QUANTUM OPTICS WITH SINGLE-PHOTON NANOANTENNA

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ABSTRACT

QUANTUM OPTICS WITH SINGLE-PHOTON NANOANTENNA

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Single-photon sources (SPSs) are at the core of quantum technologies with their purely non-classical light emission. In this connection; quantum dots, diamond N-V centers, trapped-ions are some of important SPSs. Besides all these, practicality on-chip applications of two-dimensional materials, room temperature operation, high brightness and photostability make hexagonal Boron Nitride (hBN) defects hot topic for research. In this work, I studied hBN color centers together with plasmonic nanoantennae in order to enhance the performance of single photon emission. First, computationally I investigate quality factors, absorption and scattering properties of plasmonic nanoantennae and their light focusing features into ultra small volumes. Fabrication of nanoantennae are realized by size and shape optimization in the direction of computations. Thereafter, hBN defect centers are hunted using μ photoluminescence spectroscopy. Power-resolved and angle-resolved measurements are performed to characterize a specific defect center. Photon statistics of hunted color centers are made via single-photon detectors in a Hanbury-Brown-Twiss interferometer. Second-order correlation measurements show that our defect centers exhibit antibunched photon emission. In the coupling phase, Emission characteristics of a single

defect center is modified using plasmonic nanoantennae. By dewetting thin films on hBN multilayers, plasmonic nanoantennae are obtained in a controllable way with no harm on the defect. A very same defect is investigated with and without nanoantenna in order to demonstrate clearly the modification of its emission. Based on the film thickness in dewetting process, on-demand enhancement and quenching effects are observed. For a true deterministic coupling, a further electromagnetic simulation is employed in the light of experiments. Fluorescence lifetime, radiative and nonradiative emission rate calculations are used for estimating the spatial configuration of the defect-nanoantenna system as well as confirming the experimental findings. The approach provides a very cheap and easy coupling opportunity as an alternative to the scanning probe technique.

Keywords: Quantum Emitters, Plasmonic Nanoantennas, Single-Photon Sources, hBN defects, Colour Centers, Purcell Effect.

TEK-FOTON NANOANTEN İLE KUANTUM OPTİK

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Kuantum ışık kaynakları, kuantum teknolojilerinin odak noktasıdır. Tek-foton kaynakları (SPS) tamamıyla klasik olmayan ışıma özellikleriyle mükemmel bileşenlerdir. Bu bağlamda; quantum noktalar, elmas kusurları, tuzaklanmış atomlar önemli birer SPS kaynağıdır. Tüm bunların yanında, iki-boyutlu malzemelerin çip uygulamalarında kullanışlı olması, oda sıcaklığında çalışabilmesi, yüksek parlaklık ve fotokararlılık özellikleri hexagonal Boron Nitride (hBN) kusur noktalarını araştırma için moda bir konu haline getiriyor. Bu çalışmada, tek foton ışınım performansını artırmak amacıyla, hBN ışıma noktaları ve gümüş nanoantenleri ile çalıştım. Evvela hesaplamalı olarak, nanokavitelerin kalite faktörlerini ve kırınım limiltlerinin ötesinde ışığı çok küçük hacimlere odaklama özelliklerini inceledim. Hesaplar doğrultusunda, nanoanten üretimi boyut ve şekil optimizasyonu ile gerçekleştirildi. Akabinde, hBN kusur noktaları mikro-fotoışınım düzeneği ile avlandı. Güç ve açıya bağımlı ölçümler, belirli bir kusuru karakterize etmek amacıyla yapıldı. Avlanan kusur noktasının foton istatistiği tek-foton detektörler vasıtasıyla yapıldı. Atomik yapıların yaşamömrü 1-15 nanosaniye civarında gözlendi. İkinci-derece korelasyon ölçümleri, kusur noktalarının birer tek foton kaynağı olduğunu gösterdi. Eşleştirme safhasında, çeşitli kusur noktaları tanımlandı. Tam olarak aynı kusur noktaları, üzerlerine nanoanten fabrikasyonunun ardından yeniden avlandı ve ölçüldü. Yarı-belirleyici bir şekilde, nanoantenlerin parlaklığı iki farklı şekilde değiştirdiğini gösterdim. Bazı boyutlarda nanoantenler ışınımsızlığı baskın olan bir etki altında kalırken, göreli olarak daha büyük nanoantenler, ışıma miktarını artırıyor. Uyarılmış yaşam süresi ise iki farklı durum için de kısalıyor. Son olarak, bu iki durum için hesaplanmış kuantum verimlilik ve Purcell faktörü değerleri, deneysel bulguları teyit ediyor.

Anahtar Kelimeler: Kuantum Işıyıcılar, Plazmonik Nanoantenler, Tek-Foton Kaynakları, hBN Kusurları, Işıma Merkezleri, Purcell Etkisi. Dedicated to my family...

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LIST OF ABBREVIATIONS

MNP	Metal Nano Particle
SPS	Single Photon Source
HBT	Hanbury-Brown-Twiss Interferometer
FEM	Finite Element Method
μPL	Micro-Photoluminescence
SEM	Scanning Electron Microscopy
AgNI	Silver Nano Island
AgNP	Silver Nano Particle
AgNW	Silver Nano Wire
SD	Spontaneous Decay
Pc	Plasmon Cavity
cQED	Cavity Quantum Electrodynamics
PcQED	Plasmon Cavity Quantum Electrodynamics
hBN	Hexagonal Boron Nitride
QE	Quantum Emitter
FDTD	Finite Difference Time Domain
IRF	Instrument Response Function
ZPL	Zero Phonon Line
PSB	Phonon Side Band
CW	Continuous Wavelength
LDOS	Local Density of States

CHAPTER 1

INTRODUCTION

1.1 Concise introduction

In this thesis, defect centers embedded in hexagonal Boron Nitride (hBN) are studied. Their emission properties are modified using plasmonic nanoantennae. Computational investigations are performed in order to characterize nanocavity parameters. In the quantum emitter part, hBN defect emission characteristics are studied experimentally and it is demonstrated to have bright and stable quantum emitter features. For the coupling part, first, hBN flakes spread over a vast area are surveyed and spotted emissive defect centers were spatially marked and characterized using angle-, power-, time-resolved photoluminescence spectroscopy and HBT interferometer. After fabricating nanoantennas on hBN multilayers, defect centers are re-found and measurements are repeated. As a result, depending on size of the nanoantennae, quenching and enhancement of photon emission effects are observed. It is also shown that sub-Poissonian photon statistics of a defect is not affected by a plasmon cavity. Finally, the experimental findings are confirmed via simulation results.

1.2 General introduction

Quantum information is the ultimate solution to the secure communication. Singlephoton sources are building blocks to realize this with no-cloning theorem [5]. Solidstate based single photon emitters are good candidates with their high stability [6]. Diamond color centers and quantum dots are some examples that have been studied many years. The defect centers in 3D crystals cause technical challenges during

applications. Location of defect centers in 3D materials is one of them. Coupling with a waveguide or a cavity is the main difficulty of 3D structures. Furhermore, total internal reflection is one another technical problem. On the other side, quantum dots appear with their low temperature operation requirements. In this context, hexagonal Boron Nitride defect center is an unprecedented solution for single-photon emitter demand. It is embedded in a 2D lattice and defect centers are ready to coupling with either a cavity or a waveguide. Also, room temperature operation is one of the most crucial factor. Defect centers in hBN exhibit a wide range of emission frequency due to large bandgap of host crystal. It is nearly 6 eV [7]. In this thesis, by exploiting easy-coupling property of hBN defects, silver nanoantennas are semideterministically coupled with hBN defect centers. Using computational techniques, light-matter interaction tendencies of silver nanoantennas are investigated. In the direction of these knowledges, silver nanoislands are fabricated. On the other hand, hBN defects are characterized using μ -PL and HBT interferometer. As a super tough business, one specific defect center is hunted two times for comparison purposes. Features of defect centers before and after metal nanoislands are studied. Through this method, enhancement and quenching tendencies are observed. Finite element method computations are performed in order to support experimental findings. As a result, the quenching dominant particle sizes exhibited quenching. Although excited state lifetime of the single quantum system is shortened slightly, the brightness of the single photon emission is reduced. However, for scattering dominant particle sizes, the hunted defect showed that the excited state lifetime is shortened voluminously and the photon emission rates are enhanced in a respectable amount.

1.3 Organization of the thesis

Structure of the thesis is a bit different than the most widely prefered ones. I here aim to focus on the efforts in a direct way. Detailed explanations of the theory and the computational parts were given in the complement chapters. Starting with chapter two, all works are regulated in the order of their realization sequences. For example, fabricating plasmon structures desires some properties like radius, length, wavelength or thickness etc. Determination of these parameters become a primary work with simulations. For this reason, computations were given at first. Then exploitation of the results were done in the fabrication part. That is to say, the work flow of the whole thesis was reflected into the script.

Arousing interest and to be understandable, the phases for each chapter are presented with explanatory figures. As it is seen, computational and experimental methods are used along the thesis.



Figure 1.1: Summary figures for chapter-2.

In the second chapter, plasmon nanoantennas are studied with full electromagnetic solutions. Helmholtz wave equation is (derived in Complement-1A) solved within a simulation domain. Scattered electromagnetic field responses are used to find nanoantenna characterization parameters such as scattering cross section or extinction efficiency. Size effect of plasmon nanoparticles are shown over different radius Agspheres. Using all these information, fabrication experiments are performed. With the aim of obtaining high local density of state but low quality factor nanoresonators, particles are fabricated with nearly 15 nm radius. Also, larger size particles around 60 nm radius are fabricated for the sake of high scattering efficiency. Scanning electron microscope studies showed that we have actually hemispheroid shape nanois-lands. Therefore, the simulations are further improved with shape effect study. Same nanoantenna parameters are calculated for those hemispheroids.

Third chapter presents at the begining that single quantum emitters' difference from other light sources with an essence manner. Emphasizing that molecular structures



Figure 1.2: Summary figures for chapter-3.

are a bit different than those single atom or bulk materials, vibrational states and Franck-Condon princple are used to introduce quantum emission from hBN defect centers. Thereafter, the efforts that have been made are presented. By directly reflecting what it is done during the experiment, the procedures are introduced. Photoluminescence measurements, with 1.5 micron spotsize, are used to hunt defect centers. Angle-resolved measurements showed that the hunted defects are dipole-like structures. Then, power-resolved measurements are performed. Power saturation curves are presented. At the end of the chapter, time-resolved measurements are done. Using a fast APD (avalanche photodiode) and a time tagging module, pulsed laser excitation of selected defect center is observed. The excited state lifetime of the defect is recorded. Antibunched photon emission is proved by HBT interferometer by using two single photon detector and a beam splitter. Pulsed second-order correlation measurements are performed. As it is expected, the emissions are non-classical which obey with sub-Poissonian photon statistics.

Finally, the fourth chapter combines the techniques and outcomes of chapter two and three. The coupling procedures and results are presented. For the beginning, computationally, inhomogeneous environment effect is studied on a point electric dipole which is placed in the vicinity of a silver nanoisland. The reliability of these calcu-



Figure 1.3: Summary figures for chapter-4.

lations are confirmed using the results of two different paper. Same conditions are regenerated on our simulation domain and the outputs are compared with the results presented in the papers. Since Purcell factor is a representation of spatial, spectral and polarization match of the quantum emitter and the cavity. The simulations are performed by spectral and spatial parametric sweeps at certain dipole orientation. The results showed that plasmon nanoantennas are good candidates as a nanocavity if appropriate coupling configurations are obtained. In this sense, experiments with 30 nm diameter radius particles coupled with defect centers are presented. Then, 120 nm diameter particles are used in the experiments. The coupling results are presented at the end of this section. Finally, for the measured defect centers at single frequency, normalized radiative and nonradiative decay rates are computed by considering experimental outputs. Quantum efficiency, quenching and Purcell factor graphs are given at last for confirmation and further interpretation.

1.4 History of the literature

Light is explained in many aspects in the past. However, Max Planck's black body radiation [8] is accepted as quantum physics' birthday. Einstein's A and B coefficients in order to explain light emission and absorption [9] caused the idea that emission and absorption properties only belonging to atom's itself. After the second quantization framework of quantum mechanics described by Dirac [10], the well-known description of light is presented.

Without no external stimulation, photon emission from an atom is named as spontaneous emission. The emission process is defined as a transition of excited electron to a lower energy level. However, spontaneous emission has been considered an intrinsic material property.

In 1946, E. M. Purcell proposed that spontaneous emission rates can be manipulated by changing their environment [11]. By this way, the local density of photonic states are modified. This effect is known as Purcell effect. Purcell discusses in his paper that an optical cavity can be used as manipulation tool. While the quality factor of the resonator is inversely proportional to the excited state lifetime of the atom, the mode volume -physical volume of the cavity- is directly proportional to the lifetime. It is possible to state that parameters enter the Purcell formula (λ , n, Q, V) are manipulation tools for enhancement and inhibition of emission from an atom.

As a consequence of the Purcell effect, Q/V ratio gained a special importance [12]. Here, Q quantifies how much energy stored and how this energy is dissipated. On the other side, mode volume is considered as physical volume for a specific mode. It is simply the integrated optical energy density normalized with its maximum value. This definition causes problems at different type of cavities (e.g. open cavities) [13, 14]

Serge Haroche and his research group in Paris, demonstrated for the first time the lifetime modification of Rydberg atoms. The resonator was a Fabry-Perot cavity. Two spherical Niobium mirrors are positioned with 25 mm separation between them [15, 16]. The quality factor they reached, was 7.5×10^5 . The problem here the mode volume is about 70 mm³ which is too high. That is why the emission was not at optical frequencies due to high V does not support this.

Fast growing technologies allowed to fabricate smaller size cavities and a sort of competition has started between experimental scientists working on the field. Micro cavities became a hot topic research with their high quality but low modal volumes [17].

The smaller photonic cavity competition has faced an obstacle since they have reached mode volume on the order of λ^3 [18]. At this level, the quality factor is faced with difficulties with scattering due to fabrication imperfections. The diffraction limit [19] put a boundary for the mode volume, V, because one can not focus light into a volume smaller than λ^3 .



Figure 1.4: Ernst Abbe's formula for the diffraction limit. A stone monument in Jena.

Surface plasmon polaritons come to the help of focusing light into subwavelength volume [20]. Plasmonic cavities at this stage have become a trend research focus in order to confine electromagnetic fields into nanoscale volumes. Physical cavities using plasmon properties are called as plasmon cavities [21] however, plasmon nanoantennas -metal nanoparticles with a special shape and size- are also refered sometimes as plasmon cavities. Basically, collective oscillation of electrons and photons at a specific frequency forms this phenomenon [22].



Figure 1.5: Demonstration of surface plasmon polaritons standing at the interface of a silver thin film and glass.

Strong light-matter interaction is within the possibilities of plasmon nanostructures due to high enery confinement rates [2]. However, these systems are highly dissipated and lossy. This makes them low quality resonators. Using the Purcell factor for plasmonic nanoantennas brings tough duties. Spectral, spatial and polarization matches are required. For a perfect coupling scenario; spectral match selects the highest possible quality factor for the plasmonic antenna while spatial match selects a point where the highest optical energy is available. In other words, spatial match for mode volume and spectral match for the quality factor.

1.5 Motivation

Almost all of the scientific journals and thesis claim that quantum information technology and its demands are the motivation behind the single photon sources. Any work in the literature states as an introductory argument that present or future technologies. However, for me, the motivation behind this work is completely different than those introductory arguments.

When Albert Einstein discussed the photon absorption and emission phenomenon in his letter in 1917 [9], quantum physics was a baby and it was considered as an advanced mathematical exercise. Since there were no application for quantum physics in those days, physicists were not able to find support and excluded from societies. The potential was underestimated and many physicists were suffered from impatient people who fond of technology applications of science.

The paper of Einstein presents a discussion about light emission and absorption using thermodynamics. Only atom's itself is quantized and electromagnetic field is a classical continuous wave. Paul Dirac presents the second quantization formalism which quantizes electromagnetic field as well. Light emission and absorption are considered with only atom's perspective. It was considered that the emission is only about atom's internal property. In 1946, Purcell stated in his short paper that environment can alter the emission property of an atom. Serge Haroche showed this phenomenon experimentally [15]. Last two sentences include two Nobel Physics Prize. Addition to that, many physicists for decades struggling with high quality resonators or smaller cavities. Some efforts have been made about emission inhibition. As a summary, all these efforts are about manipulation of an atom and observing the interesting dynam-

ics in the nature. This is the motivation. Physics is the motivation. Understanding one small piece of knowledge and opportunity of practicing those knowledges are quite exciting.

COMPLEMENT 1A

Surface waves

$$\rho_{tot} = \rho_{ext} + \rho_{int}$$
 $\mathbf{J}_{tot} = \mathbf{J}_{ext} + \mathbf{J}_{int}$

The external charge and current densities drive the system while the internal ones respond to the external stimuli. Starting with the macroscopic Maxwell's equations ;

$$\nabla \times \mathbf{H} = \mathbf{J}_{ext} + \frac{\partial \mathbf{D}}{\partial t}, \qquad \text{AMPÉRE-MAXWELL LAW} \quad (1.1)$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J}_{ext} + \mu_0 \frac{\partial \mathbf{D}}{\partial t} \qquad (\text{where} \quad \mathbf{H} = \frac{1}{\mu_0} \mathbf{B})$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \qquad \text{FARADAY'S LAW} \quad (1.2)$$

$$\nabla \times \nabla \times \mathbf{E} = -\frac{\partial (\nabla \times \mathbf{B})}{\partial t}$$

$$\nabla \times \nabla \times \mathbf{E} = -\frac{\partial}{\partial t} (\mu_0 \mathbf{J}_{ext} + \mu_0 \frac{\partial \mathbf{D}}{\partial t})$$

$$\nabla \times \nabla \times \mathbf{E} = -\frac{\partial}{\partial t} (\mu_0 \frac{\partial \mathbf{D}}{\partial t}) \qquad (\text{in the absence of } \mathbf{J}_{ext})$$

$$\nabla \times \nabla \times \mathbf{E} = -\mu_0 \frac{\partial^2 \mathbf{D}}{\partial^2 t}$$

$$\nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\mu_0 \frac{\partial^2 \mathbf{D}}{\partial^2 t}$$

$$\nabla \cdot \mathbf{D} = \rho_{ext}$$
$$\nabla \cdot (\epsilon \mathbf{E}) = \rho_{ext}$$
$$(\nabla \epsilon) \mathbf{E} - \epsilon (\nabla \cdot \mathbf{E}) = 0$$
$$-\epsilon (\nabla \cdot \mathbf{E}) = (\nabla \epsilon) \mathbf{E}$$
$$(\nabla \cdot \mathbf{E}) = -\frac{\mathbf{E}}{\epsilon} (\nabla \epsilon)$$

(*in the absence of external stimuli*)

GAUSS'S LAW (1.3)

IMPORTANT NOTE: $\nabla \epsilon$ term can be neglible for the distances around one optical

wavelength or less!

$$(\nabla \cdot \mathbf{E}) = -\frac{\mathbf{E}}{\epsilon}(\nabla \epsilon) = 0$$

$$\nabla (\nabla - \mathbf{E})^{\bullet} = -\mu_0 \frac{\partial^2}{\partial^2 t} \mathbf{D}$$

$$\nabla^2 \mathbf{E} = \mu_0 \frac{\partial^2}{\partial^2 t} \mathbf{D}$$

$$\nabla^2 \mathbf{E} = \mu_0 \epsilon_0 \epsilon \frac{\partial^2}{\partial^2 t} \mathbf{E}$$

$$\nabla^2 \mathbf{E} = \frac{\epsilon}{c^2} \frac{\partial^2}{\partial^2 t} \mathbf{E}$$

$$\nabla^2 \mathbf{E} = \frac{\epsilon}{c^2} \frac{\partial^2}{\partial^2 t} \mathbf{E}$$
(Wave equation) (1.4)

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}(\mathbf{r})e^{-i\omega t} \qquad (ANSATZ) \qquad (1.5)$$
$$\frac{\partial \mathbf{E}(\mathbf{r},t)}{\partial t} = \mathbf{E}(\mathbf{r})\frac{\partial}{\partial t}(e^{-i\omega t}) = (-i\omega)\mathbf{E}(\mathbf{r})e^{-i\omega t}$$

$$\frac{\partial \mathbf{E}(\mathbf{r},t)}{\partial t} = (-i\omega)\mathbf{E}(\mathbf{r},t) \qquad \qquad \therefore \frac{\partial}{\partial t} \to (-i\omega)$$

$$\frac{\partial^2 \mathbf{E}(\mathbf{r},t)}{\partial t^2} = (-\omega^2)\mathbf{E}(\mathbf{r},t) \qquad \qquad \therefore \frac{\partial^2}{\partial t^2} \to (-\omega^2) \qquad (1.6)$$

$$\nabla^2 \mathbf{E} - \frac{\epsilon}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{E} = 0 \qquad (continue with the wave equation (1.4))$$

$$\nabla^{2}\mathbf{E} - \frac{(-\omega^{2})}{c^{2}}\epsilon\mathbf{E} = 0 \qquad (substitution \to k_{0} = \frac{\omega}{c})$$
$$\nabla^{2}\mathbf{E} + k_{0}^{2}\epsilon\mathbf{E} = 0 \qquad \text{HELMHOLTZ EQUATION} \quad \blacksquare \quad (1.7)$$

The Helmholtz equation is necessery to find electic and magnetic fields. However, waves propagate on a geometry and they have a propagation direction. For a one-dimensional symbolic geometry;

$$\begin{split} \mathbf{E}(x,y,z) &= \mathbf{E}(z)e^{i\beta x} & \beta \Rightarrow \beta_x \to k \text{ propagation constant} \\ \nabla^2 \mathbf{E} &= \nabla^2(\mathbf{E}(z)e^{i\beta x}) & \nabla^2 \to (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) \\ \nabla^2 \mathbf{E} &= \mathbf{E}(z)(-\beta^2)e^{i\beta x} + e^{i\beta x}\frac{\partial^2 \mathbf{E}(z)}{\partial z^2} \\ \nabla^2 \mathbf{E} &= (-\beta^2)\mathbf{E} + \frac{\partial^2 \mathbf{E}}{\partial z^2} \end{split}$$

$$\nabla^{2}\mathbf{E} + k_{0}^{2}\epsilon\mathbf{E} = 0 \qquad \text{HELMHOLTZ EQUATION}$$
$$(-\beta^{2})\mathbf{E} + \frac{\partial^{2}\mathbf{E}}{\partial z^{2}} + k_{0}^{2}\epsilon\mathbf{E} = 0$$
$$\boxed{\frac{\partial^{2}\mathbf{E}}{\partial z^{2}} + (k_{0}^{2}\epsilon - \beta^{2})\mathbf{E} = 0}$$
(1.8)



Figure 1.6: The geometry on which Helmholtz equations are solved

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \times \mathbf{H} = \mathbf{J}_{ext} + \frac{\partial \mathbf{D}}{\partial t}$$
$$\frac{\partial E_z}{\partial y} - \frac{\partial E_y}{\partial z} = i\omega\mu_0 H_x \qquad \qquad \frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} = -i\omega\epsilon_0\epsilon E_x$$
$$\frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = i\omega\mu_0 H_y \qquad \qquad \frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} = -i\omega\epsilon_0\epsilon E_y$$
$$\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = i\omega\mu_0 H_z \qquad \qquad \frac{\partial H_y}{\partial x} - \frac{\partial H_z}{\partial y} = -i\omega\epsilon_0\epsilon E_z$$

The propagation is in x-direction $\Rightarrow \frac{\partial}{\partial x} = i\beta \Rightarrow \frac{\partial}{\partial y} = 0$

$$\begin{aligned} -\frac{\partial E_y}{\partial z} &= i\omega\mu_0 H_x & -\frac{\partial H_y}{\partial z} &= -i\omega\epsilon_0\epsilon E_x \\ \frac{\partial E_x}{\partial z} &- i\beta E_z &= i\omega\mu_0 H_y & \frac{\partial H_x}{\partial z} &- i\beta H_z &= -i\omega\epsilon_0\epsilon E_y \\ i\beta E_y &= i\omega\mu_0 H_z & i\beta H_y &= -i\omega\epsilon_0\epsilon E_z \end{aligned}$$

Equation sets of (2.9) and (2.10) are TM (p) and TE (s) modes, respectively.

$$E_{x} = -i\frac{1}{\omega\epsilon_{0}\epsilon}\frac{\partial H_{y}}{\partial z}$$

$$E_{z} = -\frac{\beta}{\omega\epsilon_{0}\epsilon}H_{y} \begin{cases} \frac{\partial E_{x}}{\partial z} - i\beta E_{z} = i\omega\mu_{0}H_{y} \end{cases} \frac{\partial^{2}H_{y}}{\partial z^{2}} + (k_{0}^{2}\epsilon - \beta^{2})H_{y} = 0$$
(1.9)

$$H_{x} = i \frac{1}{\omega \mu_{0}} \frac{\partial E_{y}}{\partial z} \\ H_{z} = \frac{\beta}{\omega \mu_{0}} E_{y} \right\} \frac{\partial H_{x}}{\partial z} - i\beta H_{z} = -i\omega\epsilon_{0}\epsilon E_{y} \bigg\} \frac{\partial^{2} E_{y}}{\partial z^{2}} + (k_{0}^{2}\epsilon - \beta^{2})E_{y} = 0$$

$$(1.10)$$

The solution of (1.9) TM waves;

$$\begin{aligned} H_{y}(z) &= A_{2}e^{i\beta x}e^{-k_{2}z} \\ E_{x}(z) &= iA_{2}\frac{k_{2}}{\omega\epsilon_{0}\epsilon_{c}}e^{i\beta x}e^{-k_{2}z} \\ E_{z}(z) &= -A_{2}\frac{\beta}{\omega\epsilon_{0}\epsilon_{c}}e^{i\beta x}e^{-k_{2}z} \end{aligned} \right\} z > 0 \quad (in \ the \ dielectric, \epsilon_{d}) \\ H_{y}(z) &= A_{1}e^{i\beta x}e^{k_{1}z} \\ E_{x}(z) &= -iA_{1}\frac{k_{1}}{\omega\epsilon_{0}\epsilon_{d}}e^{i\beta x}e^{k_{1}z} \\ E_{z}(z) &= -A_{1}\frac{\beta}{\omega\epsilon_{0}\epsilon_{d}}e^{i\beta x}e^{k_{1}z} \end{aligned} \right\} z < 0 \quad (in \ the \ conductor, \epsilon_{c}) \\ E_{z}(z) &= -A_{1}\frac{\beta}{\omega\epsilon_{0}\epsilon_{d}}e^{i\beta x}e^{k_{1}z} \end{aligned}$$

The solution of (2.10) TE waves;

$$E_{y}(z) = A_{2}e^{i\beta x}e^{-k_{2}z}$$

$$H_{x}(z) = -iA_{2}\frac{k_{2}}{\omega\mu_{0}}e^{i\beta x}e^{-k_{2}z}$$

$$H_{z}(z) = A_{2}\frac{\beta}{\omega\mu_{0}}e^{i\beta x}e^{-k_{2}z}$$

$$E_{y}(z) = A_{1}e^{i\beta x}e^{k_{1}z}$$

$$H_{x}(z) = iA_{1}\frac{k_{2}}{\omega\mu_{0}}e^{i\beta x}e^{k_{1}z}$$

$$H_{z}(z) = -A_{1}\frac{\beta}{\omega\mu_{0}}e^{i\beta x}e^{k_{1}z}$$

$$\left. z < 0 \quad (in the conductor, \epsilon_{c}) \right.$$

$$k_i \Rightarrow k_{z,i} \perp xy$$
-plane, $\hat{z} = \frac{1}{|k_z|},$ (1.11)

 $\hat{z} \stackrel{\text{\tiny def}}{=}$ the evanescent decay length of the fields,

The reciprocal value of k_z quantifies confinement of the wave.
At the interface (z = 0) for TM ¹,

$$H_{y}(z) = A_{2}e^{i\beta x}e^{-k_{2}z}\big|_{z=0}, \qquad H_{y}(z) = A_{1}e^{i\beta x}e^{k_{1}z}\big|_{z=0}$$
$$A_{2}e^{i\beta x}e^{-k_{2}z}\big|_{z=0} = A_{1}e^{i\beta x}e^{k_{1}z}\big|_{z=0}$$
$$A_{2}e^{-k_{2}z}\big|_{z=0} = A_{1}e^{k_{1}z}\big|_{z=0}$$
$$A_{1} = A_{2}$$

$$E_z(z) = -A_2 \frac{\beta}{\omega \epsilon_0 \epsilon_c} e^{i\beta x} e^{-k_2 z} \Big|_{z=+\delta}, \qquad E_z(z) = -A_1 \frac{\beta}{\omega \epsilon_0 \epsilon_d} e^{i\beta x} e^{k_1 z} \Big|_{z=-\delta}$$

$$\mathcal{A}_{2} \frac{\beta}{\omega\epsilon_{0}\epsilon_{c}} e^{i\beta x} e^{-k_{2}z} \Big|_{z=+\delta} = \mathcal{A}_{1} \frac{\beta}{\omega\epsilon_{0}\epsilon_{d}} e^{i\beta x} e^{k_{1}z} \Big|_{z=-\delta}$$

$$\frac{1}{\epsilon_{c}} e^{-k_{2}z} \Big|_{z=+\delta} = \frac{1}{\epsilon_{d}} e^{k_{1}z} \Big|_{z=-\delta}$$

$$e^{-k_{2}z\epsilon_{d}} \Big|_{z=+\delta} = e^{k_{1}z\epsilon_{c}} \Big|_{z=-\delta}$$

$$-k_{2}z\epsilon_{d} \Big|_{z=+\delta} = k_{1}z\epsilon_{c} \Big|_{z=-\delta}$$

$$\lim_{\delta \to 0} (-k_{2})z\epsilon_{d} \Big|_{z=+\delta} = \lim_{\delta \to 0} k_{1}z\epsilon_{c} \Big|_{z=-\delta}$$

$$-k_{2}\epsilon_{d} = k_{1}\epsilon_{c}$$

$$\frac{k_{1}}{k_{2}} = -\frac{\epsilon_{d}}{\epsilon_{c}}$$
(1.12)

 $\exists \text{ Surface Waves } \iff [Re(\epsilon_d) > 0 \land Re(\epsilon_c) < 0] \lor \\ [Re(\epsilon_d) < 0 \land Re(\epsilon_c) > 0]$

$$\begin{cases} k_1^2 = \beta^2 - k_0^2 \epsilon_d \\ k_2^2 = \beta^2 - k_0^2 \epsilon_c \end{cases} \iff equation (1.9)$$
 (1.13)

(1.12) and (1.13) gives the *dispersion relation*;

$$\beta = k_0 \sqrt{\frac{\epsilon_d \epsilon_c}{\epsilon_d + \epsilon_c}}$$

¹ Surface waves exist for only TM modes \therefore continuity of TE modes gives $A_1 = A_2 = 0 \implies$ no wave

CHAPTER 2

PLASMONIC NANO-CAVITIES

A plasmonic system can be labeled in many different ways based on the physical approach. It may be considered as a single particle (quasiparticle), localized fields, an electron sea, a collective harmonic oscillator, an antenna or a cavity. Basically, it is a small metal particle with a characteristic size and shape which absorbs and scatters incoming fields. For the field of interest, prevalently considered terms are nanoantenna and nanocavity. Despite the fact that both terms refer to the same object, physical meanings of them are quite different. The former term is used because the particle conveys the far-field electromagnetic energy to the near-field and the other way around. That is why it is called as an antenna. The latter term is used because similar to a Fabry-Pérot cavity, integer number of electromagnetic modes occur as a standing wave at the interface of the MNP and the dielectric surrounding of the particle (see Complement 2A).

In this chapter, fabrication of nanostructures and their full-electromagnetic solutions are investigated. To do that, first, spherical metal nanoparticles embedded in air are studied. Aim of this section is to illustrate that the model gives results compatible with the results in literature. And then, the fabrication of particles and their size distributions are given. At the last section, the actual simulation model is built with a progressive manner. All the shape, size and substrate effects are studied thoroughly.

2.1 Preliminary electromagnetic simulations

Fabrication of plasmonic nanostructures require certain foreknowledge about size, shape, field enhancement and electromagnetic cross sections. Actually, all these items

are correlated to each other. In terms of the geometry optimization and parameter estimation, preliminary simulations are timesaver and obligatory tools. Since the subject is resonator, \mathbb{Q} -factor is crucial for measuring the resonance quality. To do that, some concepts about electromagnetic field interactions with small particles are critical (see Complement 2B).

The second parameter, mode volume (V) is a perplexing one. It is a vital factor that is mainly responsible for light-matter interaction in cavity quantum electrodynamics (cQED). However, the mode volume is not a physical volume for our context and its calculation requires a source. Electric and magnetic field distributions radiated by the source show up in the mode volume expression. Moreover, dielectric function, $\epsilon(\mathbf{r}, \omega)$, differs from the ones used for microcavities because plasmonic cavities are quite dissipative systems. As the mode volume has particular importance for plasmonic cavity quantum electrodynamics (PcQED), it will be scrutinized in next chapters, thoroughly.

To build a proper model, first of all, an incoming plane wave is traversed Method through an air domain (figure 2.1) surrounded by perfectly match layers (PML). Then, a single silver nano-sphere is planted into the air domain. The main objective of this subsection is to demonstrate the field (E, B) distributions. Later on, the substrate is introduced in the simulation domain. The energy attenuated in the incoming light (the extinction) and the energy localized near to the particle surface are investigated for different geometries. As a result, four picture types arise: Incoming fields, scattered fields, localized fields and total fields. The finite element method (FEM) is used within the COMSOL®MULTIPHYSICS. Wave Optics: Electromagnetic Waves, Frequency Domain study package is a proper tool in order to calculate Maxwell Equations in wavelength/frequency domain for single, dual and randomly distributed multiple metal nanostructures such as sphere, wire and spherelike particles. Optical response of air is defined as $\epsilon_0 = 1$. By the help of material library, optical responses of silver and silicon substrate are taken into account by the interpolation list that is defined experimentally for the complex dielectric function [23]. Reliability is compared by the literature values. General tendencies of electromagnetic cross sections, their efficiencies and \mathbb{Q} values that are found in published papers and other online numerical tools are appropriate indicators to check the reliability. After confirmation, whole model will be built inside this model just by replacing geometries, mesh sizes and desired output variables.

For the sake of completeness, it is appropriate to start with introducing simulation domain and incoming linearly polarized plane wave. The wave is propagating along the z-axis while the electric field, **E**, is polarized along the y-axis.



Figure 2.1: (a) A generic plane wave propagation, (b) through air and (c) Si-substrate

First of all, a 25 nm radius of silver (Johnson & Christy [23]) nanosphere is planted into the model. Then, by using double-parametric sweep study; sphere geometries for eight different radius, together with a hundred wavelengths ranging from 200 to 1100 nm, are calculated. All the effective cross sections and their efficiencies are derived inside the simulation environment using corresponding equations in Complement 2B. The Q-factor calculations are made by extracting resonance frequency, ω_r , and the full width half maximum, $\Delta \omega$, from the extinction efficiency, Q_{ext} , the spectra give the quality factor as

$$\mathbb{Q} = \frac{\omega_r}{\bigtriangleup \omega}$$

Furthermore, the E field enhancement [24], δ^e , and field localization parameter, \hat{z} , are measured by implementing point probes into the near field of the particle along the axis in polarization direction. The last but not least part is numerically extracting all field values and the corresponding 3-dimensional spatial coordinates with ultra high resolution. This valuable data set will be used in subsequent chapters for the calculation of Green's dyadic function and the local density of photonic state, LDOS.

Results and Discussion For 25 nm radius silver particle results are used for reliability check at the beginning. The resonance wavelength of the particle is calculated as 364 nm. As it is seen in the figure (2.3), the quality factor is found as 24. The Drude model calculation for the same scenario in [25] including bound electron contributions show that the quality factor is 24 however it gives the value of 21 when it is using tabulated data (Johnson & Christy). Also, it is observed that the resonance frequency does not match exactly. Contrary to this, the Bohren & Huffman code[26] using Johnson & Christy parameters confirms our model so that the resonance wavelength and the quality factor values are exactly same. One may want to check this code by him/herself can visit the following link which is available as an online widget (http://nordlander.rice.edu/miewidget). Moreover, the small shifts are observed for the same case of scattering on silver sphere in different approaches. The first obvious reason lies behind the method. Analytical methods and their numerical evaluations are clearly giving different spectral values than the calculations made with the 'full electrodynamics solution'.



Figure 2.2: Effective cross sections

Figure 2.3: Efficiency of EM interception

The differences in the model with smaller geometries or the miscalculated data can be originated from the degree of approximation. In order to test this, as a primitive example; same case given above was calculated one more time but with a coarser mesh size which defines the discretization of finite elements. Applying only fine mesh onto the particle, the scattering cross section values, for high energies, started to change and in some values close to the zero they became to have negative values. These miscalculation effect is faced when getting smaller diameter in higher frequencies. The actual simulations are made mostly with extra fine mesh and it is seen that the unexpected data is meliorated.

After that the effect of larger physical cross section on EM cross section was demonstrated in figure (2.4). As it was mentioned in [27], the spectral shift, towards to the infrared, has occured.





Figure 2.4: Scattering cross section for different sizes

Figure 2.5: Extinction cross section for different sizes



Figure 2.6: Scattering Efficiencies

The comparison of extinction efficiency, indicator of far field excitation coupling into smaller volumes, shows that there exists an optimized geometry for the best nanoan-



Figure 2.7: Absorption Efficiencies



Figure 2.8: Extinction efficiency comparison for different sizes

tenna because its spectral response has to be narrow, as well.



Figure 2.9: Quality factor values for different size particles at their resonance frequency

2.1.1 Nanoisland scattering model

The actual model is built to define a proper scattering model that gives explanatory results for the fabricated nanoparticles. By the help of information that we obtained from the previous section, an actual simulation model is developed for fabricated shapes. As we observed from the tilted SEM images, shape of the particles are like hemispherical. Also, they are numerously formed. For the sake of reliability and clarity of the results, the actual model is built step by step in a progressive manner. The graph which is obtained at the end will contain different contributions such as substrate, shape, size and material. Therefore, each small changes in the model is given in steps. Accordingly; effects of shape, substrate and number of particles are studied, respectively. Size effect is investigated in each step.

Hemispheroid-shape effect

In section 2.1, a sphere surrounded by air is studied. The only change in this subsection is to cut the sphere (figure 2.11) from the bottom. The particle suspended in midair which is surrounded by 200 nm *perfectly matched layer* (PML). The physical



Figure 2.10: Field confinement in the vicinity of MNPs



Figure 2.11: Geometry of the simulation domain.

domain is excited by a linearly polarized plane wave from the top port (the ceiling boundary of the physical domain). While the top and the bottom boundaries in the geometry are assigned as ports, the lateral boundaries are defined as periodic boundary conditions to assure that incoming light does not scattered at the side walls. The mesh sizes are defined by considering the sharp edges and the particle's radius. For the nanoparticle domain, maximum element size is set as 2 nm and minimum element size is set as 1 nm. The remaning part in the physical domain is meshed as 'extremely fine' from the local mesh directory.

Each model is computed with parametric sweep and proceeded around 26-27 hours



Figure 2.12: Electromagnetic cross section values and their efficiencies. (a,b) 15 nm radius. (c,d) 60 nm radius.

with a powerful computer. The computer has 20 cores and 40 processors with maximum 3.2 GHz speed and 192 GB random access memory (RAM). One model is computed at a time with %60 utilization.

As a result of this subsection, it is obvious that the larger particle with 120 nm diameter has more effective cross section. The 30 nm diameter particle is absorption dominant while the larger one is dominant in the scattering regime. As it is expected, the quality factor of the resonance is decreased with the size increment.

For the main purpose of this model, the figure (2.18) clearly shows the comparison of how the hemispheroid shape differs from a perfect sphere. For the 30 nm size, the centre wavelength is shifted from 358 nm to 379 nm and the absorption efficiency



Figure 2.13: Electromagnetic efficiency comparison of perfect sphere versus hemispheroid. The black lines are always for scattering while the red is for absorption.

becomes 17 while the sphere has the value of 11. When the particle gets larger size, hemispheroid shape again cause a shift in resonance wavelength and an increase in the total efficiency. For 120 nm, the centre wavelength is observed around 450 nm and the scattering efficiency is increased from 8 to 13. The extinction efficiencies shows that the smaller particle has the larger value which is quite meaningful because the extinction efficiency is an indicator of how strong the incoming light and the nanoantenna interact. The smaller one interacts with the incoming light more than the larger one but works in absorption dominant regime.

2.2 Fabrication of metal nano-particles

Cavities, as it was mentioned previously, are not physical cavities. The main objective is to built surface waves on the metal-dielectric interface for a desired resonance frequency. The surface waves are expected to be forming a standing wave just like it happens in Fabry-Perot type cavities. So, it is possible to use a wide range of types to obtain a nano cavity exploiting features of SPPs. The structures that are fabricated throughout this work are hemispheroid particles. Roughly speaking, there is no physical cavity in which the quantum emitter is located. Another perspective about this, in the weak coupling regime, the plasmon particle acts like it is a mirror so that it reflects the emission back into the point where it is emitted. This configuration may be considered as a physical cavity.

Laser marking This step is required for the later purposes and very significant however in the application procedure, it comes at the very beginning and the cleaning is crucial after this step. The reason to do this is also important. The quantum emitters that are embedded in microlevel flakes are hunted and investigated in chapter 3. Just after that, other procedures are required. At last step, the same flake should be found for a reinvestigation. Finding exactly same flake on the substrate is quite tough business. It is similar to find a specific hair in someone's scalp. So, the marking is a simple trick for creating microlevel avenues on the substrate. And silhouettes of flakes are streets to find true address later on.

Laser marking is made on a 10x10 mm silicon chip. The numbers (as two digits: 00, 01, 02, 03, ..., 99) around 100 μm in size. These numbers are written by engraving substrate surface by a laser which has 70 μm spot size. The opening between them are around 500 μm . The process is extremely dirty and imprecise. During the scribing, clean surface of a silicon substrate turns in to a contaminated one (see figure 2.14). The melted particles of silicon are splashed around the numbers.

Substrate cleaning is the first step of the fabrication. To begin with, single side polished, n-type Si-substrates were dipped into 5-10% diluted hydrofluoric acid, HF, in order to etch the silicon dioxide, SiO₂, layer. To remove all the organic contam-



Figure 2.14: Surface image of silicon substrate after laser marking without cleaning.

inants, *standart clean-1* $(SC-1)^1$ was applied. Since this process oxides the surface, diluted HF solution was again used for etching the oxide layer. At this point, it is important to rinse organic residue with deionized, DI, water. After that, the metal impurities were cleaned with *standart clean-2* $(SC-2)^1$ process. At last, HF process and rinsing etched metal ions with DI water are the final steps.

SC-1	$\mathrm{NH}_4\mathrm{OH}:\mathrm{H}_2\mathrm{O}_2:\mathrm{H}_2\mathrm{O}$	(1:1:5)
SC-2	$\mathrm{HCl}:\mathrm{H}_{2}\mathrm{O}_{2}:\mathrm{H}_{2}\mathrm{O}$	(1:1:5)

The surface of Si-substrate is expected to be highly hydrophobic as it is shown in



Figure 2.15: Before and after the SC-1, SC-2 cleaning

figure 2.16. During the experiment, the final HF and rinsing steps are recurred just before the metal evaporation process in order to prevent formation of oxide layer.

Agglomeration is a disintegration process due to instabilities on the structure. It is a quite old physics and introduced by Rayleigh. The first concept was about instability

¹ The process is developed by Werner Kern at RCA laboratories. It is also known as RCA-1,2 clean.



Figure 2.16: The hydrophobicity of clean Si-substrate.

on jets of fluids [28]. An infinite cylinder of water can not be in equilibrium and it discomposes into smaller pieces[29]. The matter here is about surface instabilities. As a general expression, it is said that the surface area of a thin film gets too large so that surface to volume ratio of the thin film reach some kind of maximum value. Instability starts because of this high surface/volume ratio. In order to balance this ratio by reducing surface, a driving force occurs. This happens by a diffusion mass transfer. All molecules in a liquid move by thermal effects. The dynamics depends on temperature, viscosity and the film thickness [30].



Figure 2.17: Void formation and growth on Ag thin film.

Capillary instability on thin films are explained in two steps: void formation and void growth according to [31]. Suface of the film changes its shape from a flat view to the one shown in 2.17. The metastability of a thin film causes to dewett and form too many nano islands [32]. Instability condition can occur much below the melting temperature of the thin film. So, all the process happen in the solid state phase. In order to increase the capillary force, film thickness should be decreased so that the agglomeration can be controlled as well. As a result, dewetting temperature is a



function of film thickness. It can be manipulated by changing film thickness [33].

Figure 2.18: Dewetting on a thin film.

In the experiment, the procedure starts with emplacing a clean substrate on the target holder of the physical vapor deposition sysytem 2.20. The material which is desired to be coated on the substrate is placed into the Molybdenum, Mo boat (source holder). In this work, silver and gold are used to evaporate. For this reason, the melting point of the boat material should be higher than the soruce material. Under ultra high vacuum (UHV) around $\sim 5 \times 10^{-6}$ [Torr]; a piece of silver is evaporated onto the substrate. The boat in which 100 - 150 [A] electric current flows provides the heat to melt the source metal. As a result, the large surface area of silver, Ag, thin film is obtained.



Figure 2.19: General demonstration of PVD system.

A quality thin film is the desideratum however the oxidation appears as a major problem at this point. Because the plasmon resonances, that are studied at the begining of this chapter, are killed due to an oxygen layer on the metal. That is why the film is taken immediately into the tube furnace after the vacuum chamber of the PVD is opened. Tube furnace has its own pipe in which nitrogen flows through. Temperature of the furnace provides the instability condition and void formation starts 2.17. Further annealing causes to void growth and finally the nano islands are formed[34, 35].

It is possible realize infinite number of experiments with the combination of temperature, film thickness and some other parameters. However, this distracts the aim of the work. So, certain temperatures are tried and observed via scanning electron microscope imaging. With particle size statistics over the surface, the appropriate film thicknesses are defined.



Figure 2.20: Tilted images of dewetted silver nanoparticles.

Particle size statistics The last process of this chapter is image analysis of electron microscope results and size statistics of particles. The main goal is to define an approximate size for each film thickness. For a trial value of temperature, a series of experiment are performed 2.1. As it is concluded from the chart, change in film thickness exhibits a noticable change in particle sizes while the annealing duration does not affect much. Nevertheless, this results do not quarantee anything. For any other thermal evaporator system, vacuum environment, furnace and other factors should be investigated again in order to conclude a reliable recipe. Even the hydrophobicity of the substrate surface can be a strong factor that affects the driving force. Apart from these, type of the substrate is one of the main parameters. Every single substrate should be re-characterized [36].

All the statistics are made with Gwyddion image analysis tool

Thickness [nm]	$T \circ C$	Annealing [min]	\approx Radius [nm]
10	200	30	65 - 70
10	200	45	70 - 75
10	200	60	70 - 80
7.5	200	30	60
7.5	200	45	60
7.5	200	60	60
5	200	30	40
5	200	45	40
5	200	60	40

Table 2.1: Annealing duration experiment of Ag-Thin film.



Figure 2.21: Ag particle size distribution for 10 nm film thickness at 200 $^{\circ}C$ a) 35 minutes and b) 60 minutes annealing time.



Figure 2.22: Ag particle size distribution for 7.5 nm film thickness at 200 $^{\circ}C$ a) 30 minutes and b) 60 minutes annealing time.



Figure 2.23: Ag particle size distribution for 5 nm film thickness at 200 $^{\circ}C$ a) 30 minutes and b) 45 minutes annealing time.



Diameter (nm)





Diameter (nm)





Figure 2.24: Particle size distribution histograms

COMPLEMENT 2A Cavity analogy

A conventional Fabry-Pérot resonator is formed by two reflecting mirrors. For the most basic case, two parallel-mirrors should have a well-defined opening, d, between them. If one of the mirrors experience 180° -phase shift according to the wave reflecting on the other mirror, waves perpetually propagate back and forth -for the ideal case- between the mirrors. As a result, standing wave patterns occur with an integer number, q, for the longitudinal modes. For a monochromatic plane wave, the wave function is expressed as,

$$\psi(\mathbf{r},t) = U(\mathbf{r})\exp(i2\pi\nu t) \tag{2.1}$$

Complex amplitude, $U(\mathbf{r})$, satisfies the Helmholtz equation, $\nabla^2 U + k^2 U = 0$, with

$$k = \frac{2\pi\nu}{c} \tag{2.2}$$

The solution of the Helmholtz equation is,

$$U(\mathbf{r}) = A\sin(kz) \tag{2.3}$$

The spatial function, $U(\mathbf{r})$, and the coefficient, A, vanish on the mirrors, z = 0, z = d.

$$\sin(kz)\big|_{z=d} = 0 \quad \Longrightarrow \quad kd = q\pi \tag{2.4}$$

$$k_d = \frac{q\pi}{d} \tag{2.5}$$

where q = 1, 2, 3, ... which is being the mode number. The discretized frequency, ν ,

$$\nu = \frac{ck}{2\pi} = q\frac{c}{2d} \tag{2.6}$$

Lastly, the resonance wavelength and the resonator length are respectively,

$$\lambda_q = \frac{c}{\nu_q} = \frac{2d}{q}, \qquad d = \frac{q}{2}\lambda_q \tag{2.7}$$

Surface waves coupled with photons, propagate on the dielectric-metal interface, can be described with a very similar method;

$$\begin{split} \mathbf{E}(\mathbf{r},t) &= \mathbf{E}(\mathbf{r})e^{-i\omega t} \\ \mathbf{E}(\mathbf{r}) &= \mathbf{E}(z)e^{i\beta x}, \end{split} \qquad where \ \beta = \ k_0 \sqrt{\frac{\epsilon_d \epsilon_c}{\epsilon_d + \epsilon_c}} \end{split}$$

which are defined in Complement 1A. In the Euler form of the function, sin term will survive due to the non-zero coefficient. And applying the boundary condition, the resonance of a MNP is given by,

$$\left. \sin(k_{eff}z) \right|_{z=L} = 0,$$

where L is the length of the particle[27]. It is measured in the direction of Epolarization. **Important point** is the wave number, k_{eff} , which is different than β . Since surface waves depend on charge densities on different type of surfaces, the wave number can not be generalized directly by using dielectric constants. So, it is expressing a crucial factor for *Plasmon Cavity Design*.



Figure 2.25: Standing SPP wave on a nanoantenna excited with λ

$$k_{eff}L = q\pi, \qquad (q=1,2,3,...)$$

$$k_{eff} = \frac{2\pi}{\lambda_{eff}}, \qquad effective wave number \qquad (2.8)$$

$$L = \frac{q}{2}\lambda_{eff}, \qquad effective length \qquad (2.9)$$

In order to find out properties of k_{eff} , one should explicitly define the effective wavelength [37], λ_{eff} , of the surface plasmon resonance. The **wavelength scaling rule** (equation 2.10) is rigorously defining the relation between geometry parameters, excitation wavelength and the effective wavelength.

$$\lambda_{eff} = n_1 + n_2 \frac{\lambda}{\lambda_p} \tag{2.10}$$

$$n_1 = 2\pi R \left[13.74 - 0.12 \left[\epsilon_{\infty} + \epsilon_d (141.04) \right] - \frac{2}{\pi} \right]$$
(2.11)

$$n_2 = 2\pi R \left[0.12 \frac{\sqrt{\epsilon_\infty + \epsilon_d (141.04)}}{\epsilon_d} \right]$$
(2.12)

where ϵ_{∞} , ϵ_d , n_1 , n_2 and λ_p are the infinite frequency limit of dielectric function, permittivity of the surrounding medium, two geometry parameters and the plasma wavelength of the free electron oscillations in the metal, respectively. In order to confirm the equations above, the numerical calculation of the Letter [37] was recalculated with a different computation tool built in section (2.1).



Figure 2.26: Electric field intensity enhancements for different mode numbers of Au-Johnson nanorods / Regenerated simulation results of the Letter parameters.

With an arbitrary length and 5 nm radius gold nanorod (Johnson) was defined. The parameters of *wavelength scaling rule* were taken as $\epsilon_{\infty} = 11$, $\epsilon_d = 1$ and $\lambda_p = 138nm$. Unlike the paper's method, the nanorod was excited with a single frequency.

And the mode number, q, became the only input variable to form a phase-matched standing SPP waves on the plasmon cavity. Each value of mode number yielded different lengths of particle together with the effective wavelength. The excitation wavelength was taken as 1150 nm which is found in the paper as well. The results (see figure 2.19) confirmed the plasmon cavity analogy as much as paper's itself.

COMPLEMENT 2B

Electromagnetic cross section and efficiency

The subject is energy transfer. The energy flux of electromagnetic radiation is the energy flowing through a unit area in a unit time. It is given by Poynting² vector, **S**. The electric and magnetic fields were found in Complement 1A as $\mathbf{E} = \mathbf{E}(\mathbf{r})e^{-i\omega t}$ and $\mathbf{H} = \mathbf{H}(\mathbf{r})e^{-i\omega t}$ in equation (1.5). where $\mathbf{E}(\mathbf{r}) = \mathbf{E}_{\mathbf{r}}$ and $\mathbf{H}(\mathbf{r}) = \mathbf{H}_{\mathbf{r}}$ are phasors.

$$\begin{split} \mathbf{S} &= \mathbf{E} \times \mathbf{H} \end{split}$$
(2.13)
$$\mathbf{S}(t) &= \Re(\mathbf{E}_{\mathbf{r}}e^{-i\omega t}) \times \Re(\mathbf{H}_{\mathbf{r}}e^{-i\omega t}) \qquad \text{instantaneous Poynting vector} \\ \mathbf{S}(t) &= \frac{1}{2}(\mathbf{E}_{\mathbf{r}}e^{-i\omega t} + \mathbf{E}_{\mathbf{r}}^{*}e^{i\omega t}) \times \frac{1}{2}(\mathbf{H}_{\mathbf{r}}e^{-i\omega t} + \mathbf{H}_{\mathbf{r}}^{*}e^{i\omega t}) \\ \mathbf{S}(t) &= \frac{1}{4}(\mathbf{E}_{\mathbf{r}} \times \mathbf{H}_{\mathbf{r}}^{*} + \mathbf{E}_{\mathbf{r}}^{*} \times \mathbf{H}_{\mathbf{r}} + \mathbf{E}_{\mathbf{r}} \times \mathbf{H}_{\mathbf{r}}e^{-2i\omega t} + \mathbf{E}_{\mathbf{r}}^{*} \times \mathbf{H}_{\mathbf{r}}^{*}e^{2i\omega t}) \\ \mathbf{S}(t) &= \frac{1}{2}\Re(\mathbf{E}_{\mathbf{r}} \times \mathbf{H}_{\mathbf{r}}^{*}) + \frac{1}{2}\Re(\mathbf{E}_{\mathbf{r}} \times \mathbf{H}_{\mathbf{r}}e^{-2i\omega t}) \end{split}$$

Time average of the instantaneous Poynting vector,

$$\begin{split} \langle \mathbf{S}(t) \rangle &= \frac{1}{T} \int_0^T \mathbf{S}(t) dt \\ \langle \mathbf{S}(t) \rangle &= \frac{1}{T} \int_0^T \left[\frac{1}{2} \Re(\mathbf{E}_{\mathbf{r}} \times \mathbf{H}_{\mathbf{r}}^*) + \frac{1}{2} \frac{\Re(\mathbf{E}_{\mathbf{r}} \times \mathbf{H}_{\mathbf{r}} e^{-2i\omega t})}{1} \right] dt \\ \langle \mathbf{S}(t) \rangle &= \frac{1}{T} \int_0^T \frac{1}{2} \Re(\mathbf{E}_{\mathbf{r}} \times \mathbf{H}_{\mathbf{r}}^*) dt \\ \langle \mathbf{S}(t) \rangle &= \frac{1}{2} \Re(\mathbf{E}_{\mathbf{r}} \times \mathbf{H}_{\mathbf{r}}^*) \end{split}$$

$$\mathbf{S}_{inc} = \frac{1}{2} \Re \{ \mathbf{E}_{inc} \times \mathbf{H}^*_{inc} \}$$
(2.14)

$$\mathbf{S}_{sca} = \frac{1}{2} \Re\{\mathbf{E}_{sca} \times \mathbf{H}^*_{sca}\}$$
(2.15)

$$\mathbf{S}_{ext} = \frac{1}{2} \Re \{ \mathbf{E}_{inc} \times \mathbf{H}^*_{sca} + \mathbf{E}_{sca} \times \mathbf{H}^*_{inc} \}$$
(2.16)

² John Henry Poynting (1884)

 S_{inc} and S_{sca} are time-averaged electromagnetic power flows for incoming and scattered fields. Incoming and scattered fields also interfere with each other. This interaction causes an additional power expression which is being S_{ext} in equation (2.16).

$$\mathbf{S}_{tot} = \mathbf{S}_{inc} + \mathbf{S}_{sca} + \mathbf{S}_{ext}, \qquad \text{CONSERVATION OF ENERGY}$$
(2.17)

$$\mathbf{S}_{tot} = \frac{1}{2} \Re \{ \mathbf{E}_{tot} \times \mathbf{H}^*_{tot} \}$$
(2.18)

$$\mathbf{E}_{tot} = \mathbf{E}_{inc} + \mathbf{E}_{sca} \qquad \& \qquad \mathbf{H}_{tot} = \mathbf{H}_{inc} + \mathbf{H}_{sca} \tag{2.19}$$

The crucial point is to obtain the energy values relevant to the particle. In the model (2.1), the surface, s, and volume, v, of the particle are defined as boundary and domain. And the integrations are performed as;

•

$$P_{sca} = \int_{s} \mathbf{S}_{sca} ds, \qquad \qquad Scattered \ energy \ over \ the \ particle \qquad (2.20)$$

$$P_{abs} = -\int_{s} \mathbf{S}_{tot} ds, \qquad Absorbed energy over the particle \qquad (2.21)$$

$$P_{ext} = -\int_{s} \mathbf{S}_{ext} ds$$
, Total energy removed from the incident field (2.22)

The scattering and the absoption processes remove energy from the incident field. Throughout the interaction of light with the nanoparticle, incoming fields experience an obstacle larger than the particle's cross sectional area. The electromagnetic cross sections are given as [2];

$$\sigma_{sc} = \frac{P_{sca}}{|\mathbf{S}_{inc}|}, \qquad \sigma_{abs} = \frac{P_{abs}}{|\mathbf{S}_{inc}|}, \qquad \sigma_{ext} = \frac{P_{ext}}{|\mathbf{S}_{inc}|} = \sigma_{sc} + \sigma_{abs}$$
(2.23)

As a criterion of how the interception area has a larger value than the actual cross sectional area, the efficiencies are given as;

$$Q_{sc} = \frac{\sigma_{sc}}{area}, \qquad Q_{abs} = \frac{\sigma_{abs}}{area}, \qquad Q_{ext} = \frac{\sigma_{ext}}{area} = Q_{sc} + Q_{abs}$$
 (2.24)

$$Q_{ext} \implies$$
 Strong interaction with the incoming fields

CHAPTER 3

SINGLE QUANTUM EMITTER

All light sources are quantum emitters or collection of quantum emitters. Even it is a gigantic celestial body or a material reflecting incoming light. In any case, the emission process occurs at the level of an atom. Light sources are characterized by their photon emission statistics. This is known as **photon statistics** and it is the key point in order to define type of the emitter [38, 39]. Photon number states with annihilation and creation operators [40];

$$\begin{aligned} a_k^{\dagger} a_k |n_k\rangle &= n_k |n_k\rangle \\ a_k |n_k\rangle &= \sqrt{n_k} |n_k - 1\rangle \\ a_k^{\dagger} |n_k\rangle &= \sqrt{n_k + 1} |n_k + 1\rangle \end{aligned}$$

$$N = a_k^{\dagger} a_k$$
 : Number operator $|n_k
angle$: Fock states

Creation, a_k^{\dagger} , operators create photon number states from the vacuum state, $|0\rangle$;

$$|n_k\rangle = \frac{1}{\sqrt{n_k!}} (a_k^{\dagger})^{n_k} |0\rangle \tag{3.1}$$

Eigenstates of the annihilation operator are coherent (Glauber) states;

$$a|\alpha\rangle = \alpha|\alpha\rangle \tag{3.2}$$

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n} \frac{\alpha^n}{\sqrt{n!}} |n\rangle$$
(3.3)

The probability of finding n number of photon in coherent states;

$$P(n) = |\langle n | \alpha \rangle|^2 = e^{-|\alpha|^2} \frac{|\alpha|^{2n}}{n!}$$
(3.4)



Figure 3.1: Photon statistics comparison. The figures are taken from Fox-2006

Thus, coherent light sources have Poissonian statistics. Lasers are well-known example for this type. Coherent light sources are classical light sources. The shape of the Poissonian distribution can be broadened in some situations. In this case, the square root of the mean number is smaller than the standart deviation while they are equal in Poissonian distribution.

Poissonian statistics	$\Delta n = \sqrt{\overline{n}}$	classical
super-Poissonian statistics	$\Delta n > \sqrt{\overline{n}}$	classical
sub-Poissonian statistics	$\Delta n < \sqrt{\overline{n}}$	non-classical

The most perfectly coherent light sources also obey with the Poissonian statistics because the emitting medium consists of multiple other sources e.g. atoms, molecules. In order to obtain a light source which has almost no fluctuation in its intensity, a single quantum system should be employed. Only with this way, it is possible to obtain sub-Poissonian distribution. Moreover, if the standart deviation becomes zero, $\Delta n = 0$, the photon statistics appear as a Dirac delta, (δ), function. This is actually being the photon number state's itself as illustrated in figure 3.1. As a result, it is a purely quantum mechanical event and there is no classical counter-part of it.

Non-classical light emission from single quantum sysytems are studied in literature with a wide range of material types. Trapped ion or atom [41, 42], single molecule [43, 44, 45], quantum dot [46] and other type of solid state emitters including colour centres [47, 48] are studied in order to observe non-classical light emission.

The photon absorption with no energy transfer to vibrational states cause a direct transition from the lowest level of HOMO to the lowest level of LUMO. This transi-

tion is known as a **zero-phonon line**. Atomic defects cause photon emission which is similar to single molecule photon emission. Throughout this work, colour centres (also known as luminescence, F, defect centres) in *hexagonal Boron Nitride*, hBN, are investigated.

The most important feature of hBN defects is to be a room-temperature quantum emitter[7]. hBN is a Van der Waals crystal that can be found in the form of monolayer or multilayer. This exhibits a similar properties with graphene. In a Van der Waals crystal in-plane bonds are much stronger than out-of-plane bonds [49, 50]. All quantum emitters in two-dimensional materials have wide bandgap. Energy levels of a defect structure sit between this wide bandgap. hBN has 6 eV bandgap[51] which is greater than any two dimensional materials. That is why it may have many optically active defects.



Figure 3.2: Some defect types [1]. Oxygen, carbon, nitrogen antisites with nitrogen vacancy, respectively.

Defects are formed due to a vacancy, an antisite, an additional dopant atom or combination of these. In the absence of nitrogen or boron atom in hBN, the local structure is defined as vacancy. Additionally, the neighbouring atom may be interchanged with another atom. This is called as antisite. If a nitrogen atom leaves and the neighbouring atom to this is replaced by a carbon atom, it is called carbon antisite nitrogen vacancy, $C_B N_v$. There are many types of defects with a characteristic emission wavelength (e.g. oxygen, carbon, silicon, sulfur, flourine and phosphorus antisite[1]).



Figure 3.3: Jablonski diagram[2].

3.1 Experimental investigation of quantum emitters in hBN

The defect centers in 3D crystals cause technical challenges during applications. Location of defect centers in 3D materials is one of them. Coupling with a waveguide or a cavity is the main difficulty of 3D structures. Furhermore, total internal reflection is one another technical problem. On the other side, quantum dots appear with their low temperature operation requirements. In this context, hexagonal Boron Nitride defect center is an unprecedented solution for single-photon emitter demand. It is embedded in a 2D lattice and defect centers are ready to coupling with either a cavity or a waveguide. Also, room temperature operation is one of the most crucial factor. Defect centers in hBN exhibit a wide range of emission frequency due to large bandgap of host crystal. It is nearly 6 eV [7]. Brightness of them are another significant advantageous of hBN colour centers [52, 53].

Here, I investigate experimentally room temperature single photon emissions from hBN defect centers embedded in multilayered flakes.

 μ -Photoluminescence is a powerful tool in order to study the optical and electronic properties of single nanostructures. Photoluminescence experiment starts with photoexcitation and it ends with detection of the photons created by relaxation of the system. The word ' $\mu i cro$ ' emphasis the spatial resolution of the experiment. It allows to survey nanostructures due to harvesting photons in a very small region typically around one or two micrometer. It is also possible with several hundred nanometer spot size.



Figure 3.4: Photoluminescence process on a defect in hBN ref-[1].

For a true deterministic coupling [54] and reliable comparison, quantum emitters are placed before nanoantennas to make sure that we did not change QE's location and emission properties by any transferring process. hBN Flakes (Graphene Supermarket) are drop cast onto the substrate and annealed at 350 ^{o}C for 10 min. The purpose of the annealing process is to assure that the selected defect will not be affected in that temperature level later on.

The experiment starts with real-space sample surface observation. Using a white light source and CMOS camera assembled to the setup, the surface of the substrate is displayed on the monitor. The resolution of the image is around several micrometer by the help of an objective that has a 50x magnification and 0.75 numerical aperture. Before any measurement, a scan is made in order to find a proper hBN bulk which is potantially a host for stable and bright defects.

The defect hunting in an hBN flake is made on a nanopositioner xyz-stage which is assembled to a micro-photoluminescence (μ -PL) setup. The specimen is excited by a CW laser ($\lambda_{exc} = 532 \ nm$, Verdi-V6 Coherent) and a pulsed diode laser ($\lambda_{exc} = 483 \ nm$, 65 ps pulse width, 80 MHz repetition rate, Advanced Laser Diode Systems). Focusing and harvesting light are achieved with an objective (50x/0.75 NA, Optika). For investigating excitonic effects, different excitation power values are created by a motorized ND filter (round continuously variable metallic neutral density filter). The optimum polarization angle of the excitation is defined with a motorized halfwaveplate (HWP).

For the detection part of our setup, the rayleigh scattered part is cut with a 540 nm notch filter. The sample surface is viewed by a CMOS camera. Andor Shamrock-750 monochromator is used with 3 MHz Newton.

While simultaneous capturing the fluorescence emission spectra, the selected bulk is scanned to determine a stable and bright colour center. Once the desired defect is found, it is studied in terms of its polarization and power series. At the HWPangle which the emission intensity has the maximum value, the emission spectrum is recorded with a higher exposure time in order to reduce noise to signal ratio. The lifetime measurement of the quantum emitter is captured by one of the photon counting avalanche photodiodes in the HBT interferometer (APD, connected to time tagging module, TTM8000, Roithner Laser Technik).

The defect investigation is done by using a sub-bandgap excitation in order to avoid excitonic effects. [7, 55]



Figure 3.5: μ -PL setup

3.2 Defect hunting in an hBN bulk

A defect or colour center randomly occurs inside the hBN layers. The hBN bulks can be both monolayer or multilayer. Microlevel size of an hBN-bulk allows one to recognize it. However, the defects are atomic systems and can not be identified by optical/electron microscope scanning. Raman spectroscopy is a spear in order to hunt defect centers. An incoming light is absorbed and scattered back at frequency that is different than the incoming frequency. The scattered light frequency and the shape of the spectra are the focus of our interest. In other words, it carries the information about the quantum system.

To begin with, a bulk is selected randomly. Then, the flip mirror of the white light is by-passed to allow only laser illumination on the sample. About a $10 \ \mu m^2$ area on the bulk region, the laser beam is focused at a fixed point. By the help of piezopositioners on the XYZ-stage, the sample is scanned by a 100 nm steps. In real-time, spectra of the bulk is observed on the screen. While doing this, the Raman peak of hBN guides and says that the laser spot is still on the hBN bulk. Once a sharp and stable peak is found, more sensitive spatial scanning is made to capture the best shape of photoluminescence (PL) peak.



Figure 3.6: Optical microscope image of hBN bulks on the left. SEM image of a typical hBN bulk on the right



Figure 3.7: Capture from a single point in the bulk which is in red circle at figure 3.6. a) Full spectra and the zoom view of the defect-PL, b) the baseline substracted spectra after peak analysis.

As it is seen in figure 3.7-a, there are many peaks corresponding to different frequencies. Before the investigation about the dipole orientation and the power responses, one should interpret each peaks in the spectra.

Interpretation of peaks The peaks can be response of the substrate, hBN, oxide layer, zero phonon line or phonon side band of a defect center. To understand this, the Raman shift values are used in the following formula for 532 nm excitation wave-

length;

$$\lambda_{Raman}[nm] = \frac{1}{\frac{1}{\lambda_{exc}[nm]} - \frac{Raman-shift[cm^{-1}]}{10^7}}$$

For single-crystal silicon the Raman shift is 520 $[cm^{-1}]$ [56] and the formula gives wavelength value of 548 nm. The Raman shift of hBN is around 1366 $[cm^{-1}]$ [57] which yields to 574 nm. Also, the small peak around 625 nm (1.98 eV) is the sideband of the hBN peak (574nm, 2.15eV). The crowded region, next to the hBN peak around 578 nm, has contributions to the 632 nm peak. So, the background contribution should be substracted as it is seen in figure 3.7. Lastly, the defect center at 632 nm has a phonon sideband at around 691 nm. In order to find this, the zero phonon line wavelength value should be used in the formula as λ_{exc} . So, the λ_{Raman} appears as λ_{PSB} . The asymmetric shape of the defect line is because of the phonon interactions [58]. For the most cases, other defects are observed at different wavelengths. There is no special frequency band to observe more defect centers in a bulk hBN.



Figure 3.8: Emission spectra with 483 nm pulsed laser excitation.

Realizing same measurements with a pulsed laser is important in terms of finding the defect with pulsed laser. It is sometimes possible that measuring all features about a defect with 532 nm CW laser but after switching to the pulsed laser, the spectrum disappears and becomes impossible to refind it. Availability of the defect center under the excitation of a pulsed laser is required for the lifetime measurements.

Polarization and power measurements For the polarization-resolved measurement, a motorized half-wave-plate (HWP) is employed. The measurement is started from 0° to 180° with 5° steps. The photoluminescence intensity is captured automatically while polarization angle changes. In data analysis part[59], since there are different background effects in the spectra for each polarization angle, all of them are substracted carefully. Using the peak analyzer of OriginPro, the area of the baseline substracted data sets are plotted as a function of corresponding angles3.9. Fitting function of the polar plot is chosen as $cos^2\theta$ [54, 7]. More specifically, the function is;

$$y = y_0 + A\cos^2(\theta \frac{\pi}{180} + x)$$

y = Dependent variable, $\theta = Independent variable,$ $y_0, A, x = Parameters$



Figure 3.9: Polarization-resolved measurement of defect-632nm in 3.6. a) Full spectra for the given angles. Inset: Spectra between 616-650 nm with baselines, b) Polar plot of the selected data and fit

Fluorescence intensity of the defect center as a function of laser power is studied. Output power of the laser is attenuated with a round shape neutral density filter in
order to increase the power gradually. So, the emission spectra is captured for different excitation power in figure 3.10-a. Same procedure is followed for background substracting from the original spectrum. Area under the intensity plot gives the power values. In a selected wavelength interval in the inset of 3.10-a, the data analysis is performed and results are plotted in (b). The saturation power is observed as 663 μW . The fitting function is [7];

$$I = I_{\infty} \times \frac{P}{P + P_{sax}}$$



Figure 3.10: Power measurements of the defect-632nm in 3.6. a) Full spectra for the given excitation powers. Inset: Spectra between 626-646 nm, b) Power saturation plot and fitting of the experimental data. Inset: same plot with log-log scale.

As a result of power measurements over many experiments, hBN defect centers are quite bright quantum light sources and perfect candidates for potential technologies.

Time-resolved measurement Fluorescence lifetime measurement is very sensitive technique. Photons from the excitation source and the quantum emitter are correlated with a time tagging module. Basically, just after the short-pulse excitation, arrival times of photons, which are radiated from the emitter, are measured. The arrival time of each photon is tagged by a time-correlator. The difference between two time measurements shows the delay after excitation[60]. Laser pulse starts and the first photon emitted from the defect stops the counting by triggering the detector (see figure 3.11).



Figure 3.11: Time tagging demonstration. The figures are taken from PicoQuant's TCSPC-tutorial



Figure 3.12: Time-correlated single-photon counting a) for two successive pulses, b) one pulse-cycle with normalized intensity.

The photons are captured with a single photon sensitive detectors e.g. photomultiplier tube (PMT), micro channel plate (MCP), a single photon avalanche diode (SPAD) or a hybrid PMT [61]. Photons of the two events are converted into electrical signals. Processing time of the electronics are around nanoseconds. This causes a *dead time* after each measurement. That is why only one photon is taken into account for each measurement cycle and this is being the first photon arriving to the detector. Any

other photon arriving to the detector in same cycle may lead to the 'pile-up' effect. Also, the fluorescence photon in the next pulse-cycle coming into the detector is lost. As a result, the count rates of the emitter gain importance[62, 63].

In the setup, *IDQ's ID120 Single-Photon Detector* is employed. Quantum efficiency of the detector is 80%. For the time tagging part, *TTM8000, Roithner LaserTechnik* is used. The results are captured as it is seen in figure 3.12-a. After experiment, data analysis is made and one measurement cycle is selected. The exponential decay on the plot 3.12-b is fitted with the function;

$$y = y_0 + A_1 exp(-x/\tau_1) + A_2 exp(-x/\tau_2)$$

where A_1 and A_2 are fitting parameters. Since we have three-level model, doubleexponential is used as a fitting function. Thereby, lifetime of the excited state, τ_1 , is found as 2.4 ns while the metastable state lifetime, τ_2 , is 11.5 ns. This is the expected result. One comment about fitting may be that playing with the fitting function or fitting parameters can easily cause a small changes in lifetimes. This is ignorable. Especially, within this work, the comparison of lifetime is important. As long as fitting functions are same for different experiments, lifetimes can be compared safely.



Figure 3.13: Semilog plot of the fluorescence lifetime with a double-exponential fit.

Photobleaching Defects interact with its environment. For example, with oxygen atoms or neighbouring unknown atoms/molecules. As a result of this ambiguous phenomena, fading on the fluorescence intensity occurs. This irreversible process is called in the literature as photobleaching. Although in some areas (e.g. fluorescence microscopy) photobleaching is exploited for several aims, in our case it is an undesired situation[64, 65, 66, 67]. According to hands on experiences, defect centers are mostly stable and photobleaching is observed quite rarely. However, in some cases, the excitation power exceeds some certain level for the defect and photobleaching happens. After several excitation cycle full-bleach happens if the power is too high for that specific defect structure. Simply, in order to avoid photobleaching, external conditions should be kept properly. For instance; keeping sample in an inert environment or avoiding high power excitations, etc.

Photoblinking Singlet-singlet transitions are dominant in count rates which is corresponding to the observed values of 1-15 ns lifetime. However, through the experiments of single molecule structure, it is seen that sudden interruptions are appears on the spectrum. This is because milisecond dark periods intervene singlet-singlet transitions. These are known as triplet-singlet excursions. [2, 68]

3.3 Photon antibunching

In order to explain the difference of sub-Poissonian photon statistic from Poissonian statistics; daily used concepts about coherent light sources such as power, intensity and flux are good starting point for the explanation of quantum nature of photon and its detection. As a coherent light source, considering a laser beam,

$$\Phi = \frac{IA}{\hbar\omega} = \frac{P}{\hbar\omega} \quad \left[\frac{photons}{second}\right] \tag{3.5}$$

This is an average number of photons per unit time through a cross section of the beam. If a device with quantum efficiency, η , and an active counting time, *T*, starts to count photons, average number of counted photons,

$$N(T) = \eta T \Phi = \frac{\eta T P}{\hbar \omega}$$
(3.6)

The average count rate over one counting cycle,

$$R = \frac{N(T)}{T} = \eta \frac{P}{\hbar\omega}$$
(3.7)

Every detector has a dead time as previously mentioned. The quantum efficiency of a detector is the number of detected photons normalized with the number of total incoming photons. Count rate has an upper limit due to detector's recovery time. So, intensity is the main parameter to focus. For example, a cylindrical shape laser beam has C number of photons in a $3x10^8$ m length segment. If one cuts this long segment into a smaller 3 m segment, number of photons would be $Cx3x10^{-8}$. If C is equal to a hundred million of photons, then only 3 photons are appeared in 3 meters segment of the laser beam. The problem arises after this stage. If one further cuts into 3 cm segment, the number of photons would not be 0.03 photon! This is not possible. So, if measurement trials are made on this 3 cm segment which is equivalent to 0.1 ns in time scale, different numbers would appear on the detector's screen. This is the source of shot noise. This fluctuation is the subject of counting discrete light particles. Even with a perfectly coherent light source, fluctuations are appeares. In conclusion of the discussion, shot noise is sourced by quantum fields.

Fluctuations are characterized by an autocorrelation function. Famous Hanbury-Brown-Twiss interferometer [69] is the tool that is used to study these fluctuations.



Figure 3.14: Demonstration of an HBT setup. (This figure is taken from picoquant.com)

Coherence is the interference exhibition capacity of a system. The difference between photon and shot noise is called excess photon noise. It is too small to be detected with a one photodetector. In the figure 3.14 two fast detectors correlates an incoming photon. Shot noise currents, the space-charge smoothing effects and the multiplication noise in the two detectors are uncorrelated. So, long time detection of two photocurrents by tagging their times provides how the two photocurrents are correlated to each other [70].

For a chaotic light detection experiment,

$$I(t) = \langle I \rangle + \Delta I(t)$$
$$\frac{I(t)}{2} \approx I_1(t) = I_2(t)$$

Output of the HBT experiment gives,

$$\langle \Delta I(t) \Delta I(t+\tau) \rangle$$

If the time delay τ is zero, the output would be,

$$\langle \Delta I(t) \Delta I(t+\tau) \rangle_{\tau=0} = \langle \Delta I(t) \Delta I(t) \rangle$$

= $\langle \Delta I(t)^2 \rangle$

This is expected to be zero but it is not due to chaotic nature of the source. One important result is here that output of the experiment is **non-zero** for $\tau = 0$.

First-order coherence function quantifies electric field fluctuations. However, intensity fluctuations are observed by using second-order correlation function [39, 40];

$$g^{1}(\tau) = \frac{\langle E^{*}(t)E(t+\tau)\rangle}{\langle |E(t)|^{2}\rangle}$$

$$g^{2}(\tau) = \frac{\langle E^{*}(t)E^{*}(t+\tau)E(t+\tau)E(t+\tau)E(t)\rangle}{\langle E^{*}(t+\tau)E(t+\tau)E(t+\tau)E(t)\rangle}$$
(3.8)

$$\langle E^{*}(t)E(t)\rangle\langle E^{*}(t+\tau)E(t+\tau)\rangle$$

$$q^{2}(\tau) = \frac{\langle I^{*}(t)I(t+\tau)\rangle}{\langle I^{*}(t)I(t+\tau)\rangle}$$
(3.9)

$$g^{2}(\tau) = \frac{\langle U \rangle \langle U \rangle \langle I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle}$$
(3.9)

The function above is purely time dependent and measures the temporal coherence of incoming photons. Since measured intensity values are corresponding to number of incoming photons, then it is possible to express second-order correlation function

$$g^{2}(\tau) = \frac{\langle n_{1}(t)n_{2}(t+\tau)\rangle}{\langle n_{1}(t)\rangle\langle n_{2}(t+\tau)\rangle}$$

where $n_1(t)$ and $n_2(t)$ are number of photons impinged on detector one and two, respectively. If photon statistics of the quantum emitter is antibunched, in other words, photons travel with a regular gap between them, then the quantum emitter is called single photon source. The value of $g^2(0)$ is an experimental sign of this phenomenon [39, 71].

$g^2(0) > 1$	Bunched	Chaotic
$g^2(0) = 1$	Random	Coherent
$g^2(0) < 1$	Antibunched	Single quantum emitter

First experimental demonstration of photon antibunching is made by [72] in the Letter 'Photon Antibunching in Resonance Fluorescence'. In this work, two single-photon detection modules (IDQ-ID120 Single-photon detector) are employed in the setup with a 50:50 beam splitter. The detector time tagging module is TTM8000 (Roithner Laser Technik).

COMPLEMENT 3A Radiation of an atom

Atomic dipole oscillator Although the exact description of light emission from an atom is quantum mechanical, the idea of that light emission from an oscillating electric dipole and the consideration of atoms as oscillators are found before the foundation of quantum mechanics. Henrick Lorentz (1878) proposed the idea that atom is an oscillating dipole. The heavy nucleus is fixed in space and the electron is attached to the center with a spring. The displacement of the electron from its equilibrium position on an orbit causes the spring to act in opposite direction. This is the reaction force. So, the natural frequency of the atom is given by,

$$\omega_0 = \sqrt{\frac{K_s}{\mu}} \tag{3.10}$$

where the K_s is the reaction (restoring) force and the μ is the reduced mass (or approximately the electron's mass). One smart person may ask how Lorentz proposed this idea in 1878 while the electron and the nuclei is discovered in 1897 and 1911. Because this is a simple postulation without knowing the existence of electrons.

Dielectric permittivity The equation of motion for an electron,

$$m_{0}\frac{d^{2}x}{dt^{2}} + m_{0}\gamma\frac{dx}{dt} + m_{0}\omega_{0}^{2}x = -eE, \qquad (3.11)$$

$$E(t) = E_{0}\exp(-i\omega t + \phi), \quad x(t) = X_{0}exp(-i\omega t + \phi')$$

$$-m_{0}\omega^{2}X_{0}e^{(-i\omega t)} - im_{0}\gamma\omega X_{0}e^{(-i\omega t)} + m_{0}\omega_{0}^{2}X_{0}e^{(-i\omega t)} = -eE_{0}e^{(-i\omega t)}$$

$$X_0 = \frac{-eE_0/m_0}{\omega_0^2 - \omega^2 - i\gamma\omega}, \quad p(t) = -ex(t)$$
(3.12)

where γ is damping of the oscillation, X_0 is displacement of the electron and the p(t) is time varying dipole moment. If there is N number of atom per unit volume, the

resonant polarization (Presonant) becomes,

$$P_{resonant} = Np$$

$$= -Nex$$

$$= \frac{Ne^2}{m_0} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)} E$$
(3.13)

The electric displacement field, D is given by,

$$D = \epsilon_0 E + P$$

$$= \epsilon_0 E + P_{background} + P_{resonant}$$

$$= \epsilon_0 E + \epsilon_0 \chi E + P_{resonant}$$

$$= \epsilon_0 E + \epsilon_0 \chi E + \frac{Ne^2}{m_0} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)} E$$

$$= \epsilon_0 E (1 + \chi + \frac{1}{\epsilon_0} \frac{Ne^2}{m_0} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)}) = \epsilon_0 \epsilon_r(\omega) E$$
(3.14)

So, the relative dielectric constant is,

$$\epsilon_r(\omega) = \frac{1}{\epsilon_0} \frac{Ne^2}{m_0} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)}$$
(3.15)

$$\epsilon_{real}(\omega) = 1 + \chi + \frac{Ne^2}{\epsilon_0 m_0} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2) + (\gamma \omega)^2}$$
$$\epsilon_{imaginary}(\omega) = \frac{Ne^2}{\epsilon_0 m_0} \frac{\gamma \omega}{(\omega_0^2 - \omega^2) + (\gamma \omega)^2}$$

In the case of multiple resonances, there should be many oscillators with different frequencies ω_j ,

$$P = \left(\frac{Ne^2}{m_0} \sum_{j} \frac{1}{(\omega_j^2 - \omega^2 - i\gamma_j\omega)}\right) E$$
(3.16)

$$\epsilon_r(\omega) = 1 + \frac{Ne^2}{\epsilon_0 m_0} \sum_j \frac{1}{(\omega_j^2 - \omega^2 - i\gamma_j \omega)}$$
(3.17)

This expression gives the material's behaviour for different frequencies. The frequency dependent refractive index and absorption line of the matter can be found with this expression. However, there is a problem about the contribution of each oscillator. Different frequency of oscillations cause different effects. The explanation of this phenomenon is possible only with quantum mechanical transition rates. That is why an oscillatory strength term, f_j , is added in order to express different oscillator's contribution.

$$\epsilon_r(\omega) = 1 + \frac{Ne^2}{\epsilon_0 m_0} \sum_j \frac{f_j}{(\omega_j^2 - \omega^2 - i\gamma_j \omega)}$$
(3.18)

for each electron $\sum_{j} f_{j} = 1$, \Leftarrow quantum mechanical, for each oscillator $f_{j} = 1$, \Leftarrow classical model

For the quantum mechanical interpretation, it is said that a particular electron can be count in different transitions at a time.

Luminescence Atoms emit photons by a transition from excited state to its ground state. Before it happens, the atom should be excited. The energy of the incoming photon causes the atom to be excited by absorption. This is for two-level system or a single atom. Due to Pauli exclusion principle, electrons/fermions can not sit in same energy level and they exclude each other. So, two identical atoms' electrons cause that one energy level splits into two levels. In consideration of many identical atoms, one energy level for an electron causes infinetely many levels. Energy bands in solids arise from this phenomenon. So, the excitation of a solid requires an amount of energy between valance and conduction band or more. The conduction band is the new excited state while the valance band is the new ground state of the system. After this point, relaxation mechanism occurs with a probabilistic manner for different electrons in a continuous band. The relaxation happens in any case through the energy transfer. However, the radiation by emitting a photon is not the only option that the energy of the excited electron flows through. There are other channels like phonons. If the energy transfer process is radiative, this is called luminescence. And the channel is called as radiative. On the other hand, if the relaxation happens through the heat distribution, it is called as non-radiative channel. Another definition is about the type of excitation. If the system is excited by an external light source, then the radiation process is called photoluminescence. Statistical distribution of the electrons and holes in a solid changes the photoluminescence (PL) shape.

$$\left(\frac{dN}{dt}\right)_{radiation} = -AN = -\frac{N}{\tau_r}: Radiative emission rate$$
(3.19)
$$N(t) = N(0)e^{-At} = N(0)e^{-t/\tau_r}: Population at time t in the excited state$$
$$A_{i \to f}, \quad B_{i \to f}: Einstein coefficients$$

For a single isolated atom, $A_{i\to f}$ and $B_{i\to f}$ are equal but in case of a solid material these two coefficients are proportional, not equal, because phonon emission may occur as well. By taking these heat losses into account, the radiative emission rate will be diminised. This happens if non-radiative relaxation is faster than the radiative relaxation.

$$\left(\frac{dN}{dt}\right)_{total} = -N\left(\frac{1}{\tau_r} + \frac{1}{\tau_{nr}}\right): \quad \text{Total emission rate}$$
(3.20)

$$\eta_r = \frac{\text{radiative emission rate}}{\text{total emission rate}} = \frac{1}{1 + \tau_r / \tau_{nr}} \quad \text{Luminescent efficiency} \quad (3.21)$$

In order to built an efficient light emitting device, $\tau_r \ll \tau_{nr}$ should be satisfied.

COMPLEMENT 3B Molecular radiation

Atomic orbitals are characterized by quantum numbers (n, l, m, and s). Basically; energy, angular momentum, magnetic moments (vectorial components of the angular momentum) and spin properties of the electron engender variations on the wavefunction which gives a mathematical description of electron's position with time. In case of interaction between different atomic orbitals, they establish bond(s) and conjugated atoms form new orbitals for the combined system which is being *molecular orbitals* (MO). MOs can be categorized by bonding type (σ , π , etc.). Electrons of the consituent atoms in a molecule cause bonds between atoms. The highest energy level with electron is called *the highest occupied molecular orbital*, **HOMO**, and the first energy level above the HOMO is called as *the lowest unoccupied molecular orbital*, **LUMO**.

The ground state level has zero total spin quantum number due to the paired antiparallel spins. In case of an excitation, one of the electrons jumps up to the excited state and makes electrons unpaired which affects the total spin number as S = 0 or S = 1. If S = 0, the states are known as **singlets** and if S = 1, the states are known as **triplets**. This is crucial for the optical spectra that are scrutinized in this work with details.

The singlet-singlet transitions form the main mechanism for the absorption and emission. Excited state lifetime for the singlet state is around 1 - 10 ns (dipole allowed transition). However, the transition from an excited triplet state to a ground singlet state takes much more time than the transition between $S_1 \rightarrow S_0$.

Vibrational energy levels arise from the vibration of an atom around their bonds. Vibrational states change during the transition. These states are called **vibronic** states. Vibronic transitions are consist of four steps; absorption, non-radiative relaxation, emission and again a non-radiative relaxation as it is seen in figure 3.15.



Figure 3.15: a) Vibronic transition in a singlet-singlet system, b) four steps during a vibronic process (Franck-Condon principle), c) energy levels with molecular configurations for a diatomic molecule. (The images are taken from Fox, 2001)

Franck-Condon principle In molecules, electronic and nuclear components of a wavefunction are seperated. This is known as *Born-Oppenheimer approximation*. So, it is possible to draw energy diagrams versus the distance between nuclei of constituent atoms in a molecule (figure 3.15c). And electronic transitions occur much faster than the movement of the nuclei. As a result of this, the distance between two atoms is set as r_1 and r_2 before and after relaxation (figure 3.15b). The coordinates r_1, r_2 do not change during the absorption and emission (or vibronic transitions). Within the vibronic bands of the molecule, non-radiative relaxations take place. Due to these relaxations, emitted photon energy becomes smaller than the absorbed photon energy. This is why emission spectra are observed as red-shifted.

Fluorescence	$: S_1 \to S_0$	\implies High probability / short radiation lifetime
Phosphorescence	$: T_1 \to S_0$	\implies Low probability / long radiation lifetime

Rotational transitions	:	$\lambda > 100 \mu m,$	far infrared
Vibrational transitions	:	$\lambda \approx 1 - 100 \mu m,$	infrared
Electronic transitions	:	$\lambda < 1\mu m,$	ultraviolet and visible

COMPLEMENT 3C

Semiclassical atom-radiation interaction

Inadequacy of the Einstein's theory for transition probabilities of atom [9] brings detailed questions about light emission and absorption. So, Einstein's B coefficient can be explained with time-dependent quantum mechanics using Schrödinger equation. Normally, the atom-field interaction requires the second quantization or full quantum mechanical treatment so that both atom and electromagnetic field are quantized. However, semiclassical approach is enough to give a defitinion about atomic transitions.

Starting with time dependent Schrödinger's equation;

$$\hat{H}\psi(\boldsymbol{r},t) = i\hbar \frac{d\psi(\boldsymbol{r},t)}{dt}$$
(3.22)

For an isolated atom, Hamiltonian of the system only can be represented by sum of kinetic and potential energies of constituent particles. This gives stationary energy eigenvalues. If atom is a two-level system, the energy eigenvalues are E_1 and E_2 ;

$$\hat{H}_A \psi_1(\boldsymbol{r}) = E_1 \psi_1(\boldsymbol{r}) \tag{3.23}$$

$$\hat{H}_A \psi_2(\boldsymbol{r}) = E_2 \psi_2(\boldsymbol{r}) \tag{3.24}$$

Now, it is possible to define the *transition frecuency*, ω_0 , as

$$\hbar\omega_0 = E_2 - E_1$$

Electromagnetic field has time-varying electric and magnetic field components. That means the Hamiltonian now is time dependent.

$$\hat{H} = \hat{H}_A + \hat{H}_I \tag{3.25}$$

Actually, the total Hamiltonian is given as sum of atom, field and interaction Hamiltonian but again, field is not quantized here yet [39].

Time dependent wavefunction with superposition principle,

$$\psi(\boldsymbol{r},t) = C_1(t)\psi_1(\boldsymbol{r},t) + C_2(t)\psi_2(\boldsymbol{r},t)$$

And, Schrödinger's equation for interaction Hamiltonian,

$$\hat{H}_{I}(C_{1}\psi_{1} + C_{2}\psi_{2}) = i\hbar\left(\psi_{1}\frac{dC_{1}}{dt} + \psi_{2}\frac{dC_{2}}{dt}\right)$$
(3.26)

Multiply each side by ψ_1^* and integrate,

$$\psi_1^* \hat{H}_I (C_1 \psi_1 + C_2 \psi_2) = i\hbar \psi_1^* \left(\psi_1 \frac{dC_1}{dt} + \psi_2 \frac{dC_2}{dt} \right)$$
(3.27)

$$\int dV \psi_1^* \hat{H}_I (C_1 \psi_1 + C_2 \psi_2) = i\hbar \int dV \psi_1^* \left(\psi_1 \frac{dC_1}{dt} + \psi_2 \frac{dC_2}{dt} \right)$$
(3.28)

Use normalization and Dirac's notation,

$$\int dV |\psi(\mathbf{r}, t)|^2 = |C_1(t)|^2 + |C_2(t)|^2 = 1$$
(3.29)

$$\int dV \psi_1^* \hat{H}_I \psi_1 = \langle 1 | \hat{H}_I | 1 \rangle \tag{3.30}$$

$$i\hbar \frac{dC_1}{dt} = \langle 1|\hat{H}_I|1\rangle C_1 + \langle 1|\hat{H}_I|2\rangle C_2 e^{-i\omega_0 t}$$
(3.31)

Similarly for ψ_2

$$i\hbar \frac{dC_2}{dt} = \langle 2|\hat{H}_I|2\rangle C_2 + \langle 2|\hat{H}_I|1\rangle C_1 e^{-i\omega_0 t}$$
(3.32)

The wavefunction can be determined using C_1 and C_2 which are only time dependent.

Interaction Hamiltonian in case of an incoming electric field,

$$\hat{H}_{I} = \boldsymbol{\mu} \boldsymbol{E}$$
$$\hat{H}_{I} = e \boldsymbol{r_{i}} \boldsymbol{E_{0}} cos(\omega t)$$

Since \hat{H}_I is real with odd parity,

$$\langle 1|\hat{H}_{I}|1\rangle = \langle 2|\hat{H}_{I}|2\rangle = 0$$
$$\langle 1|\hat{H}_{I}|2\rangle = \langle 2|\hat{H}_{I}|1\rangle^{*}$$
$$\langle i|\hat{H}_{I}|f\rangle = eE_{0}M_{if}cos(\omega_{0}t)$$
$$\langle 1|\hat{H}_{I}|2\rangle = eE_{0}M_{12}cos(\omega_{0}t)$$

 M_{12} is the transition dipole matrix element. For the energy between two states of our two level-atom;

$$\hbar\nu = eE_0M_{12}$$

As a result, C_1 and C_2 are shown as,

$$\frac{dC_1}{dt} = -iC_2\nu\cos(\omega t)e^{-i\omega_0 t}$$
(3.33)

$$\frac{dC_2}{dt} = -iC_1\nu\cos(\omega t)e^{-i\omega_0 t}$$
(3.34)

Solution of this coupled expression yields a second order differential equation. Einstein's B coefficient can be found with this solution. If the atom is in its initial state at time t=0, the probability of finding atom at a later time requires square of norm of complex amplitude. So, initial state is $|1\rangle$ and the probability of getting an excited atom at a later time t is $|C_2|^2$ for B_{12} ;

$$B_{12} \propto |C_2|^2 / t$$
 (3.35)

Transition matrix element in general is written as,

$$\langle 1|\hat{H}_{I}|2\rangle = \frac{1}{2}eE_{0}M_{12}e^{-i\omega t} = \frac{1}{2}\hbar\nu e^{-i\omega t}$$

Finally, the transition rate, $1/\tau$, is given by [39],

$$\frac{1}{\tau} = |C_2|^2 / t = \frac{1}{2} \pi \nu^2 \delta(\omega_0 - \omega)$$
(3.36)

Fermi's golden rule, for a single atom, becomes,

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_{f} |\langle f | \hat{H}_I | i \rangle|^2 \delta(\omega_f - \omega_i)$$
(3.37)

or

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \int d\omega_f |\langle f | \hat{H}_I | i \rangle|^2 \delta(\omega_f - \omega_i)$$
(3.38)

CHAPTER 4

NANOANTENNA - QUANTUM EMITTER COUPLING

Spontaneous emission modification is the subject of this chapter. Metal nanoparticle alter the emission rates and excited state lifetime of the single photon emitter. In order to understand the dynamics which is critical, the formalism is given as an introduction to this chapter [73, 74, 75, 76].

Initial and final states The excited state and ground state of a two-level atom are given as;

 $|e\rangle, |g\rangle$

Atom is in excited state is represented as;

$$|i\rangle = |e\rangle \otimes |0\rangle$$

which says that while atom is excited, photon number is zero because there is no emission yet. The one-photon state is given by

$$|1_{(k,\mu)}\rangle = |1\rangle$$

where k is the propagation vector and μ is polarization. Using the formalism in previous chapter about number states, the final state is represented as;

$$|f\rangle = |g\rangle \otimes a_k^{\dagger}|0\rangle$$

Fermi's Golden Rule Using Heisenberg Picture (operators are time-dependent), the emission rate is expressed as;

$$\gamma = \frac{2\pi}{\hbar^2} |\langle f | \hat{H}_I | i \rangle|^2 \delta(\omega_i - \omega_f)$$
(4.1)



Figure 4.1: Transition from excited state to a set of final states. The figure is taken from Novotny, 2006.

Since we have a continuum of final states, the above expression should be sum over all final states;

$$\gamma = \frac{2\pi}{\hbar^2} \sum_{f} |\langle f | \hat{H}_I | i \rangle|^2 \delta(\omega_i - \omega_f)$$
(4.2)

$$|\langle f|\hat{H}_{I}|i\rangle|^{2} = \langle i|\hat{\mu}.\hat{E}|f\rangle\langle f|\hat{\mu}.\hat{E}|i\rangle$$
(4.3)

$|f\rangle\langle f| \rightarrow$ projection operator which is a scanner for f states

Interaction Hamiltonian is composed of contributions of atom and photon. Since electromagnetic field is also quantized in this picture, for fully quantum mechanical description, the electric field is express with an operator as well;

$$\hat{E} = \sum_{k} [E_k^{\dagger} \hat{a}_k(t) + E_k^{-} \hat{a}_k^{\dagger}(t)] \qquad \text{property of the photon}$$
(4.4)

$$\hat{\mu} = \mu |e\rangle \langle g| + \mu |g\rangle \langle e|$$
 property of the atom (4.5)

Here, electric field operator is composed of positive and negative field parts which are responsible for photon creation and annihilation. On the other side, the operator $\hat{\mu}$ implies with the first and second terms; absorption and emission photon, respectively.

Arranging above expressions, Fermi's expression turns into the following;

$$\gamma = \frac{2\pi}{\hbar^2} \sum_k [\mu \cdot (E_k^+ E_k^-) \cdot \mu] \delta(\omega_i - \omega_f)$$
(4.6)

$$E_k^{\ +} = \sqrt{\frac{\hbar\omega_k}{2\epsilon_0}} u_k, \qquad E_k^{\ -} = \sqrt{\frac{\hbar\omega_k}{2\epsilon_0}} u_k^* \tag{4.7}$$

As a result, decay rate is expressed as;

$$\gamma = \frac{2\omega}{3\hbar\epsilon_0} |\mu|^2 \rho_\mu(\vec{r}_0, \omega_0)$$

$$\rho_\mu(r_0, \omega_0) = \frac{6\omega_0}{\pi c^2} \left[\mathbf{n}_\mu . Im\{\overleftarrow{G}(r_0, r_0, \omega_0)\} . \mathbf{n}_\mu \right]$$
(4.8)

Partial local density of states, ρ_{μ} , represent the final photon states. The result is given above without intermediate steps [2]. Nevertheless, this expressions are quite enough to read physical dynamics through the computation and experiments that are listed at following sections.

The normal modes in electric field operators are solved through vectorial form Helmholtz equation and express oscillation modes [77]. Green's function, which is actually being a unit electric field response at a point in space, can be represented as a series of normal modes, u_k . However, quasinormal mode calculation is using different expression special to plasmon resonances. As a result, finding Green's function is enough to define all the other quantities related to our analysis.

$$\nabla \times \nabla \times \boldsymbol{u}_{\boldsymbol{k}} - \frac{\omega_k^2}{c^2} \boldsymbol{u}_{\boldsymbol{k}} = 0$$
(4.9)

$$\nabla \times \nabla \times \overleftrightarrow{G}(r_0, r, \omega_0) - \frac{\omega_k^2}{c^2} \overleftrightarrow{G}(r_0, r, \omega_0) = \overleftrightarrow{I} \delta(r_0 - r)$$
(4.10)

4.1 Computational investigation of the quantum emitter

According to Fermi's Golden Rule and fluctuation-dissipation theorem, continuous modes should be taken into account in order to investigate the quantum mechanical

description of an inhomogeneous lossy medium. It is also possible to consider the lossy medium as a continuous photonic reservoir.

It is showed in complement chapter that the quantum emitter is a radiating electric dipole. Normalized quantum mechanical decay rate is equal to the power radiated from a point dipole in an inhomogeneous environment [2]. The radiated power has to be normalized with the power in the absence of the inhomogeneous environment as well. With this method, some important features about the quantum mechanical system can be obtained in a remarkable way.

$$\frac{\gamma}{\gamma_0} = \frac{P}{P_0} \tag{4.11}$$

By starting with the classical radiation power rate of an electric dipole, it is possible to survey the effects of the inhomogeneous environment's contribution to the quantum emission. After that quantum mechanical concepts can be scrutinized through Fermi's Golden Rule. Green's function, local density of photonic state, quantum efficiency, radiative and non-radiative decay rates can be calculated.

First of all, the method of computation should be assured with a reliability check.

4.1.1 Reliability test - Comparison with FDTD results

An electric point dipole near a metal nanosphere is studied in this subsection. Normalized non-radiative and radiative decay rates of a point dipole are investigated. Together with these results, local density of state is calculated for the point where the electric dipole is located. In order to ensure that the results are reliable, the very first model is a remade one based on an FDTD simulation from Lumerical's application gallery¹.

Within this model, a nanosphere with 20 nm radius is embedded in an air domain. The material is selected as gold (Palik) for the nanosphere. The electric point dipole is located at z = 15 nm above the sphere's surface (figure 4.2). The dipole orientation is perpendicular to the surface along the z-direction. In mesh sizes, around the region between the point dipole and the metal nanosphere, it uses 5 nm for the first simulation with coarse mesh and 2.5nm for the second simulation with fine mesh.

¹ Application gallery > More examples > NanoPhotonics > Plasmonics > Fluorescent enhancement



Figure 4.2: Demonstration of geometries for Lumerical and COMSOL environments. Both are embedded in a rectangular simulation box.

Note that this is not an ordinary result comparison with another simulation program. Lumerical already checks the reliability in this model with theoretical calculations. If the result gives values between green and red lines in 4.3, it confirms the reliability. That is to say, the model built for this thesis is checked double; one check with the theoretical calculation and the other one is more precise comparison with the Lumerical results.

In COMSOL side, same geometry and position values are regenerated. The only differences is about the type of material. Within the COMSOL material library, Au-Palik is not available. For this reason, Au-Johnson is used. Furthermore, the mesh sizes are exaggerrated. For example, a 2x2x2 nm mesh box is placed above the MNP, so that the electric dipole is located at the center of this box and then the box is meshed with maximum 0.3 nm and minimum 0.1 nm element sizes. For the MNP, maximum 3 nm and minimum 1 nm element sizes are used. Remaining part of the geometry is adjusted with extra fine mesh. So, a third check is possible with the trends in mesh sizes. Therefore, one obvious result of the comparison arises about the computation time because of extremely fine mesh sizes. While the lumerical calculation takes a couple hours for fine mesh, the model prepared in COMSOL is lasted 42 hours, 27 minutes and 27 seconds. The reason of long computation time is not only mesh sizes but also parametric sweep with 2 nm step and larger simulation domain.



Figure 4.3: FDTD results of Lumerical. a) Normalized radiative decay rate with coarse mesh, b) normalized loss decay rate with coarse mesh, c) radiative decay rate with fine mesh, d) normalized loss decay rate with fine mesh.Blue lines are the results that are interested in. Green and red lines are the results for one mesh size closer and farther dipole position.

As a result, the model built in COMSOL is confirmed with the result of FDTD calculation. Moreover, mesh trends show that finer mesh causes decrement in both radiative and non-radiative graphs. Especially in (b) and (d) of the figure 4.3, the peak point of the blue line decreases from 55 to 35. This means that coarse mesh results gives more loss than the results with finer mesh. The figure 4.4 also confirms same effect.

About the quantum efficiency, the equation 3.21 in (Complement 3A) is used. The radiative decay rate values are normalized with the sum of loss decay rate values and radiative decay rate values for each wavelength.

As a summary, the power radiated from the point dipole is integrated over the boundaries of the small mesh box and the total simulation domain for loss decay rate and



Figure 4.4: FEM results of COMSOL. a) Normalized radiative decay rate with extremely fine mesh, b) normalized loss decay rate with extremely fine mesh.



Figure 4.5: Quantum efficiency of the point electric dipole above a gold nanosphere. a) FDTD with Lumerical, b) FEM with COMSOL.

radiation decay rate, respectively. Another simulation is run with only removing the MNP from the model and the power integration data are normalized with corresponding data set.

Green's function In the context of this thesis, Green's function is a knowledge capsule that contains unit electric field response of a radiating quantum system which can be either a scattering nanoparticle or a quantum emitter. In the presence of a nanoparticle, the Green's tensor gives the unit electric field response of the geometry. This is important because the electric field values are calculated already or it is potentially computable for any kind of geometry combination by considering the previous numerical models with reliability. Green's dyadic function is a 3x3 matrix which can be interpreted physically in terms of dipole orientation and components of the radiated electric field by the dipole.

$$\overleftrightarrow{G} = \begin{bmatrix} G_{xx} & G_{yx} & G_{zx} \\ G_{xy} & G_{yy} & G_{zy} \\ G_{xz} & G_{yz} & G_{zz} \end{bmatrix}, \qquad G(r, r_0) = \frac{E(r)c^2\epsilon_0}{\omega^2\mu}$$
(4.12)

The physical meaning of the above expression, $G(r, r_0)$ is that a function measuring the electric field at r emitted by the source located in r_0 . So, the physical meaning of the matrix is little bit more complicated, it may be interpreted as electric field components radiated by each dipole orientation at a single point in space. For example, G_{yz} is the z-component of the electric field which is radiated by a dipole oriented along y-direction.

In Fermi's Golden Rule for a single isolated atom, $\delta(\omega_i - \omega_f)$ expresses the transition between specific frequencies. In case of many atoms and many photons, the final states become continuous. The number of final single-photon states are called **photonic density of states** (LDOS), $\rho(r_0, \omega_0)$, where r_0 is the position of the two-level quantum emitter.

Partial LDOS is defined as;

$$\rho_{\mu}(r_0,\omega_0) = \frac{6\omega_0}{\pi c^2} \left[\mathbf{n}_{\mu}.Im\{\overleftarrow{G}(r_0,r_0,\omega_0)\}.\mathbf{n}_{\mu} \right]$$
(4.13)

and the total density of photonic state is the total electromagnetic modes per unit volume and unit frequency at a single location, r_0 ;

$$\rho(r_0,\omega_0) = \frac{6\omega_0}{\pi c^2} \frac{1}{3} \left[Im\{\overleftrightarrow{G}_{xx}(r_0,r_0,\omega_0) + \overleftrightarrow{G}_{yy}(r_0,r_0,\omega_0) + \overleftrightarrow{G}_{zz}(r_0,r_0,\omega_0)\} \right]$$
$$= \frac{2\omega_0}{\pi c^2} Im\{Tr\left[\overleftrightarrow{G}_{(r_0,r_0,\omega_0)}\right]\}$$
(4.14)

For free space;

$$\rho_0 = \frac{\omega_0}{\pi^2 c^3} \quad and \quad \gamma_0 = \frac{\omega_0^3 |\vec{\mu}|^2}{3\pi\epsilon_0 \hbar c^3}$$
(4.15)

where $\mu = \langle f | \hat{\mu} | i \rangle$ is the transition dipole matrix element.

One more time, a gold sphere-point dipole system is considered. Two types of excitation are made. First one is the point excitation. A point dipole source radiates in the vicinity of a nanoparticle. And the second one is the far field excitation. Therefore, this is a plane wave source.

$$\overleftrightarrow{G}(\mathbf{r}_0, \mathbf{r}, \omega) = \overleftrightarrow{G}_H(\mathbf{r}_0, \mathbf{r}, \omega) + \overleftrightarrow{G}_S(\mathbf{r}_0, \mathbf{r}, \omega)$$
(4.16)



Figure 4.6: Demonstration of homogeneous and scattering part of Green's function.

The point source and the observation point for the Green's function can be in same or different medium. The method of scattering superposition is used [78]. If the source and the observation point are in same medium and there is no other scatterer around them, then only the homogeneous part of the Green's function survive. However, whenever another scatterer object is placed around them, this time total Green's function must be taken into account. One another possible case is about being in different media. This time only the scattering part of equation 4.16 survives.

After that the Green's function enters to the LDOS expression by a vector multiplica-

tion;

$$\mathbf{n}_{\mu} \overleftarrow{G} (\mathbf{r}_{0}, \mathbf{r}, \omega) \mathbf{n}_{\mu} = \begin{bmatrix} n_{x} & n_{y} & n_{z} \end{bmatrix} \begin{bmatrix} G_{xx} & G_{yx} & G_{zx} \\ G_{xy} & G_{yy} & G_{zy} \\ G_{xz} & G_{yz} & G_{zz} \end{bmatrix} \begin{bmatrix} n_{x} \\ n_{y} \\ n_{z} \end{bmatrix}$$
(4.17)

For a point dipole oriented along z-direction located above a sphere in z-axis,

$$\mathbf{n}_{z} \overleftarrow{G} (\mathbf{r_{0}}, \mathbf{r_{0}}, \omega) \mathbf{n}_{z} = \begin{bmatrix} 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} G_{xx} & G_{yx} & G_{zx} \\ G_{xy} & G_{yy} & G_{zy} \\ G_{xz} & G_{yz} & G_{zz} \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$
$$= G_{zz}$$
(4.18)

Since the observation point is the place where the dipole emitter is located, the Green's function is expressed as $\overleftrightarrow{G}(\mathbf{r}_0, \mathbf{r}_0, \omega)$. In addition to that scattering component of the Green's function is given by G_{zz} . With another word, one wants to find the response of scattering fields from the gold nanosphere on the point that the dipole is located ($\mathbf{r} = \mathbf{r}_0$). By taking imaginary part of this, it is possible to obtain local density of photonic state in dipole's position. As an extra example, one another scenario can be considered so that a probe point which is located at any point in space other than dipole's position (also out of the gold nanosphere). In this case, the homogeneous part is needed together with the scattering component.

4.1.2 Reliability test - Comparison with QNM calculations

In this part, a model is reproduced by considering two different letters [3, 4]. A gold nanorod, with 15 nm radius and 100 nm length, is placed in a medium with n=1.5 refractive index. The quantum emitter is located 10 nm apart on the length axis of the cylinder. The dipole orientation is set along the x direction.

This time $2 nm^3$ mesh box or a monitoring box is used for the loss calculation. Outer surface of the physical domain is selected as a radiative monitor. In addition to that a point probe is located in the point of quantum emitter for the Green's function.

Both works [3, 4] present quasi normal mode (QNM) calculation method which can be found in the appendix of the paper [79]. In order to avoid distracting the main purpose of this part, the QNM method details are not presented.



Figure 4.7: Model geometry and results from papers. a) Quantum dot at r_a in the vicinity of gold nanorod and Purcell factor graph [3]. b) Same geometry and parameters from another letter [4].



Figure 4.8: COMSOL results of the regenerated model. a) Purcell factor in frequency domain, b) wavelength domain in order to compara with corresponding letters cited above.

The quantum emitter is only located at r_a . In figure 4.7-a, it is given extra quantum dot configurations. The comparison is made between figure-4.7 and figure-4.8. One

important point that should be concerned is the difference between normalized decay rate and the Purcell factor. At first glance, both look same but they are not. The former one is only the ratio of two cases in the absence and the precence of the nanoparticle. However, Purcell factor includes the refractive index effect. The normalized decay rate should be multiplied by $(\frac{1}{n})$.

4.1.3 Quantum emitter near a silver hemisphere

The simulations above demonstrate radiative and non-radiative channels for the specific emitter state and the geometry that are presented in the cited letters. Also, it is a comparison for a reliability check. From this point on, structures are nanoislands that are explained previously. With exactly same manner, only by changing geometry and position of the emitter, radiative and non-radiative contributions are computed.

Once again, the non-radiative part expresses only photon losses, not phonon-losses. In order to take into account phonon-losses, probably a heat transfer module should be employed within COMSOL Multiphysics. As a note for those who want to compute this, the results of electromagnetic module should be used to calculate the electromagnetic energy that is transferred from the quantum emitter to the plasmon particle. This energy is the initial value for the heat transfer calculation. As a result, one can compute the Joule losses which corresponds to phonon losses.

4.1.3.1 Spectral effect

Computations are made by wavelength sweeping since the spectral response of inhomogeneous environment is investigated. In order to observe two different regimes, 30 nm and 120 nm diameter particles are modelled and compared for each case.

The Purcell factor is known for the weak coupling regime as, [4]

$$F = \frac{3}{4\pi^2} (\frac{\lambda_0}{n})^3 \frac{Q}{V}$$
(4.19)

The term λ_0/n is the resonance wavelength in the material with refractive index of n. Quality factor (Q) and the mode volume (V); these factors are main tools for manipulation of any quantum emitter located in a resonant medium. The quality factor is directly about the resonator's itself. However the mode volume, V, is an electromagnetic quantity [80] that measures the local density of photonic states while it is known as a physical volume for dielectric cavities.

Any field distribution found in the computation is used to calculate Purcell factor with spectral mismatches. This is necessary because plasmon cavities are highly dissipative systems. So,metal nanostructures have common problems about radiative leakage, absorption and material dispersion. The expression above 4.19 is for an ideal situation. In case of any mismatch, Purcell factor expression can be represented as; [4]

$$\frac{\Gamma}{\Gamma_0} = F \frac{\omega_0^2}{\omega^2} \frac{\omega_0^2}{\omega_0^2 + 4Q^2(\omega - \omega_0)^2}$$
(4.20)

- Γ : Spontaneous decay rate into the cavity mode
- Γ_0 : Spontaneous decay rate into the cavity mode
- $Q: \ensuremath{\mathsf{Quality}}$ factor of the cavity
- ω_0 : Frequency of the resonant medium
- $\omega:$ Frequency of the emitter

If the equation is regulated to obtain a proper expression for analytical calculation in terms of wavelengths,

$$F = \frac{\Gamma}{\Gamma_0} \frac{\omega^2}{\omega_0^2} \frac{\omega_0^2 + 4Q^2(\omega - \omega_0)^2}{\omega_0^2}$$

$$F = \frac{\Gamma}{\Gamma_0} \frac{\omega^2}{\omega_0^2} \left(\frac{4Q^2(\omega - \omega_0)^2}{\omega_0^2} + 1 \right)$$

$$\omega = \frac{2\pi c}{\lambda}, \qquad \omega_0 = \frac{2\pi c}{\lambda_0}$$

The modified Purcell factor in terms of wavelength;

$$F = \frac{\Gamma}{\Gamma_0} \frac{\lambda_0^2}{\lambda^2} \left(4Q^2 \lambda_0^2 \left(\frac{1}{\lambda} - \frac{1}{\lambda_0} \right)^2 + 1 \right)$$
(4.21)

The variable F in the above equation is substituted by the expression in equation 4.19,

$$\frac{3}{4\pi^2} \left(\frac{\lambda_0}{n}\right)^3 \frac{Q}{V} = \frac{\Gamma}{\Gamma_0} \frac{\lambda_0^2}{\lambda^2} \left(4Q^2 \lambda_0^2 \left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)^2 + 1 \right)$$
$$\frac{\lambda_0}{n^3} \frac{1}{V} = \frac{4\pi^2}{3} \frac{\Gamma}{\Gamma_0} \frac{1}{\lambda^2} \left(4Q \lambda_0^2 \left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)^2 + \frac{1}{Q} \right)$$
$$\frac{1}{V} = \frac{4\pi^2}{3} \frac{\Gamma}{\Gamma_0} \frac{1}{\lambda^2} \left(4Q \lambda_0^2 \left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)^2 + \frac{1}{Q} \right) \frac{n^3}{\lambda_0}$$
$$= \frac{4\pi^2}{3} \frac{\Gamma}{\Gamma_0} \frac{1}{\lambda^2} \left(4Q \left(\frac{(\lambda_0 - \lambda)^2}{\lambda^2}\right) + \frac{1}{Q} \right) \frac{n^3}{\lambda_0}$$
$$= \frac{4\pi^2 n^3}{3} \frac{\Gamma}{\Gamma_0} \frac{1}{\lambda^2 \lambda_0} \left(\frac{4Q^2 \left(\frac{(\lambda_0 - \lambda)^2}{\lambda^2}\right) + 1}{Q} \right)$$
$$= \frac{4\pi^2 n^3}{3} \frac{\Gamma}{\Gamma_0} \frac{1}{\lambda^2 \lambda_0} \left(\frac{4Q^2 (\lambda_0 - \lambda)^2 + \lambda^2}{\lambda^2 Q} \right)$$

In order to calculate spectral mismatches, the mode volume expression becomes,

$$V = \frac{3}{4\pi^2 n^3} \frac{\Gamma_0}{\Gamma} \left(\frac{\lambda_0 \lambda^4 Q}{4Q^2 (\lambda_0 - \lambda)^2 + \lambda^2} \right)$$
(4.22)

The mode volume is a complex electromagnetic quantity which always has been considered in literature as spatial integration of the electromagnic energy. However, it is made only at a point where the intensity has the maximum value. This put a constraint for plasmonic cavities because they are dissipative open cavities. The quantum emitter can be located at any point around a particle. At this point, it is important to find LDOS of the point where quantum emitter is located. Any deviations including resonance wavelength are calculated from the equation 4.22. The real and imaginary parts are responsible for on and off resonances. Re(V) emphasizes the on resonances therefore supports the radiative part while the Im(V) emphasizes the off resonances. In other words, the imaginary part is corresponded by the non-radiative LDOS and the real part is corresponded with radiative LDOS.

Things to do;

- 1) Obtain non-radiative decay rates and normalize,
- 2) Obtain radiative decay rates and normalize,
- 3) Obtain the total normalized decay rates and quantum efficiency values,
- 4) Calculate Purcell factor analytically using item-3,

5) Calculate mode volume deviations from the resonance wavelength using item-1,2 for real and imaginary parts,



6) Use Re(V) and Im(V) to obtain rLDOS and nonrLDOS respectively.

Figure 4.9: COMSOL results for point dipole in the vicinity of 5 nm radius hemisphere. a) Normalized radiative decay rate, b) normalized loss decay rate, c) quantum efficiency, d) total normalized loss decay rate. The polarization of the dipole is along the x-direction which is perpendicular to the nanoparticle.

The figure 4.10 shows the computation results for r=15 nm structure and normalized decay rates are presented with quantum efficiencies. For two different spatial position of the electric dipole is computed. At first, 5 nm away from the nanoparticle surface and then 10 nm away from the surface are considered. The figure 4.10-d gives the total normalized decay rates. Currently, this yields the Purcell factor. In the literature it is found as the summation of radiative and nonradiative normalized decay rates.

However, only specific quality factor values are available for plasmon cavities due to specific resonance frequency.



Figure 4.10: COMSOL results for point dipole in the vicinity of 15 nm radius hemisphere. a) Normalized radiative decay rate, b) normalized loss decay rate, c) quantum efficiency, d) total normalized loss decay rate. The polarization of the dipole is along the x-direction which is perpendicular to the nanoparticle.

4.2 Experimental coupling of an hBN defect center with Ag-nanoislands

In this experiment, after all procedures about substrate cleaning and HF treatment, hBN solution (Graphene Supermarket) is diluted around 40-50 % with ethanol. 50 μl solution is drop casted on the substrate and annealed around 350 °C for 20 minutes. Under a high NA, 50x-objective and camera, surface is scanned by skimming through microstuructures.

Once an hBN bulk silhouette is captured, a detailed searching process continues with photoluminescence measurement by changing white light source to a 532 nm CW laser. This time 1.5 μm laser spot is scanned over 6-8 μm bulk by 100 nm steps. Meanwhile, captured spectrum for each step is observed in order to catch a PL spectrum which is corresponding to a potential defect center. If the PL spectrum is bright enough, stable and isolated from other peaks, then the defect is being hunted. Also, a sort of asymmetry on the PL shape and a phonon sideband at the corresponding wavelength are other factors to make sure that it is a defect center.



Figure 4.11: Tilted scanning electron microscope image of Ag-nanoislands on hBN flakes

About the size distribution of particles, it should be stated that the size distribution is not uniform. The substrate effects the stability and driving force which causes different void formation. As it is observed from scanning electron microscope images,
particle size tends to be smaller than those are formed on silicon.



Figure 4.12: Scanning electron microscope image of a) the laser scribed addressing number, b) the selected hBN bulk (the inset: optical microscope image of same bulk), c) the selected bulk in $1\mu m$ scale surrounded by silver nanoislands. A 3d demonstration of Ag-nanoparticles and an hBN bulk at the bottom-right.

4.2.1 Smaller particles' effect

The results of experiments and simulations that are made in chapter-2 are used here in order to decide size of nanoparticles. So, for smaller particle regime, the mean value of statistics of particle size are given in figure 4.13.

In this subsection, studied defect has 663 nm spectral peak position. Phonon side band of the defect is around 729 nm as it is seen in figure 4.14. The peak is at 574 nm is belonging to hBN with phonon side band at 623 nm. Other peaks may be corresponding to other defects or phonon side band of the defects which are located out of the spectrum at higher energies.

Angled-resolved measurements show that the dipole emission is not destroyed by nanoantennas. However, the dipole orientation is shifted. This result is computationally confirmed as well at the following section. The meaning of this angle shift is



Figure 4.13: SEM image of dashed circle region in figure 4.12-c. The histogram shows the particle size statistics. (Gwyddion image analysis)



Figure 4.14: Normalized spectra of the spot (dashed circle 4.12-c). The black and red lines are for only hBN and with Ag nanoparticles, respectively.

relevant to location of the defect center relative to the plasmon particle which is participated to the interaction. One another interpretation about this, using angle-resolved measurement of a quantum emitter coupled with nanoislands, one may approximately determine the location of it using particular computation results.



Figure 4.15: Angled-resolved measurement of the defect-663nm. a) Before baseline substraction spectra for scanned HWP angles, b) polar plot with cos^2 fit function

Power-resolved photoluminescence results are actually expected to observe enhanced photon emission. The results in figure-4.16 shows that the intensity of the emission is reduced.Smaller particles, around 10-40 nm diameter, are in absorption dominant regime. So the quenching is very high. One may ask why smaller particles are used by expecting enhancement. Especially the simulation results are figured out in chapter-2. Well, the reason is obvious. Smaller redius particles have higher quality factors. The problem is about spatial coupling of these structures. Although the light-matter interaction is stronger compared to the larger sizes, spatial coupling ability is weak. Furthermore, the resonance wavelength of smaller diameters are smaller than others. If the resonance is occured at around 350-400 nm, the most probably, the resonance coupling is out of tune. So, the quality factor gets very small values. As a result of this, with very high mode volume and out of resonance conditions engender reduction in radiative emission rate.

On the other hand time-resolved photoluminescence results exhibits lifetime reduction, around 35%. Reduction in lifetime due to inverse proportional relation with emission rates means that an enhancement should have been occured. However, re-



Figure 4.16: Power series for the defect-663 nm. The square-blue data show power series collected from hBN Raman peak.

laxations are occured through nonradiative channels and photons can not emitted. Therefore they can not be observed radiatively at the far-field distances.

In both graph of spectra and power series, SERS (Surface Enhanced Raman Spectroscopy) effect can be seen. Not a single quantum system's response but collective response of all molecules is enhanced. Interaction of silver nanoantennas with hBN lattice increase the Raman peak of hBN molecules. As it is expected, SERS effect is observed for hBN bulks.

Finally, the defect center is demonstrated that emitted photons are antibunched in figure-4.18. This is the proof that investigations have been made with a real singlequantum system. As a result, single quantum system is expected to emit one photon at a time. Another result of $g^2(\tau)$ graph is that the plasmon resonances do not kill the emission statistics by a random sampling or any other mechanism because the measurement is performed after MNPs.



Figure 4.17: Lifetime of the defect center before and after MNPs for the defect-663 nm.



Figure 4.18: Pulsed second-degree correlation measurement for the defect-663 nm.



Figure 4.19: Scanning electron microscope image of the laser scribed addressing number-52. An unknown sign structure at the corner of number 2. Optical microscope image with 50x objective. At the bottom line: The selected hBN bulk (the inset: optical microscope image of same bulk). The selected bulk in a $1.3\mu m$ circle that shows laser spot area. Tilted image of same region at the bottom-right.

4.2.2 Larger particles' effect

Same experimental procedures are followed except particle size. On hBN dewetting hindered easy fabrication of large MNPs. Normally, it is easier to fabricate larger ones but it became an obstacle. After experimental practices, by manipulating annealing temperature and increasing film thicknesses, relatively larger particles are obtained on hBN flakes.

At the first measurement without nanoantennas, almost a perfect peak is hunted at 615-616 nm. In order to check that it is a defect, the PSB is confirmed. After MNP effect, other hunted defects pointed that an obvious enhancement has occured however the defect emissions of them were not strong enough. Consequently, they are either lost or stayed under the enhanced background due to enhanced hBN surface. A clean an isolated defect peak is then a requirement for this type of coupling.

It can be seen easily from the figure 4.20 that enhancement has occured. However, for a more quantitative analysis, power series data analysis have been made in figure-



Figure 4.20: Spectra for the defect-616 nm. The red and black lines are for with and without Ag nanoantennas, respectively.



Figure 4.21: Larger particle size statistics over the region where the measurements have been made.

4.22. Apparently the saturation intensity of the defect center is increased around 2.5 times.

For the time-resolved measurements, a striking result can be seen in figure-4.23. The



Figure 4.22: Power series for the defect-616 nm.



Defect - 615 nm with large MNPs

Figure 4.23: Time-resolved measurements for the defect-616 nm.

lifetime of the defect-616nm is reduced around 98%. The lifetime reduction is remarkably high. This brings a question about the measurement resolution. Instrument response (IRF) is given with the purple histogram in figure-4.23. Also, the lifetime of the defect without particles presents that it is a two-level system. However, after MNPs, it is observed as three level system. One may interpret it with metastable states or intersystem crossings. Another comment can be made that there is more than one nanoantenna around and it is highly possible to interact with two of them. As a scenario, the defect is located in the vicinity of a nanoantenna very closely and this configuration causes the 16ns-to-270ps reduction. Addition to that, another nanoantenna is located near to the defect causes the 16ns-to-11ns reduction. The latter one may be a smaller particle formed on hBN.



Figure 4.24: Normalized power map on 3D nanoisland surface. There is no substrate. The particles are embedded inside air. The reddish and purplish figures are belonging to 15 nm and 60 nm radius nanoantennas. The image at the corner, with a large box, show 48 nm separation in a scale multiplied 100 times.

4.2.3 Computations with experimental findings

Two cases which are studied in previous section are modeled. Here, spatial effect is studied. This is the mode volume related part of the Purcell effect. The spectral position is already defined with the hunted defects' emission wavelength. For this reason, computations are done at single frequency. The controlled parameter is the separation, s, which is describing the quantum emitter's position from the bottom surface of the nanoisland.



Figure 4.25: Computed radiative and nonradiative decay rates as a function of point dipole separation.

These results reflect the inhomogeneous environment's response. So, they are not related to the hBN defect properties at all. The normalized values emhasize that the dipole moment term is cancelled out with its corresponding free-space values. Only the one nanoisland's tendencies for a specific dipole emitter position.

In the first model, 15 nm radius hemisphere embedded in air is modelled. The dipole emitter is located on the bottom along the x-axis. Similar to the methods of previously told mesh and modelling features, 60 nm radius is prepared in another model. For both model, at first, a free space reference computations have been run for each configuration of the quantum emitter. After that, 663 nm and 616 nm point dipole excitations for 30 nm and 120 nm diameters, respectively are performed.



Figure 4.26: Quantum efficiency and Purcell factor for two cases as a function of point dipole separation

Radiative contribution of 120nm-diameter is around 110 while the smaller one is only about 17 for 1 nm separation. One should remember that these are already out of tune from the silver resonances. Therefore, high nonradiative decay rates are quite understandable.

Since the point dipole gets away from the 30 nm particle's surface, quantum efficiency is increased up to 8 nm separation. An ultimate result concluded from FEM results that larger particle has a larger Purcell factor and radiative rates. This is actually the main theme in supporting the experimental findings.



Figure 4.27: Color maps. Blue-top: Power for dipole-orientation shift effect. Purplebottom: Electric field norm for the quantum emitter-nanoantenna hybrid system.

Finally, the polarization-angle shift when the dipole emitter gets closer to the nanoantenna can be seen in figure-4.27. This is an important result confirming the experiments. As an idea, it may be possible to define defect center position in two dimensional materials using plasmon nanoislands. Dipole orientation shifts and Purcell enhancement values in computations can be tuned by adjusting them according to values which are obtained from experiments. Obtained configuration may give the information about the actual defect location.

CHAPTER 5

CONCLUSION

In summary, I demonstrate that plasmon nanoantennas are used as nanocavities. Their quality factors are weak but mode volumes are much better compared to dielectric photonic cavities. With a proper coupling conditions, plasmonic nanocavities are remarkable candidates for quantum emitter coupling applications.

I experimentally showed that hBN defect centers exhibit non-classical light emission. They are single-photon emitters at room-temperature. Ultra brightness and photostability features of hBN colour centers are presented. In contrast to 3D material defect centers, hBN defects are embedded in 2D monolayers or multilayers. I showed that coupling and light harvesting of them is quite easy and applicable. Only with a cheap protection environment, even after two months, they are extremely stable. Moreover, during 'after-MNP effect' experiments, hBN defect centers are exposed to temperature levels around 300-400°C in Nitrogen tube furnace. They are still survived in that high temperature levels.

Another result I present is that plasmonic nanoantennae alter the polarization pattern of quantum emitters. Quantum emitter's separation parameter correlated to the shift in polarization orientation angle of the hybrid system. This phenomenon is demonstrated experimentally and computationally. However, all of them are done in two dimensions. That is to say, the emitter may be located in a level which is above or under the nanoantenna. In this case, Purcell factor may be used to infer position of the QE in the third dimension. So, for the first time I propose the idea that exact positions of defect centers in 2D materials may be determined using plasmonic nanoislands with a nanometer resolution. The asymmetric shape of hemispheroids is the key feature to realize this idea. I demonstrate the cheapest method for plasmon nanocavity coupling with a quantum emitter. Other cheap and simple methods are also experienced. The Fischer-Net structures are not simple to fabricate but more difficult to couple randomly. On the other hand, chemically synthesized metal nanoparticles are used but almost no proper coupling is observed. The dewetting thin film technique provides that all the surface is covered by nanoparticles. As a result, it is almost impossible to find an uncoupled fluorescent center with MNP. So, experiments showed that efficiency of re-finding a defect center that coincidents an antenna is around 10-20%. This is a perfect result because an automated system dedicated only for this job in the future can easily find any defect center coupled with nanoantennas.

Ultimately, hexagonal Boron Nitride defect centers are remarkable structures for single-photon emission. They can easily be coupled with a cavity or a waveguide. Also, room temperature operation is one of the most crucial advantegeous of them. Wide range of emission frequency option provides a rich application range. Efforts on the coupling of hBN fluorescent centers with nanocavities brings exciting results as well as technical obstacles. Using Purcell factor as a representation of spectral, spatial and polarization match of the emitter and the resonant medium, it is easy to modify and improve the performance of the fluorescent emission of hBN defects.

REFERENCES

- S. A. Tawfik, S. Ali, M. Fronzi, M. Kianinia, T. T. Tran, C. Stampfl, I. Aharonovich, M. Toth, and M. J. Ford, "First-principles investigation of quantum emission from hbn defects," *Nanoscale*, vol. 9, pp. 13575–13582, 2017.
- [2] L. Novotny and B. Hecht, *Principles of Nano-Optics*. Cambridge University Press, 2006.
- [3] R.-C. Ge and S. Hughes, "Quantum dynamics of two quantum dots coupled through localized plasmons: An intuitive and accurate quantum optics approach using quasinormal modes," *Phys. Rev. B*, vol. 92, p. 205420, Nov 2015.
- [4] 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.*, vol. 110, p. 237401, Jun 2013.
- [5] M. A. Nielsen and I. L. Chuang, "Quantum computation and quantum information," 2000.
- [6] C. Kurtsiefer, S. Mayer, P. Zarda, and H. Weinfurter, "Stable solid-state source of single photons," *Physical review letters*, vol. 85, no. 2, p. 290, 2000.
- [7] T. T. Tran, K. Bray, M. J. Ford, M. Toth, and I. Aharonovich, "Quantum emission from hexagonal boron nitride monolayers," *Nature Nanotechnology*, vol. 11, pp. 37 EP –, Oct 2015.
- [8] M. K. E. L. Planck, "Zur Theorie des Gesetzes der Energieverteilung im Normalspectrum," Verhandl. Dtsc. Phys. Ges., vol. 2, p. 237, 1900.
- [9] A. Einstein, "Zur quantentheorie der strahlung," *Phys. Z.*, vol. 18, pp. 121–128, 1917.
- [10] P. A. M. Dirac and N. H. D. Bohr, "The quantum theory of the emission and absorption of radiation," *Proceedings of the Royal Society of London. Series A*,

Containing Papers of a Mathematical and Physical Character, vol. 114, no. 767, pp. 243–265, 1927.

- [11] E. M. Purcell, "Spontaneous emission probabilities at radio frequencies," *Physical Review*, vol. 69, p. 681, 1946.
- [12] G. Solomon, M. Pelton, and Y. Yamamoto, "Modification of spontaneous emission of a single quantum dot," *physica status solidi* (a), vol. 178, no. 1, pp. 341– 344.
- [13] D. E. Chang, A. S. Sørensen, P. R. Hemmer, and M. D. Lukin, "Quantum optics with surface plasmons," *Phys. Rev. Lett.*, vol. 97, p. 053002, Aug 2006.
- [14] T. K. Sarkar, M. N. Abdallah, M. Salazar-Palma, and W. M. Dyab, "Surface plasmons-polaritons, surface waves, and zenneck waves: Clarification of the terms and a description of the concepts and their evolution.," *IEEE Antennas and Propagation Magazine*, vol. 59, pp. 77–93, June 2017.
- [15] M. Gross and S. Haroche, "Superradiance: An essay on the theory of collective spontaneous emission," *Physics reports*, vol. 93, no. 5, pp. 301–396, 1982.
- [16] P. Goy, J. M. Raimond, M. Gross, and S. Haroche, "Observation of cavityenhanced single-atom spontaneous emission," *Phys. Rev. Lett.*, vol. 50, pp. 1903–1906, Jun 1983.
- [17] K. J. Vahala, "Optical microcavities," *Nature*, vol. 424, pp. 839 EP –, Aug 2003.
- [18] J.-M. Gérard and B. Gayral, "Strong purcell effect for inas quantum boxes in three-dimensional solid-state microcavities," *Journal of lightwave technology*, vol. 17, no. 11, pp. 2089–2095, 1999.
- [19] E. Abbe, "Beiträge zur theorie des mikroskops und der mikroskopischen wahrnehmung," Archiv für mikroskopische Anatomie, vol. 9, pp. 413 – 468, 2009.
- [20] G. M. Akselrod, C. Argyropoulos, T. B. Hoang, C. Ciracì, C. Fang, J. Huang, D. R. Smith, and M. H. Mikkelsen, "Probing the mechanisms of large purcell enhancement in plasmonic nanoantennas," *Nature Photonics*, vol. 8, pp. 835 EP –, Oct 2014.

- [21] E. J. R. Vesseur and A. Polman, "Controlled spontaneous emission in plasmonic whispering gallery antennas," *Applied Physics Letters*, vol. 99, no. 23, p. 231112, 2011.
- [22] T.-l. Liu, Plasmonic Cavities for Enhanced Spotaneous Emission. PhD thesis, 2013.
- [23] P. B. Johnson and R. W. Christy, "Optical constants of the noble metals," *Phys. Rev. B*, vol. 6, pp. 4370–4379, Dec 1972.
- [24] A. E. Krasnok, I. S. Maksymov, A. I. Denisyuk, P. A. Belov, A. E. Miroshnichenko, C. R. Simovski, and Y. S. Kivshar, "Optical nanoantennas," *Physics-Uspekhi*, vol. 56, no. 6, p. 539, 2013.
- [25] G. Colas des Francs, S. Derom, R. Vincent, A. Bouhelier, and A. Dereux, "Mie Plasmons: Modes Volumes, Quality Factors, and Coupling Strengths (Purcell Factor) to a Dipolar Emitter," *International Journal of Optics*, vol. 2012, p. 8, 2012.
- [26] C. Bohren and D. R. Huffman, Absorption and Scattering of Light by Small Particles. Wiley Science Paperback Series, 1998.
- [27] V. Giannini, A. I. Fernández-Domínguez, S. C. Heck, and S. A. Maier, "Plasmonic nanoantennas: Fundamentals and their use in controlling the radiative properties of nanoemitters," *Chemical Reviews*, vol. 111, no. 6, pp. 3888–3912, 2011. PMID: 21434605.
- [28] L. Rayleigh, "On the instability of jets," *Proceedings of the London mathemati*cal society, vol. 1, no. 1, pp. 4–13, 1878.
- [29] A. L. Yarin, A. Oron, and P. Rosenau, "Capillary instability of thin liquid film on a cylinder," *Physics of Fluids A: Fluid Dynamics*, vol. 5, no. 1, pp. 91–98, 1993.
- [30] W. W. Mullins, "Theory of thermal grooving," *Journal of Applied Physics*, vol. 28, no. 3, pp. 333–339, 1957.
- [31] E. Jiran and C. V. Thompson, "Capillary instabilities in thin films," *Journal of Electronic Materials*, vol. 19, pp. 1153–1160, Nov 1990.

- [32] C. V. Thompson, "Solid-state dewetting of thin films," Annual Review of Materials Research, vol. 42, pp. 399–434, 2012.
- [33] E. Thouti, N. Chander, V. Dutta, and V. K. Komarala, "Optical properties of ag nanoparticle layers deposited on silicon substrates," *Journal of Optics*, vol. 15, no. 3, p. 035005, 2013.
- [34] S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green, "Surface plasmon enhanced silicon solar cells," *Journal of Applied Physics*, vol. 101, no. 9, p. 093105, 2007.
- [35] T. Temple, G. Mahanama, H. Reehal, and D. Bagnall, "Influence of localized surface plasmon excitation in silver nanoparticles on the performance of silicon solar cells," *Solar Energy Materials and Solar Cells*, vol. 93, no. 11, pp. 1978 – 1985, 2009.
- [36] I. Tanyeli, H. Nasser, F. Es, A. Bek, and R. Turan, "Effect of surface type on structural and optical properties of ag nanoparticles formed by dewetting," *Optics express*, vol. 21, no. 105, pp. A798–A807, 2013.
- [37] L. Novotny, "Effective wavelength scaling for optical antennas," *Phys. Rev. Lett.*, vol. 98, p. 266802, Jun 2007.
- [38] M. Scully and M. Zubairy, *Quantum Optics*. Cambridge University Press, 1997.
- [39] R. Loudon, *The quantum theory of light*. Oxford science publications, Clarendon Press, 1983.
- [40] M. Fox, *Quantum Optics: An Introduction*. Oxford Master Series in Physics, OUP Oxford, 2006.
- [41] F. Diedrich and H. Walther, "Nonclassical radiation of a single stored ion," *Phys. Rev. Lett.*, vol. 58, pp. 203–206, Jan 1987.
- [42] D. B. Higginbottom, L. Slodička, G. Araneda, L. Lachman, R. Filip, M. Hennrich, and R. Blatt, "Pure single photons from a trapped atom source," *New Journal of Physics*, vol. 18, no. 9, p. 093038, 2016.
- [43] W. E. Moerner and L. Kador, "Optical detection and spectroscopy of single molecules in a solid," *Phys. Rev. Lett.*, vol. 62, pp. 2535–2538, May 1989.

- [44] M. Orrit and J. Bernard, "Single pentacene molecules detected by fluorescence excitation in a p-terphenyl crystal," *Phys. Rev. Lett.*, vol. 65, pp. 2716–2719, Nov 1990.
- [45] T. Basché, W. E. Moerner, M. Orrit, and H. Talon, "Photon antibunching in the fluorescence of a single dye molecule trapped in a solid," *Phys. Rev. Lett.*, vol. 69, pp. 1516–1519, Sep 1992.
- [46] P. Michler, A. Kiraz, C. Becher, W. V. Schoenfeld, P. M. Petroff, L. Zhang,
 E. Hu, and A. Imamoglu, "A quantum dot single-photon turnstile device," *Science*, vol. 290, no. 5500, pp. 2282–2285, 2000.
- [47] I. Aharonovich, D. Englund, and M. Toth, "Solid-state single-photon emitters," *Nature Photonics*, vol. 10, pp. 631 EP –, Sep 2016. Review Article.
- [48] I. Aharonovich and E. Neu, "Diamond nanophotonics," Advanced Optical Materials, vol. 2, no. 10, pp. 911–928, 2014.
- [49] J.-H. Park, J. C. Park, S. J. Yun, H. Kim, D. H. Luong, S. M. Kim, S. H. Choi, W. Yang, J. Kong, K. K. Kim, and Y. H. Lee, "Large-area monolayer hexagonal boron nitride on pt foil," *ACS Nano*, vol. 8, no. 8, pp. 8520–8528, 2014.
- [50] L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, and P. M. Ajayan, "Large scale growth and characterization of atomic hexagonal boron nitride layers," *Nano Letters*, vol. 10, no. 8, pp. 3209–3215, 2010.
- [51] F. Xia, H. Wang, D. Xiao, M. Dubey, and A. Ramasubramaniam, "Twodimensional material nanophotonics," *Nature Photonics*, vol. 8, pp. 899 EP –, Nov 2014. Review Article.
- [52] E. Neu, D. Steinmetz, J. Riedrich-Möller, S. Gsell, M. Fischer, M. Schreck, and C. Becher, "Single photon emission from silicon-vacancy colour centres in chemical vapour deposition nano-diamonds on iridium," *New Journal of Physics*, vol. 13, no. 2, p. 025012, 2011.
- [53] I. Aharonovich, S. Castelletto, D. A. Simpson, A. Stacey, J. McCallum, A. D. Greentree, and S. Prawer, "Two-level ultrabright single photon emission from diamond nanocrystals," *Nano letters*, vol. 9, no. 9, pp. 3191–3195, 2009.

- [54] S. Schietinger, M. Barth, T. Aichele, and O. Benson, "Plasmon-enhanced single photon emission from a nanoassembled metal- diamond hybrid structure at room temperature," *Nano letters*, vol. 9, no. 4, pp. 1694–1698, 2009.
- [55] K. Watanabe, T. Taniguchi, and H. Kanda, "Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal," *Nature materials*, vol. 3, no. 6, p. 404, 2004.
- [56] J. H. Parker, D. W. Feldman, and M. Ashkin, "Raman scattering by silicon and germanium," *Phys. Rev.*, vol. 155, pp. 712–714, Mar 1967.
- [57] R. V. Gorbachev, I. Riaz, R. R. Nair, R. Jalil, L. Britnell, B. D. Belle, E. W. Hill, K. S. Novoselov, K. Watanabe, T. Taniguchi, A. K. Geim, and P. Blake, "Hunting for monolayer boron nitride: Optical and raman signatures," *Small*, vol. 7, no. 4, pp. 465–468.
- [58] F. Vialla, Y. Chassagneux, R. Ferreira, C. Roquelet, C. Diederichs, G. Cassabois, P. Roussignol, J.-S. Lauret, and C. Voisin, "Unifying the low-temperature photoluminescence spectra of carbon nanotubes: The role of acoustic phonon confinement," *Physical review letters*, vol. 113, no. 5, p. 057402, 2014.
- [59] A. Gustafsson, M.-E. Pistol, L. Montelius, and L. Samuelson, "Local probe techniques for luminescence studies of low-dimensional semiconductor structures," *Journal of Applied Physics*, vol. 84, no. 4, pp. 1715–1775, 1998.
- [60] B. R. Masters, "Principles of fluorescence spectroscopy," *Journal of Biomedical Optics*, vol. 13, no. 2, p. 029901, 2008.
- [61] "Picoquant, tcspc tutorial," 2014.
- [62] D. O'Connor, *Time-correlated single photon counting*. Academic Press, 2012.
- [63] W. Becker, Advanced time-correlated single photon counting techniques, vol. 81. Springer Science & Business Media, 2005.
- [64] H. N. M. Duong, M. A. P. Nguyen, M. Kianinia, H. Abe, T. Ohshima, K. Watanabe, T. Taniguchi, J. H. Edgar, I. Aharonovich, and M. Toth, "Effects of high energy electron irradiation on quantum emitters in hexagonal boron nitride," *arXiv* preprint arXiv:1805.08589, 2018.

- [65] H. Giloh and J. Sedat, "Fluorescence microscopy: reduced photobleaching of rhodamine and fluorescein protein conjugates by n-propyl gallate," *Science*, vol. 217, no. 4566, pp. 1252–1255, 1982.
- [66] L. Song, E. Hennink, I. T. Young, and H. J. Tanke, "Photobleaching kinetics of fluorescein in quantitative fluorescence microscopy," *Biophysical journal*, vol. 68, no. 6, pp. 2588–2600, 1995.
- [67] C. Elbadawi, T. T. Tran, O. Shimoni, D. Totonjian, C. J. Lobo, G. Grosso, H. Moon, D. R. Englund, M. J. Ford, I. Aharonovich, *et al.*, "Ultra-bright emission from hexagonal boron nitride defects as a new platform for bio-imaging and bio-labelling," in *SPIE BioPhotonics Australasia*, vol. 10013, p. 1001314, International Society for Optics and Photonics, 2016.
- [68] P. Michler, A. Imamoglu, M. D. Mason, P. J. Carson, G. F. Strouse, and S. K. Buratto, "Quantum correlation among photons from a single quantum dot at room temperature," *Nature*, vol. 406, pp. 968 EP –, Aug 2000.
- [69] R. HANBURY BROWN and R. Q. TWISS, "A test of a new type of stellar interferometer on sirius," *Nature*, vol. 178, pp. 1046 EP –, Nov 1956.
- [70] B. R. Hanbury, T. R. Q., L. A. C. Bernard, and s. givenName, "Interferometry of the intensity fluctuations in light - i. basic theory: the correlation between photons in coherent beams of radiation," *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. 242, pp. 300–324, Nov 1957.
- [71] L. Mandel and E. Wolf, *Optical coherence and quantum optics*. Cambridge university press, 1995.
- [72] H. J. Kimble, M. Dagenais, and L. Mandel, "Photon antibunching in resonance fluorescence," *Phys. Rev. Lett.*, vol. 39, pp. 691–695, Sep 1977.
- [73] V. Karanikolas, C. A. Marocico, and A. L. Bradley, "Spontaneous emission and energy transfer rates near a coated metallic cylinder," *Phys. Rev. A*, vol. 89, p. 063817, Jun 2014.

- [74] C. A. Marocico and J. Knoester, "Intermolecular resonance energy transfer in the presence of a dielectric cylinder," *Phys. Rev. A*, vol. 79, p. 053816, May 2009.
- [75] H. Mertens, A. F. Koenderink, and A. Polman, "Plasmon-enhanced luminescence near noble-metal nanospheres: Comparison of exact theory and an improved gersten and nitzan model," *Phys. Rev. B*, vol. 76, p. 115123, Sep 2007.
- [76] C. A. Marocico and J. Knoester, "Effect of surface-plasmon polaritons on spontaneous emission and intermolecular energy-transfer rates in multilayered geometries," *Phys. Rev. A*, vol. 84, p. 053824, Nov 2011.
- [77] H. Goldstein, C. P. Poole, and J. L. Safko, *Classical Mechanics: Pearson New International Edition*. Pearson Higher Ed, 2014.
- [78] C. T. Tai, *Dyadic Green's Functions in Electromagnetic Theory*. IEEE Press, 2nd ed., 1994.
- [79] M. Kamandar Dezfouli and S. Hughes, "Regularized quasinormal modes for plasmonic resonators and open cavities," *Phys. Rev. B*, vol. 97, p. 115302, Mar 2018.
- [80] J.-M. Gérard, Solid-State Cavity-Quantum Electrodynamics with Self-Assembled Quantum Dots, pp. 269–314. Berlin, Heidelberg: Springer Berlin Heidelberg, 2003.
- [81] D. E. Aspnes and A. A. Studna, "Dielectric functions and optical parameters of si, ge, gap, gaas, gasb, inp, inas, and insb from 1.5 to 6.0 ev," *Phys. Rev. B*, vol. 27, pp. 985–1009, Jan 1983.
- [82] S. Arya and A. D'Amico, "Preparation, properties and applications of boron nitride thin films," *Thin Solid Films*, vol. 157, no. 2, pp. 267 – 282, 1988.
- [83] D. Golla, K. Chattrakun, K. Watanabe, T. Taniguchi, B. J. LeRoy, and A. Sandhu, "Optical thickness determination of hexagonal boron nitride flakes," *Applied Physics Letters*, vol. 102, no. 16, p. 161906, 2013.