

FOCUS ARTICLE

Ab Initio Approaches to Simulate Molecular Polaritons and Quantum Dynamics

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ABSTRACT

Molecular polaritons are hybrid states formed by the quantum mechanical interaction between light and matter. Recent experiments have shown the ability to drastically modify chemical reactions in both the ground and excited states through the hybridization of the electronic and photonic degrees of freedom. Ab initio simulations of molecular polaritons have demonstrated similar effects for simple ground and excited state reactions. However, the theoretical community has been limited in its ability to describe the complicated dynamical processes of many-molecule collective effects with a high-level treatment of all degrees of freedom within a rigorous Hamiltonian. In this review, we provide a general description and overall procedure for exploring molecular polaritons, leveraging standard many-body electronic structure calculations combined with the exact, non-relativistic quantum electrodynamics light-matter Hamiltonian.

This article is categorized under:

Electronic Structure Theory > Ab Initio Electronic Structure Methods

Software > Quantum Chemistry

Structure and Mechanism > Reaction Mechanisms and Catalysis

1 | Introduction

Coupling matter (atoms, molecules, or solid-state materials) to the quantized electromagnetic field inside an optical cavity creates a set of new photon-matter hybrid states, so-called polariton states [1–3]. These polariton states have delocalized excitations among molecules and the cavity mode, which have been shown to facilitate new chemical reactivities [1, 3, 4]. Theoretical

investigations play a crucial role in understanding new principles in this emerging field and have suggested interesting reaction mechanisms enabled by cavity quantum electrodynamics (QED) [5–14].

Unlike traditional coherent control strategies [15, 16], polariton chemistry does not rely on fragile electronic coherence [15, 16] and is robust against decoherence [10]. Compared to the classical

laser-matter interactions, which operate with a large number of photons, cavity QED enables the hybrid system to initiate chemical reactions even without photons initially present in the cavity [3]. Thus, polariton chemistry provides a new strategy for controlling chemical reactivity in a general way by tuning the fundamental properties of photons and provides a new paradigm for enabling chemical transformations that can profoundly impact catalysis, energy production, and the field of chemistry at large [17–19]. There are two main regimes for polariton chemistry: one is related to electronic (excitonic) strong coupling and photochemistry [3, 20], operating under an external laser field to initiate photochemistry, and the other is vibrational strong coupling [4, 21–23] and the change of ground-state reactivities, operating under the “dark condition” without any external laser pumping. We will mainly focus on the theoretical approaches developed for ESC and briefly discuss theoretical methods for VSC at the end of this review.

Despite the encouraging progress, recent experimental demonstrations [1, 3, 4, 24, 25] of modifications of chemical reactivity are not well understood and, in some cases, not reproducible [26, 27]. Since these polaritonic systems often require a quantum mechanical description of the photonic modes, existing physical chemistry theories for chemical reactions are no longer directly applicable to these hybrid systems, requiring a more exact QED approach. While the fundamental theories of QED has been known for decades, directly translating this knowledge to explain measurements of polariton chemistry remains a major challenge in both theoretical chemistry and quantum optics. Namely, the mechanism behind the strong coupling of a mesoscopic ensemble of molecules to a single optical cavity is still not fully understood. The basic theory for describing the modes in different types of cavity is also briefly discussed in Sections 2 and 5.3.

Additionally, simulating the time-dependent polariton quantum dynamics of the hybrid matter-field systems is often a necessary and essential task, as these polariton photochemical reactions often involve a complex dynamical interplay among the electronic, nuclear, and photonic degrees of freedom (DOFs). However, accurately simulating polaritonic quantum dynamics remains a challenging task and is beyond the paradigm of traditional photochemistry, which does not include quantized photons, and quantum optics, which does not have a well-defined theory to include the influence of nuclear degrees of freedom to describe reactivity, nor properly account for molecular structures [28]. Over the past years, enormous progress has been made to address this interdisciplinary challenge. We have witnessed how electronic structure theory (Section 3.2) and non-adiabatic quantum dynamics (Section 4) communities have actively participated in the progress of this exciting field.

In Section 2, we discuss the rigorous theoretical background of molecular cavity QED. We first review the basic theory of the molecular Hamiltonian (Section 2.1) and introduce the necessary formalism for molecular quantum electrodynamics (Section 2.2). Section 3 focuses on solving the polaritonic eigenvalue equation using various approaches from direct diagonalization in the adiabatic-Fock basis (Section 3.1.1) and polarized Fock basis (Section 3.1.2) as well as the self-consistent solution

at the mean-field (Section 3.2.2) and correlated (Section 3.2.3) levels of theory. Using the tools put forth in the previous two sections, Section 4 explores the rich quantum dynamics of strongly coupled light-matter systems, laying out common approaches toward simulating exact (Section 4.1) and realistic (Sections 4.2.1–4.2.3) molecules in the extended Hilbert space of the coupled electron-photon system as well as motivating the need for an accurate description and efficient calculation of the nuclear gradients (Section 4.3) used in the exact Pauli-Fierz Hamiltonian. Finally, in Section 5, we provide three directions toward a more complete picture of the molecular polariton picture in experiments, including machine learning polariton gradients (Section 5.1), the simulation and effects of cavity loss (Section 5.2), and the extension to many molecules and many cavity modes (Section 5.3).

The purpose of this review is to introduce and outline state-of-the-art techniques toward the simulation of realistic, *ab initio* molecular polaritons for the readers in the emergent field of polariton chemistry. This review captures much of the recent work, but not all, toward the description of polaritonic states and properties, as well as their quantum dynamics. Specifically, this work focuses on the methods and approaches needed for one to explore these complicated problems in more depth and does not primarily focus on connecting theory to experiment. While this connection is intrinsic to the answers one seeks from simulation, the discussion of experimental progress and its setbacks is beyond the scope of this review aimed at *ab initio* computational approaches. We hope that this work allows readers of all kinds to become acquainted with the simulation of molecular polaritons to explore the many unknown possibilities this novel tool has in order to manipulate chemical reactions as well as physical phenomena, and to help the community address the many open questions.

2 | QED Theoretical Background

2.1 | Molecular Hamiltonian

The molecular Hamiltonian \hat{H}_M can be written in terms of the nuclear kinetic energy operator \hat{T}_R and the electronic Hamiltonian \hat{H}_{el} as,

$$\hat{H}_M = \hat{T}_R + \hat{H}_{el} = \hat{T}_R + \hat{T}_r + \hat{V} \quad (1)$$

where \hat{T}_r is the electronic kinetic energy operator and $\hat{V}(\mathbf{R}) = \hat{V}_{NN} + \hat{V}_{eN} + \hat{V}_{ee}$ is the electronic potential including the nuclear-nuclear \hat{V}_{NN} , electron-nuclear \hat{V}_{eN} , and electron-electron \hat{V}_{ee} interactions. The electronic Hamiltonian $\hat{H}_{el} = \hat{H}_M - \hat{T}_R$ is routinely diagonalized via standard electronic structure packages, which attempt to solve the following eigenvalue problem,

$$\hat{H}_{el} | \psi_\alpha(\mathbf{R}) \rangle = E_\alpha(\mathbf{R}) | \psi_\alpha(\mathbf{R}) \rangle \quad (2)$$

which defines the adiabatic electronic states $| \psi_\alpha(\mathbf{R}) \rangle$ and potential energy surfaces $E_\alpha(\mathbf{R})$ for the α_{th} state. Note that both the eigenvalues and eigenfunctions are parameterized by the nuclear positions in the Born-Oppenheimer approximation. In this basis, the molecular Hamiltonian \hat{H}_M can be written as,

$$\hat{H}_M = \sum_{\alpha} E_{\alpha}(\mathbf{R}) |\psi_{\alpha}\rangle \langle \psi_{\alpha}| - \frac{\hbar^2}{2\mathbf{M}} \sum_{\alpha\beta} [\nabla_{\mathbf{R}}^2 \delta_{\alpha\beta} + 2\mathbf{d}_{\alpha\beta}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} + D_{\alpha\beta}(\mathbf{R})] |\psi_{\alpha}\rangle \langle \psi_{\beta}| \quad (3)$$

where $\hat{\mathbf{P}}$ is the nuclear momentum operator, \mathbf{M} is the tensor of nuclear masses, and $\nabla_{\mathbf{R}}$ is the nuclear gradient. Note that we have used the shorthand notation $|\psi_{\alpha}\rangle \equiv |\psi_{\alpha}(\mathbf{R})\rangle$. Additionally, $\mathbf{d}_{\alpha\beta}$ is the derivative coupling, expressed as

$$\mathbf{d}_{\alpha\beta}(\mathbf{R}) = \langle \psi_{\alpha} | \nabla_{\mathbf{R}} | \psi_{\beta} \rangle = \frac{\langle \psi_{\alpha} | \nabla_{\mathbf{R}} \hat{H}_{\text{el}} | \psi_{\beta} \rangle}{E_{\beta} - E_{\alpha}} \quad (4)$$

and $D_{\alpha\beta}(\mathbf{R})$ is the second-derivative coupling, expressed as,

$$D_{\alpha\beta}(\mathbf{R}) = \langle \psi_{\alpha} | \nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{R}} | \psi_{\beta} \rangle = \langle \psi_{\alpha} | \nabla_{\mathbf{R}}^2 | \psi_{\beta} \rangle \quad (5)$$

The coupling between light and matter, as we will see later, is mediated via the molecular dipole operator $\hat{\boldsymbol{\mu}} = \sum_i z_i \hat{\mathbf{R}}_i - \sum_k \hat{\mathbf{r}}_k$ and the quantized electric field of the optical cavity $\hat{\mathbf{E}}$. The matrix elements of the dipole operator in the adiabatic basis can be written as,

$$\tilde{\mu}_{\alpha\beta}(\mathbf{R}) = \langle \psi_{\alpha} | \hat{\boldsymbol{\mu}} | \psi_{\beta} \rangle \quad (6)$$

For large systems with many electrons, the maximum number of electronic states becomes impractically large for standard electronic structure calculations, even considering only the single excitation manifold. Further, for single-reference methods, such as linear response time-dependent density functionally theory (LR-TD-DFT), the efficient and accurate calculation of high-energy excited states is not always trustworthy, so in practice we employ a smaller Hilbert space than that implied by the total molecular Hamiltonian \hat{H}_M in Equation (3), which can be defined through the following projection operator,

$$\hat{\mathcal{P}} = \sum_{\alpha=0}^{\mathcal{N}_{\text{el}}-1} |\psi_{\alpha}\rangle \langle \psi_{\alpha}| \quad (7)$$

where \mathcal{N}_{el} is the number of included adiabatic electronic states (ordered by increasing energy). The identity operator for the total Hilbert space can be written as $\hat{\mathcal{I}}_{\text{el}} = \hat{\mathcal{P}} + \hat{\mathcal{Q}}$, where $\hat{\mathcal{Q}}$ is composed of all non-included states. The projected molecular Hamiltonian can be written as,

$$\hat{\mathcal{P}} \hat{H}_M \hat{\mathcal{P}} = \sum_{\alpha=0}^{\mathcal{N}_{\text{el}}-1} E_{\alpha} |\psi_{\alpha}\rangle \langle \psi_{\alpha}| - \frac{\hbar^2}{2\mathbf{M}} \cdot \sum_{\alpha\beta=0}^{\mathcal{N}_{\text{el}}-1} [\nabla_{\mathbf{R}}^2 \delta_{\alpha\beta} + 2\mathbf{d}_{\alpha\beta} \cdot \nabla_{\mathbf{R}} + D_{\alpha\beta}] |\psi_{\alpha}\rangle \langle \psi_{\beta}| \quad (8)$$

For the remainder of this work, it will be assumed that all Hamiltonians and operators reside in the truncated Hilbert space $\hat{\mathcal{P}} \hat{H}_M \hat{\mathcal{P}} \rightarrow \hat{H}_M$. The dipole operator can also be written in the truncated Hilbert space as,

$$\hat{\mathcal{P}} \hat{\boldsymbol{\mu}} \hat{\mathcal{P}} = \sum_{\alpha,\beta=0}^{\mathcal{N}_{\text{el}}-1} \boldsymbol{\mu}_{\alpha\beta} |\psi_{\alpha}\rangle \langle \psi_{\beta}| \quad (9)$$

Later, in Section 3.1.2, we will examine an entangled basis for the electron and photon degrees of freedom, which we call the polarized Fock state (PFS) basis. In order to construct this basis, we require a unitary transformation of the electronic states such that the dipole operator in the truncated Hilbert space is diagonal. In this way, we can define the dipole operator as,

$$\hat{\mathcal{P}} \hat{\boldsymbol{\mu}} \hat{\mathcal{P}} = \sum_{\nu=0}^{\mathcal{N}_{\text{el}}-1} \boldsymbol{\mu}_{\nu\nu} |\phi_{\nu}\rangle \langle \phi_{\nu}| \quad (10)$$

where $|\phi_{\nu}\rangle$ is the eigenstate of the projected dipole operator $\hat{\mathcal{P}} \hat{\boldsymbol{\mu}} \hat{\mathcal{P}}$ with

$$|\phi_{\nu}\rangle = \sum_{\alpha=0}^{\mathcal{N}_{\text{el}}-1} c_{\alpha}^{\nu}(\mathbf{R}) |\psi_{\alpha}(\mathbf{R})\rangle \quad (11)$$

and $c_{\alpha}^{\nu} = \langle \psi_{\alpha} | \phi_{\nu} \rangle$. These states are commonly referred to as Mulliken-Hush (MH) states. Under this basis, the electronic Hamiltonian rotates to an off-diagonal matrix as,

$$\hat{H}_{\text{el}} = \sum_{\nu\mu}^{\mathcal{N}_{\text{el}}-1} V_{\nu\mu}(\mathbf{R}) |\phi_{\nu}(\mathbf{R})\rangle \langle \phi_{\mu}(\mathbf{R})| \quad (12)$$

2.2 | Pauli-Fierz Hamiltonian

Often, for finite molecular systems, the Pauli-Fierz (PF) Hamiltonian \hat{H}_{PF} is chosen to model the interactions between the molecular and photonic degrees of freedom inside an optical or plasmonic cavity. We will first introduce the single-mode, single-molecule description. Later in Section 2.3, we will generalize to the collective many-mode, many-molecule Hamiltonian needed to describe experimental conditions. At this level, the PF Hamiltonian can be written as,

$$\begin{aligned} \hat{H}_{\text{PF}} &= \hat{H}_M + \hat{H}_{\text{ph}} + \hat{H}_{\text{el-ph}} + \hat{H}_{\text{DSE}} = \hat{H}_M + \hbar\omega_c \left(\hat{a}^{\dagger} \hat{a} + \frac{1}{2} \right) \\ &\quad + \sqrt{\frac{\omega_c}{2}} \boldsymbol{\lambda} \cdot \hat{\boldsymbol{\mu}} \left(\hat{a}^{\dagger} + \hat{a} \right) + \frac{1}{2\hbar} (\boldsymbol{\lambda} \cdot \hat{\boldsymbol{\mu}})^2 \\ &= \hat{H}_M + \frac{1}{2} \hat{p}_c^2 + \frac{1}{2} \omega_c^2 \left(\hat{q}_c + \frac{\boldsymbol{\lambda}}{\omega_c \sqrt{\hbar}} \cdot \hat{\boldsymbol{\mu}} \right)^2 \end{aligned} \quad (13)$$

where ω_c is the cavity frequency and \hat{a}^{\dagger} (\hat{a}) is the creation (annihilation) ladder operator for the photon field. The Hamiltonian can be factored into the form of a shifted harmonic oscillator via the definition of the canonical coordinates (i.e., the operators of positions and momentum) of the quantum harmonic oscillator: $\hat{q}_c = \sqrt{\frac{\hbar}{2\omega_c}} (\hat{a}^{\dagger} + \hat{a})$ and $\hat{p}_c = \sqrt{\frac{\hbar\omega_c}{2}} (\hat{a}^{\dagger} - \hat{a})$. Here $\boldsymbol{\lambda}$ is the light-matter coupling strength commonly used in the literature. Another common choice is the transverse vector potential of the photonic field \mathbf{A}_0 , related to $\boldsymbol{\lambda}$ as

$$\boldsymbol{\lambda} = \sqrt{\frac{\hbar}{\epsilon \mathcal{V}}} \hat{\mathbf{e}} \quad \text{and} \quad \mathbf{A}_0 = \sqrt{\frac{\hbar}{2\omega_c \epsilon \mathcal{V}}} \hat{\mathbf{e}} = \sqrt{\frac{1}{2\omega_c}} \boldsymbol{\lambda} \quad (14)$$

where \mathcal{V} is the quantization volume of the photon field, ϵ is the electric permittivity, and $\hat{\mathbf{e}}$ is the unit vector of the electric field polarization. Equation (13) is composed of four

main elements: the molecular Hamiltonian \hat{H}_M , the photonic Hamiltonian \hat{H}_{ph} , the light-matter interaction \hat{H}_{el-ph} , and the dipole self-energy \hat{H}_{DSE} . Similarly to the molecular Hamiltonian, we wish to solve an eigenvalue problem without the nuclear kinetic energy operator \hat{T}_R , which we define the polaritonic Hamiltonian \hat{H}_{pl} (analogously to the electronic Hamiltonian \hat{H}_{el}) as,

$$\hat{H}_{pl} = \hat{H}_{PF} - \hat{T}_R = \hat{H}_{el} + \hat{H}_{ph} + \hat{H}_{el-ph} + \hat{H}_{DSE} \quad (15)$$

whose eigenvalue equation can be written as,

$$\hat{H}_{pl} | \mathcal{E}_j(\mathbf{R}) \rangle = \mathcal{E}_j(\mathbf{R}) | \mathcal{E}_j(\mathbf{R}) \rangle \quad (16)$$

where $\mathcal{E}_j(\mathbf{R})$ are the Born-Oppenheimer polaritonic potential energy surfaces and $| \mathcal{E}_j(\mathbf{R}) \rangle$ are the adiabatic polaritonic states. The focus of Section 3 will be to explore solving such eigenvalue problems in various choices of basis states and to calculate chemically and physically relevant properties from such polaritonic wavefunctions.

2.3 | Collective Hamiltonian

Although many successful single-molecule experiments [29, 30] and theoretical [10, 31, 32] work have been instrumental in probing the basic physics of polaritonics, most experiments are constructed such that a large ensemble (often $\sim 10^8$ or more) of molecules is coupled simultaneously to many modes of the cavity [3, 33–35]. These many coupled DOFs generate collective upper and lower polaritonic states [9, 33, 36] as well as the dense manifold of “dark states” which contain minuscule amounts of photonic character and negligible transition dipole [33].

The direct generalization of Equation (13) for many molecules \mathcal{N}_{mol} and cavity modes \mathcal{N}_{mode} , including both parallel k_x (quasi-continuous) and perpendicular k_z (discrete) modes, can be written as,

$$\begin{aligned} \hat{H}_{PF}^G = & \hat{H}_M + \sum_{\mathbf{k}} \sum_p^{\mathcal{N}_{mode}} [\hbar\omega_{\mathbf{k}} (\hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}} + \frac{1}{2}) \\ & + \sum_A^{\mathcal{N}_{mol}} \sqrt{\frac{\omega_{\mathbf{k}}}{2}} \lambda_{\mathbf{k},p} \cdot \hat{\mu}_A(\mathbf{R}_A) (\hat{a}_{\mathbf{k}} e^{i\mathbf{k}_x \cdot \mathbf{x}_A} + \hat{a}_{\mathbf{k}}^\dagger e^{-i\mathbf{k}_x \cdot \mathbf{x}_A}) \\ & + \sum_{A,B}^{\mathcal{N}_{mol}} \frac{1}{2\hbar} (\lambda_{\mathbf{k},p} \cdot \hat{\mu}_A(\mathbf{R}_A)) (\lambda_{\mathbf{k},p} \cdot \hat{\mu}_B(\mathbf{R}_B)) e^{-i\mathbf{k}_x \cdot (\mathbf{x}_A - \mathbf{x}_B)}] \end{aligned} \quad (17)$$

Here, \mathbf{x}_A denotes the center-of-mass position of molecule A and \mathbf{R}_A denotes the nuclear coordinates of molecule A . For typical Fabry-Perot cavities, the photon energy required to excite the cavity mode with the wavevector, $\mathbf{k} = \langle k_x, k_z \rangle$, is $E_{ph}(\theta) = \frac{\hbar}{n_c} c \sqrt{k_z^2 + k_x^2} = \frac{\hbar}{n_c} c k_z \sqrt{1 + \tan^2 \theta}$, which depends on the angle θ ($\tan \theta = k_x / k_z$) of the external probe. Here, c is the speed of light in vacuum, n_c is the refractive index inside the cavity, and $\hbar\mathbf{k}$ is the momentum of the photon. While the collective Hamiltonian (Equation 17) is an extremely important physical object to describe experimental conditions, we will focus the majority of our discussion on the single-molecule, single-mode

case (Equation 13) and return to the collective case in Section 5 where we will describe extensions toward the realistic modeling of polaritonic states and their dynamics.

3 | Obtaining Polariton Eigenstates and Their Properties

3.1 | Direct Diagonalization

Diagonalizing Hamiltonians is the main task of all of quantum mechanics. If one can achieve the exact diagonalization of the Hamiltonian for all DOFs, the exact answer is returned, given a complete basis set. In reality, one is unable to achieve this due to the basis set limitations and/or the complexity of the many-body problem itself. As such, one seeks to find the best alternative toward providing approximate solutions to the many-body problem that returns the correct physics. For the electronic Hamiltonian, the community at large has spent nearly 90 years working on this problem, providing methods such as Hartree-Fock theory (HF), density functional theory (DFT), configuration interaction (CI), coupled cluster (CC), among others, including their excited state analogues like time-dependent DFT (TD-DFT). Each of these methods returns, to varying degrees of computational expense and accuracy, the solutions to the electronic Hamiltonian.

Considering the photonic part of the light-matter hybrid system, we know these DOFs are explicitly harmonic (i.e., their bare Hamiltonian \hat{H}_{ph} is simply the quantum harmonic oscillator), and their exact eigenstates are known to be the Fock (or number) states of the quantized field. In this way, we already know the solutions to the unperturbed parts of the light-matter Hamiltonian *exactly* for the photons and *approximately* for the electrons. If one can directly diagonalize the light-matter Hamiltonian (Equation 15), then one additionally receives the exact correlation between these DOFs.

In contrast to a direct diagonalization, many recent works have shown that one can reconstruct the self-consistent schemes used in the many-electron problem and solve the many-electron and many-photon problem simultaneously. In this sense, the basis states are optimized (or are allowed to respond to interactions with the photonic DOFs) to achieve a minimization of the energy, subject to the underlying approximations of the theory (e.g., density functional theory). Further, the electron-electron, electron-photon, and photon-photon correlations are forced to be described on the same footing. In the following, we will focus our description on direct diagonalization techniques to achieve the *exact* electron-photon correlation, making use of standard electronic structure packages that have been thoroughly tested and are both freely and commercially available. In the last section (Section 3.2), we will briefly motivate cases where a self-consistent approach would be advantageous and outline the idea behind such schemes.

3.1.1 | Adiabatic-Fock Basis

In the adiabatic electronic basis $| \psi_a \rangle$ (eigenstates of \hat{H}_{el}) paired with the Fock (or number) basis for the photonic DOFs $| n \rangle$ (eigenstates of $\hat{H}_{ph} = (\hbar\omega_c \hat{a}^\dagger \hat{a} + \frac{1}{2})$), the matrix elements of the polaritonic Hamiltonian can be written as.

$$\begin{aligned}
 (\hat{H}_{\text{pl}})_{\alpha\beta, nm}(\mathbf{R}) &= \left[E_{\alpha} + \hbar\omega_c \left(n + \frac{1}{2} \right) \right] \delta_{\alpha\beta} \delta_{nm} \\
 &+ \sqrt{\frac{\omega_c}{2}} \lambda (\tilde{\mu}_{\alpha\beta} \cdot \hat{\mathbf{e}}) \left(\sqrt{n} \delta_{n,m-1} + \sqrt{n+1} \delta_{n,m+1} \right) \\
 &+ \frac{1}{2\hbar} \lambda^2 \sum_{\gamma=0}^{\mathcal{N}_{\text{el}}-1} (\tilde{\mu}_{\alpha\gamma} \cdot \hat{\mathbf{e}}) (\tilde{\mu}_{\gamma\beta} \cdot \hat{\mathbf{e}}) \delta_{nm} \\
 &= \varepsilon_{\alpha,n}(\mathbf{R}) \delta_{\alpha\beta} \delta_{nm} + \tilde{\mu}_{\alpha\beta}(\mathbf{R}) \eta_{nm} + D_{\alpha\beta}(\mathbf{R}) \delta_{nm}
 \end{aligned} \quad (18)$$

where $\{\alpha, \beta, \gamma\}$ label the electronic adiabatic states (in the subspace defined by the \mathcal{N}_{el} lowest-energy states), $\{n, m\}$ label the photonic Fock states (in the subspace defined by the \mathcal{N}_{F} lowest-energy states), $\hat{\mathbf{e}}$ is the polarization unit vector of the electric field, $\varepsilon_{\alpha,n} = E_{\alpha} + \hbar\omega_c \left(n + \frac{1}{2} \right)$, $\tilde{\mu}_{\alpha\beta} = \sqrt{\frac{\omega_c}{2}} \lambda (\hat{\mathbf{e}} \cdot \tilde{\mu}_{\alpha\beta})$, $\eta_{nm} = \left(\sqrt{n} \delta_{n,m-1} + \sqrt{n+1} \delta_{n,m+1} \right)$, and $D_{\alpha\beta} = \frac{1}{2\hbar} \lambda^2 \sum_{\gamma} (\tilde{\mu}_{\alpha\gamma} \cdot \hat{\mathbf{e}}) (\tilde{\mu}_{\gamma\beta} \cdot \hat{\mathbf{e}})$. Here, from the perspective of electronic structure, only the electronically adiabatic state energies E_{α} and dipole matrix elements $\mu_{\alpha\beta}$ are required as input. Note that in the last line of Equation (18), we have explicitly inserted the dependence on the nuclear positions \mathbf{R} for clarity, but in general we choose to neglect writing such dependence for the sake of conciseness. The photonic basis is in principle infinite, since the harmonic oscillator has infinite eigenstates, so, similar to the electronic subspace which is truncated at \mathcal{N}_{el} (Equation 7), we also introduce a truncation of the photonic Hilbert space including only the lowest \mathcal{N}_{F} Fock states. The polaritonic Hamiltonian can be easily constructed via Kronecker products (e.g., $\hat{\mu} \otimes \hat{a}$) of the sub-space operators; however, it is worth noting the extreme sparsity afforded by the Fock basis. To make this clear from a visual perspective, the block-like nature of the matrix in this basis can be written as,

$$\begin{aligned}
 \hat{H}_{\text{pl}} &= \begin{bmatrix} E_0 + D_{00} & D_{01} & \cdots & \tilde{\mu}_{00} & \tilde{\mu}_{01} & \cdots \\ D_{01} & E_1 + D_{11} & \cdots & \tilde{\mu}_{01} & \tilde{\mu}_{11} & \cdots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ \tilde{\mu}_{00} & \tilde{\mu}_{01} & \cdots & E_0 + \omega_c + D_{00} & D_{01} & \cdots \\ \tilde{\mu}_{01} & \tilde{\mu}_{11} & \cdots & D_{01} & E_1 + \omega_c + D_{11} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \\
 &= \begin{bmatrix} \mathbf{M}_0 & \tilde{\mu} & 0 & 0 & \cdots & 0 \\ \tilde{\mu} & \mathbf{M}_1 & \sqrt{2}\tilde{\mu} & 0 & \cdots & 0 \\ 0 & \sqrt{2}\tilde{\mu} & \mathbf{M}_2 & \sqrt{3}\tilde{\mu} & \cdots & 0 \\ 0 & 0 & \sqrt{3}\tilde{\mu} & \ddots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \sqrt{\mathcal{N}_{\text{F}}}\tilde{\mu} \\ 0 & 0 & 0 & \cdots & \sqrt{\mathcal{N}_{\text{F}}}\tilde{\mu} & \mathbf{M}_{\mathcal{N}_{\text{F}}} \end{bmatrix}
 \end{aligned} \quad (19)$$

A few important properties of this matrix are as follows: (I) The \mathcal{N}_{F} block diagonals \mathbf{M}_n are composed of the diagonal energies and diagonal DSE elements $\varepsilon_{\alpha,n} + D_{\alpha\alpha}$ in addition to the off-diagonal DSE elements $D_{\alpha\beta}$. (II) The super- and sub-diagonal blocks are composed only of the matter dipole operator matrix elements $\tilde{\mu}_{\alpha\beta}$ weighted by the photon number of the larger diagonal Fock state label n . Note here that for clarity, we have neglected the zero-point energy of the photonic mode and \mathbf{R} dependence. One can easily see from the right-most side of

Equation (19) that this matrix is extremely sparse, especially for larger number of included Fock basis states (needed for convergence), so many approximate diagonalization schemes can be used which rely on the properties of sparse matrices, such as the Lanczos and Krylov subspace techniques [37–39], are able to return the lowest eigenvalues and eigenvectors without loss of physics but with a large computational speed-up.

Upon diagonalization of Equation (19), the polaritonic states are represented as linear combinations of the adiabatic-Fock basis states (with contracted notation $|\psi_{\alpha}(\mathbf{R})\rangle \otimes |n\rangle = |\psi_{\alpha}(\mathbf{R}, n)\rangle$) as,

$$|\Phi_j(\mathbf{R})\rangle = \sum_{\alpha}^{\mathcal{N}_{\text{el}}} \sum_n^{\mathcal{N}_{\text{F}}} C_{\alpha n}^j |\psi_{\alpha}(\mathbf{R}, n)\rangle \quad (20)$$

where $C_{\alpha n}^j = \langle \psi_{\alpha}(\mathbf{R}, n) | \Phi_j(\mathbf{R}) \rangle$. Here, \mathcal{N}_{el} and \mathcal{N}_{F} are treated as convergence parameters such that the polaritonic observables are adequately converged (see more details in Section 3.1.3). The obvious first choice is the convergence of the lowest-energy eigenvalues of Equation (19). In our experience with realistic ab initio systems, the convergence with respect to the number of Fock states is rapid, only requiring $\mathcal{N}_{\text{F}} \sim 5$ to obtain ~ 10 meV accuracy. However, due to the complicated and highly off-diagonal dipole matrix [40] in real molecules, the convergence with respect to electronic states is slow, possibly requiring $\mathcal{N}_{\text{el}} \sim 100$ or more states to achieve ~ 10 meV accuracy [41, 42]. In Section 3.2, we will briefly address other approaches, namely self-consistent schemes, to converge complicated systems which contain many strongly dipole-connected states as well as systems with large light-matter coupling that necessitate a more advanced and rigorous approach toward obtaining the polaritonic eigenstates in a self-consistent way.

Figure 1a–d presents excited state potential energy surfaces of formaldehyde as a function of the C–O bond length, showing the two lowest-energy excited states with ground-to-excited transition dipole along the C–O bond direction (which is parallel to the cavity polarization direction, $\hat{\mathbf{e}}$). The bare electronic states (Figure 1a) show two local minima in the lower-energy excited state as well as an avoided crossing (see inset). Upon coupling to the cavity, the local minima near C–O bond length of 1.50 Å can be removed with a negatively detuned cavity ($\omega_c = 6.5$ eV, Figure 1b, color bar indicates the average photonic character $\langle \hat{a}^{\dagger} \hat{a} \rangle$). Alternatively, the avoided crossing can be systematically reduced via a positively detuned cavity ($\omega_c = 9.5$ eV, Figure 1c, see inset). An important feature of this change in the avoided crossing is that the character of both states involved is retained (i.e., mainly electronic excitation character) where both states exhibit negligible amounts of photonic contributions. Direct control over the relative energy of electronic states while maintaining their original character is a useful concept and design principle in processes controlled by non-adiabatic coupling between the excited electronic states.

Figure 1d presents the matter-projected polaritonic transition density in real space.

$$\rho_{0j}^{\text{M}}(\mathbf{r}) = \langle \mathbf{r} | \text{Tr}_{\text{ph}} [\hat{\rho}_{0j}] | \mathbf{r} \rangle = \sum_{\alpha\beta}^{\mathcal{N}_{\text{el}}} \sum_n^{\mathcal{N}_{\text{F}}} C_{\alpha n}^0 \left(C_{\beta n}^j \right)^* \cdot \xi_{\alpha\beta}^{\text{M}}(\mathbf{r}) \quad (21)$$

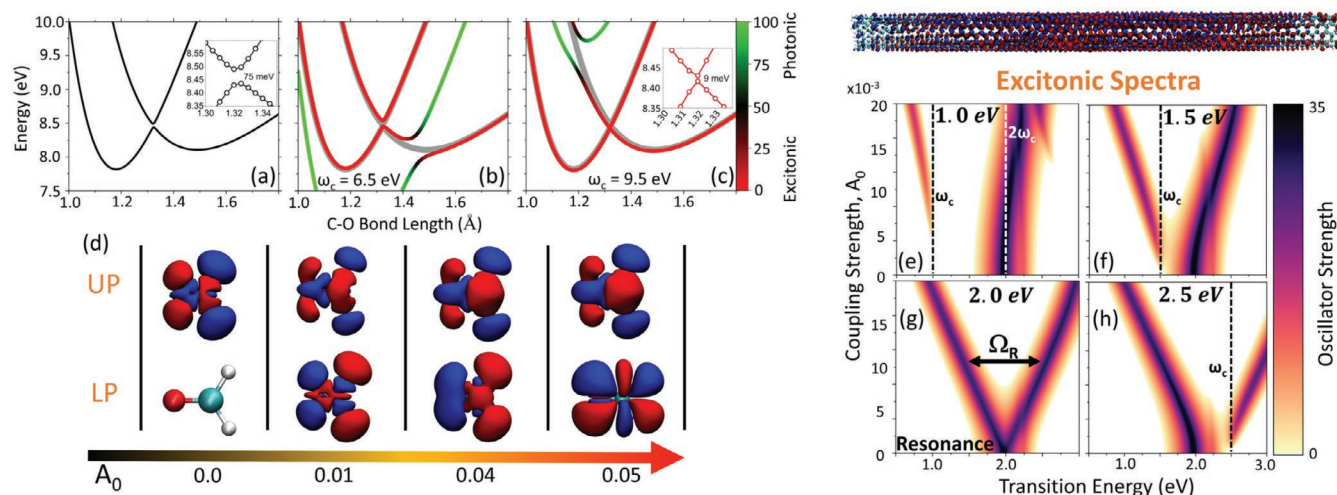


FIGURE 1 | (a) Adiabatic potential energy surface of the formaldehyde molecule's A_1 -symmetry excited states as a function of the C–O bond length, R_{CO} . The inset presents the avoided crossing between the two adiabatic states. (b, c) Polariton excited state energy $\mathcal{E}_j(R_{CO}) - \text{MIN}[\mathcal{E}_0(R_{CO})]$ of the formaldehyde-cavity hybrid system, with the coupling strength of $A_0 = 0.04$ a.u., and a cavity frequency (b) $\omega_c = 6.5$ eV and (c) $\omega_c = 9.5$ eV. The cavity polarization is parallel to the C–O bond. For panels (b, c), the color map indicates the photonic character, and the cavity-free electronic states are shown as thick gray lines. The inset in panel c shows the reduction of the avoided crossing from 75 to 9 meV. (d) Polaritonic transition density $\rho_{ij}^M(\mathbf{r})$ of the upper (UP) and lower (LP) polaritons for $A_0 = 0, 0.01, 0.04$, and 0.05 a.u. at $\omega_c = 7.92$ eV with a C–O bond length of 1.22 Å. (e, h) Excitonic absorption spectra of a (6, 5) single-walled carbon nanotube (SWCNT) coupled to an optical cavity plotted as a function of the transition energy and coupling strength A_0 . The Lorentzian energy-broadening parameter is $\sigma = 0.1$ eV. The cavity frequency is taken to be (e) $\omega_c = 1.0$ eV (half-resonance), (f) $\omega_c = 1.5$ eV, (g) $\omega_c = 2.0$ eV (resonant with bright molecular transition, E_{11}), and (h) $\omega_c = 2.5$ eV. (Above) The polaritonic transition density at $A_0 = 0.0$ a.u. is shown above the spectra for the ground-to-bright E_{11} transition. Panels (a)–(h) were taken from Reference [41].

where the photonic DOFs have been traced out, leaving only the electronic contributions. Here, $\xi_{\alpha\beta}^M(\mathbf{r}) = \psi_{\beta}^*(\mathbf{r})\psi_{\alpha}(\mathbf{r})$ is the $\alpha\beta$ th electronic transition density in real space \mathbf{r} and $\hat{\rho}_{ij} = |\Phi_j\rangle\langle\Phi_0|$ is the $0j$ th polaritonic density operator. More details on calculating observables can be found in Section 3.1.3. The light-matter hybridization leads to superpositions between photon-dressed electronic states, which leads to various electronic transition densities mixing through the polaritonic expansion coefficients in the adiabatic-Fock basis (see Equation 20). The matter-projected polaritonic transition density [41, 43] is only one of many ways to examine the character of the molecular part of the polaritonic excitation. Other examples of matter-projected polaritonic observables are the difference density [44, 45], the natural transition orbitals [41], the transition density matrix [41], and others yet to be applied for the polaritonic case.

The changes of the polaritonic transition density are presented as a function of the coupling strength A_0 (varied along the horizontal axis of panel d) for the upper and lower polaritons, with a C–O bond length of 1.22 Å and at cavity energy $\omega_c = 7.92$ eV. Under this configuration, the cavity is nearly resonant with the molecular adiabatic transition from the ground state to the $\psi_1^{A_1}$ state at the Franck-Condon points. Through the coupling-dependent mixing of the various electronic transition densities, the polaritonic transition density is modified for each coupling strength, and the results showcase how tuning the cavity parameters can modify the local electronic properties to facilitate chemical reactions or photophysical changes.

Figure 1e–h shows the excitonic spectra of a (6, 5) single-walled carbon nanotube (SWCNT) system inside an optical cavity for cavity frequencies $\omega_c =$ (e) $\frac{1}{2}E_{11}$, (f) $\frac{3}{4}E_{11}$, (g) E_{11} ,

and (h) $\frac{5}{4}E_{11}$, where E_{11} is the lowest energy bright transition in the pristine SWCNT. This system has been the subject of recent exploration by the polaritonic community and has yielded many interesting results [46–51]. It is well known that pristine SWCNTs are relatively dark to emission due to low-lying, optically inactive electronic transitions. Here (panel e), the $|\psi_0, 2\rangle$ photon-dressed ground state is in resonance with the bright $|E_{11}\rangle \equiv |\psi_6, 0\rangle$ state. At resonance (panel g), the bright character of the E_{11} state is split nearly symmetrically as a function of the light-matter coupling strength, A_0 . For the negatively detuned cavity (panels e, f), the bright character is blueshifted. For a positively detuned cavity (panel h), the bright character is redshifted to below the manifold of low-lying dark states, effectively brightening the emission of the SWCNT system without the need for chemical functionalization [52–59] or solvent doping [60, 61].

3.1.2 | Polarized Fock State Basis

In Section 3.1.1, we have described one possible basis for the representation of the PF Hamiltonian (Equation 13). However, this is not the only choice. In fact, the adiabatic-Fock representation is useful in the weak coupling limit, since the basis is simply the basis that diagonalizes the unperturbed electronic (\hat{H}_e) and photonic (\hat{H}_{ph}) Hamiltonians. In this sense, when the contributions of the interaction (\hat{H}_{e-ph}) or dipole self-energy (\hat{H}_{DSE}) become large, the many adiabatic and Fock states will be needed in the description of the polaritonic wavefunctions. Other choices exist for the description of the photonic DOFs, such as the grid basis, which diagonalizes $\hat{q}_c \propto \hat{a}^\dagger + \hat{a}$ and has been extensively used [5, 62–64].

The choice of basis can significantly enhance computational efficiency or reduce the conceptual complexity of a problem, depending on the light-matter coupling strength and cavity frequency parameters. One such basis, aimed for use in the strong light-matter coupling regime, is the recently proposed polarized Fock State (PFS) basis introduced in Reference [65]. Here, the Pauli-Fierz Hamiltonian is rewritten using an entangled electronic-photonic basis, where the electronic states are represented by the eigenstates of the dipole operator $\sum_v \hat{\mu} \hat{P} = \mu_{vv}(\mathbf{R}) |\phi_v\rangle \langle \phi_v|$ and is referred to as the Mulliken-Hush (MH) representation (Equation 11). The polaritonic Hamiltonian (see Equation 13) in the MH basis can be written as,

$$\hat{H}_{\text{pl}} = \hat{H}_{\text{el}} + \frac{\hat{p}_c^2}{2} + \sum_v \frac{\omega_c^2}{2} [\hat{q}_c + q_v^0(\mathbf{R}) |\phi_v\rangle \langle \phi_v|]^2 \quad (22)$$

where $q_v^0(\mathbf{R}) = -\frac{\lambda}{\omega_c} \cdot \mu_{vv}(\mathbf{R})$. Considering the Hamiltonian of the bare photonic field, $\hat{H}_{\text{ph}} = \frac{1}{2}(\hat{p}_c^2 + \omega_c^2 \hat{q}_c^2)$, one may notice that the QED Hamiltonian is simply shifted in the position coordinate \hat{q}_c by the value $-q_v^0(\mathbf{R})$ and is hence a shifted harmonic oscillator (or “polarized Fock state” since the field is polarized by the molecular electric multipole), unique for each MH electronic state $|\phi_v\rangle$. At zero light-matter coupling or infinitely large cavity frequency, the original MH and un-shifted (or “vacuum”) Fock states are returned. The light-matter Hamiltonian (Equation 22) can be now block-diagonalized using the PFS basis $\{ |n_v(\mathbf{R})\rangle \}$ for each MH state $|\phi_v\rangle$, which is defined as,

$$\begin{aligned} \frac{1}{2}[\hat{p}_c^2 + \omega_c^2(\hat{q}_c + q_v^0(\mathbf{R}))^2] |n_v(\mathbf{R})\rangle &\equiv \left(\hat{b}_v^\dagger \hat{b}_v + \frac{1}{2} \right) \hbar \omega_c |n_v(\mathbf{R})\rangle \\ &= \left(n_v + \frac{1}{2} \right) \hbar \omega_c |n_v(\mathbf{R})\rangle \end{aligned}$$

where \hat{b}_v^\dagger (\hat{b}_v) is the creation (annihilation) ladder operator for the shifted harmonic oscillator specific to the v_{th} MH state. Defining the total basis as the tensor product of the MH states and the PFS basis, $|\phi_v(\mathbf{R})\rangle \otimes |n_v(\mathbf{R})\rangle \equiv |\phi_v(\mathbf{R}), n_v(\mathbf{R})\rangle$, which is an entangled light-matter basis since the molecular dipole appears in the definition of the shifted Fock state, the matrix elements of the light-matter Hamiltonian can be expressed as

$$\begin{aligned} \left(\hat{H}_{\text{pl}} \right)_{v\mu, n_\mu, m_\mu} &= \left[V_{vv} + \hbar \omega_c \left(n_v + \frac{1}{2} \right) \right] \delta_{v\mu} \delta_{n_\mu, m_\mu} \\ &+ \langle n_\mu | m_\nu \rangle V_{v\mu} \left(1 - \delta_{v\mu} \delta_{n_\mu, m_\mu} \right) \end{aligned} \quad (23)$$

Note here that we have dropped the explicit dependence on the nuclear position \mathbf{R} for clarity. In this basis, the diagonal matrix elements are the diagonal MH energies V_{vv} (Equation 12) and PFS harmonic oscillator eigenvalues $\omega_c \left(n_v + \frac{1}{2} \right)$, while the off-diagonal contributions are now the MH coupling elements $V_{v\neq\mu}$ reduced in magnitude by the overlaps $\langle n_\epsilon | m_\nu \rangle \in [-1, 1]$ between two PFS harmonic oscillator states with n_v photons and m_μ photons associated with two different electronic MH states ϕ_v and ϕ_μ . In this compact basis, the light-matter coupling and dipole self-energy are all neatly housed in the MH coupling and PFS overlaps, $\langle n_\mu | m_\nu \rangle V_{v\mu}$, and thus all interactions between

light and matter DOFs are carried through this single term. Note also that the calculation of the PFS overlaps is analytic and can be written as,

$$\langle n_\epsilon | m_\nu \rangle = (-2\xi)^{n-m} e^{-2\xi^2} \sqrt{\frac{m!}{n!}} * L_g(4\xi^2, m, n-m), \quad \text{for } m < n \quad (24)$$

where L_g is the associated Laguerre polynomial and $\xi = (q_v^0 - q_\mu^0) / \sqrt{2\omega_c}$ with $q_v^0 = \frac{\lambda}{\omega_c} \cdot \mu_{vv}$. This basis is expected (and has been explicitly shown for model systems [65]) to efficiently converge the photonic basis, especially when the permanent dipoles μ_{vv} in the MH basis are large. For additional discussion on the PFS basis, see Reference [65]. Further, a similar basis has been used in quantum optics and recently in the polariton communities, which is referred to as the generalized coherent state (GCS) basis [45, 66–68], which also relies on the molecular dipole information to define a new photonic basis. The polaritonic Hamiltonian in the PFS basis is, in general, not as sparse as that of the adiabatic-Fock matrix (see Equation 19) since all shifted Fock states between different MH electronic states ϕ_v are connected via their shifted harmonic oscillator overlaps, so sparse matrix techniques cannot be as readily applied. The main advantage of the PFS basis is that many of the overlaps will be near zero due to the widely varying magnitudes of the molecular dipole μ_{vv} elements. In this way, the PFS basis, in principle, will allow one to use many fewer shifted Fock states as a basis than the vacuum Fock states used in the adiabatic-Fock basis (see Section 3.1.1) and therefore may perform more efficiently in many cases. More rigorous testing is required for real, ab initio molecular systems where the dipole matrices are extremely non-diagonal in the many-state adiabatic basis compared to many of the tested model systems, such as the harmonic oscillator or the double-well potentials, where the dipole matrix is nearly diagonal, hence the adiabatic states are already almost equal to the MH states themselves. In our experience, the photonic basis is more easily converged in ab initio systems compared to the convergence of the electronic basis, which often requires many states to provide a useful convergence (see Section 3.2 for additional discussion).

Figure 2 presents the polariton potential energy surfaces predicted by various quantum optics model Hamiltonians for the model LiF molecule shown in Figure 2a,b (the details of the model can be found in Reference [65]). Here, only two diabatic states were considered, which are denoted as the ionic state $|I\rangle$, and covalent state $|C\rangle$. These two diabatic states are coupled through a diabatic coupling $V_{\text{IC}}(R)$ (dotted yellow line in Figure 2a) that causes a splitting (avoided crossing) near the anti-crossing of the diabatic potentials $V_C(R)$ and $V_I(R)$ (solid red and blue line in Figure 2a, respectively). The adiabatic electronic states, ground $|G(R)\rangle$ and excited $|E(R)\rangle$ states can be obtained by diagonalizing the electronic Hamiltonian $\hat{H}_{\text{el}} = V_I(R) |I\rangle \langle I| + V_C(R) |C\rangle \langle C| + V_{\text{IC}}(R) (|I\rangle \langle C| + |C\rangle \langle I|)$ at each R (see Equation 12).

The electronic dipole matrix at each R is diagonal in this diabatic representation. This is because the diabatic states $|I\rangle$ and $|C\rangle$, also referred to as the Mulliken-Hush diabatic states, are by definition the eigenstates of the electronic transition dipole

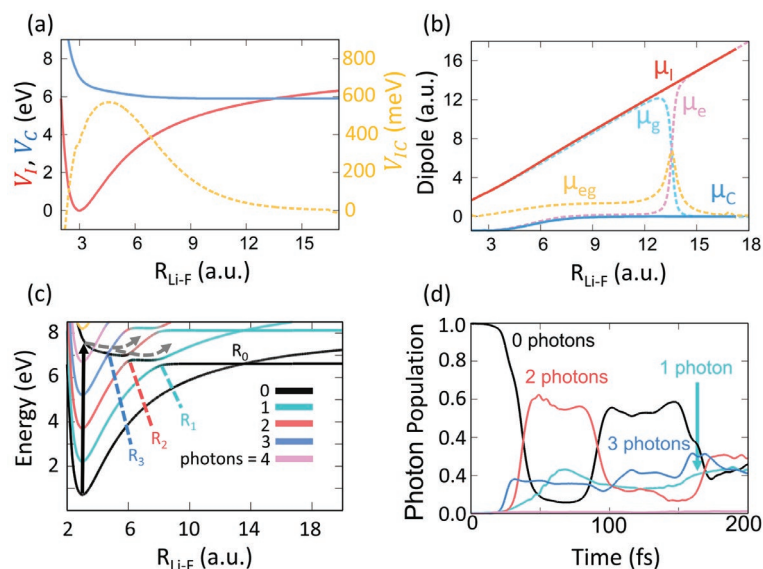


FIGURE 2 | (a) Diabatic Mulliken-Hush (MH) potentials $V_I(R)$ (red) and $V_C(R)$ (blue), with diabatic coupling V_{IC} (gold line). (b) Matrix elements of $\hat{\mu}$ in the adiabatic representation (dashed curves) μ_{gg} (pink), μ_{ee} (cyan), and μ_{eg} (gold), as well as in the diabatic representation (solid lines) μ_{II} (red) and μ_{CC} (blue). Here $\mu_{II} = \mu_I$ (red) and $\mu_{CC} = \mu_C$ in the MH representation since no off-diagonal dipole elements are present in the dipole operator. (c) Polaritonic potentials color-coded according to the number of photons with four relevant avoided crossings labeled as R_0 , R_1 , R_2 , and R_3 . The black solid vertical arrow indicates the initial photoexcitation, and the dashed lines illustrate the dynamics of the hybrid system. (d) Time-dependent photon populations. For panels (c, d), the light-matter coupling strength is set to $A_0 = 0.127$ a.u. with a cavity frequency of $\omega_c = 1.5$ eV. Panels (a)–(d) were taken from Reference [65].

operator (see discussion around Equation 10). Figure 2b presents the matrix elements of $\hat{\mu}$ in both the diabatic (solid lines) and the adiabatic (dashed lines) representations. As expected, the permanent dipole for the ionic state $|I\rangle$ (corresponding to Li^+F^-) $\mu_I(R)$ linearly increases, while the permanent dipole for the $|C\rangle$ state (corresponding to covalently bonded $\text{Li}-\text{F}$) $\mu_C(R)$ remains nearly zero with increasing interatomic separation R . The adiabatic states switch their characters around $R \approx 13.5$ a.u., as a result, the adiabatic permanent dipole switches in that region, and $\mu_{eg}(R)$ peaks at $R \approx 13.5$ a.u.

Figure 2c shows the polaritonic potential energy surfaces for a cavity frequency $\omega_c = 1.5$ eV and light-matter coupling strength $A_0 = 0.127$ a.u. The coloring indicates the average photon number of the polaritonic state. Given an initial excitation from $|G(R), 0\rangle \rightarrow |E(R), 0\rangle$ (vertical black arrow) at the ground state minimum (outside the cavity's influence), the time-dependent average photon number was calculated (see Reference [65] for more details) and shown in Figure 2d. Thus, through nuclear motion and light-matter coupling, excited photons can be generated.

3.1.3 | Calculating Relevant Polaritonic Properties

Exciton-polaritons have many characteristic features, such as the Rabi splitting observed in linear spectroscopy when the cavity frequency is in resonance with a well-separated electronic transition (e.g., historically found in single-atom spectroscopy). Of course, there are many spectroscopic footprints of polariton formation that are of interest to the community for finding and exploring the physics of such quasi-particles; however, the spectroscopic results available experimentally may not be the most

informative for probing local phenomena such as chemical reactions, charge transfer, or exciton diffusion. In these examples, the main features are stored in the excitonic part of the polariton, which is usually not directly visible in most experimental configurations due to the fast photon loss mechanisms and mirror absorption. However, examining the photonic contribution to the spectroscopy will give *indirect* information regarding the changes to the excitonic part of the polaritonic wavefunctions. In this section, we will outline the necessary steps to compute observables of polaritonic states using the direct diagonalization approach already discussed. We will focus on the local excitonic changes due to the formation of hybrid light-matter states, which are *directly* relevant to the local chemical reactivity, excited-state charge transfer, and exciton diffusion processes.

Any polaritonic observable \hat{O} can be described with any basis of light and matter, for example, adiabatic-Fock (Section 3.1.1), PFS (Section 3.1.2), or any other. Note that this is a more general case than was done in Equation (21). Here, we will choose the adiabatic-Fock basis for conceptual simplicity, but all of the main points are easily transferable to another basis by unitary transformation. The matrix elements of the polaritonic observable \hat{O} can be expanded in the adiabatic-Fock basis (Equation 20) as,

$$\begin{aligned} \langle \Phi_j | \hat{O} | \Phi_k \rangle &= \sum_{\alpha\beta} \sum_{nm} C_{\alpha n}^j C_{\beta m}^k \langle \psi_\alpha | \hat{O} | \psi_\beta, m \rangle \\ &= \sum_{\alpha\beta} \sum_{nm} C_{\alpha n}^j C_{\beta m}^k \langle \psi_\alpha | \hat{A}_{\text{el}} | \psi_\beta \rangle \langle n | \hat{B}_{\text{ph}} | m \rangle \end{aligned} \quad (25)$$

where $C_{\beta m}^k = \langle \psi_\beta, m | \Phi_k \rangle$. Note here that since the polaritonic Hamiltonian, Equation (15), is real-valued, then the

expansion coefficients in the adiabatic-Fock or PFS basis will also be real-valued, that is, $(C_{\beta m}^k)^* = C_{\beta m}^k$. In general, any polaritonic observable, even restricting to ground-to-excited elements, are linear combinations of *all* matrix elements present in the electronic and photonic sub-systems. As such, highly non-trivial mixing of matrix elements can appear when the light-matter coupling becomes large. Here $\hat{O} = \hat{A}_{\text{el}} \otimes \hat{B}_{\text{ph}}$ are factorized electronic and photonic operators, respectively, which is not a requirement of \hat{O} but is often the case for simple, non-entangled observables, such as the average photon number $\hat{O} = \hat{\mathcal{T}}_{\text{el}} \otimes \hat{a}^\dagger \hat{a}$ [69]. Another example is linear spectroscopy where the polaritonic dipole matrix elements can be expressed as $\hat{\mu}_{\text{pol}} \sim \hat{\mu}_{\text{el}} \otimes \hat{\mathcal{T}}_{\text{ph}} + \hat{\mathcal{T}}_{\text{el}} \otimes \hat{q}_c$. In experiment, the relative magnitudes of the excitonic and photonic contributions are highly dependent on the experimental configuration and are usually understood to be dominated by the photonic contributions (i.e., keeping only the \hat{q}_c term in $\hat{\mu}_{\text{pol}}$) and is often called the “visibility spectrum” or “transmission spectrum.” [70] In this case, the local information regarding the excitonic spectrum is present only in an *indirect* sense. However, often one is interested in examining the changes to the excitonic subsystem for purposes of exploring electronic reorganization through the mixing of electronic adiabatic states via hybridization with light [17, 41, 43, 44, 67, 71–74]. As such, to achieve an observable that will give direct information on the excitonic subsystem, we will ignore the second term in the polaritonic dipole operator to exclude photonic contribution, and in this way, we have traced out the photonic DOFs. An arbitrary matter-projected polaritonic operator can now be written as,

$$\hat{O}_{jk}^{\text{M}} = \langle \Phi_j | \hat{A}_{\text{el}} \otimes \hat{\mathcal{T}}_{\text{ph}} | \Phi_k \rangle = \sum_{\alpha\beta}^{\mathcal{N}_{\text{el}}} \sum_n^{\mathcal{N}_{\text{F}}} C_{\alpha n}^j C_{\beta n}^k \langle \psi_\alpha | \hat{A}_{\text{el}} | \psi_\beta \rangle \quad (26)$$

where we have made use of the orthogonality of the vacuum Fock states, $\langle n | m \rangle = \delta_{nm}$. For example, one may be interested in the polaritonic transition density [41, 43, 75] $\rho_{0j}^{\text{M}}(\mathbf{r})$ (see Equation 21) or the polaritonic difference density [17, 44, 45] $\Delta\rho(\mathbf{r}) = \rho_{jj}^{\text{M}} - \xi_{jj}$ of the molecule inside the cavity.

With the pQED approach, chemical reactions can be explored. Several theoretical studies have recently shown [17, 19] that the cavity can *completely switch selectivity of well-known chemical reactions*. If successful, cavity QED could revolutionize fundamental knowledge of organic chemistry [72] by understanding the cavity-induced modifications of electronic degrees of freedom and their interactions inside the cavity [76, 77]. One such reaction is the electrophilic bromination of nitrobenzene [17] shown in Figure 3a. This is a textbook reaction [78, 79], where only the *meta*-substitution product is possible, and the *ortho*-substituted (or *para*-substituted) product is not observed experimentally. This has been well-explained due to the stability of the catatonic active complex $\text{PhNO}_2\text{-Br}^+$, for example, using the resonance structure or using *ab initio* calculations. By coupling this reaction to an optical cavity which mixes the character of the ground and excited electronic states, it was observed that one can fundamentally change the selectivity of this reaction, making the *ortho*-substituted product possible. Figure 3b presents

the relative energy difference between the *meta*-substituted and the *ortho*-substituted catatonic active complex $\text{PhNO}_2\text{-Br}^+$, where the blue region of the figure indicates where the *meta*-substitution is more stable, and red region of the figure indicates where the *ortho*-substitution is more stable. Figure 3c,d presents the ground state density difference ($\Delta\rho(\mathbf{r})$, defined below Equation 26 using Equation 21) for the *meta*- and *ortho*-substituted intermediate coupled inside the cavity and outside the cavity. This density difference aids in the understanding of the cavity QED effects on modified relative energies of the intermediate species. This observable has a close connection with the intuitive resonance structure arguments, since the difference density shows how the electronic distribution is modified by the presence of the cavity [17]. As such, coupling to the cavity enables *ortho*-substituted nitro-benzene, thus making impossible reactions possible. Additionally, Reference [17] predicts that the experimental condition for this change requires the cavity frequency of $\omega_c = 1.8$ eV and the field intensity of 2 – 10 V/nm, both of which can be accomplished with the state-of-the-art plasmonic cavity designs [29, 30, 80].

3.2 | Iterative Approaches

In the previously discussed QED approach, one is required to compute the many-body electronic states $\{|\psi_\alpha\rangle\}$ for use in a direct diagonalization procedure of the Pauli-Fierz Hamiltonian (Equation 18) coupled with some basis for the photonic DOFs (e.g., Fock/number states, polarized Fock states) to arrive at a description of the polaritonic states in these choices of basis. This method, in the infinite basis limit, provides the exact results for the polaritonic states, capturing the exact correlation between the electronic and photonic DOFs. The primary limitation of this approach is that the electronic basis converges very slowly for strong light-matter coupling strengths, requiring the calculation of highly excited electronic states (~ 100) to converge even the lowest polaritonic energies [41, 42]. Contrary to this, the photonic basis only requires a relatively small number of basis states to converge for realistic, *ab initio* systems [17, 41].

Due to this limitation of the direct diagonalization approach, the community seeks other approximations in line with previous electronic structure approaches that now include the photonic interactions to some degree to arrive at a self-consistent description of the problem. In principle, this approach will require many fewer basis states than a single, direct diagonalization, but with similar approximations for the electron-photon and photon-photon interactions that are intrinsic to the many-body method of choice. In this way, these approaches will be able to capture the cases where strong light-matter coupling is too strong to utilize the direct diagonalization approach with a frozen basis. We define these self-consistent analogues to the commonly used electronic structure approaches as scQED-X, where X can be any of the standard approaches, such as Hartree-Fock theory (HF) [45, 67, 68, 72, 81], density functional theory (DFT), linear response time-dependent DFT (LR-TD-DFT) [43, 82, 83], coupled cluster (CC) [44, 45, 68, 71], configuration interaction (CI) [67, 84], full configuration interaction (FCI) [85], second-order Møller-Plesset perturbation theory (MP2) [86], quantum Monte Carlo (QMC) approaches [87–89], and density matrix renormalization group (DMRG) [90].

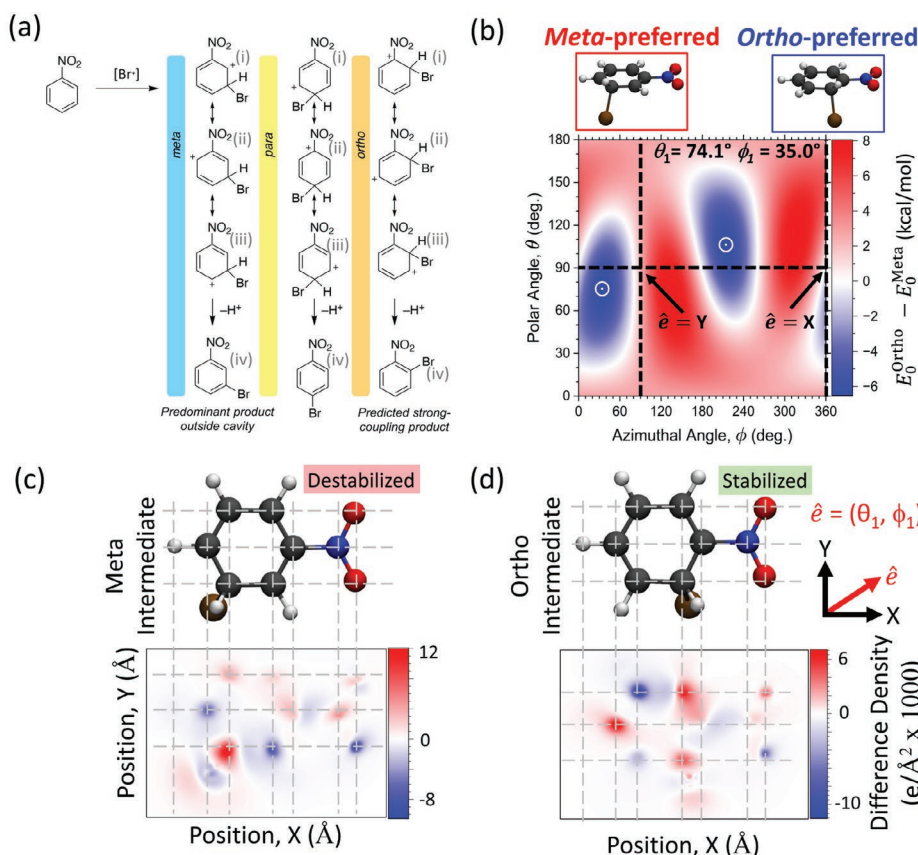


FIGURE 3 | (a) Schematic of possible reaction pathways of the electrophilic bromination of nitrobenzene. (b) Relative energy of the polaritonic ground states between *ortho*-PhNO₂-Br⁺ and *meta*-PhNO₂-Br⁺ intermediates with various cavity polarization directions. Ground state density difference between coupling to the cavity and outside the cavity case, for (c) the *meta*-cationic intermediate and (d) the *ortho*-cationic. Panels (a)–(d) were taken from Reference [17].

3.2.1 | Generalized Coherent State Transformation

In a similar manner as done in the construction of the polarized Fock states in Section 3.1.2, the generalized coherent state (GCS) transformation is a specific instance of polarizing the photonic basis by a parameter proportional to the molecular dipole moment. The GCS basis has been used in many recent works exploring the self-consistent solution to the ground polaritonic state [44, 45, 68, 72]. The unitary transformation can be written as,

$$\hat{U}_{\text{GCS}} = e^{\mathcal{Z}\hat{a}^\dagger - \mathcal{Z}^*\hat{a}} \quad (27)$$

where the GCS shift parameter \mathcal{Z} is chosen to be,

$$\mathcal{Z} = -\frac{\lambda \cdot \langle \hat{\mu} \rangle_{\text{GS}}}{\sqrt{2\omega_c}} \quad (28)$$

where $\langle \hat{\mu} \rangle_{\text{GS}}$ is the expectation value of the molecular dipole in the ground state. For this choice of GCS parameter, one can rewrite the Pauli-Fierz Hamiltonian, $\hat{U}_{\text{GCS}}^\dagger \hat{H}_{\text{pl}} \hat{U}_{\text{GCS}} = \hat{H}_{\text{pl}}^{\text{GCS}}$,

$$\hat{H}_{\text{pl}}^{\text{GCS}} = \hat{H}_{\text{el}} + \hbar\omega_c \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) + \sqrt{\frac{\omega_c}{2}} (\lambda \cdot \Delta \hat{\mu}) (\hat{a}^\dagger + \hat{a}) + \frac{1}{2\hbar} (\lambda \cdot \Delta \hat{\mu})^2 \quad (29)$$

in terms of the deviation of the molecular dipole from its expectation value in the ground state $\Delta \hat{\mu} = \hat{\mu} - \langle \hat{\mu} \rangle_{\text{GS}}$ and its variance $\langle \Delta \hat{\mu}^2 \rangle$. In the following section (Section 3.2.2), we will see that $\langle \Delta \hat{\mu} \rangle_{\text{SD}} = 0$ for many-body methods that employ only a single-determinant (SD) wavefunction, such as Hartree-Fock (SD \rightarrow HF) or density functional theories (SD \rightarrow DFT), allowing for a drastic simplification of the coupled electron-photon Hamiltonian. Note that contributions from the dipole self-energy (DSE, final term in Equation 29) survive, since $\langle \langle \Delta \hat{\mu}^2 \rangle \rangle_{\text{SD}} = \langle \hat{\mu}^2 \rangle_{\text{SD}} - \langle \hat{\mu} \rangle_{\text{SD}}^2 \neq 0$, even for a single-determinant approach.

It is important to note that simply using the GSC transformation does not yield a fully origin invariant Fock matrix or single-particle orbital energies. Reference [72] discusses such drawbacks and proposes the so-called strong coupling variant of the Hartree-Fock theory (SC-QED-HF), which transforms the Pauli-Fierz Hamiltonian in a similar way as the GSC rotation but now contains orbital specific rotations, similar to the polarized Fock state basis (see Section 3.1.2). Since the orbitals are involved and the transformation depends on the dipole operator, the single-particle Hamiltonian is first rotated to the dipole basis (similar to Equation 12 but for single-particle molecular orbitals instead of many-body states).

Furthermore, one should note that this choice of \mathcal{Z} (Equation 28) or the case of SC-QED-HF in Reference [72] only applies in the limit of infinite light-matter coupling. Recent

works have performed a variational optimization procedure on the shift parameter \mathcal{Z} , for example, choosing \mathcal{Z}_{OPT} under the condition $\frac{\partial \mathcal{E}(\mathbf{R})}{\partial \mathcal{Z}} = 0$, which further minimizes the energy of the ground state [86, 91]. This minimization is done on top of the self-consistent iterations and can be interpreted as an additional DOF for the self-consistent procedure. Given this rotation of the Hamiltonian, both the DSE as well as the bilinear interaction term would remain, even for single-determinant approaches, but would be scaled (or partially shifted away) by some optimal factor proportional to $\Delta\lambda = \lambda - \mathcal{Z}_{\text{OPT}}$ and $(\Delta\lambda)^2$, respectively. This partial transformation can be interpreted as a rotation that pushes the maximal amount of complicated many-body electron-photon and photon-mediated electron-electron correlations into the mean-field solution of the QED problem.

3.2.2 | Single-Determinant Ground Polaritonic States

Assuming a single-reference (i.e., single-determinant) wavefunction for the electronic DOFs $|\text{HF}\rangle$ (taken as Hartree-Fock determinant) for the polaritonic ground state in the GCS basis (see Section 3.2.1), then the deviation in the molecular dipole $\Delta\hat{\mu} = \hat{\mu} - \langle\hat{\mu}\rangle_{\text{GS=HF}} = 0$ since $\langle\text{HF}|\hat{\mu}|\text{HF}\rangle = \langle\hat{\mu}\rangle_{\text{GS=HF}}$, effectively removing the bilinear coupling term in the GCS light-matter Hamiltonian (Equation 29). However, the DSE term remains since $\langle(\Delta\hat{\mu})^2\rangle_{\text{HF}} \neq 0$ even for the single-determinant approximation. To be clear, for approaches with multiple determinants (i.e., the use of excited Slater determinants in a CIS-like expansion), the direct coupling term will survive. For a single-reference ground state, Equation (29) can then be simplified to,

$$\hat{H}_{\text{pl}}^{\text{GCS}} = \hat{H}_{\text{el}} + \hbar\omega_{\text{c}}\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) + \frac{1}{2\hbar}(\lambda \cdot \Delta\hat{\mu})^2 \quad (30)$$

where the only photonic operator that appears is that of the photonic Hamiltonian $\hat{H}_{\text{ph}} = \hbar\omega_{\text{c}}\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$ whose eigenstates are the vacuum Fock states $|\tilde{n}\rangle$ in the rotated GCS basis (which have the same frequency but with a shift in position q_{c} by \mathcal{Z} compared to the vacuum Fock states). One should note that the Pauli-Fierz Fock states can be re-obtained by applying the reverse unitary coherent state transformation \hat{U}_{GCS} (Equation 27) to the resulting Fock states after the self-consistent solution (discussed below) of Equation (30) has been achieved, whose average photon number will depend on the self-consistent solution of the dipole moment $\langle\hat{\mu}\rangle_{\text{HF}} = 0$, suggesting that molecules with strong ground-state dipole moments will exhibit stronger polaritonic effects [44, 92].

The ground polaritonic state can be defined as the $|\text{HF}, \tilde{0}\rangle$ wavefunction. Neglecting the photonic zero-point energy (i.e., $\langle\tilde{0}|\hat{H}_{\text{ph}}|\tilde{0}\rangle = \frac{\hbar\omega_{\text{c}}}{2}$), the electron-photon Fock matrix can be written as,

$$F_{pq} = F_{pq}^{\text{HF}} + \frac{1}{2\hbar} \left[\sum_o^{\text{Nocc}} (\lambda \cdot \mu_{po}) (\lambda \cdot \mu_{oq}) - \sum_v^{\text{Nvir}} (\lambda \cdot \mu_{pv}) (\lambda \cdot \mu_{vq}) \right] \quad (31)$$

where o , v , and (p, q) are occupied, virtual, and any molecular orbitals, respectively. Noting that the solution to the bare

molecular Fock matrix is achieved if $\mathcal{F}_{\text{ov}}^{\text{HF}} = 0$, the scQED-HF energy can be written as [45],

$$E_{\text{QED-HF}} = E_{\text{HF}} + \frac{1}{2\hbar} \langle (\lambda \cdot \Delta\hat{\mu})^2 \rangle_{\text{HF}} = E_{\text{HF}} + \frac{1}{\hbar} \sum_{\text{ov}} (\lambda \cdot \mu_{\text{ov}})^2 \quad (32)$$

which is then variationally minimized in a self-consistent way, updating the coherent shift \mathcal{Z} at each iteration. More details on the scQED-HF scheme in varying complexity can be found in References [45, 67, 72].

Following a similar procedure, the single-determinant nature of density functional theory can be used to simplify the Pauli-Fierz Hamiltonian to that of the GSC representation without the direct coupling term. However, due to the ad hoc nature of density functional theory, there are many ways to approximate the exchange-correlation kernel to arrive at various levels of corrections to the electron-electron, electron-photon, and photon-photon correlations. In fact, the simplest choice (albeit the least motivated) is to ignore the electron-photon and photon-photon terms in the exchange-correlation kernel. In this case, the only responses of the single-particle orbitals $\{p, q\}$ are those induced by the dipole self-energy contributions (the last term in Equation 31). This is the simplest approach since no novel exchange-correlation functionals need to be used/created, and one can rely on the already-developed, high-level functionals for the complicated electron-electron correlation, such as CAM-B3LYP [93], ω B97XD [94, 95], and SCAN [96, 97]. Recently, novel exchange-correlation functionals for electronic and photonic DOFs have been constructed based on a variety of frameworks, such as the optimized effective potential (OEP) approach [98, 99], photon-free effective Hamiltonians [100], and the fluctuation-dissipation theorem approach [101]. In any case, the ground state energy can be loosely written as

$$E_{\text{QED-DFT}} = E_{\text{DFT}} + E_{\text{ex-corr}}^{\text{el-ph}} + E_{\text{ex-corr}}^{\text{ph-ph}} \quad (33)$$

where the last two terms (or more specifically, the exchange-correlation functionals of the density $E[\rho]$), in addition to the first term for standard DFT, are not known explicitly and must be approximated [102]. Note that a fraction of Hartree-Fock exchange can still be included in the electron-electron exchange term within E_{DFT} . For more details, we refer the reader to the original references regarding density functional theory, References [99–101], and, as well as others who have explored and utilized similar Hartree-Fock [44, 45, 67, 68, 72, 103] and density functional theories for electron-photon systems [43, 62, 75, 82, 98, 101, 104–114].

3.2.3 | Addressing Correlations and Excited States

Capturing higher-order correlations between electrons has a well-defined procedure using post-HF approaches, such as configuration interaction (CI) or coupled cluster (CC) expansions in the basis of excited Slater determinants. The polaritonic community has also used such wavefunction approaches for computing the polaritonic electronic-bosonic states [40, 44, 45, 67, 68, 71, 73, 74, 91, 115] in addition to other approaches such as time-dependent DFT

(TD-DFT) [43, 74, 75, 82, 92, 99, 107, 109], reduced density matrix (RDM) theory [116], quantum Monte Carlo [87, 88], Møller-Plesset Theory (MP-n) [86], and density matrix renormalization group (DMRG) [90, 117–119]. While mean-field approaches (e.g., HF, DFT) yield useful ground state information, even in the absence of correlation, it is not yet clear to what extent the correlated excitations of the matter and photonic DOFs will impact the results, even in the ground polaritonic state. Further, the need for polaritonic excited states is ubiquitous in the photophysics and photochemistry of excited polaritons. Additionally, the determination of the light-matter coupling strength is often predicated on the magnitude of the Rabi splitting between the light and matter excitations at resonance. While our goal is not to outline all possible many-body approaches that go beyond mean-field, we will briefly outline and discuss QED coupled cluster theory (QED-CCSD) since in the electronic structure community coupled cluster theory is one of the most widely used approximations for capturing electronic correlation in a wide variety of molecules.

The CC ansatz for the ground-state polaritonic wavefunction is [45, 85]

$$|\mathcal{E}_0^{\text{CC}}\rangle = e^{\hat{\mathcal{T}}} |\mathcal{E}_0^{\text{HF}}\rangle = e^{\hat{\mathcal{T}}} [|\psi^{\text{HF}}\rangle \otimes |0\rangle_z] \quad (34)$$

where $|\mathcal{E}_0^{\text{HF}}\rangle$ is the polaritonic ground state calculated at the uncorrelated HF level (see Equation 32) and $|\psi^{\text{HF}}\rangle$ is the uncorrelated HF electronic ground state. Here, $|0\rangle_z$ is the photon vacuum state in the rotated coherent state representation with $|0\rangle_z = \hat{U}_z |0\rangle$ (see Equation 27) at the optimal coherent state parameter \mathcal{Z} after the HF self-consistent procedure. $\hat{\mathcal{T}}$ is the cluster operator (not to be confused with the kinetic energy operator \hat{T}_R or \hat{T}_r in Equation 1). This cluster operator involves a sum of electronic, photonic, and mixed electron-photon excitations as follows

$$\hat{\mathcal{T}} = \sum_{\alpha} t_{\alpha} \hat{\tau}_{\alpha} + \sum_n t_n \hat{\tau}_n + \tilde{\alpha}, \tilde{n} \sum_{\tilde{\alpha}\tilde{n}} t_{\tilde{\alpha}\tilde{n}} \hat{\tau}_{\tilde{\alpha}\tilde{n}} \quad (35)$$

where $\hat{\tau}_{\alpha}$ represents creation and annihilation operators for an α_{th} -order electronic excitation. For example, with $\alpha = 1$ (single electronic excitation), $\hat{\tau}_i^a = \hat{c}_a^{\dagger} \hat{c}_i$ excites an electron from an occupied orbital i to an unoccupied orbital a . Similarly, $\alpha = 2$ implies $\hat{\tau}_{ij}^{ab} = \hat{c}_a^{\dagger} \hat{c}_b^{\dagger} \hat{c}_i \hat{c}_j$ which will excite two electrons $i \rightarrow a$ and $j \rightarrow b$, respectively. The photon excitation operator is commonly written as the standard photonic ladder operator $\hat{\tau}_n = (\hat{a}^{\dagger})^n$ [44, 45]. It should be noted that this is not the only way to define the bosonic excitations. The authors of Reference [85] defined an idempotent form of the excitation operator as $\hat{\tau}_n = |n\rangle\langle 0|$ for a finite number of Fock states $\{|n\rangle\} = \{|0\rangle, |1\rangle, \dots, |N_F\rangle\}$. However, the two cases are not formally equivalent, and a rigorous comparison of the quality of the results has not been performed. In a similar manner, the coupled electron-photon excitation operator $\hat{\tau}_{\tilde{\alpha}\tilde{n}}$ can be written, for example, as $\hat{c}_a^{\dagger} \hat{c}_i (\hat{a}^{\dagger})^n$ for a one-electron electronic excitation coupled to an n_{th} -level photonic excitation while $\hat{c}_a^{\dagger} \hat{c}_b^{\dagger} \hat{c}_i \hat{c}_j (\hat{a}^{\dagger})^n$ will provide the two-electron and n_{th} -level photonic coupled excitations. Each of these excitation operators is connected with a unique cluster amplitude $\{t_{\alpha}, t_n, t_{\tilde{\alpha}\tilde{n}}\}$.

The amplitudes t_{α} , t_n , and $t_{\tilde{\alpha}\tilde{n}}$ can be solved by projection (Equation 36). This requires the evaluation of the

similarity-transformed Hamiltonian operator $\hat{H}_{\text{PF}} = e^{-\hat{\mathcal{T}}} \hat{H}_{\text{PF}} e^{\hat{\mathcal{T}}}$, where \hat{H}_{PF} is expressed in Equation (13) and is usually rotated to the coherent state basis (see Section 3.2.1). This leads to the ground state coupled cluster energy $\mathcal{E}_0^{\text{CC}}$ as a solution to the following set of equations,

$$\langle \mathcal{E}_0 | \hat{H} | \mathcal{E}_0 \rangle = \mathcal{E}_0^{\text{CC}}, \quad \{\mathcal{L}_{\Gamma}\} = \langle \mathcal{E}_{(\Gamma)} | \hat{H} | \mathcal{E}_0 \rangle = 0 \quad (36)$$

with $|\mathcal{E}_{(\Gamma)}\rangle = \hat{\tau}_{(\Gamma)} |\mathcal{E}_0^{\text{HF}}\rangle$, where $\{\Gamma\} = \{\alpha, n, \tilde{\alpha}\tilde{n}\}$ is the set of possible excitations in the cluster operator $\hat{\mathcal{T}}$ (Equation 35) leading to the set of projection equations $\{\mathcal{L}_{\Gamma}\}$. These projections lead to the equations for the excitation amplitudes $t_{(\Gamma)}$ and are usually solved in a self-consistent manner. A similar CC projection formalism can be found in any electronic structure textbook [120].

There are many different notations for the methods developed by changing the highest level of excitation for each term in the cluster operator. The most straightforward notation is CCSD-jm-n, which implies that the electronic DOFs are treated up to double (SD) excitations in the cluster operator, the photonic excitation is limited to n levels, and the mixed excitation is set to j electronic and m photonic. As per usual CC theory, the cutoff value of the excitation levels leads to effects that include even higher excitations through the exponential treatment of the cluster operator $\hat{\mathcal{T}}$, thus effectively outperforming similar methods such as CI with the same excitation level cutoff. However, due to the $\mathcal{O}(N^{6*} \mathcal{N}_{\text{F}}^{\mathcal{N}_{\text{mode}}})$ scaling (with N electrons/basis functions and $\mathcal{N}_{\text{modes}}$ cavity modes each with \mathcal{N}_{F} Fock states) of the scQED-CC method in general, including more than two Fock states has been a challenge even for small molecular systems [18, 44, 45, 121], and limited study has been performed including up to 10 Fock states for a half-filled four-site Hubbard model with direct comparison to the full configuration interaction result [85]. This will have unfavorable scaling on multi-mode cavities with quasi-continuous dispersion relations (where $N_{\text{mode}} > 10$). Nevertheless, QED-CCSD remains one of the most accurate [85, 87, 88] approaches for simulating ab initio polaritons.

4 | Polariton Quantum Dynamics

In this section, we address and outline various approaches to simulate the quantum dynamics of polaritons at various levels of theory. The essential task is trying to solve the time-dependent Schrödinger equation (TDSE)

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}_{\text{PF}} |\Psi(t)\rangle \quad (37)$$

where $|\Psi(t)\rangle$ is the total quantum state of the electronic-nuclear-photonic hybrid system. The time-evolution of such a system is governed by the Pauli-Fierz QED Hamiltonian \hat{H}_{PF} (Equation 13). Depending on this complexity of the molecular system, one may perform the dynamics exactly as dictated by the TDSE (which may be prohibitively expensive for more than a few nuclear DOFs) or resort to various approximations, such as mixed quantum-classical (MQC) approaches, semi-classical approaches, various approximate master equation approaches (e.g., Lindblad,

Redfield, etc.), or approximate wavefunction approaches (e.g., multi-configurational Hartree-Fock). In the following discussion, we will briefly introduce an exact method for solving polariton quantum dynamics (Section 4.1) as well as a few popular mixed quantum-classical approaches (Section 4.2). Additionally, we will address the calculation of the exact nuclear gradients and their effects on the quantum dynamics (Section 4.3).

4.1 | Exact Polaritonic Quantum Dynamics

We begin by briefly discussing how to solve Equation (37) exactly, thus giving an exact solution to the polaritonic quantum dynamics. There are, in principle, many possible strategies for exact quantum dynamics propagation, and we only outline one of the most commonly used strategies based on the Born-Huang expansion [122] and subsequent propagation in the energy basis. We describe the total wavefunction of the electron-photon-nuclear DOFs using the adiabatic-Fock basis as,

$$|\Psi\rangle = \sum_{\xi}^{\mathcal{N}_G} \sum_{\alpha}^{\mathcal{N}_{el}} \sum_n^{\mathcal{N}_F} \chi_{an}(\mathbf{R}_{\xi}) |\mathbf{R}_{\xi}\rangle \otimes |\psi_{\alpha}(\mathbf{R}_{\xi})\rangle \otimes |n\rangle \quad (38)$$

where $\chi_{an}(\mathbf{R}_{\xi}) = \langle \mathbf{R}_{\xi}, \psi_{\alpha}, n | \Psi \rangle = (\langle \mathbf{R}_{\xi} | \otimes \langle \psi_{\alpha}(\mathbf{R}_{\xi}) | \otimes \langle n |) | \Psi \rangle$ is the ξan expansion coefficient and \mathcal{N}_G is the number of grid points for the nuclear basis set in a grid or spectral basis (e.g., discrete variable representation) [123]. Here $\{|\psi_{\alpha}(\mathbf{R})\rangle\}$ are the electronic adiabatic states at nuclear configuration \mathbf{R} , $\{|n\rangle\}$ are the photonic Fock states, and $\{|\mathbf{R}_{\xi}\rangle\}$ are the basis functions of the grid describing the nuclear DOFs.

Within this representation, the matrix elements of the total light-matter Hamiltonian $\hat{H}_{PF} = \hat{T}_R + \hat{H}_{pl}$ are written as,

$$\left(\hat{T}_R + \hat{H}_{pl} \right)_{\xi\xi', \alpha\beta, nm} = \left(\hat{T}_R \right)_{\xi\xi', \alpha\beta} \delta_{nm} + \left(\hat{H}_{pl} \right)_{\alpha\beta, nm}(\mathbf{R}_{\xi}) \delta_{\xi\xi'} \quad (39)$$

$$\left(\hat{T}_R \right)_{\xi\xi', \alpha\beta} = -\frac{1}{2} \sum_a^{\mathcal{N}_R} \frac{1}{M_a} \left[\langle \mathbf{R}_{\xi} | \nabla_a^2 | \mathbf{R}_{\xi'} \rangle \delta_{\alpha\beta} + 2\mathbf{d}_{\alpha\beta}^a(\mathbf{R}_{\xi}) \cdot \langle \mathbf{R}_{\xi} | \nabla_a | \mathbf{R}_{\xi'} \rangle + D_{\alpha\beta}^a(\mathbf{R}_{\xi}) \delta_{\xi\xi'} \right] \quad (40)$$

$$\left(\hat{H}_{pl} \right)_{\alpha\beta, nm}(\mathbf{R}_{\xi}) = \left[E_{\alpha}(\mathbf{R}_{\xi}) + \hbar\omega_c \left(n + \frac{1}{2} \right) \right] \delta_{\alpha\beta} \delta_{nm} + \tilde{\mu}_{\alpha\beta}(\mathbf{R}_{\xi}) \eta_{nm} + D_{\alpha\beta}(\mathbf{R}_{\xi}) \delta_{nm} \quad (41)$$

where the individual terms in \hat{H}_{pl} (i.e., $\tilde{\mu}_{\alpha\beta}$, η_{nm} , and $D_{\alpha\beta}$) were defined previously in Equation (18). Additionally, $\mathbf{d}_{\alpha\beta}^a(\mathbf{R}_{\xi}) = \langle \psi_{\alpha} | \nabla_a | \psi_{\beta} \rangle$ is the non-adiabatic coupling and $D_{\alpha\beta}^a(\mathbf{R}_{\xi}) = \langle \psi_{\alpha} | \nabla_a^2 | \psi_{\beta} \rangle$ is the second-derivative coupling, which were defined in Equations (4) and (5), respectively. \mathcal{N}_R is the number of nuclear DOFs in the system. We refer the reader to References [123, 124] for evaluating quantities (e.g., the nuclear kinetic energy) using the grid or spectral basis for the nuclear DOFs.

Upon diagonalization of this Hamiltonian $\hat{H}_{PF} = \hat{T}_R + \hat{H}_{pl}$ (Equation 39), the electronic-nuclear-photonic eigenstates can be obtained as,

$$\hat{H}_{PF} |\mathcal{E}_p\rangle = \left(\hat{T}_R + \hat{H}_{pl} \right) |\mathcal{E}_p\rangle = \mathcal{E}_p |\mathcal{E}_p\rangle \quad (42)$$

The electronic-nuclear-photonic wavefunction can then be propagated in time as,

$$|\Psi(t)\rangle = e^{-i\hat{H}_{PF}t} |\Psi(t=0)\rangle = \sum_p c_p e^{-i\mathcal{E}_p t} |\mathcal{E}_p\rangle \quad (43)$$

where \mathcal{E}_p is the p_{th} eigenvalue and c_p is the projection onto initial total wavefunction onto the p_{th} eigenstate $|\mathcal{E}_p\rangle$,

$$c_p = \langle \mathcal{E}_p | \Psi(t=0) \rangle \quad (44)$$

where $|\Psi(t=0)\rangle$ is an arbitrary initial condition (in the same form as Equation 38). Additional details on the exact propagation can be found in References [63, 125, 126].

There are many ways in which to evaluate the exact (or approximately exact) dynamics of a quantum mechanical system in addition to the one outlined above, which may be one of the simplest to write down. However, other approaches exist, such as the Multi-configuration time-dependent Hartree (MCTDH) [64, 127–130], the exact factorization (XF) [11, 131], the hierarchical equation of motion (HEOM) [132, 133], and so forth, which have been already used for exploration in polaritonic systems. Additionally, ab initio multiple spawning (AIMS) [134, 135], Ehrenfest multiple cloning (EMC) [73, 136], and their variants [137–139] could also be adapted for polaritonic dynamics to give nearly exact results.

4.2 | Trajectory-Based Approaches

In lieu of an exact propagation of the total wavefunction, including electron, photon, and nuclear DOFs as quantum mechanical DOFs, we now move to a discussion of Mixed Quantum-Classical (MQC) and Semi-classical approaches. These methods are trajectory-based schemes of varying complexity and accuracy in the sense that the nuclear (and in some cases photonic) distribution is now composed of an ensemble of trajectories in order to compute observables over the entire nuclear (and/or photonic) initial distribution as ensemble averages. Further, usually the trajectories are taken to be completely independent of one another, aside from the initial nuclear distribution, with some recent exceptions of the coupled-trajectory approaches and quasi-coupled trajectory approaches stemming from the exact factorization scheme [140–143].

Two schemes exist for applying the MQC approach: (I) treating the nuclear and photon DOFs classically or (II) treating *only* the nuclear DOFs classically. While both approaches will yield interesting results, we will focus on scheme (II) where the photon is treated fully quantum mechanically. In the following two sections, we will briefly outline two approaches commonly used in quantum dynamics, namely the mean-field Ehrenfest and fewest switches surface hopping.

4.2.1 | Mean-Field Ehrenfest

Ehrenfest (EH) dynamics is an MQC approach for propagating the coupled electron-photon-nuclear dynamics [136, 144, 145]. We choose to treat the electronic and photonic DOFs as fully quantum mechanical while treating the nuclear DOFs as classical ones. In this way, one can write the total wavefunction for the quantum sub-system (Equation 38) in an approximate form, including only the electronic and photonic DOFs explicitly as follows

$$|\Psi(t)\rangle = \sum_{\alpha}^{\mathcal{N}_{\text{el}}} \sum_n^{\mathcal{N}_{\text{F}}} c_{\alpha n}(t) |\psi_{\alpha}(\mathbf{R}(t)), n\rangle \quad (45)$$

where $c_{\alpha n}(t) = \langle \psi_{\alpha}(\mathbf{R}(t)), n | \Psi(t) \rangle$ is the αn_{th} time-dependent, adiabatic-Fock expansion coefficient, $|\psi_{\alpha}(\mathbf{R}(t))\rangle$ is the α_{th} electronic adiabatic wavefunction parameterized by the nuclear positions at time t , $\mathbf{R}(t)$, and $|n\rangle$ is the time-independent photonic Fock state. The time-dependent electronic-photonic wavefunction $|\Phi(t)\rangle$ is evolved by approximating the time-dependent Schrödinger equation (TDSE), $i\frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}_{\text{PF}} |\Psi(t)\rangle$ (see Equations 13 and 18), as the following set of differential equations for the expansion coefficients in the adiabatic-Fock basis,

$$\begin{aligned} \dot{c}_{\alpha n}(t) = & -i\varepsilon_{\alpha, n} c_{\alpha n}(t) - \sum_{\beta}^{\mathcal{N}_{\text{el}}} \left[\frac{d\mathbf{R}(t)}{dt} \cdot \mathbf{d}_{\alpha\beta}(\mathbf{R}(t)) - iD_{\alpha\beta} \right] c_{\beta n}(t) \\ & - i \sum_{\beta}^{\mathcal{N}_{\text{el}}} \sum_m^{\mathcal{N}_{\text{F}}} \tilde{\mu}_{\alpha\beta} \eta_{nm} c_{\beta m}(t) \end{aligned} \quad (46)$$

Here, $\mathbf{d}_{\alpha\beta}(\mathbf{R}(t)) = \langle \psi_{\alpha}(\mathbf{R}(t)) | \nabla_{\mathbf{R}} | \psi_{\beta}(\mathbf{R}(t)) \rangle$ is the derivative coupling (Equation 4) and $\frac{d\mathbf{R}(t)}{dt}$ is the classical nuclear velocity. The matrix elements $\varepsilon_{\alpha, n}$, $\tilde{\mu}_{\alpha\beta}$, η_{nm} , and $D_{\alpha\beta}$ were defined previously in Equation (18). To achieve this expression, one assumes that the second-derivative couplings are vanishingly small and that the nuclear distribution is sharply peaked around its average position. Additionally, we have made use of the orthogonality of the vacuum Fock states, $\langle n | m \rangle = \delta_{nm}$ as well as noting that the nuclear gradient does not act on the photonic basis states (i.e., $\langle n | \nabla_{\mathbf{R}} | m \rangle = 0$) since they do not depend on the nuclear positions \mathbf{R} . This non-dependency of the photonic basis states leads to a large amount of sparsity in the matrices, and as noted earlier in Section 3.1.1, sparse matrix methods could be employed to achieve more efficient calculations. Note that this is not true, for example, when employing the PFS photonic basis (Section 3.1.2), where the definition of the photonic basis states relies on the nuclear positions through the use of the molecular dipole operator [65].

In order to propagate the classical nuclear DOFs, the classical-like force is simply the sum of all contributions from the elements of the reduced density matrix, $\rho_{\alpha n, \beta m}(t) = c_{\alpha, n}^*(t) c_{\beta, m}(t)$. In this way, the force can be written as,

$$\begin{aligned} \mathbf{F}(t) = & - \left\langle \Psi(\mathbf{R}(t)) | \nabla_{\mathbf{R}} \hat{H}_{\text{pl}} | \Psi(\mathbf{R}(t)) \right\rangle \\ = & - \sum_{\alpha\beta}^{\mathcal{N}_{\text{el}}} \sum_{nm}^{\mathcal{N}_{\text{F}}} \rho_{\alpha n, \beta m}(t) \left\langle \psi_{\alpha}(\mathbf{R}(t)), n | \nabla_{\mathbf{R}} \hat{H}_{\text{pl}} | \psi_{\beta}(\mathbf{R}(t)), m \right\rangle \end{aligned} \quad (47)$$

where the nuclear gradients on the Hamiltonian $\nabla_{\mathbf{R}} \hat{H}_{\text{pl}}$ will be discussed in detail in Section 4.3. For a similar description in terms of the polaritonic basis, see Reference [40].

4.2.2 | Linearized Spin-Mapping

In the fully linearized spin-mapping framework [146–149], any electronic-only, two-operator correlation function can be written as,

$$C_{AB}(t) = \langle A_{\text{W}}(\mathbf{Z}(0)) B_{\text{W}}(\mathbf{Z}(t)) \rangle_{\text{spin-LSC}} \quad (48)$$

where $A_{\text{W}}(F_{\text{W}})$ is the Stratonovich-Weyl (SW) transform of operator \hat{A} (\hat{B}). The measurement of an arbitrary operator at time t can be written as,

$$[\hat{B}]_{\text{W}}(\mathbf{Z}, t) \equiv B_{\text{W}}(\mathbf{Z}(t)) = \text{Tr} [\hat{B} \hat{\omega}_{\text{W}}(\mathbf{Z}(t))] \quad (49)$$

The SW kernel can be written as,

$$\hat{\omega}_{\text{W}}(\mathbf{Z}, t) = \frac{1}{2} \sum_{\alpha\beta}^{\mathcal{N}_{\text{el}}} \sum_{nm}^{\mathcal{N}_{\text{F}}} \left(Z_{\alpha n}(t) Z_{\beta m}^*(t) - \gamma_{\text{W}} \delta_{\alpha\beta} \delta_{nm} \right) |\psi_{\alpha}, n\rangle \langle \psi_{\beta}, m| \quad (50)$$

in a diabatic basis for the \mathcal{N}_{pol} polaritonic states. The SW kernel is evaluated as a function of the complex-valued, time-evolved mapping variables $\mathbf{Z} = \{Z_1, Z_2, \dots, Z_{\mathcal{N}_{\text{pol}}}\}$ with a fixed zero-point energy parameter $\gamma_{\text{W}} = \frac{2}{\mathcal{N}_{\text{pol}}} \left(\sqrt{\mathcal{N}_{\text{pol}} + 1} - 1 \right)$. It should be noted that the approach outlined here is one of many realizations for spin-mapping dynamics. In this work, we focus on the so-called spin-mapping dynamics confined to the W-sphere, which shows the most accurate results for the widest variety of systems [146, 147, 150–152].

The correlation function for the time-evolved density matrix $\rho_{\alpha n, \beta m}$ given an initial excitation to state arbitrary state σl (i.e., $\hat{A} = |\sigma l\rangle \langle \sigma l|$ in Equation 48) is evaluated using focused initial conditions such that,

$$\rho_{\alpha n, \beta m}(t) \approx \int d\mathbf{R} d\mathbf{P} d\mathbf{Z} \rho_{\text{b}}(\mathbf{R}, \mathbf{P}) \rho_{\text{W}}^{(\sigma l)} [|\psi_{\alpha}, n\rangle \langle \psi_{\beta}, m|]_{\text{W}}(\mathbf{Z}(t)) \quad (51)$$

where $\rho_{\text{b}}(\mathbf{R}, \mathbf{P})$ is the Wigner distribution for the nuclear DOFs, and $\rho_{\text{W}}^{(\sigma l)}$ is the initially focused distribution for the mapping variables,

$$\rho_{\text{W}}^{(\sigma l)} = \frac{\delta(|Z_{\sigma l}|^2 - \gamma_{\text{W}} - 2) \Pi_{\alpha n \neq \sigma l} \delta(|Z_{\alpha n}|^2 - \gamma_{\text{W}})}{\int d\mathbf{Z} \delta(|Z_{\sigma l}|^2 - \gamma_{\text{W}} - 2) \Pi_{\alpha n \neq \sigma l} \delta(|Z_{\alpha n}|^2 - \gamma_{\text{W}})} \quad (52)$$

For a given initial state σl , the mapping variables \mathbf{Z} are initialized as,

$$\begin{aligned} Z_{\sigma l} &= \sqrt{2 + \gamma_{\text{W}}} e^{i\theta_{\sigma l}} & (\text{Initially focused state}) \\ Z_{\alpha n} &= \sqrt{\gamma_{\text{W}}} e^{i\theta_{\alpha n}}, & \alpha n \neq \sigma l \end{aligned} \quad (53)$$

with $\{\theta\}$ randomly sampled between 0 and 2π , independently from one another.

The propagation of the mapping and nuclear variables can be done identically to Equation (47) with the state-dependent forces $F_e(\mathbf{R}, \mathbf{Z})$,

$$F_e(\mathbf{R}, \mathbf{Z}) = -\frac{1}{2} \sum_{\alpha\beta}^{\mathcal{N}_{\text{el}}} \sum_{nm}^{\mathcal{N}_{\text{F}}} \rho_{\alpha n, \beta m} \left\langle \psi_{\alpha}, n \left| \nabla_{\mathbf{R}} \hat{H}_{\text{pl}}(\mathbf{R}) \right| \psi_{\beta}, m \right\rangle \quad (54)$$

with

$$\rho_{\alpha n, \beta m} = \frac{1}{2} \left(Z_{\alpha, n}^*(t) Z_{\beta, m}(t) - \gamma_{\text{W}} \delta_{\alpha\beta} \delta_{nm} \right) \quad (55)$$

For more details on the linearized spin mapping approach, we refer the reader to References [146, 147, 149]. We also want to point out extensions of the spin mapping approach to partially linearized methods [149, 153–155] as well as a recently developed surface hopping-inspired spin mapping formalism [156–158].

4.2.3 | Surface Hopping

We now move to an alternative description of mixed quantum classical treatment of the dynamics known as Fewest Switches Surface Hopping (FSSH), which is one of many variants of surface hopping [159, 160]. This method approaches the problem in a more classical way, propagating the nuclei on a single adiabatic surface until a discontinuous hop is performed. Once a hop is achieved, which must satisfy energy conservation through a rescaling of the classical nuclear velocities, then the nuclear forces are now derived from the new adiabatic state. The electronic DOFs are propagated according to the Schrodinger equation, and the probabilities for hopping between adiabatic states are proportional to the first-order non-adiabatic couplings $\mathbf{d}_{\alpha\beta}$ between adiabatic states. This approach has also been recently used to simulate polariton chemistry [31, 32, 84, 125, 161–163].

It is well-known that surface hopping approaches perform better when the propagation is done in the adiabatic (i.e., polariton) basis. However, many “tricks” exist to propagate the quantum mechanical DOFs in a locally diabatic basis for higher accuracy and to work around the sharply peaked non-adiabatic couplings throughout the nuclear dynamics. The total wavefunction for the quantum mechanical DOFs (i.e., the electrons and photons) can be written as,

$$|\Psi(t)\rangle = \sum_j^{\mathcal{N}_{\text{pol}}} c_j(t) |\Phi_j(\mathbf{R}(t))\rangle \quad (56)$$

where $c_j(t) = \langle \Psi(t) | \Phi_j(\mathbf{R}(t)) \rangle$ is the time-dependent expansion coefficient for polaritonic state j and \mathcal{N}_{pol} is the number of polaritonic states. During the nuclear dynamics, the active polaritonic state S dictates the nuclear forces, which can be written as,

$$\mathbf{F}(t) = -\left\langle \Phi_S(\mathbf{R}(t)) \left| \nabla_{\mathbf{R}} \hat{H}_{\text{pl}} \right| \Phi_S(\mathbf{R}(t)) \right\rangle = -\nabla_{\mathbf{R}} \mathcal{E}_S(\mathbf{R}(t)) \quad (57)$$

At each nuclear time-step Δt , the probability to hop from the current active polaritonic state S to any other polaritonic state j is computed as,

$$\mathcal{P}_{S \rightarrow j}(t) = \text{MAX} \left[-\frac{\sigma_{Sj}(t)}{\rho_{SS}(t)}, 0 \right] \quad (58)$$

with,

$$\sigma_{Sj}(t) = 2\text{Re}[\rho_{Sj}(t)] \frac{d\mathbf{R}(t)}{dt} \cdot \mathbf{d}_{Sj}(\mathbf{R}(t)) \quad (59)$$

Here, $\mathbf{d}_{Sj}(\mathbf{R}(t))$ is the non-adiabatic coupling between polaritonic states, $\frac{d\mathbf{R}(t)}{dt} = \dot{\mathbf{R}}(t)$ are the classical nuclear velocities, and $\rho_{Sj}(t) = c_S^*(t)c_j(t)$ is the reduced density matrix in the polaritonic basis. Between nuclear time-steps, the electronic DOFs are updated via direct propagation of the time-dependent Schrodinger equation as,

$$\dot{c}_j(t) = -iE_j(\mathbf{R}(t))c_j(t) - \sum_k^{\mathcal{N}_{\text{pol}}} c_k(t) \dot{\mathbf{R}}(t) \cdot \mathbf{d}_{jk}(\mathbf{R}(t)) \quad (60)$$

It is well known [160] that FSSH suffers from producing overly coherent results (or, equivalently, a lack of proper decoherence between quantum states) within the expansion of electronic coefficients and will subsequently be problematic for the polaritonic coefficients [160]. Many ad hoc corrections exist to modify the expansion coefficients in FSSH to account for decoherence, such as the instantaneous decoherence correction (IDC) [136, 164], the energy-based decoherence correction (EDC) [165], and so forth, as well as other forms of the surface hopping scheme, such as the augmented surface hopping (A-FSSH) [166], the decoherence-induced surface hopping (DISH) [167], and the global flux surface hopping [168] schemes. More recently, a spin-mapping [146–154, 169] analogue of the surface hopping approach was constructed and mitigates much of the shortcomings of the standard FSSH procedure without ad hoc adjustments [156, 157].

A major simplicity afforded by the FSSH method is that the derivative coupling vectors $\mathbf{d}_{jk}(\mathbf{R}(t))$ are not explicitly required, as the nuclear forces (unlike in the mean-field MQC methods) do not require this quantity for time-evolution of the electronic or nuclear DOFs, except at the hops for the nuclear velocity rescaling. To be clear, the electronic propagation only requires the scalar non-adiabatic coupling terms $\mathbf{d}_{jk}(\mathbf{R}(t)) \cdot \dot{\mathbf{R}}(t) = \left\langle \Psi_j \left| \frac{d}{dt} \right| \Psi_k \right\rangle$, which can be easily obtained via finite difference wavefunction overlaps of the polaritonic states throughout the trajectory [170, 171]. This procedure is drastically cheaper than the direct computation of the non-adiabatic coupling vectors themselves, as one only needs to compute the non-adiabatic coupling vectors to rescale the nuclei at the moment of a hop [164]. Further, one can ignore the asymmetric nuclear velocity rescaling altogether and perform uniform energy-based rescaling, which is known to provide slightly worse dynamics but alleviates the computation of the vector non-adiabatic couplings altogether, providing a substantial speed-up in ab initio simulations. It is also worth mentioning that the first-order non-adiabatic couplings of the electronic subsystem $\mathbf{d}_{\alpha\beta}(\mathbf{R}(t))$ can be approximated using the scalar non-adiabatic coupling and the diagonal gradients [172, 173].

4.3 | Exact QED Nuclear Gradients

In the aforementioned mean-field, MQC Ehrenfest approach as well as other mean-field approaches not discussed here [147, 149, 153, 174, 175], the nuclear force is written as a weighted average over the reduced density matrix involving both the diagonal gradients of the adiabatic states as well as the off-diagonal non-adiabatic couplings (see Equation 47). Here, $\nabla_{\mathbf{R}}\hat{H}_{\text{pl}}$ is,

$$\nabla_{\mathbf{R}}\hat{H}_{\text{pl}} = \nabla_{\mathbf{R}}\hat{H}_{\text{el}} + \sqrt{\frac{\omega_c}{2}}\lambda(\hat{a}^\dagger + \hat{a})\nabla_{\mathbf{R}}\hat{\mu} + \frac{\lambda^2}{2}\nabla_{\mathbf{R}}\hat{\mu}^2 \quad (61)$$

Note here that the matrix elements of $\nabla_{\mathbf{R}}\hat{H}_{\text{ph}}$ are zero in the adiabatic-Fock basis and that the matrix elements of $\nabla_{\mathbf{R}}\hat{H}_{\text{el}}$ will lead to the usual electronic gradient of the adiabatic PESs, $\nabla_{\mathbf{R}}E_a(\mathbf{R})$, as well as the non-adiabatic couplings, $\mathbf{d}_{a\beta}(\mathbf{R})$ (Equation 4). Additional terms arise in the nuclear force that are proportional to the gradient on the molecular dipole matrix elements $\nabla_{\mathbf{R}}\hat{\mu}$, and these terms may contribute large amounts to the nuclear force in regions of large light-matter coupling λ .

Using the chain rule [125], the matrix elements of the nuclear gradient operator for the a_{th} nuclear DOF acting on the polaritonic Hamiltonian can be written as,

$$\left[\nabla^a\hat{H}_{\text{pl}}\right] = \nabla^a\left[\hat{H}_{\text{pl}}\right] - \left[\hat{H}_{\text{pl}}\right]\left[\hat{d}^a\right] + \left[\hat{d}^a\right]\left[\hat{H}_{\text{pl}}\right] \equiv \nabla^a\left[\hat{H}_{\text{pl}}\right] + X^a \quad (62)$$

where $\left[\nabla^a\hat{H}_{\text{pl}}\right]$, $\left[\hat{H}_{\text{pl}}\right]$ and $\left[\hat{d}^a\right]$ are the matrix representations (in the adiabatic-Fock basis) of $\nabla^a\hat{H}_{\text{pl}}$, \hat{H}_{pl} , and the non-adiabatic coupling operators, respectively, along the a_{th} nuclear DOF, and we have defined the matrix

$$X^a \equiv \left[\hat{d}^a\right]\left[\hat{H}_{\text{pl}}\right] - \left[\hat{H}_{\text{pl}}\right]\left[\hat{d}^a\right] \quad (63)$$

Note that $\left[\hat{d}^a\right]$ is the same as that of Equation (4) but in the full electron-photon Hilbert space as $\hat{d} \otimes \hat{\mathcal{F}}_{\text{ph}}$. As a concrete example, for a polaritonic system composed of two electronic adiabatic states $\{|g\rangle, |e\rangle\}$ and two photonic Fock states $\{|0\rangle, |1\rangle\}$, the 4×4 gradient matrices can be written explicitly, with the $\nabla^a\left[\hat{H}_{\text{pl}}\right]$ expressed as,

$$\nabla^a\left[\hat{H}_{\text{pl}}\right] = \begin{bmatrix} \nabla^a(E_g + D_{gg}) & \nabla^a D_{ge} & \nabla^a \tilde{\mu}_{gg} & \nabla^a \tilde{\mu}_{ge} \\ \nabla^a D_{eg} & \nabla^a(E_e + D_{ee}) & \nabla^a \tilde{\mu}_{eg} & \nabla^a \tilde{\mu}_{ee} \\ \nabla^a \tilde{\mu}_{gg} & \nabla^a \tilde{\mu}_{ge} & \nabla^a(E_g + D_{gg}) & \nabla^a D_{ge} \\ \nabla^a \tilde{\mu}_{eg} & \nabla^a \tilde{\mu}_{ee} & \nabla^a D_{eg} & \nabla^a(E_e + D_{ee}) \end{bmatrix} \quad (64)$$

and $[X^a]$ as,

$$[X^a] = \begin{bmatrix} 2d_{ge}^a D_{eg} & d_{ge}^a(E_e - E_g + D_{ee} - D_{gg}) & 2d_{ge}^a \tilde{\mu}_{ge} & d_{ge}^a(\tilde{\mu}_{ee} - \tilde{\mu}_{gg}) \\ d_{ge}^a(E_e - E_g + D_{ee} - D_{gg}) & 2d_{eg}^a D_{eg} & d_{ge}^a(\tilde{\mu}_{ee} - \tilde{\mu}_{gg}) & 2d_{eg}^a \tilde{\mu}_{ge} \\ 2d_{ge}^a \tilde{\mu}_{ge} & d_{ge}^a(\tilde{\mu}_{ee} - \tilde{\mu}_{gg}) & 2d_{ge}^a D_{eg} & d_{ge}^a(E_e - E_g + D_{ee} - D_{gg}) \\ d_{ge}^a(\tilde{\mu}_{ee} - \tilde{\mu}_{gg}) & 2d_{eg}^a \tilde{\mu}_{ge} & d_{ge}^a(E_e - E_g + D_{ee} - D_{gg}) & 2d_{eg}^a D_{eg} \end{bmatrix} \quad (65)$$

Note that $\tilde{\mu}_{\alpha\beta} \equiv \omega_c A_0 (\hat{\mathbf{e}} \cdot \boldsymbol{\mu}_{\alpha\beta})$ and $D_{\alpha\beta} = \omega_c A_0 \sum_{\gamma} \mathcal{N}_{\text{el}} (\hat{\mathbf{e}} \cdot \boldsymbol{\mu}_{\alpha\gamma})(\hat{\mathbf{e}} \cdot \boldsymbol{\mu}_{\gamma\beta})$, where \mathcal{N}_{el} is the number of electronic adiabatic states (i.e., $\mathcal{N}_{\text{el}} = 2$ in this example), as defined in Equation (18). For additional details regarding the nuclear gradients, we refer to interested reader to References [125, 163]. These nuclear gradients have been the hardest hurdle to overcome in performing on-the-fly simulations with realistic, ab initio systems, since the nuclear gradients on the molecular dipole are not widely available analytically [176]. However, some recent work has been done in achieving MQC dynamics at the Jaynes-Cummings level (i.e., without the dipole self-energy term and ignoring the highly oscillatory terms in the light-matter interaction Hamiltonian) through iterative schemes [32] or through the approximation of the gradient via a Taylor expansion [177]. However, for further theoretical advancement, the community requires work toward the efficient and analytic evaluation of these nuclear gradients to enable another theoretical leap in the simulation of polariton dynamics for realistic systems.

Figure 4 presents an example of the effects of the nuclear gradients on the quantum dynamics of the system [125]. As before, the one-electron Shin-Metiu model is used and provides access to a realistic ab initio system, albeit simplified. Figure 4a–c shows the bare electronic properties, lowest two potential energy surfaces $E_a(R)$, the non-adiabatic coupling $d_{ge}(R)$ (Equation 4), and the molecular dipole matrix elements $\mu_{\alpha\beta}(R)$. Figure 4d extends Figure 4a to include the quantized cavity photon in the four-state basis of $|g, 0\rangle$, $|e, 0\rangle$, $|g, 1\rangle$, and $|e, 1\rangle$. The colorbar indicates the average photon number $\langle \hat{a}^\dagger \hat{a} \rangle$. The gradients in this basis take the form of Equation (62). Figure 4e shows only a few of these matrix elements as a function of the nuclear coordinate. For example, the $\nabla[V]_{e0,g1} \equiv \nabla[H_{\text{pl}}]_{e0,g1}$ is the off-diagonal gradient of the Hamiltonian shown in Equation (64), and the other elements are of the quantity $X = [d][H_{\text{pl}}] - [H_{\text{pl}}][d]$ which relates to the cavity-mediated non-adiabatic couplings. Due to the light-matter couplings, the $|g, 0\rangle$ and $|g, 1\rangle$ are coupled through the gradient on the permanent dipole moment μ_{gg} as well as through the non-adiabatic coupling multiplied by the transition dipole moment μ_{ge} , in total, proportional to $\nabla\mu_{gg}(R) + 2d_{ge}(R)\mu_{ge}(R)$. This can be seen directly in the $X_{g0,g1}$ curve in Figure 4e given that the permanent dipole moment μ_{gg} has a constant gradient near $R = 0.0$ and thus provides a plateau for $X_{g0,g1}$ in the same region. Most importantly, the redistribution of d_{ge} among all the basis states allows for a complex and interesting non-adiabatic events that would be absent without the light-matter coupling. Finally, Figure 4e shows the quantum dynamics simulation using the exact nuclear gradients (solid curves, Equation 62) in addition to showing the approximate population dynamics using the approximate gradients of the Jaynes-Cummings Hamiltonian in the $|e, 0\rangle$, $|g, 1\rangle$ subspace (dashed curves, see Ref. [125] for more details). Clearly, additional states beyond the JC subspace will be explored by the quantum dynamics of the hybrid system due

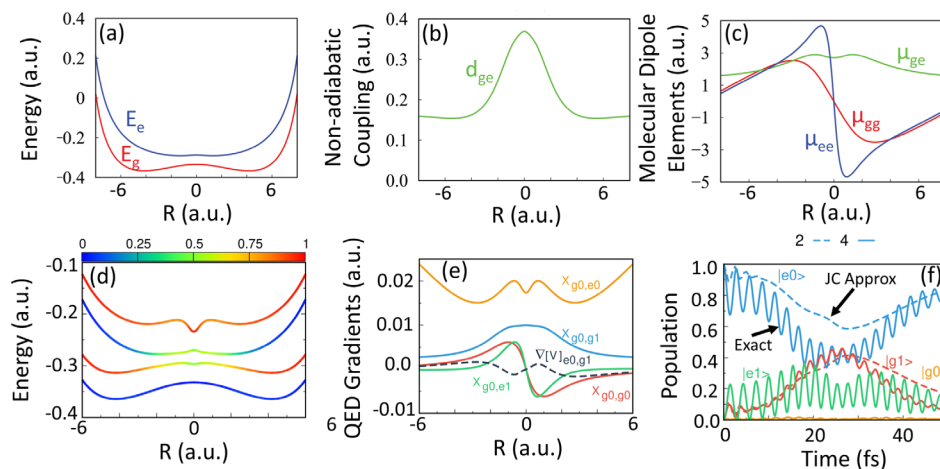


FIGURE 4 | (a) Two-state, one-dimensional Shin-Metiu (SM) model along with the (b) non-adiabatic coupling matrix element d_{ge} element and (c) dipole matrix elements μ_{gg} , μ_{ge} , μ_{ee} as functions of the nuclear coordinate R (d) SM model coupled to an optical cavity of frequency $\omega_c = 0.1$ a.u. and coupling strength $A_0 = 0.05$ a.u. using a highly truncated basis of two electronic states $\{|g\rangle, |e\rangle\}$ and two photonic Fock states $\{|0\rangle, |1\rangle\}$. The average photon number in the length gauge $\langle \hat{a}^\dagger \hat{a} \rangle$ is shown with the colorbar, where $\langle \hat{a}^\dagger \hat{a} \rangle = 0.0$ represents purely electronic character. (e) Various contributions to the nuclear gradient as functions of nuclear position R . (f) Exact quantum solution for the population dynamics using the approximate (dashed curves) gradient at the Jaynes-Cummings level (i.e., with completely uncoupled $|g, 0\rangle$ and basis $|e, 1\rangle$ states) and the Pauli-Fierz gradient (solid curves). Panels (a)-(f) were taken from Reference [125].

to the NACs among these states. The population of the $|e1\rangle$ state is mainly contributed from the population transfer from the $|e0\rangle$ state due to the light-matter coupling originating from the permanent dipole μ_{ee} . In addition, the population transition between $|e0\rangle$ and $|g1\rangle$ is mediated by the cavity-induced coupling near $R = 0.0$, where the PES exhibits a strong mixing between these two states as shown in Figure 4d.

As a concrete example of the above-mentioned MQC dynamics applied to a “realistic ab initio” system, the authors of Reference [163] explore the one-electron Shin-Metiu model system (shown in Figure 5a). This model system is composed of four charged particles: two heavy ions with fixed positions in space (red and blue) with unit positive charge, as well as a mobile proton (black) and a quantum mechanical electron (green). Below the system, Figure 5a shows the potential energy of the proton (black curve) as well as that of the electron (green curve) as a function of the proton coordinate R . For a detailed explanation of the parameters of this asymmetric Shin-Metiu model, we refer the interested reader to Reference [163]. The two lowest energy Born-Oppenheimer potential energy surfaces (i.e., the ground and first excited adiabatic states), E_g and E_e , are shown in Figure 5b, which exhibit an avoided crossing near $R = 2.0$ a.u.

Using these two electronic states as well as two photon number states, $|0\rangle$ and $|1\rangle$, as a basis, the four polaritonic Born-Oppenheimer surfaces were constructed at a light-matter coupling strength $A_0 = 0.01$ (Figure 5c) with the curves colored by their average photon number, $\langle \hat{a}^\dagger \hat{a} \rangle$ (see colorbar). The cavity frequency is $\omega_c = 0.1$ a.u. After vertical excitation from the $R = -4.0$ a.u. to the $|e, 0\rangle$ basis state (i.e., a linear combination of polaritonic states), the quantum dynamics of the system was performed using the (Figure 5d) MQC spin-LSC, (Figure 5e) MQC Ehrenfest, and (Figure 5f) MQC FSSH approaches [163]. The MQC results are shown in circles while the exact results are shown as solid curves. For these MQC simulations, the exact

nuclear gradient was implemented (as discussed in the previous section, Section 4.3) in order to compute the exact polaritonic nuclear force. At short times (< 20 fs), the nuclear wavepacket starts in and quickly leaves the region of strong light-matter coupling, showcasing a fast decay in coherent oscillations from the light-matter coupling. At ~ 20 fs, the nuclear wavepacket crosses the electronic non-adiabatic region near $R = 2.0$ a.u. where much of the population decays to the total ground state, $|g, 0\rangle$, before the simulation ends. In this example, spin-LSC MQC dynamics performs better than either Ehrenfest or FSSH. It should be noted here that FSSH can generally be improved by using various decoherence corrections [165]. Specifically, spin-LSC is able to capture the weak population of the $|e, 1\rangle$ state (green) while Ehrenfest (and to a lesser extent FSSH) dramatically overpopulates this state. Furthermore, Ehrenfest and FSSH do not accurately predict the electronic non-adiabatic crossing time, instead showing a delay of 5–10 fs.

5 | Toward Realistic Polaritons

5.1 | Machine Learning

As pointed out in previous sections (e.g., Section 4), performing trajectory-based ab initio polaritonic dynamics requires multiple properties of the molecular system, including the energy matrix, $\langle \hat{H} \rangle_{\alpha\beta}$, transition dipole matrix, $\langle \hat{\mu} \rangle_{\alpha\beta}$, and the nuclear gradients of both $\langle \nabla_{\mathbf{R}} \hat{H} \rangle_{\alpha\beta}$ and $\langle \nabla_{\mathbf{R}} \hat{\mu} \rangle_{\alpha\beta}$. The gradient on the energy leads to the usual state gradients $\nabla_{\mathbf{R}} E_\alpha$ as well as the first-order non-adiabatic couplings $\nabla_{\mathbf{R}} \mathbf{d}_{\alpha\beta}$ (Equation 4). These non-adiabatic couplings may be analytically available in some electronic structure software, such as QCHEM [178], MOLPRO [179, 180], NEXMD [164], and so forth but not all, and largely depend on the level of electronic structure itself. Further, the nuclear gradients of the transition dipole matrix elements, to our knowledge, is not implemented in an analytical form in any common electronic structure software.

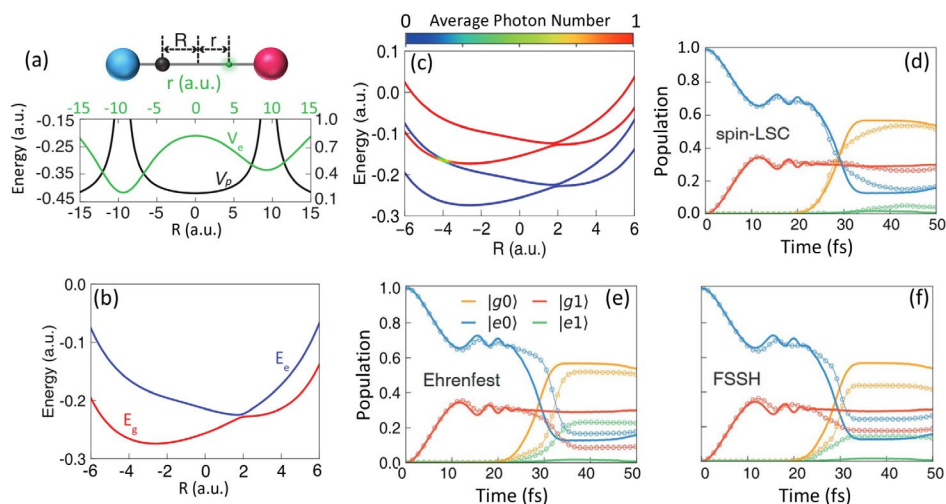


FIGURE 5 | (a, top) Depiction of the one-electron Shin-Metiu model system, with two fixed nuclei (red and blue) of unit positive charge, one proton at position R (black), and one electron (green) at position r . (a, bottom) The potential energy of the proton V_p (black) and of the electron V_e (green). (b) The ground and first electronic states of the Shin-Metiu model system as functions of the proton position R , showcasing an avoided crossing near $R = 2.0$ a.u. (c) Polaritonic potential energy surfaces as a function of the proton coordinate R for two choices of light-matter coupling strength $A_0 = 0.01$ a.u. (d–f) Population dynamics for various MQC methods (d) spin-LSC, (e) Ehrenfest, and (f) FSSH. The initial conditions are $|e, 0\rangle$ at the proton position $R = -4$ and for the same choice of light-matter coupling strength as panel (c). The exact results are shown in solid curves whereas the approximate MQC results are shown as circles. All polaritonic states were described in a truncated basis of two electronic states $|g\rangle$ and $|e\rangle$ and two photon vacuum states $|0\rangle$ and $|1\rangle$. Panels (a)–(f) were taken from Reference [163].

With this current limitation in obtaining the exact polaritonic gradient (see Section 4.3), we turn toward the use of machine learning, which will allow one to train the molecular dipole as a function of the nuclear coordinates. Then the nuclear gradient can be obtained analytically from the gradient of the trained dipole function. One of the many possible techniques is the kernel ridge regression (KRR) scheme, which relies on supervised learning of the molecular dipole matrix and has been used in several recent works [181–183]. In this approach, the molecular property, $\mu_{\alpha\beta}^{x_k}(\mathbf{R})$ (the $\alpha\beta$ th matrix element of the transition dipole moment in the x_k^{th} spatial direction), is trained based on a function of the nuclear coordinates which are represented by a molecular descriptor m such that,

$$\mu_{\alpha\beta}^{x_k}(m) = \sum_s \mathcal{N}_s w_s K(m, m^{(s)}), \quad K(m, m^{(s)}) = e^{-\frac{|m - m^{(s)}|^2}{2\sigma^2}} \quad (66)$$

where $m^{(s)}$ is the molecular descriptor for the s_{th} nuclear configuration (with \mathcal{N}_s total training configurations), K is the Gaussian kernel function with w_s as the regression coefficient and σ as the width. This choice of kernel function is a radial basis function and only depends on the absolute distance between m and m_s with a single parameter σ . The coefficients w_s are trained by minimizing a cost function C defined as,

$$C \equiv \sum_s \left[\mu_{\alpha\beta}^{x_k}(m^{(s)}) - \mu_{\alpha\beta}^{\text{ref}}(\mathbf{R}) \right]^2 + \lambda \mathbf{W}^T \mathbf{K} \mathbf{W} \quad (67)$$

Here $\mu_{\alpha\beta}^{\text{ref}}(\mathbf{R})$ is the reference molecular property value (often calculated numerically by finite-difference methods), λ is a Lagrange multiplier, and \mathbf{W} is the matrix of regression

coefficients. The choice of molecular descriptor m for the nuclear geometry can be one of many, but one of the simplest choices is the Coulomb matrix, $m_{\mathbf{R}_a \neq \mathbf{R}_b} = Z_a Z_b / |\mathbf{R}_b - \mathbf{R}_a|$ where \mathbf{R}_a is the spatial coordinates of nucleus a and Z_a its nuclear charge. Once the dipole matrix elements are trained as a function of molecular descriptor, $\mu_{\alpha\beta}^{x_k}(m)$, the nuclear gradient can be obtained by the chain rule as,

$$\frac{\partial \mu_{\alpha\beta}^{x_k}(m)}{\partial R_a^{x_j}} = \sum_l \frac{\partial \mu_{\alpha\beta}^{x_k}(m)}{\partial m_l} \frac{\partial m_l}{\partial R_a^{x_j}} \quad (68)$$

Here m_l is an element of the molecular descriptor and $R_a^{x_j}$ are the coordinates of nucleus a in the direction x_j . For additional details on using the KRR method for molecular properties in polaritonics, we refer the reader to Reference [184].

Figure 6 presents recent work [184] by Hu and Huo using the KRR approach to parameterize the transition and permanent dipoles of the azomethane molecule (Figure 6a), which exhibits a conical intersection between the ground S_0 and excited S_1 electronic states as a function of the dihedral angle. Inside the cavity (Figure 6b), the ground and excited states hybridize (black box) to form exciton-polaritons $\{\mathcal{E}_j\}$ with mixed electronic (primarily S_0 and S_1) and well as photonic character (primarily $n = 0$ and 1 vacuum Fock states). To perform the quantum dynamics simulations, the molecular dipole and its gradient were trained based on the KRR approach to yield the analytic dipole matrix elements, shown in Figure 6c against the exact results using the CASSCF electronic structure method as the training/exact data. The total polaritonic gradient of the first $\nabla_{\mathbf{R}} \mathcal{E}_1$ and second $\nabla_{\mathbf{R}} \mathcal{E}_2$ excited polaritonic states is shown in Figure 6d (see Equation 64). Using these learned values, the quantum dynamics simulation

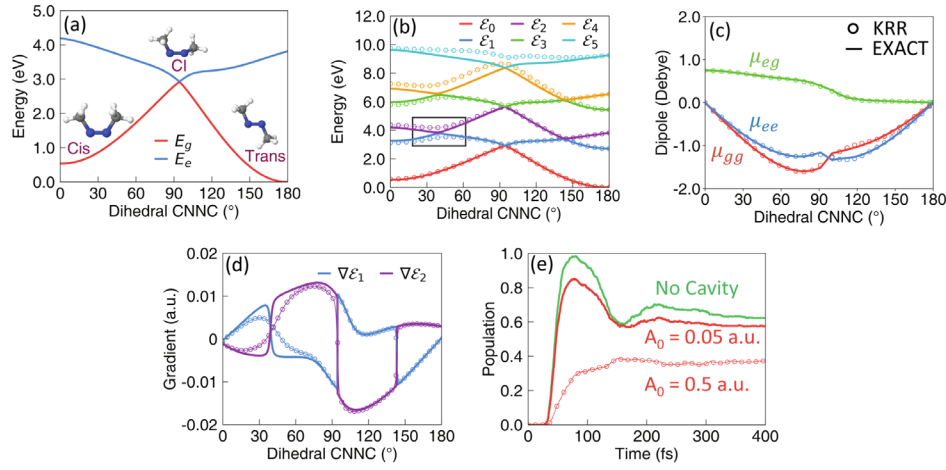


FIGURE 6 | (a) Ground and first excited potential energy surface of bare azomethane as computed by CASSCF along its CNNC dihedral angle coordinate, showcasing a conical intersection (CI). (b) Polaritonic potential energy surfaces at light-matter coupling strength $A_0 = 0.05$ a.u. (solid curves) and $A_0 = 0.5$ a.u. (circles). (c) Dipole matrix elements along the CNNC dihedral coordinate and projected along the Y-axis of the molecule (perpendicular to the molecular plane) computed by CASSCF (solid curves) and the machine learning framework (open circles). (d) The nuclear gradient on the polariton potential energy surfaces. (e) Population dynamics at varying coupling strengths $A_0 = 0.05$ a.u. (red solid curve, middle) and $A_0 = 0.5$ a.u. (open circles, bottom) as well as outside the cavity (green, top). Panels (a)-(d) were taken from Reference [185]. Panels (e)-(f) were taken from Reference [184].

of the photoisomerization of azomethane results are shown in Figure 6e. Inside the cavity, at a small coupling strength of $A_0 = 0.05$ a.u., the avoided crossing between the first and second excited polaritonic states (black box in Figure 6b) reduces the amount of product formed by the photo-reaction by bifurcating the wavepacket before reaching the conical intersection. At an increased coupling strength ($A_0 = 0.50$ a.u.), this effect is increased, reducing the overall population of the trans-product to less than 40% from the original product yield of 60% by increasing the population transfer at the polaritonic avoided crossing region.

5.2 | Simulating Cavity Loss With Trajectory Methods

Lindblad decay theory can be used to simulate the effects of photonic loss channels in semi-classical dynamics methods. The most general Markovian description of a dissipative environment (i.e., modes external to the cavity) interacting with the electron-photon subsystem $\hat{\rho}(t)$ of interest that is both norm-preserving and always provides a positive-valued population is the Lindblad master equation. For the current problem, this can be written as,

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] + \Gamma \left(\hat{L} \hat{\rho} \hat{L}^\dagger - \frac{1}{2} \{ \hat{L}^\dagger \hat{L}, \hat{\rho} \} \right) = \mathcal{L}_{\text{Coh.}} [\hat{\rho}] + \mathcal{L}_{\text{Diss.}} [\hat{\rho}] \quad (69)$$

where $\hat{\rho}$ is the reduced density operator of the quantum subsystem including the electronic and photonic DOFs, \hat{H} is the polaritonic Hamiltonian including the non-adiabatic terms, \hat{L} is a Lindblad jump operator that mediates the dissipation due to an effective environment (i.e., loss channel), Γ is the dissipation rate, $\{ \hat{A}, \hat{B} \} = \hat{A}\hat{B} + \hat{B}\hat{A}$ is the anti-commutator of matrices \hat{A} and \hat{B} and $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is the commutator. $\mathcal{L}_{\text{Coh.}}$ and $\mathcal{L}_{\text{Diss.}}$ are super-operators in Liouville space which describe the quantum mechanical evolution of the electron-photon subsystem

under the Hermitian Hamiltonian \hat{H} which governs the coherent evolution of the system and \hat{L} which governs the dissipation (i.e., incoherent evolution). Lindblad dynamics ensure the conservation of the total population of the system. The Lindblad jump operator that governs the photon dissipation channel in Fabry-Perot cavities is defined as,

$$\hat{L} = \hat{L}_{\text{el}} \otimes \hat{a} = \hat{L}_{\text{el}} \otimes \sum_n^{\mathcal{N}_F} \sqrt{n} |n-1\rangle \langle n| \quad (70)$$

where \hat{a} is the photonic annihilation operator and \hat{L}_{el} is the identity operator for the electronic subspace. This jump operator \hat{L} facilitates population transfer from one photonic Fock state to the one below ($|n\rangle \rightarrow |n-1\rangle$) while also creating decoherence between the original state ($|n\rangle$) and all other states ($|m \neq n\rangle$).

The evolution of the reduced density matrix $\hat{\rho}$ in the Liouville space can be written as,

$$\hat{\rho}(t+dt) = e^{(\mathcal{L}_{\text{Coh.}} + \mathcal{L}_{\text{Diss.}})dt} [\hat{\rho}(t)] \approx e^{\frac{1}{2} \mathcal{L}_{\text{Diss.}} dt} e^{\mathcal{L}_{\text{Coh.}} dt} e^{\frac{1}{2} \mathcal{L}_{\text{Diss.}} dt} [\hat{\rho}(t)] \quad (71)$$

where a short-time evolution by dt can be approximated to first-order by the symmetric, factorized product of individual exponentiated Liouville operators. This leads to a time-reversible and symplectic propagation for the simulated cavity loss, at a similar level to a velocity-Verlet-like scheme. The time-evolution can then be obtained as a step-wise propagation using the following equations of motion,

$$\dot{\rho}(t) = \frac{\Gamma}{2} \left(\hat{L} \hat{\rho}(t) \hat{L}^\dagger - \frac{1}{2} \{ \hat{L}^\dagger \hat{L}, \hat{\rho}(t) \} \right), \quad \dot{\rho}(t) = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}(t)], \quad (72)$$

We can expand the equations of motion in the adiabatic-Fock basis (Section 3.1.1). We define the matrix elements of the

polaritonic Hamiltonian including the first-order non-adiabatic couplings as $H_{an,\beta m} = (H_{pl})_{an,\beta m} - i\hbar \mathbf{d}_{\alpha\beta} \cdot \dot{\mathbf{R}} \delta_{nm}$, where we have used the fact that the Fock states have no dependence on the nuclear coordinates $\mathbf{d}_{an,\beta m} = \mathbf{d}_{\alpha\beta} \delta_{nm}$ and that $\dot{\mathbf{R}}$ is the classical velocity of the nuclei. Further, the matrix elements of the Lindblad jump operator can be written as $L_{an,\beta m} = \sqrt{m} \delta_{n,m-1} \delta_{\alpha\beta}$, which has no effect on the electronic states. Figure 7 presents results of the computational method by combining (Figure 7a–d) Ehrenfest and (Figure 7e,f) surface hopping dynamics with a stochastic extension to the previously outlined Lindblad decay. For details pertaining to the stochastic analogue to the aforementioned Lindblad loss approach, see Reference [185]. This approach stochastically maps the dynamics in Liouville space to dynamics in the Hilbert space. We refer to this method as the \mathcal{L} -MFE approach. The convergence of this approach [185] with respect to the number of trajectories is similar to any mixed quantum-classical method; thus, the addition of the stochastic cavity loss does not increase the computational cost. This is a general scheme that can be easily incorporated into any trajectory-based dynamics approaches, such as Ehrenfest, FSSH, or mapping approaches, or additionally to any trajectory-guided wavepacket-based methods, such as ab initio multiple spawning or ab initio multiple cloning.

The model system [13] portrays an isomerization reaction containing two electronic states $|g\rangle$ and $|e\rangle$ and two photonic Fock states $|0\rangle$ and $|1\rangle$ with a spin-boson bath for the nuclear DOFs to mediate electronic transitions. Due to the use of the Jaynes-Cummings Hamiltonian in the single-excited subspace, the ground state is “uncoupled” from the excited states

via direct light-matter interaction; however, due to the cavity loss, the Lindblad decay mediates population transfer from $|g, 1\rangle \rightarrow |g, 0\rangle$ with a rate of Γ .

Figure 7a,b shows the potential energy surfaces of the three states with light-matter coupling A_0 set to 0.0 eV (Figure 7a) and 0.136 eV (Figure 7b) with a cavity frequency of $\omega_c = 1.632$ eV. Figure 7c,d presents the polariton population dynamics in the adiabatic-Fock basis with loss rates of $\Gamma = 0$ meV (Figure 7c) and $\Gamma = 1$ meV (Figure 7d). The numerically exact results are obtained using the discrete variable representation (DVR) basis [123] for the nuclear DOF and Fock states for the photonic basis. As shown in Figure 7c, the \mathcal{L} -MFE dynamics (dotted line) capture the essential physics of the problem but deviate from the exact simulations (solid) at a longer time, which is a known problem of the mean-field Ehrenfest approach and is not the main point of this discussion. The dynamics portrayed with a loss rate of $\Gamma = 0.0$ meV (Figure 7c) reduce exactly to the dynamics of a closed quantum system with zero population residing in the uncoupled ground state, at any time t . At increased cavity loss of $\Gamma = 1$ meV (Figure 7d), the system slowly populates the ground polaritonic states by funneling population from $|g, 1\rangle$ to $|g, 0\rangle$. This gives rise to plateaus in the ground state population curve when the majority of the population is present in the $|e, 1\rangle$ state during the coherent population transfer processes, most pronounced at short times $t < 1.0$ ps.

Figure 7e,f provides a direct application of this method to an ab initio on-the-fly dynamics study of the isomerization of azomethane (a direct extension to the results shown in Figure 6)

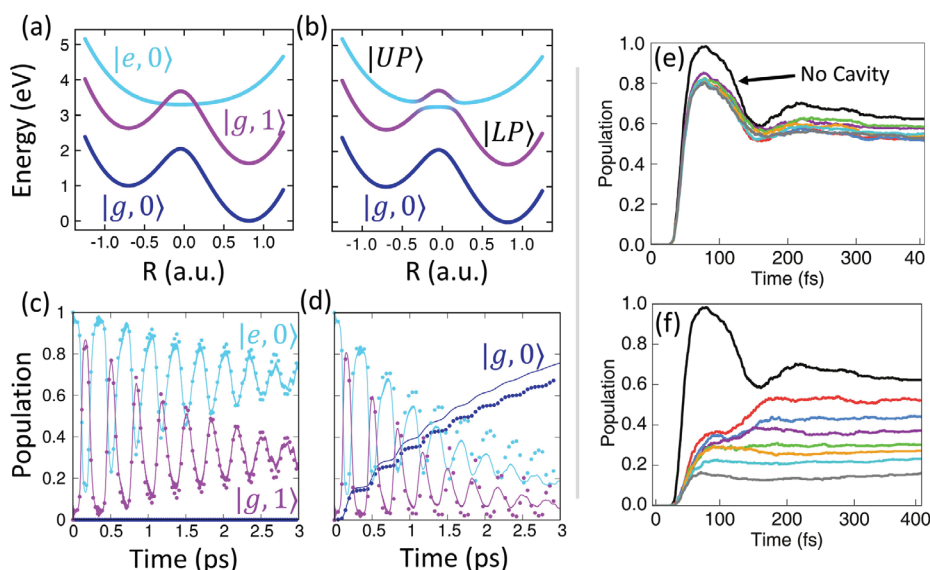


FIGURE 7 | Potential energy surfaces (PESs) and population dynamics of the model isomerization reaction coupled to the cavity. Panel (a) presents the diabatic PESs where the dark blue line is the $|g, 0\rangle$ PES, the cyan line is the $|e, 0\rangle$ PES, and the magenta line is the $|g, 1\rangle$ PES. Panel (b) presents the adiabatic PESs where the dark blue line is the uncoupled ground state $|g, 0\rangle$ PES, the middle line (labeled $|LP\rangle$) is the lower polariton PES, and the upper line (labeled $|UP\rangle$) is the upper polariton PES. The colors along the adiabatic PESs represent the diabatic character at each nuclear position. Panels (c, d) present the polaritonic population dynamics with a decay rate of (c) $\Gamma = 0$ and (d) $\Gamma = 1$ meV. The solid lines are exact Lindblad dynamics, while the dotted lines are the approximate L-MFE method. The colors of the curves represent the population of various adiabatic-Fock basis states: $|g, 0\rangle$ (dark blue), $|e, 0\rangle$ (cyan), and $|g, 1\rangle$ (magenta). For the same on-the-fly ab initio isomerization as shown in Figure 6, panels (e, f) show the trans isomer population dynamics for various cavity loss rates $\Gamma = 0, 2, 4, 8, 16, 32$, and 64 meV (colors, top to bottom) at light-matter coupling strengths of $A_0 =$ (e) 0.05 a.u. and (f) 0.5 a.u. The results outside the cavity are shown as a solid black curve. Panels (a)–(d) were taken from Reference [185]. Panels (e)–(f) were taken from Reference [184].

[184]. The polaritonic potential energy surfaces can be found in Figure 6b. The loss rate Γ was varied (colors) from $\Gamma = 0.0$ to 64 meV for a light-matter coupling strengths $A_0 =$ (Figure 7e) 0.05 a.u. and (Figure 7f) 0.5 a.u. At low coupling strength, the effects of the cavity loss are minimal. The dynamics at increased coupling strength allow for additional population to transfer to $|g, 1\rangle$, leading to fast decay into the cis-ground state $|g, 0\rangle$ without allowing enough time for the nuclear rearrangement to the trans-isomer before relaxing. This almost completely removes the isomerization pathway previously available to the system, effectively turning off the isomerization process for increased cavity loss rate.

In the present cases, the effects of cavity loss provide an additional factor when considering cavity-modified reaction rates—in the present ab initio case, the cavity loss coincides with the effects of the light-matter coupling strength, which decreases the reaction yield. Overall, explicitly including cavity loss in realistic polaritonic dynamics is required for a rigorous and consistent comparison to experiment, where the cavity loss rates are substantial enough to cause dramatic effects on the population dynamics and subsequent photo-reaction pathways accessible to the system.

5.3 | Extending to Many-Molecule and Many-Mode Simulations

In reality, optical cavities are composed of many photonic modes/wavevectors (i.e., cavity dispersion relations) whose form depends on the type of cavity. For example, in typical Fabry-Perot (parallel mirror cavities, Figure 8a), the dispersion relation can be written as $E_{ph}(\theta) = \frac{\hbar}{n_c} c \sqrt{k_z^2 + k_x^2} = \frac{\hbar}{n_c} c k_z \sqrt{1 + \tan^2 \theta}$, which

depends on the angle of the external probe, $\theta = \tan^{-1}(k_x/k_z)$. Here c is the speed of light in vacuum, n_c is the refractive index inside the cavity, and $\hbar \mathbf{k}$ is the momentum of the photon. It should be noted that there are many other cavity designs, most notably the plasmonic cavity, which contain many varied geometrical arrangements of nanoparticles-on-metal surfaces, which lead to a wide variety of cavity dispersion relations [187]. As shown in Figure 8a, the total wavevector $\mathbf{k} = \langle k_x, k_z \rangle$ is related to the quasi-continuous parallel k_x and strictly quantized perpendicular k_z modes. Additionally, there may be many molecules \mathcal{N}_{mol} collectively coupled to these cavity modes \mathcal{N}_{mode} . The scaling of such a Hilbert space (given by the Hamiltonian in Equation 17) can be written as $\dim[\hat{H}] \propto \mathcal{N}_{el}^{\mathcal{N}_{mol}} \times \mathcal{N}_F^{\mathcal{N}_{mode}}$, which is exponential in both the number of molecules as well as the number of photon modes. While not the focus of this review, for extended systems (i.e., solids), the incorporation of k-points raises further issues regarding the conservation of momentum between the electron and photon systems. This has been discussed in a few recent works [188, 189]. In any case, making the long wavelength approximation nullifies any mismatch between the electron and photon momenta.

To overcome this unfeasible scaling, many works have shown that excited polaritonic states at weak-to-moderate light-matter coupling strengths can be simulated in the so-called first-excited subspace of the total Hamiltonian (Equation 17). In singly excited subspace, the overall scaling can be written as $\dim[\hat{H}] \propto \mathcal{N}_{el} \mathcal{N}_{mol} \mathcal{N}_F \mathcal{N}_{mode}$, which is now linear scaling in all quantities. The zeroth S_0 and singly excited S_1 subspaces can be explicitly written as,

$$|S_0\rangle = \bigotimes_A^{\mathcal{N}_{mol}} |g\rangle^{(A)} \otimes \bigotimes_M^{\mathcal{N}_{mode}} |0\rangle^{(M)} \quad (73)$$

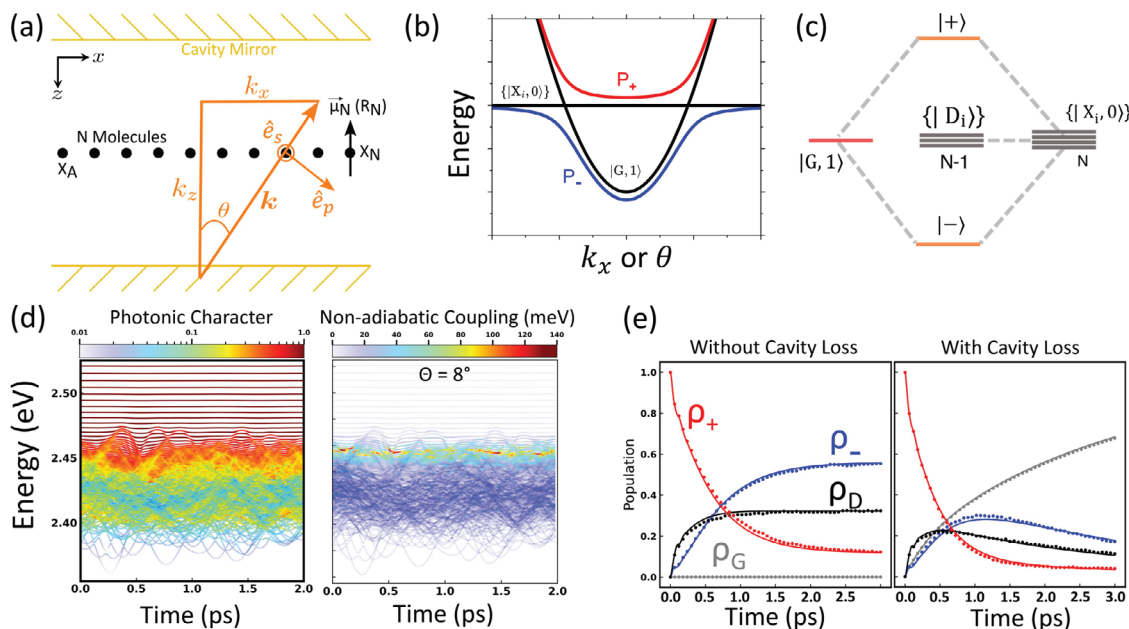


FIGURE 8 | (a) Schematics of N molecules coupled to a FP cavity. (b) Polariton Eigenspectrum predicted by the Tavis-Cummings (TC) model. (c) Polariton Eigenspectrum predicted by the Jaynes-Cummings (JC) model. (d) Time-dependent polaritonic energies are colored by (left) photonic character and (right) non-adiabatic coupling from a representative trajectory. (e) Time-dependent polaritonic populations of the ground state (gray), upper polariton states (red), lower polariton states (blue), as well as the total population of the dark states (black). Panels (d, e) were taken from Reference [186].

$$|S_1\rangle = \sum_A \left(\bigotimes_{B<A}^{\mathcal{N}_{\text{mol}}} |g\rangle^{(B)} \otimes |e\rangle^{(A)} \otimes \bigotimes_{B>A}^{\mathcal{N}_{\text{mol}}} |g\rangle^{(B)} \right) \otimes |0\rangle + \sum_A^{\mathcal{N}_{\text{mol}}} |0\rangle^{(A)} \otimes \sum_M^{\mathcal{N}_{\text{mode}}} \left(\bigotimes_{M<N}^{N-1} |0\rangle^{(M)} \otimes |1\rangle^{(N)} \otimes \bigotimes_{M>N}^{\mathcal{N}_{\text{mode}}} |0\rangle^{(M)} \right) \quad (74)$$

where we assumed only a single molecular ground and excited state per molecule $\{|g\rangle, |e\rangle\}$ and a single excited photon $\{|0\rangle, |1\rangle\}$ per mode, which is already a major approximation for most molecules with many nearby excited states. Higher-order subspaces have also been explored [190], but even including the second excited subspace produces highly unfavorable scaling with a realistic number of molecules $\mathcal{N}_{\text{mol}} \sim 10^6$. Figure 9 presents the numerical scaling (i.e., the number of possible configurations/basis states) as solid curves as well as the required memory to store the Hamiltonian (dashed curves) as a function of the number of molecules. Here, we assume only two electronic states per molecule, a single photonic mode with two Fock states, and a real-valued Hamiltonian (i.e., complex would simply double the memory requirements). The thick gray line represents 100 GB of memory, a typical node on a typical high-performance computing cluster. In the S_1 subspace (black), the 100-GB line is reached with a little over 10^5 molecules, while for the second excited subspace S_2 (red), this line is reached with a little less than 1000 molecules. The third subspace S_3 (green) only allows for 100 molecules. The full Hilbert space scales exponentially (blue). This exemplifies the need for the truncation of the total Hilbert space in order to perform meaningful theoretical explorations with realistic cavity designs and environments.

Upon the diagonalization of the many-molecule, many-mode Hamiltonian (Equation 17) in the singly excited subspace S_1 , polariton eigenenergies and eigenstates are obtained, as shown in Figure 8b for a collection of quasi-continuous parallel cavity

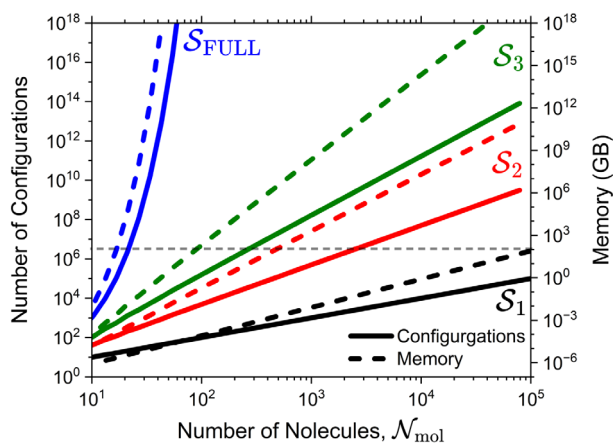


FIGURE 9 | Numerical scaling of the Pauli-Fierz Hamiltonian in various subspaces: S_1 (black), S_2 (red), S_3 (green) as well as the full Hilbert space S_{FULL} (blue) as a function of the number of molecules. The number of configurations/basis states is shown as solid curves, and the required memory to store the Hamiltonian is shown as dashed curves. The thin, dashed gray line represents 100 GB of memory. Here, we assume only two electronic states per molecule, a single photonic mode with two Fock states, and a real-valued Hamiltonian (i.e., the complex-valued Hamiltonian would simply double the memory requirements).

modes and Figure 8c for a single resonant mode. Here, the formation of the upper and lower polariton branches $P_{+/-}$ (Figure 8b) or states $|+/-\rangle$ (Figure 8c) can be observed. Furthermore, due to the presence of the other molecules (which are all degenerate with the cavity frequency), many degenerate polaritonic states can be found at the same energy as the bare molecular transition. These states are referred to as “dark states” $\{D_i\}$ since they contain no transition dipole moment between the polaritonic ground state, nor do they contain any photonic character (in the absence of molecular disorder). The Rabi splitting in this case famously scales as $\Omega_R \propto \sqrt{\mathcal{N}_{\text{mol}}}$ [29, 40]. In the presence of molecular fluctuations (e.g., thermal fluctuations), the photonic character becomes distributed among the “dark states.”

Figure 8d shows the time-dependence of the polariton eigenenergies colored by the (left) photonic character $\langle \psi_j | \hat{a}^\dagger \hat{a} | \psi_j \rangle$ and (right) non-adiabatic coupling $\sigma_j = \sum_k \langle \psi_j | \frac{d}{dt} | \psi_k \rangle$ for each polaritonic state j (both on log colorbar scales). The exchange of character mediates population dynamics between such polariton states (i.e., cavity-mediated non-adiabatic couplings). Figure 8e presents mixed quantum-classical mapping approach to surface hopping (MASH) [156, 157] dynamics where a LASER drives population from the collective ground state $|G\rangle$ to the upper polariton $|+\rangle$ (left) without and (right) with cavity loss. The dynamics suggest that the dark states quickly accumulate much of the population at initial times. Without cavity loss, the polaritonic states reach equilibrium by 3.0 ps, while with cavity loss, none of the states retain significant population due to the rapid transfer to the ground state and the ongoing polariton-polariton non-adiabatic couplings.

As discussed above in Figure 9, the explicit inclusion of many molecules yields unfavorable conditions for the direct diagonalization (Section 3.1) of the Hamiltonian. In the case of self-consistent approaches (Section 3.2), one encounters a similar bottleneck where the inclusion of many sets of one-molecule single-particle orbitals $N_{\text{sp}} = N_{\text{occ}} \times N_{\text{vir}}$ leads to a many-molecule ground state density matrix of $\dim[\hat{\rho}] \propto N_{\text{sp}} \times \mathcal{N}_{\text{mol}}$. The off-diagonal blocks of which will include the long-range Coulomb, short-range exchange, and intermolecular DSE interactions. In recent work [191], it was argued that the off-diagonal blocks of the total density matrix can be decoupled in the cavity Born-Oppenheimer (BO) approximation [62] in which the cavity photon is treated as a parameter (similar to the nuclear BO approximation). Thus, the diagonal blocks of the density matrix and treated as effectively independent, reducing the memory cost of the self-consistent treatment back to $\dim[\hat{\rho}] \propto N_{\text{sp}}$ but with \mathcal{N}_{mol} such matrices. However, without approximations, such as cavity BO, treating many molecules coupled to many cavity modes is still beyond the reach of direct simulation. Relying on efficient semi-empirical or tight-binding approaches [192–195] may provide the most direct route toward the direct simulation of many molecule QED, including both ground and excited states, and has already been used to simulate plasmonic systems [196–198].

5.4 | Intermolecular Interactions

In experiment, often the molecules are spatially confined in a polymer matrix (e.g., Poly(methyl methacrylate), PMMA).

In such cases, the molecules are often close enough to exhibit strong dipolar interactions with one another. Alternatively, molecular aggregates can be formed directly [199]. In these cases, from the perspective of polaritonic structure theory, the inclusion of molecular interactions must be considered carefully. The most rigorous approach is to consider all molecules simultaneously in a self-consistent sense (Section 3.2), which will naturally capture all molecule-molecule interactions, including those at or beyond dipole, such as the entire Coulomb and exchange interactions. Additionally, the cavity itself provides intermolecular interactions through the DSE term in the Hamiltonian and thus provides a competition between bare molecular interactions and cavity-mediated molecular interactions. These cavity-induced effects on non-bonded interactions (i.e., van der Waals, hydrogen bonding, etc.) were directly explored with the high-level scQED-CCSD approach for two molecules [68]. Though, for the extension to many-molecules, including all molecules in the self-consistency, is difficult and scales poorly with the number of molecules. Hence, one should turn toward an approximate model which captures the leading-order physics, in the same sense as the parameterized QED approach aims to do (see Section 3.1).

Intermolecular interactions have been well-studied for molecules in the absence of a cavity [200], including effects beyond the bare Coulomb interactions [201]. Here, we will focus only on the direct Coulomb interactions at the dipole level for brevity. Such interactions can be written as $\hat{H}_{\text{Agg}} = \hat{H}_{\text{el}} + \hat{J}$, where

$$\hat{J} = \frac{\hat{\mu}_A \cdot \hat{\mu}_B - 3(\hat{\mu}_A \cdot \hat{\mathbf{e}}_A)(\hat{\mu}_B \cdot \hat{\mathbf{e}}_B)}{|\mathbf{R}_A - \mathbf{R}_B|^3}$$

where \hat{H}_{el} is the bare electronic Hamiltonian (diagonal in the adiabatic representation) and \hat{J} is the dipole-dipole interaction term [54]. \mathbf{R}_A is the location of molecule A , and $\hat{\mathbf{e}}_A$ is the unit vector of molecule A (not to be confused with the unit vector of the cavity polarization \mathbf{e}). Adding the interaction term \hat{J} to the many-molecule Hamiltonian in Equation (17) will lead to additional physics and direct competition between the intermolecular DSE terms and the direct Coulomb interactions. These two interactions were shown to cancel each other when there is no electron density overlap (i.e., in the absence of exchange couplings) [108, 202]. However, this textbook result [202] has, to our knowledge, never been explicitly investigated in molecular cavity QED. Thus, in this modified light-matter Hamiltonian, the molecules now communicate between one another through both the light-matter and Coulomb interactions, and each molecule's electronic structure can be evaluated individually with massively parallelized electronic structure calculations [36, 177, 203].

6 | Summary

6.1 | Capabilities and Limitations of Methods

Throughout this review, we introduced many computational approaches aimed at a high-level, ab initio description of exciton-polaritons. However, due to the wide variety of approaches, it is

useful to establish an understanding of the strengths and weaknesses of each approach. We will very briefly discuss when to use each method by comparing their costs and scaling in various situations.

For the self-consistent polaritonic structure approaches, for example, scQED-HF, scQED-CC, the correlations achieved by each are well-known from standard electronic structure theory. Recently, scQED-HF has been shown to overestimate the QED effects (i.e., electron-photon correlations) [87, 89] compared to methods that include higher-level correlations, such as QED-CC. This is because the mean-field contribution in the standard dipole-gauge PF Hamiltonian only includes contributions from the DSE term, which is positive definite. scQED-CC, for example, partially addresses the bilinear term, which acts oppositely to the DSE contribution by including excitations in both the electron and photon degrees of freedom. However, one can perform variational unitary transformations on the PF Hamiltonian [72, 91, 204] to move the majority of the electron-photon correlations (and introduce electron-photon entanglement) into the mean-field part. These transformations allow for the use of post-HF methods with a better reference, which already includes much of the electron-photon and QED-mediated electron-electron correlations.

Next, we will address the applicability of self-consistent QED (scQED) and parameterized QED (pQED) approaches. Simply, the scQED approaches are exceptionally useful for exploring the coupled electron-photon ground state since only a ground state many-body approach is required, for example, scQED-HF or scQED-CC. pQED relies on the knowledge of excited states to build the polaritonic Hamiltonian, thus requiring at least the ability to compute the energies and transition dipole matrix in some representation (often TDDFT energies and dipoles), thus proving to be more expensive than simply using a ground state approach. Further, the ground state QED effects are dominated by the DSE term, which is proportional to the square of the transition dipole matrix $\hat{\mu}^2$. This term relies on highly off-resonant terms in the Hamiltonian and leads to difficult-to-converge situations where the number of excited states needed from TDDFT can reach $N_{\text{el}} \sim 100 - 1000$ and is necessary for strict convergence of the ground state energy [17, 41].

Both pQED and scQED approaches can be readily applied to explore excited states in which a single molecule is coupled to a photon mode, since both require an excited state approach, for example, TDDFT for pQED and scQED-TDDFT, and including the photonic component does not significantly impact the computational cost. However, the more experimentally relevant case is when many molecules $N_{\text{mol}} > 1000$ N_{mode} are coupled with many photon modes $N_{\text{mode}} > 1000$, for example, within a Fabry-Perot optical cavity. In this case, the number of degrees of freedom becomes intractably large, and one already needs to resort to the singly excited subspace. As an example, the scQED-CIS scales as $\sim (N_{\text{mol}}N_{\text{AO}} + N_{\text{Fock}}N_{\text{mode}})^4$ while the near-equivalent pQED calculation scales as $N_{\text{mol}}N_{\text{AO}}^4 + (N_{\text{mol}}N_{\text{el}} + N_{\text{Fock}}N_{\text{mode}})^3$ (performing N_{mol} electronic structure calculations plus the diagonalization of the polaritonic Hamiltonian of dimension $N_{\text{mol}}N_{\text{el}} + N_{\text{Fock}}N_{\text{mode}}$). Not only is the scaling reduced, but the number of atomic orbitals per molecule could be $N_{\text{AO}} \sim 500$ for a reasonably large

molecule, while $N_{\text{el}} \sim 50$ for the same molecule, yielding another order of magnitude difference in scaling. Further, the pQED simulation can be trivially parallelized by calculating each molecule on a different core or node before constructing and diagonalizing the Hamiltonian. In this case, the pQED approach is expected to drastically outperform the equivalent scQED approach.

Finally, we will comment on the use of various methods combined with non-adiabatic approaches. As is well-known in the non-adiabatic community, the need for analytic expressions for non-adiabatic couplings [205] is paramount for combining an electronic structure method with on-the-fly dynamics efficiently. In addition, the efficient calculation of wavefunction overlaps at adjacent nuclear configurations [171] is often useful for electronic propagation via local or quasi-diabatization. The need for these quantities carries over into the electron-photon problem with an additional caveat: the nuclear gradients on the molecular dipole $\nabla_{\mathbf{R}}\hat{\mu}$ are also required. In principle, if all ingredients are available [176], then any quantum dynamics method can be combined to simulate polaritonic systems on-the-fly.

Before we move to the conclusion, we also want to briefly mention recently developed theoretical approaches for simulating vibrational strong coupling (VSC) and vibrational polaritons. There has been exciting progress in the past few years toward simulating VSC and understanding how cavity modes are coupled to the molecular vibrations and lead to changes in the modifications to rate constants. Among them, CavMD [206] is one of the most popular approaches that treats the Hamiltonian in Equation (22) classically, including the cavity mode $\hat{q}_c \rightarrow q_c$ and molecular vibrations. CavMD has successfully produced polariton linear spectra under VSC, providing valuable insights into how cavity modes redistribute vibrational energy and facilitate vibrational energy transfer [207], which enables the community to begin to shed light on VSC-modified chemistry [208]. A related work using ab initio on-the-fly simulations to evolve molecular systems in the ground polaritonic state, while treating vibrational DOFs and cavity mode classically, while including some photon-induced electron–electron correlations to the ground state via the QEDFT approach [209].

Vibrational polaritons may also require approaches that consider the quantum nature of nuclei. This is because the quantum state description is essential to accurately provide the frequency of the optical transition [133, 210] and reliably give rise to the resonant features in VSC experiments [210–212]. For a model system, one could choose the vibrational state descriptions (either the adiabatic or localized diabatic vibrational states) [210]. For atomistic systems, the Nuclear-Electronic Orbital (NEO) approach [213] can reliably treat the nuclear wavefunction on consistent equal footing as the electronic wavefunction and has been recently used in VSC applications [213]. However, other choices are available: for example, one can use an imaginary path integral-based approach to quantize nuclei or photonic DOFs in the extended phase space (often referred to as a ring polymer), for example, path-integral MD (PIMD) and the ring-polymer MD (RPMD), both of which have been applied to VSC problems recently [214].

6.2 | Conclusions

As the experimental demonstrations of molecular cavity QED in the strong and ultrastrong coupling regimes become more frequent and accessible to the broader community, there is a need for the development of new theoretical tools that can accurately and efficiently describe such complex light-matter interactions found in experiments. This review summarizes some of these exciting theoretical advances in polariton chemistry, showcasing methods ranging from improvements in the fundamental framework and description of these hybrid systems to the computational challenges, techniques, and applications spanning from modifying reactivity in the ground state to understanding spectral signatures of excited-state photochemistry.

In Section 2, we discussed the rigorous theoretical background of molecular cavity QED. We first reviewed the basic theory of the molecular Hamiltonian (Section 2.1) and introduced the necessary formalism for molecular quantum electrodynamics (Section 2.2). Section 3 focused on solving the polaritonic eigenvalue equation using various approaches from direct diagonalization in the adiabatic-Fock basis (Section 3.1.1) and polarized Fock basis (Section 3.1.2) as well as the self-consistent solution at the mean-field (Section 3.2.2) and correlated (Section 3.2.3) levels of theory. Using the tools put forth in the previous two sections, Section 4 explored the rich quantum dynamics of the strongly coupled light-matter systems, laying out common approaches toward simulating exact (Section 4.1) and realistic (Sections 4.2.1–4.2.3) molecules in the extended Hilbert space of the coupled electron-photon system as well as motivating the need for an accurate description and efficient calculation of the nuclear gradients (Section 4.3) used in the exact Pauli-Fierz Hamiltonian. Finally, in Section 5, we provide three directions toward a more complete picture of the molecular polariton picture in experiment, including machine learning polariton gradients (Section 5.1), the simulation and effects of cavity loss (Section 5.2), and the extension to many molecules and many cavity modes (Section 5.3).

Overall, with the recent new capabilities demonstrated in experiments, there has been a recent push to rigorously simulate polariton systems in the strong coupling regime. This has led to a number of theoretical innovations that start to explain and predict these experimental results. However, there are still many mysteries to solve as the systems get increasingly more complex with more molecules and cavity modes. From the theoretical perspective, the single-molecule case has made significant progress due to the relative numerical simplicity of the simulations compared to highly expensive many-mode and many-molecule (with many electronic levels) simulations that have yet to be fully explored. From the experimental perspective, single-molecule spectroscopy in plasmonic cavities is extremely challenging and has not been widely achieved; however, the results stemming from such simple hybrid systems will afford a much greater leap forward in understanding.

The purpose of this review was to introduce and outline state-of-the-art techniques toward the simulation of realistic, ab initio molecular polaritons for readers in the emergent field of polariton chemistry. This review captures much of the recent work,

but not all, toward the description of polaritonic states and properties as well as their quantum dynamics. Specifically, this work focused on the methods and approaches needed for one to explore these complicated problems in more depth and did not focus on connecting theory to experiment. While this connection is intrinsic to the answers one seeks from simulation, the discussion of experimental progress and its setbacks is well beyond the scope of this review. We hope this work allows readers of all kinds to dive into the simulation of molecular polaritons to explore the many unknown features of this novel tool to manipulate chemical reactions as well as physical phenomena, and to help the community address the many open questions still unexplored by theory and simulation.

Author Contributions

Braden M. Weight: conceptualization (equal), data curation (lead), formal analysis (equal), investigation (equal), methodology (equal), software (lead), validation (lead), visualization (lead), writing – original draft (lead), writing – review and editing (equal). **Pengfei Huo:** conceptualization (equal), formal analysis (equal), funding acquisition (lead), investigation (equal), methodology (equal), project administration (lead), resources (lead), software (supporting), supervision (lead), validation (equal), visualization (equal), writing – original draft (supporting), writing – review and editing (equal).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon a reasonable request.

Related WIREs Articles

[Ab Initio Approaches to Simulate Molecular Polaritons and Quantum Dynamics](#)

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