Correlated exciton dynamics in semiconductor nanostructures

by

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B.S. Chemistry, University of California Berkeley (2007)

Submitted to the Department of Chemistry in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in Chemistry

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2013

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Submitted to the Department of Chemistry
on May 10, 2013, in partial fulfillment of the
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Abstract

The absorption and dissipation of energy in semiconductor nanostructures are often determined by excited electron dynamics. In semiconductors, one fundamentally important electronic state is an exciton, an excited electron bound to a positively charged vacancy. Excitons can become correlated with other excitons, mutually influencing one another and exhibiting collective properties. The focus of this dissertation concerns the origins, effects, and control of correlated excitons in semiconductor nanostructures.

Correlated Coulomb interactions can occur between excitons, resulting in energy shifts and dephasing in each exciton. Two-dimensional Fourier-transform optical spectroscopy is a powerful tool to understand Coulomb correlations; the technique relates exciton dynamics during distinct time periods. However, the technique is still limited by weak spectral features. Using two-dimensional pulse shaping methods, waveforms of excitation fields were tailored to selectively amplify spectral features of correlated exciton states in gallium arsenide quantum wells. With the aid of theoretical models, 2D spectra of quantum wells revealed clear contributions of Coulomb correlations to the exciton dynamics. Time and power dependent properties of the 2D spectra indicate several mechanisms for exciton interactions that are neglected in commonly used theoretical models.

If a semiconductor material is fabricated within a microcavity, optical fields can be trapped around the semiconductor, strongly distorting properties of the semiconductor excitons and forming new quasi-particles called exciton-polaritons. Theoretical work has suggested exciton-polariton Coulomb correlation strengths can be reduced compared to that of excitons. Using two-dimensional Fourier-transform optical spectroscopy, control of Coulomb correlations was demonstrated by varying the cavity structure. The cavity fields were also shown to induce high-order correlated interactions among exciton-polaritons.

A macroscopic quantum degenerate system of exciton-polaritons can also become correlated, exhibiting long-range order typical of a Bose-Einstein condensate. However, unlike a Bose-Einstein condensate, exciton-polaritons are not typically in ther-
mal equilibrium. Using a sample with exciton-polariton lifetimes longer than previous samples, the macroscopic behavior of exciton-polaritons was investigated by imaging the exciton-polariton photoluminescence. Condensation depended significantly on spatially-varying potential energy surfaces. Using optically-induced harmonic potential barriers, thermal equilibrium among exciton-polaritons was achieved, with exciton-polaritons forming a Bose-Einstein distribution at densities above and below the condensation phase transition.

Thesis Supervisor: Keith A. Nelson
Title: Professor of Chemistry
Acknowledgments

Many people provided invaluable support throughout my time at MIT: mentors, colleagues, friends, and family. Without these people, the work presented here would not be possible.

My advisor Keith Nelson provided much more than scientific guidance; he was a constant source of enthusiasm and inspiration. I am very grateful that he has always supported my ideas and work.

Additional guidance came from other mentors in the group. Specifically, Kathy Stone, Duffy Turner, and Kenan Gundogdu taught me how to work in lab and their research inspired many of the ideas in this thesis.

Dylan Arias joined the 2D spectroscopy project at the same time as myself. From learning how to align optics to writing this thesis, his friendship enlivened even the most challenging moments in graduate school. Of course, the times we found reasons to celebrate were even better.

Yongbao Sun toiled in lab with me for the last two years. Chapter 8, in particular, would not be possible without his help. I am very grateful for his hard work, his questions, which pushed me to learn more, his ideas, and his company during those long days and nights in lab.

Several collaborators contributed directly to the research in this thesis with their expertise and advice. Professor Jeremy Baumberg and Gabriel Christmann at the University of Cambridge provided invaluable expertise in the initial exciton-polariton experiments described in Chapter 7. Professor David Snoke at the University of Pittsburgh acted almost as a second advisor for the research described in Chapter 8. Professor Snoke and his students, Bryan Nelsen and Gangqiang Liu, were extremely helpful during those experiments.

The entire Nelson group provided a collegial and fun environment to work in. Challenging experiments and late hours were made so much easier by smart colleagues and good friends.

A great community of friends surrounded me throughout my time at MIT; Dan,
who made the transition to MIT so much easier; Kara and Lemon, friends from year one; the Puerto Rico crew; Kevin, Scott, Nicole, and David; everyone who was always ready for the Muddy, a camping trip, or a spontaneous trip to karaoke; and the great scientists and friends that live in the basement of MIT.

I also need to thank my family: Mom, Dad, and my brother, Aki. Their support and encouragement have been essential during my time at MIT. I have had many fortunate opportunities in my life, which would not be possible without the sacrifices of my parents.

Finally, I need to thank Sharmini, who was there to celebrate my successes, listen to my frustrations, and provide encouragement when I needed it most. Although we have lived in different cities for the last six years, she has shaped my experiences at MIT more than anyone else. I am grateful for her love and support.
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Chapter 1

Introduction

1.1 Motivation and background

Nanomaterials have been used by humans for centuries. By dispersing gold or silver nanoparticles into molten glass, ancient glassmakers created stained glass that reflected red or yellow light[99]. In the last several decades, with the advent of techniques such as scanning tunneling microscopy[42], scientists and engineers have achieved much of the dream that Richard Feynman laid out in his seminal lecture “Plenty of Room at the Bottom”[45]: the properties of materials can be engineered atom by atom. Nanomaterials fabricated from semiconductor materials have attracted perhaps the most attention, especially towards goals of solving global energy challenges[59] and engineering technologies for next-generation computers[74].

Of fundamental importance to semiconductor nanomaterials is the exciton[46, 153], an electron that is excited into a high energy state but remains bound to the vacancy left behind in the valence band by the electron. Excitons are often the lowest energy excited state of a semiconductor material and play an important role in the properties of semiconductors; how energy is absorbed and dissipated by a semiconductor material is often largely determined by how an exciton absorbs or dissipates energy. In turn, properties of an exciton can be controlled through the engineering of the semiconductor nanostructure. For example, the confinement of exciton wavefunctions determines the emission spectrum in quantum dot light-emitting diodes[106, 72].
Excitons can be correlated with other excitons, mutually influencing each other so that the excitons are best described as a combined system rather than individual excitons. The correlations between excitons can originate from several sources and have profound effects on properties of semiconductor materials. Coulomb interactions between excitons can correlate the time evolution of excitons, modifying the energies and relaxation of the correlated excitons\[30\]. Excitons can also become correlated through the formation of a macroscopic quantum degenerate system, which is possible due to the bosonic nature of excitons, exhibiting properties typically associated with a Bose-Einstein condensate\[19, 68\]: long-range order and coherence over the entire system of degenerate excitons. In either case, by exploiting or even controlling how excitons correlate with each other, semiconductor nanomaterials can be engineered to control how energy is absorbed or evolves in the material.

One possible method to control the correlations between excitons is through optical fields, which can couple to the charges of excitons, driving the dynamics of the excitons in space and time. Under the right circumstances, excitons can be strongly influenced by optical fields such that the excitons are best described as new particles called exciton-polaritons\[53, 54, 47\]. One method to create exciton-polaritons is to trap optical fields around semiconductor materials using a microcavity\[156\], a cavity that is engineered to precisely control how the trapped optical fields interact with the semiconductor material.

This dissertation is focused on the origins, effects, and control of correlated excitons and exciton-polaritons in semiconductor nanostructures. There are three main types of correlations described in this work: Coulomb correlations between excitons, Coulomb correlations between exciton-polaritons, and macroscopic exciton-polariton correlations. In the remainder of this section, a qualitative overview is provided of the correlations and the challenges associated with understanding these correlations.

1.1.1 Correlated Coulomb Interactions between Excitons

Because an exciton is composed of a pair of positive and negative charges, excitons can interact with other excitons through Coulomb forces. The charges can repel and
attract one another, causing excitons to scatter with each other. However, the number of excitons and states in a typical semiconductor material cause the Coulomb interactions to become quite complex: interactions between two excitons, for example, are influenced by other excitons and carriers, causing the interaction between the two excitons to evolve in a complex manner[30]. This complex interaction between two excitons is called a four-particle correlation (or two-exciton correlation)[11]. Four-particle correlations can have very important effects on exciton nonlinear dynamics; the energies and relaxation times of an exciton can be strongly modified by the correlated interaction with another exciton. Two excitons of opposite spin, for example, can become correlated so that the two negative charges orbit around the two positive charges, analogous to the formation of a hydrogen molecule, lowering the combined energy of both excitons[83].

In the last decade, the understanding of multi-exciton correlations has been advanced by the development of two-dimensional Fourier-transform optical spectroscopy (2D FT OPT)[57], which can directly resolve coherences of multiple excitons. Using 2D FT OPT, correlated interactions between two excitons[132, 60], three excitons[140], and free carriers with excitons[88] have been directly resolved. Despite these advances, 2D FT OPT can still be limited by weak signal or overlapping spectral features, both of which can obscure the interpretation of spectra. In Chapter 3, methods to selectively amplify spectral features in 2D FT OPT are presented. It is shown that by coherently controlling the excited state dynamics in an exciton system, specific exciton and multiexciton spectral features can be enhanced in 2D FT OPT. The complexity of correlated Coulomb interactions is another major challenge. Major approximations in the theoretical descriptions of Coulomb correlations limit the sources for correlated interactions to include only coherent excitons[123] and excitons excited in the limit of perturbation theory[11]. Chapter 5 discusses two experiments using 2D FT OPT that indicated both of these approximations can be too limiting.
1.1.2 Correlated interactions between exciton-polaritons

Exciton-polaritons can be formed inside of semiconductor microcavities that trap optical fields around a semiconductor material. Trapped optical fields can generate exciton polarizations in the semiconductor material. In turn, the exciton polarizations can generate optical fields that remain trapped within the cavity and are reabsorbed by the semiconductor material. The rapid exchange of energy between the cavity field and the semiconductor material distorts the exciton polarization[65], splitting the resonance energy of the exciton into new energies, and causing the system to be better described as an exciton-polariton[53, 54, 47].

The trapped optical fields can also alter the correlated interactions between excitons. By distorting the exciton energies, the correlated motions of multiple excitons can also be modified. Theoretical work suggests that correlations can be significantly reduced by tuning the coupling between excitons and cavity fields which can reduce correlation-induced dephasing [80, 120]. Chapter 7 discusses a set of experiments that directly resolve exciton-polariton correlations using 2D FT-OPT. The experiments clearly indicate that a semiconductor microcavity can be used to tune the strength of correlated interactions. The experiments also clearly resolve correlations between three and four polaritons, a higher number of correlated particles than observed in semiconductor materials that are not embedded inside of a microcavity. The results indicate a new source for correlated interactions: trapped optical fields can cause polaritons to mutually influence one another.

1.1.3 Spontaneous macroscopic correlations

Under the right conditions, exciton-polaritons can spontaneously form a macroscopic quantum degenerate system in the ground polariton state[37]. The quantum degenerate polaritons exhibit many of the properties of a Bose-Einstein condensate including spontaneous long-range coherence and superfluid propagation[37, 62, 13, 7]. Because of the small effective mass of polaritons, reduced by about eight orders of magnitude compared to the mass of rubidium, room temperature Bose-Einstein condensation
is theoretically possible[19, 68, 32]. Semiconductor microcavities could also be integrated into solid-state devices; several experiments have demonstrated the use of polariton condensates as ultrafast switches[4] and transistors[14, 48].

Although quantum degenerate polaritons exhibit many of the properties of a Bose-Einstein condensate, there is significant controversy regarding whether polaritons truly qualify as a Bose-Einstein condensate[129, 26, 27, 38]. In particular, Bose-Einstein condensation is a phase transition driven by the thermodynamic properties of a system of bosons[43]. Exciton-polaritons, however, are often well insulated from phonon interactions, preventing polaritons from establishing thermal equilibrium[135].

Recently, new progress in sample fabrication has improved the lifetime of polaritons, by at least an order of magnitude, pushing polariton lifetimes into the realm of thermal equilibrium[100]. Chapter 8 discusses the thermodynamic properties of long lifetime polaritons and polariton condensates. The chapter describes how optically-induced harmonic barriers can manipulate the thermodynamic properties of polaritons, causing polaritons to be in thermal equilibrium throughout a condensation phase transition.

1.2 Outline of dissertation

The dissertation is organized as follows. In Chapter 2, 2D FT OPT is discussed including the theoretical background and the methods and instruments used. In Chapter 3, techniques are shown to selectively enhance spectral features in 2D spectra. In Chapter 4, the origins of many-body interactions are described using both microscopic and phenomenological theories. In Chapter 5, experiments focused on understanding many-body interactions in gallium arsenide quantum wells using 2D FT OPT are discussed. In Chapter 6, the physical origins of exciton-polariton states in semiconductor microcavities are described using both a semiclassical approximation and a full quantum framework. The chapter also describes the semiconductor microcavity samples used in the next two chapters. In Chapter 7, the Coulomb correlations between
exciton-polaritons, and the strong influence of the cavity field on the correlations, are discussed. In Chapter 8, the Bose-Einstein condensation of exciton-polaritons is discussed. The chapter presents experiments demonstrating how optical trapping of polaritons can control the thermodynamic properties of a polariton condensate.
Two-dimensional Fourier transform optical spectroscopy (2D FT OPT) is a type of coherent nonlinear spectroscopy that can provide unprecedented insight into the nonlinear electronic response of material. As with other types of coherent nonlinear spectroscopy, 2D FT OPT is based on the excitation of a material using coherent fields of light: microscopic dipoles in the material become excited by coherent fields, evolve in time, and eventually emit a signal field. The energies of the emitted light can be used to understand the excited states of the dipoles. In 2D FT OPT, not only are emission energies recorded, but the emission energies are correlated to an initial excitation energy providing clear experimental signatures of the nonlinear dynamics of the dipoles. 2D FT OPT is a direct extension of 2D FT infrared spectroscopy[102, 69], which was developed to study the nonlinear vibrational responses of materials. In turn, 2D FT infrared spectroscopy is an analog of 2D NMR spectroscopy[16], which can be used to study the nonlinear nuclear spin responses of materials.

2D FT OPT, and multidimensional spectroscopy in general, provide several advantages over one-dimensional spectroscopy: congested spectral features are spread over two dimensions, coupled states can be directly resolved as cross-peaks, inhomogeneous broadening can be separated from homogeneous broadening, and multiple-quantum coherences can be directly resolved[57]. Despite the advantages of mul-
tidimensional spectroscopy, 2D spectra are still plagued by many of the difficulties associated with one-dimensional spectra. In particular, spectral congestion and weak transition dipoles can still make the collection and analysis of 2D spectra difficult. One possible method to overcome these challenges is to use waveforms that can selectively enhance the signal for target peaks in 2D spectra, as demonstrated for 2D NMR[147].

In this chapter, 2D FT OPT is discussed. In the first section, the theoretical background for coherent nonlinear spectroscopy and Fourier-transform multidimensional spectroscopy are described. In the second section, the methods to achieve 2D FT OPT, using 2D pulse shaping, are described. The experimental methods described in this section are also relevant to the results in Chapters 5 and 7. Additional methods to selectively enhance peaks in 2D spectra are demonstrated in the next chapter.

2.1 Theoretical description of two-dimensional Fourier transform optical spectroscopy

2.1.1 Semiclassical description of coherent nonlinear spectroscopy

A theoretical description of coherent nonlinear spectroscopy is derived in this section. The purpose of the theoretical description is to understand how electric fields can induce a nonlinear response in a material of interest and how the nonlinear response can be detected in spectra. The interaction between electric fields with a material of interest is described semiclassically: electric fields are treated as classical electromagnetic waves and the material response to the electric fields is derived from the quantum microscopic description of the material. This approach has become widely used to describe nonlinear spectroscopy[97, 57, 31, 138], because the description can provide an intuitive framework for understanding nonlinear spectroscopy and still accurately describe common experimental conditions of nonlinear spectroscopy.

In coherent nonlinear spectroscopy, coherent electric fields propagate through a
material. The coherent fields excite dipoles in the material, such as those associated with vibrational modes or electronic excited states. The macroscopic collection of all dipoles excited by the coherent fields results in a polarization:

$$ P(r, t) = \sum_m \mu_m(t) \delta(r - r_m) $$

(2.1)

where $\mu_m(t)$ is the time-dependent dipole (i.e. charge displacement) at $r_m$ that is driven by the electric fields. $\mu_m(t)$ includes all charges that are displaced at $r_m$. The polarizations oscillate, generating additional electric fields as described by the wave equation:

$$ c^2 \frac{\partial^2}{\partial t^2} E(r, t) = 4\pi \frac{1}{c^2} \frac{\partial^2}{\partial t^2} P(r, t) $$

(2.2)

where $c$ is the speed of light, $E(r, t)$ is an electric field, and $P(r, t)$ is the polarization of the material. Note that although $E(r, t)$ and $P(r, t)$ are vectors, only one polarization component is considered in this chapter to simplify the mathematical description. The electric fields generated by $P(r, t)$ depend on the dipoles excited in the material and are often called signal fields because properties of the fields (e.g. spectral features) can be used to understand properties of the material. In order to solve Equation 2.2, $P(r, t)$ must be derived.

**Derivation of nonlinear polarization**

The macroscopic polarization, $P(r, t)$, can be derived from the microscopic response of the material to electric fields. Considering a material that is spatially homogeneous, Equation 2.1 is simplified so that the polarization is given by the dipole expectation value: $P(t) = \langle \mu(t) \rangle$. In order to find $\langle \mu(t) \rangle$, the state of the material needs to be found as a function of time. Using the density matrix formalism in the Schrodinger picture, the state of the material is given by the time-dependent density matrix, $\rho(t)$, and $\langle \mu(t) \rangle$ can be solved by taking the trace of the time-independent dipole matrix,
\( P(t) = < \mu(t) > \)
\[ = \text{Tr}[\mu \rho(t)] \]  \hspace{1cm} (2.3)

Of course, in order to solve Equation 2.3, \( \rho(t) \) must also be solved.

\( \rho(t) \) evolves in time because of the influence of a potential created by the electric fields, \( V(t) = \mu \cdot E(t) \). \( V(t) \) describes the action of the electric field, \( E(t) \), on dipole transitions in the material. The time dependence of \( \rho(t) \) can be solved using perturbation theory: the electric field and density matrix are expanded to different orders in the field amplitude. The total Hamiltonian of the material under the influence of \( V(t) \) is:

\[ \mathcal{H} = \mathcal{H}_0 + V(t) \]  \hspace{1cm} (2.4)

where \( \mathcal{H}_0 \) is the material Hamiltonian. The time evolution of the density matrix is given by the Liouville-Von Neumann equation:

\[ \frac{\partial \rho_I}{\partial t} = -\frac{i}{\hbar} [V_I(t), \rho_I(t)] \]  \hspace{1cm} (2.5)

where the potential and the density matrix have been transformed into the interaction picture, \( V_I(t) = U_0^\dagger V(t) U_0 \) and \( \rho_I(t) = U_0^\dagger \rho(t) U_0 \) with \( U_0 = \text{exp}(-i\mathcal{H}_0 t) \). Equation 2.5 can be solved by integrating both sides of the equation from an initial time point, \( t_0 \), to a time variable, \( t \):

\[ \rho_I(t) = \rho_I(t_0) - \frac{i}{\hbar} \int_{t_0}^{t} dt_1 [V_I(t_1), \rho_I(t_1)] \]  \hspace{1cm} (2.6)

\( \rho_I(t_0) \) is just the initial value of the density matrix. In a nonlinear spectroscopy experiment, usually \( \rho_I(t_0) \) is given by equilibrium conditions of the material. Equation 2.6 gives the density matrix in terms of the initial density matrix and a density matrix during a new time variable, \( t_1 \). By iteratively inserting Equation 2.6 into itself, \( \rho_I(t) \)
can be solved exactly using the following equation:

\[
\rho_f(t) = \rho_f(t_0) - \frac{i}{\hbar} \int_{t_0}^{t} dt_1 [V_f(t_1), \rho_f(t_0)] + \\
+ \left( -\frac{i}{\hbar} \right)^2 \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 [V_f(t_2), [V_f(t_1), \rho_f(t_0)]] + ... \\
+ \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} dt_n \int_{t_0}^{t_{n-1}} dt_{n-1} ... \int_{t_0}^{t_2} dt_1 [V_f(t_n), [V_f(t_{n-1}), ... [V_f(t_1), \rho_f(t_0)]]] \\
+ ...
\]  

(2.7)

Equation 2.7 gives the solution to \( \rho(t) \) as a sum of terms, where each term depends on the perturbing electric fields to different orders: the first term on the right hand side of Equation 2.7 does not depend at all on the electric fields, the second term has a first-order dependence on the electric fields, the third term has a second-order dependence, and so on. For fields that are not too strong, \( \rho(t) \) can be accurately solved by truncating Equation 2.7 up to a certain order determined by the strength of the electric fields that interact with the material.

Finally, \( P(t) \) can be solved up to a specific order in the electric field by inserting Equation 2.7 into Equation 2.3 and truncating the density matrix terms up to the desired order. The polarization that has an \( n \)-order dependence on the electric fields can be written as:

\[
P^{(n)}(t) = \int_{0}^{\infty} d\tau_n ... \int_{0}^{\infty} d\tau_1 R^{(n)}(\tau_1, \tau_2, ..., \tau_n) E(t - \tau_n - ... - \tau_1) ... E(t - \tau_n)  
\]  

(2.8)

\( R^{(n)} \) is the material response function and is just the nested commutator found in the terms on the right hand side of Equation 2.7 with the electric fields factorized out:

\[
R^{(n)}(\tau_1, \tau_2, ..., \tau_n) = \left(-\frac{i}{\hbar}\right)^n \theta(\tau_1)\theta(\tau_2) ... \theta(\tau_n) \\
Tr \{[...[\mu_f(\tau_n + ... + \tau_1), \mu_f(\tau_{n-1} + ... + \tau_1)], ..., \mu_f(t_0)] \rho(t_0)\} 
\]  

(2.9)
The new time variables, \( \tau_n \), are intervals defined by:

\[
\begin{align*}
    t_n &= t - \tau_n \\
    t_{n-1} &= t - \tau_{n-1} - \tau_n \\
    &\quad\vdots \\
    t_1 &= t - \tau_1 - \tau_2 - \ldots - \tau_n
\end{align*}
\]

(2.10)

A time ordering, \( t_1 \leq t_2 \leq \ldots \leq t_n \), has also been enforced. The new time variables, \( \tau_j \), and the enforced time ordering are used because a time ordering between multiple pulses of electric fields is used in most forms of time-resolved spectroscopy and Fourier-transform 2DS. It should be stressed that \( \tau_j \) are variables and not the time delays of the perturbing electric fields; in order to calculate Equation 2.8, the full n-order integral must be calculated from zero to infinity for every time delay of each pulse, \( T_j \), if the impulsive limit is not assumed. However, the new time variables, \( \tau_j \), and the enforced time ordering can be used to simplify \( P^{(n)} \) assuming that the perturbing fields are pulses of light that are much faster than the material response function, \( R^{(n)}(t) \). In this case, the perturbing fields can be approximated as delta functions at a specific time delay, \( E_j(t) = |E_j|\delta(t-T_j) \). By inserting the delta functions into Equation 2.8, it can be found that the nonlinear polarization is directly proportional to the response function of the material, where the time variables, \( \tau_j \), now represent the time interval between pulses:

\[
P^{(n)}_{\text{impulse}}(t) = R^{(n)}(\tau_1, \tau_2, \ldots, \tau_{n-1}, t)|E_1||E_2|\ldots|E_n|
\]

(2.11)

For any given set of pulse delays, the values of \( \tau_j \) are just constants. Technically, a different variable should be used to represent \( \tau_j \) as a time variable in Equation 2.8 and a parameter in Equation 2.11. However, in many time-domain coherent spectroscopy experiments, a set of perturbing fields are often delayed, in which case the values of \( \tau_j \) in Equation 2.11 are varied. By convention, the time delays between pulses are represented by \( \tau_j \) in Equation 2.11.

The nested commutator in Equation 2.9 is a sum of \( 2^n \) terms, with each term
representing the dipole operator acting on the density matrix in different sequences. Furthermore, the action of each dipole operator can be sequenced in an intuitive manner to represent the interaction of a field on the bra or ket side of the density matrix. For example, one of the terms of $R^{(2)}$ is given by $R_a^{(2)}$:

$$R_a^{(2)} = \text{Tr} \left[ \mu_I(\tau_1 + \tau_2)\mu_I(0)\rho(t_0) \right]$$
$$= \text{Tr} \left[ U_0^\dagger(\tau_1 + \tau_2)\mu U_0(\tau_1 + \tau_2)U_0^\dagger(\tau_1)\mu U_0(\tau_1)\rho(t_0) \right]$$
$$= \text{Tr} \left[ U_0^\dagger(\tau_1)U_0^\dagger(\tau_2)\mu U_0(\tau_2)U_0(\tau_1)U_0^\dagger(\tau_1)\mu U_0(\tau_1)\rho(t_0) \right]$$
$$= \text{Tr} \left[ U_0^\dagger(\tau_1)U_0^\dagger(\tau_2)\mu U_0(\tau_2)U_0(\tau_1)U_0^\dagger(\tau_1)U_0^\dagger(\tau_2) \right]$$
$$= \text{Tr} \left[ \mu U_0(\tau_2)\mu U_0(\tau_1)\mu \rho(t_0)U_0^\dagger(\tau_1)U_0^\dagger(\tau_2) \right]$$
$$= \text{Tr} \left[ \mu U_0(\tau_2)\mu \left( U_0(\tau_1)\mu \rho(t_0)U_0^\dagger(\tau_1) \right) U_0^\dagger(\tau_2) \right]$$

The parenthesis in the last step have been added for clarity of the proper sequence of action on $\rho(t_0)$. The density matrix starts in an initial state, $\rho(t_0)$, is multiplied by the dipole matrix on its ket side, evolves in time during $\tau_1$ according to the evolution operator, is multiplied by the dipole matrix on its ket side again, and evolves in time during $\tau_2$. In a similar fashion, a second term of $R^{(2)}$ can be derived, $R_b^{(2)}$, where the density matrix starts in an initial state, $\rho(t_0)$, is multiplied by the dipole matrix on its bra side, evolves in time during $\tau_1$, is multiplied by the dipole matrix on its ket side, and evolves in time during $\tau_2$. The last two terms that contribute to $R^{(2)}$ represent interactions of the dipole matrix twice on the bra side, which is just the conjugate of $R_a^{(2)}$, and an interaction of the dipole matrix first on the ket side followed by the bra side, the conjugate of $R_b^{(2)}$. Similarly, the third-order response function $R^{(3)}$ can be decomposed into four terms $R_{a}^{(3)}$-$R_{d}^{(3)}$ and the four matching conjugate terms, with each term representing different orderings of the dipole matrix acting on the density matrix and evolving during $\tau_1$, $\tau_2$, and $\tau_3$. Typically, the evolution of a density matrix element during the time delay $\tau_j$ is given by $\exp(-i\omega_{ab}\tau_j - \Gamma_{ab}\tau_j)$, where $a$ and $b$ are the elements of the density matrix, $|a><b|$, $\omega_{ab} = \omega_a - \omega_b$, and $\Gamma_{ab}$ is the dephasing time of the $|a><b|$ coherence if $a \neq b$ or the relaxation rate for the $a$ state if $a = b$. 

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Diagrammatic perturbation theory

The different contributions to $R^{(n)}$ can be represented in Feynman diagrams, similar to those used to represent many-body interactions. The eight contributions to the third-order response, $R_a^{(3)} - R_d^{(3)}$ and $R_a^{(3)*} - R_d^{(3)*}$, are given in Figure 2-1. The time evolution of the density matrix is given by the solid vertical lines. The density matrix element at the bottom of each diagram represents all initially occupied states $|a><a|$. The action of each dipole matrix on the density matrix is given by arrows on the right and left of the diagram, representing multiplication of the dipole matrix on the bra and ket side of the density matrix. After each arrow, another density matrix element is written representing all the nonzero density matrix elements after the action of that dipole matrix. The density matrix evolves in time between the dashed lines according to the evolution operator of the system. Finally, the wavy arrows represent the emission that is given off by the polarization due to the specific response function represented by the diagram.

The Feynman diagrams in Figure 2-1 are written for a generic material with single excitation states, $x_j$, that have nonzero transition moments to the ground state and double-excitation states, $b_j$, that are dipole coupled to the single excitation states. The selection rules that determine the possible transitions from the ground state, $g$, to any of the $x_j$ states and from the $x_j$ states to the $b_j$ states are given by the dipole matrix $\mu$. The labels X and B in the Feynman diagrams represent any possible state that could be excited as determined by $\mu$. By convention, only the Feynman diagrams that emit from the left side of the diagram, giving a signal field of positive oscillation frequency, are shown. Similar Feynman diagrams that emit from the right side of the diagram, giving a signal field of negative oscillation frequency, can also be drawn.

Phase matching considerations

The signal fields can be found by inserting Equation 2.8 into Equation 2.2 and solving for the electric field. For a thin sample, the electric fields emitted from the sample,
Figure 2-1: (a) Energy levels of generic material with a single ground state, $g$, a set of single excitation states, $x_j$, and a set of double excitation states, $b_j$. (b) Feynman diagrams representing different terms in the third-order response of the generic material given in (a). $X$ and $B$ represent any of the single or double excitation states, respectively. $X'$ can also represent any of the single excitation states and may be different from $X$. Only Feynman diagrams that emit from the left side of the diagram are shown, by convention. No $R1^*$ diagrams emit from the left side. The diagrams are labeled as rephasing (R), nonrephasing (NR), and two-quantum (2Q), corresponding to the types to third-order 2D scans discussed in the text.
\( E_{\text{sig}}(t) \), can be found to be:

\[
E_{\text{sig}}(t) = i l P(t) \text{sinc} \left( \frac{\Delta kl}{2} \right) e^{i\Delta kl/2}
\]  

(2.13)

where \( \Delta k \) is the difference in wave vector between \( E_{\text{sig}}(t) \) and \( P(t) \). So far, the wave vector dependence of the fields and polarization have been neglected and suppressed in the notation. However, each excitation field has a well defined wave vector, \( k \). The dependence of the sinc function on \( \Delta k \) means that the magnitude of \( E_{\text{sig}}(t) \) decays as its wave vector deviates from \( k_{\text{sig}} \), given by \( k_{\text{sig}} = \sum_{j=1}^{n} k_j \), where \( k_j \) are the wave vectors of the \( n \) excitation fields in Equation 2.8. As a result, different orders of \( P^{(n)}(t) \) can be isolated by isolating the signal field corresponding to a specific wave vector direction. If \( \Delta k = 0 \), the signal field is proportional to the polarization, with a phase shift of \( \pi/2 \).

Phase matching and time ordering can be used to selectively excite different contributions to the nonlinear response function. As can be seen by the Feynman diagrams in Figure 2-1, the multiplication of the dipole matrix on different sides of the density matrix can result in the excitation of coherences that oscillate at frequencies of opposite sign. By convention, a coherence written as \( |g><X| \) oscillates at a negative oscillation frequency, given by a phase factor \( \exp[i(\omega_X - \omega_g)t] \). An electric field can be written as a complex sum of a component with positive frequency and its complex conjugate:

\[
E(r, t) = E_0(t)\exp[-i(\omega - \omega_0)t - ik \cdot R] + E_0^*(t)\exp[i(\omega - \omega_0)t + ik \cdot R].
\]

By inserting this decomposition of the field into the equation for the nonlinear polarization, Equation 2.8, it can be seen that the nonconjugate (conjugate) part of the electric field is needed to induce absorption (stimulate emission) on the ket side of the Feynman diagrams. The nonconjugate (conjugate) part of the electric field is needed to stimulate emission (induce absorption) on the bra side of the Feynman diagrams. Therefore, by choosing a phase matching condition that depends on the positive or negative wave vector of each field, different contributions to the response function can be excited in Equation 2.8. For example, considering a third-order polarization \( P^{(3)} \) in the direction \( k_{\text{sig}} = k_a + k_b - k_c \), diagrams \( R1, R4, \) and \( R2^* \) can
contribute to the nonlinear polarization if the time ordering of the pulses is such that a nonconjugate field at \( \mathbf{k}_a \) or \( \mathbf{k}_b \) comes first, followed by the conjugate field at \( \mathbf{k}_c \), and the last nonconjugate field arrives at the material last. By utilizing both the phase matching condition of \( E_{\text{sig}} \) and the time ordering of the pulses, specific Feynman diagrams and the excited-state dynamics they represent can be studied using nonlinear spectroscopy.

**Fifth and seventh order spectroscopy**

In addition to third-order experiments, higher order nonlinear polarizations can be excited by considering a higher number of field interactions. Due to the larger number of field interactions, higher-order polarization are often excited in the self-diffraction geometry: \( P^{(n)} \) generates \( E_{\text{sig}} \) in a direction \( \mathbf{k}_{\text{sig}} = (n - m)\mathbf{k}_a - m\mathbf{k}_b \) after \( n \)-\( m \) interactions with an electric field at \( \mathbf{k}_a \) and \( m \) interactions with an electric field at \( \mathbf{k}_b \). The reduced number of distinct wave vectors simplifies the experiment but requires all nonconjugate field interactions to occur simultaneously and all conjugate field interactions to occur simultaneously. The Feynman diagrams for fifth-order and seventh-order 2D spectra in the self-diffraction geometry are shown in Figures 2-2 and Figure 2-3.

**2.1.2 Fourier-transform multidimensional spectroscopy**

In Fourier transform two-dimensional spectroscopy (FT 2DS), \( P^{(n)} \) is measured as a function of two time intervals. Typically, \( P^{(n)} \) is measured as a function of the emission time, \( t \), and one of the delay times between pulses, \( \tau_j \), in Equation 2.8. In this case, a set of \( M \) field interactions are used to excite coherences in the sample before a delay time, \( \tau_{\text{scan}} \). After \( \tau_{\text{scan}} \), the remaining electric fields needed to generate \( P^{(n)} \) are sent to the sample, causing the emission of \( E_{\text{sig}} \) during \( t \). By detecting \( E_{\text{sig}} \) in a spectrometer overlapped with a reference pulse, the full complex value of \( E_{\text{sig}} \) can be spectrally resolved. During \( \tau_{\text{scan}} \), the coherences in the material oscillate at resonance frequencies set by the response function and time propagator of the material. The
Figure 2-2: (a) Energy levels of generic material, identical to Figure 2-1a except with a set of triple excitation states, $t_j$. (b) Feynman diagrams representing different terms in the fifth-order response of the generic material given in (a). $X$, $B$, and $T$ represent any of the single, double, and triple excitation states, respectively. $X'$ can also represent any of the single excitation states and may be different from $X$. The diagrams do not represent all terms in the fifth-order response function but represent only the terms that are relevant for the self-diffraction geometry. The diagrams are labeled as rephasing (R) or three-quantum (3Q).
Figure 2-3: (a) Energy levels of generic material, identical to Figure 2-2a except with a set of quadruple excitation states, $q_j$. (b) Feynman diagrams representing different terms in the fifth-order response of the generic material given in (a). X, B, T, and Q represent any of the single, double, triple, and quadruple excitation states, respectively. The diagrams do not represent all terms in the seventh-order response function but only the terms that are relevant for the self-diffraction geometry. The diagrams are labeled as rephasing (R) or four-quantum (4Q).
oscillations of the density matrix result in phase shifts of $P^{(n)}$ which are measured in $E_{\text{sig}}$. By scanning $\tau_{\text{scan}}$ over a range of time delays, the spectrum of $E_{\text{sig}}$ can be measured as a function of $\tau_{\text{scan}}$. Fourier transformation of the signal along the $\tau_{\text{scan}}$ axis gives a full 2D spectrum, so that the full complex value of $E_{\text{sig}}$ is measured as a function of coherence frequencies during $\tau_{\text{scan}}$ and coherence frequencies during $t$.

Types of 2D spectra

2D spectra are categorized according to different types of Feynman diagrams that contribute to them. As discussed in the previous subsection, which Feynman diagrams contribute to the nonlinear signal depends on the phase matching conditions and time-ordering of pulses. Generally, 2D spectra can be categorized into three types of spectra: rephasing, nonrephasing, and multiple-quantum 2D spectra (also called S1, S2, and S3 2D spectra, respectively). Rephasing spectra correspond to the excitation of coherences with oscillation frequencies of opposite signs during $\tau_{\text{scan}}$ and $t$. For a third-order experiment with $\mathbf{k}_{\text{sig}} = \mathbf{k}_a + \mathbf{k}_b - \mathbf{k}_c$, a rephasing scan corresponds to $\tau_{\text{scan}} = \tau_1$, and $\mathbf{k}_c$ arrives first. The diagrams labeled as R in Figure 2-1b represent diagrams that contribute to a third-order 2D rephasing spectrum. Nonrephasing spectra correspond to the excitation of coherences with the same sign during $\tau_{\text{scan}}$ and $t$. In a third-order experiment, a nonrephasing scan corresponds to $\tau_{\text{scan}} = \tau_1$, and $\mathbf{k}_a$ or $\mathbf{k}_b$ arrives first. The diagrams labeled as NR in Figure 2-1b represent diagrams that contribute to a third-order 2D nonrephasing spectrum. Finally, multiple quantum scans correspond to excitation with all nonconjugate fields first, exciting a coherence between a multiple-quantum state and the ground state during $\tau_{\text{scan}}$. In a third-order experiment, $\tau_{\text{scan}} = \tau_2$ and $\mathbf{k}_a$ and $\mathbf{k}_b$ arrive before $\mathbf{k}_c$. The diagrams labeled as 2Q in Figure 2-1b represent diagrams that contribute to a third-order 2D two-quantum spectrum. The Feynman diagrams are also marked in Figures 2-2 and 2-3 according to the rephasing and multiple-quantum labels.

Because the real and imaginary parts of $E_{\text{sig}}$ are detected, the complex material response can be extracted from 2D spectra. However, the real and imaginary parts of $E_{\text{sig}}$ are actually a mixture of the real and imaginary parts of the response function.
A phase twist originates from a discontinuity caused by acquiring 2D spectra in the rephasing, nonrephasing, and multiple-quantum pulse sequences since the signal is collected by varying $\tau_{\text{scan}}$ from $\tau_{\text{scan}} = 0$ to $\infty$ instead of $\tau_{\text{scan}} = -\infty$ to $\infty$. Because $P(n)$ is a convolution of the electric fields and the material response, as given by Equation 2.8, the discontinuity results in mixing of the real and imaginary parts of the response function upon Fourier transformation of $E_{\text{sig}}[57]$. The real and imaginary parts of the response function can be separated by adding the 2D rephasing and nonrephasing spectra, equivalent to acquiring the 2D spectra from $\tau_{\text{scan}} = -\infty$ to $\infty$, resulting in 2D spectra that are called 2D correlation spectra. The real and imaginary parts of 2D rephasing, nonrephasing, and correlation spectra are shown in Figure 2-4.

As shown in the figure, the real and imaginary parts of the 2D correlation spectra are usually absorptive and dispersive, respectively. However, for materials without the typical response function (of the form $\exp(i\omega T - \Gamma \tau)$ for a single time period), the real and imaginary parts may not correspond to absorptive and dispersive lineshapes.

In addition to scanning the time delay that determines the type of 2D spectrum obtained, $\tau_{\text{scan}}$, time delays between other field interactions may yield insight into material properties. For example, after the first two field interactions in a third order rephasing scan, the excitations in the density matrix of the material are given by population terms and superpositions of single excited states, as can be seen in the Feynman diagrams in Figure 2-1b. By delaying the time between the second and third fields, the dynamics of material during this population time can be resolved. A similar population time can be scanned for nonrephasing spectra after the first two interactions, as long as the first two interactions are given by fields in the nonconjugate and conjugate directions. Typically, both a 2D rephasing and nonrephasing spectrum are obtained for different population times and added together to obtain a 2D correlation spectrum as a function of population wait times. Additionally, the time between the first two excitation fields in a third-order 2D two-quantum scan can also be delayed. In this case, the excitations in the density matrix of the material are given by single-quantum coherences. By scanning the time period between the first and second field interactions, the oscillation frequencies in all three time periods of a
Figure 2-4: Real (a-c) and imaginary (d-f) parts of a third-order 2D rephasing (a,d), nonrephasing (b,e), and correlation (c,f) of a single excited state. The real and imaginary parts of the correlation spectra show the usual absorptive and dispersive lineshapes. The diagonal line represents excitation and emission of the same energy. The colorbar in (c) and (f) applies for all spectra in the top row and all spectra in the bottom row, respectively.
Figure 2-5: 2D rephasing spectra showing two excited states that are coupled (a) and uncoupled (b). The magnitude of the signal is shown. The diagonal line represents excitation and emission of the same energy. All peaks in both figures are represented by Feynman diagrams R2 and R3 in Figure 2-1b, with $X=X'$ for the diagonal peaks and $X\neq X'$ for the off-diagonal peaks. The integrated four-wave mixing spectra are shown for both (a) and (b) below the 2D spectra, showing nearly identical one-dimensional spectra. The colorbar in (b) gives the intensity of the signal for both 2D spectra.

two-quantum scan can be resolved[141].

Advantages of FT 2DS

There are several crucial capabilities of FT 2DS. First, coupling between states can be immediately revealed by cross-peaks in rephasing and nonrephasing spectra, as shown in Figure 2-5. One common coupling mechanism between excited states is a common ground state. In this case the two ground-excited state transitions are coupled since each depletes (or for higher-order interactions with the light fields, replenishes) the ground state that is needed for the other transition. Other coupling mechanisms can also create cross-peaks in 2D spectra such as many-body interactions between excited states, as discussed in Chapters 4 and 5.
Figure 2-6: 2D rephasing spectra of a single excited state that is broadened mostly by inhomogeneous dephasing (a) and by homogeneous dephasing (b). The integrated one-dimensional spectra, shown below the 2D spectra, show similar linewidths. The colorbar in (b) gives the intensity of the signal for both 2D spectra.

Another capability of FT 2DS is the separation of inhomogeneous and homogeneous broadening in 2D rephasing spectra. An inhomogeneous distribution of resonance frequencies causes the total nonlinear polarization emitted from a material to dephase during $\tau_{\text{scan}}$. During a rephasing scan, however, the response function oscillates with frequencies of opposite sign during $t$ from the frequencies during $\tau_{\text{scan}}$ so that the inhomogeneous dephasing is reversed when $t = \tau_{\text{scan}}$. In the frequency domain, the rephasing of the inhomogeneous frequencies results in the separation of inhomogeneous and homogeneous broadening into the diagonal and antidiagonal linewidths of a peak, although the two types of broadening are not completely separated[126]. Simulations of the inhomogeneously and homogeneously broadened 2D spectra are shown in Figure 2-6. The inhomogeneously broadened spectrum is similar to the spectrum in Figure 2-5b with additional peaks centered at all the intermediate frequencies between the two shown.

FT 2DS can also be used to directly resolve multiple-quantum coherences. Be-
Figure 2-7: A two-quantum coherence is directly resolved in a 2D two-quantum spectrum. The diagonal line represents excitation at twice the energy as the emission energy. The peak represents a double excitation state that is at an energy slightly less than twice the emission energy. The peak is given by the R1 Feynman diagram labeled as 2Q.

cause the excitation and emission of multiple-quantum coherences require multiple fields, the signals from multiple-quantum coherences are very difficult to observe in one-dimensional spectra. However, by measuring $E_{\text{sig}}$ as a function of the multiple-quantum coherence time, the frequencies, dephasing times, phases, and relative amplitudes of multiple-quantum coherences are all directly resolved during $\tau_{\text{scan}}$. A simulated multiple-quantum 2D spectrum is shown in Figure 2-7.

Finally, as already mentioned, the real and imaginary parts of a material response function can be characterized using the real and imaginary parts of $E_{\text{sig}}$. Typically, the real and imaginary parts of a peak in a 2D correlation spectrum show absorptive and dispersive lineshapes, corresponding to the response function terms that represent the dephasing and resonance frequency of the peak, respectively, as shown in Figure 2-4. However, as discussed extensively in Chapter 4 and 5, the phase of the material response is very sensitive to many-body interactions.

2.1.3 Optical Bloch equations

A useful method to model multidimensional spectra is based on the optical Bloch equations (OBE)[3]. The OBE are differential equations that describe the time-
dependent evolution of the density matrix elements of a material that are excited by optical fields, which can be used to solve for the nonlinear polarization through Equation 2.3. Of course, the nonlinear polarization can be solved as outlined in Section 2.1.1 by solving the nth order integral in Equation 2.8. However, as derived in Chapter 4, the OBE can be easily modified to incorporate phenomenological terms that represent many-body interactions in semiconductor materials. In this section, OBE are derived that give the third-order polarization. The OBE are also used in the last section of this chapter to describe the effects of arbitrarily shaped waveforms on 2D spectra.

The OBE can be derived starting with an arbitrary n-level Hamiltonian. Off-diagonal elements of the Hamiltonian can be used to account for one-photon dipole-allowed transitions between different states. In this section, the OBE are solved for a three-level system representing a ground state (g), a single excited state (X), and a double excited state (B), starting with a three-level Hamiltonian:

\[ H = -i \begin{bmatrix} 0 & \Omega_{Xg}(t) & 0 \\ \Omega_{Xg}^*(t) - i\gamma_{Xg} & \omega_{Xg} - i\Gamma_X & \Omega_{BX}(t) - i\gamma_{BX} \\ 0 & \Omega_{BX}^*(t) - i\gamma_{BX} & \omega_{Bg} - i\Gamma_B \end{bmatrix} \] (2.14)

where \( \omega_{ab} \) and \( \gamma_{ab} \) represent the frequency and dephasing rate between the a and b states and \( \Gamma_a \) is the lifetime of the a state. \( \Omega_{ab}(t) \) represents the electric field interaction between the a and b states and is given by \( \Omega_{ab}(t) = \mu_{ab} \cdot E(t)e^{i\mathbf{k}\mathbf{R}} \), where \( \mu_{ab} \) is the dipole transition between the a and b states. An electric field can excite a transition from g \( \rightarrow \) X and X \( \rightarrow \) B.

The 3 x 3 elements of the density matrix, \( \rho \), can be solved by inserting Equation (2.14) into the Liouville equation:

\[ \frac{d}{dt}\rho = -[\rho, H] \] (2.15)

Equation (2.15) gives a differential equation for each density matrix element, \( \rho_{ab} = |a \rangle \langle b| \), in terms of population elements, \( \rho_{ab} = n_a \) for \( a = b \), and coherence elements,
\( \rho_{ab} = p_{ab} \) for \( a \neq b \):

\[
\frac{d}{dt} n_a = -\Gamma_a n_a + i \left[ (p_{a,a-1} - p_{a+1,a}) \Omega(t) - (p_{a-1,a} + p_{a,a+1}) \Omega^*(t) \right] \quad (2.16)
\]

and

\[
\frac{d}{dt} p_{ab} = -\gamma_{ab} + i \left[ \omega_{ab} p_{ab} + (n_a - n_b + p_{a,b-1} - p_{a+1,b}) \Omega(t) + (-n_b + n_a - p_{a-1,b} + p_{a,b+1}) \Omega^*(t) \right] \quad (2.17)
\]

where \( a \pm 1 \) represents the state that is one transition above or below the \( a \) state, if such a state exists (e.g. \( p_{g+1} = p_X \) but \( p_{g-1} = 0 \)).

In order to solve for the third-order signal, the wavevector dependence of the density matrix terms must be included. This is accomplished by the spatial Fourier expansion [91] of \( n_a \) and \( p_{ab} \). To reduce the number of equations, the self-diffraction geometry is considered, with signal given in the \( 2k_a - k_b \) direction. This simplifies the calculations and is valid as long as the two nonconjugate fields are identical in the experiment. Furthermore, the algebra is simplified if the two beams are incident to the sample with wavevectors \( K + k \) and \( K - k \) so that the excitation fields can be written as \( E_-(t)e^{i(K-k)R} \) and \( E_+(t)e^{i(K+k)R} \). Then the density matrix elements in Equations (2.16) and (2.17) can be expanded in terms of the wavevector \( k \):

\[
n_a = \sum_{m=-M}^{M} n_{a,m} e^{i m k R} \quad (2.18)
\]

and

\[
p_{ab} = \sum_{m=-M}^{M} p_{ab,m} e^{i (b-a) K + m k R} \quad (2.19)
\]

For third-order spectroscopy, the signal depends on two interactions with the field along \( K + k \) and one interaction with the conjugate of the field along \( K - k \) so that the signal will be along the \( K + 3k \) direction. Therefore, to solve for \( \rho^{(3)} \), the \( p_{ab} \) and \( n_a \) terms in Equations (2.18) and (2.19) need to be solved up to \( M = 3 \).

The spatially expanded density matrix terms, Equations (2.18) and (2.19), and
the spatially expanded electric fields are inserted into Equations (2.16) and (2.17), giving coupled differential equations:

\[
\frac{d}{dt} p_{Xg}^{(3)} = \left[ -\gamma_{Xg} + i\omega_{Xg} \right] p_{Xg}^{(3)} + i\mu \cdot [E_{-}(t)p_{Bg}^{(2)} + E_{+}(t)(n_{g}^{(2)} - n_{X}^{(2)})] \tag{2.20}
\]

\[
\frac{d}{dt} p_{BX}^{(3)} = \left[ -\gamma_{BX} + i(\omega_{B} - \omega_{X}) \right] p_{BX}^{(3)} + i\mu \cdot [-E_{-}(t)p_{BX}^{(2)} + E_{+}(t)n_{X}^{(2)}] \tag{2.21}
\]

\[
\frac{d}{dt} n_{g}^{(2)} = -\Gamma_{g}n_{g}^{(2)} + i\mu \cdot [E_{-}^{*}(t)p_{Xg}^{(1)} - E_{+}(t)p_{Xg}^{(1)*}] \tag{2.22}
\]

\[
\frac{d}{dt} n_{X}^{(2)} = -\Gamma_{g}n_{X}^{(2)} + i\mu \cdot [-E_{-}^{*}(t)p_{Xg}^{(1)} + E_{+}(t)p_{Xg}^{(1)*}] \tag{2.23}
\]

\[
\frac{d}{dt} p_{Bg}^{(2)} = \left[ -\gamma_{Bg} + i\omega_{B} \right] p_{Bg}^{(2)} + i\mu \cdot E_{+}(t)p_{Xg}^{(1)} \tag{2.24}
\]

\[
\frac{d}{dt} p_{Xg}^{(1)} = \left[ -\gamma_{Xg} + i\omega_{Xg} \right] p_{Xg}^{(1)} + i\mu \cdot E_{+}(t)n_{g}^{(0)} \tag{2.25}
\]

where \( n_{g}^{(0)} \), the initial population in the ground state, is set equal to one and the superscript value refers to the order \( M \) in which each of these terms depends on \( k \). By solving Equations (2.20)-(2.25), the third-order signal can be calculated for arbitrarily defined excitation fields. As given by Equation 2.3, the third-order polarization is found from the third order terms, \( p_{Xg}^{(3)} \) and \( p_{BX}^{(3)} \), by multiplying the two terms by the dipole matrix elements connecting the \( X \rightarrow g \) states and connecting the \( B \rightarrow X \) states, respectively, and summing the two signals. In the case of a two-quantum scan, Equations (2.20)-(2.25) are solved as a function of scan time between \( E(K + k) \) and \( E(K - k) \), with \( E(K + k) \) arriving first. Using the simplified two-beam geometry of this derivation, nonrephasing signals cannot be calculated.

2.2 Pulse-shaping based multidimensional spectroscopy

Multidimensional spectroscopy can be used to study different types of material excitations depending on the frequencies of the electric fields used to excite the material. There are technical challenges for obtaining 2D spectra using fields in all the different frequency regimes. The main technical challenge of optical multidimensional
spectroscopy, 2D FT OPT, is the ability to delay the timing of optical pulses while still maintaining phase stability between all fields. The conventional method to delay pulses, by sending different optical beams through different path lengths using delay stages, requires active stabilization of the phase shifts caused by jitter of different optics [22, 33]. Active phase stabilization was first demonstrated with 2D rephasing and nonrephasing spectra, since the phase stability requirements between the second and third fields are relaxed in rephasing and nonrephasing scans compared to two-quantum scans. Alternatively, pulse shaping methods to delay pulses, using spatial light modulators instead of delay stages, do not require active phase stabilization because all optical beams travel the same path and jitter in any optic imparts the same phase shift in all beams. The first demonstration of pulse shaping based 2D FT OPT used only a single optical beam, creating multiple pulses of light in the single beam [137]. However, such an approach suffers from greater noise, because the signal is not collected in a background free direction, and from the limitations of the spatial light modulator to shape a single pulse into multiple pulses.

For the work in this dissertation, 2D FT OPT was accomplished using a pulse shaping based setup, as previously detailed [149, 50, 132, 142]. The setup permits the generation of multiple optical beams from a single input beam, with a beam geometry that is easily reconfigurable. The setup also provides control of the temporal waveforms of the pulses in each beam, while maintaining full phase stability between all the beams. A schematic illustration of the essential components of the setup is shown in Figure 2-8, which shows four main components: an oscillator, a beam shaper, a pulse shaper, and a spectrometer. This setup was used to collect the 2D spectra that will be reported in Chapters 5 and 7 and in the next section of this chapter. Each of the components in Figure 2-8 will be discussed in this section. The procedure to process the raw signal acquired from the setup into 2D spectra will also be discussed.
Figure 2-8: A schematic illustration of the pulse shaping based setup used in the experiments. The output from an oscillator, which generated ultrafast near-infrared pulses, was sent to a beam shaper that generated multiple beams in a reconfigurable geometry. All the excitation beams were sent to the pulse shaper which shaped the temporal waveform of the pulses in each beam. The beams were focused onto a sample, generating signal that was overlapped with a reference beam and sent to the spectrometer.
Oscillator

The Ti:Sapphire oscillator generated pulses of near infrared optical fields at a repetition rate of 92.5 MHz. Depending on the experiment, the center wavelength of the pulses was tuned between 750 nm to 850 nm and the pulse duration was tuned from 50 fs to 100 fs. The optical beam was sent through an optical isolator to prevent back reflections from destabilizing the oscillator.

Two-dimensional spatial light modulators

In both the beam shaper and the pulse shaper, the key instrument was a two dimensional spatial light modulator (2D SLM) from Hamamatsu (Model X8267). The front face of the device is a uniform layer of liquid crystals that was held at a bias voltage of about 4 Volts. The back of the liquid crystal layer is a photoconductive semiconductor layer that applied a variable voltage to the front liquid crystal layer. A control laser diode, in the back of the device, was incident on the photoconductive semiconductor layer and modulated the voltage applied to the front liquid crystal layer depending on the incident intensity. The intensity of the control laser diode was attenuated spatially by an intermediate liquid crystal mask, which was set by a user defined image. The pixelation of the intermediate mask effectively created pixels in the otherwise uniform front layer of liquid crystals. In this 2D SLM model, there are 768 by 768 pixels, with each pixel a 24x24 micron square. Optical fields that were incident on each of these pixels experienced different phase shifts depending on the orientation of the pixels, which depended on the applied voltage. The voltage applied to the front liquid crystal layer can be attenuated by 256 values, which are called grayscale values.

Interferometric calibration was used to calibrate the phase shifts induced by the front surface of the 2D SLM[148]. An input beam was split into two beams by a phase mask and each beam was focused onto different sides of the 2D SLM. The retroreflection off the 2D SLM and back into the phase mask was separated from the input beam with a beam splitter and sent to a photodiode detector. By scanning one
Figure 2-9: (a) Schematic of beam shaper with an input beam focused onto the surface of the two-dimensional spatial light modulator which diffracts light into different orders based on the applied diffraction pattern. (b) A diffraction pattern corresponding to the output beam geometry shown in (c).

Of 2D SLM through the 256 grayscale values, the phase change caused by each grayscale value can be characterized. The bias voltage was adjusted so that the 256 grayscale values would correspond to a range of phase shifts from zero to $2\pi$.

**Beam shaper**

The beam shaper was used to generate multiple beams in a reconfigurable geometry. The input beam was focused onto the surface of a 2D SLM using a long focal length lens (150 cm). A diffraction pattern was applied to the 2D SLM, diffracting the input beam into different orders. The 2D SLM was at a slight angle (less than one degree relative to the incident beam) so that the diffracted beams were collimated by a second lens (150 cm). By configuring the diffraction pattern at the 2D SLM, different beam geometries can be easily obtained. A schematic illustration of the beam shaper along with an example of a diffraction pattern and its corresponding beam geometry are shown in Figure 2-9.

**Pulse shaper**

The pulse shaper was used to shape the temporal waveforms of the beams generated by the beam shaper. The beams were first focused above a mirror, that was used as a
pick-off mirror for the outgoing shaped pulses, and then the beams were recollimated by a second lens. The collimated beams were spectrally dispersed by a grating-cylindrical lens pair, as shown in Figure 2-10a. The front surface of a 2D SLM was positioned at the spectral plane so that the horizontal dimension of the 2D SLM controlled the phase of the optical fields as a function of the wavelength of the optical field components. Any beams that occupy the same horizontal space cannot be controlled independently. Horizontal stripes, with heights of roughly 100 pixels, were uniquely defined for beams that occupied a different horizontal space on the 2D SLM. A sawtooth pattern was applied along the vertical dimension of the 2D SLM, shown in Figure 2-10b. The retroreflections of the beams were focused by the second input lens so that all beams of the same diffraction order from the vertical sawtooth pattern were focused to the same spot at the position of the pick-off mirror. The first diffraction orders of all beams were reflected by the pick-off mirror and sent to the sample. Because the output beams of the pulse shaper were the first order diffraction beams from the sawtooth pattern, the method is described as diffraction-based pulse shaping.

Diffraction-based pulse shaping gives control of both the phase profiles and the amplitude profiles of the optical pulses. The frequency dependent sawtooth pattern, given by a function $S(\omega)$, permits control of the optical pulse amplitudes as a function of frequency:

$$E(\omega) = \exp(i2\pi \Delta/d_s) \text{sinc}[\pi(1 - S(\omega))]$$

(2.26)

where $d_s$ is the periodicity of the sawtooth pattern and $\Delta$ is the vertical displacement of the pattern, as shown in Figure 2-10b. The phase shifts of optical pulses are controlled by shifting the sawtooth pattern vertically. In this case, the possible number of phase values that the pulse shaper can impart on optical pulses is given by the number of pixels used to define one sawtooth pattern. In the experiments discussed in this dissertation, 12 pixels were used to define one sawtooth pattern so that the pulse shaper could change the phase of the optical pulses by $2\pi/12$. As discussed below, the decreased precision in the phase control, which increased the minimum
\( \tau_{\text{delay}} \) that could be achieved by the pulse shaper, was compensated through binning of the 2D SLM columns. In addition to providing control of the pulse amplitudes, diffraction-based pulse shaping is also advantageous over phase-only pulse shaping because first-order diffraction beams do not contain replica pulses, caused by the pixelation of the 2D SLM, that are found in zero-order beams [148].

The columns of pixels in each horizontal stripe change the phase of each beam as a function of wavelength. In order to calibrate the columns of pixels to the wavelength of light that each column controls, each optical beam was sent to the spectrometer and a single column of pixels was scanned across the corresponding horizontal stripe. If the 2D SLM was not precisely positioned in the spectral imaging plane of the grating/lens pair, the pixel-to-wavelength calibrations for different beams were slightly different.

By controlling the phases of optical pulses as functions of frequency, the temporal waveforms could also be controlled by considering the Fourier relationships between pulse shapes in the time domain and frequency domain. A time delay in a pulse, \( \tau_{\text{delay}} \), is created by applying a linearly increasing phase to the pulse as a function frequency: \( \phi(\omega) = (\omega - \omega_c)\tau_{\text{delay}} \), where \( \omega \) is the frequency of the pulse and \( \omega_c \) is a user-defined frequency, called the carrier frequency. Because the phase sweep is centered around \( \omega_c \), the phase at the \( \omega_c \) does not vary with \( \tau_{\text{delay}} \). In the time domain, oscillations in the signal phase during \( \tau_{\text{delay}} \) are decreased by \( \omega_c \) so that phase oscillations of the signal during \( \tau_{\text{delay}} \) can be accurately resolved with a lower Nyquist limit. The detection of the signal during \( \tau_{\text{delay}} \) with a nonzero \( \omega_c \) is called rotating frame detection and was first used in NMR [16].

The minimum and maximum time delays that can be generated using the 2D pulse shaper are determined by both the parameters of the 2D SLM device and the spectral imaging determined by the grating and cylindrical lens [142]. The minimum time delay, \( \tau_{\text{min}} \), is determined by the smallest linear phase increase as a function of frequency that can be achieved with the 2D SLM, which is determined by the spatial dispersion of the frequencies on the 2D SLM and the size of the pixels. The minimum time delay is improved by binning a number of pixels together and changing the phase as a function of the different bins of pixels. In this case, the minimum time delay is

50
Figure 2-10: (a) Layout of 2D pulse shaper with an incoming beam that is diffracted off a grating, a cylindrical lens, and a 2D spatial light modulator (SLM) in the spectral imaging plane. (b) Sawtooth pattern that is applied on 2D SLM in the vertical dimension of the screen. The periodicity of the sawtooth pattern is given by $d_s$ and the offset of the sawtooth pattern is given by $\Delta$.

given by:

$$\tau_{\text{min}} = \frac{\Delta \phi_{\text{min}} \times N_{\text{bin}}}{\Delta \omega}$$ (2.27)

where $\Delta \phi_{\text{min}}$ is the minimum change in phase over one pixel, $N_{\text{bin}}$ is the number of pixels in one bin, and $\Delta \omega$ is the spread of frequencies over one pixel. In the experiments discussed in this dissertation, $\tau_{\text{min}} = 25$ fs was achieved with four bins of 192 pixels.

The maximum time delay is limited by the pixelation of the 2D SLM. The top-hat shape of each pixel is imparted to the frequency domain pulse shapes, which results in a sinc function in the time domain pulse shapes. The sinc function gives a decrease in the intensity of the optical pulses as a function of $\tau_{\text{delay}}$:

$$E_{\text{out}}(\tau_{\text{delay}}) \propto \exp\left(-\pi^2 \delta \nu^2 \tau_{\text{delay}}^2\right) \text{sinc}(\delta \nu \tau_{\text{delay}})$$ (2.28)

where $\delta \nu = \delta x \Delta \omega / w_{\text{px}}$, $w_{\text{pixel}}$ is the width of one pixel, $\delta x = 4 F \lambda / \pi D$, $F$ is the focal length of the cylindrical lens, $D$ is the input beam diameter, and $\lambda$ is the center wavelength of the optical pulse. For the gratings and cylindrical lenses used in this dissertation, the sinc full width half maximum was about 10 ps.
Figure 2-11: The setup to route the local oscillator (LO) around the sample, in the self-diffraction geometry. Excitation fields at $k_1$ and $k_2$ were focused onto the sample ($S$), generating signal that was overlapped with the local oscillator at $k_{LO} = 2k_2 - k_1$. In order to route the LO around $S$, a phase mask (PM) was placed one focal length before the first lens (L). A second PM was placed one focal length after the second L to recombine the optical fields. The usual beam paths, without the use of the two masks, are shown as solid lines. The beam paths routed around the sample are shown as dashed lines.

Spectral signal detection

The output of the pulse shaper was sent to a sample, generating signal in a phase matched direction that was overlapped with a reference field, called the local oscillator (LO), and both fields were sent to a spectrometer. In all experiments discussed in this dissertation, the sample was held in a cold-finger cryostat at liquid helium temperatures (4 K to 10 K, unless otherwise noted). In most cases, the LO beam was generated by the beam shaper and co-propagated with the other excitation beams through the pulse shaper and the sample. However, the 2D spectra of semiconductor microcavity samples (Chapter 7) were obtained by routing the LO beam around the sample and recombining the LO beam after the sample using a matching pair of transmissive diffractive optics called phase masks, as shown in Figure 2-11. The phase masks were placed one focal length before and after the lenses used to focus and collimate the beams around the sample, respectively. Routing of the beam around the sample was necessary because most of the light was reflected from the surface of the semiconductor microcavity sample, preventing complete spectral overlap of the signal and LO fields in the spectrometer.

The interference between the signal field, $E_{\text{sig}}$, and the LO, $E_{LO}$, in the spectrometer can be used to extract the full complex value of $E_{\text{sig}}$ through a procedure
called spectral interferometry\[87]\). The procedure is outlined in Figure 2-12. The interference spectrum of $E_{\text{sig}}$ and $E_{\text{LO}}$, $I_{SI}$, is given by:

\[
I_{SI}(\omega) = |E_{\text{sig}}(\omega) + E_{\text{LO}}(\omega)|^2 \\
= |E_{\text{sig}}(\omega)|^2 + |E_{\text{LO}}(\omega)|^2 + 2|E_{\text{sig}}(\omega)||E_{\text{LO}}(\omega)|\cos[\phi_{\text{sig}}(\omega) - \phi_{\text{LO}}(\omega)]
\] (2.29)

where the phases of the signal and the LO are given by $\phi_{\text{sig}}(\omega)$ and $\phi_{\text{LO}}(\omega)$, respectively. $I_{SI}$ has been interpolated from the wavelength domain, as measured by the spectrometer, to the frequency domain. The last term on the right hand side, which contains the phase of the signal, can be isolated by measuring the spectrum of the LO and signal fields and subtracting the spectrum from $I_{SI}$, giving the interference spectrum of Figure 2-12b.

The phase of $E_{\text{sig}}$ can be extracted through Fourier filtering. The cross term of Equation 2.29 can be written as:

\[
2|E_{\text{sig}}(\omega)||E_{\text{LO}}(\omega)|\cos[\phi_{\text{sig}}(\omega) - \phi_{\text{LO}}(\omega)] = 2|E_{\text{sig}}(\omega)||E_{\text{LO}}(\omega)|e^{-i[\phi_{\text{sig}}(\omega) - \phi_{\text{LO}}(\omega)\tau_{\text{LO}}]} + c.c. \\
= \mathcal{F}^{-1}[B^+(t) + B^-(t)]
\] (2.30)

where $B^+(t)$ and $B^-(t)$ are the Fourier transforms of the two terms on the right hand side of the first line of Equation 2.30. As can be seen in Figure 2-12c, $B^+(t)$ and $B^-(t)$ are signals at positive and negative times. By filtering out the negative time domain signal and performing an inverse Fourier transformation back into the frequency domain, only the first term on right hand side of the first line of Equation 2.30 is isolated, giving a complex signal. The final step is to remove the $\phi_{\text{LO}}$. Assuming that the only phase difference between the $E_{\text{sig}}$ and $E_{\text{LO}}$ is given by a time delay in the LO, $\tau_{\text{LO}}$, then $\phi_{\text{LO}}(\omega) = (\omega - \omega_c)\tau_{\text{LO}}$. By multiplying $2|E_{\text{sig}}(\omega)||E_{\text{LO}}(\omega)|e^{-i[\phi_{\text{sig}}(\omega) - \phi_{\text{LO}}(\omega)\tau_{\text{LO}}]}$ by $e^{-i\phi_{\text{LO}}(\omega)}$ and dividing by the square root of the LO spectrum, the complex signal field can be derived, shown in Figure 2-12d. The phase between $E_{\text{sig}}$ and $E_{\text{LO}}$ can be checked by comparing the integrated 2D correlation spectrum with the spectrum of a pump-probe experiment because the pump-probe spectrum is independent
of the phase of the excitation fields and should be identical to the integrated 2D spectrum\cite{57}.

**Polarization control**

A combination of quarter and half waveplates placed in the paths of the beams were used to change the relative polarization configurations of each optical field: the configurations included collinear, crosslinear, cocircular, and crosscircular polarizations. In the cross polarization configurations, one (or more for fifth or higher-order spectroscopy) nonconjugate field(s) were perpendicular in polarization from the other nonconjugate field(s). By conservation of polarization, the signal and the conjugate fields were also cross-polarized. In the BOXCARS geometry, this polarization control can be accomplished by using a large quarter waveplate that can rotate the polarization of all four beams and four small quarter waveplates that rotate the polarization of each beam individually. Using different combinations of the large and small quarter waveplates, all four of the desired polarization conditions can be achieved. The waveplates were placed between the pulse shaper and the sample.

For experiments in the self-diffraction geometry, polarization control can also be accomplished by a combination of a large quarter waveplate that controls all the beams and small quarter waveplates that control each beam. However, because of the beam geometry, all nonconjugate field interactions must be the same polarization and all conjugate field interactions must be the same polarization. However, a pseudo cross-circular polarization scheme can be achieved by setting the nonconjugate fields to a linear polarization, the conjugate fields to one specific circular polarization, and using a waveplate/polarizer combination to detect only the opposite circular polarization of the signal. In order to conserve the total polarization, the two nonconjugate field interactions must be with cross-circular field components.

**Phase cycling**

$E_{\text{sig}}$ can be isolated from the background scatter by a procedure called phase cycling, first utilized in NMR\cite{16}. Although $E_{\text{sig}}$ is generated in a phase-matched direction,
Figure 2-12: (a) Spectrum of the signal field, $|E_{\text{sig}}|^2$, the local oscillator, $|E_{\text{LO}}|^2$, and the interference of the two fields $|E_{\text{sig}} + E_{\text{LO}}|^2$. (b) The cross term of $|E_{\text{sig}} + E_{\text{LO}}|^2$ that depends on both the phase of the signal field, $\phi_{\text{sig}}$, and the phase of the local oscillator, $\phi_{\text{LO}}$. (c) Fourier transformation of the cross term in (b), giving signal at both positive and negative times. A step function filter (green) selects for the signal at positive times. (d) Inverse Fourier transformation of the signal at positive times in (c) with the phase and spectrum of the local oscillator removed, giving the phase of $E_{\text{sig}}$. 
scattering of the excitation fields into the signal direction can still hinder the detection of $E_{\text{sig}}$, particularly because the signal field strength is typically orders of magnitude smaller than the excitation fields. In this case, the intensity that the spectrometer detects, $I_{\text{det}}$, is given by:

$$I_{\text{det}}(\omega, \phi_{\text{LO}}, \phi_{\alpha}, \phi_{\beta}, ... \phi_{n}) = \left| E_{\text{LO}} e^{i\phi_{\text{LO}}(\omega)} + E_{\text{sig}} e^{i\phi_{\text{sig}}(\omega)} + \sum_{n}^{N} E_{n} e^{i\phi_{n}(\omega)} \right|^2$$

(2.31)

where $E_n$ are the excitation fields used to generate the signal that have scattered into the signal direction with phases given by $\phi_n$. Phase cycling involves isolating the signal cross term, given in Equation 2.30, by summing $I_{\text{det}}(\omega, \phi_{\text{LO}}, \phi_{\alpha}, \phi_{\beta}, ... \phi_{n})$ over different values of $\phi_{\text{LO}}$ and $\phi_n$. The exact values of the phase shifts and the number of cycles that are used to isolate the signal depend on the number of field interactions that each excitation field contributes to generate the signal. For all experiments in this dissertation, eight-step phase cycling was used to isolate the signal field. For third-order experiments in the BOXCARS geometry, the phase cycling was accomplished in eight steps by shifting all excitation fields and combinations of excitation fields by $\pi$, as detailed previously[148]. For all experiments in the self-diffraction geometry, the phase cycling was also accomplished in eight steps but the phase of the LO was also varied and the value of the phase shift depended on the order of the signal, as detailed previously[142].
Chapter 3

Coherent control in 2D spectroscopy

Even with the advantages of 2D FT OPT, broadening of peaks relative to the energy separation between the peaks may still produce 2D spectra that are difficult to interpret. A state with a weak dipole moment relative to that of a neighboring state may be completely obscured by the lineshape of the neighboring peak. Spectral congestion is often worse when measuring multiple-quantum coherences because there are often a greater number of multiple-quantum peaks, since correlations can exist among many combinations of single-quantum states, and the peaks are usually broader due to faster homogeneous dephasing times [60].

The isolation of weak or overlapping peaks may be further improved by tailoring waveform amplitude and/or phase profiles to excite or probe specific resonances, as has been well developed in the strong-field regime for 2D NMR [147]. Toward this goal, evolutionary algorithms in 2D FT OPT have been theoretically and experimentally explored [1, 112, 150]. In these works, the shapes of excitation fields are based on adaptive feedback loops that optimize target spectral signatures of a particular sample. Generally, the optimal pulse shapes are not easily adaptable to enhancing spectral signatures in other systems.

Tailored pulse shapes that are based on calculations considering a limited number of system parameters may be adaptable to many systems. Such an approach has
recently been tested in the 2D FT OPT of atomic rubidium gas by the selective amplification of peaks using tailored phase profiles in the first two excitation pulses [90]. Atomic rubidium gas provided a good test system because its excited states are energetically well separated relative to their linewidths. However, application of coherent control techniques in the 2D FT OPT of many systems of interest, such as molecular aggregates and nano-structured solid state systems, requires selective amplification of peaks that are overlapping. In addition, because the lineshapes in 2D spectra can be distorted in undesirable ways by frequency-dependent phase profiles in the excitation pulses [136], modifications in the lineshapes of 2D spectra due to applied phase profiles must be carefully analyzed. Finally, control techniques to selectively amplify multiple-quantum coherences, and not just coherences in single electronic excited states, have yet to be developed for 2D FT OPT.

Using only energy levels of the system as input parameters, tailored pulse sequences were designed to optimize specific peaks in the 2D spectra of gallium arsenide quantum wells (GaAs QWs). Optimal pulse shapes were designed using simple calculations based on perturbative coherent control techniques that have been previously developed in one-dimensional spectroscopy: double pulse (DP) shapes that selectively enhance different resonance frequencies and pulses with a frequency-dependent phase window (PW) that selectively enhance different two-quantum resonances [151, 41]. The pulse shapes were incorporated in the laboratory using pulse shaping-based 2D FT OPT, as discussed in the previous section. As will be discussed in detail in Chapters 4 and 5, the 2D spectra of GaAs QWs are dominated by many-body effects giving rise to peaks due to different biexciton states, unbound two-exciton correlations between various combinations of single-exciton states, and even triexciton states [88, 132, 133, 25, 33, 140, 60]. All of these multi-exciton coherences may interfere with each other and single-exciton peaks. The many-body effects also produce distortions in the lineshapes of 2D spectra. Despite these complications, selective amplification of final emission pathways and signals from biexciton states are demonstrated using DP and PW shapes, respectively. The effects of the shaped pulses on the lineshapes of target peaks are considered by comparison to calculated 2D spectra.
3.1 Methods

3.1.1 GaAs quantum well energy states

The sample structure consists of ten layers of 10 nm thick GaAs sandwiched between 10 nm thick Al_{0.3}Ga_{0.7}As. As will be detailed in Chapter 4 and 5, the electronic excited states of the GaAs QWs are strongly influenced by many-body interactions. However, for the purposes of this section, the electronic energy states can be represented by the simple energy diagram shown in Figure 3-1a. The diagram shows the ground state, g, the single-exciton heavy-hole, H, and light-hole, L, states, and the biexciton states composed of two H excitons, HH, two L excitons, LL, and a H and L exciton, HL. Each biexciton energy is reduced by a binding energy relative to the combined two-exciton energies. Polarization selection rules may be used to isolate specific exciton and biexciton resonances but because we are interested in demonstrating the selectivity of the DP and PW pulse shapes, we utilize only collinear (all parallel polarizations) or crosslinear (vertical and horizontal polarizations for the first two fields and for the third and LO fields, respectively) for all experiments. In both polarization configurations, all exciton and biexciton states may be excited. Additionally, in the collinear polarization configuration, unbound two-exciton correlations can also give rise to peaks in the 2D spectra at energies equal to the sum frequencies of the two excitons, energies that are larger than the biexciton peaks by the biexciton binding energies. In the crosslinear polarization excitation scheme, the unbound correlations are suppressed.

The possible Feynman pathways for 2D rephasing and two-quantum spectra of GaAs QWs are shown in Figures 3-1b and 3-1c. For the rephasing Feynman pathways, Figure 3-1b, the first and third fields can excite coherences of the same exciton state (pathways A1 and A1’) or different exciton states (pathways A2 and A2’), resulting in diagonal and off-diagonal peaks, respectively. Additionally, red-shifted shoulders
Figure 3-1: (a) A diagram showing the relative energy orderings of the ground (g), heavy-hole or light-hole exciton (H or L), and biexciton (HH, HL, or LL) states. (b) and (c) Feynman pathways showing coherent excitation of the various exciton and biexciton states in rephasing (b) and two-quantum (c) scans. The first two excitation fields in two-quantum scans were kept time coincident for all 2D spectra in this work.
to the peaks A1, A1', A2, and A2', due to emission from the various biexciton states
to single-exciton states, are anticipated in Figure 3-1b as pathways A3, A3', A4, and
A4'. Two-quantum Feynman pathways, Figure 3-1c, describe the coherent excitation
of various biexciton states. After excitation of a biexciton state, the biexciton can be
converted into a single exciton coherence with the ground state, as in pathways B1,
B1', B2, and B2', leading to emission from H or L, or a coherence between the biex-
citon and a single-exciton state can be excited, as in pathways B3, B3', B4, and B4',
leading to red-shifted shoulders to the first four pathways. Different Feynman path-
ways contributing to the 2D rephasing and two-quantum spectra can be selectively
enhanced using the DP and PW shapes, as discussed in the next two subsections.
The DP can be used to enhance selected single-quantum coherences, such as the final
emission pathways in either the 2D rephasing or two-quantum spectra. The PW pulse
shapes can be used to selectively enhance between different two-quantum coherences
in the 2D two-quantum spectra.

3.1.2 Double pulses

In 2D spectra, as in many nonlinear optical experiments, emission from different
excited states may contribute to the observed spectrum. Depending on the dipole
strengths, energies, and linewidths, the emission from one state may dominate over
that from another, obscuring the spectroscopic observation of some states. In the
Feynman pathways in Figure 3-1, the final (signal) emission is represented by the final
curry arrow on the left sides of all the pathways. In both rephasing and two-quantum
pathways, there are several emission pathways which may overlap. For example,
the rephasing pathways A1 and A2 are generally well separated because the energy
difference between the two emission pathways, given by the energy difference between
the H and L excitons, is large relative to the linewidths of the peaks. However, the
emitted signals from the two-quantum pathways B1 and B3 are strongly overlapped
because the energy difference between the two emission pathways is given by only the
binding energy of the HH biexciton state, which is on the order of the linewidths of
the peaks.
Figure 3-2: (a) A single Gaussian pulse is shaped into a double pulse with well-defined pulse delay, $\tau_{DP}$, and phase difference $\phi_{DP}$. (b) Two nonresonant excitation pathways (left) normally interfere destructively but can be made to interfere constructively by placing a phase window in the excitation fields (right), enhancing the two-quantum signal.
Selection for different emission pathways can be accomplished using phase-controlled pulse pairs or longer sequences that induce constructively or destructively interfering coherent oscillations in the system, a technique that is ubiquitous in the coherent control literature [154, 66, 39]. In particular, using a DP for the final field interaction of a third-order optical spectroscopy measurement can enable selective enhancement and suppression of different emission pathways [151]. A DP, as shown in Figure 3-2a, is defined as two Gaussian shaped pulses that are separated by a time difference, $\tau_{DP}$, and a relative phase difference between the two pulses, $\phi_{DP}$. In this case, the third-order density matrix of the system can be written as:

$$
\rho^{(3)}(t) = \frac{-i}{\hbar^3} \int_0^\infty \int_0^\infty \int_0^\infty d\tau_3 d\tau_2 d\tau_1 E(t - \tau_3 - \tau_2 - \tau_1) E(t - \tau_3 - \tau_2) \\
\exp(-i\phi_{DP}) R(3)(\tau_1, \tau_2, \tau_3)
$$

where the polarizations and wave vector dependences of the fields have been suppressed. After the first pulse in the DP, an induced coherence accumulates a phase during $\tau_{DP}$. The coherence can be made in or out of phase with a second coherence induced by the second pulse through control over $\phi_{DP}$, amplifying or suppressing the peak in the 2D spectra corresponding to this specific coherence. If there are two neighboring peaks, selective amplification of one peak and suppression of the other can be achieved by selecting $\tau_{DP}$ such that the phases accumulated at the frequencies of the two coherences are $\pi$ out of phase with each other and selecting $\phi_{DP}$ to enhance the desired peak. By shaping the third electric field to be a DP, Feynman pathways with different emission frequencies can be selectively enhanced. Similar strategies are possible with any of the incident fields.

In order to demonstrate the selectivity of the DP technique, the final electric fields in rephasing and two-quantum scans were shaped into a DP. For the rephasing scans, the parameters of the DP were chosen to discriminate between the Feynman pathways in Figure 3-1 that emit out of the H exciton coherence with the ground state (A1 and A2') and the Feynman pathways in Figure 3-1 that emit out of the L exciton coherence.
with the ground state (A2 and A1'). For the two-quantum scans, the parameters of the DP were chosen to discriminate between the two-quantum Feynman pathway in Figure 3-1 that emits out of the H exciton (B1) and the Feynman pathway in Figure 3-1 that emits out of the HH biexciton coherence with the H exciton (B3).

### 3.1.3 Phase window pulse shapes

Two-quantum coherences that are present in 2D two-quantum spectra are often obscured by other two-quantum coherences that overlap. For example, three biexciton states exist in GaAs QWs that may overlap in the two-quantum frequency domain spectra: the HH biexciton (excited in the pathways B1 and B3 in Figure 3-1), the HL biexciton (excited in the pathways B2, B2', B4, and B4' in Figure 3-1), and the LL biexciton (excited in the pathways B1' and B3' in Figure 3-1). In the GaAs QWs, the spectral crowding is made worse because of unbound two-exciton coherences and free carrier scattering caused by many-body interactions[60, 132, 133].

Dudovich and coworkers have shown that selectivity in the excitation of two-quantum coherences, assuming a resonant intermediate state, may be achieved by applying a PW shape to the two electric fields used in the two-photon excitation[41]. A PW shape, shown on the right side of Figure 3-2b, is defined by a $\pi/2$ phase offset over a range of frequencies in the electric field. The selective enhancement is based on coherent addition of contributions to the two-quantum coherence that is produced by the two field interactions. Considering a three-level ladder system, shown on the left of Figure 3-2b, with one-photon transitions allowed from the ground state, $g$, to the intermediate state, $i$, and from the intermediate to the final state, $f$, the second-order density matrix can be written as [41]:

$$
\rho^{(2)}_{fg} = \frac{-1}{\hbar^2} \mu_{fi} \mu_{ig} [i \pi E(\omega_i)E(\omega_{fg} - \omega_i) + CPV \int_{-\infty}^{\infty} d\omega' \frac{E(\omega)E(\omega_{fg} - \omega')}{\omega_{fg} - \omega}] 
$$

(3.2)

where $E(\omega)$ is an excitation field that interacts twice with the sample, $\mu_{mn}$ and $\omega_{mn}$ are the dipole and frequency of the transition from state $n$ to state $m$, and $CPV$ is the Cauchy principle value. The first term on the right hand side of Equation 2
describes a resonant process, whereby the components of the fields resonant with $\omega_{ig}$ and $\omega_{fi}$ contribute to the density matrix. The second term describes two nonresonant pathways: one with the first field interaction detuned to the red from $\omega_{ig}$ (path 1 in Figure 3-2b) and one where the first field interaction is detuned to the blue from $\omega_{ig}$ (path 2 in Figure 3-2b). In both nonresonant pathways, the second interaction must be detuned from $\omega_{fi}$ such that the total energy of the two-photon process is still given by $\omega_{ig} + \omega_{fi}$.

Although nonresonant pathways can contribute to $\rho^{(2)}$, the two nonresonant pathways are $\pi$ out of phase: as apparent from Equation 2, the contributions have opposite signs and the net contribution to $\rho^{(2)}$ is zero. However, applying a $\pi/2$ phase offset between $\omega_{ig}$ and $\omega_{fi}$ in the two excitation fields, as shown on the right side of Figure 3-2b, results in a net phase factor of $\pi$ in only path 2 so that the two nonresonant pathways contribute constructively to $\rho^{(2)}$. As shown by Dudovich and coworkers, the two-photon signal amplitudes in rubidium gas can be increased seven-fold compared to the amplitudes induced by ordinary Gaussian pulses.

By applying a PW shape in the first two electric fields of a two-quantum scan, different two-quantum coherences can be selectively enhanced in 2D two-quantum spectra. To demonstrate the selectivity of the PW shape, the parameters of the PW were chosen to enhance the HL biexciton by applying a $\pi/2$ phase shift over the range of frequencies between the two transition energies needed to excite the HL biexciton in the Feynman pathways B2, B2', B4, and B4' shown in Figure 3-1c. Specifically, a $\pi/2$ phase shift is applied between the frequency of the H exciton, $\omega_H$, and the frequency needed to excite the H exciton to the HL biexciton, $\omega_{HL} - \omega_H = \omega_L - \delta_{HL}$.

For coherent measurement of two-quantum states, not only is the amplitude of $\rho^{(2)}$ important, but so is the phase. The work by Dudovich and coworkers demonstrated the increase in two-photon absorption by incoherent emission from a neighboring high-energy single-photon state. Consequently, modifications to the phase of $\rho^{(2)}$ due to the PW in the excitation fields were not characterized. As discussed below, the effect of the PW on the phase of the two-quantum coherence is a calculable constant phase factor for each of the peaks of interest, which was experimentally verified using
the complex value of the 2D spectra.

3.1.4 Theoretical modeling

To simulate the effects of pulse shaping on the 2D spectra, and in particular to understand possible phase distortions caused by the PW shape, 2D spectra were calculated by solving the OBE, as derived in Section 2.1.3. The equations were derived using a three-level Hamiltonian, representing the QW ground state, the H exciton state, and the HL biexciton state. All other exciton and biexciton states were ignored because the purpose of the calculations was to calculate the phase shifts caused by the PW shape in a two-quantum peak. Although phenomenological density-dependent terms are often added to simulate many-body interactions in QWs, as discussed in Chapter 4, these terms were neglected because only changes in the phase caused by the PW are of interest in this section, not the absolute phase of any specific 2D spectrum. As seen below, neglecting the many-body interactions did not prevent accurate prediction of the phase shifts caused by the PW pulse shapes.

3.2 Results and discussion

3.2.1 2D spectra without selective enhancements

A 2D rephasing spectrum of GaAs QWs is shown in Figure 3-3b, consistent with previous 2D spectra of the system [88]. Peaks corresponding to the H and L states, with an intensity ratio of 9 : 1 (after normalization for the relative amplitudes of the laser spectrum, shown in Figure 3-3a) due to the relative transition dipole strengths of the H and L states, are found along the diagonal. The shared ground state led to off-diagonal peaks between the H and L states. All red-shifted shoulders to peaks are attributed to excited-state absorption to the biexciton state (pathways A3, A3, A4, and A4 in Figure 3-1b).

2D two-quantum spectra of GaAs QWs are shown in Figures 3-3c and d for crosslinear and collinear polarization conditions, consistent with previous 2D spectra.
Figure 3-3: (a) Spectral intensity of optical fields used to excite the sample. (b) A 2D rephasing spectrum taken in the collinear polarization configuration, without double pulse or phase window shaped pulses. (c) 2D two-quantum spectrum taken in the crosslinear polarization configuration, without double pulse or phase window shaped pulses. (d) Same as (c) except electric fields are in the collinear configuration. Features in the spectra are labeled according to Feynman pathway diagrams in Figure 3-1b and c. Colorbar in (d) is used for all figures in this chapter.
of the system[25]. Peaks appear corresponding to the excitation of various biexcitons and emission out of H or L, as labeled by the Feynman pathway diagrams in Figure 3-1c. The peak corresponding to HL emitting out of H is obscured slightly by a vertical stripe corresponding to scatter from free carriers into the H exciton state[162], which was not completely suppressed in the crosslinear polarization.

3.2.2 Selective enhancements using DP shapes

The relative intensities of peaks were manipulated by replacing a single Gaussian pulse with a DP. To demonstrate this capability, the peaks in a rephasing spectrum that appear due to emission from H, pathways A1 and A2' in Figure 3-4b, and emission from L, pathways A2 and A1', were selectively enhanced or suppressed. In Figure 3-4a, \( \tau_{DP} = 170 \) fs and \( \phi_{DP} = 2\pi \omega_H \tau_{DP} \). In Figure 3-4b, \( \tau_{DP} \) was the same as in Figure 3-4a but \( \phi_{DP} \) was shifted by \( \pi \). The ratio of the diagonal peak amplitudes, corresponding to H and L emission pathways, was switched from 31:1 to 1:1, compared to the ratio of 9:1 using the normal pulse sequence shown in Figure 3-3a.

The control shown in Figure 3-4a and b can be understood by considering the interference between the different Feynman pathways that contribute to the 2D spectra. As with the 2D rephasing spectra without spectral enhancements, three electric fields along \( k_a, k_b, \) and \( k_c \) were sent to the sample. The conjugate beam, \( E_c(k_c) \), and one of the nonconjugate beams, \( E_a(k_a) \), were normal Gaussian pulses but the third electric field, \( E_b(k_b) \), was shaped into a DP. In a subset of the excitons initially excited by \( E(k_c) \) and \( E(k_a) \), the first pulse in the DP initiated coherences oscillating at either the H exciton frequency \( \omega_H \), pathways A1 and A2', or the L exciton frequency \( \omega_L \), pathways A2 and A1'. After the delay between the two pulses in the DP, the phase difference between the excitons in H and L emission pathways was given by \( \Delta \phi = 2\pi(\omega_L - \omega_H)\tau_{DP} \). The value of \( \tau_{DP} = 170 \) fs was chosen so that \( \Delta \phi = \pi \).

To enhance the H emission pathways, the second pulse in the DP must excite coherences that were in phase with the coherences started by the first pulse in the DP, i.e. the phase of the second pulse was chosen to match the phase of the H emission pathways started by the first pulse, \( \phi_{DP} = 2\pi \omega_H \tau_{DP} \). Simultaneously, the L emission
Figure 3-4: (a) A 2D rephasing spectrum recorded under the same conditions as Figure 3-3b except a double pulse is used in the last field to enhance H emission. (b) Same as (a) except the double pulse parameters were selected to amplify L emission. (c) A 2D two-quantum spectrum recorded under the same conditions as Figures 3-3c except a double pulse was used to enhance pathway B1. (d) Same as (c) except the double pulse was used to enhance pathway B3.
pathways were suppressed due to the selection of $\tau_{DP}$. It is important to note that the signal was detected in the four-wave mixing direction so that each of the three beams incident on the sample at wavevectors $k_a$, $k_b$, and $k_c$ contributed exactly one field interaction with the sample. Thus a subset of the excitons generated by the first two fields was acted upon by the first pulse in the $E_b$ DP, and another subset of the excitons was acted upon by the second pulse in the $E_b$ DP. It is the interference between the different subsets excited by the different pulses in the DP that gives the enhancement or suppression of the signal. To suppress the H emission pathways and amplify the L emission pathways, $\phi_{DP}$ was flipped by $\pi$.

Selective enhancement between two peaks using the DP was useful even if the target peaks overlap, such as the two peaks given by Feynman pathways B1 and B3 in Figure 3-1c, which are separated only by the HH biexciton binding energy in the emission dimension. To selectively enhance either of these peaks, the third electric field in a two-quantum scan, $E_c(k_c)$, was shaped into a DP with $\tau_{DP} = 700$ fs and $\phi_{DP} = 2\pi \omega_H \tau_{DP}$ to enhance pathway B1 or $\phi_{DP} = 2\pi \omega_H \tau_{DP} + \pi$ to enhance pathway B3. Because the energy separation between these two transitions, given by the binding energy of HH, is much smaller than the energy separation between the H and L transitions to the ground state, $\tau_{DP} = 700$ fs was much longer than $\tau_{DP}$ used to distinguish between H and L emission. Even in this case of overlapping peaks, the ratio of the amplitudes of the two pathways can be switched from 3:4 to 7:4. A high energy tail appears in the emission of Figure 3-4d. Because there are no peaks expected at this position, the high energy tail is most likely due to constructive interference of the emission from the high energy side of the H exciton linewidth in pathway B1.

The selectivity between two overlapping peaks was reduced compared to two peaks that are well separated because, in order to reach a $\pi$ phase shift between these two coherences, $\tau_{DP}$ must be comparable to their dephasing times and the coherences excited by the first pulse in the DP decay during $\tau_{DP}$. Assuming two peaks of equal linewidths, $\gamma$, and an energy separation of $\delta \omega$, the DP selectivity, measured by the relative change in ratio of the two peak amplitudes, decays as $\exp(-\pi \gamma / 2 \delta \omega)$. 

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if $2\pi\delta_\omega \tau_{DP} = \pi$. Therefore, the DP is a useful approach to selectively amplify or suppress neighboring peaks within the limitations determined by $\gamma$ and $\delta_\omega$. In a 2D two-quantum spectrum, $\gamma$ is due to both homogeneous and inhomogeneous broadening. However, in a rephasing scan the inhomogeneity of a sample is isolated along the diagonal of the 2D spectrum so that the DP technique is only limited by the homogeneous broadening. Furthermore, because the 2D rephasing spectrum can be thought of as the sum of Feynman pathways with an inhomogeneous distribution of absorption and emission energies[57], the parameters $\tau_{DP}$ and $\phi_{DP}$ can be chosen in a rephasing scan to selectively enhance different contributions of the inhomogeneous distribution. Such selectivity could be accomplished by choosing a portion of the inhomogeneous distribution to be enhanced and a portion to be suppressed. The central frequencies of these two portions could then be used to choose $\tau_{DP}$ and $\phi_{DP}$ to selectively enhance a portion of the inhomogeneous distribution. However, the GaAs QW sample used in this paper has comparable inhomogeneous and homogeneous linewidths, as seen by the nearly round peaks in the rephasing spectra in Figure 3-3a, so the DP shapes used in this paper did not discriminate between different contributions to the inhomogeneous distribution.

### 3.2.3 Selective enhancements using PW shapes

The PW was able to selectively enhance two-quantum peaks, even in the presence of overlapping signals. As an example, the HL peak was selectively enhanced in a 2D two-quantum spectra despite the fact that it overlaps with an elongated peak due to free-carrier scattering in the H state. To enhance the HL peak, a $\pi/2$ phase shift was applied to fields $E_1(k_a)$ and $E_2(k_b)$, between the $H \rightarrow HL$ transition frequency, $\omega_{HL-H}$, and the $g \rightarrow H$ transition frequency, $\omega_{H}$. The magnitude 2D spectrum obtained using PW pulses is shown in Figure 3-5. Relative to the magnitude of the HH peak, the magnitude of the HL peak increased by nearly three times, corresponding to an enhancement in the electric field intensity by nine times, similar to the enhancements measured in Rb gas [41]. A binding energy of 1.7 meV was measured for the HL peak, in agreement with previous results[132]. Because the PW was only in the
Figure 3-5: A 2D two-quantum spectra taken under the same conditions as Figure 3-3d except that a phase window was applied to the first two excitation fields.

The spectral region between the two transition energies, $\omega_{HL-H}$ and $\omega_H$, the resonant contribution to Equation 2 was unaffected by the PW shape. However, the nonresonant contribution was greatly enhanced by constructively interfering the pathways that were blue-detuned and red-detuned from $\omega_H$. The selective amplification of the HL peak was demonstrated despite the presence of many-body interactions that generated overlapping signal, specifically the peak representing free-carrier scattering into the H exciton state. Because free-carrier scattering into the H exciton state cannot be described by a two-photon transition with an intermediate state, the scattering was not enhanced by the PW.

The PW also caused a phase shift in the signal. The real parts of the 2D spectra are shown in Figure 3-6, which differ from the usual dispersive line shape due to phase shifts caused by many-body interactions[88]. The imaginary parts were also determined, and the phases of the 2D spectra at any frequency were found from the real and imaginary parts of the 2D spectra at that frequency. A cut of the phase of the 2D spectra along the two-quantum energy at the energy of the HL biexciton was used to find the change in phase at that same cut when a PW was applied, as shown in Figure 3-6c for two different PW widths. As can be seen, the change in phase depends on the width of the window used. A shift of approximately $\frac{\pi}{3}$ at the HL peak emitting out of H was recorded for a PW width of 5.5 meV, as used in Figure 3-6b. For a PW width of 2.6 meV, a phase shift of about $\frac{\pi}{3}$ was observed.
Figure 3-6: (a) The real part of the 2D two-quantum spectra shown in Figure 3-3b. (b) The real part of the 2D two-quantum spectra shown in Figure 3-5. (c) Calculated and experimental phase shifts in 2D spectra due to phase windows of two different spectral widths.
Although the phase of the 2D spectrum was altered using PW pulses, the change in phase was easily calculated using the OBE. Calculated 2D spectra with and without PW pulse shapes are shown in Figure 3-7, with the parameters of the three-level system Hamiltonian chosen to match the properties of the ground, H exciton, and HL biexciton states of the sample used in the experiment. As can be seen by comparing Figures 3-7a and 3-7c, when incorporating a PW in the first two excitation fields, the magnitude of the signal due to the biexciton coherence increased by about a factor of two, similar to the experimental observation of a threefold increase in signal. The calculated phase changes of the 2D spectra are shown in Figure 3-6c as the dotted lines. The theoretically calculated phase changes were within 5% of the experimentally measured phase shifts.

The phase change dependence on the PW width can be understood by considering the limiting cases of a PW of zero width, which gives zero change in phase since no phase pattern is applied, and a PW of infinite width, which gives a phase shift of $\pi$ since each field contributes a shift of $\frac{\pi}{2}$ for all frequencies to the 2D spectra. Even in the presence of many-body interactions that alter the phases of the 2D spectra features, the calculations demonstrate that, although the PW pulse shape alters the
phase of the 2D spectra, the real and imaginary parts of the 2D spectra can still be
determined. The phase shifts in the signals could be used for relative enhancements
or suppression of one feature relative to another by appropriate selection of the PW
frequency range and the LO heterodyne phase.

3.3 Conclusions

Pulse sequences have been designed and applied to selectively enhance exciton and
biexciton peaks in GaAs QW 2D spectra. The peaks were enhanced by using double
pulse sequences and phase window profiles in the excitation fields. Despite overlapping
peaks and complex many-body interactions, both methods were able to selectively
enhance or suppress selected peaks. The phase window shapes caused a phase shift
in the 2D spectra that could be calculated using optical Bloch equations. In theory,
the pulse shapes should be applicable to other systems by adapting a small number
of control parameters (e.g. double pulse time delays, phase shifts, and phase win-
dow frequency limits) appropriately. The parameter values can be calculated with
simple third-order perturbation theory. Selective amplification of resonances in 2D
FT OPT is expected to be particularly relevant for systems in which overlapping or
weak features prevent clear elucidation of coupling mechanisms or multiexciton peaks.
More generally, the present demonstration suggests the use of other types of shaped
waveforms in third-order and higher-order multidimensional spectroscopy.
Chapter 4

Theoretical description of many-body interactions in semiconductors

Many-body interactions play a crucial role in the dynamics of excited electrons in semiconductor materials. The interactions are a result of long-range Coulomb interactions that couple charged carriers in the semiconductor. For example, an electron excited into the conduction band of a semiconductor can relax into an orbital around the vacancy the electron left behind in the valence band, forming a hydrogen-like bound state called an exciton, which can live for nanoseconds, depending on the material, until the electron relaxes back into the valence band through radiative or nonradiative recombination.

The binding of an excited electron into an exciton state is only one type of Coulomb interaction found in semiconductors: additional Coulomb interactions can occur among excitons, strongly influencing the dynamics of the excitons. Coulomb interactions can cause excitons to scatter with each other, exchanging energy and momentum during the scattering process. Furthermore, the Coulomb interactions among excitons can occur in a correlated manner[30]. The interactions between two excitons, for example, can modify the configuration of each exciton over a finite period of time as the two excitons mutually evolve in time. The correlated interactions
among excitons can cause the excitons to form bound multiexciton states, much like two hydrogen atoms can form a hydrogen molecule, as well as a continuum of unbound correlated states.

The ideal theoretical description of many-body interactions would elucidate the precise mechanisms and effects of Coulomb interactions in semiconductor materials. The complexity of many-body problems, however, often obscures the physical intuition that might be derived from a theoretical model. Fortunately, under the right approximations, theoretical equations can be derived that accurately describe some of the mechanisms and effects of Coulomb interactions. Not coincidentally, the approximations that are made to simplify the theoretical description can also reflect the conditions of nonlinear spectroscopy experiments; the theoretical models address the central question of how Coulomb interactions modify the excited states and nonlinear dynamics of semiconductor electrons.

In this chapter, two theoretical descriptions of many-body interactions are discussed. The first section discusses the microscopic origins of the exciton bound state and various types of interactions among excitons, including the correlated Coulomb interactions among excitons. The second section discusses a simpler phenomenological model that can be used to explain how many-body interactions influence the nonlinear dynamics of excitons.

4.1 Microscopic theory of many-body interactions

4.1.1 The semiconductor Hamiltonian

The theoretical description of many-body interactions starts with the Hamiltonian of electrons in a semiconductor. In the quantized k-space basis set, the Hamiltonian can be written as:

\[ \mathcal{H} = \mathcal{H}_{\text{mat}} + \mathcal{H}_{\text{coul}} + \mathcal{H}_f \]  

(4.1)
\( \mathcal{H}_{\text{mat}} \) is the material Hamiltonian that gives the kinetic energy of electrons in the conduction band or valence band, \( \epsilon_c \) or \( \epsilon_v \) respectively, of a semiconductor:

\[
\mathcal{H}_{\text{mat}} = \sum_{\lambda, k} \epsilon_\lambda(k) a^\dagger_{\lambda, k} a_{\lambda, k}
\]  

(4.2)

where \( a^\dagger_{\lambda, k} \) and \( a_{\lambda, k} \) are the creation and annihilation operators of an electron in the band \( \lambda \). The summation over \( \lambda \) includes all states in the conduction band and the valence band. The creation and annihilation operators can be derived from real-space representations of electron density operators\[51\] but can be intuitively understood in analogy to the raising and lowering operators of a harmonic oscillator: the creation (annihilation) operator increases (decreases) by one the excitation number in the specified band and \( k \) state. \( \mathcal{H}_{\text{coul}} \) is the Coulomb Hamiltonian that gives the Coulomb coupling among electrons:

\[
\mathcal{H}_{\text{coul}} = \frac{1}{2} \sum_{k, k', q \neq 0, \lambda, \lambda'} V(q) a^\dagger_{\lambda, k+q} a^\dagger_{\lambda', k'-q} a_{\lambda', k'} a_{\lambda, k}
\]  

(4.3)

where \( V(q) \) is the Coulomb coupling between two electrons separated by a distance in \( k \)-space by \( q \). In two dimensions, which is the main focus of this dissertation, \( V_{2D}(q) = \frac{2 \pi e_0}{\epsilon_0 L^2 |q|} \) where \( \epsilon_0 \) is the background dielectric constant that accounts for the polarizability of the valence electrons and the lattice, \( e \) is the charge of an electron, and \( L^2 \) is the area of the crystal. \( \mathcal{H}_I \) is the interaction Hamiltonian between electrons and an optical field:

\[
\mathcal{H}_I = \sum_{c, v, k} E(t) (a^\dagger_{c, k} a_{v, k} d_{cv} + h.c.)
\]  

(4.4)

The optical field can excite an electron from a state in the valence band, \( v \), to a state in the conduction band, \( c \), depending on the transition moment given by \( d_{cv} \). The interactions with lattice nuclear motions have been neglected for two reasons: the primary focus of this chapter is on the Coulomb interactions among electrons and because the main effect of phonons in coherent nonlinear spectroscopy is to cause dephasing, which can be added phenomenologically as a dephasing constant.
The Coulomb interaction, given by Equation 4.3, is the source of many-body interactions among electrons in the semiconductor and must be carefully considered in order to understand the energies and dynamics of optically excited electrons in a semiconductor material. The term couples electrons in different bands and different \( k \)-states, depending on the coupling term \( V(q) \) which depends on the material parameters. As Equation 4.3 is written, the effects of the Coulomb coupling are not obvious, but there are several levels of approximations that can be made to elucidate the role of many-body interactions in the excited states. Two approximations are commonly considered: the Hartree-Fock approximation[51] and the coherent approximation[123]. By applying the Hartree-Fock approximation, also called the mean-field approximation, it will be shown that Coulomb interactions result in a bound hydrogen-like state between a single excited electron in the conduction band and a single vacancy in the valence band, called a hole. By applying the coherent approximation, it will be shown that Coulomb interactions can result in correlations among two excited electrons in the conduction band and two vacancies in the valence band. The four-particle correlations can result in the formation of a bound hydrogen molecule like state as well as correlated scattering among the particles.

In either approximation, the primary focus of the theoretical model will be the description of the electronic excited state dynamics. The simplest excitation condition is the direct excitation of an electron from the valence band into the conduction band with an optical field. In this case, there is an excitation in the conduction band and one less occupancy in the valence band, as represented by the polarization expectation value, \( P_k \):

\[
P_k(t) = < a_{v,k}^\dagger a_{c,k}(t) > \quad (4.5)
\]

In order to find the time dependence of Equation 4.5, the equation can be inserted into the Heisenberg equation:

\[
\frac{d}{dt} P(t) = i \frac{\hbar}{\hbar} [\mathcal{H}, P(t)] + \frac{\partial}{\partial t} P(t) \quad (4.6)
\]

After some algebra, the equation of motion describing the excited state of one electron
in the conduction band and one hole in the valence band at a wave vector $\mathbf{k}$ can be found:

$$h \left[ \frac{d}{dt} - (\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})) \right] P_k = N_k(t) \delta_{\mathbf{q}0} E(t) + \sum_{k', q \neq 0} V(q) B_{k,k',q}(t)$$

(4.7)

$N_k(t)$ is the difference between the number of electrons in the conduction band, $n_{c,k}(t)$, and valence band, $n_{v,k}(t)$, at $\mathbf{k}$. $n_{\lambda,k}(t)$ is given by:

$$n_{\lambda,k}(t) = \langle a^\dagger_{\lambda,k} a_{\lambda,k}(t) \rangle$$

(4.8)

$B_{k,k',q}(t)$ is the correlation among four particles, given by:

$$B_{k,k',q}(t) = \langle a^\dagger_{c,k+q} a^\dagger_{v,k-q} a_{c,k'} a_{c,k}(t) \rangle + \langle a^\dagger_{v,k'+q} a^\dagger_{v,k-q} a_{c,k} a_{c,k}(t) \rangle$$

(4.9)

Equation 4.7 describes the time-dependent dynamics of a coherently excited electron-hole pair: the first term on the right-hand side describes the optical coupling of a population of electrons in either the conduction or valence bands and the second term describes the many-body Coulomb interactions that modify the dynamics of the polarization. The many-body interactions couple the two-particle correlations given by $P_k(t)$ to the four-particle correlations given by $B_{k,k',q}(t)$. Furthermore, the equation of motion for the four-particle correlations depend on six-particle correlations, the six-particle correlations depend on eight-particle correlations, and so on for each order of particle correlations. The hierarchy of correlations is one of the main difficulties of calculating many-body interactions but can be overcome by considering the Hartree-Fock approximation or the coherent approximation.

### 4.1.2 Exciton correlations

The Hartree-Fock approximation assumes that correlations occur between at most two particles so that higher-order correlations can be written as products of particle
populations and the polarization correlation function. For example, a four-particle correlation \(<a_{c,k}^\dagger a_{c,k} a_{c,k'} a_{c,k'}^\dagger>\) can be rewritten to be \(P_{c,k'} n_{c,k} \). Physically, the simplification implies that the phase between a pair of particles can be correlated but the phase with other pairs of particles is averaged. The Hartree-Fock approximation results in a simplified equation of motion for the polarization:

\[
\hbar \left[ i \frac{d}{dt} - (\epsilon_c(k) - \epsilon_v(k)^\prime) \right] P_k(t) = N_k(t) d_{cv} E(t) + \sum_{q \neq k} V(k - q) P_{v,q}(t) N_k(t)
\] (4.10)

The energy of the \(\lambda\) band has been renormalized as:

\[
\epsilon_{\lambda}(k)^\prime = \epsilon_{\lambda}(k) - \sum_{q \neq k} V(k - q) n_{\lambda,q}
\] (4.11)

Under the Hartree-Fock approximation, the main effects of the Coulomb interactions are to renormalize the energies of the conduction and valence bands and to couple the polarizations with populations of electrons. Equation 4.10 describes the excited state dynamics under the assumption that four or higher-order particle correlations have no effect on the dynamics and is often also called a mean-field approximation. Equation 4.10 can be used to describe nonlinear spectroscopy experiments if experimental conditions of the optical fields are considered (e.g. pulse timings, wave vectors of optical beams, etc). In fact, Equation 4.10 is the basis for a widely used set of equations called the semiconductor Bloch equations[51] which describes the influence of Hartree-Fock interactions on the nonlinear dynamics of excitons. A more general set of equations, including the influence of four-particle correlations, will be discussed in more detail in Section 4.1.3.

In the case of a single coherent excitation (i.e. a single polarization is created between an electron in the valence band and a hole in the conduction band), Equation 4.10 can be simplified by the fact that the entire population of electrons is essentially in the valence band: \(n_{c,k}(t) = 0, n_{v,k}(t) = 1\), and \(N_k(t) = -1\). The simplification precisely describes the dynamics of an electron orbiting a positive charge, such as the hydrogen atom. This can be understood by plugging the values of the
population terms into Equation 4.10 and taking the Fourier transformation in both space and time:

$$\left[h(\omega + i\delta) - E_g + \frac{\hbar^2 \Delta^2}{2m_r} + V(r)\right] P_{sc}(r, \omega) = -d_c E(\omega) \delta(r) L^3$$ \hspace{1cm} (4.12)

The difference in energy between the conduction band and valence band has been approximated as parabolic using the effective mass approximation, \(E_c - E_v = E_g + \frac{\hbar^2 \Delta^2}{2m_r}\), where \(m_r\) is the effective mass of an electron in the conduction band and \(E_g\) is the bandgap of the semiconductor. \(L^3\) is the volume of the semiconductor crystal. Equation 4.12 describes exactly the behavior of an electron about a positive charge. Just as the case for an electron in the hydrogen atom, a single excited electron in the conduction band of a semiconductor will be bound to a hole in the valence band, decreasing its resonance energy relative to the bandgap of the semiconductor by some binding energy. Furthermore, just like the electron in a hydrogen atom, the electron can occupy higher energy orbitals of p-type symmetry, d-type symmetry, and so on until the energy of the electron is higher than the binding energy and becomes a free particle. The major differences between an electron in a hydrogen atom and an electron in an exciton are a much smaller binding energy in the semiconductor (about 10 meV in GaAs compared to 13.6 eV in hydrogen) and a larger Bohr radius for the electron in the semiconductor (about 10 nm in GaAs compared to 50 pm in hydrogen). Additionally, radiative recombination limits the lifetime of the electron in the semiconductor, on the order of 1 ns.

### 4.1.3 Two-exciton correlations

In addition to correlations between a pair of particles, Coulomb interactions also create correlations among larger numbers of particles which can also have profound influences on the excited state dynamics of semiconductor electrons. In Equation 4.7, the excited state polarization, \(P_k(t)\), depends on the four-particle correlation term, \(B_{k,k',q}(t)\). As written, however, the exact influences of the four-particle correlations are not clear. Furthermore, the time dependence of the four-particle correlation

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The term $B_{k,k',q}(t)$ can be shown to depend on a six-particle correlation term, with the time dependence of the six-particle correlation term depending on an eight-particle correlation term, and so on, with the time dependence of each correlation term found by solving the Heisenberg equation of motion. The infinite hierarchy of equations not only obscures the interpretation of Equation 4.7, but also creates an infinite number of coupled differential equations that need to be solved in order to solve for the excited state dynamics of even just $P_k(t)$.

The hierarchy of equations can be truncated using the coherent approximation. This approximation assumes that excitations in the semiconductor are excited entirely through coherent optical fields. The key simplification of this approximation is that the correlation functions can be truncated up to a certain order in the optical fields, using perturbation theory: a single light-matter interaction can only excite correlations between a single electron-hole pair, two light-matter interactions can only excite correlations between up to two electron-hole pairs, and so on. The truncation of the correlation functions limits the hierarchy of equations so that Equation 4.7 can be solved with a finite number of coupled differential equations.

The truncation scheme using the coherent approximation is called the dynamics-controlled truncation scheme (DCTS), as first derived by Axt and Stahl[11]. The derivation is also detailed in-depth by Schafer and Wegner[123] and Takayama and coworkers[134]. The main goal of these works is to describe the excited state dynamics at the level of third-order nonlinear spectroscopy in which two nonconjugate optical fields and one conjugate optical field interact with the semiconductor, as described in the previous chapter. The key results of the DCTS can be summarized as:

\[
\begin{align*}
& (i\hbar \frac{d}{dt} - \epsilon_{1s} - i\gamma_{1s}) \tilde{P}^{(3)}_{\pm}(t) = \tilde{d}_{1s} E(t) A_{PSF} \tilde{P}^{(1)}_{\pm}(t) \tilde{P}^{(1)}_{\pm}(t) \\
& \quad + V_{HF} \tilde{P}^{(1)}_{\pm}(t) \tilde{P}^{(1)}_{\pm}(t) \tilde{P}^{(1)}_{\pm}(t) \\
& \quad + 2 \tilde{P}^{(1)}_{\pm}(t) \int_{-\infty}^{+\infty} dt' G^+(t-t') \tilde{P}^{(1)}_{\pm}(t') \tilde{P}^{(1)}_{\pm}(t') \\
& \quad + \tilde{P}^{(1)}_{\pm}(t) \int_{-\infty}^{+\infty} dt' [G^+(t-t') + G^-(t-t')] \\
& \quad \tilde{P}^{(1)}_{\pm}(t') \tilde{P}^{(1)}_{\pm}(t') \quad (4.13)
\end{align*}
\]

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Equation 4.13 is written in the exciton basis set: the polarization \( \bar{P}_n \) is composed of the solutions to the homogeneous portion of Equation 4.10 with the form \( \bar{P}_n = \sum_k \phi_n(k) P_k \). To simplify the equation, all exciton states except for the 1s exciton state are ignored. In this case, the only possible excitations are the spin up and spin down 1s exciton, given by the subscripts ±. The spin up and spin down exciton states are a result of the possible spin configurations of the electron in the conduction band. \( \epsilon_{1s} \) and \( \gamma_{1s} \) are the 1s exciton energy and dephasing rate. The dephasing is added phenomenologically. \( A^{PSF} \) is a phase-space filling constant that accounts for saturation of the semiconductor bands and arises because the polarizations are written in the exciton basis set.

The final three terms, \( V_{HF} \), \( G^+(t-t') \), and \( G^-(t-t') \) are Coulomb coupling terms written in the exciton basis. \( V_{HF} \) describes the uncorrelated interaction among exciton polarizations; it is the Hartree-Fock interaction discussed in the previous section but weighted for the interaction among 1s excitons instead of electron-hole pairs. \( V_{HF} \) is given by:

\[
V_{HF} = \sum_{k,q} V(k - q)|\phi(k)|^2 \phi(q)(\phi(k)^* - \phi(q)^*) \tag{4.14}
\]

Finally, the two integrals on the right hand side of Equation 4.13 give the contribution of the two-exciton correlations. Instead of writing a separate differential equation for the two-exciton correlation function, the two-exciton correlations are written in terms of a Green's function that correlates two exciton polarizations, with the Green's function accounting for all the Coulomb interactions that couple the composite electron and holes of each of the excitons. The key advantage of the DCTS is the ability to formulate the two-exciton correlations in a closed form, without a dependence of higher-order correlations, such that the two-exciton correlations can be written in the form \( B(t) = \int G(t-t')P(t')P(t') \). A full derivation of the (approximate) Green's functions, starting from the differential equations for the two-exciton correlations, can be found in the previously cited references [11, 123, 134].

Equation 4.13 can be used to derive the third-order susceptibility, \( \chi^{(3)} \), of the semiconductor material. Using perturbation theory, as described in the previous
chapter, the first-order and third-order polarizations are given by $P^{(1)} = \chi^{(1)} E(\omega)$ and $P^{(3)} = \chi^{(3)} E(\omega) E(\omega) E^*(\omega)$, respectively. These definitions suggest that taking the Fourier transformation of Equation 4.13 and writing the terms for $P^{(1)}(\omega)$ in terms of $\chi^{(1)} E(\omega)$ can give an equation for $\chi^{(3)}$. The full derivation is detailed by Kwong and coworkers\cite{Kwong2020} and the results are:

$$\chi^{(3)}(\omega_a, \omega_b, \omega_c) = -\frac{\chi^{(1)}(\omega_a) \chi^{(1)}(\omega_b) \chi^{(1)}(\omega_c) \chi^{(1)}(\omega_a + \omega_b - \omega_c)}{|d_{ls}|^4}$$

$$\times \left[ \delta_+ G^{PSF}(\omega_a, \omega_b) + T_m(\omega_a + \omega_b) \right]$$

(4.15)

where $\chi^{(1)}(\omega)$ is the first-order exciton susceptibility:

$$\chi^{(1)}(\omega) = -\frac{|d_{ls}|^2}{\hbar \omega - \epsilon_{ls} + i\gamma_{ls}}$$

(4.16)

Each first-order exciton susceptibility depends on a separate frequency domain, given by the variable $\omega_i$, which are related to the experimentally observed frequency variable, $\omega$ given by the equation for the third-order polarization in the frequency domain:

$$P^{(3)}_L(\omega) = \frac{1}{(2\pi)^2} \sum_{m,n,p} \int d\omega_a d\omega_b d\omega_c \delta(\omega_a + \omega_b - \omega_c - \omega) \chi^{(3)}_{lmnp}(\omega_a, \omega_b, \omega_c)$$

$$\times E(\omega_a) E(\omega_b) E^*(\omega_c)$$

(4.17)

Again, the exciton resonances that are considered are the spin up and spin down 1s exciton states. The third-order susceptibility is labeled with the index $\pm$, representing the susceptibility that gives the third-order polarizations of the singlet, $-$ and triplet, $+$, configurations. Because the spin is assumed to be conserved, excitation of the triplet configuration implies that all four excitations are of the same spin and excitation of the singlet configuration implies that two spins are opposite the other two spins. The phase space filling term, $G_{PSF}$, only contributes to the triplet configuration, given by the delta function, $\delta_+$, because the saturation of one spin state
does not saturate the other spin state. $G_{PSF}$ is given by:

$$G_{PSF} = |d_{1s}|^2 \left[ \frac{1}{\chi^{(1)}(\omega_a)} + \frac{1}{\chi^{(1)}(\omega_b)} \right]$$  \hspace{1cm} (4.18)

Multiplied with the first-order susceptibility terms, the phase space filling term is just the third-order susceptibility of a material with a resonance at the $1s$ exciton resonance frequency.

The last term, $T_\pm(\omega_a + \omega_b)$, gives the Coulomb interactions and depends on the spin configuration:

$$T_+(\omega_a + \omega_b) = V^{HF} + 2G_+(\omega_a + \omega_b)$$  \hspace{1cm} (4.19)

$$T_-(\omega_a + \omega_b) = G_+(\omega_a + \omega_b) + G_-(\omega_a + \omega_b)$$  \hspace{1cm} (4.20)

The matrices $T_\pm(\omega_a + \omega_b)$ are just the Fourier transformations of the Green's functions of Equation 4.13, with the Hartree-Fock term added to the Green's function of the triplet configuration so that all Coulomb interactions are captured by the $T_\pm(\omega_a + \omega_b)$ matrices. The $T_\pm(\omega_a + \omega_b)$ matrices couple the two excitons excited by the first two optical fields which oscillate in the frequency space given by the variables $\omega_a$ and $\omega_b$. The frequency dependence of $G_\pm(\omega_a + \omega_b)$ is the result of the time-dependence of the two-exciton correlation function, given by $G_\pm(t - t')$. Because the Hartree-Fock term describes only uncorrelated interactions, $V^{HF}$ is independent of time and frequency. Based on Equation 4.15, $\chi^{(3)}$ has contributions from phase-space filling, mean-field Coulomb repulsion, and two-exciton Coulomb correlations in the same-spin configuration but only contributions from two-exciton Coulomb correlations in the spin-paired configuration.

The frequency dependence of $T_\pm$ depends significantly on the spin configuration. The matrices were calculated by Takayama, Kwong, and coworkers using material parameters reflecting GaAs\cite{134, 79} considering only the $1s$ exciton. The figures are reproduced in Figure 4-1. There is a sharp peak in the imaginary part of $T_-$ at the biexciton resonance, approximately 2 meV below twice the bare exciton resonance\cite{79}, and a continuum of states at higher energies representing the unbound biexciton.
states. The real part of $T_-$ shows the dispersive shape characteristic of a resonance at the biexciton energy. $T_+$ features no bound biexciton state and its magnitude increases with frequency beginning at roughly twice the bare exciton energy. In the imaginary parts of both $T_+$ and $T_-$, the continuum correlations can increase the dephasing of exciton polarizations which can be understood with a density of states argument: the larger density of states at higher energies provides more pathways for scattering into different states which, in turn, causes exciton polarizations to dephase. The real part of the two matrices can cause renormalizations of the exciton energies which can occur even at two-exciton energies without a large density of states: two exciton polarizations can interact with each, shifting the energies of each other, without scattering to other exciton states.

The calculations of correlations among six or more particles have been limited in scope. The calculations of six-particle correlations that have been reported so far have focused on an incoherent contribution to the six-particle correlations. Specifically, the calculations have considered the possibility of transitions between an incoherent population and two correlated excitons. The calculations did not include coherent six-particle correlations, which would be the analog of the four-particle (or two-exciton) correlations described in Figure 4-1. As a result, the possibility of triexciton correlations or unbound three-exciton correlations has not been confirmed theoretically.

4.1.4 Calculation of 2D spectra using the DCTS

A full 2D spectrum can be calculated using the third-order susceptibility, Equation 4.15, in the equation for the third-order polarization, Equation 4.17, and varying the time delay of specific optical fields. A time delay, $\tau$, of the optical fields is given by a linear phase sweep in the frequency domain:

$$E(\omega) = g(\omega) \exp[i(\omega - \omega_{carrier})\tau]$$  \hspace{1cm} (4.21)
Figure 4-1: Imaginary (top) and real (bottom) parts of the two-exciton interaction matrix, $T_{\pm}$, that determines the Coulomb-mediated interactions of two excitons. The solid black lines represent the interactions between two excitons in the singlet configuration ($T_{+}$) and the dashed blue lines represent the interactions between two excitons in the triplet configuration ($T_{-}$). The frequency-dependence of the interaction matrices (and corresponding time-dependence of the Fourier transformation of the interaction matrices) give the interactions that correlate the dynamics of two exciton polarizations, as opposed to Hartree-Fock (i.e. mean-field) interactions. The interaction matrices are normalized by the Bohr radius of the exciton, $a_0$. 
where $\omega_{\text{carrier}}$ is a carrier frequency that sets the center of the phase sweep and $g(\omega)$ is the Gaussian envelope of the pulse. The time delays of pulses can be chosen based on the time delays needed for the 2D spectra: in rephasing 2D spectra the conjugate field arrives first, $E(\omega_c)$ in Equation 4.17, while in two-quantum 2D spectra, the nonconjugate fields arrive first, $E(\omega_a)$ and $E(\omega_b)$ in Equation 4.17. Fourier transformation along the scanned time delay dimension gives a full 2D spectrum.

Rephasing and two-quantum 2D spectra are shown in Figures 4-2 and 4-3 with and without different many-body contributions. The rephasing 2D spectra show the usual absorptive peak without many-body interactions. No two-quantum signal is calculated without many-body interactions. The Hartree-Fock interactions and triplet correlations cause the peak in the rephasing spectra to have a dispersive shape. Both interactions give two-quantum signal, which also have a dispersive shape for both types of interactions. The fact that both Hartree-Fock interactions and the full triplet correlations give similar 2D spectra might not be too surprising given the two-exciton interaction matrix, $T_+$, in Figure 4-1; the frequency dependence of the triplet interactions is relatively weak at energies below the two-exciton sum frequency indicating that the interactions among two excitons in the triplet configuration at low energies are mostly uncorrelated. The contributions of the singlet interactions cause a red-shifted shoulder to appear in the 2D spectrum due to the biexciton and a bound biexciton peak to appear in the two-quantum 2D spectra. The biexciton peak appears below a peak at exactly twice the exciton energy due to the unbound interactions between two excitons in the singlet configuration. As can be seen, 2DS is an important tool to probe many-body interactions because the signatures of different types of interactions can be readily identified.
Figure 4-2: Calculated real parts of rephasing 2D spectra using the dynamics-controlled truncation scheme including only the phase-space filling terms (a), only the Hartree-Fock interactions among excitons of the same spin (b), the fully correlated interactions among excitons of the same spin (c), and the fully correlated interactions among excitons of different spins (d). The colorbar in (d) applies for all 2D spectra.
Figure 4-3: Calculated real parts of two-quantum 2D spectra using the dynamicscontrolled truncation scheme including only the Hartree-Fock interactions among excitons of the same spin (a), the fully correlated interactions among excitons of the same spin (b), and the fully correlated interactions among excitons of different spins (c). The colorbar in (c) applies for all 2D spectra. Note that the bound biexciton signals in (c) are relatively weak compared to the unbound interactions.

4.2 Phenomenological theory of many-body interactions

Because of the complexity of the microscopic many-body theory, a phenomenological model based on the optical-Bloch equations (OBE), which were introduced in Chapter 2, has been widely utilized to explain the influence of many-body interactions on nonlinear spectroscopy: the modified optical Bloch equations (MOBE). The MOBE treat a semiconductor as a simple N-level system, with the number of levels determined by the number of bound exciton and multiexciton states to be considered, and includes phenomenological terms to represent many-body interactions. While a microscopic calculation provides detail about many-body interactions that a phenomenological model cannot, such as the two-exciton Green’s function discussed in Section 4.1.3, the phenomenological model still allows one to identify the signatures of specific many-body interactions such as excitation-induced shifts (EIS), excitation-induced dephasing (EID), local field effects (LFE), and bound multiexciton states. As a result, the MOBE have been widely utilized to understand the nonlinear dynamics of semiconductor excitons[76, 155, 15, 17, 127, 108, 125, 88, 132].
In this section, the MOBE are derived starting from the basis set of a four-level system, to account for the possibility of up to a bound triexciton state. The derivation largely follows the procedure for the derivation of the optical Bloch equations in Chapter 2 except that more energy levels are included, to account for triexciton states, and phenomenological terms are added to account for many-body interactions. Differential equations are derived that describe the exciton polarization. The exciton polarizations will be expanded in terms of the wave vector of the excitation fields to account for the phase matching conditions used in nonlinear spectroscopy experiments. Phase matching conditions will be considered that describe experimental conditions of up to fifth-order nonlinear spectroscopy experiments. As in third-order nonlinear spectroscopy, many-body interactions can dramatically modify the line shapes, frequencies, and phases of peaks in fifth-order nonlinear spectroscopy. However, as discussed in Section 4.1.3, microscopic calculations of fifth-order signal are even more difficult than third-order microscopic calculations and Green’s functions for three-exciton correlations have not been calculated. As shown in the next chapter, the fifth-order MOBE are a useful model to understand the many-body interactions of unbound correlations in fifth-order 2D spectroscopy.

4.2.1 Derivation of coupled equations of motion

A four-level Hamiltonian is used to represent the ground (g), exciton (X), biexciton (BX), and triexciton (TX) states. Optical transitions are allowed between states with ±1 number of electron-hole pairs composing the states.

\[
H = -i \begin{bmatrix}
0 & \Omega(t) - i\gamma_X & 0 & 0 \\
\Omega^*(t) - i\gamma_X & \epsilon_X - i\Gamma_X & \Omega(t) - i\gamma_{BX} & 0 \\
0 & \Omega^*(t) - i\gamma_{BX} & \epsilon_{BX} - i\Gamma_{BX} & \Omega(t) - i\gamma_{TX} \\
0 & 0 & \Omega^*(t) - i\gamma_{TX} & \epsilon_{TX} - i\Gamma_{TX}
\end{bmatrix}
\]  \hspace{1cm} (4.22)

where \(\epsilon_n\), \(\gamma_n\), and \(\Gamma_n\) represent the energy, dephasing rate, and lifetime of the \(n = X, BX, \text{and } TX\) states. \(\Omega(t)\) represents the electric field interaction with the system,
given by the multiplication of the dipole moment of the transition, \( d_{nm} \), and the electric field \( E(t) \).

Using Equation 4.22, coupled differential equations for the 4 x 4 elements of the density matrix, \( \rho \), can be derived using the Liouville equation as outlined in Section 2.1.3. The resulting differential equations for the population terms, \( n_a \), and coherence terms, \( p_{ab} \), are identical to population and coherence terms derived in Section 2.1.3: \( n_a \) and \( p_{ab} \) are given by Equations 2.16 and 2.17, respectively. The differential equations can be used to describe fifth-order nonlinear spectroscopy by expanding the density matrix in terms of the wave vector of the optical field and isolating the terms that contribute to the signal in the fifth-order direction[91], just as the OBE terms were expanded in Section 2.1.3. The wave vectors of the excitation fields are assumed to be in a two-beam geometry (i.e. \( 3k_2 - 2k_1 \) for fifth-order spectroscopy experiments), and represented as \( K \pm k \).

The derivation so far has followed exactly as the third-order OBE in Chapter 2 except the density matrix terms of higher spatial expansion order, up to \( M = 5 \), are included in the equations. In theory, there are 16 density matrix elements that are each expanded to the fifth order resulting in 80 coupled differential equations. However, only a subset of these equations are nonzero with the initial condition \( n_g = 1 \) and all other density matrix elements equal to zero. To the zeroth order in the field, only \( n_{g,0} \neq 0 \). To the first order in the field, \( n_{g,0} \Omega(t) \) and \(-n_{g,0} \Omega^*(t)\) act as source terms for \( p_{12,\pm 1} \) and \( p_{21,\pm 1} \), respectively. Thus, a hierarchy of density matrix elements is formed, where lower order terms (with respect to \( k \)) act as sources for higher order terms. This is visualized in Figure 4-4. As an example, the differential equations for the fifth order terms \( p_{Xg,5} \), \( p_{BX,5} \), and \( p_{TB,5} \) are:

\[
\frac{d}{dt}p_{Xg,5} = [-\gamma_{Xg} + i\omega_{Xg}]p_{Xg,5} + id \cdot [-E^\dagger(t) \cdot p_{BS,4} - E(t) \cdot n_{g,4} + E^\ast(t) \cdot n_{X,4}] \quad (4.23)
\]
Figure 4-4: Hierarchy of differential equations for signal in positive k-directions, originally published in [143]. Lower order terms act as source terms for higher order terms. Solid (dashed) lines represent multiplication of lower order terms with \(d \cdot E_+ (t)\) \((d \cdot E_- (t)\) before addition (black lines) or subtraction (red lines) to differential equation of higher order term. Differential equations for signal in negative k-directions are represented by the same figure except solid (dashed) lines represent multiplication by \(d \cdot E_- (t)\) \((d \cdot E_+ (t)\) and all elements have negative k-indices (e.g. \(p_{gX,-1}\) instead of \(p_{gX,1}\)).
Many-body interactions may be included in the Bloch equations by adding phenomenological terms to represent LFE, Eis, and EID. Local fields, due to polarizations of neighboring excitons, act as a density-dependent source term. Local field interactions in the MOBE are equivalent to the Hartree-Fock interactions in the DCTS; the LFE couple polarizations in an uncorrelated fashion. The relationship between the local field term in the MOBE and the Hartree-Fock term in the DCTS has been formally derived by Kwong and coworkers[78]. Here, only first-order polarizations are considered as sources for LFE. The spatial Fourier expansion coefficients of the first-order polarizations, K + k and K − k, are equivalent to the Fourier coefficients of the E+ and E− fields, respectively, and act as sources if E+ or E− are sources. LFE are therefore included by redefining the electric field to be:

\[ \Omega(t) = \Omega^{\text{laser}}(t) + \Omega^{\text{LFE}}(t) \]  

where \( \Omega^{\text{laser}}(t) = \mu \cdot E_-(t) e^{i(K-k)R} + \mu \cdot E_+(t) e^{i(K+k)R} \), with \( \mu \) the transition dipole matrix, and \( \Omega^{\text{LFE}} \) is given by:

\[ \Omega^{\text{LFE}}(t) = dN \left( dp_{12,-1} e^{i(K-k)R} + dp_{12,1} e^{i(K+k)R} \right) \]

\( N \) is the excitation density and \( l \) is the Lorentz field parameter. To simplify algebra, the electric and local fields are grouped according to wave vector direction:

\[ \Omega(t) = \Omega_+(t) + \Omega_-(t) \]
EIS and EID can be included in the MOBE by including density-dependent phenomenological constants that modify the real and imaginary parts of the equations of motion, respectively. The EIS and EID terms can be used to approximate changes in the dynamics due to correlated Coulomb coupling. However, as discussed below, the EIS and EID terms do not actually correlate exciton coherences in the MOBE. The phenomenological constants, $\omega'$ and $\gamma'$, are multiplied with the calculated exciton density to capture the EIS and EID interactions. To the right side of Equation 2.17, the EIS and EID terms are added with a term $\frac{d}{dt}E_{\text{EI}}$:

$$\frac{d}{dt}E_{\text{EI}} = (\gamma' + i\omega')N \sum_{\sigma = X,B,T} n_{c_r} p_{ab}$$

(4.29)

The spatial Fourier expansions of the density matrix elements, Equations 2.18 and 2.19, must be inserted into 4.29. Populations with wave vector $k = r$, $n_{c_r}$, couple with polarizations with wave vector $k = q - r$, $p_{ab,q-r}$, and act as source terms for polarization with wave vector $k = q$, $p_{ab,q}$:

$$\frac{d}{dt}E_{\text{EI}}' = (\gamma' + i\omega')N \sum_{\sigma = X,B,T} n_{c_r} p_{ab,q-r}$$

(4.30)

Note that in a fifth order experiment, $n_{T,r}$ is zero for all orders of $k$ so the summation is effectively over $c = X, B$. Proper selection of $n_{c_r}$ and $p_{ab,q-r}$ is a tedious but straightforward algebraic exercise.

By solving Equation 4.29 up to the order desired, the nonlinear signal of any order can be calculated with arbitrarily defined excitation fields. For example, we can calculate the third-order nonlinear signal by solving the following differential equations:

$$\frac{d}{dt}P_{Xg}^{(3)} = [-\gamma_{Xg} + i\omega_{Xg}]P_{Xg}^{(3)} + i\mu \cdot \left[ E_{-}^{*}(t)P_{Bg}^{(2)} + E_{+}(t) \left( n_{g}^{(2)} - n_{X}^{(2)} \right) \right] + (\gamma' + i\omega')N n_{X,2} p_{Xg,1}$$

(4.31)

$$\frac{d}{dt}P_{BX}^{(3)} = [-\gamma_{BX} + i(\omega_{Bg} - \omega_{Xg})]P_{BX}^{(3)} + i\mu \cdot \left[ -E_{-}^{*}(t)P_{Bg}^{(2)} + E_{+}(t)n_{X}^{(2)} \right]$$

(4.32)
\[
\frac{d}{dt} n_g^{(2)} = -\Gamma_g n_g^{(2)} + i\mu \cdot \left[ E_+^*(t)p_{Xg}^{(1)} - E_+(t)p_{Xg}^{(1)*} \right]
\]  
(4.33)

\[
\frac{d}{dt} n_X^{(2)} = -\Gamma_g n_X^{(2)} + i\mu \cdot \left[ -E_-^*(t)p_{Xg}^{(1)} + E_-(t)p_{Xg}^{(1)*} \right]
\]  
(4.34)

\[
\frac{d}{dt} p_{Bg}^{(2)} = \left[ -\gamma_{Bg} + i\omega_{Bg} \right] p_{Bg}^{(2)} + i\mu \cdot E_+(t)p_{Xg}^{(1)}
\]  
(4.35)

\[
\frac{d}{dt} p_{Xg}^{(1)} = \left[ -\gamma_{Xg} + i\omega_{Xg} \right] p_{Xg}^{(1)} + i\mu \cdot E_+(t)n_g^{(0)}
\]  
(4.36)

And the complete equation for the fifth-order exciton polarization \( p_{Xg,5} \) is:

\[
\frac{d}{dt} p_{Xg,5} = \left[ -\gamma_{Xg} + i\omega_{Xg} \right] p_{Xg,5} + id \cdot \left[ -\Omega_+(t) \cdot p_{Bg,4} - \Omega_-^*(t) \cdot n_{g,4} \right] + \Omega_+^*(t) \cdot n_{X,4} + (\gamma' + i\omega')N(n_{X,4}p_{Xg,1} + n_{B,4}p_{Xg,1} + n_{X,2}p_{Xg,3}) + n_{B,2}p_{Xg,3}
\]  
(4.37)

which depends on fourth-order terms as well as the third-order terms.

A simplified version of the final form of the differential equations may be informative. Coherences are of the form:

\[
\frac{d}{dt} p = \left[ -\left( \gamma + \gamma'N \sum n_A \right) + i \left( \omega + \omega'N \sum n_A \right) \right] p + i \left( \sum n_A + \sum p_B \right) \Omega(t)
\]  
(4.38)

Populations are of the form:

\[
\frac{d}{dt} n = -\Gamma n + i \sum p_A \Omega(t)
\]  
(4.39)

where indices \( A \) and \( B \) keep track of state indices and spatial expansion coefficients and the summations are over all possible states that are allowed under the Hamiltonian (Equation 4.22) and under the spatial Fourier expansion. The simplified equations show that LFE act similarly to electric fields. The EID and EIS terms provide density-dependent modifications to the real and imaginary parts, respectively, of coherences. The LFE and EIS influence the differential equation for the coherence in a similar fashion; both terms multiply a coherence term with a population term and influence the real part of the equation. This result is the same for third-order MOBE
Extended to the fifth order, the MOBE contain more states and terms that couple the differential equations, but the physical intuition of the equations remains largely the same.

4.2.2 Calculation of 2D spectra using the MOBE

Third-order rephasing and two-quantum 2D spectra can be calculated using Equations 4.31 to 4.36 and varying the time ordering of the pulses appropriately: the nonconjugate optical field, $E_+$, arrives first in the two-quantum scan and the conjugate optical field, $E_-$, arrives first in the rephasing scan. Fourier transformation of the scanned time gives a full 2D spectrum.

Third-order rephasing and two-quantum 2D spectra with and without various many-body interactions are shown in Figures 4.2.2 and 4.2.2. Without many-body interactions, the calculations are of a simple two-level system (2LS) which gives an absorptive peak in the rephasing 2D spectrum and no two-quantum signal. The inclusion of EIS causes the rephasing peak to become dispersive, much like the Hartree-Fock interactions and triplet correlations caused the rephasing peak to become dispersive. The main effect of the EID term is to cause elongation of the exciton peak in the scanned dimension. Both EIS and EID terms cause two-quantum signal to appear at exactly twice the exciton energy, indicating unbound interactions between two excitons. Finally, inclusion of a biexciton state causes a red-shifted shoulder to appear in the rephasing 2D spectrum and a bound biexciton state in the two-quantum 2D spectrum. Unlike the 2D spectrum calculated using the DCTS, there are no unbound two-exciton coherences in the calculations of the biexciton but they can be included by adding EIS or EID terms into the differential equations that include the biexciton.

4.2.3 Microscopic origins of phenomenological terms

The relationship between the DCTS and the MOBE is not obvious. The MOBE are useful because of the separation of the many-body interactions into the LFE, EID, and EIS terms but the relationships among these terms and the Coulomb interac-
Figure 4-5: Calculated real parts of rephasing 2D spectra using the modified optical Bloch equations including no many-body interactions (a), excitation-induced shift (b), excitation-induced dephasing (c), and a biexciton state (d). Local field effects give similar results as excitation-induced shift.

Figure 4-6: Calculated real parts of two-quantum 2D spectra using the modified optical Bloch equations including excitation-induced shift (a), excitation-induced dephasing (b), and a biexciton state (c).
tions derived in the microscopic calculations, governed by the $G_\pm$ and $V_{HF}$ terms in Equations 4.13 and 4.15, are not clear. The relationship between the two models is particularly confusing because there are no mechanisms in the MOBE to correlate coherences (i.e. mechanisms that would cause the time dependence of one coherence to be modified by another coherence with a time-dependent coupling term such as the Green's functions in the DCTS).

Although the phenomenological terms do not capture the physical picture of correlated excitons, the LFE, EIS, and EID terms are able to replicate changes in the energy, phase, and dephasing by fine tuning the phenomenological constants to match the experiment. The MOBE allows one to fine tune shifts in both the real and imaginary parts of exciton coherences by changing the LFE, EIS, and EID terms. These terms can then be used to change the phases, energies, and dephasing rates of the coherences. Generally, the LFE and EIS terms modify the phases and energies of the exciton coherences and the EID term modifies the dephasing rates. Furthermore, interactions that cause exciton coherences to form bound multiexciton states are added phenomenologically in the initial Hamiltonian used to derive the MOBE, Equation 4.22, by including higher-lying excited states. In the DCTS, shifts in the phases, energies, and dephasing rates are all accounted for in the Hartree-Fock term and Green's function; the ability to tune the real and imaginary parts of the Coulomb coupling is not possible. Additionally, the bound biexciton coherence is a result of the time-dependent correlations governed by the singlet Green's function. Because the MOBE do not actually include correlations among excitons, the MOBE cannot be used to identify whether Coulomb interactions occur through correlations or Hartree-Fock interactions. The formal mathematical relationship between the DCTS and the MOBE was derived by Kwong and coworkers[78].

4.3 Conclusions

Both microscopic and phenomenological theories can be used to describe many-body interactions in semiconductor materials. The microscopic theory, derived from the
semiconductor Hamiltonian, accounts for correlated interactions among excitons, but
the equations are fairly complex and difficult to calculate. The microscopic equa-
tions can be simplified through the Hartree-Fock approximation, which neglects the
correlated interactions among excitons. Phenomenological theories approximate the
semiconductor as a simple N-level system and incorporate many-body interactions as
phenomenological constants that represent excitation-induced dephasing, excitation-
induced shift, and local field effects. The phenomenological equations are much
simpler to derive and calculate but cannot distinguish between correlated and un-
correlated interactions. However, as will be shown in the next chapter, either the
microscopic or phenomenological models can be used to distinguish different types of
many-body interactions in two-dimensional spectra.
Chapter 5

Many-body interactions in semiconductor quantum wells probed by two-dimensional spectroscopy

Since 2005, two-dimensional spectroscopy (2DS) has been utilized to identify and understand the mechanisms of exciton many-body interactions. The advantages of 2DS permit the clear identification of many-body interactions in the exciton nonlinear dynamics. As discussed in Chapter 2, the key advancements of 2DS include the direct resolution of multiple-quantum coherences, the detection of both the real and imaginary parts of nonlinear optical signals, and the resolution of cross-peaks that readily identify coupling between states. All of these advantages help identify how Coulomb interactions affect the exciton nonlinear dynamics. Furthermore, because different many-body interactions produce different spectral signatures in 2D spectra, the contributions of different types of interactions can be identified; as discussed in Chapter 4, the types of many-body interactions originate from both uncorrelated interactions (called Hartree-Fock or mean-field interactions) and correlated interactions, which are strongly dependent on the exciton spin configuration. These
interactions cause effects such as excitation-induced shift (EIS), excitation-induced dephasing (EID), local field effects (LFE), and bound multiexciton states, which are the many-body interactions usually included in phenomenological models.

2DS of many-body interactions has mainly been focused on the interactions in semiconductor QWs. As discussed in Chapter 1, semiconductor QWs are thin layers of semiconductor materials such that the exciton wavefunction is confined in one-dimension. QWs are an ideal platform to study many-body correlations because high quality samples can be fabricated using molecular beam epitaxy and the confinement in one dimension can split the energy of the heavy-hole (H) and light-hole (L) exciton states. Additionally, propagation effects of the optical fields are generally not observed in QWs because the optical fields generally propagate in a direction normal to the plane of the QW. Propagation effects in bulk semiconductor samples that could complicate the analysis of many-body correlations include distortions of the spectral lineshapes[161], cascaded nonlinear signals[18, 145], and bulk polariton effects[105, 124]. As discussed in Chapter 6, polariton effects may strongly influence the many-body interactions.

This chapter discusses the use of 2DS to study many-body interactions in GaAs QWs. Section 5.1.2 discusses the nonlinear spectroscopy of many-body interactions using one-dimensional spectroscopy. Section 5.2 discusses the many-body interactions that contribute to the single exciton nonlinear dynamics. The different contributions are identified by taking correlation spectra of exciton states. By varying the population time of the correlation spectra, the time dependence of each of these contributions is resolved[144]. The results indicate that the coherent approximation made in both the microscopic and phenomenological models is too limiting: incoherent exciton populations also play an important role in the nonlinear exciton dynamics. Section 5.3 discusses the 2DS of bound multiexciton states. Bound biexciton and triexciton coherences are directly resolved in multiple-quantum 2D spectra. Finally, Section 5.4 discusses the interactions that result in unbound two-exciton coherences. Two-quantum rephasing 2D spectra are used to identify the inhomogeneous and homogeneous dephasing times of the two-exciton coherences[143]. Non-perturbative
power-dependent effects on the two-exciton interactions are also identified. In all of the experiments described, 2D spectra of gallium arsenide (GaAs) QWs are recorded using the methods and sample structure described in Chapter 2.

5.1 Nonlinear spectroscopy of gallium arsenide quantum wells

5.1.1 Energy levels of gallium arsenide quantum wells

The two lowest energy exciton states in GaAs QWs, the H and L exciton states, arise from the energy splitting of states with different angular momentum. The total angular momentum of an electron in the conduction band (CB), \( J_e \), or a hole in the valence band (VB), \( J_h \), is given by \( J = L + s \), with the orbital angular momentum of the particle, \( p \), given by \( L \) and the spin of the particle given by \( s \). Both electrons and holes have a spin of \( \pm \frac{1}{2} \). The orbital angular momentum of the electron or hole depends on the symmetry of the CB or VB, respectively. The lowest energy CB state is of s-type symmetry so that the only possible orbital angular momentum state for the electron is \( |L_e| = 0 \) and the total angular momentum of the electron is given by \( |J_e| = \frac{1}{2} \). The possible angular momentum states of the electron are \( m_j^e \) = \( \pm \frac{1}{2} \). The highest energy VB state is of p-type symmetry so that the possible orbital angular momentum states for the hole are given by \( |L_h| \in \{1,0\} \) and the total angular momentum of the hole is given by \( |J_h| \in \{\frac{3}{2}, \frac{1}{2}\} \). Holes with total angular momentum of \( |J_h| = \frac{1}{2} \) are energetically separated from holes with total angular momentum of \( |J_h| = \frac{3}{2} \) by about 0.5 eV and are not considered in this dissertation. Holes with total angular momentum \( |J_h| = \frac{3}{2} \) can have angular momentum of \( m_j^h = \pm \frac{3}{2} \) and \( \pm \frac{1}{2} \). Due to the one-dimensional confinement of the QW structure, the particles have a finite momentum that split the \( m_j^h = \pm \frac{3}{2} \) and the \( m_j^h = \pm \frac{1}{2} \) angular momentum states, giving the heavy-hole and light-hole bands. A representation of the band structure is shown in Figure 5-1a.

Optical transition selection rules are given by the change in angular momentum.
Promotion of an electron from $m^h_j = \pm \frac{3}{2}$ to $m^e_j = \pm \frac{1}{2}$ results in a change of angular momentum of $\mp 1$, which can be excited by the two circular polarizations of light. By convention, the transition requiring a change of angular momentum of $+1$ can be excited by right-circularly polarized light. Therefore, the electron residing in the $m^e_j = +\frac{1}{2}$ is excited by left-circularly polarized light. On the other hand, the promotion of an electron from $m^h_j = \pm \frac{1}{2}$ to $m^e_j = \pm \frac{1}{2}$ results in a change of angular momentum of $\pm 1$. Therefore, the excitation of an electron from either H or L states into the CB state with the same angular momentum requires light of opposite circular polarizations. Co-circularly polarized light excites electrons from the H and L states into different angular momentum states in the CB. This is most easily seen in Figure 5-1b which gives the energy states at $k = 0$.

As discussed in Section 4.1.2, an electron that is promoted from the VB to the CB forms a bound exciton state with the hole left in the VB. A common representation is the exciton basis set, shown in Figure 5-1c, where the ground state is given by a full VB and empty CB and the excited states are exciton states composed of one electron and one hole in different combinations of angular momentum states. Using the notation $(m^h_j, m^e_j)$, the H exciton spin up and spin down states are $(+\frac{3}{2}, +\frac{1}{2})$ and $(-\frac{3}{2}, -\frac{1}{2})$, respectively, and the L exciton spin up and spin down states are $(+\frac{1}{2}, -\frac{1}{2})$ and $(-\frac{1}{2}, +\frac{1}{2})$.

5.1.2 One dimensional four-wave mixing of many-body interactions in quantum wells

Two seminal experiments using four-wave mixing (FWM) demonstrated the importance of many-body interactions in semiconductor QWs[70, 86, 157]. In both experiments, optical pulses with wave vectors $k_a$ and $k_b$ were used to generate nonlinear signal in the direction $2k_b - k_a$. As discussed in Chapter 2, the third-order signal in the direction $2k_b - k_a$ is generated by two interactions with the optical pulse at $k_b$ and one interaction with the optical pulse at $k_a$. The nonlinear excitation can be thought of as a self-diffraction process; the interference of the optical fields at $k_a$ and
Figure 5-1: (a) A schematic of the energy band structure of gallium arsenide. The lowest two states are the heavy-hole (H) and light-hole (L) states in the valence band, given by the black and blue lines, respectively. The highest energy state is the lowest energy conduction band. The angular momentum of each state is given by $m_j$. (b) Energy states and optical transition selection rules for zero in-plane momentum. The red, dashed (blue, solid) arrows represent right-circularly (left-circularly) polarized light. (c) Energy states and optical transition selection rules in the exciton basis set. The H and L spin states are composed of electron and hole pairs in various angular momentum states, as defined in the text.

$k_b$ generate an excitation grating which the optical field at $k_b$ can scatter off of, into the signal direction at $2k_b-k_a$. Signal should not be generated if the optical pulse at $k_b$ arrives before the pulse at $k_a$: the excitation grating is formed after the field at $k_b$ has already left the sample. Furthermore, the intensity of the diffracted light should decrease with time as the excitations created by the optical fields decay. However, neither of these predictions are true in semiconductor QWs: FWM signals are generated even if the pulse at $k_b$ arrives first and, even when the pulse at $k_b$ arrives last, the maximum intensity of the FWM signal field is delayed with respect to the optical pulse at $k_b$. Both of these results are summarized in the Figure 5-2.

The signal at negative times and the delay in the signal intensity are a result of many-body interactions. Not only can the optical pulse at $k_b$ scatter off of the excitation grating, but polarizations excited by the pulse at $k_b$ can also scatter off the grating if the polarizations are coupled to the excitation grating. The coupling in GaAs QWs can occur through Coulomb interactions or LFE. If the pulse at $k_b$ arrives before the pulse at $k_a$ but within the dephasing times of the polarizations,
the polarizations excited by $k_b$ can create an excitation grating with the polarizations created by $k_a$ and scatter off the excitation grating into the signal direction. The signal at negative time delays can also arise from the excitation of biexciton coherences; the two interactions at $k_b$ excite a two-photon transition into a biexciton coherence with the ground state and the third pulse at $k_a$ generates a single-quantum coherence that emits third-order signal at $2k_b - k_a$. Finally, if the pulse at $k_a$ arrives first, the scattering of the polarizations excited by the pulse at $k_b$ can give rise to a delay in the signal intensity relative to the time that the pulse at $k_b$ arrives at the sample.

The initial FWM experiments on QWs clearly demonstrated the importance of many-body interactions on the nonlinear dynamics of excitons. However, the ideal experiment would identify how each of the types of many-body interactions, in either the microscopic or phenomenological models, contributes to the nonlinear dynamics of the excitons. As shown below, the 2DS of semiconductor QWs can clearly resolve key signatures of various many-body interactions such as Hartree-Fock and correlation contributions in the microscopic picture and EIS, EID, and LFE contributions in the phenomenological picture.

Figure 5-2: A sketch of the time-integrated four-wave mixing signal as a function of the delay between excitation pulses[86] (a) and the time-resolved four-wave mixing signal at a fixed delay between excitation pulses[70, 157] (b) of a simple two level system (2LS, wide gray lines) and of a gallium arsenide quantum well (QW, thin black lines).
5.2 Two-dimensional spectroscopy of exciton states

The first 2DS experiments of GaAs QWs focused on understanding the contributions of different many-body interactions to the coherent nonlinear dynamics of excitons using third-order rephasing and nonrephasing 2D spectra[22, 88, 160, 162]. In particular, 2DS proved fruitful in identifying the many-body interactions that can couple H and L exciton coherences[162], cause scattering from free-carriers into both H and L exciton coherences[22], and shift the phase of exciton coherences[88]. Furthermore, the specific types of many-body interactions that cause these effects could be identified by comparison to theoretical models.

The signatures of many-body interactions in 2D spectra depend strongly on the polarizations of the excitation fields, as expected from the discussion of many-body interactions in Chapter 4. A natural basis set to understand the different contributions of many-body interactions is the set of spin up and spin down states because the interactions can be separated for excitons of different spins or of the same spin. Therefore, the focus of this chapter will be on polarization conditions that can separate the same-spin interactions and the different spin interactions (triplet and singlet interactions, respectively, for the case of only two excitons). As will be discussed in the next section, the main effect of interactions between excitons of different spin, bound multiexciton states, can be easily observed using multiple-quantum 2DS with cross-circularly polarized optical fields. Interactions between excitons of the same spin will be the focus of this section. In particular, the many-body interactions that contribute to the co-circular 2D correlation spectra will be discussed. Because 2D correlation spectra permit unambiguous identification of the real and imaginary lineshapes in the 2D spectra (see Chapter 2), the correlation spectra will clearly show the contribution of many-body interactions to the phase of the exciton coherence. Furthermore, by varying the population time, the time dependence of different many-body interactions can be studied.

All optical fields were co-circularly polarized so that a single spin state of the H exciton was excited and a single spin state of the L exciton was excited, but with
opposite spin to the H exciton. These two states do not share a common ground state. The optical beams were in the BOXCARS geometry, with excitation pulses in the $k_a$, $k_b$, and $k_c$ directions and the reference and signal beams were in the $k_a + k_b - k_c$ direction. Pulses were 100 fs and centered around the L resonance so that both resonances were excited.

2D correlation spectra were collected by summing rephasing and nonrephasing 2D spectra. Rephasing (nonrephasing) 2D spectra were collected by sending an optical pulse in the $k_c$ ($k_a$) direction to the sample first, followed by sending an optical pulse in the $k_a$ ($k_c$) direction after a variable delay time, $\tau_1$. The first two optical pulses excited populations of H and L excitons (assuming no coupling between the two exciton states) that existed during another variable delay time, $\tau_2$, before the third optical pulse, in the $k_b$ direction, interacted with the sample. The population delay time, $\tau_2$ was varied by sending the last excitation pulse and the reference pulse to a delay stage. The full electric field of the signal was collected by overlapping the signal field with the reference field in a spectrometer. Fourier transformation of the signal with respect to $\tau_i$ gives rephasing and nonrephasing 2D spectra as a function of specified population times. All of the 2D spectra were also collected by collaborators at JILA using a setup where all delays were introduced by actively phase stabilized delay stages.

The real part of the correlation spectra with a population time of 0.2 ps is reported in Figure 5-3. There are four main peaks: two diagonal peaks representing the excitation and emission of the same exciton state, either H or L, and two cross peaks representing the excitation and emission of different exciton states. The diagonal peaks are labeled by H and L to designate the excitation and emission from the same exciton state. Because H and L states are of opposite spin, the cross-peaks labeled by $X'$ and $X''$ cannot be described by Feynman pathways; the two states are not coupled by a common ground or excited state. Finally, the continuum scattering also cannot be described by Feynman pathways as discussed below.

The correlation spectra in Figure 5-3 show three features that cannot be explained without the consideration of many-body interactions. First, the H diagonal peak has
Figure 5-3: Real part of correlation 2D spectra with a population time of 0.2 ps. The labels H and L correspond to the excitation and emission from the same exciton state, either the heavy-hole (H) or light-hole (L) exciton. The labels X and X' represent coupled peaks between the heavy hole and light hole exciton states due to many-body interactions. The labels CS represent continuum scattering into the exciton states, also due to many-body interactions.

a dispersive shape instead of the usual absorptive feature expected for the real part of the 2D spectra. Second, there are vertical stripes representing the excitation of a continuum of high energy carriers emitting at both the H and L energies. Finally, there are cross peaks between the H and L states even though these states should be uncoupled when all optical fields are co-circularly polarized. All three of these features can be explained by comparing the results to either the microscopic or phenomenological theories.

The phase shift of the H diagonal peak was due to the uncorrelated coupling to other excitons. As shown in Section 4.1, the change from an absorptive to a dispersive lineshape can be accounted for in 2D spectra by including only Hartree-Fock interactions: the uncorrelated interaction between two excitons of the same spin caused the phase shift in the exciton coherence. In the phenomenological model, the phase shift can be accounted for by modifying the real part of the exciton differential equation, Equation 4.31, using the EIS term. Considering both the DCTS and MOBE models, the phase shift can be understood as a modification to the real part of the coherent exciton time evolution due to the uncorrelated coupling with other exciton coherences. The phase shift has been previously observed in rephasing 2D spectra and compared to MOBE and DCTS calculations[88, 162].
The cross peaks and the continuum scattering were due to correlated interactions. Unlike the 2D spectra calculated in Sections 4.1 and 4.2, the L exciton and the free carriers must be included in the calculations to account for the cross peaks and the continuum scattering, respectively. Calculations that include a continuum of free-carrier states, in either the DCTS[162] or the MOBE[22] models, can account for the continuum scattering by considering the two-exciton triplet correlations in the DCTS model and EID in the MOBE model. The triplet two-exciton correlations are also needed to observe the cross peaks in calculated 2D spectra[162]. In contrast to the phase shift of the H diagonal peak, the interactions between different exciton states and the free carriers were correlated and characterized by a modification to the imaginary part of the coherent exciton time evolution.

The relative importance of correlations between the different exciton states and the free carriers can be understood by considering the triplet two-exciton correlation functions (see Section 4.1.3). In the triplet configuration, the interactions between two exciton polarizations (or carrier polarizations) are more strongly correlated as the energies of the polarizations increase. As already discussed, the increase in correlation strength occurs because of the higher densities of states: the imaginary part of the correlation function corresponds to excitation-induced dephasing and increases as the number of states increases because the polarizations can scatter into a larger number of states. The interactions between two H excitons are far enough in energy away from the continuum of states that the correlations that cause EID do not play a large role in their dynamics. However, the interactions involving L excitons and free carriers, which are energetically closer to the continuum of states, are correlated and give rise to EID.

The time dependence of the different many-body interactions was studied by varying the population time of the correlation spectra, as shown in Figures 5-4. The phase shift of the H diagonal peak decayed on the order of the dephasing time of the H exciton (10 ps) while the continuum scattering and the cross peaks only decreased in amplitude by half for the maximum population time used in the experiment (35 ps). Based on either the DCTS or the MOBE, the decay of the phase shift on the order
of the dephasing time is expected. In either model, the coherent limit is assumed: interactions occur between polarizations and all population terms are written in the coherent limit (i.e. $n \propto p(t)p^*(t)$). Any interaction that occurs in either model decays on the time scale of the dephasing rate. The longer lived features (the continuum scattering and the cross peaks) indicate that there were incoherent contributions to the many-body interactions that are not accounted for in the coherent models.

As the exciton and free carriers dephase, the coherences can turn into incoherent populations. The long lifetime of the cross peaks and the continuum scattering indicate that the incoherent population can also cause coupling between carriers and exciton states. The result clearly shows the need to develop models that include incoherent contributions to the many-body interactions in exciton nonlinear dynamics.

### 5.3 Two-dimensional spectroscopy of bound multiexciton states

The 2DS of GaAs QWs has also been used to study bound multiexciton states. Two excitons in the singlet configuration can bind to form a biexciton, similar to the binding of two hydrogen atoms into a hydrogen molecule. In the DCTS, the correlations between two excitons in the singlet configuration cause the energy lowering of the two excitons into the biexciton state (Figure 4-1). Similar calculations of three-exciton correlations, or correlations of even higher numbers of excitons, have not been
The multiexciton states can be directly probed by multiple-quantum 2DS. As discussed in Chapter 2, all optical beams must be phase stable so that a number of field interactions, \(N\), can create a \(N\)-quantum coherence with the ground state that can be converted into a single quantum coherence with \(N-1\) additional fields. FWM, six-wave mixing, and eight-wave mixing can be used to study biexciton, triexciton, and even quadexciton coherences, respectively.

The first direct observation of the biexciton coherence was reported by Stone and coworkers\[132\] using two-quantum 2DS based on FWM. The real parts of the 2D spectra were subsequently reported\[60, 133\]. In these experiments, two cross-circularly polarized pulses were used to excite a biexciton coherence, composed of two H excitons, with the ground state. A third optical pulse was used to convert the two-quantum coherence into a one-quantum coherence. As the time between the first two pulses and the third pulse was varied, the biexciton coherence oscillated at a frequency slightly less than twice the frequency of a single H exciton due to the binding energy of the biexciton state. Fourier transformation of the signal with respect to this time delay directly gives the biexciton coherence energy. The real part of the calculated 2D spectrum using the DCTS is reproduced in Figure 5-5, zoomed into the region of interest. There are two main peaks, with different line shapes: an unbound two-exciton coherence with a dispersive line shape (indicative of EIS type interactions, as discussed in Section 5.2) and a biexciton coherence shifted slightly below the unbound coherence with an absorptive line shape. The experimental real 2D spectrum\[60, 133\] match the theoretical real 2D spectra in Figure 5-5 although the magnitude of the unbound two-exciton coherence is much weaker in the first report of the biexciton coherence\[132\]. The measured biexciton binding energy was 0.9 ± 0.2 meV\[132\]. The results clearly indicate the correlation of the H excitons into a biexciton coherence. 2D spectra using co-circular polarization conditions also showed a bound mixed biexciton coherence between a H exciton and a L exciton with a binding energy of 1.42 ± 0.41 meV\[60, 132, 133\]. A biexciton between two L excitons was not observed, perhaps because the signal for the L exciton is generally...
Figure 5-5: Theoretical real part of a two-quantum 2D spectrum. The calculations include the singlet correlated interactions and are based on the dynamics-controlled truncation scheme (see Section 4.1). The feature labeled U is the unbound two-exciton coherence with a dispersive lineshape and the feature labeled B is the bound biexciton coherence with an absorptive line shape.

much weaker due to the smaller transition moment.

The existence of a bound triexciton coherence was confirmed using three-quantum 2DS based on six-wave mixing[140]. In these experiments, the self diffraction phase matching geometry was used to detect signals in the fifth-order direction: three interactions with an optical field in the direction $k_b$ excite a three-quantum coherence with the ground state before two interactions with an optical field in the direction $k_a$ convert the three-quantum coherence into a one-quantum coherence that emits signal. Again, the Fourier transform of the time period between the first three interactions and the last two interactions gives the oscillation frequencies of the three-quantum coherences. Using collinearly polarized optical fields, a peak was observed at $1.7 \pm 0.2$ meV less than the energy of three $H$ excitons. The results indicate that the additional interaction of a third exciton with two others can lower the energy of all three excitons into a correlated triexciton. Triexciton coherences between all possible combinations of $H$ and $L$ excitons were also observed: a HHL triexciton, with a binding energy $1.8 \pm 0.2$ meV, a HLL triexciton, with a binding energy $2.4 \pm 0.3$ meV, and even a LLL triexciton, with a binding energy $2.4 \pm 0.4$ meV were all observed. Furthermore, unbound coherences (other than continuum scattering into the exciton states) were not observed in either collinearly polarized or co-circularly polarized excitation conditions. One possible explanation of this result is that the correlations between bound

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multiexciton states are removed energetically from the continuum of free carrier states that would induce decoherence and decouple the unbound three-exciton coherences. Theoretical calculations of triexciton correlations have not yet been reported (see Section 4.1.3).

Finally, four-quantum 2DS was attempted using eight-wave mixing[140]. The self-diffraction geometry was again used, but the signal was detected in the seventh-order direction. In this experiment, the only signal detected in the 2D spectra using either co-circular or collinear polarization conditions was the continuum scattering indicating that four excitons do not bind into a quadexciton.

5.4 Two-dimensional spectroscopy of unbound exciton correlations

The interactions that give rise to unbound two-exciton coherences are an important contribution to exciton nonlinear dynamics; the unbound interactions are the only source of many-body interactions between two excitons of the same spin and can be the dominant source of interactions between two excitons of different spins[60, 133]. The unbound two-exciton coherences appear at exactly twice the H and L exciton energies and have a dispersive line shape in the real part of the 2D spectra. The dispersive line shape can be accounted for entirely by including Hartree-Fock interactions, which are uncorrelated Coulomb interactions, in calculations of the two-quantum 2D spectra (see Section 4.1.3).

The homogeneous and inhomogeneous dephasing of the unbound two-exciton coherences can be studied using rephasing measurements of the two-quantum coherence, the fifth-order extension of single-quantum rephasing measurements. The two-quantum rephasing measurement can be accomplished using the self-diffraction geometry: two interactions with an optical field in the direction $k_b$ excite a two-quantum coherence in the sample which is converted into a single-quantum coherence by three interactions with an optical field in the direction $k_a$ and the signal is collected in
the $3k_a - 2k_b$ direction. Two-quantum coherences oscillate during the time between the first two interactions and the last three interactions with a frequency opposite in sign relative to the frequencies of single-quantum coherences that oscillate after the last field interaction. As a result, just like in third-order rephasing 2D spectra, the homogeneous and inhomogeneous linewidths will be separated along the diagonal and antidiagonal parts of the 2D spectra. In the experiments described in this section, however, the first two optical field interactions were split into two different wave vectors, $k_{a1}$ and $k_{a2}$, so that the excitation and reference beams formed a Y-shape, shown in Figure 5-6. The advantage of this phase matching geometry is the ability to uniquely control the polarization conditions and timing of the first two interactions.

The real part of the two-exciton rephasing 2D spectrum is shown in Figure 5-7a for low excitation fluences ($1 \mu J/cm^2$). The spectrum features a single peak at exactly twice the H exciton energy with a dispersive line shape, consistent with previous measurements of the two-exciton coherence using third-order two-quantum 2D$S[60, 133]$. The dispersive lineshape indicates that the coherence is mediated by uncorrelated Hartree-Fock Coulomb interactions. Furthermore, the peak is elongated along the diagonal: the diagonal linewidth is 3.6 meV and the antidiagonal linewidth is 1.0 meV. The diagonal linewidth gives a measure of the inhomogeneity of the two-exciton coherences due to fluctuations in the quantum well width. At higher excitation fluences (up to 25 $\mu J/cm^2$), the antidiagonal linewidth increases while the diagonal linewidth remains the same, as shown in Figure 5-7b. The ratio of the antidiagonal linewidth over the diagonal linewidth is plotted in Figure 5-7c for a range of excitation fluences and varies from about 0.3 to 0.6. The changes in the line shape are somewhat expected: inhomogeneity should remain constant, so that the diagonal linewidth is constant, while an increased density of excitons should increase scattering between carriers which should increase the homogeneous dephasing. Finally, a blue shift of
Figure 5-7: Real part of rephasing two-quantum 2D spectra at an excitation fluence of 1 μJ/cm² (a) and 25 μJ/cm² (b). All excitation field are co-circularly polarized so that all excitons have the same spin. The ratio of the antidiagonal linewidth over the diagonal linewidth as a function of excitation fluence is shown in (c).
about 1 meV in the exciton energy is observed.

From the power dependence of the lineshape in the 2D spectra, it is clear that there are contributions to the dynamics of two-exciton coherences that depend on greater than fifth-order field interactions. One possible source of the change in lineshape, for example, could be populations of excitons excited by each optical field that contribute to the blue shift and dephasing of the two-exciton coherence. Each optical field can excite a population of excitons through two interactions, one interaction with the nonconjugate component and one interaction with the conjugate component, so that the net wave vector of the excitation is zero and the signal is still emitted in the fifth-order direction. In addition, as the exciton coherences are driven to higher energies, the possibility arises that the types of interactions between the excitons might change, particularly as the exciton energy becomes closer to the energy of the continuum of states where the correlated interactions that cause EID are more significant (see Section 4.1). Models based on the DCTS are not capable of explaining these power-dependent effects because the equations are based on third-order interactions with the optical fields. However, the MOBE can be used to study the power-dependent phenomena as the equations were spatially expanded using the wave vectors of the optical fields, not truncated up to any order in the field interactions.¹

In order to calculate two-quantum rephasing 2D spectra, the MOBE were solved up to the fifth order in the wave vector, as derived in Section 4.2. The biexciton and triexciton states were not included in the calculations because the bound multiexciton states were not excited in the co-circular polarization conditions of the experiment. Each spectrum was calculated by solving the set of coupled differential equations using an adaptive Runge-Kutta algorithm in approximately 15 minutes on a PC that had a 2 GHz processor and 2 Gb RAM. The two-quantum time dimension was calculated in 500 steps over 10 ps while the emission time dimension was calculated in about 1000 steps over 50 ps. The adaptive algorithm uses small (large) time steps when

¹The equations derived in Section 4.2 were truncated by wave vector so that excitation terms in the directions of seventh order or higher were ignored. These terms should have a much smaller contribution to the fifth-order signal than the population terms that can be excited through only two field interactions.
Figure 5-8: Real part of calculated two-quantum rephasing 2D spectra at an excitation density roughly matching the excitation fluence of 1 µJoule/cm² (a) and 10 µJoule/cm² (b). The calculations include mostly EIS (\(\omega' = 5 \times 10^{-24} \text{THz/m}^3\)) but do include some EID (\(\gamma' = 0.5 \times 10^{-24} \text{THz/m}^3\)) for both 2D spectra.

The oscillation amplitude is large (small), so the emission dimension was interpolated to a linear spaced time axis after the signal was computed. The resulting time-time matrix was fast Fourier transformed to yield the 2D spectrum.

The calculated two-quantum rephasing spectra are shown in Figure 5-8 for two different excitation densities, which were matched to the experimental excitation fluences of roughly 1 µJ/cm³ and 10 µJ/cm³. In both calculations the EIS and EID parameters, \(\omega'\) and \(\gamma'\), were kept at values of \(\omega' = 5 \times 10^{-24} \text{THz/m}^3\) and \(\gamma' = 0.5 \times 10^{-24} \text{THz/m}^3\). Both spectra compare well to the experimental two-quantum rephasing spectra in Figure 5-7. In particular, the blue-shift and elongation of the anti-diagonal features are qualitatively reproduced. The dispersive line shape at both powers is accounted for by mostly EIS interactions. The small contribution of the EID term causes the vertical elongation of the node. The constant values of the EIS and EID terms suggest that the types of many-body interactions contributing to the two-exciton coherences remain constant, at least for the fluences used in this experiment. The calculations also show that the interactions can be largely characterized as EIS for all excitation fluences studied.
5.5 Conclusions

Two-dimensional Fourier-transform optical spectroscopy has led to significant progress in understanding the origins and effects of Coulomb interactions in gallium arsenide quantum wells. Specific many-body contributions to the nonlinear exciton dynamics can be identified by the direct resolution of coupled states, multiexciton coherences, inhomogeneous and homogeneous dephasing, and phases of exciton coherences. With the aid of both microscopic and phenomenological theories, the origins of many-body contributions can be identified. Two results presented in this chapter, however, suggest limitations to common theoretical models. First, by resolving the time-dependence of different many-body contributions to correlation 2D spectra, Coulomb interactions were shown to persist for times much longer than the exciton coherence times. This result indicates that Coulomb interactions with incoherent populations of excitons, which are neglected in most theoretical models, can contribute to the nonlinear exciton dynamics. Second, by isolating the homogeneous dephasing times of two-exciton coherences, the interactions between two excitons were shown to have a higher-order dependence on the excitation fields, at only moderate field strengths. This result indicates that theories based on perturbation theory may not adequately account for the effects of many-body interactions in exciton nonlinear dynamics.

As suggested by the results above, the understanding of many-body interactions is still far from complete. In particular, despite the difficulty of developing theoretical models, many-body interactions in gallium arsenide quantum wells are relatively well studied compared to other nanostructures and materials. For example, biexciton states in quantum dots are split in energy due to the three dimensional confinement in quantum dots. Because of the large inhomogeneous distribution found in most colloidal quantum dot samples, even just the relative energy ordering of biexciton states is unknown. By separating the homogenous and inhomogeneous linewidths, 2D spectroscopy could help map out the biexciton energy structure. Another area that requires more research is how many-body interactions might be controlled. As discussed in the next two chapters, engineering of the semiconductor nanostructure
and strong coupling to optical fields both have profound effects on many-body interactions, and could lead the way toward controlling many-body interactions.
Exciton-polaritons in semiconductor microcavities

Exciton-polaritons are exciton polarizations that are strongly coupled to optical fields. The strong coupling results in a hybridized state between the optical field and the excitons; exciton-polaritons have characteristics of both excitons and optical fields. In bulk semiconductor materials, exciton-polaritons can be formed between optical fields that propagate through the bulk material and the exciton polarizations in the path of the field[53, 54, 47]. Exciton-polaritons can also be formed in two-dimensional, one-dimensional, and zero-dimensional semiconductor nanostructures when a microcavity is used to confine optical fields around the material. Using a microcavity, exciton-polaritons have been formed with quantum wells (QWs)[156], micropillars[158], and quantum dots[113]. Exciton-polaritons have also been formed in organic materials using a microcavity[89]. Regardless of the material platform, the evidence for an exciton-polariton state usually comes from changes in the linear spectra of the material. Specifically, the energies of the excitons and optical fields split into lower and higher energy modes. The strong coupling between optical fields and excitons can also have profound influence on the nonlinear dynamics; the scattering of exciton-polaritons with each other and with phonons are dramatically different from that of excitons with each other and with phonons.

In this chapter, the polariton states in semiconductor microcavities are derived.
This chapter, and the remaining chapters of this dissertation, focus entirely on the exciton-polariton states formed between exciton states in QWs and the cavity field in semiconductor microcavities. The polariton states will be derived using two approaches to describe the strong coupling between the exciton resonance in the QW and the confined optical fields in the microcavity. In Section 6.1.1, a semiclassical approach is described where the cavity optical fields drive polarizations in the QW. The oscillations of the optical fields and the polarizations become strongly coupled, described through Maxwell's equation. In Section 6.1.2, a full quantum mechanical approach to the strong coupling is described, with the cavity fields treated as quantized photons. The polariton states are found by diagonalizing the Hamiltonian that describes both the exciton and cavity photon states. In both the semiclassical and quantum derivations, nonlinear interactions between carriers and the interaction between phonons and carriers are neglected. The interactions between carriers will be discussed in Chapter 7 and the interactions between carriers and phonons will be discussed in Chapter 8. Finally, in Section 6.2, two semiconductor microcavity samples are discussed. Optical measurements of the linear properties of these two samples are also presented, clearly showing evidence for the formation of exciton-polariton states.

The semiconductor microcavity structures discussed in this chapter are composed of two distributed Bragg reflectors (DBRs) that are fabricated around QWs. DBRs are multiple stacks of alternating material, that are very efficient mirrors due to the interference of reflected and transmitted light off of the alternating layers of material. Optical fields that are resonant with an exciton state of the QWs can be trapped between the two DBRs by engineering the distance between the two DBRs so that the optical fields can form a standing wave in the cavity. The QWs are embedded in bulk semiconductor materials that are used as spacers so that the QWs can be precisely positioned at the antinodes of the confined optical fields, maximizing the coupling between the optical field and the exciton state of the QWs. The absorption energy of the spacer semiconductor material is generally much higher than the energy of the exciton or cavity modes so that light is not absorbed by the bulk material. The structure of a typical semiconductor microcavity is shown in Figure 6-1. In the
Figure 6-1: Structure of a semiconductor microcavity, drawn to scale except for the thickness of the quantum well. The normal direction is the growth direction and the parallel direction is one of the dimensions parallel to the plane of the quantum well (QW). The distributed Bragg reflectors (DBRs) are composed of fourteen alternating layers of GaAs/AlAs (white and gray stripes), with refractive indices of roughly 3.6/3.0. Each layer is a length equal to $\lambda/4$, where $\lambda$ is the optical wavelength that is resonant with the exciton mode of the QW (blue stripe) at the center of the microcavity. The cavity length is equal to $\lambda/2$ and composed of GaAs, with the single QW placed at the center of the cavity such that the QW is at an antinode of a standing wave of the resonant optical field (see inset, where the red line shows the relative field amplitude as a function of position). The resonance wavelength is 850 nm in the figure.

figure, the microcavity has a length given by $\lambda/2$ and a single QW is embedded at the antinode.

6.1 Derivations of exciton-polariton states in semiconductor microcavities

6.1.1 Semiclassical description of exciton-polaritons in semiconductor microcavities

The semiclassical description of exciton-polaritons treats the optical field as a classical wave and the exciton mode as a quantum state of the QWs. The propagation of an optical field through the semiconductor microcavity structure is governed by the wave
equation:

\[ \frac{n^2(z, \omega) \omega^2}{c^2} + \frac{\partial^2}{\partial z^2} E(z, \omega) = -4\pi \frac{\omega^2}{c^2} P(z, \omega) \]  

(6.1)

where the propagation direction, \( z \), is in the direction of the optical field. The index of refraction, \( n(z, \omega) \), depends on the properties of each layer of material in the microcavity. Equation 6.1 is the frequency domain version of the wave equation given by Equation 2.2. Polarizations in a material, \( P(z, \omega) \), act as source terms for electric fields, \( E(z, \omega) \). The vector notation of \( E(z, \omega) \) and \( P(z, \omega) \) has been suppressed for simplicity but the orientation of \( P(z, \omega) \) is given by the polarization of \( E(z, \omega) \), neglecting any nonlinear processes. Except for the QWs, all materials in the semiconductor microcavity are assumed not to have a resonant response to the optical fields so that the frequency dependence of \( n(z, \omega) \) can be neglected and \( P(z, \omega) \) is zero. Under the conditions of nonresonant optical fields, a general solution to the wave equation is the sum of right, \( E^+(z, \omega) \), and left, \( E^-(z, \omega) \), propagating waves:

\[ E(z, \omega) = E^+(z, \omega) + E^-(z, \omega). \]  

(6.2)

Given an arbitrarily defined initial field of a form given by Equation 6.2, \( E(0, \omega) = E^+(0, \omega) + E^-(0, \omega) \), the propagation of optical fields through the semiconductor microcavity can be solved using transfer matrix methods[65]. In transfer matrix methods, the change in the optical fields that travels a distance, \( a \), can be found by multiplying a vector of the right and left going fields with a propagation matrix \( M_a \):

\[ \begin{bmatrix} E^+(0, \omega) \\ E^-(0, \omega) \end{bmatrix} = \begin{bmatrix} M_a & 0 \\ 0 & M_a \end{bmatrix} \begin{bmatrix} E^+(a, \omega) \\ E^-(a, \omega) \end{bmatrix} \]  

(6.3)

For the propagation of optical fields through a layer of material with a refractive index \( n \), the change in the optical fields is given by a phase change acquired from the propagation over the length of the material. In this case, the transfer matrix \( M_a \) is given by:

\[ M_{\text{prop}} = \begin{bmatrix} e^{ika} & 0 \\ 0 & e^{-ika} \end{bmatrix} \]  

(6.4)
If the optical field crosses an interface, where materials of refractive indices \( n_1 \) and \( n_2 \) are on either side of the interface, the reflection and transmission of the field through the interface must be considered. The transfer matrix can be found to be:

\[
M_{\text{int}} = \frac{1}{2n_2} \begin{bmatrix} n_1 + n_2 & n_2 - n_1 \\ n_2 - n_1 & n_1 + n_2 \end{bmatrix}
\]  

(6.5)

The transfer matrix matrix method is summarized in Figure 6-2a. Using the propagation and interface transfer matrices, \( M_{\text{prop}} \) and \( M_{\text{int}} \), the total propagation of optical fields across a semiconductor microcavity structure without QWs can be solved by multiplying transfer matrices in the order that an incident optical field propagates through the structure. The total transfer matrix, \( M_{\text{tot}} \), is given by:

\[
M_{\text{tot}} = \prod_j M_j
\]  

(6.6)

where the product is over all the layers of the semiconductor microcavity structure.

The reflection and transmission of optical fields through a DBR and the entire microcavity structure are shown in Figures 6-3a and 6-3b. In the calculations, the DBRs are composed of alternating layers of GaAs and AlAs, with refractive indices of \( n_{\text{GaAs}} = 3.59 \) and \( n_{\text{AlAs}} = 2.98 \). The thickness of each layer is \( \lambda_{\text{DBR}}/4 \), where \( \lambda_{\text{DBR}} \) is the wavelength of light that is optimally reflected by the DBR. A single pass through one \( \lambda_{\text{DBR}}/4 \) layer of the DBR causes an optical field to acquire a phase shift of \( \pi/2 \), as can be confirmed with \( M_{\text{prop}} \). In addition, a reflection off of the interface of a layer with higher refractive index causes a phase shift of \( \pi \), as can be confirmed with \( M_{\text{int}} \) for an optical field propagating initially in only one direction. As shown in Figure 6-2b, the reflections off of a two-layered DBR will be in phase. The analysis can be extended to show that the transmission through the DBR destructively interferes. By increasing the number of layers, a DBR reflects optical fields with nearly 100% efficiency over a frequency range called the stop band due to the constructive (destructive) interference of reflected (transmitted) light from all the layers in the DBR. The stop band is centered at a frequency corresponding to \( \omega_{\text{DBR}} = c/\lambda_{\text{DBR}} \).
Figure 6-2: (a) Schematic illustration showing the transfer matrix method. Right and left going optical fields ($E^+(x)$ and $E^-(x)$) are propagated in a material using a propagation matrix $M_{\text{prop}}$. The propagation across an interface is calculated using $M_{\text{int}}$. (b) A schematic illustration showing a simple semiconductor microcavity, where a pair of layers, with refractive indices $n_1$ and $n_2$, act as a Bragg reflector on either side of a cavity, with refractive index $n_1$. $n_2$ is greater than $n_1$ so that a reflection off the front face of a $n_2$ layer gives a $\pi$ phase shift. The layers in the Bragg reflector are a length $\lambda/4$ and the cavity length is $\lambda/2$, where $\lambda$ is the wavelength of light incident on the sample (blue arrows). As a result, a single pass through a layer in the Bragg reflector near normal incidence results in a $\pi/4$ phase shift and a single pass through the cavity near normal incidence results in a $\pi/2$ phase shift. The angle of the incident light is exaggerated to clearly show the reflections. The reflected light components off the first Bragg reflector are all in phase (with phases of 0, $\pi$, and 3$\pi$) and the light components off the second Bragg reflector are in phase with each other (with phases of 4$\pi$, 6$\pi$, and 8$\pi$) but out of phase with the reflections from the first Bragg reflector. The interference between the two Bragg reflectors gives the cavity mode.
In Figure 6-3, $\lambda_{\text{DBR}} = 850$ nm. Beyond either side of the stop band are dips in the reflection where light can leak through the DBR. The bandwidth of the stopband increases with the number of DBR layers.

In the microcavity, a transmissive mode exists, where the wavelength of the mode is given by the standing wave that can form in the cavity. The condition to form a standing wave is that the wavelength of the optical field must have nodes or antinodes given by the length of the cavity (i.e. $L = m\frac{\lambda}{2}$, where $L$ is the cavity length, $m$ is a positive integer and $\lambda$ is the wavelength of the optical field). An optical field that satisfies the standing wave condition, propagates through the cavity, and reflects off the second DBR. The light reflected from the second DBR has a phase that is shifted by $\pi$, or an odd integer multiple of $\pi$, relative to optical fields that are reflected from the first DBR. Therefore, the optical fields that reflect off the first and second DBRs in a microcavity structure will interfere destructively, creating a dip in the reflection spectrum. The destructive interference between the reflections off the front and back DBRs is shown schematically in Figure 6-2b. The analysis can be extended to show that the transmission through the microcavity will constructively interfere for optical fields that satisfy the standing wave condition.

The mode that transmits through the microcavity, with frequency $\omega_c$, is called the cavity mode. The linewidth of the cavity mode, $\delta\omega_c$, gives a measure of the range in frequency around which some degree of destructive (constructive) interference occurs between light reflected off (transmitted through) the two DBRs. The quality of the microcavity, called the Q-factor, is given by:

$$Q = \frac{\omega_c}{\delta\omega_c}. \quad (6.7)$$

The Q-factor can also be thought of as time that light is trapped inside the cavity before most of the light leaks out of the cavity. The Q-factor increases as the DBR reflectively goes to 100%.

The propagation of optical fields through the QWs in the semiconductor microcavity must include the resonant responses of the exciton states of the QWs, which cause
Figure 6-3: The calculated reflection (R, black) and transmission (T, red) of a distributed Bragg reflector (a) and a model semiconductor microcavity without a quantum well (b) and with a quantum well (c). In all three calculations, the structure matches the microcavity in Figure 6-1, where the Bragg reflector is only one of the reflectors in the figure (e.g. the first fourteen pairs of layers). The Bragg reflector is nearly 100% reflective around 350 THz, the center of its stop band region. In the microcavity without a quantum well, a single transmissive peak is calculated representing the cavity mode. Two transmissive peaks are calculated when the quantum well is included in the microcavity. The transmissive peaks in the microcavity are magnified in Figure 6-4.
optical fields to drive polarizations in the QWs and are a source of optical fields in the wave equation (Equation 6.1). As described in Chapter 2, the polarization is simply given by the multiplication of the optical field with the first-order susceptibility:

\[ P(z, \omega) = \frac{1}{4\pi} \chi^{(1)}(z, \omega) E(z, \omega) \quad (6.8) \]

where \( \chi^{(1)}(z, \omega) = (1/\omega_X - \omega - i\gamma_X) \) assuming only one exciton resonance frequency for all QWs in the microcavity. \( \omega_X \) and \( \gamma_X \) are the exciton resonance frequency and dephasing time, respectively. The polarization generated at a QW can be inserted into the wave equation, Equation 6.1, to find the propagation of optical fields through the QW. The output optical fields can be found using Green’s function methods[65]. The reflection and the transmission through a single QW layer, \( r_{QW} \) and \( t_{QW} \) respectively, are given by:

\[ r_{QW}(\omega) = \frac{i\Gamma_0}{\omega_0 - \omega - i(\Gamma_0 + \gamma)} \quad (6.9) \]

and

\[ t_{QW}(\omega) = 1 + r(\omega) \quad (6.10) \]

where \( \Gamma_0 \) is the radiative lifetime of the exciton.

\( r_{QW} \) and \( t_{QW} \) can be used to find the transfer matrix that represents propagation across a QW. The propagation of an incident field across a QW can be written:

\[ M_{QW} \begin{bmatrix} 1 \\ r_{QW} \end{bmatrix} = \begin{bmatrix} t_{QW} \\ 0 \end{bmatrix} \quad (6.11) \]

However, assuming that the QW is symmetric and is surrounded identically by the same materials, the transfer matrix must also describe an incident optical field from the opposite direction:

\[ M_{QW} \begin{bmatrix} 0 \\ t_{QW} \end{bmatrix} = \begin{bmatrix} r_{QW} \\ 1 \end{bmatrix} \quad (6.12) \]
Figure 6-4: The reflection (R, black lines) and the transmission (T, red lines) of an empty semiconductor microcavity (a) and a semiconductor microcavity with a quantum well (b) are calculated using the microcavity structure in Figure 6-1. One peak is observed in the microcavity without the quantum well due to the resonance frequency of the cavity, given by the half-wavelength standing wave that is supported by the cavity length. The addition of a quantum well, with an exciton resonance wavelength equal to the cavity wavelength, causes the reflection and transmission to have two peaks representing the upper and lower polariton modes.

A transfer matrix that satisfies both Equations 6.11 and 6.12 is given by:

\[
M_{QW} = \frac{1}{t_{QW}} \begin{bmatrix} t_{QW}^2 - r_{QW}^2 & r_{QW} \\ -r_{QW} & 1 \end{bmatrix}
\]  

(6.13)

Using the transfer matrices for all the layers of the semiconductor microcavity, including \( M_{QW} \) for the QW, the propagation of optical fields through the semiconductor microcavity structure of Figure 6-1 can be solved. The results are shown in Figure 6-3c. The optical properties of a microcavity with and without a QW inside the microcavity are compared in Figure 6-4. The main effect of adding the QW into the microcavity is the splitting of the single cavity peak into two peaks representing the lower polariton (LP) and upper polariton (UP). The two polariton peaks are a result of the strong coupling between the exciton polarization and the optical fields in the cavity that drive the polarizations. The oscillatory motion of both the exciton polarizations and the optical fields are therefore coupled. The strong coupling modifies the oscillatory motions of the driven exciton polarizations into lower and higher
frequencies, giving the LP and UP frequencies.

The frequencies of the LP and the UP depend on the wave vector of the incident light due to the dispersion of the cavity mode. The quantized energy of an optical field mode that is confined in the microcavity can be written as $\hbar \omega_c = \hbar (c/n_e) \sqrt{k_\parallel^2 + k_z^2}$, where $k_\parallel$ and $k_z$ are the components of the optical wave vector parallel and perpendicular to the plane of the QW (i.e. $k_z$ is the cavity confinement direction). $k_z$ is fixed by the cavity length, $k_z = 2\pi/L_c$. The energy of the cavity mode can be approximated as:

$$\hbar \omega_c = \frac{\hbar}{n_e} \sqrt{k_\parallel^2 + k_z^2}$$

$$\approx \frac{\hbar}{n_e} k_z \left(1 + \frac{k_\parallel^2}{2k_z^2}\right) = \frac{\hbar^2 k_\parallel^2}{2m_c} + \hbar \omega_c(k_\parallel = 0) \quad (6.14)$$

where the energy at normal incidence is given by $\hbar \omega_c(k_\parallel = 0) = \hbar c/n_e L_c$ and the effective mass of the cavity is given by $m_c = \hbar n_c/c L_c$. The effective mass of the cavity is typically $10^{-5} - 10^{-4}$ times the effective mass of an exciton. The dispersion of the cavity mode causes the polariton modes to have a much smaller effective mass than an exciton in a bare QW. The energies of the LP and UP can be found precisely by solving for the allowed optical modes at oblique angles, considering the phase shift caused by the angle of the incident light[65]. However, it is much simpler to solve for the dispersion of the polariton modes using a fully quantum description of both the cavity and exciton modes so a full discussion of the polariton dispersion will be left to the next section. Finally, it is convenient to relate the wave vector of light to its angle of incidence. The relationship is given by $k_\parallel = (\omega/c)\sin(\theta)$. This relation is useful for angle-resolved optical measurements, as will be discussed extensively in Chapter 8.
6.1.2 Quantum description of exciton-polaritons in semiconductor microcavities

The quantum description of the exciton-polariton states in semiconductor microcavities begins with the Hamiltonian for the system, written in the exciton and cavity basis set:

\[ \mathcal{H} = \mathcal{H}_X + \mathcal{H}_C + \mathcal{H}_{XC} + \mathcal{H}_{ext} + \mathcal{H}_{NL} \]  \hfill (6.15)

\( \mathcal{H}_X \) and \( \mathcal{H}_C \) are the exciton and cavity mode Hamiltonians:

\[ \mathcal{H}_X = \sum_{\lambda,k} \epsilon_X(k) a_{\lambda,k}^{\dagger} a_{\lambda,k} \]  \hfill (6.16)

and

\[ \mathcal{H}_C = \sum_{\lambda,k} \epsilon_C(k) b_{\lambda,k}^{\dagger} b_{\lambda,k} \]  \hfill (6.17)

The operators \( a^{\dagger} (b^{\dagger}) \) and \( a (b) \) are the raising and lowering operators of the exciton (cavity) modes analogous to the harmonic oscillator raising and lowering operators, as discussed in Chapter 4. The energies of the exciton and cavity states are given in the effective mass approximation as \( \epsilon_n(k) = \epsilon_n(k_{\perp} = 0) + \frac{\hbar^2 k_{\perp}^2}{2m_n} \) where \( n \) is the exciton, \( X \), or cavity state, \( C \). The effective mass of the exciton is several orders of magnitude larger than the cavity effective mass so that the wave vector dependence of \( E_X(k) \) is negligible. The summation over \( \lambda \) is over the different exciton states of the QW and the corresponding polarization modes of the cavity. Assuming only the 1s exciton state, the only exciton states are the spin up and spin down states which are uncoupled if \( \mathcal{H}_{NL} \) is neglected. The only cavity polarization modes are right and left circularly polarized modes, which are also uncoupled without the nonlinear Hamiltonian, \( \mathcal{H}_{NL} \). The index \( \lambda \) will be suppressed for the remainder of this section.

The summation over \( k \) occurs over points in \( k \)-space. Because of the confinement in both the QW and the microcavity, the summation occurs over only the in-plane wave vector component, \( k_{\parallel} \), with the perpendicular wave vector component given by the QW thickness, \( k_z = \frac{2\pi}{L_{QW}} \), for the exciton state and the microcavity length,
\[ k_z = 2\pi/L_c, \] for the cavity state. The exciton and cavity modes are coupled through the \( \mathcal{H}_{XC,k} \) term, given by:

\[
\mathcal{H}_{XC} = \sum_k g_0 (b_k^+ a_k + b_k a_k^+) \tag{6.18}
\]

where \( g_0 \) is the exciton-photon dipole interaction strength. The cavity mode is coupled to external optical fields through the \( \mathcal{H}_{ext} \) term, given by:

\[
\mathcal{H}_{ext} = g_{ext} \sum_k E_{ext}(t) b_k^+ + H.c. \tag{6.19}
\]

where \( g_{ext} \) is the coupling constant between the external field, \( E_{ext}(t) \), and the cavity modes. The final term in Equation 6.15, \( \mathcal{H}_{NL} \), includes all nonlinear interactions such as Coulomb interactions and exciton-phonon interactions and will be neglected in this section.

Neglecting the external coupling and the nonlinear interaction terms, the Hamiltonian in Equation 6.15 is just a 2x2 matrix for every point in \( k \)-space with the exciton and cavity modes as the basis set. The 2x2 matrices can be diagonalized resulting in a new Hamiltonian given by:

\[
\mathcal{H} = \sum_k \epsilon_{LP}(k) P_k^+ P_k + \sum_k \epsilon_{UP}(k) Q_k^+ Q_k \tag{6.20}
\]

where the energies, \( \epsilon_{LP}(k) \) and \( \epsilon_{UP}(k) \), are the energies of the LP and the UP. The \( P_k^+ \) (\( Q_k^+ \)) and \( P_k \) (\( Q_k \)) operators are the raising and lowering operators of the LP (UP). The LP and UP operators are written in terms of the exciton and cavity raising and lowering operators as:

\[
P_k = X(k) a_k + C(k) b_k \tag{6.21}
\]

\[
Q_k = -C(k) a_k + X(k) b_k
\]

where the coefficients, \( X(k) \) and \( C(k) \), are called the exciton and cavity Hopfield coefficients\[53\]. The polariton modes are superpositions of the exciton and cavity modes.
modes, with the LP (UP) given by the constructive (destructive) addition of the exciton and cavity modes. The contributions of the exciton and cavity modes to the LP are given by the magnitudes of the exciton and cavity Hopfield coefficients squared, $|X_k|^2$ and $|C_k|^2$ respectively. The contributions of the exciton and cavity modes to the UP are given by $|C_k|^2$ and $|X_k|^2$, respectively. A LP (UP) can be qualitatively described as exciton-like (photon-like) if the exciton (cavity) Hopfield coefficient is much greater than the cavity (exciton) Hopfield coefficient. Of course, a more exciton-like LP implies a more photon-like UP.

The energies and Hopfield coefficients of the LP and UP depend on both the value of $k$ and the detuning of the cavity energy from the exciton energy. The energies of the LP and UP states are given by:

$$\epsilon_{LP,UP}(k) = \frac{1}{2} \left[ \epsilon_X(k) + \epsilon_C(k) \mp \sqrt{4g_0^2 + (\delta_e(k))^2} \right]$$  \hspace{1cm} (6.22)

The Hopfield coefficients are given by:

$$|X(k)|^2 = \frac{1}{2} \left( 1 + \frac{\delta_e(k)}{\sqrt{\delta_e(k)^2 + 4g_0^2}} \right)$$

$$|C(k)|^2 = \frac{1}{2} \left( 1 - \frac{\delta_e(k)}{\sqrt{\delta_e(k)^2 + 4g_0^2}} \right)$$  \hspace{1cm} (6.23)

where $\delta_e(k) = \epsilon_C(k) - \epsilon_X(k)$. The value of $\delta_e(k)$ at $k = 0$ is called the detuning energy. In the limit that $\delta_e(k) \gg g_0$, $|X_k|^2$ goes to one, and the LP (UP) is essentially an exciton (cavity) mode. In the opposite limit as $\delta_e(k)$ becomes a very large negative value and $|\delta_e(k)| \gg g_0$, then the LP (UP) is essentially a cavity (exciton) mode. The Hopfield coefficients and the polariton energies are plotted as functions of $k$ and $\delta_e(k = 0)$ in Figure 6-5.

At zero detuning energy, the LP and UP eigenfunctions are roughly composed of equal parts exciton and cavity modes near $k = 0$. The LP and the UP are hybrid states between the exciton and cavity modes. The difference between the two polariton states is that the energy exchange between the exciton and cavity modes is
Figure 6-5: The energies of the polariton (P, thick black lines) and uncoupled states (U, thin red lines) are shown as a function of in-plane wave vector (a) and detuning of the cavity energy from the exciton energy, $\epsilon_{\text{cavity}} - \epsilon_{\text{exciton}}$ (b). The lower polariton, upper polariton, exciton, and cavity states are labeled as LP, UP, X, and C, respectively. For the detuning curve in (b), the energies of all the states are given by the energies at $k = 0$. The magnitude of the Hopfield coefficients squared, giving the fraction of exciton or photon character in the lower polariton, are shown as a function of in-plane wave vector (c) and cavity detuning energy (d). The solid line gives the exciton fraction, $|X|^2$, and the dashed line gives the cavity fraction, $|C|^2$. 
Figure 6-6: The energy of the lower polariton as a function of both in-plane wave vector dimensions ($k_x$ and $k_y$).
in-phase for the LP and out-of-phase for the UP. Both the LP and UP dispersion curves can be fit to parabolic curves near \( k = 0 \), with effective masses several times smaller than the exciton effective mass. At larger wave vectors, however, the LP is not parabolic and has an inflection point around \( 0.25 \mu m^{-1} \) before becoming flat. This is because for \( |k| >> 0 \), the cavity energy is much higher than the exciton energy and the LP is essentially an exciton mode. The UP is essentially a cavity mode at high wave vectors and its shape remains parabolic. The wave vector dependence of the LP and UP character is reflected in the wave vector dependence of the Hopfield coefficients (Figure 6-5c).

The polariton energies exhibit the typical anticrossing behavior of strongly coupled systems as a function of \( \delta_r(k = 0) \): the energies of the LP and UP are split by a minimum separation when \( \delta_r(k = 0) = 0 \), and the LP and UP tend to the energies of the exciton and cavity modes at large values of \( |\delta_r(k = 0)| \). The minimum energy separation at \( \delta_r(k = 0) = 0 \) is called the Rabi energy, \( \Omega_R \), and is given by \( \Omega_R = 2g_0 \).

### 6.2 Optical properties of semiconductor microcavity samples

Two semiconductor microcavity samples are described here. Both microcavity samples are based on GaAs and doped GaAs materials. A short lifetime microcavity was fabricated by Dr. John S. Roberts at the University of Sheffield and provided by Professor Jeremy J. Baumberg from the University of Cambridge. A long lifetime microcavity was fabricated by Dr. Loren N. Pfeiffer and Dr. Ken West at Princeton University and provided by Professor David W. Snoke at the University of Pittsburgh. The samples were grown using molecular beam epitaxy[131]. The lifetimes of the polariton states are limited by the radiative coupling to the external fields, which is determined by the Q-factor of the microcavity. The short lifetime sample has a Q-factor of around 5000 and a cavity lifetime of around 1 ps based on the linewidth of the polariton states, typical of GaAs semiconductor microcavities. The long lifetime
sample has a Q-factor of $10^6$ and a cavity lifetime of at least 100 ps, with the estimate limited by the spectral resolution of the polariton linewidth in optical reflection measurements\cite{100}. Both microcavity samples were grown so that the length of the cavity varies along one spatial dimension, creating a wedged cavity dimension. The detuning of the cavity varies as a function of the wedged dimension.

### 6.2.1 Short lifetime semiconductor microcavity

The short lifetime semiconductor microcavity is composed of 10 nm In$_{0.06}$Ga$_{0.94}$As QWs embedded inside a GaAs microcavity, identical to previously reported samples\cite{122} and shown in Figure 6-7a. The cavity length is $3/2$ times the exciton resonance wavelength of 850 nm. A set of three QWs, separated by 10 nm thick GaAs layers, is at each of the two antinodes. The exciton-photon coupling strength, $\Omega_R$, is 7 meV, as given by the LP and UP splitting at zero detuning. The two ends of the cavity are composed of DBRs consisting of 17 GaAs/Al$_{0.18}$Ga$_{0.82}$As layers in the top DBR and 20 GaAs/Al$_{0.18}$Ga$_{0.82}$As layers in the bottom DBR. The bottom DBR is on top of a thick layer of GaAs substrate. In all experiments using this sample, the microcavity was mounted onto a cold finger in a Janis ST-100 cryostat using cryogenic Apiezon vacuum grease and kept between 6-10K.

The energies of the LP and UP were measured using the transmission of a 100 fs optical pulse with a frequency centered at 850 nm, plotted in Figure 6-7b. Transmission spectra were measured as a function of position on the sample along the wedged dimension of the microcavity. The energies of the LP and UP were extracted from each transmission spectrum and plotted in Figure 6-7c. As can be seen, the LP and UP energies exhibit the expected anticrossing curves of a strongly coupled polariton system. By measuring the energies of the lower and upper polaritons at the extreme ends of the microcavity, the uncoupled cavity mode and exciton mode was extracted and the detuning energy was found as a function of sample position, as shown in Figure 6-8c.
Figure 6-7: (a) The structure of the short lifetime semiconductor microcavity sample. Two sets of three 10 nm In$_{0.06}$Ga$_{0.94}$As quantum wells are placed at the antinodes in a 3λ/2 cavity. The distributed Bragg reflectors are made of alternating λ/4 layers of GaAs and Al$_{0.18}$Ga$_{0.82}$As with 17 pairs on the front reflector and 20 layers in the back reflector. Only one layer of the reflectors are shown in the figure. (b) The transmission spectrum of a 100 fs optical pulse, centered between the lower polariton and upper polariton peaks. (c) The energies of the lower and upper polaritons at \( k = 0 \) measured as a function of position on the sample, where the position is varied along the wedged dimension of the microcavity.
6.2.2 Long lifetime semiconductor microcavity

The long lifetime semiconductor microcavity is composed of 7 nm GaAs QWs embedded inside a GaAs microcavity, identical to previously reported samples[100] and shown in Figure 6-8a. The cavity length is 1/2 times the exciton resonance wavelength of 780 nm. Three sets of four QWs, separated by 3 nm thick AlAs barriers, are at the antinodes in the structure, with two sets of the QWs between the last two layers of the front and back DBRs. By placing the QWs inside the layers of the DBRs, the cavity length can be kept short while still increasing the number of QWs that couple to the cavity field. In this sample, $\Omega_R = 13$ meV. The two ends of the cavity are composed of DBRs consisting of 32 Ga$_{0.8}$Al$_{0.2}$As/AlAs layers in the top DBR and 40 Ga$_{0.8}$Al$_{0.2}$As/AlAs layers in the bottom DBR. The larger number of layers in each DBR increases the Q-factor of the microcavity. After the bottom DBR is a thick layer of GaAs substrate. Because the GaAs substrate has a resonance below the polariton state, all experiments using this sample were done in reflection mode. In all experiments using this sample, the microcavity was mounted onto a cold finger in a Janis ST-300MS cryostat using silver paste.

The photoluminescence of the long-lifetime sample was measured as a function of in-plane momentum, giving the dispersion curves of the LP. The imaging setup is shown in Figure 6-9. A c.w. laser was used to nonresonantly pump carriers in the QW, which relaxed to the LP state through carrier-phonon scattering (as discussed in Chapter 8). The c.w. laser diode was stabilized by the retro reflection off a grating, in the Littman-Metcalf configuration[52, 92]. The retro reflection narrowed the linewidth of the diode output and tuned the center wavelength of the laser spectrum depending on the angle of the grating. In order to couple the nonresonant c.w. laser into the microcavity, the wavelength of the laser was tuned to the wavelength of a dip in the microcavity reflection spectrum, which depended on the detuning energy of the microcavity and varied from about 705 nm to 712 nm. The c.w. laser beam was focused onto the sample to a 10 µm spot using a microscopic objective with a numerical aperture of 0.28. The photoluminescence at around 780 nm was separated.
Figure 6-8: (a) The structure of the long lifetime semiconductor microcavity. Three sets of four 7 nm gallium arsenide quantum wells are at the antinode in a $\lambda/2$ cavity and between the last two layers of the surrounding distributed Bragg reflectors. The Bragg reflectors were made of alternating sets of $\text{Ga}_{0.8}\text{Al}_{0.2}\text{As}/\text{AlAs} \, \lambda/4$ layers, with 32 pairs in the front reflector and 40 in the back reflector, with only two pairs of layers shown in the figure for each reflector. (b) A spectrally dispersed far-field image of the photoluminescence of the long-lifetime semiconductor microcavity at zero detuning. The greyscale gives the normalized intensity of the photoluminescence. (c) The energy of the lower polariton branch at $k = 0$ (circles) measured as a function of detuning of the cavity energy from the exciton energy, which was varied by scanning the wedged dimension of the microcavity. The dashed lines have a slope of zero and one, representing the exciton and cavity energies as a function of cavity detuning energy. The asymptotes of the exciton and cavity energies were given by the energies of the lower polariton at the extreme ends of the sample.
Figure 6-9: The imaging setup used to measure the photoluminescence from the semiconductor microcavity sample as a function of both in-plane wave vector and energy. A grating-stabilized diode laser resonant with a dip in the semiconductor microcavity reflection spectrum, at roughly 705 nm, was focused onto the surface of the sample, held in a cold finger cryostat, with a microscope objective of 0.28 numerical aperture. Photoluminescence light was collected by the same objective and separated from the input laser light with a dichroic mirror. The photoluminescence was focused and then collimated by an 80 cm and 10 cm lens pair. Far-field images of the sample were formed on the slits of the imaging spectrometer. With the slits closed, the spectrometer gave images of the photoluminescence with the spectrally dispersed dimension along one axis of the image and the in-plane wave vector of the light along the other axis.

from the excitation beam using a dichroic mirror. The photoluminescence was imaged in the far field on the slit of an imaging spectrometer. The photoluminescence along the slit was a one-dimensional slice of the far field image and the photoluminescence along the second dimension was spectrally dispersed. Therefore, the photoluminescence was measured as a function of energy and in-plane wave vector on the C.C.D camera in the spectrometer, with the intensity of the light given by the counts on the camera.

An image of the photoluminescence is plotted in Figure 6-8b as a function of energy and in-plane wave vector. The image was taken near zero detuning. No photoluminescence was observed from the UP, most likely because carriers in the UP lived long enough to relax into the LP before radiative recombination occurred. The PL from the LP appears parabolic because only a limited wave vector range around the bottom of the LP branch was observed using a numerical aperture of
0.28. Dispersion curves were also recorded as a function of detuning energies. The energy of the LP at $\mathbf{k} = 0$ is plotted as a function of position on the sample in Figure 6-8c. The LP energies at extreme limits of the sample position was used to fit linear lines with zero slope and finite slope, representing the uncoupled exciton and cavity modes, respectively. From these energies, the cavity detuning from the exciton energy was extracted, giving the x-axis of Figure 6-8c. The spectrally resolved far-field photoluminescence images will be discussed extensively in Chapter 8.
In the previous chapter, strong coupling between the optical modes of a microcavity and the exciton modes of a quantum well was shown to have profound effects on exciton dynamics; the two modes couple to form exciton-polariton states that have a mixture of light-like and exciton-like character. Although the many-body interactions between polaritons were completely neglected in the previous chapter, Coulomb interactions between polaritons can play an important role in polariton nonlinear dynamics. Just as the nonlinear dynamics of excitons in a quantum well are strongly influenced by correlated interactions, the nonlinear dynamics of polaritons can be strongly influenced by correlated interactions between polaritons.

In this chapter, the correlated interactions between polaritons are discussed. Section 7.1 discusses previous experiments, based on four-wave mixing (FWM), that
Figure 7-1: A schematic illustration of the three-quantum fifth-order spectroscopy experiments. The energies of LP and UP are plotted as a function of in-plane momentum. Three spin-up polaritons (red arrows) are excited by three interactions with field $E(k_2)$, and their correlations through various coupling mechanisms (dashed red circle) result in a three-quantum coherence at $3k_2$; after a variable delay $\tau_{3Q}$, a field at $E(k_1)$ stimulates scattering, curved red arrows, into the $k_1$ and $k^{(5)} = 3k_2 - 2k_1$ directions, resulting in two polaritons in the $k_1$ state (gray) and one polariton in the $k^{(5)}$ state (straight black arrow), along which the signal emerges.

clearly demonstrated the importance of correlated interactions between exciton-polaritons.

In Section 7.2, two-quantum 2D spectra of polaritons are reported. The 2D spectra directly reveal the interactions between polaritons and the spectra show that correlated interactions between polaritons can be controlled by tuning the energy of the cavity mode. Section 7.3 discusses the role of high-order correlations in polariton nonlinear dynamics and presents three-quantum and four-quantum 2D spectra. In addition to Coulomb correlations, the strong coupling with light is shown to be an important source of correlations through multiple interactions with the cavity field.

In all the experiments described in this chapter, the sample structure was the short lifetime semiconductor microcavity described in Section 6.2.

2D spectra were recorded using 2D spatial and temporal pulse shaping techniques as described in Chapter 2. Nonlinear signals, up to seventh order in the excitation fields, were generated using single or multiple field interactions of the pulses in two excitation beams, with wave vectors $k_2$ and $k_1$, pulse widths of 100 fs, and wavelengths centered at 850 nm. The beams were kept less than two degrees from normal incidence. Using a pair of identical transmissive diffractive optics, a reference beam was directed around the sample and superimposed with the coherent signal beam.
that emerged from the sample, as shown in Figure 2-11 in Chapter 2. The signal was emitted in the wave vector direction $2k_2 - k_1$, $3k_2 - 2k_1$, or $4k_2 - 3k_1$ for third, fifth, or seventh-order measurements, respectively. The dispersed frequency components of the signal field were measured through spectral interferometry. For third and fifth-order spectra, the beam at $k_2$ was kept horizontally polarized while the beam at $k_1$ and the detection polarization were either co-circularly or cross-circularly polarized. Assuming that the spins of the polaritons in the final states ($k_{\text{sig}}$ and $k_1$) preserve the spins of the initially excited polaritons (in $k_2$), this polarization scheme allows us to selectively detect the signal due to polaritons with the same spin (co-circular) or the signal due to polaritons where one has a spin opposite to the other(s) (cross-circular). For seventh-order spectra, all beams were co-circularly polarized. A schematic illustration of the fifth-order experiment is shown in Figure 7-1.

## 7.1 Evidence of correlated interactions between microcavity polaritons

Two earlier experiments demonstrated that correlated interactions can play a significant role in polariton nonlinear dynamics. The first experiment[77] showed that the spectrally resolved FWM signal of a GaAs-based semiconductor microcavity is polarization dependent. The FWM signal was generated using the $2k_2 - k_1$ beam geometry, with time-coincident optical pulses centered around the LP and UP. The FWM signal was detected in a spectrometer and showed two peaks at the LP and the UP energies. The relative intensities of the two peaks depended on the polarization conditions of the excitation pulses, which were varied between the collinear, crosslinear, co-circular, and cross-circular polarization conditions. In Figure 7-2, the FWM signals for the co-circular and cross-circular polarization conditions are plotted. The signals were derived by summing the 2D spectra, to be discussed in the next section, but are qualitatively similar to the FWM signals in [77]. A theoretical analysis of the polarization dependence[79, 80] showed that the relative peak intensities can only be explained by
including correlated interactions between polaritons; correlated interactions mediate scattering between polaritons, causing scattering within the same polariton state or into the other polariton state, depending on the polarization conditions.

The second experiment that clearly demonstrated the importance of correlated interactions between polaritons was the observation of parametric amplification, also in a GaAs-based semiconductor microcavity[122]. In this experiment, a relatively strong pump beam (kept below saturation levels) was sent to the microcavity at an angle corresponding to the inflection point of the LP, \( k_{pu} \), at approximately 16°. The shape of the LP dispersion curve is such that two polaritons excited by the pump beam can scatter into different momentum states, one into the \( k = 0 \) state and one into the \( k = 2k_{pu} \) state, conserving both energy and momentum. A weak probe beam was sent to the \( k = 0 \) state, stimulating the parametric scattering such that the probe beam was amplified by 5000 times. All optical beams were kept in the same circular polarization. The parametric amplification can be thought of as a FWM process as shown in Figure 7-3: two interactions with the pump optical field, at \( k_{pu} \), and one interaction with the probe optical field, at \( k_{pr} = 0 \), generates signal in an
Figure 7-3: The parametric amplification experimental configuration from [122]. A strong pump beam at $k_{pu}$ excited lower polariton (LP) coherences of the same spin (red arrows). A weak probe beam at $k_{pr} = 0$ stimulated pairwise scattering (curved black arrows) from the pump state into the probe and the idler, $k_{id} = 2k_{pu} - k_{pr}$, states (gray arrows).

idler direction, at $k_{id} = 2k_{pu} - k_{pr}$. Although the parametric amplification of the probe beam can be qualitatively understood without considering correlated interactions, a theoretical analysis showed that the massive gain can only be explained by considering the correlated interaction between polaritons[120]. Specifically, the theoretical analysis showed that the correlated interactions that typically cause dephasing, excitation-induced dephasing as discussed in Chapter 4, do not contribute strongly to the interactions among LPs. Essentially, the strong coupling with the cavity mode causes exciton polarizations to be driven to lower energies, isolating the polarizations from the high density of states that typically lead to excitation-induced dephasing (see Figure 4-1 and the related discussion). The decrease in correlated interactions resulted in the massive gain observed in the parametric amplification experiments.

Although the correlated interactions between polaritons play key roles in the nonlinear polariton dynamics, correlated exciton-polariton pairs have never been observed directly. In both the spectrally resolved FWM and the parametric amplification experiments, the effects of the correlated interactions are only observed in the final emission; the initially excited pair of polaritons that scatter into the final emission states were not measured. As shown in the next section, the direct measurement of the initially excited two-polariton coherences gives a clearer picture of how correlated interactions mediate the nonlinear polariton dynamics.

Additionally, higher-order correlations between polaritons have never been con-
sidered in the microcavity system. As discussed in Chapter 5, triexciton correlations have been resolved using three-quantum 2DS. A natural question is whether or not higher-order correlations are also observed between exciton-polaritons. Higher-order correlations are discussed in Section 7.3.

7.2 Correlated interactions controlled by exciton-photon coupling

7.2.1 Two-polariton interactions probed by two-dimensional spectroscopy

In Figures 7-4a and b two-quantum 2D spectra are shown, where two-polariton coherences were excited by two time-coincident fields before a third field generated FWM nonlinear emission from a single polariton state. The polarizations of the excitation and reference beams were controlled so that the two initially excited polaritons that contributed to the signal have either the same spin (Figure 7-4a) or were spin paired (Figure 7-4b). The cavity resonance was 2 meV higher than the exciton resonance for both spectra. The 2D spectra show peaks representing excitation of different combinations of LP and UP: two LPs (LP₂), two UPS (UP₂), and a mixed combination of LP and UP (MP₂). The 2D spectra reveal how LP₂, UP₂, and MP₂ coherences contributed to the nonlinear signals at LP and UP frequencies: LP₂ and UP₂ emitted into only LP or UP, respectively, but MP₂ emitted into either LP or UP.

The relative intensities of the two-polariton coherences were dramatically modified if the cavity energy was detuned relative to the exciton energy. In Figures 7-4c and d, two-quantum 2D spectra are shown where the cavity energy was detuned by -4 meV from the exciton energy. As can be seen, the relative intensities of the different coherences varied dramatically not only from the spectra at 2 meV detuning, but also between the two polarizations. For example, at -4 meV detuning the interaction between two LPs was almost completely suppressed in the cross-circular configuration but remained strong in the co-circular configuration.
Figure 7-4: Two-quantum coherences. Experimental magnitude two-quantum 2D spectra, taken with the cavity resonance 2 meV higher than the exciton resonance, in the same-spin (a) or spin-paired (b) configuration. Same-spin and spin-paired 2D spectra taken for a cavity resonance 4 meV lower than the exciton resonance are shown in (c) and (d). Peaks on the diagonal dashed lines are LP$_2$ and UP$_2$ two-quantum coherences, which were generated by the first two field interactions and emitted signal at the LP and UP frequencies, respectively, after the third field interaction. Off-diagonal peaks are MP$_2$ two-quantum coherences that emitted signal at either the LP or UP frequencies.
The change in the relative intensities of the two-quantum peaks can be characterized by a ratio, \( R \), equal to the integrated intensity of MP\(_2\) over the integrated intensity of LP\(_2\). The integrated intensity was calculated along the two-quantum dimension at the LP emission energy and accounts for both the peak intensity and linewidth of each peak. The value of \( R \) was calculated for 2D spectra taken for a range of cavity detuning energies \( \pm 3 \text{meV} \) and plotted in Figure 7-5. As the cavity energy was tuned to lower energies, the value of \( R \) remained nearly constant for polaritons of the same spin but varied from one to nearly three for polaritons of different spin.

As discussed in Chapter 6, the character of the LP and UP change as the cavity energy is tuned from the exciton energy; the polariton states can become more or less exciton-like or light-like depending on the detuning energy as given by the Hopfield coefficients. However, the change in Hopfield coefficients is the same regardless of the spin state. Therefore, the change in the ratio \( R \) cannot be explained by the change in polariton character. Instead, as shown by comparison below to theoretical models, the change in the ratio \( R \) can be explained by considering the correlated interactions between polaritons; the correlated interactions are strongly dependent on both the cavity detuning energy and the polariton spin states.

### 7.2.2 Theoretical model of correlated two-polariton interactions

In order to understand the polarization and detuning dependence of \( R \), 2D spectra were calculated following the calculations of one-dimensional FWM spectra by Kwong and coworkers \[79, 80\]. The calculations were based on calculations of the third-order susceptibility of quantum wells, including the correlated many-body interactions between up to two excitons, derived using the dynamics-controlled truncation scheme (see Section 4.1). In the calculations, the contributions to the third-order susceptibility can be clearly identified: mean-field Coulomb repulsion and non-binding two-exciton Coulomb correlations contribute to the same-spin third-order susceptibility and only two-exciton Coulomb correlations contribute to the spin-paired third-order
susceptibility. First, the procedure to calculate four-wave mixing signals in a semiconductor microcavity structure is reviewed[79, 80]. The procedure is then extended to calculate two-quantum 2D spectra.

As discussed in Section 6.1.1, the linear optical properties of the semiconductor microcavity can be solved by considering the wave equation for optical fields, Equation 6.1, and using standard transfer matrix calculations. In that section, the linear responses of the excitons in a QW were included by using the first-order exciton susceptibility to include first-order exciton polarizations in the wave equation, which acted as sources for optical fields. The key challenge to calculate the nonlinear spectra of exciton-polaritons is to calculate the nonlinear polarizations generated in the QW, which also act as sources for optical fields in the wave equation, Equation 6.1.

The third-order polarization was calculated by standard perturbation theory. In the frequency domain, the third-order polarization at the position of the QW is given
by [31]:

\[
E^{(3)}_l(\omega) = \frac{1}{(2\pi)^2} \sum_{m,n,p} \int d\omega_1 d\omega_2 d\omega_3 \delta(\omega_1 + \omega_2 - \omega_3 - \omega) \chi^{(3)}_{lmnp}(\omega_1, \omega_2, \omega_3) 
\]

\[
E_{Qm}(\omega_1) E_{Qn}(\omega_2) E_{QP}^*(\omega_3)
\]  

(7.1)

where \(\chi^{(3)}_{lmnp}\) is the third-order exciton susceptibility describing interactions between excitons in the \(m, n,\) and \(p\) spin states contributing to the polarization in the spin state \(l\). Assuming the conservation of spin, \(\chi^{(3)}_{lmnp}\) can be labeled with two spin indices representing the two initially excited spin states \(\chi^{(3)}_{mn}\). Equation 7.1 is identical to Equation 4.17 except that the optical fields in Equation 7.1 are not the applied fields external to the semiconductor microcavity, but are the optical fields at the position of the QW, which have peaks at the LP and UP resonances, as given by the propagation of the external light field to the position of the quantum well using transfer matrices (see Chapter 6).

Microscopic calculation of the third-order susceptibility is extremely challenging because of the many-body Coulomb interactions. Kwong and coworkers [79, 80] calculated the susceptibility using the dynamics-controlled truncation scheme giving the results described in Section 4.1. In particular, the third-order susceptibility is given by Equation 4.15 and the many-body interactions are given by the T matrices plotted in Figure 4-1. As discussed in Section 4.1, the frequency dependence of \(T_{nm}\) depends significantly on the spin configuration. There is a sharp peak in \(T_{-}\) at the biexciton resonance, approximately 2 meV below twice the bare exciton resonance for a GaAs sample [79, 80]. Although \(T_{+}\) increases with frequency beginning at roughly twice the bare exciton energy due to the increasing density of states, there is no similar resonance in its spectrum. By inserting the third-order susceptibility (Equation 4.15) into Equation 7.1, the transmitted third-order optical field can be computed for different spin configurations. The frequency-dependent values of \(T_{\pm}\) used in all calculations were given by Ref. [79, 80]. Although the sample structure in the calculations were based on a GaAs quantum well instead of an InGaAs quantum well, the calculations qualitatively reproduced key features in the 2D spectra. Note that the 1s exciton
energy was shifted to match the exciton energy of InGaAs but the biexciton binding energy was not modified from [79, 80].

A full 2D spectrum can be calculated by variably delaying the excitation fields in Equation 7.1. A time delay, \( \tau \), of the optical fields is given by a linear phase sweep in the frequency domain, as given in Equation 4.21. Conveniently, time delays in the experiment were generated in the frequency domain by a pulse shaper, exactly as indicated in Equation 4.21, with an experimentally chosen carrier frequency [142]. Equation 4.21 was inserted into Equation 7.1 and the transmitted third-order optical field was calculated for time delays between the two time-coincident non-conjugate fields, \( E_1 \) and \( E_2 \), and the third, conjugate field, \( E_3 \). Fourier transformation along the scanned time delay dimension resulted in the 2D spectra shown in Figure 7-6.

Same-spin and spin-paired two-quantum 2D spectra were calculated for various detuning values and used to find values of \( R \) as a function of detuning, shown in Figure 7-5. \( R \) was nearly one in the same-spin configuration but varied from one to over two in the spin-paired configuration, across a range of detuning values similar to the experimental values. The calculations replicated the spin-dependent change in the interaction strengths between various polariton states.

The dramatic detuning dependence of the spin-paired \( R \) can be attributed to the correlated interactions between polaritons, which are strongly frequency dependent.
for the spin-paired polaritons due to the biexciton correlations. As the cavity detuning was varied, LP₂ and MP₂ moved in or out of resonance with the biexciton energy and became more or less strongly correlated through a biexciton interaction. Specifically, as the cavity energy was lowered and the LP became more light-like, the LP₂ energy moved out of resonance with the biexciton until biexciton interactions no longer correlated the two LPs. Because the UP became more exciton-like as the cavity energy was lowered, biexciton interactions could correlate MP₂ much more than LP₂ for negative detuning energies. In fact, for negative detuning energies in the spin-paired configuration, correlations between LP and UP were the main source of nonlinear signal. Although the same-spin Coulomb correlation strength is also frequency dependent, the correlation strength is not sharply peaked but increases relatively gradually with negative detuning frequency\[79\]. At least for the detuning values in Figure 7-4c, the frequency dependence of the same-spin Coulomb correlations did not cause strong frequency dependence in the strength of polariton nonlinear interactions. Regardless of the spin configuration, the relative nonlinear signal strengths at LP or UP depended on the strengths of the LP₂, UP₂, and MP₂ correlations which are normally integrated over in typical FWM experiments such as the spectrally resolved FWM experiment discussed in Section 7.1. By clearly separating the LP₂ and MP₂ coherences, the role of the biexciton correlation in polariton nonlinear dynamics was clearly resolved.

### 7.2.3 Biexciton strong coupling

There has been some work detailing how biexcitons may become strongly coupled to the cavity light field. Although the biexciton itself does not directly couple to light, FWM experiments have shown that the exciton-to-biexciton transition may become strongly coupled to the light mode when the exciton transition becomes saturated\[117, 101\]. Since the work described in the previous section was in the perturbative limit, with excitation powers at least an order of magnitude lower than the saturation threshold, such effects were not observed. The signal showed a third-order power dependence, up to the highest powers used in the experiments. The fifth-order and seventh-order signals, reported in the next section, also depended on
the power as expected, confirming that we were below the saturation point for all 2D spectra reported.

Additionally, the possibility exists that the biexciton can couple to two-photon cavity modes, forming what is often described as a bipolariton. Normally, such coupling does not lead to significant changes in biexciton energy or linewidth since the biexciton interaction occurs over a much larger k-space range than that within which the cavity light field is coupled to the exciton[115, 23]. However, some work has demonstrated the existence of a bipolariton state when the biexciton binding energy is equal to the Rabi splitting of the cavity[12, 103], as mentioned above. Light fields can also couple to the biexciton when considering the bulk (or zero-order) photon modes[56], although such effects are not unique to microcavities. A two-quantum 2D spectrum should provide a sensitive probe to the bipolariton dispersion or detuning dependence. However, for the specific sample used in the experiments reported in this chapter, the Rabi splitting (7meV) was most likely several times larger than the biexciton binding energy (2meV in GaAs[132]) and no shifts in energy at the positions of the LP₂, MP₂, or UP₂ peaks were observed, indicating that bipolariton effects were not significant in the sample studied.

7.3 High-order correlations between exciton-polaritons

7.3.1 Three-polariton and four-polariton interactions probed by two-dimensional spectroscopy

Polariton nonlinear dynamics may also be mediated by higher-order correlations. In bare GaAs QWs, three excitons have recently been shown to correlate into a bound triexciton state if the spin of one of the excitons is opposite to the other two (see Section 5.3). Other work studying QWs using six-wave mixing has shown that the biexciton coherence and exciton population may mix, and even correlate [21, 85]. There have been no reported observations of correlations or coherent mixing between three or more excitons of the same spin in bare exciton systems. If polariton in-
teractions were mediated only by exciton nonlinearities, then triexciton correlations and biexciton-exciton mixing should mediate three-polariton coherences and no coherences of three or more polaritons with the same spin should be observed. However, as shown in Figures 7-7 and 7-8, three-quantum and four-quantum coherences were detected in the six-wave mixing (SWM) and eight-wave mixing (EWM) directions, respectively, including coherences between polaritons of the same spin. The 2D spectra show peaks representing various combinations of LP and UP with the same spin (Figure 7-7a and 7-8) and with one spin opposite the others (Figure 7-7b). In the three-quantum spectra, mixed polariton coherences (LP2UP) are again stronger relative to the pure LP coherence (LP3) if one spin is opposite to the others.

In addition to high-order Coulomb correlations, the high-order multiple polariton coherences that were observed may occur through multiple third-order exciton nonlinearities. A 2k₂ - k₁ polariton generated from third-order exciton nonlinearities can interact with two polaritons that were directly excited by the k₂ and k₁ input fields to generate a 3k₂ - 2k₁ polariton with a fifth-order dependence on the input fields[145, 18]. The fifth-order polariton can interact with two more first-order polaritons in yet another third-order process, yielding a seventh-order 4k₂ - 3k₁ signal, and so on. The coupling of two-exciton Coulomb correlations with a third polariton through the cavity mode is shown on the left side of Figure 7-9.

Such "cascaded" third-order signals were not observed in bare QWs[140] but have been observed in bulk samples [105, 124]. The signals in bulk samples represent sequential interactions mediated by emitted fields propagating through the sample, with no influence on the earlier exciton participants by the later ones, rather than interactions that mutually influence and correlate all the excitons involved. In microcavities, a coherent exciton-polariton field can play a similar role in generating a new high-order coherence, but instead of leaving the sample, the field components are confined and continue to interact with the electronic coherences, mutually correlating them. In other words, the two coherences are mutually influenced and correlated through their associated fields, and the signal that emerges from the sample represents a true multi-exciton-polariton correlation that is denoted as "field-coupled". In order
Figure 7-7: Three-quantum coherences. (a),(b) Experimental magnitude three-quantum 2D spectra taken with the cavity resonance 1 meV lower than the exciton resonance. The spectra show correlations among three LPs (LP3) and two LPs with one UP (LP2UP) emitting into LP. LP2UP and a correlation between one LP and two UPs (LPUP2) emitting into UP. All three polaritons had the same spin in (a) and one is opposite the other two in (b). (c),(d) Calculated three-quantum 2D spectra matching the experimental conditions in (a) and (b) respectively.
Figure 7-8: Four-quantum coherences. (a) Experimental magnitude 2D spectra taken with the cavity resonant with the exciton energy showing four-quantum coherences emitting into the LP state. All polaritons have the same spin. (b) Calculated 2D spectra matching the experimental conditions. From bottom to top, coherences were observed and calculated among four LPs (LP4) and among three LPs and one UP (LP3UP).

Figure 7-9: Different types of coupling mechanisms between polaritons in a single QW embedded inside a microcavity. Polaritons can be correlated through Coulomb interactions between the exciton component of the polariton (straight black arrows between black circles) and light fields (curvy red lines).

to separate the two mechanisms for high-order correlations, high-order Coulomb correlations and field-coupled correlations, theoretical models are developed in the next section.

7.3.2 Theoretical model of high-order correlations

There are two mechanisms for fifth-order signal to be generated in exciton systems: two coupled third-order exciton correlations or a fifth-order exciton correlation. For the case of two field-coupled third-order exciton interactions, the fifth-order polariz-
tion is given by:

\[
P^{(5)}_{\text{field, } l}(\omega) = \frac{1}{(2\pi)^2} \sum_{m,n,p} \int d\omega_1 d\omega_2 d\omega_3 \delta(\omega_1 + \omega_2 - \omega_3 - \omega) \chi_{\text{lmnp}}^{(3)}(\omega_1, \omega_2, \omega_3)
\]

\[
E^{(3)}_{Q_m}(\omega_1) E^{(1)}_{Q_n}(\omega_2) E^{(1)*}_{Q_p}(\omega_3)
\]

Equation 7.2

The fifth-order polarization in Equation 7.2 is generated by two third-order exciton interactions; one third-order interaction generates the polariton given by the \(E^{(3)}_{Q_m}\) term, and the other third-order interaction couples this polariton with two other polaritons directly excited by the external fields. Crucially, all interactions described in Equation 7.2 occur at the position of the QW. Normally, first-order coherences in thin QWs do not couple to third-order fields emitted from the same QW samples[140], but in a microcavity structure the fields are confined and can continue to interact at the QW layer. In bulk samples, sequential cascaded interactions also generate fifth-order signal similar to the signal described in Equation 7.2 but at different positions in the sample[145, 18]; the third-order field generated at one position of the sample propagates along the sample, interacting with the first-order excitation fields as it arrives at different positions on the sample.

The field-coupled signals emitted from microcavities are fundamentally different from sequential cascades from bulk samples. In the microcavity case, the field components are not just the incident fields but dynamic polariton fields. The correlated nature of the coupled third-order exciton interactions may not be obvious from Equation 7.2. This is because the optical fields in Equation 7.2 are treated semiclassically[79, 80]; the optical field operators and the exciton operators have been factorized and the former written as a classical field. The consequence of this formulation is that the optical fields are not actually influenced by the exciton correlations. However, considering the confinement by the microcavity, the quantum nature of the optical field can be important in nonlinear experiments. The relationship between quantum correlation and semiclassical factorization in semiconductor microcavities was first elucidated by Savasta and coworkers and more recently extended to higher-orders by Portolan and coworkers[121, 111]. In these works, the
optical field was described by its own dynamic equation and was correlated to the
exciton through Pauli-blocking interaction[121]. This correlation, in turn, was mutual-
tually influenced by both multi-exciton correlations and multi-photon cavity corre-
lations. Two-exciton-photon correlations have been demonstrated by measuring cor-
related intensity fluctuations in twin beams generated by FWM in a semiconductor
microcavity[116]. Despite the role of quantum correlations, the application of the
semiclassical approximation in Equation 7.2 should not detrimentally affect our abil-
ity to compare qualitative characteristics (e.g. relative peak intensities) between the
fifth-order signal calculated by Equation 7.2 and the experimental fifth-order signal
since such characteristics are usually given by the exciton correlations described in
χ(3). For certain experimental configurations (e.g. if the Rabi splitting was equal to
the biexciton binding energy[12, 103]), the multi-exciton correlations become strongly
dressed by the multi-photon states, significantly altering the line shapes and energies
of the multi-polariton correlations, but the sample used in our experiments does not
appear to show these effects, as discussed in the last section.

Fifth-order polarizations may also be generated by fifth-order Coulomb interac-
tions. In this case, the polarization is given by:

\[ P_{\text{coul},i}(\omega) = \frac{1}{(2\pi)^2} \sum_{j,k,l,m,n} \int d\omega_1 d\omega_2 d\omega_3 \delta(\omega_1 + \omega_2 + \omega_3 - \omega_4 - \omega_5 - \omega) \]
\[ \chi_{\text{mmnpq}}^{(5)}(\omega_1, \omega_2, \omega_3, \omega_4, \omega_5) \]
\[ E_{Qm}(\omega_1)E_{Qn}(\omega_2)E_{Qp}(\omega_3)E_{Qq}^{*}(\omega_4)E_{Qr}^{*}(\omega_5) \]

(7.3)

The fifth-order exciton susceptibility in Equation 7.3 accounts for three-exciton Coulomb
correlations such as bound triexciton interactions. Fifth-order optical fields can be
generated by both \( P_{\text{field}} \) and \( P_{\text{coul}} \). Unfortunately, calculation of the fifth-order ex-
citon susceptibility, including three-exciton Coulomb correlations, is extremely chal-
lenging and outside the scope of this dissertation so only \( P_{\text{field}} \) is included in the
calculations. Full 2D spectra are calculated as described above for third-order 2D
spectra and shown in Figures 7-7c and 7-7d.
Seventh-order nonlinear signals can be generated through similar mechanisms: three coupled third-order exciton interactions, a third-order exciton interaction coupled to a fifth-order interaction, and a seventh-order exciton interaction can all contribute signal in the seventh-order direction. Without a calculation of the fifth-order or seventh-order exciton susceptibility, however, only the contribution from three coupled third-order exciton interactions can be calculated:

\[
P^{(7)}_{\text{field},l}(\omega) = \frac{1}{(2\pi)^2} \sum_{m,n,p} \int d\omega_1 d\omega_2 d\omega_3 \delta(\omega_1 + \omega_2 - \omega_3 - \omega) \chi^{(3)}_{\text{linmp}}(\omega_1, \omega_2, \omega_3)
\]

\[
P^{(5)}_{\text{field},Qm}(\omega_1)E_{Qm}(\omega_2)E_{Qp}^*(\omega_3)
\]

where \(E^{(5)}_{\text{field},Qm}\) is the field at the QW due to the polarization from Equation 7.2. The two coupled third-order exciton interactions calculated in Equation 7.2 are coupled to two other polaritons through another third-order exciton interaction. Full 2D spectra are calculated using Equation 7.4 and shown in Figure 7-8b.

The calculated 2D spectra qualitatively reproduce the experimental results. In particular, the relative strengths of LP\(_3\) and LP\(_2\)UP for the two spin configurations of the fifth-order 2D spectra (Figure 7-7) were well reproduced, indicating that field-coupled correlations may explain the polarization dependence of the fifth-order 2D spectra. In the mixed-spin spectra, for example, the relatively strong peak at LP\(_3\)UP can be attributed to a LP and UP that interacted strongly through biexciton attraction and both were field coupled to another LP. The calculated seventh-order 2D spectra in Figure 7-8b are also qualitatively similar to the experimental 2D spectra: the emission from UP is diminished and correlations involving at least three LPs are the strongest features.

Based on these calculations, contributions from high-order Coulomb correlations to high-order polariton correlations cannot be excluded. As previously mentioned, triexciton interactions should mediate correlations between three polaritons with mixed spins. Considering a total binding energy of approximately 3 meV[140], triexciton interactions would be the strongest for LP\(_2\)UP at the detuning shown in Figure 7-7. Triexciton interactions would therefore give qualitatively similar correlation
strengths as field-coupled third-order exciton-polariton nonlinear interactions. Careful calculations of the triexciton binding energy should help separate the field-coupled and high-order Coulomb contributions to the three-quantum coherences, but such calculations remain at or beyond the limit of current theoretical capabilities[104]. Additionally, although unbound three-exciton or four-exciton correlations were not observed in bare QWs, unbound three-exciton or four-exciton correlations may still play a role between polaritons because the high-order Coulomb and field-coupled correlations should be frequency dependent, just as the two-exciton correlation is frequency-dependent. Full understanding of the origins of these high-order multipolariton coherences will require further theoretical work describing the high-order correlation functions.

7.4 Conclusions

Using two-dimensional spectroscopy, the contributions of multipolariton correlations to nonlinear polariton dynamics were resolved. The strong coupling to light modified two-exciton correlations by tuning the oscillation frequencies of the constituent polariton. Depending on the spectral overlap with the biexciton resonance, two spin-paired polaritons were strongly correlated through biexciton Coulomb interactions. In particular, for negative detuning energies and spin-paired polaritons, the correlation between the LP and UP were the dominant source of nonlinear emission from the LP state. The ability to control the nonlinear LP signal by controlling the correlations with the UP could be an interesting mechanism for nonlinear devices. Additionally, correlations among up to four polaritons were observed, a higher order than observed in bare QWs, demonstrating that high-order correlations can be mediated through the polariton fields. The maximum order of the Coulomb correlations could not be clearly elucidated: multiple third-order Coulomb interactions, coupled through the cavity light field, give calculated correlation signals that are qualitatively similar to the experimental spectra, but high-order Coulomb correlations may still contribute to the observed multi-exciton-polariton signals.

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Further experimental and theoretical work could help detail the exact nature of these correlations. For example, the two mechanisms for high-order correlations might be separated using a microcavity structure with two different quantum wells embedded at different antinodes in the cavity; multiple-quantum peaks representing coherences between polariton states of different quantum wells would immediately indicate a multi-polariton correlation mediated entirely by field coupling. Additionally, the experiment reported here could be repeated but with the $k_2$ and/or $k_1$ field interactions separated into different beams so that wave vector combinations that are resonant with both biexciton and high-order correlations could be examined. Finally, five-quanta and higher-order multiple-quantum coherences could also be explored by detecting the ninth-order and higher signal.
Chapter 8

Polariton condensation

Under the right conditions, a system composed of bosons in thermal equilibrium can undergo Bose-Einstein condensation (BEC), a phase transition characterized by the spontaneous occupation of the ground state in the system by a large fraction of the bosons\(^\text{[43]}\). The phase transition is accompanied by novel effects such as long range coherence and superfluid behavior\(^\text{[20, 107]}\). Superfluid helium was discovered in 1938 by Allen and Misener\(^\text{[2]}\) and although it was postulated almost immediately by London that superfluid helium is a consequence of BEC\(^\text{[93]}\), the exact connection between the two phenomena was not obvious. The first clear experimental observation of BEC was achieved using ultracold atoms\(^\text{[8, 34]}\). BEC of excitons in semiconductor materials have attracted a great deal of interest: room temperature BEC can theoretically occur in some semiconductor materials and the materials could be fabricated into solid-state devices relatively easily, at least compared to ultracold atoms\(^\text{[19, 68]}\). Some materials that have attracted interest include bulk cuprous oxide, coupled double quantum-wells, and semiconductor microcavities\(^\text{[128]}\).

After several early reports of polariton BEC in semiconductor microcavities\(^\text{[37, 62, 13]}\), a large body of experimental and theoretical literature has been amassed reporting on the properties of polariton BEC and related phenomena such as superfluid behavior\(^\text{[81, 7, 6, 118, 119]}\). In these experiments, the lifetimes of polaritons were on the order of several picoseconds or less, shorter than the time that is usually necessary for polaritons to reach thermal equilibrium, which can be achieved through scattering...
with phonons or collisions with other carriers. Despite the relatively short lifetime, experimental and theoretical works have demonstrated that many of the characteristics of BEC, such as long-range spatial coherence[37, 62, 13] and superfluid behavior[7], can be observed in semiconductor microcavities. Furthermore, polaritons have been shown to reach thermal equilibrium under very specific conditions; by detuning the cavity energy away from the exciton energy, polaritons can be tuned to be more "exciton-like", with a longer lifetime and stronger interactions with both phonons and other particles[36, 63].

Recently, fabrication methods have improved so that the lifetime of polaritons, limited by the radiative lifetime of the cavity mode, can be improved by about two orders of magnitude to 100 ps[100]. Due to the longer lifetime, polaritons in the new samples demonstrate very novel effects such as condensation behavior that is strongly dependent on the long-range potential energy surface of the microcavity sample[100]. Because the lifetime of the sample is longer than both the phonon scattering time and interparticle collision time, the polaritons should reach equilibrium within their lifetime and be well described by Bose-Einstein statistics. However, because of spatially varying potentials in the microcavity caused by both the structure of the sample and optically induced excitation densities in the material, a ground state in the material is very poorly defined and the condensation does not follow a simple BEC theory.

In this chapter, experiments investigating the Bose-Einstein statistics of long-lifetime polaritons are reported. Polaritons were trapped in an optically induced 2D harmonic potential and the thermal distribution of polaritons was measured as a function of polariton density, through the critical density required for BEC. The polaritons were well described by a Bose-Einstein distribution throughout the phase transition. The results show that long-lifetime polaritons can reach thermal equilibrium at densities well below the critical density for BEC, and that polaritons form a condensate that is also well described by a Bose-Einstein distribution.

This chapter is organized as follows. In the first section, the background of polariton BEC is discussed. The second section discusses the methods used to characterize the sample, the methods to measure the polariton thermal distribution, and the
methods to optically trap the polariton condensate. The third section discusses the thermal properties of trapped condensates in long lifetime samples.

8.1 Polariton Bose-Einstein condensation

8.1.1 Theory of Bose-Einstein condensation

In this section, some of the key physics of BEC are explained. There are a large number of textbooks that derive the full theory of BEC and related phenomena[114, 110, 159]. This section will focus on key topics that are relevant to the polariton BEC experiment discussed at the end of this chapter: the quantities that define a BEC phase transition, the importance of the dimensionality of a system to BEC, and the influence of interactions on the properties of a condensate.

BEC phase transition

BEC can be most simply understood in the case of an ideal gas of noninteracting bosons that are in equilibrium with a reservoir. In this case, the bosons can exchange energy and particles with the reservoir, establishing a temperature, $T$, and a chemical potential, $\mu$, that describe the distribution of states that are occupied by the bosons. The average number of bosons that occupy a state with energy $\epsilon_i$ is given by:

$$n_i(\epsilon_i, T, \mu) = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \quad (8.1)$$

where $\beta^{-1} = k_B T$ and $k_B$ is the Boltzmann constant. In this chapter, $\epsilon_i$ is measured with respect to the ground state of the system which means that $\mu < 0$; otherwise $n_i$ could be a negative number. In order to define a phase transition, the total number of bosons in the ground state, $N_0(T, \mu)$, can be separated from the total number of
bosons that occupy states of higher energies, $N_{th}(T, \mu)$:

$$
N(T, \mu) = n_0(T, \mu) + \sum_{i \neq 0} n_i(\epsilon_i, T, \mu) \\
= N_0(T, \mu) + N_{th}(T, \mu)
$$

(8.2)

where $N(T, \mu)$ is the total number of bosons in the system. The mechanism for BEC is based on the fact that as $\mu$ goes to zero, $N_0(T, \mu)$ diverges. However, it is important to consider that in a real system, $N$ must remain finite and the fraction $N_0/N_{th}$ might still be negligible even as $\mu$ goes to zero because $N_{th}$ might diverge as well. Therefore, a critical number of bosons, $N_c$, is defined by:

$$
N_c(T) = N_{th}(T, \mu = 0)
$$

(8.3)

In order for a system to be considered a Bose-Einstein condensate, $N_c$ must be finite and the total number of bosons in the system must be greater than $N_c$ so that $N_0$ is non-negligible: $N > N_c$. Similarly, a critical temperature, $T_c$ can be defined for a given $N$ such that all bosons occupy a state higher in energy than the ground state:

$$
N_{th}(T_c, \mu = 0) = N
$$

(8.4)

At temperatures below $T_c$, $N_0$ becomes non-negligible. To determine whether or not a system of bosons can undergo BEC, $N_c$ and $T_c$ must be found, both of which depend on the dimensionality of the system.

**Dimensionality constraints to BEC**

$N_c$ can be solved, given that the density of states of the system, $\rho(\epsilon)$, is known:

$$
N_c = \int_0^{\infty} d\epsilon \rho(\epsilon) \frac{1}{e^{\frac{\epsilon}{T_c}} - 1}
$$

(8.5)
\( \rho(\epsilon) \) depends on the dimensionality of the system. Considering infinite uniform systems of one, two, and three dimensions, one can find that \( \rho(\epsilon) \) is given by\([110, 159]\):

\[
\rho_d(\epsilon) = \Omega_d \left( \frac{L}{2\pi} \right)^d \frac{1}{2} \frac{m^{\frac{d}{2}}}{\hbar^2} \epsilon^{\frac{d}{2} - 1}
\]

(8.6)

where

\[
\Omega_d = \begin{cases} 
4\pi & \text{if } d=3 \\
2\pi & \text{if } d=2 \\
1 & \text{if } d=1
\end{cases}
\]

(8.7)

\( L \) is the length of the system along one dimension, \( m \) is the mass of the bosons, and \( \hbar \) is the reduced Planck’s constant. The system is considered to be infinite when \( L \) is large compared to the size of the bosons and no variations in the densities or energies of states are considered with respect to \( L \). The subscript, \( d \), denotes the dimensionality of the system. \( \rho_d(\epsilon) \) is plotted in Figure 8-1 for the different dimensionalities and, as can be seen, only for uniform 3D systems does \( \rho_d(\epsilon) \) go to zero as \( \epsilon \) goes to zero. By inserting Equation 8.6 into Equation 8.5, one can find that \( N_c \) does not remain finite for uniform 2D and 1D systems, indicating that a phase transition corresponding to BEC does not exist for uniform 2D or 1D systems. After some algebra, however, the critical density of a uniform 3D system, \( n_c(T) = N_c(T)/L^3 \), can be found:

\[
n_c(T_c) \approx 2.612 \frac{1}{\lambda_{T_c}^3}
\]

(8.8)

where \( \lambda_{T_c} \) is the thermal de Broglie wavelength at the critical temperature:

\[
\lambda_{T_c} = \sqrt{\frac{2\pi\hbar^2}{mk_BT_c}}
\]

(8.9)

Equation 8.8 gives a clear interpretation of the condensation threshold. As the density increases, or the temperature decreases, the BEC phase transition occurs as the spatial separation between bosons becomes on the order of \( \lambda_{T_c} \). When the density of bosons is high enough and the temperature of the bosons is cold enough,
Figure 8-1: Density of states, $\rho$, for a uniform 1D (a), 2D (b), and 3D (c) system as a function of energy, $\epsilon$.

Figure 8-2: The fraction of bosons occupying different energies, $\epsilon$, in a uniform 3D system for three different chemical potential values, $\mu$. The chemical potential is shown in units of $\beta^{-1}$, where $\beta^{-1} = k_B T$ and $k_B T$ is the thermal energy of the system.

The wavefunctions of nearby bosons begin to overlap and the collective behavior of all bosons in the system begins to become important. In Figure 8-2, the number of bosons as a function of energy for a uniform 3D system is shown for several values of $\mu$. As can be seen, the BEC transition is accompanied by a sharp increase in the occupation of the lower energy states.

Although BEC cannot occur in uniform 2D and 1D systems, a confining potential can restore the possibility for BEC. A 2D harmonic confining potential is given by:

$$V(x, y) = \frac{1}{2} m\omega_{HO}^2(x^2 + y^2)$$

(8.10)
where $\omega_{HO}$ is the harmonic constant. In order for a system to undergo BEC, the energy spacing between states in the harmonic potential, $h\omega_{HO}$, must be small enough so that the bosons in the potential can form a thermal distribution (i.e. $h\omega_{HO} \ll k_BT$). The density of states in a harmonic potential, $\rho_{HO}(\epsilon)$ is given by:

$$\rho_{HO}(\epsilon) = \frac{\epsilon}{(h\omega_{HO})^2}$$ (8.11)

As for a 3D system, $N_c$ can be found by inserting $\rho_{HO}(\epsilon)$ into the equation for $N_{th}(T, \mu = 0)$, Equation 8.5. After some algebra, it can be found that the critical density and temperature are defined by the following relationship:

$$n_{c2D}^2 = \pi^2 \frac{1}{6 \lambda_{Tc}}$$ (8.12)

As for a 3D system, the condensation threshold is reached when the density is large enough or the temperature is cold enough such that the spatial separation between bosons is on the order of the thermal de Broglie wavelength.

**Influence of interactions on Bose-Einstein condensates**

The description of BEC has so far only considered noninteracting bosons. However, the interactions between bosons cause a Bose-Einstein condensate to have very interesting properties such as the massive occupation of a single state, long-range coherence, and superfluid behavior. All of these properties can be understood by considering the energetics of a quantum degenerate gas of bosons (i.e. a gas of bosons that occupy the same state). Full theoretical descriptions of all of these phenomena can be found in various textbooks and courses[114, 110, 159]. However, a qualitative description of these phenomena will be provided here.

A Bose-Einstein condensate occupies a single collective state, not just a set of degenerate or nearly-degenerate single-particle states near the ground state. The fragmentation of the quantum degenerate gas into degenerate but separate states would result in a net increase in energy due to the exchange energy between the
Figure 8-3: (a) Cartoon picture of the interaction between two fragmented condensates. Exchange interactions raise the energy of the system so that a single condensate is preferred. (b) Cartoon picture of the interaction between a condensate at zero wave vector, shown in blue, and thermal excitations at wave vectors greater than zero, shown as red spots. The interactions with thermal excitations lock the phase of the condensate, resulting in spontaneous long-range coherence after the Bose-Einstein condensation transition. (c) The dispersion curve of a free boson (solid black line) transforms into a linear dispersion curve (dashed red line) when a condensate of large enough density occupies the ground state. The red dashed line is called the Bogoliubov excitation spectrum.

fragments, as shown in Figure 8-3a. Because the population of each fragment is large, the exchange energy cost would be so huge that the occupation of a single state is favored. One novel result of the fragmentation energy is that the transition to a Bose-Einstein condensate is accompanied by localization in not only energy but also in the distribution of spatial and momentum states.

A Bose-Einstein condensate can also exhibit superfluid properties. A large occupation of the $k = 0$ state causes the dispersion curve around $k = 0$ to be transformed from the usual parabolic shape into a linear dispersion curve, called the Bogoliubov excitation spectrum[20], as shown in Figure 8-3b. The linear slope of the Bogoliubov excitation spectrum gives a maximum velocity, $v_c$, at which the condensate may propagate and any excitation of bosons from the condensate into an excited state would not be allowed by energy and momentum conservation. A condensate that propagates below $v_c$, called the Landau criterion[84], can propagate without friction.

Finally, a Bose-Einstein condensate is also characterized by spontaneous long-range coherence. The coherence is a result of the interaction energy between the
condensate, \( N_0 \), and a population of Bugoliubov excitations, \( N_q \), which is greatly reduced if the phase of all bosons in \( N_q \) are \( \pi \) out of phase with the phase of the condensate, as shown in Figure 8-3c. Because of the large number of bosons in the condensate, the energy gain is so massive that a long-range coherence is established over the entire condensate. As a result, the photoluminescence emitted from a Bose-Einstein condensate of exciton-polaritons is coherent.

### 8.1.2 Polariton condensation and polariton lasing

BEC of exciton-polaritons in semiconductor microcavities has attracted quite a bit of interest in the last fifteen years. There have been several reports of polariton BEC based on the observation of spontaneous long-range coherence, spectral narrowing, and spatial localization above a critical density\[37, 62, 13\]. Other phenomena associated with BEC and quantum degenerate gases have also been reported, including superfluid behavior\[81, 7, 6, 118, 119\] and the observation of the Bogoliubov excitation spectrum\[146, 75\]. The strong interest in polariton BEC stems from the much higher \( T_c \) compared to atomic BEC; the effective mass of a polariton is on the order of \( 10^{-5} \) of an electron and \( 10^{-8} \) of an atom so that \( T_c \) is increased by orders of magnitude from the \( T_c \) required to observe atomic BEC. Using a gallium nitride based semiconductor microcavity, spontaneous coherent emission from the lower polariton state has been reported at room temperature\[32\]. Additionally, a semiconductor microcavity would be more easily integrated into a device that could exploit the unique properties of the condensate. Toward this goal, polariton switches\[4\] and transistors\[14, 48\] have both been demonstrated. There are now many reviews about polariton condensation and related phenomena, including in-depth reviews of the physics\[67, 35\] and more cursory summaries of recent results\[64, 38\].

Despite the successes, reports of polariton BEC have not been without controversy. The largest source of controversy is centered on whether or not it is correct to describe the spontaneous occupation of the polariton ground state as BEC when the system is often not in thermal equilibrium, meaning that the polaritons do not occupy a distribution of states described by a Bose-Einstein distribution, either before or after
the phase transition[129, 26, 27, 38]. Many researchers have adopted the label of polariton laser to describe the coherent emission from the ground state, although there is not yet a consensus on the terminology.

In either case, the debate is not just one about nomenclature but also about the mechanisms that cause condensation into the polariton ground state. In most reports of polariton BEC (or polariton lasing), a high energy c.w. laser pumps high energy carriers inside the quantum well of the microcavity. As sketched in Figure 8-4, the relaxation of high energy carriers into the ground state can occur through two mechanisms: scattering with phonons and scattering with electrons (i.e. free carriers, excitons, and polaritons). At relatively low carrier densities, the relaxation to the top of the lower polariton branch occurs through phonon scattering[109]. At the top of the lower polariton branch, radiative coupling to the cavity mode causes the lifetime of carriers to decrease depending on the cavity lifetime, on the order of 1-2 ps for typical semiconductor microcavity samples[35]. If the lifetime is shorter than the scattering time of the phonon interactions, the carriers will not fully relax to the lower energy states. This effect is called the phonon bottleneck[135]. Above a certain carrier density, however, scattering between polaritons and other carriers result in the relaxation of polaritons into the ground state at $k = 0$. The occupation of the ground state by a small number of polaritons stimulates other polaritons into the ground state, causing massive occupation of the ground state to occur above a critical density, not necessarily related to the critical density described above for BEC[55, 73, 122]. In the case that the spontaneous occupation of the ground state occurs through carrier scattering, the distribution of polaritons cannot be described by a temperature and the transition is often called a kinetically-driven transition, as opposed to a thermodynamically-driven transition.

Reports so far indicate that polaritons can thermalize to a Bose-Einstein distribution under a limited set of experimental conditions. Initial theoretical work showed that polariton thermalization is aided by tuning the cavity energy to be greater than the exciton energy[28]. In this case, the lower polaritons are more exciton-like, with a longer radiative lifetime and a stronger interaction with phonons and other carri-
Figure 8-4: The mechanisms of Bose-Einstein condensation in exciton-polariton systems, adapted from [135]. The dispersion curves of the upper polariton and lower polariton are shown as solid lines and the dispersion curves of the exciton, cavity, and free carriers are shown as dashed blue lines. The relaxation process occurs in three wave vector regions: the thermal region (TR), the bottleneck region (BR), and the strong coupling region (SC). Note that the box on the right shows a range of wave vectors that is four orders of magnitude wider than the box on the left. After the generation of high energy free carriers, usually from a nonresonant optical pump, carriers can scatter to the exciton and lower polariton branches at high wave vectors in the TR, usually through phonon scattering. The carriers can relax to the top of the lower polariton at the BR through additional phonon scattering, shown as the red arrows. However, due to the phonon bottleneck effect, relaxation to the SC through phonon scattering can be limited. At high carrier densities, however, polaritons can scatter with carriers and relax to the ground state of the lower polariton branch at zero wave vector.
ers. This prediction was confirmed in time-dependent measurements of the polariton energy distributions[36], which were measured on a streak camera after the resonant injection of polaritons at high wave vectors with a pulsed laser. The polariton distributions, measured as a function of time and fit to a Bose-Einstein distribution, thermalized to the lattice temperature after about 40 ps if the cavity was detuned from the exciton energy by $0.25\Omega_R$, where $\Omega_R$ is the Rabi splitting of the polariton states. Subsequent theoretical work showed that phonon and carrier scattering could account for the time-dependent behavior[40]. The first, and only, experimental report demonstrating that polaritons can form a steady-state thermal distribution was reported using a nonresonant, high energy c.w. laser[63]. Over a detuning range of $0.19\Omega_R$ to $0.4\Omega_R$, the distribution of polaritons could fit to a Bose-Einstein distribution for a range of pump powers around the condensation threshold, although only the low energy "thermal tail" of the distribution could be fit. It should also be noted that the steady-state measurements were done using a cadmium telluride semiconductor microcavity, which typically has larger disorder and stronger interactions between carriers than the GaAs microcavities used in the time-resolved measurements and used in this dissertation.

8.1.3 Polariton trapping

The dimensionality of polariton condensation is another area of interest. In most reports of polariton BEC, polaritons were formed using the exciton states of quantum wells. In theory, BEC should not be possible because the quantum well is an infinite uniform 2D system. One possible explanation for the observation of condensation is that polaritons are pinned by disorder to specific positions on the sample[95]. However, in such a case, the ground state of the system would be poorly defined unless the disorder were carefully characterized. As shown by Balili and coworkers[13], creating a harmonic trap using mechanical stress in the plane of the quantum well creates a well-defined ground state in which the polaritons can condense. Creating a well-defined ground state is especially important for long-lifetime samples, in which polaritons can propagate on the order of a millimeter during their lifetime[100].
this case polariton BEC will not be observed because polaritons will accelerate away from the pump spot due to spatial variations in the polariton potential energy surface created by the high density of carriers at the pump spot, as shown in the next section.

There is also general interest in manipulating the spatial properties of polariton condensates. As demonstrated by work done in the trapping of atomic condensates, trapping of polariton condensates could open up new possibilities in understanding and manipulating the spatial properties of polariton condensates. Magnetic [9] and optical [130] traps used to confine atomic condensates have been used to demonstrate new quantum behaviors that depend on the system dimensionality [49] and symmetry [98]. By manipulating the spatial profile of the potential energy surface of exciton-polaritons, similar control over polariton condensates should be feasible.

There have been several reports of the spatial manipulation of polariton condensates. Fabrication methods are one way to create spatial patterns in the polariton potential energy surface: patterned microcavities [58, 44], deposited metallic thin films [82, 71], and naturally present defects in sample growth [96] have all been used to trap polariton condensates. These techniques are able to create well defined potential trap profiles, but they are necessarily static and determined at the time of sample fabrication. Other techniques that have been demonstrated include inducing mechanical strain [13] and surface acoustic waves [29], but the flexibility of these methods to control the polariton potential energy surface is still limited. Recently, all-optical manipulation of polariton potential energy surfaces has been achieved by exploiting the repulsive interactions between polaritons and exciton densities. So far, such works used focused Gaussian spots to create point-like potential barriers in quantum well polaritons [5] and in micropillar polaritons [158] and two focused Gaussian spots to create a one-dimensional harmonic potential [139].
8.2 Methods

8.2.1 Characterization of long-lifetime sample

The semiconductor microcavity sample is described in detail in Section 6.2.2. The samples were designed with a Q-factor of around $10^6$, corresponding to a cavity lifetime of 400 ps[100]. Previous reports on the thermalization properties of exciton-polaritons in semiconductor microcavities used samples with cavity lifetimes of 1-2 ps[36, 63]. The samples were fabricated by Dr. Loren Pffiefer and Dr. Ken West at Princeton and provided by Professor David W. Snoke at the University of Pittsburgh.

The setup to image the photoluminescence (PL) is shown in Figure 8-5. The output of a diode laser was grating stabilized in the Littrow configuration and modulated at 900 Hz with a duty cycle of 1% to prevent sample heating effects. Depending on the detuning of the cavity energy from the exciton energy, the wavelength of the diode laser was tuned from 704 nm to 711 nm. To excite the sample with a single Gaussian pump spot, the diode laser was focused onto the surface of the sample using a microscope objective with numerical aperture of 0.28. The sample was mounted on a cold finger cryostat using silver paste from SPI Supplies and kept at 6.7 K using liquid helium unless otherwise specified. The PL was collected by the objective and separated from the input laser beam using a dichroic mirror.

The PL was sent along two different paths for far-field and near-field imaging. For far-field imaging, an 80 cm lens was used to create a near-field image before a 10 cm lens. The 10 cm lens generated a far-field image on the slits of an imaging spectrometer. The intermediate near-field image plane was used to filter the PL as a function of spatial position using a pinhole. The pinhole diameter corresponded to a 50 μm spot size in the near-field image. Spectrally resolved far-field images gave the intensity of the PL as a function of both the energy and outgoing wave vector of the PL. The far-field imaging path is shown in Figure 8-5b.

For near-field imaging, a 10 cm lens was placed 20 cm away from the near-field image formed by the 80 cm lens, generating another near-field image 20 cm away on the slits of the imaging spectrometer. Note that a different optical path was used.
Figure 8-5: (a) The imaging setup used to measure polariton photoluminescence. The output of a grating-stabilized diode laser was focused onto the surface of the sample using a microscope objective with numerical aperture of 0.28. The sample was held in a cold finger cryostat at 6.7 K. The photoluminescence was separated from the pumping laser using a dichroic mirror and sent through a pair of imaging lenses, which projected the near-field (NF) or far-field (FF) image onto the slits of an imaging spectrometer. (b) The imaging lenses used to create a FF image on the spectrometer, with \( f_1 = 80 \text{ cm} \) and \( f_2 = 10 \text{ cm} \). (c) The imaging lenses used to create a NF image on the spectrometer, with the same focal lengths as in (b) but the \( f_2 \) lens was placed \( 2f_2 \) from the first NF image, forming a second NF image \( 2f_2 \) after the \( f_2 \) lens.

after the 80 cm lens for the two imaging conditions, accounting for the different path lengths of the imaging setups. The spectrally resolved near-field image gives the intensity of the PL as a function of both energy and spatial position of the PL. The near-field imaging path is shown in Figure 8-5c.

The cavity length varied as a function of position on the sample. In order to characterize the energy detuning of the cavity mode from the exciton energy, \( \delta_e \), the energy of the lower polariton was measured as a function of position. For these measurements, the output of the laser diode was directly focused onto the surface of the sample in a Gaussian pump spot of about 10 \( \mu \text{m} \). The power of the diode laser was kept at least an order of magnitude lower than the condensation threshold. A far-field image is shown in Figure 8-6. The image shows the PL as a function of both energy and outgoing wave vector. Instead of the expected parabola, associated with the lower polariton dispersion curve for wave vectors close to zero, the PL is smeared toward one side which is not observed using microcavity samples with short lifetimes. As previously reported[100], the smearing of the PL is due to polaritons accelerating
Figure 8-6: Spectrally resolved far-field exciton-polariton photoluminescence in long-lifetime samples. The photoluminescence is shown as a function of both in-plane wave vector and energy. The colorbar gives the intensity of the photoluminescence.

down the slope of the cavity wedge.

In order to isolate the PL from a single position on the sample, a 50 μm pinhole was placed in the intermediate near-field image plane after the 80 cm lens. The pinhole was centered on the excitation pump spot, giving the spectrally resolved far-field images shown in Figure 8-7 for various positions on the sample. The intensity of the PL was still asymmetric due to the acceleration of the polaritons down the slope of the cavity wedge but the PL was clearly in the shape of a parabola. The energy of the parabola at $k = 0$ was used to map out the energy of the lower polariton as a function of position, shown in Figure 8-8 as blue dots. The energy of the lower polariton for very short and long cavity lengths has asymptotes that are lines of zero and finite slopes, giving the energies of the uncoupled exciton and cavity modes, respectively. The energy difference between the two modes gives the detuning energy, $\delta_\varepsilon = \varepsilon_C - \varepsilon_X$, which is used to label the dispersion curves in Figure 8-7 and as the x-axis in Figure 8-8. The energy difference of $\varepsilon_{LP}$ from the energy of $\varepsilon_X$ and $\varepsilon_C$ at the position that the two uncoupled modes cross gives half the Rabi energy, $\Omega_R$. $\Omega_R$ and $\delta_\varepsilon$ can be used to fit $\varepsilon_{LP}$ and calculate the upper polariton energy, $\varepsilon_{UP}$, using Equation 6.22 from Chapter 6:

$$\varepsilon_{LP/UP}(k) = \frac{1}{2} \left[ \varepsilon_X(k) + \varepsilon_C(k) \mp \sqrt{\Omega_R^2 + \delta_\varepsilon(k)^2} \right]$$ (8.13)
Figure 8-7: Spatially filtered spectrally resolved far-field exciton-polariton photoluminescence in long-lifetime samples. The photoluminescence is shown as a function of both in-plane wave vector and energy. The colorbar gives the intensity of the photoluminescence. The spatial filter was centered on the optical pump spot which was focused at a position on the sample corresponding to a cavity detuning energy, $\delta_c$ of 9.8 meV (a), 0 meV (b), -6.8 meV (c), and -16 meV.

where all values are taken at $k = 0$. The calculated values of $\epsilon_{LP}$ and $\epsilon_{UP}$ are shown as the solid lines in Figure 8-8.

Because the pump laser was much higher energy than the lower polariton resonance, the carriers that were initially excited by the pump laser were scattered into different momentum, energy, and polarization states of the lower polariton, as described in Section 8.1. In order to characterize the propagation behavior of these polaritons, spectrally resolved near-field images of the PL were recorded of polaritons that had come to rest, which were isolated by placing a pinhole in a far-field image plane to isolate the PL from $k = 0$ polaritons. Near-field images of the $k = 0$ polaritons for different $\delta_c$ are shown in Figure 8-9. Depending on the detuning, the polaritons propagated up to 600 $\mu$m. The long propagation distances were a result of the fast propagation time, about a hundredth of the speed of light depending on
the detuning, and the long lifetime of the cavity. Perhaps surprisingly, the polaritons propagated toward higher energies. However, as previously reported[100], the uphill propagation can be understood by the fact that polaritons that propagated toward states of higher energy slowed down as the lower polariton state at $k = 0$ increased in energy. As the polaritons eventually reached $k = 0$, the polaritons emitted PL that was detected in the near-field images of Figure 8-9. Polaritons that propagated toward lower energy states accelerated, so that the wave vectors of the polaritons increased and their luminescence were not collected in the near-field images in Figure 8-9. It should be stressed that the long propagation distances observed in these samples are not observed in short-lifetime microcavity samples and have only recently been reported in samples that are identical to ours by the Snoke group at Pittsburgh[100].

8.2.2 Optical trapping of polaritons

The multiple-spot pumping and optical imaging setup to trap and measure the polariton PL is shown in Figure 8-10, which was nearly identical to the imaging setup for a Gaussian pump spot except for the use of two lenses and a phase mask before the sample. The diode laser was focused with a 10 cm lens onto a phase mask, a transmissive piece of glass with a two-dimensional grating pattern of 20 $\mu$m groove
Figure 8-9: Spectrally resolved near-field images of the photoluminescence from long-lifetime samples. The sample was excited at positions corresponding to cavity detuning energies, $\delta_c$, of -40 meV (a) and -15 meV (b). The photoluminescence was detected only from the $k = 0$ state.

spacing. The far-field image of the phase mask was projected onto the surface of the sample using a second 10 cm lens and the microscope objective before the sample. A near-field image of the reflected light off of the sample is shown in Figure 8-10b. The four bright spots are the first diffraction orders from the phase mask. The weaker spot in the center is the zero diffraction order. In order to change the spatial separation of the pump spots, the positions of the phase mask and lenses were adjusted. In the figures shown in Figure 8-10b, the separation between first diffraction orders was 40 $\mu$m. The use of four distinct spots to create a 2D trap, instead of a ring-shaped beam, provided a higher density of carriers, which was needed to achieve the condensation of polaritons.

In order to characterize the optical trap, the two first-order diffraction pump spots along the vertical direction were centered on the slits of the spectrometer and spectrally resolved near-field images of the PL were recorded as a function of pump power, giving the images shown in Figure 8-11. The pump beams were centered on the sample at a position corresponding to $\delta_c = 0$ meV in Figures 8-11a and b and $\delta_c = -5$ meV in Figures 8-11c and d. For each detuning position, spectrally resolved near-field images are shown for pump powers of 1 mW (a and c) and 22 mW (b and d). The images show relatively low energy polaritons at the pump spots and a cloud of polaritons at higher energies that were delocalized spatially. The bimodal
distribution of polariton energies can be understood as polaritons that were at high wave vectors (and energies) that could propagate in the sample plane and polaritons that were near $k = 0$ that could not propagate. The images suggest that the large density of carriers at the pump spots, including a large population of excitons that were uncoupled to the cavity mode, could scatter with polaritons to create the large population of polaritons at $k = 0$ at the pump spots. For optical traps created close to cavity energies of zero detuning, a larger population of polaritons at lower energies could be observed between the pump spots. The distribution of polariton energies in the middle of the trap gives a measure of the polariton temperature, as discussed in the next section.

Depending on the pump power, the potential energy of the polaritons was blue-shifted by the pump beam, forming a harmonic trap between the two pump spots. The minimum energy of the PL emitted between the pump spots can be fit to a harmonic potential:

$$\epsilon_{LP_{\text{min}}}(x) = U_{HO}x^2 + s_{cav}x + \epsilon_{LP}(x = 0)$$

The linear constant, $s_{cav}$, is the slope of the cavity wedge, $\epsilon_{LP}(x=0)$ is the energy of the lower polariton at the pump spot, and $U_{HO}$ is the harmonic constant. $s_{cav}$ was measured by the detuning dependence of the sample, shown in Figure 8-8, giving a
Figure 8-11: Spectrally resolved near-field images of the optically-induced polariton trap, with the trap centered at positions on the sample corresponding to cavity detuning energies of 0 meV (a and b) and -5 meV (c and d) with total pump powers of 1 mW (a and c) and 22 mW (b and d). The fitting of the photoluminescence to a harmonic potential, as described in the text, is shown as the solid lines. The harmonic constant, $U_{HO}$ is shown in (e) as a function of pump power. The blue (black) lines give the fitting for polaritons at a detuning energy of 0 meV (-5 meV).
value of $s_{\text{av}} = 0.440$ eV/cm. The fits to the harmonic trap are shown on top of the images in Figure 8-11 as the solid lines. By recording the spectrally resolved near-field images for a range of pump powers, $U_{HO}$ was measured as a function of pump power, shown in Figure 8-11e. For the range of pump powers shown in Figure 8-11e, the polariton density was kept below the condensation threshold. The trap constant increased linearly with pump power, as expected, because the blue shift of the lower polariton state increases linearly with carrier density, which increases linearly with pump power. Considering that the Coulomb interactions between exciton-like polaritons should be stronger than the Coulomb interactions between photon-like polaritons, the increase in $U_{HO}$ for both detuning energies was surprisingly similar. One explanation could be that the larger population of polaritons in the center of the harmonic potential for $\delta_e = 0$ meV caused blue shifts in the center of the potential that decreased $U_{HO}$.

8.3 Polariton Bose-Einstein condensation in long-lifetime samples

8.3.1 Thermal properties of long-lifetime polaritons at low excitation densities

In order to characterize the thermal properties of long-lifetime polaritons at low excitation densities, polaritons were optically pumped with a single Gaussian pump spot and the distribution of polariton energies was fit to a Bose-Einstein distribution. The procedure is shown in Figure 8-12 for polaritons measured at $\delta_e = 5$ meV and a low pump power equal to 1 mW. The energy and number of polaritons of each in-plane wave vector state was found, $\epsilon_{LP}(k)$ and $N_{LP}(k)$ respectively. $\epsilon_{LP}(k)$ was extracted from the spectrally resolved far-field images by finding the energy corresponding to the maximum PL intensity for each $k$ state. In all reported pump powers below, $\epsilon_{LP}(k)$ fits the expected shape of the lower polariton, given by Equation 8.13, with the only free parameter being $\epsilon_C(k)$. $\epsilon_C(k)$ is fit to a parabola, giving the effective
Figure 8-12: (a) Spectrally resolved far-field images of the photoluminescence at a position on the sample corresponding to a cavity detuning energy of 5 meV and a pump power of 1 mW. The solid line gives the fit of the maximum intensity to the energy of the lower polariton mode. (b) Exciton Hopfield coefficient squared, $|X_k|^2$, calculated by the parameters extracted from the dispersion curve in (a) and the detuning curve in Figure 8-8. Note that the cavity Hopfield coefficient squared is given by $1 - |X_k|^2$. The lifetime of the lower polariton, $\tau_{LP}$, is shown as the dashed lines, with the values given on the right y-axis. (c) The number of polaritons measured by the PL intensity, $N_{LP}$, as a function of energy of the lower polariton, $\epsilon_{LP}$. The fit to a Bose-Einstein distribution, with $T = 21.2$ K ± 1.0 K and $\mu = -4.1$ meV ± 0.2 meV, is shown as the solid line.
using:

\[
\frac{1}{\tau_{LP}(k)} = \frac{|X(k)|^2}{\tau_X} + \frac{|C(k)|^2}{\tau_C}
\]  

(8.15)

where \(|C(k)|^2\) and \(|X(k)|^2\) are the Hopfield coefficients, \(\tau_X\) is the radiative lifetime of the exciton, about 1 ns, and \(\tau_C\) is the radiative lifetime of the cavity, about 100 ps. The Hopfield coefficients can be calculated using Equation 6.23 from Chapter 6:

\[
|C_k|^2 = \frac{1}{2} \left( 1 - \frac{\delta_e(k)}{\sqrt{\delta_e(k)^2 + \Omega^2_R}} \right)
\]

\[
|X_k|^2 = \frac{1}{2} \left( 1 + \frac{\delta_e(k)}{\sqrt{\delta_e(k)^2 + \Omega^2_R}} \right)
\]  

(8.16)

All the values in Equation 8.16 were given by the fit of the lower polariton energy. \(|X_k|^2\) is plotted for \(\delta_e = 5\,\text{meV}\) in Figure 8-12b, showing the expected increase in the exciton character for larger values of \(|k|\).

Finally, \(N_{LP}(k)\) was converted into a function of \(\epsilon_{LP}\) to give the energy distribution of polaritons, \(N_{LP}(\epsilon_{LP})\). Because \(\epsilon_{LP}(k)\) is symmetric about \(|k| = 0\), the values of \(N_{LP}(k)\) for positive and negative wave vectors were added together for states with the same value of \(|k|\). The values of \(N_{LP}(\epsilon_{LP})\) are plotted in Figure 8-12c (crosses) for \(\delta_e = 5\,\text{meV}\) and a pump power of less than 1 mW. The \(N(\epsilon_{LP})\) values were fit to a Bose-Einstein distribution:

\[
N(\epsilon_{LP}) = \frac{1}{e^{-(\epsilon_{LP} - \mu)/(k_B T)} - 1}
\]  

(8.17)

where \(\epsilon_{LP}\) is measured with respect to \(\epsilon_{LP}\) at \(k = 0\). The fit to \(N(\epsilon_{LP})\) is shown as the solid lines in Figure 8-12c, with \(T = 25.8\,\text{K} \pm 3.5\,\text{K}\) and \(\mu = -12.2\,\text{meV} \pm 1.7\,\text{meV}\). The temperature of the lattice was kept at 6.7 K, indicating that the temperature of the polaritons was roughly four times the temperature of the lattice. The deviations from the lattice temperature and the errors in the fit will be discussed in the next section.

It is worth discussing the role of the conversion constant from CCD counts to number of photons, because estimates of such constants are very difficult to precisely
determine. The main effect of the conversion constant from CCD counts to number of photons was to modify the fitted value of the chemical potential; the number of polaritons at $\epsilon = 0$ meV gives the chemical potential, as can be seen from Equation 8.17. The trends in the temperature and chemical potential were largely insensitive to the conversion constant value. However, due to the nonlinearity of Equation 8.17, the absolute value of the temperature does depend on the conversion constant. This is a basic limitation of all thermalization fitting experiments[61]. It is important to note that the same conversion constant was used to calculate $N_{LP}(k)$ for every pump power, detuning value, and temperature. Additionally, the occupancy of polaritons in the ground state was on the order of one at the condensation threshold, indicating that the estimate of the conversion constant was at least the right order of magnitude.

The fitting of $N_{LP}(\epsilon_{LP})$ strongly depends on $\delta_{\epsilon}$. $N_{LP}(\epsilon_{LP})$ measured at $\delta_{\epsilon} = 8$ meV and at $\delta_{\epsilon} = 0$ meV are shown in Figures 8-13a and 8-13b, respectively. The fit to a Bose-Einstein distribution changes from $T = 23.3$ K $\pm 4.0$ K and $\mu = -11.5$ meV $\pm 2.0$ meV to $T = 56.3$ K $\pm 24.8$ K and $\mu = 29.5$ meV $\pm 13.2$ meV. Clearly, $N_{LP}(\epsilon_{LP})$ that were collected at positions corresponding to more photon-like lower polaritons, i.e. decreasing values of $\delta_{\epsilon}$, cannot be fit to a Bose-Einstein distribution; a hump in $N_{LP}(\epsilon_{LP})$ is visible at energies greater than zero that is due to the acceleration of polaritons down the microcavity energy gradient.

This is a similar result to that previously reported for short lifetime microcavity samples in which the photon-like polaritons also could not thermalize to the lattice[36, 63]. In the short lifetime samples, however, the acceleration of polaritons down the microcavity potential gradient does not have an effect on the thermalization of photon-like polaritons. Instead, the thermalization of polaritons in short lifetime samples is limited by the phonon bottleneck, with most of the polaritons decaying at finite wave vector states that are symmetric about $k = 0$. In the long-lifetime samples, the polaritons accelerated away from the pump spot before thermal equilibrium could be reached at the pump region, as evidenced by the asymmetric distributions in Figure 8-7. Essentially, the ground state of the system was not given by the $k = 0$ state at the pump region.
Figure 8-13: (a) The number of polaritons measured by the photoluminescence intensity, $N_{LP}$, as a function of energy of the lower polariton, $\epsilon_{LP}$. The fit to a Bose-Einstein distribution, with $T = 23.3 \pm 4.0$ K and $\mu = -11.5$ meV $\pm$ 2.0 meV, is shown as the solid line. The polaritons are excited and measured at a position corresponding to a cavity detuning energy $\delta_c = 10$ meV with 1 mW pump power. (b) The same as (a) except $\delta_c = 0$ meV and $T = 56.3 \pm 24.8$ K and $\mu = 29.5$ meV $\pm$ 13.2 meV. (c) and (d) The fitted temperature, $T$ (c), and chemical potential, $\mu$ (d), as a function of $\delta_c$. 
8.3.2 Condensation of untrapped polaritons

In order to characterize the condensation behavior of untrapped polaritons, the PL was collected as a function of pump power, using a single Gaussian pump spot. Spectrally resolved near-field images and far-field images are shown in Figure 8-14 for several pump powers. For all images, the Gaussian pump spot was centered at a position corresponding to $\delta_c = -5$ meV. At low pump powers, the near-field PL formed a cloud around the pump spot that was delocalized in both space and energy. As can be seen in Figures 8-14a and 8-14d, the polaritons occupied many different wave vector states and spatial positions. For higher pump powers, the PL was smeared toward one side of the sample, as shown in Figure 8-14c), but the energy of the PL narrowed toward high energies, corresponding to the occupation of a high momentum state (Figure 8-14f). The fringes in the near-field image at high pump powers were due to a back reflection from a neutral density filter, indicating that the PL became coherent at high pump powers. The energy of the lower polariton at $k = 0$, measured at low excitation densities, is shown as the solid line in Figure 8-14a, giving the change in polariton energy due to the wedge in the cavity length. Surprisingly, at high pump powers the polaritons accelerated toward the side of higher cavity energies. Note that unlike the PL shown in Figure 8-9, in which a filter was used to collect only the PL emitted from $k = 0$, the PL shown in Figure 8-14c was due mostly to polaritons at high wave vectors, as shown in Figure 8-14f.

The power dependence of the untrapped polariton PL can be understood by considering the density-dependent blue shift of the lower polariton state at the pump spot, which caused the polaritons to move away from the pump spot. The spatially varying potential energy which give rise to the energy variations shown as the solid curves in Figures 8-14b and c, can be estimated from the cavity detuning energy, shown in Figure 8-14a, and the blue shift caused by the pump spot, represented as a Gaussian with a height equal to the blue shift at the center of the pump spot and a full-width half maximum equal to the pump spot size. At very high pump powers, the change in energy due to the cavity wedge was relatively small compared to the
Figure 8-14: Spectrally resolved near-field (a-c) and far-field (d-f) images of the photoluminescence (PL) for pump powers of 1 mW (a,d), 7.6 mW (b,e), and 15.5 mW (c,f). Note that the intensity of each image has been normalized. The solid lines show the energy of the lower polariton state at $k = 0$ in (a-c) and the energy of the lower polariton state as a function of $k$ in (d-f).

large blue shift caused by the pump spot. In this case, one might expect two equally distributed populations of polaritons on either side of the pump spot. However, the blue-shifted pump spot and the increase in potential energy due to the cavity wedge formed a slight trap, causing some polaritons to be trapped on the right side of the pump spot. The much larger population of polaritons on one side of the pump spot could be caused by the bosonic nature of the polaritons; a population of polaritons stimulated other polaritons to occupy the right side of the image. Furthermore, because polaritons on the right side of the image had a larger exciton Hopfield coefficient, the stimulated interactions given by the exciton Coulomb interactions were stronger. A similar result was reported with an identical sample[100]. In that report, above a certain pump power, the polaritons eventually relaxed to $k = 0$ in the trap formed between the pump spot and the cavity detuning energy. However, for the diode laser used in these experiments, there was not enough pump power to observe the relaxation to $k = 0$.
Figure 8-15: Spectrally resolved near-field image of trapped polariton photoluminescence at zero detuning (a and b) and -5 meV detuning (c and d) with pump powers of at 90% of the threshold power (a and c) and at the threshold power (b and d).

8.3.3 Condensation of trapped polaritons

Although untrapped polaritons clearly did not form a Bose-Einstein distribution, at pump powers above or below the condensation threshold, the behavior of trapped polaritons was very different. Spectrally resolved near-field images of the PL are shown in Figure 8-15 for $\delta_c = 0$ meV (a and b) and $\delta_c = -5$ meV at pump powers just lower than the threshold power, $0.9P_{\text{thresh}}$ (a and c), and pump powers at $P_{\text{thresh}}$ (b and d). Note that the trap size was decreased slightly from the trap used in Figure 8-11 in order to increase the power density, which was necessary to observe condensation. The biggest qualitative difference between the traps at the two different detuning values is that the trap was deeper for $\delta_c = -5$ meV. However, for both detuning positions, the condensate formed between the two pump spots.
Figure 8-16: Spectrally resolved far-field images of trapped polariton photoluminescence at zero cavity detuning energy using a total pump power for all four beams of 1 mW (a), 6 mW (b), 10 mW (c), and 19 mW (d). The solid lines give the energy of the lower polariton extracted from the maximum photoluminescence.

**Condensation at zero detuning**

In order to characterize the distribution of the trapped polaritons, the far-field PL was collected only from the trapped region by using a 50 μm pinhole in the intermediate near-field image plane and plotted in Figure 8-16. At low pump powers, Figure 8-16a, the distribution of polaritons was centered around a slightly nonzero wave vector, corresponding to the acceleration of polaritons down the wedge of the cavity energy. As the pump power was increased, and the trap began to form, the polariton distribution was centered around $k = 0$, as shown in Figures 8-16b and 8-16c. At very high pump powers, Figure 8-16d, the trapped polaritons condensed around $k = 0$. In contrast, the untrapped polaritons formed a narrow distribution around a very high $k$ state, Figure 8-14f.

Using the far-field images, the distribution of polaritons was extracted for a range of pump powers. $N_{LP}(e_{LP})$ is shown in Figures 8-17a to 8-17c for three pump powers.
At low pump powers, (Figure 8-17a), $N_{LP}(\epsilon_{LP})$ fits to a Bose-Einstein distribution with a relatively high temperature and uncertainty, $T = 27.4 \pm 3.0$ K and $\mu = 6.4$ meV $\pm 0.8$ meV. Because the polaritons were not trapped at low pump densities, the deviations from the Bose-Einstein distribution can be attributed to the propagation of polaritons down the wedge of the microcavity. The fitting of $N_{LP}(\epsilon_{LP})$ remains relatively constant for pump powers below 4 mW, above which the fitting improves.

At pump powers of 12 mW (17 mW), $N_{LP}(\epsilon_{LP})$ is fit by $T = 20.5 \pm 0.8$ K ($T = 7.3 \pm 0.5$ K) and $\mu = -1.2$ meV $\pm 0.05$ meV ($\mu = 0.03$ meV $\pm .003$ meV). The condensation threshold can be found by the change in power dependence of the total number of polaritons, shown in Figure 8-17e, and occured at a pump power of 16 mW. As can be seen, the distribution smoothly fits to a Bose-Einstein distribution throughout a range of densities approaching the phase transition from low and high density. It should be noted that for very high powers above the pumping threshold for BEC, the PL emitted from excited states was generally very weak, so that $N_{LP}$ could only be collected over a narrow range of energies. However, the entire distribution curve can fit to a Bose-Einstein distribution, including the low energy peak; in short lifetime samples, only the high energy “thermal tail” of the distribution curve can fit to a Bose-Einstein distribution[63]. Additionally, in short lifetime samples the thermalization of polaritons before and after the BEC transition only occurs for exciton-like detunings, corresponding to $\delta_\epsilon = 0.19\Omega_R$ to $\delta_\epsilon = 0.4\Omega_R$[63, 36]. The thermalization at $\delta_\epsilon = 0$ meV indicates that the longer cavity lifetime improves the ability for polaritons to come to equilibrium at densities below and above the BEC critical density.

**Detuning dependence**

In order to characterize how the condensation behavior depends on the strong coupling to the cavity mode, the distribution of polaritons was characterized for several cavity detuning energies. The four pump beams were centered around regions of $\delta_\epsilon = 6.8$ meV and $\delta_\epsilon = -5$ meV, corresponding to lower polaritons that were more exciton-like and photon-like, respectively. For each cavity detuning energy, spectrally resolved

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Figure 8-17: Number of polaritons as a function of the lower polariton energy, \( N(\varepsilon_{LP}) \), using pump powers of 2 mW (a), 12 mW (b), and 17 mW (c) at a position corresponding to zero cavity detuning energy. The raw data are given as crosses and the fits to a Bose-Einstein distribution are given as the solid lines. The fitting parameters used for (a)-(c) were the temperature, \( T \), and chemical potential, \( \mu \), and are shown in (d) and (e), respectively. The total number of polaritons, given by summing \( N(\varepsilon_{LP}) \) for each pump power, is shown as a function of pump power in (e).
Figure 8-18: Spectrally resolved far-field images of trapped polariton photoluminescence at a cavity detuning energy of 6.8 meV for pump powers of 1 mW (a), 2 mW (b), 4 mW (c), and 7 mW (d). The solid lines give the energy of the lower polariton state extracted from the maximum intensity of the photoluminescence.

far-field images of the PL were collected from the region between the four pump spots (Figures 8-18 and 8-20). $N_{LP}(\epsilon_{LP})$ was extracted and fit to a Bose-Einstein distribution (Figures 8-19 and 8-21). For each detuning energy, the wavelength of the diode laser was tuned to remain resonant with a dip in the semiconductor microcavity reflectivity. Due to the limitations of the diode laser used in this experiment, the pump power for the excitation at $\delta_c = 6.8$ meV was much lower than at the other detuning energies and was not enough to observe condensation.

The power dependence of the fitting parameters at $\delta_c = 6.8$ meV are very similar to the power dependence at $\delta_c = 0$ meV, at least for pump powers below the condensation threshold. As shown in Figures 8-19d and 8-19e, the temperature and chemical potential that fit $N_{LP}(\epsilon)$ remain relatively constant for pump powers up to about 2 mW, above which the fitting uncertainty decreases, the fitted temperature decreases, and the chemical potential shifts toward zero. At a pump power of 1 mW, $T = 26.0$ K ± 1.9 K and $\mu = -6.1$ meV ± 0.5 meV, and at a pump power of 6 mW, $T = 7.8$ K
Figure 8-19: Number of polaritons as a function of the lower polariton energy, $N(\epsilon_{LP})$, using pump powers of 1 mW (a), 4 mW (b), and 6 mW (c) at a position corresponding to a cavity detuning energy of 6.8 meV. The raw data are given as crosses and the fits to a Bose-Einstein distribution are given as the solid lines. The fitting parameters used for (a)-(c) were the temperature, $T$, and chemical potential, $\mu$, and are shown in (d) and (e), respectively. The total number of polaritons, given by summing $N(\epsilon_{LP})$ for each pump power, is shown as a function of pump power in (e).
Figure 8-20: Spectrally resolved far-field image of trapped polariton photoluminescence at a cavity detuning energy of -5 meV for pump powers of 3 mW (a), 13 mW (b), 24 mW (c), and 45 mW (d). The solid lines give the energy of the lower polariton state extracted from the maximum intensity of the photoluminescence.

$\pm 0.5 \, \text{K and } \mu = -0.7 \, \text{meV} \pm 0.05 \, \text{meV}$. The better fit to a Bose-Einstein distribution at lower powers for $\delta_c = 6.8 \, \text{meV}$, compared to $\delta_c = 0 \, \text{meV}$, can be attributed to two reasons: more exciton-like polaritons had a stronger interaction with phonons and the acceleration to lower cavity energies was a smaller effect.

In contrast, the power dependent behavior of the fitting parameters at $\delta_c = -5 \, \text{meV}$ is very different from the power dependent behavior at $\delta_c \geq 0 \, \text{meV}$, as can be seen in Figure 8-21. At very low pump powers, the fitting of $N_{LP}(\epsilon_{LP})$ to a Bose-Einstein distribution is poor (Figure 8-21a), as expected, due to the acceleration of polaritons to lower cavity energies. For higher pump powers still below the condensation threshold, the fitting of $N_{LP}(\epsilon_{LP})$ to a Bose-Einstein distribution is actually worse, with a larger population of polaritons occupying a finite wave vector (Figure 8-21b). Only above the condensation pump power does $N_{LP}(\epsilon_{LP})$ fit to a Bose-Einstein distribution (Figure 8-21c). For this detuning position, condensation was observed at 35 mW, as shown in Figure 8-21f.
Figure 8-21: Number of polaritons as a function of the lower polariton energy, $N(\epsilon_{LP})$, using pump powers of 4 mW (a), 34 mW (b), and 44 mW (c) at a position corresponding to a cavity detuning energy of -5 meV. The raw data are given as crosses and the fits to a Bose-Einstein distribution are given as the solid lines. The fitting parameters used for (a)-(c) were the temperature, $T$, and chemical potential, $\mu$, and are shown in (d) and (e), respectively. The total number of polaritons, given by summing $N(\epsilon_{LP})$ for each pump power, is shown as a function of pump power in (e).

Figure 8-22: The fitting parameters used to fit the polariton distributions at a cavity detuning energy of -5 meV, as shown in Figure 8-21 but shown in this figure for only the pump powers above condensation threshold. The temperature, $T$, is shown in (a) and the chemical potential, $\mu$, is shown in (b).
sation threshold are shown in Figure 8-22 for clarity. For a pump power of 43 mW, 
\[ T = 30.7 \text{ K} \pm 3.9 \text{ K} \] and \[ \mu = 0.1 \text{ meV} \pm 0.01 \text{ meV}. \]

\[ N_{LP}(\epsilon_{LP}) \] shown in Figure 8-20 indicates that the distribution of polaritons inside 
the trap region for \( \delta_c < 0 \) was determined by the acceleration of polaritons away 
from the pump spots for pump powers below the critical power, and not by the 
thermalization of polaritons by phonons or collisions. To some extent, this result 
might be expected based on the condensation behavior of polaritons generated at 
a single pump spot. As discussed in the previous section, polaritons generated at 
a single pump spot occupied a high wave vector state due to the acceleration away 
from the pump spot. At a critical pump power, all polaritons occupied a single high 
wave vector state, as shown in Figures 8-14e and 8-14f. The fact that the polaritons 
clearly do not fit a Bose-Einstein distribution indicates that the condensation into a 
high wave vector state was kinetically driven; occupation of a high wave vector state 
stimulated additional occupation of the same state. Above a second critical pump 
power, which was not achievable with the laser diode used in this work, polaritons 
are expected to condense into the \( k = 0 \) state, trapped by the single pump spot and 
the gradient in the cavity energy[100]. Similarly, polaritons generated by four pump 
beams accelerated away from each pump spot, occupying a high wave vector state. 
Below the condensation threshold, polaritons in the trap region between the four 
pump spots did not fully relax and occupied finite wave vector states with energies 
greater than the ground state. It should be noted that the polaritons occupied a 
wave vector state greater than \( 2 \mu m^{-1} \) at the region of each pump spot, as shown in 
Figure 8-14e and 8-14f, but occupied a wave vector state of only about \( 0.2 \mu m^{-1} \) in 
the trap region, indicating that some degree of deceleration was occurring in the trap 
region. Above the condensation pump power, the polaritons relaxed into the \( k = 0 \) state, with a distribution that fits to a Bose-Einstein distribution. The fact that 
condensation to \( k = 0 \) was observed using four pump beams but not using a single 
pump beam indicates that the pump power that is needed to trap the polaritons 
between the pump spot and the cavity wedge is higher than the pump power needed 
to trap polaritons between the four pump spots.

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The thermal properties of polaritons in the long-lifetime samples were fundamentally different than the thermal properties of polaritons in short lifetime samples\[36, 63\]. In short lifetime samples, the thermalization is limited by the number of phonon interactions that can occur within the lifetime of the polariton\[36, 63\]; only exciton-like polaritons can thermalize because photon-like polaritons do not interact strongly with phonons and decay faster. Furthermore, the thermalization properties of short lifetime samples are not affected by the acceleration of polaritons to lower cavity energies; the distributions of polaritons about $k = 0$ are symmetric. The thermalization of polaritons in long-lifetime samples, however, were strongly influenced by the acceleration of polaritons to lower cavity energies, as evidenced by the asymmetry in $N_{LP}(k)$ about $k = 0$ observed in the untrapped polaritons. Polaritons that were excited at $\delta_c \geq 0$ meV thermalized within the optically induced trap, fitting to a Bose-Einstein distribution well before and after the phase transition into a Bose-Einstein condensate. Polaritons that were excited at $\delta_c < 0$ meV did thermalize within the trap, although only for pump powers above the threshold for Bose-Einstein condensation. That the polaritons at $\delta_c = -5$ meV above the critical density thermalized indicated that although the phase transition may not have been thermodynamically driven, the polaritons still formed a Bose-Einstein distribution after the BEC phase transition. Such a phase transition had previously been termed a “kinetically-driven Bose-Einstein condensate”\[63\].

**Temperature dependence**

Finally, the temperature dependence of the BEC transition was tested. The temperature of the sample was varied, using a heater on the bottom of the cold finger, between 8.7K to 28.7K, in steps of 2.5K. Spectrally resolved far-field images were collected as a function of pump power for each temperature and $N_{LP}(\epsilon_{LP})$ was extracted and fit to a Bose-Einstein distribution for each pump power and temperature. For all temperature dependent measurements, $\delta_c = 0$ meV. $N_{LP}$ and the fits to $N_{LP}$ are shown in Figure 8-23 for three temperatures at a pump power of 20 mW. The power dependence of the fitted temperatures are shown in Figures 8-24a to 8-24d for four
Figure 8-23: The distribution of polaritons, $N_{LP}$, is shown for three different temperatures: 8.7 K (blue), 13.7 K (black), and 21.2 K (red). The data points are given by the crosses and the fits to a Bose-Einstein distribution are given by the solid lines. For all temperatures, the pump power was 20 mW and the cavity detuning energy was 0 meV.

different temperatures.

For all temperatures below 23.7 K, the fitted temperature roughly follows the same trend as for 6.7K: the fitting of $N_{LP}(\epsilon_{LP})$ is poor at low pump powers because of the acceleration of the polaritons but the fitting improves for high pump powers. $N_{LP}(\epsilon_{LP})$ fit to temperatures close to the lattice temperatures, shown as the dashed black lines, at pump powers slightly below and above the BEC pump threshold, shown as the dashed red lines. However, as mentioned above, the PL emitted from $k = 0$ was very weak at some pump powers above the critical power. For situations where no PL was detected at $k = 0$, the fitted temperature went to zero, regardless of the lattice temperature. This can be seen most prominently in Figure 8-24c where the temperature dips below the lattice temperature for all pump powers above threshold. In fact, the emission fluctuated between a thermalized distribution and a population of polaritons entirely at $k = 0$, as seen in Figure 8-24a and 8-24b. Such fluctuations might be expected as $\mu$ goes to zero and $N_0$ diverges.

The threshold pump power is shown as a function of lattice temperature in Figure 8-24g. A linear line is fit to the data points, shown as the blue line, with an $R^2 = 0.96$, where $R$ is the coefficient of determination. However, the linear line does not intercept the origin, as expected for an ideal gas. If the origin is included in the fit, shown as the black line, then $R^2 = 0.67$. Although there is a clear increase in
Figure 8-24: Temperature dependence of trapped polariton BEC. The fitted temperatures to polariton distributions measured as a function of pump power at $T = 8.7$ K (a), 13.7 K (b), 18.7 K (c), and 23.7 K (d). The black dashed lines give the lattice temperature and the red dashed line gives the threshold pump power. The number of polaritons in the ground state, $N_0$, and the spectral FWHM of the integrated far-field images are shown in (e) and (f), respectively, for $T = 11.2$ K (blue), $T = 16.2$ K (black), and $T = 28.7$ K (red). The threshold pump power is plotted as a function of lattice temperature in (g) with the data given by the crosses and linear fits with and without the origin given by the dashed black line and the solid blue line, respectively.
the threshold pumping power with the lattice temperature, the power dependence also clearly deviates from an ideal gas, which is expected considering the interactions between polaritons[94]. Additionally, the phase transition could be affected by the unique pumping parameters of the experiment since the trap potential depended on the density of polaritons. Further theoretical work should be done to simulate the expected phase transition for polaritons under the experimental conditions reported here.

8.4 Conclusions

The results presented in this chapter show that exciton-polaritons in long-lifetime microcavity samples exhibit fundamentally different physics than short lifetime samples. In particular, the long-lifetime polaritons were strongly influenced by spatial variations in their potential energy surfaces due to both changes in the cavity length and optically induced traps. Polaritons came to thermal equilibrium within traps at densities below and above the critical densities required for the Bose-Einstein condensation phase transition. The strong coupling to the cavity mode had a large influence on the ability of polaritons to reach thermal equilibrium; polaritons that were mostly photon-like could not reach thermal equilibrium before the condensation threshold density due to reduced interaction strengths with phonons and carriers. For polaritons that were in thermal equilibrium, the condensation threshold increased linearly with temperature. The results demonstrate that BEC of long-lifetime polaritons can be well described by thermodynamics. Finally, the results show how the spatial manipulation of long-lifetime polaritons can dramatically control the nonlinear polariton properties.
Bibliography


