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Quantum Optics of Polaritonic Nanocomposites

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Graduate Program in Physics

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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QUANTUM OPTICS OF POLARITONIC NANOCOMPOSITES

(Thesis format: Integrated Article)

by

Christopher D.C. Racknor

Graduate Program in Physics

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Abstract

In this thesis, we study the quantum optical interaction in polaritonic nanocomposites. These systems are made by the combination of two or more micro- or nano-scale structures with complementary optical properties, such as polaritonic materials, excitonic materials, photonic crystals (PCs), quantum dots (QDs), waveguides, couplers, metal nanorods (MNRs), bionanoparticles. The nanocomposites systems studied included QDs doped within a polaritonic PC, an excitonic waveguide coupler, and a metamaterial waveguide. Also addressed are systems consisting of MNRs paired with biological labelling dye or QDs.

The application of a strain field, known as the acousto-optic effect, was found to control photon transmission in polaritonic PC, and through that, the spontaneous emission of a QD doped within the crystal. Furthermore, a theory of reservoir induced-transparency (RIT) was developed in the QD-exciton-polaritonic coupler and QD-metamaterial waveguide nanocomposites. Transparent states in the absorption spectrum of the QD can be induced via the presence of bound polariton states in the coupler/waveguide. The nature of the states could be controlled by the separation of the couplers or the thickness of the metamaterial.

Energy transfer is found and an explanatory theory is developed for MNRs with QD/biological labelling dye nanocomposites. Decrease in fluorescence lifetime from the dye is shown to be greater for excitation through that two-photon process. Increase of two-photon intensity is shown to significantly increase enhancement of the energy transfer.

Keywords

Polaritonics, phonon-polariton, exciton-polariton, surface plasmon-polariton, nanocomposites, photonic crystals, quantum dots, metal nanorods, metamaterials, Schrödinger equation method, density matrix method
Co-Authorship Statement

This thesis contains both material from previously published manuscripts and unpublished results.

For the material presented in chapters 3, 4, & 6, Chris Racknor and Mahi Singh developed the theoretical formalism and wrote the manuscripts. Chris Racknor performed the numerical calculations and produced the results in consultation with Mahi Singh.

In chapter 5, Chris Racknor and Mahi Singh developed the theoretical formalism and wrote most of the manuscript. Chris Racknor performed the numerical simulations and produced the results in consultation with Mahi Singh. Yu Chen wrote the portions of the manuscript pertaining to the experimental methods. Yinan Zhang, David Birch and Yu Chen performed the experimental work.

In chapter 7, Chris Racknor and Mahi Singh developed the theoretical formalism and wrote the manuscript. Chris Racknor performed the numerical simulations and produced the results in consultation with Mahi Singh. Marek Brzozowski produced the first three figures and edited the manuscript.
For my daughter, Adelaide
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<td>AFD</td>
<td>Alexa Fluor Dye</td>
</tr>
<tr>
<td>BEP</td>
<td>Bound Exciton-Polariton</td>
</tr>
<tr>
<td>CRLH</td>
<td>Composite Right/Left Handed</td>
</tr>
<tr>
<td>DDI</td>
<td>Dipole-Dipole Interaction</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>EIT</td>
<td>Electromagnetically Induced Transparency</td>
</tr>
<tr>
<td>ETR</td>
<td>Energy Transfer Rate</td>
</tr>
<tr>
<td>GNR</td>
<td>Gold Nanorod</td>
</tr>
<tr>
<td>MNR</td>
<td>Metallic Nanorod</td>
</tr>
<tr>
<td>PC</td>
<td>Photonic Crystal</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum Dot</td>
</tr>
<tr>
<td>RIT</td>
<td>Reservoir Induced Transparency</td>
</tr>
<tr>
<td>SPP</td>
<td>Surface Plasmon-Polariton</td>
</tr>
<tr>
<td>TE</td>
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<td>Transverse Magnetic</td>
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Chapter 1

Fundamentals

In this chapter the fundamental concepts required in the thesis are presented. Providing a more indepth look at the components, structures, and processes used will give the reader an improved base with which to better understand the thesis as it is written.

1.1 Polaritons

Polaritons are quasiparticles resulting from electric or magnetic dipole-carrying excitations within a material strongly coupling to electromagnetic waves that travel within them. Thus, the photons of light moving within a dispersive, or polaritonic, material are not freely propagating but are held back by their interaction with the present dipoles. This forms what is known in quantum optics as a dressed state where the photon is in essence "dressed" with the material excitation. An important feature of polaritonic materials is the formation of photonic band gaps in the dispersion relation of the material without any constructed periodicity in the material structure. Bands of energies forbidden to travel in the material occur when the coupling between the photons and the medium's excitations are approximately at resonance. The condition of resonance we refer to is that of both waves having nearly equal frequencies and wavevectors [1].

A few such sources of dipole carrying excitations are excitons, optical phonons, surface-plasmons, and magnons. By their different manner of coupling with light in the formation of a unique type of polaritons, each develop their own dispersion relation to govern the wave light
Figure 1-1: Graphical representation of the optical mode of a phonon. Here, the + and - represent the charge on the ions in the material. The arrows show the directions of motion of the mode.

...will propagate within them. Of these excitations, the first three will be addressed in this thesis.

1.1.1 Phonon-Polaritons

Phonon-polaritons are the result of photons interacting with transverse optical phonons [1]. In some literature they are sometimes referred to as just polaritons. Optical phonons may only be found in materials with more than one type of atom in their unit cell. The optical phonon is the out-of-phase oscillation of the oppositely charged atoms in the lattice creating a time-varying dipole moment. Adjacent atoms are always moving in opposite directions. A visual representation is shown in Fig 1-1. The acoustic mode, which is the two different atoms move together, does not result in a dipole excitation to which photons may couple. Optical phonons are excited by infrared radiation and will interact with photons with frequencies between 100 GHz and 10 THz to form phonon-polaritons. Examples of dispersive materials which will support the formation of phonon-polaritons are GaP, MgO, LiNbO₃, LiTaO₃, NaCl, GaAs, and LiH. The first four of these will be used in the studies performed in this thesis.

1.1.2 Exciton-Polaritons

Exciton-polaritons are, as their name suggests, the coupled interaction of photons with excitons within a material [2]. Excitons are most commonly found in insulators and semiconductors. Materials such as these have ranges of energies where electrons are free to move within the
atomic lattice, called the conduction band, and where they are confined to their individual atoms, called the valence band. They are commonly known as excitonic materials. Within both bands the electronic states are arranged into discrete levels that depend on the size and shape of the structure containing them. Commonly, there is a region between these bands called the electronic band gap. Similar to the photonic band gap, these are energies where no electron states are allowed to exist. An exciton is made by an absorbed photon exciting an electron from the valence band into the conduction band leaving behind a positively-charged electron hole, as shown in Fig 1-2. This creates a dipole in which the photon will couple with to create an exciton-polariton. They are also sometimes also referred to as ‘dressed excitons’.

1.1.3 Surface Plasmon-Polaritons

The last of the polaritons of interest are surface plasmon-polaritons. Plasmons are described in a classical picture as the collective oscillation of the free electrons with respect to the positive ions in a metal [3]. The oscillation will proceed with at what is called the plasmon frequency. They exist in the bulk of a metal or along its surface. Surface plasmons are confined to the surface of a metal and strongly interact with photons resulting in a polariton. Surface plasmon-polaritons have tight spatial confinement and may be present along a flat two dimensional interface or along the outer surface of finite sized metallic nanostructures. A visual representation of surface plasmon-polaritons propagation in both situations is shown in Fig 1-3. Surface plasmon-polaritons maybe be formed from photons of frequencies in the infrared.
or visible light ranges.

1.1.4 Dispersion relation

The dispersion relation of each type of polariton will change in a different manner with the frequency of incident light.

\[ \varepsilon = \frac{hc}{n(\varepsilon)k} \]

Here \( \varepsilon \) is the energy of polaritons in the material while \( k \) is their wavevector. \( c \) is the speed of light and \( n(\varepsilon) \) is the refractive index of the polariton material. You’ll note that the refractive index depends on the energy of the polaritons. The manner in which \( n \) varies with \( \varepsilon \) will differ for each different type of polariton. A graphical representation of the dispersion relation of a phonon-polariton is shown in Fig 1-4 where there are two bands of propagation separated by a band gap. Near the band gap the polariton acts more phonon-like and away from the gap more photon-like. Dispersion relations for exciton-polaritons and surface plasmon-polaritons are calculated in chapters 4 and 7.
1.2 Structures

To facilitate the creation and investigate the effects these polaritons, structures are needed in which to study them. In this thesis, as in the whole study of nanocomposite hybrid systems, there are a multitude of possible components to choose from. We have used photonic crystals, waveguides, quantum dots, metal nanorods, biological labeling dye, and metamaterials to do our studies.

1.2.1 Photonic Crystals

Photonic crystals are a very recently developed structure made to localize and control the flow of light within it [4]. They are materials made with the periodic arrangement of dielectric materials with differing dielectric constants and this periodically may be in one, two, or three spatial dimensions. A visual representation of this is shown in Fig 1-5. In one dimension, these are called Bragg reflectors. Internal reflection and destructive interference of photons in
Figure 1-4: Sample dispersion relation for a phonon-polaritonic material. The red line is the light line, it shows the uncoupled dispersion of the photon. The black lines are the coupled dispersion relation. Note the band gap. This is the region of photon energies that are forbidden to propagate in the material. The further from the band gap, the more the polariton will act like an uncoupled photon. The closer to the band gap, the more the polariton will act like an uncoupled phonon.

this structure cause an energy gap to appear in its photonic dispersion relation. Just as the polaritonic band gaps, this makes for a specific range of frequencies forbidden to propagate in the photonic crystal. Though reliant on the particular construction of the photonic crystal, the band gap has the potential for customization that polaritonic band gaps, which are mostly limited to the nature of the chosen dispersive material, lack. Photonic crystals do present a potential photonic analogue to semiconductors for optical devices.

One dimensional photonic crystals are easily made by growing layers of alternating dielectric materials on top of each other. A 2-D photonic crystal may be made by growing an array of nanorods out of one material then filling the area between them. Lastly, one possible method for creating a three-dimensional photonic crystal is to periodically arrange spheres of a material in a container then and fill the empty space with another material to act as the background. Once the spheres are dissolved this is a with photonic crystal made from air spheres in a background dielectric material [4].
1.2.2 Quantum Dots

Quantum dots are a semiconductor component that is as important to photonics as it is to electronics [5]. They are a three-dimensional semiconductor nanostructure that will confine its excitons in all three spatial dimensions. At typically spheres of size less than 3 nm in diameter quantum dots have electronic characteristic, such as electronic band gap and energy levels, closely tied to their size and shape and thus they are highly tunable. Even though they are semiconductors and contain excitons, exciton-polaritons do not propagate within them because of their extremely small size. Fluorescence occurs in quantum dots when an exciton recombines with its hole and emits a photon, which can also be described as the excited electron decaying back down to its ground state. The light will have an energy equal to the difference between the excited and ground states.

Spontaneous emission is the term given to the process whereby this electron will decay to the ground state without being stimulated to do so. The rate at which the exciton will recombine once excited is called the decay rate and is described by Fermi’s golden rule. The background medium in which the quantum dot finds itself will affect its decay rate through the
density of states, which is the number of available photon per unit energy in the system and depends on the derivative of its dispersion relation with respect to energy. Thus, the properties of the quantum dot may also be changed by manipulating the surrounding material. The ability of quantum dots to be doped into other structures makes them very effective for probing the optical properties of those structures. If the surrounding material has a band gap within which the emitted energy would exist (i.e. a photonic or polaritonic crystal) the emission would be suppressed and the photon would be confined to the quantum dot. This may also be used to allow emission only in certain spatial directions.

Quantum dots can self assemble under certain circumstances through molecular beam epitaxy in a process called Stranski–Krastanov growth. When a material is grown on a substrate without matching the two lattices it is strained and will collect into small ‘islands’ instead of as a smooth layer. Normally this island formation is something to be avoided as it would ruin multiple layer materials. However, these islands make for excellent quantum dots once they are buried in a material with an electron band gap. Quantum dots can also be made from core-shell structures where colloidal chemistry methods produce one semiconductor crystal wrapped in another. Notable core-shell pairs are CdS/ZnS, CdSe/ZnS, CdSe/CdS, and InAs/CdSe [5].

1.2.3 Waveguides

Another structure to manipulate the flow of light in a system is a waveguide [6]. A waveguide can be any structure that confines light to only travel in one or two spatial directions. One that confines light only in one direction is often referred to as a fiber waveguide, those that confine to two are called slab waveguides. Any of these types of waveguides consist of two parts: a core region that allows the light to flow and a cladding region that provides the confinement. Construction of two waveguiding components close enough to couple yet still separated by a cladding region is called a coupler. These couplers may have as any number of coupled layers making for a range of different propagation possibilities. Waveguides can be structured with a high index of refraction material surrounding one of lower index. The confinement of the optical waves in these types of waveguides is by total internal reflection. This is how modern fiber optic cables work. A more efficient confinement mechanism is one using materials with band gaps where the light transmitted through the core region of the waveguide
exists within the band gap of the cladding. Polaritonic crystals can be made into a waveguiding structure such as this by either layering one crystal between slabs of another or wrapping a wire of one with the other. You can also take one built with either one, two, or three dimensions of periodicity and remove one or more layers of one of the alternating dielectrics. An example is shown in Fig 1-6 for a waveguiding region in a 2-D photonic crystal.

1.2.4 Metamaterials

In the pursuit of better waveguiding capabilities and novel optical properties researchers have come to develop artificial materials, known as metamaterials, to aid them in their work. They are developed for the expressed purpose of finding new properties that are not found in nature. One such property is negative index of refraction. This concept has been popularized for its science fiction inspiring potential to create a cloaking device. Built around a unit cell structure that is smaller than the wavelength of light by which you want to interact with, a metamaterial is made to be seen as a homogeneous material to the light. The goal is to
create a material whose permittivity and permeability are dependent on the frequency of the incident light, much like in metals, polaritonic materials, and photonic crystals. This makes it possible to find a region in which both permittivity and permeability are negative. Plasmonic metamaterials contain surface plasmons to couple and interact with incident light. Interaction will give rise to SPPs and these metamaterial would be highly tunable and customizable in application [3].

The plasmonic metamaterial of interest to this thesis is a composite right/left handed (CRLH) metamaterial. This metamaterial is made using capacitors and inductors. Right-handed materials are those within which the electric and magnetic fields, and the direction of propagation of light obeys the right hand rule. In left-handed materials the direction of propagation is the opposite, thus the waves in that kind of material would obey the left-hand rule. The unit cell of a CRLH metamaterial is one that contains an equivalent circuit of both right-handed and left-handed natures. A schematic of this unit cell can be found in Fig 7-2. Depending on the frequency of interaction, it may show right-handed or left-handed behaviour [7].

1.3 Processes

1.3.1 The Acousto-Optic Effect

In this work we have utilized a few methods for interacting with our hybrid system components. The acousto-optic effect is a method for altering the refractive index by the application of a strain field to the crystal [8]. Since phonon-polaritons are mitigated by optical phonons, the acousto-optic effect is a specific case of photoelasticity whereby a mechanical strain field will change the permittivity of a material. This would have an effect on the dispersion relation in the material and potentially change the location of the band gap.

1.3.2 Two-Photon Process

Two-photon absorption is a nonlinear optical process by which two photons are simultaneously absorbed to excite an electron from one state to another [9]. The energy difference between the two states must be equal to the sum of the energies of the two photons. The process requires
high light intensity, which was not available to researchers until the invention of the laser. Two-photon absorption occurs without the presence of an intermediate state, though it can be treated as a “virtual” state facilitates the transition. This is shown in Fig 1-7. Two-photon excited fluorescence, or simply a two-photon process, is the action of exciting a transition with two photons that will then be emitted as one photon with energy that is the sum of the two incident photons. Two-photon processes are important to bioimaging because the human body is opaque to visible wavelength of light. Using two-photon absorption with fluorescent dyes in biological situations allows one to use the far infrared region of the spectrum to image living tissue. Two-photon microscopy has deeper tissue penetration, more efficient light detection, and a vast reduction in phototoxicity [10].
Bibliography


Chapter 2

Introduction

In the previous chapter we explained the fundamental physics required to understand this thesis. The concepts such as those of polaritonic materials, quantum dots, photonic crystal, and metamaterials are all addressed. This chapter will present an overview of the research literature covering the material studied in this thesis.

2.1 Phonon-Polaritonic Nanocomposites

Polaritonic materials represent a vast potential for bridging the gap between photonics and electronics research in the creation of unique and efficient optoelectronic devices. Nanocomposites are systems made by combining two or more micro- or nano-scale structures to have capabilities beyond those of each component. Those containing polaritonic material will be an important component of future quantum optics research. Nanocomposites are also known as hybrid systems. Phonon-polaritonic materials operate at frequencies ranging from hundreds of GHz to several THz in the regime connecting photonics and electronics. Polaritons are quasiparticles formed in the strong coupling interaction of an incident transverse electromagnetic wave photons with transverse optical phonons in the host material. Significant to their operation, polaritonic materials have a range of photon energies that are forbidden to propagate in them, called a photonic band gap, that arises naturally out of the resonant coupling of the phonons and photons [1].

The natural photonic band gap makes polaritonic materials of interest in the development of
photonic counterparts to electronic devices such as transistors, sensors, and integrated circuits that exploit the well known speed advantage in photons over electrons. These materials have also been explored for applications in high-bandwidth signal processing, THz imaging and THz spectroscopy [2],[3].

Maragkou et al. [4] have proposed that polaritonic materials may be used to create lasers that operate at reduced thresholds making them more efficient to use. Polariton band gaps in the THz range have been studied in periodic and quasi-periodic multilayer systems [5]. Reflection and absorption measurements have also been obtained for polaritonic materials in the THz-frequency range [6]. Polaritonic waveguides and resonators have been fabricated from LiNbO$_3$ and LiTaO$_3$ host crystals [2],[3],[7], while polaritonic wires made from an isotropic dielectric material coated with metal have also been investigated [8]. It has been shown that suppression of spontaneous emission occurs when a quantum dot is placed within a polaritonic material [9],[10], and the optoelectronic behaviour of a polaritonic nanowire is optimal to developing all-optical switches [11].

Photonic crystals are another well known advance in photonic devices. Realized in 1987 [12], they are structures with a periodic arrangement of dielectric materials with differing dielectric constants. This structure was found to cause an energy gap to appear in the photonic dispersion relation. Again, this is a range of energies that would be forbidden to propagate in the crystal. This range is determined by the contrast between the pair of dielectric materials and the spacing distances. This gives some control over the band gap to the researcher in fabrication.

There is a problem though in how high a contrast is actually required to form a full photonic band gap [13]. For example, inverse opal photonic crystals require dielectric contrast of a factor of eight to obtain a photonic band gap in the optical regime. This restriction causes a great deal of difficulty in terms of fabrication. Materials with energy dependent dielectric constants, such as polaritonic materials, are the best alternative to overcome this barrier. This work will consider photonic crystals fabricated using polaritonic materials.

There has been some recent work done on polaritonic photonic crystals [14]-[24]. Huang et al. [14]- [16] have demonstrated that polaritonic photonic crystals will exhibit near-dispersionless bandwidth field localization in the polaritonic material and metal-like bands with complete flux expulsion in an extremely small frequency interval around the characteristic phonon frequency.
Sigalas et al. [17] have calculated the transmission coefficient for a 2-D square lattice of GaAs and air and found it to have a band gap to be in the THz range. Zeng et al. [18] have used 2-D polaritonic photonic crystals as waveguides, and showed that propagation loss decays with increasing waveguide wall thickness. Högström and Ribbing [19] have verified the presence of a polaritonic band gap for thicknesses of 1-D photonic crystals lower than the wavelength for SiO₂/Si and SiO₂/air.

Furthermore, Kuzmiak et al. [20] calculated the photonic band structure for an infinite array of polaritonic rods in a vacuum. They found that for larger values of the volume filling fraction, the dispersion relation produced a complete 2-D photonic band gap for transverse electric electromagnetic waves. Rung and Ribbing [21] showed that in a polaritonic photonic crystal, the photonic gap can be shifted across the polaritonic gap by varying the crystal's lattice constant. Chern et al. [22] used an interfacial operator approach to study the effect of structural and polaritonic parameters on four different polaritonic photonic crystal structures. Gantzounis and Stefanou [23] used layer-multiple-scattering to study the optical properties of 3-D polaritonic photonic crystals and their transmission characteristics. In addition, they [24] also studied and the optical response of finite slabs of 2-D and 3-D periodic structures of air cavities in polaritonic materials, which revealed existence of strong resonant modes.

The acousto-optic effect is a method capable of altering the refractive index by the application of a strain field to a material. This is of particular interest to polaritonics research since the polariton is formed by photons coupling to phonons. Changing the refractive index would change both the natural photonic band gap of the polaritonic material but also the band gap of any photonic crystal that material was part of. The photon transmission of some wavelengths of light could then be changed.

Research into the acousto-optic in photonic crystals has already found promising results [25]-[27]. For example, Courjal et al. [25] have studied an active 2-D lithium niobate photonic crystal driven by stationary Rayleigh surface acoustic waves. The configuration relies on two interdigital transducers that modulate the refractive index through the acousto-optic effect. Their experiments showed a significant enhancement of the elasto-optical interaction. Haakestad and Engan [26] have studied experimentally the acoustic and acousto-optic properties of a solid core photonic crystal fiber. Acousto-optic interaction is used to couple light from the lowest order
to the first higher order optical modes of the solid core fiber. Lim et al. [27] have measured the multiple resonance peaks in an all-fiber acousto-optic tunable filter built with a photonic crystal fiber. They explained their experiments by using the physics of acousto-optic mode coupling.

2.2 Exciton-Polaritonic Nanocomposites

There is significant research interest in the optoelectronic interaction of nanocomposites [28]-[32]. These hybrid systems can consist of many combinations of nanoscale components, such as graphene [28], metallic nanoparticles [29], metamaterials [30], quantum dots [29] and nanowires [31], to name just a few. A significant component of the research field is devoted to studying the interaction of exciton-polariton carrying materials with excitons in quantum dots in a nanocomposite. Quantum dots are three-dimensional nanostructures with a valence band and conduction band in the ranges of allowable electron energies. There is an electronic band gap between the two and when an electron is excited from the valence band to the conduction band it leaves behind a positively charged hole, resulting in a dipole. The same is true for excitonic materials.

Excitonic materials built into one- or two-dimensional structures, such as wires and waveguides or couplers, have the ability for light incident on them to couple with excitons and propagate through them as exciton-polaritons [33]. Just as with phonon-polaritons, excitons-polaritons have natural photonic band gaps in their dispersion relation that limits some frequencies of light from propagating within them. In these materials, that gap is generally found in the visible range whereas phonon-polaritonic material gaps are in the infrared [34]. This makes exciton-polaritonic devices useful for controlling interaction at optical wavelengths.

Quantum dots play a very important role in hybrid nanostructure research, for example, quantum dot-metal nanoparticle hybrid systems interact strongly via exciton-surface plasmon coupling and could prove to be an efficient mechanism for the transmission of quantum information between qubits for applications in quantum communication [29]. Quantum dots have been doped at the interfaces of waveguides consisting of plasmonic metamaterials [30] and have shown enhancement in their photoluminescence as a result of their coupling with the metamaterial waveguide. The emission spectra of quantum dots has also been shown to be enhanced
Optical waveguide couplers have numerous applications and garner a considerable amount of research attention. They are physical structures capable of directing the flow of light through a system [35] and they represent a scientific frontier in communication [36],[37] and sensing technologies [38] among others.

Couplers are multiple waveguides in close enough proximity to have coupled properties different from those waveguides on their own [39]-[42]. Khomeriki and Leon [39] have proposed an all-optical amplification scenario based on the properties of light propagation in two coupled subwavelength metallic slab waveguides and confirmed it via numerical simulations. Gosciniak et. al. [40] have done experimental studies on compact fiber-coupled dielectric-loaded plasmonic waveguide directional couplers for operation at telecom wavelengths. A directional coupler based on metal-insulator-metal plasmonic waveguide has been investigated by Pu et. al. [41] where they show that the coupling length increases nearly linearly with the wavelength and propose the design of a wavelength division multiplexer to take advantage of this property. Thorhauge et. al. [42] have demonstrated efficient directional couplers made from photonic crystals based on a planar hexagonal photonic crystal lattice of holes.

Exciton materials have a potential for use in on-chip polaritonic circuit applications and are currently of great interest to Bose-Einstein condensate studies [44]. Organic nanowire exciton-polariton resonators have been shown to emit two-photon-pumped blue lasing with a near-infrared femtosecond pulse laser [45]. In the field of waveguides, excitonic materials have been made into organic semiconductor optical slab waveguides where the momentum of the polaritons can be controlled by changing the thickness of the waveguide [46]. Strong coupling between guided mode polaritons in the waveguide with excitons in nearby quantum wells and discs [47],[48] has been experimentally observed. Exciton-polaritonic couplers are also proposed to possibly be made from closely spaced graphene layers by Smirnova et. al. [49]. They have analytically studied the nonlinear properties of graphene couplers and predict that the interlayer power-dependent coupling would provide a mechanism for optical beam control and manipulation at realistic input power levels.
2.3 Plasmon-Polaritonic Natural Material Nanocomposites

The number of possible combinations of components for nanocomposite hybrid systems is nearly endless [50]-[54]. To enhance or decrease optical interactions and effects, hybrid systems are made from the combination of two or more nano-scale components and are strong tools in the future of biotechnology [55]-[57] and solar energy collection [58]-[59].

An important component of many nanocomposites are plasmonic nanoparticles, commonly made of noble metals [50]. Surface plasmons are the collective oscillation of the free electrons with respect to the positive ions confined to the surface of a metal [60]. Noble metals are the best natural source of surface plasmons [62]. These excitations will strongly interact with photons and as a result form a coupled quasiparticle called surface plasmon-polaritons. Surface plasmon-polaritons may be found along flat two dimensional interfaces or the outer surfaces of metallic nanostructures.

Metal nanostructures are very common hybrid system components. They are used in systems to interact with quantum dots [29], organic dyes [61], [65], and enzymes [63]. The organic dye-metal nanoparticle nanocomposites have shown great progress as fluorescent probes that improve the quenching efficiency and photostability [65]. The future of bioimaging will be reliant on the development of new experimental tools that enable the manipulation of biomolecules. Nanocomposites with metal nanoparticle are one of those tools that will be essential in information gathering for biological applications. In quantum dot-metal nanorod systems they show promise as sensors based on the exciton-plasmon interaction [66].

The surface plasmon-polariton energies are sensitive to the shape and size of their material. They can be used in structures such as nanowires [31], nanoparticles [29], nanoshells [4], and nanorods [27]. Metal nanoparticles also now make up integral pieces of some solar cell designs [67] that improve the absorption while decreasing the thickness of the absorbing layer.

There have been considerable efforts to study the nonlinear processes such two-photon process and second harmonic generation in hybrid systems. Two-photon effects are well known phenomena [68],[69] and have a wide range of applications [70], specifically to bioscience imaging [71]-[73]. Emission from single 10–15-nm-diameter core/shell CdTe/CdS nanoparticles can be readily observed in a two-photon scanning microscopy setup [74]. The multi-photon properties of quantum dots have been readily observed [75],[76]. Singh [77] has investigated the second
harmonic generation and dipole-dipole interaction in a quantum dot and spherical metallic nanoparticle hybrid system and found the signals produced by the system are enhanced by the interaction. Two-photon emission and second harmonic generation have also been investigated theoretically and experimentally by Cox et. al [78].

In particular, three level quantum dots have shown coherent population trapping and electromagnetically induced transparency experimentally [79]-[81]. Recent theoretical work on quantum dots has been done on their nonlinear optical absorption and rectification [82] as well as linear absorption and dispersion in the presence of plasmonic nanostructures [83].

Metallic nanoparticles hybrid systems have also been fabricated by several groups [84]-[88]. Goncalves et al. [85] have grown gold nanoparticles on the graphene surfaces using a simple chemical method in aqueous medium. They found that the graphene-gold hybrid system may function as a substrate for surface enhanced Raman scattering. They found a significant enhancement of the Raman spectrum. Yan et. al. [86] have studied midinfrared generation from difference frequency in self-assembled quantum dots near metal nanoparticles with two-color interband excitations. They found signal enhancement as a result of competition between local electric field enhancement and excitonic lifetime shortening and they propose this hybrid system as a candidate for a midinfrared quantum dot laser.

2.4 Plasmon-Polaritonic Metamaterial Nanocomposites

There is considerable interest in the study of the physical properties of artificial materials [90]-[98]. The first artificial materials were proposed by an Indian scientist, Bose, who studied the rotation of the plane of polarization by human-made twisted structures. These structures are artificial chiral structures by today’s definition [90]. Later Lindell et al. studied artificial chiral media formed by a collection of randomly oriented small wire helices [91]. Veselago [92] theoretically studied the uniform plane-wave propagation in an artificial materials which have both real negative permittivity and permeability values. He found that the direction of the Poynting vector of a monochromatic plane wave is opposite to that of its phase velocity. These materials are known as “left-handed materials” or metamaterials. Smith et al. [93] based on the work of Pendry et al. [94] constructed a metamaterial in the microwave regime
by arranging periodic arrays of small metallic wires and split-ring resonators. They found that these materials show the anomalous refraction at their boundaries that is the result of negative refraction. Since then, negative refraction has subsequently been realized in THz waves and at optical wavelengths [95]-[97]. The fabrication of metamaterials that will operate at optical wavelengths is an important research area [97],[98].

Optical waveguides play an important role in many fundamental studies of optical physics at nanoscale with applications to nanophotonic. Therefore, in order to obtain novel optical properties beyond the conventional dielectric waveguides, optical waveguides based on metamaterials have been studied [99]-[107]. Huang et. el. [100] studied wave propagation in nanowire waveguides made from extremely anisotropic metamaterials. They found that at a critical radius, the waveguide supports degenerate forward- and backward-wave modes with zero group velocity. He et al. [101] propose nanoscale metamaterial optical waveguides with ultrahigh refractive indices based on metal–dielectric multilayer indefinite metamaterials with ultrahigh effective refractive indices. They found that waveguide modes depend on the cross sectional area of the waveguide.

Very recently a hyperbolic metamaterial waveguide has been proposed to have a high efficiency rainbow trapping effect. Trapped “rainbow” storage of light by the use of metamaterials and plasmonic graded surface gratings is of great interest for on-chip slow light and could have a broad impact on photon-harvesting technologies [102]. Furthermore, on the subject of slow-light metamaterial waveguides, Yao et. al. [103] found enhanced Purcell factors and Lamb shifts in the far-field emission spectra for a system containing a quantum dots near the surface of those waveguides. Specifically composite right/left handed metamaterials have been applied in a half-mode substrate integrated waveguide. It is found to support backward-wave propagation of the below the characteristic waveguide cutoff frequency in the left-handed region and the forward-wave propagation in the right-handed region [104]. Nanostructure metamaterials with hyperbolic dispersion have been shown to have significant effect on the photonic density of states [105]. Other novel optical properties such as slow-light propagation, subwavelength mode compression and surface mode guidance have also been studied [106],[107].
2.5 Objective and Outline of Thesis

The aim of the thesis is to study the quantum optics of polaritonic nanocomposites. These systems are made by the combination of two or more micro- or nano-scale structures with complementary optical properties. One of these components is a material that is capable of carrying propagating phonon-, exciton-, or surface plasmon-polaritons. The combined optical properties of the composite will have capabilities that go beyond those of their constituent parts. The motivation behind this work is driven by the common scientific knowledge that our current electronic technology is reaching intrinsic speed and efficiency limits that simple advances will not fix. Switching mechanisms, like those laid out in this thesis, can be applied to make new types of optoelectronic devices that operate at faster speeds and higher efficiencies. This would allow these new components to circumvent the fundamental limits of the common electronic components. As a further application, these one- and two-photon mechanisms can also be made into sensing components. By this function, the presence of particular substances may be detected or have its own optical properties probed by a change in an optical response of a nanocomposite. The sheer number of available nanostructure components is ever growing along with recent advances in nanofabrication techniques. Nanocomposites hybrid systems have the potential to be the next generation of nano-sensors, communication networks, and computational devices. In this thesis, the optical properties of several types of nanocomposite hybrid systems are theoretically and numerically investigated.

The thesis is organized as follows: In Chapter 3, we present the acousto-optic effect on the photon transmission in a polaritonic photonic crystal. We have also investigate how it affects the spontaneous emission of quantum dots doped into the polaritonic photonic crystals to make a nanocomposite. We have considered that photonic crystals are fabricated from polaritonic materials such as $GaP$, $MgO$, $LiNbO_3$ and $LiTaO_3$. The decay rate of quantum dots as well as the band structure and photon transmission coefficient of the polaritonic photonic crystal have been calculated. The spontaneous decay rate of the quantum dot can be controlled by an external strain field. This finding is significant because it is well known that the spontaneous emission is source of undesirable noise in different types of electronic and optical devices. We have also found the system can be switched from transmitting state to reflecting state by applying the external strain field. These are new and interesting results and can be used to
fabricate new types of photonic couplers and fibers which in turn can be used to fabricate all photonic switches.

In Chapter 4, we develop a theory of the quantum mechanism of reservoir induced-transparency in quantum dot and exciton-polaritonic coupler hybrid systems. The coupler is fabricated from excitonic materials by embedding two $CdS$ slabs between layers of $ZnO$. An ensemble of non-interacting quantum dots are doped in the waveguide coupler. It is well known that exciton-polaritonic materials have a band gap in their energy spectrum. Polaritonic bound states are found within the band gap of $ZnO$. These bound exciton-polaritons interact with the excitons present in the quantum dots via the exciton-bound exciton-polariton interaction. In other words the coupler is acting as a reservoir. A probe laser is applied to measure the absorption in the quantum dot. It is found that when the two $CdS$ waveguiding cores are far away ($\sim 150$ nm) from each other that the absorption spectrum has one minima which corresponds to a transparent state. Further, when the waveguides are close to each other ($\sim 80$ nm) the absorption spectra has two transparent states. It is found that the transparent states can be switched on and off by the application of a control field. These are noteworthy results which can be used to make new types of polaritonic devices such as optical switches and transistors.

In Chapter 5, we demonstrate energy transfer enhanced fluorescence in a biological labelling dye (Alexa Fluor 405) and gold nanorods nanocomposite both experimentally and theoretically. The fluorescence lifetime imaging microscopy and density matrix method are used to study a hybrid system of dye and nanorods under one- and two-photon excitations. Energy transfer between dye and nanorods via the dipole-dipole interaction is found to cause a decrease in the fluorescence lifetime change. Enhanced energy transfer from dye to nanorods is measured in the presence of an increased density of nanorods. This study has potential applications in fluorescence lifetime-based intra-cellular sensing of bio-analytes as well as nuclear targeting cancer therapy.

In Chapter 6, we investigate the nonlinear energy transfer in a quantum dot and metallic nanorod hybrid system. The quantum dot is taken to have three excitonic states. An intense probe laser field is applied between the ground state and first excited state and a control laser field is applied between the first and second excited states. Induced dipoles are created in the quantum dot and metallic nanorod and both are interacting via the dipole-dipole interaction.
Surface plasmon-polaritons are also created in the metallic nanorod due to a coupling of charge fluctuations and laser fields. Therefore, there is an interaction between excitons in quantum dot and surface plasmon-polaritons in the metallic nanorod. Due to these interactions the energy is transferred from the quantum dot to metallic nanorod. Using the density matrix method the energy transfer rate between the components of the system is evaluated. Numerical simulations have been performed on the energy transfer in the hybrid system. Shifting of the peak energy transfer rate to off resonance position due to nonlinear interactions is found. Enhancement of the energy transfer rate is found to be controlled by the probe field intensity and transparency of the system by the control field. The presented hybrid system can be used to fabricate nanosensors, nano-switches and energy transfer devices.

In Chapter 7, the effect of surface plasmon-polaritons on the absorption coefficient of quantum dots in a nanocomposite with metamaterial waveguides is studied. The waveguides are made by sandwiching a metamaterial between two dielectric material layers. An ensemble of quantum dots are deposited near the waveguide interfaces. It is found that when the thickness of the waveguide is of the order of the wavelength of the interaction light, the surface plasmon polariton energy states are split. Excitons of the quantum dot are interacting with surface plasmon-polaritons of the waveguide, which is acting as reservoir. It is observed that when the exciton resonance frequency lies near the surface plasmon-polariton frequencies of the waveguide we get transparent states in the absorption spectrum. This effect is due to strong coupling between excitons and surface plasmon-polaritons. However, when the excitons energy does not lie near the surface plasmon-polariton energies, all of the transparent states disappear due to weak coupling. This work can be used to make new types of optical devices for sensing and imaging applications based on metamaterials.

Lastly, in Chapter 8, the main results of the thesis are summarized and possible future research directions are discussed.
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Chapter 3

Acousto-Optics in Polaritonic Photonic Crystal Nanocomposites

In the previous chapter, the background material pertaining to the topics and systems studied in this thesis was reviewed. In this chapter we study the physical properties of photonic crystals made from polaritonic materials. The acousto-optic responses of the photonic crystals will be investigation when they are doped with quantum dots$^1$.

3.1 Introduction

The interest in polaritonic materials comes from their natural band gaps $[1]$. Their use in photonic crystals brings with them the ability to create new and improve current light controlling features for the structures. They also form an important partnership in nanocomposites with quantum dots (QDs) to unveil novel quantum optical features.

Much research has been done on polaritonics as of late $[2]$$-[8]$, particularly on waveguides $[2],[3],[7]$ and wires $[8],[9]$. Devices designed to utilize these unique attributes have applications as high bandwidth signal processing, THz imaging and THz spectroscopy $[2],[3]$.

Photonic crystals are currently the brightest light in photonics research for guiding the movement of light. In a photonic crystal the band gap is formed due to a periodic variation

in refractive index, as was explained in chapter 2. This proves to have many advantages to controlling light yet still faces some challenges. The effective index of refraction of a polaritonic material is dependent on the frequency of an incident photon and is also sensitive to manipulation of the phonons in the material. Polaritonic materials are currently of great interest to improve upon or solve some of the challenges to photonic crystal performance and fabrication [10]-[12]. Manipulation of the state of phonons in a material with an aim at changing that material’s refractive index is called the acousto-optic effect and this mechanism has seen some research on photonic crystals [13],[14] and photon crystal fibers [15],[16]. It is these features that we will examine in this chapter for the possible construction of better photonic crystals and control of their interactions with nearby QDs in a nanocomposite hybrid system.

3.1.1 System Studied

This chapter will investigate photonic crystals made from polaritonic materials. We will numerically investigate their physical properties and have done so for four different polaritonic materials. Those materials are GaP, MgO, LiNbO$_3$ and LiTaO$_3$. Additionally we will study the same polaritonic photonic crystal system doped with QDs to make a nanocomposite system. We use the acousto-optic effect to change the index of refraction in the polaritonic material. By having control over the allowed propagating wavelength of light in the polaritonic photonic crystal surrounding the quantum dot, we can suppress its spontaneous emission via the decay rate.

3.2 Theoretical Formalism

3.2.1 Polaritonic Photonic Crystals

We consider that a photonic crystal is made from dielectric spheres which are arranged periodically in a background polaritonic material, where the polaritonic background material has a frequency dependent refractive index. For simplicity, the dielectric material is taken as air. This type of crystal is similar in form to Yablonovite, which was fabricated by drilling air spheres into silica in a periodic manner [17]. Here the radius of the dielectric spheres is taken as $r_s$ and the lattice constant of the crystal is denoted by $L$. See Fig 3-1.
Figure 3-1: 2-D cross-sectional view of the considered 3-D polaritonic photonic crystal. The photonic crystal is air spheres periodically arranged in a polaritonic crystal background. The periodicity is denoted by the lattice constant, $L$, and the radius of the air spheres is $r_s$.

The index of refraction of a polaritonic material, $n_p$, is frequency (energy) dependent and is written as [12]

$$n_p(\varepsilon_k) = \left( \epsilon_{\infty} \left( \frac{\varepsilon_k^2 - \varepsilon_L^2 - i\gamma\varepsilon_k}{\varepsilon_k^2 - \varepsilon_T^2 - i\gamma\varepsilon_k} \right) \right)^{1/2},$$

(3.1)

where $\varepsilon_T$ and $\varepsilon_L$ are the transverse and longitudinal phonon energy, respectively. $\varepsilon_k$ is the energy of polaritons and the constant $\epsilon_{\infty}$ is the high frequency dielectric constant which is the contribution due to ion core electrons. $\gamma$ is the energy loss factor. The band structure of the polaritonic photonic crystal considered here has been modelled using the technique developed by John and Wang [18]. This model has been used widely to study the quantum optics of photonic crystals [19]-[28]. According to this model the band structure of the photonic crystal is given as

$$\cos(kL) = F(\varepsilon_k),$$

(3.2)
where
\[
F(\varepsilon_k) = \sum_{\pm} \left[ \pm \left( \frac{(n_p(\varepsilon_k) \pm n_s)^2}{4n_p(\varepsilon_k)n_s} \right) \cos \left( \frac{\varepsilon_k (n_p(\varepsilon_k)2a \pm n_s(L - 2a))}{hc} \right) \right].
\] (3.3)

Here \( \varepsilon_k \) is energy of polaritons and \( k \) is their wave vector in the photonic crystal. The physical parameter \( a \) is chosen where \( r_s = \frac{1}{2} a \), and \( r_s \) is the radius of the spheres. \( n_p \) is the refractive index of the polaritonic background material and \( n_s \) is that of the spheres.

### 3.2.2 Acousto-Optic Effect

When an external mechanical strain (i.e. acoustic wave) is applied to a polaritonic material, its refractive index is modified due to photon-phonon interaction. This is known as the acousto-optic effect. Let us apply an acoustic (phonon) wave to our system with intensity \( I_a \). The intensity of the acoustic wave is written as
\[
I_a = \frac{1}{2} \rho v_s^3 S_a^2,
\] (3.4)

where \( \rho \) is the density, \( v_s \) is the phonon wave speed and \( S_a \) is the magnitude of the strain.

Let us consider that a longitudinal acoustic wave is travelling along the \( x \)-direction and the displacement (deformation) of the material is \( u_x \). The strain \( S_a \) is then defined as
\[
S_a = \pm \frac{du_x}{dx},
\] (3.5)

where + and − stand for the compression and dilation of the system, respectively. As the elastic material is deformed due to the external strain (acoustic wave), the optical impermeability \( \eta \) of the system is related to the strain as [29]
\[
\Delta \eta = p S_a,
\] (3.6)

where \( p \) is called the photoelastic or acousto-optic constant. The optical impermeability is related to the dielectric constant \( \epsilon \) of a material as
\[
\eta = \sqrt{\frac{\epsilon_0}{\epsilon}},
\] (3.7)
where $\varepsilon_0$ is the dielectric constant in a vacuum.

In the presence of the external strain the dielectric constant of the material is modified. Therefore, the refractive index of the system can be obtained by solving Maxwell’s equations by using the coupled wave theory. The refractive index of the system is obtained as

$$n_T(\varepsilon_k) = n_p \left[ \frac{\varepsilon_k^2 - \varepsilon_T^2 - i\gamma_s k \pm \frac{1}{2} p S_s (\varepsilon_k^2 - \varepsilon_L^2 - i\gamma_s k)}{\varepsilon_k^2 - \varepsilon_T^2 - i\gamma_s k} \right].$$

Note that if we neglect the effect of the external strain (i.e. $S_s = 0$) the above expression reduces to Eq. (3.1). Let us express $S_s$ in terms of the intensity of strain field (acoustic wave) by rearranging Eq. (3.4), which gives

$$S_s = \left( \frac{2I_a}{\rho v^3} \right)^{1/2}. \quad (3.9)$$

Putting the above expression of $S_s$ into Eq. (3.8) we find

$$n_T(\varepsilon_k) = n_p \left[ \frac{\sqrt{\varepsilon_\infty (\varepsilon_k^2 - \varepsilon_T^2 - i\gamma_s k) \pm \left( \frac{1}{2} \eta I_a \right)^{1/2} (\varepsilon_k^2 - \varepsilon_L^2 - i\gamma_s k)}}{\sqrt{\varepsilon_\infty (\varepsilon_k^2 - \varepsilon_T^2 - i\gamma_s k)}} \right]. \quad (3.10)$$

where $\eta$ is a constant with units of $\text{m}^2/\text{W}$, and is defined as

$$\eta = \frac{\varepsilon_\infty P^2}{\rho v_s^3}. \quad (3.11)$$

Note that total refractive index of the system now depends on the intensity of the acoustic wave and the material dependent parameter $\eta$. When the intensity of the acoustic wave is zero we get back our original expression for the refractive index. Note that we have considered that the wavelength of the strain field is very large compared to photon wave length so that the system does not have space variation in the refractive index.

Yariv and Yeh [29] have studied acousto-optic effect in homogenous medium. When acoustic wave propagate in the medium the refractive index of the medium periodically modulated both in time and space and an index grating is created. The scattering of photons with this grating gives Bragg-diffraction condition. In most calculations the time dependence of the refractive index is neglected since the frequencies of photons are much greater than the phonons.
frequencies [30]. In this case the system is treated as a static (frozen) periodic modulated medium.

3.2.3 Transmission Coefficient

Photons with energies lying within the photonic band gap of a photonic crystal do not propagate within it; conversely, photons with energies lying outside the photonic band gap do propagate in the photonic crystal. The photon transmission coefficient $T(\varepsilon_k)$ of the polaritonic photonic crystal is calculated using the method of reference [31]. It is found as

$$T(\varepsilon_k) = 1 - \Phi [1 - \Lambda(\varepsilon_k)],$$

where $\Lambda(\varepsilon_k)$ is obtained from the photonic dispersion relation and is written as

$$\Lambda (\varepsilon_k) = \Pi_+ (\varepsilon_k) + \Pi_- (\varepsilon_k),$$

where

$$\Pi_\pm = \left( \frac{\left[n_T (\varepsilon_k, I_a) \pm n_s\right]^2}{4n_s n_T (\varepsilon_k, I_a)} \right) \cos \left( \frac{2\varepsilon_k [an_T (\varepsilon_k, I_a) \pm n_s (L - 2a)]}{\hbar c} \right).$$

Here $\Phi$ is the Heaviside step function and has the following property

$$\Phi(x) = 1 \quad \text{for} \quad x > 1$$

$$\Phi(x) = 0 \quad \text{for} \quad x < 1$$

3.2.4 Spontaneous Emission

We consider that the polaritonic photonic crystal is doped with a two-level QD. Energy levels of the QD are denoted as $|a\rangle$ and $|b\rangle$ where the former is the ground state and latter is the excited state. See Fig. 3-2. Let us consider that initially the QD is in the excited state. Therefore, it is interacting with the polaritonic photonic crystal which is acting as reservoir. In the dipole and rotating wave approximation the Hamiltonian of the system is written in the interaction representation as
Figure 3.2: Schematic of the two level quantum dot. The ground state is $|a\rangle$ and the excited state is $|b\rangle$. It is coupled to the phonon-polaritons in the polaritonic photonic crystal.

$$H = H_A + H_P + H_{AP} \quad (3.16)$$

where

$$H_A = (\sigma_z + \frac{1}{2}) \varepsilon_{ba} + hc \quad (3.17)$$
$$H_P = \sum_k \varepsilon_k a_k^+ a_k + hc \quad (3.18)$$
$$H_{AP} = -\sum_{k_z} \left( \frac{\mu_{ba}}{\hbar} \sqrt{\frac{\varepsilon_k}{2 \epsilon_0 V}} \right) a_k \sigma^+ e^{i(\varepsilon_{ba} - \varepsilon_k)t/\hbar} + hc \quad (3.19)$$

where $\sigma_z = |b\rangle \langle b| - |a\rangle \langle a|$, $\sigma^+ = |b\rangle \langle a|$ and $\sigma^- = |a\rangle \langle b|$. The operators $a_k$ and $a_k^+$ are called the photon annihilation and creation operators of the reservoir, respectively. Here $\varepsilon_k$ is photon energy in the photonic crystal and can be obtained by solving the band structure Eq. (3.2) and $\varepsilon_{ba}$ the transition energy between states $|a\rangle$ and $|b\rangle$. The first and second terms in Eq. (3.16) correspond to the Hamiltonian of a quantum dot and photons in the photonic crystal, respectively. The third term describes the coupling between a quantum dot and photonic crystal. Here $V$ is the volume of the crystal and $\mu_{ba}$ is the dipole moment of the quantum dot.

The self energy $\Xi_{ba}$ for the spontaneous emission can be calculated from Eq. (3.16) by using the Schrödinger equation method developed in reference [32], and is obtained as
\[ \Xi_{ba} = \lim_{s \to 0^+} \int d\varepsilon_k D(\varepsilon_k) \left( \frac{\hbar (\varepsilon_k \mu_{ba})^2}{2e_0 \varepsilon_k V} \right) \frac{1}{(\varepsilon_k - \varepsilon_{ba}) - is} . \] (3.20)

where \( D(\varepsilon_k) \) is the density of states. The DOS is calculated from equations (3.1) and (3.2) and found as

\[ D(\varepsilon_k, I_a) = \left( \frac{V k^2}{3\pi^2 e} \right) \frac{\xi(\varepsilon_k)}{\sqrt{1 - F^2(\varepsilon_k)}}, \] (3.21)

where

\[ \xi(\varepsilon_k, I_a) = A (\cos \theta_+ - \cos \theta_-) + B \left( n_T(\varepsilon_k, I_a) + n_s \right)^2 \sin \theta_+ - \left( n_T(\varepsilon_k, I_a) - n_s \right)^2 \sin \theta_- , \] (3.22)

\[ A = \frac{cn_T(\varepsilon_k, I_a)}{Ln_s n_T^2(\varepsilon_k, I_a)}, \] (3.23)

\[ B = \left( \frac{2a}{\hbar L} \right) \left[ \frac{n_T(\varepsilon_k, I_a) + \varepsilon_k n_T'(\varepsilon_k, I_a)}{4n_T(\varepsilon_k, I_a) n_s} \right], \]

\[ \theta_\pm = \left( \frac{2\varepsilon_k}{\hbar c} \right) \left[ n_T(\varepsilon_k, I_a) a \pm n_s (L - 2a) \right] \]

and \( n_T' \) is the derivative of \( n_T \) with respect to \( \varepsilon_k \). Note that the DOS has a singularity where the function \( F(\varepsilon_k) \) becomes unity. Generally this function becomes unity at the band edges. The DOS also depends on the intensity of the acoustic wave.

The self energy is a complex quantity and its imaginary part (i.e. \( \Gamma_{ba} = \text{Im}(\Xi_{ba}) \)) gives the spontaneous emission decay rate or linewidth. After some mathematical calculations we get the following expression for the linewidth

\[ \Gamma_{ba} = \gamma_0 \left( \frac{\xi(\varepsilon_k, I_a)}{\sqrt{1 - F^2(\varepsilon_k, I_a)}} \right). \] (3.24)

where

\[ \gamma_0 = \frac{\mu^2 \varepsilon_{ba}^3}{3\pi e_0 \hbar^4 c^3}. \] (3.25)
Here $\gamma_0$ is the linewidth for an energy level of an atom when it is located in a vacuum. Note that the decay rate depends on the intensity of the acoustic wave. We have shown that the DOS has a very large value near the band edges. Therefore, the spontaneous decay rate has a very large value when the resonance energy $\varepsilon_{ba}$ lies near photonic band edges. It should be noted that asymptotic increase of the DOS at the band edges is peculiar to one dimensional crystals and not to three-dimensional crystals. However, we want to point out that the DOS increases exponentially near the band edges in 2-D and 3-D photonic crystals [33]-[37]. In our calculations we did not use the value of DOS at the band edges.

### 3.3 Results and Discussion

In this section numerical calculations are performed on the transmission coefficient, dispersion relation and the spontaneous emission decay rate. We have done these calculations for four polaritonic photonic crystals fabricated from GaP, MgO, LiNbO$_3$ and LiTaO$_3$ with air. These material are chosen since they are widely used in fabrication and characterization of polaritonic devices. The parameters used in our numerical calculations for each of the polaritonic materials are given in Table 2.1. These parameters are taken from references [1],[10],[38],[39].

<table>
<thead>
<tr>
<th>Polaritonic Material</th>
<th>$\epsilon_\infty$</th>
<th>$\varepsilon_T$ (meV)</th>
<th>$\varepsilon_L$ (meV)</th>
<th>$\rho$ ($10^3$kg/m$^3$)</th>
<th>$v_s$ ($10^3$m/s)</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>8.5</td>
<td>45</td>
<td>51</td>
<td>4.13</td>
<td>6.35</td>
<td>0.18</td>
</tr>
<tr>
<td>MgO</td>
<td>2.75</td>
<td>38</td>
<td>72</td>
<td>3.58</td>
<td>5.35</td>
<td>0.18*</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>20.6</td>
<td>31</td>
<td>65</td>
<td>4.7</td>
<td>6.57</td>
<td>0.29</td>
</tr>
<tr>
<td>LiTaO$_3$</td>
<td>13.4</td>
<td>18</td>
<td>31</td>
<td>7.45</td>
<td>6.19</td>
<td>0.15</td>
</tr>
</tbody>
</table>

*Note, we were unable to find reliable numbers for the photoelastic constant of MgO so the number for GaP has been used instead.

We have calculated the effective dielectric constant of the polaritonic materials as a function of incident photon energy. The results for the real part of the dielectric are shown in Fig. 3-1, where the solid and dashed curves correspond to GaP and MgO, respectively and the dotted and dot-dashed curves represent LiNbO$_3$ and LiTaO$_3$, respectively. Here we have used an experimental value of $\gamma = 0.014\varepsilon_T$ for all materials [40].
Figure 3-3: The dielectric constant, $\varepsilon$, is plotted as a function of energy, $\varepsilon_k$. The solid curves correspond to GaP, the dashed curve to MgO, the dotted to LiNbO$_3$, and the alternating dots and dashes to LiTaO$_3$.

Note that in Fig. 3-3, we find that all materials have a singularity in their dielectric constant near the optical photon energy when the decay constant is taken as zero. However, when we consider the effect of the decay constant (i.e. $\gamma = 0.6 \text{meV}$) the singularity disappears. One can also see that the energy difference between $\varepsilon_L$ and $\varepsilon_T$, which represents the inherent energy bandgap in polaritonic materials, is greatest for GaP and LiNbO$_3$, then LiTaO$_3$, and MgO in succession.

The results from our numerical simulations of the photonic dispersion relations for the four polaritonic photonic crystals are given in Fig. 3-4a and 3-4b, where we have used the parameters $L = 200 \text{ nm}$ and $2L/a = 0.3$ for each crystal. The solid and dotted lines in Fig. 3-4a correspond to GaP and MgO, respectively. Similarly, the dashed and dot-dashed lines in Fig. 3-4b correspond to LiNbO$_3$ and LiTaO$_3$, respectively.
The photonic band gap width of a crystal is defined as $\Delta \varepsilon = \varepsilon_c - \varepsilon_v$, where $\varepsilon_c$ and $\varepsilon_v$ are the upper and lower band edges of the gap, respectively. We have calculated the photonic band gap widths for the four polaritonic photonic crystals, which were found to be $\Delta \varepsilon_{GaP} = 0.35\text{ eV}$, $\Delta \varepsilon_{MgO} = 0.13\text{ eV}$, $\Delta \varepsilon_{LiNbO_3} = 0.46\text{ eV}$ and $\Delta \varepsilon_{LiTaO_3} = 0.42\text{ eV}$. It is interesting to note that the band gap of the LiNbO$_3$ photonic crystal has the largest value whereas the band gap for MgO crystal has the smallest value. The order of the band gap widths seems to be the same as the contributions due to the high frequency dielectric constant, $\varepsilon_\infty$. Therefore, our calculations predict that the high frequency dielectric constant has the greatest effect on the width of the photonic band gaps in polaritonic photonic crystals. MgO, though, has its band edges at the greatest energy, GaP follows with the next highest then LiTaO$_3$ and LiNbO$_3$, respectively. This varies inversely with the factor $\varepsilon_\infty \varepsilon_L^2 / \varepsilon_T^2$, where $\varepsilon_L$ and $\varepsilon_T$ are the longitudinal and transverse optical phonon energies.

Huang et al. [11] have also calculated the band structure of a photonic crystal fabricated from LiTaO$_3$, with the parameters $L = 29.7 \mu\text{m}$ and $2L/a = 0.25$ and found a photonic band gap below the polariton gap. This has been verified by our method. They also found a band gap...
gap for CsI and TlCl in the same optical region for similar crystal parameters.

Generally, photonic crystals are characterized by their gap to midgap ratio. This ratio is defined as

\[ R = \frac{\Delta \varepsilon}{(\varepsilon_c + \varepsilon_v)/2}. \]

We have calculated this ratio for our four polaritonic photonic crystals and found \( R_{\text{GaP}} = 37.0\% \), \( R_{\text{MgO}} = 11.1\% \), \( R_{\text{LiNbO}_3} = 60.0\% \) and \( R_{\text{LiTaO}_3} = 49.2\% \). Note that the photonic crystal made from LiNbO\(_3\) has the largest value and the crystal made from MgO has the lowest value. This again seems to be related to the relative values of \( \epsilon_\infty \) whose effect on the photonic band gap width is greater than the factors that effect the band edge location.

From Fig. 3-4a we also see that the upper band edge of MgO lies just below that of GaP. One can fabricate photonic crystal waveguides or fibers by embedding an MgO photonic crystal into a GaP photonic crystal. This is an encouraging result for the study of waveguides and fibers fabricated from photonic crystals. The present calculation will help to choose the proper materials for the fabrication of these systems. Similarly in Fig. 3-4b it is found that the upper band edge of LiNbO\(_3\) lies below to that of LiTaO\(_3\). Therefore, we conclude that these photonic crystals can be used to fabricate photonic waveguides and fibers.

We have investigated the effect of the energy loss constant \( \gamma \) on the band gap of these materials. We have varied \( \gamma \) through realistic values \( 0.001 \epsilon_T \) to \( 0.1 \epsilon_T \) [11]. It is found this constant does not have a significant effect on the photonic band gaps of these materials. This is consistent with results found by Huang et al. [11], where it was predicted that the loss factor would be minimal far above \( \epsilon_T \).

We have studied the acousto-optic effect on the band structure of the four polaritonic photonic crystals. The results for GaP are plotted in Fig. 3-5, where the solid line represents \( \varepsilon_v \) for \( I = 0 \) W/m\(^2\) and the dashed line for varying \( I \) from \( I = 10^6 \) W/m\(^2\) to \( I = 10^9 \) W/m\(^2\). We can see that the energy difference \( (\varepsilon_v(I) - \varepsilon_v(0)) \) increases with intensity. Similar results are found for both \( \varepsilon_v \) and \( \varepsilon_c \) of all materials considered in this study.

We have calculated the DOS as a function of resonance energy of the QD. Note that the decay rate of spontaneous emission depends on the density of states. The results from our simulations are plotted in Fig. 3-6a and 3-6b when the resonant energy \( \epsilon_{ab} \) lies in the upper
Figure 3-5: The lower band edge energy, $\varepsilon_v$, of GaP is plotted as a function of acoustic strain intensity. The solid line represents $\varepsilon_v$ for $I = 0$ W/m$^2$ and the dashed line for varying $I$ from $I = 10^6$ W/m$^2$ to $I = 10^9$ W/m$^2$.

and lower bands.

In Fig. 3-6a the solid and dashed curves represent GaP and MgO polaritonic photonic crystals, respectively. Both curves have symmetric shapes in both bands. The DOS has large values near the photonic band edges for both crystals. This behaviour is because the DOS has a singularity near the photonic band edges. Similarly, the DOS for LiNbO$_3$ and LiTaO$_3$ are plotted in Fig 3-6b. The dotted curve corresponds to the LiNbO$_3$ crystal whereas the alternating dashes and dots correspond to the LiTaO$_3$ crystal. For both crystals, the DOS has a singularity at the band edges.

We have considered the influence of the acousto-optic effect on spontaneous emission of the two-level quantum dot. The DOS is plotted in Fig 3-7a and 3-7b as function strain field intensity for the LiNbO$_3$ photonic crystal. The results are plotted in separate figures because
Figure 3-6: The DOS is plotted as a function of photon energy of the quantum dot. The crystal parameters are taken as $L = 200$ nm and $2L/a = 0.3$. (a) The solid curves corresponds to GaP and the dashed curves to MgO, respectively. (b) The dotted lines correspond to LiNbO$_3$ and the alternating dots and dashes to LiTaO$_3$.

The difference between the solid and dashed curves cannot be distinguished in one figure. Similar results are also found for other crystals and are not plotted here. The solid curve is for $I = 0$ W/m$^2$ and the dashed curve is for $I = 10^9$ W/m$^2$. Note that in the presence of the strain field the DOS (decay rate) is modified. The decay rate is increased when the resonance energy of the quantum dot lies within the lower band. Similarly when the resonance energy lies within the upper band of the decay rate is decreased. This means that spontaneous emission of the quantum dot can be controlled by the external strain field. This is a new and interesting finding that is significant because spontaneous emission is the source of undesirable noise in different types of electronic and optical devices. The control of the spontaneous emission also plays a very significant role in quantum computation and quantum information processing.

The transmission coefficient of the LiNbO$_3$ polaritonic photonic crystal has been calculated as function of photon energy. Here the transmission coefficient refers to the semi-infinite crystal and not to a finite slab of it. The results are plotted in Fig. 3-8a and 3-8b and are indicated by the solid curve. These results are displayed in separate figures because the difference between the solid and dashed curves cannot be distinguished in one figure. The photonic band gap is
Figure 3-7: The DOS is plotted as a function of photon energy of the quantum dot for varying strain intensity, I. The solid line corresponds to LiNbO$_3$ when $I = 0$ W/m$^2$ and the dashed line corresponds to $I = 10^9$ W/m$^2$ where (a) shows the lower band and (b) shows the upper band.

found to be in the THz range. The lower band edge, $\varepsilon_v$, is located where the solid line contacts the x-axis in figure 3-8a, while the upper band edge, $\varepsilon_c$, is located where the solid line contacts the x-axis in figure 3-8b. Note that when the energy of photons lies below $\varepsilon_v$ photons are able to propagate through the crystal. Similarly, when the photon energy lies above $\varepsilon_c$, photons propagate through the crystal. For both cases the transmission coefficient is one. This means that the crystal is transparent for these photon energies. However, when the photon energy lies within the band gap photons are totally reflected and the transmission coefficient becomes zero. Sigalas et al. [41] calculated the transmission coefficient of a GaAs polaritonic photonic crystal and found the band gap in the THz region.

The acousto-optic effect has been considered in numerical calculations of the transmission coefficient of the polaritonic photonic crystal. The solid and dashed curves are plotted in the absence ($I = 0$ W/m$^2$) and the presence ($I = 10^9$ W/m$^2$) of the acoustic wave intensity. The presence of mechanical strain has the band gap edges $\varepsilon_v$ and $\varepsilon_c$ shifted to new positions $\varepsilon'_v$ and $\varepsilon'_c$. $\varepsilon'_v$ is located where the dashed line contacts the x-axis in Fig 3-8a, while $\varepsilon'_c$ is located where the dashed line contacts the x-axis in Fig 3-8b. Photons with energy just below $\varepsilon_v$ but above
Figure 3-8: The transmission coefficient is plotted as a function of energy for LiNbO$_3$. The solid curve corresponds to when strain intensity $I = 0.0$ W/m$^2$ and the dashed curves corresponds to $I = 10^9$ W/m$^2$. (a) shows the lower band edges and (b) shows the upper band edges.

$\varepsilon'_0$ will be transmitted through the crystal in the absence of the strain field but will be totally reflected in its presence. This change is also evident for photons with energy below $\varepsilon_c$ but above $\varepsilon'_c$ that will be totally reflected in the absence of the strain field but will transmit when the strain field is present. This means that the system can be switched from the reflecting state to transmitting state, or vice versa depending on which band edge is used as the switch, by applying an external strain field. In other words, when the system is in reflecting state it can be considered to be in the OFF position, and when the system is in a transmitting state it can be considered as ON. This is a new and very interesting result which can be used to fabricate switches from polaritonic photonic crystals.

We have also plotted the effect of strain field intensity on the photonic band gap of LiNbO$_3$. The results are plotted for $(\Delta \varepsilon(I) - \Delta \varepsilon(0))$ as a function of the strain intensity in Fig. 3-9. It is shown that the band gap increases as the intensity increases, but the change is on the order of meV. It is found that the shift in the upper band edge due to same intensity is more than the lower band edge. Similar results are found for all materials considered in this study.
Figure 3-9: The band gap width of LiNbO$_3$ is plotted as a function of acoustic strain intensity.

We have also examined the effect of the strain intensity on the DOS in Fig. 3-10a and 3-10b for LiNbO$_3$. Fig. 3-10a depicts the lower band of the DOS. The solid line is for photon energy $\varepsilon = 0.530$ eV, the dotted line for $\varepsilon = 0.535$ eV, and the dashed line for $\varepsilon = 0.540$ eV. It is clear that at energies closer to the band gap, the DOS is more affected by the strain field intensity. The upper band of the DOS is shown in Fig. 3-10b, where the solid line is for resonance energy $\varepsilon = 1.030$ eV, the dotted line for $\varepsilon = 1.035$ eV, and the dashed line for $\varepsilon = 1.040$ eV. In the upper band, for energies closer to the band gap, the effect on the DOS is similar to the lower band.

Finally, we would like to make a comment on the band structure model used in the present paper. This model was proposed by Sajeev John’s group [18] and is widely used to understand the optical properties of photonic crystals because of its simplicity [19]-[28]. Typically, the band structures of 2-D and 3-D photonic crystals are determined with rigorous numerical approaches such as the plane wave expansion and the transfer matrix methods. These methods produce photonic band gaps and large values for the DOS near the band edges [33]-[37], but do not show an asymptotic behaviour for the DOS at the edges. As one can realize, it is very complicated to use numerical band structure methods to study spontaneous emission and photon transmission in these structures. One of the aims of the present paper is to get analytical expressions of the
above quantities. It is important to note that using numerical approaches, one cannot obtain the analytical expressions we want. On the other hand, John’s band structure model is very useful because it gives an analytical expression for the spontaneous emission and transmission coefficient. These analytical expressions can be used for experimentalists to analyze their data easily or to initiate new experiments. The expressions derived here give a qualitative explanation of these phenomena. Therefore, the findings of the paper will not change even if one uses a numerical method for the band structure. Of course, to get a quantitative explanation one has to use a numerical method for the band structure.

3.4 Conclusions

We have investigated the acousto-optic effect on the photon transmission and spontaneous emission in a polaritonic photonic crystal. The polaritonic photonic crystals considered are made from dielectric spheres which are arranged periodically in a background polaritonic material. The following polaritonic materials were used in our numerical calculations: GaP, MgO, LiNbO$_3$ and LiTaO$_3$. The dielectric spheres are made from air for simplicity. A two-level quantum dot
is doped in the a polaritonic crystal to study the spontaneous emission. The decay rate of the quantum dot due to spontaneous emission has been calculated using the Schrödinger equation. The band structures and photon transmission coefficients for these crystals have also been calculated. It is found that the band gap widths and the decay rates of quantum dots depend strongly on the high frequency dielectric constant, $\varepsilon_\infty$, of the polaritonic crystals, while the photonic band and DOS midgaps vary inversely according to the factor $\varepsilon_\infty \varepsilon_L^2 / \varepsilon_T^2$. The decay rate can be modified by applying an external strain field. The findings of this paper are significant because it is well known that the spontaneous emission is source of undesirable noise in different types of electronic and optical devices. The control of the spontaneous emission also plays a very significant role in quantum computation and quantum information processing. We have also predicted that these polaritonic photonic crystals can be switched from transmitting states to reflecting states by applying an external strain field. This result can be used to fabricate new types of photonic sensors.
Bibliography


Chapter 4

Reservoir Induced Transparency in Exciton-Polaritonic Nanocomposites

In the previous chapter, the acousto-optic properties of polaritonic photonic crystals are studied. There the interaction in the hybrid system was between phonon-polaritons in the polaritonic photonic crystals and excitons in the semiconductor quantum dots (QDs). The switching was controlled by the acousto-optic effect. In this chapter, we examine the light matter interaction in excitonic material couplers doped with QDs to be a nanocomposite system. The interaction is between exciton-polaritons in the couplers and excitons in the QDs. A control laser field is found to control the transparent states of the system\textsuperscript{1}.

4.1 Introduction

The study of the interaction between excitons and exciton-polaritons in nanocomposites is an important research field in directing fabrication toward useful systems \textsuperscript{[1]}-[\textsuperscript{3}]. A hybrid system consisting of components such as QDs and exciton-polaritonic couplers will be very important to light controlling mechanisms at optical wavelengths. When excitonic materials interact with light to form the exciton-polariton quasiparticle, there arises a band gap of disallowed energies that is generally found in the visible range \textsuperscript{[4]}.

\textsuperscript{1}The material presented in this chapter has been communicated to \textit{Nanotechnology} for publication.
QDs are a major component for hybrid nanostructure research as they interact strongly with other components and can enhance interesting optical features [5]-[7]. Rising potential in the use of QD with waveguides in hybrid systems could create efficient single-photon sources [8].

Couplers are two or more optical waveguides coupled together to have new physical properties. Optical waveguide themselves have numerous applications and garner a considerable amount of research attention as physical structures capable of directing the flow of light through a system [9]. Waveguides are thought to hold promising potential in communication [10],[11] and sensing technologies [12]. Couplers are another exciting tool to be used in the control of light [13]-[17] through which properties can be realized that could not be achieved with one waveguide alone.

To make these coupler that interact and control light flow in the visible range we use excitonic materials with their inherent band gaps that forbid the propagation of certain photon energies from through the material [4]. It comes from the excitons (electron-hole pairs) present in the material coupled to incident visible light, forming exciton-polaritons. Some examples of excitonic materials are ZnO, CdS, GaAs, CdSe, and InAs. Excitonic materials are of current interest to Bose-Einstein Condensate studies [18] and as resonators for emitting two-photon-pumped blue lasing [19]. As waveguides, excitonic materials have been made into organic semiconductor optical slab waveguides [1] and have been observed to couple with excitons in nearby quantum wells and discs [2],[3].

4.1.1 System Studied

In this chapter, a nanocomposite system of a QD and an exciton-polariton coupler is investigated. The coupler is built out of two CdS waveguiding slabs placed between layers of ZnO, as shown in Fig. 4-1. An ensemble of non-interacting QDs are doped within the CdS portions of the coupler. Bound mode of exciton-polaritons will be found in the coupler that will interact with the excitons present in the QDs. The coupler will thus be acting as a reservoir to the QDs.

We develop a theory for a quantum mechanism of reservoir induce-transparency (RIT) in this nanocomposite. Here the interaction of the coupler and QD will make the QD transparent to certain frequencies of light that it would not be if doped in another material. We measure the
absorption in the QD and find that when the two \( \text{CdS} \) waveguiding cores are far away \( (h = 150 \text{ nm}) \) from each other that the absorption spectrum has one minima which corresponds to a transparent state. Additionally, when the waveguides are close to each to other \( (h = 80 \text{ nm}) \) we find two transparent states in the absorption spectra. Furthermore, we find that a control laser will be able to switch these transparent states off. These are noteworthy results which can be used to make new polaritonic devices such as optical switches, sensors, and transistors.

4.2 Theoretical Formalism

4.2.1 Dispersion Relation

We explore the physics of a coupler made from excitonic materials. A coupler is two slabs of a waveguiding material, denoted material A, embedded in another cladding material, this one labelled as material B. We have taken \( \text{CdS} \) as material A and \( \text{ZnO} \) as material B. A schematic of coupler is displayed in Fig. 4-1.

The exciton-polariton dispersion relation for an excitonic material is written as \[ k_i = F_i(\varepsilon), \] (4.1)
Figure 4-2: Dispersion relations of (a) ZnO and (b) CdS. The curves show the energy of the exciton-polaritons, $\varepsilon$, versus their wavevector, $k$. Band gaps can be seen between energies $\varepsilon_{T_1}$ & $\varepsilon_{L_1}$ and $\varepsilon_{T_2}$ & $\varepsilon_{L_2}$ where there are no possible exciton-polariton energy states.

where $i = A, B$ and

$$F_i(\varepsilon) = \frac{\varepsilon}{\hbar c} \sqrt{\varepsilon_b \left( 1 + \frac{\left( \varepsilon_{L_2}^2 - \varepsilon_{T_1}^2 \right) \left( \varepsilon_{L_1}^2 - \varepsilon_{T_1}^2 \right)}{\varepsilon_{T_1}^2 - \varepsilon_{T_2}^2 - i\varepsilon \Gamma_1} \right) + \frac{\left( \varepsilon_{L_1}^2 - \varepsilon_{T_2}^2 \right) \left( \varepsilon_{L_2}^2 - \varepsilon_{T_2}^2 \right)}{\varepsilon_{T_1}^2 - \varepsilon_{T_2}^2 - i\varepsilon \Gamma_2} \right)}$$

(4.2)

with $\varepsilon_{L_{i1}}$ and $\varepsilon_{L_{i2}}$ being the longitudinal resonance energies and $\varepsilon_{T_{i1}}$ and $\varepsilon_{T_{i2}}$ are the transverse resonance energies.

We have plotted the dispersion relation for ZnO and CdS excitonic materials in Fig. 4-2a and 4-2b, respectively. The physical parameters used in the calculations for CdS and ZnO are given in Table 3.1[4].

<table>
<thead>
<tr>
<th>Table 4.1: Exciton-polaritonic Material Constants</th>
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<tbody>
<tr>
<td>$\epsilon_b$</td>
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<tr>
<td>CdS</td>
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<tr>
<td>ZnO</td>
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</table>
One can see that both CdS and ZnO each have two band gaps in their dispersion relations. The largest of the four band gaps is the upper one of ZnO which lies between $\varepsilon_{T_2} = 3.381$ eV and $\varepsilon_{L_2} = 3.392$ eV with $\Delta \varepsilon_{gap} = \varepsilon_{L_2} - \varepsilon_{T_2} = 11$ meV. Within this band gap of ZnO there can be no propagation of exciton-polaritons within the material. We have exploited this characteristic to create confinement of exciton-polaritons in material A of our coupler system. When the energy of propagating polaritons in CdS lies within the band gap of ZnO the polaritons are reflected from ZnO. In other words, the polaritons are confined in CdS.

Note that we have considered that our CdS/ZnO coupler lies along z direction and light propagate in x and z plane with wave vectors $k_x$ and $k_z$. There is no propagation in y direction. We can easily include the propagation y direction but it will not change the physics of this paper. The width of the two CdS slabs are taken to be the same and is denoted by $d$. The distance between the stabs is $h$. Following the method of reference [9] we get the following dispersion relation for the exciton-polaritons in the coupler

$$k_{Ax}^+ \tan \left[ 2d k_{Ax}^+ - \tan^{-1} \left( \frac{k_{Bx}^+}{k_{Ax}^+} \right) \right] - k_{Bx}^+ \tanh \left[ k_{Bx}^+ h/2 \right] = 0, \quad (4.3)$$

$$k_{Ax}^- \tan \left[ 2d k_{Ax}^- - \tan^{-1} \left( \frac{k_{Bx}^-}{k_{Ax}^-} \right) \right] - k_{Bx}^- \coth \left[ k_{Bx}^- h/2 \right] = 0,$$

where $k_{Bx}^\pm = \sqrt{(k_{Ax}^\pm)^2 + F_A^2 - F_B^2}$. The + and − stand for the exciton-polariton energies of the even and odd modes.

According to the above expression the wave vector $k_{Ax}$ is quantized with quantum number $n$. These quantized modes propagate along the z-direction. According to eqn. (4.1) if $k_{Ax}$ is quantized then the energy of the polaritons is also quantized. It is denoted as $\varepsilon_{nk_z}^\pm$ where it is quantization of energy in the x direction and $k_z$ stands for propagation of polaritons in the z direction. Then $k_{Az}$ is found from eqn. (4.1) as

$$k_{Az} = \sqrt{F_A^2 (\varepsilon_{nk_z}^\pm) - (k_{Anx}^\pm)^2}. \quad (4.4)$$

For $k_z = 0$, the quantized energy $\varepsilon_{nk_z}^\pm$ reduces to $\varepsilon_n^\pm$ and we get

$$k_{Anx}^\pm = F_A (\varepsilon_n^\pm). \quad (4.5)$$
by putting eqn. (4.3) into eqn. (4.1). The expression of $k_{Az}$ becomes

$$k_{Az} = \sqrt{F^2_A(c_{nk}^\pm) - F^2_A(c_{n}^\pm)}.$$  

The quantized energies $c_{nk}^\pm$ are calculated via eqn. (4.3) by numerical methods.

### 4.2.2 Hamiltonian

It is considered that the coupler is lightly doped with quantum dots. Therefore, the interaction between the quantum dots can be neglected. Four energy levels of the QDs are considered in the calculation of the absorption coefficient. It is noted that in the previous section that the bound exciton-polaritons (BEPs) in the coupler are quantized. We know that QDs also have excitons. To observe the effect of coupling excitons in the QDs and BEPs in the coupler we have considered only four levels in the QD. They are denoted as $|a\rangle$, $|b\rangle$, $|c\rangle$ and $|d\rangle$ and a schematic diagram of the QD is presented in Fig. 4-3. Here $|a\rangle$ is the ground state.

We consider a probe field with amplitude $E_p$ is applied between level $|a\rangle$ and $|b\rangle$ and a control field with amplitude $E_c$ is applied between level $|c\rangle$ and $|d\rangle$. The coupler acts as reservoir for the QDs. We consider that the exciton transition energy for $|b\rangle \leftrightarrow |c\rangle$ is in resonance with the polariton energy of the coupler. Hence there is coupling between the QD and the coupler. The coupling is called the exciton-BEP interaction. Therefore the QD is interacting with probe and control lasers and also with the coupler which as a reservoir. Hence the Hamiltonian of the QD
is written as

\[ H_{pol} = H_0 + H_{QD-L} + H_{QD-R}. \]  \hspace{1cm} (4.7)

The first term is the Hamiltonian is written as

\[ H_0 = \sum_{i=a,b,c,d} \varepsilon_i \sigma_{ii}. \]  \hspace{1cm} (4.8)

The second term in eqn. (4.7) is coupling of the QD and probe and control lasers and is found as

\[
H_{QD-L} = -\hbar \left( \Omega_p a_p^\dagger \sigma_{ba} e^{-i\varepsilon_p t/\hbar} + \Omega_p^* a_p \sigma_{ba} e^{i\varepsilon_p^* t/\hbar} \right) \\
- \hbar \left( \Omega_c a_c \sigma_{dc} e^{-i\varepsilon_c t/\hbar} + \Omega_c^* a_c^\dagger \sigma_{dc} e^{i\varepsilon_c^* t/\hbar} \right),
\]  \hspace{1cm} (4.9)

where \( \sigma_{ii}^+ = |i\rangle \langle i| \) with \( i = a, b, c, d \) and it is called the preserving operator. \( \sigma^+ \) and \( \sigma^- \) are the raising and lowering operators, respectively with \( \sigma_{ba}^+ = |b\rangle \langle a| \), \( \sigma_{ba} = |a\rangle \langle b| \), \( \sigma_{bc}^+ = |c\rangle \langle b| \) and \( \sigma_{bc} = |b\rangle \langle c| \). Here \( \varepsilon_i \) is the energy of \( |i\rangle \) and \( \varepsilon_{bc} \) is the energy difference between \( |b\rangle \) and \( |c\rangle \). \( a_{p/c} \) and \( a_{p/c}^\dagger \) are probe/control field photon annihilation and creation operators. \( \Omega_p \) and \( \Omega_c \) are the Rabi frequencies associated with the probe and control fields, respectively. \( \varepsilon_{p/c} \) is the probe/control field photon energy.

The last term in eqn. (4.7) is coupling in the exciton-BEP interaction between the QD and the coupler. It is found as

\[
H_{QD-R} = -\sum_{\pm} \sum_n \sum_{k_z} V(\varepsilon_{nk_z}) \begin{bmatrix}
n_nk_z \pm \sigma_{bc}^+ e^{-i\varepsilon_{nk_z} t/\hbar} \\+ a_{nk_z}^\dagger \pm \sigma_{bc} e^{i\varepsilon_{nk_z} t/\hbar} \end{bmatrix},
\]  \hspace{1cm} (4.10)

where

\[
\sum_{k_z} V(\varepsilon_{nk_z}^\pm) = \sqrt{\frac{2\hbar\varepsilon_{nk_z}^\pm}{2\pi\varepsilon_0 Ad_z}}
\]

with \( a_{nk_z}^\dagger \) and \( a_{nk_z} \) being the polariton creation and annihilation operators.
4.2.3 Schrödinger Equation Method

Now we solve the Schrödinger equation for the above Hamiltonian by

\[
\frac{i\hbar}{\partial t} |\Psi\rangle = (H_0 + H_{QD-L} + H_{QD-R}) |\Psi\rangle.
\]  

(4.11)

We consider that initially the electron in QD is in the ground state \( |a\rangle \) and there is one probe photon and one control photon present. Polaritons in the reservoir are in the ground state and this initial state is denoted as \( |1, 0_k, 1_a, 1_b\rangle \). We expand the wavefunction as an orthonormal set as follows

\[
|\Psi\rangle = A_a |a, 0_k, 1_a, 1_b\rangle + A_b |b, 0_k, 0_a, 1_b\rangle
\]

\[
+ \sum_{\pm} \sum_n \sum_{k_z} A_{c,nk_z}^\pm |c, 1_k, 0_a, 1_b\rangle
\]

\[
+ \sum_{\pm} \sum_n \sum_{k_z} A_{d,nk_z}^\pm |d, 1_k, 0_a, 0_b\rangle.
\]

(4.12)

where \( A_i \) are the expansion coefficients. Putting eqn. (4.11) into eqn. (4.12) we get

\[
\frac{\partial A_a}{\partial t} = i\Omega_p A_b
\]

(4.13a)

\[
\frac{\partial A_b}{\partial t} = \begin{bmatrix}
    d_{ab} A_b + i\Omega_p A_a \\
    + i \sum_{\pm} \sum_n \sum_{k_z} V (\varepsilon_{nk_z}^\pm) A_{c,nk_z}^\pm
\end{bmatrix}
\]

(4.13b)

\[
\frac{\partial A_{c,nk_z}^\pm}{\partial t} = d_{bc} A_{c,nk_z}^\pm + iV (\varepsilon_{nk_z}^\pm) A_b + i\Omega_c A_{d,nk_z}^\pm
\]

(4.13c)

\[
\frac{\partial A_{d,nk_z}^\pm}{\partial t} = d_{cd} A_{d,nk_z}^\pm + i\Omega_c A_{c,nk_z}^\pm
\]

(4.13d)

where \( \gamma_b, \gamma_c, \) and \( \gamma_d \) are the radiative linewidths of their respective levels and

\[
d_{ab} = [i\delta_{ab} - \gamma_b],
\]

(4.14)

\[
d_{bc} = [i(\delta_{ab} - \delta_{n}^\pm) - \gamma_c],
\]

\[
d_{cd} = [i(\delta_{cd} + \delta_{ab} - \delta_{n}^\pm) - \gamma_d],
\]
\[ \delta_{ab} = \varepsilon_p - \varepsilon_{ab}, \quad (4.15) \]
\[ \delta_{cd} = \varepsilon_c - \varepsilon_{cd}, \quad \delta_n^\pm = \varepsilon_n^\pm - \varepsilon_{bc}. \]

Here \( \delta_n^\pm \) is called the polariton detuning and \( \delta_{ab} \) and \( \delta_{cd} \) are the probe and control detunings, respectively. The summation in eqn. (4.13b) can be replaced by using the method of density of states. We know that polaritons in the coupler have quantized modes which propagate in \( z \)-direction. The \( z \)-component of the wave vectors is not quantized. Therefore, the summation over \( k_z \) can be replaced by the integration over energy \( \varepsilon_{nk_z} \) by using the concept of the DOS as

\[ \sum_{\pm} \sum_n \sum_{k_z} = \sum_{\pm} \sum_n \int D_n^\pm d\varepsilon_{nk_z}, \quad (4.16) \]

where \( D_n^\pm \) is defined as

\[ D_n^\pm = V \frac{dk_z}{8\pi^3 d\varepsilon_{nk_z}^\pm}, \quad (4.17) \]

where if \( k_z = \sqrt{F^2(\varepsilon_{nk_z}^\pm) - F^2(\varepsilon_n^\pm)} \) then

\[ D_n^\pm = V \frac{F'(\varepsilon_{nk_z}^\pm)}{16\pi^3 \sqrt{F^2(\varepsilon_{nk_z}^\pm) - F^2(\varepsilon_n^\pm)}}, \quad (4.18) \]

where \( F' \) is the differential of \( F \) with respect to \( \varepsilon_{nk_z}^\pm \).

### 4.2.4 Absorption Coefficient

Following the method of reference [20] and using Schrödinger equations (4.13a-4.13d) one can evaluate the absorption coefficient in the linear response theory as

\[ \alpha_{ab} = \frac{\varepsilon_p}{2\hbar^2 c \varepsilon_0} \text{Im} \left( \frac{P_{ab}^2 \rho_{ab}}{\Omega_p} \right) = \alpha_0 \text{Im} (\rho_{ab}), \quad (4.19) \]

likewise the dispersion coefficient may be found to be
\[
\beta_{ab} = \frac{\varepsilon_p}{2\hbar^2 c \varepsilon_0} \text{Re} \left( \frac{\rho_{ab}^{\rho} \rho_{ab}}{\Omega_p} \right) = \beta_0 \text{Re} (\rho_{ab}),
\]

(4.20)

where \( \rho_{ab} \) is the dipole moment for the transition \( a \to b \). \( \rho_{ab} \) is the density matrix element for the \( a \to b \) transition and can be found by solving our Schrodinger equations in eqn. (4.13a-4.13d) with

\[
\rho_{ab} = A_a A_b^*. \tag{4.21}
\]

Note that the polariton absorption coefficient depends on \( \rho_{ab} \), which in turn depends on the energy difference between the transition energy \( \varepsilon_{bc} \) and a BEP energy \( \varepsilon_{n}^{\pm} \) (i.e. \( \delta_{n}^{\pm} \)). In other words, the absorption coefficient depends on coupling of the QD and the reservoir.

### 4.2.5 Group Velocity

We can now calculate the group velocity of exciton-polaritons in the coupler as

\[
v_g = \frac{1}{\hbar} \frac{\partial \delta_{ab}}{\partial k_A} = \frac{1}{\hbar} \left[ \frac{F_i(\varepsilon_p)}{\varepsilon_p} + \frac{\partial \beta}{\partial \Delta_{ab}} \right]^{-1},
\]

(4.22)

as well as the delay time of the field at the exit point from the medium \( z = \zeta \) which is

\[
T_{del} = \hbar \frac{\partial \beta}{\partial \delta_{ab}} \zeta, \tag{4.23}
\]

and the group velocity dispersion given by is

\[
D = \hbar^2 \frac{\partial^2 \beta}{\partial \delta_{ab}^2}. \tag{4.24}
\]

### 4.2.6 Analytical Expressions

Though we will solve eqn. (4.13a-4.13d) numerically, to gain some physical insight of the effect of the QD-coupler coupling we have derived the analytical expression of the absorption coefficient in the steady state. In the steady state we get the expression of expansion coefficient \( A_b \) are found as

\[
A_b = -\frac{i \Omega_p}{\delta_{ab} + \Xi_{bc}} A_a \tag{4.25}
\]
where $\Xi_{bc}$ is a complex quantity and is generally called the self energy. It is written as

$$\Xi_{bc} = \sum_{\pm, n, k_z} \frac{|V (\varepsilon_{nk_z}^\pm)|^2 d_{cd}}{(d_{cd} d_{bc} - |\Omega_c|^2)}. \tag{4.26}$$

and by putting eqn. (4.26) into (4.21) we get an analytic expression for the density matrix

$$\rho_{ab} = -\frac{i \Omega_a \rho_{aa}}{d_{ab} + i \Xi_{bc}}, \tag{4.27}$$

where $\rho_{aa} = |A_a|^2$ is the probability of finding the particles in state $|a\rangle$.

Putting the expression of the density matrix, eqn. (4.27), into the expression of the absorption coefficient, eqn. (4.19), we get

$$\alpha_{ab} = -\frac{\varepsilon_p}{\hbar c} \text{Im} \left[ \frac{i \Omega_a \rho_{aa}}{d_{ab} + i \Xi_{bc}} \right]. \tag{4.28}$$

By rewriting the self energy in eqn. (4.26) and replacing the summation $\sum_{\pm, n, k_z}$ by the DOS defined in eqn. (4.16), we get

$$\Xi_{bc} = \sum_{\pm} \sum_n \int D_n^\pm d_{n, k_z}^\pm \left( \frac{|V (\varepsilon_{nk_z}^\pm)|^2 d_{cd}}{d_{cd} d_{bc} - |\Omega_c|^2} \right). \tag{4.29}$$

Putting expression of $d_{bc}$ and $d_{cd}$ from (4.14) in the above expression we get

$$\Xi_{bc} = \sum_{n, \pm} \int \left( \frac{|V (\varepsilon_{nk_z}^\pm)|^2 \left[ i \left( \delta_{cd} - \delta_n^\pm \right) - \gamma_d \right] D_n^\pm d_{n, k_z}^\pm}{i \left( \delta_{cd} - \delta_n^\pm \right) - \gamma_d} \right), \tag{4.30}$$

as an analytical expression for the self energy and consequently for the absorption coefficient given by eqn. (4.28). One can see from these equations that the absorption coefficient depends on the DOS, $D_n^\pm$, of the quantized propagating polaritons in the coupler. It also depends on the detuning $\delta_n^\pm = \varepsilon_n^\pm - \varepsilon_{bc}$. In other words the absorption coefficient is very sensitive to the location of QD transition energy $\varepsilon_{bc}$ and the BEP energy $\varepsilon_n^\pm$.

Note that when both $\varepsilon_n^\pm$ and $\varepsilon_{bc}$ are in resonance we get $\delta_n^\pm = \delta_{bc}$ and the coupling between QD and coupler is enhanced and the self energy becomes huge since the DOS is huge. This is because the DOS has a singularities at $\varepsilon_n^\pm = \varepsilon_{bc}$. This can be seen from eqn. (4.18). This in
turn the absorption coefficient becomes almost zero, switching it into a transparent state. A more detailed numerical calculation is presented in the next showing the above predictions.

4.3 Results and Discussion

In this section we have performed numerical simulations of bound exciton polaritons (BEP), the density of states (DOS), and the absorption coefficient. For numerical simulations we envision a waveguide coupler made from CdS and ZnO. The bound exciton-polariton energies and the density of states are solved for using the Maple software package. The Schrodinger equations of eqn. (4.13a-4.13d) are solved numerically by using a method constructed in Matlab based on the ODE45 differential equation solver. The QD we consider is a four-level N-type system that can be realized in a single-electron-charged QD [21] and has a resonance energy $\varepsilon_{bc} = 3.384$ eV, dipole moment $p_{bc} = 0.1$ e nm, $\gamma_b = 1$ meV, and $\gamma_c, \gamma_d = 0.01 \gamma_b$.

The BEP energy is plotted as a function of separation, $h$, in Fig. 4-4. The even (+) and odd (-) BEP energies are denoted by the lower and upper dashed curves, respectively. The degenerate single BEP energy for the $h = 150$ nm case is the dotted line. The solid lines show the band edges for the upper ZnO band gap. Note that as $h$ increases that the separation between the odd and even modes decreases. It can be seen that for coupler separation of $h > 140$ nm the coupler system acts like two separate single waveguides with energy $\varepsilon_n = 3.384$ eV. That means that the waveguides do not interact with each other via dipole-dipole interaction (DDI). For $h < 140$ nm the two waveguides interact with each other via the DDI and the BEP energy splits. For separations of $h < 80$ nm the even mode solution of the BEP energy lies below the band gap of ZnO and would no longer be a bound state of the coupler. This needs to be taken into account in choosing the dimensions in which to fabricate this coupler system. Split modes in the dispersion of polaritons has been seen in experimental systems [22].

The DOS for even and odd states are plotted as function of energy in Fig. 4-5. Here, the dashed line corresponds to $h = 150$ nm and the solid lines to when $h = 80$ nm. The dashed lines depict the locations of the $\varepsilon_n = 3.384$ eV, $\varepsilon^+_n = 3.382$ eV and $\varepsilon^-_n = 3.386$ eV BEP energies. The alternating dashes and dots line shows the band edges for the ZnO band gap. It can also be plainly seen that the value for the DOS becomes very large at each BEP energy state. This
means that when the resonance energy $\varepsilon_{bc}$ of the QD is resonant with $\varepsilon_n$, $\varepsilon_n^+$ or $\varepsilon_n^-$ there is large exciton-BEP coupling. This can be seen in eqn. (4.30).

The absorption coefficient depends on $\rho_{ab}$ as shown in eqn. (4.19). The density matrix element, $\rho_{ab}$, is evaluated at the steady state. We have plotted $\rho_{ab}$ against normalized time ($\tau$) in Fig. 4-6. One can see that the system oscillates in the beginning and then reaches its steady state for $\tau > 10$. Here the dotted represents the coupler with separation of $h = 150$ nm and the dashed curve for separation of $h = 80$ nm. Both are for the a detuning value of $\delta_{ab} = 1$. The frequency of oscillations is increased with the two waveguides interacting in the coupler, however the steady-state is reached at nearly the same number of time steps. The number of oscillations then depends on the self energy. As the self energy increases so do the number of oscillations.

In Fig. 4-7 we show the absorption coefficient as a function of probe detuning when separa-
Figure 4-5: Plot of the DOS (in arbitrary units) of the coupler as a function of Energy (eV) within the band gap of ZnO.

The separation between the waveguides is \( h = 150 \text{ nm} \). Here, the control field is absent, \( \Omega_c = 0 \). The solid and dotted curves correspond to the when the QD-coupler system is far off and at resonance, respectively. In this case both waveguiding slabs act independently. In the non-resonant condition the absorption profile has one peak due to the transition \( |a\rangle \leftrightarrow |b\rangle \). The splitting of the spectrum from having one peak to two peaks is due to strong exciton-BEP coupling. As we pointed out, the coupling is strong via the DOS having a large value near the bound states as shown in Fig. 4-5. Due to the strong coupling, dressed states are created in the system and are denoted as \( |b^+\rangle \) and \( |b^-\rangle \). Two absorption peaks appear due to transitions \( |a\rangle \leftrightarrow |b^+\rangle \) and \( |a\rangle \leftrightarrow |b^-\rangle \). It can be noted that the absorption spectra also has a minima at \( \delta_{ab} = 0 \), which is \( \varepsilon_{bc} = \varepsilon_n \). In this instance the QD has become transparent to the probe laser, \( \Omega_p \), at resonance with the BEP energy of the coupler, \( \varepsilon_n \).

Absorption of guided mode polaritons of a waveguide by a nearby quantum well has been experimentally seen in work by Takagi et al. [3]. In that work a waveguide and quantum well,
both made of GaAs, show a resonant coupled interaction when separated by 500 nm. Exciton-polaritons travelling through the waveguide are demonstrated to be absorbed by the nearby quantum well by drops in the transmission rate in energy regions corresponding to the lh and hh exciton transitions of the quantum well.

In Fig. 4-8 we have plotted the absorption coefficient as a function of probe detuning, this time for a distance between the waveguiding slabs of \( h = 80 \text{ nm} \). The control field is still off, \( \Omega_c = 0 \). The solid curve correspond the non-resonance condition and the dashed curve to being on resonance. Here we see the spectrum of the QD split having one peak to three peaks. This is because this case creates four dressed states. Two dressed states are degenerate and have the same energy. Hence we three transition corresponding to three peaks. This case we also have two transparent states. This means that one transparent state at \( h = 150 \text{ nm} \) coupler separation can be split into two at \( h = 80 \text{ nm} \). This is due to the coupling between the two waveguiding slabs interacting via the DDI. We call the presence of transparency in the present system reservoir induced transparency (RIT) [23]-[24]. This effect is similar to electromagnetically induced transparency (EIT). EIT has been observed in an artificial atom [25] and \( ^{87}\text{Rb} \) atoms [26] due to a control laser instead of a photonic reservoir. This is a good
Finally we have studied the switching mechanism for the RIT. We applied a control field \((\Omega_c)\) to the transition \(|c\rangle \leftrightarrow |d\rangle\). In Fig. 4-9 we have plotted the solid and dotted curves as the absorption in the presence \((\Omega_c = 0.1\gamma_b)\) and absence \((\Omega_c = 0)\) of the control field, respectively. Here the separation in the coupler is taken to be \(h = 80\) nm. There results in the shift of the transparent states. This means that the transparent states in the presence of the control field become absorbing states. Therefore one can say that the system can be switched from transparent states to absorbing states. This is a switching mechanism. As mentioned before the system may also be switched from one transparent state to two by changing the distance between the waveguiding slabs. This can also be achieved by applying stress or strain fields to the coupler to change the separation distance.

Plotted in Fig. 4-10 we have the dispersion coefficient as a function of probe detuning. As in the plot of the absorption coefficient the solid line corresponds to the non-resonant case, the dotted line to the resonant case with \(h = 150\) nm, and the dashed line to the resonant case with \(h = 80\) nm. It can be seen that the solution for the dispersion coefficient goes to zero in correspondence with to the location of the transparent states in the absorption coefficient.
Figure 4-8: The off (solid curve) and on (dashed curve) resonance absorption for $h = 80$ nm coupler separation of the QD plotted against probe laser detuning, $\delta_{ab}$ (meV).

In Fig. 4-11a and 4-11b, the delay time, $T_{del}$, and group velocity dispersion coefficient, $D$, are plotted against detuning, $\delta_{ab}$. The dotted and dashed curves correspond to $h = 150$ nm and $h = 80$ nm separation cases, respectively. The regions of negative value are due to anomalous dispersion near absorption regions and would lead to faster-than-c or negative $v_g$ [27]. In Fig. 4-11a, the peaks in $T_{del}$ are located at the $\delta_{ab} = \delta_{n}^{\pm}$, $\delta_{n}$, just as were the minima in the absorption. The derivative of $\rho_{ab}$ is discontinuous at $\delta_{ab} = \delta_{n}^{\pm}$, $\delta_{n}$ so appropriate values must be taken in the limits as $\delta_{ab} \to \delta_{n}^{\pm}$, $\delta_{n}$. Maxima values of $T_{del}$ correspond to minima values for the group velocity, $v_g$. This clearly means that $v_g$ is appreciably reduced near the regions of resonance coupling between the coupler and QD that forms RIT. Also clear in Fig. 4-11b, the group velocity dispersion, $D$, is also increased in the region of resonance and this may lead to strong confinement within the QDs.
Figure 4-9: The effect of the control laser $\Omega_c$ applied to the $|c\rangle \leftrightarrow |d\rangle$ transition on the absorption of the QD plotted against probe laser detuning, $\delta_{ab} \text{ (meV)}$, in the case of the coupler with separation $h = 80$ nm. For the dashed curve $\Omega_c = 0$ and $\Omega_c = 0.1\gamma_b$ for the alternating dashes and dots curve.

Figure 4-10: The non-resonant absorption (solid curve), the $h = 150$ nm (dotted curve) and $h = 80$ nm (dashed curve) coupler separation resonant absorption of the QD plotted against probe laser detuning, $\delta_{ab} \text{ (meV)}$. 
Figure 4-11: The (a) delay time $T_{del}$, and (b) group velocity dispersion coefficient, $D$, plotted against detuning, $\delta_{ab}$. In both the dotted curve corresponds to the coupler in case $h = 150$ nm and the dashed to $h = 80$ nm.
4.4 Conclusions

We have developed a theory for a quantum mechanism of RIT in QDs and exciton-polaritonic coupler hybrid systems. The considered coupler is built out of excitonic materials. Two \( CdS \) waveguiding slabs are embedded between layers of \( ZnO \) in the construction of the coupler. An ensemble of non-interacting QDs are doped within the \( CdS \) waveguiding regions of the coupler. The coupler acts as a reservoir to the QDs. BEPs are found within the band gap of \( ZnO \) and interact with the excitons present in the QDs via the exciton-BEP interaction. A probe laser is applied to measure the absorption in the QD. It is found that when the two \( CdS \) waveguiding cores are far away \( (h = 150 \text{ nm}) \) from each other that the absorption spectrum has one minima which corresponds to a transparent state. Further, when the waveguides are close to each other \( (h = 80 \text{ nm}) \) the absorption spectra has two transparent states. A control laser is found to be able to switch the transparent states on and off. These are noteworthy results which can be used to make new types of polaritonic devices such as optical switches and transistors.
Bibliography


Chapter 5

Fluorescence in Biological Labelling
Dye-Gold Nanorod Nanocomposites

In the previous chapter, we studied the interaction in a quantum dot (QD) and exciton-polaritonic coupler nanocomposite hybrid systems. We found reservoir induced-transparency in the system that a control laser field had the ability to switch off and on. In this chapter we study the fluorescence in a biological labelling dye (Alexa Fluor 405, AFD) and gold nanorods (GNRs) nanocomposite. There is a transfer of energy that is driven by the dipole-dipole interaction between the excitons in the AFD and surface plasmon-polaritons on the gold nanorods. We have investigated the energy transfer rate from AFD to GNRs under excitation from one-photon and two-photon resonant laser fields and its effect on the measured fluorescence lifetime change in AFD samples\textsuperscript{1}.

5.1 Introduction

To fuel the current revolution in life science imaging new experimental tools that enable the manipulation of biomolecules and the study of biological processes at the molecular level are needed. Biomolecule-nanoparticle nanocomposites represent functional information gathering units for biological applications. Interest in the development of nanoscale optoelectronic devices has

\textsuperscript{1}The material presented in this chapter has been published in: C. Racknor, M.R. Singh, Y. Zhang, D.J.S. Birch, and Y.Chen, \textit{Methods Appl. Fluoresc.} \textbf{2}, 015002 (2014).
progressed recently by combining different nanomaterials into hybrid structures [1]-[6]. These hybrid nanostructures could prove to be potentially strong tools for the future of biotechnology [7]-[9] and solar energy collection [10],[11]. To create fluorescent probes there are many types of potential hybrid matches such as organic dye-metal [12] and nanoparticle-enzyme [13]. Specifically magnetic hybrid nanostructures have applications as contrast agents in MRI technology [14]. Fluorescent dyes are combined with quantum dots in hybrid systems as photosensitizers for photodynamic therapy in cancer studies. A Methylene blue dye-semiconductor nanocrystal match points toward an improvement in the cancer cell kill efficiency [15]. A system of two linear linked dye molecules to metal oxide nanoparticles has been made to be a dye-sensitized solar cell covering a wavelength range from 400 to 950nm [11]. Organic dye molecules and noble metal nanoparticles show improved fluorescence quenching efficiency and photostability as resonant energy transfer systems [16].

Also, Silver colloids selectively bound with thiolated 23-mer oligonucleotide in a hybrid system with fluorescein were studied. Their interaction made for an observed increase in fluorescence emission [17]. An organic dye-gold nanoparticle hybrid system has been recently found to have random photoactivated fluorescence blinking whose rate depends on the size of the nanoparticles. These properties have the potential for use as light emitting nanostructures [18].

The optical excitations in metallic nanorods are the collective oscillations of conduction band electrons, called surface plasmon-polaritons. Polaritons arise from the dielectric contrast between the metal and an embedded dielectric media while the resonant frequencies of surface plasmon-polaritons are dictated by the shape and size of the metallic system. The future of nanophotonic devices and circuits utilizing the polaritons is expected to be significant in optical signals processing, nanoscale optical devices, and near-field microscopy with nanoscale resolution [19].

Two-photon effects are well known phenomena and have a wide range of applications, specifically to bioscience imaging [20]. Two-photon excitation has advantage over one-photon excitation because it has higher spatial resolution, deeper penetration and less photo-damage. Nanoparticles made of pure noble metals have high electron polarizability and produce enhanced local electric fields that are particularly important for nonlinear optical processes. Multi-photon
photoluminescence has been studied in nanostructured noble metals [21]-[23] and it is found that it is more sensitive to the local field than single-photon luminescence. One- and two-photon induced fluorescence of Pacific Blue-labeled human serum albumin has been studied in the presence of different size silver colloids. The two-photon excitation showed stronger increases in brightness compared to one-photon excitation [24].

5.1.1 System Studied

This chapter will be on a hybrid system consisting of Alexa Fluor 405 dye (AFD), a biological fluorescent labelling dye, and gold nanorods (GNRs) submerged in an aqueous solution. A schematic is shown in Fig. 5-1. Alexa Fluor dyes can act as a cell and tissue labels in fluorescence microscopy and cell biology. The Alexa Fluor 405 is efficiently activated by lasers in the wavelength range near 405 nm [25]. This work investigates the energy transfer rates for situations where the AFD is excited by one- and two-photon absorption, respectively. Alexa Fluor dyes are generally more stable, brighter, and less pH-sensitive than common dyes (e.g. fluorescein, rhodamine) of comparable excitation and emission [26]. We will be concerning ourselves with the energy transfer rate arising from the interaction of optical excitations between
these components of the system. These interactions are strong when the AFD and GNR are in close proximity and their optical excitation frequencies are resonant with each other. We find that the DDI interaction between AFD and GNRs will force a decrease in the fluorescence lifetime change in the AFD which could be a significant contribution to bioimaging, fluorescence sensing, and nuclear targeting cancer therapy.

5.2 Experimental Methods

Experiments on the fluorescence and fabrication of the AFD/GNR nanocomposite were carried out by the group of Dr. Yu Chen at the University of Strathclyde. The GNRs were synthesized by the seeded growth method with a typical length about 50nm and aspect ratio about 3.5 obtained from SEM measurement. A schematic of the hybrid solution is presented in Fig. 5-1.

The first sample S0-1 was prepared by combining the mixture solution of 500 µl 0.21nM GNRs and 150 µl 2µM AFD making for an AFD/GNR ratio of 3000:1. Similarly, a second sample S0-2 was prepared by mixing a solution of 500 µl 0.21nM GNRs and 300 µl 2µM AFD for a ratio of 6000:1. Samples were placed in an imaging chamber for microscopy studies. Fluorescence-lifetime imaging microscopy experiments were performed using a confocal microscope (LSM 510, Carl Zeiss) equipped with a time-correlated single photon counting module (SPC-830, Becker & Hickl GmbH). A femtosecond Ti:Sapphire laser (Chameleon, Coherent) with a laser pulse repetition rate of 80 MHz and duration less than 200 fs. Emission was collected using a 60 water immersion objective (N.A. 1.0) and a bandpass filter with a transmission window from 390 nm to 465 nm. The GNRs have a longitudinal plasmon mode centred at around 850 nm and a transverse band at 525 nm.

The interaction between GNRs and AFD in a mixed solution was examined by monitoring the fluorescence lifetime change. Here sample F405 is the pure AFD and samples S0-1 and S0-2 are AFD-GNR hybrids. Fig. 5-2 displays the comparison of AFD fluorescence intensity in S0-1, S0-2 and reference control solution excited at 385 nm. All measurements have been normalized in term of dye concentration so that direct comparison can be made. Both S0-1 and S0-2 showed significant drop in fluorescence intensity. Furthermore, S0-2 had a further decrease in intensity compared to S0-1.
In two separate experiments the one-photon and two-photon fluorescence lifetime change in samples F405, S0-1, and S0-2 were observed under excitation from two different lasers. In the one-photon experiment the laser with wavelength 374nm is used and emissions were collected with longpass 405nm filter. One-photon excitation fluorescence decay curves of all samples are presented in Fig. 5-3. Under one-photon excitation (374nm) the GNRs do not emit light, so the decay curve of mixture solution can be directly compared to that of the pure F405 sample. All AFD-GNR hybrid samples (S0-2 and S0-1) show significant decrease in decay time. This lifetime reduction alongside a fluorescence intensity decrease suggests an energy transfer between AFD and GNRs.

In the two-photon excitation experiments a laser with wavelength 810nm (Ti: Saphire) is used and both AFD and GNRs emit luminescence. The GNRs emit luminescence with a lifetime shorter than the system response time [27]. Fig. 5-4 shows normalized decay curves (after subtracting the effect from nanorods) of F405, S0-1, and S0-2 under two-photon excitation. Emission from GNR solution was used as system response (or prompt) to achieve good-quality fitting results. More significant decrease in lifetime (down to 2.6ns from 3.7ns) has been found, which suggests an enhanced energy transfer process when excitation wavelength matches with
longitudinal surface plasmon resonance of GNRs. This enhanced energy transfer under two-photon excitation shows a benefit to using gold nanorods in energy transfer pairs in comparison with gold nanospheres.

5.3 Theoretical Formalism

Firstly, we have considered the dipole-plasmon interaction between the dye and metal nanoparticles for the two-photon process, we call it a dipole-dipole interaction. In the literature the surface energy transfer (SET) theory has been widely used to explain experimental data [28]-[31]. The SET theory gives a $1/d^4$ distance dependence behaviour where $d$ would be the distance between the dye and a metallic nanoparticle. This theory has been developed for a one-photon process and it is valid for a special case when the one-dimensional (1D) localized plasmons are interacting with a dipole. The 1D localized plasmons are present in two-dimensional metallic surface with a semi-infinite positive back-ground [32]. In the present work, the plasmons in the nanorods are localized in all three dimensions because the size of the nanorod in all three dimensions is smaller than the wavelength of the incident light. In nanorods there is no semi-infinite positive back-ground. Hence the SET theory cannot be applied to the present case and we have developed a theory for the two-photon energy transfer between a dye and a nanorod as follows.

In the experiments, one-photon and two-photon processes are studied in the AFD. The AFD acts as a donor nanoparticle and the GNR acts as an acceptor nanoparticle in the hybrid system. According to selection rules, the one-photon excitation occurs only when the ground state and the excited state have the opposite parity. Similarly the two-photon excitation occurs only when the ground and excited states have the same parity. Therefore we consider that the AFD must have one ground state and two excited states with opposite parity. We model that the AFD’s three states which are denoted as $|1\rangle$, $|2\rangle$, and $|3\rangle$ where $|1\rangle$ is the ground state and $|2\rangle$ and $|3\rangle$ are excited states. The 374 nm laser is represented by $E_c \cos (\omega_c t)$ which excites the one-photon transition from $|1\rangle$ to $|3\rangle$ (i.e. $\omega_c \simeq \omega_{13}$). The 810 nm laser is $E_p \cos (\omega_p t)$ and it excites a two-photon transition from from $|1\rangle$ to $|2\rangle$ (i.e. $2\omega_p \simeq \omega_{12}$). We also consider that the 374nm and 810nm lasers excite one- and two-surface plasmon polaritons in the GNR with
frequency $\omega_{sp1}=\omega_c$ and $\omega_{sp2}=2\omega_p$, respectively.

One- and two-photon excitation dipoles are induced in the AFD and GNR. They interact with each other via the dipole-dipole interaction (DDI). Due to the DDI, energy transfer occurs from AFD to GNR and can be calculated as [34]

$$W_{d\rightarrow g}^i = \frac{1}{V_g} \left\langle \int [j_g^i, E_d^i] \, dV \right\rangle. \quad (5.1)$$

where $i = 1ph$ and $2ph$. Here $j_g^i$ is the induced current and $V_g$ is the volume of GNR. The arrowed brackets, $\langle \rangle$, signify a time average over the period of the oscillating laser fields. The fields $E_{d}^{1ph}$ and $E_{d}^{2ph}$ are the dipole electric fields created by the AFD due to the one- and two-photon excitations at the location of the GNR, respectively. They are written as

$$E_{d}^{1ph} = \frac{g P_{d}^{1ph}}{(4\pi \epsilon_0 \epsilon_b) \epsilon_B R^3}, \quad E_{d}^{2ph} = \frac{g P_{d}^{2ph}}{(4\pi \epsilon_0 \epsilon_b) \epsilon_B R^3}, \quad (5.2)$$

where $P_{d}^{1ph}$ and $P_{d}^{2ph}$ are induced dipoles in the AFD due to the one- and two-photon excitations. Here $\epsilon_B = (2\epsilon_b + \epsilon_d)/3\epsilon_b$ where $\epsilon_b$ and $\epsilon_d$ are the dielectric constants of the host substance, i.e. water, and the AFD. Here $g$ is called the polarization parameter with $g = 2$ or $-1$. The center-to-center distance between the AFD and GNR is denoted as $R$.

The one- and two-photon polarization in AFD can be calculated by using the density matrix method as [34]

$$P_{d}^{1ph} = \mu_{13} \varrho_{13}, \quad P_{d}^{2ph} = k_{12} \varrho_{12} E_p. \quad (5.3)$$

The physical parameters $\varrho_{12}$ and $\varrho_{13}$ are the density matrix elements between states $|1\rangle$ and $|2\rangle$ and $|1\rangle$ and $|3\rangle$, respectively. Here $\mu_{13}$ and $k_{12}$ are the one-photon and two-photon dipole moments and are given in reference [35].

The current density $j_g^i$ in the GNR is calculated by differentiating the polarization $P_g^i$ with time as such, $j_g^i = (dP_g^i/dt)/V_g$.

The nonlinear two-photon polarization $P_g^{1ph}$ in the GNR can be calculated by using the quasi-static approximation [36]. We consider a GNR of an ellipsoidal shape with major axis $l$ and minor axis $r$. The electric field seen by the GNR are $E_c$ and $E_{d}^{1ph}$, for one-photon process
and \( E_p \) and \( E^{2ph}_d \) for two-photon process. The resultant polarization of the GNR is

\[
P^{1ph}_g = \chi_1 \left( E_c + E^{1ph}_d \right), \quad P^{2ph}_g = \chi_1 E^{2ph}_d + \chi_2 E^2_p,
\]  

(5.4)

where

\[
\chi_1 = \frac{4\pi \epsilon_0 \epsilon_b V_a (\epsilon_m - \epsilon_b)}{3\epsilon_b + 3\varsigma_{l,r}(u) (\epsilon_m - \epsilon_b)}, \quad \chi_2 = \frac{m_e \zeta \chi_0^2 (\omega_p) \chi_1 (2\omega_p)}{\epsilon^3},
\]  

(5.5)

and where \( \epsilon_m(\omega) \) is dielectric constant of the GNR and taken from Ref. [34]. Here \( m_e, \zeta, \) and \( e \) are the mass of an electron, coupling constant with unit \( (m^{-1}s^{-2}) \) and the charge of the electron, respectively. Parameter \( \varsigma_{l,r}(u) \) is the depolarization factor and is defined in Ref. [37] and it depends on the shape of the nanorod \( (u = r/l) \).

With the help of eqns (5.2-5.4), eqn (5.1) the energy transfer rate calculated as

\[
W^{1ph}_{d\rightarrow g} = \frac{\omega_{13}}{2} \left[ \text{Im} \left( \chi_1^* \right) \left| E^{1ph}_d \right|^2 + \text{Im} \left( \chi_1^* E^*_d E^{1ph}_d \right) \right]
\]  

(5.6a)

\[
W^{2ph}_{d\rightarrow g} = \frac{\omega_{12}}{2} \left[ \text{Im} \left( \chi_1^* \right) \left| E^{2ph}_d \right|^2 + \text{Im} \left( \chi_2^* E^{2ph}_d \right) \left| E_p \right|^2 \right]
\]  

(5.6b)

where \( W^{1ph}_{d\rightarrow g} \) and \( W^{2ph}_{d\rightarrow g} \) are the energy transfer rate due to the one- and two-photon DDI from the AFD to the GNR. Note that energy rate depends on the one- and two-photon DDI between the AFD and GNR. A similar expression to eqn. (5.6a) for the one-photon process has been calculated in Ref. [2]. This expression depends on the density matrix element \( \rho_{13} \) which are also been calculated in that work. The two-photon energy transfer rate depends on density matrix element \( \rho_{12} \) which is calculated as follows.

We have calculated that polarization induced in the GNR in eqn. (5.4). This polarization creates a dipole field near the AFD and is written as

\[
E^{2ph}_g = \frac{g I^{2ph}_g}{(4\pi\epsilon_0) \epsilon_B R^3}.
\]  

(5.7)

The AFD and GNR interact via DDI. Using the above expression the DDI Hamiltonian of
the hybrid system is

$$H_{ddi} = \hbar (\Lambda_2 + \Lambda_{ddi}) \sigma_{21} + \hbar c,$$  \hspace{1cm} (5.8)

where

$$\Lambda_2 = \frac{g_{12} g_{12} E_p^3}{(4\pi\varepsilon_0\varepsilon_b) \varepsilon_B R^3}; \quad \Lambda_{ddi} = \frac{g_1^2 (k_{12} E_p^2)^2}{(4\pi\varepsilon_0\varepsilon_b)^2 \varepsilon_B^2 R^6}.$$

Here $\hbar c$ stands for the Hermitian conjugate and $\sigma_{ij} = \langle i | j \rangle$ is called the creation operator from state $|i\rangle$ to $|j\rangle$. Note that DDI Hamiltonian depends on $\chi_1$ and $\chi_2$ whose denominator becomes zero at $\omega_{sp} = \omega_{12}$. This means that the DDI is strongest when the frequencies of AFD and GNR are resonant ($\omega_{sp2} = \omega_{12}$).

We use the density matrix method developed for the and one- and two-photon process in Ref. [34]. Using eqn. (5.8) and two-photon rotating wave approximation we obtained the following expressions for density matrix elements

$$\rho_{22} = -\gamma_2 \rho_{22} + i \Omega_{12} \rho_{12} - i \Omega_{12}^* \rho_{21},$$

$$\rho_{12} = -[\gamma_2/2 - i (\delta_{21} + \delta_S)] \rho_{12} + i \Omega_{12}^* (\rho_{22} - \rho_{11}),$$

where $\Omega_{12} = (\Omega_2 + \Lambda_2 + \Lambda_{ddi})$, $\rho_{11} + \rho_{22} = 1$, $\rho_{12} = \rho_{21}^*$, and $\delta_S = \beta_S |\Omega_{12}|$. The detuning parameter here is $\delta_{21} = 2\omega_p - \omega_{12}$. $\gamma_2$ is the spontaneous decay rate for states $|2\rangle$ and $\beta_S = (k_{bb} - k_{aa})/4k_{ab}$ where $k_{aa}$, $k_{bb}$, $k_{ab}$ are the two-photon coefficients [34].

The energy transfer from AFD to GNR is measured via the fluorescence of the AFD. The energy transfer is observed as a decrease of the AFD’s fluorescence intensity and increase of the GNR’s. In the fluorescence measurement, the intensity emission from the AFD is measured in time. The decay time of AFD in the presence of GNRs is given as

$$I_{d-g}^{1ph} = I_0 \exp(-\gamma_3 t - \gamma_{1ph} t);$$  \hspace{1cm} (5.10a)

$$I_{d-g}^{2ph} = I_0 \exp(-\gamma_2 t - \gamma_{2ph} t)$$  \hspace{1cm} (5.10b)

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where $\gamma_3$ and $\gamma_2$ are radiative decay rates of the AFD for one- and two-photon in the absence of the GNRs, respectively. Similarly $\gamma_{1ph}$ and $\gamma_{2ph}$ are the nonradiative decay rates due to one- and two-photon energy transfer from the AFD to the GNR. It has found that the radiative and nonradiative decay rates are related to the energy transfer rate of the AFD in the absence and in the presence of the GNR, respectively by the following identity [36]

$$\frac{\gamma_{1ph}}{\gamma_3} = \frac{W_{1ph}^{d-g}}{W_{rad}^{1ph}}, \quad \frac{\gamma_{2ph}}{\gamma_2} = \frac{W_{2ph}^{d-g}}{W_{rad}^{2ph}}, \quad (5.11)$$

where $W_{rad}^{1ph}$ and $W_{rad}^{2ph}$ are one- and two-photon energy transfer rate of the AFD in the absence of the GNR, they are calculated as [36]

$$W_{rad}^{1ph} = \hbar \omega_1 \rho_{03}^{0}, \quad W_{rad}^{2ph} = \hbar \omega_2 \rho_{22}^{0}, \quad (5.12)$$

where $\rho_{22}^{0}$ and $\rho_{33}^{0}$ are the density matrix elements for $|2\rangle$ and $|3\rangle$ in the absence of the GNR and measure the population of $|2\rangle$ and $|3\rangle$, respectively. They are evaluated from eqn. (5.9) by neglecting the DDI Hamiltonian. By putting eqns 5.11 and 5.12 into 5.10a & 5.10b we get the one- and two-photon fluorescence intensities.

The AFD-GNR pair does not exist alone but in an ensemble of AFD-GNR pairs. We consider that the AFDs and GNRs are separated according to the Gaussian distribution as

$$P(R) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{1}{2} \left( \frac{R_{av} - R}{\sigma} \right)^2 \right], \quad (5.13)$$

where $R_{av}$ is the average distance between a AFD and GNR pair and $\sigma$ is the standard deviation. The fluorescence intensity decay is now the summation of all accessible distances between the AFD and GNR such that

$$I_{d\rightarrow a} = \int_0^\infty d^3R P(R) I_{d\rightarrow a}(R), \quad (5.14)$$

This is simply the weighted average of the decay for each AFD-GNR distance.
5.4 Results and Discussion

For simulations sake the 374 nm and 810 nm laser fields are taken to be resonant with their transitions, therefore $\delta_{12} = \delta_{13} = 0$. This is fair given that the intensities under comparison are normalized. The three sample solutions contain the hybrid system in an aqueous solution. For this reason, the background dielectric constant is that of water, $\epsilon_b = 1.77$. For the F405 three level model the dipole moment $\mu_{13} = 0.004 e$ nm and two-photon coupling constant $k_{12} = 2 \cdot 10^{-36}$ mC$^2$/N, $g = -1$. The radius of the nanorods is taken to be $r = 50$ nm and $u = 1/3$ while the radius for F405 molecule is 1 nm.

Using eqn. (5.10a) we have calculated the one-photon fluorescence intensity for the F405-GNR hybrid system. The results are plotted in Fig. 5-3 by solid, dashed, and dashed-dotted lines for three samples F405, S0-1 and S0-2, respectively. A good agreement between theory and experiment is found. The fluorescence intensity for the F405 sample is calculated by neglecting

![Figure 5-3: Normalized theoretical and experimental fluorescence intensity under one-photon excitation.](image)
DDI terms, $W_{d\rightarrow g}^{1ph} = 0$, in eqn. (5.10a). This gives us the decay rate for the AFD in the absence of the GNR $\gamma_3^{-1} = 0.588$ ns. For samples S0-1 and S0-2 the nonradiative decay rates were found as $\gamma_{1ph}^{-1} = 0.04$ ns and $\gamma_{1ph}^{-1} = 0.10$ ns, respectively. Both mixture solution samples show significant decrease in their decay rates. The decrease in the decay rate is due to energy transfer from the AFD to the GNR due to the one-photon DDI. Note that the decrease in the decay time in S0-2 is larger than that of the S0-1. This means the DDI interaction in the S0-2 sample is larger than in the S0-1 sample. The average centre-to-centre distance between the AFD and GNR for S0-1 and S0-2 are estimated at $R_{av} = 71$ nm and $R_{av} = 61$ nm, respectively. This also shows that the DDI in S0-2 is larger than that of the S0-1 since the DDI is inversely proportional to the distance between the AFD and GNR.

The numerical simulations for two-photon fluorescence intensity is performed by using eqn. (5.10b) and results are shown in Fig. 5-4. The solid, dashed and dashed-dotted lines again represent Fluor405, S0-1 and S0-2. Strong agreement between theory and experiments is again

Figure 5-4: Normalized theoretical and experimental fluorescence intensity under two-photon excitation.
found. The F405 is calculated for $W_{d-g}^{2ph} = 0$ and the radiative two-photon decay rate is calculated $\gamma_2^{-1} = 3.57$ ns. The nonradiative two-photon decay rates for S0-1 and S0-2 are $\gamma_{2ph}^{-1} = 0.87$ ns and $\gamma_{2ph}^{-1} = 1.37$ ns, respectively. Both sets of decay rates are displayed in Tables 5.1 and 5.2.

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<tr>
<th>Table 5.1: Radiative Decay Rates</th>
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<td>$\gamma_2^{-1}$</td>
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<td>F405</td>
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<tr>
<th>Table 5.2: Non-Radiative Decay Rates</th>
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<tr>
<td>$\gamma_{1ph}^{-1}$</td>
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<tr>
<td>S0-1</td>
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<td>S0-2</td>
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Decrease in the decay rates for both samples is consistent with the one-photon case and is motivated by the two-photon energy transfer from the AFD to the GNR. The decrease in the decay time in S0-2 is again larger than that of the S0-1 and therefore its DDI interaction is larger. These results are consistent with the result from a FLIM study in cell culture [28].

### 5.5 Conclusions

The energy transfer between biological labelling dye (Alexa Fluor 405) and gold nanorods has been studied both experimentally and theoretically. Fluorescence lifetime imaging microscopy and the density matrix method are applied to study a hybrid system of dye and nanorods under one- and two-photon excitations. The DDI interaction between AFD and GNR causes a decrease in the fluorescence lifetime change. The energy transfer provides detailed information in biological studies using metallic nanoparticles as fluorescence probes, especially when combined with the advantages of two-photon excitation microscopy [28]. The present study has potential applications in FRET imaging and fluorescence lifetime-based intra-cellular sensing of bio-analytes such as metal ions, proteins, as well as nuclear targeting cancer therapy.
Bibliography


Chapter 6

Nonlinear Energy Transfer in Quantum Dot-Metal Nanorod Nanocomposites

In the previous chapter we examined the fluorescence in a biological labelling dye and gold nanorods nanocomposite under one- and two-photon excitation. In this chapter we examine the two-photon process driven energy transfer between a quantum dot (QD) and a metallic silver nanorod (MNR). Here we will study the effects of increased probe and control fields on the hybrid system.

6.1 Introduction

The study of optoelectronic properties in nanocomposites consisting of semiconductor QDs and plasmonic nanostructures is an interesting area of current research [1]-[5]. Interactions between the metal nanostructures and QDs are strong when they are in close proximity and their optical excitation frequencies are resonant with each other. Surface plasmon polaritons (SPPs) created in metals due to the collective oscillations of conduction band electrons couple to excitons in the QDs. These resonant frequencies of SPPs can be manipulated by changing the physical

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1The material presented in this chapter has been communicated to the Journal of the Optical Society of America B for publication.
proportions of the metallic component. This ability gives them great potential for applications in ultrasensitive optical biosensing [6], photonic metamaterials [7], light harvesting [8], optical nanoantennas [9] and quantum information processing [10].

Nonlinear processes, such as the two-photon process and second harmonic generation, are the newest regime of study being focused in on hybrid systems. Two-photon effects are well known phenomena [11], [12] and have a wide range of applications [13], specifically to bioscience imaging [14]-[16] where they show higher spatial resolution, deeper penetration and less photodamage.

The multi-photon properties of QDs [17],[18] and metal nanocomponents [19]-[22] have been observed. Energy transferred between components in a hybrid system containing a QD have the means of creating windows of transparency to particular wavelengths of light in the QD. Three level QDs have shown electromagnetically induced transparency (EIT) experimentally [23]-[25]. Nanocomposites utilizing these properties may be used in the fabrication of new and better nanosensors, nano-switches and energy transfer devices.

6.1.1 System studied

The system of interest in this chapter is a nanocomposite consisting of a QD and a MNR. This type of system has been fabricated by quite a few groups [26],[5]. The QD is a three-level Lambda type system that is similar to one that has been recently experimentally studied [27]. The MNRs studied are given to be on the scale of <10nm, specifications that have been experimental produced [28].

Dipoles are induced in the QD and MNR with the application a non-linear probe laser and a linear control laser. The components will interact via the dipole-dipole interaction (DDI) and energy is transferred from the QD to the MNR. We perform our investigation using the density matrix method to numerically solve for the energy transfer rate. We find shifting of the peak energy transfer rate to off resonance position due to the nonlinear nature of the interaction. We also find enhancement of the energy transfer rate to be controlled by the probe laser intensity and transparency of the system by the control laser.
Figure 6-1: A schematic diagram of the QD and MNR. Here $R$ is distance between the QD and the MNR when the QD lies along a) the minor axis, $s_a = -1$, or b) the major axis, $s_a = 2$, of the MNR. Three exciton levels of QD are denoted by $|1\rangle$, $|2\rangle$, and $|3\rangle$. Probe and control fields are applied to monitor the $|1\rangle \leftrightarrow |2\rangle$ and $|2\rangle \leftrightarrow |3\rangle$ transitions, respectively.

6.2 Theoretical Formalism

6.2.1 Polarization in the metallic nanorod

Optical excitations in the QD are electron-hole pairs, which are called excitons. The optical excitations in the MNR are the collective oscillations of conduction band electrons, and are called surface plasmon polaritons (SPPs). The QD-MNR hybrid system is embedded in a host dielectric material such as silica. The center-to-center distance between QD and MNR is denoted as $R$. Optical excitations of the QD are excitons and have sharp and discrete states.

We consider a quantum dot having three levels $|1\rangle$, $|2\rangle$, and $|3\rangle$, where $|1\rangle$ is the ground state and $|2\rangle$ where $|3\rangle$ are the excited states. The energy difference between two of the states is denoted as $\omega_{ij}$, where $i, j$ = the numbers of the two states. A probe field $E_p \cos(\omega_p t)$ is applied between $|1\rangle$ and $|2\rangle$ so that two-photons with frequency $2\omega_p$ are absorbed. The energy conservation gives the condition $\omega_{12} = 2\omega_p$. The control field, $E_c \cos(\omega_c t)$, is applied between $|2\rangle$ and $|3\rangle$ such that $\omega_{23} = \omega_c$. A schematic diagram for the hybrid system is shown in Fig. 6-1.
In the presence of the external laser fields, induced dipole $P_{QD}$ is created in the QD. The nonlinear second order polarization $P_{QD}$ in the QD is calculated by using the method of reference [29]. It is found as

\[ P_{QD} = \chi_{QD} E_p = k_{12} \varrho_{12} E_p \] (6.1)

\[ k_{12} = \frac{1}{2h} \frac{\mu_{1n} \mu_{n2}}{(\omega_{12} - \omega_p) + i\gamma_{12}} \]

The physical parameters \( \varrho_{ij} \) are the density matrix elements between states \(|i\rangle \) and \(|j\rangle \). Here \( \mu_{1n} \) and \( \mu_{n2} \) are matrix elements of the dipole moment between \(|1\rangle \) and \(|n\rangle \) and \(|n\rangle \) and \(|2\rangle \), respectively due to the one photon process. The summation is over an intermediate state \(|n\rangle \) which is responsible for exciting the two photon transition \(|1\rangle \leftrightarrow |2\rangle \).

The QD creates an dipole electric field due to the induced dipole moment $P_{QD}$ and it is written as

\[ E_{QD} = \frac{2P_{QD} k^3}{4\pi\epsilon_B} \left( \frac{i}{(kR)^2} - \frac{1}{(kR)^3} \right) e^{ikr}, \quad (P_G \parallel R) (6.2) \]

\[ E_{QD} = \frac{P_{QD} k^3}{4\pi\epsilon_B} \left( \frac{1}{(kR)^2} + \frac{i}{(kR)^2} - \frac{1}{(kR)^3} \right) e^{ikr}, \quad (P_G \perp R) \]

where $\epsilon_B = (2\epsilon_b + \epsilon_d)/3\epsilon_b$. Here $\epsilon_b$ is the dielectric constant of the host dielectric material, and $\epsilon_d$ the dielectric constant of the QD. When the wavelength of the probe and control fields are larger than the distance between QD and MNR (i.e. $kR << 1$) then in the most of calculations $(kR)^{-1}$ and $(kR)^{-2}$ term are negligible compared to $(kR)^{-3}$ and $e^{ikr}$ is taken as one. The effect of the $(kR)^{-3}$ terms plays an important role in the two-exciton process energy transfer. The above two expressions can be combined into one as

\[ E_{QD} = \frac{g_{x,z} P_{QD}}{(4\pi\epsilon_b) \epsilon_{dr} R^3}. \] (6.3)

Here $g_{x,z}$ is called the polarization parameter with $g_x = 2$ or $g_z = -1$ for $(P_G \parallel R)$ and $g_z = -1$ for $P_G \perp R$, respectively. These two configurations are both shown in Fig. 6-1. The subscripts $x$ and $z$ stand for an electric field applied along the length and width directions of
the system, respectively. Putting eqn. (6.1) into the above equation and we get

\[ E_{QD} = \frac{g_{x,z}k_{12}\theta_{12}E_p}{(4\pi\epsilon_b)\epsilon_{dr}R^3}. \]  

(6.4)

The above field is responsible for the dipole-dipole interaction (DDI) between the QD and MNR.

SPPs are created in the MNR. These polaritons will produce an enhanced local electric field near the MNR. Therefore, the DDI between the QD and MNR is very strong in the vicinity of the MNR due to the enhanced local electric field. Specifically the DDI will be very strong when there is a resonant coupling between QD and MNR (i.e. \( \omega_{sp} = 2\omega_p \)).

Now we need to calculate the polarization in MNR, \( P_M \), due to electric field seen by it. This electric field consists of two terms which are written as

\[ E_M = E_pe^{-i\omega_p t} + E_{QD}e^{-i\omega_{ab} t} \]  

(6.5)

where the first term is the electric field from the probe field and the second term is the dipole electric field produced by the QD. Using the quai-static approximation the induced dipole polarization in the MNR due to the above electric field can be calculated as

\[ P_M = P_M^{QD} + P_M^p \]  

(6.6)

\[ P_M^{QD} = \chi_{g1}E_{QD}e^{-i2\omega_p t} + cc \]

\[ P_M^p = \chi_{g2}E_p^2e^{-i2\omega_p t} + cc \]

where

\[ \chi_{g1} = \frac{4\pi V\epsilon_0\epsilon_b{[\epsilon_m - \epsilon_b]}}{3\epsilon_b + 3\kappa_{x,z}(\epsilon_m - \epsilon_b)} \]  

(6.7a)

\[ \chi_{g2} = \frac{\epsilon_0^2 m_{b}^{3}}{(4\pi V\epsilon_0\epsilon_b)^2 N^2\epsilon^3 \chi g_1^2(\omega_p)\chi g_1(2\omega_p)} \]  

(6.7b)
Here $\varsigma_{x,z}$ is called the depolarization factor and is defined as

$$
\varsigma_x = \frac{1 - \epsilon_m^2}{\epsilon_m^2} \left[ \frac{1}{2\epsilon_m} \ln \left( \frac{1 + \epsilon_m}{1 - \epsilon_m} \right) - 1 \right]
$$

(6.8)

$$
\varsigma_z = (1 - \varsigma_t)/2,
$$

and $\epsilon_m = \sqrt{1 - (R_m/L_m)^2}$ with $R_m$ and $L_m$ being the semi-minor and semi-major radii, respectively. $V$ is the volume of the nanorod while $m$ and $e$ are the mass of an electron and the electron charge. Importantly $\beta$ is a parameter that characterizes the strength of the second-order nonlinearity as defined in [11]. Note that the first order term in the probe electric field does not appear since this term does not excite the SPPs (i.e. $\omega_p \neq \omega_{sp}$).

The MNR will create a dipole electric field (also called the near field) at the QD due to the induced dipole moment, $P_M$, and it is written as

$$
E_M = E_M^{QD} + E_M^p
$$

(6.9)

where

$$
E_M^{QD} = \left( \frac{g_{x,z}}{4\pi\epsilon_0e_b} \right)^2 \frac{1}{R^6} \chi_{M1} \chi_{QD} E_p
$$

(6.10a)

$$
E_M^p = \frac{g_{x,z}}{(4\pi\epsilon_0)} c_R^2 \chi_{g2} E_p^2
$$

(6.10b)

are the two components with $E_M^{QD}$ being due to the dipole moment $P_M^{QD}$ in MNR which was induced by the QD dipole field. This field has $1/R^6$ dependence. The second component, $E_M^p$, is due to the induced dipole moment $P_M^p$ in MNR created by the intense probe laser field. This field has $1/R^3$ dependence. The $E_M$ electric field is responsible for the DDI between the QD and MNR.

### 6.2.2 Hamiltonian

The total field seen by the QD consists of two terms. The first term is the pump field $E_p$ and the second is the dipole field $E_M$ created by the MNR. The intense field creates an exciton from
state \(|1\rangle\) to state \(|2\rangle\) in the QD due to absorption of two photons. This process satisfies the conservation energy as \(\omega_{21} = 2\omega_p\). According to reference [29] the two-photon coupling Hamiltonian for the transition \(|1\rangle \leftrightarrow |2\rangle\) is written as

\[
H_1 = \frac{1}{2} k_{12} E_p^2 \sigma_{21} e^{-i(2\omega_p - \omega_{12})t} + hc, \tag{6.11}
\]

where \(hc\) stands for the Hermitian conjugate and \(\sigma_{21}^+ = |2\rangle \langle 1|\) is called the creation operator for an exciton from state \(|1\rangle\) to \(|2\rangle\) due to two-photon absorption. The above expression can be rewritten as

\[
H_1 = \Omega_p \sigma_{21} e^{-i(2\omega_p - \omega_{12})t} + hc, \tag{6.12}
\]
\[
\Omega_p = \frac{1}{2} k_{12} E_p^2.
\]

The near dipole electric field, \(E_M\), also interacts with the QD. The interaction Hamiltonian due to the two-photon DDI electric field can be obtained as

\[
H_2 = \frac{1}{2} P_{QD} E_M \sigma_{21} e^{-i2\omega_p t} + hc, \tag{6.13}
\]

where \(P_{QD}\) is the matrix element of the polarization between \(|1\rangle\) and \(|2\rangle\) due to the second order two-photon absorption process. Putting expression of \(P_{QD}\) and \(E_M\) into the above expression we get

\[
H_2 = (\Lambda_M + \Lambda_{2p}) \sigma_{21} e^{-i(2\omega_p - \omega_{12})t} + hc, \tag{6.14}
\]
\[
\Lambda_{2p} = \frac{1}{2} \left(\frac{g_{x,z}}{4 \pi \epsilon_0} \right) \epsilon_b R_3 \chi_{QD} \chi_{q2} E_p^3,
\]
\[
\Lambda_M = \frac{1}{2} \left(\frac{g_{x,z}}{4 \pi \epsilon_0 \epsilon_b} \right)^2 \frac{1}{R_6} \chi_{q1} \chi_{QD} E_p^2.
\]

The combining both interaction terms as \(H_1\) and \(H_2\) we get the two-photon interaction Hamiltonian as

\[
H_{int} = H_1 + H_2 = V_{21} \sigma_{21} e^{-i(2\omega_p - \omega_{12})t} + hc, \tag{6.15}
\]
where

\[ V_{21} = (\Omega_p + \Lambda_M + \Lambda_{2p}) . \] (6.16)

The first term is the direct contribution from the external probe field, which is represented by the terms \( \Omega_p \). The second contribution is denoted by the term \( \Lambda_M \) and represents the dipole that arise from the QD polarizing the MNR, which in turn polarizes the QD. In other words, this contribution is the self-interaction of the QD, as it depends on the polarization of the QD. For this reason, this term is called the self-induced DDI parameters. The third and last contribution, \( \Lambda_{2p} \), comes from the MNR being polarized by probe laser before then interacting with the QD.

### 6.2.3 Density Matrix Method

We use the density matrix method to evaluate the power spectrum in MNR. Using eqn. (6.15) we obtained the following expressions for density matrix elements

\[
\frac{d\rho_{21}}{dt} = \left[i (\Delta_p + \Delta_s) - \gamma_{12}\right] \rho_{21} - iV_{23}^* \rho_{31} + iV_{21} (\rho_{22} - \rho_{11}),
\]

\[
\frac{d\rho_{32}}{dt} = (i\Delta_c - \gamma_{23}) \rho_{32} + iV_{21}^* \rho_{31} + iV_{23} (\rho_{33} - \rho_{22}),
\]

\[
\frac{d\rho_{31}}{dt} = \left[i (\Delta_p + \Delta_c + \Delta_s) - \gamma_{13}\right] \rho_{31} - iV_{23} \rho_{21} + iV_{21}^* \rho_{32},
\]

\[
\frac{d\rho_{11}}{dt} = \gamma_{22} \rho_{22} + iV_{21} \rho_{12} - iV_{21}^* \rho_{21},
\]

\[
\frac{d\rho_{33}}{dt} = -\gamma_{33} \rho_{33} + iV_{23}^* \rho_{32} - iV_{23} \rho_{23},
\] (6.17)

where

\[ \Delta_s = \Omega_R |V_{21}| , \] (6.18)

\[ V_{23} = -\frac{d_{23} E_c}{2\hbar} , \]

\[ V_{21} = (\Omega_p + \Lambda_M + \Lambda_{2p}) , \]

with the condition that \( \rho_{11} + \rho_{22} + \rho_{33} = 1 \). \( d_{23} \) is the dipole moment between the levels \(|2\rangle \) and \(|3\rangle \). Here \( \Omega_R = (k_{22} - k_{11})/2k_{12} \), and \( \Delta_s \) is the two-photon dynamic Stark shift due nonlinear coupling of the QD with external electric fields.
6.2.4 Energy Transfer Rate

We calculate the two-photon energy transfer rate from the QD dot to MNR due to the DDI. The energy transfer is calculated as [29]

\[ W_{QD} = \left\langle \int [j_M \cdot E_{MNR}] dV \right\rangle, \]  
(6.19)

where \( j_M \) is the electric current induced in the MNR. The volume integral is over the volume \( V_M \) of the QD. Here symbol \( \langle \rangle \) is the time average over the period of the oscillating laser fields.

The current density is calculated by differentiating the polarization \( P_M \) given in eqn. (6.6) with time and obtained as

\[ j_M = \frac{1}{V_M} \frac{d}{dt} \left( \frac{V_M}{d} \right), \]  
(6.20)

\[ j_M = \frac{i 2 \omega_p}{V_M} \left[ \chi g_1 E_{QD} + \chi g_2 E_p^2 \right] e^{-i 2 \omega_p t} + cc, \]

Putting eqns. (6.9) and (6.20) into (6.19) and performing some mathematical manipulation we get

\[ W_M = W_{QD}^M + W_{p}^M, \]  
(6.21)

\[ W_{QD}^M = 4 \omega_p \text{Im} (\chi g_1 |E_{QD}|^2), \]  
(6.22)

\[ W_{p}^M = 4 \omega_p \text{Im} (\chi g_2 E_p^3), \]  
(6.23)

where \( W_{QD}^M \) is the energy transfer from QD to the MNR and \( W_{p}^M \) is the energy transfer from the probe field to the MNR.

6.3 Results and Discussion

In this section we perform numerical simulations for \( W_{QD}^M \), eqn. 6.22, which is the energy transfer rate from the QD to the MNR in our hybrid system. This type of hybrid system has been used by several groups [26],[5]. We consider a QD similar to a InAs/GaAs QD which has been fabricated [27]. Physical parameters of the QD are taken as \( R_{QD} = 2 \text{ nm} \) and \( \hbar \omega_{12} = 8.9 \text{ eV} \). The dielectric constant of the QD is \( \epsilon_d = 6 \) [30] and the dipole moment of the upper QD
transition is taken to be $d_{23} = 0.7\text{ nm}$ [31]. Physical paramters for the silver MNR are taken as $L_{MNR} = 10\text{ nm}$, $h\omega_p = 8.9\text{ eV}$, and ratio $R_m/L_m = 1/3$. These parameters are consistent with experimental values found in the literature [28]. The two-photon coupling constant is $k_{12} = 8 \times 10^{-25}\text{ mC}^2\text{N}^{-1}$ and we take $k_{22} = 1.5k_{11}$ which are similar to what was used in reference [22]. We consider that QD and MNR are deposited on the substrate made from silica. The dielectric constant of the host material silica is taken as $\varepsilon_0 = 1.96$ [33]. The relaxation rates are taken to be $\gamma_2 = 1.2\mu\text{eV}$ and $\gamma_3 = 0.1\mu\text{eV}$. These values are similar to those found in other literature [34]. The density matrix elements $\rho_{ij}$ are obtained via solving eqns. (6.17) numerically using a seventh-eighth order continuous Runge-Kutta method provided by the software package Maple.
The ETR between the QD and MNP is plotted in Fig. 6-2 as a function of the probe detuning. The intensity of the probe field is \( I_p = 1 \text{ W/cm}^2 \). The dotted and dashed curves are plotted for intensity of the control field being \( I_c = 0 \text{ GW/cm}^2 \) and \( I_c = 45 \text{ GW/cm}^2 \), respectively. The separation between the MNP and QD is \( R = R_{QD} + L_{MNR} = 12 \text{ nm} \) and we will begin by considering that the QD lies along on the major axis of MNR i.e., \( s_a = 2 \). We can see that when the control field is turned off, the ETR profile has one peak. This is due to the two-photon field of the probe laser interfering with the one-photon field from the MNR. The shape of the curves may also be described by the combination of the real and imaginary components of \( \rho_{12} \). Here they are both shifted to positive detuning and add together to form the shown peak.

The spectrum then splits, as the control field is applied, from one peak to two. The control field creates dressed states in the QD that we will denoted as \( |2^+\rangle \) and \( |2^-\rangle \). The two absorption peaks the appear at transitions \( |1\rangle \leftrightarrow |2^+\rangle \) and \( |1\rangle \leftrightarrow |2^-\rangle \). The splitting creates a minima located at a detuning of \( \Delta_p + \Delta_s = 0 \) in which the QD has now become transparent to the two-photon probe laser, \( \Omega_p \). Note that \( \Delta_p = 0 \) correspond to \( \omega_{12} = 2\omega_p \). The term \( \Delta_s \) appears due to nonlinear coupling between QD and MNR and the subsequent shift in the transition energy of the QD.

A clear picture of splitting in the energy transfer rate can be seen when the probe field is weak and the non-linear effects of the two-photon and DDI interaction are no longer present. Fig. 6-3 is a plot of the ETR with \( I_p = 0.3 \text{ W/cm}^2 \) and \( R = 12 \text{ nm} \) as a function of the probe detuning. The QD is again along the major axis of the MNR, \( s_a = 2 \). The dotted and dashed curves are drawn for control field intensities of \( I_c = 0 \text{ GW/cm}^2 \) and \( I_c = 45 \text{ GW/cm}^2 \), respectively. The shape of both curves are nearly symmetric, as is expected of a linear interaction. The Stark shift contribution of \( \Delta_s \) is less than before as can be expect from eqn. (6.18) where \( \Delta_s \sim |V_{21}| \) and thus we should expect a smaller shift with a weaker probe field. When the control field is off we have a single peak that is split into two peaks with a minima between them when the control field is on. These are interesting results which can be use to make nonlinear switching devices from hybrid systems.

In Fig. 6-4 we investigate the effect of an increased intensity of probe field on the ETR in the system. The ETR is again plotted against probe detuning and both curves are plotted
Figure 6-3: The energy transfer rate, $W^{QD}_M$, plotted vs probe detuning $\Delta_p$. The intensity of the control field is $I_c = 45 \text{ GW/cm}^2$, the separation is $R = 12 \text{ nm}$, and $s_a = 2$. The dotted and dash-dotted curves are plotted for intensity of the control field being $I_p = 1 \text{ W/cm}^2$ and $I_p = 3 \text{ W/cm}^2$, respectively.

for $I_c = 0 \text{ GW/cm}^2$. The dotted curve, as before, is plotted for $I_p = 1 \text{ W/cm}^2$ while the dashed-dotted line is plotted for $I_p = 3 \text{ W/cm}^2$. Here we see a shift back to near $\Delta_p = 0$ detuning and an enhancement of the peak in the ETR spectrum with an increase in the probe field intensity. This is due to the increased intensity of the two-photon probe field dominating over the interaction field from the MNR. Also, the component from $\text{Re}(\rho_{12})$ is shifted to higher detuning than in the $I_p = 1 \text{ W/cm}^2$ case. On the other hand, the $\text{Im}(\rho_{12})$ is centred near $\Delta_p = 0$ and is much larger than the $\text{Re}(\rho_{12})$ part leading to its dominance over the shape of the curve.

We will now examine our system for the second system orientation where the QD lies along the minor axis of the MNR, $s_a = -1$. In Fig. 6-5 the ETR is plotted against probe detuning.
Figure 6-4: The energy transfer rate, $W_{MQD}^M$, plotted vs probe detuning $\Delta_p$. The intensity of the control field is $I_c = 45 \text{ GW/cm}^2$, the separation is $R = 12 \text{ nm}$, and $s_a = -1$. The dotted and dash-dotted curves are plotted for intensity of the control field being $I_p = 1 \text{ W/cm}^2$ and $I_p = 3 \text{ W/cm}^2$, respectively. The dotted curve is plotted for $I_p = 1 \text{ W/cm}^2$ while the dashed-dotted line is plotted for $I_p = 3 \text{ W/cm}^2$. The peak in the spectrum shown by the dotted curve has less of a shift than in the other orientation. The effect of the interaction field from the MNR is less. The ETR corresponding to $I_p = 3 \text{ W/cm}^2$ shows the same shape as in the previous figure where the two-photon field dominates, however we do see a greater enhancement. Also as before it is the $\text{Im}(\rho_{12})$ component that dominates over the $\text{Re}(\rho_{12})$ component to create outputted curve.

Both curves are drawn for $I_c = 0 \text{ GW/cm}^2$. The dotted curve is plotted for $I_p = 1 \text{ W/cm}^2$ while the dashed-dotted line is plotted for $I_p = 3 \text{ W/cm}^2$. The peak in the spectrum shown by the dotted curve has less of a shift than in the other orientation. The effect of the interaction field from the MNR is less. The ETR corresponding to $I_p = 3 \text{ W/cm}^2$ shows the same shape as in the previous figure where the two-photon field dominates, however we do see a greater enhancement. Also as before it is the $\text{Im}(\rho_{12})$ component that dominates over the $\text{Re}(\rho_{12})$ component to create outputted curve.

We also investigated the effect of distance between the QD and MNR on the nonlinear energy transfer. Fig. 6-6 plots the ETR versus the separation of the QD and MNR at zero detuning, $\Delta_p = -\Delta_s$ and with $s_a = 2$. The dotted curves is drawn for probe and control fields
Figure 6-5: The energy transfer rate, $W^{QD}_M$, plotted vs probe detuning $\Delta_p$. The intensity of the probe field is $I_p = 0.3 \, \text{W/cm}^2$, the separation is $R = 12 \, \text{nm}$, and $s_a = 2$. The dotted and dashed curves are plotted for intensity of the control field being $I_c = 0 \, \text{GW/cm}^2$ and $I_c = 45 \, \text{cW/cm}^2$, respectively.

of $I_p = 1 \, \text{W/cm}^2$, and $I_c = 0 \, \text{mW/cm}^2$, the dashed curve for $I_p = 0 \, \text{GW/cm}^2$, and $I_c = 45 \, \text{GW/cm}^2$ fields, and the dash-dotted curve for $I_p = 3 \, \text{W/cm}^2$, and $I_c = 0 \, \text{mW/cm}^2$. The graph shows that the ETR is most prevalent for separation of less than 20 nm. The increase in the probe field shows a direct enhancement in the energy transfer. These results are consistent with the findings of Xiao et al. [35] who found a similar effects in multiphoton luminescence spectra while varying excitation intensity and concentration of acceptors in a CdSe QD-Au nanoparticle system. Xiao et al. found an increase in the peak of the spectra with stronger laser intensity and an increased concentration of nanoparticles, which is directly related to a decrease in average separation distance of a QD and a MNR.

Shown in the inset we see the decrease in the energy transfer rate with the increase of the
control field, which goes to zero at $I_c = 45 \text{ GW/cm}^2$. One can see that in the presence of that control field that the ETR is zero for all separation at $\Delta_p = -\Delta_s$, as is shown by the dashed line in the main figure. This depicts an effective switching mechanism using the control field for any centre-to-centre separations of the QD and MNR of less than 20 nm.

### 6.4 Conclusions

We have investigated the nonlinear energy transfer rate from a QD to a MNR in a hybrid system nanocomposite. An intense probe laser field is applied between the ground state and first excited state, and a control laser field is applied between the first and second excited states.
Induced dipoles are created in the QD and MNR with applied probe and control lasers. Both components then interact via the DDI. Due to this interaction, the energy is transferred from the QD to the MNR. Numerical simulations of the density matrix solve for the energy transfer in this nanocomposite. Shifting of the peak energy transfer rate to off resonance position due to nonlinear interactions is found. Enhancement of the energy transfer rate is found to be controlled by the probe field intensity and transparency of the system by the control field. This hybrid system nanocomposite can be used to fabricate nanosensors, nano-switches and energy transfer devices.
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Chapter 7

Surface plasmon-polariton induced transparency in metamaterial waveguides nanocomposites

In the previous two chapters, we have examined the energy transfer in plasmon-polaritonic natural material nanocomposites driven by the interaction of excitons and surface plasmon-polaritons (SPPs). In this chapter we study the same interaction but now one of the components of the nanocomposite is an artificial metamaterial. Here the hybrid system consists of a quantum dot (QD), which is the source of the excitons, and a composite right/left handed (CRLH) metamaterial waveguide, in which the surface plasmon-polaritons propagate. We study absorption coefficient for QDs doped in a metamaterial waveguide. We find the absorption profile of the QD is made transparent to certain frequencies of light by the presence of the metamaterial waveguide\(^1\).

7.1 Introduction

Artificial materials are an important research area in the future of nanophotonics [1]-[14]. They are man-made structures built on a size scale that is smaller than that of the operational

\(^1\)The material presented in this chapter has been communicated to Physical Review A for publication.
wavelength and they exhibit optical properties not found in nature. An example of one of these unnatural properties is negative refractive index which has been found at THz and optical wavelengths [2]-[4]. As components of nanocomposites, metamaterials have the potential to take those new properties and use them to create new interactions.

The fabrication of optical wavelength metamaterials is a young and important research area with many possible applications [4], [5]. One such applied device would be an optical waveguide. Optical waveguides are fundamental to modern optical physics at the nanoscale and to discover new optical properties beyond those of conventional dielectric waveguides would be the ultimate goal of using metamaterials for nanophotonic applications [6]-[14].

Plasmonic metamaterial are a source of surface plasmons just as metals are. Metals are important nanocomposite components for their optical properties that complement those of semiconductor nanostructures [16]. It is possible that metamaterials can be found that will do the same job as metals in these circumstance and more. In metamaterial waveguides the SPPs that result from the photon and surface plamson coupling will propagate along the interfaces between the metamaterial and the dielectric layer. While they propagate they will not move away from the boundary region. In fact, in recent work comparing their uses as in claddings in cylindrical waveguides, metamaterials showed slowing of light and an decrease in lose when interacting with nearby atoms [15].

7.1.1 System Studied

In this chapter we study the effect of metamaterial waveguides, acting as a reservoir, on the absorption coefficient of QDs. Our QD-Metamaterial nanocomposite is made of a waveguides are built by sandwiching a metamaterial between dielectric material layers. A schematic diagram of the waveguide is shown in Fig. 7-1. Here we consider a composite right and left handed (CRLH) metamaterial [17]. The advantage of using metamaterials is that they have a energy gap in their photonic spectrum that can be manipulated by the proper choice of capacitances and inductances of the right and left handed units. QDs are doped at the interfaces of the metamaterials waveguide. Excitons of the QD will interact with SPPs of the waveguide, acting as a reservoir. A probe laser field is applied to monitor the absorption coefficient and the density matrix method [18] is used to calculate the absorption coefficient in the QDs and density
Figure 7-1: Schematic of the QD-metamaterial waveguide nanocomposite. The waveguide is made of a CRLH metamaterial between two layers of polyethylene. The polyethylene layers are doped with QDs.

of states (DOS) for the SPPs.

Numerical calculation for bound modes of SPPs, the DOS, and the absorption coefficient are carried out. It is observed that when the exciton resonance frequency lies near the SPP frequencies of the waveguide we get four transparent states in the absorption spectrum. This effect is due to strong coupling between excitons and SPPs.
7.2 Theoretical Formalism

7.2.1 CRLH Metamaterials

In this paper we consider a CRLH metamaterials used in the fabrication of a waveguide. The unit cell of this metamaterials is shown in Fig. 7-2. This is a general unit cell notation for many different types of metamaterials such as those made from a metallic thin wire and metallic split ring resonator lattice [19] or by a planar transmission line structures which are consists of a series of interdigital capacitors and shunt stub inductors [17] to name two examples.

The dispersion relation for this type of metamaterials using unit cell given in Fig. 7-2 is calculated by using the transfer matrix method as [17],[20]

\[
\sin^2\left(k_m a_m / 2 \right) = \frac{1}{4} \left( \frac{\varepsilon_r^2}{\varepsilon_f^2} + \frac{\varepsilon_i^2}{\varepsilon_f^2} - \kappa \varepsilon_i^2 \right),
\]

(7.1)

where

\[
\varepsilon_r = \sqrt{\frac{\hbar^2}{C_R L_R}}, \varepsilon_i = \sqrt{\frac{\hbar^2}{C_L L_L}},
\]

(7.2)

\[
\kappa = L_R C_L + L_L C_R
\]

where \(C_R\) and \(L_R\) are the capacitance and inductance of right handed (RH) part of the trans-
mission line while $C_L$ and $L_L$ correspond to the left handed (LH) part. The periodicity of the metamaterial is $a_m$.

Metamaterials are defined as artificial, effectively homogeneous, electromagnetic structures with unusual properties which are not found in natural materials. They have homogeneous structures and their unit cell $a_m$ is much smaller that the wavelength $\lambda_m$ of the electromagnetic wave propogating in the material. In other words the average size of the unit cell is $a_m < \lambda_m/4$ [17]. This condition is a long wavelength limit and can expressed as $k_m a_m < 1$. It follows that we can use this longwavelength approximation to make $\sin(k_m a_m/2) = k_m a_m/2$ and using this approximation reduces the dispersion relation to

$$k_m = \pm F_m (\varepsilon) = \pm \frac{1}{a_m^2} \sqrt{\left(\varepsilon^2 + \frac{\varepsilon^2}{\varepsilon_0^2} - \kappa \varepsilon_0^2\right)}.$$  

(7.3)

The longwavelength approximation is widely used in the metamaterials literature [17]. The dispersion relation given in eqn. (7.3) can also be rewritten as

$$k_m = \pm F_m (\varepsilon) = \pm \frac{\varepsilon}{(hc)} \sqrt{\varepsilon_m \mu_m},$$

(7.4)

where the metamaterial constants are $\varepsilon_m$ and $\mu_m$ and are found as

$$\varepsilon_m = \frac{C_R - h^2/\varepsilon^2 L_L}{a_m \varepsilon_0},$$

(7.5)

$$\mu_m = \frac{L_R - h^2/\varepsilon^2 C_L}{a_m \mu_0}.$$  

Note that $\varepsilon_m$ and $\mu_m$ appearing in eqn. (7.4) can be interepreted as the dielectric constant and magnetic permeability of the metamaterials.

$$\varepsilon_m = \varepsilon_\infty \left(1 - \frac{\varepsilon_P^2}{\varepsilon_0^2}\right)$$

(7.6)

$$\mu_m = \mu_\infty \left(1 - \frac{\varepsilon_P^2}{\varepsilon_0^2}\right)$$

where
\[ \varepsilon_p = \frac{\hbar}{\sqrt{C_R L_L}}, \varepsilon_\infty = \frac{C_R}{a_m \epsilon_0} \]
\[ \varepsilon_q = \frac{\hbar}{\sqrt{C_L L_R}}, \mu_\infty = \frac{L_R}{a_m \epsilon_0} \]  

Note that \( \epsilon_m \) and \( \mu_m \) have negative values for \( \varepsilon < \varepsilon_p \) and \( \varepsilon < \varepsilon_p \), respectively. Metamaterials which have both \( \epsilon_m \) and \( \mu_m \) negative are called negative index metamaterials.

### 7.2.2 Surface plasmon polaritons in metamaterials waveguides

The metamaterial waveguide is fabricated by sandwiching a CRLH metamaterial layers between two dielectric material plates. The thickness of the metamaterial layer is taken as \( d_m \). In the waveguide both materials lie in \( y-z \) plane and the \( y \) and \( z \) direction are taken to be symmetric. The first and second interfaces between the metamaterial and the dielectric lie at \( x = 0 \) and \( x = d_m \), respectively. Surface plasmon polaritons (SPPs) exist near the metamaterials interfaces.

Let the dielectric constant and magnetic permeability of the dielectric materials are denoted as \( \epsilon_d \) and \( \mu_d \), respectively and are frequency independent. The dispersion relation for the dielectric materials is written as

\[ k_d = \pm F_d (\varepsilon) = \pm \left( \frac{\varepsilon}{\hbar c} \right) \sqrt{\epsilon_d \mu_d}, \]  

We consider that electromagnetic light decays near the both interfaces along \( x \) direction in the metamaterial and in the dielectric material. We consider that the EM wave travels along the \( y-z \) plane and its wave vector in \( x \)-direction is denoted as \( \kappa_{mx} \) and \( \kappa_{dx} \) in metamaterial and dielectric, respectively. The propagating vector in \( y-z \) plane is denoted as \( \beta \). Therefore we have

\[ \kappa_{mx} = \sqrt{k_m^2 - \beta^2} \]
\[ \kappa_{dx} = \sqrt{k_d^2 - \beta^2} \]

**TM Mode:** Let us calculate the transverse magnetic (TM) mode is propagating in the waveguide. By using the boundary conditions at \( x = 0 \) and \( x = d \) for the waveguide we get a
dispersion relation for the SPPs as

$$\tanh \left( \frac{1}{2} \kappa_{m}^{+} d \right) = -\frac{\varepsilon_{m} \kappa_{d}^{+}}{\varepsilon_{d} \kappa_{m}^{+}},$$

$$\coth \left( \frac{1}{2} \kappa_{m}^{-} d \right) = -\frac{\varepsilon_{d} \kappa_{m}^{-}}{\varepsilon_{m} \kappa_{d}^{-}},$$

(7.10)

where in the above expression $+$ and $-$ stand for the even and odd SPP modes, respectively.

With the help of the above expression we can also get dispersion relation for the surface plasmon polariton for a single interface heterostructure made from a metamaterial and a dielectric. In this case the thickness of the metamaterials is very large i.e. $d \to \infty$. This means we can put $\kappa_{m} d \to \infty$ in eqn. (7.10) to get $\tanh(2\kappa_{m} d) \to 1$ and the SPP dispersion relation reduces to

$$\frac{\kappa_{d}^{x}}{\varepsilon_{d}} + \frac{\kappa_{m}^{x}}{\varepsilon_{m}} = 0$$

(7.11)

with the help of $\kappa_{d}^{x}$ and $\kappa_{m}^{x}$ from eqn. (7.9) we can change above expression into

$$\beta = \left( \frac{\varepsilon}{\hbar c} \right) \sqrt{\frac{\varepsilon_{0}^{2} (\varepsilon_{m}^{2} - \varepsilon_{d}^{2})}{(\varepsilon_{m}^{2} - \varepsilon_{d}^{2})}}$$

(7.12a)

and this is the TM mode SPP dispersion relation for a single interface.

**TE Mode:** Simialrity we can also derive the SPP dispersion relation for the transverse electric field (TE) mode propagation in the waveguide. It is found as

$$\tanh \left( \frac{1}{2} \kappa_{m}^{-} d \right) = -\frac{\mu_{m} \kappa_{d}^{+}}{\mu_{d} \kappa_{m}^{+}},$$

$$\coth \left( \frac{1}{2} \kappa_{m}^{+} d \right) = -\frac{\mu_{d} \kappa_{m}^{-}}{\mu_{m} \kappa_{d}^{-}},$$

(7.13)

where again the $+$ and $-$ stand for the even and odd SPP modes, respectively.

The TE mode dispersion relation for the SPPs of the metamaterial-dielectric single interface heterostructure may be derived as was done above. This means we can put $\kappa_{m} d \to \infty$ in the
above expression. This will make \( \tanh(2\kappa_{m,x}d) = 1 \) and will reduce eqn (7.13) to

\[
\left( \frac{\kappa_d + \kappa_m}{\mu_d + \mu_m} \right) = 0
\] (7.14)

and by putting eqn. (7.9) into eqn. (7.14) we get

\[
\beta = \left( \frac{\varepsilon}{\hbar c} \right) \sqrt{\frac{k_0^2 (\mu_m^2 n_d^2 - \mu_m^2 n_m^2)}{(\mu_m^2 - \mu_d^2)}}
\] (7.15)

The above expression is the TM mode SPP dispersion for a single interface.

The dispersion relation for the SPPs in the waveguide may be found as follows. We find the value of \( \kappa_{m,x}^{\pm} \) by solving eqn. (7.10) and (7.13) selfconsistently using the MAPLE software package and calculate the dispersion relation for the waveguide by substituting in into eqn. (7.9)

\[
\beta_{\pm} = \sqrt{F_m^2(\varepsilon) - [\kappa_{m,x}^{\pm}(\varepsilon)]^2},
\] (7.16)

It is interesting to note that from above expression the waveguide has two types of SPPs, called the even (+) and odd (−) SPP modes, whereas a single metamaterial interface has only one SPP mode as shown in eqns (7.12a) and (7.15). These equations give rise to bound SPP states for each of the even and odd modes whose energies we will denote as \( \varepsilon_{sp}^+ \) and \( \varepsilon_{sp}^- \). These energies will be calculated in the results and discussion section.

### 7.2.3 Absorption Coefficient and Hamiltonian

An ensemble of noninteracting QDs are deposited near the both interfaces of the waveguide. In this section we calculate the effect of the SPPs on the absorption coefficient of the QDs. We consider a QD that has three excitonic states denoted as \( |a\rangle, |b\rangle, \) and \( |c\rangle \) where \( |b\rangle \) is the electronic state and \( |a\rangle \) and \( |c\rangle \) are two ground state (see Fig. 7-3). The energies of these states are \( \varepsilon_a, \varepsilon_b \) and \( \varepsilon_c \). The Hamiltonian of a QD is written as

\[
H_0 = \sum_{i=a,b,c} \varepsilon_i \sigma_{ii}
\] (7.17)
Where $\sigma_{ii}^+ = |i\rangle \langle i|$ with $i = a, b$ and $c$ and it is called the exciton number operator. The energy differences for $|a\rangle \leftrightarrow |b\rangle$ and $|b\rangle \leftrightarrow |c\rangle$ are denoted as $\varepsilon_{ab} = \varepsilon_b - \varepsilon_a$ and $\varepsilon_{bc} = \varepsilon_b - \varepsilon_c$, respectively.

A probe field with energy $\varepsilon_p$ and an amplitude $E_p$ is applied to monitor the absorption coefficient for the transition $|a\rangle \leftrightarrow |b\rangle$. The absorption coefficient due to absorption of a photon for the transition $|a\rangle \leftrightarrow |b\rangle$ is calculated in the literature [21] is written as

$$\alpha = \frac{\varepsilon_p}{\hbar c} \text{Im} \left( \frac{d_{ab}\rho_{ab}}{E_p} \right),$$

where $\rho_{ab}$ is the density matrix element and $d_{ab}$ is the dipole moment induced in the QD due to the transition $|a\rangle \leftrightarrow |b\rangle$. The interacting Hamiltonian between the probe laser and QD is then found in the dipole and rotating wave approximation as

$$H_{QD-L} = -\hbar \Omega_p a_p \sigma_{ba}^+ e^{-i\varepsilon_p t/\hbar} + h.c.$$  \hspace{1cm} (7.19)

where $\sigma_{ba}^+ = |b\rangle \langle a|$ is the exciton raising operator and $a_p$ is the probe field photon annihilation operator. Here $\Omega_p$ is the Rabi frequencies associated with the probe field.

We consider that transition energy $\varepsilon_{bc}$ of the QD lies near the SPP energies $\varepsilon_{sp}^+$ and $\varepsilon_{sp}^-$ of the waveguide and it is therefore convenient for us to define a SPP detuning parameter which is $\delta_{sp}^\pm = \varepsilon_{bc} - \varepsilon_{sp}^\pm$. When the QD transition energy $\varepsilon_{bc}$ is in resonance with the SPP energy $\varepsilon_{sp}^+$ we
get $\delta_{sp}^+ = \epsilon_{bc} - \epsilon_{sp}^+ = 0$. Similarly, when the QD transition energy $\epsilon_{bc}$ is resonant with the SPP energy $\epsilon_{sp}^-$ we get $\delta_{sp}^- = \epsilon_{bc} - \epsilon_{sp}^- = 0$. Due to the transition $|a\rangle \leftrightarrow |b\rangle$ and the electron is excited to state $|b\rangle$. Since the QD transition energy $\epsilon_{bc}$ is in resonance with SPP energy $\epsilon_{sp}^\pm$, the excited electron will then decay to state $|c\rangle$. The decay process is due to the exciton-SPPs coupling between the QD and the metamterial waveguide. In other words the metamaterial waveguide is acting as reservoir for the QDs.

The QDs interact with the waveguide via the exciton-SPPs interaction. One can say that the SPP electric field induces a dipole moment $d_{bc}$ in the QD and in this way they will interact with each other. Therefore the exciton-SPPs interaction Hamiltonina can be written in the dipole and rotating wave approximation as

$$H_{EX-SPP} = -\sum_{\beta \pm} g_{bc} \left[ a_{\beta \pm} \sigma_{bc}^\dagger e^{-i(\epsilon_{bc} - \epsilon_{sp}^\pm)} + h.c. \right]$$

(7.20)

where $g_{bc}$ is coupling constant of the exciton-SPP interaction,

$$g_{bc} = \left( \frac{\epsilon_{bc} d_{bc}^2}{2\epsilon_0 \pi V_m} \right)^{1/2},$$

(7.21)

and $\sigma_{bc}^\dagger$ is called the exciton raising operator for transition $|b\rangle \leftrightarrow |c\rangle$. $a_{\beta \pm}$ is the SPP annihilation operator and $V_m$ is the volume of the metamaterial layer.

Let us calculate the density matrix element $\rho_{ab}$ appearing in eqn. (7.18) by using the Schrödinger equation method. The Schrödinger equation for the presented sytem is written as

$$i\hbar \frac{d}{dt} |\Psi\rangle = (H_0 + H_{QD-L} + H_{EX-SPP}) |\Psi\rangle.$$  

(7.22)

### 7.2.4 Schrödinger Equation

We need to expand the wave function $|\Psi\rangle$ as an orthornormal set. To find the orthonormal set we consider that initially the electron in the QD is in the ground state $|a\rangle$ and there is one probe photon present $|1_p\rangle$. SPPs in the waveguide are in the ground state $|0_{\beta \pm}\rangle$. This initial state is denoted as $|a, 0_{\beta \pm}, 1_p\rangle$. Therefore we find the three orthonormal states of the system
to be $|a, 0\beta_\pm, 1_p\rangle$, $|b, 0\beta_\pm, 0_p\rangle$, and $|c, 1\beta_\pm, 0_p\rangle$ as the wave function as follows

$$|\Psi\rangle = A_a |a, 0\beta_\pm, 1_p\rangle + A_b |b, 0\beta_\pm, 0_p\rangle + \sum_{\beta_\pm} A_{c,\beta_\pm} |c, 1\beta_\pm, 0_p\rangle.$$  \hspace{1cm} (7.23)

Solving the Schrödinger equation with eqn. (7.23) we get

$$\frac{\partial A_a}{\partial t} = i\Omega_p A_b; \hspace{1cm} (7.24a)$$

$$\frac{\partial A_b}{\partial t} = [i\delta_{ab} - \gamma_b] A_b + i\Omega_p A_a + i \sum_{\beta_\pm} g_{bc} A_{c,\beta_\pm}; \hspace{1cm} (7.24b)$$

$$\frac{\partial A_{c,\beta_\pm}}{\partial t} = [i(\delta_{ab} - \delta_{sp}) - \gamma_c] A_{c,\beta_\pm} + ig_{bc}^* A_b; \hspace{1cm} (7.24c)$$

where $\delta_{ab} = \varepsilon_p - \varepsilon_{ab}$ is the probe detuning and $\gamma_b$ and $\gamma_c$ are the radiative linewidths of levels $|b\rangle$ and $|c\rangle$, respectively.

The summation in eqn. (7.24b) can be replaced by using the method of density of states. We know that polaritons in the coupler have quantized modes which propagate in the $z$-direction. The $z$-component of the wave vectors is not quantized. Therefore, the summation over $k_z$ can be replaced by the integration over energy $\varepsilon_{mpk_z}$ using the concept of the DOS,

$$\sum_{\beta_\pm} = \sum_{\beta_\pm} \int D_{\pm}(\varepsilon) \, d\varepsilon; \hspace{1cm} (7.25)$$

where $D_{\pm}$ is defined as

$$D_{\pm} = \frac{V_m \varepsilon^2}{\pi^2 \hbar^2 c^2} \frac{d\beta_\pm}{d\varepsilon}; \hspace{1cm} (7.26)$$

Here $V_m$ is the volume. The expression of $\rho_{ab}$ appearing in eqn. (7.18) is found from the expansion coefficient as

$$\rho_{ab} = A_b A_a^* \hspace{1cm} (7.27)$$

Therefore to find $\rho_{ab}$ we will solve the above three Schrodinger equation (7.24a, 7.24b, and 7.24c). We derive the analytical expression of the absorption coefficient in the steady state as
follows. In the steady state eqn. (7.24c) gives the expression of $A_{c,\beta \pm}$ as

$$A_{c,\beta \pm} = \frac{-ig_{bc}^*}{i (\delta_{ab} - \delta_{sp}^{\pm} - \gamma_c)} A_b. \quad (7.28)$$

Putting the above expression into eqn. (7.24b) we get the expression of $A_b$ as

$$A_b = \frac{-i\Omega_p}{([i\delta_{ab} - \gamma_b] + i\Xi_{bc})} A_a, \quad (7.29)$$

where $\Xi_{bc}$ is the self energy of the decay of the excition in the QD from excited state $|b\rangle$ to $|c\rangle$ and it is written as

$$\Xi_{bc} = -i \sum_{\beta \pm} \frac{|g_{bc}|^2}{[i (\delta_{ab} - \delta_{sp}^{\pm}) - \gamma_c]}. \quad (7.30)$$

Let us replace the summation over by the DOS in the self energy and we get

$$\Xi_{bc} = -i \sum_{\beta \pm} \int d\varepsilon \frac{D_{\pm}(\varepsilon) |g_{bc}(\varepsilon)|^2}{[i (\delta_{ab} - \delta_{sp}^{\pm}) - \gamma_c]} \quad (7.31)$$

The above expression can be written into two terms as

$$\Xi_{bc} = \Xi_{bc}^+ + \Xi_{bc}^- \quad (7.32)$$

where $\Xi_{bc}^+$ and $\Xi_{bc}^-$ are separately each the self energy due to the even and odd SPPs coupling, respectively and once the equation for DOS from eqn. (7.26) is substituted into eqn. (7.31) and the integration is performed we get

$$\Xi_{bc}^\pm = \frac{-i\pi \gamma_{sp}^{\pm}}{(\delta_{sp}^{\pm} - \delta_{ab} - i\gamma_c)^{3/2}} \quad (7.33)$$

$$\gamma_{sp}^{\pm} = \frac{3hc\gamma_0}{2\pi \sqrt{F_m} (\varepsilon_{sp}^{\pm})} \quad (7.34)$$

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The expression of the density matrix can be found from eqn (7.27) and (7.29) as

\[
\rho_{ab} = \frac{i\Omega_{ab}\rho_{aa}}{(i\delta_{ab} - \gamma_b) + i(\Xi_{bc}^+ + \Xi_{bc}^-)}
\]  

(7.35)

where \(\rho_{aa} = |A_a|^2\) is nothing but the probability of finding the particles in state \(|a\rangle\). Putting the expression of the density matrix into the expression of the absorption coefficient we get

\[
\alpha = \alpha_0 \text{Im} \left( \frac{\gamma_b}{(\delta_{ab} + i\gamma_b) + \Xi_{bc}^+ + \Xi_{bc}^-} \right),
\]  

(7.36)

where

\[
\alpha_0 = \frac{2\varepsilon_p |d_{ab}|^2 \rho_{aa}}{\gamma_b \hbar c}.
\]  

(7.37)

One can see from the eqn. (7.36) that if we neglect the coupling the QD and SPPs we get \(\Xi_{bc}^\pm = 0\) and one only the absorption peak at \(\delta_{ab} = 0\). Now let us concentrate on the absorption peak which appears at \(\delta_{ab} = 0\). Note from eqn. (7.33) that the self energy \(\Xi_{bc}^+\) and \(\Xi_{bc}^-\) have large values at \(\delta_{ab} = \delta_{sp}^+\) and \(\delta_{ab} = \delta_{sp}^-\), respectively. Note also \(D_\pm(\varepsilon)\) and \(D_-\varepsilon\) given in eqn. (??) for even and odd SPPs have also singularities at \(\delta_{sp}^\pm = 0\). This means that the absorption coefficient becomes zero at \(\delta_{ab} = \delta_{sp}^\pm\). In otherwords the absorption spectrum has two minima located \(\delta_{ab} = \delta_{sp}^+\) and \(\delta_{ab} = \delta_{sp}^-\). These minima are the transparent states in the system and this is mechanism is called reservoir induced transparency (RIT) [22]-[23].

**7.3 Results and Discussion**

In this section we have performed numerical simulations of bound SPPs, the density of states and the absorption coefficient. For numerical simulations we envision a waveguide made from CRLH-TL metamaterial as a core and polyethylene as the cladding. The material constants for the polyethylene cladding are \(\mu_d = 1\) and \(\epsilon_d = 2.25\) [24]. For the metamaterial we choose capacitances and inductances of the right- and left-handed components to be \(C_R = 664 \text{ zF, L}_R = 57 \text{ fH, C}_L = 111 \text{ aF, L}_L = 51 \text{ fH. Given the periodicity } a_m = 40 \text{ nm, these parameters give rise to values of } \varepsilon_p = 8 \text{ eV and } k_p = \varepsilon_p / \hbar c = 3.92 \cdot 10^7 \text{ m}^{-1}.

The SPP dispersion relation for the TM and TE metamaterial waveguide have been calculated and their result is plotted in Fig. 7-4a and 7-4b. In both figures the dotted curves
Figure 7-4: The dispersion relation for the (a) TM and (b) TE modes of the metamaterial waveguide. Dotted curves correspond to metamaterial where $d_m \gg 400\text{nm}$, and dashed curves to $d_m = 400\text{nm}$.

corresponds to the single interface metamaterial case. This follows the condition that $k_p d_m \gg 1$ which means the waveguide needs $d_m \gg 400\text{nm}$. The dashed curves shown the SPP dispersion curve of both the TM (a) and TE (b) in a waveguide when the metamaterial layer is sufficiently small as to produce a coupled interaction between it’s two surfaces. The separation condition is $k_p d_m = 1$ or $d_m = 400\text{nm}$. In the $d_m = 400\text{nm}$ waveguide we find two distinct energy curves each of the TM and TE modes. It is worth pointing out here that a waveguide made from natural materials, such as metal, does not contain any TE SPP branches. For each of the four energy curves we derive a SPP energy, they are $\varepsilon_{TM1} = 0.371\varepsilon_p = 2.968 \text{eV}$, $\varepsilon_{TM2} = 0.603\varepsilon_p = 4.824 \text{eV}$, $\varepsilon_{TE1} = 0.150\varepsilon_p = 1.2 \text{eV}$, and $\varepsilon_{TE2} = 0.212\varepsilon_p = 1.696 \text{eV}$.

It can be plainly observed that for each curve in the $d_m \gg 400\text{nm}$ waveguide their are two for the $d_m = 400\text{nm}$. This is the result of both internal waveguide interfaces coupling with each other and removing a SPP degeneracy and each energy curve splits into even ($+$) and odd ($-$) modes. Each even and odd mode pair in the $d_m = 400\text{nm}$ waveguide approach the same limit as their $d_m \gg 400\text{nm}$ waveguide counterpart. To see the effects of the coupling in the thin waveguide we consider SPPs with a specific $k$ value (i.e. $k = 3k_p = 1.18 \cdot 10^8 \text{m}^{-1}$) that will
allow four distinct energies for each mode. These SPP energies are $\varepsilon_{\text{TM}1}^+ = 0.357\varepsilon_p = 2.856$ eV, $\varepsilon_{\text{TM}1}^- = 0.375\varepsilon_p = 3$ eV, $\varepsilon_{\text{TM}2}^+ = 0.630\varepsilon_p = 5.04$ eV, and $\varepsilon_{\text{TM}2}^- = 0.549\varepsilon_p = 4.392$ eV for the TM mode. They are $\varepsilon_{\text{TE}1}^+ = 0.154\varepsilon_p = 1.232$ eV, $\varepsilon_{\text{TE}1}^- = 0.147\varepsilon_p = 1.176$ eV, $\varepsilon_{\text{TE}2}^+ = 0.226\varepsilon_p = 1.808$ eV, and $\varepsilon_{\text{TE}2}^- = 0.208\varepsilon_p = 1.664$ eV for the TE mode.

These results are supported by the findings of Hon et. al. [25] who studied CRLH terahertz metamaterial waveguides. Their terahertz CRLH waveguide can be realized in metal-metal waveguide by introducing gaps into the top metallization to create a series capacitance, $C_L$. They found the transmitted TM mode EM field is observed to decay exponentially away from the metasurface and therefore confirms the existence of the bound surface waves.

To couple excitations of a QD to SPPs in our metamaterial waveguide we need two types of QDs, one to investigate the TM and TE modes each individually. The resonance energies of these QDs are as follows $\varepsilon_{\text{bc}}^{QD-\text{TM}} = 0.37\varepsilon_p = 2.96$ eV and $\varepsilon_{\text{bc}}^{QD-\text{TE}} = 0.215\varepsilon_p = 1.72$ eV. These energies lie in the visible light range. We are considering QDs which have been recently fabricated [26]. Other parameters for our QDs are the dipole moments, $p_{\text{bc}}^{QD-\text{TE}} = 4.8\cdot10^{-28}$ Cm and $p_{\text{bc}}^{QD-\text{TM}} = 8\cdot10^{-28}$ Cm, the linewidths of level $|b\rangle$, $\gamma_{b}^{QD-\text{TE}} = 32$ meV and $\gamma_{b}^{QD-\text{TM}} = 64$ meV, and the linewidth of the level $|c\rangle$, $\gamma_{c} = 10^{-5}$ meV.

In Fig. 7-5a and 7-5b we show the absorption coefficient as a function of probe detuning for the TM and TE modes. We have focused our investigation to the lower energy region in the TM mode, near $\varepsilon_{\text{TM}1}$, and the upper energy region in the TE mode, near $\varepsilon_{\text{TE}2}$. These SPPs will lie in the optical light range while the others will lie outside and are too far off resonance with the QD to be significant. The solid curves corresponds to the when the QD-waveguide systems are far off resonance. In this case both surfaces of the metamaterial slab act independently and the absorption profile has one peak due to the transition $|a\rangle \leftrightarrow |b\rangle$. In both figures the dotted line is drawn for a metamaterial slab of thickness $d_m \gg 400$nm while the dashed line is drawn for a $d_m = 400$nm. We show a splitting in the spectrum where the absorption profile of the $d_m \gg 400$nm slab has two peaks and of the $d_m = 400$nm slab has three peaks.

The splitting of the spectrum from having one peak to two peaks and three peaks is due to strong exciton-SPP coupling. The coupling is strong via the DOS having a large value near the bound SPP states as shown in the inset. In these insets the result for the $d_m \gg 400$nm and $d_m = 400$nm are shown by the dotted and dashed lines, respectively. Due to the strong coupling,
dressed states are created in the system. In the $d_m \gg 400\text{nm}$ metamaterial they are denoted as $|b^+\rangle$ and $|b^-\rangle$ and two absorption peaks appear due to transitions $|a\rangle \leftrightarrow |b^+\rangle$ and $|a\rangle \leftrightarrow |b^-\rangle$. For the $d_m = 400\text{nm}$ metamaterial waveguide there are four dressed states created due to the coupling of the slab surfaces. Two of these dressed states are degenerate and have the same energy. Hence we of three transition which develop three peaks in the absorption spectra.

Absorption of guided mode SPPs of a waveguide by nearby quantum dots has been experimentally seen in work by Bracher et al [27]. In that work they use Au waveguides on GaAs and measure the coupling effect on the photoluminescence of near surface InGaAs self-assembled QDs. The waveguide was 5 $\mu$m wide and 25 $\mu$m long while the InGaAs QDs were grown on GaAs substrate using Stranski–Krastanov growth. The separation of waveguide and QD varied 7 to 57 nm and the density of QDs was 120-130 dots per $\mu m^2$. The spectra measured at the end of the waveguide showed the luminescence of several dots and therefore proved the presence of a coupled interaction between components of the heterostructure.

The spectra of nonresonant case in Fig. 7-5a and 7-5b show no minima while the $d_m \gg 400\text{nm}$ and $d_m = 400\text{nm}$ metamaterial show one and two, respectively. These minima appear
at $\delta_{ab} = \delta_{sp}, \delta_{sp}^\pm$ for each energy resonance and correspond to a transparent state of the system. The splitting is due to presence of dressed state in the system due to strong exciton-SPP coupling at the resonance condition. This coupling is strong due to large DOS values, shown in the insets, near the SPPs energies. This can be seen in eqn. (7.31). This would follow for the other two energies regions of the TM and TE modes if they were near resonance with the QD.

For the $d_m \gg 400\text{nm}$ we observe a single minima at $\delta_{ab} = \delta_{sp}$, or $\varepsilon_p = \varepsilon_{TM1}$ for the TM mode and $\varepsilon_p = \varepsilon_{TE2}$ for the TE mode. In this situation the QD has become transparent to the probe laser, $\Omega_p$, at resonance with the SPP energy of the metamaterial waveguide. Both the TM and TE mode coupled spectra show two minima for the $d_m = 400\text{nm}$ case. These minima correspond to $\delta_{ab} = \delta_{sp}^\pm$. It follows that the energies, for the TM mode, where these minima occur are $\varepsilon_p = \varepsilon_{TM1}^\pm$. For the TE modes, $\varepsilon_p = \varepsilon_{TE2}^\pm$. The presence of transparency in the present system due to waveguide on the WD is called reservoir induced transparency (RIT) [22]-[23]. This effect is similar to electromagnetically induced transparency (EIT). Strong evidence for EIT has been observed [28] and one could expect that experimental realization of RIT should not be far off. We have shown how one could control the number of the transparent states present in a metamaterial waveguide-QD heterostructure system by changing the location of the SPP energies, done by altering $C_R, L_R, C_L$, and/or $L_L$. Finally, we have used the density matrix method to also calculated the absorption coefficient. With the use of the Maple software package numerically solved for the absorption coefficient and found similar results [29].

7.4 Conclusions

The effect of SPPs on the absorption coefficient of QDs in metamaterial waveguides has been studied. It is found that when the thickness of the waveguide is on the order of the wavelength of interacting light each SPP energy state can be split in two. Excitons of the quantum dot are interacting with SPPs of the waveguide which is acting as reservoir. Numerical calculation for SPPs, DOS, and absorption coefficient are carried out. It is observed that when the exciton resonance frequency lies near the SPP frequencies of the waveguide we get four transparent states in the absorption spectrum. This effect is due to strong coupling between excitons and SPPs.
Bibliography


Chapter 8

Concluding Remarks

In this thesis, we have studied the quantum optical interactions in polaritonic nanocomposites. We have investigated the acousto-optic effect on the photon transmission and spontaneous emission in a polaritonic photonic crystal. Numerical calculations were performed on polaritonic photonic crystals fabricated from GaP, MgO, LiNbO$_3$ and LiTaO$_3$. The photonic band gap width and the decay rate of quantum dots (QDs) are found to vary depending on the high frequency dielectric constant, $\epsilon_\infty$, of the polaritonic material, while the photonic band edges vary inversely with the factor $\epsilon_\infty \varepsilon_L^2/\varepsilon_T^2$. The decay rate and transmission coefficient were been calculated in the presence of an external strain field. It is found that the decay rate increases when the resonance energy of the QD lies within the lower photon propagation band and decreases when it lies in the upper band. This demonstrates that the spontaneous emission of the QD can be controlled by the external strain field. This finding is significant because spontaneous emission is the source of undesirable noise in different types of electronic and optical devices. The control of the spontaneous emission also plays a significant role in quantum computation and quantum information processing. We have also found that polaritonic photonic crystals can be switched from a transmitting state to a reflecting state by applying an external strain field. The findings presented in this paper can be used to fabricate new types of optical switches. This work opens new opportunities for controlling light-sound interactions in photonic crystals and optical fibres hybrid systems made with photonic crystals.

A QD-exciton-polariton coupler nanocomposite is investigated. The coupler is fabricated from excitonic materials by embedding two CdS slabs between layers of ZnO. An ensemble of
non-interacting quantum dots are doped in the CdS layers of the waveguide coupler and polaritonic bound states were found within the band gap of ZnO. These bound exciton-polaritons (BEPs) from the coupler, which itself is acting as a reservoir, interact with the excitons present in the QDs via the exciton-BEP interaction. It is found that when the two CdS waveguiding cores are far away (~ 150 nm) from each other that the absorption spectrum has one minima which corresponds to a transparent state and when the waveguides are close to each other (~ 80 nm) the absorption spectra has two transparent states. The transparent states are also found to be switched on and off by a control laser field. These results can be used to make new types of polaritonic devices such as optical switches and transistors.

The energy transfer fluorescence between a biological labelling dye (Alexa Fluor 405, AFD) and gold nanorods (GNRs) has been studied experimentally and theoretically. Under one- and two-photon excitations, the fluorescence lifetime imaging microscopy and the density matrix method are applied to study this hybrid system. The dipole-dipole interaction (DDI) between AFD and GNR causes a decrease in the fluorescence lifetime change. The energy transfer provides detailed information in biological studies using metallic nanoparticles as fluorescence probes. This work has applications in bioimaging, fluorescence lifetime-based intra-cellular sensing of bio-analytes, and nuclear targeting cancer therapy.

We have investigated the nonlinear energy transfer from a QD to a metallic nanorod (MNR) in a hybrid systems. Probe and control laser fields were applied to the system and induced dipoles are created in the QD and MNR and both then interact via the DDI. The subsequent energy transfer is driven by interaction of excitons in the QD with surface plasmon polaritons (SPPs) created in the MNR. A theory of the nonlinear energy transfer between QD and MNR has been developed by using the density matrix method. We numerically evaluate the energy transfer by a self consistent method in the Maple software package and find shifting of the peak energy transfer rate to an off resonance position due to nonlinear interaction. Enhancement of the energy transfer rate is found to be controlled by the probe field intensity. Transparency of the system to particular wavelengths results from the application of a control field. This nanocomposite can be used to fabricate nanosensors, nano-switches and energy transfer devices.

The effect of SPPs on the absorption coefficient of QDs in metamaterial waveguides has been studied. Numerical calculation for the DOS, spontaneous emission and the absorption
coefficient are carried out. It is observed that when the exciton resonance frequency lies near the SPP frequencies of the waveguide we get transparent states in the absorption spectrum. This effect is due to strong coupling between excitons and SPPs. This coupling depends on the DOS of the SPPs. The coupling is strongest near SPP frequencies since the DOS there has very large values. For the waveguides of thickness on the order of the wavelength of light, the split in the SPP energy states also causes a split in each transparent state.

As stated and demonstrated throughout this work, there are countless numbers of possible combinations in the formation of nanocomposite systems. As an immediate next step of the present research, there is the opportunity to apply the non-linear processes used in chapters 5 and 6 to the other systems. Phonon-polariton and exciton-polariton materials could be made into any number of further structures from waveguides, couplers, and wires to more complicated split-ring resonators. Our theory derived in the investigation of biological labelling dyes and natural plasmonic materials could be extended to other systems of different dyes or organic molecules and different shapes and types of metals nanoparticles or even graphene. Metamaterials give us more control over their dispersion characteristic and display properties not seen in nature. The investigation of some of the more exotic new features, such as negative refractive index, on metamaterial waveguide and wire structures could completely change the present bound modes.
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