

Subradiant entanglement in plasmonic nanocavities

Kalun Bedingfield, Ben Yuen, and Angela Demetriadou ^{*}

School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom



(Received 1 March 2024; revised 12 November 2024; accepted 14 November 2024; published 18 February 2025)

Plasmonic nanocavities are known for their extreme field enhancement and subwavelength light confinement in gaps of just a few nanometers. Pairing this with the ability to host quantum emitters, they form highly promising platforms to control or engineer quantum states at room temperature. Here, we use the lossy nature of plasmonic nanocavities to form subradiant entangled states between two or more quantum emitters, that persist for ~ 100 times longer than the plasmonic excitation. We develop a theoretical description that directly links quantum variables to experimentally measurable quantities, such as the extinction cross section, and unlike previous studies includes plasmonic excitations necessary to resonantly form subradiant states. This work paves the way towards engineering quantum entangled states in ambient conditions with plasmonic nanocavities.

DOI: [10.1103/PhysRevB.111.075420](https://doi.org/10.1103/PhysRevB.111.075420)

I. INTRODUCTION

Plasmonic nanocavities are formed by two or more metallic nanostructures separated by a nanometer-size gap [1–3] and have drawn significant attention in recent years due to their ability to reveal light-matter interactions in ambient conditions [4–10]. Such structures confine electromagnetic fields at extreme subwavelength volumes [5,6,9–11] and promise to generate quantum phenomena, such as quantum entanglement and nonclassical light at room temperature, which are yet to be realized. Until now, experimental investigations have primarily focused on far-field measurements for the combined system (i.e., scattering and extinction cross sections) [4–13], while theoretical studies have focused on quantum scattering processes and spontaneous emission [14–17], with quantum dynamics usually explored for weakly coupled systems that rapidly decay and arbitrary cavities that cannot be implemented for realistic plasmonic nanocavities that tightly confine fields [18,19].

Quantum entanglement serves as the foundation of many current quantum technologies, typically implemented in high-finesse cavities or other low-loss systems, and often require complex cryogenic setups. Plasmonic nanocavities, characterized by their non-Hermitian (i.e. lossy) nature, present a significant challenge to the coherent control of quantum states. However, it has been proposed that dissipation can be utilized for quantum state preparation and entanglement [20–22]. Such dissipative state engineering has been realized in traditional quantum optical systems to produce entanglement in atomic ensembles [23], Bell states, and

squeezed states of trapped ions [24,25], but it often involves complex experimental setups operating at cryogenic temperatures.

In this paper, we show that nanoplasmonic systems are ideal for forming quantum states in ambient conditions through dissipation. We demonstrate that subradiant entangled states are formed in plasmonic nanocavities through the plasmonic dissipation, paving the way towards the experimental realization of quantum state preparation with nanoplasmonics. We first incorporate the description of a resonant plasmon mode into quantum optical models, paying particular attention to carefully parametrize the input (output) coupling to external sources (loss reservoirs). This allows us to directly connect quantum variables with experimentally measurable quantities, ensuring consistency in the classical limit. Using this method, we reveal subradiant entanglement emerging between two or more quantum emitters (QEs) located in a plasmonic nanocavity, which persists for ~ 100 times longer than the lifetime of Rabi oscillations that are limited by the plasmon decay. Unlike previous studies that adiabatically eliminate the photonic excitation and therefore form subradiant states driven by virtual transitions [18,26,27], we include the excitation of the plasmonic mode, which becomes important for interactions near the cavity resonance. We show that it is the lossy nature of plasmonic nanocavities that aids the emergence of the subradiant states. Hence, our work is an important bridge between theoretical input-output modes in quantum optics [28] and descriptions of quantum plasmonics, which paves the way towards engineering quantum states via dissipation in ambient conditions with plasmonic devices.

II. QUANTUM DESCRIPTION OF PLASMONIC NANOCAVITIES

The open and lossy nature of plasmonic environments creates a non-Hermitian system and places significant theoretical impediments for their incorporation into cavity quantum-electrodynamics (cQED) descriptions, since they

^{*}Contact author: a.demetriadou@bham.ac.uk

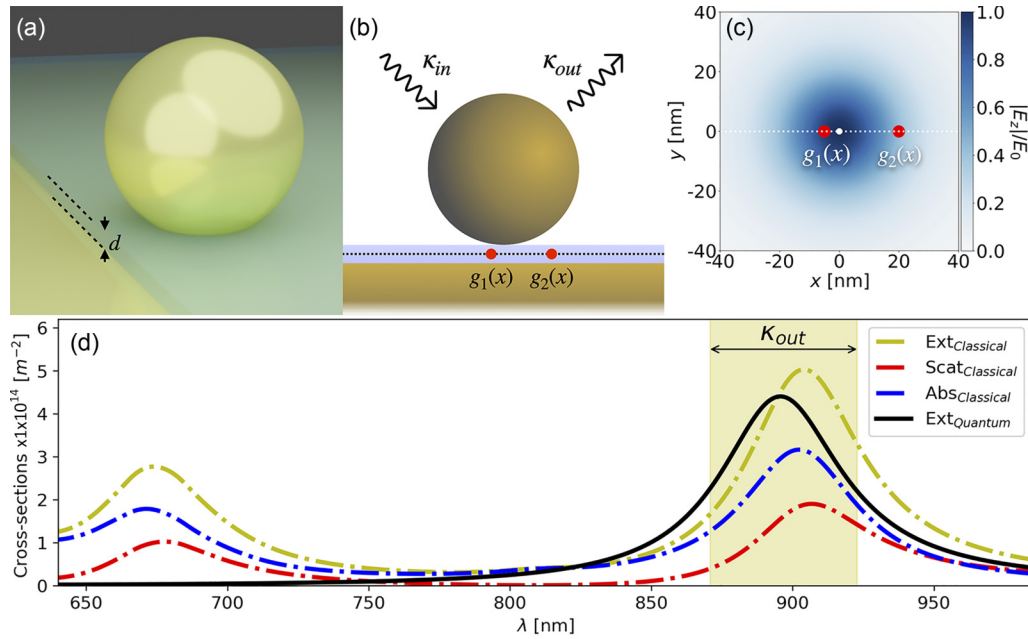


FIG. 1. (a) NPoM geometry for a 40-nm-radius spherical gold nanoparticle assembled on a flat gold mirror and separated by a spacer of refractive index $n = 2.5$ and thickness $d = 1$ nm. (b) NPoM with two QEs in the nanocavity and showing the energy coupling in (κ_{in}) and out (κ_{out}) of the system. (c) The normalized mode profile of the (1,0) plasmonic mode on a plane through the center of the cavity, with the white and red dots indicating the QE positions. (d) The classical absorption, scattering, and extinction cross sections (blue, red, and yellow dashed lines, respectively) plotted with the quantum extinction cross section (black full line) for a single plasmonic mode model.

were developed for high-finesse cavities. Recently, several quantum descriptions have been proposed that aim to overcome the non-Hermitian nature of the problem [14,29,30]. Even though each method is a significant breakthrough, this is still a developing topic with each newly proposed method having significant merits, but also limitations. Two notable examples are the Weisskopf-Wigner theory [29–34] that, in general, uses the spectral density of a plasmonic system calculated classically to perform multi-Lorentzian spectral fits for the plasmonic modes, and the symmetrizing orthonormalization transformation of quasinormal mode (QNM) operators that produces plasmonic operators that canonically commute [14]. Although both methods are probably the current state of the art for the quantization of plasmons, each has limitations. The first method does not easily facilitate the decomposition of plasmon modes, affecting both the near and far fields. The second method mixes the plasmonic modes during the symmetrizing orthonormalization transformation, producing a new set of canonical plasmonic operators that no longer correspond to the initial QNM modes. Consequently, both methods impede the design of plasmonic systems with specific modes and properties, crucial for interactions with QEs, aimed at forming specific quantum states.

Here, we therefore introduce a general open quantum system formalism, where each plasmonic mode's resonant frequency, loss, and coupling strength with a QE is obtained from classical QNM modes, and focus on how energy couples in and out of the system to obtain experimentally measurable quantities. This formalism can be applied to other quantum descriptions, including Refs. [14,34]. We start by decomposing the classical photonic response of the plasmonic system into quasinormal modes (QNMs), using the QNMEig (quasi-

normal mode eigensolver) methodology [35–37], described in detail in the Supplemental Material (SM) [38], Sec. S5. This method employs an auxiliary-field eigenvalue approach to account for the dispersive nature of the metals and linearize the electromagnetic eigenvalue problem. The eigenvectors provide the near field of each plasmon mode with complex eigenfrequencies [39,40] $\tilde{\omega}_{cav} = \omega_{cav} - i\kappa_{out}$, where ω_{cav} is the cavity resonant frequency and κ_{out} the total decay rate (radiative and Ohmic losses) of each plasmonic mode. Here, we consider the nanoparticle on mirror (NPoM) plasmonic nanocavity as shown in Figs. 1(a) and 1(b).

We divide the Hamiltonian $\mathcal{H} = \mathcal{H}_{sys} + \mathcal{H}_{res}$ into two components: the system ($\mathcal{H}_{sys}$) and reservoir ($\mathcal{H}_{res}$) Hamiltonians [41], which we discuss separately. The system Hamiltonian describes the plasmonic modes obtained from classical QNM calculations [35] ($\mathcal{H}_{cav}$), the multiple QEs as two-level systems ($\mathcal{H}_{QEs}$), the interaction between the plasmon modes and the QEs ($\mathcal{H}_{int}$) and a driving external field coupled to the cavity ($\mathcal{H}_{ext}$), such as a pump, which here represents an external illumination of the system. The system Hamiltonian is given by

$$\begin{aligned} \mathcal{H}_{sys} = & \underbrace{\Delta_{cav} a^\dagger a}_{\mathcal{H}_{cav}} + \underbrace{\sum_j \frac{1}{2} \Delta_d^{(j)} \sigma_z^{(j)}}_{\mathcal{H}_{QEs}} + \underbrace{\sum_j g(\mathbf{r}^{(j)}) (a^\dagger \sigma_-^{(j)} + a \sigma_+^{(j)})}_{\mathcal{H}_{int}} \\ & + \underbrace{i\sqrt{\kappa_{in}}(\alpha^* a - \alpha a^\dagger)}_{\mathcal{H}_{ext}}, \end{aligned} \quad (1)$$

where N is the number of QEs placed in the nanocavity, $\Delta_{cav} = \omega_{cav} - \omega_p$ and $\Delta_d^{(j)} = \omega_{QE}^{(j)} - \omega_p$ are the detunings of the cavity resonance (ω_{cav}), and each QE resonant frequency

$(\omega_{QE}^{(j)})$ from the external field's frequency (ω_p). The $\{a, a^\dagger\}$ are the bosonic operators that create and annihilate the plasmon mode, and $\sigma_z^{(j)}$ is the Pauli z operator describing the j th two-level QE (see SM [38], Sec. S2). Note that to ease the interpretation of the system's quantum dynamics and the correlations between multiple QEs residing within the plasmonic nanocavity, we design a gold NPoM nanocavity for which it is safe to assume that only one plasmon mode couples to the QEs. The interaction of the plasmonic mode with the j th QE at position $\mathbf{r}^{(j)}$ is given by $(a^\dagger \sigma_-^{(j)} + a \sigma_+^{(j)})$ with the coupling strength measured by

$$g(\mathbf{r}^{(j)}) = \sqrt{\frac{\hbar \omega_{\text{cav}}}{2 \epsilon_0 \epsilon V}} \mathbf{d}^{(j)} \cdot \mathbf{u}(\mathbf{r}^{(j)}), \quad (2)$$

where $\mathbf{u}(\mathbf{r}^{(j)})$ is the normalized electric field vector of the QNM mode, which makes the coupling strength $g(\mathbf{r}^{(j)})$ dependent on the j th QE's location $\mathbf{r}^{(j)}$ within the plasmonic nanocavity. The mode volume is obtained from the QNM calculations as $V = \frac{\int d\mathbf{r} |\mathbf{u}(\mathbf{r})|^2}{\text{Max}[|\mathbf{u}(\mathbf{r})|^2]}$ (see SM [38], Sec. S1), ϵ is the electric permittivity of the material hosting the QEs, and $\mathbf{d}^{(j)}$ is the dipole moment of the j th QE. The last term $[i\sqrt{\kappa_{\text{in}}}(\alpha^* a - \alpha a^\dagger)]$ of Eq. (1) describes an external coherent monochromatic source driving the system, where $\sqrt{\kappa_{\text{in}}}$ is the rate that energy couples into the system and α is the amplitude of the coherent state, defined by the source's photon flux $c|\alpha|^2$ (see SM [38], Secs. S1 and S3, for more discussion). Note that α can be complex, with its amplitude directly linked to the amplitude of a coherent driving field and its phase corresponding to the driving field phase. However, since in this paper we only consider one continuous incident field, the driving field phase is irrelevant and one can take α to be real.

While the system Hamiltonian describes the excitation of the system and the interaction between QEs and the plasmon mode, it contains no description of losses. Nanoplasmonic devices hosting QEs, in general, have two loss channels: (i) the plasmon modes lose energy by both radiating to the far field and via Ohmic losses, and (ii) the decoherences of QEs due to the (ro)vibrational energy states of the molecule. We represent the plasmonic loss and QE decoherences with two separate reservoirs as

$$\begin{aligned} \mathcal{H}_{\text{res}} = & \sum_j \int_0^\infty d\omega_{\text{vib}} \sigma_z^{(j)} \kappa_{\text{vib}}(\omega_{\text{vib}}) [b_{\text{vib}}^\dagger e^{i\omega_{\text{vib}} t} + b_{\text{vib}} e^{-i\omega_{\text{vib}} t}] \\ & - i \sum_\lambda \int_0^\infty d\omega \kappa_{\text{res}}(\omega) [b_\lambda(\omega) a^\dagger e^{i\Delta(\omega)t} \\ & - b_\lambda^\dagger(\omega) a e^{-i\Delta(\omega)t}], \end{aligned} \quad (3)$$

where the first term describes the coupling of the QEs to a phonon bath reservoir, with phonon frequencies ω_{vib} and strength $\kappa_{\text{vib}}(\omega_{\text{vib}})$, and $\{b_{\text{vib}}, b_{\text{vib}}^\dagger\}$ the phonon reservoir operators. The second term of Eq. (3) accounts for the coupling of the plasmonic mode to a background reservoir that represent plasmonic and photonic losses to describe the Ohmic and radiative losses of the system, respectively, with photon frequencies ω and coupling strength $\kappa_{\text{res}}(\omega)$. It is this part of the cQED method that provides the short lifetime of the system's plasmonic behavior. Note that the detuning $\Delta(\omega) = \omega - \omega_p$

is the detuning of frequency ω with the incident external field frequency (ω_p), and $\{b_\lambda(\omega), b_\lambda^\dagger(\omega)\}$ are the plasmon reservoir creation/annihilation operators.

Applying the Born-Markov approximation [42] for the reservoirs allows for the time evolution of the open quantum system to be described by the density operator ρ via the Lindblad master equation as

$$\begin{aligned} \frac{d}{dt} \rho = & -i[\mathcal{H}_{\text{sys}}, \rho] + 2\kappa_{\text{out}} a \rho a^\dagger - \kappa_{\text{out}} (a^\dagger a \rho + \rho a^\dagger a) \\ & + \sum_j \left[\kappa_{\text{vib}} \sigma_z^{(j)} \rho \sigma_z^{(j)} - \frac{\kappa_{\text{vib}}}{2} (\sigma_z^{(j)2} \rho + \rho \sigma_z^{(j)2}) \right], \end{aligned} \quad (4)$$

where the density operator ρ describes the statistically mixed state of the system (see SM [38], Sec. S2). We solve Eq. (4) numerically using DIRACPY [43]. The expectation value of any operator of the system can be obtained via $\langle O \rangle = \text{Tr}[O\rho]$, for example, the expected plasmon excitation number $\langle a^\dagger a \rangle$.

Quantum extinction cross section

To obtain experimental quantities, such as the extinction cross section, from the above cQED description (or any other quantum description), one needs a formalism on how energy couples in and out of the system. Here we represent a constant external illumination with a monochromatic plane wave by a single mode, ω_p , of the plasmon reservoir that is coherently excited. The field operators $b_\lambda(\omega_p)$ are replaced by complex amplitudes α under the mean-field approximation. These are directly related to the incident beam intensity and determine the flux of photons exciting the system. The rates with which energy is coupled into (κ_{in}) and lost (κ_{out}) from the system are schematically shown in Fig. 1(b) and can be used to find the quantum extinction cross section.

Classically, the extinction cross section is defined as the total power lost by the system (P_{out}) relative to the incident intensity (S) of the plane wave. When considering their quantum analogues in the steady state, they respectively become $P_{\text{out}} = 2\kappa_{\text{out}} \hbar \omega \langle a^\dagger a \rangle$ and $S = c_0 \hbar \omega |\alpha|^2$. The $\langle a^\dagger a \rangle = \frac{\kappa_{\text{in}} |\alpha|^2}{\kappa_{\text{out}} + \Delta_{\text{cav}}^2}$, and is proportional to $\langle a \rangle$ and $\langle a^\dagger \rangle$ (see SM [38], Sec. S4), which leads to the quantum extinction cross section,

$$\langle \sigma_{\text{ext}}^q \rangle_{\text{noQEs}} = \frac{2\kappa_{\text{in}} \kappa_{\text{out}}}{c_0} \frac{1}{\kappa_{\text{out}}^2 + \Delta_{\text{cav}}^2}, \quad (5)$$

where c_0 is the speed of light constant. We define the incoupling coefficient as $\kappa_{\text{in}} = \kappa_{\text{out}} c_0 \sigma_{\text{ext}}^c / 2$, which ensures that the quantum, $\langle \sigma_{\text{ext}}^q \rangle_{\text{noQEs}}$ and classical, σ_{ext}^c , extinction cross sections are equal, $\langle \sigma_{\text{ext}}^q \rangle_{\text{noQEs}} = \sigma_{\text{ext}}^c$, when the external illumination is on resonance with the QNM mode (i.e., $\omega_{\text{cav}} = \omega_p$ and $\Delta_{\text{cav}} = 0$).

Now, we apply this theoretical description to a specific plasmonic system. Throughout this article, we consider a NPoM geometry [see Figs. 1(a) and 1(b)] made of a spherical, gold nanoparticle of radius 40 nm assembled 1 nm above a flat gold mirror, separated by a molecular monolayer with refractive index $n = 2.5$, which is consistent with recent experimental setups [44,45]. This plasmonic nanocavity has the first-order (1,0) QNM resonance at $\tilde{\omega}_{\text{cav}} = (338.9 - i9.8)$ THz (i.e., $\lambda_{\text{cav}} \sim 900$ nm), which gives a Q factor of

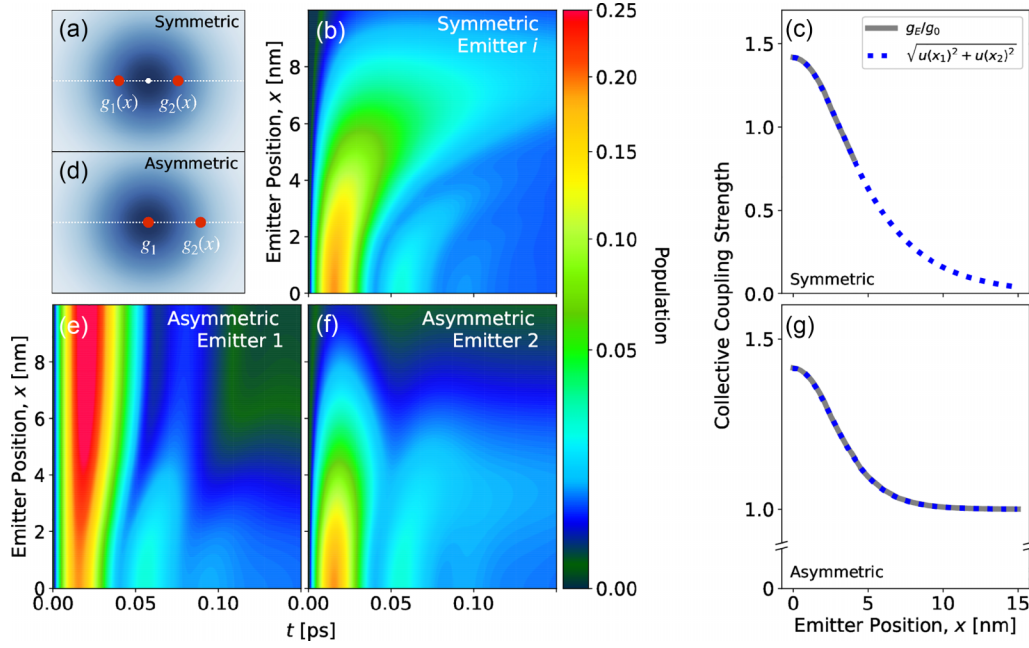


FIG. 2. (a) The symmetric QE placement in a NPoM nanocavity. (b) The population of their excited state, when the system is initialized in the excited field state. (c) The effective coupling strength of the system. (d) Asymmetric QE placement in the nanocavity, with the (e) central and (f) displaced QE excited state population, when the system is initialized in the excited field state. (g) The system's effective coupling strength.

$Q = \text{Re}(\tilde{\omega}_{\text{cav}})/2\text{Im}(\tilde{\omega}_{\text{cav}}) \sim 17$. The normalized electric field eigenvector $\mathbf{u}(\mathbf{r})$ for the (1,0) mode is shown on a slice through the center of the cavity in Fig. 1(c) and exhibits a large central extrema, with the mode volume being $\text{Re}[V] = 60.01 \text{ nm}^3 \sim 8.2 \times 10^{-8} \lambda^3$. This combination of Q factor and mode volumes takes plasmonic nanocavities far beyond traditional photonic cavities.

In Fig. 1(d), we plot the classical extinction (σ_{ext}), scattering (σ_{scat}), and absorption (σ_{abs}) cross sections that show the lowest-order mode to be spectrally isolated, and the κ_{out} obtained from the QNM calculations corresponding to the full width at half maximum of σ_{ext} . Therefore, we can safely assume that only one plasmonic mode interacts with the QEs for this specific plasmonic nanocavity. The quantum extinction cross section is in good agreement with its classical counterpart and, since we considered only one plasmonic mode for the cQED description, it only shows one peak. Note that the values of the quantum and classical σ_{ext} match exactly on resonance with the cavity [i.e., the (1,0) QNM mode: $\lambda_{(1,0)} \sim 900 \text{ nm}$]. The spectral shifts seen in Fig. 1(d) are due to the broadband contributions of higher-order modes for far-field quantities such as the classical σ_{ext} , and have been previously reported and explained [46,47]. This driven formalism is applicable to other quantum descriptions and very flexible, allowing us to initialize the system in any particular state, unlike other methods [29].

III. TWO-EMITTER QUANTUM DYNAMICS

We now consider the quantum dynamics of QEs in this cavity, which we take henceforth as Cy5 molecules with $d = 10.1 \text{ D}$ and $\kappa_{\text{vib}} = 25 \text{ meV}$ [45]. Before discussing the

details of the two-molecule dynamics, we briefly summarize the single-molecule behavior when a plasmon is initially excited and the molecule is located in the center of the cavity ($x = 0$) and starts in its ground state. In this case, Rabi oscillations occur at $\omega_{\text{Rabi}} = \sqrt{4g^2 - \kappa_{\text{out}}^2}$. The molecular dephasing at rate κ_{vib} causes these oscillations to “blur” out over time (see SM [38], Sec. S7). Introducing a second emitter at the same location and initialization, one finds the frequency of Rabi oscillations is increased to $\omega_{\text{Rabi}} = \sqrt{8g^2 - \kappa_{\text{out}}^2}$ due to the $\sqrt{N} = \sqrt{2}$ enhancement of the collective coupling strength, $\sqrt{2}g$. The populations of the two emitters also decay faster due to the combined dephasing of both emitters. Realistically, two Cy5 molecules cannot be placed at the exact same position within the nanocavity, and their coupling strength $g(\mathbf{r})$ of Eq. (2) is position dependent, according to the QNM mode's eigenvector shown in Fig. 1(c). Due to the cylindrical symmetry of the cavity and of the (1,0) mode, we need to only consider QE positions along the x axis—as indicated by the white dashed line in Figs. 2(a) and 2(d). Figure 2(a) diagrammatically shows a symmetric arrangement for the two QEs away from the center of the cavity, which means both QEs continue to experience the same coupling strength, producing identical excited state populations for all positions $|x| = x_2 = -x_1$. These are shown in Fig. 2(b) for $|x|$ up to 10 nm away from the nanocavity center. As the emitters move away from the cavity center, they experience a rapid reduction of their coupling strength and, for $|x| > 6 \text{ nm}$, the system transitions into the weak-coupling regime, where no Rabi oscillations are observed in the quantum dynamics of the system [Fig. 2(b)]. This can be quantified through the ratio of an effective coupling strength g_E obtained from the Rabi oscillations of the quantum dynamics [Fig. 2(b)]

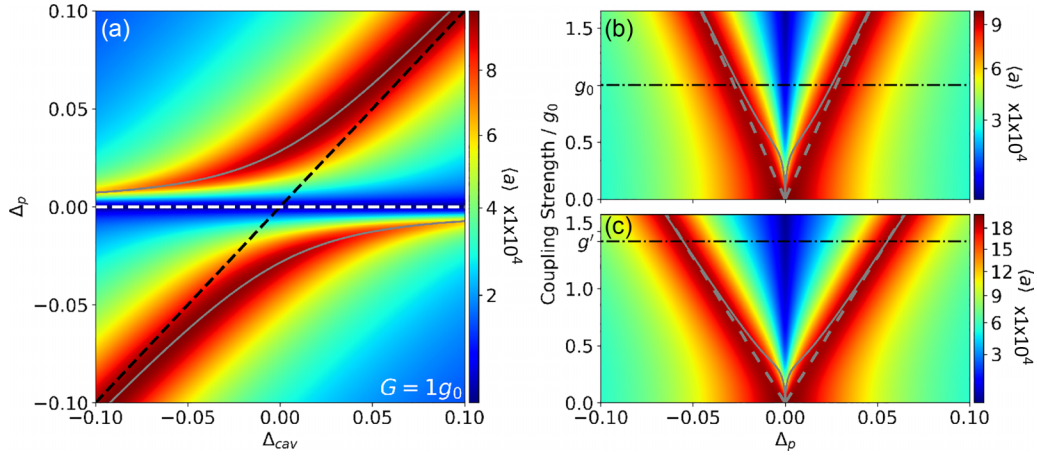


FIG. 3. (a) The $\langle a \rangle$ of the driven single QE NPoM system as a function of both cavity ($\Delta_{\text{cav}} = \frac{\omega_{\text{cav}} - \omega_{\text{QE}}}{\omega_{\text{QE}}}$) and external source ($\Delta_p = \frac{\omega_p - \omega_{\text{QE}}}{\omega_{\text{QE}}}$) detunings. The black and white dashed lines, respectively, show $\Delta_{\text{cav}} = \Delta_p$ and $\Delta_p = 0$. Rabi splitting in terms of $\langle a \rangle$ as a function of both plasmon detuning and coupling strength, for (b) one and (c) two emitters at the center of the cavity, where $g' = \sqrt{2}g_0$. Gray dashed lines trace the peaks, while the gray solid lines are solutions of Eq. (7).

normalized to the coupling of a single QE at the center of the cavity, g_0 , shown in Fig. 2(c). Due to the dependence of the coupling strength on the mode profile, the effective coupling strength (g_E) changes with the position of the emitters as $g_E/g_0 \propto \sqrt{u(x_1)^2 + u(x_2)^2}$, which becomes $\sqrt{2}u(x)$ for the symmetric placement of the QEs [since $u(x_1) = u(x_2)$]. No g_E can be determined once the system is in the weak-coupling regime since no Rabi oscillations are present in the quantum dynamics. If, instead, one QE always remains at the center of the cavity while the second QE takes various positions along the x axis (i.e., asymmetric placement), as shown in Fig. 2(d), then each QE is coupled to the plasmon mode with a different coupling strength. The population dynamics of the central emitter and displaced emitter now differ and are, respectively, shown in Figs. 2(e) and 2(f), showing that the central QE's Rabi oscillations slow down as the second emitter is placed further out from the nanocavity. Nevertheless, we find that the Rabi oscillations are still governed by the effective coupling strength $g_E/g_0 \propto \sqrt{u(x_1)^2 + u(x_2)^2}$ [see Fig. 2(g)]. This now decreases more slowly as $\sqrt{1 + u(x_2)^2}$ compared to the symmetric case, and reduces to unity once the second QE is only weakly coupled to the plasmon, which occurs at $x_2 \sim 10$ nm, where the system returns to a single-emitter strong-coupling interaction with the plasmon mode.

Hybrid states

Experimentally, the Rabi oscillations and effective coupling strength are obtained by the Rabi splitting of the system's hybrid states, measured in the far field. Usually an external field illuminates the combined system, and the scattered light (or extinction energy) is collected. Due to reciprocity, the energy loss of the system in the steady state [$P = 2\kappa_{\text{out}}\hbar\omega\langle a^\dagger a \rangle$] is equivalent to the plasmon excitation in the system by the external illumination, which is described by $P = -\sqrt{\kappa_{\text{in}}}(\alpha\langle a^\dagger \rangle + \alpha^*\langle a \rangle)$. Normalizing this energy loss with the incident energy $S = c_0\hbar\omega|\alpha|^2$ leads to the quantum extinction cross section for the combined system, i.e., $\langle \sigma_{\text{ext}}^q \rangle = -\sqrt{\kappa_{\text{in}}}(\alpha\langle a^\dagger \rangle + \alpha^*\langle a \rangle)/c_0|\alpha|^2$, in terms of the field operator

expectation values. Without loss of generality, α can be taken to be real in our case, which reduces the quantum extinction cross section to

$$\langle \sigma_{\text{ext}}^q \rangle = -2\sqrt{\kappa_{\text{in}}} \frac{\text{Re}\{\langle a \rangle\}}{c_0\alpha}, \quad (6)$$

where $\langle a \rangle$ describes the rate at which energy is removed from the excited plasmon state (i.e., extinction energy) and can be found by first solving the master equation for the density matrix in the steady state and then taking the trace with the field operator as $\langle a \rangle = \text{Tr}[a\rho]$.

For this externally driven regime, the system which is initially in the vacuum state is excited at a rate $\sqrt{\kappa_{\text{in}}}\alpha$ —such that the average photon number in the system is $N_{ph} = 10^{-6}$. This value ensures that no two-photon processes occur and corresponds to an incident power of 4π mW/cm² (see SM [38], Sec. S3). In Fig. 3(a), we plot $\langle a \rangle$ (which is proportional to $\langle \sigma_{\text{ext}}^q \rangle$) for a single emitter at the center of the nanocavity, with both the external source (Δ_p) and cavity (Δ_{cav}) resonances detuned relative to the QE resonance. This exhibits the signature avoided crossing to form two hybrid states, characteristic of strong coupling [48,49]. The black and white dashed lines show $\Delta_{\text{cav}} = \Delta_p$ and $\Delta_p = 0$, respectively. Many experimental analyses of strongly coupled systems measure these hybrid states, with other theoretical descriptions also predicting them [32,50,51]. It has been recently shown [51] that one can consider a complex mode volume that accounts for the radiative nature of plasmons, to obtain the complex frequency of the strong-coupling hybrid states (i.e., polaritons) as [51–54]

$$\tilde{\omega}_{\pm} = \frac{\tilde{\omega}_e + \tilde{\omega}_{\text{cav}}}{2} \pm \sqrt{g^2[1 - iR] + \left(\frac{\tilde{\omega}_e - \tilde{\omega}_{\text{cav}}}{2}\right)^2}, \quad (7)$$

where $R = \text{Im}[V]/\text{Re}[V]$ is the ratio of the imaginary and real components of the mode volume [55], and the imaginary components of $\tilde{\omega}_e$ and $\tilde{\omega}_{\text{cav}}$ are, respectively, κ_{vib} and κ_{out} . For systems with a large quality factor Q , the negligibly small $\text{Im}[V]$ makes it apparent that the standard description

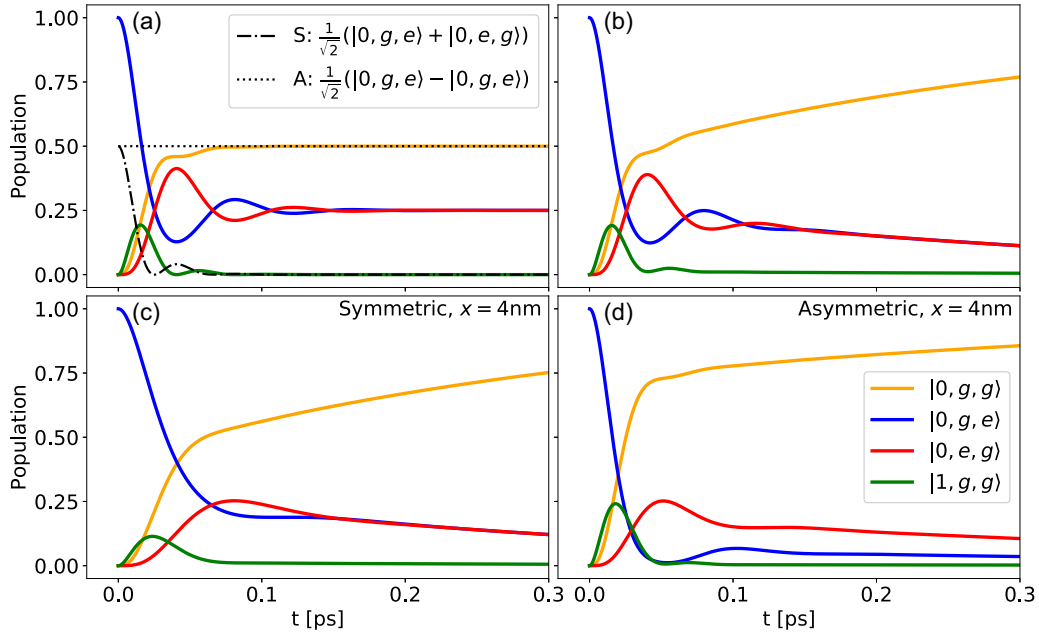


FIG. 4. The population dynamics for a system of two QEs at the center of a nanocavity (a) without ($\kappa_{\text{vib}} = 0$) and (b) with ($\kappa_{\text{vib}} = 25$ meV) the QE decoherences. S and A, respectively, describe the super- and subradiant superposition states. The population dynamics for two QE with decoherences $\kappa_{\text{vib}} = 25$ meV, when they are placed in a nanocavity (c) symmetrically ($x_2 = -x_1 = 4$ nm) and (d) asymmetrically ($x_1 = 0$ and $x_2 = 4$ nm).

is sufficient. For low- Q systems though, such as our plasmonic nanocavity, the complex nature of the mode volume has the ability to significantly alter the observed dynamics. The solutions for $\tilde{\omega}_{\pm}$ are plotted with gray lines in Fig. 3(a), demonstrating their strong agreement with our non-Hermitian cQED description for light-matter interactions.

Now, we obtain the strong-coupling hybrid states for various coupling strengths with respect to the external field detuning from the QE Δ_p [see Fig. 3(b)]. For an empty cavity ($g = 0$), a singular resonance is observed which is attributed to the absorption and reemission of the energy collected by the plasmonic mode alone. Increasing the coupling between the QE and the plasmon, one quickly sees their hybridization and emergence of the characteristic Rabi splitting, even for small coupling strengths. For small coupling strengths, the strong-coupling condition $g^2 > \kappa_{\text{out}}\kappa_{\text{vib}}$ [56] is still valid, despite the QE population dynamics showing a relatively small number of Rabi oscillations that dissipate quickly (see SM [38], Sec. S6 for the quantum dynamics). However, to acquire a more intuitive picture of the occurring interaction, it is more appropriate to separate this condition into two: one for the plasmon $g > \kappa_{\text{out}}$ and one for the QE $g > \kappa_{\text{vib}}$. For example, a single emitter at the center of our NPoM cavity (i.e., at g_0) has $g_0^2/\kappa_{\text{out}}\kappa_{\text{vib}} = 4.64$, placing the system well into the strong-coupling regime. However, $g_0/\kappa_{\text{vib}} = 9.74$, which allows the Rabi splitting to occur, while $g_0/\kappa_{\text{out}} = 0.48$, which leads to a large radiative emission and rapidly decaying Rabi oscillations. To lose the Rabi splitting and the hybrid states for the overall system, the coupling strength needs to reduce enough for the ratio $g/\kappa_{\text{vib}} < 1$, which is in agreement with both our description and Eq. (7) [51] (gray lines) shown in Fig. 3(b). For multiple QEs in the cavity, the coupling strength scales with $\sqrt{N}$, as expected, with Fig. 3(c) showing the Rabi

splitting for varying coupling strengths of two emitters in a plasmonic nanocavity obtained from our description and also in agreement with Eq. (7).

IV. SUBRADIANT ENTANGLEMENT

We now take advantage of the flexibility of our cQED description to consider a case without external illumination, by setting the input field α to zero, and initialize the system with only one QE in the excited state. To better demonstrate the dynamics presented by this preparation, we initially ignore the inherent molecular linewidths of the emitters ($\kappa_{\text{vib}} = 0$) and assume both emitters are placed at the center of the cavity. Figure 4(a) shows that the primary energy exchange and Rabi oscillations are now observed between the two emitters—with twice as much energy passed to the initially nonexcited emitter than to the plasmonic mode. Due to the asymmetric initialization, the emitters no longer interact with the field symmetrically: they instead oscillate out of phase with each other as energy is passed between them. The key observation here is that the emitters exchange energy until they reach an equal, nonzero steady-state value. This long-lived state originates from the symmetric and antisymmetric superpositions formed from the states of the two emitters,

$$|S\rangle = \frac{1}{\sqrt{2}}(|0, e, g\rangle + |0, g, e\rangle), \quad (8)$$

$$|A\rangle = \frac{1}{\sqrt{2}}(|0, e, g\rangle - |0, g, e\rangle), \quad (9)$$

which, respectively, describe the super- and subradiant states, as shown in Fig. 4(a) with dot-dashed and dotted lines. The symmetric and antisymmetric states are entangled since they cannot be factorized into a product of $|e\rangle$ and $|g\rangle$. For our

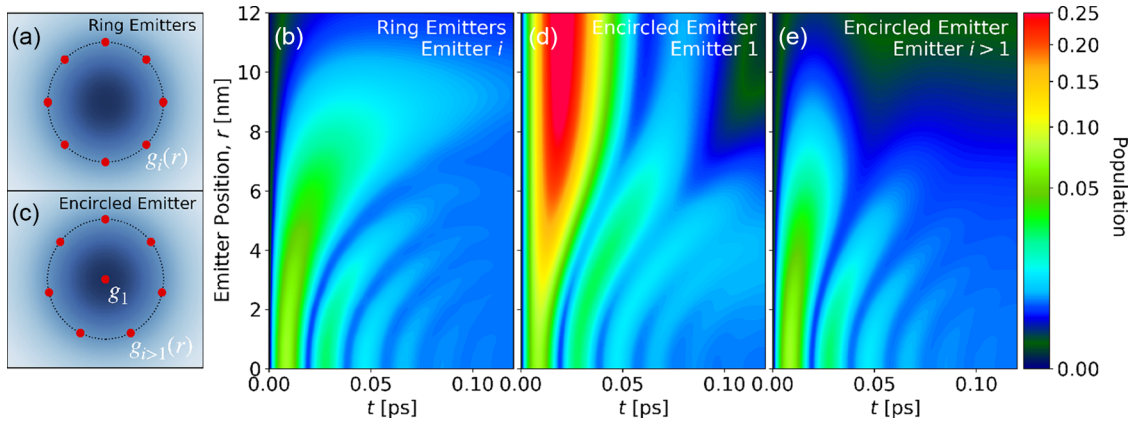


FIG. 5. (a) Eight QEs placed in a nanocavity on a ring arrangement, and (b) the population dynamics of their excited state, when the system is initialized in the excited field state. (c) Eight QEs placed in a nanocavity on an “encircled emitter” arrangement and the population dynamics of the (d) central and (e) surrounding QES, when the system is initialized in the excited field state.

system, although the superradiant state rapidly decays to zero, the subradiant state reaches a steady-state solution. This occurs due to the asymmetry of the state, with the interactions of the $|1, g, g\rangle$ state with the components of $|A\rangle$ ($|0, e, g\rangle$ and $|0, g, e\rangle$) perfectly canceling out. In fact, these states are formed via the high dissipation of the plasmonic mode, with the plasmon providing a conduit to form the subradiant entangled state (see the logarithmic-scale plot of the dynamics in SM [38], Sec. S9). Introducing the molecular decoherence rates to this calculation [Fig. 4(b)], we find that these states are still formed, but now decay nonradiatively via $\kappa_{\text{vib}} = 25$ meV and eventually the system returns to its ground state. However, since the plasmonic excitation returns to zero population at ~ 80 fs and the subradiant states only vanish at ~ 10 ps, they live for ~ 100 times longer than the plasmonic excitation, creating semipersistent subradiant entangled states in lossy plasmonic nanocavities.

For a more realistic arrangement of the emitters, Fig. 4(c) shows the quantum dynamics for a symmetric placement of QEs at $|x| = x_2 = -x_1 = 4$ nm. The equal coupling strength leads to fewer oscillations between the two QEs, but eventually the same long-lived entangled states emerges, with the same population as with both QEs at the center of the nanocavity (SM [38], Sec. S7). In contrast, the asymmetric QE placement (i.e., $x_1 = 0$ and $x_2 = 4$ nm) leads to unequal coupling strengths with the plasmon, and different rates for the energy exchange between them, which distorts the subradiant entangled states. Interestingly, we conclude that the coherence between emitters and the formation of the (semipersistent) subradiant entangled states occurs via the plasmonic dissipation and is only dependent on their relative coupling strength with each other.

V. MULTI-EMITTER SYSTEMS

Of course, one can have more than just two QEs in a plasmonic nanocavity, and with DNA origami [44,45] these can be placed with a spatial precision of ± 1 nm. Here we choose eight QEs ($N = 8$), but keep the discussion generalized as it is applicable for any reasonable number of emitters. We initially consider a symmetric QE ring configuration of radius r , shown

diagrammatically in Fig. 5(a), where all N -QEs experience the same coupling strength due to the cylindrical symmetry of the plasmon mode. The quantum dynamics of this system can be described using only three states: the vacuum state $|0, \vec{g}\rangle$, the excited field state $|1, \vec{g}\rangle$, and an N -fold degenerate state with any one of the N emitters excited $|0, \phi\rangle$. Here, $|\vec{g}\rangle = \prod_i^N \otimes |g_i\rangle$ is a state in which all of the emitters are in their ground states, and $|\phi_j\rangle = \sigma_+^{(j)} |\vec{g}\rangle$ is the state where emitter j is excited while the rest remain in their ground states. The state $|0, \phi_j\rangle$ is shown in Fig. 5(b) for this symmetric ring configuration when the system is initially in the plasmon excited state; this exhibits a $\sqrt{N}$ enhancement to the effective coupling strength and Rabi oscillation frequency. Now, instead consider the emitters placed in an encircled emitter configuration, shown in Fig. 5(c), with one emitter at the center of the nanocavity and the other $N - 1$ forming a ring of radius r . The central and surrounding QEs experience different coupling strengths and therefore have different quantum dynamics, where $|\phi_1\rangle$ of the central emitter is no longer degenerate with $|\phi_{j>1}\rangle$ of the ring emitters, shown in Figs. 5(d) and 5(e), respectively. Analogously to the asymmetric displacement of the two QEs, the central QE remains always strongly coupled to the plasmon, while the surrounding emitters experience slower Rabi oscillations as r increases, until $r \gtrsim 10$ nm where they are weakly coupled to the plasmon.

We now explore the emergence of the subradiant entangled states for a multi-emitter system. We initialize the system with one QE in its excited state, when all N -emitters are at the center of the nanocavity and there is no molecular decoherence ($\kappa_{\text{vib}} = 0$). Figure 6(a) shows the population of the state $|0, \phi_1\rangle$ for the initially excited QE (blue), together with the total population of the other $(N - 1)$ QEs (magenta). Figure 6(b) incorporates the decoherence for Cy5 molecules of $\kappa_{\text{vib}} = 25$ meV and shows the emergence of the subradiant entangled states between the N -emitters, which now decays more rapidly because of the higher total QE decoherence. If the QEs are placed on a symmetric ring at $r = 4$ nm, the subradiant entangled states are formed, but there are fewer oscillations between the QEs since the coupling strength is much weaker [Fig. 6(c)]. However, the coherent dynamics

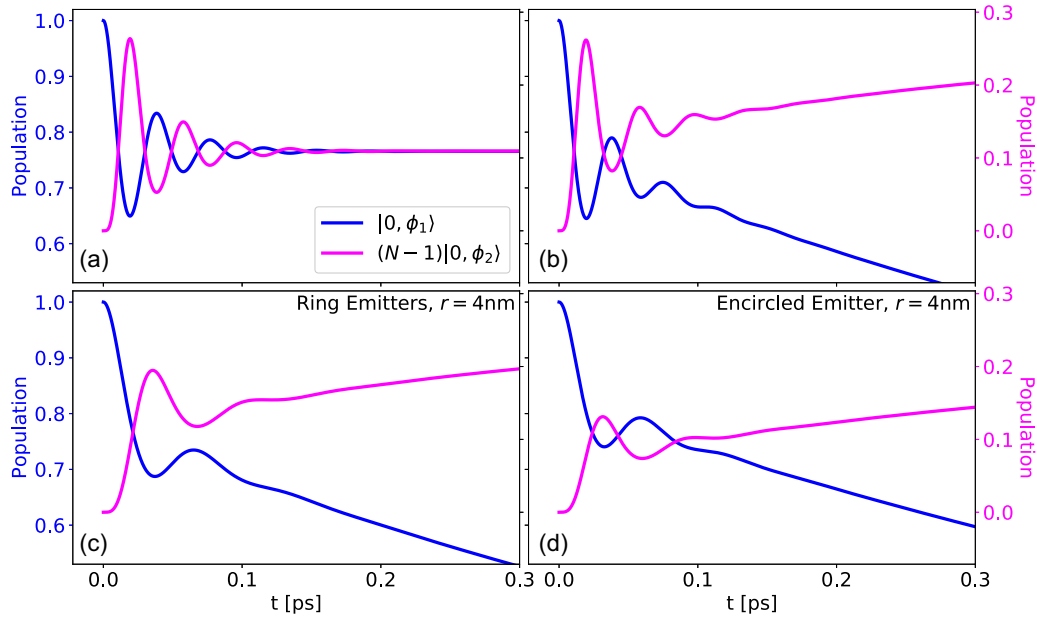


FIG. 6. The population dynamics for eight QEs in a nanocavity, initialized with one QE (blue) at its excited state and the effective excited state of the other QEs (magenta). The dynamics for the emitters placed at the center of the cavity, (a) without ($\kappa_{\text{vib}} = 0$) and (b) with ($\kappa_{\text{vib}} = 25$ meV) QE decoherences, and placing the QEs at a (c) ring and (d) encircled QE arrangements with radius $r = 4$ nm.

of the QEs helps maintain their long-lived nature, with the subradiant state population matching the same state's population for all QEs at the nanocavity center. For the asymmetric encircled emitter configuration [Fig. 6(d)], the system is initialized with the central emitter in an excited state, which maintains the quantum dynamic degeneracy of the $(N - 1)$ QEs forming the circle. However, the varying coupling strength between the central and ring QEs distorts the subradiant entangled states.

Hence, multiple QEs within a plasmonic nanocavity give rise to semipersistent subradiant states at room temperature via the plasmonic dissipation, if the system is initialized appropriately. These subradiant states form within just ~ 100 fs and persist for ~ 100 times longer than the plasmonic excitation, as long as the QEs are strongly coupled to the lossy plasmonic nanocavity. The high loss of the plasmonic nanocavity actually enables the emergence of the subradiant states since it causes the superradiant state to decay very rapidly. Their decay depends only on the molecular decoherence, and one can choose molecules, quantum dots, or other QEs with more favorable decoherence values than the ones considered here. Such systems pave the way towards engineering quantum states at room temperature via dissipation with plasmonic nanocavities, for quantum memory and quantum communication applications, avoiding complex and cumbersome experimental setups.

VI. CONCLUSION

We have introduced a theoretical formalism for the integration of quantized plasmons into quantum optical models, with particular attention given to the correct parametrization of in and out coupling in plasmonic systems. We obtain experimentally measurable quantities from the quantum formalism, with very good agreement between quantum and classically calculated extinction cross sections. Using this method, we demonstrate that multiple emitters in a plasmonic nanocavity form semipersistent subradiant states via the plasmonic dissipation. They only emerge if the system is initialized appropriately, the QEs are strongly coupled to the lossy plasmonic nanocavity, are independent of the high plasmonic losses and the coupling strength, and survive ~ 100 times longer than the plasmonic excitation. This work paves the way towards quantum state engineering quantum at room temperature with nanoplasmonics.

ACKNOWLEDGMENTS

A.D. gratefully acknowledges support from the Royal Society University Research Fellowship URF/R1/180097 and URF/R/231024, Royal Society Research Fellows Enhancement Award RGF/EA/181038, and funding from EPSRC EP/X012689/1, EP/Y008774/1, and CDT in Topological Design EP/S02297X/1.

- [1] A. Emboras, J. Niegemann, P. Ma, C. Haffner, A. Pedersen, M. Luisier, C. Hafner, T. Schimmel, and J. Leuthold, Atomic scale plasmonic switch, *Nano Lett.* **16**, 709 (2016).
- [2] D. O. Sigle, J. Mertens, L. O. Herrmann, R. W. Bowman, S. Ithurria, B. Dubertret, Y. Shi, H. Y. Yang, C. Tserkezis, J. Aizpurua, and J. J. Baumberg, Monitoring morphological

changes in 2D monolayer semiconductors using atom-thick plasmonic nanocavities, *ACS Nano* **9**, 825 (2015).

- [3] F. Benz, C. Tserkezis, L. O. Herrmann, B. De Nijs, A. Sanders, D. O. Sigle, L. Pukenas, S. D. Evans, J. Aizpurua, and J. J. Baumberg, Nano-optics of molecular-shunted plasmonic nano-junctions, *Nano Lett.* **15**, 669 (2015).

- [4] G. Zengin, M. Wersäll, S. Nilsson, T. J. Antosiewicz, M. Käll, and T. Shegai, Realizing strong light-matter interactions between single-nanoparticle plasmons and molecular excitons at ambient conditions, *Phys. Rev. Lett.* **114**, 157401 (2015).
- [5] R. Chikkaraddy, B. De Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, and J. J. Baumberg, Single-molecule strong coupling at room temperature in plasmonic nanocavities, *Nature (London)* **535**, 127 (2016).
- [6] F. Benz, M. Schmidt, A. Dreismann, R. Chikkaraddy, Y. Xiang, A. Demetriadou, C. Carnagie, H. Ohadi, B. de Nijs, R. Esteban, J. Aizpurua, and J. J. Baumberg, Single-molecule optomechanics in “picocavities,” *Science* **354**, 726 (2016).
- [7] T. B. Hoang, G. M. Akselrod, and M. H. Mikkelsen, Ultrafast room-temperature single photon emission from quantum dots coupled to plasmonic nanocavities, *Nano Lett.* **16**, 270 (2016).
- [8] J. Huang, A. Traverso, G. Yang, and M. Mikkelsen, Real-time tunable strong coupling: From individual nanocavities to meta-surfaces, *ACS Photonics* **6**, 838 (2019).
- [9] Y. Zhang, Q. Meng, L. Zhang, J. Li, J. J. Baumberg, and D. R. Smith, Sub-nanometre control of the coherent interaction between a single molecule and a plasmonic nanocavity, *Nat. Commun.* **8**, 15225 (2017).
- [10] B. Yang, G. Chen, A. Ghafoor, Y. Zhang, Y. Zhang, Y. Luo, J. Yang, V. Sandoghdar, J. Aizpurua, Z. Dong, and J. G. Hou, Sub-nanometre resolution in single-molecule photoluminescence imaging, *Nat. Photon.* **14**, 693 (2020).
- [11] T. B. Hoang, G. M. Akselrod, C. Ciraci, J. Huang, D. R. Smith, and M. H. Mikkelsen, Ultrafast spontaneous emission source using plasmonic nanoantennas, *Nat. Commun.* **6**, 7788 (2015).
- [12] J. J. Baumberg, J. Aizpurua, M. H. Mikkelsen, and D. R. Smith, Extreme nanophotonics from ultrathin metallic gaps, *Nat. Mater.* **18**, 668 (2019).
- [13] H. Kishida and M. Mikkelsen, Ultrafast lifetime and bright emission from graphene quantum dots using plasmonic nanogap cavities, *Nano Lett.* **22**, 904 (2022).
- [14] S. Franke, S. Hughes, M. K. Dezfouli, P. T. Kristensen, K. Busch, A. Knorr, and M. Richter, Quantization of quasinormal modes for open cavities and plasmonic cavity quantum electrodynamics, *Phys. Rev. Lett.* **122**, 213901 (2019).
- [15] J. Ren, S. Franke, A. Knorr, M. Richter, and S. Hughes, Near-field to far-field transformations of optical quasinormal modes and efficient calculation of quantized quasinormal modes for open cavities and plasmonic resonators, *Phys. Rev. B* **101**, 205402 (2020).
- [16] M. Schmidt, R. Esteban, A. Gonzalez-Tudela, G. Giedke, and J. Aizpurua, Quantum mechanical description of Raman scattering from molecules in plasmonic cavities, *ACS Nano* **10**, 6291 (2016).
- [17] T. Neuman, R. Esteban, G. Giedke, M. K. Schmidt, and J. Aizpurua, Quantum description of surface-enhanced resonant Raman scattering within a hybrid-optomechanical model, *Phys. Rev. A* **100**, 043422 (2019).
- [18] I. Shlesinger, P. Senellart, L. Lanco, and J. J. Greffet, Tunable bandwidth and nonlinearities in an atom-photon interface with subradiant states, *Phys. Rev. A* **98**, 013813 (2018).
- [19] S. Franke, M. Richter, J. Ren, A. Knorr, and S. Hughes, Quantized quasinormal-mode description of nonlinear cavity-QED effects from coupled resonators with a Fano-like resonance, *Phys. Rev. Res.* **2**, 033456 (2020).
- [20] B. Kraus, H. P. Buchler, S. Diehl, A. Kantian, A. Micheli, and P. Zoller, Preparation of entangled states by quantum Markov processes, *Phys. Rev. A* **78**, 042307 (2008).
- [21] F. Verstraete, M. Wolf, and J. I. Cirac, Quantum computation and quantum-state engineering driven by dissipation, *Nat. Phys.* **5**, 633 (2009).
- [22] Y.-D. Wang and A. A. Clerk, Reservoir-engineered entanglement in optomechanical systems, *Phys. Rev. Lett.* **110**, 253601 (2013).
- [23] H. Krauter, C. A. Muschik, K. Jensen, W. Wasilewski, J. M. Petersen, J. I. Cirac, and E. S. Polzik, Entanglement generated by dissipation and steady state entanglement of two macroscopic objects, *Phys. Rev. Lett.* **107**, 080503 (2011).
- [24] Y. Lin, J. P. Gaebler, F. Reiter, T. R. Tan, R. Bowler, A. S. Sorensen, D. Leibfried, and D. J. Wineland, Dissipative production of a maximally entangled steady state of two quantum bits, *Nature (London)* **504**, 415 (2013).
- [25] D. Kienzler, H.-Y. Lo, B. Keitch, L. De Clercq, F. Leupold, F. Lindenfesler, M. Marinelli, V. Negnevitsky, and J. Home, Quantum harmonic oscillator state synthesis by reservoir engineering, *Science* **347**, 53 (2015).
- [26] M. B. Plenio, S. F. Huelga, A. Beige, and P. L. Knight, Cavity-loss-induced generation of entangled atoms, *Phys. Rev. A* **59**, 2468 (1999).
- [27] A. Gonzalez-Tudela, D. Martin-Cano, E. Moreno, L. Martin-Moreno, C. Tejedor, and F. J. Garcia-Vidal, Entanglement of two qubits mediated by one-dimensional plasmonic waveguides, *Phys. Rev. Lett.* **106**, 020501 (2011).
- [28] C. W. Gardiner and M. J. Collett, Input and output in damped quantum systems: Quantum stochastic differential equations and the master equation, *Phys. Rev. A* **31**, 3761 (1985).
- [29] R.-Q. Li, D. Hernangomez-Perez, F. J. Garcia-Vidal, and A. I. Fernandez-Dominguez, Transformation optics approach to plasmon-exciton strong coupling in nanocavities, *Phys. Rev. Lett.* **117**, 107401 (2016).
- [30] A. Cuartero-Gonzalez and A. Fernandez-Dominguez, Light-forbidden transitions in plasmon-emitter interactions beyond the weak coupling regime, *ACS Photonics* **5**, 3415 (2018).
- [31] R.-Q. Li, F. Garcia-Vidal, and A. Fernandez-Dominguez, Plasmon-exciton coupling in symmetry-broken nanocavities, *ACS Photonics* **5**, 177 (2018).
- [32] A. Cuartero-Gonzalez and A. I. Fernandez-Dominguez, Dipolar and quadrupolar excitons coupled to a nanoparticle-on-mirror cavity, *Phys. Rev. B* **101**, 035403 (2020).
- [33] A. Cuartero-Gonzalez, A. Manjavacas, and A. Fernandez-Dominguez, Distortion of the local density of states in a plasmonic cavity by a quantum emitter, *New J. Phys.* **23**, 073011 (2021).
- [34] I. Medina, F. J. Garcia-Vidal, A. I. Fernandez-Dominguez, and J. Feist, Few-mode field quantization of arbitrary electromagnetic spectral densities, *Phys. Rev. Lett.* **126**, 093601 (2021).
- [35] W. Yan, R. Faggiani, and P. Lalanne, Rigorous modal analysis of plasmonic nanoresonators, *Phys. Rev. B* **97**, 205422 (2018).
- [36] P. Lalanne, Light-in-complex-nanostructures/MAN: Versions 7.1 of QNMEig and QNMPole, Zenodo (2020), doi:10.5281/zenodo.5017292.
- [37] C. Carlson, R. Salzwedel, M. Selig, A. Knorr, and S. Hughes, Strong coupling regime and hybrid quasinormal modes from a single plasmonic resonator coupled to a transition metal dichalcogenide monolayer, *Phys. Rev. B* **104**, 125424 (2021).

- [38] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.111.075420> for the derivation of the normalized mode volume; the description of the driven cavity quantum electrodynamics model; the calculation of the in-coupling constant; the derivation of the quantum extinction cross section; details of the quasinormal mode analysis; the population dynamics of single emitter, two-emitter, and multi-emitter systems; the dynamics of the subradiant state populations, and which also includes Refs. [57–72].
- [39] P. T. Kristensen, R. C. Ge, and S. Hughes, Normalization of quasinormal modes in leaky optical cavities and plasmonic resonators, *Phys. Rev. A* **92**, 053810 (2015).
- [40] K. Bedingfield, E. Elliott, A. Gisdakis, N. Kongsuwan, J. Baumberg, and A. Demetriadou, Multifaceted plasmonic nanocavities, *Nanophotonics* **12**, 3931 (2023).
- [41] H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2007).
- [42] S. M. Barnett and P. M. Radmore, *Methods in Theoretical Quantum Optics* (Oxford Academic, Oxford, 2002).
- [43] B. Yuen, DIRACPY v1.0.0, <https://github.com/b-yuen/diracpy>.
- [44] S. Simoncelli, E. Roller, P. Urban, R. Schreiber, A. Turberfield, T. Leidl, and T. Lohmuller, Quantitative single-molecule surface-enhanced Raman scattering by optothermal tuning of DNA origami-assembled plasmonic nanoantennas, *ACS Nano* **10**, 9809 (2016).
- [45] R. Chikkaraddy, V. Turek, N. Kongsuwan, F. Benz, C. Carnegie, T. van de Goor, B. de Nijs, A. Demetriadou, O. Hess, and J. J. Baumberg, Mapping nanoscale hotspots with single-molecule emitters assembled into plasmonic nanocavities using DNA origami, *Nano Lett.* **18**, 405 (2018).
- [46] A. Lombardi, A. Demetriadou, L. Weller, P. Andrae, F. Benz, R. Chikkaraddy, J. Aizpurua, and J. J. Baumberg, Anomalous spectral shift of near- and far-field plasmonic resonances in nanogaps, *ACS Photonics* **3**, 471 (2016).
- [47] P. Alonso-Gonzalez, P. Albella, F. Neubrech, C. Huck, J. Chen, F. Golmar, F. Casanova, L. E. Hueso, A. Pucci, J. Aizpurua, and R. Hillenbrand, Experimental verification of the spectral shift between near- and far-field peak intensities of plasmonic infrared nanoantennas, *Phys. Rev. Lett.* **110**, 203902 (2013).
- [48] T. G. Eck, Level crossings and anti-crossings, *Physica* **33**, 157 (1967).
- [49] P. Törmä and W. L. Barnes, Strong coupling between surface plasmon polaritons and emitters: A review, *Rep. Prog. Phys.* **78**, 013901 (2015).
- [50] A. Demetriadou, J. Hamm, Y. Luo, J. Pendry, J. Baumberg, and O. Hess, Spatiotemporal dynamics and control of strong coupling in plasmonic nanocavities, *ACS Photonics* **4**, 2410 (2017).
- [51] T. Wu, M. Gurioli, and P. Lalanne, Nanoscale light confinement: The Q's and V's, *ACS Photonics* **8**, 1522 (2021).
- [52] L. C. Andreani, G. Panzarini, and J. M. Gérard, Strong-coupling regime for quantum boxes in pillar microcavities: Theory, *Phys. Rev. B* **60**, 13276 (1999).
- [53] K. Santhosh, O. Bitton, L. Chuntonov, and G. Haran, Vacuum Rabi splitting in a plasmonic cavity at the single quantum emitter limit, *Nat. Commun.* **7**, ncomms11823 (2016).
- [54] K.-D. Park, M. A. May, H. Leng, J. Wang, J. A. Kropp, T. Gougousi, M. Pelton, and M. B. Raschke, Tip-enhanced strong coupling spectroscopy, imaging, and control of a single quantum emitter, *Sci. Adv.* **5**, eaav5931 (2019).
- [55] P. Lalanne, W. Yan, K. Vynck, C. Sauvan, and J.-P. Hugonin, Light interaction with photonic and plasmonic resonances, *Nanophotonics* **12**, 1700113 (2018).
- [56] A. Kuhn and D. Ljunggren, Cavity-based single-photon sources, *Contemp. Phys.* **51**, 289 (2010).
- [57] C. Sauvan, J. P. Hugonin, I. S. Maksymov, and P. Lalanne, Theory of the spontaneous optical emission of nanosize photonic and plasmon resonators, *Phys. Rev. Lett.* **110**, 237401 (2013).
- [58] R.-C. Ge and S. Hughes, Design of an efficient single photon source from a metallic nanorod dimer: A quasi-normal mode finite-difference time-domain approach, *Opt. Lett.* **39**, 4235 (2014).
- [59] P. T. Kristensen and S. Hughes, Modes and mode volumes of leaky optical cavities and plasmonic nanoresonators, *ACS Photonics* **1**, 2 (2014).
- [60] Q. Bai, M. Perrin, C. Sauvan, J.-P. Hugonin, and P. Lalanne, Efficient and intuitive method for the analysis of light scattering by a resonant nanostructure, *Opt. Express* **21**, 27371 (2013).
- [61] D. A. Powell, Resonant dynamics of arbitrarily shaped meta-atoms, *Phys. Rev. B* **90**, 075108 (2014).
- [62] X. Zheng, V. K. Valev, N. Verellen, V. Volskiy, L. O. Herrmann, P. Van Dorpe, J. J. Baumberg, G. A. E. Vandenbosch, and V. V. Moschchalkov, Implementation of the natural mode analysis for nanotopologies using a volumetric method of moments (V-MoM) algorithm, *IEEE Photon. J.* **6**, 1 (2014).
- [63] R.-L. Chern, Chien C. Chang, and C. Chung Chang, Surface and bulk modes for periodic structures of negative index materials, *Phys. Rev. B* **74**, 155101 (2006).
- [64] A. Taflove, A. Oskooi, and S. Johnson, *Advances in FDTD Computational Electrodynamics: Photonics and Nanotechnology* (Artech House, Boston, 2013).
- [65] J. Zimmerling, L. Wei, P. Urbach *et al.*, Efficient computation of the spontaneous decay rate of arbitrarily shaped 3D nanosized resonators: A Krylov model-order reduction approach, *Appl. Phys.* **A 122**, 158 (2016).
- [66] R. Zhao, Y. Luo, A. I. Fernández-Domínguez, and J. B. Pendry, Description of van der Waals interactions using transformation optics, *Phys. Rev. Lett.* **111**, 033602 (2013).
- [67] A. Raman and S. Fan, Photonic band structure of dispersive metamaterials formulated as a Hermitian eigenvalue problem, *Phys. Rev. Lett.* **104**, 087401 (2010).
- [68] J. Zimmerling, L. Wei, P. Urbach, and R. Remis, A Lanczos model-order reduction technique to efficiently simulate electromagnetic wave propagation in dispersive media, *J. Comput. Phys.* **315**, 348 (2016).
- [69] R. M. Joseph, S. C. Hagness, and A. Taflove, Direct time integration of Maxwell's equations in linear dispersive media with absorption for scattering and propagation of femtosecond electromagnetic pulses, *Opt. Lett.* **16**, 1412 (1991).
- [70] N. Kongsuwan, A. Demetriadou, M. Horton, R. Chikkaraddy, J. J. Baumberg, and O. Hess, Plasmonic nanocavity modes: From near-field to far-field radiation, *ACS Photonics* **7**, 463 (2020).
- [71] COMSOL MULTIPHYSICS v. 6.0, www.comsol.com (COMSOL AB, Stockholm, Sweden).
- [72] E. Elliott, K. Bedingfield, J. Huang, S. Hu, B. de Nijs, A. Demetriadou, and J. J. Baumberg, Fingerprinting the hidden facets of plasmonic nanocavities, *ACS Photonics* **9**, 2643 (2022).