17th International Congress on Artificial Materials for Novel Wave Phenomena - Metamaterials 2023
Crete, Greece, Sep. 11$^{\text{th}}$ - 16$^{\text{th}}$ 2023

Photonic Modelling of Two-Photon Purcell Effect Near Plasmonic Nanostructures

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***Abstract* – We present a novel photonic model that enables an efficient computation of the two-photon Purcell effect of a quantum emitter in the vicinity of an arbitrary photonic structure. Our framework is relevant for the plasmonic nanocavities used to enhance higher-order light-matter interactions, as it goes beyond the dipolar approximation. The computation of Purcell factors through classical electromagnetic simulations determines the influence of the environment without tedious analytic calculations. We demonstrate that placing a hydrogen-like emitter close to a silver nanodisk enhances the transition rate by 5 and 11 orders of magnitude via electric dipole and quadrupole two-photon transitions, respectively. This process has exciting implications for future research, including the potential for efficient entangled two-photon sources.**

I. Introduction

Spontaneous emission is a fundamental process in the field of light-matter interaction in which an excited quantum emitter, such as an atom, molecule, or quantum dot, releases a specific amount of energy in the form of a single quantum or multiple quanta, and transitions to a lower energy state [1]. Nowadays, it is well known that the emission rate of an emitter is influenced by its environment, known as the Purcell effect [2]. To study this phenomenon, the electric dipole approximation is commonly used. However, current devices aimed at enhancing light-matter interactions [3], such as photonic crystals [4] and plasmonic nanocavities [5], exhibit a significant spatial variation of the light fields, which causes the breakdown of the electric dipole selection rule [6]. As a result, previously inaccessible transitions such as multipolar and multiquanta emission processes become possible [7].

In this work we focus on the two-photon spontaneous emission (TPSE) process, which is typically eight to ten orders of magnitude slower than the competing single-photon spontaneous emission [7]. Unfortunately, the current study of TPSE near arbitrary objects is hampered by the absence of efficient theoretical and numerical methods. An expression for the TPSE transition rate of a quantum emitter as a function of the one-photon Purcell factors under the electric dipole approximation was previously derived for symmetric structures [8]. Our work presents a more general and efficient framework for calculating the TPSE rate of a quantum emitter close to an arbitrary structure and beyond the dipolar approximation, i.e., by also taking into account the magnetic dipole and the electric quadrupole contribution to the TPSE rate. This field holds significant promise for numerous applications [9], including efficient entangled two-photon sources for quantum applications, new platforms in spectroscopy, and broadband absorbers and emitters.

II. Framework: connection between TPSE rates and Purcell factors

We consider a system composed of a quantum emitter in close proximity to a photonic environment. Using a perturbative approach, the probability per unit time that the system carries out a second-order transition by emitting two quanta from an initial state to a final state is given by Fermi's golden rule. Moreover, the interaction Hamiltonian is studied up to the electric quadrupolar order, since the dipolar approximation is no longer valid near plasmonic nanostructures [6].

To establish the connection between TPSE rates and Purcell factors, the steps are as follows: normalize the rates derived from Fermi's Golden rule by these related to vacuum, rewrite them as a function of the dyadic Green's function, and make the link between the components of the Green's function and the Purcell factors [**?**].

In this way we derive the two-electric dipole (2ED) contribution to the TPSE rate [**?**]:

$$\frac{\gamma^{(2)}_{\text{2ED}}(\omega;\mathbf{R})}{\gamma^{(2)}_{\text{2ED,0}}(\omega)} = \hat{\mathcal{D}}^{eg}_{ia}(\omega,\omega_{eg}-\omega)\left(\hat{\mathcal{D}}^{eg}_{jb}(\omega,\omega_{eg}-\omega)\right)^{*} F^{ED}_{ij}(\omega;\mathbf{R})\, F^{ED}_{ab}(\omega_{eg}-\omega;\mathbf{R}) \tag{1}$$

where $\gamma^{(2)}_{\text{2ED,0}}$ denotes the 2ED transition rate in vacuum and $\hat{\boldsymbol{\mathcal{D}}}^{eg}$ stands for the normalized second-order electric dipole transition moment between the excited state $|e\rangle$ and the ground state $|g\rangle$ of the emitter. Note that the tensor $\hat{\boldsymbol{\mathcal{D}}}^{eg}$ involves a summation over all possible and virtual intermediate states of the system. In this equation ω and ω_{eg} are the frequencies of the two emitted quanta with $\hbar\omega_{eg}$ the transition energy, $\mathbf{R}$ is the emitter's position taken at the center of its charge distribution, and the components of the tensor $\mathbf{F}^{\text{ED}}$ are defined as a function of the one-photon Purcell factors:

$$F^{\text{ED}}_{ii}(\omega;\mathbf{R}) := \frac{6\pi c}{\omega}\text{Im}G_{ii}(\omega;\mathbf{R},\mathbf{R}) = P^{\text{ED}}_{i}(\omega;\mathbf{R}), \tag{2}$$

$$F^{\text{ED}}_{ij}(\omega;\mathbf{R}) := \frac{6\pi c}{\omega}\text{Im}G_{ij}(\omega;\mathbf{R},\mathbf{R}) = P^{\text{ED}}_{ij}(\omega;\mathbf{R}) - \frac{1}{2}\left(P^{\text{ED}}_{i}(\omega;\mathbf{R}) + P^{\text{ED}}_{j}(\omega;\mathbf{R})\right) \tag{3}$$

with $i,j = 1,2,3$ and $i \neq j$ and where $\text{Im}\mathbf{G}$ is the imaginary part of the Green's function.

Concerning the Purcell factors $\mathbf{P}^{\text{ED}}_{i}$ and $\mathbf{P}^{\text{ED}}_{ij}$, they correspond, respectively, to the ratio between the ED transition rate of an emitter that has its transition electric dipole moment aligned along one of the basis vectors (i.e., $\hat{\mathbf{d}}^{eg} := \hat{\mathbf{e}}_i$ with $i = 1,2,3$) and along the bisector of two basis vectors (i.e., $\hat{\mathbf{d}}^{eg} := (\hat{\mathbf{e}}_i + \hat{\mathbf{e}}_j)/\sqrt{2}$ with $i,j = 1,2,3$ and $i \neq j$) with the corresponding rate in vacuum. Note that in the most general case, six Purcell factors need to be calculated by considering six different orientations of the electric dipole moment. For example, in a cartesian basis we need to calculate these six factors: $\left\{P^{\text{ED}}_{x}, P^{\text{ED}}_{y}, P^{\text{ED}}_{z}, P^{\text{ED}}_{yz}, P^{\text{ED}}_{xz}, P^{\text{ED}}_{xy}\right\}$.

Similarly, the same relation can be derived for the two-magnetic dipole (2MD) and the two-electric quadrupole (2EQ) contributions. Note that for the quadrupolar one there are, in the most general case, fifteen Purcell factors to calculate, which correspond to different orientations of the electric quadrupole moment.

It is important to remark that, first, the derived equations are valid regardless of the emitter environment, not only for symmetric structures. Second, the contribution of the emitter and of the photonic environment is decoupled in the equations, and thus can be calculated separately. Third, the Purcell factors can be computed classically by the ratio of the power emitted by a classical emitter [2], and thus by modelling point sources in classical electromagnetic simulations. Fourth, the contribution of the radiative and the non-radiative emission channels can be computed through the decomposition of Purcell factors into radiative and non-radiative parts [2]. Fifth, to obtain a full TPSE spectrum, the Purcell factors need to be calculated over a range of frequencies and for different source orientations. However, the number of Purcell factors to calculate can be reduced depending on the symmetry of the photonic environment.

III. Application

As an application of the developed framework, we study the two-photon Purcell effect for an $s \rightarrow s$ transition of a hydrogen atom placed under a plasmonic silver nanodisk. As our framework is more general, we can calculate the 2EQ contribution and we can study this effect for any position of the emitter (not only on the axis of symmetry of the disk), which was not possible in a previous study [10]. The multipolar second-order transition moments are calculated analytically via the emitter's wavefunctions while Purcell factors are computed with COMSOL Multiphysics® [11]. Fig. 1 shows TPSE spectra. At $\omega = \omega_{eg}/2$, the photon-pair emission rate drawn in blue dots is enhanced by, respectively, 5 and 11 orders of magnitude for the 2ED and 2EQ transitions. When the emitter is shifted in the direction parallel to the disk, additional modes are excited leading to additional peaks.

IV. Conclusion

In this work we present a photonic model for efficiently calculating the two-photon Purcell effect of a quantum emitter in the vicinity of an arbitrary shaped nanostructure. Our approach is based on an analytical calculation of the emitter contribution but especially on a classical computation of the one-photon Purcell factors for the environment contribution. We employ classical point emitters in electromagnetic simulations to calculate these

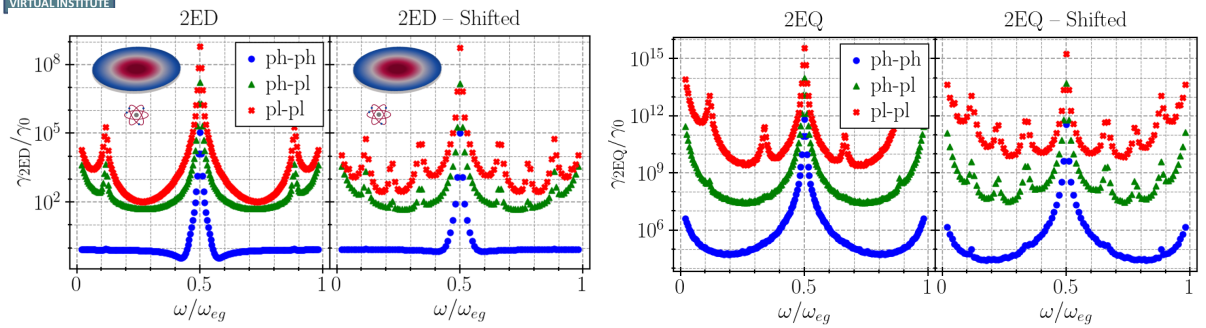

Fig. 1: Photon-photon (ph-ph), photon-plasmon (ph-pl), and plasmon-plasmon (pl-pl) emission channels of the TPSE rate for the 2ED and the 2EQ transitions. The emitter is placed 10 nm under a D=25 nm diameter and 5.2 Å thickness silver disk, and its transition frequency is $\hbar\omega_{eg}$ = 2.64 eV. The emitter is either on the axis of symmetry of the disk or shifted by D/4 in the direction parallel to the disk.

factors, which allows us to study complex geometries that lack analytical models. Importantly, our framework goes beyond the dipolar approximation by accounting for second-order multipolar interactions, making it relevant for plasmonic nanostructures with highly confined light. Additionally, our framework enables the separate calculation of radiative and non-radiative emission channels, which is essential to distinguish for many applications.

As a proof-of-concept, we demonstrate the potential of our framework by using the COMSOL Multiphysics® software to show significant enhancement in the electric dipole and quadrupole two-photon transitions of respectively 5 and 11 orders of magnitude for an $s \rightarrow s$ transition of a hydrogen-like emitter placed under a plasmonic silver nanodisk. This result illustrates the potential of our framework to optimize the design of nanostructures, for example, to harness a particular multipolar emission channel of the TPSE process. Finally, our method is applicable to a wide range of quantum emitters and can be extended to include interference between the multipolar emission channels of the TPSE process [6].

Acknowledgements

We acknowledge support from the FRS-FNRS (Research project T.0166.20) and from Action de Recherche Concertée (project ARC-21/25 UMONS2).

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