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Polaritons: From Theory to Applications

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Bachelor's thesis

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Polaritons are quasiparticles created by strong interaction between photons and matter. This thesis deals only with exciton-polaritons.

Excitons are electron and electron hole pairs usually found in different materials, such as semiconductors. An exciton is created when electron is excited to higher energy state at the conduction band, leaving electron hole behind at the valence band. Compared to the surroundings electron has negative charge and hole has positive charge. Electron and hole start to attract each other because of the Coulomb force. When they combine, a photon can be emitted.

By placing semiconductor material between two reflectors, an optical cavity is created. Energy can then be pumped into cavity with a laser or electricity to form excitons inside. When recombining, excitons emit light back into cavity, whereupon the emitted photons can get reflected back into material and create new exciton. The emitted light can also escape from the cavity or get attenuated within the cavity. When the energy of light that is trapped inside the cavity exceeds the energy of light that emits out or gets attenuated, the interaction of material and light moves into strong coupling regime. Through strong coupling the polariton is created. The polariton can be experimentally detected from light emitted out of cavity by using angle-resolved spectroscopy.

One theoretical model that explains the properties observed in polariton emission is the Tavis-Cummings model. In this model, we assume that there are N number of excitons in the cavity and one photon capable of interacting with the excitons. By placing the cavity in the right state, when it is in resonance with, for example the first singlet state, two new eigenstates called upper and lower polaritons are created. The energy of the upper polariton is at a higher level and the energy of the lower polariton is lower. These states begin to dominate the photochemical interactions in matter. All other states become, so called dark states or exciton reservoir, and excitons in these energy states are unable to emit light properly out of the cavity.

Excitons can move through different routes from the reservoir to either upper or lower polaritons. However, they are not able to emit light from the upper polariton state easily but must use different mechanisms to move to the lower polariton, from which they can emit light.

Exciton polaritons can be used in many different applications. The most common current research targets are, for example, the room temperature Bose-Einstein condensate, polariton lasing, and polariton OLEDs or POLEDs.

Although the applications mentioned above have already been successfully tested in experimental conditions and seem promising, more research is still needed so that they can be used in practical applications in everyday use.

Key words: Polariton, Exciton-polariton, Polariton laser, Room temperature Einstein-Bosen condensate, POLED.

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Polaritonit ovat fotonien ja materiaalin vuorovaikutuksesta syntyviä kvasihiukkasia. Tämä tutkielma käsittelee ainoastaan eksitonipolaritoneja.

Eksitonit ovat erilaisissa materiaaleissa, kuten puolijohteissa, esiintyviä elektroni ja elektroniaukko pareja. Eksitoni syntyy, kun elektroni virittyy korkeammalle energiatilalle ja siirtyy johtovyölle. Elektronin virittyessä sen alkuperäiselle paikalle jää elektroniaukko, joka on positiivisesti varautunut verrattuna ympäristöönsä. Vastaavasti elektronilla on negatiivinen varaus verrattuna ympäristöönsä ja se alkaa Coloumbin voiman seurauksesta kiertämään elektroniaukkoa. Kun elektroni ja aukko yhdistyvät, voivat ne emittoida fotonin.

Asettamalla puolijohdetta kahden heijastavan pinnan väliin voidaan luoda optinen kaviteetti. Kun puolijohteeseen pumpataan esimerkiksi korkea energistä laservaloa, alkaa puolijohteeseen syntymään eksitoneja. Yhdistyessään eksitonit emittoivat valoa takaisin kaviteettiin, jolloin emittoitu valo voi heijastua heijastavasta pinnasta takaisin materiaaliin ja luoda uuden eksitonin. Emittoitu valo saattaa myös vaimeta kaviteetin sisällä tai karata kaviteetista kokonaisuudessaan. Kun kaviteetissa pysyvän valon energia ylittää siellä vaimentuvan ja karkaavan valon energioiden summan, siirtyy valon ja materiaalin vuorovaikutus vahvan kytkennän alueelle, joka luo polaritonin. Polaritoni pystytään kokeellisesti havaitsemaan kaviteetista emittoituvan valon avulla kulmaerotteisella spektroskopialla (Angle-resolved spectroscopy).

Eräs teoreettinen malli, joka selittää polaritonin emissiosta havaittavat ominaisuudet on Tavis-Cummings-malli (Tavis-Cummings model). Tässä mallissa oletetaan kaviteetissa olevan N määrä eksitoneja ja yksi fotoni, joka pystyy olemaan vuorovaikutuksessa eksitonien kanssa. Asettamalla kaviteetti oikeaan tilaan, jolloin se on resonanssissa esimerkiksi ensimmäisen singlettitilan (singlet state) kanssa, syntyy kaksi uutta ominaistilaa nimeltään ylä- ja alapolaritoni. Yläpolaritonin energia on suuremmalla tasolla ja alapolaritonin energia taas alemmalla. Nämä tilat alkavat dominoimaan fotokemiallisia vuorovaikutuksia aineessa. Kaikki muut tilat muuttuvat niin sanotusti pimeiksi tiloiksi tai toiselta nimeltänsä eksitonireserviksi, ja eksitonit näillä energiatiloilla eivät pysty emittoimaan valoa kunnolla ulos kaviteetista.

Eksitonit voivat siirtyä eri reittejä reservistä joka ylä- tai alapolaritoneille. Ne eivät kuitenkaan pysty emittoimaan valoa yläpolaritonitilasta helposti, vaan niiden täytyy eri mekanismeja hyödyntäen siirtyä alapolaritonille, josta ne voivat emittoida valoa.

Eksitonipolaritoneja voidaan käyttää monissa eri sovelluksissa. Yleisimpiä tämän hetkisiä tutkimuskohteita ovat esimerkiksi huoneenlämmössä esiintyvä Bose-Einsteinin kondensaatti, polaritonilaseri sekä polaritoni OLEDit eli POLEDit.

Vaikka edellä mainitut sovellukset onkin jo onnistuneesti testattu testiolosuhteissa ja vaikuttavat lupaavilta, tarvitaan kuitenkin vielä enemmän tutkimustyötä, jotta niitä voidaan hyödyntää käytännön sovelluksissa arkikäytössä.

Avainsanat: Polaritoni, Eksitonipolaritoni, Polaritonilaseri, Bose-Einsteinin kondensaatti huoneenlämmössä, POLED

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1 Introduction

Throughout the history, scientific community has had heated discussion about nature of light. Two competing theories asserted that light was either particle or wave propagating through space. Between 19th and 20th centuries truth about nature of light started being unravelled. Experimental results started to show that light had both wave and particle like properties. New field of studies called quantum mechanics was born.

Through further observations it was concluded that particles like electrons also experience this wave-particle duality. Suddenly the boundary between particles and waves, matter and light wasn't so clear anymore. How matter and light would interact between each other became one of the focuses of both theoretical and experimental research. It wouldn't take long until it would be theorized that light and matter could be coupled to form new hybrid states with new properties. Later this new hybrid state would be known as a polariton.

Polariton is a quasiparticle which arises through coupling of electromagnetic wave and a dipole. This thesis focuses mainly on one of the subgroups of polaritons called exciton-polaritons. Exciton-polaritons are born through electromagnetic wave interacting with electron and electron hole pairs which are named excitons. Other examples of photon and matter interactions that results with polaritons are photon-phonon and photon-plasmon interactions.

Polaritons, although first considered theoretically already in start of the 1950s [1], have started to garner much more attention in recent decades. Interesting applications like polariton lasers, POLEDs or even room temperature Bose-Einstein condensates are being experimented on. Theoretical research also continues towards understanding different mechanics behind light-matter coupling. Understanding this interaction more will help towards realizing better ways to implement above mentioned applications and even creating new ones in the future.

In this thesis we are first going through basic theory behind exciton-polaritons. After that, overview of the current and future applications of exciton-polaritons such as polariton lasers, room temperature Bose-Einstein condensate and OLEDs are given. Lastly some future more theoretical applications are discussed.

2 Theoretical Background of Exciton-Polaritons

As was mentioned in the introduction section, exciton-polaritons are quasiparticles that arise through photon-exciton interaction. To understand mechanics behind this interaction we are first going to need to understand concepts such as excitons, strong coupling, optical oscillators and cavities.

In this section we are going to introduce each of above-mentioned concepts one by one to understand mechanics behind polaritons. This section concludes with presentation of theoretical model for exciton-polaritons called Tavis-Cummings model.

2.1 Light and Photons

Through emergence of quantum mechanics came better understanding of light's wave-particle duality nature. Thomas Young demonstrated in his famous double slit experiment light to be wave in 1803 when he was able to detect diffraction pattern of light going through two slits.

At the turn of the 18th century, it became clear that light being just a wave couldn't explain all experimental results, such as the ones of Heinrich Hertz who was the first to observe the photoelectric effect.

Light would first be theorized as an elementary particle, later called a photon, by Albert Einstein in 1905. This photon would have energy dependent on its frequency through which we can deduce that its energy is inversely dependent to its wavelength. Equation for energy of a photon is presented in equation (2.01) where E is energy of a photon, ω is the radial frequency, h and $\hbar$ are Planck constant and reduced Planck constant, c is speed of light in vacuum and λ is wavelength.

$$E = \hbar\omega = \frac{hc}{\lambda} \tag{2.01}$$

From this it can be deducted that photons with different wavelengths carry different amount of energy with them. When photon interacts with particles like electrons this energy can then be transferred to electron and transfer it to excited state.[2]

2.2 Excitons

Exciton is a quasiparticle usually found in insulators and semiconductors. In condensed material excited electron can have enough energy to transfer itself from valence band to

conduction band. This can happen when electron absorbs photon with enough energy or in other words with certain wavelength. By doing so it will leave behind a hole which means absence of an electron from a place where there could be one. Compared to the surrounding this electron hole has a positive charge. Because of Coulomb force, this electron which has negative charge and hole can form a system where they both attract each other forming new state called exciton.

Exciton has a net charge of zero, but it still has energy it acquired from photon. This is called exciton's binding energy. Exciton can be approximated as hydrogenic state which means that it can be thought as a hydrogen atom. Therefore, different properties of exciton follow closely Bohr model.

Equations for binding energy and Bohr radius is presented below (equation (2.02) and (2.03) respectively) where q is a charge of the electron, a_0 is Bohr radius, ϵ_r and ϵ_0 are dielectric constant and vacuum permittivity respectively, $\hbar$ is the reduced Planck constant, m_r^* is the reduced effective mass of exciton and n is principal quantum number of excited state. We can see that one of the main properties of the material affecting both binding energy and Bohr radius is its dielectric constant ϵ_r.

$$E_B = -\frac{q^2}{8\pi a_0(\epsilon_r\epsilon_0)n^2} \tag{2.02}$$

$$a_0 = \frac{4\pi(\epsilon_0\epsilon_r)\hbar^2}{m_r^* q^2} \tag{2.03}$$

Exciton can move through crystal lattice thus making it a particle that is able to transfer energy through the lattice without net transfer of charge. This energy can be then released by recombination of electron and electron hole back to valence band. Energy that exciton did hold will be then released as photon with similar wavelength as with the photon that excited that electron in the first place. This photon can then interact with another electron, forming a new exciton.

There are different types of excitons which are categorized by their location relative to the hole and its Bohr radius. Two most common are called Frenkel exciton and Wannier-Mott exciton. Illustration of both exciton types are presented in figure 2.1.

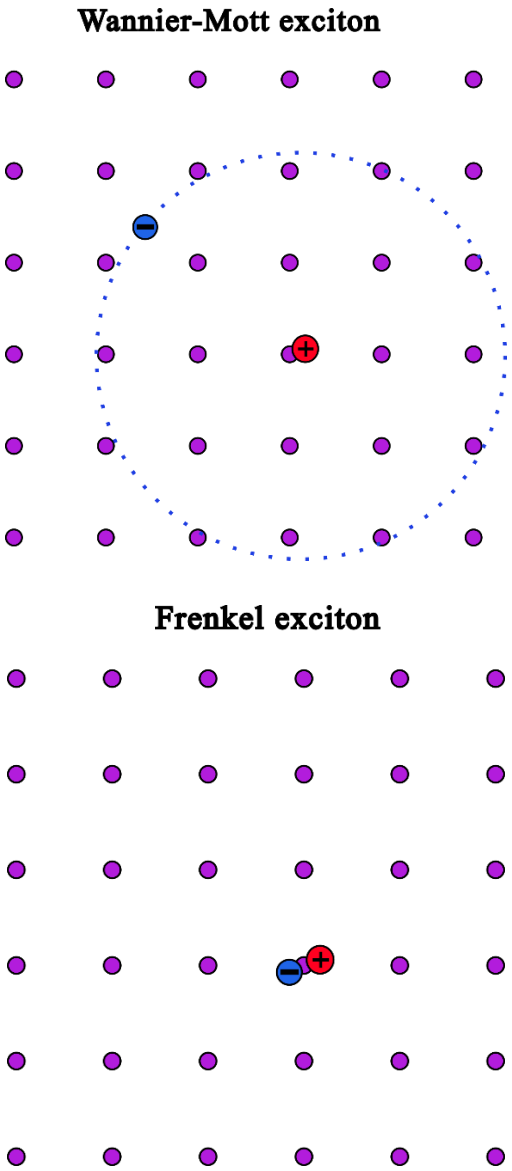

Figure 2.1. Comparison of the Wannier-Mott and Frenkel excitons. Wannier-Mott exciton is up and Frenkel exciton below. Purple dots represent either atoms or molecules, blue dots represent electrons and red dots electron holes.

Wannier-Mott excitons are characterized by their large Bohr radius. They are generally found in inorganic semiconductors where dielectric constant is stronger, resulting into much smaller Coulomb force between hole and electron. Wannier-Mott excitons have binding energy generally around ~5-50 meV. This low binding energy makes them more unstable at room temperature. By engineering inorganic semiconductors, binding energy can be raised to make them act more like Frenkel excitons.

Compared to the Wannier-Mott excitons, Frenkel excitons have much smaller radius. Frenkel excitons are usually confined to single or adjacent molecules in solids. They can easily move from molecule to molecule and diffuse within the material. Frenkel excitons have much

higher binding energies (~0,5-1 eV) compared to Wannier-Mott excitons, making them much more stable at higher temperatures. Due to this they can be more easily exhibited at room temperature. [3, Para. 3.6.5]

2.2.1 Singlet and Triplet States

Singlet state in exciton is a state where hole and electron have opposite spins, resulting for spin quantum number of $S = 0$. When considering classical mechanics, spin can be thought as angular momentum of a particle (though this isn't really the case). When calculating the spin of the system in singlet state, the angular momentum is 0 ($\frac{1}{\sqrt{2}}(\downarrow\uparrow - \uparrow\downarrow) = 0$) and there is only one possible configuration for this state. This is what defines a singlet state.

On the other hand, in triplet states electron and hole pair has spin quantum number of $S = 1$ and angular momentum of either -1, 0 or 1 ($\downarrow\downarrow = -1$, $\frac{1}{\sqrt{2}}(\downarrow\uparrow + \uparrow\downarrow) = 0$ or $\uparrow\uparrow = 1$) so there are three of these configurations.

In semiconductors triplet states are usually dominant while singlet states are rarer. This is because ratio of the two states is $\frac{1}{3}$ meaning that of all states 25% are singlet states and 75% are triplet states. Triplet states usually take also more time to decay which means moving to their ground state or in excitons electron-hole combination.[3]

Singlet states usually decay by emitting photons or sometimes phonons to other singlet states or into ground state. This is called fluorescence. On the other hand, for triplet states their decay path usually consist of them emitting energy so they will be transferred to another singlet state or into ground state. This is called in turn phosphorescence. Other way for two triplet states to interact is by annihilating themselves, converting them into singlet exciton.[4] Another way for the triplet state to decay is to transfer their energy to nearby molecules and excite them in return. This energy transfer can sometimes also create phonon withing crystal lattice.

Phonons are quantized energy packets of vibrations in solids. Due to their nature, they can be thought as a bosonic particle that can transfer energy through crystal lattice. This energy can be also transferred to excitons.[5]

2.3 Optical Cavity

Optical cavity also known as optical resonator is one of the most crucial parts to achieve right conditions for polaritons to appear in the material. They are used to confine light into certain space.

The most basic type of optical cavity would be to place two flat mirrors or other reflectors certain distance parallel from each other. This type of resonator is also called Fabry-Perot cavity. When light is inserted into the cavity it starts to bounce off from mirror to mirror. Due to wave like nature of the light it may form a standing wave inside the cavity. Due to this light oscillation, certain modes with resonance frequencies are formed inside the cavity. These modes are called cavity modes. This means that if light which is pumped inside the cavity has a broad wavelength spectrum, those wavelengths that match cavity's modes will remain while other wavelengths get dampened.

If material like semiconductor is placed between reflectors light will bounce countless times through material and reflectors before decaying out of the cavity through different pathways making cavity lose some of its energy.

When characterizing optical cavity, so called quality factor is used. Quality factor Qtells us cavity energy storage within certain timeframe which means that it will tell us how much light it can retain within. Equation (2.04) is the equation for calculating quality factor[6]:

$$Q = \frac{\lambda_0}{\delta\lambda_0} \tag{2.04}$$

where λ_0 is the resonance wavelength and $\delta\lambda_0$ is the fullwidth half maximum of the resonance wavelength λ_0.

When researching polaritons, optical cavities called microcavities are normally used. Microcavities have length between reflectors usually under micrometres (μm). If we assume both reflectors to be ideal, then we can get resonance wavelength of the cavity from equation (2.05):

$$L_c = m\frac{\lambda}{2} \tag{2.05}$$

Where L_c is length of the cavity, m is an integer and λ is the wavelength. We can see from the equation 2.05 that smallest possible microcavity that can be manufactured can be half of the wavelength of the wave of light that is wanted inside the microcavity ($m = 1$).

Reflectors in microcavity can be as simple as two metal sheets that are easier to manufacture or more complex ones like distributed Bragg's reflectors (DBR).

Metal microcavities have few advantages over DBR ones, like easier ways to inject electricity and smaller mode volume but their reflectivity is limited by the thickness of the metal sheet. This is why they usually have quality factor under 500. [7]

DBR consists of alternating layers of materials with high and low refraction indexes. Some of the light is always reflected from each alternating surface, meaning that DBR microcavity's quality factor depends on the number of alternating pairs in DBR. To work properly, optical thickness of each layer needs to match the quarter of the desired reflected wavelength λ so that reflections inside DBR interferes constructively instead of destructively within desired spectral range. [8]

Example of DBR microcavity structure is given in figure 2.2. Generally, DBR cavities have much higher *Q* value than their metallic counterparts, making them much more desirable when doing polariton research although they are much harder to manufacture.

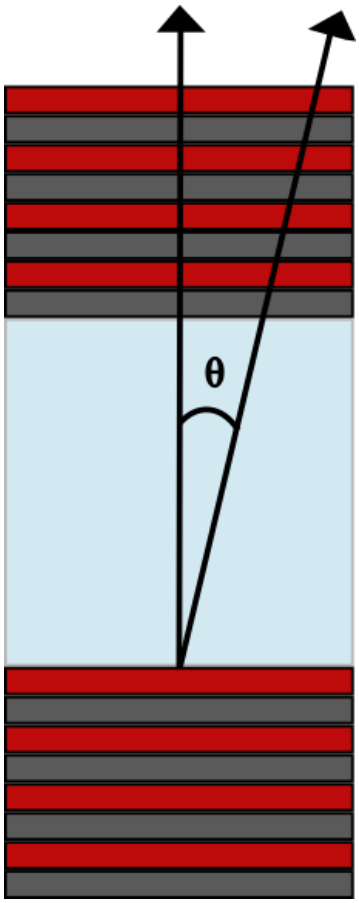

Figure 2.2. Structure of Fabry-Perot microcavity using DBR. Grey areas are materials with high refraction index while red ones are materials with low refraction index. Light blue area indicates emitter material inside the cavity. θ is angle of emission.

2.4 Weak and Strong Coupling

As mentioned above in chapter 2.3 confining photons is essential for the emergence of polaritons. This is due to the need to keep light-matter interaction ongoing and stronger. We call this light-matter coupling. This rate of interaction is usually categorized into two regimes called weak and strong couplings.

Photons and matter interact through different mechanisms like absorption, spontaneous and stimulated emission.

Absorption means that atom or molecule absorbs photon so that one or few of its electrons rise to higher energy level (in case of excitons from valence band to conduction band). Spontaneous emission means that excited electron will move from higher energy level to lower one releasing photon with the same energy as the difference of the energy of higher and lower levels.

Stimulated emission happens when excited atom or molecule interacts with the photon with same energy as the difference between higher and lower energy levels corresponding that energy state. As a result, the interacting photon will be absorbed and a photon with the same energy, phase and direction or momentum is released. Stimulated emission is one of the key interactions used in lasers. Figure 2.3 illustrates above mentioned photon-exciton interactions.[7]

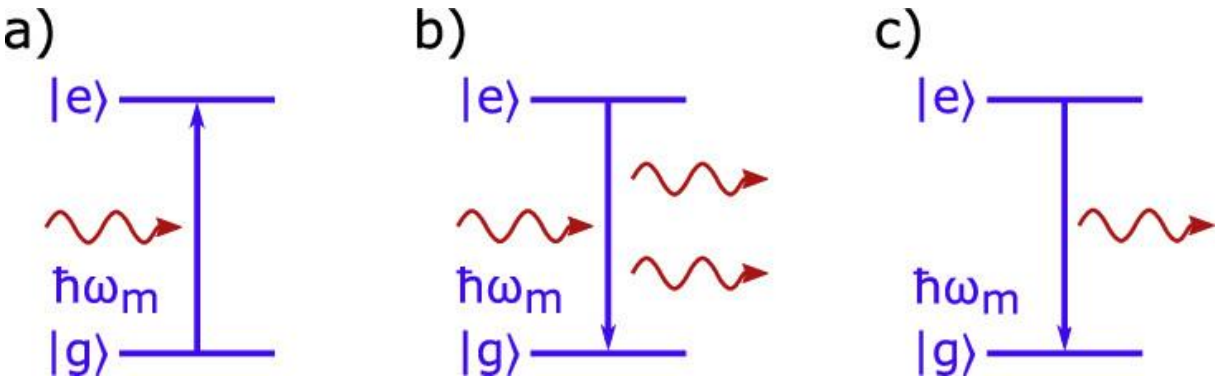

Figure 2.3. Illustrations of different types of interactions between photon and exciton. $|g\rangle$ denotes the ground state where electron is at rest, $|e\rangle$ denotes exciton where electron is excited and electron-hole pair has been formed. a is absorption, b is stimulated emission and c is spontaneous emission. From Ref [9] figure 1, used under Commons CC-BY 4.0 licence.

We are next going to go through the basic characteristics of each coupling regimes.

2.4.1 Weak Coupling

When considering weak coupling in the case of an atom in vacuum, we usually consider only absorption of a photon and then its spontaneous emission afterwards. This process would be irreversible in this case.

In bulk material, the situation is much different as the photon can then be reabsorbed by the next atom and so on until it exits the material. Purcell was one of the first to propose that there would be a way to enhance the rate of spontaneous emission when material was placed inside spectrally resonant light field.[10]

When emitter material like semiconductor is placed inside a microcavity with optical resonant modes this effect can be achieved experimentally. One of these experiments achieved five-fold rate enhancement of spontaneous emission. On the other hand, rate decrease has been also experimentally observed in the case of emitters that were out of resonance with cavity modes. Both of these can happen at the same time.[11], [12]

This change of rate for spontaneous emissions in microcavity is happening because photon can bounce of multiple times through cavity's reflectors back into material, before decaying out of cavity through different means like imperfect reflection or scattering.

When overall energy change inside microcavity is negative, light-matter coupling is called weak, and this interaction is irreversible. This can experimentally be seen from light emission out of microcavity as there won't be any new energy states rising from the interaction and properties of the cavity material remain mostly the same. Equation for the condition for weak coupling is presented below (equation (2.06)) where g represents energy kept in interaction, $\gamma_{ex,nr}$ represents rate of photons non resonant decay inside the cavity and γ_{em} is the rate of photons emitted out of the microcavity.[13]

$$g < \gamma_{ex,nr}, \gamma_{em} \tag{2.06}$$

While weak coupling is an interesting interaction and it can be used in lasers and other applications, research usually focuses on strong coupling regime due to the new properties that rise from stronger light-matter interaction.

2.4.2 Strong Coupling

Strong coupling regime is reached when overall energy change inside microcavity is net zero or above. This means that energy exchange rate between emitters and photons is bigger than the decay rate of photons out of and inside the microcavity. Condition for strong coupling is presented in equation (2.07). Variables of equation (2.07) are the same as in equation (2.06).

$$g \geq \gamma_{ex,nr}, \gamma_{em} \tag{2.07}$$

In this interaction, photons which get emitted by emitter (excitons in our case) get either reabsorbed by another exciton or reflected by reflectors in microcavity and reabsorbed and then emitted again. This interaction becomes periodic, and system starts to oscillate coherently between cavity photons and excitons. This oscillation between cavity photon and exciton energy states is called Rabi frequency (Ω_R). Through this oscillation, cavity photon and exciton energy states become hybridized and two new energy states replace previous one which become the system's new eigenstates. (Figure 2.4) This is called exciton-polariton which have unique properties from both cavity photons and excitons.

These new system eigenstates are called the upper polariton (UP) for the higher energy state and the lower polariton (LP) for the lower energy state. These two new states now behave like any other states, absorbing and emitting photons. Energy difference between UP and LP at the emission angle of zero ($\theta = 0$) is called Rabi splitting ($\hbar\Omega_R$) where $\hbar$ is reduced Planck's constant. Energy difference ($\hbar\Omega_R$) of these two states corresponds to the strength of the coupling which means that the bigger the Rabi splitting the stronger the exciton and cavity photon coupling.[13]

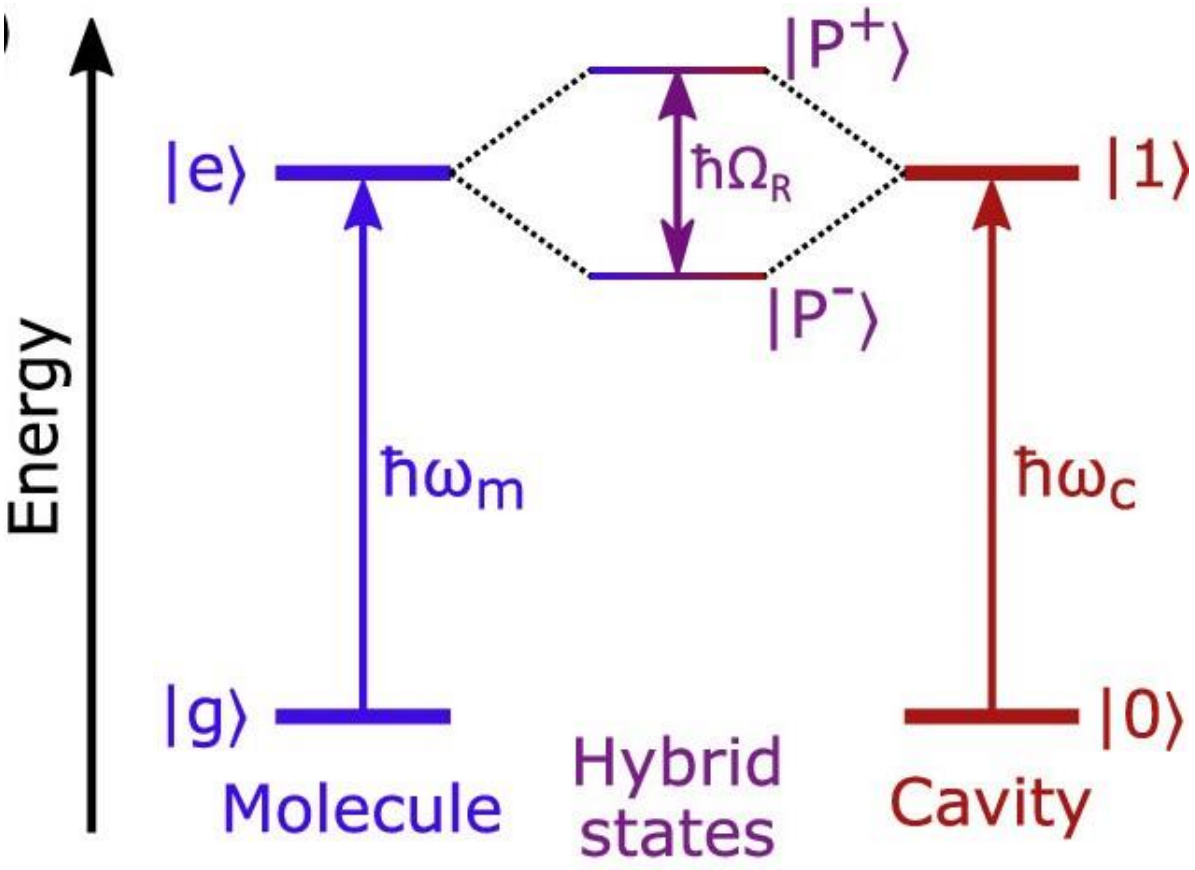

Figure 2.4. Rabi splitting $\hbar\Omega_R$ and new hybrid eigenstates of upper ($|P^+\rangle$) and lower ($|P^-\rangle$) polariton represented in energy diagram. From Ref [9] figure 3b, used under Commons CC-BY 4.0 licence.

One way to measure coupling strength is to use normalized coupling factor g. Equation (2.08) where $\hbar\Omega_R$ is Rabi splitting and ω_m is resonance frequency of the exciton, represents way to calculate g:

$$g = \frac{2\hbar\Omega_R}{\hbar\omega_m} \tag{2.08}$$

Higher the value of g means larger strong coupling between the system and the cavity photon.[14]

To experimentally observe strong coupling inside microcavity, spectroscopy is usually used. When light is emitted out of the microcavity its angle resolved absorption, transmission, photoluminescence etc. can be observed. This was first time experimentally observed in 1992 with DBR microcavity using GaAs quantum well as a cavity material between two reflectors.[15]

After experimental observation of exciton-polaritons and Rabi splitting and oscillation, work for theoretical framework started for this observable phenomenon. There have been few models made to understand this interaction more. These models range from semi-classical to full quantum theory models. In next section one of these theoretical models known as Tavis-Cummings model is introduced and explained in more detail.

2.5 Exciton-polariton through Tavis-Cummings model

When trying to understand strong coupling interaction inside microcavity theoretically it's good to approximate the system by a two-level system (ground state and another energy state) and only one cavity photon in cavity mode coupled together. This kind of model is called the Jaynes-Cummings model.

Jaynes-Cummings Hamiltonian is the operator of the above-mentioned system. Hamiltonian describes the systems total energy, and it can be also expressed as sum of energy of its parts. Jaynes-Cummings model is described in equation (2.09).[16]

$$\widehat{H}_{JC} = \widehat{H}_{ex} + \widehat{H}_{ph} + \widehat{H}_{int} = E_{ex}\widehat{\sigma_z} + E_{ph}\hat{b}^{\dagger}\hat{b} + g_0\left(\widehat{\sigma_+}\hat{b} + \widehat{\sigma_-}\hat{b}^{\dagger}\right) \qquad (2.09)$$

Where $\widehat{H}_{JC}$, $\widehat{H}_{ex}$, $\widehat{H}_{ph}$ and $\widehat{H}_{int}$ are Hamiltonian operators of system, uncoupled exciton, uncoupled photon and interaction energy of exciton and photon respectively. $\widehat{\sigma_z}$ is a operator which represents single exciton either in ground state or as excited. $\hat{b}$, $\hat{b}^{\dagger}$ are creation and annihilation operators of photon. E_{ex} and E_{ph} are energies of exciton and photon respectively. g_0 is the energy of exciton photon interaction and its coupling strength. If we now recall equations (2.06) and (2.07) and substitute g from those two with g_0 from equation (2.09) we can determine if system is in weak or strong coupling regime over time from this model.

Jaynes-Cummings model is useful in only the case of perfect system with one exciton and photon interacting. In most experimental applications we need to consider cases with *N* number of molecules able to form excitons. Upgraded version of Jaynes-Cummings model which takes this into account is called Tavis-Cummings model. In this model interaction

energy g_0 becomes $g = \sqrt{N} * g_0$. Note that we are still going to assume that there is one excitation or photon at any given moment inside the cavity. Tavis-Cummings model is presented in equation (2.10) where $\hat{H}_{TC}$ means Hamiltonian operator of the system and $\hat{a}$, $\hat{a}^{\dagger}$ are creation and annihilation operators of exciton.

$$\hat{H}_{TC} = \hat{H}_{ex} + \hat{H}_{ph} + \hat{H}_{int} = E_{ex}\hat{a}^{\dagger}\hat{a} + E_{ph}\hat{b}^{\dagger}\hat{b} + g\left(\hat{a}^{\dagger}\hat{b} + \hat{a}\hat{b}^{\dagger}\right) \quad (2.10)$$

By diagonalizing equation (2.10) we get equations for upper and lower polaritons:

$$H|P^{+}\rangle = E_{UP}|P^{+}\rangle = E_{UP}(\alpha|e,0\rangle + \beta|g,1\rangle) \quad (2.11)$$

$$H|P^{-}\rangle = E_{LP}|P^{-}\rangle = E_{LP}(\beta|e,0\rangle - \alpha|g,1\rangle) \quad (2.12)$$

Equation (2.11) is the energy of upper polariton and (2.12) is the energy of lower polariton. $|e,0\rangle$ goes through every possible excitation one by one while photon doesn't exists inside the cavity. Opposite is true for the $|g,1\rangle$ operator where photon exist inside the cavity while every exciton is at ground state. α and β are the probability amplitudes of excitons and cavity photons respectively. Both probability amplitudes describe the contribution of the exciton and cavity photons at any given time. They are in superposition which means that both states can exist simultaneously, and they must satisfy the normalization condition of $|\alpha|^2 + |\beta|^2 = 1$. $|\alpha|^2$ and $|\beta|^2$ are also called Hopfield coefficients. When $|\alpha| > |\beta|$ system rests towards excitons in UP state and towards photons in LP and when $|\alpha| < |\beta|$ system rests towards excitons in LP state and towards photons at UP.

Figure 2.5 shows an illustration of diagonalized equations (2.11 and 2.12) in graph as function of the emission angle θ.

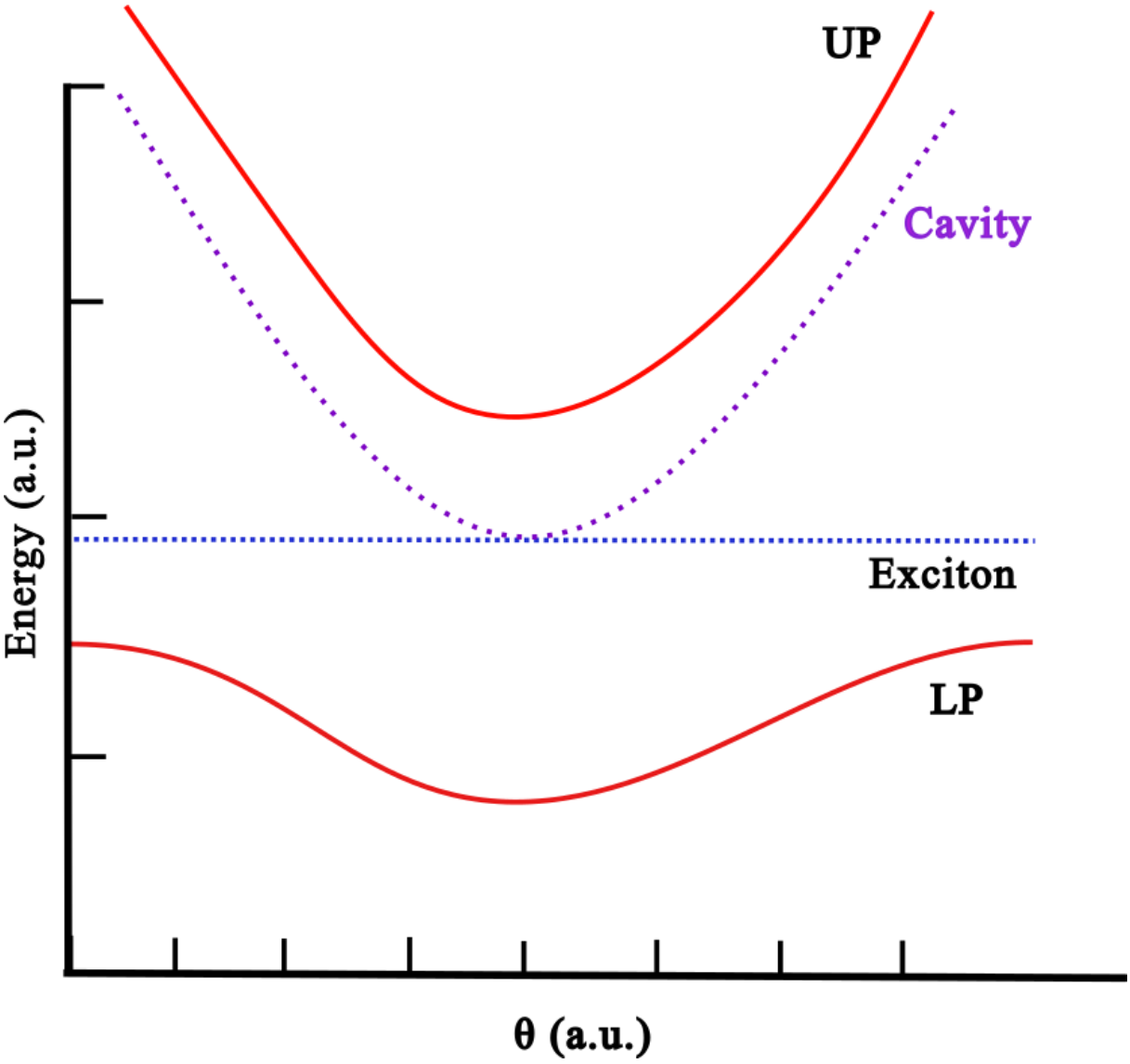

Figure 2.5. Illustration of both polariton branches' emission energy as function of the angle θ. UP means upper polariton and LP is lower polariton (red curves). Purple dotted curve represents cavity photon and blue dotted line represents energy of exciton.

This model can be tuned by changing difference of exciton energy and photon energy which is called detuning $\Delta = E_{ex} - E_{ph}$. This also changes Hopfield coefficients. These effects are shown in figure 2.6. Where $E_{ex} = E_{ph}$ the separation of both polariton branches is at minimum and the Rabi splitting equals $2\hbar\Omega_R$ which can be used to determine Rabi splitting of the system.[8], [17]

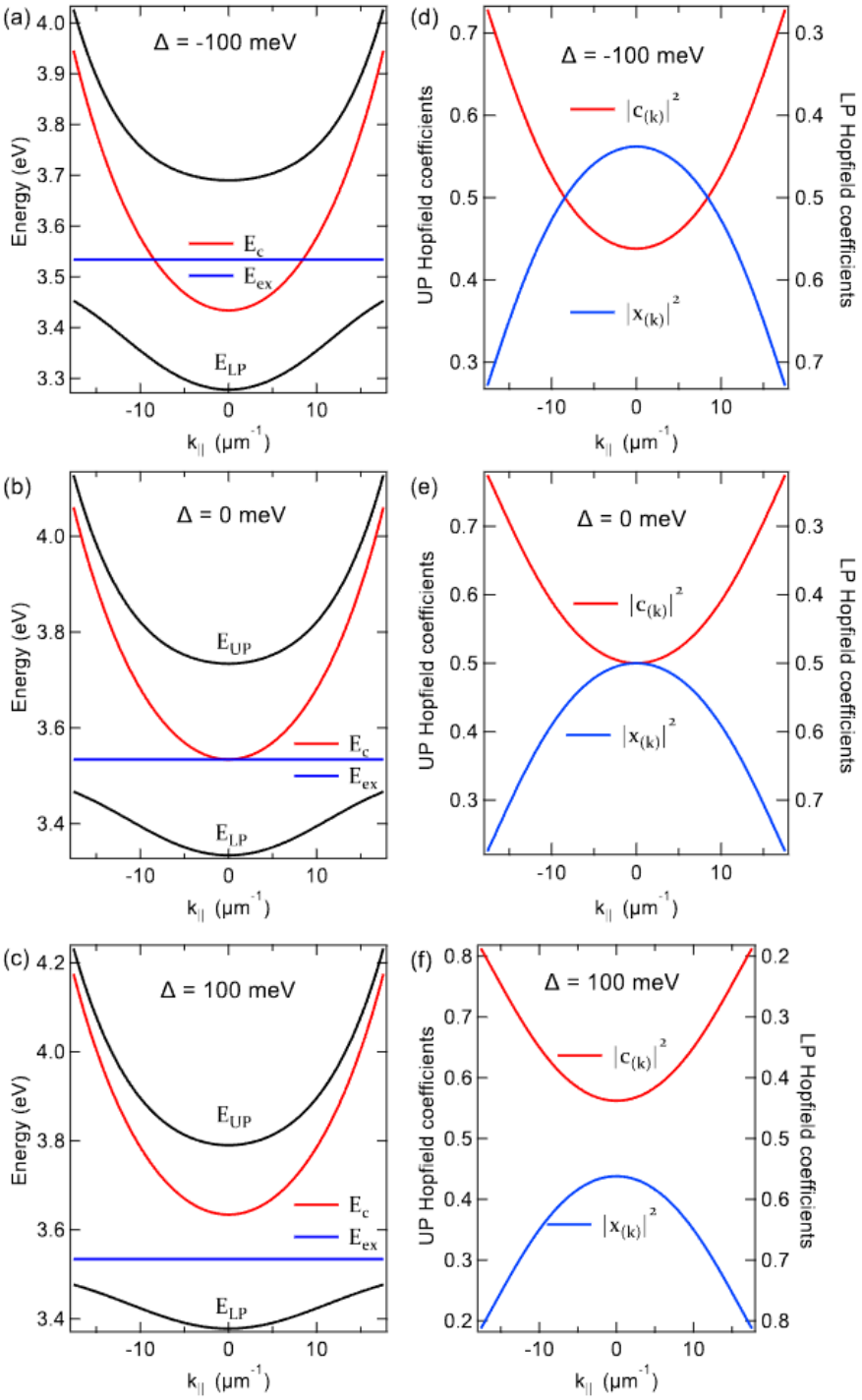

Figure 2.6. Example of the effects of the detuning Δ. a-c represents polariton dispersion while d-f are corresponding Hopfield coefficients. In this example the exciton energy E_{ex} is 3.534 eV and Rabi splitting is 0.4 eV. a and d correspond to $\Delta = -100$ meV. b and e correspond to $\Delta = 0$ meV. c and f correspond to $\Delta = 100$ meV. Reproduced by permission from ref [8] figure 2.10.

Usually, microcavity is tuned to only one of the singlet states occurring within material. Now singlet states that are between these new UP and LP branches are not able to interact so well within this new system, needing them to first decay through different means, for example by

emitting photon or phonon to relax into LP branch and from there to decay to the ground state. These singlet states are still valid eigenstates of the system, so they become what is known as dark states or exciton reservoir. Making these excitons within reservoir to interact with the polariton and understanding their different relaxation and decay paths is part of the ongoing studies. Understanding dark states' mechanics more could enable these states being used more effectively to bring exciton-photon interaction from weak to strong coupling regime. These dark states will be discussed more in next chapter.

3 Dark States and Decay Paths

When photon excites electron, it is usually excited to the first singlet state rapidly. This excitation usually relaxes fast by intramolecular relaxation. Photochemistry and physics between molecules now get dominated by that singlet state. In the case of strong coupling regime if this singlet state is affected, new hybrid states of UP and LP now govern around this localized singlet state instead.

If N number of molecules and one cavity photon hybridize, we now get N+1 number of states where two of those states are now UP and LP which are separated by Rabi splitting. This now makes N-1 number of other states inactive and they don't contribute almost anything. This is happening for many reasons like destructive interference of emitted photons. These now become dark states or exciton reservoir.

When exciton first gets excited to the UP state it decays back to dark state and usually fast which is faster than normal emissive process. This is due to density of the reservoir (N-1) when compared to the low density of the LP state of what there are only one. From reservoir, relaxation can occur towards LP state, ground state or a another triplet state.[9], [18]

Relaxation from reservoir to the LP state can happen in two ways. First is through vibrationally assisted scattering. In vibrationally assisted scattering, exciton is relaxed to lower energy level when releasing energy by vibrating nearby molecules radiating its energy into the material.[19], [20]

Second way for the exciton relaxation is by radiative pumping. Molecule that is in the exciton reservoir that has been excited suddenly emits a single photon. After this, exciton gets absorbed by lower polariton.[9], [21]

Vibrational assisted scattering and radiative pumping are both competing pathways for relaxation from reservoir to the LP. In general, radiative pumping is more dominant in molecules like organic dyes while vibrationally assisted scattering is more dominant in molecules like J-aggregates.

Figure 3.1 illustrates different relaxation and decay pathways. (i) Represents relaxation from UP to reservoir as was discussed in this chapter. (ii) Is a relaxation from UP straight to LP. This has been experimentally observed only couple of times but are usually attributed as an error with distinguishing it from different decay pathway through exciton reservoir. (iii) Has

been observed for some J-aggregates but is very uncommon. There has been some attempts to explain this phenomena, thermal activated repopulation of UP, simulation suggesting this is due to more photonic nature of the polaritons.[9], [22]

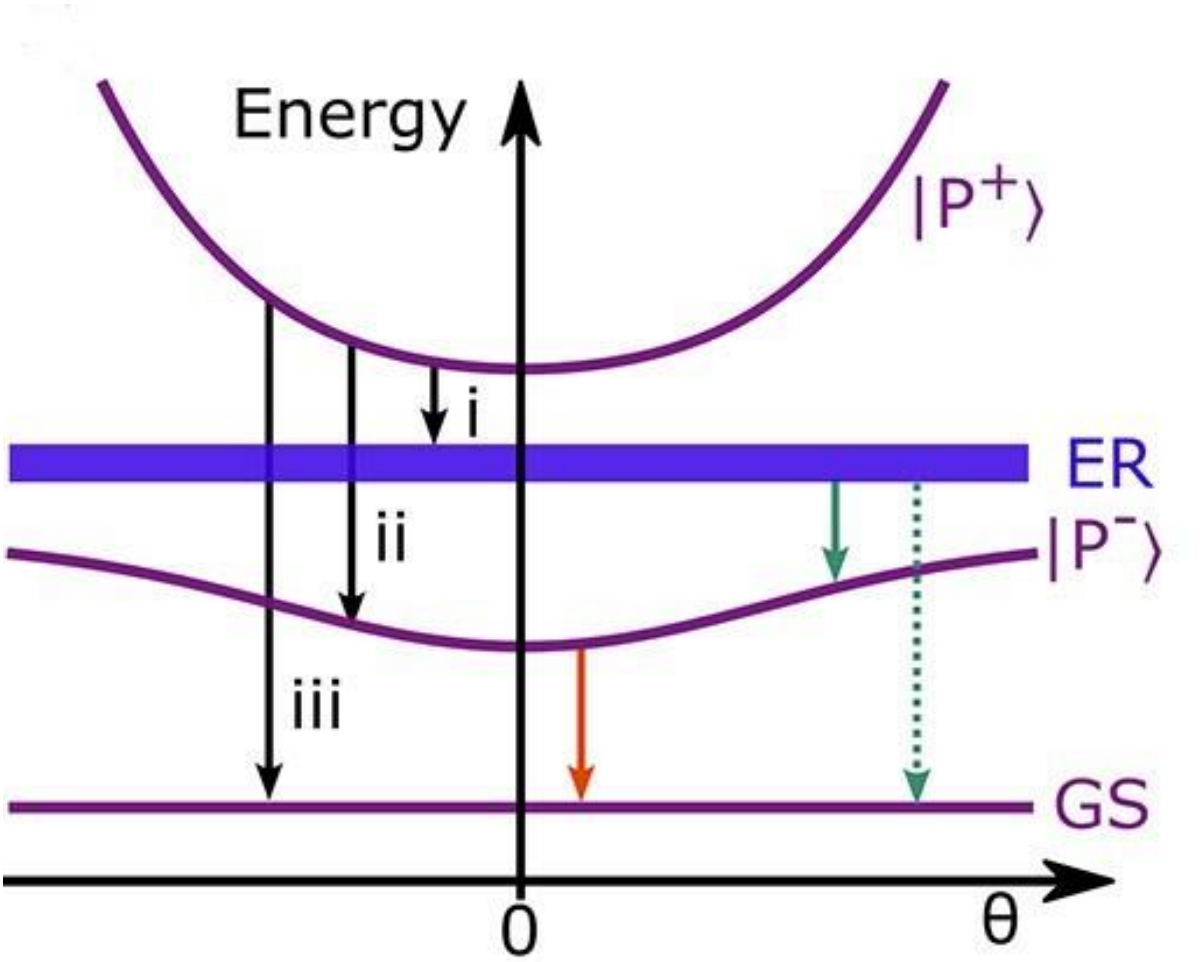

Figure 3.1. Different decay paths of excitons from UP and exciton reservoir to LP and ground state. (i) Relaxation from UP to reservoir. (ii) Relaxation from UP to LP. (iii) Decay from UP to ground state. Green arrow represent relaxation from reservoir to LP. Green dotted arrow represent decay from reservoir straight into ground state. Red arrow represents decay from LP to ground state. ER means exciton reservoir. GS means ground state. $|P^+\rangle$ and $|P^-\rangle$ are upper and lower polaritons respectively. From ref [9] figure 5(a), used under Commons CC-BY 4.0 licence.

From LP branch exciton has pathway to decay into ground state using emission. As UP branch decays very fast into reservoir it is not very visible when compared to LP branch which decays usually much slower. One study has found that this rate is as fast as 150 fs for UP relaxation to reservoir and comparatively slow for relaxation from reservoir to LP branch which was measured to be around 3,2 ps in J-aggregated cyanine dye which was strongly coupled.[23]

Usually, emission from LP concentrates on around the angle of 0° (figure 3.1). One of the theories that try to explain this phenomenon is assuming that LP branch consists of numerous discrete sets of states. When exciton relaxes from reservoir into LP branch it will go into one of these states. Exciton is then excited back to reservoir and then relaxes back into lower state within LP branch by emitting phonons. This goes on until exciton is at lowest point of the LP branch and then decays into its ground state.[8], [9]

4 Applications

There has been surge of interest in recent years towards exciton-polaritons. Some of it is through interest towards understanding this quantum mechanical phenomena. But while others are trying to understand the theory behind polaritons, others are working towards realizing useful applications that could help in basic research or replace older technologies. In this section we are going to go through three such applications that are being in development now. These applications are room temperature Bose-Einstein condensate, polariton lasers and polariton OLEDs.

4.1 Room Temperature Bose-Einstein Condensate

Bose-Einstein condensate is one of the states of matter first theorized by Albert Einstein in around 1924. He credited this discovery to Indian mathematician and physicist Satyendra Nath Bose as well who had made a pioneering paper about quantum statistics prior of his own works.

Both researchers worked in collaboration to develop concept known as Bose-Einstein statistics which describes two different ways how identical and non-interacting particles can occupy same discrete energy states. Particles that follow this statistic model are known as bosons. Bosons do now follow Pauli exclusion principle as their spin values are integers.

When macroscopic collection of these particles occupies same energy state at the same time it is called Bose-Einstein condensate. Usually, this state is lowest single particle energy state. Bose-Einstein condensate can be achieved only in very cold temperatures around absolute zero with low density gaseous bosons like rubidium atoms.[24]

As excitons are bosonic particles in nature, they are able behave like particles following Bose-Einstein statistics. They are then able to also form kind of quasi-Bose-Einstein condensate as well. Condensation temperature is inversely proportional to the mass of the particle by following relation, $T_c \propto \frac{n^{\frac{2}{3}}}{m}$ where T_c is condensation temperature, n is number density and m is the mass of the particle. Compared to the rubidium atoms, mass of the polaritons is much smaller, around 10^{10} smaller. This makes polaritons great platform to form condensate. Organic semiconductors within microcavity now pose great opportunity as they can form Frenkel excitons that have binding energy high enough to survive in room temperature. This

now opens new possibilities to research properties of the Bose-Einstein condensates in room temperature using exciton polaritons.[8]

In case of exciton-polaritons, this low energy state is LP branch where excitons concentrate after relaxing there from reservoir through different means discussed in the chapter 3.

To achieve condensation, in most experiments microcavity is pumped with non-resonant light with energies above that of exciton excitation states. This creates population of excitons into reservoir that in the end relax into polariton states. Below threshold excitons in reservoir scatter all around LP branch through their decay paths. With certain amount of stimulation scattering to the angle $\theta = 0$ becomes most likely as it overtakes the rates of other pathways of decay and system enters state above threshold. We now have high density of excitons at the lowest points of the LP branch. Sharp and non-linear increase of photoluminescent emission is observed originating from the bottom of LP branch. This emission is also observed to be coherent meaning that it is spatially and temporally coherent. Figure 4.1 is an example of polariton Bose-Einstein condensate in real space.[9], [25]

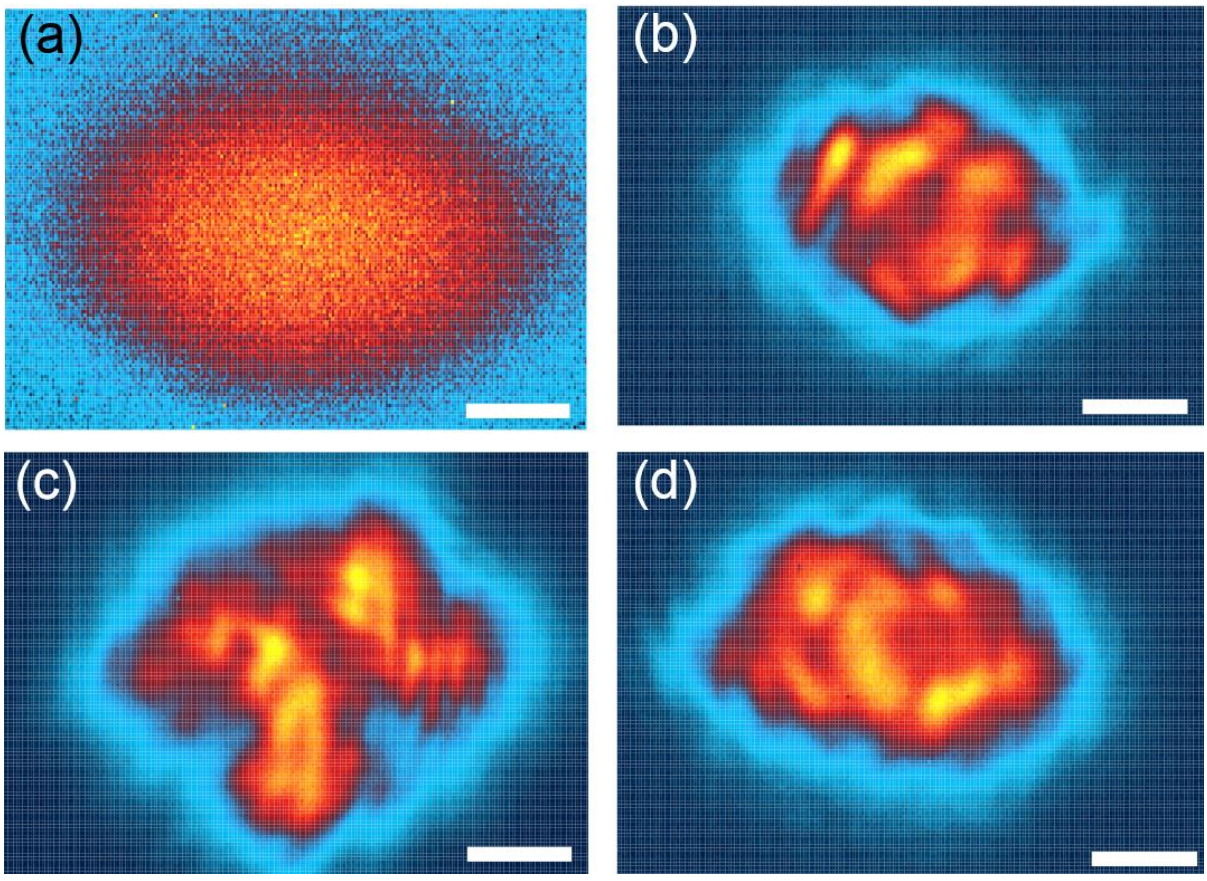

Figure 4.1. Polariton Bose-Einstein condensate emission in real space. a is below threshold and b-d is above threshold. Image of b has been taken from same spot as a but c and d are from different spot. The scale bar is 5 μm. Reproduced by permission from ref [8] figure 5.5.

One of the interesting features of Bose-Einstein condensates is to form what is known as superfluid, which is fluid like phase of matter with zero viscosity. In exciton-polaritons superfluidity can be observed within microcavity that has 2D quantum well embedded within.

One experiment in 2017 was able to observe superfluid in polariton condensate using TDAF molecules to form Frenkel excitons. Quantum well was burned with laser to form artificial defect into material. When not in superfluid phase, dark cone would be formed behind defect and in front there would be a fringe-like pattern, when observing defect in real space image. Dark cone and fringe pattern would almost disappear when superfluid is formed.

It was found out that polariton density played a key role for superfluidity to happen. When density was $0{,}5 * 10^6 \frac{\text{pol}}{\mu m^2}$ superfluid wasn't formed, but at density of $10^7 \frac{\text{pol}}{\mu m^2}$ superfluid was observed. This study also found out that in different conditions high group velocity of polaritons inhibited the superfluid behaviour. One of the theorized practical applications of this phenomena would be to shield photonic devices from scattering that is caused by polariton-polariton interactions. Another useful thing would be to make studying of superfluid behaviour in room temperature conditions instead of temperatures close to absolute zero.[26]

4.2 Polariton Lasers

As was mentioned about polariton condensation, we observe coherent photoluminescent emission from the lowest point of the LP branch. Lasers are devices that emit coherent beam of light. We can now start to wonder if the coherent emission from polariton condensate could be utilized as a new type of laser.

Typical lasers work by using stimulated emission. First light or electricity is pumped inside of the laser into material containing either gas, crystal, or semiconductor material. Excitations form inside the laser into emitter material which is called population inversion. After this at above lasing threshold spontaneous emissions become stimulated emissions, creating coherent light emission. Normal laser can be also placed inside the cavity to bolster the stimulated emission with cavity feedback.[27]

Figure 4.2 illustrates difference of the working principles behind polariton and photon lasers.

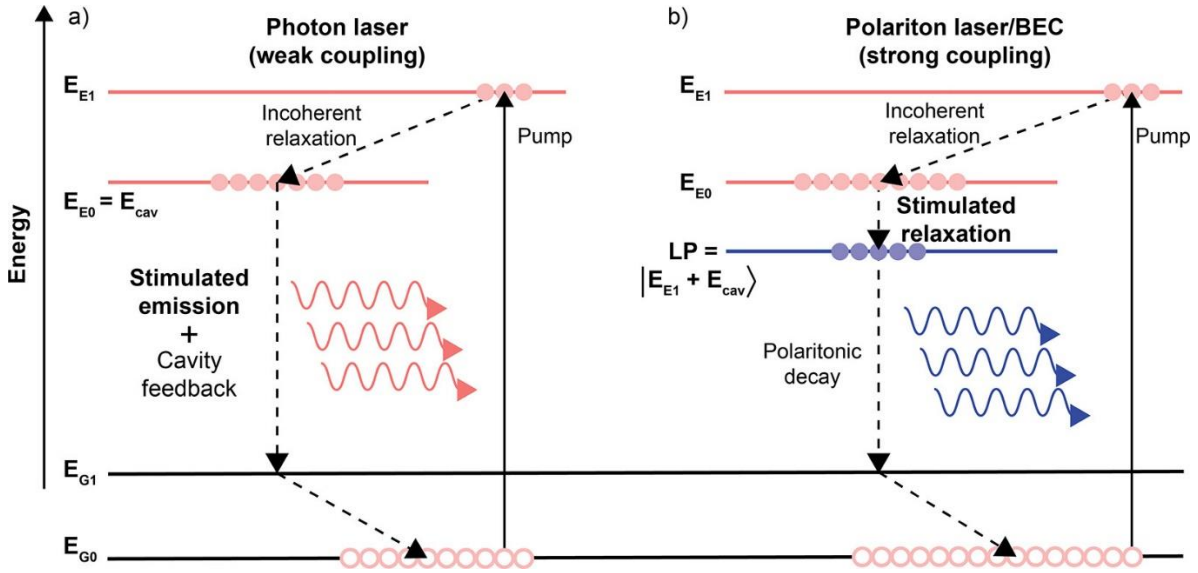

Figure 4.2. Working principle of regular photon laser (a) and a polariton laser (b) through relaxation processes. From [9] figure13, used under Commons CC-BY 4.0 licence.

Main difference between polariton laser and photon laser is where emission is coming as both can be achieved with electrical and light pumping.[28] Photon laser emits light through stimulated emission from the material while key working principle of the polariton laser is that emission comes from condensate concentrated into LP branch. Coherence now comes from the excitons that are coupled with cavity photons. Now there is no need for population inversion. Now the main objective is to obtain density high enough for condensation to happen. Downside of this is that it takes time for excitons to concentrate into LP from exciton reservoir. While this is happening polaritons have time to decay. Therefore, key point is to find right conditions where excitons can relax into LP, which builds up density at higher rate than they decay out of LP branch into ground state, which decreases the density.[9]

One of the key advantages of the polariton laser is their lower threshold compared to more conventional ones. This is because there is no need for population inversion. First polariton lasers worked by optical pumping but in 2013 first electrically pumped polariton lasing was observed in DBR microcavity containing four integrated InGaAs quantum wells. This has been seen as great leap towards realizing more practical applications of these new kinds of lasers. [28]

4.3 POLED

OLEDs are light emitting diodes that (in contrast to normal LED that use inorganic semiconductors) use instead organic semiconductors as emitters. Typically, OLED device consists of two electrodes and in between are multiple layers of organic materials sandwiched.

When in operation, electron holes are injected from anode and electrons are injected from cathode inside the organic semiconductor material. When inside the emitter material, holes and electrons recombine and excite the emitter material which in turn emits photon when it relaxes into ground state.[29]

As interest into OLEDs has increased in recent years for example in display industry and other applications, researchers have started to experiment with polaritons light emitting properties to see if they could be utilized as new kinds of OLED devices.

Polariton OLED or POLED structurally resembles typical OLED devices with exception of reflectors that sandwiches emitting material. Now when electrons and holes combine inside emitter material photons get trapped inside microcavity and strong coupling occurs inside, forming polaritons. Organic materials are again used due to need of forming Frenkel excitons that can survive at room temperature.

When experiments are performed with POLEDs usually instead of strong coupling regime, ultrastrong coupling regime is used. Ultrastrong coupling regime is reached when normalized coupling factor g is around 20% or above.[14]

It has also been discovered that wavelength of electroluminescence in POLED device can be changed by changing the Rabi splitting. This can be achieved through changing volume of the microcavity. This is one way to change the colour of the light emitted by device.[30]

Appeal of the POLEDs again is their much lower possible threshold for emission to occur when compared to conventional OLEDs. In 2018, POLED made from a coumarin fluorescent dye, was electrically pumped into USC regime as it achieved coupling strength of 37%. Fabricated device had luminance of 700 $\frac{\mathrm{cd}}{\mathrm{m}^2}$ in that region and was at that time speculated to have had highest values when compared to previous devices of that size.[31]

Main aims of the POLED research focus on making them brighter and at the same time keeping them more energy efficient. One of main goals is therefore to increase polariton flux so that more excitons relax into wider area of LP branch so called energy valley at the bottom. This requires different ways to utilize exciton reservoir more so that greater number of excitons relax into LP branch.

One of the recent discoveries have concerned different ways to convert triplet states from reservoir into singlet or polariton states. One study in 2021 was able to convert triplet state

straight into LP branch using triplet-triplet annihilation (TTA). This happened because TTA mechanism was changed from endothermic into exothermic reaction. Phenomena was temperature dependent as exciton-exciton TTA started to occur at higher temperatures. Other proposed way to make use of triplet states is through inversion of triplet state into more useful singlet state. Another experiment performed in 2019 with microcavity that used TADF material sandwiched between TPBi buffer and Ag mirrors was able to perform this. When microcavities with higher Rabi energies were used it was observed that energy of LP was much lower with all incident angles (figure 4.3), thus giving evidence of triplet to singlet inversion in the system.[31], [32], [33]

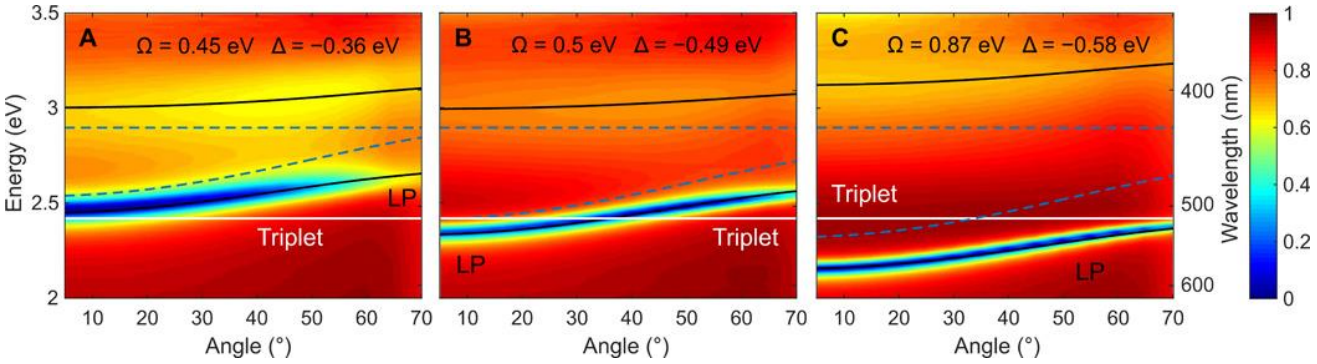

Figure 4.3. Angle resolved reflectivity from 3 different cavities. Only TE-polarized light is measured. Dashed lines are energies of cavity photon and exciton. Black lines are fitted dispersion curves for UP and LP branches. White line is the energy of triplet state. A. is microcavity with 64 nm of TPBi-3DPA3CN. B. with 81 nm of TPBi-3DPA3CN. C. 70 nm of only 3DPA3CN. Complete inversion can be seen in C. where energy of triplet state is higher in all incidence angles when compared to LP. From ref [33] figure 3, used under CC-BY 4.0 licence.

5 Conclusions

In conclusion, this thesis went through basic theory about what exciton-polaritons are and how they are formed. After that three applications under development were introduced. These were room temperature Bose-Einstein condensate, polariton laser and lastly POLED.

We started by introducing concept of exciton and what are the characteristics of different types of excitons such as Frenkel or Wannier-Mott excitons. One of the key differences were their binding energy which means that Frenkel excitons were more likely to form and survive in room temperature, making them ideal in many applications.

Next, we explained what optical cavity is and how they operate. Key concept of quality factor was explained and what it means for photons inside microcavity. This thesis only went through workings of Fabry-Perot cavities. Distributed Bragg reflector was also introduced and the fact that it has usually higher quality factor.

By combining microcavity and semiconductor material and pumping energy via pump laser or electrical pumping inside the cavity, interaction between photons and excitons starts. When energy of these interactions is lower than dampening energy inside and energy emitted out of cavity, the whole system is in what is called weak coupling regime. On the other hand, when energy of interaction gets larger, the system enters strong coupling regime and new eigenstates gets formed called upper and lower polaritons. These can be detected by using angle-resolved spectroscopy.

We then finally introduced theoretical model called Tavis-Cummings model to explain and interpret the emission graphs we get from angle-resolved spectroscopy. We also learned about tuning of the model and cavity as well.

Before going into applications, introduction to the kinematics of polaritons was introduced with very important concept of dark states or also known as exciton reservoir. We learned that emission mostly comes from lower polariton, and that exciton reservoir plays an important part in mechanics that govern polariton emission.

After theoretical parts, we went over 3 above mentioned applications. We discovered that exciton-polaritons can form room temperature Bose-Einstein condensate, which can be seen as coherent light emission from the lowest part of lower polariton branch. It is also able to form superfluid.

Using polariton BEC emission as a polariton laser was introduced and their benefits over conventional ones. We also discovered that decay rate from reservoir into lower polariton plays huge role in polariton lasing which still needs to be improved for realisation of everyday applications.

Last application discussed was polariton OLEDs. Differing from conventional ones with introduction of microcavity, POLEDs may be more energy efficient than conventional ones. Much more research into POLEDs needs to be done before they can overtake normal OLEDs in everyday use.

Polariton research has made huge leaps over couple of decades. They garner much interest in doing basic physics research and studying quantum mechanics and photochemistry. They look also promising for many kinds of applications as well. More research needs to be done to realize full potential of these interesting quasiparticles. Especially working of internal mechanics and how to utilize exciton reservoir to increase lifespan of polariton emission.

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