A theoretical perspective on molecular polaritonics

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Abstract

In the last decade, much theoretical research has focused on studying the strong coupling between organic molecules (or quantum emitters, in general) and light modes. The description and prediction of polaritonic phenomena emerging in this light-matter interaction regime have proven to be difficult tasks. The challenge originates from the enormous number of degrees of freedom that need to be taken into account, both in the organic molecules and in their photonic environment. On the one hand, the accurate treatment of the vibrational spectrum of the former is key, and simplified quantum models are not valid in many cases. On the other hand, most photonic setups have complex geometric and material characteristics, with the result that photon fields corresponding to more than just a single electromagnetic mode contribute to the light-matter interaction in these platforms. Moreover, loss and dissipation, in the form of absorption or radiation, must also be included in the theoretical description of polaritons. Here, we review and offer our own perspective on some of the work recently done in the modelling of interacting molecular and optical states with increasing complexity.

1 Introduction

Polariton is a general term used to describe a hybrid light-matter excitation, and has been employed in many different situations in the history of physics.1 In this Perspective, we focus on a small subset of these situations, namely those in which molecules (often organic dyes) are used to provide the material component. Even within this small subset, a wide range of new phenomena are enabled by polariton formation, among them Bose-Einstein condensation and polariton lasing,2,3 quantum information processing,4 long-range excitation transport5,6 and control of chemical reaction rates.7 After a short overview of basic physical concepts, we discuss our view on the current state of the field and the challenges it faces, interesting recent developments, and promising future directions. Despite the focus on molecules, we here restrict the discussion mostly to “physical” properties, and ignore “chemical” properties such as (photo)reactivity that have been the focus of a recent related perspective on polaritonic chemistry.8

Polaritons arise when the interaction strength between light modes and material excitations in a system becomes large enough that the eigenstates of the system are not even approximately represented by pure matter excitations or pure electromagnetic excitations (photons), and instead become mixed. Polariton formation is thus intimately related to the regime of strong coupling (SC) between light and matter,9,10 reached when the interaction strength overcomes the loss rates of the constituents. We note that strong coupling itself is not necessarily a quantum effect, and can often be modelled through classical electromagnetism (EM).10,11 In that case, the material excitations are represented through the dielectric function of the medium (e.g., through a resonance of Drude-Lorentz form), or through a polarizable dipole for single emitters.12,13

Before introducing strong coupling in more detail, we note that the apparently simple question of what should be called a “light mode” is actually somewhat subtle, and, as for any question of
semantics, its answer is to some degree arbitrary. The only “pure” light modes are free-space modes in vacuum. A cavity is a material structure that confines the EM field, such that the confined “cavity photon modes” are always partially material excitations.\(^\text{8,14}\) As an operational definition, the cavity modes are usually understood as the modes supported by those parts of the full system for which the relevant dynamics can be well-approximated through macroscopic electromagnetism under linear response. This distinction leads naturally to the framework of macroscopic QED,\(^\text{14–21}\) discussed in more detail below. The resulting EM modes then include those of optical (Fabry-Pérot) cavities\(^\text{22,23}\) (as depicted in the left bottom panel of Fig. 1), photonic crystals,\(^\text{24,25}\) and often also plasmonic nanostructures (as illustrated in the left top panel of Fig. 1), whose resonances are formed due to geometrical restriction of the free electron motion in metals and allow strongly subwavelength field confinement to be achieved.\(^\text{26–28}\) However, plasmon modes are physically quite distinct from “optical” modes. In Fabry-Pérot or photonic crystal cavities, the energy is mostly stored in the electric and magnetic fields, and the dielectric functions of the materials can often be treated as approximately constant within the relevant range of frequencies. In contrast, the energy in plasmonic resonances is stored in the electric field and the kinetic energy of the electrons,\(^\text{29}\) such that the resulting modes are more correctly referred to as surface plasmon polaritons. The dominantly electrostatic (or more precisely, quasistatic) character of the fields in deep-subwavelength cavities also has fundamental consequences on the light-matter interaction, as the electric fields are then to a good approximation purely longitudinal and not represented by the vector potential in the standard Coulomb gauge.\(^\text{8,14,30}\) Furthermore, plasmonic systems can have complicated internal dynamics after excitation, e.g., leading to hot electron generation which in turn can have significant effects on chemistry.\(^\text{31,32}\) In this Perspective, we do not discuss such hot-electron effects.

Once a suitable definition of what constitutes the light modes in the system has been chosen, it becomes possible to distinguish between the weak and strong coupling regime within that model. For a single quantum emitter approximated as a two-level system coupled to a single photon mode within the rotating wave approximation, the dynamics is described by the Jaynes-Cummings model.\(^\text{33}\) When the emitter and photon mode are on resonance, the strong coupling regime is entered when their mutual interaction overcomes decoherence in the system. In this regime, energy exchange between light and matter becomes a coherent process: if only one of the components is initially excited, this energy exchange is seen as an oscillatory behaviour of the population between both subsystems, the so-called vacuum Rabi oscillations occurring at the vacuum Rabi frequency (or Rabi splitting)

\[
\Omega_R = 2g = \frac{2}{\hbar} \vec{\mu} \cdot \vec{E}_{1\text{ph}},
\]

where \(\vec{\mu}\) is the dipole transition moment of the emitter and \(|\vec{E}_{1\text{ph}}| = \sqrt{\hbar \omega_c / 2 \epsilon_0 V}\) is the quantized electric field strength of the mode, associated with one photon, at the emitter position. Here, \(\omega_c\) is the cavity mode frequency and \(V\) is its effective mode volume, whose definition in nanophotonic devices has been the object of intense theoretical activity lately.\(^\text{34–36}\) Physically, vacuum Rabi oscillations thus correspond to the situation where a photon can be emitted and reabsorbed several times before it disappears from the system. In these conditions, the eigenstates of the coupled system are hybrid light-matter states, and a thorough understanding of the system can only be reached by considering the coupled system as a whole. The two original excited states (emitter and photon) transform into polaritonic states that are shifted up and down in frequency by the coupling strength, with their difference in energy given by the Rabi splitting. These two states are conventionally called the lower po-
lariton (LP) and upper polariton (UP).

We mention here that some care should be taken to distinguish between the concepts of polaritonic states and polaritons. The former are the hybrid eigenstates of the coupled system, which do not depend on the state of the system at any point in time and in that sense always exist. The latter are the excitations of the system in a quasi-particle picture, and thus only exist when the system is in one of the polaritonic states. As a further complication, for (approximately) linear systems that are well-modeled as harmonic oscillators, polaritons behave approximately like bosons. It is then convenient to use the concept of (bosonic) polaritonic modes, each of which describes a (formally) infinite number of polaritonic Fock states \(|0\rangle_P, |1\rangle_P, |2\rangle_P, \ldots\). In this picture, having \(n\) polaritons in mode \(P\) means that the system is in state \(|n\rangle_P\). In the literature, the distinction between polaritons, polaritonic states, and polaritonic modes is not always made explicit, which can cause some confusion. Which of the three is meant is usually clear from the context.

For single emitters, reaching the SC regime is extremely challenging, as the single-emitter coupling strength \(g\) has to become comparable to the emitter and cavity decoherence rates. This can be achieved by either increasing the coupling strength or decreasing the decoherence rates sufficiently. This was first achieved in 1985 by working with long-lived emitters and cavities at cryogenic temperatures, in a microwave cavity with superconducting mirrors. Rabi oscillations in the system were explicitly measured two years later. In 2004, the SC regime for a single quantum dot in a semiconductor micropillar cavity was achieved, with a Rabi splitting \(\sim 100\ \mu\text{eV}\). These approaches, where the absolute coupling strength is a small fraction of the excitation energy, necessarily require very long-lived emitters and cavity modes, which in turn implies cryogenic temperatures. More recently, the strong coupling regime has been approached at room temperature for single organic molecules by using extremely localized surface plasmons in narrow gaps, which support light confinement in deeply subwavelength volumes. The estimated single-molecule Rabi splitting achieved in Ref. was 90 meV, at the limit of the strong coupling regime. Very recently, strong coupling and quantum nonlinearity have been observed for a single molecule at cryogenic temperature, where the molecule behaves as an effective two-level system.

Strong light-matter coupling is much easier to achieve in the collective case where an ensemble of \(N\) close to identical quantum emitters interacts with a photonic mode (as described by the Tavis-Cummings model\(^{[46]}\)). In that case, the effective coupling strength increases with the number of emitters as \(g_N = g\sqrt{N}\). This enhancement significantly simplifies entering the strong coupling regime and is the basis for most experiments in the field of molecular polaritonics. It occurs because an excitation in this case can be coherently distributed over the \(N\) emitters, forming a so-called bright state with increased light-matter coupling. At the same time, all \(N-1\) orthogonal ways of distributing an excitation over the emitters show negligible coupling to the cavity mode due to destructive interference between the dipole transitions in the different emitters. These superpositions are the so-called dark states (DS), which play a major role in molecular polariton dynamics\(^{[48,49]}\).

Collective strong coupling was first realized in 1975 using molecular vibrations coupled to surface phonon polariton modes, and soon later for molecular excitons coupled to surface plasmon polaritons, and Rydberg atoms coupled to a high-Q microwave cavity. Strong coupling to semiconductor (Wannier) excitons was first realized in 1992. Such systems reach Rabi splittings in the range of \(1-20\ \text{meV}\). Organic semiconductors support much larger Rabi splittings, \(\Omega_R \gtrsim 100\ \text{meV}\), due to their high density and large dipole moments, so that strong coupling can be observed at room temperature. We note that the maximally reachable Rabi splitting for a given material is determined by the density of dipoles, but largely independent of the specifics of the photon mode. This can be understood by noticing that

\[
g_N \propto \mu \sqrt{N/V} \propto \mu \sqrt{\rho}, \tag{2}
\]

where \(\rho\) is the molecular number density and we have used that the effective mode volume is related to the physical volume occupied by the mode. The number of molecules interacting with the mode is thus proportional to the molecular density times the volume. A more careful calculation shows that the Rabi splitting depends on the dipole density multiplied by a “filling factor” between 0 and 1 that determines what fraction of the mode volume is filled with the molecular material (weighted with the position-dependent quantized field strength). When a cavity is com-
pletely filled with the material in question, the Rabi splitting is equal to the bulk polariton splitting obtained by Hopfield in 1958. These facts explain why similar Rabi splittings have been observed in the literature for very different photonic systems, such as Fabry-Pérot cavities, plasmonic surfaces, plasmonic hole arrays, isolated particles and arrays of them, and nanoparticle-on-mirror setups. Several kinds of organic materials can reach the ultrastrong coupling regime, in which the Rabi splitting is a significant fraction of the bare excitation energy, with record values close to and above $\Omega_R = 1 \text{ eV}$. These large values also mean that cavity modes with very large decay rates $\kappa$ (or equivalently, short lifetimes $\tau = 1/\kappa$ or low quality factors $\omega_c/\kappa$) can be used while still reaching the strong coupling regime.

Organic molecules are very well-suited for reaching large Rabi splittings due to the large transition dipole moments and high densities. However, they have complex internal structure due to their rovibrational degrees of freedom and often cannot be approximated as two-level systems. On the one hand, this complicates their use and study as idealized (two-level) quantum emitters. On the positive side, this opens up the opportunity to modify their internal structure and dynamics through strong light-matter coupling, or conversely to exploit the internal dynamics to achieve new photonic functionalities. The former type of applications are exemplified by the field of polaritonic chemistry, which aims at modifying chemical processes such as photochemical reactions through strong light-matter coupling. The latter type of applications typically rely on the fact that molecules show strong exciton-vibration interactions, such that molecular vibrations can drive polariton relaxation or transfer between different polaritonic states. This can enable processes such as organic exciton-polariton lasing and condensation or energy transfer between different molecular species even over long spatial distances. Note that it has been also shown that, even under the two-level system approximation, SC phenomena involving organic molecules offer possibilities for nonclassical light generation not attainable by means of other types of quantum emitters.

When describing light-matter interactions in molecular systems, in particular in the strong coupling regime, including all the degrees of freedom in both constituents is an arduous task. Then, many models are focused on taking into account the complexity of one of them, i.e., the theoretical effort is focused either on the description of the complexity of the photonic structures or to include to some extent the vibrational structure of the molecules. In what follows, we summarize some of the theoretical challenges that remain in both paths.

### 2 Complex EM fields under strong coupling

Many different kinds of “cavities” can be used to achieve strong coupling in the collective regime, while few- or single-molecule strong coupling necessarily requires deep subwavelength confinement of light. In general, any cavity setup is determined by “macroscopic” structures consisting of large numbers of atoms, such as Fabry-Pérot cavities, photonic crystals, and metallic nanoparticles or surfaces. Within these setups, one or several microscopic quantum emitters such as atoms, molecules or point defects are placed. As discussed above, it is then customary to treat the macroscopic structure through Maxwell’s equations and formally treat the modes arising from these equations as the EM modes of the system.

In order to describe light-matter interactions on a quantum level, these EM modes have to be quantized, which is significantly more challenging than the quantization of free EM modes in conventional quantum electrodynamics. For one, the presence of material structures complicates the solution of eigenmodes, which often is only possible numerically. Nowadays, many commercial and open source packages are available to solve Maxwell’s equations. Furthermore, these light modes will be lossy, often highly so, both due to material losses and leakage to the far field. Only in some approximations do lossless states exist, e.g., when assuming the existence of perfectly conducting mirrors or infinitely long lossless and defect-free waveguides, etc. None of these are typically good approximations for the kinds of structures used in molecular polaritons. Still, when losses are small enough, it can be a reasonable strategy to quantize fully bound modes in a fictitious lossless system, and then treat the losses as small perturbations on top of that.

Alternatively, when dealing with small enough nanoparticles with localized resonances (such as plasmonic nanoparticles) for which radiative losses are small due to inefficient emission, the so-called quasistatic approximation is often applicable. In
this approximation, retardation effects, and therefore EM propagation into free-space (or bulk dielectric media) is neglected, resulting in purely longitudinal fields. In this limit, semi-analytical solutions are often again possible, e.g., using transformation optics, with the resulting modes being fully bound while still describing the material losses. Since subwavelength confinement is a prerequisite for the quasistatic approximation, these material losses will always be significant. One advantage of the quasistatic approximation is that the EM modes can be described by a scalar potential, which simplifies the treatment of beyond-dipole interactions. Another advantage of the quasistatic approximation is that for metals described by a dielectric function of Drude form, the resulting eigenmodes will always correspond to uncoupled Lorentzians in the spectral density (discussed in more detail below), which allows for a straightforward quantization procedure of the resulting modes. Radiative losses can also be included a posteriori, e.g., by calculating the effective dipole moment of the localized resonances.

When the quasistatic approximation is not appropriate and retardation effects have to be taken into account, the most general and powerful approach to nonetheless obtain a quantized description of the EM field is macroscopic QED. This is a formalism that quantizes the EM field in arbitrary structures, including dispersive and absorbing materials. A particularly appealing feature of this approach is that the quantized EM modes are fully described by the dyadic Green’s function $G(r, r', \omega)$ of the classical Maxwell equations, which can be obtained from any numerical solver. This can be conceptually understood from the fact that Maxwell’s equations are the wave equations describing the dynamics of EM fields, which remains true after quantization. A recent review about macroscopic QED in the context of nanophotonics can be found in Ref. 14. We note here that, although the classical description of the EM environment is valid for a wide variety of physical situations, it breaks down when the material and the emitters are physically close enough that electronic wave functions overlap, which happens at subnanometer separations.

For an emitter where a single dipole transition is relevant (i.e., when treating only two electronic levels), the so-called spectral density $J(\omega)$ completely characterizes the electromagnetic environment and its interaction with the emitter (a schematic picture of this physical magnitude is rendered in the top right panel of Fig. 1). This quantity is given by

$$J(\omega) = \frac{\hbar \omega^2}{\pi \epsilon_0 c^2} \mathbf{\mu} \cdot \text{Im} G(r, r, \omega) \cdot \mathbf{\mu},$$

where $\mathbf{\mu}$ is the transition dipole and $r$ is the position of the emitter. For the many situations where the classical EM spectral density can be used, the EM environment is then a continuum which can be treated as a bath. This makes all the theoretical tools of the field of open quantum systems available. In the weak-coupling regime, the bath can be treated perturbatively through the Markov approximation, which just induces level shifts (often assumed to be included in the emitter frequency $\omega_0$ and thus neglected) and radiative decay with rate $\gamma_r = 2\pi J(\omega_0)$.

In the more interesting situation where the Markovian approximation is not applicable, there are several available methods to treat a bath of harmonic oscillators (the photon modes) exactly using advanced computational tools. One of these tools is the cumulant expansion, which is based on solving the Heisenberg equations of motion for the correlations between operators and truncating the resulting expansion at a given order. It is in this sense an extension of mean-field approaches to arbitrary order. For small numbers of molecules (or a single one), relatively high orders of the correlations are needed to accurately describe the dynamics even in the presence of photonic continua, while for large numbers of molecule, the expansion converges much earlier.

Several other commonly used approaches rely on the so-called chain mapping, an orthogonal transformation that maps the Hamiltonian of one emitter coupled to a continuum of modes to a chain-like Hamiltonian where the emitter is only coupled to the first site, which corresponds to a reaction mode, i.e., a collective environment mode, in an infinite string of modes coupled through nearest-neighbor interactions. Fig. 2a shows a sketch of this transformation. In this form, tensor network approaches that represent a high-dimensional wave function as a product of many lower-dimensional matrices (a so-called matrix product state) become highly efficient as the entanglement in an effective 1D system such as a chain is limited. Tensor network approaches depend exactly on a truncation of the possible entanglement between different parts of the system. In the context of molecular polaritonics, they have been shown to allow the descrip-
Figure 2: (a): Sketch of the chain mapping model. (i) quantum system coupled to a discrete set of environment modes; (ii) quantum system coupled to the (collective) reaction mode, with this mode coupled to a residual bath of modes; (iii) chain mapping for the environment modes after n steps, with a residual bath of N-n modes at the end of the chain. (b): Sketch of the few-mode quantization model for one quantum emitter. The spectral density of the model can be fitted to the one obtained classically from the Green's function. Therefore, the couplings to the interacting modes $g_i$, their frequencies and coupling $\omega_{ij}$ and the dissipative terms $\kappa_i$ can be known. Reproduced with permission.
tion of several molecules coupled to complex environments. A fully converged tensor network calculation gives exact results, but becomes computationally challenging when long propagation times are desired as the entanglement grows over time. Furthermore, the formally infinite chain has to be truncated at finite length in any realistic calculation, with the required length increasing with propagation time (to prevent unphysical reflections from the end of the chain). In order to decrease the length of the chain and access long times with low computational effort, it is possible to introduce fictitious losses along it that lead to damping of the propagating excitations (similar to the absorbing potentials used in many areas of physics).

Another approach is to employ transfer tensors, which can be used to propagate to arbitrary times with linear computational cost.

While the description of the EM modes as a structured continuum described by the spectral density is formally exact, it is often advantageous and desired to obtain a description of the environment in terms of a few discrete modes, corresponding to the physical image of isolated cavity modes. When losses are included, these are not true eigenmodes of the system, but resonances with a given linewidth embedded in the continuum. Several methods to achieve such a few-mode quantized description have been developed in the past few years. One is based on quasinormal modes, which are eigenmodes of the Maxwell equations including losses with complex frequencies. They can be used to expand the electric field solutions based on a master equation approach, or explicitly quantized such that the EM field is represented in terms of discrete bosonic modes. An alternative approach that does not require calculation and explicit quantization of quasinormal modes is based on the fact that two systems with the same spectral density are indistinguishable for an emitter. This allows the construction of a model system consisting of a few coupled discrete modes that are themselves coupled to a background bath and reproduce the full spectral density. Fig. 2b shows a sketch of that model. The parameters of the model, which are obtained through fitting of the spectral density, are the coupling between the emitter and the discrete modes \( g_i \), the frequencies of these modes and their couplings \( \omega_{ij} \), and their dissipation \( \kappa_i \). The coupling to the background modes is spectrally flat (by construction) and thus leads to Markovian dynamics that can be represented in a Lindblad master equation, such that the full EM continuum is represented by a collection of lossy and coupled discrete modes in the master equation. This approach is not only computationally efficient, but also allows to describe the EM environment in the language of cavity QED and quantum optics. The fact that the discrete modes are mutually coupled makes it able to reproduce even complex interference phenomena between the EM modes in the spectral density. While originally developed for a single emitter, we have recently extended the approach to the case of several emitters, or one emitter with several contributing transitions (such as different orientations of the dipole moments). This is enabled by defining a generalized spectral density that fully encodes the interaction between the EM modes and several emitters,

\[
\mathcal{J}_{nm}(\omega) = \frac{\hbar \omega^2}{\pi \epsilon_0 c^2} \mathbf{n}_n \cdot \text{Im} \left[ G(\mathbf{r}_n, \mathbf{r}_m, \omega) \right] \cdot \mathbf{n}_m, \tag{4}
\]

and which is again determined by the classical dyadic Green’s functions. Here, \( \mathbf{n}_n \) is the unit vector describing the orientation of the dipole transitions that are taken into account, while \( \mathbf{r}_n \) is the position of the corresponding emitter. Note that in this definition, the dipole moment is not included in the spectral density as emitters with many levels and dipole transitions between them can be treated.

3 Introducing molecular complexity

For the description of the molecules, we focus on approaches that are well-adapted for describing “good” molecular emitters, meaning ones where the first electronically excited state is relatively stable against nonradiative decay and photochemical reactions do not take place. For such emitters, it is often a good approximation to represent the nuclear potential energy surfaces as harmonic oscillators, which significantly simplifies the treatment. When more chemical detail is needed, a wide variety of methods are nowadays available, but doing so typically limits the level of description of nuclear motion.

As detailed in the introduction, the simplest approach is to treat molecules as two-level systems. This can be well-justified for studies at cryogenic temperatures where vibrational sublevels are individually resolved and addressable. At room temperature, the influence of the vibrational mo-
tion of the molecule can be approximately included by adding a pure dephasing term in a Lindblad master equation description. This can be understood as arising from an exciton-vibration coupling term treated through the Markov approximation. However, since under strong coupling the molecular exciton state gets distributed over the polaritonic modes, the Markov approximation that was originally performed for the emitter by itself to obtain a pure dephasing term is not valid anymore.\textsuperscript{111} Including it without further modification in the strongly coupled system leads to artificial population transfer between the polaritons and dark states, with equal rates for pumping of energy from the reservoir of vibrations to the system as for loss of energy from the system to the reservoir. This is unphysical when the Rabi splitting is comparable to or larger than the thermal energy, a condition that is essentially always fulfilled in molecular exciton-polariton strong coupling. This problem can be resolved by applying the Markov approximation after taking into account the strong coupling, e.g., by using a Bloch-Redfield approach.\textsuperscript{76,112,113}

When exciton-phonon coupling is sufficiently strong that the above approach breaks down, it becomes necessary to explicitly include the vibrational modes of the molecules. The simplest approach is the so-called Holstein model, which treats only a single vibrational mode and describes each molecule as two displaced harmonic oscillators. For multiple emitters, this leads to the so-called Holstein-Tavis-Cummings model,\textsuperscript{114,115} within which each electronic level is represented by several vibrational sub-levels. Within this model, the effect of the vibronic coupling can be studied, so an analysis of nuclear dynamics in molecules under strong coupling is feasible. Along this line, it has been predicted that electron transfer between different excited states can be enhanced or suppressed.\textsuperscript{115} The inclusion of vibronic sublevels and the concomitant emergence of dark vibronic polaritons (collective light-matter states that weakly absorb but strongly emit radiation) allows for a better description of the spectroscopy and dynamics of organic microcavities in the strong coupling regime.\textsuperscript{116–118} The inclusion of vibrational levels is also highly relevant for the description of phenomena such as organic polariton lasing and polariton condensation.\textsuperscript{114,119,120}

An extension of the Holstein-Tavis-Cummings model that allows for more realistic molecular structure is to consider more complex potential energy curves instead of harmonic oscillators, permitting the treatment of vibrational nonlinearities and (photo)chemical reactions within a relatively simple model (especially if only a single vibrational degree of freedom is treated). The hybridization of the potential energy surfaces in the strong coupling regime then leads to hybridized polaritonic potential energy surfaces (PoPES), which have mixed photon-matter properties.\textsuperscript{48,121,122} A schematic representation of these PoPES can be found in the right bottom panel of Fig. 1.

Assuming that vibrational modes are harmonic oscillators but taking into account all degrees of freedom for the molecules (typically hundreds), and potentially of the surrounding solvent or polymer host material, one can again rely on tensor network techniques as discussed above for the photonic modes. The molecular vibrations are then represented by an independent chain of harmonic oscillators.\textsuperscript{99–101} Alternatively, the bath of harmonic vibrational modes can be represented through its correlation function and simulated using the time-evolving matrix product operator (TEMPO) method.\textsuperscript{123,124} This uses a tensor network to describe the system’s history over a finite memory time and can thus represent non-Markovian dynamics. Combining this technique with a mean-field approximation further reduces the problem size.\textsuperscript{125}

We note at this point that although many effects can be understood by the use of the previous models, all of them constitute strong approximations for the molecular structure. In particular, the use of harmonic oscillators to describe the vibrational modes precludes the description of any nonlinear vibrational effects or of chemical transition states, conical intersections, etc. However, a full quantum description of the molecules is an extremely challenging task and only possible for small molecules. To give a more complete picture by including all degrees of freedom inside the molecules requires utilizing quantum chemistry and ab-initio approaches.\textsuperscript{8}

4 Summary and outlook

In this article we have provided a perspective on the current status of the theoretical investigation devoted to analyzing the exciting physics in the emergent field of molecular polaritonics. This area of research deals with the strong light-matter coupling regime that appears between electronic/vibrational excitations within (organic) molecules and confined
light fields. As for the light field component, a photonic structure that acts as a cavity is needed. Depending on the cavity used, strong coupling can be reached by utilizing a large ensemble of molecules or just one or a few of them, depending on whether or not subwavelength confinement is achieved.

The theoretical description of the EM modes that arise in these photonic structures, which in general are lossy, is then a challenging task. When the cavities present small losses, they can be treated perturbatively, while for small enough subwavelength cavities, the quasistatic approximation can be used, which allows for semi-analytical solutions. However, in many physical situations, a fully quantized description of the EM field in photonic structures is required. Here we have shown how the macroscopic QED formalism provides the necessary theoretical and numerical tools to accurately describe light-matter strong coupling in arbitrary structures. Within this framework, the spectral densities that characterize the coupling between one or several quantum emitters and confined EM modes are fully determined by the classical Green’s functions, which are calculated using standard numerical solvers of Maxwell’s equations in complex EM media. Based on macroscopic QED, it is then feasible to develop approaches that allows for a tractable treatment of complex photonic environments. Among these simplified treatments, the most promising approaches are those based on the concept of quasinormal EM modes and a very recent one that relies on the construction of a model system involving a small number of lossy and interacting EM modes whose parameters are fitted to exactly reproduce the spectral densities associated with the photonic structure under study.

Regarding the matter component, organic molecules also have a complex internal structure, which prevent them from being theoretically modelled as just two-level systems in many situations. To include molecular complexity in the theoretical description, it is then mandatory to add some ingredients to the standard two-level model to describe the vibrational modes of the molecules. Depending on the strength of the vibronic coupling, a pure dephasing term, the Bloch-Redfield approximation or the explicit inclusion of the vibrational modes need to be utilized. Within this last approach, the most used framework is the so-called Holstein-Tavis-Cummings model, which only takes into account one vibrational mode, modelled as a harmonic oscillator, which has proven to be very successful in providing physical insight. Going beyond this model can be achieved either by including more of the (typically hundreds of) vibrational modes of a molecule, or by substituting the harmonic oscillators by more realistic potential energy surfaces. The first approach captures vibration-induced dephasing and decoherence, while the second naturally accounts for the vibrational nonlinearities and has also allowed for a fundamental description of (photo)chemical reactions induced by strong light-matter coupling. Nevertheless, in order to have a more accurate description of the internal structure of organic molecules, numerical formalisms that rely on quantum chemistry codes or ab initio approaches need to be utilized.

At this stage, for the case of collective strong coupling in which a large (macroscopic) number of molecules is involved, the current status of the theoretical research on molecular polaritonics does not allow for both a realistic treatment of the internal structure of the organic molecules and a detailed account of the complex EM media. This is indeed very frustrating as the majority of the experiments carried out in this field belong to the category of collective strong coupling. Therefore, a quantitative agreement between ab-initio theory and experiment is not within reach nowadays. This is why during the last decade, most of theoretical research has focused either on giving fundamental support to some of the experimental findings or to propose new effects that result from theoretical approaches based on simplified models. On a more positive note, for the case in which only a single or few molecules participate in the strong coupling phenomenon, after ten years of intense research, we now have the adequate theoretical and numerical tools to accurately describe both the internal vibrational modes of the organic molecules and the complexity of the sub-wavelength EM fields associated with nanoplastic (mainly plasmonic) structures. Then, we expect that all this theoretical knowledge will help to open new and exciting avenues for research in molecular polaritonics.

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