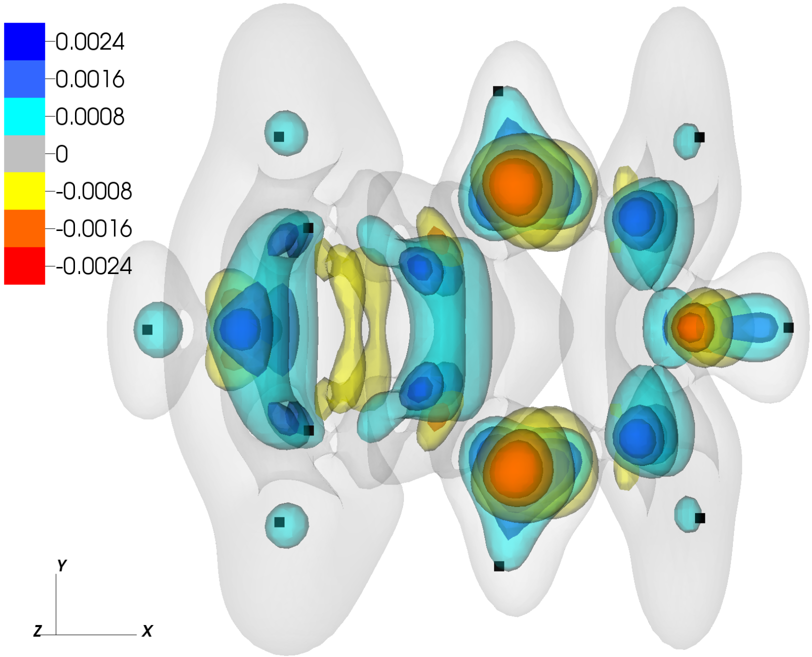

Figure 14: Difference in electronic ground-state density $n_{\lambda=0.08}(\mathbf{r}) - n_{\lambda=0}(\mathbf{r})$ of Azulene (complementing visualization, see P4) when affected by the cavity with a polarization in x-direction and $\omega = 0.0856\ a.u.$ Small black squares indicate the position of nuclei. The reorganization of electronic density involves many eigenstates in a non-trivial fashion. A stripe-like, alternating pattern along the direction of polarization can be observed in which electronic density is shifted in/out-wards of the molecular (x-y) plane.

observed under those conditions is that the electronic ground-state density when coupled to the cavity tends to avoid the polarization direction of the field for strong coupling (see P4, [107] and P2). In Fig. 2 of P2, a clear accumulation of charge perpendicular to the direction of polarization can be observed. However, for substantially stronger coupling (see Fig. 2 of P2), the opposite behavior appears, the density tends to orient along the polarization direction. We can understand this when considering that two components compete for the energy of the system, the repulsive self-polarization and the bilinear displacing interaction $\propto \hat{q}\hat{\mathbf{R}}$. The self-polarization now commonly dominates the ground state, aiming to reduce the local polarization thus decoupling from the cavity. The same behavior was observed in P4. However, the excited states behave contrary (see e.g. Fig. 3 of P2) as now the bilinear coupling $\mathcal{O}(\lambda^1)$ will dominate the self-polarization contribution $\mathcal{O}(\lambda^2)$ for as long as the extension criterion $\lambda^2/4\varepsilon_i^2 \ll 1$ is sufficiently fulfilled (see P1). In combination with the control of the polarization, it opens further interesting opportunities how charge can be redistributed via the cavity. For instance Fig. 10 of P4 illustrates that the density of a chain of sodium dimers can be accumulated onside the atomic position, reducing the charge overlap between the dimers. According to P3, this shifts the electronic configuration into the domain characterized by static correlation. However, when switching the polarization perpendicular to the chain, the opposite effect is present, charge overlap increases, and it becomes apparent that electronic devices can be partially controlled by strong light-matter interaction. Furthermore, with the tendency to accumulate charge where charge is already present, a molecule in the equilibrium configuration will accumulate charge in the bonding region. The nuclei will then relax into a configuration with a reduced bond length (see e.g. [61]). Figure 14 visualizes the effect of the cavity on the electronic ground state for Azulene as investigated in P4. Clearly, a real molecule reacts in a much more complex way, the previous conclusions should be perceived as overall tendencies. The stripe-like pattern of alternating in- and outwards shifting of density will clearly also enact forces on the nuclei. The molecular structure will relax accordingly and its previous symmetries (e.g. rotational) will break. Especially the capability to break the symmetry of a given system in a non-intrusive fashion might be of fundamental interest (see also Sec. 7).

In conclusion, the cavity does not only allow us to introduce polaritonic excited states, it furthermore reshapes the complete equilibrium electronic and nuclear structure when the coupling is sufficiently strong. So far, the strength of light-matter interaction on an individual molecule does not reach the level that would be demanded to consistently access those effects in experiment. It might be however instructive and beneficial for the future to account for those features, especially for systems with high collectivity and plasmonic devices.

Imprinting correlation Imprinting correlation between far apart components with the help of the cavity is in contrast surely accessible with state-of-the-art cavities, indeed represents a corner-stone of collective light-matter coupling, and first steps to utilize this mechanism for quantum informatic purposes were already investigated [58]. The first-principles description will be demanding as especially Fig. 12 of P3 illustrates that the role of electronic correlation imprinted by the cavity can be non-negligible while light and matter remain largely uncorrelated. Density-functional theory for instance will be able to reliably describe the local molecular structure but it is unclear if the strong electronic correlation can be captured. We should remind ourself that classical correlation is similarly relevant and already mixed quantum-classical methods are able to qualitatively resemble correlated dynamics (see for instance the $G^{(2)}$ function calculated in P6). The precise description of quantum correlation on the other hand might demand steps towards non-equilibrium Green's functions or similar techniques (see P7 and [99]).

Extended systems Extended systems show typically even stronger polaritonic features as the sheer amount of charge contributing to the polarization is massive. The only conceptual differences are the apparent momentum dependence of the coupled excitons, i.e. the polaritons posses a mixed band-dispersion, and the theoretical question if the long-wavelength approximation is applicable. Various experimental realizations provided insight into the creation and control of exciton polaritons [35, 224, 225]. The massive amount of charge in those systems might provide a further interesting direction and the question to which extent a novel collective state can be imprinted by the cavity when various competing interactions are present. For instance, this can include shifting the phase-transition of superconductivity, theoretically [226, 227] and experimentally shown [131]. In general, the cavity has the capability to shape the excitation structure [228], electronic and phononic, as well as their interplay. In addition to electric fields, the interplay with magnetic fields becomes interesting in extended systems. It gives rise to the (fractional) quantum hall effect and to Landau polaritons for which the light-matter coupling can reach rather large values such that the collective Lamb shift $\mathcal{L}$ (see P2) and the counter-rotating components become entirely non-negligible [229].

7 Work in progress

MANY aspects of this work, as common to science, never stopped developing or never worked out the way intended. This includes various extensions of for instance QEDFT, realizations of non-equilibrium perturbation theory in the light-matter context and attempts to shape chemistry or materials with the confining structure of a cavity. In addition to previous comments within the manuscript, we present here a short list of projects that are currently in progress but have not yet reached the level of submission.

One of the major obstacles that is holding back QEDFT so far, is the lack of a simple working functional similar to the local density approximation (LDA). While the OEP is rather accurate and able to collect a set of physically demanded features, such as the $1/r$ long-range decay, it is computationally demanding to converge and intractable for larger systems. A simplification of the OEP along the lines of the KLI approximation, as in P4 and further investigations, showed that it sacrifices too much of the desirable features of the OEP, e.g. translational invariance and the zero-force theorem. At the heart of DFT is the homogeneous electron gas (HEG) that leads to the LDA functional and from there on to a manifold of other DFT functionals. Together with Michael Ruggenthaler, Florian Eich, Vasilis Rokaj and Angel Rubio, we are currently investigating how the HEG and subsequently the LDA is shaped inside the cavity. In its simplest realization, we obtain a simple functional that incorporates effectively a simplification to the response of the HEG, delivering very good results for one-dimensional atomic systems. Improvements that are necessary to capture physical features that arise in higher dimensions are currently investigated.

QEDFT has an incomparable advantage as it allows to self-consistently and in real-space describe the electronic, photonic and nuclear motion for realistic systems. Together with Enrico Ronca, Johannes Flick, Prineha Narang and Angel Rubio, we currently exploit this strength to describe in real-space and real-time the slow-down of a reaction inside a single-mode cavity as measured by Thomas et al. [43]. We observe not just that the reaction is taking place as expected outside the cavity but we furthermore observe the slow-down of the reaction under resonant coupling and we are able to distinguish two competing mechanism preventing the reaction. Further calculations extending the statistical ensemble are currently performed.

When a system is externally driven, it can be forced into new equilibrium states, sometimes rendering previously unstable configurations now stable. An instructive example is the Kapitza pendulum for which driving the pivot point leads to the pendulum flipping on its head rather than hanging down. Driving with classical fields, i.e. Floquet physics, has proven to deliver all kinds of desirable and fascinating features. For example might it induce superconductivity [230] and allows to manipulate topological (Weyl)points in solid state materials [231]. We have seen that Floquet and cavity physics are conceptually very similar with the major advantage that the cavity does not demand pumping and consequently avoids heating.

A in Nature Materials accepted perspective, written together with Hannes Hübener, Umberto De Giovannini, Enrico Ronca, Johan Andberger, Michael Ruggenthaler, Jerome Faist and Angel Rubio, illustrates and promotes the immense possibilities that arise from this realization, especially for chiral cavities.

An ongoing debate is the question if for the thermodynamic limit or sufficient light-matter coupling, a novel state of matter appears in the ground state, i.e. the so called superradiant phase transition takes place. Indeed, a no-go-theorem exists for a dilute gas of atoms that prohibits such a transition [123, 127]. On the other hand, when the system becomes interacting, especially the limit in which the approximate cancellation of self-polarization and Coulomb interaction ('contact-free limit') is no longer fulfilled, this can change [123, 232]. Considering further investigations in the domain of excitonic insulators [130] and the shaping of superconductivity [131, 226, 233], proof that this limit is surely of interest. However, the question which gauge is delivering the correct results and how components of the Hamiltonian have to relate to each other becomes essential when the collective coupling reaches such immense values. Together with Enrico Ronca and Angel Rubio, we investigate the thermodynamic limit starting from a finite system in various approximations and gauges to extrapolate into a regime of interest and remain control of physical features, such as the violation of the Thomas-Reiche-Kuhn sumrule and the scaling of correlation.

We might often be able to approximate the cavity-field as a few or even a single mode. Nanoplasmonic environments, on the other hand, in which a complicated interplay between longitudinal and transversal modes appears on microscopic scales that are on the order of the structures itself, might drive an interest for a true first-principles description. As hinted in P1, the improvement of model descriptions could be greatly fostered by this approach. The coupled Maxwell-Kohn-Sham algorithm part of the OCTOPUS code [153] allows to solve the light-matter system self-consistently on the mean-field level for any arbitrary mode-geometry. This powerful tool can be conveniently combined with the MTEF ansatz to account for a set of quantum statistical features and in combination with the excellent scalability, we obtain a methodology that will be able to provide theoretical predictions consistent with the experimental realizations. To which extent the experimental observations are driven by quantum character is still up to debate and will very much depend on the specific application in mind. The high resilience of this effect, present even under rough ambient conditions such as room temperature and low-quality cavities [20, 30, 33–52], indicates that classical, semiclassical and full quantum light-matter coupling descriptions will have their fair share of usage for the community and scientific progress. Recall here especially the results of Section 6 and Publication P3 which indicate that for excitation energy transfer especially electronic correlations, originating from longitudinal (Coulomb) and transversal ($\hat{q}_\alpha \boldsymbol{\lambda}_\alpha \cdot \hat{\mathbf{R}}$ and $(\boldsymbol{\lambda}_\alpha \cdot \hat{\mathbf{R}})^2$) interaction, are essential while explicit light-matter correlations are in contrast of negligible relevance in those situations. In this context, building a connection to macroscopic QED [72, 73] might be furthermore beneficial.

The cavity allows spatially separated components to interact, for instance within a molecular ensemble. When we try to employ quantum chemical methods to accurately describe the local chemical reaction, we have to find a way to account for this collective non-local interplay. So far, the full ensemble was included fully as e.g. in P4, or via approximate models that allowed to effectively parallelize the system [118, 119]. Those approaches delivered already remarkable insight into the collective interplay. The alteration of chemical reactions however seems to suggest that the collectivity extends far beyond the domain of a few molecules. To which extent the full ensemble of billions of molecules at room temperature and subject to solvent effects is indeed (quantum) correlated is yet to be investigated but the relevance of interplay between many molecules is undoubtedly present in experiments. Taking the ambient conditions into account, it seems indeed unlikely that a true entanglement will be at the heart of the mechanism and an effective correlation of polarizability seems more likely. If this is the case, it would pave a way to consider local light-matter couplings as reshaped by a collectively dressed photonic field. For instance, the dressed propagator in Sec. 5.1.2 could approximately account for the ensemble polarizability. This way a single component in an ensemble bath can be effectively described and the result will be conceptually similar to a first-principles version of the Dicke model, focusing just on the bright states.
We have observed in Sec. 5.1.2 the relevance and emergence of polaritonic states in the construction of QEDFT functionals and MBPT at the example of the bare [10] and dressed (App. 10.1) TDOEP equation. Although the computational complexity disqualifies the time-dependent OEP from its application to larger realistic systems, it can provide very valuable insight for small molecules, atoms or models. We are currently investigating possibilities to construct an efficient algorithm that allows us to obtain the TDOEP in frequency space by means of the Sternheimer response equation with adjusted polaritonic poles according to our previous considerations. This would not just provide us with an improved and potentially ensemble adjustable TDOEP solution but will furthermore foster any future development of QEDFT functionals.

Let us to this end abstract our gathered insights towards quantum information. With the recent progress into the quantum supremacy regime [234], quantum information took a step into a mature domain of research. Common realizations depend on superconducting qubits implying the demand for specific ambient conditions. So far the rather small light-matter interaction prevented realizations build around photonic systems [235]. With the step towards theoretical first-principles predictions of functional materials and light-matter interaction, a new chapter in this story might be opened. Inspired by our observations regarding long-range correlation imprinted by the cavity and in combination with the developed theoretical first-principles methodologies, we hope to provide a novel perspective to drive further progress in the development of scalable quantum information devices.

8 Scientific contributions

The following publications are ordered by their didactic flow and we suggest the reader to follow this order.

Due to possible copyright claims the following publications are not included in this electronically published version. The reader is referred to the references [1] to [7]. Additional information can be obtained upon request from the author: `christian.schaefer.physics@gmail.com`**.**

8.1 P1 Relevance of the quadratic diamagnetic and self-polarization terms in cavity quantum electrodynamics

8.2 P2 Ab initio nonrelativistic quantum electrodynamics: Bridging quantum chemistry and quantum optics from weak to strong coupling

8.3 P3 Modification of excitation and charge transfer in cavity quantum-electrodynamical chemistry

8.4 P4 Ab Initio Optimized Effective Potentials for Real Molecules in Optical Cavities: Photon Contributions to the Molecular Ground State

8.5 P5 Dressed-Orbital Approach to Cavity Quantum Electrodynamics and Beyond

8.6 P6 Capturing vacuum fluctuations and photon correlations in cavity quantum electrodynamics with multitrajectory Ehrenfest dynamics

8.7 P7 Benchmarking semiclassical and perturbative methods for real-time simulations of cavity-bound emission and interference

8.8 P8 Octopus, a computational framework for exploring light-driven phenomena and quantum dynamics in extended and finite systems

This publication is not suited to be part of this thesis and we refer the interested reader to https://arxiv.org/abs/1912.07921 for the full manuscript that is currently under review.

9 Conclusion

NON-RELATIVISTIC QED exists since many decades and dominates our perception of this world as it describes the energy scale on which we experience this piece of paper in our hand or on our screen. Would we ignore transversal or longitudinal fields, we could neither read the ink on this paper nor would it materialize in our hands. If we zoom down to the molecular scale, the intricate interplay of charged particles via transversal photons and Coulomb interaction is in most situations an unsolvable and yet so essential problem. We have seen how the fundamental equations of non-relativistic QED are approximated by focusing on specific subspaces of interest and treating the remaining components merely qualitatively. The historically deviating strategies, one addressing the matter itself via quantum chemical methods and the other the quantized interplay of light with matter, demand now a consideration on equal footing as we enter domains of strong light-matter interaction in which none of the two strategies alone provides satisfying predictions. In the course of this thesis (P1, P2, P3), we have shown that many ad-hoc combinations will lead to serious violations of basic physical constrains, such as gauge, coordinate and basis independence as well as the stability of the light-matter correlated system itself. It is of uttermost importance for the future of cavity QED and its application in chemistry that first-principles descriptions and complementary models lead to conclusive and reasonable predictions. The design of accordingly suited models will greatly benefit from the here derived conclusions and will be fostered by the now arising first-principles approaches.

Quantum electrodynamic density-functional theory (QEDFT) presents now such a feasible and accurate method to describe realistic cavity-matter systems. While QEDFT will still demand many years of research to reach the same highly sophisticated level that conventional density-functional theory possesses in quantum chemistry, the first steps taken within this (P4, P5) and previous work prove how efficient and accurate this approach is. We have been able to develop and apply functionals that describe the correlated ground and excited states of realistic systems to high accuracy by means of dressed quasiparticle approaches and the optimized effective potential with its subsequent simplifications and improvements. For the first time, quantum chemistry and optics are truly considered on equal footing. The reshaping of electronic density, the creation of the novel polaritonic quasiparticles and the nuclear reorganization are all accessible and of uttermost interest. Our efforts pushed not just QEDFT as a method but furthermore cavity QED itself to novel heights, presenting truly magnificent perspectives. We have shown (P6, P7) that when the interplay of many emitters or the dynamic of many modes becomes relevant, the extensively benchmarked semiclassical and perturbative methods provide a path to complement QEDFT by an additional edge. While purely classical propagation in terms of Ehrenfests equation of motion might omit phase-relations, advanced (linearized) semiclassical methods are able to recover some of this information. This way, we provided cavity QED with an complementary angle for efficient first-principles predictions.

Many promising applications are waiting for those tools, some already presented in this work or other publications. That energy transfer and entanglement can be rendered almost distance independent inside the cavity (P3) is just a first indication of the impact that cavity QED will have on various domains of modern science. The control of (photo)chemical reactions via electronic or vibrational strong coupling is already changing the perception of how steering and catalysis of chemical reactions can take place. The similarity between coherently driving matter with an external field and the cavity environment enables many further applications far beyond the scope of this work. The exploration of strong light-matter interaction represents a novel knob to tune physical systems, chemical reactions and many more features in a way we can barely imagine at this moment. Our theoretical impact, presented in this thesis and especially P1-P7, provided the field with novel perspectives, tools, unseen predictions and unknown conclusions, comprising to a large extent the state-of-the-art of first-principles cavity QED. The recent years signalized an ever increasing interest and grow of the community, accounting for physicists, chemists, biologists, computer scientists and mathematicians. Breathtaking steps in experimental realizations that vary between ultra-strong single emitter coupling, controlling chemical reactions and the modification of superconductivity push the limits of this fast expanding field of research. This process sheds new light on many previous considerations, e.g. the question of phase transitions (see for instance the Mermin-Wagner theorem [236]), that are worth revisiting. On the interface between quantum electrodynamics and electronic structure theory, a highly interdisciplinary field of research is growing that proves once more that human curiosity is the catalyst needed to overcome the hurdles awaiting us.

10 Appendix

10.1 The polaritonic propagator approximation

Let us start from a 2-site, 1-mode model in PZW gauge represented by Pauli matrices (recall Sec. 4.1). The coupling to a single cavity mode is

$$\hat{H} = -t\hat{\sigma}_x + g(\hat{a}^\dagger + \hat{a})\hat{\sigma}_z + \omega(\hat{a}^\dagger\hat{a} + \frac{1}{2}) + \frac{\lambda^2}{2}$$

with $g = \sqrt{\frac{\omega}{2}}\lambda$ and dipole $|R_{01}| = 1$. The hopping between the two sites, i.e. the element $t = \langle\Phi_1|\frac{\nabla^2}{2}|\Phi_2\rangle$ (assumed symmetric), provides the energetic scale of excitations $\omega_a = 2t$. As this model practically implies a pinned dipole, the self-polarization reduces for a 2-level system in its center-of-mass to a constant. Recall that this breaks gauge invariance and therefore Coulomb and PZW gauge only agree in their predictions if photonic and atomic system are resonant (see Sec. 4.3, P2 and P1). The difference in occupation between the two sites (relative density) is represented in Fig. 9 and 10 according to $\sigma_z = n_1 - n_2$. We apply the unitary transformation $\hat{U} = \sqrt{\frac{1}{2}}(\hat{\sigma}_x + \hat{\sigma}_z)$ which switches the Pauli matrices $\sigma_z \leftrightarrow \sigma_x$ and changes the representation of eigenstates from the discrete site-basis (with explicit hopping) into the energetic representation. By furthermore shifting the energetic origin as we transform $\hat{U}\hat{H}\hat{U}^\dagger - (\frac{\omega}{2} + \frac{\lambda^2}{2})\mathbb{1} = \hat{H}_{Rabi}$, we arrive at the Rabi Hamiltonian

$$\hat{H} = -\frac{\omega+\delta}{2}\hat{\sigma}_z + g(\hat{a}^\dagger + \hat{a})\hat{\sigma}_x + \omega\hat{a}^\dagger\hat{a}\ ,\ \text{with } \delta = \omega_a - \omega \text{ detuning .}$$

Notice please that this similarly demands to transfer any initial state $|\phi_a(0)\rangle_{g\sigma_x} = \hat{U}|\phi_a(0)\rangle_{g\sigma_z}$. By performing the RWA $(\hat{a} + \hat{a}^\dagger)\hat{\sigma}_x = (\hat{a} + \hat{a}^\dagger)(\hat{\sigma}_+ + \hat{\sigma}_-) \approx \hat{a}\hat{\sigma}_+ + \hat{a}^\dagger\hat{\sigma}_-$, we obtain a 2-by-2 block structure (just transitions between $|e,n\rangle \leftrightarrow |g,n+1\rangle$ are allowed) that can be directly solved. Relevant quantities are

$$\begin{aligned}
\Omega_n(\delta) &= \sqrt{\delta^2 + 4g^2(n+1)} \text{ Rabi-frequency}\\
E^n_\pm &= \omega(n+\frac{1}{2}) \pm \frac{1}{2}\Omega_n(\delta) \text{ Rabi-splitting}\\
\alpha_n &= \tan^{-1}(2g\sqrt{n+1}/\delta) \text{ detuning angle}\\
|n,+\rangle &= \cos(\alpha_n/2)|n,e\rangle + \sin(\alpha_n/2)|n+1,g\rangle, \quad e^{-i\hat{H}t}|n,\pm\rangle = e^{-iE^n_\pm t}|n,\pm\rangle\\
|n,-\rangle &= -\sin(\alpha_n/2)|n,e\rangle + \cos(\alpha_n/2)|n+1,g\rangle, \quad e^{-i\hat{H}t}|0,g\rangle = e^{-i\frac{\omega+\delta}{2}t}|0,g\rangle
\end{aligned} \tag{13}$$

with the identity operator

$$\mathbb{1} = \sum_{n=0}^{\infty}(|n,g\rangle\langle n,g| + |n,e\rangle\langle n,e|) = |0,g\rangle\langle 0,g| + \sum_{n=1}^{\infty}(|n,+\rangle\langle n,+| + |n,-\rangle\langle n,-|)\ .$$

An arbitrary initial state $|\phi(0)\rangle = \sum_{n=0}^{\infty} c_n(b_g|n,g\rangle + b_e|n,e\rangle)$ evolves in time according to

$$\begin{aligned}
|\phi(t)\rangle =& c_0 b_g e^{+i\frac{\omega+\delta}{2}t}|0,g\rangle \\
&+\sum_{n=0}^{\infty}\Big\{ c_{n+1}b_g\big[\sin(\alpha_{n+1}/2)e^{-iE_+^{n+1}t}|n+1,+\rangle + \cos(\alpha_{n+1}/2)e^{-iE_-^{n+1}t}|n+1,-\rangle\big] \\
&\quad + c_n b_e\big[\cos(\alpha_n/2)e^{-iE_+^{n}t}|n,+\rangle - \sin(\alpha_n/2)e^{-iE_-^{n}t}|n,-\rangle\big]\Big\}\,.
\end{aligned} \tag{14}$$

We refer the interested reader now to [96, 160, 161] for a detailed introduction into many-body perturbation theory. While the approach is conceptually simple, it is technically demanding and requires a deeper representation to be fully appreciated. The basic idea is again built around avoiding the wavefunction as descriptor such that we decide to use the one-body Green's function in its place. The Green's function describes the propagation of a particle by creating it at one point and destroying it at another point according to $G^{(1)}(\mathbf{r}_1t_1, \mathbf{r}_2t_2) = -i\langle e^{-\beta\hat{H}}\mathcal{T}\hat{\Psi}(\mathbf{r}_1t_1)\hat{\Psi}^{\dagger}(\mathbf{r}_2t_2)\rangle/\langle e^{-\beta\hat{H}}\rangle$. The time-ordering operator $\mathcal{T}$ distinguishes the different situations $t_1 \lessgtr t_2$ and accordingly (anti)commutes the operators. Those situations are then indicated by adding $G^{\lessgtr}$ and the resulting objects are referred to as lesser/greater components. We are able to represent any one-body observable with the help of $G^{(1)}(\mathbf{r}_1t_1, \mathbf{r}_2t_2)$ such that for example the ionization spectrum of a material is naturally provided. However, many-particles objects, such as excitons, demand the next higher order of Green's function to be fully described. The thermal initial state is created by $e^{-\beta\hat{H}}$ and can be conveniently included into the propagation scheme by construction of an imaginary time, the Matsubara track. Applying the Heisenberg equation of motion leads to a hierarchy of coupled equations (Martin-Schwinger hierarchy). This hierarchy can be formally closed on the one-body level by using Wicks theorem (any higher-order correlator can be broken down in a determinant/permanent of free propagators) and introducing a self-energy Σ which accumulates all many-body scatterings $G^{(1)}(\mathbf{r}_1t_1, \mathbf{r}_2t_2) = G_0^{(1)}(\mathbf{r}_1t_1, \mathbf{r}_2t_2) + \int\int d\mathbf{r}_3dt3\mathbf{r}_4t_4G_0^{(1)}(\mathbf{r}_1t_1, \mathbf{r}_3t_3)\Sigma(\mathbf{r}_3t_3, \mathbf{r}_4t_4)G^{(1)}(\mathbf{r}_4t_4, \mathbf{r}_2t_2)$. The self-energy encodes therefore all interactions (classical = Hartree, fermion symmetry = exchange, and correlation) that affect the propagation of a particle and therefore leads to correlated quasiparticles. The photonic system follows the same conceptual steps with the difference that the Heisenberg equation of motion $\partial_t^2\hat{q}(t) + \omega^2\hat{q}(t) = \omega\boldsymbol{\lambda}\cdot\hat{\mathbf{R}}(t)$ is of second order, giving rise to a slightly adjusted structure. [24] The photonic system can feature large coherent shifts which is the reason why Maxwell's equations provide often satisfying results. As a consequence, the creation and annihilation operators are hardly truncating and it is much more elegant to design the perturbative ladder around the field fluctuations (see e.g.

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[24] To generate self-consistent approximations, by means of a sensible self-energy that conserves energy and momentum, the functional derivative of the Φ functional can be used [96, 161]. The lowest order self-consistent Φ functional is a bubble diagram (see e.g. [237, 238]) featuring two electronic propagators enclosing one photonic propagator $\frac{1}{2}GDG$. Functional derivatives with respect to the electronic propagators δ_G deliver the electronic self-energy $\Sigma \propto GD$ while δ_D leads to the photonic self-energy or polarization $\Pi \propto GG$. Disconnected diagrams are canceled by the partition function in the denominator of the propagators.

[237, 238])

$$\Delta\hat{q}_\alpha(t_1) = \frac{1}{\sqrt{2\omega_\alpha}}(\hat{a}_\alpha(t_1) + \hat{a}^\dagger_\alpha(t_1)) - \langle\hat{q}(t_1)\rangle \ .$$

The photonic propagator at zero temperature for a pure state can then be defined as

$$D_{\alpha\alpha}(t_1, t_2) = -i\langle\mathcal{T}\Delta\hat{q}_\alpha(t_1)\Delta\hat{q}_\alpha(t_2)\rangle \ . \tag{15}$$

The equation of motions for the electronic and photonic Green's functions, the Kadanoff-Baym equations, are naturally correlated. The lowest order of self-consistently dressed interaction (GW or self-consistent Born approximation) will describe a self-consistently updated single photon scattering for the electronic equation $\propto G(\mathbf{r}_1t_1, \mathbf{r}_2t_2)D(\mathbf{r}_1t_1, \mathbf{r}_2t_2)$. Vice versa, the photonic operator is driven by the polarization of the matter system, the corresponding self-energy, $\Pi(\mathbf{r}_1t_1, \mathbf{r}_2t_2) \propto G(\mathbf{r}_2t_2, \mathbf{r}_1t_1)G(\mathbf{r}_1t_1, \mathbf{r}_2t_2)$ accounts for exciton creation.

We calculate now the time-ordered components of the perturbatively dressed propagator $D^{\lessgtr}_{RWA}$ in the Schrödinger frame by substituting Eq. (14) into Eq. (15) and can express the propagation with the help of Eq. (13). The symmetry $\langle\hat{a}^\dagger(t_2)\hat{a}(t_1)\rangle = \langle\hat{a}^\dagger(t_1)\hat{a}(t_2)\rangle^*$ such that $D^{\gtrless,*}(t_2, t_1) = -D^{\lessgtr}(t_2, t_1) = -D^{\gtrless}(t_1, t_2)$ and assuming $\delta = 0$ will render this procedure more convenient. We arrive at

$$\begin{aligned}
2i\omega D^{>}_{RWA}(t_2, t_1) =& \frac{|b_e|^2}{4} e^{+i\omega(t_2-t_1)} \left[e^{+igt_2} - e^{-igt_2}\right] \left[e^{-igt_1} - e^{+igt_1}\right] \\
&+ \frac{|b_g|^2}{2} e^{-i\omega(t_2-t_1)} \left[e^{+ig(t_2-t_1)} + e^{-ig(t_2-t_1)}\right] \\
&+ \frac{|b_e|^2}{4} e^{-i\omega(t_2-t_1)} \Big\{ (\sqrt{2}+1) \left[e^{+i(\sqrt{2}-1)g(t_2-t_1)} + e^{-i(\sqrt{2}-1)g(t_2-t_1)}\right] \\
&\qquad\qquad - (\sqrt{2}-1) \left[e^{+i(\sqrt{2}+1)g(t_2-t_1)} + e^{-i(\sqrt{2}+1)g(t_2-t_1)}\right] \Big\} \\
&- b_e^2 b_g^2 \Re \left[e^{-i(\omega-g)t_2} - e^{-i(\omega+g)t_2}\right] \Re \left[e^{-i(\omega-g)t_1} - e^{-i(\omega+g)t_1}\right] \ .
\end{aligned}$$

For $g \to 0$ the free propagator is obtained. The excellent performance of the RWA dressed TDOEP indicates that the linearized Sham-Schlüter equation employed to derive the starting point of the OEP (see [10]) is indeed the minor issue. Similarly, for coupling λ well below one, vertex corrections are apparently of minor impact. The interested reader might refer to the phononic context and Migdal's theorem [239]. Instead, the failure of the bare TDOEP on resonance is very intuitively arising because the propagator does not consider the adjusted quasiparticle eigenstates, therefore the essential component of strong coupling and its effect on the photonic fluctuations is disregarded. Future developments should consequentially always consider those components and the rather low demand to design conserving approximations [170] might allow very efficient strategies. The computational complexity and instability will likely prohibit the TDOEP from true first-principles utilization for large realistic systems. By consistently combining insight from models and extending the size of the latter, one might however find the ideal field of application for a dressed TDOEP, interpolating between models and first-principles.

11 Abbreviations

Abbreviation	Definition
BBGKY	Bogoliubov–Born–Green–Kirkwood–Yvon
(c)BO	(cavity) Born-Oppenheimer
CI	Configuration interaction
(TD)DFT	(time-dependent) Density-functional theory
DMFT	Dynamical mean-field theory
DMRG	Density-matrix renormalization group
FBTS	Forward backward trajectory solution
FRET	Förster resonant energy-transfer
FSSH	Fewest switches surface hopping
FWHM	Full width half maximum
HEG	Homogeneous electron gas
Hxc	Hartree-exchange-correlation
(TD)KLI	(time-dependent) Krieger-Li-Iafrate
KS	Kohn-Sham
Laser	Light amplification by stimulated emission of radiation
LDA	Local density approximation
LSC	Linearized semiclassical
MBPT	Many-body perturbation theory
MCTDH	Multiconfiguration time-dependent Hartree
MTEF	Multi-trajectory Ehrenfest
(TD)OEP	(time-dependent) Optimized effective potential
PES	Potential energy surface
PZW	Power-Zienau-Wooley
QCLE	Quantum Classical Liouville Equation
QED	Quantum electrodynamics
QEDFT	Quantum electrodynamic density-functional theory
RWA	Rotating wave approximation
VSC	Vibrational strong coupling

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