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Quantum light from a metal nanoparticle

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Recent progress in quantum technologies has opened the possibility to control the quantum properties of light and manipulate with single photons [1,2]. Single-photon sources have found numerous applications in spectroscopy, quantum optics, and quantum technologies. They can be used for measurements of weak absorption, quantum information processing, quantum communication, quantum cryptography, quantum computing, and quantum metrology [1–4].

Single-photon sources are subjected to a fundamental limitation in the speed of operation dictated by the spontaneous emission rate of quantum emitters (QEs). The current paradigm of the rate acceleration suggests coupling of a QE to a metal nanostructure, in particular, a metal nanoparticle (MNP). Here, we demonstrate that, in contrast to this approach, a MNP itself being excited via a strong coupling with a QE can emit light with quantum properties. We determine both the first- and second-order correlation functions of light spontaneously emitted by a MNP in such a compound and show that this light should exhibit sub-Poissonian photon statistics and perfect photon antibunching. This discovery opens a prospect to single-photon sources with generation rates up to 100 THz.

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I. INTRODUCTION

Recent progress in quantum technologies has opened the possibility to control the quantum properties of light and manipulate with single photons [1,2]. Single-photon sources have found numerous applications in spectroscopy, quantum optics, and quantum technologies. They can be used for measurements of weak absorption, quantum information processing, quantum communication, quantum cryptography, quantum computing, and quantum metrology [1–4].

A key element of a single-photon source is a quantum emitter (QE) such as an atom, ion, molecule, color center, semiconductor nanocrystal, or quantum dot. Single emitters being excited by an external source, either optically or electrically, emit light spontaneously delivering photons one at a time, which is known as photon antibunching. To emit a next photon, the excitation-emission cycle should be completed that limits the repetition rate of single-photon emission and hence the speed of any single-photon device operation. The shortest emission lifetimes of 300 ps are typical for quantum dots, which leads to the highest rate of photon emission, 1 GHz [1].

The current commonly adopted paradigm in accelerating the QE spontaneous emission suggests to introduce a dielectric or metallic (plasmonic) environment in the vicinity of the QE which modifies the electromagnetic local density of states for the optical transition [5,6]. The underlying mechanism of this modification is the Purcell effect [7], which can be alternatively considered as a result of the interaction of the QE with its own field reflected from the cavity walls or plasmonic nanostructure [8]. The most pronounced effect takes place when the QE emission frequency is close to the frequencies of localized surface plasmons (LSPs), which are the normal modes of the collective electron oscillations in the nanostructure. The estimates show [9] that in such a case the plasmonic approach to the spontaneous emission enhancement can provide two orders of magnitude larger enhancement as compared to all-dielectric structures, reaching the ultimate level of single-photon emission of the order of 1 THz. Recently, experimental demonstrations of ultrafast room-temperature single-photon emission with rates up to 80 GHz from quantum dots coupled to plasmonic nanostructures have been reported [10,11].

In all studies to date, a plasmonic nanostructure in this context has been considered as a passive element which modifies the local environment of a QE. In the most simple configuration the nanostructure is reduced to a metal nanoparticle (MNP) acting as a nanoantenna which concentrates light from the far field and enhances the outcoupling of the QE radiation into the far field [12]. Due to its subwavelength dimensions the QE-MNP compound system can be regarded as a dipole “superemitter” [13]. This phenomenon has been investigated in different configurations, both experimentally [13–15] and theoretically [16–29]. One distinguishes between the weak-coupling regime where only the relaxation dynamics of the QE is modified [16,18,20,22,23,25,28] and the strong-coupling regime where the emission spectrum is modified as well due to the fast Rabi oscillations between the QE and MNP states [17,19,21,24,26,27,29,30]. It has been also noticed that the photon antibunching in the QE emission can be controlled in the vicinity of a MNP [31].

In contrast to the situation discussed above, a MNP can emit light itself. Being optically excited above the onset of the interband transitions, noble-metal nanoparticles can demonstrate rather strong visible photoluminescence [32–34]. There is experimental evidence that the nonradiative relaxation channel in such a case can involve the generation of LSPs which subsequently radiate light [34]. The coupling of a MNP with a QE can lead to the enhancement of MNP photoluminescence [35]. On the other hand, LSPs can be excited directly, either by fast electrons [36,37] or by light resonant to the LSP mode [36]. The emission rate of a dipole LSP in a MNP is proportional to its volume and can reach the values of the order of 1 PHz = 10^3 THz [38], three orders of magnitude larger than the ultimate rate expected for QEs coupled to metal nanostructures.
of frequency \( \omega_{\text{LSP}} \) of an isolated MNP. The resonant laser excitation ladder of the plasmonic Fock states is represented by an infinite equidistant resonance with the higher plasmonic Fock states.

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...one should say here regarding the term “strong coupling,” which is somewhat context sensitive. In this paper, following Ref. [26], we define the strong-coupling regime for a MNP-QE compound as the range where the coupling strength exceeds the linewidths of the two coupled systems. In other words, the system is in the strong-coupling regime whenever the Rabi splitting is experimentally observable. This definition is somewhat different from the one adopted in cavity quantum electrodynamics where strong coupling implies that the interaction between two subsystems dominates over all decay mechanisms [39].

The paper is organized as follows. Section II introduces the adopted theoretical model and describes the energy spectrum of the system, relaxation processes, and master equations. In Sec. III both the first- and second-order correlation functions of the emitted light are calculated. In Sec. IV the single-photon generation rate is discussed for different scenarios. The main results of the paper are summarized in Sec. V.

II. THEORETICAL MODEL

A. Energy spectrum

We consider first the model system shown in Fig. 1(b). The QE, which has three energy levels \(|g\rangle, |e\rangle, \) and \(|u\rangle, \) is incoherently excited at the optically active transition \(|g\rangle \rightarrow |u\rangle, \) the transition frequency \( \omega_{\text{g,u}} \) of the other optically active transition \(|g\rangle \rightarrow |e\rangle, \) is close to the frequency \( \omega_{\text{c}} \) of the dipole LSP mode of the MNP [40]. Let us note that such a model does not specify the MNP as far as its dipole LSP resonance can be engineered by the choice of the MNP composition, size, shape, and its dielectric environment [41]. We assume also that the upper excited QE state \(|u\rangle \) undergoes fast nonradiative decay to the state \(|e\rangle \) and the frequency of the transition \(|g\rangle \rightarrow |u\rangle, \) is below the onset of interband transitions in the MNP, so that its photoluminescence is not excited.

This model assumes that the QE interacts effectively only with the MNP dipole plasmon mode and the interaction with the higher-order multipole modes can be neglected. Such a model was adopted in a number of publications (see, e.g., Refs. [17,22,23,25,29,35]). It is a reasonable approach when the energy of the interaction between the QE dipole and the MNP multipoles is much smaller than the energy intervals between the MNP dipole LSP mode and the higher-order multipole modes. The quantum-mechanical operators of the multipole moments of a spherical MNP are found in Ref. [38]. Using these results one can estimate the interaction between the QE transition dipole moment, \( d_{\text{QE}}, \) and the field, \( E^{(1)} \), of the MNP \( l \)th multipole \( Q^{(l)}, \) both being in vacuum, as

\[
V^{(l)} = d_{\text{QE}} E^{(1)} \sim d_{\text{QE}} Q^{(l)} \frac{l}{Z^{2}},
\]

where \( Q^{(l)} = \sqrt{4\pi l} R^{l+1} Z^{l+1}/2, \) \( \omega_{l} = \) the frequency of the \( l \)th LSP multipole mode, \( R \) is the MNP radius, and \( Z \) is the distance between the QE and the MNP center. Assuming for an estimate that \( Z \approx R \) and \( \omega_{l} \approx \omega_{1}, \) one finds that the interaction energy \( V \sim d_{\text{QE}} \sqrt{4\pi l}/Z^{l+1} \) and does not depend significantly on the multipole order \( l. \) Taking here \( d_{\text{QE}} = e r_{0} \) with \( e \) being the electron charge and \( r_{0} = 0.7 \) nm, a typical value for quantum dots [16,22], \( \omega_{l} = \omega_{\text{Ag}} \sqrt{r_{0}^{3}} \) with \( \omega_{\text{Ag}} = 9.2 \) eV being the Ag plasmon energy quantum [42] and \( Z = 30 \) nm one obtains \( V \approx 10 \) meV, which is much smaller than the energy gaps between the LSP dipole and the \( l \)th multipole modes, \( h (\omega_{l} - \omega_{1}), \) which are of the order of a few tenths of electronvolt [17,24]. On the other hand, this value of the interaction strength is above the onset of strong MNP-QE coupling which is considered in this paper [17].

FIG. 1. Energy levels of the system under consideration. (a) Plasmonic Fock states of an isolated MNP. The resonant laser excitation of frequency \( \omega_{\text{LSP}} = \omega_{\text{c}} \) (red solid arrows) populates all Fock states \( |N\rangle \) that leads to spontaneous emission at the transitions \(|N\rangle \rightarrow |N - 1\rangle \) (green dashed arrows). (b) The levels of isolated MNP and QE involved in the coupling. The relaxation at the transition \(|u\rangle \rightarrow |e\rangle \) is nonradiative (blue dashed arrow). The higher plasmonic Fock states are not populated and are not shown here. (c) The levels of the compound system “MNP+QE.” The laser excitation of frequency \( \omega_{\text{c}} = \omega_{\text{LSP}} \) is resonant to the transition \(|G\rangle \rightarrow |\rangle \), but is out of resonance with the higher plasmonic Fock states.

In the quantum description [38], the spectrum of the dominant dipole LSP mode is represented by an infinite equidistant ladder of the plasmonic Fock states \( |N\rangle \) with \( N \) being the number of quanta in the dipole plasmonic state [Fig. 1(a)]. Spontaneous emission in such a system results from downward transitions between the adjacent Fock states. Upon illumination by resonant laser light, which is described by a coherent state [1], all plasmonic Fock states are populated. There is therefore a certain probability that a few photons of the same frequency can be emitted simultaneously which is a disadvantage when one aims to achieve a single-photon emission.

This drawback would be avoided if one could prepare a MNP as a two-level system which involves only the vacuum and single-plasmon Fock states while the contribution of the other plasmonic states could be disregarded. The present paper is therefore focused on this issue. We show that a MNP being strongly coupled to a QE behaves effectively as a two-level system which exhibits extremely rapid radiative relaxation. We consider two different scenarios of the MNP-QE compound excitation. In the first one, a three-level QE is excited by laser light through the transition which is nonresonant with the MNP LSP mode (nonresonant scenario). In the second one, the system is excited resonantly to one of its lower transitions (resonant scenario). We analyze these schemes in terms of single-photon generation rate and propose them as a platform for single-photon sources with unprecedented efficiency.
The QE and the MNP are coupled with each other through the electrostatic interaction $\hat{V}$ so that the Hamiltonian of the system is written as $\hat{H} = \hat{H}_{\text{QE}} + \hat{H}_{\text{MNP}} + \hat{V}$, where $\hat{H}_{\text{QE}}$ and $\hat{H}_{\text{MNP}}$ are the Hamiltonians of the noninteracting components. We assume that the matrix elements of $\hat{V}$ are much less than the energy intervals $\hbar\omega_0$ and $\hbar\omega_1$, but may be comparable with $2\Delta = \hbar(\omega_0 - \omega_1)$. This condition implies that the regime of ultrastrong coupling is not realized in the system under discussion that guarantees the validity of both the rotating wave approximation and Markov approximations [44]. Then in the lowest order the eigenstates of the system involved in the MNP-QE coupling are approximated by the states $|G\rangle = |g\rangle|0\rangle$, $|U\rangle = |u\rangle|0\rangle$, and

$$|\rangle = \cos \theta |g\rangle|1\rangle - \sin \theta |e\rangle|0\rangle, \quad (2)$$

$$|\rangle = \sin \theta |g\rangle|1\rangle + \cos \theta |e\rangle|0\rangle. \quad (3)$$

with $\tan 2\theta = V_0/\Delta$ and $V_0 = \langle 1|\langle\hat{V}|\hat{V}\rangle|0\rangle = V_0^2$. The states $|\rangle$ and $|\rangle$, Eqs. (2) and (3), can be identified as the QE states dressed by the MNP plasmonic field [39]. The doublet of the dressed states is separated by the energy $2\Delta$ with $\Omega \equiv \sqrt{\Delta^2 + V_0^2}/\hbar$ being the frequency of the Rabi oscillations between the states $|g\rangle|1\rangle$ and $|e\rangle|1\rangle$ [Fig. 1(c)] [45]. In the case of strong MNP-QE coupling which is considered in this paper the splitting between the levels of the doublet is larger than the linewidths of the $|\rangle \rightarrow |G\rangle$ transitions. These transitions do not overlap therefore with each other and are well spectrally resolved.

Besides the energy levels which correspond to the states $|\rangle$ and $|\rangle$, there are also levels which originate from the coupling between the states $|g\rangle|N+1\rangle$ and $|e\rangle|N\rangle$ with $N \geq 1$ and which are not shown in Fig. 1(c) [39]. The splittings between them, $2\Omega_N = 2\sqrt{\Delta^2 + V_0^2}(N + 1)/\hbar$, are larger than the linewidths of the $|\rangle \rightarrow |G\rangle$ transitions under consideration. As a result, the transitions between the higher dressed states contribute to another spectral lines and can be filtered out.

### B. Relaxation processes

In what follows, we will be interested in the correlation functions of light emitted at the transitions $|\rangle \rightarrow |G\rangle$. The radiative relaxation rates are proportional to the square of the transition matrix elements of the dipole moment operator of the compound system “MNP+QE,” $\hat{D}^S = \hat{\mathbf{D}} + \hat{\mathbf{d}}$, where $\hat{\mathbf{D}}$ and $\hat{\mathbf{d}}$ are the dipole moment operators of the MNP and QE, respectively. For the transitions under discussion,

$$D_{G-}^S = D_{01} \cos \theta - d_{ge} \sin \theta \approx D_{01} \cos \theta \equiv D_{01}^-, \quad (4)$$

$$D_{G+}^S = D_{01} \sin \theta + d_{ge} \cos \theta \approx D_{01} \sin \theta \equiv D_{01}^+, \quad (5)$$

where we have taken into account that $d_{ge} \ll D_{01}$ and assumed $V_0 \sim |\Delta|$. For a spherical MNP of radius $R$ in vacuum the transition dipole moment is given by $D_{01} = \sqrt{\hbar\alpha_0 R^2}/2$ [38]. Taking here the value of $\omega_1$ for an Ag sphere as before and $R = 20$ nm one obtains $D_{01} = eR_0$ with $R_0 \approx 120$ nm. If besides that $r_0 = 0.7$ nm as before, the approximations in Eqs. (4) and (5) are valid if $|\tan \theta|, |\cot \theta| \ll 170$. In such case the contribution of the QE is negligible and the emission originates primarily from the MNP.

Under the same assumptions, this leads to the radiative relaxation rates $\Gamma_r^\pm \approx \Gamma_r \cos^2 \theta$ and $\Gamma_r^\pm \approx \Gamma_r \sin^2 \theta$ for the transitions $|\rangle \rightarrow |G\rangle$ and $|\rangle \rightarrow |G\rangle$, respectively, where $\Gamma_r$ is the radiative relaxation rate of an isolated MNP. In particular, for a spherical MNP in vacuum [36,38],

$$\Gamma_r = \frac{2\omega_0^0 R^3}{3\epsilon_\infty} \quad (6)$$

with $c$ being the speed of light in vacuum. One concludes therefore that the relaxation rate is determined by the squared amplitude of the admixture of the one-plasmon state.

Analogously, the nonradiative relaxation rates $\Gamma_{nr}^\pm \approx \Gamma_{nr} \cos^2 \theta$ and $\Gamma_{nr}^\pm \approx \Gamma_{nr} \sin^2 \theta$ due to the dominant contribution of the nonradiative decay rate of the MNP one-plasmon state, $\Gamma_{nr}$. Here the quantity $\Gamma_{nr}$ is a sum of the relaxation rates in all possible nonradiative relaxation channels which lead to the depopulation of the one-plasmon Fock state. It includes, in particular, the Landau damping that originates from the decay of the LSP into electron-hole pairs [46,47]. We thus have for the total longitudinal (energy) relaxation rates $\Gamma_r^\pm \approx \Gamma_r \cos^2 \theta$ and $\Gamma_{nr}^\pm \approx \Gamma_{nr} \sin^2 \theta$ with $\Gamma_1 = \Gamma_r + \Gamma_{nr}$.

By the same token, $\Gamma_{\perp}^\pm \approx \Gamma_{\perp} \cos^2 \theta$ and $\Gamma_{\perp}^\pm \approx \Gamma_{\perp} \sin^2 \theta$ for the transverse (phase) relaxation rates at the transitions $|\rangle \rightarrow |G\rangle$ with $\Gamma_\perp$ being the phase relaxation rate of the plasmonic Fock state [1]. The latter quantity equals one-half of the relaxation rate $\Gamma$ which enters the Drude dielectric function of the MNP that follows from the quasistatic limit for the MNP polarizability [38]. It is associated with collisions of electrons with each other and with the MNP boundary. The relaxation rate $\Gamma$ can be written in the form [42]

$$\Gamma = \Gamma_\infty + a\nu_F R, \quad (7)$$

where $\Gamma_\infty$ is the relaxation constant for an unbounded metal, $\nu_F$ is the Fermi velocity, $R$ is a characteristic size of the MNP, and the prefactor $a$ is in the order of one and depends in particular on the geometry of the MNP.

Similar arguments can be applied to write $\gamma^- \equiv \gamma \sin^2 \theta$ and $\gamma^\pm \equiv \gamma \cos^2 \theta$ for the rates of the decays $|U\rangle \rightarrow |\rangle$ with $\gamma$ being the nonradiative decay rate at the transition $|U\rangle \rightarrow |e\rangle$.

### C. Master equations

#### 1. Nonresonant scenario

The evolution of the system is described by the Liouville equation for the density matrix, $\rho$, which is split into the balance equations for the state populations:

$$\dot{\rho}_{GG} = -\mathcal{R}\rho_{GG} + \Gamma_{--}\rho_{--} + \Gamma_{+-}\rho_{+-}, \quad (8)$$

$$\dot{\rho}_{UU} = \mathcal{R}\rho_{GG} - (\gamma^- + \gamma^+)\rho_{UU}, \quad (9)$$

$$\dot{\rho}_{--} = \gamma^-\rho_{UU} - \Gamma_{--}\rho_{--}, \quad (10)$$

$$\dot{\rho}_{++} = \gamma^+\rho_{UU} - \Gamma_{++}\rho_{++}, \quad (11)$$

and the equations for the coherences of interest:

$$\dot{\rho}_{--} = -(\Gamma_{--} + i\omega_-)\rho_{--}, \quad (12)$$

$$\dot{\rho}_{++} = -(\Gamma_{++} + i\omega_+)\rho_{++}, \quad (13)$$
where $R$ is the pumping rate of the external field and $\omega_L = (\omega_0 + \omega_1)/2 \pm \Omega$ are the frequencies of the transitions $|\pm\rangle \rightarrow |G\rangle$. Here we have neglected the rate of the decay $|U\rangle \rightarrow |G\rangle$ in comparison with the rates $\gamma_{\pm}$.

The set of Eqs. (8)–(11) is solved by applying the Laplace transform with the initial condition $\rho(0) = 1$ and all other populations being equal to zero. In the steady-state limit ($t \gg \Gamma_1^{-1}$) the populations of interest are given by

$$\rho_{\pm\pm}(\infty) = \frac{R\gamma^+\Gamma_1^-}{Q} \sin^4 \theta,$$  
(14)

$$\rho_{\mp\mp}(\infty) = \frac{R\gamma^+\Gamma_1^-}{Q} \cos^4 \theta,$$  
(15)

where $Q = (\gamma^- + \gamma^+ + R)\Gamma_1^+\Gamma_1^- + R(\gamma^+\Gamma_1^- + \gamma^-\Gamma_1^+)$.

2. Resonant scenario

We assume here that the laser field of amplitude $E_L$ and frequency $\omega_L$ resonantly excites one of the transitions, either $|-\rangle \rightarrow |G\rangle$ or $|+\rangle \rightarrow |G\rangle$. In such a case the evolution of the system is described by the standard optical Bloch equations [43]. In the regime far below saturation the steady-state populations of the upper state (either $-\rangle$ or $+\rangle$) is given by

$$\rho_{\pm\pm}(\infty) = \frac{2\bar{\Omega}_{L}^{(\pm)}}{\Gamma_1^{\mp} + \Gamma_1^{\pm}},$$

(16)

where $\bar{\Omega}_{L}^{(\pm)} = D_{0\pm}^E E_L/\hbar$ is the Rabi frequency characterizing the coupling the MNP-QE compound with the laser field and $\delta^\pm = \omega_L - \omega_{\pm}$ is the frequency detuning. The applicability of this approach implies that the power broadening is negligible or, equivalently,

$$\bar{\Omega}_{L}^{(\pm)} \ll \Gamma_1^{\mp} \Gamma_1^{\pm}.$$  
(17)

Strictly speaking, the population of the states which are not involved in the selected two-level system modifies the populations of the states $|G\rangle$ and $|\pm\rangle$. However, the corrections due to this effect give the relative contribution of the order of $\bar{\Omega}_{L}^{(\pm)} / (\Gamma_1^{\pm} + \Gamma_1^{\pm})$ and will be neglected in what follows.

III. CORRELATION FUNCTIONS OF THE EMITTED LIGHT

The electromagnetic field spontaneously emitted by a compound quantum dipole source in the far-field region is written as a sum of the positive-frequency and negative-frequency parts [48]

$$E(r, t) = E^+(r, t) + E^-(r, t),$$

(18)

where

$$E^+(r, t) = -\frac{\omega_{ul}^2}{4\pi\epsilon_0 c^3 R^3} \left[ (\mathbf{D}_L \times r) \times r \right] \sigma_{-\tilde{t}},$$

(19)

and $E^-(r, t) = (E^+(r, t))^\dagger$. Here $\omega_{ul}$ is the frequency of the transition from the upper state $|u\rangle$ to the lower state $|l\rangle$, $\mathbf{D}_L$ is the transition dipole moment of the system, $\sigma_\pm = |l\rangle\langle u|$ is the lowering operator, and the time argument $\tilde{t} \equiv t - r/c$ takes into account retardation.

The experimentally observed quantities can be expressed in terms of the first- and second-order correlation functions [48]

$$\langle E^-(t)E^+(t + \tau) \rangle \propto g_{+1}(t, t + \tau)$$

(20)

and

$$\langle E^-(t)E^-(t + \tau)E^+(t + \tau + \tau) \rangle \propto g_{+2}(t, t + \tau)$$

(21)

where $\sigma_\pm = |u\rangle\langle l|$ is the raising operator and the averaging is taken over the “system (S) + reservoir (R)” states with the reservoir being the electromagnetic vacuum $|\emptyset\rangle$, so that $\rho_{S+R}(t) = \rho(t)|\emptyset\rangle\langle\emptyset|$. The correlation functions $g_{+1}(t, t + \tau)$ and $g_{+2}(t, t + \tau)$ are found with the use of the quantum regression theorem [48–50] which relates the $\tau$ evolution of the operators under the trace symbol in Eqs. (20) and (21) with the evolution of $\rho(t)$. As a result, one obtains for the steady-state limits $g_{+1}^{(1)}(\tau) \equiv \lim_{t \rightarrow \infty} g_{+1}^{(1)}(t, t + \tau)$ (here and in what follows the subscript or superscript “$\pm$” indicates the transitions $|\pm\rangle \rightarrow |G\rangle$)

$$g_{+1}^{(1)}(\tau) = \rho_{\pm\pm}(\infty) e^{-i(\bar{\Omega}_{L}^{(\pm)} + i\omega_{ul})\tau},$$

(22)

where the steady-state populations $\rho_{\pm\pm}(\infty)$ are given by Eqs. (14) and (15). Accordingly, the spectra of spontaneous emission at these transitions are found as

$$S_{\pm}(\omega) = \int_{-\infty}^{\infty} e^{i\omega \tau} g_{+1}^{(1)}(\tau) d\tau = \frac{2\bar{\Omega}_{L}^{(\pm)} \rho_{\pm\pm}(\infty)}{(\omega - \omega_{ul})^2 + (\Gamma_{1\pm}^*)^2},$$

(23)

where the functions $g_{+1}^{(1)}(\tau)$ for negative $\tau$ are defined as $g_{+1}^{(1)}(-\tau) = g_{+1}^{(1*)}(\tau)$ [50]. The linewidths of the doublet are related with each other as $\Gamma_{1\pm}^* = \tan^2 \theta$ while their intensities at the maximums, taking into account Eqs. (4) and (5), are related as $L_1/L = \cot^2 \theta$ (see Fig. 2).

The second-order correlation function depends on the excitation scenario and is considered below.
A. Nonresonant scenario

The steady-state limits of the second-order coherences, $S^{(2)}_\pm(\tau) \equiv \lim_{t \to -\infty} S^{(2)}_\pm(t, t + \tau)$, are given by

$$g^{(2)}_\pm(0) \approx [g^{(1)}_\pm(0)]^2 \times \left(1 - \frac{\cal R + \gamma}{\Gamma_\parallel} e^{-\gamma \tau} + \frac{\cal R + \gamma}{\Gamma_\pm} e^{-\Gamma_\pm \tau}, \right),$$

(24)

where we have adopted a reasonable assumption that $\gamma, \cal R \ll \Gamma_\parallel$ and have taken the lowest order in $\gamma/\Gamma_\parallel$ and $\cal R/\Gamma_\parallel$. We have also used here the relation $\rho_{\pm \pm}(\infty) = S^{(1)}_{\pm \pm}(0)$ [see Eq. (22)].

Equation (24) reveals that $g^{(2)}_{\pm}(0) = g^{(2)}_{\pm}(0) = 0$, i.e., both lines of the doublet exhibit perfect photon antibunching. When the delay between two photons $\tau \gg (\cal R + \gamma)^{-1}$, $g^{(2)}_{\pm}(0) \approx [g^{(1)}_\pm(0)]^2$ and two fields are completely uncorrelated. For finite delays $\tau > 0$ $g^{(2)}_{\pm}(\tau) < [g^{(1)}_\pm(0)]^2$, which indicates the sub-Poissonian photon statistics (Fig. 3) [51].

B. Resonant scenario

Due to the strong MNP-QE coupling the two transitions $|G\rangle \to |\pm\rangle$ are well spectrally resolved and one can excite either the $|-\rangle$ or the $|+\rangle$ state. In such case, the correlation functions of the spontaneously emitted light can be found from the solution of the optical Bloch equations in the lowest nonvanishing order with respect to the Rabi frequency of the corresponding transition, $\Omega^{(2)}_L$. In the particularly simple case of exact resonance ($\omega_\pm = \omega_\pm$) this approach gives

$$S^{(2)}_\pm(\tau) \approx [S^{(1)}_\pm(0)]^2 \times \left(1 - \frac{\Gamma_\pm}{\Gamma_\parallel} e^{-\Gamma_\parallel \tau} + \frac{\Gamma_{\pm \pm}}{\Gamma_\parallel} e^{-\Gamma_{\pm \pm} \tau}, \right),$$

(25)

which reveals both the sub-Poissonian photon statistics and perfect antibunching as before (Fig. 3).

C. Numerical values

The numerical results represented in Figs. 2 and 3 are given in terms of dimensionless parameters normalized to either $\Gamma_\parallel$ or $\Gamma_\perp$. In order to have a relation with experimentally measured quantities one needs to know the absolute values of these relaxation constants.

As we have mentioned before, the quantity $\Gamma_\parallel$ equals one-half of the relaxation constant in the Drude model for the dielectric function of the MNP [see Eq. (7)]. For the two most common plasmonic materials, Au and Ag, the quantity $\Gamma_\parallel$ equals 72 and 21 meV, respectively, and $v_F = 1.4 \times 10^6$ m/s for both metals [42]. For example, for a spherical MNP of radius $R = 20$ nm this gives $\Gamma_\parallel \approx 38$ meV for Au and $\Gamma_\parallel \approx 33$ meV for Ag.

The two main contributions to the quantity $\Gamma_\parallel$ come from the radiative damping, Eq. (6), and the Landau damping which can be estimated as the size-dependent part of $\Gamma$, Eq. (7) [47]. Taking the plasmon energy 9.1 and 9.2 eV for Au and Ag, respectively [42], one obtains for the same model of a MNP as before $\Gamma_\parallel \approx 8.0 \times 10^{14}$ s$^{-1}$ (0.50 eV) for Au and $\Gamma_\parallel \approx 8.4 \times 10^{14}$ s$^{-1}$ (0.53 eV) for Ag. The Landau damping has a much smaller magnitude of 44 meV for both metals. As a result, the quantum yield of the MNP light emission $\eta = \Gamma_\gamma/\Gamma_\parallel \approx 0.9$.

IV. PHOTON GENERATION RATE

The probability of photon emission per unit time, $p$, is determined as the product of the probability that the system occupies the excited state with the radiative emission rate from this state, i.e., $p = \rho_{\pm \pm}(\infty) \Gamma_\parallel$, where we assume the steady-state operation.

In the case of the nonresonant scenario the dressed state populations are determined by Eqs. (14) and (15). Using the same assumption that $\gamma, \cal R \ll \Gamma_\parallel$ as before, one finds

$$\rho_{- -}(\infty) \approx \frac{\tan^2 \theta}{\Gamma_\parallel} \left(1 + \frac{1}{\gamma} \right)^{-1},$$

(26)

$$\rho_{++}(\infty) \approx \frac{\cot^2 \theta}{\Gamma_\parallel} \left(1 + \frac{1}{\gamma} \right)^{-1}. \quad (27)$$

Taking for an estimate $\tan \theta \sim \cot \theta \sim 1$ one concludes from here that, not depending on the ratio between the rate constants $\cal R$ and $\gamma$, $p_{\pm} \sim \eta \min(\cal R, \gamma)$. Therefore the optimal pumping rate is determined by the condition $\cal R \sim \gamma$ and in such case $p_{\pm} \sim \eta \gamma$.

The emission quantum yield of a MNP depends on its size and shape. For example, for Au nanorods of diameter 20 nm and length 60 nm $\eta \approx 0.1$ [52], while for Au and Ag spherical nanoparticles of radius 20 nm $\eta \approx 0.9$ (see above). One can expect that $\eta$ increases with the MNP size. For a spherical MNP of radius $R$ the radiative relaxation rate scales as $R^3$ whereas the size-dependent part of the nonradiative damping rate scales as $1/R$ [53].

The typical value of the nonradiative relaxation rate in quantum dots is $\gamma \sim 10^{12}$ s$^{-1}$ (0.6 meV) [54], which justifies the assumption $\gamma \ll \Gamma_\parallel$ made before. For the quantum yield $\eta \sim 1$ this can provide a single-photon emission rate up to
1 THz. Although this value is far above the generation rates of the currently available single-photon sources, this stage in the excitation channel presents a “bottleneck” as compared to the ultimate radiative relaxation rates achievable in MNPs.

In the case of the resonant scenario the steady-state populations of the dressed states are given by Eq. (16) provided the condition (17) is fulfilled. Taking for an estimate $\delta = 0$, $\Omega_L^{(\pm)} / (\Gamma_\parallel \Gamma_\perp) \sim 0.05$, $\Gamma_\parallel \sim 10^{15}$ s$^{-1}$, and $\eta \sim 1$, one obtains for the single-photon generation rate $p_\pm \sim 0.1 \times \Gamma_\parallel^2 \sim 10^5$ THz.

It is instructive to estimate the laser intensity necessary to realize different scenarios of the MNP-QE compound excitation. For the nonresonant scenario the optimum condition requires $R \sim 10^{12}$ s$^{-1}$. Taking the typical value of the absorption cross section for quantum dots $\sigma_a \sim 10^{-14}$ cm$^2$ [55,56] and the transition energy $\hbar \omega_{gs} \sim 2.8$ eV [56] one obtains that this condition is fulfilled at the laser intensity $I_L \sim 4.4 \times 10^7$ W/cm$^2$. Such a high intensity is above the threshold for destruction of metals and can only be implemented in a pulsed regime [57]. On the contrary, for the resonant scenario it is sufficient to have $\Omega_L^{(\pm)} \sim (0.05 \times \Gamma_\parallel \Gamma_\perp)^{1/2}$. Taking for an estimate $\Gamma_\parallel \sim 10^{15}$ s$^{-1}$, $\Gamma_\perp \sim 10^{13}$ s$^{-1}$, and $R_0 = 120$ nm as before, one obtains $I_L \sim 1.7 \times 10^9$ W/cm$^2$, which is acceptable for a continuous excitation.

**V. CONCLUSION**

In this paper, we have demonstrated that a MNP strongly coupled to a QE behaves effectively as a two-level system and should spontaneously emit light which obeys sub-Poissonian statistics and exhibits perfect antibunching. We have considered two different scenarios of excitation: (i) the MNP is excited nonresonantly via coupling with a three-level QE, and (ii) the MNP-QE compound is excited resonantly far below saturation. We have found that in the first case the single-photon generation rate is fundamentally limited by the nonradiative relaxation rate in the excitation channel. On the contrary, the latter scenario is seen as a simple and promising approach which can ensure a repetition rate of single-photon emission of the order of 100 THz.

To realize the full potential of a MNP as a single-photon source, it should be coupled to a high-$Q$ resonant cavity which can enhance the spontaneous emission, channel the emitted photons, and narrow the spectral range of emission [1]. This can be implemented, for example, in a photonic nanowire which has been demonstrated to be a highly efficient platform for a single-photon source [58]. A superemitter coupled to a cavity represents a hybrid photonic system with a rich spectrum of the local density of optical states which can be engineered in a wide range [59].

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