Nested-open-quantum-systems approach to photonic Bose-Einstein condensation

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The photonic Bose-Einstein condensate is a recently observed collective ground state of a coupled light-matter system. We describe this quantum state based on macroscopic quantum electrodynamics in dispersing and absorbing environments. To model the coupled photon-dye dynamics, we derive a master equation using a nested-open-quantum-systems approach yielding all parameters essential to describe the condensation process. This approach allows us to describe photon condensates of arbitrary shapes because all geometry-dependent decay constants can be expressed in terms of the Green's tensor. In particular, we obtain the cavity mode absorption and emission rates of the dye molecules.

I. INTRODUCTION

Photonic Bose-Einstein condensation is a phenomenon where photons reach thermal equilibrium with a well-defined effective temperature and macroscopically occupy the lowest energy state possible in the system. It is analogous to an atomic Bose-Einstein condensate (BEC), but the conditions for photons to achieve this state are different. The first BECs were observed with atoms [1–4], and since then experiments have demonstrated BECs of magnons, polaritons, and excitons [5–10].

For a long time, it was assumed that photons cannot form a BEC because of their noninteracting nature and because they disappear in the cavity walls when decreasing the temperature, as described in the blackbody radiation model. It turns out that photon condensate is possible if one uses a dye-filled microcavity with highly reflective mirrors [11–14]. The dye allows for the photons to reach thermal equilibrium through multiple absorption-emission cycles. The thermalization time must be much faster than the rate at which photons are lost from cavity modes due to spontaneous or cavity decay. When the photons reach thermal equilibrium, their effective temperature is equal to the temperature of the dye whose absorption-emission spectrum must obey the Kennard-Stepanov relation [15].

The mirrors provide a trapping potential that endows the photons with an effective mass and prevents them from escaping the cavity before reaching thermalization. Condensation can be achieved at room temperature when a critical number of photons in the system is reached.

Recent reports demonstrate photon condensation with 68 photons [16] and even as few as 7 photons [17]. Other work has demonstrated the condensation of photons inside a one-dimensional fiber cavity [18]. Here, the thermalization of

photons was achieved by many interaction cycles of photons and Er and Yb. One of the recent reports demonstrates the coupling of condensate through tunneling by exploiting two minima in a mirror potential where symmetric and antisymmetric eigenstates of the condensate have been formed [19].

The BEC is a promising candidate for many applications, e.g., atomic and photonic lasers [20–25], atomic interferometry [26,27], and in quantum information processing [14]. Despite being a quantum phenomenon, condensation has also been theoretically predicted and observed for classical light, allowing applications in imaging [28,29].

On the theory side, one of the first works [30] has shown that a photon BEC can be achieved if the grand canonical ensemble can be applied for photons. Some of the theoretical work has assumed that photons are already in thermal equilibrium [31,32], while other work has focused on the nonequilibrium dynamics describing the condensation from laser theory by considering two-level atom interaction with photons [33]. The latter does not take into account the rovibrational coupling of dye molecules which is an important ingredient for the thermalization of photons. One of the recent papers demonstrates that photon condensation can occur in three dimensions with thermalization mechanisms other than dye [25].

So far, the most in-depth work is the microscopic model developed by Keeling and Kirton [34,35], which provides the nonequilibrium dynamics of the photons and can describe fluctuations and correlations of the condensate. It allows for predicting the photon condensation threshold by considering multiple parameters important in the experiment. Two of them, namely, absorption and emission rates of the dye molecules, are derived using an open quantum systems description while others, namely, spontaneous and cavity decay rate and incoherent pumping rate, are included phenomenologically. The theory has been further developed to describe the spatial profile of the photon BEC with respect to the spot

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size of the laser pump and polarization dynamics in the condensate [36,37]. The extended version of this model has also been used to study the transition between BEC, multimode condensation, and lasing [38].

In this paper, we develop a first-principles theory of photonic Bose-Einstein condensation by combining open quantum systems and macroscopic quantum electrodynamics (QED) [39,40]. There are three advantages to our approach. First, we derive all dynamic equations of condensate from first principles. Second, this approach allows us to calculate all the necessary parameters which is particularly useful for planning new experiments. Third, it is formally possible to calculate the condensate dynamics for arbitrary geometries since we use Green's tensor formalism. It could be applied, for example, for cascaded mirrors with two dimples [19], periodic structures [16], or even arbitrarily shaped potentials [41].

The theoretical model consists of multiple systems and baths interacting with each other. In Sec. II we give a short introduction to nested open quantum systems. In Sec. III we start the development of the theory by constructing the Hamiltonian of the photon-molecule interaction inside the cavity. Next, we exploit the concept of nested open quantum systems: In step 1 (see Sec. IV), we derive the master equation in Lindblad form for the cavity and molecular decay and pumping constants. Then, in step 2 (see Sec. V), we separate the remaining system Hamiltonian into the new system, bath, and interaction parts and derive the master equation for absorption and emission rates, which are now influenced by the previously derived rates from step 1. Along with the derivation, we demonstrate that spontaneous molecular decay and absorption and emission rates are proportional to Green's tensor and the dipole moment of the dye molecule.

II. NESTED OPEN QUANTUM SYSTEMS

Figure 1 shows the concept of a nested open quantum system. The goal of this approach is to describe the interaction of a system (here S_1) with two baths (B and S_2) where the second bath itself is subject to dissipative dynamics due to the influence of the first bath. This is achieved in a two-step process. First, we have two Hamiltonians $\hat{H}_{S1}$ and $\hat{H}_{S2}$ describing two systems $S1$ and $S2$ interacting with each other via interaction term $\hat{H}_{S1S2}$. They both are immersed in a common bath described by $\hat{H}_B$. For simplicity, we assume that only $S1$ is directly interacting with the bath via the term $\hat{H}_{S1B}$.

Starting from the unitary evolution of the total density matrix ρ (top of figure), we trace out $\hat{H}_B$. This leads to the dissipative dynamics of the density matrix ρ_{S1+S2}, where $\mathcal{D}_B$ is the dissipator in Lindblad form (middle of the figure). Next, we trace out $\hat{H}_{S2}$ as the new bath. This results in an additional dissipative term $\mathcal{D}_{S2}(\mathcal{D}_B)$ which is a function of $\mathcal{D}_B$. Thus, the nested-systems approach allows us to capture the influence of $\mathcal{D}_B$ on $\mathcal{D}_{S2}$.

III. HAMILTONIAN

Figure 2 shows a schematic illustration of a model to describe a photon BEC. It consists of a cavity made of two highly reflective mirrors where in between there are dye molecules. Photons from the laser enter the cavity via the
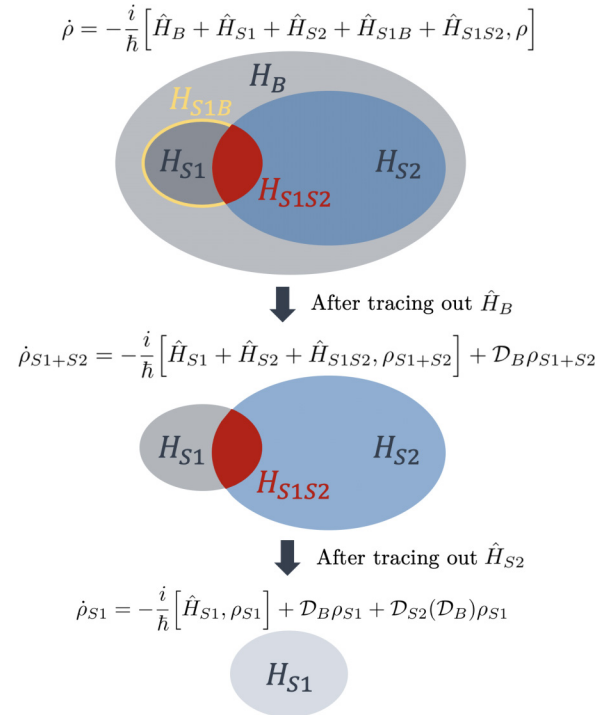
$$\dot{\rho} = -\frac{i}{\hbar}\left[\hat{H}_B + \hat{H}_{S1} + \hat{H}_{S2} + \hat{H}_{S1B} + \hat{H}_{S1S2}, \rho\right]$$

After tracing out $\hat{H}_B$

$$\dot{\rho}_{S1+S2} = -\frac{i}{\hbar}\left[\hat{H}_{S1} + \hat{H}_{S2} + \hat{H}_{S1S2}, \rho_{S1+S2}\right] + \mathcal{D}_B\rho_{S1+S2}$$

After tracing out $\hat{H}_{S2}$

$$\dot{\rho}_{S1} = -\frac{i}{\hbar}\left[\hat{H}_{S1}, \rho_{S1}\right] + \mathcal{D}_B\rho_{S1} + \mathcal{D}_{S2}(\mathcal{D}_B)\rho_{S1}$$

FIG. 1. Schematic representation of a nested-open-quantum-systems approach. We have two systems described by $\hat{H}_{S1}$ and $\hat{H}_{S2}$ embedded into an environment described by H_B. In step 1 we trace out H_B to obtain the master equation for density matrix ρ_{S1+S2} where $\mathcal{D}_B$ is the Markov approximated Lindblad dissipator. In step 2 we treat H_{S2} as an environment and trace it out to obtain the master equation for ρ_{S1} with an additional Lindblad dissipator $\mathcal{D}_{S2}(\mathcal{D}_B)$ which is now a function of (influenced by) $\mathcal{D}_B$.

dye molecules by being absorbed (with a pumping rate $\Gamma_\uparrow$) and emitted into the cavity mode ν [with a rate $\Gamma(-\delta_\nu)$]. Molecules can also absorb the photons from the cavity mode [with a rate $\Gamma(\delta_\nu)$]. There are two ways photons are lost from the cavity: they may leak from the cavity mirrors (with a rate κ) or spontaneously decay into a noncavity mode (with a rate $\Gamma_\downarrow$). A photon BEC is formed once a critical number of photons (or the pumping rate $\Gamma_\uparrow$) is exceeded inside the cavity, which is illustrated in Fig. 2 as a bright yellow line around the optical axis.

The starting point is a well-known macroscopic QED description of molecules, photons, and their interaction [42]. Here we employ a model of identical molecules i as two-level systems where each level is dressed by rovibrational states. Electronic levels of the molecule are represented by Pauli matrices $\hat{\sigma}_i$ with the electronic molecular transition frequency being ω_{10}. The rovibrational (phonon) modes are described by harmonic oscillators with mode operators $\hat{b}_i$ and $\hat{b}_i^\dagger$ and the transition frequency between modes Ω. Here, ω_{10} and Ω are assumed to be the same for all molecules. Note that $\Omega \ll \omega_{10}$. We assume that the molecule is described by only one rovibrational mode. In principle, it is possible to include multiple electronic and phononic modes that would give rise to multiple peaks in the absorption or emission spectrum of the molecule. However, the simplified model is sufficient to describe the photon BEC dynamics. The two-level system
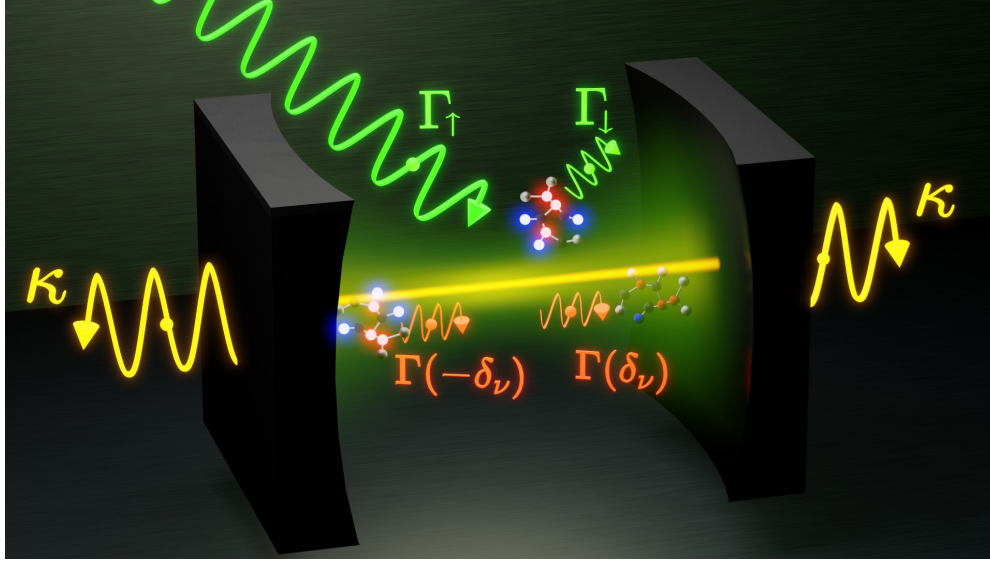
FIG. 2. Photon BEC setup. Dye molecules inside a cavity are pumped with a laser at a rate $\Gamma_\uparrow$. The molecules can emit photons into a cavity mode ν with a rate $\Gamma(-\delta_\nu)$ and absorb them with a rate $\Gamma(\delta_\nu)$. Excitations are lost from the cavity by spontaneous emission from the molecule with a rate $\Gamma_\downarrow$ or by a cavity decay with a rate κ.

and rovibrational states couple with each other with coupling strength given by the Huang-Rhys parameter S. The Hamiltonian for a total of N molecules then reads

$$\hat{H}_M = \sum_{i=1}^{N} \left[\frac{\hbar}{2} \omega_{10} \hat{\sigma}_i^z + \hbar \Omega \hat{b}_i^\dagger \hat{b}_i + \hbar \Omega \sqrt{S} \hat{\sigma}_i^z (\hat{b}_i + \hat{b}_i^\dagger) \right]. \quad (1)$$

This description of rovibrational excitations is known as the polaron model [43]. Related harmonic-oscillator models for phonon-induced damping have been used in a variety of contexts such as quantum dots [44], optomechanics [45], and quantum transport [46,47].

To describe cavity-assisted photons, we quantize the field in media and obtain the fundamental field operators $\hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega)$ and $\hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega)$ at position $\mathbf{r}$ and frequency ω. They are related to the polarization and magnetization of the medium [40] and obey the commutation relation $[\hat{\mathbf{f}}_\lambda(\mathbf{r}', \omega'), \hat{\mathbf{f}}_{\lambda'}^\dagger(\mathbf{r}, \omega)] = \delta_{\lambda\lambda'} \delta(\omega - \omega') \delta(\mathbf{r} - \mathbf{r}')$. The total photon field can then be expressed as the sum of electric and magnetic excitations (e, m) and the integral of $\hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega)$ and $\hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega)$ over the entire space in position and frequency:

$$\hat{H}_F = \sum_{\lambda=e,m} \int d^3r \int_0^\infty d\omega \, \hbar\omega \, \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega). \quad (2)$$

Interactions between the molecules and photons take place when a photon gets absorbed (emitted) from a ground (excited) state of a two-level system. The molecule-field interaction is then taken in dipole approximation to be

$$\hat{H}_{MF} = -\sum_i (\mathbf{d}_{01} \hat{\sigma}_i + \mathbf{d}_{10} \hat{\sigma}_i^\dagger) \cdot \hat{\mathbf{E}}(\mathbf{r}_i), \quad (3)$$

where $\mathbf{d}_{10}$ is the dipole moment and $\hat{\mathbf{E}}(\mathbf{r}_i)$ is the electric field operator at a molecule's position $\mathbf{r}_i$. The electric field can be

expressed in terms of the Green's tensor $\mathbf{G}_\lambda$ and operators $\hat{\mathbf{f}}_\lambda$ [40]:

$$\hat{\mathbf{E}}(\mathbf{r}_i) = \sum_{\lambda=e,m} \int d^3r \int_0^\infty d\omega \left\{ \mathbf{G}_\lambda(\mathbf{r}_i, \mathbf{r}, \omega) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega) \right.$$
$$\left. + \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega) \cdot \mathbf{G}_\lambda^{*\mathrm{T}}(\mathbf{r}_i, \mathbf{r}, \omega) \right\}, \quad (4)$$

where $\mathbf{G}_e$ and $\mathbf{G}_m$ are defined as

$$\mathbf{G}_e(\mathbf{r}, \mathbf{r}', \omega) = i \frac{\omega^2}{c^2} \sqrt{\frac{\hbar}{\pi \varepsilon_0} \mathrm{Im}\varepsilon(\mathbf{r}', \omega)} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega),$$

$$\mathbf{G}_m(\mathbf{r}, \mathbf{r}', \omega) = i \frac{\omega}{c} \sqrt{\frac{\hbar}{\pi \varepsilon_0} \frac{\mathrm{Im}\mu(\mathbf{r}', \omega)}{|\mathrm{Im}\mu(\mathbf{r}', \omega)|^2}} [\nabla' \times \mathbf{G}(\mathbf{r}', \mathbf{r}, \omega)]^{\mathrm{T}}, \quad (5)$$

with $\varepsilon(\mathbf{r}, \omega)$ and $\mu(\mathbf{r}, \omega)$ being the electric permittivity and magnetic permeability of the medium, ε_0 being vacuum permittivity, and c being the speed of light.

As we have now stated the Hamiltonian describing photons, molecules, and their interactions, we will identify different parts of the Hamiltonian responsible for different dissipation processes. As described in the Introduction and Sec. II, we will use a nested-open-quantum-systems approach. Figure 3 shows a schematic diagram of a nested open quantum system for our model. In step 1, there are baths responsible for cavity and spontaneous decay and laser pumping. The system Hamiltonians $\hat{H}_S^a$ and $\hat{H}_S^\sigma$ are coupled to the bath Hamiltonians $\hat{H}_F^\kappa$, $\hat{H}_F^{\Gamma_\downarrow}$, and $\hat{H}_F^{\Gamma_\uparrow}$ through the respective interaction Hamiltonians $\hat{H}_I^\kappa$, $\hat{H}_I^{\Gamma_\downarrow}$, and $\hat{H}_I^{\Gamma_\uparrow}$. Once we derive the master equation for the corresponding system, in step 2, we separate the remaining system Hamiltonian again into the system, bath, and interaction Hamiltonians. Then we trace out the bath and
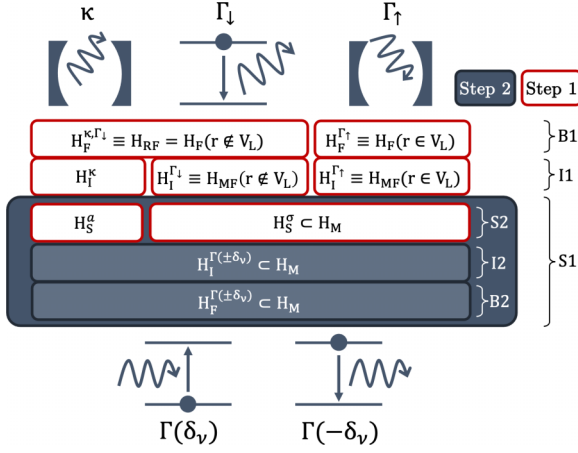
FIG. 3. Schematic representation of a nested-open-quantum-systems approach for our model. In step 1 we derive the rates κ, $\Gamma_{\downarrow}$, and $\Gamma_{\uparrow}$ from baths (B1) $\hat{H}_F^{\kappa}$, $\hat{H}_F^{\Gamma_{\downarrow}}$, and $\hat{H}_F^{\Gamma_{\uparrow}}$ and their interaction (I1) with systems (S1) $\hat{H}_S^a$ [see Eq. (17)] and $\hat{H}_S^{\sigma}$ [see Eq. (23)]. Here, $\hat{H}_F^{\kappa,\Gamma_{\downarrow}} \equiv \hat{H}_{RF} = \hat{H}_F(\mathbf{r} \notin V_L)$ [(see Eqs. (19) and (18)], and $\hat{H}_F^{\Gamma_{\uparrow}} = \hat{H}_F(\mathbf{r} \in V_L)$ [see Eq. (9)]. Also, $\hat{H}_I^{\Gamma_{\downarrow}} = \hat{H}_{MF}(\mathbf{r} \notin V_L)$ [see Eq. (24)], and $\hat{H}_I^{\Gamma_{\uparrow}} = \hat{H}_{MF}(\mathbf{r} \in V_L)$ [see Eq. (22)]. There are additional terms $\hat{H}_F^{\Gamma(\pm\delta_v)}$ and $\hat{H}_I^{\Gamma(\pm\delta_v)}$ which we treat as part of the system (S1) in step 1. In step 2, they take on the roles of bath (B2) and system-bath (I2) interaction and from their interaction with the remaining system (S2) H_S^a and H_S^{σ} we derive $\Gamma(\pm\delta_v)$.

obtain the emission and absorption rates for the photons in the cavity modes $\Gamma(\pm\delta_v)$. In Fig. 3 we denote the corresponding partition of the Hamiltonian with B1, I1, and S1 as bath, interaction, and system parts for step 1. Correspondingly, B2, I2, and S2 represent partition into bath, interaction, and system in step 2.

The main reason why we exploit this approach is that in general, both $\Gamma(\pm\delta_v)$ are influenced (broadened) by incoherent processes in the cavity, in this case, κ, $\Gamma_{\downarrow}$, and $\Gamma_{\uparrow}$. Exploiting the nested approach allows us to capture this influence.

To derive the master equation with dissipative constants of interest, the first step is to perform a separation of the total photon field into different fields which we will treat as baths responsible for dissipative processes. Thus, we separate $\hat{H}_F$ into the laser field (responsible for $\Gamma_{\uparrow}$; see Appendix C), resonant cavity modes, the remaining field responsible for spontaneous decay ($\Gamma_{\downarrow}$), and cavity leakage (κ).

Within the laser source region V_L there is a coherent field and everywhere else there are vacuum fluctuations. Thus, we can separate the total field state as follows [48]:

$$|\psi\rangle_F = |\{\hat{\mathbf{f}}_{\lambda}(\mathbf{r},\omega)\}\rangle_{\mathbf{r}\in V_L} \otimes |\{0\}\rangle_{\mathbf{r}\notin V_L}. \qquad (6)$$

If we act with an annihilation operator on this state we obtain the number instead of an operator at the laser source:

$$\hat{\mathbf{f}}_{\lambda}(\mathbf{r},\omega)|\psi\rangle_F = \begin{cases} \mathbf{f}_{\lambda}(\mathbf{r},\omega)|\psi\rangle_F, & \mathbf{r} \in V_L, \\ 0, & \mathbf{r} \notin V_L. \end{cases} \qquad (7)$$

We can then separate Eq. (2) as follows:

$$\hat{H}_F = \hat{H}_F(\mathbf{r} \notin V_L) + \hat{H}_F(\mathbf{r} \in V_L)$$

$$= \sum_{\lambda=e,m} \int_{\mathbf{r}\notin V_L} d^3r \int_0^{\infty} d\omega\, \hbar\omega\, \hat{\mathbf{f}}_{\lambda}^{\dagger}(\mathbf{r},\omega) \cdot \hat{\mathbf{f}}_{\lambda}(\mathbf{r},\omega)$$

$$+ \sum_{\lambda=e,m} \int_{\mathbf{r}\in V_L} d^3r \int_0^{\infty} d\omega\, \hbar\omega\, \hat{\mathbf{f}}_{\lambda}^{\dagger}(\mathbf{r},\omega) \cdot \hat{\mathbf{f}}_{\lambda}(\mathbf{r},\omega). \qquad (8)$$

Next, we assume that the laser field is independent of the position $\mathbf{r}$. Because the laser field is pumping molecules, it works as an amplifier in the open-quantum-systems context; thus, we redefine the second part of Eq. (8) in terms of inverted oscillator operators $\hat{h}(\omega'')$ and define it to be [49]

$$\hat{H}_F(\mathbf{r} \in V_L) \equiv \hat{H}_F^{\Gamma_{\uparrow}} = -\int d\omega''\, \hbar\omega''\, \hat{h}(\omega'')\hat{h}^{\dagger}(\omega''). \qquad (9)$$

Note that the inverted oscillator operator $\hat{h}(\omega'')$ and its Hermitian conjugate are exactly opposite to the photon field operator $\hat{\mathbf{f}}_{\lambda}(\mathbf{r},\omega)$ and it obeys the commutation relation

$$[\hat{h}(\omega),\hat{h}^{\dagger}(\omega')] = -\delta(\omega-\omega'). \qquad (10)$$

The average values are given the opposite of usual photon occupation number,

$$\langle\hat{h}^{\dagger}(\omega)\hat{h}(\omega)\rangle = (N(\omega)+1)\delta(\omega-\omega'), \qquad (11)$$

$$\langle\hat{h}(\omega)\hat{h}^{\dagger}(\omega)\rangle = N(\omega)\delta(\omega-\omega'), \qquad (12)$$

where $N(\omega)$ is the Bose-Einstein distribution with a negative laser temperature, $T_{\text{laser}} < 0$:

$$N(\omega) = \frac{1}{e^{-\hbar\omega/k_B T_{\text{laser}}} - 1}. \qquad (13)$$

The next step is to separate the field of the Hamiltonian $\hat{H}_F(\mathbf{r} \notin V_L)$ into that of the cavity modes and that of the remaining field. The cavity modes are described by operators $\hat{a}_{m\zeta}$ and $\hat{a}_{m\zeta}^{\dagger}$, where the cavity resonance has a Lorentzian shape. They can destroy (create) a photon of a cavity mode with labels m, ζ. As an example for the planar cavity, m determines the number of standing-wave modes along the cavity axis, while ζ is the mode by the transversal wave number $k^{\parallel}$, which has an expression $k^{\parallel^2} = k^2 - (m\pi/d)^2$ where d is the length of the cavity and k is the total wave number. The annihilation operator reads [50]

$$\hat{a}_{m\zeta} = \sqrt{\frac{\gamma_{m\zeta}}{2\pi}} \int_{-\infty}^{\infty} d\omega\, \frac{\hat{a}(\omega,\zeta)}{\omega-\omega_{m\zeta}+i\gamma_{m\zeta}/2}, \qquad (14)$$

where $\hat{a}(\omega) \equiv \hat{a}(\mathbf{r}_i,\omega)$ at a molecule's position $\mathbf{r}_i$ is defined through the Green's tensor [see Eq. (5)] $\mathbf{G}_{\lambda}$ [42]:

$$\hat{a}(\omega,\zeta) = -\frac{1}{\hbar g(\mathbf{r}_i,\omega_{m\zeta},\zeta)}$$

$$\times \sum_{\lambda=e,m} \int d^3r' \int_0^{\infty} d\omega\, \mathbf{d}_{10} \cdot \mathbf{G}_{\lambda}(\mathbf{r},\mathbf{r}',\omega) \cdot \hat{\mathbf{f}}_{\lambda}(\mathbf{r}',\omega),$$

$$(15)$$

with the interaction strength between photons and molecules being

$$g^2(\mathbf{r}, \omega_{m\zeta}, \zeta)$$

$$= \frac{\mu_0}{\pi \hbar} \omega_{m\zeta}^2 \mathbf{d}_{10} \cdot \text{Im}\mathbf{G}(\mathbf{r}, \mathbf{r}, \omega_{m\zeta}, \zeta) \cdot \mathbf{d}_{01} = \frac{\Omega_R^2}{2\pi \gamma_{m\zeta}}, \quad (16)$$

where $\Omega_R = \sqrt{\frac{2}{\hbar} \mu_0 \gamma_{m\zeta} \omega_{m\zeta}^2 \mathbf{d}_{10} \cdot \text{Im}\mathbf{G}(\mathbf{r}, \mathbf{r}, \omega_{m\zeta}, \zeta) \cdot \mathbf{d}_{01}}$ is the Rabi frequency, $\gamma_{m\zeta}$ is the width of the resonance at the resonant frequency $\omega_{m\zeta}$, and μ_0 is the magnetic permeability. Note that

$$\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) = \int d\zeta \, \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega, \zeta).$$

For notation convenience, we subsume the two mode labels within a multi-index ν, i.e., $m\zeta \equiv \nu$. We separate the first part of Eq. (8) into the Hamiltonian of the resonant cavity modes and a remaining field bath by adding and subtracting $\hat{H}_S^a = \sum \hbar \omega_\nu \hat{a}_\nu^\dagger \hat{a}_\nu$:

$$\hat{H}_F(\mathbf{r} \notin V_L) = \hat{H}_{RF} + \hat{H}_S^a, \quad (17)$$

where the remaining field (RF) reads

$$\hat{H}_{RF} = \sum_{\lambda=e,m} \int_{\mathbf{r}\notin V_L} d^3r \int_0^\infty d\omega \, \hbar\omega \, \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega)$$

$$- \sum_{\nu=1}^\infty \hbar \omega_\nu \hat{a}_\nu^\dagger \hat{a}_\nu. \quad (18)$$

$\hat{H}_{RF}$ is responsible for the spontaneous decay of the molecules; thus, we label it as $\hat{H}_{RF} \equiv \hat{H}_F^{\Gamma_\downarrow}$.

To account for the cavity leakage, we need to add another bath Hamiltonian. It turns out that the remaining field Hamiltonian can account not only for the spontaneous decay but also for the leakage of the cavity modes. But, for the interaction Hamiltonian with cavity modes to be well defined, it has to be recast into a different form, which we define as

$$\hat{H}_F^\kappa = \hat{H}_{RF} = \int_0^\infty d\omega' \, \hbar\omega' \, \hat{a}^\dagger(\omega')\hat{a}(\omega'). \quad (19)$$

Now that we have separated the total field into multiple baths of interest, we do a similar procedure for the molecule-field interaction term (3). For the setup of interest, the laser frequency is near resonant, $\omega \approx \omega_{10}$; thus, we can perform the rotating-wave approximation and the interaction Hamiltonian (3) reads

$$\hat{H}_{MF} = -\sum_{i}^N \sum_{\lambda=e,m} \int d^3r \int_0^\infty d\omega$$

$$\times \left\{ \mathbf{d}_{10} \cdot \mathbf{G}_\lambda(\mathbf{r}_i, \mathbf{r}, \omega, \zeta) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega)\hat{\sigma}_i^\dagger \right.$$

$$\left. + \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega) \cdot \mathbf{G}_\lambda^{*T}(\mathbf{r}_i, \mathbf{r}, \omega, \zeta) \cdot \mathbf{d}_{01}\hat{\sigma}_i \right\}. \quad (20)$$

Now we proceed in a similar manner as we did for the photon field by separating the interaction term. First, we split $\hat{H}_{MF}$ into

$$\hat{H}_{MF} = \hat{H}_{MF}(\mathbf{r} \notin V_L) + \hat{H}_{MF}(\mathbf{r} \in V_L). \quad (21)$$

The interaction part $\hat{H}_{MF}(\mathbf{r} \in V_L)$ for the laser is semiclassical as can be obtained if $\hat{\mathbf{E}}(\mathbf{r}_i)$ is applied to the state in Eq. (6) [48]. The explicit expression is given by Eq. (C1). But to employ the open-quantum-systems context, similarly as in Eq. (9), we redefine $\hat{H}_{MF}(\mathbf{r} \in V_L)$ to be a quantized interaction between $\hat{H}_F^{\Gamma_\uparrow}$ and $\hat{H}_S^\sigma$:

$$\hat{H}_{MF}(\mathbf{r} \in V_L) \equiv \hat{H}_I^{\Gamma_\uparrow}$$

$$= \sum_i \int_0^\infty d\omega'' \, \hbar\mu(\omega'')(\hat{h}(\omega'')\hat{\sigma}_i^\dagger + \hat{h}^\dagger(\omega'')\hat{\sigma}_i), \quad (22)$$

with the coupling strength $\mu(\omega'')$. In Appendix C we demonstrate how the pumping term $\Gamma_\uparrow$ is related to the laser parameters. The Hamiltonian of N two-level molecules from Eq. (1) is identified as

$$\hat{H}_S^\sigma = \sum_{i=1}^N \frac{\hbar}{2} \omega_{10} \hat{\sigma}_i^z. \quad (23)$$

Treating the interaction term $\hat{H}_{MF}(\mathbf{r} \notin V_L)$, in the same manner as we did for the field in Eq. (17), we add and subtract the resonant interaction term $\sum_{\nu,i} \frac{1}{2}\hbar\Omega_R(\mathbf{r}_i, \omega_\nu, \zeta)[\hat{a}_\nu\hat{\sigma}_i^\dagger + \hat{a}_\nu^\dagger\hat{\sigma}_i]$ which is analogous to the Jaynes-Cummings model. Then we define the remaining-field interaction (RI) term as

$$\hat{H}_{RI} = -\sum_{\lambda=e,m} \sum_i^N \int d^3r \int_0^\infty d\omega \left\{ \mathbf{d}_{10} \cdot \mathbf{G}_\lambda(\mathbf{r}_i, \mathbf{r}, \omega) \cdot \hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega)\hat{\sigma}_i^\dagger \right.$$

$$\left. + \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega) \cdot \mathbf{G}_\lambda^{*T}(\mathbf{r}_i, \mathbf{r}, \omega) \cdot \mathbf{d}_{01}\hat{\sigma}_i \right\}$$

$$- \sum_{\nu,i} \frac{1}{2}\hbar\Omega_R(\mathbf{r}_i, \omega_\nu, \zeta)[\hat{a}_\nu\hat{\sigma}_i^\dagger + \hat{a}_\nu^\dagger\hat{\sigma}_i]. \quad (24)$$

The remaining-field interaction Hamiltonian $\hat{H}_{RI}$ is related to the spontaneous decay; thus, we define it to be the interaction Hamiltonian between $\hat{H}_F^{\Gamma_\downarrow}$ and $\hat{H}_S^a$, $\hat{H}_{RI} \equiv \hat{H}_I^{\Gamma_\downarrow}$.

The other resonant interaction term together with the third part of Eq. (1) we define as

$$\hat{H}_I^{\Gamma(\pm\delta_\nu)} = \sum_{\nu,i} \frac{1}{2}\hbar\Omega_\nu[\hat{a}_\nu\hat{\sigma}_i^\dagger + \hat{a}_\nu^\dagger\hat{\sigma}_i]$$

$$+ \sum_i \hbar\Omega\sqrt{S}\hat{\sigma}_i^z(\hat{b}_i + \hat{b}_i^\dagger), \quad (25)$$

where $\Omega_\nu \equiv \Omega_R(\mathbf{r}_i, \omega_\nu, \zeta)$.

To account for the cavity leakage, we need to add the interaction between the remaining field from Eq. (19) with the cavity modes from the second part of Eq. (18):

$$\hat{H}_I^\kappa = \sum_\nu \int_0^\infty d\omega' \, \hbar\lambda(\omega')[\hat{a}(\omega')\hat{a}_\nu^\dagger + \hat{a}^\dagger(\omega')\hat{a}_\nu], \quad (26)$$

with the coupling strength $\lambda(\omega')$. In Appendix A we demonstrate that the cavity leakage κ is related to the width of the cavity resonance γ_ν.

Finally, the rovibrational states Hamiltonian from Eq. (1) in the open-quantum-systems context we define as

$$\hat{H}_F^{\Gamma(\pm\delta_\nu)} = \sum_i \hbar\Omega \hat{b}_i^\dagger \hat{b}_i. \tag{27}$$

We treat it as a system term in step 1 and as a bath term in step 2, respectively.

The complete Hamiltonian describing the model is $\hat{H} = \hat{H}_S^a + \hat{H}_S^\sigma + \hat{H}_F^{\Gamma\downarrow} + \hat{H}_F^{\Gamma\uparrow} + \hat{H}_F^\kappa + \hat{H}_I^{\Gamma\downarrow} + \hat{H}_I^{\Gamma\uparrow} + \hat{H}_F^{\Gamma(\pm\delta_\nu)} + \hat{H}_I^{\Gamma(\pm\delta_\nu)}$ (see Fig. 3).

IV. INTERMEDIATE MASTER EQUATION

A. Transforming into the interaction picture

As we have separated the system of interest in the respective bath, interaction, and system Hamiltonians, we are ready to derive the dynamics of the reduced system of photons and electronic transitions of molecules with all the relevant constants.

The first step is to transform interaction Hamiltonians to the interaction picture, which read

$$\hat{H}_I^\kappa(t) = \sum_\nu \int_0^\infty d\omega' \, \hbar\lambda(\omega')[\hat{a}(\omega')e^{-i\omega't}\hat{a}_\nu^\dagger e^{i\omega_\nu t} + \hat{a}^\dagger(\omega')e^{i\omega't}\hat{a}_\nu e^{-i\omega_\nu t}], \tag{28}$$

$$\hat{H}_I^{\Gamma\downarrow}(t) = -\sum_{\lambda=e,m}\sum_i^N \int d^3r \int_0^\infty d\omega[\, \mathbf{d}_{10}\cdot\mathbf{G}_\lambda(\mathbf{r}_i,\mathbf{r},\omega)\cdot\hat{\mathbf{f}}_\lambda(\mathbf{r},\omega)e^{-i\omega t}\hat{\sigma}_i^\dagger e^{i\omega_{10}t} + \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r},\omega)e^{i\omega t}\cdot\mathbf{G}_\lambda^{*\mathrm{T}}(\mathbf{r}_i,\mathbf{r},\omega)\cdot\mathbf{d}_{01}\hat{\sigma}_i e^{-i\omega_{10}t}]$$

$$-\sum_{\nu,i}\frac{1}{2}\hbar\Omega_R(\mathbf{r}_i,\omega_\nu,\zeta)\left[\sqrt{\frac{\gamma_{m\zeta}}{2\pi}}\int_{-\infty}^\infty d\omega\,\frac{\hat{a}(\omega,\zeta)e^{-i\omega t}}{\omega - \omega_{m\zeta} + i\gamma_{m\zeta}/2}\hat{\sigma}_i^\dagger e^{i\omega_{10}t} + \sqrt{\frac{\gamma_{m\zeta}}{2\pi}}\int_{-\infty}^\infty d\omega\,\frac{\hat{a}^\dagger(\omega,\zeta)e^{i\omega t}}{\omega - \omega_{m\zeta} - i\gamma_{m\zeta}/2}\hat{\sigma}_i e^{-i\omega_{10}t}\right], \tag{29}$$

$$\hat{H}_I^{\Gamma\uparrow}(t) = \sum_i \int_0^\infty d\omega'' \, \hbar\mu(\omega'')[\hat{h}(\omega'')e^{-i\omega''t}\hat{\sigma}_i^\dagger e^{i\omega_{10}t} + \hat{h}^\dagger(\omega'')e^{i\omega''t}\hat{\sigma}_i e^{-i\omega_{10}t}]. \tag{30}$$

We have used two approximations: the rovibrational energies are typically much smaller than the electronic and photon energies, $\Omega \ll \omega_\nu, \omega, \omega', \omega''$, and assuming that the interaction between atoms and photons is not ultrastrong, $\Omega_\nu \ll \omega_\nu, \omega, \omega', \omega''$. On this basis, we can neglect the interaction picture contribution from $\hat{H}_F^{\Gamma(\pm\delta_\nu)}$ and $\hat{H}_I^{\Gamma(\pm\delta_\nu)}$.

B. Constructing the master equation

We start with the usual Markov-approximated density matrix equation in the interaction picture [39]:

$$\dot{\tilde{\rho}}_S(t) = \frac{1}{\hbar^2}\int_0^\infty d\tau\left\{\mathrm{tr}_{F^\kappa}\left[\hat{H}_I^\kappa(t),\left[\hat{H}_I^\kappa(t-\tau),\tilde{\rho}_S(t)\rho_{F^\kappa}\right]\right]\right.$$

$$+ \mathrm{tr}_{F_\downarrow^{\Gamma\mathrm{tot}}}\left[\hat{H}_I^{\Gamma\downarrow}(t),\left[\hat{H}_I^{\Gamma\downarrow}(t-\tau),\tilde{\rho}_S(t)\rho_{F_\downarrow^{\Gamma\mathrm{tot}}}\right]\right]$$

$$- \mathrm{tr}_{F_\downarrow^{\Gamma\mathrm{r}}}\left[\hat{H}_I^{\Gamma\downarrow}(t),\left[\hat{H}_I^{\Gamma\downarrow}(t-\tau),\tilde{\rho}_S(t)\rho_{F_\downarrow^{\Gamma\mathrm{r}}}\right]\right]$$

$$\left. + \mathrm{tr}_{F^{\Gamma\uparrow}}\left[\hat{H}_I^{\Gamma\uparrow}(t),\left[\hat{H}_I^{\Gamma\uparrow}(t-\tau),\tilde{\rho}_S(t)\rho_{F^{\Gamma\uparrow}}\right]\right]\right\}, \tag{31}$$

where $\tilde{\rho}_S(t)$ is the system density matrix in the interaction picture. Here, $\mathrm{tr}_{F^\kappa}[,\ ]$ means that the trace has been taken with respect to the bath coming from Hamiltonian $\hat{H}_F^\kappa$, and in the same fashion other traces have been taken with respect to their respective baths. It has been shown [51] (Appendix B2) that if the interaction between baths is weak, then for each bath there is one Lindbladian superoperator and we can neglect cross terms between different baths. Thus, we split the double commutator and its trace into three parts for each bath. Since for bath $F^{\Gamma\downarrow}$ we have separated the resonant photon modes from the total field in the Hamiltonian $\hat{H}_F^{\Gamma\downarrow}$, we need to also

account for that when calculating the bath density matrix. Thus, we split the density matrix by writing $\rho_{F^{\Gamma\downarrow}} = \rho_{F_\downarrow^{\Gamma\mathrm{tot}}} - \rho_{F_\downarrow^{\Gamma\mathrm{r}}}$, where $\rho_{F_\downarrow^{\Gamma\mathrm{r}}}$ and $\rho_{F_\downarrow^{\Gamma\mathrm{tot}}}$ account for the cavity-photon and total bath density matrices, respectively.

To expand the double commutator in Eq. (31), we identify the system $A_i(t)$ and bath $B_i(t)$ operators by writing the interaction Hamiltonian in the form $\sum_\alpha A_\alpha(t)\otimes B_\alpha(t)$. In this way $\hat{H}_I^\kappa$ leads to

$$A_1(t) = \sum_\nu \hat{a}_\nu^\dagger e^{i\omega_\nu t},$$

$$A_2(t) = \sum_\nu \hat{a}_\nu e^{-i\omega_\nu t}, \tag{32}$$

$$B_1(t) = \int_0^\infty d\omega' \hbar\lambda(\omega')\hat{a}(\omega')e^{-i\omega't},$$

$$B_2(t) = \int_0^\infty d\omega' \hbar\lambda(\omega')\hat{a}^\dagger(\omega')e^{i\omega't}, \tag{33}$$

whereas $\hat{H}_I^{\Gamma\downarrow}$ implies

$$A_3(t) = \sum_i \hat{\sigma}_i^\dagger e^{i\omega_{10}t},$$

$$A_4(t) = \sum_i \hat{\sigma}_i e^{-i\omega_{10}t}, \tag{34}$$

$$B_3(t) = -\sum_{\lambda=\mathrm{e,m}} \int d^3r \int_0^\infty d\omega \, \mathbf{d}_{10} \cdot \mathbf{G}_\lambda \cdot \hat{\mathbf{f}}_\lambda e^{-i\omega t},$$

$$\tag{35}$$

$$B_4(t) = -\sum_{\lambda=\mathrm{e,m}} \int d^3r \int_0^\infty d\omega \, \hat{\mathbf{f}}_\lambda^\dagger \cdot \mathbf{G}_\lambda^{*\mathrm{T}} \cdot \mathbf{d}_{01} e^{i\omega t},$$

and

$$A_{3'}(t) = \sum_i \hat{\sigma}_i^\dagger e^{i\omega_{10}t},$$

$$A_{4'}(t) = \sum_i \hat{\sigma}_i e^{-i\omega_{10}t},$$

$$\tag{36}$$

$$B_{3'}(t) = -\sum_\nu \frac{1}{2}\hbar\Omega_R(\mathbf{r}_i, \omega_\nu, \zeta)$$

$$\times \sqrt{\frac{\gamma_{m\zeta}}{2\pi}} \int_{-\infty}^\infty d\omega \, \frac{\hat{a}(\omega, \zeta)e^{-i\omega t}}{\omega - \omega_{m\zeta} + i\gamma_{m\zeta}/2},$$

$$B_{4'}(t) = -\sum_\nu \frac{1}{2}\hbar\Omega_R(\mathbf{r}_i, \omega_\nu, \zeta)$$

$$\times \sqrt{\frac{\gamma_{m\zeta}}{2\pi}} \int_{-\infty}^\infty d\omega \, \frac{\hat{a}^\dagger(\omega, \zeta)e^{i\omega t}}{\omega - \omega_{m\zeta} - i\gamma_{m\zeta}/2}, \tag{37}$$

and finally, from $\hat{H}_I^{\Gamma\uparrow}$ we deduce

$$A_5(t) = \sum_i \hat{\sigma}_i^\dagger e^{i\omega_{10}t},$$

$$\tag{38}$$

$$A_6(t) = \sum_i \hat{\sigma}_i e^{-i\omega_{10}t},$$

$$B_5(t) = \int_0^\infty d\omega'' \, \hbar\mu(\omega'')\hat{h}(\omega'')e^{-i\omega''t},$$

$$\tag{39}$$

$$B_6(t) = \int_0^\infty d\omega'' \, \hbar\mu(\omega'')\hat{h}^\dagger(\omega'')e^{i\omega''t}.$$

Note that $A_3(t) = A_{3'}(t) = A_5(t)$ and $A_4(t) = A_{4'}(t) = A_6(t)$. The correlation functions read, for example, for the first bath F^κ,

$$C_{12}(\tau) = \mathrm{tr}_{F^\kappa}\{B_1 B_2(-\tau)\rho_{F^\kappa}\}, \tag{40}$$

$$C_{21}(\tau) = \mathrm{tr}_{F^\kappa}\{B_2 B_1(-\tau)\rho_{F^\kappa}\}. \tag{41}$$

Because the baths are independent from each other, all correlations between different baths yield zero: $C_{13} = C_{23} = C_{14} = C_{35} = \cdots = 0$. Note that all correlations with the same index yield zero as well, i.e., $C_{11} = C_{22} = \cdots = 0$, since the average of the product of the same bath operators vanishes. Transforming back to the Schrödinger picture and by expanding the double commutator in the integral we obtain the master equation,

$$\dot{\rho}_S(t) = -\frac{i}{\hbar}[\hat{H}_S, \rho_S(t)] - \frac{1}{\hbar^2}\int_0^\infty d\tau \Bigg\{ \sum_\nu [\hat{a}_\nu^\dagger, \hat{a}_\nu e^{i\omega_\nu\tau}\rho_S(t)]C_{12}(\tau) + [\rho_S(t)\hat{a}_\nu e^{i\omega_\nu\tau}, \hat{a}_\nu^\dagger]C_{21}(-\tau)$$

$$+ [\hat{a}_\nu, \hat{a}_\nu^\dagger e^{-i\omega_\nu\tau}\rho_S(t)]C_{21}(\tau) + [\rho_S(t)\hat{a}_\nu^\dagger e^{-i\omega_\nu\tau}, \hat{a}_\nu]C_{12}(-\tau)$$

$$+ \sum_i [\hat{\sigma}_i^\dagger, \hat{\sigma}_i e^{i\omega_{10}\tau}\rho_S][C_{34}(\tau) - C_{3'4'}(\tau)] + [\rho_S(t)\hat{\sigma}_i e^{i\omega_{10}\tau}, \hat{\sigma}_i^\dagger][C_{43}(-\tau) - C_{4'3'}(-\tau)]$$

$$+ [\hat{\sigma}_i, \hat{\sigma}_i^\dagger e^{-i\omega_{10}\tau}\rho_S(t)][C_{43}(\tau) - C_{4'3'}(\tau)] + [\rho_S(t)\hat{\sigma}_i^\dagger e^{-i\omega_{10}\tau}, \hat{\sigma}_i][C_{34}(-\tau) - C_{3'4'}(-\tau)]$$

$$+ \sum_i [\hat{\sigma}_i^\dagger, \hat{\sigma}_i e^{i\omega_{10}\tau}\rho_S(t)]C_{56}(\tau) + [\rho_S(t)\hat{\sigma}_i e^{i\omega_{10}\tau}, \hat{\sigma}_i^\dagger]C_{65}(-\tau)$$

$$+ [\hat{\sigma}_i, \hat{\sigma}_i^\dagger e^{-i\omega_{10}\tau}\rho_S(t)]C_{65}(\tau) + [\rho_S(t)\hat{\sigma}_i^\dagger e^{-i\omega_{10}\tau}, \hat{\sigma}_i]C_{56}(-\tau) \Bigg\}, \tag{42}$$

where $\rho_S(t)$ is the system density matrix in the Schrödinger picture and the system Hamiltonian reads

$$\hat{H}_S = \hat{H}_S^a + \hat{H}_S^\sigma + \hat{H}_F^{\Gamma(\pm\delta_\nu)} + \hat{H}_I^{\Gamma(\pm\delta_\nu)}. \tag{43}$$

C. Evaluating environmental correlation functions

Assuming the thermal excitations to be much smaller than the electronic and photonic cavity excitations in the system [11], i.e., $\omega, \omega_\nu, \omega' \gg k_B T/\hbar$ and $\omega'' \gg k_B T_{\mathrm{laser}}/\hbar$, we can neglect the respective thermal occupation numbers, $n(\omega) = n(\omega_\nu) = n(\omega') = N(\omega'') \approx 0$.

We present the calculation of the first bath correlation functions in detail, which read

$$C_{12}(\tau) = \langle B_1 B_2(-\tau)\rangle \approx \int_0^\infty d\omega' \, \hbar^2\lambda^2(\omega')e^{-i\omega't}, \quad (44\mathrm{a})$$

$$C_{21}(\tau) \approx 0. \tag{44b}$$

Next, we use the relation

$$\int_0^\infty d\tau e^{\pm i\omega\tau} = \pi\delta(\omega) \pm i\mathcal{P}\frac{1}{\omega} \tag{45}$$

to evaluate time-frequency integrals with $\delta(\omega)$ being the Dirac delta function and $\mathcal{P}$ being the Cauchy principal value. For example, the time integral of the coefficient $C_{12}(\tau)$ is given by

$$\frac{1}{\hbar^2}\int\limits_0^\infty d\tau\, C_{12}(\tau)e^{i\omega_\nu\tau} = \frac{1}{\hbar^2}\int\limits_0^\infty d\tau \int\limits_0^\infty d\omega'\, \hbar^2\lambda^2(\omega')e^{-i(\omega'-\omega_\nu)\tau}$$

$$= \pi\lambda^2(\omega_\nu) - i\mathcal{P}\int\limits_0^\infty \frac{d\omega'}{\omega'-\omega_\nu}\lambda^2(\omega').$$

(46)

Finally, we define the cavity decay rate κ and the Lamb shift Δ_κ as

$$\frac{\kappa}{2} = \pi\lambda^2(\omega_\nu),$$

(47a)

$$\Delta_\kappa = \mathcal{P}\int\limits_0^\infty \frac{d\omega'}{\omega'-\omega_\nu}\lambda^2(\omega').$$

(47b)

For instance, for a planar cavity, the cavity decay rate is given by [52]

$$\kappa = \frac{2\delta c}{d},$$

(48)

where δ, d, and c are mirror transmission, spacing between mirrors, and the speed of light, respectively.

The correlation functions from the second bath read (derivation in Appendix B)

$$C_{34}(\tau) \approx \int\limits_0^\infty d\omega\, \frac{\hbar\mu_0}{\pi}\omega^2 \mathbf{d}_{10}\cdot\mathrm{Im}\mathbf{G}(\mathbf{r}_i,\mathbf{r}_i,\omega)\cdot\mathbf{d}_{01}e^{-i\omega\tau},$$

(49)

$$C_{43}(\tau) \approx 0.$$

(50)

Again, we evaluate the time-frequency integral using Eq. (45):

$$\frac{1}{\hbar^2}\int\limits_0^\infty d\tau\, C_{34}(\tau)e^{i\omega_{10}\tau}$$

$$= \frac{\mu_0}{\hbar}\omega_{10}^2 \mathbf{d}_{10}\cdot\mathrm{Im}\mathbf{G}(\mathbf{r}_i,\mathbf{r}_i,\omega_{10})\cdot\mathbf{d}_{01}$$

$$- i\mathcal{P}\int\limits_0^\infty \frac{d\omega}{\omega-\omega_{10}}\frac{\mu_0}{\hbar\pi}\omega^2 \mathbf{d}_{10}\cdot\mathrm{Im}\mathbf{G}(\mathbf{r}_i,\mathbf{r}_i,\omega)\cdot\mathbf{d}_{01}.$$

(51)

Similarly as before, we define the spontaneous decay rate of all photon modes $\Gamma_\downarrow^{\mathrm{tot}}$ and the shift $\Delta_{\Gamma_\downarrow^{\mathrm{tot}}}$ as

$$\frac{\Gamma_\downarrow^{\mathrm{tot}}}{2} = \frac{\mu_0}{\hbar}\omega_{10}^2 \mathbf{d}_{10}\cdot\mathrm{Im}\mathbf{G}(\mathbf{r}_i,\mathbf{r}_i,\omega_{10})\cdot\mathbf{d}_{01},$$

(52a)

$$\Delta_{\Gamma_\downarrow^{\mathrm{tot}}} = \mathcal{P}\int\limits_0^\infty \frac{d\omega}{\omega-\omega_{10}}\frac{\mu_0}{\hbar\pi}\omega^2 \mathbf{d}_{10}\cdot\mathrm{Im}\mathbf{G}(\mathbf{r}_i,\mathbf{r}_i,\omega)\cdot\mathbf{d}_{01}.$$

(52b)

For instance, the spontaneous decay rate in a spherical microcavity has been derived in Ref. [53].

For the resonant correlation functions we have a sum of interaction strength over modes ν:

$$C_{3'4'}(\tau) = \sum_\nu \frac{1}{4}\hbar^2\Omega_R^2\frac{\gamma_\nu}{2\pi}\int\limits_{-\infty}^\infty d\omega\, \frac{e^{-i\omega t}}{(\omega-\omega_\nu)^2+\gamma_\nu^2/4},$$

(53)

$$C_{4'3'}(\tau) \approx 0.$$

(54)

Then we evaluate the time-frequency integral:

$$\frac{1}{\hbar^2}\int\limits_0^\infty d\tau\, C_{3'4'}(\tau)e^{i\omega_{10}\tau}$$

$$= \sum_\nu \frac{\gamma_\nu}{2\pi}\int\limits_0^\infty d\tau \int\limits_{-\infty}^\infty d\omega\, \frac{1}{4}\frac{\Omega_R^2}{(\omega-\omega_\nu)^2+\gamma_\nu^2/4}e^{-i(\omega-\omega_{10})t}$$

$$= \sum_\nu \frac{\Omega_R^2}{2}\frac{\gamma_\nu/4}{(\omega_{10}-\omega_\nu)^2+\gamma_\nu^2/4}$$

$$- i\sum_\nu \mathcal{P}\int\limits_{-\infty}^\infty \frac{\Omega_R^2}{2\pi}\frac{d\omega}{\omega-\omega_{10}}\frac{\gamma_\nu/4}{(\omega-\omega_\nu)^2+\gamma_\nu^2/4}$$

$$= \frac{\Gamma_\downarrow^r}{2} - i\Delta_{\Gamma_\downarrow^r},$$

(55)

where we have defined the resonant decay rate $\Gamma_\downarrow^r$ and shift $\Delta_{\Gamma_\downarrow^r}$ as

$$\frac{\Gamma_\downarrow^r}{2} = \sum_\nu \frac{\Omega_R^2}{2}\frac{\gamma_\nu/4}{(\omega_{10}-\omega_\nu)^2+\gamma_\nu^2/4},$$

(56a)

$$\Delta_{\Gamma_\downarrow^r} = \sum_\nu \mathcal{P}\int\limits_{-\infty}^\infty \frac{\Omega_R^2}{2\pi}\frac{d\omega}{\omega-\omega_{10}}\frac{\gamma_\nu/4}{(\omega-\omega_\nu)^2+\gamma_\nu^2/4}.$$

(56b)

For the third bath the correlation values read

$$C_{56}(\tau) \approx 0,$$

(57)

$$C_{65}(\tau) \approx \int\limits_0^\infty d\omega''\, \hbar^2\mu^2(\omega'')e^{i\omega''\tau}.$$

(58)

By evaluating the time-frequency integral with the coefficient $C_{65}(\tau)$ we obtain

$$\frac{1}{\hbar^2}\int\limits_0^\infty d\tau\, C_{65}(\tau)e^{-i\omega_{10}\tau}$$

$$= \frac{1}{\hbar^2}\int\limits_0^\infty d\tau \int\limits_0^\infty d\omega''\, \hbar^2\mu^2(\omega'')e^{i\omega''\tau}e^{-i\omega_{10}\tau}$$

$$= \pi\mu^2(\omega_{10}) + i\mathcal{P}\int\limits_0^\infty \frac{d\omega''}{\omega''-\omega_{10}}\mu^2(\omega'').$$

(59)

We define the laser pumping rate $\Gamma_\uparrow$ and the shift $\Delta_{\Gamma_\uparrow}$ as

$$\frac{\Gamma_\uparrow}{2} = \pi \mu^2(\omega_{10}), \tag{60a}$$

$$\Delta_{\Gamma_\uparrow} = \mathcal{P} \int_0^\infty \frac{d\omega''}{\omega'' - \omega_{10}} \mu^2(\omega''), \tag{60b}$$

with the coupling constant $\mu^2(\omega)$ being

$$\mu^2(\omega) = \frac{d_{01}^2 I(\omega)}{2c\varepsilon_0 \hbar^2}. \tag{61}$$

We find $\mu^2(\omega)$ in Appendix C, where we derive the expression of the parameter $\Gamma_\uparrow$ related to the laser output intensity $I(\omega)$ and demonstrate that it does not depend on the frequency distribution of the light source in the broadband limit. Additionally, we find the frequency shift induced by the laser source $\Delta_{\Gamma_\uparrow}$.

D. Resulting master equation

Now we can write the master equation in shorter form, retaining only the nonvanishing correlation functions:

$$\dot{\rho}_S(t) = -\frac{i}{\hbar}[\hat{H}_S, \rho_S(t)] - \frac{1}{\hbar^2} \int_0^\infty d\tau \left\{ \sum_\nu [\hat{a}_\nu^\dagger, \hat{a}_\nu e^{i\omega_\nu \tau} \rho_S(t)] C_{12}(\tau) + [\rho_S(t)\hat{a}_\nu^\dagger e^{-i\omega_\nu \tau}, \hat{a}_\nu] C_{12}(-\tau) \right.$$

$$+ \sum_i [\hat{\sigma}_i^\dagger, \hat{\sigma}_i e^{i\omega_{10}\tau} \rho_S(t)][C_{34}(\tau) - C_{3'4'}(\tau)] + [\rho_S(t)\hat{\sigma}_i^\dagger e^{-i\omega_{10}\tau}, \hat{\sigma}_i][C_{34}(-\tau) - C_{3'4'}(-\tau)]$$

$$\left. + \sum_i [\rho_S(t)\hat{\sigma}_i e^{i\omega_{10}\tau}, \hat{\sigma}_i^\dagger] C_{65}(-\tau) + [\hat{\sigma}_i, \hat{\sigma}_i^\dagger e^{-i\omega_{10}\tau} \rho_S(t)] C_{65}(\tau) \right\}. \tag{62}$$

Using all the rate parameters defined above, the master equation reads

$$\dot{\rho}_S(t) = -\frac{i}{\hbar}[\hat{H}_S, \rho_S(t)] - \left\{ \sum_\nu [\hat{a}_\nu^\dagger, \hat{a}_\nu \rho_S(t)]\left[\frac{\kappa}{2} - i\Delta_\kappa\right] + [\rho_S(t)\hat{a}_\nu^\dagger, \hat{a}_\nu]\left[\frac{\kappa}{2} + i\Delta_\kappa\right] \right.$$

$$+ \sum_i [\hat{\sigma}_i^\dagger, \hat{\sigma}_i \rho_S(t)]\left[\left[\frac{\Gamma_\downarrow^{\text{tot}}}{2} - i\Delta_{\Gamma_\downarrow^{\text{tot}}}\right] - \left[\frac{\Gamma_\downarrow^r}{2} - i\Delta_{\Gamma_\downarrow^r}\right]\right] + [\rho_S(t)\hat{\sigma}_i^\dagger, \hat{\sigma}_i]\left[\left[\frac{\Gamma_\downarrow^{\text{tot}}}{2} + i\Delta_{\Gamma_\downarrow^{\text{tot}}}\right] - \left[\frac{\Gamma_\downarrow^r}{2} + i\Delta_{\Gamma_\downarrow^r}\right]\right]$$

$$\left. + \sum_i [\rho_S(t)\hat{\sigma}_i, \hat{\sigma}_i^\dagger]\left[\frac{\Gamma_\uparrow}{2} - i\Delta_{\Gamma_\uparrow}\right] + [\hat{\sigma}_i, \hat{\sigma}_i^\dagger \rho_S(t)]\left[\frac{\Gamma_\uparrow}{2} + i\Delta_{\Gamma_\uparrow}\right] \right\}. \tag{63}$$

Note that for the last bath correlation the shifts $\Delta_{\Gamma_\uparrow}$ have the opposite sign as compared to $\Delta_{\Gamma_\downarrow^{\text{tot}}}$, $\Delta_{\Gamma_\downarrow^r}$, and Δ_κ.

After using the Lindblad superoperator definition $\mathcal{L}[\hat{X}]\rho = \hat{X}^\dagger \hat{X}\rho + \rho\hat{X}^\dagger\hat{X} - 2\hat{X}\rho\hat{X}^\dagger$ for a generic operator $\hat{X}$ and collecting all Lamb shifts we obtain the master equation describing cavity and spontaneous decay and laser pump rate:

$$\dot{\rho}_S(t) = -\frac{i}{\hbar}[\hat{H}_S, \rho_S(t)] - i\sum_{\nu,i} \left\{ \Delta_\kappa[\hat{a}_\nu^\dagger \hat{a}_\nu, \rho_S(t)] + \Delta_{\Gamma_\downarrow}[\hat{\sigma}_i^\dagger \hat{\sigma}_i, \rho_S(t)] - \Delta_{\Gamma_\uparrow}[\hat{\sigma}_i \hat{\sigma}_i^\dagger, \rho_S(t)] \right\}$$

$$- \left\{ \sum_{\nu,i} \frac{\kappa}{2}\mathcal{L}[\hat{a}_\nu]\rho_S(t) + \frac{\Gamma_\downarrow}{2}\mathcal{L}[\hat{\sigma}_i]\rho_S(t) + \frac{\Gamma_\uparrow}{2}\mathcal{L}[\hat{\sigma}_i^\dagger]\rho_S(t) \right\}, \tag{64}$$

where $\Gamma_\downarrow = \Gamma_\downarrow^{\text{tot}} - \Gamma_\downarrow^r$ and $\Delta_{\Gamma_\downarrow} = \Delta_{\Gamma_\downarrow^{\text{tot}}} - \Delta_{\Gamma_\downarrow^r}$. Absorbing the Lamb shifts into a redefined system Hamiltonian, the master equation reads

$$\dot{\rho}_S(t) = -\frac{i}{\hbar}[\hat{H}_S, \rho_S(t)]$$

$$- \sum_{\nu,i} \left\{ \frac{\kappa}{2}\mathcal{L}[\hat{a}_\nu] + \frac{\Gamma_\downarrow}{2}\mathcal{L}[\hat{\sigma}_i] + \frac{\Gamma_\uparrow}{2}\mathcal{L}[\hat{\sigma}_i^\dagger] \right\} \rho_S(t). \tag{65}$$

The new frequencies in the system Hamiltonian $\hat{H}_S$ coming from the Lamb shift we redefine to be

$$\omega_{10} + \Delta_{\Gamma_\downarrow} + \Delta_{\Gamma_\uparrow} \to \omega_{10}$$

and

$$\omega_\nu + \Delta_\kappa \to \omega_\nu.$$

V. NESTED OPEN QUANTUM SYSTEMS

We have now derived the master equation for spontaneous and cavity decay and accounted for laser pumping. Now we treat the remaining system Hamiltonian as the total Hamiltonian of the subsystem $\hat{H}_S \equiv \hat{H}$ [see Eq. (43)].

Also, we define the new system Hamiltonian to be $\hat{H}_S^a + \hat{H}_S^\sigma \equiv \hat{H}_S$, whereas $\hat{H}_I^{\Gamma(\pm\delta_\nu)}$ and $\hat{H}_F^{\Gamma(\pm\delta_\nu)}$ remain unchanged. For notational convenience, we will now drop the superscripts $\Gamma(\pm\delta_\nu)$ from the field and interaction Hamiltonians. If the coupling between rovibrational states, electronic transitions, and photons is strong, it is convenient to transform the

Hamiltonian using the polaron transformation $\hat{H} \rightarrow \hat{U}^\dagger \hat{H} \hat{U}$, where the polaron operator $\hat{U}$ reads

$$\hat{U} = e^{\sum_i \sqrt{S} \hat{\sigma}_i^z (\hat{b}_i - \hat{b}_i^\dagger)}. \tag{66}$$

The Hamiltonian after applying the polaron transformation can be written as

$$\hat{H} = \sum_{\nu,i} \frac{1}{2} \hbar \omega_{10} \hat{\sigma}_i^z + \hbar \omega_\nu \hat{a}_\nu^\dagger \hat{a}_\nu + \hbar \Omega \hat{b}_i^\dagger \hat{b}_i \tag{67}$$

$$+ \hbar \Omega_\nu [\hat{a}_\nu \hat{\sigma}_i^\dagger \hat{D}_i + \hat{a}_\nu^\dagger \hat{\sigma}_i \hat{D}_i^\dagger], \tag{68}$$

with the interaction Hamiltonian being

$$\hat{H}_I = \sum_{\nu,i} \hbar \Omega_\nu [\hat{a}_\nu \hat{\sigma}_i^\dagger \hat{D}_i + \hat{a}_\nu^\dagger \hat{\sigma}_i \hat{D}_i^\dagger] \tag{69}$$

and the displacement operator $\hat{D} = e^{2\sqrt{S}(\hat{b}_i^\dagger - \hat{b}_i)}$.

To obtain the master equation for $\hat{H}_I$, here we use a more general treatment, called the projection operator technique [49]. Because now $\hat{H}_I$ in the interaction picture will not only evolve unitarily but will also exhibit an exponential decay coming from κ, $\Gamma_\downarrow$, and $\Gamma_\uparrow$. We start with the master equation from the previous section:

$$\dot{\rho} = -\frac{i}{\hbar}[\hat{H}, \rho]$$
$$- \sum_{\nu,i} \left\{ \frac{\kappa}{2} \mathfrak{L}[\hat{a}_\nu] + \frac{\Gamma_\downarrow}{2} \mathfrak{L}[\hat{\sigma}_i] + \frac{\Gamma_\uparrow}{2} \mathfrak{L}[\hat{\sigma}_i^\dagger] \right\} \rho. \tag{70}$$

Note that we have redefined the density matrix of the subsystem as $\rho_S \equiv \rho$.

Let us redefine commutators and Lindblad dissipators into Liouville superoperator form:

$$\mathcal{L}_{F,S,I} \rho = -\frac{i}{\hbar}[\hat{H}_{F,S,I}, \rho] \tag{71}$$

and

$$\mathcal{D}\rho = - \sum_{\nu,i} \left\{ \frac{\kappa}{2} \mathfrak{L}[\hat{a}_\nu] + \frac{\Gamma_\downarrow}{2} \mathfrak{L}[\hat{\sigma}_i] + \frac{\Gamma_\uparrow}{2} \mathfrak{L}[\hat{\sigma}_i^\dagger] \right\} \rho. \tag{72}$$

The master equation then reads

$$\dot{\rho} = (\mathcal{L}_F + \mathcal{L}_S + \mathcal{L}_I + \mathcal{D})\rho = \mathcal{L}\rho. \tag{73}$$

The goal is to derive the master equation for the subsystem of interest (photon number and molecular excitations), which can be achieved by projecting on the relevant part of the density matrix $\mathcal{P}\rho = \text{tr}_F[\rho] \otimes \rho_F = \rho_S \otimes \rho_F$ and tracing out the bath (phonon modes of molecules). The irrelevant part reads as $\mathcal{Q}\rho = (1 - \mathcal{P})\rho$.

As for step 1, this step is based on the rotating-wave and Markov approximations and we assume that the rovibrational level spacing is smaller than the frequency of the electronic transition under consideration, $\Omega \ll \omega_{10}$. In this step (step 2), the rovibrational levels of all molecules act as a thermal bath for the coupled dynamics of electronic molecular transitions and cavity modes. This requires that the rovibrational levels

reach thermal equilibrium on time scales that are short with respect to decay by electronic transitions and the mode leakage outside the cavity. The former condition is equivalent to the validity of the Kennard-Stepanov relation. We follow the derivation along the lines of Ref, [49] (Chap. 5.1.2) and obtain

$$\dot{\rho}_S = (\mathcal{L}_S + \mathcal{D})\rho_S(t)$$
$$- \frac{1}{\hbar^2} \text{tr}_F[\hat{H}_I, \int_0^\infty d \, e^{(\mathcal{L}_F + \mathcal{L}_S + \mathcal{D})s} [\hat{H}_I, \rho_S(t - s) \otimes \rho_F]]. \tag{74}$$

Up to second-order expansion in coupling g from $\hat{H}_I$ it can be shown that Eq. (74) can be written as [54]

$$\dot{\rho}_S = (\mathcal{L}_S + \mathcal{D})\rho_S(t)$$
$$- \frac{1}{\hbar^2} \text{tr}_F[\hat{H}_I, \int_0^\infty ds \, [e^{(\mathcal{L}_F^\dagger + \mathcal{L}_S^\dagger + \mathcal{D}^\dagger)s}(\hat{H}_I), \rho_S(t) \otimes \rho_F]], \tag{75}$$

where $e^{(\mathcal{L}_F^\dagger + \mathcal{L}_S^\dagger + \mathcal{D}^\dagger)s}$ is acting only on $\hat{H}_I$ and the adjoint Lindbladian superoperator for an arbitrary operator $\hat{A}$ is defined as

$$\mathfrak{L}^\dagger[\hat{X}]\hat{A} = \hat{X}^\dagger \hat{X} \hat{A} + \hat{A} \hat{X}^\dagger \hat{X} - 2\hat{X}^\dagger \hat{A} \hat{X}. \tag{76}$$

The interaction Hamiltonian now corresponds to the dissipative interaction picture.

Calculating the Liouville superoperator for all interaction Hamiltonian operators, we obtain the following relations:

$$\hat{a}(t) = e^{(\mathcal{L}_F^\dagger + \mathcal{L}_S^\dagger + \mathcal{D}^\dagger)t} \hat{a} = e^{(\mathcal{L}_S^\dagger + \mathcal{D}^\dagger)t} \hat{a} = \hat{a} e^{-i\omega_\nu t - \frac{\kappa}{2}t}, \tag{77}$$

$$\hat{a}^\dagger(t) = \hat{a}^\dagger e^{i\omega_\nu t - \frac{\kappa}{2}t}, \tag{78}$$

$$\hat{\sigma}(t) = \hat{\sigma} e^{-i\omega_{10}t - \frac{\Gamma_\downarrow + \Gamma_\uparrow}{2}t}, \tag{79}$$

$$\hat{\sigma}^\dagger(t) = \hat{\sigma}^\dagger e^{i\omega_{10}t - \frac{\Gamma_\downarrow + \Gamma_\uparrow}{2}t}, \tag{80}$$

$$\hat{D}(t) = e^{i\sum_i \hbar \Omega \hat{b}_i^\dagger \hat{b}t} \hat{D} e^{-i\sum_i \hbar \Omega \hat{b}_i^\dagger \hat{b}t} = e^{2\sqrt{S}(\hat{b}_i^\dagger e^{i\Omega t} - \hat{b}_i e^{-i\Omega t})}, \tag{81}$$

$$\hat{D}^\dagger(t) = e^{2\sqrt{S}(\hat{b}_i e^{-i\Omega t} - \hat{b}_i^\dagger e^{i\Omega t})}, \tag{82}$$

where the last two expressions are obtained by using the Baker-Campbell-Hausdorff formula. We have used the following relations to obtain $\hat{a}(t)$ and $\hat{\sigma}(t)$ and their conjugates:

$$\mathfrak{L}^\dagger[\hat{a}]\hat{I} = \mathfrak{L}^\dagger[\hat{\sigma}]\hat{I} = \mathfrak{L}^\dagger[\hat{\sigma}^\dagger]\hat{I} = 0, \tag{83}$$

$$\mathfrak{L}^\dagger[\hat{a}]\hat{a} = \hat{a}, \tag{84}$$

$$\mathfrak{L}^\dagger[\hat{a}]\hat{a}^\dagger = \hat{a}^\dagger, \tag{85}$$

$$\mathfrak{L}^\dagger[\hat{\sigma}]\hat{\sigma}^\dagger = \mathfrak{L}^\dagger[\hat{\sigma}^\dagger]\hat{\sigma}^\dagger = \hat{\sigma}^\dagger, \tag{86}$$

$$\mathfrak{L}^\dagger[\hat{\sigma}]\hat{\sigma} = \mathfrak{L}^\dagger[\hat{\sigma}^\dagger]\hat{\sigma} = \hat{\sigma}. \tag{87}$$

We are now in a position to write the master equation by evaluating the double commutator under the integral

in Eq. (75), which reads

$$
\begin{aligned}
\dot{\rho}_S(t) = & -\frac{i}{\hbar}[\hat{H}_S, \rho_S(t)] + \mathcal{D}\rho_S(t) \\
& - \int_0^\infty d\tau \sum_{\nu,i} \Big\{ [\hat{a}_\nu \hat{\sigma}_i^\dagger, \hat{a}_\nu^\dagger \hat{\sigma}_i e^{i\delta_\nu \tau} \rho_S(t)] C_{78}(-\tau) \\
& + [\rho_S(t) \hat{a}_\nu^\dagger \hat{\sigma}_i e^{i\delta_\nu \tau}, \hat{a}_\nu \hat{\sigma}_i^\dagger] C_{87}(\tau) \\
& + [\hat{a}_\nu^\dagger \hat{\sigma}_i, \hat{a}_\nu \hat{\sigma}_i^\dagger e^{-i\delta_\nu \tau} \rho_S(t)] C_{87}(-\tau) \\
& + [\rho_S(t) \hat{a}_\nu \hat{\sigma}_i^\dagger e^{-i\delta_\nu \tau}, \hat{a}_\nu^\dagger \hat{\sigma}_i] C_{78}(\tau) \Big\},
\end{aligned}
\tag{88}
$$

where $\delta_\nu = \omega_\nu - \omega_{10}$.

To cast this result into a simpler form, we define the quantities $K(\delta_\nu)$, $K(-\delta_\nu)$, $K^*(\delta_\nu)$, and $K^*(-\delta_\nu)$:

$$
\begin{aligned}
K(\delta_\nu) &= \int_0^\infty d\tau \, C_{87}(-\tau) e^{-i\delta_\nu \tau} \\
&= \hbar^2 \Omega_\nu^2 \int_0^\infty d\tau \, \langle \hat{D}_i^\dagger \hat{D}_i(\tau) \rangle e^{-i\delta_\nu \tau} e^{-\frac{\Gamma}{2}\tau},
\end{aligned}
\tag{89}
$$

$$
\begin{aligned}
K(-\delta_\nu) &= \int_0^\infty d\tau \, C_{78}(-\tau) e^{i\delta_\nu \tau} \\
&= \hbar^2 \Omega_\nu^2 \int_0^\infty d\tau \, \langle \hat{D}_i^\dagger \hat{D}_i(\tau) \rangle e^{i\delta_\nu \tau} e^{-\frac{\Gamma}{2}\tau},
\end{aligned}
\tag{90}
$$

$$
\begin{aligned}
K^*(\delta_\nu) &= \int_0^\infty d\tau \, C_{87}(\tau) e^{i\delta_\nu \tau} \\
&= \hbar^2 \Omega_\nu^2 \int_0^\infty d\tau \, \langle \hat{D}_i^\dagger \hat{D}_i(-\tau) \rangle e^{i\delta_\nu \tau} e^{-\frac{\Gamma}{2}\tau},
\end{aligned}
\tag{91}
$$

$$
\begin{aligned}
K^*(-\delta_\nu) &= \int_0^\infty d\tau \, C_{78}(\tau) e^{-i\delta_\nu \tau} \\
&= \hbar^2 \Omega_\nu^2 \int_0^\infty d\tau \, \langle \hat{D}_i^\dagger \hat{D}_i(-\tau) \rangle e^{-i\delta_\nu \tau} e^{-\frac{\Gamma}{2}\tau},
\end{aligned}
\tag{92}
$$

with $\Gamma = \kappa + \Gamma_\downarrow + \Gamma_\uparrow$. We have used the relation

$$
\langle \hat{D}_i(\tau)\hat{D}_i^\dagger \rangle = \langle \hat{D}_i^\dagger(\tau)\hat{D}_i \rangle,
\tag{93}
$$

which follows from the relations $\hat{D}^\dagger(\alpha) = \hat{D}(-\alpha)$ and $\langle n, -\alpha | n, -\beta \rangle = \langle n, \alpha | n, \beta \rangle$. With these definitions, the master equation reads

$$
\begin{aligned}
\dot{\rho}_S(t) = & -\frac{i}{\hbar}[\hat{H}_S, \rho_S(t)] + \mathcal{D}\rho_S(t) \\
& - \sum_{\nu,i} [\hat{a}_\nu \hat{\sigma}_i^\dagger, \hat{a}_\nu^\dagger \hat{\sigma}_i \rho_S(t)] K(-\delta_\nu) + [\rho_S(t)\hat{a}_\nu^\dagger \hat{\sigma}_i, \hat{a}_\nu \hat{\sigma}_i^\dagger] K^*(\delta_\nu) \\
& + [\hat{a}_\nu^\dagger \hat{\sigma}_i, \hat{a}_\nu \hat{\sigma}_i^\dagger \rho_S(t)] K(\delta_\nu) + [\rho_S(t)\hat{a}_\nu \hat{\sigma}_i^\dagger, \hat{a}_\nu^\dagger \hat{\sigma}_i] K^*(-\delta_\nu).
\end{aligned}
\tag{94}
$$

Separating the coefficients $K(\delta)$ into real and imaginary parts, we can define constants for absorption and emission out of or into the cavity modes:

$$
\Gamma(\pm \delta_\nu) = 2K'(\pm \delta_\nu),
\tag{95}
$$

where $K'(\pm\delta_\nu) \equiv \mathrm{Re}K(\pm\delta_\nu)$. With these definitions and collecting terms in Eq. (94) into Lindbladian forms, we obtain a final master equation that describes the dye-photon dynamics in a photon-BEC setup:

$$
\begin{aligned}
\dot{\rho}_S = & -\frac{i}{\hbar}[\hat{H}_S', \rho_S] - \sum_{\nu,i} \Big\{ \frac{\Gamma_\downarrow}{2}\mathfrak{L}[\hat{\sigma}_i] + \frac{\kappa}{2}\mathfrak{L}[\hat{a}_\nu] + \frac{\Gamma_\uparrow}{2}\mathfrak{L}[\hat{\sigma}_i^\dagger] \\
& + \frac{\Gamma(\delta_\nu)}{2}\mathfrak{L}[\hat{a}_\nu \hat{\sigma}_i^\dagger] + \frac{\Gamma(-\delta_\nu)}{2}\mathfrak{L}[\hat{a}_\nu^\dagger \hat{\sigma}_i] \Big\} \rho_S.
\end{aligned}
\tag{96}
$$

The modified system Hamiltonian $\hat{H}_S'$ has absorbed the Lamb shifts and reads

$$
\begin{aligned}
\hat{H}_S' = & \hbar \sum_{\nu,i} [\omega_{10} + K''(-\delta_\nu)]\hat{\sigma}_i^\dagger \hat{\sigma}_i + [\omega_\nu + K''(\delta_\nu)]\hat{a}_\nu^\dagger \hat{a}_\nu \\
& + [K''(-\delta_\nu) - K''(\delta_\nu)]\hat{a}_\nu^\dagger \hat{a}_\nu \hat{\sigma}_i^\dagger \hat{\sigma}_i,
\end{aligned}
\tag{97}
$$

where $K''(\pm\delta_\nu)$ denotes the imaginary part of $K(\pm\delta_\nu)$.

VI. CONCLUSIONS

We have constructed a general theory and derived the necessary parameters to describe photon Bose-Einstein condensation in a dye-filled cavity using a microscopic description of the molecule-photon interaction. Adding to the previous dissipative studies, we have derived parameters $\Gamma_\uparrow$, $\Gamma_\downarrow$, and κ, where the last two depend on the geometry of the system. Also, we have demonstrated that all the rates (except $\Gamma_\uparrow$) are related to the Green's tensor, which is essentially related to the geometrical setup. Furthermore, we have shown how $\Gamma(\pm\delta_\nu)$ are influenced by $\Gamma_\uparrow$, $\Gamma_\downarrow$, and κ since molecule rovibrational states are influenced by cavity and spontaneous decay and laser pumping.

The next step will be to apply this technique to different geometries and calculate the threshold of the condensate. The simplest geometry for which the Green's tensor can be analytically calculated is the planar cavity. For example, the spontaneous emission rate $\Gamma_\downarrow$ would then be calculated from the imaginary part of the Green's tensor multiplied by the dipole moment of the molecule, as demonstrated in the main section. If the cavity mirrors are highly reflective, it is relatively easy to calculate the cavity decay κ. It can be obtained from the Green's tensor intrinsic structure by taking a Taylor expansion of the denominator in the Green's tensor, which is responsible for multiple reflections from mirrors. For the laser pump rate $\Gamma_\uparrow$ one needs to know the laser intensity and dipole moment of the molecule.

For a more realistic setup, mirrors with a spherical curvature even including two dips [19] can be considered, which are used in real experiments. Naturally, the complexity of calculating the Green's tensor for such a system largely increases.

APPENDIX A: CAVITY DECAY DEMONSTRATION

Here we demonstrate that photons decay with the same rate as Lorentzian linewidth describing the quality of the cavity γ. We have defined the creation and annihilation operators in the cavity to be [50]

$$
\hat{a}_\nu^\dagger = \sqrt{\frac{\gamma_\nu}{2\pi}} \int\limits_{-\infty}^{\infty} d\omega \frac{\hat{a}^\dagger(\omega)}{\omega - \omega_\nu - i\gamma_\nu/2},
$$

$$
\hat{a}_\nu = \sqrt{\frac{\gamma_\nu}{2\pi}} \int\limits_{-\infty}^{\infty} d\omega \frac{\hat{a}(\omega)}{\omega - \omega_\nu + i\gamma_\nu/2}.
\tag{A1}
$$

As we will show, the effective dynamics of these non-monochromatic narrow-band operators will be nonunitary and decay with a rate γ_ν for mode ν. We start from Heisenberg equations of motion for $\hat{a}(\omega)$ and their conjugate:

$$
\begin{aligned}
\dot{\hat{a}}^\dagger(\omega) &= i\omega\hat{a}^\dagger(\omega), \\
\dot{\hat{a}}(\omega) &= -i\omega\hat{a}(\omega).
\end{aligned}
\tag{A2}
$$

Taking the time derivative of Eqs. (A1) and using Eqs. (A2), we obtain

$$
\dot{\hat{a}}_\nu^\dagger = \sqrt{\frac{\gamma_\nu}{2\pi}} \int\limits_{-\infty}^{\infty} d\omega \frac{i\omega\hat{a}^\dagger(\omega)}{\omega - \omega_\nu - i\gamma_\nu/2},
$$

$$
\dot{\hat{a}}_\nu = \sqrt{\frac{\gamma_\nu}{2\pi}} \int\limits_{-\infty}^{\infty} d\omega \frac{-i\omega\hat{a}(\omega)}{\omega - \omega_\nu + i\gamma_\nu/2}.
\tag{A3}
$$

These equations can be rewritten in the form

$$
\begin{aligned}
\dot{\hat{a}}_\nu^\dagger &= i\hat{F}^\dagger + \left(i\omega_\nu - \frac{\gamma_\nu}{2}\right)\hat{a}_\nu^\dagger, \\
\dot{\hat{a}}_\nu &= -i\hat{F} + \left(-i\omega_\nu - \frac{\gamma_\nu}{2}\right)\hat{a}_\nu,
\end{aligned}
\tag{A4}
$$

with $\hat{F} = \sqrt{\frac{\gamma_\nu}{2\pi}} \int d\omega\, \hat{a}(\omega)$. To find the equation of motion of the number operator $\langle \hat{a}_\nu^\dagger \hat{a}_\nu \rangle$, we use Eqs. (A4) and the chain rule. We start by taking derivative of the expectation value:

$$
\frac{d}{dt}\langle \hat{a}_\nu^\dagger \hat{a}_\nu \rangle = -\gamma_\nu \langle \hat{a}_\nu^\dagger \hat{a}_\nu \rangle - i\langle \hat{a}_\nu^\dagger \hat{F} \rangle + i\langle \hat{F}^\dagger \hat{a}_\nu \rangle.
\tag{A5}
$$

Let us evaluate the last two terms:

$$
-i\langle \hat{a}_\nu^\dagger \hat{F} \rangle = -i\frac{\gamma_\nu}{2\pi} \int\limits_{-\infty}^{\infty} d\omega \frac{n(\omega)}{\omega - \omega_\nu - i\gamma_\nu/2},
\tag{A6}
$$

$$
i\langle \hat{F}^\dagger \hat{a}_\nu \rangle = i\frac{\gamma_\nu}{2\pi} \int\limits_{-\infty}^{\infty} d\omega \frac{n(\omega)}{\omega - \omega_\nu + i\gamma_\nu/2},
\tag{A7}
$$

where we have used the fact that $\langle \hat{a}^\dagger(\omega)\hat{a}(\omega') \rangle = n(\omega)\delta(\omega - \omega')$. Summing these terms,

$$
i\langle \hat{F}^\dagger \hat{a}_\nu \rangle - i\langle \hat{a}_\nu^\dagger \hat{F} \rangle = \frac{\gamma_\nu^2}{2\pi} \int\limits_{-\infty}^{\infty} d\omega \frac{n(\omega)}{(\omega - \omega_\nu)^2 + (\gamma_\nu/2)^2},
\tag{A8}
$$

the total time evolution equation reads

$$
\begin{aligned}
\frac{d}{dt}\langle \hat{a}_\nu^\dagger \hat{a}_\nu \rangle = &-\gamma_\nu \langle \hat{a}_\nu^\dagger \hat{a}_\nu \rangle \\
&+ \frac{\gamma_\nu^2}{2\pi} \int\limits_{-\infty}^{\infty} d\omega \frac{n(\omega)}{(\omega - \omega_\nu)^2 + (\gamma_\nu/2)^2},
\end{aligned}
\tag{A9}
$$

where $n(\omega)$ is thermal photon number following Bose-Einstein distribution:

$$
n(\omega) = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}.
\tag{A10}
$$

In the experimental setup the thermal excitations are much smaller than the cavity excitations; thus, $n(\omega) \approx 0$. Equation (A9) then shows that the photon decay rate κ is identical with the width of the resonance γ_ν.

APPENDIX B: CORRELATION COEFFICIENTS FOR THE TOTAL PHOTON FIELD BATH

In this section we demonstrate explicitly how $C_{34}(\tau)$ and $C_{43}(\tau)$ are calculated. Before carrying out the calculation we mention that the average value of fundamental fields reads

$$
\langle \hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega)\hat{\mathbf{f}}_{\lambda'}^\dagger(\mathbf{r}', \omega') \rangle = [n(\omega') + 1]\boldsymbol{\delta}(\mathbf{r} - \mathbf{r}')\delta_{\lambda\lambda'}\delta(\omega - \omega'),
\tag{B1a}
$$

$$
\langle \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega)\hat{\mathbf{f}}_{\lambda'}(\mathbf{r}', \omega') \rangle = n(\omega')\boldsymbol{\delta}(\mathbf{r} - \mathbf{r}')\delta_{\lambda\lambda'}\delta(\omega - \omega'),
\tag{B1b}
$$

where $n(\omega)$ is the same as in Eq. (A10).

Note that $C_{33} = C_{44} = 0$, because $\langle \hat{\mathbf{f}}_\lambda(\mathbf{r}, \omega)\hat{\mathbf{f}}_{\lambda'}(\mathbf{r}', \omega') \rangle = \langle \hat{\mathbf{f}}_\lambda^\dagger(\mathbf{r}, \omega)\hat{\mathbf{f}}_{\lambda'}^\dagger(\mathbf{r}', \omega') \rangle = 0$.

The explicit calculation of the correlation coefficient $C_{34}(\tau)$ is as follows: we take the average of the product of the bath operators $\langle B_3 B_4(-\tau) \rangle$ from Eqs. (35) which is just an average over $\hat{\mathbf{f}}_\lambda$ operators.

Simplifying the result by using the integral relation [40]

$$
\begin{aligned}
\sum_{\lambda=e,m} \int d^3s\, \mathbf{G}_\lambda(\mathbf{r}, \mathbf{s}, \omega) \cdot \mathbf{G}_{\lambda'}^{*\,T}(\mathbf{r}', \mathbf{s}, \omega') \\
= \frac{\hbar\mu_0}{\pi}\omega^2 \mathrm{Im}\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega),
\end{aligned}
\tag{B2}
$$

we find

$$
C_{34}(\tau)
$$

$$
= \int_0^\infty d\omega \, \frac{\hbar\mu_0}{\pi} \omega^2 \mathbf{d}_{10} \cdot \mathrm{Im}\, \mathbf{G}(\mathbf{r}_i, \mathbf{r}_i, \omega) \cdot \mathbf{d}_{01}[n(\omega) + 1] e^{-i\omega\tau}.
$$

$$
\text{(B3)}
$$

The coefficient $C_{43}(\tau)$ is calculated in similar manner:

$$
C_{43}(\tau) = \langle B_4 B_3(-\tau) \rangle
$$

$$
= \int_0^\infty d\omega \, \frac{\hbar\mu_0}{\pi} \omega^2 \mathbf{d}_{10} \cdot \mathrm{Im}\, \mathbf{G}(\mathbf{r}_i, \mathbf{r}_i, \omega) \cdot \mathbf{d}_{01} n(\omega) e^{i\omega\tau}.
$$

$$
\text{(B4)}
$$

APPENDIX C: DERIVATION OF LASER DRIVING CONSTANT

In this section, we derive the laser driving constant from the properties of the laser. We follow a similar procedure as Loudon (Chap. 2 of Ref. [55]). We start from the Hamiltonian that describes the interaction of a two-level atom with an incoherent, broad-band classical light field:

$$
\hat{H} = \hat{H}_A + \hat{H}_I = \frac{1}{2}\hbar\omega_{10}\hat{\sigma}_z
$$

$$
+ \hat{\mathbf{d}} \cdot \int_0^\infty d\omega \, [\mathbf{E}(\mathbf{r}_i, \omega) e^{-i\omega t} e^{-i\phi_\omega} + \mathbf{E}^*(\mathbf{r}_i, \omega) e^{i\omega t} e^{i\phi_\omega}],
$$

$$
\text{(C1)}
$$

where $\mathbf{E}(\mathbf{r}_i, \omega)$ is the electric field at the molecule's position $\mathbf{r}_i$ at frequency ω. The phase for each frequency is described by ϕ_ω and $\hat{\mathbf{d}} = \mathbf{d}_{10}|1\rangle\langle 0| + \mathbf{d}_{01}|0\rangle\langle 1|$ is the dipole moment of the molecule. To calculate the time dynamics of the excited atom state, we need to solve Schrödinger's equation, $\hat{H}\Psi = i\hbar\dot{\Psi}$. We expand the wavefunction as a linear superposition of orthonormal basis states which has a time dependence from the atomic Hamiltonian:

$$
|\Psi\rangle = C_0(t) e^{i\frac{E_0}{\hbar}t}|0\rangle + C_1(t) e^{i\frac{E_1}{\hbar}t}|1\rangle.
$$

$$
\text{(C2)}
$$

Transforming to the interaction picture, Schrödinger's equation reads

$$
\hat{H}_I|\Psi\rangle = i\hbar(\dot{C}_0(t)|0\rangle + \dot{C}_1(t)|1\rangle).
$$

$$
\text{(C3)}
$$

Multiplying Eq. (C3) by $\langle 0|$ and $\langle 1|$ we obtain two differential equations:

$$
i\hbar\dot{C}_0(t) = \mathbf{d}_{01} \cdot \int_0^\infty d\omega \, [\mathbf{E}(\mathbf{r}_i, \omega) e^{-i\omega t} e^{-i\phi_\omega}
$$

$$
+ \mathbf{E}^*(\mathbf{r}_i, \omega) e^{i\omega t} e^{i\phi_\omega}] e^{-i\omega_{10}t} C_1(t),
$$

$$
i\hbar\dot{C}_1(t) = \mathbf{d}_{10} \cdot \int_0^\infty d\omega [\mathbf{E}(\mathbf{r}_i, \omega) e^{-i\omega t} e^{-i\phi_\omega}
$$

$$
+ \mathbf{E}^*(\mathbf{r}_i, \omega) e^{i\omega t} e^{i\phi_\omega}] e^{i\omega_{10}t} C_0(t), \qquad \text{(C4)}
$$

where we have used the fact that the dipole operator has odd parity, meaning $\mathbf{d}_{00} = \mathbf{d}_{11} = 0$. Using the rotating-wave approximation and assuming that the dipole operator is real, $\mathbf{d}_{01} = \mathbf{d}_{10}$, the equations read

$$
i\hbar\dot{C}_0(t) = \mathbf{d}_{01} \cdot \int_0^\infty d\omega \, \mathbf{E}^*(\mathbf{r}_i, \omega) e^{i(\omega-\omega_{10})t} e^{i\phi_\omega} C_1(t),
$$

$$
\text{(C5)}
$$

$$
i\hbar\dot{C}_1(t) = \mathbf{d}_{01} \cdot \int_0^\infty d\omega \, \mathbf{E}(\mathbf{r}_i, \omega) e^{-i(\omega-\omega_{10})t} e^{-i\phi_\omega} C_0(t).
$$

To solve these equations we employ the perturbation expansion of $\mathbf{d}_{01} \cdot \mathbf{E}(\mathbf{r}_i, \omega)$ up to the first order, since $\mathbf{d}_{01} \cdot \mathbf{E}(\mathbf{r}_i, \omega) \ll \hbar\omega_{10}$. We pose the initial conditions, where the atom is assumed to be initially in the ground state, namely, $C_0(0) = 1$ and $C_1(0) = 0$. The solution for the first coefficient is constant $C_0(t) = 1$. The solution for $C_1(t)$ reads

$$
C_1(t) = \frac{i}{\hbar}\mathbf{d}_{01} \cdot \int_0^\infty d\omega \, \mathbf{E}(\mathbf{r}_i, \omega)\frac{1 - e^{i(\omega_{10}-\omega)t}}{i(\omega_{10} - \omega)} e^{-i\phi_\omega}. \quad \text{(C6)}
$$

Upon expressing the complex exponential in terms of the sine function, we obtain

$$
C_1(t) = -2\frac{i}{\hbar}\mathbf{d}_{01} \cdot \int_0^\infty d\omega \, \mathbf{E}(\mathbf{r}_i, \omega) e^{\frac{i}{2}(\omega_{10}-\omega)t} e^{-i\phi_\omega}
$$

$$
\times \frac{\sin\left[\frac{1}{2}(\omega_{10} - \omega)t\right]}{\omega_{10} - \omega}.
$$

$$
\text{(C7)}
$$

We are interested in the excited-state probability,

$$
|C_1(t)|^2 = \left(\frac{2d_{01}}{\hbar}\right)^2 \left| \int_0^\infty d\omega \, \mathbf{E}(\mathbf{r}_i, \omega) e^{\frac{i}{2}(\omega_{10}-\omega)t} \right.
$$

$$
\left. \times \, e^{-i\phi_\omega}\frac{\sin\left[\frac{1}{2}(\omega_{10} - \omega)t\right]}{\omega_{10} - \omega} \right|^2,
$$

$$
\text{(C8)}
$$

where for simplicity we have assumed that the dipole moment is parallel to the electromagnetic field $\mathbf{d}_{01} \parallel \mathbf{E}(\mathbf{r}_i, \omega)$. For incoherent light, a phase average results in

$$
\langle e^{i(\phi_{\omega'}-\phi_\omega)} \rangle = 0, \quad \text{for } \omega \neq \omega'. \quad \text{(C9)}
$$

Relating the electric field with the intensity of light using the well-known relation

$$
I = c\varepsilon_0 \mathbf{E}^2(\mathbf{r}_i, t) = \int_0^\infty d\omega \, I(\mathbf{r}_i, \omega), \quad \text{(C10)}
$$

the excitation probability can be expressed as

$$
|C_1(t)|^2 = \frac{2}{c\varepsilon_0\hbar^2}d_{01}^2 \int_0^\infty d\omega \, I(\mathbf{r}_i, \omega)\frac{\sin^2\left[\frac{1}{2}(\omega_{10} - \omega)t\right]}{(\omega_{10} - \omega)^2}.
$$

$$
\text{(C11)}
$$

The intensity of a light source typically has some frequency distribution since it is not completely monochromatic. Thus, it can be described with a certain line shape function $L(\omega)$ such that $I(\omega) = I_0 L(\omega)$ with $L(\omega_{10}) = 1$ and $I_0 = I(\omega_{10})$.

The excitation probability then reads

$$|C_1(t)|^2 = \frac{2}{c\varepsilon_0\hbar^2}d_{01}^2 I_0 \int_0^\infty d\omega \, L(\omega)\frac{\sin^2\left[\frac{1}{2}(\omega_{10}-\omega)t\right]}{(\omega_{10}-\omega)^2}. \tag{C12}$$

When we evaluate the integrals, we assume that arbitrary line shape is centered at $\omega = 0$ for the convenience of the calculations, which do not influence the physical results. First we take $L(\omega)$ to be a rectangular constant function centered at zero frequency, meaning that $L(\omega) = 1$ in the interval $[-1/2\gamma, 1/2\gamma]$. We calculate the following integral in the limit $\gamma t \gg 1$:

$$\int_{-1/2\gamma}^{1/2\gamma} d\omega \, \frac{\sin^2\left(\frac{\omega t}{2}\right)}{\omega^2} \approx \frac{\pi t}{2}. \tag{C13}$$

Second, we take $L(\omega)$ to be Gaussian centered at zero frequency, $L(\omega) = e^{-\frac{1}{2}\frac{\omega^2}{\gamma^2}}$. This integral in the limit $\gamma t \gg 1$ is

$$\int_{-\infty}^{\infty} d\omega \, e^{-\frac{1}{2}\frac{\omega^2}{\gamma^2}}\frac{\sin^2\left(\frac{\omega t}{2}\right)}{\omega^2} \approx \frac{\pi t}{2}. \tag{C14}$$

Third, we evaluate the same integral with a narrow Lorentzian profile centered at zero. This integral in the limit $\gamma t \gg 1$ is

$$\int_{-\infty}^{\infty} d\omega \, \frac{\frac{\gamma^2}{4}}{\left(\omega^2+\frac{\gamma^2}{4}\right)}\frac{\sin^2\left(\frac{\omega t}{2}\right)}{\omega^2} \approx \frac{\pi t}{2}. \tag{C15}$$

So regardless of the specific line shape, we find that in the limit $\gamma t \gg 1$

$$|C_1(t)|^2 \approx \frac{\pi d_{01}^2 I_0}{c\varepsilon_0\hbar^2}t = \Gamma_\uparrow t, \tag{C16}$$

where

$$\Gamma_\uparrow = \frac{\pi d_{01}^2 I_0}{c\varepsilon_0\hbar^2}. \tag{C17}$$

Using perturbation theory, we also calculate the frequency shift of the ground and excited states when subjected to laser light. By expanding the second of Eqs. (C5) up to zeroth order and solving it, we obtain the zero-order solution for $C_1^{(0)}(t)$:

$$C_1^{(0)}(t) = \frac{\mathbf{d}_{01}}{\hbar}\cdot\int_0^\infty d\omega \, \mathbf{E}(\mathbf{r}_i,\omega)\frac{e^{-i\phi_\omega}e^{-i(\omega-\omega_{10})t}}{\omega-\omega_{10}}C_0(t)$$

$$-\frac{\mathbf{d}_{01}}{\hbar}\cdot\int_0^\infty d\omega \, \frac{\mathbf{E}(\mathbf{r}_i,\omega)e^{-i\phi_\omega}}{\omega-\omega_{10}}C_0(t). \tag{C18}$$

We disregard the last term because it will have an oscillatory time dependence with frequency $\omega - \omega_{10}$. Substituting this into the first of Eqs. (C5), we obtain the differential equation for $C_0(t)$:

$$i\dot{C}_0(t) = \frac{1}{\hbar^2}\int_0^\infty\int_0^\infty d\omega' d\omega[\mathbf{d}_{01}\cdot\mathbf{E}^*(\mathbf{r}_i,\omega)][\mathbf{d}_{01}\cdot\mathbf{E}(\mathbf{r}_i,\omega')]$$

$$\times\frac{e^{i(\omega-\omega')t}e^{i(\phi_\omega-\phi_{\omega'})}}{\omega'-\omega_{10}}C_0(t). \tag{C19}$$

To simplify the double integral, we once more take a phase average and express the result in terms of light intensity to obtain

$$i\dot{C}_0(t) = \frac{d_{01}^2}{2c\varepsilon_0\hbar^2}\int_0^\infty d\omega \, \frac{I(\mathbf{r}_i,\omega)}{\omega-\omega_{10}}C_0(t). \tag{C20}$$

This differential equation shows that the electric field induces a frequency shift (or light shift), which is proportional to the intensity and detuning of the laser field.

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