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Coherent Response of Two Dimensional Electron Gas probed by Two Dimensional Fourier Transform Spectroscopy

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Coherent Response of Two Dimensional Electron Gas probed by Two Dimensional Fourier Transform Spectroscopy

by

Jagannath Paul

A Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy Department of Physics College of Arts and Sciences University of South Florida

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Keywords: Mahan Exciton, Modulation Doped Quantum Well, 2D Electron Gas, Two Dimensional Fourier Transform Spectroscopy, Quantum Coherence, Magnetoexcitons

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Dedication

To my parents and sisters.
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Abstract

Advent of ultrashort lasers made it possible to probe various scattering phenomena in materials that occur in a time scale on the order of few femtoseconds to several tens of picoseconds. Nonlinear optical spectroscopy techniques, such as pump-probe, transient four wave mixing (TFWM), etc., are very common to study the carrier dynamics in various material systems. In time domain, the transient FWM uses several ultrashort pulses separated by time delays to obtain the information of dephasing and population relaxation times, which are very important parameters that govern the carrier dynamics of materials. A recently developed multidimensional nonlinear optical spectroscopy is an enhanced version of TFWM which keeps track of two time delays simultaneously and correlate them in the frequency domain with the aid of Fourier transform in a two dimensional map. Using this technique, the nonlinear complex signal field is characterized both in amplitude and phase. Furthermore, this technique allows us to identify the coupling between resonances which are rather difficult to interpret from time domain measurements. This work focuses on the study of the coherent response of a two dimensional electron gas formed in a modulation doped GaAs/AlGaAs quantum well both at zero and at high magnetic fields.

In modulation doped quantum wells, the excitons are formed as a result of the interactions of the charged holes with the electrons at the Fermi edge in the conduction band, leading to the formation of Mahan excitons, which is also referred to as Fermi edge singularity (FES). Polarization and temperature dependent rephasing 2DFT spectra in combination with TI-FWM measurements, provides insight into the dephasing mechanism of the heavy hole (HH) Mahan exciton. In addition to that strong quantum coherence between the HH and LH Mahan excitons is observed, which is rather surprising at this high doping concentration. The binding energy of Mahan excitons is expected to be greatly reduced and any quantum
coherence be destroyed as a result of the screening and electron-electron interactions. Such correlations are revealed by the dominating cross-diagonal peaks in both one-quantum and two-quantum 2DFT spectra. Theoretical simulations based on the optical Bloch Equations (OBE) where many-body effects are included phenomenologically, corroborate the experimental results. Time-dependent density functional theory (TD-DFT) calculations provide insight into the underlying physics and attribute the observed strong quantum coherence to a significantly reduced screening length and collective excitations of the many-electron system. Furthermore, in semiconductors under the application of magnetic field, the energy states in conduction and valence bands become quantized and Landau levels are formed. We observe optical excitation originating from different Landau levels in the absorption spectra in an undoped and a modulation doped quantum wells. 2DFT measurements in magnetic field up to 25 Tesla have been performed and the spectra reveal distinct difference in the line shapes in the two samples. In addition, strong coherent coupling between landau levels is observed in the undoped sample. In order to gain deeper understanding of the observations, the experimental results are further supported with TD-DFT calculation.
Chapter 1

Introduction

In a direct band gap semiconductor, the optical properties near the band gap at low temperature is governed by Coulomb bound electron-hole pair or excitons. In low dimensional semiconductors, the effect of confinement changes the optical properties dramatically, leading to observation of many novel phenomena. Quantum well is an example of reduced dimensional structure where the motion of carrier are confined to a quasi 2D plane. This leads to the increase in exciton binding energy compared to bulk due to increased Coulomb interaction. Additionally, exciton-exciton correlation results in the formation of biexciton. Charged excitons or trions are formed due to correlation between excitons and electrons or holes. All these quasi particles contribute to the optical properties of semiconductor quantum well. Quantum wells have been subject of extensive research since its invention in 1070 by Esaki and Tsu [1]. Epitaxial growth techniques, such as Molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), facilitated the growth of these reduced dimensional structures with monolayer precision. Modulation doped heterostructures were introduced by Dingle et al. [2], that led to the development of various optoelectronic devices [3–5]. Very high carrier mobility has been achieved in modulation doped heterostructures because of the reduced ionized impurity scattering. Many interesting optical and transport phenomena [6] were observed.

Ultrafast spectroscopy is an elegant tool to study the exciton dynamics in semiconductors. Advent of ultrafast lasers provide the required high time resolution to probe phenomena that occur on the order of few femtoseconds to several tens of picoseconds. Pump-probe,
transient FWM are very common techniques to probe the exciton dynamics in semiconductors. A recently developed multidimensional nonlinear optical spectroscopy has gained attention due to its ability to obtain information that are not accessible by the conventional one-dimensional time domain techniques. In two dimensional coherent spectroscopy, two time delays are monitored simultaneously, which are then correlated in a two dimensional map in the frequency domain with the aid of Fourier transform. The time delays are scanned with an interferometric precision in order to obtain a meaningful Fourier transformation and phase is preserved. This technique allows to characterized the nonlinear complex signal field both in amplitude and phase. Furthermore, this technique uncovers coherent coupling between resonances which are rather difficult to interpret from time domain measurements. In this thesis, the technique is referred to as two dimensional Fourier transform spectroscopy (2DFTS) and has been employed to explore the exciton dynamics of quasi two dimensional semiconductor heterostructures. It uses three pulse FWM technique to probe the third order nonlinear response (involving $\chi^{(3)}$). Higher order nonlinearities have also been explored using 2DFTS [7–11]. It has been implemented in the UV [12–14], visible [15–19], mid-IR [20–22] and terahertz [23, 24], covering a broad frequency range. Coherent response various materials such as atomic vapors [25–27], molecules [7, 28–32], biological complexes [16, 17, 33–35], and semiconductor nanostructures [8, 36–40], have been studied using 2DFTS.

1.1 Outline of the thesis

The focus of this thesis is to study the non-linear optical properties of a two dimensional electron gas system, using transient four wave mixing and a recently developed two dimensional Fourier transform spectroscopy (2DFTS) techniques. The thesis is organized as follows. The basic optical properties of excitons in bulk and quantum well (undoped and doped) followed by a brief discussion on the effect of magnetic field on the optical properties of the quantum wells are presented in chapter 2.

Basic concepts of two dimensional Fourier transform spectroscopy is covered in chapter
3. Different types of transient four wave mixing (TFWM) techniques are discussed first, followed by third order non-linear response function and Optical Bloch Equation (OBE) using density matrix formalism. A diagrammatic approach to coherently track all possible quantum pathways in Liouville space using double sided Feynman diagram is also presented. Finally, the principles of 2DFTS as well as different types of 2D spectra and advantages of 2DFTS are discussed.

In chapter 4, the 2DFTS experimental setup is presented together with a discussion on spectral interferometry. The scanning procedure is discussed briefly at the end of this chapter. All the experimental results are covered in chapters 5 and 6. In chapter 5, the coherent dynamics of Mahan excitons observed in a modulation doped quantum well at zero magnetic field is presented. Experimental results for the heavy hole (HH) Mahan exciton, including photoluminescence (PL), time-integrated FWM (TIFWM), polarization dependent rephasing and two quantum 2DFTS measurements, as well as effect of temperature on the exciton homogeneous linewidths are discussed in section 5.2. Observation of strong quantum coherence between the HH and LH Mahan excitons followed by theoretical interpretation with simulations based on OBE and time dependent Density Functional Theory (TD-DFT) are presented in section 5.3.

Finally, the dynamics of magnetoexcitons in an undoped and a modulation doped quantum well are explored in chapter 6. Rephasing 2DFT spectra and TIFWM measurements at various magnetic field up to 25 Tesla for both samples together with theoretical interpretation are discussed. Theoretical calculations based on the OBE and the TD-DFT are included in the appendices.
Chapter 2

Excitons in Semiconductor

In general, a semiconductor with a direct gap at the center of the Brillouin zone can be represented in momentum space by the band diagram shown in Fig. 2.1, where the valence bands is completely occupied by the electrons and the conduction band is unoccupied, when the system is in thermal equilibrium. Valence band consists of a heavy hole (HH), a light hole (LH) and a spin split-off (SO) sub-bands [41]. In bulk semiconductor, the HH and LH sub-bands are degenerate at \( k = 0 \) under normal pressure. The split-off band (SO) is due to spin orbit coupling and is separated from the HH and LH valence sub-bands by \( \Delta SO \) at

![Figure 2.1: Schematic of band structure of a direct band gap III-V bulk semiconductor near the Γ point.](image)

hole (LH) and a spin split-off (SO) sub-bands [41]. In bulk semiconductor, the HH and LH sub-bands are degenerate at \( k = 0 \) under normal pressure. The split-off band (SO) is due to spin orbit coupling and is separated from the HH and LH valence sub-bands by \( \Delta SO \) at
\( \mathbf{k} = 0 \). In the parabolic band approximation, the effective mass, \( m^* \) for electrons and holes at the band minima is defined as [42]:

\[
m^* = \left( \frac{1}{\hbar^2} \frac{d^2E}{dk^2} \right)^{-1}.
\]

The expression for the effective mass is also related to the curvature of the bands. HH (LH) valence band has larger (smaller) effective mass and smaller (larger) curvature compared to the LH valence band. In direct band gap semiconductors, such as bulk GaAs, the conduction band is \( s \)-like (orbital angular momentum \( L = 0 \), spin angular momentum \( S = \pm 1/2 \)) and is two fold degenerate. The valence band is \( p \)-like (orbital angular momentum, \( L = 1 \), \( S = \pm 1/2 \)) is four-fold degenerate at \( \mathbf{k} = 0 \). The total angular momentum and the projection of the total angular momentum along the \( Z \)-axis are defined as: \( J = L + S \) and \( J_Z \), respectively. Thus for conduction band, \( J = 1/2 \) and \( J_Z = \pm 1/2 \), and for valence band, \( J = 1/2, 3/2 \). The valence sub-band with \( J = 3/2 \) and \( J_Z = \pm 3/2 \) is known as the heavy hole (HH) whereas, the sub-band with \( J = 3/2 \) and \( J_Z = \pm 1/2 \) is designated as the light hole (LH). The other valence sub-band with \( J = 1/2 \) is called the split-off band (SO).

When a semiconductor is excited by a photon with energy \( \hbar \omega \) such that \( \hbar \omega \geq E_g \), electrons from the valence bands advances to the conduction band leaving behind a +ve hole in the valence band. Since the photon momentum is negligible compared to the electron, this transitions takes place at \( \mathbf{k} \approx 0 \) of the Brillouin zone. Due to Coulomb attraction, these optically generated electron-hole pair becomes correlated, which leads to the formation of a bound state known as exciton. These excitons are quasi-particles that do not possess any net charge but carry momentum and take part in energy transport. In order to form an exciton, the group velocity \( (v_g) \) of the electron and the hole must be equal for \( \mathbf{k} \approx 0 \). The group velocity is defined as:

\[
v_g = \frac{1}{\hbar} \frac{\partial E}{\partial k}.
\]

Furthermore, correlation between two such excitons with opposite spins can form an-
other bound state known as biexciton. In some semiconductor materials, exciton can couple with another electron or hole to form charged exciton known as trion. A positive trion is formed with two holes and one electron whereas, the negative trion is a correlation of two electrons and a hole. All these quasi particles contribute to the optical properties of semiconductors near the band gap at low temperature. However, at higher temperature, effects of optical phonon scattering becomes dominant and may suppress these excitonic effects in the optical spectra in some materials.

Excitons are classified into two types depending on how strong the electron-hole pair is coupled. When the Coulomb attraction between an electron and a hole is very strong, as in the case of ionic crystals, the electron and the hole are very tightly coupled and resulting excitons are known as Frenkel excitons. Whereas, relatively weak coupling between an electron and a hole results in Wannier-Mott excitons which are generally observed in most semiconductors. Due to large dielectric constant in semiconductors, the Coulomb potential is strongly screened and hence the excitons are weakly bound. This is illustrated in Fig. 2.2 where Wannier exciton Bohr radius extends over many lattice cites.
2.1 Excitons in Bulk Semiconductor

Exciton energy levels can be expressed in terms of hydrogen atom energy levels. In center of mass frame, the exciton reduced mass is defined as:

\[ 1/\mu = 1/m_e + 1/m_h, \quad (2.3) \]

where, \( m_e \) and \( m_h \) are the electron and hole effective masses, respectively. The energy of the \( n^{th} \) state of an exciton in bulk semiconductors can be written as:

\[ E^{3D}_X(n) = E_g - \frac{E_{RX}}{n^2}, \quad (2.4) \]

where, \( E_{RX} \) (exciton Rydberg constant) represents the binding energy of the excitonic ground state, and is expressed as:

\[ E_{RX} = \frac{\hbar^2}{2a_B^2}. \quad (2.5) \]

In Eq. 2.5, \( a_B = (\mu \epsilon^4/2\epsilon^2\hbar^2) \) is the exciton Bohr radius, and \( \mu, \epsilon \) are the reduced mass of exciton and the background lattice dielectric constant of the material, respectively. The exciton oscillator strength for the \( n^{th} \) exciton state of a bulk semiconductor is:

\[ f^{(3D)}_n \propto \frac{1}{n^3}. \quad (2.6) \]

The oscillator strength represents how well the electron and hole wave functions overlap. Exciton absorption spectra near the band gap shows several discrete lines. Fig. 2.3 (b) shows the comparison of the strength of the exciton absorption spectrum for the excited states near the band gap. As \( n \) increases, excitonic absorption decreases and eventually merge with the continuum states. The absorption coefficient is proportional to the oscillator strength. For example, the absorption coefficient for \( n = 2 \) state is 1/8th of that of the first excited state. Typical bulk GaAs values at low temperature at \( \Gamma \) point: \( E_g = 1.5195 \pm 0.0005 \)
In center of mass frame, the motion of the exciton has center of mass motion in addition to the relative motion of the two particles about the center of mass and the total energy of exciton can be expressed as [45]:

\[
E(n, \mathbf{K}) = E_g - \frac{E_{RX}}{n^2} + \frac{\hbar^2}{2M} |\mathbf{K}|^2,
\]

(2.7)

where, \( \mathbf{K} = \mathbf{k}_e + \mathbf{k}_h \) is the total exciton wave vector and \( M = m_e + m_h \) is the total exciton mass. The excitonic absorption occurs where a photon dispersion curve (represented by \( E = \frac{hcK}{n} \), where \( c \) is the speed of light in vacuum and \( n \) is the refractive index of the semiconductor) intersect the exciton dispersion curve. The photon dispersion is depicted as a dotted line. The coupling between a photon and an exciton leads to the concept of another quasi particle known as polariton [46, 47].
2.2 Excitons in Quantum Well

A quantum well is a low dimensional heterostructure formed by introducing a layer of low band gap material, such as GaAs, between two higher band gap materials, such as AlGaAs. In these structures, the motion of the charge carriers are confined in one directions (in the growth direction) which restrict their motion to the quasi-two dimensional quantum well region. The confinement leads to unique optical properties compared to the bulk materials. The crystal structures of III-V compounds such as GaAs, AlAs, and Al$_x$Ga$_{1-x}$ are of zinc blend type and have cubic symmetries at normal pressure. A quantum well formed with GaAs/Al$_x$Ga$_{1-x}$As heterostructure system is shown in Fig. 2.4. GaAs with band gap 1.52 eV (4.2 K) is sandwiched between two Al$_x$Ga$_{1-x}$As layers which has a band gap of $\approx$ 1.95 eV (4.2 K) for $x = 0.3$. Al$_x$Ga$_{1-x}$As is direct band gap semiconductor for $x < 0.45$, and $E_{AlGaAs}(x) \approx 1.424 + 1.247x$ eV at room temperature [48]. For $x > 0.45$, it becomes indirect. $\Delta E_C$ and $\Delta E_V$ are the conduction and valence band offsets, respectively which represent the confinement potential for the respective bands. Usually the GaAs/Al$_x$Ga$_{1-x}$As heterostructures are grown on (001)-GaAs substrate. The lattice parameters of GaAs and Al$_x$Ga$_{1-x}$As alloy are very similar which allows to grow these heterostructures with very
small lattice mismatch (less than 0.15%). The high quality quantum wells are grown by molecular beam epitaxy (MBE) or by metal organic chemical vapor deposition (MOCVD) techniques. With these techniques the structures can be grown with monolayer precision. These techniques made possible to the development of numerous optoelectronic devices based on quantum well heterostructures.

### 2.2.1 Exciton Binding Energy in Quantum Well

The exciton binding energy and the oscillator strength of a quantum well with infinite barrier can be expressed as:

\[
E_{RX}^{(2D)} = \frac{E_{RX}}{(n - \frac{1}{2})^2}, \tag{2.8}
\]

and

\[
f_n \propto \frac{1}{(n - \frac{1}{2})^3}, \tag{2.9}
\]

Figure 2.5: Binding Energy of HH and LH excitons in undoped GaAs/AlGaAs QW. This Figure is reproduced from [49] with permission.
respectively. The binding energy of excitons in quantum well is larger than that in bulk \([49–52]\). In quantum well with infinite barrier, the exciton binding energy increases monotonically with the decrease in the well width thickness \([49–51]\) and attains a upper limit of four times the binding energy of the bulk semiconductor, i.e., \(E_{RX}^{(2D)} = 4E_{RX}\). However, for finite barrier, the binding energies are found to be lower than the bulk. For example, in GaAs/AlGaAs quantum well with 10 nm well width, the binding energy of the HH exciton ground state is \(\approx 8.5\) meV \([50]\). It was shown that for a finite barrier height, the excitonic binding energy first increases with decrease in well width and then decreases when the well width becomes very narrow \([49, 52, 53]\). The oscillator strength is also enhanced in quantum well. From Eq. (2.9), for \(n = 1\), \(f_{2D} = 8f_{3D}\).

### 2.2.2 Selection rules in GaAs Quantum Wells

The quantum confinement acts as a perturbation which results in lifting the degeneracy of the HH and LH at \(k = 0\). The simple level scheme for the HH and LH single excitonic transitions for circularly polarized excitation is shown in Fig. 2.6. The HH exciton transitions are represented by \((-\frac{3}{2}, -\frac{1}{2})\) and \((\frac{3}{2}, \frac{1}{2})\), whereas, the LH excitonic transitions are \((-\frac{1}{2}, \frac{1}{2})\) and \((\frac{1}{2}, -\frac{1}{2})\). The dipole allowed transitions for right circularly polarized (left circularly
polarized) light denoted by $\sigma^+$ ($\sigma^-$) are shown with dashed (solid) blue (red) arrows. The transition dipole moments, $\mu$, for the HH and LH transitions can be written as [54]:

\begin{align*}
\mu \left( \frac{3}{2}, -\frac{1}{2} \right) &= \mu_0 \sigma^+ = \frac{1}{\sqrt{2}} \mu_0 (\hat{x} + i\hat{y}), \\
\mu \left( -\frac{1}{2}, -\frac{1}{2} \right) &= \frac{1}{\sqrt{3}} \mu_0 \sigma^+ = \frac{1}{\sqrt{6}} \mu_0 (\hat{x} + i\hat{y}), \\
\mu \left( \frac{3}{2}, \frac{1}{2} \right) &= \mu_0 \sigma^- = \frac{1}{\sqrt{2}} \mu_0 (\hat{x} - i\hat{y}), \\
\mu \left( -\frac{1}{2}, \frac{1}{2} \right) &= \frac{1}{\sqrt{3}} \mu_0 \sigma^- = \frac{1}{\sqrt{6}} \mu_0 (\hat{x} - i\hat{y}),
\end{align*}

where, $\hat{x}$ and $\hat{y}$ are the unit vectors and $\mu_0$ is the modulus of transition dipole. However, this simple single exciton level scheme neglects the interaction between excitons and does not explain many experimental observations. For example, the observation of negative delay signal in the time integrated TFWM measurement performed on a GaAs/AlGaAs multiple quantum well [55] could not be explained adequately by the single excitons level scheme. Exciton-exciton correlation leads to the formation of bound and unbound two-exciton states. Fig. 2.7 shows the extended level scheme for GaAs/AlGaAs quantum well where two excitons states are included. The allowed transitions for RCP (LCP) lights are shown with blue solid (red dashed) arrows.
2.3 Modulation Doped Quantum Well

The optical properties of modulation doped heterostructures have been studied extensively in past few decades. A modulation doped heterostructure was first grown by Dingle et al. [2], which led to the development of various high speed semiconductor devices such as high electron mobility transistors (HEMT) [3], modulation doped FET (MODFET) [4], selectively doped heterojunction transistor (SDHT) [5], etc. In modulation doped (also known as δ-doped) quantum wells, a thin layer of donor impurity atoms is inserted within the barrier region (e.g. Si in the AlGaAs barrier in GaAs/AlGaAs quantum well). The excess electrons becomes spatially separated from the parent donor atoms and move into the quantum well region. As a result, the electrons leave behind ionized impurities in the barrier region and get confined by the quasi-triangular potential formed at the interface. This results in the formation of a quasi two dimensional electron gas (2DEG) in the quantum well region. The fact that the carriers are now separated from the ionized impurities, an enhancement of carrier mobilities occurs due to reduced ionized-impurity scattering at low temperature. The formation of 2DEG in a GaAs/AlGaAs heterostructure is depicted in Fig. 2.8. Similarly, when

![Diagram of 2DEG formation in a GaAs/AlGaAs heterostructure](image-url)
barrier regions are doped with acceptor (e.g., Be in the AlGaAs barrier in GaAs/AlGaAs quantum well), a two-dimensional hole gas (2DHG) is formed.

Figure 2.9: (a) Modulation Doped Quantum Well structure where both the AlGaAs barriers are doped with Si. (b) The details of the structure of a 12 nm MDQW.

The transport and optical properties of the modulation doped heterostructures structure strongly depend on the parameters such as concentration of dopants, the spacer-layer thickness [56, 57], and the concentration of Al [58] in the AlGaAs barrier. The mobility in a high quality MDQW is $\sim 10^6 \text{ cm}^2/\text{V} \cdot \text{s}$ and a value exceeding $10^7 \text{ cm}^2/\text{V} \cdot \text{s}$ [59–61] has also been reported at low temperatures. It was shown that the mobility increases with increasing spacer thickness [62]. For heavily doped QW, the band structure gets modified significantly due to various many-body effects such as, band gap normalizations (BGR), band tailing, and band gap shrinkage.

Fig. 2.9 (a) shows an n-type modulation doped quantum well structure used in our study where both AlGaAs layers are doped with Si with a doping concentration of $\sim 1 \times 10^{12}$ cm$^{-2}$ and the detailed structure of the modulation doped quantum well is illustrated in Fig. 2.9 (b). The measurements were performed on doped quantum wells with two different well
In an n-type MDQW, the barrier layers are usually heavily doped with donor atoms and resulting high density of excess electrons populate the quantum well region forming a 2D degenerate electron gas. As a consequence, the Fermi level resides inside the conduction band and all the states up to the Fermi level are completely occupied by this 2DEG and any electron transition from the valence band to the conduction band at $k \approx 0$ are restricted due to Pauli exclusion principle. Thus, upon optical excitation, unlike a direct band gap semiconductor, the absorption can not take place at $k \approx 0$, instead, it occurs in the vicinity of the Fermi level, i.e., at wave vector $k \approx k_F$ ($k_F$ is the Fermi wave vector), whereas, the recombination predominantly takes place from the bottom of the conduction band and up to the Fermi level leading to a Stokes-shifted photoluminescence (PL) from the absorption. The
energy difference $\Delta E$ between the PL and the absorption is similar to Moss-Burstein (MB) shift [63] observed in doped bulk semiconductor. The 2D electron density can be determined from the energy shift as [64] (considering only first excited state of the conduction band is filled):

$$N_s = \frac{m_e}{\pi \hbar^2} \Delta E,$$

where, $N_s$ is the number of electrons per unit area (2D sheet density). In semiconductors, the heavy hole mass is generally much heavier than the electron mass. Thus, for a given value of doping concentration, the Fermi energy, $E_F$, is larger in n-doped quantum wells compared to p-doped quantum wells.

Although the bound excitonic state is no longer stable at high carrier density due to screening, phase-space filling and short-range exchange interaction between carriers in the Fermi sea, a bound state with respect to the Fermi level still forms. This phenomenon was first discussed by Mahan in highly doped bulk semiconductors and in metals and is referred in the literature as ”Mahan exciton” [65, 66] or Fermi edge singularity (FES). This bound state results from the sharpness of the Fermi edge and Pauli exclusion principle’s restriction of the electron’s scattering. The mechanism of PL and absorption process in modulation doped quantum well is illustrated in Fig. 2.10. The absorption spectra in MDQW follows a power law with respect to the Fermi level. The PL spectra from an n-type MDQW at low temperature exhibits strong enhancement near the Fermi edge. This phenomena is analogous to soft-X-ray emission and absorption in metals [67, 68]. The FES is very strongly dependent on temperature. The absorption or PL peak diminish and become broad as the temperature increases, which has been observed in previous studies.

### 2.4 Quantum Well in Magnetic Field

In semiconductors under the application of magnetic fields, the energy states of the conduction band and the valence bands become quantized which results in the formation
of discrete Landau levels. The Landau levels are separated by cyclotron energy. Optical excitation in the presence of magnetic field leads to the formation of Coulomb correlated excitons. Furthermore, Coulomb correlation between two such excitons with opposite spin can form biexciton. The excitons and biexcitons remain bound even at high magnetic fields, until the cyclotron energy becomes comparable to their binding energies. In weak magnetic field when the exciton binding energy is larger than the cyclotron energy, excitons show a quadratic diamagnetic shift in energy with the external field, whereas, at high magnetic field, when the cyclotron energy is greater than the exciton binding energy, the exciton energy shift linearly, provided the valence band mixing is neglected [69–73].

In modulation doped quantum well, when the Fermi sea is subjected to large magnetic fields, Landau levels are formed, and optical excitations originating from different Landau levels can be observed [74–76]. The dephasing of optical excitations in 2DEG in external magnetic fields has been studied theoretically and experimentally, using coherent FWM spectroscopy [77–86]. The 2D electron gas form a strongly-correlated system in high magnetic field and this quantization of energy states leads to unique transport phenomena at low temperature, such as fractional and integer quantum hall effect [6]. Light scattering and photoluminescence measurement in the quantum Hall regime were performed early on and have provided important insights into the physics of optical excitations at high magnetic fields [87–99]. The light scattering experiments have lead to the observation of magnetorotons and have provided details into the physics of composite fermions at different fractional filling factors [100–107] and explored the interactions of bilayer quantum Hall systems [108–115]. The energy eigen values of a 2DEG are derived in Appendix A.

2.5 Relaxation Mechanism

When a semiconductor is excited with a ultra short laser pulse, it establishes a coherence between the ground state and the excited state of the system. As soon as the laser pulse
is turned-off, this phase coherence starts to decay due to various scattering processes and it remains coherent until time $T_2$. This characteristic decay time is referred to as the dephasing time or the decoherence time of the system, and can be expressed as [116]:

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*},$$  \hspace{1cm} (2.15)

where, $T_2^*$ represents the pure dephasing time and $T_1$ is the population relaxation time. $T_2$ is related to the homogeneous linewidth $\Gamma_{hom}$ of optical transitions as:

$$\Gamma_{hom} = \frac{2\hbar}{T_2^*}. \hspace{1cm} (2.16)$$

Eq. 2.15 implies that $T_2 \leq 2T_1$, i.e., the upper limit of dephasing time $T_2$ is set by the population relaxation time. The pure dephasing time is usually much smaller than the population time in many semiconductor materials and thus, $T_2$ is a good measure of the pure dephasing time in those materials.

Semiconductors are very sensitive to excitation conditions. At higher excitation density, exciton-exciton and free carrier-exciton scattering are enhanced which cause faster dephasing, and hence broadened linewidth. The excitation density dependent homogeneous linewidth can be expressed as [117]:

$$\Gamma_{hom}(n_X) = \Gamma_{hom}(0) + \gamma_{XX} a_B^2 E_B n_X,$$  \hspace{1cm} (2.17)

where $a_B$, $E_B$ , and $n_X$ are the exciton Bohr radius, exciton binding energy, and exciton density, respectively. $\gamma_{XX}$ is a dimensionless parameter.
Scattering with phonons is another major source that causes significant linewidth broadening. The temperature dependent homogeneous linewidth can be expressed as [117]:

$$\Gamma_{\text{hom}}(T) = \Gamma_{\text{hom}}(0) + aT + \frac{b}{\exp\left(\frac{\hbar \omega_{\text{LO}}}{k_B T}\right) - 1},$$

(2.18)

where, the first term is independent of temperature and represents the homogeneous linewidth due to scattering with ionized impurities, interface roughness, etc. The second term is proportional to the temperature and is due to acoustic phonon scattering ($a$ is the acoustic phonon scattering parameter). The third term represents the linewidth broadening due to scattering with optical phonons with energy $\hbar \omega_{\text{LO}}$ and $b$ is optical phonon scattering parameter. In semiconductors, acoustic phonon scattering dominates at the low temperature range (up to $\sim 80$K for GaAs) [118] whereas optical phonon scattering becomes dominant at higher temperature ($> 80$K for GaAs).
Chapter 3

Principles of Multidimensional non-linear Optical Spectroscopy

Multidimensional Fourier-transform spectroscopy is an important tool to study light-matter interactions in various materials. The concept originates from the development of nuclear magnetic resonance (NMR) [119] and it has been implemented in two-dimensional spectroscopy [120]. Two dimensional Fourier transform spectroscopy (2DFTS) has been used both in optical and infrared regime using ultrashort laser pulse. In the infrared, it has been used to probe the coherent dynamics of the vibrational states in molecules [15, 25, 36, 121–128] whereas, in the optical frequency regime, electronic transitions in molecules [15, 25] and semiconductors [36, 124] have been studied. In 2DFTS, excitation laser pulses separated by different times delays induces a non-linear signal in the sample. The phase of this signal can be coherently tracked with respect to the time delays [125]. Upon Fourier transformation of the time domain data set, one can obtain a two dimensional spectrum in frequency domain. 2DFTS has several advantages over the time-domain measurement techniques which will be discussed in the following sections.

3.1 Transient Four Wave Mixing (TFWM) Techniques

Interaction of light with a dielectric medium induces a macroscopic polarization in the system which is proportional to the electric field associated with the light if the incident light intensity is low, and the system can be characterized by a linear response function. Physical properties such as absorption, reflection and refraction are considered linear. For sufficiently intense light field, the optical properties of the medium cannot be described by the linear term, and other higher order non-linear terms must be considered. In such case,
the induced polarization can be expressed as:

\[ P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots, \]  

(3.1)

where \( P, E \) and \( \chi^{(n)} \) are the macroscopic induced polarization, electric field associated with the incident light and the \( n \)-th order susceptibility, respectively. In the above expression, \( P \) and \( E \) are vectors while \( \chi^{(n)} \) is tensor of rank \((n + 1)\). The first term \( \chi^{(1)} \) is the linear with field. The second higher order term \( \chi^{(2)} \) and all other even order terms are for a system with inversion symmetry. The third term \( \chi^{(3)} \) is the first non-vanishing non-linear term that governs the non-linear optical processes in such system. In order to probe the third-order response of the system interaction of three incident electric field is necessary. Various nonlinear spectroscopic techniques have been employed in order to study the non-

\[ \text{k_{Sig} = 2k_B - k_A} \]

Figure 3.1: Two pulse TFWM.

linear optical properties which are generally performed either in time domain (also known as transient) or in frequency domain. Coherent transient four wave mixing (TFWM) is an example of such technique which has been used to study the coherent dynamics of various material systems.

This spectroscopy technique is performed using both two-pulse and three-pulse configuration. In a two-pulse transient FWM technique, two laser pulses are incident on a sample and one of the two pulses acts twice in order to generate the third order non-linear signal.
Let us consider two pulses with wave vectors $k_A$ and $k_B$, separated by delay $\tau$, are incident on the sample. For $\tau > 0$, $k_A$ arrives on the sample first. The third order signal is generated in the phase matched direction $k_S = 2k_B - k_A$ where the second pulse acts twice. In three-pulse TFWM (Fig. 3.2), three laser beams with wavevectors $k_A$, $k_B$ and $k_C$ are incident on the sample. The interaction of the first pulse ($k_A$) with the sample establishes a coherence between the ground state and the excited state. The second pulse ($k_B$) arrives on the sample after a delay $\tau$ and converts the coherence to an excited state population. This population varies sinusoidally as the electric fields associated with the two pulses interfere and results in the formation of a dynamic grating with a spatial period of $k_B - k_A$. The periodicity of the grating is given by $\Lambda = \lambda/[2\sin(\theta/2)]$, where $\lambda$ and $\theta$ are the wavelength of the excitation beams and the angle between the two beams at the focus, respectively. In other words, when the fields of the two pulses are in phase, they interfere constructively and creates an excited state population. On the other hand, when they are out of phase, they interfere destructively leading to depopulation. The third pulse ($k_C$) interacts with the sample after a delay $T$ from the arrival of the second pulse and generates the non-linear signal. Three-pulse TFWM has advantage over the two-pulse TFWM as the intensity of the FWM signal can be monitored by scanning two time delays $\tau$ and $T$. The dephasing rate can be obtained by scanning $\tau$ for a fixed $T$, while scanning $T$ for a fixed $\tau$ yields the population decay rate.

\[
k_{\text{sig}} = -k_A + k_B + k_C
\]

Figure 3.2: Three pulse TFWM in non-collinear BOX geometry.
signal detection method, namely time-integrated (TI-FWM), time-resolved (TR-FWM) and spectrally resolved (SR-FWM). All three types of techniques are summarized in Fig. 3.3 for a three pulse excitation scheme where pulses are arranged in a box geometry.

### 3.1.1 Time integrated Four Wave Mixing (TI-FWM)

In a three pulse time integrated FWM experiment, the intensity of the non-linear signal is monitored by a slow detector. The signal intensity can be expressed as:

\[ S_{TI}(\tau, T) \propto \int_0^\infty |P^{(3)}(\tau, T, t)|^2 dt, \]  

(3.2)

where \( P^{(3)}(\tau, T, t) \) is the third order polarization term. If we consider a homogeneously broadened two-level system, then, in the impulsive pulse limit, i.e., when the pulse is much shorter than the dephasing time and can be approximated as delta function in time, the FWM signal can be expressed within the Markovian approximation as [129]:

\[ S_{TI}(\tau, T) \propto \Theta(\tau)\Theta(T)e^{-2\gamma\tau}e^{-\Gamma_{gr}T}, \]  

(3.3)
where $\gamma$, $\Gamma_{gr}$, and $\Theta(t)$ are the homogeneous linewidth, the population decay rate, and the Heaviside step function, respectively. For an inhomogeneously broadened system, the TFWM signal is emitted as a photon echo after a time $t = \tau$ after the arrival of the third pulse and can be expressed as:

$$S_{TI}(\tau, T) \propto \Theta(\tau)\Theta(T)e^{-4\gamma\tau}e^{-\Gamma_{gr}T}.$$  \hspace{1cm} (3.4)

An important aspect of many body effect in semiconductors is the appearance of transient FWM signal for negative delays. This phenomenon was first reported by Leo et al. [55] in a GaAs/AlGaAs MQW using two pulse time integrated FWM technique. The TIFWM

![Figure 3.4: TIFWM Signal for negative delay. This Figure is reproduced from Ref. [55] with permission.](image)

signal intensity with time delays at three different temperatures is shown in Fig. 3.4. The slope of the negative time delay signal was found to be about half the slope of the positive
decay signal, i.e., the rise time of the signal is half the decay time. This observation was attributed to exciton-exciton correlation.

3.1.2 Time-Resolved Four Wave Mixing (TR-FWM)

Time integrated FWM does not predict if the non-linear signal is a photon echo or a free polarization decay (FPD). In time resolved FWM technique, the TFWM signal is up-converted using a delayed reference pulse by a time $t$ in a non-linear optical crystal and the resulting non-linear signal intensity is measured as a function of the real time $t$. The TR-FWM signal has the form:

$$S_{TR}(\tau, T, t) \propto \int_{-\infty}^{\infty} |P^{(3)}(\tau, T, t')|^2 \cdot |E_{ref}(t - t')|^2 \, dt', \quad (3.5)$$

where $E_{ref}(t)$ is the electric field of the reference pulse.

3.1.3 Spectrally Resolved Four Wave Mixing (SR-FWM)

In spectrally resolved technique, the FWM signal is heterodyned with a reference pulse, also called local oscillator (LO), and the resulting interferogram is dispersed in a grating spectrometer and is then detected by a CCD. Using this technique, the phase of the complex signal field can be extracted, thus providing complete information, i.e. both amplitude and phase, of the signal field. The spectrally resolved FWM signal can be written as:

$$S_{SR}(\tau, T, \omega_t) \propto \int_{-\infty}^{\infty} |P^{(3)}(\tau, T, t)|^2 e^{i\omega_t t} \, dt, \quad (3.6)$$

where $\omega_t$ is the frequency of the emitted signal. The details of this technique is discussed in the Section 3.5.
3.1.4 Quantum beat Vs. Polarization Interference

In many systems, the optical transitions are often found to be coupled as they originate from a common ground state. This coupling manifests itself in the form of a beating in the transient FWM signal and is referred to as quantum beating (QB). Beating in the TFWM signal can also be observed due to the interference of FWM signals on the detector originating from two isolated two level systems, and is known as polarization interference (PI). It is often very difficult to distinguish between these two types of beating observed in TFWM signal.

Figure 3.5: Illustration of a three level coupled system: Two excited states sharing a common ground state.

Let us consider a three level system as shown in Fig. 3.5, where two closely lying excited states denoted by $|A\rangle$ and $|B\rangle$ with energies $E_A$ and $E_B$, respectively, have a common ground state $|g\rangle$ with energy $E_g$. The separation between the two excited states ($\Delta E = E_A - E_B$) being small, both states can be excited resonantly with a ultra short laser pulse with sufficient spectral width. The interaction of the laser pulse creates a coherence between the ground state and the excited states which decays at a rate characterized by the dephasing time. This coherence manifests itself as a beating in the TFWM signal with a beating period equal to $T_B = h/\Delta E$, and the beating lasts until the system dephase. For example, in GaAs/AlGaAs quantum well, the HH and the LH valence sub-bands are energetically separated due to
confinement and can be simultaneously excited by a ultra short laser pulse. The excitonic transitions from HH and LH form a 3 level system, and beating between HH and LH can be observed in TFWM measurements [130, 131]. QB between free and bound excitons has also been observed in GaAs/AlGaAs MQW [132], although, it was later pointed out that those were due to polarization interference. QB between bi-exciton and exciton was observed in 2P-TFWM signal in GaAs/AlGaAs MQW [133, 134]. Furthermore, QB of magneto-excitons in GaAs was studied by Bar-Ad et al. [135]. The beating was also observed in bulk CdSe [136].

Spectrally resolved FWM technique was also used to investigate the nature of beating in two different material systems and was able to distinguish between the two types of beating [137]. Two dimensional Fourier transform spectroscopy can detect the presence of quantum beating in a system without any ambiguity. Any coherent optical transitions appear along the diagonal of a two dimensional map and any coherent coupling between them appear as separate peaks along the cross-diagonal direction. The details of this technique will be presented in section 3.5.

### 3.2 Non-linear Response Function

Interaction of light with a dielectric medium induces a macroscopic polarization which can be characterized by a multi-dimensional non-linear response function [138]. For a three-pulse four wave mixing experiment, three pulses $A$, $B$ and $C$ with wavevectors $\mathbf{k}_A$, $\mathbf{k}_B$ and $\mathbf{k}_C$ interact with a given system at times $t_A$, $t_B$ and $t_C$, respectively. Pulse $A$ and pulse $B$ are separated by the coherence time, $\tau = t_B - t_A$ while pulse $B$ and pulse $C$ are separated by population time, $T = t_C - t_B$. $t$ is the detection time. Thus, the carrier dynamics of the system can be represented by a third order response function, $R^{(3)}$. The electric field for the
three pulses can be written as:

\[
E_j (r, t) = \left[ \varepsilon_j^+ (t) e^{i (k_j \cdot r - \omega_j t)} + \varepsilon_j^- (t) e^{-i (k_j \cdot r - \omega_j t)} \right] \hat{e}_j, \tag{3.7}
\]

where \(k_j, \omega_j, \) and \(\hat{e}_j\) are the wavevectors, carrier frequency, and unit polarization vector, respectively for the \(j\)-th pulse \((j = A, B, C)\). \(\varepsilon_j^+ (t) (\varepsilon_j^- = (\varepsilon_j^+)^*)\) is the positive (negative) frequency component of the slowly varying pulse envelope. Thus, the pulse sequence can be expressed as:

\[
E (r, t) = \sum_{j=A,B,C} E_j (r, t - t_j), \tag{3.8}
\]

where \(j\) represents the time ordering of the incident pulses. The overall third-order polarization can be expressed as:

\[
P^{(3)} (r, t_A, t_B, t_C) = \int_0^\infty \int_0^\infty \int_0^\infty R^{(3)} (r, t'_A, t'_B, t'_C) \cdot E_A (r, t'_A - t_A) E_B (r, t'_B - t_B) E_C (r, t'_C - t_C) dt'_A dt'_B dt'_C, \tag{3.9}
\]

where \(R^{(3)} (r, t'_A, t'_B, t'_C)\) is the time dependent third-order non-linear response function. The \(n\)-th order response function \(R^{(n)}\) can be expressed as a combination of \(n + 1\) order correlation functions of the dipole moment operator [139, 140]. In the limit of impulsive excitation, the pulse envelope is assumed to be much shorter than any time scale of the system and the
delays between the pulses. In such case, the electric fields associated with each pulse can be approximated as delta function. With this assumption, Eq. 3.9 can be evaluated analytically and can be expressed as [54]:

\[
P^{(3)}(\mathbf{r}, t_A, t_B, t_C) = R^{(3)}(t_A, t_B, t_C) \cdot \varepsilon^\pm_A \varepsilon^\pm_B \varepsilon^\pm_C \cdot e^{i(\pm \mathbf{k}_A \pm \mathbf{k}_B \pm \mathbf{k}_C) \cdot \mathbf{r}} \cdot e^{-i(\pm \omega_A \pm \omega_B \pm \omega_C) t} \\
\times e^{i(\pm \omega_A \pm \omega_B t_B + \omega_A t_B) t_C} \cdot e^{i(\pm \omega_A \pm \omega_B t_B) t_B} \cdot e^{i(\pm \omega_A t_A).}
\]

(3.10)

The expression for polarization in Eq. 3.10 contains all possible time ordering for the three pulses. Each pulse sequence corresponds to a separate FWM signal in the phase-matched direction \( k_s = \pm k_A \pm k_B \pm k_C \). This implies eight possible phase-matching signal directions. Under rotating wave approximation (RWA) * only four are independent as signal directions \( k_s \) and \( -k_s \) are conjugate to each other and does not contribute to any new phenomenon. Thus we have the following possible signal directions: \( k_I = -k_A + k_B + k_C, k_{II} = k_A - k_B + k_C, k_{III} = k_A + k_B - k_C, \) and \( k_{IV} = k_A + k_B + k_C, \) and corresponding emission frequencies are \( \omega_I = -\omega_A + \omega_B + \omega_C, \omega_{II} = \omega_A - \omega_B + \omega_C, \omega_{III} = \omega_A + \omega_B - \omega_C, \) and \( \omega_{IV} = \omega_A + \omega_B + \omega_C, \) respectively. As a result, the third-order polarization in Eq. 3.10 can be rewritten as a sum of four polarizations terms corresponding to the phase matched signal directions \( k_I, k_{II}, k_{III}, \) and \( k_{IV} \):

\[
P^{(3)}(\mathbf{r}, t, t_A, t_B, t_C) = \sum_{s=I}^{IV} P_s (t_A, t_B, t_C) e^{i(k_s \cdot \mathbf{r} - \omega_s t)} + c.c.
\]

(3.11)

For \( s = I, II, III \) or \( IV \), the polarization term \( P_s (t_A, t_B, t_C) \) can be expressed as following:

\[
P_I (t_A, t_B, t_C) = R_{I}^{(3)}(t_A, t_B, t_C) \varepsilon^+_A \varepsilon^+_B \varepsilon^+_C \cdot e^{i(-\omega_A + \omega_B + \omega_C) t_C} e^{i(-\omega_A + \omega_B) t_B} e^{-i \omega_A t_A},
\]

(3.12)

\[
P_{II} (t_A, t_B, t_C) = R_{II}^{(3)}(t_A, t_B, t_C) \varepsilon^+_A \varepsilon^-_B \varepsilon^+_C \cdot e^{i(\omega_A - \omega_B + \omega_C) t_C} e^{i(\omega_A - \omega_B) t_B} e^{i \omega_A t_A},
\]

(3.13)

\[
P_{III} (t_A, t_B, t_C) = R_{III}^{(3)}(t_A, t_B, t_C) \varepsilon^+_A \varepsilon^-_B \varepsilon^-_C \cdot e^{i(\omega_A + \omega_B - \omega_C) t_C} e^{i(\omega_A + \omega_B) t_B} e^{i \omega_A t_A},
\]

(3.14)

\[
P_{IV} (t_A, t_B, t_C) = R_{IV}^{(3)}(t_A, t_B, t_C) \varepsilon^+_A \varepsilon^+_B \varepsilon^-_C \cdot e^{i(\omega_A + \omega_B + \omega_C) t_C} e^{i(\omega_A + \omega_B) t_B} e^{i \omega_A t_A}.
\]

(3.15)

*In RWA, the fast oscillating terms are neglected [138].
Eq. 3.18 can be ignored within rotating wave approximation (RWA) [54] as this corresponds to a fast oscillations of the polarization. The third-order polarization for each phase matched directions can be obtained in the form of sum-over-states expression of the non-linear response function. The response function needs to be evaluated for all possible coherent pathways in the Liouville space, which can be coherently tracked by double-sided Feynman diagrams. In order to gain better understanding of the diagrammatic approach, Optical Bloch Equation (OBE) will be discussed first in the next section followed by the double sided feynman diagram.

3.3 Optical Bloch Equation (OBE)

The density matrix operator for a system with wavefunction $|\psi(t)\rangle$ is defined as:

$$\rho(t) \equiv |\psi(t)\rangle\langle\psi(t)|,$$

(3.16)

and the wavefunction can be represented in terms of a basis $|i\rangle$ as:

$$|\psi(t)\rangle = \sum_i a_i(t) |i\rangle .$$

(3.17)

In Eq. 3.20, $a_i(t)$ is the coefficient for the eigenstate $|\psi(t)\rangle$. Using Eqs. (3.16) and (3.17), the density matrix elements for the system is:

$$\rho_{ij} = a_i(t) a_j^* (t) .$$

(3.18)

The diagonal elements $\rho_{ii} = |a_i(t)|^2$ represent the probability of the system in a population state and is known as population density; the off-diagonal elements $\rho_{ij}$ ($i \neq j$) represent the coherence between states $i$ and $j$. The trace of the density matrix operator, denoted by Tr, provides the expectation value of any observable for the system. E.g., the expectation value
of the polarization operator $\hat{P}$ can be expressed as:

$$\langle \hat{P} \rangle = \langle \psi(t) | \hat{P} | \psi(t) \rangle = \text{Tr} \left[ \hat{P} \rho(t) \right].$$  \hspace{1cm} (3.19)

The normalization condition is given by the trace of the density matrix operator, i.e., $\text{Tr} [\rho(t)] = 1$. Let us consider an example of a two-level system with a ground state $|1\rangle$ and an excited state $|2\rangle$. The wavefunction for the system can be expressed as: $|\psi(t)\rangle = a_1(t) |1\rangle + a_2(t) |2\rangle$. The corresponding density matrix is:

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} = \begin{pmatrix} a_1 a_1^* & a_1 a_2^* \\ a_2 a_1^* & a_2 a_2^* \end{pmatrix}.$$  \hspace{1cm} (3.20)

The diagonal elements $\rho_{11} = |a_1|^2$ and $\rho_{22} = |a_2|^2$, represent the population densities of the ground and excited states, respectively. On the other hand, the off-diagonal elements $\rho_{12} = a_1 a_2^2 = \rho_{21}^*$ represent the coherent coupling between the ground and excited states, and are proportional to the dipole moment between the two states.

The equation of motion for the system can be obtained from the Schrödinger equation and has the form:

$$\dot{\rho} = \frac{1}{i\hbar} [H, \rho].$$  \hspace{1cm} (3.21)

Let us now consider an interaction of this two-level system with an applied electric field $E(t)$. The interaction leads to a potential, $V$, which is proportional to the applied field. The Hamiltonian of the system can be written as:

$$H = H_0 + V = \begin{pmatrix} \hbar \omega_1 & V_{12} \\ V_{21} & \hbar \omega_2 \end{pmatrix},$$  \hspace{1cm} (3.22)

where $H_0$ is the free particle Hamiltonian, and $\omega_1, \omega_2$ are the eigen frequencies of the two
states, respectively. The interaction potential elements can be expressed as: \( V_{12} = V_{21} = -\mu_{12} E(t) \), where \( \mu_{12} \) is the transition dipole moment between the ground and excited states. Using Eqn. 3.21, the equation of motion for the system can be written as [141]:

\[
\dot{\rho} = \frac{1}{i\hbar} \sum_k (H_{ik}\rho_{kj} - \rho_{ik}H_{kj}) - \Gamma_{ij}\rho_{ij},
\]

(3.23)

where the term \( \Gamma_{ij} \) represents the total decay rate of the system, and has been introduced phenomenologically. The total decay rate can be written as:

\[
\Gamma_{ij} = \frac{1}{2} (\gamma_i + \gamma_j) + \gamma_{ij}^{ph},
\]

(3.24)

where \( \gamma_i, \gamma_j \) are the decay rates of the states \( i, j \), and \( \gamma_{ij}^{ph} \) represent the pure dephasing rate of the system. Using Eqns. 3.22 and 3.23 the time evolution of density matrix for the two-level system can be written as:

\[
\dot{\rho}_{11} = -\gamma_1\rho_{11} + \frac{i}{\hbar}\mu_{12}E(t)(\rho_{12} - \rho_{21}),
\]

(3.25)

\[
\dot{\rho}_{22} = -\gamma_2\rho_{22} - \frac{i}{\hbar}\mu_{12}E(t)(\rho_{12} - \rho_{21}),
\]

(3.26)

\[
\dot{\rho}_{12} = -\Gamma_{12}\rho_{12} + i\omega_0\rho_{12} - \frac{i}{\hbar}\mu_{12}E(t)(\rho_{22} - \rho_{11}),
\]

(3.27)

where \( \omega_0 = (\omega_2 - \omega_1) \), is the oscillation frequency. Various many-body effects (MBEs) such as local field corrections (LFC), excitation induced dephasing (EID) and excitation induced shift (EIS) are incorporated phenomenologically into the above OBEs [142].

### 3.4 Double sided Feynman Diagrams

The equations of motion (OBEs) described in the previous section, are usually solved perturbatively. In perturbation theory, the time evolution of the density matrix elements can be facilitated with the help of double-sided Feynman diagrams which allows us to represent any physical process taking place in a system in a very simple way. The diagram consists
of two vertical lines of propagation, one for the ket side (left side) and the other for the bra side (right side) of density matrix elements with time increasing vertically upward [138]. If the electric field of an incident light is indicated by an arrow, then any interaction of the system with the electric field is represented by the vertex of the arrow. Any arrow pointing towards the left vertical line (ket side) represents absorption with the field indicated by $E_j \cdot \exp(i k_j \cdot r - i \omega_j t)$, while the arrow pointing towards the right vertical line represents the absorption due to a conjugate field indicated by $E_j^* \cdot \exp(-i k_j \cdot r + i \omega_j t)$. On the other hand, an arrow pointing away from the vertical lines represent emission of photon. The resultant wavevector for any diagram is the sum of the individual wavevectors interacting with the system at different time intervals. The sign of a diagram is determined by $(-1)^n$ where $n$ is the number of interactions on the right vertical line (bra side). The system initially starts from the ground state density matrix and after interacting with the field, it jumps to higher excited states.

Let us consider a system with ground state $|g\rangle$, two single excited states $|e\rangle$ and $|e'\rangle$, and a double excited state denoted by $|f\rangle$. The system is excited with three pulses as described in section 3.2. The level scheme and the corresponding Feynman diagrams for each phase matched direction are shown in Fig. 3.2. For the phase matched direction $k_I$, three Feynman diagrams are shown in Fig. 3.7 (a) which represent three general process, namely ground state bleaching (GSB), excited state emission (ESE), and excited state absorption (ESA) [125] which are labeled as (1), (2), and (3), respectively. For diagram (1), the phase conjugate pulse with wave vector $k_A$ arrives first (acting on the right vertical line) which creates a coherence between the ground state $|g\rangle$ and the excited state $|e\rangle$. The second pulse with wave vector $k_B$ (acting away from the right vertical line) arrives after a delay $\tau$ brings the system to be back to the ground state. The interaction of the third pulse (acting on the left vertical line) with wave vector $k_C$ excites the system to the state $|e'\rangle$ and after a time $t$ from the arrival of the third pulse, the system comes back to the ground state by radiating a
signal in the phase matched direction $\mathbf{k}_I$. The other possible transitions for the system can be described by diagrams (2) and (3) in a similar way. For the phase matched direction $\mathbf{k}_{II}$, the possible Feynman diagrams are shown in Fig. 3.7 (b). In this pulse sequence (also known as non-rephasing pulse sequence) pulse $\mathbf{k}_B$ arrives first followed by the phase conjugate pulse $\mathbf{k}_A$ which comes after a delay $\tau$ from the first pulse. Finally, for the phase matched direction $\mathbf{k}_{III}$ there are two possible Feynman diagrams both involving the double-excited state $|f\rangle$, and are shown in Fig. 3.7 (c): (7)-(8). The third-order response function for a specific phase matched directions can be obtained by considering the sum-over contributions from all the
respective Feynman diagrams. The response functions $R^{(3)}_I$, $R^{(3)}_{II}$ and $R^{(3)}_{III}$ corresponding to the phase matched directions $k_I$, $k_{II}$ and $k_{III}$, respectively can be expressed as following [54]:

\[
R^{(3)}_I (\tau, T, t) = \left( \frac{i}{\hbar} \right)^3 \sum_{ee'} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{e'g} \cdot \hat{e}_C)(\mu_{e'S} \cdot \hat{e}_S) e^{(i\omega_{eg} - \Gamma_{eg}) \tau} e^{-\Gamma_{gs} T} e^{-(i\omega_{e'S} + \Gamma_{e'S}) t} \\
+ \sum_{ee'} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{e'g} \cdot \hat{e}_C)(\mu_{e'S} \cdot \hat{e}_S) e^{(i\omega_{eg} - \Gamma_{eg}) \tau} e^{-(i\omega_{e'S} + \Gamma_{e'S}) T} e^{-(i\omega_{e'S} + \Gamma_{e'S}) t} \\
- \sum_{ee'f} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{e'g} \cdot \hat{e}_C)(\mu_{e'S} \cdot \hat{e}_S) e^{(i\omega_{eg} - \Gamma_{eg}) \tau} e^{-(i\omega_{e'S} + \Gamma_{e'S}) T} e^{-(i\omega_{f'S} + \Gamma_{f'S}) t},
\]

(3.28)

\[
R^{(3)}_{II} (\tau, T, t) = \left( \frac{i}{\hbar} \right)^3 \sum_{ee'} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{e'g} \cdot \hat{e}_C)(\mu_{e'S} \cdot \hat{e}_S) e^{-(i\omega_{eg} + \Gamma_{eg}) \tau} e^{-(i\omega_{ee'} + \Gamma_{ee'}) T} e^{-(i\omega_{eg} + \Gamma_{eg}) t} \\
+ \sum_{ee'} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{e'g} \cdot \hat{e}_C)(\mu_{e'S} \cdot \hat{e}_S) e^{-(i\omega_{eg} + \Gamma_{eg}) \tau} e^{-(i\omega_{ee'} + \Gamma_{ee'}) T} e^{-(i\omega_{ee'} + \Gamma_{ee'}) t} \\
- \sum_{ee'f} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{e'g} \cdot \hat{e}_C)(\mu_{e'S} \cdot \hat{e}_S) e^{-(i\omega_{eg} + \Gamma_{eg}) \tau} e^{-(i\omega_{ee'} + \Gamma_{ee'}) T} e^{-(i\omega_{f'S} + \Gamma_{f'S}) t},
\]

(3.29)

\[
R^{(3)}_{III} (\tau, T, t) = \left( \frac{i}{\hbar} \right)^3 \sum_{ee'f} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{e'g} \cdot \hat{e}_C)(\mu_{e'S} \cdot \hat{e}_S) e^{-(i\omega_{eg} + \Gamma_{eg}) \tau} e^{-(i\omega_{f'g} + \Gamma_{f'g}) T} e^{-(i\omega_{e'S} + \Gamma_{e'S}) t} \\
- \sum_{ee'f} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{e'g} \cdot \hat{e}_C)(\mu_{e'S} \cdot \hat{e}_S) e^{-(i\omega_{eg} + \Gamma_{eg}) \tau} e^{-(i\omega_{f'g} + \Gamma_{f'g}) T} e^{-(i\omega_{f'g} + \Gamma_{f'g}) t},
\]

(3.30)

where $\mu_{ij}$, $\omega_{ij}$, and $\Gamma_{ij}$ are the dipole moment, transitions frequency, and the dephasing rate of the $i \rightarrow j$ transitions, respectively. The macroscopic polarizations in Eqs. 3.6-3.8 can be
obtained using the response functions (Eqs. 3.22-3.24). The FWM signal field is related to
the macroscopic polarization by the following expression:

\[ E(\tau, T, \omega_t) = \frac{L}{2n(\omega_t)c\epsilon_0}i\omega_t P^{(3)}(\tau, T, \omega_t), \quad (3.31) \]

where, \( L, n(\omega_t), c, \) and \( \epsilon_0 \) are the thickness of the sample, refractive index of the sample, speed of light in vacuum, and permittivity of the free space, respectively.

### 3.5 Two Dimensional Fourier Transform Spectroscopy

The 2DFT spectroscopy is an extended version of one-dimensional transient four wave mixing (TFWM) technique where two time delays are monitored simultaneously and are then correlated in a two dimensional map in frequency domain with the aid of Fourier transformation. In order to have a meaningful Fourier transformation, the time delays are stepped with sub-wavelength precision and the TFWM signal is measured through spectrally resolved heterodyne detection. This technique allows us to extract both the amplitude and the phase of the complex FWM signal. The phase is preserved throughout the experiment and the pulses are actively phase stabilized. A simple schematic of the 2DFT setup is illustrated in Fig. 3.8 where three phase stabilized ultrashort laser pulses, namely A*, B, and C with wave vectors \( \mathbf{k}_A, \mathbf{k}_B, \) and \( \mathbf{k}_C, \) respectively, are arranged in a BOX-geometry. Pulse A* and pulse B are separated by coherence time \( \tau, \) where as pulse B and pulse C are separated by population time \( T. \) The interaction of these three pulses results in the FWM signal in one of the phase matched directions \( \mathbf{k}_I = -\mathbf{k}_A + \mathbf{k}_B + \mathbf{k}_C, \mathbf{k}_{II} = \mathbf{k}_A - \mathbf{k}_B + \mathbf{k}_C, \mathbf{k}_{III} = \mathbf{k}_A + \mathbf{k}_B - \mathbf{k}_C. \) The fourth pulse (REF/Tracer) acts as reference or tracer pulse which traces the signal direction. During the measurement, tracer beam is kept blocked. A reference beam (also called the local oscillator) is derived from the phase stabilized fourth beam and is co-linearly recombined with the FWM signal with an appropriate delay between them to form heterodyne. The resulting spectral interferogram is dispersed in a grating spectrograph
Figure 3.8: Schematic of the 2DFTS setup in transmission geometry: the four phase stabilized ultra-short laser pulses obtained from the MONSTR instrument are focused on the sample. A portion of the laser pulse has been split off and co-linearly recombined with the FWM signal for heterodyne detection. The combined beams are dispersed in the spectrometer resulting in the spectral interferogram.

and is then detected by a CCD [143].

Performing 2DFT measurements in box geometry has some advantages over the co-linear excitation scheme as the FWM signal in all three phase matched directions can be obtained by altering the time ordering of the phase conjugate pulse $A^*$. The pulse sequence for each of these phase matching conditions is depicted in Fig. 3.9. The 2DFT signal for the phase matched directions $k_I$, $k_{II}$ and $k_{III}$ are labeled as $S_I$, $S_{II}$ and $S_{III}$, respectively, and each describes different physical processes [139].

All possible pulse time ordering in a 2DFT measurement using three pulse scheme in box geometry is shown in Fig. 3.9. The pulse sequence where the conjugate pulse $A^*$ arrives on the sample first, followed by pulse B and C is depicted in Fig. 3.9 (a). For an inhomogeneously broadened system, the FWM signal appears as a "photon echo" and this pulse ordering is referred to as "rephasing" pulse sequence (labeled as $S_I$) in the literature. In rephasing measurements, the coherence time $\tau$ (Axis 1) is scanned while the population
time $T$ is kept fixed and the evolution of the FWM signal is recorded in real time $t$ (Axis 2). Fourier transformation with respect to the two time delays ($\tau$, $t$) results in a 2D map in frequency domain ($\omega_\tau$, $\omega_t$). In the same pulse ordering when the population time $T$ is scanned for a fixed $\tau$, we can monitor any non-radiative decay of the system. This pulse ordering is shown in Fig. 3.9 (b) where the signal is measured as a function of the population time $T$ (Axis 1) and the real time $t$ (Axis 2). When pulse B interacts with the sample first followed by the conjugate pulse $A^*$ and pulse C, the pulse sequence is termed as "non-rephasing" and the corresponding pulse ordering is shown in Fig. 3.9 (c). In this case, the effect of inhomogeneous broadening is not canceled. All three pulse sequences mentioned above do
not lead to any direct bi-exciton or unbound two exciton state as the direct transitions to a
two-exciton state from ground state is optically forbidden. However, two exciton correlations
can be monitored with the pulse sequence shown in Fig. 3.9 (d) where pulse C and pulse
B are incident on the sample with a constant delay $\tau$ between them followed by pulse $A^*$
and the time ordering is labeled as $S_{III}$. The interaction of the first two pulses brings the
system to a double excited state, consequently, the absorption axis on the 2D spectrum is
twice the emission axis. In our study, we have used the rephasing ($S_I$) and the two-quantum
2DFTS ($S_{II}I$) measurements and these two processes are discussed in detail in the following
subsections.

### 3.5.1 $S_I$ 2D Spectra

The pulse sequence for an $S_I$ process in 2DFTS is analogous to ”spin echo” pulse se-
quence in NMR, and is shown in Fig. 3.10 (b). The FWM signal is collected as a function
of coherence time $\tau$ and the real time $t$ (time delay $T$ is held constant). Upon Fourier transfor-
mation of the $\tau$ axis, the signal is displayed on a 2D map in frequency domain as a function
of $(\omega_\tau, T, \omega_t)$, and can be expressed in terms of amplitude and phase as:

$$S_I(\omega_\tau, T, \omega_t) = \int_{-\infty}^{\infty} E(\tau, T, \omega_t) e^{i\omega_\tau \tau} d\tau,$$

(3.32)

where $E(\tau, T, \omega_t)$ is the detected signal field.

In order to describe the process, let us consider a 3 level system consisting of a ground
state, a single excited state manifold, and a double excited state manifold denoted by $|g\rangle$, $|1\rangle$, and $|2\rangle$, respectively, as shown in Fig. 3.10 (a), where the optical transitions corresponding
to one of the quantum pathways are shown with black and red arrows. The phase conjugated
pulse $A^*$ arrives on the sample first and creates a coherent superposition between the ground
state and single exciton states ($|g\rangle \leftrightarrow |1\rangle$). After a time delay $\tau$, the second pulse generates a
ground state population (or higher excited state population, not shown in the diagram). The
third pulse interacts with the system after a times delay $T$ and converts the population back into a $(|g⟩ \leftrightarrow |1⟩)$ coherence and system radiates as FWM signal (indicated by red arrow in the diagram). During the first time interval $\tau$, the system phase evolves with $e^{i\omega_1 \tau}$. For an inhomogeneously broadened system, the oscillators have a distribution of frequencies, thus each oscillator evolve with different frequency and the system dephase subsequently. The temporal phase of the final coherence being $e^{-i\omega_1 t}$, all the oscillators oscillate in phase at time $t = \tau$ after the interaction of the third pulse and the signal emits as a photon echo. This process is referred to as rephasing because the system evolves with opposite phases during the two time intervals. This pulse sequence permits separation of the homogeneous linewidths from the inhomogeneous broadening. The diagonal linewidth are due to the convolution of inhomogeneous and homogeneous broadening, whereas cross-diagonal linewidth represents homogeneous broadening.
3.5.2 \textit{S}_{III} type 2D Spectra

As mentioned earlier, a distinctive feature of many body interactions in semiconductors is the presence of “negative delay” signal observed in TFWM measurements which predominantly arises due to interactions and correlations between a pair of excitons. This phenomenon can be studied using two-quantum 2DFTS technique with a pulse sequence (referred to as $S_{III}$) shown in Fig. 3.11 (b), which corresponds to the case of negative delay signal that isolates the two quantum coherence [8, 64, 126, 144–148]. For a three level system as indicated in the previous section (also shown in Fig. 3.11 (a)), direct transition to the doubly excited state is optically forbidden but can be achieved through a two step process. The first pulse creates a coherent superposition between the ground state and single exciton states. After a time delay $\tau$, the second pulse brings the system to a two exciton state, thus establishing the coherence superposition between the ground and the two exciton states, ($|g\rangle \leftrightarrow |2\rangle$). Here, the first two pulses are in resonance with the ($|g\rangle \leftrightarrow |1\rangle$) and

\[
S_{III}(\tau, 2\omega_{T_{2Q}}, \omega_{t})
\]

Figure 3.11: Illustration of two-quantum 2DFTS pulse sequence. (a) A three level system with a ground state, a single excited manifold, and a double excited manifold. (b) Illustration of a two-quantum 2DFTS Pulse Sequence.
(\ket{1} \leftrightarrow \ket{2}) transitions, respectively. The phase conjugate pulse $A^*$ arrives on the sample last after a time delay $T_{2Q}$ and converts the two quantum coherence (\ket{g} \leftrightarrow \ket{2}) to a single quantum coherence (either \ket{g} \leftrightarrow \ket{1} or \ket{1} \leftrightarrow \ket{2}), which radiates as FWM signal. In this case, Fourier transform with respect to time delays $T_{2Q}$ (Axis 1) and $t$ (Axis 2) results in a two-quantum 2D spectrum in the frequency domain ($\omega_{T_{2Q}}, \omega_t$) where the two quantum energy axis is twice the emission energy axis. An illustration of two-quantum 2DFT amplitude spectrum is shown in Fig. 3.12 for a three level system as described previously. The diagonal peaks A and B represent unbound two exciton states with absorption (emission) energies $2\hbar \omega_A$ ($\hbar \omega_A$) and $2\hbar \omega_B$ ($\hbar \omega_B$), respectively. Both peak A and peak B originate from the correlation of two identical excitons. Any bound two exciton state or biexciton will be shifted from the unbound diagonal peak along the emission axis. The off-diagonal peaks (also referred as cross peaks) C and D originate due to coherent coupling of two mixed exci-
ton states. Both off-diagonal peaks appear at the same energy, $\hbar(\omega_A + \omega_B)$. Similarly, any mixed biexciton state will be shifted off the cross-peaks along the emission axis. Although, the mixed biexciton states are very difficult to observe as the coupling between two such mixed excitons are rather weak compared to the identical excitons. Various quantum pathways contribute to the FWM signal in the S_{III} process and the corresponding double sided Feynman diagrams are shown in B.4 (Appendix B) for a GaAs QW system with level scheme shown in Fig. 2.7.

### 3.5.3 Advantages of 2DFT Spectroscopy

One of the advantages of 2DFT spectroscopy is to identify the coupling between resonances. In 2D spectra the resonances appear on the diagonal and any coupling between them manifests as off-diagonal peaks. Fig 3.13 (a) shows the rephasing 2D spectrum for a two independent two level systems where two resonances at transition frequencies $\omega_1$ and $\omega_2$ appear on the diagonal at $(\omega_1, -\omega_1)$ and $(\omega_2, -\omega_2)$, respectively. Fig 3.13 (b) shows a 2D

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**Figure 3.13:** Rephasing 2D spectrum for (a) a two independent two-level system, (b) a three level system with shared ground state, (c) a two independent two level system with incoherent population relaxation from higher excited state to a lower excited state.

†In rephasing 2DFT spectra, any point on this 2D map is represented by the co-ordinate $(\omega_t, -\omega_t)$. The absorption axis $(\omega_t)$ is negative, hence the energy increases downwards.
spectrum for a 3-level system with two transitions having a common ground state. These two transitions are not independent any more and the coupling between the two resonances result in the appearance of two additional off-diagonal cross-peaks at \((\omega_1, -\omega_2)\) and \((\omega_2, -\omega_1)\). On the other hand, if there is any population relaxation from a higher excited state to a lower excited state in a two independent two level system, the resulting 2D spectrum reveals only one cross-peak as shown in Fig 3.13 (c). The cross-peak appear at an absorption frequency which is greater than the emission frequency, indicating the presence of incoherent population relaxation from higher excited state to the lower excited state. A finite value of the time delay \(T\) in the rephasing pulse sequence is needed in order to observe any incoherent population relaxation [149].
Chapter 4

2DFT Spectroscopy: Experimental Setup

A multidimensional optical non-linear spectrometer (MONSTR) apparatus has been extensively used in the past decade to study the coherent dynamics of excitons in semiconductor nanostructures [40, 144, 150–152], atomic vapor [26, 27], biological complexes [16, 17, 33–35], etc., using 2DFTS technique. The MONSTR is based on a three pulse FWM excitation scheme, using the fourth pulse as a phase-stable reference pulse. Implementation of multidimensional Fourier transform spectroscopy techniques is quite challenging as it requires sub-wavelength stability. Passive [127, 128, 153] and active phase stabilization [37, 38, 40, 154–159] techniques have been used primarily in order to achieve the phase stability. The usefulness of the apparatus has been demonstrated with several 2DFT measurements, including a 2D two-quantum coherences where all four excitation pulses need to be phase stabilized [144]. In 2DFTS, phase cycling [160–162] is often used to eliminate the contribution of scattered light from the pump beams. An all optical method [163] is employed to obtain the global phase of complex FWM signal. The details of the MONSTR setup can be found in Ref. [159, 164] and will be briefly discussed here.

The MONSTR apparatus houses three folded and nested Michelson interferometers. It has two separate decks, namely bottom and top decks, each containing a Michelson interferometer, and a third interferometer (between deck) is formed when the top deck is stacked on top of the bottom deck. The beam path in each deck are shown in Fig. 4.1. Each deck contains two linear translation stages. The bottom deck stages, namely stage X and stage C, have 20 cm and 5 cm of travel, respectively. Similarly, the top deck contains two
identical stages (labeled as A and B); both have 5 cm of travel. All stages have resolution ∼ 1 nm. The ultrashort laser pulse enters the bottom deck from the side as indicated by the red arrow in the diagram. A part of the input beam is split-off at the first beam splitter (BS) and guided by the mirror P1 on to the mirror P2 of the top deck. The transmitted beam is further split-off at a second beam splitter (BS) after traveling through stage X. The reflected beam at the second BS generates beam C while the transmitted beam generates the reference beam after passing through stage C. In a similar way, the top deck produces two parallel beams, A* and B, respectively. The top deck is folded and placed on top of the bottom deck so that all four beams (A, B, C, and Ref) are positioned at the corners of a one inch square box. The ultrashort beams pass through compensation plates (CP) which compensate for the dispersion in each arm of the interferometers. The whole apparatus has

Figure 4.1: Schematic of the Top and Bottom decks of the MONSTR. This figure is reproduced from Ref. [165] with permission.
three piezoelectric transducers (PZT) mounted at the back of three mirrors to control the phase of the four beams using active phase stabilization method. The required servo loop filters and the Piezo controllers were designed and custom built at the JILA electronic shop. A CW laser passes through the same path as the ultrashort laser pulse and is reflected back by a long pass 2 inch dichroic mirror (DCM) attached to front of the bottom deck so that the all four ultrashort pulses pass through the same DCM when the two decks are assembled together. The reflected CW beams produces error signals from the respective interferometers (indicated by dashed lines with arrows) and are sent to the photo diodes (not shown in Fig. 4.1). The entire assembly of the MONSTR apparatus is shown in Fig. 4.2.

A second MONSTR apparatus was developed for the measurements performed at the National High Magnetic Field Laboratory, in Tallahassee, where the installed linear translational stages have lower resolution (∼ 5 nm). Additionally, the servo loop filters for the active phase stabilization were designed with NI-FPGA modules. Commercially available Piezo controllers (Thorlabs: MDT693B and MDT694B) were used to control the voltage of
The complete 2DFTS experimental setup in transmission geometry is shown in Fig. 4.3. Ultrashort pulse is generated from a mode-locked Ti:Sapphire laser oscillator (Coherent MIRA 900) which is pumped by a 532 nm CW diode laser (Coherent Verdi V-10). The laser oscillator operates at a repetition rate of $\sim 76$ MHz with $\sim 130$ fs pulse duration and is tunable in the range of 720 to 960 nm. An optical parametric oscillator (OPO, Coherent APE, not shown in Fig. 4.3) pumped by the Ti:Sapphire oscillator is used for generating ultrashort pulses in the range of 500 to 1400 nm. Input ultrashort laser pulse enters the
MONSTR apparatus and generates four pulses which are actively phase stabilized. A CW laser follows the same path as the ultrashort laser pulse inside the MONSTR apparatus. The CW laser beams are reflected from the DCM to produce interference fringes from the three interferometers. These fringes are detected by three photodiodes as error signals and are fed back to servo loop filters which then corrects for any deviation of the optical path lengths in the interferometers due to any mechanical drift by controlling the voltages of the piezoelectric transducers (PZTs). Phase stabilization of $\sim \lambda/100$ to $\lambda/400$ could be achieved using this technique, where $\lambda$ is the laser wavelength. A sinusoidal wave from a function generator is fed to the PZTs to optimize the error signals at the detectors. Optical isolators are placed in front of the CW lasers to prevent any retro-reflected beams getting back onto the CW laser that would cause instabilities in the laser. The four output beams from the MONSTR pass through a set of polarizations optics and are focused on to the sample by a single two inch diameter lens ($L_1$). The FWM signal generated by the three of the four pulses is then collimated by a second lens ($L_2$) and is guided to the spectrometer. The fourth beam, Tracer, follows the signal path and is used for initial alignment. A portion of the Ref/Tracer beam is split-off before the first lens which passes through an external delay stage and then co-linearly recombined with the FWM at a beam splitter (BS with 10% reflectivity) to form heterodyne. The resulting spectral interferogram is then dispersed into a grating spectrograph, and is detected by a thermoelectric cooled CCD. A polarizer is placed in front of the spectrometer to select different polarization states of the FWM signal in accordance with the excitation polarization conditions. Both reference and the signal are focused onto the slit ($\sim 50 \mu m$) of the spectrometer by a 5 cm lens ($L_3$). In order to maintain the phase stability between the FWM signal and the reference beam another interferometer is formed (External loop) with the help of a separate CW laser that follows the signal and reference beam paths (indicated by the blue dashed lines in the diagram) between two dichroic mirrors (DCM 1 and 2). The resulting interference fringes from the CW laser are detected by a fourth photodiode as an error signal and is fed back to the servo
loop filter which corrects for any path length fluctuation in the External loop by controlling the voltage of a PZT mounted at the back of a mirror placed in the reference beam path. The cryostat is held by a sturdy custom built mount which minimizes any vibration. The cryostat is not part of the external loop and any phase drift due to cryostat vibration is not compensated by the PZT. In order to find the time zero positions of all four beams, a beam sampler is placed between the first lens (L\textsubscript{1}) and the sample to create a replica focus of the overlapping beams. A 40X microscope objective is placed at the replica focus and the magnified image of the spatial interference fringes formed between the beams is recorded by a camera attached to the objective. First, the field correlation between the two beams from the top deck, i.e., between pulse A\textsuperscript{*} and pulse B, is recorded by keeping pulse A\textsuperscript{*} (stage B) fixed and scanning pulse B (stage A). The field correlation yields a sinusoidal pattern which is then fitted with a Gaussian envelope to obtain the time zero position of pulse B with respect to pulse A\textsuperscript{*}. Similarly, field correlations between pulses A\textsuperscript{*} and pulse C (between deck), and

Figure 4.4: The field correlation between the Pulse C and Ref beam. The black lines represent the measured data whereas the fit is depicted by the orange dashed lines.
between Pulse C and the reference (bottom deck), provide the time zero positions of pulse C and reference, respectively. An example of the field correlation data (black lines) and its fit (orange dash-dot lines) are shown in Fig. 4.4. The images of the spatial interference fringes from each deck and from all three decks (overlap of all four beams) are shown in the inset of Fig. 4.3 in a cyclic order (starting with top deck), where all pulses are at their respective time zero values.

Figure 4.5: 2DFT setup in reflection geometry. In order to maintain phase stability between the FWM signal and the reference beam, the HeNe or the 488.5 nm laser propagates through the same path. The metrology laser light is reflected back by dichroic mirrors and the interference pattern is detected with the photodiode. Any mechanical drifts are compensated using a piezoelectric transducer driven by a fourth high speed loop filter.

The 2DFT spectroscopy can also be performed in reflection geometry and the experimental setup is shown in Fig. 4.5. The sample is mounted on a microstat which is placed at an angle off the excitation direction to send the FWM signal away from the excitation beams. The signal is recombined with a reference beam as described previously. This is advantageous because experiments can be performed without removing the substrate.
4.1 Spectral Interferometry

In 2DFT Spectroscopy technique, the TFWM signal is heterodyne detected by employing spectral interferometry [154, 166–168], which permits retrieval of the signal amplitude and phase. In this method, the TFWM signal is recombined with a delayed local oscillator (reference pulse), and the combined pulses propagate collinearly to form spectral interferogram, which is dispersed in a grating spectrometer equipped with thermoelectric cooled CCD. Usually, the delay between the signal and the local oscillator is chosen such that the local oscillator arrives ahead of the signal. Interference fringes between the signal and local oscillator are formed even though the two pulses are temporarily separated. This is because the ultrashort pulse widths are broadened due to linear dispersion in the grating [169], thus allowing temporal overlap of the pulses. The delay is set to about 8-10 ps to achieve dense fringes. The density of fringes is limited by the finite spectrograph resolution. If the electric fields associated with the TFWM signal and the local oscillator are $E_S(\omega_t)$ and $E_{LO}(\omega_t)$, respectively, then, the power spectrum detected by the CCD an be written as:

$$|E_S(\omega_t) + E_{LO}(\omega_t)|^2 = |E_S(\omega_t)|^2 + |E_{LO}(\omega_t)|^2 + 2 \text{Re}\{E_S(\omega_t)E_{LO}^*(\omega_t)e^{i\omega t_0}\}, \quad (4.1)$$

where, $t_0$ is the delay between the signal and the local oscillator. The first two terms in Eq. (4.1) represent the power spectrum of the signal and the local oscillator, respectively, and can be subtracted from the spectral interferogram to extract the oscillatory interferometric term shown below:

$$S(\omega_t) = 2 \text{Re}\{E_S(\omega_t)E_{LO}^*(\omega_t)e^{i\omega t_0}\}. \quad (4.2)$$

The power spectra of the FWM signal and the reference pulse, and the interferometric term is shown in Fig. 4.6. The expression in Eq. 4.2 is in frequency domain which upon inverse Fourier transform yields the real time signal in the time domain and can be written as:

$$S(t) = \mathcal{F}^{-1}S(\omega_t) = f(t - t_0) + f(-t - t_0). \quad (4.3)$$
Eq. 4.3 contains two terms for both positive and negative times of which, \( f(t - t_0) \) satisfies the causality principle. This time domain data is then multiplied with a Heaviside step function \( \Theta(t - t'_0) \) which filters out any noise from the pump beams and a Fourier transform of the product is performed to retrieve the amplitude and phase of the signal in the frequency domain as shown below:

\[
E_S(\omega_t) = \frac{\mathcal{F}[\Theta(t - t'_0)\mathcal{F}^{-1}S(\omega_t)]e^{-i\omega_t t_0}}{E_{LO}^*(\omega_t)}. \tag{4.4}
\]

In Eq. (4.4), the phase factor \( e^{-i\omega_t t_0} \) is used to remove the linear phase corresponding the delay between the signal and the local oscillator. The phase of the signal retrieved by the Fourier transformation process bears a constant phase offset (difference between the
signal and local oscillator phase) because the phase of the local oscillator is not known. In 2DFTS, the global phase of the signal can be found from a separate spectrally resolved transient absorption (SRTA) measurement. In this measurements, two excitation laser pulses are used in pump-probe geometry. One of the beams (pulse C) acts as pump while other one (the tracer pulse) acts as probe. The excitation power of the pump beam is set twice as that of the probe beam replicating the excitation conditions of the 2DFTS measurements. The cross-diagonal profile of the real part 2D spectrum is then matched with the differential transmission spectrum obtained from the SRTA measurement by adjusting the phase offset in the data processing. The global signal phase can also be obtained by employing an all optical method where SRTA is not applicable. The details of the method is described in Ref. [163]. In the present study neither of the two methods were employed to extract the phase of the complex FWM signal as only amplitude 2DFT spectrum was sufficient to interpret the coherent response of the systems under study.

### 4.2 Scanning Procedure

In 2DFTS, the time delays (e.g., delay $\tau$ in a rephasing measurement) are scanned with interferometric precision, which is necessary for a meaningful Fourier transformation. The spectral interferogram is acquired at each delay with a step size equal to an integral multiple of $\lambda/4$, where $\lambda$ is the wavelength of the CW laser. A single longitudinal mode He-Ne CW laser is used for measurements performed in the near IR, while for the visible range, a 488.5 nm single longitudinal mode CW laser (Coherent Sapphire) is used. The $\lambda/4$ optical path length delay of one of the ultrashort laser pulses is obtained by moving the respective stage and it corresponds to a movement of half a He-Ne wavelength (632.82 nm), i.e., 316.41 nm. The stages have a resolution $\sim 1$ nm and unequal stepping may occur as it moves. The error accumulates significantly over long scan length which may lead to imperfect 2D spectra after the Fourier transformation of the scanning delay. This is eliminated by correcting for the overstepping/under-stepping of the stages after each delay by measuring the error signals of
the PZTs when it is locked and is unlocked after each step. The movement of the stages in terms of the He-Ne interference fringes (error signal) are monitored on an Oscilloscope. During the scan, with the stages at time zero, all the PZTs are engaged (locked). After acquiring the spectral interferogram, the PZTs are unlocked, and once the stages are moved to next delay point (including the correction for the over or under stepping of the stages), the PZTs are locked again for the acquisition of next spectral interferogram. This process continues until the desired scan length is achieved. The entire scanning procedure is shown in Fig. 4.7.
Chapter 5

Dynamics of Mahan Excitons in a 2DEG

5.1 Introduction∗

The dynamics of excitons in semiconductors are very sensitive to many-body interactions [117, 170, 171]. In modulation doped quantum well, excess carriers get separated from the donor atom and moves into the quantum well region, and form a two dimensional electron gas system. This results in the reduction of effective ionized impurity scattering and increased carrier mobility. Due to the presence of high carrier density, the Coulomb interactions are screened in a 2DEG, and form an interesting system for quantitatively investigating the role of many-body interactions [172, 173]. The 2DEG in modulation doped semiconductor quantum systems is subject of renewed interest as a result of the discovery of three-dimensional topological insulators [174]. Furthermore, in a strong magnetic field, the two-dimensional electrons form a correlated system that exhibits unique electronic transport properties such as the integer and fractional quantum Hall effect [6]. The optical properties of 2DEG were extensively investigated using light scattering and photoluminescence measurements in the quantum Hall regime [87–99]. The light scattering experiments have lead to the observation of magnetorotons and have provided details into the physics of composite fermions at different fractional filling factors [100–107] and explored the interactions of bilayer quantum Hall systems [108–115].

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Modulation doped quantum wells (MDQW) provide an ideal system to study the Fermi edge singularity (Mahan exciton), because the quantum confinement increases the interaction of the hole with the Fermi sea and the scattering with ionized impurities is suppressed as compared to doped bulk semiconductors. In the first experiments, Kim et al. measured the dephasing from two modulation doped GaAs/Al$_{0.3}$Ga$_{0.7}$As quantum wells as a function of excitation photon energy in the absence of magnetic fields [175]. The samples consisted of 60 and 100 quantum well periods with electron concentrations $\sim2 \times 10^{11}$ cm$^{-2}$ and $\sim6 \times 10^{11}$ cm$^{-2}$, corresponding to a Fermi energy of 7 meV and 20 meV, respectively. The dephasing time decreased drastically for excitation pulses with even small excess energy above the Fermi edge singularity peak, observed in the photoluminescence excitation spectrum. Most of the variations in dephasing time occurred for laser energies above the Fermi edge. An echo behavior was observed, which led to the conclusion that the continuum states in a semiconductor can be considered inhomogeneously broadened in momentum space, an intrinsically inhomogeneously broadened system.

5.2 Dynamics of HH Mahan Exciton

The modulation doped two dimensional electron gas (2DEG) samples consist of a single 18 nm and 12 nm thick GaAs/AlGaAs quantum wells. The Barrier layers (AlGaAs) are doped with Si with a concentration of $1 \times 10^{12}$ cm$^{-2}$ result in a well carrier concentration of $\sim4 \times 10^{11}$ cm$^{-2}$, corresponding to Fermi energies of 13.1 meV and 13.9 meV for the 18 nm and 12 nm quantum well, respectively. A detailed schematic of the sample is shown in Fig. 5.1(b). The sample was kept in vacuum and in thermal contact with the liquid helium cooled finger inside the cryostat. The FWM signal was collected in reflective geometry as shown in Fig. 5.1(b) by mounting the cryostat at a small angle off-normal. The implementation of this geometry was very advantageous since it does not require substrate removal. The 130 femtosecond laser pulses used for excitation at the exciton energy were obtained from a commercial oscillator (Mira 900, Coherent). The phase stability between the FWM signal
and the reference beam shown in Fig. 5.1(b) is maintained using the methods described in [164].

Figure 5.1: (a) The schematic of the band structure. (b) The 2DFT setup in reflection geometry: Four phase stabilized beams are obtained from the MONSTR instrument described in [159, 164]. (c) The sequence of the laser pulses used in the rephasing ($S_I$) experiments, where $A^*$ corresponds to the phase conjugate pulse. (d) The sequence of the pulse used in the $S_{III}$ experiments. (Sample ID: VA0605 and VA0607).

In order to probe the fundamental interactions in a 2DEG, we performed temperature and polarization dependent $S_I$ and $S_{III}$ 2DFT spectroscopy. The nonlinear response of semiconductors can, in most cases, be described by the third-order polarization induced by the optical fields [176, 177]. In semiconductor quantum wells, the Coulomb interaction between various polarization components cannot be ignored and the optical Bloch equations must be suitably modified to include Coulomb correlations [170, 171]. The Coulomb interactions can lead to excitation induced dephasing [178–180], excitation induced shifts [142], and biexcitonic effects [181–184]. The lineshapes of 2DFT spectra are very sensitive to many-body interactions and therefore 2DFTS provides an elegant tool for studying these phenomena.
5.2.1 Photoluminescence and Spectrally Resolved FWM

The temperature dependent photoluminescence (PL) spectra of the two modulation-doped quantum wells are shown in Fig. 5.2. The spectra show one strong peak with a small shoulder at high energy which is typically observed in modulation doped quantum wells [186]. The PL peak corresponds to recombination originating from the bottom of the conduction band, as shown schematically in Fig. 5.1 (a). The PL spectra have a long tail at the high energy side which ends with a weak shoulder corresponding to the Fermi edge $E_F$. The weak shoulder becomes more pronounced but broadens with temperature.

The absorption and photoluminescence processes in a modulation doped quantum well are schematically shown in Fig. 5.3 (a). Absorption occurs at the Fermi energy with a wave vector $\vec{k} = \vec{k}_F$, whereas photoluminescence occurs predominantly at the bottom of the conduction band in GaAs/AlGaAs modulation doped quantum wells since the holes are not localized. Therefore, the FWM spectra are energetically shifted with respect to the
Figure 5.3: (a) Schematic of the band diagram for modulation doped quantum wells. Direct absorption taking place at the Fermi edge (green arrow) whereas photoluminescence originates predominantly due to recombination of electron at the bottom of the conduction band (red arrow). (b) Spectrally resolved FWM from the 12 nm thick MDQW (black line). The excitation laser spectrum is shown above (green line). Two FWM peaks are observed as a result of absorption from the heavy hole (HH) and light hole (LH) valence sub-bands. The PL spectrum is shown for comparison. FWM originating from the bulk GaAs buffer layer appears at a much lower energy (blue line). (c) The excitation laser pulse is tuned towards higher energy leading to an enhancement of the LH FWM peak. (d) Spectrally resolved FWM from the 18 nm thick MDQW.

PL. However, Fermi level enhancement has been suggested to occur in this system where momentum conservation is provided by collective excitation of the Fermi sea [187]. In Fig. 5.3 (b) and (c) the spectrally resolved FWM is shown together with the PL spectra obtained from the 12 nm quantum well. In Fig. 5.3 (b) the exciting laser pulses are centered at the lower energy peak (heavy hole to Fermi edge transitions) whereas in Fig. 5.3 (c) the laser spectrum is centered at the higher energy peak (light hole to Fermi edge transition). The PL originating from the recombination of holes with electrons at the bottom of the conduction band is \( \sim 14 \) meV lower in energy than the corresponding FWM peak, which reflects the energy shift between PL and absorption. The FWM peak originating from the bulk GaAs buffer layer appears at a much lower energy and is shown for comparison. Similar behavior
is observed for the 18 nm quantum well and is shown in Fig. 5.3 (d).

### 5.2.2 Time-integrated FWM of HH Mahan Exciton

The dephasing of the heavy hole Mahan excitons of two modulation doped quantum wells of width 12 and 18 nm was studied using time integrated FWM technique at temperatures from 5K to 30K. The data are shown in Fig. 5.4 (a)-(d) for temperatures at 5K and at 25K, respectively, for the two samples. The excitation laser pulse was in resonance with the HH Mahan exciton and the FWM signal was found to decay exponentially at a rate proportional to \( \exp(-2\tau/T_2) \), where \( T_2 \) is the dephasing time. At 5K, dephasing time of

![Figure 5.4](image-url)

Figure 5.4: Time integrated FWM data at temperatures of 5K and 25K for (a) & (b) a 12 nm MDQW nm and (c) & (d) a 18 nm MDQW, respectively. A single exponential fit was used to find the decay of the FWM signal. The instrumental response is shown by a green dashed curve in (a) & (c).

0.51 ps and 0.68 ps were obtained from the single exponential fitting of the data for the 12 nm and 18 nm MDQW, respectively. At low temperature, ionized impurity scattering is dominant mechanism behind the dephasing. As temperature increases, scattering due to
acoustic and optical phonons cause the excitons to dephase at faster rate. This behavior is observed at 25K where dephasing time of 0.19 ps and 0.28 ps were obtained for the 12 and 18 nm MDQW samples, respectively. Previous studies on GaAs quantum well have shown that for temperature below 50K, scattering due to acoustic phonons are responsible for excitonic dephasing whereas optical phonon scattering becomes dominant at higher temperature.

The dephasing of the Mahan HH excitons in 12 nm MDQW are found to be faster than that of the 18 nm MDQW. The homogeneous linewidths ($\Gamma$) were obtained from the dephasing time using the relation $\Gamma = 2\hbar/T_2$, and the linewidths were found to increase linearly with temperature. The homogeneous linewidths were also obtained directly from the rephasing 2DFTS measurements and were comparable to the values obtained from the TIFWM measurements. The result of the temperature dependence of the average linewidths (see Fig. 5.7) obtained from the two measurements is discussed in the following section.

5.2.3 Polarization dependent $S_I$ 2DFT Spectra

In the rephasing, $S_I$ measurement, the complex FWM signal is represented in frequency domain via Fourier transform with respect to the $\tau$ and $t$ time delays, and that results in a two-dimensional map where the $\omega_\tau$ and $\omega_t$ axes are now correlated. The two-dimensional lineshapes provide insight into the various types of interactions taking place in the system. The many body interactions on the carrier dynamics can be identified phenomenologically. The amplitude (left) and the real part (right) of the $S_I$ 2DFT spectra for both, the 18 and 12 nm quantum wells, are shown in Fig. 5.5 (a)-(f). The measurements were performed at two different polarizations, and are labeled as (HHHH) and (HVVH). Here, the polarization sequence (HHHH) corresponds to pulse $A^*$, B, C and detection, respectively, and is termed as colinear. Similarly, (HVVH) is termed as cross-linear. The line shapes display a slight asymmetry in the width which is larger below than above the diagonal. The asymmetry can be more easily observed in the amplitude spectrum in Fig. 5.5 (a) and 5.5 (c) and is more
Figure 5.5: (a) and (b) Amplitude and real part 2DFT spectra originating from the 18 nm MDQW using co-linear (HHHH) polarizations. The polarization sequence (HHHH) corresponds to pulse A*, B, C and detection, respectively. (c) and (d) Amplitude and real parts of the 2DFT spectra for the 12 nm MDQW using co-linear (HHHH) polarizations at $T = 0$ fs. (e) and (f) Amplitude and real part 2DFT spectra for the 12 nm MDQW using cross-linear (HV VH) polarizations at $T = 0$ fs.

pronounced for the 12 nm quantum well. This elongation of the line shape occur due to the coupling of the HH Mahan exciton to the continuum states.

The cross-linear 2DFT spectra for the 12 nm quantum well are shown in Fig. 5.5 (e) and 5.5 (f). The spectra show a single peak on the diagonal and the intensity is much weaker as compared to the colinear polarization. The many-body interactions are suppressed for the cross-linear polarizations because the first two excitation pulses are crossed with respect to each other. As a result, there is no spatial modulation of the net population [54, 150]. For this polarization configuration, only certain quantum pathways are allowed which suppresses the single excitonic resonances and enhances the contribution of two exciton resonances. The
single peak on the diagonal of the 2DFT spectrum for the 12 nm quantum well arise due to the transition from an two exciton state to a single exciton state. No biexciton formation is observed. The line shape also are found to be more symmetric compared to the co-linear spectra which indicates suppression of many body effects [150]. The cross-linear peak for the heavy hole to Fermi edge transition in the 18 nm quantum well is very weak and is not shown here.

5.2.4 Temperature dependent $S_I$ 2DFT Spectra

In semiconductor, scattering with phonons is the dominant mechanism of excitonic dephasing at higher temperature. In order to probe the effect of exciton-phonon scattering, rephasing 2DFT measurements were performed at different temperatures between 5 and 30K. In this temperature range, scattering with acoustic phonons is dominant, which results in faster dephasing. It has been observed that the linewidth (inversely proportional to the dephasing time) increases linearly with temperature [188] for scattering due to acoustic phonons. The temperature dependent 2DFT spectra of the HH Mahan excitons at colinear

Figure 5.6: (a)-(f) Amplitude and real part 2DFT spectra ($T = 0$ fs) originating from the 12 nm MDQW using co-linear polarizations at different temperatures. The cross-diagonal profiles of the 2DFT data (black squares) are shown with the Lorentzian fit (red line). The cross-diagonal profile provides the homogeneous linewidth which increases with increasing temperature.
polarization are shown in Fig. 5.6 (a)-(f). The homogeneous linewidth are obtained from the Lorentzian fitting of the cross-diagonal profile (shown next to each 2DFT spectrum). The 2DFT spectra show linewidth broadening with the increase in temperature. The average values of the homogeneous linewidths obtained from the TIFWM measurements and the 2DFT spectra are plotted as a function of temperature in Fig. 5.7 for both quantum wells. The homogeneous linewidths increases linearly with temperature, but at a higher rate compared to undoped quantum wells [118].

![Homogeneous linewidth obtained from the 2DFT spectra vs. temperature for both MDQWs and the corresponding linear fittings.](image)

The homogeneous linewidths Vs. temperature data were fitted according to the relation \( \Gamma = \Gamma_0 + \alpha T \), where \( \Gamma \) is the temperature dependent linewidth, \( \Gamma_0 \) is the temperature independent linewidth, and \( \alpha \) is the acoustic phonon scattering coefficient. The temperature independent linewidths \( \gamma_0 \) were found to be 1.40 meV and 1.42 meV, whereas the acoustic phonon scattering coefficients \( \alpha \) were 110 \( \mu eV/K \) and 158 \( \mu eV/K \) for the 18 nm and 12 nm quantum well, respectively. These values are about one order of magnitude larger than what has been observed in undoped quantum wells (5 − 10 \( \mu eV/K \)) and bulk GaAs (17 \( \mu eV/K \)) [118]. In undoped quantum well, a reduction in exciton-phonon scattering due to the quantum confinement was observed for Wannier exciton [189]. There are two possibilities

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that could lead to the appreciably higher dephasing rate with temperature in the narrower 12 nm quantum well. The narrower quantum well could have larger in-well carrier concentration, which could lead to a higher scattering rate with acoustic phonons. However, the energy shift between the PL and FWM in Fig. 5.3 (b) and 5.3 (d) is the same for both quantum wells within less than 1 meV, indicating similar Fermi energy and in-well carrier concentration. The increased quantum confinement in the 12 nm well could lead to an increased carrier-phonon scattering rate that causes more efficient dephasing in the narrower quantum well.

5.2.5 Polarization dependent $S_{III}$ 2DFT Spectra

The two quantum 2DFT spectra ($S_{III}$) that isolate two-quantum coherences and correspond to the negative delay case in a FWM experiment are shown in Fig. 5.8 (a)-(d) for the 18 and 12 nm quantum well, respectively, for colinear polarization. A single diagonal peak

Figure 5.8: (a) and (b) Amplitude and real part 2DFT spectra originating from the 18 nm MDQW using co-linear (HHHH) polarizations. (c) and (d) Amplitude and real part 2DFT spectra originating from the 12 nm MDQW using co-linear (HHHH) polarizations. The polarization sequence (HHHH) corresponds to pulse B, C, A* and detection, respectively. The pulse sequence for the $S_{III}$ 2DFT spectra is shown in the upper inlet. (e) and (f) Amplitude and real part $S_I$ 2DFT spectra originating from the 12 nm MDQW using co-circular ($\sigma^+\sigma^+\sigma^+\sigma^+$) polarizations. (g) and (h) Amplitude and real part $S_{III}$ 2DFT spectra originating from the 12 nm MDQW using co-circular ($\sigma^+\sigma^+\sigma^+\sigma^+$) polarizations.
corresponding to an unbound two exciton state is observed for both samples. The peak is stronger in the 12 nm QW compared to the 18 nm QW, and could be due to the increased confinement in the narrower QW. 2DFT spectra using circularly polarized excitations provide clear spin selection rule. For this polarization, the many body effects are suppressed and any coupling between resonances are enhanced. The $S_I$ and $S_{III}$ 2DFT spectra using $(\sigma^+\sigma^+\sigma^+\sigma^+)$ polarizations are shown in Fig. 5.8 (e)-(f) and 5.8 (g)–(h), respectively. For cross-circular polarizations $(\sigma^+\sigma^-\sigma^-\sigma^+)$ the signal for both $S_I$ and $S_{III}$ was absent, indicating spin selection rules imposed by the Pauli exclusion principle which differ from those of undoped quantum wells [144, 150]. The $S_I$ 2DFT data in Fig. 5.8 (e)-(f) show a more pronounced asymmetry than in the co-linear case, which can be better observed in the real part of Fig. 5.8 (f).

5.2.6 Conclusion

In conclusion, we performed 2DFT measurements on two single modulation doped quantum wells of 12 nm and 18 nm thickness. The nature of the temperature dependent photoluminescence spectra indicate the presence of Fermi edge singularity. The PL spectra are found to be red-shifted with respect to the spectrally resolved FWM (SR-FWM), indicating the absorption taking place at the Fermi energy ($k \approx k_F$), whereas the recombination predominantly occurs at the bottom of the conduction band ($k = 0$). The energy shift of 13.1 meV and 13.9 meV are observed between the PL and SR-FWM for the 18 nm and 12 nm MDQW samples, respectively. Transitions from the HH and LH valence bands to the Fermi energy level leading to the formation of Mahan excitons were observed in the SR-FWM spectra. The homogeneous linewidths of the HH Mahan excitons in both modulation doped single quantum wells of 12 nm and 18 nm thickness and with in-well carrier concentration of $\sim 4 \times 10^{11} \text{ cm}^{-2}$ were obtained from the dephasing rate using time-integrated four-wave mixing (TIFWM). From rephasing 2DFT spectra, the linewidths were obtained directly from the cross-diagonal profile. The homogeneous linewidths were observed to vary linearly with
temperature for both samples at a rate higher compared to undoped quantum wells. Also, the dephasing rate is much faster in the narrower quantum well, which could result from increased exciton-phonon scattering due to higher quantum confinement. The lineshapes obtained from the polarization dependent rephasing 2DFT spectra show asymmetry, indicating the presence of many body interactions.

5.3 Strong Quantum Coherence between Mahan Excitons

In modulation doped quantum well the Mahan excitons are formed as a result of the interactions of the charged holes with the electrons at the Fermi edge in the conduction band. Strong quantum coherence is observed between the HH and LH Mahan excitons which is quantitatively stronger than the observed coherence between HH and LH Wannier excitons in undoped quantum wells. This quantum coherence appears as cross-peaks in the 2DFT spectra. The observed cross-peaks are stronger than that of undoped quantum wells. The line shape and the peaks strengths of 2DFT spectra in quantum wells are very sensitive to the polarizations of the excitation pulses. As a result, certain polarizations can enhance two-quantum contributions to the 2DFT spectra and lead to stronger cross-peaks. The one-quantum $S_I$ 2DFT spectra show stronger cross-peaks using circularly polarized excitation pulses. However, the $S_{III}$ 2DFT spectra originate solely from two-quantum contributions to the nonlinear optical response. Therefore cross-peaks observed in the $S_{III}$ spectra unambiguously confirm the nature of the cross-peaks as originating from quantum coherence. Furthermore, the observed lineshapes of the cross-peaks in the $S_I$ spectra which extend energetically above the LH excitonic resonance indicate contributions from virtual ‘continuum states’ above the Fermi level. Such collective excitations above the Fermi energy are a clear demonstration of the many-body nature of the Mahan exciton and are modeled here by a series of closely spaced resonances above the LH energy that dephase very rapidly. The experimental 2DFT spectra are qualitatively well reproduced using the optical Bloch equa-

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tions where the many-body effects such as excitation induced dephasing (EID) and excitation induced shift (EIS) are included phenomenologically.

5.3.1 Polarization dependent $S_I$ and $S_{III}$ 2DFT Spectra

![Image of 2DFT Spectra](image)

Figure 5.9: Experimental $S_I$ 2DFT spectra at four different polarizations namely (HHHH), (HVVH), $(σ^+σ^+σ^+σ^+)$, and $(σ^+σ−σ−σ^+)$, where the polarizations correspond to $A^*$, B, C and detection, respectively. The spectrally resolved FWM (black line) and the excitation laser spectrum (red line) are shown above the experimental spectra. Lower row: Theoretical spectra calculated using the optical Bloch equations where many-body effects such as EID and EIS are included phenomenologically.

The rephasing 2DFT measurements were performed on a modulation doped GaAs/AlGaAs single quantum well with 12 nm thickness. The in-well carrier concentration of $\sim 4 \times 10^{11}$ cm$^{-2}$ was estimated from the energy separation of the PL and SR-FWM spectra. The experimental $S_I$ 2DFT spectra were measured at four different polarizations, namely (HHHH), (HVVH), $(σ^+σ^+σ^+σ^+)$, and $(σ^+σ−σ−σ^+)$, where the polarizations correspond to $A^*$, B, C and detection, respectively, and are shown in Fig. 5.9. All measurements were performed
with zero delay between pulse B and pulse C ($T = 0$). The nonlinear response function are represented by the density matrix in the optical Bloch equations and all the coherent pathways can be tracked conveniently using double sided Feynman diagrams in Liouville space (see Appendix B). Each polarization sequence corresponds to a specific pathways in Liouville space, thus for different polarization sequences, a different set of coherent pathways contribute to the nonlinear response function. This may lead to unequal cross peak strengths with respect to the diagonal peaks. At (HHHH) polarization we observed two peaks on the diagonal of the $S_I$ 2DFT spectra corresponding to the HH (labeled as A) and LH (labeled as B) Mahan excitons, respectively. A strong cross peak C below the diagonal can also be observed with an absorption energy of the LH but emission energy of the HH. For cross-linear polarization sequence (HVVH), we only observe a single peak (labeled as A) on the diagonal which corresponds to the HH exciton. The coherent pathways for this polarization sequence do not allow the formation of any cross peaks. However, the LH exciton peak is not observed because the LH is much weaker compared to the HH. Also, the excitation laser pulse frequency could have been shifted towards the HH.

For co-circular ($\sigma^+\sigma^+\sigma^+\sigma^+$) and cross-circular ($\sigma^+\sigma^-\sigma^-\sigma^+$) polarization sequences, 2DFT spectra are dominated by two very strong cross peaks below the diagonal (labeled C) and above the diagonal (labeled D), indicating the HH and LH Mahan excitons are strongly coupled. For these polarizations, the double sided Feynman diagrams involving two quantum transitions predominantly contribute to the non-linear 2DFT signal. As a result, the cross peaks are stronger and indicates quantum coherence between peaks A and B. This is because the cross peaks above and below the diagonal from two-quantum contributions can only originate from coherent coupling of two resonances. Unwanted peaks may appear in the rephasing 2DFT spectra due to imperfect polarizations. In order to verify the observed quantum coherence in the rephasing measurement, we further performed two quantum 2DFT ($S_{II}$) measurements. In this process, the signal arises from contribution of
two exciton states and the presence of any cross-peaks would confirm the quantum coherence (see section 3.5.2).

Figure 5.10: Left: Experimental $S_{III}$ 2DFT spectra at polarization $(\sigma^+\sigma^+\sigma^+\sigma^+)$, where the polarizations correspond to pulses $A^*$, $B$, $C$ and detection, respectively. Right: Theoretical spectra calculated using the optical Bloch equations where many-body effects such as EID and EIS are included phenomenologically.

The $S_{III}$ 2DFT data at $(\sigma^+\sigma^+\sigma^+\sigma^+)$ is shown in Fig. 5.10 (Left). Due to the fact that the $S_{III}$ 2DFT spectra are based on the negative delay signal, they are rather weak. However, in addition to the two-exciton diagonal peaks A and B, two cross peaks can be observed. The cross peaks are enclosed in the white circles for clarity and are labeled as C and D. It should be pointed out here that the $\Omega_T$ axis corresponds to $\Omega_T = 2 \times \Omega_t$ because the $S_{III}$ 2DFT spectra originate from two-quantum transitions [144]. The experimental spectra are reproduced in Fig. 5.10 (Right) using the optical Bloch equations and the same parameters used to reproduce the $S_I$ experimental spectra.

5.3.2 Results from TD-DFT Calculations

Finally, in order to gain deeper understanding into the physics behind the observed quantum coherence we performed state-of-the-art theoretical calculations which go beyond the phenomenological approach using the optical Bloch equations. The theoretical 2DFT
spectra are modeled within the density matrix version of TDDFT [190–194]. In the density-matrix TDDFT approach, the time-dependent Kohn-Sham (KS) equation is solved using time-dependent Hartree and exchange correlation potentials. In general, TDDFT has recently been successfully applied to study the excitonic effects in the frameworks of the time-dependent optimized effective potential approach [195, 196], in combination with the Bethe-Salpeter equation [197, 198], and by solving the TDDFT version of the semiconductor Bloch equations in the density-matrix representation [191, 192]. Additionally, the last approach was recently generalized to include biexcitonic effects [193, 194].

Figure 5.11: Left: Calculated $S_I$ 2DFT spectra for (HHHH) polarizations using TDDFT. Right: Calculated binding energies for HH, LH excitons and HH-LH biexcitons as a function of doping using TDDFT.

In order to calculate the $S_I$ 2DFT we used the density matrix TDDFT technique [193] with the screened Slater exchange-correlation kernel [194]. The TDDFT analysis was performed by using the static DFT Kohn-Sham wave functions and eigenenergies as input. The last quantities were obtained by using the Quantum Expresso package [199]. The corresponding $S_I$ 2DFT spectra at (HHHH) polarizations calculated using this approach is shown in Fig. 5.11 (Left). Calculated 2DFT spectra agrees well with the experimental data of Fig. 5.9, where the diagonal peaks corresponding to the HH and LH Mahan excitons, as
well as the cross-diagonal peak C are reproduced. Furthermore, we obtained the binding energies of the HH, the LH excitons, and the HH-LH biexcitons as a function of doping. The results are shown in Fig. 5.11 (Right) and suggests that at doping concentration of the samples studied here ($1 \times 10^{12}$ cm$^{-2}$), the Mahan excitons form bound state with binding energies of $\sim4.5$ meV, $\sim1.0$ meV, and $\sim0.9$ meV for the HH exciton, LH exciton, and HH-LH biexciton, respectively. It also shows that these excitons form bound states at even much higher doping levels and show very moderate decrease in binding energy with doping concentration. It is well known fact that due to the presence of large number of free carriers, bare Coulomb interaction is reduced in dielectric medium because of screening effect. In modulation doped quantum wells, the Coulomb interaction gets further reduced due to the confinement. Thus, the reduced dielectric screening parameter due to the quantum confinement in the 12 nm quantum well leads to the formation of the bound sates, despite a large number of additional scattering centers, namely electron dopants, the attractive potential between the electrons and holes remains reasonably strong even at rather high doping levels in the order of $10^{12} - 10^{13}$ cm$^{-2}$.

The effect of the screening of Coulomb interaction can be demonstrated by estimating the Thomas-Fermi screening radius, $r_{TF} = \sqrt{\pi \epsilon a_B / 4 k_F m}$. This can be represented in the relevant quantum well units as $r_{TF} \approx 0.366 \sqrt{\epsilon / m} (l/N)^{1/6}$, where $\epsilon$ is the dielectric constant, $m$ is the particle mass in units of $m_0$, $l$ is the width of the well in nm and $N$ is the number of electrons per cm$^{-2}$ divided by $10^{11}$. Using $\epsilon \sim 12.9$, the mass of the electron $m_e \approx 0.067$, the mass of the heavy hole $m_{hh} \approx 0.45$, the mass of the light hole $m_{lh} \approx 0.082$, the quantum well width $l = 12$ and number of electrons $N = 1$, we obtain for the electron $r_{TF}^e \approx 7.6$ nm, heavy hole $r_{TF}^{hh} \approx 3.0$ nm, and light hole $r_{TF}^{lh} \approx 7.0$ nm. Although this estimation is rather simple, it demonstrates that the screening length is comparable to the quantum well width $l \sim 12$ nm. This indicates that the screening is greatly reduced as compared to the bulk case. Using this approach we can estimate the increase in doping needed to reduce the binding
energy by half. The number of electrons needs to increase by a factor of $2^6 = 64$, which corresponds to an increase from $10^{11}$ to $64 \times 10^{11} cm^{-2}$ close to two orders of magnitude. This simple estimation is in excellent agreement with the TDDFT calculations shown in Fig. 5.1.1. At a doping concentration of $64 \times 10^{11} cm^{-2}$ indeed excitons start to dissociate.

### 5.3.3 Conclusion

In conclusion, we performed 2DFTS measurements on a high mobility two dimensional electron gas. The rephasing 2D spectra revealed two peaks on the diagonal corresponding to HH and LH Mahan excitons, as well as two additional strong cross-peaks, indicating coherently coupling between the two resonances. The observed quantum coherence Mahan excitons are stronger in the doped sample compared to that between LH and HH Wannier type excitons in the undoped quantum well. This is very surprising since the Mahan excitons occur as a result of the interaction of the positively charged holes with the ensemble of electrons in the conduction band. Therefore, screening and electron-electron interactions should destroy the quantum coherence. Instead the reduced screening as a result of the quantum confinement in the quantum well combined with collective nature of the electronic excitations at the Fermi edge enhanced the quantum coherence. The experimental results were supported by theoretical calculation based on OBE and TDDFT calculations.
Chapter 6

Dynamics of Magnetoexcitons in doped and undoped Quantum Wells

6.1 Introduction

In our study, we observe distinct differences in the Landau levels originating from undoped and modulation doped quantum wells. In the undoped sample elongated stripes are observed and have been attributed to coupling to a higher continuum states [36, 38, 200]. This behavior was expected to be stronger in the modulation doped sample due the high concentration of free carriers. Surprisingly, the striping is completely absent in the lowest Landau level in the modulation doped quantum well sample between 8 and 10 Tesla. In order to get a deeper understanding of the different nature of the line shape, we performed time dependent density functional theory (TD-DFT) calculations which reveals the underlying physics. The observed elongation of the lineshapes is attributed to inhomogeneities in the exchange-correlation potential caused by Coulomb interactions, leading to the coupling of discrete landau levels to a continuum state. Whereas, the absence of the stripes along the $\omega_\tau$ direction in the doped samples is attributed to a combination of screening of the Coulomb interactions and orbital-localization effects.

Additionally, we observe strong coherent coupling between Landau levels is observed which manifest as distinct cross-diagonal peaks in the 2DFT spectra. Inter-Landau level coherent coupling was first observed as a beating in the time integrated FWM signal[83, 85]. Although, it is often difficult to distinguish between quantum coherence and polarization interference from the one dimensional TFWM data, the presence of cross-peaks in 2DFT spectra demonstrates the quantum coherence [185] due to it’s ability to isolate various co-
herent pathways that contribute to the nonlinear FWM signal and present them in a two
dimensional map in frequency domain. Finally, we observe an increase in the quantum co-
herence at the lowest Landau level LL0 as compared to the first Landau level LL1. The
increased quantum coherence of the lowest LL0 is likely a result of a lower population as
compared to the first Landau level LL1, which leads to reduced carrier scattering. The exper-
imental results and discussion of the measurements up to 10 Tesla are presented in Section
6.2, whereas the results from measurements between 10 and up to 25 Tesla are discussed in
Section 6.3.

6.2 Experimental Results (up to 10 Tesla) and Discussion

In our studies, two samples, one undoped and a modulation doped GaAs/AlGaAs mul-
tiple (four periods) quantum wells, were used. The undoped (intrinsic) and the modulation
doped quantum wells are 10 nm and 18 nm thick, respectively. The estimated in-well carrier
concentration for the modulation doped quantum well is \(\sim 4 \times 10^{11} \text{ cm}^{-2}\). All magnetic field
measurements are performed in transmission geometry. The sample substrate was etched
by wet chemical method. For the measurements up to 10 Tesla, the samples were held at
1.6 Kelvin inside a Oxford Spectromag magneto-optical cryostat (superconducting magnet).
The magnetic field was applied in the Faraday geometry perpendicular to the sample surface.

Figure 6.1: Schematic of the experimental 2DFT setup in Magnetic Field.
The experimental setup is shown in Fig. 6.1.

6.2.1 Magneto-absorption Spectra of undoped and modulation doped quantum wells

The absorption spectra of the undoped quantum well measured with a white light source with right hand circular polarization (RCP) at different magnetic field up to 10 Tesla and at 1.6K is shown in Fig. 6.2. At zero field, the HH and LH exciton peaks are well resolved. As the field is increased, both peaks shift diamagnetically towards higher energy. The shift of the HH peak is marked with dashed black line. The line is drawn as a guide to the eye.

Figure 6.2: Absorption Spectra of undoped GaAs/AlGaAs multiple quantum well with right circular polarized (RCP) light from 0 to 10 Tesla at 1.6K. The energy shift of the HH transitions with magnetic field is marked with a black dashed line. The line is a guide to the eyes only.

of the HH peak is marked with dashed black line. The line is drawn as a guide to the eye.
At higher field, several Landau levels appear in the optical spectra. The identification of the higher Landau levels has been discussed in the literature and is not the subject of the present study [69–71, 201–205].

Figure 6.3: a) Absorbance of the modulation doped 18 nm GaAs quantum well with right circular polarized light showing the two lowest Landau levels at different magnetic fields from 1 to 25 Tesla. Both Landau levels shift linearly with temperature marked by the dashed lines. c) Polarization dependent absorption spectra of the LL0 at 10 Tesla. d) Polarization dependent absorption spectra of the LL1 at 6.5 Tesla.

The formation of Landau levels in a modulation doped quantum well with various magnetic field up to 25 Tesla is shown in Fig. 6.3 (a) where the absorption was measured at 10K with right circular polarized light. At lower magnetic field we observe two lowest Landau levels denoted by LL0 and LL1. Between 4 and 5 Tesla LL1 is populated first and shifts toward higher energy linearly with increasing magnetic field as expected for Landau levels. The lowest Landau level LL0 becomes populated at about 8 Tesla and also shifts linearly with increasing magnetic field. The formation of Landau levels is depicted in Fig.
6.3 (b). We also measured the absorbance with left circularly polarized (LCP) light and the comparison of absorption LL1 and LL0 is shown in Fig. 6.3 (c) and (d) for RCP ($\sigma^+$) and LCP ($\sigma^-$). The first Landau level LL1 shows only a small energy shift between the $\sigma^+$ and $\sigma^-$ polarizations, whereas the lowest Landau level LL0 appears to be strongly polarization dependent. The lowest Landau level at fixed momentum only accommodates only particles with one projection of spin, while the next level is filled with particles with both spins. This likely leads to the strong polarization dependence of the lowest Landau level.

6.2.2 $S_I$ 2DFT Spectra of the undoped Quantum Well

In Fig. 6.4 (a) and (b), 2DFT spectra of the Landau levels originating from the undoped quantum well are shown at magnetic fields 6 and 10 Tesla, respectively. The full widths at half maximum (FWHM) of the Landau levels along the $\omega_t$ spectral direction of the 2DFT spectra are measured to be below 1 meV, whereas, the spectra shows much larger and elongated lineshapes along the $\omega_\tau$ direction. The linewidths along $\omega_t$ become even narrower at 10 Tesla. Furthermore, at 10 Tesla we observe two Landau levels indicated by the two peaks on the diagonal of the 2DFT spectra (Fig. 6.4 (b)). We also observe two additional cross-diagonal peaks which indicates strong quantum coherent coupling between the two Landau levels. Furthermore, we probe the excitonic ground state at 6 and 10 Tesla shown in Fig. 6.4 (c) and (d), respectively. At 6 Tesla both the exciton and biexciton peak are clearly visible in Fig. 6.4 (c) and are marked by the red arrows. As previously observed, these resonances do not show the vertical elongation along the $\omega_\tau$ direction, but are slightly elongated along the diagonal of the 2DFT spectra due to inhomogeneous broadening. Rephasing 2DFT spectra with the cross-linear polarization enhances the contribution of the biexciton peaks and are shown in Fig. 6.5 at magnetic fields of 2 and 4 Tesla. The biexciton peaks (labeled as BX) at both fields are $\sim$2 meV red-shifted from the excitonic peak along the emission axis. The energy shift corresponds to the biexciton binding energy, which in this case is about 2 meV. Both co-linear and cross-linear data suggest that the biexciton remains bound even at 6
Figure 6.4: Experimental $S_f$ 2DFT spectra of the undoped GaAs quantum well at (HHHH) polarizations under high magnetic fields. The (HHHH) polarizations correspond to $A^*$, $B$, $C$ and detection, respectively. The spectrally resolved FWM (blue line) and the absorbance (black line) are shown above the experimental spectra. Left: 2DFT spectra of the Landau levels from the undoped GaAs quantum well at magnetic fields of (a) 6 Tesla and (b) 10 Tesla. Right: 2DFT spectra of the excitation region from the undoped GaAs quantum well at magnetic fields of (c) 6 Tesla and (d) 10 Tesla.

Tesla. Biexciton binding energy of $\sim 2$ meV has been observed previously at zero field from the 10 nm undoped quantum well sample, which suggest the binding energy does not change much in the low fields. However, at 10 Tesla, the biexciton peak is absent.

The elongated lineshapes along the $\omega_\tau$ direction in the undoped sample have been observed in previous studies at zero magnetic field and the origin of the elongated peaks has been attributed to the coupling to the continuum states [36, 38, 206]. However, in the present
Figure 6.5: SI 2DFT Spectra of the undoped quantum well with cross-linear polarization. The biexciton peak is labeled as BX.

In the case the discrete nature of the Landau levels and the quantum confinement of the quantum well in the magnetic field direction should not lead to such continuum state interactions. These elongated lineshapes first occur with the appearance of Landau levels and narrow further along the $\omega_t$ direction with increasing field.

Figure 6.6: Time-integrated FWM of the LL1 at 4.5 Tesla (black circles) and LL0 at 10 Tesla (blue squares). The red lines are the exponential fittings.

The time-integrated FWM was measured for LL1 and LL0 at 4.5 and 10 Tesla, re-
spectively, and is shown in Fig. 6.6. A rapid dephasing of several hundred femtoseconds is observed for both Landau levels. The fast dephasing is followed by a much slower component lasting several picoseconds. The longer decay component is measured to be 4.6 ps for LL1 and increases further to 6.2 ps for LL0. The longer dephasing for LL0 is likely due to underpopulation of the level as compared to LL1, and hence reduced scattering effects. On the other hand, the initial $\sim 100$ fs relaxation for both levels is due to similar ultra-fast pre-equilibration of the quasi-free excitations.

Figure 6.7: Left: Experimental $S_I$ 2DFT spectra using $(\sigma^+\sigma^+\sigma^+\sigma^+)$ polarizations of LL1 at three different magnetic fields (4T, 4.5T, and 5.5T). Right: Experimental SI 2DFT spectra using $(\sigma^+\sigma^+\sigma^+\sigma^+)$ polarizations of LL0 at three different magnetic fields (8, 9, and 10 Tesla).

### 6.2.3 $S_I$ 2DFT Spectra of Modulation doped Quantum Well

The 2DFT spectra at $(\sigma^+\sigma^+\sigma^+\sigma^+)$ polarizations for the modulation doped quantum well are shown in Fig. 6.7 for LL1 (left) and LL0 (right) at three different magnetic fields.
Surprisingly, the striping lineshapes observed in the undoped quantum well are substantially reduced for LL1 and are completely absent for LL0 in the modulation doped sample. Despite the much higher concentration of the free carriers in the modulation doped sample, there is no stripe-like elongation for the lowest Landau level at fields between 8T and 10T. In order to gain deeper understanding of the physics behind the counterintuitive behavior of the Landau
levels in doped and undoped quantum wells, we performed density matrix time-dependent DFT calculations for both samples, which are shown in Fig. 6.8. The theory reproduces well the linenshapes of the Landau levels in the undoped sample as shown in Fig. 6.8 (a), as well as the cross-peaks due to quantum coherent coupling shown in Fig. 6.8 (b). In addition, at lower excitation energies the presence of the bound exciton and biexciton peaks in the 2DFT spectra at 6 Tesla are reproduced, as shown in Fig. 6.8 (c), followed by the dissociation of the exciton at 10 Tesla, as the cyclotron energy approaches the excitonic binding energy (Fig. 6.8 (d)). The Density matrix time-dependent DFT calculations reveal the underlying physics and attributes the elongated linenshapes to breaking of the translational invariance by inhomogeneities in the exchange-correlation potential. The inhomogeneities are obtained from first-principle DFT calculations of the exchange-correlation kernel and are caused by the Coulomb interactions, which couples the discrete Landau levels to a continuum state. The electron and hole charge distribution becomes increasingly separated as the magnetic field is increased, which leads to an overlap of charge densities comparable to the in-plane lattice constant. The charge inhomogeneities with the overlap leads to breakdown of Kohn’s theorem [207–209], and acts as a perturbation that coherently couple discrete and degenerate states, which is manifested by the elongated linenshapes in the 2DFT spectra.

Next we discuss the simulations of the 2DFT LL1 and LL0 spectra for the modulation doped quantum well. The simulations based on time-dependent DFT calculations reproduce the observed absence of elongated linenshapes for the LL0 at 10 Tesla. The time-dependent DFT provides insights into this seemingly counterintuitive observation. The screening generated by the free carrier weakens the strength of the Coulomb interactions, which leads to reduced effect of the inhomogeneities in the electron-hole charge density overlap; and restores Kohn’s theorem (see Appendix C). Furthermore, the narrowing of the Landau level radius with magnetic field leads to a substantial decrease of scattering probability with free electrons. The combined effect leads to the disappearance of elongation in the $\omega_\tau$ frequency.
direction and reduction of free-carrier induced dephasing. As a result, the LL0 state reaches a homogeneous linewidth of $\sim 0.27$ meV at 10 Tesla, obtained experimentally from the cross-diagonal profile of the 2DFT spectra, well in agreement with the measured dephasing time using time-integrated FWM.

Finally, we use a simple diagrammatic description in order to summarize the essential physics obtained from the time-dependent DFT calculations. In Fig. 6.9 the band structure and Landau levels are shown for both undoped and doped case. The laser pulse promotes an electron into the Landau levels creating a positively charged hole in the valence band. The attractive Coulomb attraction between the electron and hole is depicted by the dashed field lines. In the undoped case, the bare Coulomb interaction between the electron and hole, as well as the repulsive electron-electron interaction, lead to spatial inhomogeneities in the exchange correlation potential. These inhomogeneities break the translational symmetry due to a non-trivial dispersion of the in-plane charge excitations. These interactions are non-linear in nature and involve multiple quasi-particles. As a result, the degeneracy of Landau
levels is lifted and Landau levels are coupled to continuum state. In the modulation doped case, the Coulomb interactions are substantially weakened due to the screening provided by the electron doping. Furthermore, orbital-localization effects with the increasing magnetic fields lead to an additional reduction in quasi-particle scattering. Therefore, the Landau levels remain discrete.

6.3 Experimental Results (up to 25 Tesla)

We conclude the experimental section of this chapter by reporting the 2DFTS and TI-FWM measurements performed at high magnetic field up to 25 Tesla. A DC resistive magnet (Florida Split-Helix) was used for the measurements up to 25 Tesla. Fig. 6.10 shows the absorption spectra of the undoped quantum well for right hand circularly polarized light at various magnetic field up to 25 Tesla, measured at 10K, and depicts the formation of several LL’s with increasing field.

Figure 6.10: Absorption Spectra of undoped GaAs/AlGaAs multiple quantum well with right circular polarized (RCP) light from 10 to 25 Tesla at 10K.
Figure 6.11: SI 2DFT Spectra of the LL’s of an undoped quantum well measured at 10K with colinear polarization at magnetic fields up to 25 Tesla. The spectrally resolved FWM are shown above the 2D spectra.

The rephasing 2DFT spectra measured with colinear polarization at several magnetic field from 12 to 25 Tesla are shown in Fig. 6.11. The excitation laser pulse with a duration of $\sim 40$ fs was centered at 790 nm ($\sim 1.570$ eV) to resonantly excite the higher LL’s. We observe several peaks on the diagonal of the 2DFT spectra which corresponds to the peaks on the SR-FWM spectra (shown on top of each 2DFT spectrum), as well as some cross peaks indicating coupling between LL’s. The lineshapes of the LL’s are found to be elongated along the absorption axis, as observed previously in the 2DFT spectra measured at a field up to 10 Tesla. Please note that, we observed a very strong FWM signal originating from the buffer

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layer at \(\sim 1.520\) eV compared to the other LL’s from the quantum well, that dominated the 2DFT spectrum. The peak due to the bulk was subtracted to make other peaks visible.

6.4 Conclusion

In conclusion, we employed TFWM and 2DFTS techniques to study the dynamics of Landau levels in an undoped and a modulation doped GaAs/AlGaAs quantum wells in an external magnetic field up to 25 Tesla. The 2DFT spectra revealed distinctly different lineshapes in the two quantum well samples. The lineshapes of the Landau levels for the undoped quantum well show elongation along the absorption axis; whereas, the elongation is much reduced in the LL0 and is completely absent in LL1 of the doped sample. Theoretical simulations based on TD-DFT were performed on the measurements up to 10 Tesla and suggested that the elongations appears due to coupling of the LL’s to the continuum states in the undoped sample. The absence of elongations in the modulation doped sample was attributed to the combination of Coulomb screening and orbital localization effects.
Chapter 7

Conclusion and Outlook

The focus of our study was to explore the exciton dynamics of a two dimensional electron gas in a modulation doped quantum well using three pulse transient FWM (TFWM) and two dimensional Fourier transform spectroscopy (2DFTS) techniques. A custom built multidimensional nonlinear optical spectrometer (MONSTR) was developed together with the employment of an active phase stabilization method, to facilitate the implementation of these techniques. We observed the characteristic spectral signature of the 2DEG in modulation doped quantum wells in the PL spectra. Although, the carrier concentration is very high in these quantum well, bound states are still formed with respect to the Fermi level. These bound states are referred to as Mahan excitons in the literature. TFWM and rephasing 2DFTS measurements demonstrated that the Mahan excitons dephase at a much faster rate compared to undoped GaAs/AlGaAs quantum wells. The temperature dependent homogeneous linewidths were found to increase linearly with temperature, and the fitting of the data suggested that the excitons dephase faster due to scattering with acoustic phonons at temperature \( \sim 30\text{K} \). Polarization dependent rephasing 2DFT spectra revealed distinct lineshapes, indicating the presence of many body interactions. Furthermore, we observed unusual strong quantum coherence between the HH and LH Mahan excitons. The quantum coherence was demonstrated by the presence of two strong cross-peaks in both one and two quantum 2DFTS spectra. The experimental observations were reproduced with the simulations based on OBE, where many body interactions such as excitation induced dephasing (EID) and excitation induced shift (EIS) were included phenomenologically. Further theoretical analysis based on time dependent DFT calculations provided the underlying physics
and attributed the observed coherence to a considerably reduced Coulomb screening and collective excitation of the Fermi sea.

we further studied the dynamics of Landau levels in an undoped and a modulation doped GaAs/AlGaAs quantum wells in an external magnetic field up to 25 Tesla. The 2DFT spectra revealed distinctly different lineshapes in the two quantum well samples. An elongated line shape along the absorption axis of the rephasing 2DFT spectra was observed for the Landau levels in the undoped quantum well, whereas, the elongation was found to be much reduced in the LL0 and was completely absent in LL1 of the doped sample. Theoretical simulations based on TD-DFT were performed on the measurements up to 10 Tesla and suggested that the elongations appeared due to coupling of the LL’s to the continuum states in the undoped sample. The absence of elongations in the modulation doped sample was attributed to the combination of Coulomb screening and orbital localization effects.

The work presented in this thesis further strengthens the efficiency of 2DFTS, which offer several advantages over the more conventional one dimensional spectroscopy techniques. The ability to isolate homogeneous linewidth in the presence of inhomogeneous broadening and to identify coherent coupling between resonances, makes 2DFTS an invaluable spectroscopy tool for studying the carrier dynamics in various materials system. This has been implemented in a wide wavelength range starting from UV to terahertz. Maintaining phase stability, specially at the shorter wavelength, has been dealt with several methods and are constantly being developed to improve its performance.
Appendix A

2DEG Energy Levels in a uniform Magnetic Field

When a uniform magnetic field is applied in a direction (along z axis) perpendicular to the plane of the two dimensional electron gas (confined in the xy plane of area $A_S = L_x L_y$), the Hamiltonian of the system can be written as:

$$H = \frac{1}{2m} \left[ \left( p_x + \frac{e}{c} A_x \right)^2 + \left( p_y + \frac{e}{c} A_y \right)^2 \right], \quad (A.1)$$

where $m$ is the electron effective mass, $e$ is the electronic charge, and $A(\mathbf{r})$ is the magnetic field vector potential. In Eq. A.1, the interaction of spin magnetic moment with field is neglected. The vector potential can be written in terms of the first Landau gauge as:

$$A(\mathbf{r}) = (-B_y, 0, 0) \quad (A.2)$$

$$\nabla \times A(\mathbf{r}) = B(0, 0, 1). \quad (A.3)$$

Using Eqs. A.2 and A.3, the Hamiltonian of the system (Eq. A.1) can be written in the following form:

$$H = \frac{1}{2m} \left[ \left( p_x - \frac{eB}{c} y \right) + p_y^2 \right]. \quad (A.4)$$

Eqn. A.4 can be further written as:

$$H = \frac{1}{2m} \left[ (\hbar k_x - \frac{eB}{c} y) + p_y^2 \right] \quad (A.5)$$

$$= \frac{1}{2m} p_y^2 + \frac{1}{2} m \omega_c^2 (y - y_0)^2,$$
where \( \omega_c = eB/mc \) represents the cyclotron resonance frequency, \( y_0 = (\hbar c/eB)k_x \) is the center of cyclotron motion, and \( l = \sqrt{\hbar c/eB} \) is the magnetic length of the system. The expression in Eq. A.5 represents the Hamiltonian of a displaced harmonic oscillator with frequency \( \omega_c \), and the corresponding eigen values are:

\[
E_{nk_x} = \left( n + \frac{1}{2} \right) \hbar \omega_c. \tag{A.6}
\]

where \( n = 0, 1, 2, \ldots \) representing the Landau Levels of the system. The Eq. A.6 suggests that the energy levels becomes discrete in a magnetic field and are separated by cyclotron energy \( \hbar \omega_c = (e\hbar mc)B = 2\mu_B B \), where \( \mu_B = (e\hbar/2mc) \) is the Bohr magneton and has a value of 0.05788 meV/Tesla.

The energy eigen values of the Landau levels in Eq. A.6 are degenerate in \( k_x \) and the allowed values of \( k_x \) satisfy the condition \( 0 \leq k_x < (eB/\hbar c)L_y \). Thus, the orbital degeneracy of each Landau level \( n_L(B) \) can be written as:

\[
n_L(B) = \frac{L_x}{2\pi} \frac{eB}{\hbar c} L_y = \frac{e}{\hbar c} B A_S. \tag{A.7}
\]

Thus, the orbital degeneracy is proportional to the magnetic field.
Appendix B

Perturbative Expansion of the Optical Bloch Equation

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B.1 S⃗{\text{I}} Perturbative Expansion of the OBE

For the phase matching condition, \( \mathbf{K}_I = -\mathbf{K}_A + \mathbf{K}_B + \mathbf{K}_C \), the third order density matrix element for the double-sided Feynman diagram in figure is:

\[
\rho^{(3)}_{gG} = \frac{i\mu_{gG}}{2\hbar} e^{i\mathbf{K}_C \mathbf{r}} \int_{-\infty}^{t} dt'' e^{-i(\omega_{gG} - i\gamma_{gG}) (t''-t)} \hat{E}_C(t'') e^{-i\omega_C t'''} \\
\quad \times \frac{i\mu_{gG}}{2\hbar} e^{i\mathbf{K}_B \mathbf{r}} \int_{-\infty}^{t''} dt''' e^{-i(\omega_{gG} - i\gamma_{gG}) (t'''-t'')} \hat{E}_B(t'') e^{-i\omega_B t'''} \\
\quad \times \frac{-i\mu_{gG}}{2\hbar} e^{-i\mathbf{K}_A \mathbf{r}} \int_{-\infty}^{t'''} dt''' e^{-i(\omega_{gG} - i\gamma_{gG}) (t'''-t')} \hat{E}_A^*(t') e^{i\omega_A t'} \rho^{(0)}_{gg},
\]  

(B.1)

where the dipole moment, transition frequency and dephasing rate between state \( j \) and \( k \) are \( \mu_{jk} \), \( \omega_{jk} \), and \( \gamma_{jk} \), respectively.

The field is defined as \( E_i = \hat{E}_i(t) e^{-i\omega_i t} \) for \( i = A, B, C \). In the limit that the pulse duration is short with respect to the time delays, the field’s amplitude can be defined as \( \hat{E}_i(t) = \delta (t - t_i) \) where \( t_i \) is the arrival time of pulse \( i = A, B, C \). Using this definition, the
Figure B.1: (a) Example of double sided Feynman diagram for SI phase matching condition. (b) Energy level scheme used in the calculation.

The integral can be carried out:

\[
\rho_{ehg}^{(3)} = \frac{-i\mu_{elg}h_{ehg}h_{eLg}\rho_{gg}^{(0)}}{8\hbar^3} e^{iK_{I}\tau} \hat{E}_A^* (t_A) \hat{E}_B (t_B) \hat{E}_C (t_C) \theta (t - t_C) \theta (t_C - t_B) \theta (t_B - t_A)
\]

\[
\times e^{-i\omega t} e^{-i\gamma_{el} t} e^{i[(\omega_{eh} - \omega_{el})t_B]} e^{(\gamma_{el} - \gamma_{eL})t_B} e^{i(\omega_{eL} - \omega)t_A} e^{\gamma_{eL} t_A}
\]

In Eq. (B.2), we assumed \( \omega = \omega_A = \omega_B = \omega_C \) and \( \theta (t) \) is the Heaviside step function.

Defining the operator \( \rho_{ehg}^{(3)} = \rho_{ehg}^{(3)} e^{-i\omega t} \) and using the time ordering definitions \( t \equiv t - t_C, T \equiv t_C - t_B, \tau \equiv t_B - t_A \), the operator can be written as:

\[
\hat{\rho}_{ehg}^{(3)} = \frac{-i\mu_{elg}h_{ehg}h_{eLg}\rho_{gg}^{(0)}}{8\hbar^3} e^{iK_{I}\tau} \hat{E}_A^* \hat{E}_B \hat{E}_C \theta (t) \theta (T) \theta (\tau)
\]

\[
\times e^{\gamma_{eh} t - \gamma_{eL} T - \gamma_{eL} \tau} e^{i(\omega - \omega_{eh}) t} e^{-i\omega_{eL} T} e^{-i(\omega + \omega_{eL}) \tau}.
\]

The trace of the density matrix with the dipole moment operator provides the macroscopic polarization, \( \hat{P}^{(3)} \). To account for any inhomogeneous frequency distribution, the polariza-
g(\omega_{geL}, \omega_{eHG}) = \sqrt{\frac{a_{11}a_{22} - a_{12}^2}{\pi}} \times e^{\left[a_{11}(\omega_{geL} - \omega_{geL}^c)^2 - 2a_{12}(\omega_{geL} - \omega_{geL}^c)(\omega_{eHG} - \omega_{eHG}^c) + a_{22}(\omega_{eHG} - \omega_{eHG}^c)^2\right]}, \quad (B.4)

where \omega_{geL}^c and \omega_{eHG}^c are the center frequencies. The third order polarization integral is:

\hat{P}_{eHG}^{(3)} = N \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mu_{eHG} \hat{P}_{eHG}^{(3)} g(\omega_{geL}, \omega_{eHG}) d\omega_{geL} d\omega_{eHG}. \quad (B.5)

We define the following terms:

Figure B.2: All possible double sided Feynman diagrams for SI phase matching condition for the extended level scheme.

\[ R = \frac{a_{12}}{\sqrt{a_{11}a_{22}}}, \quad \text{(B.6)} \]

\[ \delta_{\omega_{geL}} = \sqrt{\ln(2)} \frac{a_{22}}{a_{11}a_{22} - a_{12}^2}; \quad \text{(B.7)} \]

\[ \delta_{\omega_{eHG}} = \sqrt{\ln(2)} \frac{a_{11}}{a_{11}a_{22} - a_{12}^2}; \quad \text{(B.8)} \]
where $R$ is the correlation between $\omega_{geL}$ and $\omega_{eHg}$; $\delta\omega_{geL}$ and $\delta\omega_{eHg}$ are the full width at half maximum of the distribution along $\omega_{geL}$ and $\omega_{eHg}$, respectively. Using the relations (B.6) and solving the integral in Eq. (B.5), we obtain

\[
\hat{P}^{(3)}_{eHg} = \frac{-i\mu_{eHg}\mu_{eHg}^{(0)}}{8\hbar^3} e^{iK_{j,r}} \hat{E}_A^* \hat{E}_B \hat{E}_C \theta(t) \theta(T) e^{\gamma_{eHg}T - \gamma_{eHgL}T - \gamma_{eHg}\tau} \\
\times e^{-i\omega_{eHg}T} e^{-i(\omega_{eHg} - \omega_{eHg})t} e^{i(\omega_{eHg} - \omega_{eHg})t} e^{iK_{A,r}r} \left[ (\delta\omega_{geL})^2 - 2R\delta\omega_{geL} \delta\omega_{eHg}\tau + (\delta\omega_{eHg})^2 \right]
\]

where we have used $\gamma_{geL} = \gamma_{eLg}$ and $\omega_{geL} = -\omega_{eLg}$. Using Eq. (B.7) we obtain the radiated electric field from the following equation:

\[
E(\tau, T, \omega_t) = \frac{L}{2n(\omega_t)} P^{(3)}(\tau, T, \omega_t),
\]

where $L$ is the sample thickness and $n(\omega_t)$ is the frequency dependent refractive index. In order to obtain the total radiated signal, this calculation needs to be performed for each allowed Feynman diagram which are shown in figure (B.2).

### B.2 $S_{III}$ Perturbative Expansion of the OBE

For the phase matching condition $K_{III} = K_B + K_C - K_A$, the third order density matrix element for the double-sided Feynman diagram in figure is:

\[
\rho^{(3)}_{eHg} = \frac{i\mu_{eHg}\mu_{eHg}^{(0)}}{2\hbar} e^{iK_{j,r}} \int_{-\infty}^{t} dt'' e^{-i(\omega_{eHg} - i\gamma_{eHg})}(t - t'') \hat{E}_A^* (t'') e^{i\omega_A t''} \\
\times \frac{i\mu_{eHg}\mu_{eHg}^{(0)}}{2\hbar} e^{iK_{r,C}} \int_{-\infty}^{t} dt' e^{-i(\omega_{eHg} - i\gamma_{eHg})}(t' - t') \hat{E}_C (t') e^{-i\omega_C t'} \\
\times \frac{-i\mu_{eHg}\mu_{eHg}^{(0)}}{2\hbar} e^{-iK_{r,B}} \int_{-\infty}^{t} dt e^{-i(\omega_{eHg} - i\gamma_{eHg})}(t' - t) \hat{E}_B (t) e^{-i\omega_B t'} \rho_{gg}^{(0)}
\]

where the dipole moment, transition frequency and dephasing rate between state $j$ and $k$ are $\mu_{jk}$, $\omega_{jk}$, and $\gamma_{jk}$, respectively. In a similar fashion, as described in the previous section, the field is defined as $E_i = \hat{E}_i (t) e^{-i\omega_i t}$ for $i = A, B, C$. In the limit that the pulse duration is
short with respect to the time delays, the field’s amplitude can be defined as $E_i(t) = \delta(t - t_i)$ where $t_i$ is the arrival time of pulse $i = A, B, C$. Using this definition, the integral can be carried out:

$$\rho_{eHg}^{(3)} = \frac{-i\mu eHfH\mu_fH\mu_eHg\rho_{gg}^{(0)}}{8\hbar^3} e^{iK_{III}r} \tilde{E}_A^* (t_A) \tilde{E}_B (t_B) \tilde{E}_C (t_C) \theta (t - t_A) \theta (t_A - t_C) \theta (t_C - t_B)$$
$$\times e^{-i\omega eHg t} e^{-\gamma eHg T} e^{(\omega_{eHg} + \omega_{fHg}) t_A} e^{(\gamma_{eHg} - \gamma_{fHg}) t_A}$$
$$\times e^{(\omega_{fHg} - \omega_{eHg}) t_C} e^{(\gamma_{fHg} - \gamma_{eHg}) t_C} e^{(\omega_{eHg} - \omega) T} e^{i(2\omega_{fHg} - \omega_{eHg}) T} e^{i(\omega_{eHg} - \omega) \tau} .$$

(B.12)

In Eq. (A.10), we assumed $\omega = \omega_A = \omega_B = \omega_C$ and $\theta (t)$ is the Heaviside step function. Defining the operator $\rho_{eHg}^{(3)} = \rho_{eHg}^{(3)} e^{-i\omega t}$ and using the time ordering definitions $t \equiv t - t_A, T \equiv t_A - t_C, \tau \equiv t_C - t_B$, the operator can be written as:

$$\hat{\rho}_{eHg}^{(3)} = \frac{-i\mu eHfH\mu_fH\mu_eHg\rho_{gg}^{(0)}}{8\hbar^3} e^{iK_{III}r} \tilde{E}_A^* \tilde{E}_B \tilde{E}_C \theta (t) \theta (T) \theta (\tau)$$
$$\times e^{\gamma_{eHg} t - \gamma_{fHg} T - \gamma_{eHg} \tau} e^{i(\omega_{eHg} - \omega) T} e^{i(2\omega_{eHg} - \omega) T} e^{i(\omega_{eHg} - \omega) \tau} .$$

(B.13)

The trace of the density matrix with the dipole moment operator provides the macroscopic polarization, $\hat{P}^{(3)}$. To account for any inhomogeneous frequency distribution, the polariz-
tion can be integrated over a distribution function of the form:

$$g(\omega_{f_{fg}}, \omega_{e_{fg}}) = \frac{\sqrt{a_{11}a_{22} - a_{12}^2}}{\pi} \times e^{\left[a_{11}(\omega_{f_{fg}} - \omega_{f_{fg}}^c)^2 - 2a_{12}(\omega_{f_{fg}} - \omega_{f_{fg}}^c)(\omega_{e_{fg}} - \omega_{e_{fg}}^c) + a_{22}(\omega_{e_{fg}} - \omega_{e_{fg}}^c)^2\right]}$$  \quad(\text{B.14})$$

where $\omega_{f_{fg}}^c$ and $\omega_{e_{fg}}^c$ are the center frequencies. The third order polarization integral is:

$$\hat{P}_{e_{fg}}^{(3)} = \sum_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mu_{e_{fg}} \hat{P}_{e_{fg}}^{(3)} g(\omega_{f_{fg}}, \omega_{e_{fg}}) d\omega_{f_{fg}} d\omega_{e_{fg}} .$$  \quad(B.15)$$

We define the following terms:

$$R = a_{12} \sqrt{a_{11}a_{22} - a_{12}^2} ,$$

$$\delta_{\omega_{f_{fg}}} = \sqrt{\ln(2) \frac{a_{22}}{a_{11}a_{22} - a_{12}^2}} ,$$

$$\delta_{\omega_{e_{fg}}} = \sqrt{\ln(2) \frac{a_{11}}{a_{11}a_{22} - a_{12}^2}} ,$$  \quad(B.16)$$

where $R$ is the correlation between $\omega_{f_{fg}}$ and $\omega_{e_{fg}}$; $\delta_{\omega_{f_{fg}}}$ and $\delta_{\omega_{e_{fg}}}$ are the full width at half maximum of the distribution along $\omega_{f_{fg}}$ and $\omega_{e_{fg}}$, respectively. Using the relations (\text{B.14}) and solving the integral in Eq. (\text{B.13}), we obtain:

$$\hat{P}_{e_{fg}}^{(3)} = -\frac{i\mu_{e_{fg}}}{8\hbar^3} \mathcal{E}_A \mathcal{E}_B \mathcal{E}_C \theta(t) \theta(T) \theta(T - t) e^{-\gamma_{e_{fg}} t - \gamma_{f_{fg}} T - \gamma_{e_{fg}} T} \times e^{\left[i(2\omega - \omega_{f_{fg}})T\right]} e^{i(\omega - \omega_{e_{fg}})t} e^{i(\omega - \omega_{e_{fg}})t} e^{\frac{1}{\hbar} \left[\left(\delta_{\omega_{f_{fg}}} T\right)^2 + 2R \delta_{\omega_{f_{fg}}} \delta_{\omega_{e_{fg}}} T t + \left(\delta_{\omega_{e_{fg}}} T\right)^2\right]}$$  \quad(B.17)$$

In order to obtain the total radiated signal, Eq. (\text{B.15}) can be inserted in Eq. (\text{B.8}) and this calculation needs to be performed for each allowed Feynman diagram shown in Figure (\text{B.4}).

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Figure B.4: All possible double sided Feynman diagrams for SIII phase matching condition for the extended level scheme.
Appendix C

Time dependent Density Functional Theory Calculations

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C.1 Binding Energies

For the undoped quantum well, the Density-Matrix Time-Dependent Density Functional Theory (DM-TDDFT) equation for the binding energies has the following form:

\[ \sum_{k'} \left[ (\varepsilon_{k+q}^c - \varepsilon_k^v) \delta_{kk'} + F_{kk'}^{cvvc}(\omega) \right] P_{k'+\mu q}(\omega) = \omega P_{k+\mu q}(\omega), \] (C.1)

where \( q \) is the exciton momentum, \( \mu \) is the reduced pair mass, and \( \varepsilon_k^c \) and \( \varepsilon_k^v \) are the dispersions of the conduction and of the valence bands. The effective electron-hole interaction described by the matrix elements in Eq. C.1 can be defined as (in time domain):

\[ F_{kqk'q'}^{abcd}(t_1, t_2) = \int dr_1 dr_2 \varphi_a^* (r_1) \varphi_b(r_1) \varphi_{a'}^* (r_2) \varphi_{b'}(r_2) f_{XC} (r_1, t_1; r_2, t_2) \varphi_{a'}^* (r_2) \varphi_{b'}(r_2), \] (C.2)

where \( \varphi_k^a (r) \) are the static Kohn-Sham wave functions for band \( a \) and momentum \( k \), obtained from the solution of static DFT equations. The matrix \( F_{kqk'q'}^{abcd}(t_1, t_2) \) describes the strength of the electron-hole attraction and is a function of the exchange-correlation (XC) kernel:

\[ f_{XC} (r, t; r', t') = \frac{\delta V_{XC} (r, t)}{\delta n (r', t')}, \] (C.3)
where \( V_{XC}(r, t) \) is the XC potential. In the present work, we use the Slater XC Kernel:

\[
f_{XC}^{\text{Slater}}(r, t; r', t') = -\delta(t - t') \frac{2|\sum_{j,k} \varphi_j^*(r) \varphi_k^j(r')|^2}{\varepsilon |r - r'| n_0(r)n_0(r')}.
\] (C.4)

In the doped quantum well, the left-hand side exciton equation (Eq. C.1) will have an additional term \( \sum_{kk'} w_{kk'kk'} P_{k'+\mu q}(\omega) \).

To calculate the biexciton binding energies, we solve the following DM-TDDFT equation:

\[
i \frac{\partial B_{ccv\bar{v}}}{\partial t} = \left( \varepsilon_{k_1}^e + \varepsilon_{k_2}^e - \varepsilon_{q_1}^v - \varepsilon_{q_2}^v \right) B_{ccv\bar{v}}^{k_1k_2q_1q_2} + \sum_{v',k,q} \left[ F_{c^{\prime}v^{\prime}c^{v}v}^{k_1q,kq} \right] \nonumber \]

\[
+ \sum_{p_1,p_2} w_{ccv_p_{p_1}p_{p_2}} B_{ccv_{p_1}p_{p_2}q_1q_2} + \sum_{v',v''p_1,p_2} u_{c^{v'}v''v_{p_1}p_2} B_{ccv_{p_1}p_{p_2}}. \]

(C.5)

Eq. C.5 represents the eigen-energy equation for the biexciton function \( B_{ccv\bar{v}}^{k_1k_2q_1q_2} \), where \( k_1, k_2 \) and \( q_1, q_2 \) are the electron and hole momenta, respectively. The first line represents the free four-particle spectrum; the second line corresponds to the electron-hole attraction parts, described by the matrix potential (Eq. C.2), and the third line accounts for the electron-electron and hole-hole repulsion parts of the equation. The corresponding matrix elements for the electron interaction is

\[
w_{cccc}^{abcd} = \frac{1}{\varepsilon_{ee}} \int dr_1dr_2 \psi_{k}^{a*}(r_1) \psi_{q}^{b*}(r_2) \frac{1}{|r_1 - r_2|} \psi_{k'}^{c}(r_1) \psi_{q'}^{d}(r_2) \] (C.6)

where \( \varepsilon_{ee} \) is the static dielectric screening parameter. Eq. C.5 can be symbolically written in the matrix form \( i \frac{\partial \tilde{B}}{\partial t} = \hat{A} \tilde{B} \), where \( \tilde{B} \) is a vector in the momentum space with dimensionality \( d = N^4 \) and \( N \) is the number of k-points in the Brillouin zone. The eigen-energies of this equation can be found after numerical diagonalization of the matrix \( \hat{A} \).
C.2 Interplay between Dephasing Time and Doping Density

In order to gain an insight on the dephasing mechanism and to estimate the dephasing times from TDDFT, we analyze the linear part of the general exciton polarization equations, which has the same approximate form for both excitons, and can be written as:

\[ i \frac{\partial}{\partial t} P_{kq}(t) = [\varepsilon_k^c \varepsilon_k^c] P_{kq}(t) + \sum_{k',q'} \alpha_{kqk'q'} P_{k'q'}(t) + \sum_{k'} \beta_{kk'k'k'} P_{k'q'}(t) + d_{kq}^w E(t), \]  

(C.7)

where

\[ \alpha_{kqk'q'} = 2 \int dr_1 dr_2 \varphi_{k}^*(r_1) \varphi_{q}^*(r_1) f_{XC}(r_1; r_2) \varphi_{k'}^*(r_2) \varphi_{q'}^*(r_2), \]

\[ \beta_{kk'k'k'} = 2 \int dr_1 dr_2 \varphi_{k}^*(r_1) \varphi_{q}^*(r_1) \frac{1}{\varepsilon_{ee}|r_1 - r_2|} \varphi_{k'}^*(r_2) \varphi_{q'}^*(r_2) \]

are the TDDFT electron-hole and electron-electron interaction potentials, respectively. To estimate the value of the dephasing time, we approximate the electron-hole interaction term in the linear equation above by

\[ \sum_{k',q'} \alpha_{kqk'q'} P_{k'q'}(t) \approx \left[ \alpha_{kqkq} - i\tau_d \right] P_{kq}(t), \]

where \( \alpha_{kqk'q'} \) is a real function that defines the excitonic binding energy, and the inverse dephasing time is approximated as

\[ \frac{1}{\tau_d} = -Im \left[ \sum_{k',q'} \alpha_{kqk'q'} \right]. \]  

(C.8)

By definition, the repulsion potential \( \beta_{kk'k'k'} \) is real, thus it leads only to a reduction of the binding energy. From the expression for \( \alpha_{kqk'q'} \) and the screened Slater XC kernel

\[ f_{XC}^{Slater}(r; r') = -\frac{2|\sum_{j,k} \varphi_j^k(r) \varphi_j^{k*}(r')|^2}{\varepsilon|r - r'| n_0(r) n_0(r')} , \]  

(C.9)

we show how the value of the dephasing time has a nontrivial doping dependence. Indeed, as doping concentration increases, the denominator of \( f_{XC}^{Slater}(r; r') \sim \frac{1}{n_0(r)n_0(r')} \) grows faster than the numerator, since \( n_0(r) = \sum_{j,k} \varphi_j^k(r) \varphi_j^{k*}(r) (j \text{ stands for the valence and conduction bands}) \), and in the conduction band (in the end the summation is performed up to the
Thus, $f^{Slater}_{XC}(r; r')$ is expected to decrease with the doping increasing. This is an expected result: increase in doping leads to a screening, e.g. reduction of the electron-hole attraction potential. On the other hand, at higher doping, the summation over the conduction band momenta $k'$ in Eq. C.8 leads to an increase of $1/\tau_d$, i.e. to the decrease of $\tau_d$. This effect dominates at large Fermi momenta. Thus, while at low doping the properties of the Mahan excitons, including the dephasing time, are defined mostly by the strength of the attraction between the hole and the many-electron system, at higher doping, electron-electron repulsion dominates.

To estimate the excitonic dephasing times, we proceed as follows. Eq. C.9 can be approximately written as $f^{Slater}_{XC}(r; r') \approx -\frac{2}{\varepsilon R_X}$, where $R_X$ is the excitonic radius and substituting it into Eq. C.8 yields $\frac{1}{\tau_d} \sim \frac{2}{\varepsilon R_X} n$, where $n$, is the total number of electrons per unit cell. Taking $\varepsilon \sim 12.9$, $R_X \sim 10$ nm, and $n \sim 4$, we get $\tau_d \sim 1.3$ ps.

Similarly, to estimate the two-exciton dephasing time, we obtain an approximate scattering term in the biexcitonic equation from the linear from the linear terms that include the interaction potential. Indeed, the corresponding part will consist of four terms of the same order as the excitonic one, $1/\tau_d$ (describing two holes attracting to two electrons). This allows us to estimate the biexciton dephasing time as $1/4$ of the excitonic one, i.e. $\sim 0.3$ ps.

### C.3 Four Wave Mixing Spectra

The 2DFT spectra can also be theoretically modeled within the DM-TDDFT [191, 192]. In the case of three-band approximation, the third order DM-TDDFT equation for the heavy hole and the light hole excitation polarizations $P_{1k}(t)$ and $P_{2k}(t)$ have the following form
\[
\frac{i}{\partial t} P_{1k}(t) = [\varepsilon^c_k - \varepsilon^{\text{v1}}_k] P_{1k}(t) + \sum_q \int_{-\infty}^{t} dt' \alpha_{1kq}(t, t') P_{1q}(t') + d^{\text{cv1}}_k E(t) \\
+ \sum_{q,p,Q} P_{1q}^* \int_{-\infty}^{t} dt' F_{11kqpQ}(t, t') P_{1p}(t') P_{1Q}(t') \\
+ \sum_{q,p,Q} P_{2q}^* \int_{-\infty}^{t} dt' F_{12kqpQ}(t, t') P_{1p}(t') P_{2Q}(t') ,
\]

\(\text{(C.10)}\)

\[
\frac{i}{\partial t} P_{2k}(t) = [\varepsilon^c_k - \varepsilon^{\text{v2}}_k] P_{2k}(t) + \sum_q \int_{-\infty}^{t} dt' \alpha_{2kq}(t, t') P_{2q}(t') + d^{\text{cv2}}_k E(t) \\
+ \sum_{q,p,Q} P_{2q}^* \int_{-\infty}^{t} dt' F_{22kqpQ}(t, t') P_{2p}(t') P_{2Q}(t') \\
+ \sum_{q,p,Q} P_{1q}^* \int_{-\infty}^{t} dt' F_{21kqpQ}(t, t') P_{2p}(t') P_{1Q}(t') ,
\]

\(\text{(C.11)}\)

where \(\varepsilon^c_k, \varepsilon^{\text{v1}}_k\) and \(\varepsilon^{\text{v2}}_k\) are the dispersions for the conduction electron, heavy and light holes, respectively, and:

\[
d^{\text{cv1}}_k = \int dr \varphi^c_k(r) r \varphi^{\text{v1}}_k(r) 
\]

\(\text{(C.12)}\)

are the dipole moment matrix elements \((i = 1, 2)\) that describe the magnitude of the response of the system to the multi-pulse electric field \(E(t)\). The functions \(\alpha_{ikq}(t, t')\) are given by:

\[
\alpha_{ikq}(t, t') = 2 F^{cv1, cv1}_{kqk'q'}(t, t') ,
\]

\(\text{(C.13)}\)

where \(F^{cv1, cv1}_{kqk'q'}(t, t')\) are defined in Eq. C.2, describe the strengths of the electron-hole attraction.

Thus, the first line in Eqs. C.10 and C.11 are the linear TDDFT equations for the excitons with zero total momentum, that correspond to the standard many-body Wannier equation in the case \(\alpha_{ikq}(t, t')\) equal to the non-retarded bare Coulomb electron-hole attraction potential \(\delta(t - t') |k - q|^{-2}\). The nonlinear terms (lines two and three) in Eqs. C.10, C.11 correspond to the same band (second line) and different band (third line) exciton-exciton
interactions, described by the matrix elements:

\[
F_{ijkqpQ}(t, t') = \frac{1}{3!} \iiint dr dr' dr'' \varphi^*_{k}(r) \varphi^*_{q}(r') \varphi_{i}(r) \varphi_{v}(r') \varphi_{c}(r') \varphi_{p}(r') \varphi_{Q}(r')
\]

\[
g_{XC}(r, r', t; r'', t') \varphi_{c}^c(r) \varphi_{q}^q(r') \varphi_{c}^q(r') \varphi_{Q}^q(r')
\]

and

\[
F_{ijkqpQ}(t, t') = \frac{1}{3!} \iiint dr dr' dr'' \varphi^*_{k}(r) \varphi^*_{q}(r') \varphi_{i}(r) \varphi_{v}(r') \varphi_{c}(r') \varphi_{p}(r') \varphi_{Q}(r') \varphi_{Q}(r')
\]

\[
\times g_{XC}(r, t; r', t; r'', t') \varphi_{c}^c(r) \varphi_{q}^q(r') \varphi_{c}^q(r') \varphi_{Q}^q(r')
\]

\[
\times [\varphi_{p}^c(r'') \varphi_{p}^{v*}(r'') \varphi_{Q}^c(r'') \varphi_{Q}^{v*}(r'')
\]

\[
+ \varphi_{p}^c(r'') \varphi_{p}^{v*}(r'') \varphi_{Q}^c(r'') \varphi_{Q}^{v*}(r'')]
\]

In Eqs. C.14 and C.15,

\[
g_{XC}(r, t; r', t; r'', t') = \frac{\delta^3 V_{XC}(r, t)}{\delta n(r, t') \delta n(r'', t') \delta n(r'''', t'''')}
\]

\[
= \frac{\delta^2 f_{XC}(r, t; r', t')}{\delta n(r'', t') \delta n(r'''', t'''')}
\]

is the third order XC kernel function that describes the exciton-exciton interaction. We assume that this function has the separable form:

\[
g_{XC}(r, t; r', t; r'', t') = g_{XC}^{Slater}(r, r', r'', t') j_{XC}(t - t')
\]

where the static spatial part is obtained from the Slater XC kernel Eq. C.17:

\[
g_{XC}^{Slater}(r, r', r'', t') = \frac{\delta^2 f_{XC}(r, r')}{\delta n(r) \delta n(r'')}
\]

We have used two types of the time-dependent part \( j_{XC}(t - t') \) of the kernel C.18: the instant kernel

\[
j_{XC}(t - t') = \delta(t - t')
\]
and the non-adiabatic kernel

\[ j_{XC}(\omega) = \frac{1}{\omega - E_{XX} + \frac{i}{\tau_{XX}}} \] (C.20)

(in frequency representation), where the values for the biexciton binding energy and scattering time \( E_{XX} \) and \( \tau_{XX} \) are found by solving Eq. C.18:

\[
i \frac{\partial B_{ccvv}^{k_1 k_2 q_1 q_2}}{\partial t} = \left( \varepsilon_{k_1}^c + \varepsilon_{k_2}^c - \varepsilon_{q_1}^v - \varepsilon_{q_2}^v \right) B_{ccvv}^{k_1 k_2 q_1 q_2}
\]

\[
+ \sum_{k,q} \left[ F_{ccvw}^{k_1 q_1 q_2 k k_2 q q_2} B_{ccvw}^{k k_2 q q_2} + F_{ccvw}^{k_2 q_1 k k_2 q q_2} B_{ccvw}^{k k_2 q q_2} + F_{ccvw}^{k_2 q_1 q_2 k k_2 q q_2} B_{ccvw}^{k k_2 q q_2} \right]
\]

\[
+ \sum_{p_1, p_2} \left[ w_{cccc}^{k_1 k_2 p_1 p_2} B_{ccvw}^{p_1 p_2 q_1 q_2} + w_{vvvv}^{q_1 q_2 p_1 p_2} B_{ccvw}^{k_1 k_2 p_1 p_2} \right].
\] (C.21)
Appendix D

Time dependent DFT calculations in magnetic field

D.1 Electronic Properties

At zero magnetic field, the time dependent DFT Kohn-Sham equation for the effective electronic wave function $\Psi_k(r, t)$ has the following form:

$$\left[ -\nabla^2 + V_{\text{ion}}(r) + V_H[n](r, t) + V_{\text{XC}}[n](r, t) + V_{\text{ext}}(r, t) \right] \Psi_k(r, t) = i \frac{\partial \Psi_k(r, t)}{\partial t}, \quad (D.1)$$

where the first term in the brackets is the kinetic energy operator, $V_{\text{ion}}(r)$ is the ion potential, $V_H[n](r, t)$ is the Hartree potential, $V_{\text{XC}}[n](r, t)$ is the XC potential, and $V_{\text{ext}}(r, t)$ is the external potential. Since the Hartree and the XC potentials depend on the charge density, Eq. (D.1) has to be solved self-consistently with the particle number equation

$$n(r, t) = \sum_{k \leq k_F} |\Psi_k(r, t)|^2. \quad (D.2)$$

To describe the effects of electron-electron, electron-exciton, and exciton-exciton interactions, we expand the XC potential up to the third-order with respect to the density fluctuations:

$$V_{\text{XC}}[n](r, t) \approx V_{\text{XC}}[n](r, t = 0) + \int dr' dt' f_{\text{XC}}(r, t; r', t') \delta n(r', t') + \int dr' dt' \int dr'' dt'' g_{\text{XC}}(r; r', t'; r'', t'') \delta n(r', t') \delta n(r'', t'') \delta n(r''', t'''), \quad (D.3)$$

where,

$$f_{\text{XC}}(r, r'; t, t') = \left. \frac{\delta V_{\text{XC}}[n](r, t)}{\delta n(r', t')} \right|_{n=n(r, t=0)}, \quad (D.4)$$
is the XC kernel and
\[
g_{\text{XC}}(r; r', r''; t, t', t'') = \frac{\delta^3 V_{\text{XC}}(r, t)}{\delta n(r', t') \delta n(r'', t'') \delta n(r''', t''')}
\equiv \frac{\delta^2 f_{\text{XC}}(r, r'; t, t')}{\delta n(r'', t'') \delta n(r''', t''')}. \tag{D.5}
\]

The laser-pulse potential can be approximated by a "dipole" potential and can be expressed as:
\[
V_{\text{ext}}(r, t) = -e \vec{E}(t) \cdot \vec{r}, \tag{D.6}
\]

This corresponds to the case when the characteristic field frequency is bigger than the level spacing. In our case, \( \vec{E}(t) \) consists of three separate pulses.

In order to solve the system of Eqs. D.1 and D.2, in the density matrix formalism [191–194], the electron wave function needs to be expanded in a basis of static KS wave function:
\[
\Psi_k(r, t) = \sum_l c^l_k(t) \phi^{l(0)}_k(r), \tag{D.7}
\]

where, \( \phi_k^{l(0)}(r) \) are the wave function solutions of static KS equation:
\[
H(r, t) \phi_k^{l(0)}(r) = \phi_k^{l(0)}(r) \varepsilon_k^{l(0)}, \tag{D.8}
\]

and \( \varepsilon_k^{l(0)} \) are the corresponding eigenenergies.

In Eq. D.7, \( c^l_k(t) \) are unknown time dependent coefficients. In the density matrix formalism, one looks for solution of another function, the density matrix, which is a linear combination of these coefficients:
\[
\rho_k^{lm}(t) = c^l_k(t)c^{m*}_k(t) \tag{D.9}
\]
and satisfies the Liouville equation:

\[ \frac{i}{\partial t} \rho_{lm}^k(t) = [H(t), \rho(t)_k^{lm}] . \]  \hspace{1cm} (D.10)

In Eq. D.10,

\[ H_{lm}^k(t) = \int d^3r \phi^{l(0)*}_k H(r,t) \phi^{m(0)}_k(r) \]  \hspace{1cm} (D.11)

are the matrix elements of the KS Hamiltonian. Eq. D.10 is equivalent to the Time-dependent DFT Bloch equations:

\[ \frac{i}{\partial t} \rho_{lm}^k(t) = (\varepsilon^l_k - \varepsilon^m_k) \rho_{lm}^k(t) + \sum_n \left[ V_{lm}^k(t) \rho_{lm}^{kn}(t) - \rho_{lm}^{kn}(t) V_{lm}^{kn} \right] , \]  \hspace{1cm} (D.12)

where,

\[ V_{lm}^k(t) = \int d^3r \int d^3r' \phi^{l(0)*}_k(r) \phi^{m(0)}_k(r) [V_{XC}[n](r,t) - V_{XC}[n](r,t = 0)] \]  \hspace{1cm} (D.13)

and \( V_{XC}[n](r,t) \) is defined in Eq. D.3 with

\[ \delta n(r,t) = n(r,t) - n(r,t = 0) \]

\[ = \sum_{n,s,q<q_F} \phi^{n(0)*}_q(r') \phi^{s(0)}_q(r') \left[ \rho^{sn}_q(t') - \rho^{sn}_q(t' = 0) \right] . \]  \hspace{1cm} (D.14)

Eq. D.12 has to be solved with the initial conditions

\[ \rho^{sn}_q(t = 0) = \delta^{sn} n^{s}_q . \]  \hspace{1cm} (D.15)

where, \( n^{s}_q \) are the initial state occupancies.

In the presence of magnetic field, it is rather difficult to obtain the exact static solutions of the DFT equation. However, since our main goal is to understand the properties of interacting spin-polarized electrons and holes in the magnetic field, and other complex
magnetic field effects are not of our interest, with rather good accuracy one can assume that in strong fields, the spectrum consists of discrete Landau Levels,

\[ E_{n\sigma} = \left( n + \frac{1}{2} + \sigma \right) \hbar \omega_B, \quad (D.16) \]

split by inhomogeneity-induced in-plane excitations (we assume that z-component of the momentum is zero in case of quantum well). In Eq. (D.16), \( \hbar \omega_B = \hbar eB/\mu c \sim 0.116 \text{meV} \times B(T)/\mu(m_0) \), \( n \) is an integer and \( \sigma \) is the spin (half-integer) number.

Next, we consider the KS in the presence of the magnetic field which we assume to be modified similar to the case of system with square dispersion and can be expressed as:

\[ \phi^{l(0)}_k(r) \rightarrow \phi^{l(0)}_k(r)\chi_n(y), \quad (D.17) \]

where,

\[ \chi_n(y) = \frac{1}{\pi^{1/4}a_B^{1/2}} \frac{1}{\sqrt{2^n n!}} e^{-\frac{(y-y_0)^2}{a_B^2}} H_n \left( \frac{y-y_0}{a_B} \right), \quad (D.18) \]

and

\[ H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}, \quad (D.19) \]

are the Hermite polynomials.

\[ y_0 = -\frac{e p_x}{e H}, \quad (D.20) \]

and

\[ a_B = \sqrt{\frac{\hbar c}{e B}} \approx \frac{25.7}{\sqrt{mB}} nm. \quad (D.21) \]

A localization of the wave functions caused by the magnetic field leads to a significant decrease of the values matrix elements of the electron-hole and other interactions. As a result, this leads to zero binding energies for the exciton and biexcitons at \( H > 8T \) in the undoped case. In the doped case, the binding states are absent even at lower fields due to extra suppression of the electron-hole interaction by the increased ground state density of
D.2 Dephasing

In finite field, from the structure of the TDDFT equations for polarizations, one can also gain insight on the nature of the dephasing mechanism for the excitons and the difference between the cases of LL0 and LL1. In particular, from the spectrum in Eq. (D.16), one can see that there is a degeneracy for states \((n, \sigma = 1/2)\) and \((n + 1, \sigma = -1/2)\). This means that the lowest energy level is occupied by particles with one component of spin, and the next level with both spins \((n = 0, \sigma = 1/2, \text{ and } n = 1, \sigma = -1/2)\). This is shown in Fig. (D.1).

Figure D.1: Schematic of the occupancies of the lowest Landau levels in doped quantum well system in a magnetic field.

Similar to the zero field case, the inverse dephasing time can be estimated as \(\frac{1}{\tau_d} \sim -\text{Im} \left[ \sum_{k', q'} \alpha_{kqk'q'} \right]\), where the summation is performed over combined momentum-spin indices. Since in the case of LL0, the summation in the last equation is performed only over one spin, this leads to significantly longer dephasing time for this level as compared to LL1. Estimated dephasing times for the LL1 and LL0 are found to be 3 ps and 5 ps, respectively.
These values are in good agreement with the experimental results shown in Fig. 6.6.

### D.3 The charge inhomogeneity effects

The inhomogeneity effects become important when the characteristic field-related length scales, i.e., the overlap of the electron-hole wave functions become comparable or smaller than the in-plane lattice constant. In this case, the exciton eigenenergies will have a non-trivial dependence on the in-plane momentum. The charge density fluctuations within the overlap of the wave functions lead to a breakdown of the jellium model and of the Kohn’s theorem.

There are four characteristic lengths we need to consider in this case: the in-plane lattice constant, the electron and hole Landau level orbitals $l_B$, the exciton Bohr radius $r_X$, and the electron-hole overlap. The value of the lattice constant ($a$) and the dielectric constants are 5.654 Å and 12.9, respectively. The 3D and 2D Bohr radii are $r_{3D}^X = \varepsilon \hbar^2/\mu e^2 = \frac{a_B (\varepsilon m_0/\mu)}{2}$ and $r_{2D}^X = \varepsilon \hbar^2/2\mu e^2 = \frac{a_B}{2} (\varepsilon m_0/\mu)$, respectively. The reduced electron-heavy hole mass is $\mu = 0.058 m_0$, where $m_0$ is the free electron mass. Since the system is neither 2D or 3D, and extrapolated value for the Bohr radius $r_X = (r_{3D}^X + r_{2D}^X)/2 = 3a_B/4 (\varepsilon m_0/\mu) \approx 112$

![Figure D.2: The magnetic length, and the 3D and 2D excitonic Bohr radii as function of the magnetic field.](image)
9 nm, can be used. This is depicted in Fig. D.2. On the other hand, magnetic length (represented by the black curve in Fig. D.2) depends on the strength of the magnetic field. The value of $l_B$ becomes comparable with the Bohr radius of the 3D exciton at $B_{3D}^{10} = 4.76 \text{T}$, and to the corresponding radius of the 2D exciton at $B_{2D}^{10} = 19.02 \text{T}$. In the case of strong magnetic fields ($l_B < a_B$), the excitons transform into magnetoexcitons with the binding energy $\frac{e^2}{\varepsilon l_B} \sqrt{\frac{\pi}{2}}$ and radius $l_B$ instead of $\frac{e^2}{\varepsilon a_B}$ and $a_B$. However, at fields between 5 to 10 T, the values of $l_B$ and $a_B$ are similar, and the discussion and conclusions below remain valid for both types of excitons.

![Figure D.3: The difference between the electron and hole charges at B = 10T.](image)

A more detailed examination of spatial electron and hole charge distributions (Fig. D.3) suggests that at fields larger than 4 to 5T, the Landau level electron and hole charge density distributions become sufficiently separated, such that the electron and hole charge density overlap involves less than half of total charges. This leads to a qualitative change of the excitonic features in the system, involving distinctly separated in space electron and
hole charge densities.

The electron and hole hole clouds in Fig. D.3 at 10T (large field case) suggests that the distance between them is on the order of unit lattice cell. Thus, the inhomogeneity effects defined by the lattice structure becomes important. The charge fluctuations within the overlap region, which are taken into account by the cross-correlation potential, becomes significant. Thus, along with the standard length scale (Landau level radius) $\sim 5$-10 nm, which for GaAs is much larger than the lattice constant, magnetic field introduces an additional length scale, namely, the spatial distance between the electron and hole Landau orbits, described by their charge density distribution. This length scale is on the order of $\sim 1$ nm and makes the spatial inhomogeneity over the unit cell important. Thus, the inhomogeneity affect the lineshapes of 2DFT spectra. This becomes clear when analyzing the expression for effective electron-hole scattering matrix (defined in Eqn. C.2) that provides the solution of the excitonic spectrum described by the Eqn. C.1. In the Slater XC kernel in Eqn. C.4, the spatial dependence of the equilibrium (zero perturbation) charge density over cell $n_0(r)$ becomes important at higher magnetic fields as shown in Fig. D.3, which leads to a non-trivial in-plane momentum dependence of the exciton dispersion.

Figure D.4: (a) 2DFT spectrum of the undoped quantum well at 6 T. (b) The corresponding spectrum obtained by using interaction functions for a unit cell expanded four times in the in-plane directions.

To demonstrate the importance of inhomogeneity effects, we compare the 2DFT spectrum for the undoped quantum well at 6T for two different configurations (shown in Fig. D.4). First, we calculate the 2DFT spectrum for the optimized unit cell, and then for the
unit cell expanded four times in the in-plane direction. In the last case, the in-plane unit cell parameters is larger than the distance between the electron and hole charge distributions. As a result, the charge inhomogeneity within the overlap of electron and hole charge density is artificially weakened. Thus, we obtain the usual lineshape that does not show the elongation along the $\omega_\tau$ direction. This clearly indicates the origin of peculiar lineshapes we observe in the 2DFT spectra for the undoped samples. However, the screening introduced by the dopant in the doped sample, reduces the perturbation effect on the electron and hole overlap. It leads to a reduced amplitude of the matrix element, which in a sense is equivalent to weakening of these fluctuations. Thus, the Kohn’s theorem is restored and the Landau levels remain discrete.
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