Study of Transition Metal Dichalcogenides Via Linear and Non-Linear Spectroscopy

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Study of Transition Metal Dichalcogenides Via Linear and Non-Linear Spectroscopy

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of
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Keywords: Super Radiance, Biexciton Coherence, Exciton Dynamics, Time Integrated Four Wave Mixing

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Dedication

To my son, Oliver.
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Abstract

Beginning with the discovery of graphene, two-dimensional materials have amassed a strong interest. Like graphene, transition metal dichalcogenides (TMDs) can be coaxed into atomically thin sheets which have some impressive properties. Unlike graphene, TMDs also has a change in their electronic band structure causing an indirect band gap to a direct gap transition in its monolayer form. Additionally, these materials lose their inversion symmetry as a monolayer. These unique properties make TMDs a strong candidate for being used in optoelectronic and valleytronic devices. In order for these devices to be successful, the optical properties of TMDs must be thoroughly understood. Due to this class of material’s strong Coulomb interaction, the optical properties are dominated by excitons, a quasiparticle made up of an electron-hole pair. Therefore, the success of these devices relies, in part, on understanding and manipulating excitons. One key parameter of excitons is their dephasing rate which characterizes the lifetime of the coherent superposition of two states (i.e. how the coherence decays which is caused by excitons interacting with their environment).

In this work, two optical properties are investigated: (1) How the linear absorption of the TMDs A-exciton peak varies as the material increases in thickness. By looking at how the absorption varies by sample thickness, the interaction between emitters can be understood. Experimental results for the diamagnetic shift are presented which are used to determine the lateral excitonic size. Through theoretical calculations, based on the semiconductor Maxwell-Bloch equations, additional insight into the radiative coupling of the systems are obtained. (2) How the coherence profile of the exciton changes in the presence of an external magnetic field and specific valley excitation. By varying the polarization scheme in the four wave mixing measurement, specific valley excitation can be selected, allowing for insight
into the dephasing mechanisms. By applying an external magnetic field, the energy levels of the electron and hole can be discretized and the corresponding effects on the system’s coherence seen. In conjunction with time-dependent density function theory calculations and the experimental results, a deeper understanding of exciton dynamics and multi-exciton complexes was obtained. Finally, a new system is proposed in which complex spectroscopic techniques can be performed on micron sized samples as well as devices in the presence of an external magnetic field at cryogen temperatures. This system will allow for the investigation of the optical properties of stacked monolayers (heterostructures) as well as devices.
Chapter 1

Introduction

With the discovery of graphene, and its unique properties, there has been a strong interest in other layered semiconductors [1–3]. Some of these layered materials fall into a class known as Transition Metal Dichalcogenides (TMDs) which range from insulators to semiconductors to conductors. While this class of materials have been investigated for decades, new advances, developed mainly from the research on graphene, opened the door to many new research applications. Of this class of materials, the group VI TMDs of the form $\text{MX}_2$ ($\text{M} = \text{Mo or W}, \text{X} = \text{S or Se}$) have shown some very interesting properties and potential for device application. In 2010, it was found that MoS$_2$ has a indirect to direct band gap transition when taken down to a monolayer [4]. Additionally, these layered materials allow for easy fabrication of single-layered samples through mechanical exfoliation. This is due to the strong in-plane and weak out-of-plane attraction. Furthermore, these materials form a 2D hexagonal lattice, and when a monolayer, inversion symmetry is broken. This, in combination with the strong spin-orbit coupling, allows for selective valley excitation of the $\text{K}$ or $\text{K'}$ valley via circularly polarized light [5]. These unique properties provide a wonderful platform for exploring spin and valley physics as well as many-body effects. Devices using TMDs have already been developed in electronic and electro-optical applications such as transistors and photo detectors [6–9]. More devices are beginning to be fabricated using heterostructures, which are just beginning to be thoroughly investigated [10].
1.1 Outline of Dissertation

The focus of this dissertation is in studying the optical (linear and non-linear) properties of TMDs as well as fundamental exciton dynamics through quantitative absorption measurements as well as transient four wave mixing techniques. This dissertation is organized as follows: Background into the materials measured in later chapters is presented in chapter 2. This includes electronic and optical properties of TMDs, a brief introduction to excitons, and sample fabrication methods. In chapter 3, concepts of linear and non-linear spectroscopy are covered. First, linear absorption and the specific case of superradiance is discussed. Followed by an introduction to different non-linear measurements that can be performed using four wave mixing techniques. Next, the third-order response of the system, originating from the Optical Bloch Equations (OBE) is discussed. Followed by a diagrammatic approach to easily track the coherent pathways is described. Finally, the experimental apparatus used is explained in detail.

Experimental results are presented in chapters 4-6. In chapter 4, the quantitative absorption for two representative TMDs are explored. The absorption percentage at the A - exciton peak was measured as a function of layer thickness and compared to the Beer-Lambert law as well as a theoretical model based on the Maxwell-Bloch equations. In the model, a specific case where the system is superradiant is also presented. In chapter 5, Time-Integrated Four Wave Mixing (TI-FWM) measurements are presented as a function of applied external field up to 25T for MoSe$_2$. Additionally, the effects of valley selection on the dephasing times is discussed. Finally, in chapter 6, the development of a new tabletop system designed to run experiments on samples only several microns in size in an external magnetic field up to 7.5T is discussed.
Chapter 2

Basics of Transition Metal Dichalcogenides

Transition Metal Dichalcogenides have become a highly investigated class of materials in recent years due to their unique and desirable properties. Similar to graphene, TMDs are a layered material, which are held together by strong in-plane covalent bonding and a weak out-of-plane interaction via Van der Waals attraction. Additionally, like graphene, when taken down to a single layer, new and exciting properties emerge. Group VI TMDs have the general $\text{MX}_2$ form ($\text{M} = \text{Mo, W}; \text{X} = \text{S, Se}$) and form a hexagonal 2D structure. Each layer is formed by one transition metal layer in between two chalcogen layers. Due to the weak bonding in the z-direction, these materials are capable of being cleaved down to monolayers via mechanical exfoliation [2, 4, 11, 12].

When TMDs are a monolayer, the hexagonal lattice lacks spatial inversion symmetry which leads to an intrinsic magnetic moment corresponding to the valley index. Additionally, the lack of inversion symmetry allows for valley Hell effect and valley polarization selection (discussed more in section 2.2) [13]. Due to the relatively high binding energies (in the range of a few hundred meV) TMDs have strong excitonic effects [14–17]. The combination of these stout excitons with relatively large effective masses, and valley polarization selection, make TMDs a great platform to optically investigate valley and spin effects as well as many-body interactions.

A periodic table can be seen in figure 2.1 with the transition metals (M) and chalcogen (X) atoms highlighted. The properties of the TMDs varies greatly depending on the electronic structure of the transition metal. For example, $\text{NbS}_2$ is a metal, $\text{MoSe}_2$ is a
Figure 2.1: Periodic table with the transition metals (M) and the chalcogen atoms (X) highlighted, forming TMDs of the MX$_2$ form. The green shaded transition elements are those that can be made into monolayers.

Semiconductor, and TiS$_2$ is an insulator. In this dissertation, two semiconducting TMDs linear and non-linear properties are investigated, MoSe$_2$ and WSe$_2$. These materials can have several different polytypes: 2H (hexagonal symmetry, trigonal prismatic coordination, AB-AB layer stacking), 3R (rhombohedral symmetry, trigonal prismatic coordination, ABC-ABC layer stacking), and 1T (tetragonal symmetry, octahedral coordination, one layer per unit cell) [18]. These different polytypes can be seen in figure 2.2. Measurements in this dissertation were made on samples of the 2H polytype.

Figure 2.2: In (a), the different polytypes can be seen: 2H (hexagonal symmetry), 3R (rhombohedral symmetry), and 1T (tetragonal symmetry). In (b), the structure of a monolayer is seen which has an intralayer spacing for 6.5 Å. This figure is partially reproduced with permission from ref. [18].
2.1 Electronic and Optical Properties

The band structure for TMDs have been widely investigated, both experimentally [19,20] and theoretically [21–24], leading to a very clear picture of the band structure in the bulk and monolayer limit. Both MoSe$_2$ and WSe$_2$ have an indirect to direct band gap transition from the bulk to monolayer limit. Below, the band structure for these two materials is discussed in both cases. The band structure presented in this section were calculated via density functional theory in the local density approximation by Kumar, et al. [22]. Through calculating the lattice parameters and density of states, a more complete picture was obtained. The electronic structure can be seen in figure 2.3 for both MoSe$_2$ (left two) and WSe$_2$ (right two) for both the bulk and monolayer limit. It can be seen that the band structure for these two materials is very similar, and thus the following description applies to both materials.

![Figure 2.3: Theoretical band structure for MoSe$_2$ (left two) and WSe$_2$ (right two) in the bulk and monolayer limit. The arrow shows the smallest energy value for the band gap. In bulk, it is an indirect gap and a direct gap for a monolayer. This figure is reproduced with permission from ref. [22].](image)

The clear difference between the bulk and monolayer limit is the nature of the band gap. In bulk, it is an indirect gap, and at a monolayer, it is a direct gap. The room temperature band gap energy for bulk is 1.1 eV and 1.2 eV for MoSe$_2$ [25] and WSe$_2$ [26], respectively. For a monolayer, the band gap energy is 1.58 eV for MoSe$_2$ and 1.61 eV for WSe$_2$ [22]. As the material is thinned, the indirect gap energy gradually blue shifts up to the bilayer limit.
Figure 2.4: Band gap energy shift for the indirect gap (solid line, triangles) and the direct gap (solid line, circles) at the K point as a function of number of layers. The dashed (solid) horizontal lines are the direct (indirect) gap energy in the bulk limit. This figure is reproduced with permission from ref. [22].

Then, the indirect to direct gap transition occurs from bilayer to monolayer. This blueshift in energy can be seen in figure 2.4. The solid line with triangles is the indirect gap energy and the solid line with circles is the direct gap energy as a function of layers [22].

Secondly, the band structure for the monolayer samples can be broken into three different regions, each with different electron orbital contributions. The first region is from -12 eV to -15 eV (not shown). The bands in this region are mainly from the chalcogen s orbitals. Above this region, there is a large gap before arriving at the band structure seen in figure 2.3. The next region is from the band gap to -8 eV below the gap and the bands above the gap. This region is attributed to both the p orbitals of the chalcogen and d orbitals of the transition metal. The final region is the bands at the gap, which are primarily from the d orbital of the transition metal [22, 27, 28]. The band structure is also strongly influenced by the hybridization of the d orbital of the transition metal and the s orbital of the chalcogen below the Fermi energy [27–29].

Since these materials have a direct bandgap in the visible portion of light, they are being highly investigated for optoelectronic devices. With the change in band structure from bulk to monolayer, the absorption, photoconductivity, and photoluminescence all see corresponding changes [4, 30–33]. The absorption spectra shows two main peaks corresponding to the A and B excitons. The transition is at the K-point of the Brillouin zone at the split valance
bands to the minimum of the conduction band [4]. Additionally, the PL signal increases greatly from multiple layers down to bulk, which is expected due to the change from an indirect to direct band gap. The PL signal for both (a) MoSe$_2$ and (b) WSe$_2$ are seen in figure 2.5 for one, two, and three layers. The corresponding spectras have by multiplied such that the details can be compared. Note that the single layer PL is extremely strong when compared to even a bilayer. For MoSe$_2$, the monolayer has a single peak at $\sim 780$ nm and for a WSe$_2$ monolayer, a peak at $\sim 750$nm [32].

2.2 Spin, Orbit and Valley Properties

As previously mentioned, monolayer TMDs have several fortuitous properties that lead to a strong spin-orbit splitting and spin-valley coupling. Monolayers are non-centrosymmetric (or bulk with an odd number of layers) and therefore lack inversion symmetry. This can be seen in the monolayer structure in figure 2.2. In addition to the asymmetry, the electron motion is confined to in-plane motion. Finally, the high mass of the atoms increase the screening of the nucleus. All of these properties increase the strength of the spin-orbit
splitting. For example, the maximal spin splitting from the upper valence band at the K point is calculated to be 183 meV for MoSe$_2$ and 456 meV for WSe$_2$ [34]. In comparison, in quantum wells, the spin-orbit splitting is $\sim$ 30 meV, an order of magnitude smaller [35, 36] and even smaller in graphene [37].

Furthermore, the lack of inversion symmetry has another effect on the spin and valley properties. Due to this lack of symmetry, another index becomes relevant, the valley index. The valley index refers to valley points that have the same energies, but different locations in momentum space [38]. This effect is exploited in valleytronic devices. For TMDs, this occurs near the K and K’ points. The coupling between the spin and valley leads to the spin and valley indices being locked. This lets the individual valleys be selected through optical selection rules. Using circularly polarized light ($\sigma^+$ or $\sigma^-$), excitons in either the K or K’ valley can be selectively excited [39].

2.3 Excitons in Semiconductors

When a semiconductor is excited with a photon of energy larger than the band gap energy, $E_b$, an electron is excited from the valence band to the conduction band. In a direct gap semiconductor, this can happen without the need for a phonon to assist in the transition (the transition is aligned in momentum space, therefore the phonon is not necessary to conserve momentum) but is necessary in an indirect gap semiconductor. When the electron is excited, it leaves behind a vacancy in the valence band. This vacancy can be thought of as a positively charged quasiparticle, known as a hole. The excited electron is free to radiatively or non-radiatively decay back to the valence band, removing the hole. However, if $\hbar \omega \approx E_b$, then the electron and hole can become a bound quasiparticle state called an exciton. Excitons form due to Coulomb forces between the positively charge hole and negatively charged electron in the valence and conduction band, respectively. In an absorption spectra, excitons will show as a strong absorption line just below $E_b$. 
Excitons can be classified into two classes, which are characterized by their Bohr radius. If the exciton has a Bohr radius less than or equal to the length of the unit cell, then it is referred to as a Frenkel exciton. On the other hand, if the Bohr radius is much larger than the length of the unit cell, it is referred to as a Wannier-Mott exciton. Excitons in the TMDs studied in this dissertation are of the Wannier-Mott type [40,41].

For a better understanding of Wannier-Mott excitons, consider the comparison to the hydrogen atom, where some simple substitutions can be made. First, the reduced mass, $\mu$, becomes:

$$\frac{1}{\mu} = \frac{1}{M_{\text{proton}}} + \frac{1}{m_{\text{electron}}} \approx \frac{1}{m_{\text{electron}}} \rightarrow \frac{1}{m^*} = \frac{1}{m_e} + \frac{1}{m_v}$$

where $m^*$, $m_e$ and $m_v$ are the reduced effective mass, conduction band,- and valence band effective masses, respectively. Secondly, the electronic charge is replaced with $e^2/\epsilon$, where $\epsilon$ is the dielectric constant of the crystal. These substitutions yield the energy shift below the band gap $E_{ex}$, and Bohr radius, $a_{ex}$, as [42]:

$$E_{ex} = \frac{e^2}{2a_o^2} = \frac{m^*}{m} \frac{1}{e^2} \frac{e^2}{2a_o} = \frac{m^*}{m} \frac{1}{\epsilon^2} (13.6) \text{eV}$$

$$a_{ex} = \frac{\hbar^2}{m^*(e^2/\epsilon)} = \epsilon \frac{m}{m^*} a_o$$

Thus, bound excitons can form at energies below the band gap with a hydrogenic-like spectra.

In addition to excitons, several multi-particle complexes can form. If two excitons are in close proximity to each other, they can form a biexciton. The biexciton can either be bound or unbound depending on the symmetry of the two-exciton wave function. If the wave function is symmetric, the biexciton is a bound state with lower energy. If it is anti-symmetric, it is an unbound biexciton [43]. Another possibility is the trion, which consists of either two electrons and one hole or two holes and one electron. Trions are a charged quasiparticle with charge equal to $\pm e$ depending on the combination. Both trions [44–47] and biexcitons [48–51] have been seen to play a role in the optical properties of TMDs.
2.4 Sample Fabrication

Consistently and reliably producing samples is a necessary requirement for using TMDs in potential device applications. In this section two different sample fabrication approaches will be discussed: the top down approach and bottom up approach.

The simpler of the two approaches, the top down method, is done through mechanical exfoliation of bulk crystals. This method is more commonly known as the “scotch tape method” and has been used to fabricate graphene [2, 4, 9, 31, 52, 53]. In this process, some sort of adhesive tape is applied to bulk crystals. When the tape is peeled off, layers of material are peeled with it. This process is repeated several times and is only possible because the layers are held weakly together by the Van der Waals force. Once the materials have been adequately cleaved, the tape, with the material on it, is pressed onto a clean substrate. When the tape is removed, some of the material will remain on the substrate and can be identified via an optical microscope [54, 55]. In this process, flakes ranging from monolayer to bulk will be transferred onto the substrate. Using mechanical exfoliation, the samples are of high quality and free of impurities and defects (assuming high quality bulk crystals are used). Once the required sample is identified, it can be used in device fabrication [4, 9, 31, 54, 56–58] or its fundamental properties measured [4, 31, 53, 59]. However, there is two major setbacks with this fabrication method: the process can not be scaled up for larger samples and there is no way to control the sample thickness.

However, different chemical exfoliation techniques have been developed to help resolve these issues. One such method, the intercalation method [11, 60–64], involves the “host” material absorbing a secondary ion, in this case lithium. After the TMD has been submerged in the chemical and allowed to absorb the ion for approximately a day, the TMD is taken out and submerged in water. The water and lithium ion violently reacts producing H$_2$ gas and separating the layers [11, 62]. While this method does repeatedly produce monolayers, the chemical process can change the electronic and structural properties of the material.
Although, it has been shown that these properties can be restored by thermal annealing [62]. This process has been performed on MoS$_2$, WS$_2$, MoSe$_2$ and SnS$_2$ [65, 66].

Additional methods for exfoliation are still being developed. For example, by placing the crystals in either organic solvents, aqueous surfactant solutions, or polymers in solvents, the TMD can be sonicated [67–70]. This ultrasonication exfoliates the crystals to flakes that are a few hundred nanometers in size. However, the effects of this method on the electronic and structural properties are still being researched.

Instead of mechanically exfoliating, or cleaving bulk crystals down to monolayer samples, chemical vapor deposition (CVD) is a bottom up method to grow the samples [71]. CVD methods have shown great promise at producing high-quality, high yield thin films for TMDs [72, 73]. The process involves heating solid material to high temperatures, vaporizing the powdered material [74, 75]. For an example, to produce a thin film of MoS$_2$, sulphur and MoO$_3$ powders can be used. The two materials deposit onto a nearby substrate coating it in a thin film where the number of layers can be roughly controlled by the exposure time and the concentration of the vapor. These methods have had success in synthesizing large-scale devices using graphene [76–78].

2.5 Linear and Non-linear studies in TMDs

For optoelectronics and valleytronic devices using TMDs to be successful, it is of utmost importance to understand and control the carrier selection [29, 38, 79]. Early work on this was done using helicity-resolved photoluminescence (PL) which showed that approximately 30% of the PL signal maintained the circular polarization of the excitation source in MoS$_2$ [39]. Improving upon these results, a second group was able to obtain 50% valley polarization through similar PL measurements [29]. Finally, a third group was able to obtain complete dynamic valley polarization in MoS$_2$ [80]. Additionally, measurements on the valley polarization of the both the A- and B- exciton has been measured and compared. It was shown
that the B-exciton has a higher valley polarization than the A-exciton. This was attributed
to the shorter lifetime of the B-exciton [81]. The robustness of the valley polarization has
also been measured through temperature dependent measurements as well as in the presence
of an external magnetic field. It was found that at \( \sim 4 \) K 90\% polarized emission was seen
while at room temperature, 40\% was still present. Additionally, an applied external field up
to 9 T left the degree of polarization unchanged [82]. Similar valley polarization results have
also been shown for other TMDs [38,83].

In addition to the strong valley polarization in these materials, it has been shown that the
excitonic lifetime is on the order of picoseconds. Through time-resolved PL measurements, it
has been approximated at 4 ps in MoS\(_2\) [84]. The valley polarization is ultimately destroyed
by various scattering channels in the form of phonons and non-radiative interband electron-
hole recombination [85]. Using femtosecond transient absorption and microscopy Shi et al.
found that the relaxation dynamics are much more complicated. They observed three differ-
ent decay times, 2.6 ps, 74 ps, and 850 ps for a suspended MoS\(_2\) monolayer [86]. Additionally,
through four wave mixing measurements, the coherence time has been measured for MoS\(_2\),
MoSe\(_2\), and WSe\(_2\) for both atomically thin, and bulk crystals. The experimental values for
the dephasing time were measured to be 200 fs, 279 fs, and 394 fs for monolayer MoS\(_2\), WSe\(_2\),
and MoSe\(_2\), respectively. Additionally, the population time was measured for WSe\(_2\), which
showed two decays: an initial rapid decay \( \sim 3 \) ps, and a second longer decay \( \sim 100 \) ps [87]. It
was also found that the limiting factor of the optical coherence is limited by electron-phonon
interactions, namely the E’ and E” phonon modes. These results point to TMDs being an
excellent class of materials for valleytronic and optoelectronic devices. However, more work
needs to be done to further understand their excitonic properties and limitations.
Chapter 3

Spectroscopic Techniques and Theory

When light interacts with a dielectric medium, a macroscopic polarization is induced. Providing the incident light is sufficiently weak, the system can be describe by simply the linear response in the system. Interactions that are considered linear include reflection, transmission, and absorption. To begin the discussion the induced polarization, \( \mathbf{P} \), in a system can be defined as:

\[
\mathbf{P} = \epsilon_0 \chi \mathbf{E}
\]  
(3.1)

where \( \epsilon_0 \) is the permittivity of free space, \( \chi \) is the linear susceptibility and \( \mathbf{E} \) is the electric field. If \( \chi \) in equation 3.1 is expanded in a power series, then:

\[
\chi = \chi^{(1)} + \chi^{(2)} \mathbf{E}(t) + \chi^{(3)} \mathbf{E}^2(t) + \cdots
\]  
(3.2)

and

\[
\mathbf{P} = \epsilon_0 \chi^{(1)} \mathbf{E}(t) + \epsilon_0 \chi^{(2)} \mathbf{E}^2(t) + \epsilon_0 \chi^{(3)} \mathbf{E}^3(t) + \cdots = P^{(1)} + P_{NL}
\]  
(3.3)

where \( P_{NL} \) is the non-linear contribution to the polarization.

It can be shown that \( P^{(1)} \) can be expressed in terms of a linear response function [88], \( S^{(1)}(r, t) \), (non-linear response function will be discussed in section 3.5) and has the form:

\[
P^{(1)}(r, t) = \int dr_1 \int_0^t dt_1 S^{(1)}(r - r_1, t - t_1) E(r_1, t_1)
\]  
(3.4)
combining equation 3.4 with the Maxwell-Liouville equations, we arrive at:

\[ \nabla \times \nabla \times E(\mathbf{r}, t) + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \int d\mathbf{r}_1 \int_0^t dt_1 \varepsilon(\mathbf{r} - \mathbf{r}_1, t - t_1) E(\mathbf{r}_1, t_1) = -\frac{4\pi}{c^2} \frac{\partial^2 P_{NL}(\mathbf{r}, t)}{\partial t^2} \]  

(3.5)

where the dielectric function, \( \varepsilon(\mathbf{r} - \mathbf{r}_1, t - t_1) \), is:

\[ \varepsilon(\mathbf{r} - \mathbf{r}_1, t - t_1) \equiv \delta(t - t_1)\delta(\mathbf{r} - \mathbf{r}_1) + 4\pi S^{(1)}(\mathbf{r} - \mathbf{r}_1, t - t_1) \]  

(3.6)

Equation 3.5 can be solved for specific cases yielding useful insight into the interaction of light and matter. One such case will be discussed in the next section.

### 3.1 Linear Absorption

Using equation 3.5, one can solve for the specific case of linear absorption by an isotropic medium. First, equation 3.5 needs to be split into the transverse and longitudinal components. This is done by making use of several vector calculus identities. This transforms equation 3.5 into:

\[ \nabla^2 E^\perp(\mathbf{r}, t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \int d\mathbf{r}' \int_0^t dt'[\varepsilon(\mathbf{r} - \mathbf{r}', t - t') E(\mathbf{r}', t')]^\perp = -\frac{4\pi}{c^2} \frac{\partial^2 P_{NL}^\perp(\mathbf{r}, t)}{\partial t^2} \]  

(3.7)

After this transformation, the specific case for linear absorption can be applied by setting \( P_{NL} \) to zero and assuming a solution of the form:

\[ E(\mathbf{r}, t) = E_0 \exp(i k z - i \omega t) \]  

(3.8)

By substituting this into equation 3.7 yields:

\[ \frac{k^2 c^2}{\omega^2} = \varepsilon(\mathbf{k}, \omega) \]  

(3.9)
where

\[ \varepsilon(k, \omega) = 1 + 4\pi \chi^{(1)}(k, \omega) = 1 + 4\pi \int \! \! dr \int_{0}^{\infty} dt S^{(1)}(r, t) \exp(-i k \cdot r + i \omega t) \] (3.10)

and by definition, the dispersion is:

\[ \frac{k c}{\omega} = \sqrt{\varepsilon(k, \omega)} \equiv n(\omega) + i\kappa(\omega) \] (3.11)

where \( n \) is the refractive index and \( \kappa \) is the extinction coefficient. Solving equation 3.11 for the wave vector \( k \) and substituting it into the electric field yields:

\[ E(z, t) = E_0 \exp[i \frac{\omega}{c} (n(\omega) + i\kappa(\omega))z - i \omega t] = E_0 \exp[i k'z - \frac{\kappa'_a(\omega)z}{2} - i \omega t] \] (3.12)

where

\[ k' \equiv \frac{\omega n(\omega)}{c} \] (3.13)

\[ \kappa'_a(\omega) \equiv \frac{2\omega \kappa(\omega)}{c} \] (3.14)

and \( \kappa'_a(\omega) \) is the absorption coefficient. The field intensity can then be calculated through:

\[ I(z) \equiv |E(z, t)|^2 = I_0 \exp[-\kappa'_a(\omega)z] \] (3.15)

or in a more common form:

\[ I(z) = I_0 \exp[-\kappa_a \rho_0 z] \] (3.16)

where \( \rho_0 \) is the density of absorbers in the material and \( \kappa_a \) is the absorption cross section. This equation is the attenuation of light through a material for non-interacting absorbers and is the same as the Beer-Lambert law. It can be related to a layered material by instead
of the density of a material or gas using the number of layers the light traveled through. Additionally, by redefining the absorption coefficient as the absorption percentage per layer.

3.1.1 Superradiance

In contrast to the case presented in the previous section, here the absorbers (emitters) will be able to interact with each other leading to a cooperative process known as “superradiance”. This phenomena was first investigated by Dicke in 1954 [89]. Since then, it has been experimentally seen in a wide range of systems; multiple quantum well structures [90–94], qubits [95], and several astronomical systems [96, 97] to name a few. Below, the case of N two-level identical atoms is described and originally presented by Dicke [89].

To begin, each atom can be in either the ground $|g\rangle$ or excited state $|e\rangle$ with energy difference $\hbar \omega_o$ and $\lambda_o = \frac{2\pi c}{\omega_o}$. The atoms are symmetrically coupled, leading to them being interchangeable. Additionally, the atoms are motionless and confined to a volume with dimensions much smaller when compared to the optical wavelength (this guarantees that all emitters are in phase). The system can only change through coupling of the atoms and the radiation field. Several operator definitions need to be made relating to the transition of the system:

\begin{align}
D^+_i &= |e\rangle\langle g| \\
D^-_i &= |g\rangle\langle e| \\
D^3_i &= \frac{1}{2}[|e\rangle\langle e| - |g\rangle\langle g|]
\end{align}

where $D^+_i$ ($D^-_i$) is the raising (lowering) off diagonal operators and $D^3_i$ is the diagonal operator. Additionally, the operators only act on the $i^{th}$ atom such that:
\[ [D^3_i, D^\pm_j] = \pm \delta_{ij} D^\pm_i \]  
(3.20)

\[ [D^+_i, D^-_j] = 2\delta_{ij} D^3_i \]  
(3.21)

The system will start off such that all the atoms are in the excited state, \( |e\rangle \),

\[ |\Psi(0)\rangle |e, e, e, ..., e\rangle \]  
(3.22)

For convenience, it is better to describe the system as a singlet, spin 1/2 system. In this case, \( |e\rangle \) is the spin up and \( |g\rangle \) is the spin down states. By doing this, the operators \( D^\pm_i \) and \( D^3_i \) are the same as the Pauli spin matrices. With the assumption that the states are invariant by atom permutation, the system is then a symmetrical superposition of \( N \) spin 1/2 states with a maximum angular momentum \( J = N/2 \). There are therefore \( N + 1 \) states which can be obtained by:

\[
\sum_i D^-_i |\Psi(0)\rangle = \sqrt{(J + M)! \over N!(J - M)!} (\sum_i D^-_i)^{(J-M)} |e, e, e, ..., e\rangle = |J, M\rangle
\]  
(3.23)

where \( \sum_i D^-_i |\Psi(0)\rangle \) is the collection of dexcitation operators, and \( |J, M\rangle \) is the fully symmetrical state. Here, \( J + M \) atoms are in the excited state and \( J - M \) are in the ground state. Several additional operators can now be defined as:

\[ D^\pm = \sum_i D^\pm_i \]  
(3.24)

\[ D_3 = \sum_i D^3_i \]  
(3.25)

\[ D^2 = {1 \over 2} (D^+ D^- + D^- D^+) + D^2_3 \]  
(3.26)
by applying $D_3$ and $D^2$ onto $|J, M\rangle$ yield the eigenvalues $M$ and $J(J+1)$, respectively. Additionally, the following relations also hold:

\[
\langle J, M | \sum_i D_i^+ D_i^- | J, M \rangle = J + M \tag{3.27}
\]

\[
\langle J, M | \sum_i D_i^- D_i^+ | J, M \rangle = J - M \tag{3.28}
\]

which represent the number of atoms in the excited and ground state. By using these definitions, it creates a picture for the system in the form of a “ladder”; where the top rung has all of the atoms in the excited state and the bottom rung has all of the atoms in the ground state. This can be seen in figure 3.1.

Now, for a single atom, the rate of photon emission is defined as [99]:

\[
\omega_i = \Gamma \langle D_i^+ D_i^- \rangle \tag{3.29}
\]

where $\Gamma$ is the atomic natural linewidth for the transition $|e\rangle \rightarrow |g\rangle$. This definition can be
generalized to the case of \( N \) atoms by:

\[
\omega_N = \Gamma \langle D^+ D^- \rangle = \Gamma (J + M)(J - M + 1)
\]  

(3.30)

where \( \langle D^+ D^- \rangle \) is the expectation value. Solving the expectation value is done directly by relating the system to the angular momentum "ladder" system, using the eigenvalues defined above. This leads to the case where if all atoms are excited, \( M = J \), then \( \omega_N = 2J \Gamma = N \Gamma \) and if only half are excited, \( M = 0 \), then \( \omega_N = \Gamma J (J + 1) = 1/2N(1/2N + 1) \Gamma \). This means that as the system loses energy, the rate of emission strongly increases from \( \sim N \) to a maximum of \( \sim N^2 \). This faster rate of emission, and proportionality to \( N^2 \) are the hallmarks of superradiance.

Relating this effect to absorption measurements is quite simple. Since the radiative decay rate in enhanced in the system, the chance of the photon being irreversibly absorbed (converted into vibrational energy or transitioning to a dark state) decreases. Therefore, the overall absorption of the system will decrease. In terms of a layered material, the absorption percentage per layer is decreased [33]. This ends the discussion on linear spectroscopy.

### 3.2 Four-Wave Mixing

Referring back to equation 3.3, the following sections will now focus on the non-linear polarization, \( P_{NL} \). It can be shown that for a centrosymmetric material that all even order terms are zero [100]. This leads to the first non-zero non-linear term as the term \( \sim \chi^{(3)} \). The third order response of the system can by probed through Four Wave Mixing (FWM) techniques, of which there are two and three pulse methods. In two-pulse FWM, one pulse must interact twice in order to generate the third order response. Labeling the pulses as A and B, with wave vector \( k_A \) and \( k_B \), and assuming pulse B acts twice, then the coherent third order non-linear signal will propagate in the phase matched direction \( k_s = 2k_B - k_A \).
Figure 3.2: Box geometry for FWM measurements. Time delay between pulses is shown. FWM signal propagates along the phase-matched direction, \( k_S = -k_A + k_B + k_C \).

In three-pulse FWM measurements, three pulses (labeled A*, B, and C) with the same frequencies interact with the material. Each pulse has a corresponding wave vector, \( k_a, k_b, k_c \). The first pulse, A* interacts with the material creating a coherence between the ground and excited state. After a time delay, \( \tau \), the second pulse, B, converts the coherence into a population. The amplitude of the population is determined by the relative phase of electric field of pulse B and the polarization induced in the sample and varies sinusoidally with a spatial period of \( k_B - k_A \). This amplitude will be at a maximum (minimum) when the two constructively (deconstructively) interfere. After a second time delay, T, the third pulse, C, arrives and induces a second polarization which scatters off the grating created by the first two pulses. This results in the FWM signal in the phase-matched direction \( k_S = -k_A + k_B + k_C \), as seen in figure 3.2.

By using the three-pulse over the two-pulse method, both time delays can be scanned, allowing for different dynamics to be investigated. For instance, the dephasing rate can be measured by scanning time delay \( \tau \) while keeping a fixed \( T \). Alternatively, if \( \tau \) is kept fixed, and \( T \) is scanned, the population decay rate is measured. Several different detection methods can be employed to measure the signal; time-integrated (TI-FWM), time-resolved (TR-FWM), and spectrally resolved (SR-FWM).
3.2.1 Time-Integrated Four Wave Mixing

In TI-FWM measurements, the FWM signal is detected by a slow detector, and integrated during the emission time, t. The signal is recorded as a function of one time delay ($\tau$ for dephasing dynamics and $T$ for population dynamics) and can mathematically be expressed as:

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

(3.31)

where $P^{(3)}(\tau, T, t)$ is the third-order polarization. Assuming the pulses are much shorter then the dephasing time, then the pulses can be approximated as Dirac delta functions and the signal has the form [43,101]:

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

(3.32)

where $\Theta(\tau)$ is the Heaviside step function, $\gamma$ is the homogeneous linewidth, and $\Gamma_{gr}$ is the population decay rate. If the system is inhomogeneously broadened, then the signal is emitted as a photon echo and the signal has the form [43,101]:

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

(3.33)

When comparing equation 3.32 and 3.33, it can be seen that the system decays proportionally to the homogeneous linewidth even if there is inhomogeneous broadening in the system. Additionally, in the TI-FWM signal, there can exist signal at negative time delays. This was first reported by Leo in ref [102] when investigating GaAs/AlGaAs multiple quantum wells. A negative delay signal was seen which has a rise time which was twice as fast as the positive delay signal. It has been shown theoretically that for homogeneously-broadened two-level systems that the rise time is twice as fast as the decay time [43,102,103]. The negative delay signal is attributed to many body effects (i.e. exciton-exciton correlations).
3.2.2 Time-Resolved Four Wave Mixing (TR-FWM)

If instead of using a slow-detector, the FWM signal is up-converted using a delayed reference pulse and non-linear crystal (if the dephasing times are sufficiently short, < 10 ps). If the dephasing time is sufficiently long, no up-conversion is necessary. The resulting signal is measured as a function of the emission time, \( t \). The signal has the following form:

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

(3.34)

where \( E_{ref}(t) \) is the electric field of the reference pulse. TR-FWM measurements can be used to determine if the signal has been emitted as a photon echo or a free-polarization decay. These two possibilities are indicative in determining the homogeneous and inhomogeneous parts of the linewidth [104].

3.2.3 Spectrally-Resolved Four Wave Mixing (SR-FWM)

In SR-FWM, the signal is heterodyned with a reference pulse. This enables the full phase information to be retrieved. SR-FWM yields the FWM signal amplitude and phase through Fourier analysis. The signal has the form:

\[
S_{SR}(\tau, T, \omega_t) \propto \int_{-\infty}^{\infty} |P^{(3)}(\tau, T, t')|^2 e^{i\omega_t t} dt
\]  

(3.35)

where \( \omega_t \) is the frequency of the signal.

3.2.4 Dephasing Dynamics

Once a semiconductor is excited by an ultra short laser pulse, a coherence is created between the ground and excited state. The coherence begins to decay away once the pulse stops interacting with the material and is due to different scattering processes. The characteristic homogeneous dephasing time of a system, \( T_2 \), includes both the pure dephasing, \( T_2^* \),
and the population relaxation contribution, $T_1$, are related by [105]:

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$$  \hspace{1cm} (3.36)

Additionally, the homogeneous linewidth is linked to the dephasing rates, and thus $T_2$ by:

$$\Gamma_{hom} = \frac{2\hbar}{T_2}$$  \hspace{1cm} (3.37)

In the case where the pure dephasing time is much smaller then the population time, measuring $T_2$ is a good measure of the pure dephasing of the system. This is true for many semiconductor materials.

The effects of exciton-exciton collisions is one main pathway for excitons to dephase. This was first measured by Honold et al. [106, 107] where the GaAs quantum well sample was pre-excited by a pulse that had its intensity varied. The pulse arrived 20 ps prior to the measurement to ensure that any exciton population was incoherent when the dephasing time was measured. They found that the homogeneous linewidth had the following dependence:

$$\Gamma_h(n_x) = \Gamma(0) + \gamma_{xx}a_B^2E_bn_x$$  \hspace{1cm} (3.38)

where $a_B$, $E_b$, $n_x$ are the exciton Bohr radius, exciton binding energy, and exciton density per unit area, respectively. $\gamma_{xx}$ is the linear slope relating to the effects of exciton-exciton collisions.

Another dephasing mechanism is exciton-phonon interactions. This again was measured by Honold et. al. [107], where temperature dependent measurements were performed. More recently, these measurements were also performed on TMDs [87]. It was found that the
homogeneous linewidth can be fit with an equation of the following form [43]:

\[ \Gamma_h(T) = \Gamma_h(0) + aT + \frac{b}{e^{\frac{\hbar \omega_{LO}}{k_B T}} - 1} \]  \hspace{1cm} (3.39)

where \( \hbar \omega_{LO} \) is the optical phonon energy. The first term is independent of temperature and is the homogeneous linewidth from scattering and other processes. The second term (\( \sim T \)) is the acoustic phonon contribution, and the last term is the optical phonon scattering.

### 3.3 Non-linear Response Function

Similar to the procedure presented in the introduction of this chapter (equation 3.4), the non-linear polarization can be expressed in terms of a non-linear response function. In a three-pulse experiment, the pulses are labeled A*, B, and C, with wave vectors \( \mathbf{k}_a, \mathbf{k}_b, \) and \( \mathbf{k}_c, \) and time orderings \( \tau \equiv t_B - t_A, \) \( T \equiv t_C - t_B, \) and \( t \) is the detection time. Here, \( \tau \) is the coherence time and \( T \) is the population time. The pulse sequence and time orderings can be seen in figure 3.3. Using these definitions, the third order polarization can be written in terms of the non-linear response function, \( S^{(3)} \), in the following form:

\[
P^{(3)}(r,t_A,t_B,t_C) = \int_0^\infty \int_0^\infty \int_0^\infty S^{(3)}(r,t'_A,t'_B,t'_C)E_{A}(\mathbf{R},t'_A-t_A)E_{B}(\mathbf{R},t'_B-t_B) \times E_{C}(\mathbf{R},t'_C-t_C)dt'_A dt'_B dt'_C \]  \hspace{1cm} (3.40)

where

\[
E_j(r,t) = \left[ \varepsilon_j^+(t)e^{i(\mathbf{k}_j \cdot r - \omega_j t)} + \varepsilon_j^-(t)e^{-i(\mathbf{k}_j \cdot r - \omega_j t)} \right]\hat{e}_j \]  \hspace{1cm} (3.41)

in which \( \mathbf{k}_j \) is the wave vector, \( \omega_j \) the frequency, and \( \hat{e}_j \) the unit polarization vector of the \( j^{th} \) pulse. Additionally, \( \varepsilon_j^+ \) and \( \varepsilon_j^- \) is the positive and negative component of the slowly varying pulse envelope.
The third-order non-linear response function can be calculated using time-dependent perturbation theory and expressed as a combination of $n+1$ order correlation functions of the dipole moment operator [88,108]. As before, in the limit that the pulses are much shorter than the time scales of the evolution of the system, then each pulse can be approximated as Dirac delta functions pulses. With this assumption, equation 3.40 becomes:

$$P^{(3)}(r, t, t_A, t_B, t_C) = S^{(3)}(t_A, t_B, t_C) \cdot e^{\pm \frac{\pm k_A \pm k_B \pm k_C}{2}} \cdot e^{i(\pm k_A \pm k_B \pm k_C) \cdot r} \cdot e^{-i(\pm \omega_A \pm \omega_B \pm \omega_C) \cdot t} \times e^{-i(\pm \omega_A \pm \omega_B \pm \omega_C) \cdot t_C} \cdot e^{i(\pm \omega_A \pm \omega_B) \cdot t_B} \cdot e^{i(\pm \omega_A) \cdot t_A}$$ (3.42)

where all possible time orderings of the three pulses are included. Of the 8 possible phase-matched directions ($k_S = \pm k_A \pm k_B \pm k_C$), only 4 are independent. This is due to the fact that $k_S$ and $-k_S$ are the complex conjugate of each other and no new phenomenon contribute. Therefore, we have the following phased-match directions for the signal: $k_I = -k_A + k_B + k_C$, $k_{II} = k_A - k_B + k_C$, $k_{III} = k_A + k_B - k_C$, and $k_{IV} = k_A + k_B + k_C$ with emission frequencies, $\omega_I = -\omega_A + \omega_B + \omega_C$, $\omega_{II} = \omega_A - \omega_B + \omega_C$, $\omega_{III} = \omega_A + \omega_B - \omega_C$, and $\omega_{IV} = \omega_A + \omega_B + \omega_C$. Therefore, the third order polarization for each pulse ordering can be defined as follows:
\[ P^{(3)}_I(t_A, t_B, t_C) = S^{(3)}_I(t_A, t_B, t_C) \varepsilon^+_A \varepsilon^+_B \varepsilon^+_C e^{i(-\omega_A+\omega_B+\omega_C)t_C} e^{i(-\omega_A+\omega_B)} \cdot B e^{-i\omega_A t_A} \] (3.43)

\[ P^{(3)}_{II}(t_A, t_B, t_C) = S^{(3)}_{II}(t_A, t_B, t_C) \varepsilon^+_C \varepsilon^+_B \varepsilon^+_A e^{i(\omega_A-\omega_B-\omega_C)t_C} e^{i(\omega_A-\omega_B)} \cdot B e^{i\omega_A t_A} \] (3.44)

\[ P^{(3)}_{III}(t_A, t_B, t_C) = S^{(3)}_{III}(t_A, t_B, t_C) \varepsilon^+_B \varepsilon^+_C \varepsilon^+_A e^{i(\omega_A+\omega_B-\omega_C)t_C} e^{i(\omega_A+\omega_B)} \cdot B e^{i\omega_A t_A} \] (3.45)

\[ P^{(3)}_{IV}(t_A, t_B, t_C) = S^{(3)}_{IV}(t_A, t_B, t_C) \varepsilon^+_C \varepsilon^+_B \varepsilon^+_A e^{i(\omega_A+\omega_B+\omega_C)t_C} e^{i(\omega_A+\omega_B)} \cdot B e^{i\omega_A t_A} \] (3.46)

The third order polarization for each phase-matched directions can be obtained by performing a sum-over-states of the non-linear response function. In order to understand the response function, a visual approach is used in section 3.6. There, double-sided Feynman diagrams are explained and related to the non-linear response function. But first, the Optical Bloch Equations (OBE) need to be introduced.

### 3.4 Optical Bloch Equations (OBE)

In order to derive the Optical Bloch Equations, the density matrix formalism will be used. To begin, the density matrix operator is defined as:

\[ \rho(t) \equiv |\Psi(t)\rangle \langle \Psi(t)| \] (3.47)

for a system with a wave function \( |\Psi(t)\rangle \). The wave function can be written in terms of the eigenstates of the system by:

\[ |\Psi(t)\rangle = \sum_t c_t(t)|\phi_t\rangle \] (3.48)

where \( c_t(t) \) is the time-dependent coefficient for state \( |\phi_t\rangle \). Using equations 3.47 and 3.48, the density matrix elements for the system are:

\[ \rho_{ij} = c_i(t)c_j^*(t) \] (3.49)
and the diagonal components, \( c_{ii}(t) = \left| c_i(t) \right|^2 \), give the probability of finding the system in state \( i \), and is the population density. The off-diagonal elements \( (i \neq j) \), give the probability of the system being in a superposition of state \( i \) and state \( j \).

As an example, consider a simple two-level system which has a ground state \( \ket{g} \) and excited state \( \ket{e} \). In this case the wave function has the form \( \ket{\Psi(t)} = c_1(t)\ket{g} + c_2(t)\ket{e} \) and the density matrix will be:

\[
\rho = \begin{pmatrix}
    \rho_{gg} & \rho_{ge} \\
    \rho_{eg} & \rho_{ee}
\end{pmatrix} = \begin{pmatrix}
    c_g c_g^* & c_g c_e^* \\
    c_e c_g^* & c_e c_e^*
\end{pmatrix}
\]

Here, the diagonal elements, \( \rho_{gg} \) and \( \rho_{ee} \) represent the population density of the ground and excited states, respectively. The off-diagonal elements, \( \rho_{ge} = c_g c_e^* = \rho_{eg}^* \) represent the coherence between the ground and excited state of the system. Once the density matrix is defined, the expectation value of any observable can easily be calculated by performing the trace of the matrix. The trace is defined as:

\[
\langle \hat{P} \rangle = \langle \Psi(t)|\hat{P}|\Psi(t)\rangle = Tr(P\rho(t)) \quad (3.50)
\]

and is the summation of the operators diagonal components. In order to determine the individual density matrix elements, the equations of motion need to be determined. They are derived from the Schrödinger equation as follows:

\[
\dot{\rho} = -\frac{i}{\hbar}[H, \rho] = -\frac{i}{\hbar}(H \cdot \rho - \rho \cdot H) \quad (3.51)
\]

For the simple two-level system, the Hamiltonian is:

\[
H = H_0 + H_I = \begin{pmatrix}
    \hbar \omega_g & V_{ge} \\
    V_{eg} & \hbar \omega_e
\end{pmatrix}
\]
where $H_0$ is the free particle Hamiltonian, $\hbar\omega_g$ and $\hbar\omega_e$ are the eigenenergies for states $|g\rangle$ and $|e\rangle$, respectively. The interaction potential can be defined as $V_{eg} = V_{ge} = -\mu_{eg}E(t)$ in the dipole approximation where $\mu_{eg}$ is the transition dipole moment between state $|g\rangle$ and $|e\rangle$. In order to include dephasing into the description of the system, it is added phenomenologically to the equations of motion by:

$$\dot{\rho}_{ij} = -\frac{i}{\hbar} \sum_k (H_{ik}\rho_{kj} - \rho_{ik}H_{kj}) - \Gamma_{ij}\rho_{ij}$$

where $\Gamma_{ij}$ accounts for the dephasing and relaxation of the system and is defined as:

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

with $\gamma_i$ being the decay rate of state $i$ and $\gamma_{ij}^{ph}$ being the coherence pure dephasing rate and is zero when $i = j$. By using equations 3.51 and 3.52, the equations of motion for the system are obtained:

$$\dot{\rho}_{gg} = -\gamma_g \cdot \rho_{gg} + \frac{i}{\hbar} \cdot \mu_{eg}E(t) \cdot (\rho_{ge} - \rho_{eg})$$

(3.54)

$$\dot{\rho}_{ee} = -\gamma_e \cdot \rho_{ee} + \frac{i}{\hbar} \cdot \mu_{eg}E(t) \cdot (\rho_{ge} - \rho_{eg})$$

(3.55)

$$\dot{\rho}_{eg} = -\Gamma_{eg} \cdot \rho_{eg} + i\omega_0\rho_{ge} - \frac{i}{\hbar} \cdot \mu_{eg}E(t) \cdot (\rho_{ee} - \rho_{gg})$$

(3.56)

where $\omega_0 = (1/\hbar)(E_e - E_g)$. These equations are known as the Optical Bloch Equations. Different many-body effects can be added phenomenologically into the OBEs to further accurately model systems [109]. The OBEs are perturbatively solved in appendix A.

### 3.5 Double-Sided Feynman Diagrams

In order to easily track the evolution of the density matrix elements, double-sided Feynman diagrams will now be introduced. Each diagram represents a coherent pathway in
Liouville space. In figure 3.4, a sample diagram is shown. In the diagram, the vertical lines represent the bra (right) and ket (left). The time evolution of the system is seen vertically upwards. The density matrix elements are tracked within the diagram indicating the progression of the system due to each interaction. The arrows indicate the electric field interacting with the system. If the arrow is pointing towards the diagram it is an absorption, and if the arrow is pointing away from the system, it is emission. Additionally, if the arrow is pointing towards the right, the electric field has the form $E_i \exp(ik_i \cdot r - i\omega_it)$ and if the arrow is pointing to the left, the field is the complex conjugate and has the form $E_i \exp(-ik_i \cdot r + i\omega_it)$. The overall sign of the diagram is determined by the number of arrows interacting with the bra (right side), $n$, by $(-1)^n$.

![Diagram](image)

Figure 3.4: Sample double-side Feynman diagram for pulse ordering $A^*$, B, then C. Moving vertically upwards indicates progression in time. The two vertical lines represent the ket (left side) and bra (right side). The arrows indicate the incident light onto the system and the density matrix elements can be tracked in between the vertical lines.

The number of coherent pathways, and therefore diagrams, is determined by the level scheme of the system. However, there are three unique forms the diagrams can take. These are seen in figure 3.5 for phase matched direction $k_S = -k_A + k_B + k_C$ [110]. These diagrams are for a system with a ground state, $|g\rangle$, first excited state $|e\rangle$, and doubly excited state $|d\rangle$. As it can be seen in figure 3.5 (a), the first pulse, $A^*$ is absorbed on the right, making the transition from $|g\rangle$ to $|e\rangle$, creating a coherence between these two states. The second pulse, B, then interacts and causes the system to emit a photon through the transition $|e\rangle$ to $|g\rangle$. The third pulse, C, then is absorbed and the system is once again excited from
Finally, the FWM signal is produced from the transition $|e\rangle$ to $|g\rangle$. A similar description can be done for diagrams (b) and (c). The three diagrams each represent different processes, (a) is ground state bleaching, (b) is excited state emission, and (c) is excited state absorption [88]. For the other pulse orderings, a similar process can be done resulting in their unique double-sided Feynman diagrams. For $k_S = k_A - k_B + k_C$ there are three and for $k_S = k_A + k_B - k_C$ there are only two.

![Feynman Diagrams](image_url)

Figure 3.5: Three characteristic double-sided Feynman diagrams for $k_S = -k_A + k_B + k_C$ and corresponding three level system. In (d), $|g\rangle$ is the ground states, $|e\rangle$ is the first excited state and $|d\rangle$ is the doubly excited state.

From the complete set of double-sided Feynman diagrams for each phase-matched direction, the third order non-linear response function can be determined. For $k_S = -k_A + k_B + k_C$, the non-linear response function is [88,108,110]:

$$S^{(3)}_1(\tau, T, t) =$$

$$= \left( \frac{i}{\hbar} \right)^3 \sum_{ee'd} (\mu_{ge} \cdot \hat{e}_A)(\mu_{eg} \cdot \hat{e}_B)(\mu_{e'g} \cdot \hat{e}_C)(\mu_{g'g} \cdot \hat{e}_S) e^{(i\omega_{eg} - \Gamma_{eg})\tau} e^{-(i\omega_{e'g} + \Gamma_{e'g})t}$$

$$+ \sum_{ee'} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{eg} \cdot \hat{e}_C)(\mu_{e'g} \cdot \hat{e}_S) e^{(i\omega_{eg} - \Gamma_{eg})\tau} e^{-(i\omega_{e'g} + \Gamma_{e'g})T} e^{-(i\omega_{e'g} + \Gamma_{e'g})t}$$

$$- \sum_{ee'd} (\mu_{ge} \cdot \hat{e}_A)(\mu_{ge'} \cdot \hat{e}_B)(\mu_{e'd} \cdot \hat{e}_C)(\mu_{de} \cdot \hat{e}_S) e^{(i\omega_{eg} - \Gamma_{eg})\tau} e^{-(i\omega_{e'd} + \Gamma_{e'd})T} e^{-(i\omega_{e'd} + \Gamma_{e'd})t} \quad (3.57)$$

where $\mu_{ij}$ is the dipole moment, $\omega_{ij}$ is the transition frequency, and $\Gamma_{ij}$ is the dephasing rate for the transition $i \rightarrow j$. Each summation in equation 3.57 corresponds to single a
double-sided Feynman diagram. The first sum is from diagram (a), the second from (b), and the third from (c) in figure 3.5. The third-order non-linear response function can then be inserted into equation 3.43 to obtain the third order polarization. From the polarization, the FWM signal can easily be calculated from Maxwell’s equations to obtain:

$$E(\tau, T, \omega_t) = \frac{L}{2n(\omega_t)c\varepsilon_0} i\omega_t P^{(3)}(\tau, T, \omega_t)$$

(3.58)

where $L$ is the sample thickness, $n(\omega_t)$ is the sample’s refractive index, $c$ is the speed of light in vacuum, and $\varepsilon_0$ is the permittivity of free space.

3.6 Experimental Implementation: MONSTR Apparatus

In the past decade, a new apparatus has been designed to perform three pulse FWM measurements while also stabilizing the relative phase of the pulses. This apparatus is a multidimensional optical non-linear spectrometer (MONSTR) and has been used on quantum wells [111–115], quantum dots [116], atomic gases [117, 118], and TMDs [87, 119]. The MONSTR allows for multidimensional Fourier transform spectroscopy techniques to be performed as the MONSTR can obtain sub-wavelength stability through active [111, 120–127] or passive [128–130] phase stabilization. Detailed explanations of the MONSTR apparatus can be found in ref. [127,131], but a brief summary will be presented here.

The MONSTR instrument incorporates three nested Michaelson interferometers which are mounted on two different decks (labeled top and bottom deck). Each deck has one interferometer as well as a third that is formed when the two decks are stacked on top of each other (between deck). The beam path and outputs can be seen in figure 3.6. Both a continuous wave laser (in this case a HeNe) and an ultrafast laser are colinearly sent into the MONSTR on the bottom deck. From here, the laser is split at the beam splitter (BS), sending one beam to the top deck via the periscope mirror (P1) and the second beam onto stage X.
Figure 3.6: Beam path for the MONSTR apparatus. Three nested interferometers are encapsulated in the instrument consisting of the bottom deck, top deck and between deck. The pulses combinations that interfere are C and reference (bottom deck), A* and B (top deck), and A*, B, C, and Ref (between deck). This figure is reproduced from ref. [131] with permission.

The beam on the bottom deck passes through another beam splitter sending one beam to stage C and the other out of the MONSTR (or back reflected by the dichroic mirror, DCM). The beam sent to the top deck follows a similar path, going onto stage B and C and out of the MONSTR. Along each beam’s path in the MONSTR, they pass through a compensator plate (CP) which compensate for dispersion. When the beams exit the MONSTR, the HeNe is back reflected by the dichroic mirror, representing the end of the interferometers. The ultrafast laser pulses pass through the DCM at the four corners of a 1 inch by 1 inch square box (geometry seen in figure 3.2).

The system has three piezoelectric transducers (PZT) mounted on the back of mirrors which are used in the active phase stabilization of the system. The relative phase of the pulses are monitored by the output of each arm of the interferometer and a photodiode. This
“error signal” (dashed lines) is part of a feedback loop which controls the PZTs voltages, compensating for any phase drift. With each beam having its own translation stage, the pulses can be delayed with respect to each other independently. This allows for a seemly transition between scanning different time delays. Stages A, B, and C each have 5 cm of travel, whereas stage X has 20 cm of travel. The entire assembled MONSTR apparatus is see in figure 3.7.

A complete experimental setup is shown in figure 3.8 for a dephasing measurement. While the MONSTR has phase stabilization capabilities, it is not necessary for these measurements and are excluded from the diagram. The four pulses exit the MONSTR in the ”box” geometry and pass through a half-wave plate, linear polarizer, and quarter-wave plate, consecutively. By using a half-wave plate in combination with a linear polarizer, the laser power for each beam can be individually controlled. The quarter-wave plates can easily be removed if linear polarizations are desired, or left in for circular polarizations. The four beams then pass through a focusing lens onto the sample. After passing through the sample, the beams are collimated by a second lens. The signal is allowed to pass through an iris which blocks the
Figure 3.8: Experimental setup for dephasing scans using the MONSTR apparatus. The abbreviations $\lambda/2 = \text{quarter wave plate}$, $\text{pol} = \text{linear polarizer}$, $\lambda/4 \text{ quarter wave plate}$, $\text{FM} = \text{flip mirror}$. 

three beams so that only the signal is collected. The signal then passes through an analyzing polarizer (quarter-wave plate is included if circular polarizations are used) and sent to a single channel detector to record the signal. For imaging purposes, a white light source is shown which sends light onto the back of the sample via a flip mirror (FM). The light is sent to the CCD camera by the 8%/92% (R/T) pellicle beam splitter. A pellicle beam splitter is used to remove the double image caused by transitional beam splitters. For a dephasing scan, the forth beam (ref) is used strictly as an alignment beam. Due to the geometry of the beams, the path the reference beam follows will be the phase-matched direction for the signal.

Additionally, the beam splitter also sends a portion of the focusing beams towards a CCD camera. This branch is used to determine time-zero (when the three pulses arrive at the same time). By imaging the replica focus of the beams in the CCD camera, the interference pattern is magnified and imaged. Depending on the orientation of the pulses that are interfering, the interference pattern will either be vertical or horizontal. In order to determine when the pulses are arriving at the same time, the following procedure is followed. First, Pulse $A^*$ is fixed at a specific stage position and pulse $B$ is scanned relative to it. This determines when pulse $B$ arrives at the same time as pulse $A^*$. Then, pulse $C$ is scanned relative to pulse $A^*$ determining its time-zero position. Finally, the reference pulse is scanned
Figure 3.9: Field correlation used to determine the time-zero position of each stage. The black line is the recorded data from the CCD camera and the red line is the fitting data. Against pulse C. When all four pulses arrive at the same time and interfere, a checkerboard pattern is seen. To find the exact stage position when the pulses overlap, the field correlation is recorded in the camera. The correlation yields a pulse envelope with a fast oscillating sine wave inside of it, as seen in figure 3.9. The correlation is then fit with a Gaussian envelope to obtain the accurate time zero value.
Chapter 4

Superradiant Coupling in Transition-Metal Dichalcogenides

Quantitative absorption measurements on the lowest excitonic resonance were performed using broadband incoherent white light. Two representative transition-metal dichalcogenides, MoSe$_2$ and WSe$_2$, were explored. The number of layers (N) were varied from a single layer up to hundreds of layers, allowing additional insight into the radiative coupling for these systems to be obtained. The excitonic resonance does not saturate for samples with hundreds of layers. Additionally, the absorption percentage does not vary consistently with the layer thickness. The experimental results were modeled using a semi-classical theory of radiatively coupled two-dimensional excitons revealing that not only is radiative coupling necessary to reproduce the results, but in a certain region of layer thicknesses the coupling is superradiant in nature.

4.1 Introduction

When incoherent white light is shined on a single two-level system two effects can take place; absorption and scattering. If the energy of the photons do not match the resonant energy of the system, then the photons will be redirected without otherwise altering them (scattering). If the energy of the photon does match that of the system’s resonance, then the photon will be absorbed, exciting it. The excited system will return to its ground state by either transferring the energy into random atomic motion (i.e. heat) or reemit the photon [132]. The photons that are not re-emitted are the true absorption of the system.

\footnote{Contents of this chapter are published in “C. E. Stevens et al. Optica 5, 749-755 (2018)”}
Additionally, if you have the situation in which two two-level systems are within close proximity to each other a process known as radiative coupling can occur. This was first investigated by Dicke [89] and was found to be a cooperative process. Generally speaking, radiative coupling occurs when an ensemble of oscillators interacts with a common light field. The interaction of a single emitter with the light field will cause the formation of a multitude of modes that describe the entire system instead of the effects of the individual emitter. This effect even occurs when one of the systems are in its ground state.

It has been shown by Hopfield [133] that if resonantly excited homogeneous semiconductors are radiatively coupled that the absorbed photons will be in a perpetual cycle of emission and absorption with an infinite radiative lifetime creating a exciton-polariton state. This infinite radiative lifetime is due to the infinite system dimensions which restricts the photon from leaving the system. The polariton will instead decay due to non-radiative dephasing processes and leads to the irreversible absorption of energy from the optical field. For a material where each layer absorbs a fixed percentage of incoming light, an exponential decrease in transmitted light at the resonance as a function of material thickness is expected. This is known as the Beer-Lambert Law.

On the contrary, a photon that was absorbed and then emitted by a local oscillator can escape the sample creating a radiative decay channel. The radiative decay rate in determined by the oscillator strength, $f_\lambda$, which controls the reversible light absorption as well as the emission. For energy transition $E_\lambda$, the radiative decay rate is $\Gamma_\lambda = f_\lambda E_\lambda / \hbar$ [90–92]. In the case of an ensemble of these local oscillators, the cooperative effects depend strongly on the relative phase of the emitted light. If, for example, $N$ oscillators are in a small region, compared to the wavelength, then the overall emission is in phase and a peak intensity of the emitted light is $\propto N^2$. With this increase in peak intensity, there is a corresponding reduction in the radiative lifetime. This phenomenon is called ‘superradiance’ [89].
4.2 Samples and Experimental Technique

The measurements presented in this chapter were performed on flakes of MoSe$_2$ and WSe$_2$ which were prepared by mechanical exfoliation via the “Scotch tape method” [3]. Samples were exfoliated onto quartz substrates and identified first through an optical microscope followed by atomic force microscopy (AFM) to obtain the number of layers per sample. For the atomically thin samples, photoluminescence and Raman spectroscopy was also employed to confirm the AFM results. A sample PL, Raman, and AFM measurement is shown in figure 4.1. The full list of AFM scans is shown in appendix B.1.

The samples were loaded into a Janis ST-300-MS compact cryostat and held at 4.5 K. The measurements were performed using the experimental setup seen in figure 4.2(a). The white light was obtained from a commercial spectroscopy grade incandescent light source (StellarNet Inc. SL1-Filter Tungsten Halogen lamp) and focused onto the samples via a 50x microscope objective. The transmitted light was collected by a second 50x objective and directed into a spectrometer where it was dispersed onto a CCD detector. The reflected light was collected through the initial microscope objective and guided into the spectrometer. To switch between the transmitted and reflected paths, a flip mirror was used. For each measurement, a reference spectra was obtained for the transmitted and reflected light from the substrate. Additionally, the reflected and transmitted signal from the sample was obtained, taking great care as to not let any light leak around the samples.
Figure 4.2: (a) Experimental setup for absolute absorption measurements. Samples are held inside of a cryostat at 4.5 Kelvin allowing for both reflection and transmission measurements to take place. The broadband white light is focused onto the sample via a 50x objective and collimated on the other side by another 50x objective. The reflected and transmitted light is sent into a spectrometer and measured by a CCD detector. A flip mirror is used to switch between the reflected and transmitted paths. (b) Representative transmission ($1 - T$), reflection ($R$), and absorption ($1 - T - R$) spectra.

4.3 Experimental Results and Discussion

For each sample, the absolute absorption was calculated using $A = 1 - T - R = 1 - \frac{I_T}{I_0} - \frac{I_R}{I_0}$, where $I_0$, $I_T$, and $I_R$ are the intensities of the incident, transmitted and reflected light, respectively. Representative spectra for $A$, $1 - T$, and $R$ are shown in figure 4.2(b). Using the absolute absorption spectra, the absorption at the A - exciton peak was determined for each sample and plotted as a function of layer thickness as seen in figure 4.3 (blue circles). The error bars for absorption percentage were determined by the confidence level in the absolute absorption spectra. The error in the number of layers is ±2 layers based on the sensitivity/clarity of the AFM scans.

From the experimental data, it can be clearly seen that the absorption for both MoSe$_2$ and WSe$_2$ do not saturate until the samples are hundreds of layers thick. These results were compared to the prediction of Beer’s law assuming N independent layers, each absorbing a fixed percentage. The absorption percentage per layer used for the comparison are the
Figure 4.3: Quantitative absorption percentage at the A-exciton absorption energy for MoSe\textsubscript{2} (left) and WSe\textsubscript{2} (right) as a function of layer thickness. The experimental data is shown as the blue circles. The green solid line is the theoretical peak absorption for the full geometry and the red dashed line shows the absorption in the superradiant geometry. The blue dashed line shows the extinction of the transmitted intensity (1-peak intensity). For comparison, the expected absorption percentage based on the absorption for a monolayer extrapolated using Beer’s law is shown as the dashed dark yellow line. The brown line represents the Beer’s law extrapolation for a monolayer embedded within bulk material.

measured absorption percentage of a single layer on a quartz substrate (MoSe\textsubscript{2} = 10.24% WSe\textsubscript{2} = 14.29%) and the calculated percentage of a single layer embedded in bulk material (MoSe\textsubscript{2} = 3.64% WSe\textsubscript{2} = 3.78%). The predicted curve based on Beer’s law using these absorption percentages (monolayer on a quartz substrate (yellow dashed line) and a monolayer embedded in bulk material (red dashed line)) greatly differ from the experimental results. Beer’s law predicts saturation after $\sim$10 layers or $\sim$100 layers depending on which absorption percentage per layer is used. However, this is in strong disagreement with the experimental data where it does not saturate until hundreds of layers.

4.4 Theoretical Results and Discussion

4.4.1 Microscopic Model: Introduction and Model Validity

In order to obtain a deeper understanding, the experimental results were modeled using a semi-classical theory based on the Maxwell-Bloch equations for a classical optical field
interacting with equidistant two-dimensional layers. The model includes four interacting bands as well as radiatively coupled two-dimensional excitons. Screening and coupling effects are dynamically included for the four bands and all other contributions are included in the background dielectric tensor [134]. In this model, the only free parameter is related to the physical thickness of the layers. All other parameters were obtained from density functional theory calculations (see appendix C for additional details on theoretical model).

It must be noted that the screening of the surrounding layers influences the spectral position and oscillator strength of the excitons. This is due to the different dielectric environments for each layer which will lead to small shifts in the resonant frequency. Therefore, the overall response of the samples will be inhomogeneously broadened. However, this effect becomes negligible as the sample thickness becomes sufficiently large when compared to the in-plane exciton Bohr radius. Using this assumption, the linear susceptibility for each layer becomes identical for all layers.

To verify that an identical linear susceptibility is valid to use, the diamagnetic shift for the A - exciton was measured in magnetic fields up to ± 60 Tesla applied perpendicular to the layers (along the c-axis) for both MoSe$_2$ and WSe$_2$. The energy position of the A - excition can be seen in figure 4.4 (a) and (c) as a function of magnetic field for WSe$_2$ and MoSe$_2$, respectively. From the energy position, the diamagnetic shift is determined and plotted in figure 4.4 (b) and (d). Fitting the shift with a simple quadratic, yielded an average shift in position of $\sim 0.77 \, \mu eV/T^2$ for WSe$_2$ and $\sim 0.12 \mu eV/T^2$ for MoSe$_2$. Using the diamagnetic shift, the lateral exciton size, $r_X$, can be calculated via the following equation:

$$ r_X = \sqrt{\langle r \rangle^2} = \frac{\sqrt{8m_r \sigma}}{e} \quad (4.1) $$

where $m_r$ is the reduced excitonic mass and $\sigma$ is the diamagnetic shift coefficient [40]. Using a reduced excitonic mass of $0.17 m_o$ for WSe$_2$ and $0.27 m_o$ for MoSe$_2$ and the measured diamagnetic shift coefficient, the lateral exciton size is calculated to be 2.44 nm and 1.21 nm.
for WSe$_2$ and MoSe$_2$, respectively. Comparing these values to the natural layer thickness of $d = 6.5$ Å for both materials, the exciton radius is approximately two to four times larger than the interlayer distance. Therefore, for $N \geq 7$ the surface effects can be ignored and the linear susceptibility approximated as identical for all layers.

![Graphs showing energy position and diamagnetic shift for WSe$_2$ and MoSe$_2$.](image)

Figure 4.4: (a) Energy position of the $A$ - exciton in WSe$_2$ as a function of magnetic field strength up to +60 Tesla (blue squares) and down to -60 Tesla (red squares). (b) Obtained diamagnetic shift for the $A$ - exciton in WSe$_2$ (yellow squares). The dashed line is a quadratic fitting. (c) Energy position of the $A$ - exciton in MoSe$_2$ as a function of magnetic field strength up to +60 Tesla (blue squares) and down to -60 Tesla (red squares). (d) Obtained diamagnetic shift for the $A$ - exciton in MoSe$_2$ (yellow squares). The dashed line is a quadratic fitting.

### 4.4.2 Theoretical Results

Varying the number of layers effects the transmission and absorption characteristics in two ways. First it changes the background refractive index experienced by the individual
layers. The effect of this can been seen in figure 4.5 (a). For illustration, the transmission spectra for a MoSe$_2$ monolayer on a BK7 substrate (purple line) and a monolayer embedded in bulk material (blue line) with the same linear susceptibility is shown. It can be seen that the increase in the background refractive index from the bulk environment reduces the extinction by a factor of 2.5.

Secondly, increasing the number of layers introduces radiative coupling to the system. The effects of this coupling depends on the relative phase of the emitters in the system and is an additive effect when the emitters are in phase. By artificially forcing the interlayer distance to zero (superradiant geometry), the emitters can be forced into phase allowing for the comparison of the spectra obtained from using the known interlayer spacing of 6.5 Å (full geometry). This comparison can be seen in figure 4.5 (b) for MoSe$_2$ where the solid line is the full geometry and the dashed line is the superradiant geometry. Clearly, for the layer thicknesses shown, the full geometry is in good agreement with the superradiant geometry.

![Figure 4.5: (a) Calculated transmission spectra for monolayer MoSe$_2$ on a BK7 substrate (purple curve) and a monolayer embedded in bulk material (blue curve). Both curves are calculated with the same linear susceptibility. (b) Comparison of absorption per layer for different number of layers in the superradiant geometry. The solid line shows the calculated absorption per layer for MoSe$_2$ on a BK7 substrate for the full geometry. The dashed line shows the calculated results for the superradiant geometry (spacing between layers artificially set to zero).](image)

In order to compare the theoretical results with the experiment, both the full geometry (solid green) and superradiant geometry (dash red) are plotted in figure 4.3. Comparing the theoretical and experimental data, it can be clearly seen that the full geometry is needed to
replicate the data. However, within a certain range of thicknesses ($10 < N < 90$ for MoSe$_2$ and $10 < N < 60$ for WSe$_2$) the superradiant geometry, full geometry, and experimental results are in good agreement. This points to the conclusion that in this region, not only is radiative coupling necessary to replicate the results, but the coupling is superradiant in nature.

Figure 4.6: Experimental and theoretical absorption spectra for various layer thicknesses for both MoSe$_2$ and WSe$_2$. The A and B exciton peaks are labeled for clarity.

To further confirm the theoretical model has successfully replicated the results and not just the absorption percentage, several experimental and theoretical spectra are compared in figure 4.6. The full list of spectra and their comparisons can be seen in appendix B.2. It can be clearly seen that the theoretical spectra replicates many of the features of the experimental results as well as the absorption percentages.

4.5 Conclusion

In conclusion, absolute absorption measurements were performed on MoSe$_2$ and WSe$_2$ samples of varying thicknesses. The measurements show that the absorption percentage does not saturate until the samples are hundreds of layers thick and do not follow the predicted curves from the Beer-Lambert Law. Instead, to accurately describe the experimental results,
a theoretical model that includes radiative coupling had to be employed. The theoretical results were compared, not only for the absorption percentages, but the full spectra as well. Further investigation into the radiative coupling determined that in a range of layer thicknesses (10 < N < 90 for MoSe$_2$ and 10 < N < 60 for WSe$_2$) the coupling is superradiant in nature.
Time-integrated four wave mixing (TI-FWM) measurements were performed on chemical-vapor-deposition (CVD) grown MoSe$_2$ monolayers in magnetic fields up to 25 Tesla. TI-FWM measurements, coupled with theoretical calculations, more easily allows for the separation of the biexciton’s contribution from other sources as opposed to linear photoluminescence spectroscopy. A more complete picture of the FWM signal was obtained by exploring the effects of various polarization schemes as well as an applied external magnetic field. The experimental results were modeled using time-dependent density functional theory (DFT) leading to a better understanding of biexciton formation and dynamics. For a more realistic simulation, a four-band model (top two valence and bottom two conduction bands) was used.

5.1 Introduction

Monolayer two-dimensional transition metal dichalcogenides (TMDs) draw substantial interest due to their electronic properties and potential use in optoelectric devices [4,83,135–144]. The electronic properties, which were discussed in detail in chapter 2, allow for the formation of strongly bound excitons, trions, and biexcitons [6,16,44,48,50]. Additionally, with an applied external magnetic field the valleys will split due to Zeeman splitting, which can be used to magnetically tune the polarization and coherence of the excitonic valley pseudospin [145–149].

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In order to probe these effects, linear spectroscopy is a difficult tool to use as it struggle separating the contribution from the biexciton and other sources causing a non-linear increase in intensity as a function of excitation density. Instead, using coherent non-linear spectroscopy, the two- (exciton) and four- (biexciton) particle correlations through two-dimensional Fourier-transform spectroscopy are separated (2DFTS) [49, 114, 115, 150, 151]. Using 2DFTS, the resulting spectra will generate different features in the spectra corresponding to the exciton and biexciton. Alternatively, by using TI-FWM spectroscopy and theoretical calculations, some initial insights can be obtained.

5.2 Samples and Experimental Technique

In this chapter, the measurements presented were performed on CVD grown MoSe\textsubscript{2} samples. The samples were initially grown on silicon substrates directly from MoSe\textsubscript{2} bulk powder using N\textsubscript{2}+H\textsubscript{2}O vapor as a carrier. The grown samples were then transferred onto quartz substrates via a wet transfer method using PMMA. The detailed process is described in ref. [72]. The samples were then characterized via micro-photoluminescence and Raman spectroscopy as seen in figure 5.1. In the PL spectra, only a single peak is seen at 810 nm, corresponding to the direct exciton in an MoSe\textsubscript{2} monolayer. Additionally, the Raman spectra shows three main peaks: 240 cm\textsuperscript{-1}, 249 cm\textsuperscript{-1}, and 520 cm\textsuperscript{-1}. The first two peaks are from the A\textsubscript{1g} and 2E\textsubscript{2g} modes whereas the third peak is from the silicon substrate. The high PL to Raman signal points to a highly crystalline structure [72]. Room temperature absorption measurements (figure 5.1(c)) were also performed on the samples, which revealed an A-exciton peak at 795 nm and the B-exciton at 705 nm. The splitting of 90 nm between the A- and B-exciton peak is consistent with earlier measurements [152, 153]. The samples were placed in the cryostat in the 25 Tesla Split Helix DC Magnet at the National High Magnetic Field Laboratory and held at 10K.
Figure 5.1: (a) Photoluminescence spectra for MoSe$_2$ monolayer. A strong single peak is seen centered at 810 nm and is attributed to the direct excitonic transition at room temperature. (b) Raman spectra for MoSe$_2$ monolayer. The peak at 240 cm$^{-1}$ and shoulder at 249 cm$^{-1}$ correspond to the A$_{1g}$ mode and E$_{2g}^2$ shear mode, respectively. The room temperature absorption spectra is shown in (c), showing the A- and B- exciton peaks at 795 nm and 705 nm, respectively.

The measurements were performed using the multidimensional optical nonlinear spectrometer (MONSTR) instrument (discussed in section 3.6). The three pulses are oriented into the box geometry, where each pulse makes up one corner of the box and are focused onto an overlapping spot on the sample. The non-linear third order optical response leads to a FWM signal that will propagate along the phase-matched direction, $-k_a + k_b + k_c$, which will be the “missing” corner of the box. This signal is then sent to a single channel detector and analyzed by a lock-in amplifier. The lock-in amplifier is referenced off the chopper’s difference frequency, which is chopping two of the three pulses (A* and C) used to create the FWM signal. By setting the time delay between pulse B and C to zero and scanning A* from a negative delay (arriving last, figure 5.2(d)) to a positive delay (arriving first, figure 5.2(c)) the coherence time, T$_2$, can be measured. Both the negative and positive delay signals have contributions from the biexciton, however, the negative delay signal only comes from these four-particle correlations [43,88].
Figure 5.2: (a) Experimental setup for TI-FWM measurements taken in the 25 Tesla split helix magnet at the National High magnetic Field Laboratory in Tallahassee, Florida. Three beams, A*, B, and C are produced by the MONSTR and focused onto the sample inside of the magnet’s cryostat. The sample is held at 10K. The FWM signal is sent to a single channel detector and recorded. (b) Sample holder placed at the end of the sample probe such that the magnetic field is applied perpendicular to the sample surface. (c) Pulse sequence for the positive delay signal. (d) Pulse sequence for the negative delay signal.

5.3 Experimental Results and Discussion

Firstly, to investigate the effects of the magnetic field on the TI-FWM signal, without preferential valley selection, linear polarization is used. This can be seen in figure 5.3 where data taken at zero applied magnetic field and 10 Tesla is shown. The time axis represents the time delay between pulse A* and pulse B and C. From this data, it was found that the coherence time, $T_2$, changes from $\sim 400$ fs when no field is applied to $\sim 600$ fs at 10 T. The effects on the negative delay signal are even more noticeable. This result is surprising as the exciton binding energy in MoSe$_2$ has been found to be $\sim 0.5$ eV and is energetically large when compared to the Valley Zeeman splitting, which was determined to be $\sim 0.22$ meV T$^{-1}$ [14, 16, 145–148, 154, 155]. Therefore, the excitons should only be slightly perturbed as the splitting will be rather small. However, it is this splitting of the electron and hole into
Figure 5.3: TI-FWM signal obtained on a MoSe$_2$ monolayer sample using linear polarization. The blue squares are taken with zero applied magnetic field and the red circle were taken at 10 Tesla. The green dashed line is the instrumental response. The time axis is the delay between the arrival of pulse A* relative to pulse B and C. The time delay between pulse B and C is kept constant at T = 0 fs.

discrete energy levels that reduces the excitonic scattering. This, in turn, suppresses the dephasing mechanisms leading to longer dephasing times.

To continue the investigation, the polarization was switched to two different schemes using either left ($\sigma^+$) or right ($\sigma^-$) handed circular polarization. The two schemes were co-circular ($\sigma^+\sigma^+\sigma^+\sigma^+$) and cross-circular ($\sigma^-\sigma^+\sigma^-\sigma^+$), where each polarization corresponds to pulse A*, B, C, and detection, respectively. This allows for valley selection of either the K or K' valleys which are at the corner of the first Brillion zone [44, 79, 156]. By applying co-circular polarization, excitons were formed in only in the K valley, whereas when using cross-circular, excitons in both the K and K' valleys are formed [49,112]. The experimental results using these polarization schemes can be seen in figure 5.4.

In figure 5.4(a,c) the results of the co-circular polarization scheme are shown for zero magnetic field and 25 T and the cross-circular results are shown in 5.4(b,d). The green dashed line in figure 5.4 is the instrumental response of the system. It can be seen that both the negative and positive delay signals are longer for the cross-circular case when compared
Figure 5.4: Experimental results for the TI-FWM measurements using co- $(\sigma^+\sigma^+\sigma^+\sigma^+)$ (a) and (c) and cross- $(\sigma^-\sigma^+\sigma^-\sigma^+)$ (b) and (d) circular polarization schemes. In (a) and (b) there is no external applied field whereas in (c) and (d) the field is 25 Tesla. The green dashed line in all figures represents the instrumental response of the system. The time axis is the delay between the arrival of pulse A* relative to pulses B and C.

to the co-circular data at zero field and 25 T. At zero field, this increase can be attributed to the cross-circular polarization exciting both the K and K’ valleys as opposed to just the K valley. This causes excitons of opposite spins in different valleys to be created [49].

Additionally, for both polarization schemes, the negative and positive delay signals increase when an external field is applied. In monolayer TMD’s when the external field is applied, it causes valley Zeeman splitting. For MoSe$_2$ there is a linear shift between the two Zeeman levels at a rate of $\sim 0.22$ meV $T^{-1}$ [145,147]. Moreover, by lifting the degeneracy of the two valleys at the K and K’ points, the degree of circularity of the polarization for the emitted light increases [148]. By applying the magnetic field perpendicular to the atomic
plane (Faraday geometry), the two-dimensional system becomes highly confined. This reduces the quasiparticle scattering along the field direction, thus increasing the dephasing time.

5.4 Theoretical Results and Discussion

In order to understand what is causing the increase in the coherence times, the experimental results were modeled using time-dependent DFT in its density-matrix representation to develop equations of motion for the polarization dynamics [45, 114, 115, 157–159]. For realistic simulations, the top two valence bands and bottom two conduction bands were included. The four-band model was used to describe the light interaction dynamics at the $K$ and $K'$ points of the Brillouin zone. When the light excited the material, excitons were formed due to the Coulomb electron-hole interactions.

The time-integrated FWM signal is determined by the third-order non-linear polarization. As such, the important quantities the model produces is the polarizations at each valley, $\rho_{cv}^K(t)$ and $\rho_{cv}^{K'}(t)$, where the indices include $c$ and $v$ include the two conduction and two valence bands, respectively. The excitonic effects are accurately described using the screened Slater exchange-correlation potential with the nonadiabatic kernels which displays a Coulomb-like long-range behavior and include memory effects [157,160]. In order to include the biexciton contributions, the equations of motion were expanded up to the third-order. In the equations of motion, the biexcitonic contribution can be “turned off” making the results purely the exciton’s effect. In this way, the exciton’s and biexciton’s contribution to the total FWM signal for both the positive and negative delay can be determined. An indepth look at the theoretical model is presented in appendix D.

The theoretical results for the zero field co- and cross-circular data can be seen in figure 5.5. In figure 5.5 (a,b) the experimental data is seen with the theoretical results overlaid in red and in (c,d) the individual contributions to the theoretical data is seen as the blue dashed
Figure 5.5: Theoretical results for the zero field time-integrated FWM measurements using (a) and (c) co-circular ($\sigma^+\sigma^+\sigma^+\sigma^+$) and (b) and (d) cross-circular ($\sigma^-\sigma^+\sigma^-\sigma^+$) polarization schemes. The red overlay on the experimental data in figures (a) and (b) is the total theoretical modeling results. In figures (c) and (d) the theoretical results (black) is broken into the individual contributions from the exciton (blue dashed) and biexciton (red dashed). (exciton correlations) and red dashed (four particle bound biexciton correlations) to the total theoretical results (solid black). As it can be seen, the theoretical model nicely reproduces the experimental data. Looking at the breakdown of the theoretical results, it can be seen that the negative delay signal for both polarization schemes is completely dominated by the biexciton. Whereas, the positive delay signal is from both the exciton and biexciton in both cases.

Similarly, the experimental and theoretical results for 25 Tesla can be seen in figure 5.6. For the co-circular case, positive delay signal is formed by equal contributions from both the exciton and biexciton, but the increase in the negative delay signal is attributed to
Figure 5.6: Theoretical results for the 25T time-integrated FWM measurements using (a) and (c) co-circular ($\sigma^+\sigma^+\sigma^+\sigma^+$) and (b) and (d) cross-circular ($\sigma^-\sigma^+\sigma^-\sigma^+$) polarization schemes. The red overlay on the experimental data in figures (a) and (b) is the total theoretical modeling results. In figures (c) and (d) the theoretical results (black) is broken into the individual contributions from the exciton (blue dashed) and biexciton (red dashed).

the biexciton. For the cross-circular case, the negative and positive delay signal increased relative to the zero field measurements. The increase in both signals is again caused by the biexciton.

The theoretical calculations attribute the increase in the positive and negative delay signals to two main effects. Firstly, the presence of additional carrier (i.e. four particle complexes) increases the screening. This leads to longer radiative lifetimes and slower dephasing of the biexciton. Secondly, and more importantly, the applied field splits the levels which reduces scattering and allows multiple exciton correlations to form more easily.
5.5 Conclusion

In summary, the TI-FWM signal was measured on CVD grown MoSe$_2$ in magnetic fields up to 25 T. Three different polarization schemes were used; linear, co-circular, and cross-circular. The experimental results showed an increase in the decay time with increasing magnetic field. This is attributed to the reduction of scattering which leads to longer decay times. The decay times also increased as the polarization is changed from co-circular to cross-circular. The change in polarization causes excitons to only be excited in one valley (co-circular) to excitons being excited in both valleys (cross-circular).

The experimental results were modeled using time-dependent DFT calculations. The theoretical results allowed for a more complete picture for the increase in the decay times. By looking at the exciton and biexciton’s contributions to the total signal, it was discovered that the positive delay signal is from the exciton and biexciton equally at zero field and 25 T for co-circular polarization. For cross-circular, at zero field both contribute, but at 25 T the biexciton dominates. Interestingly, the negative delay signal is dominated by the biexciton at 0 T and 25 T for both cases.
Chapter 6

Characterization and Implementation of a 7.5 Tesla Superconducting Magnet

In the previous chapter, one effect of applying an external magnetic field on a transition metal dichalcogenide monolayer was investigated. The previous experiment was performed on a CVD grown monolayer at the National High Magnetic Field Laboratory with a relatively large spot size (≈300 µm). These restraints limit the experiments that can be performed and the samples that can be investigated. This led to the acquisition of a 7.5 Tesla superconducting magnet with an open bore allowing for optical components to be within a centimeter to the sample inside of a compact cryostat. With the design of the magnet, a new optical setup needed to be developed to allow for two-dimensional motion of the cryostat as well as a laser spot size of ≈10 µm. In this chapter, the characterization and specifications of the magnet as well as the experimental design are presented.

6.1 Magnet Characterization

6.1.1 Magnet Design and Specifications

The 7.5 Tesla magnet, schematically seen in figure 6.1, was purchased from Cryomagnetics Inc. The superconducting magnet weighs in at 792 pounds and has a 16 by 31.5 inch footprint. It is 38.88 inches tall, not including the remote motor for the cooling tower. The superconducting coils are made of twisted multi-filamentary NbTi wire with a copper matrix and have a critical temperature, $T_C$, ≈10K which decreases as the current density and magnetic field increase [161,162]. The coils are cooled by a 1 watt, two-stage pulse tube cryocooler (Sumitomo RP-082B2S) with a F-70 Sumitomo compressor. In order to reduce
vibrations from the compressor to the motor, the compressor transfer lines are partially enclosed in a sand trap. Additionally, the motor is mounted separately from the magnet and only connects to the cryocooler via three transfer lines which further limits vibrations.

The magnet has an open bore in the horizontal and vertical directions (figure 6.1 (b,c)) with diameters of 2 inches and 2.375 inches, respectively. The vertical bore allows for the cryostat (Janis, ST-300 compact cryostat) to be inserted into it, as seen in figure 6.1(c). When the cryostat inserted, the optical window is centered in the horizontal bore. With the horizontal bore completely open, non-magnetic optical components can be extended into it, up to the cryostat window. This allows for experiments with high spatial resolution to be performed.

### 6.1.2 Cooling and Charging Information

To charge the magnet, the coils need to be cooled to a point where they can remain superconducting while the large currents needed are added. As mentioned above, this is
done by a 1 W, two-stage pulse tube cryocooler. However, since the coils are so large, the system takes quite some time to completely cool, \( \sim 90 \) hours. This estimation is after the cryostat surrounding the core has been sufficiently evacuated. The cooling profile for the system can be seen in figure 6.2. Four temperature sensors inside the magnet allow for a detailed picture of the cooling process. The four sensors are on the 1\(^{st}\) and 2\(^{nd}\) stage of the cryocooler, the magnet shield surrounding the coils, and the coils themselves. When the system is completely cooled, the base temperatures are 57.92 K (Magnet Shield), 32.1 K (1\(^{st}\) Stage), 3.40 K (Magnet coils), 3.34 K (2\(^{nd}\) Stage). From the curves in figure 6.2, it can be seen that the cooling rate of the 1\(^{st}\) stage and the magnet shield are related as well as the 2\(^{nd}\) stage and the magnet coils. Additionally, once the 1\(^{st}\) stage (magnet coils) goes to a lower temperature then the 2\(^{nd}\) stage (magnet shield), a sharp increase in cooling speed is seen.
Once the magnet is at base temperature, the magnet coils can be charged. The charging process takes 2 hours and 55 minutes to reach full field (7.469 T). The current to field conversion ratio for this system is .08702 T/A. The charging information can be seen in figure 6.3. Plots (a-d) are the temperature information of the four sensors as the field is increased; (a) 1st stage (b) magnet shield, (c) 2nd stage, and (d) magnet coils. Plot (e) is the amount of current in the coils, and (f) is the magnetic field present in the center of the magnet. In order to safely ramp the magnet to full field without it quenching (superconducting coils changing to conducting coils) the process needs to be done in two stages. The first stage has ramping rate of 0.0098 A/s and will continue at this rate until the current in the coils is 68.67 A. At this point, (first red dashed line at ∼117 minutes) the ramping rate changes to 0.0045 A/s. This ramping rate takes the current to 86 A and is full field for the magnet. The second red dashed line in the figure is when the magnet reaches full field.

In figure 6.3 (c,d), the 2nd stage and magnet coils temperatures can be seen. The temperature profile first shows a sharp rise when the current is initially introduced into the coils but then begins to recover. Once the ramping rate changes to a lower value (first red dashed line), the temperature reacts by dropping at a quicker rate and closer to base temperature. This can also be seen when the magnet is at full field (second dashed red line) when no additional current is added into the system. After some time at full field, the magnet coils and 2nd stage recover to their starting temperatures. During the charging process, it can also be seen that the magnet shield temperature drops, while the 1st stage temperature increases. When discharging the magnet back to zero field, the reverse process occurs and shows the same temperature features in reverse.

6.1.3 External Stray Field

With such strong magnetic fields being produced by the superconducting magnet, strong external stray fields must also be present. These fields need to be characterized and labeled
Figure 6.3: Temperature, current, and magnetic field data while the system is ramping to full field. In (a-d), the temperatures of the (a) 1\textsuperscript{st} stage, (b) magnet shield, (c) 2\textsuperscript{nd} stage, and (d) magnet coils are shown. In (e), the current in the coils and (f) the magnetic field strength are presented. The first dashed red line indicates the change in ramping speed at 68.67 A. The second dashed line is when the magnet reaches full field [163].

as health and safety concerns become possible [164–168]. Magnetic fields have a wide range of effects, from health issues (disrupting cardiac pacemakers) to damaging electronic equation (wiping data on computers and credit cards). In order to not have equipment damaged, many pieces have an upper limit of magnetic field they must stay out of.

For this magnet, the estimated external stray field can be seen in figure 6.4 [162]. In the plot, the 1000 G (purple), 100 G (green), 10 G (red), and 5 G (blue) lines are seen for both the radial and z- direction. Radially, the distances for the 1000 G, 100 G, 10 G, and 5 G lines are 66 cm, 143 cm, 303 cm, and 383 cm, respectively. With the stray field extending so far from the magnet, special care needs to be taken when placing optics and electronics.

6.2 Experimental Setup and Preliminary Results

6.2.1 Experimental Setup

In order to meet the requirements imposed on the experiment by the expected sample sizes and stray magnetic field, the experimental set up had to be carefully considered. The components closest to the magnet will be experiencing well over 1000 G field. At this field, any component relying on magnetic parts for motion becomes useless and any loose
components will either be pulled into the magnet or, at the very least, their alignment altered. Therefore, all non-magnetic components need to be used. The experimental setup can be seen in figure 6.5. The experimental setup provides the necessary spot size required by the samples (which is determined by the size of the spatial filter). Using a 30 cm and 3 cm lens pair, the size of the 1 inch by 1 inch four beam box from the MONSTR’s output is sufficiently reduced to pass through the aspherical lens near the center of its optical axis. Too much deviation from the center degrades the quality of the lens giving undesired results. The aspherical and collimating lens located inside the magnet are in two aluminum lens tubes which are mounted on two non-magnetic translation stages. These non-magnetic translation stages are used to adjust the focus to the sample plane and to collimate the signal after the sample. The signal is then sent through an analyzing polarizer and collected in either a
Figure 6.5: Experimental setup used in conjunction with the magnet. All components are either non-magnetic, or rated to use used in the stray field based on their locations. Pol: Linear Polarizer, FM: Flip Mirror, Asphere: aspherical Lens. The two tubes attaching to the two-dimensional translation stages are aluminum tubes which house the aspherical lens and the 5 cm lens. Although the MONSTR’s output is four beams, the beam path is simplified for clarity. The signal can be sent to either a single channel detector or a spectrometer.

A second optical branch is shown for imaging the sample. Imaging the sample needed to be possible while the beams are focused onto the sample to verify the correct location is being probed. The imaging path uses a broadband “collimated” white light source (top right) and sent through the collection side of the sample. Using a flip mirror, the image can be seen but the signal will be blocked. Once the correct area of the sample is identified and targeted, the flip mirror can switch orientations, allowing the signal to pass to the detector. After the white light passes through the sample, it is collected by the 4 cm aspherical lens and passes to the 8%/92% (R/T) pellicle beam splitter. A pellicle beam splitter was used to remove the double image created by a traditional beam splitter. The reflected light is then sent through a lens and into a CCD camera where the image is recorded. The reflected light of the laser focal point on the sample follows the same path, allowing for both the image and laser spot to be seen at the same time. The second white light source below the MONSTR
can be used for absorption measurements. Again, the white light source will be guided into the optical path by a flip mirror. However, for the absorption measurement the 3 cm lens and the spatial filter need to be removed to obtain a small spot size.

6.2.2 Cryostat Holder

The final piece for the experimental setup that needed to be designed is the cryostat holder. Several restrictions were placed on the design in order to reduce vibrations at the sample and allow for motion to properly identify and target the samples. The cryostat needed to be decoupled from the magnet along with the table that the magnet sits on so that no vibrations from the magnet are transferred to the cryostat. Additionally, the cryostat is going to be cooled by a closed-cycle cryocooler system with recirculating helium gas. This system has additional space requirements on the cryostat holder that need to be left open so the connections can be made. In order to accomplish this, the cryostat holder seen in figure 6.6 was designed.

The cryostat is clamped to the carriage which sits in two alignment grooves to allow for horizontal translation. The translation is controlled by a fine-threaded screw seen between the two alignment grooves in figure 6.6. The horizontal translation portion of the mount is fit in 4 alignment grooves (not seen) on the cross bars. These horizontal bars support the entire system. The spacing between the support rails was chosen as to accommodate the space needs for the cryocooler connections. Two fine-threaded screws are on each side of the cross-bars allow for vertical motion. The four cross-bars attach to the two optical tables adjacent to the table that the magnet is mounted to. The four feet have vibration damping elastomer under them to further isolate the mounting system from any table vibrations. The entire system is made of non-magnetic materials so that the magnetic field does not influence the system.
Figure 6.6: Cryostat mounting bracket which suspends the cryostat above the magnet allowing the tail to be centered in the bore. The holder has X-Z translation capabilities using non-magnetic fine-threaded screws. The mounting carriage is attached to two cross bars which mount to two optical tables that are adjacent to the magnet.

6.2.3 Preliminary Results

In order to verify that (a) the sample can be imaged, (b) the sample can be located, and (c) basic measurements performed, a simple absorption measurement was performed on two different sections of a MoSe$_2$ - WSe$_2$ heterostucture sample. The sample was prepared by Dr. Xu et al. at the University of Washington - Seattle and is a MoSe$_2$ - WSe$_2$ heterostucture encapsulated in BN seen in fig 6.7(b). Using a broadband white light source, the light was focused down to a spot size of $\sim$5 microns. Then, using the X-Z translation stages on the cryostat mount, the sample was located. Once it was located, two locations were chosen to run the measurements on; one that is just an MoSe$_2$ monolayer, and one on the heterostructure. The results from these two measurements can be seen in figure 6.7(a,c).
Figure 6.7: Preliminary absorption results taken at 2.2 K and zero applied external field. In (a), the normalized absorption data on an MoSe$_2$ sample sandwiched between two layers of BN. Two peaks are seen in the absorption data at 758 nm (1.640 eV) and 673 nm (1.842 eV) which corresponds to the A and B exciton, respectively [169]. (b) Image of MoSe$_2$ - WSe$_2$ heterostructure with measurement locations labeled. (c) Absorption data on the heterostructure. Three features are seen at 767 nm (1.614 eV), 758 nm (1.64 eV), and 733 nm (1.6913 eV).

Figure 6.7(a) is the absorption results for the MoSe$_2$ monolayer taken at position (a) on the sample. The measurements were taken at 2.2 K. Two features can be seen, one at 758 nm (1.636 eV) and another at 673 nm (1.842 eV), which corresponds to the A- and B- exciton peaks, respectively [169]. Since no additional features from WSe$_2$ or the interaction on the heterostructure are seen, it can be said with confidence that only the MoSe$_2$ monolayer was correctly targeted. In (c), the absorption results from the heterostructure at position (b) on the sample is seen. Here, three features are located at 767 nm (1.616 eV), 758 nm (1.636 eV), and 733 nm (1.691 eV). The two main peaks correspond to the A-exciton for WSe$_2$ (733 nm) and MoSe$_2$ (767 nm). The MoSe$_2$ peak is red-shifted compared to the peak in figure (a) due to the change in the dielectric environment [170] (in (a), the MoSe$_2$ layer has BN on the top and bottom, in (c) it has BN on the bottom and WSe$_2$ on the top). The third peak at 758 nm, matches to that of the MoSe$_2$ monolayer. This leads to the conclusion that some light leaked off of the heterostructure and onto just the MoSe$_2$ layer.
6.3 Conclusion

The success of this simple measurement shows proof of principle for performing more complicated measurements using this system as a basis. This system allows for the location and identification of samples a few microns in size, targeting of said samples, and the ability to perform measurements in an external applied magnet field. Additionally, the unintentional effects of the magnet (stray field, vibrations, etc) have been accounted for as much as possible with the design of the cryostat mount and experimental setup.
Chapter 7

Conclusion and Future Work

In this dissertation, the linear and non-linear optical properties of TMDs were explored. First, the absorption properties at the A - excitonic resonance was measured for two representative TMDs, MoSe$_2$ and WSe$_2$. The measurements were performed on a varying number of layer thicknesses ranging from monolayer up to bulk. By measuring the absolute absorption percentage for each material, the results was compared with the prediction from the Beer-Lambert Law. It was found that the system does not follow the Beer-Lambert Law, as it does not account for radiative coupling effect. Theoretical calculations were performed, which included radiative coupling to accurately reproduce the results. Additionally, it was found that for a range of layer thicknesses ($10 < N < 90$ for MoSe$_2$ and $10 < N < 60$ for WSe$_2$) the radiative coupling was superradiant in nature (details in chapter 4). In order to confirm this effect was not a surface effect, the diamagnetic shift was measured for both materials. It was found to be $0.12 \, \mu\text{eV/T}^2$ for MoSe$_2$, $0.77 \, \mu\text{eV/T}^2$ for WSe$_2$. From the diamagnetic shift, the lateral exciton size was calculated to be $1.21 \, \text{nm}$ and $2.44 \, \text{nm}$ for MoSe$_2$ and WSe$_2$, respectively. Since the natural layer thickness is $6.5 \, \text{Å}$ for both of these materials, surface effects can confidently be ignored after $\sim$7 layers.

Furthermore, the non-linear optical properties of MoSe$_2$ were explored in an applied external field. Using a CVD grown MoSe$_2$ monolayer, dephasing measurements were made up to 25 T using several different polarization schemes. Firstly, using a co-linear polarization scheme, TI-FWM measurements were run at no external field and 10 T. These measurements show a clear increase in both the negative and positive delay signals in the presence of
an external field. The increase is caused by the discretization of the energy levels which reduces the excitonic scattering, and in turn, increasing the dephasing time. Furthermore, two circular polarization schemes were used, co-circular and cross-circular. These schemes were used to probe valley selection effects on the dephasing times. When using co-circular polarization, excitons only in the $K$ valley were excited whereas when using cross-circular polarization, excitons in both the $K$ and $K'$ valleys were excited. The measurements and corresponding simulations showed that the increase in the negative delay signal at 25 T is almost entirely caused by the biexciton. Specifically, for the cross-circular case, the positive delay is also dominated by the biexciton. For the co-circular case, the positive delay has contributions from both the exciton and biexciton. This effect is attributed to two main causes: (1) the presence of additional carriers increases the screening which slows down the dephasing of the biexciton, (2) the applied external field splits the energy levels which further reduces scattering which allows for multiple exciton correlations to form more easily.

Finally, an experimental setup was presented along with proof of principle results. The system is designed around a high spatial resolution setup with an applied external magnetic field up to 7.5 T. Several details about the magnet were discussed, including the physical magnet (size, footprint, capabilities, etc), the cooling and charging information, and the stray field and their effects on equipment. These details highlighted the constraints on the experimental setup and potential concerns that needed to be accounted for. A mounting system for the cryostat was developed with two dimensions of motion, built out of all non-magnetic components. The experimental setup was then presented, which allowed imaging micron-sized samples, movement of the cryostat for targeting samples, and a focused laser spot size on the order of $\sim 10$ microns. Preliminary results were presented in the form of absorption measurements on a MoSe$_2$ / WSe$_2$ heterostructure.
7.1 Future Direction

From recent experimental results, exploring the optical properties of stacked TMD monolayers into heterostructures is a possible avenue. With these heterostructures already being fabricated, many new experiments are already being performed [10, 47, 135, 138, 170–173]. By exploring these heterostructures via photoluminescence an interlayer exciton has been discovered [170, 173]. Additionally, heterostructures are showing promise in photovoltaic devices [10]. Based on the results presented in this dissertation as well as other works [145, 147, 148, 155], applying an external field to these materials could provide some interesting insight into the interaction of these interlayer excitons. A system in development to perform these measurements was presented in chapter 6.
Bibliography


Appendix A

Perturbative Expansion of the Optical Bloch Equations

The optical Bloch Equations, presented in chapter 3.5, can be solved through a perturbative expansion. In the expansion, the lower order density matrix element is inserted into the higher order and integrated. In this appendix, this will be performed for a three level system with the ground state \( |g\rangle \), exciton, \( |e\rangle \) and biexciton \( |d\rangle \) for phase matched direction \( \mathbf{k}_S = -\mathbf{k}_A + \mathbf{k}_B + \mathbf{k}_C \) and double-sided Feynman Diagram seen in figure A.1.

To begin, the third order density matrix element, \( \rho_{e\!g}^{(3)} \) is calculated by [101,174]:

\[
\rho_{e\!g}^{(3)} = \frac{i\mu_{eg}}{2\hbar} \int_{-\infty}^{t} dt'' e^{-i(\omega_{eg}-i\gamma_{eg})(t-t'')} \hat{E}_C(t'') e^{-i\omega_C t''} \\
\times \frac{-i\mu_{ge}}{2\hbar} \int_{-\infty}^{t''} dt'' e^{-i(\omega_{ge}-i\gamma_{ge})(t''-t')} \hat{E}_B(t'') e^{-i\omega_B t''} \\
\times \frac{-i\mu_{ge}}{2\hbar} \int_{-\infty}^{t''} dt'' e^{-i(\omega_{ge}-i\gamma_{ge})(t''-t')} \hat{E}_A^{*}(t') e^{i\omega_A t''} \rho_{gg}^{(0)}
\]

(A.1)

where the \( \mu_{ij}, \omega_{ij}, \) and \( \gamma_{ij} \) are the dipole moment, transition frequency and dephasing rate between state \( i \) and \( j \), respectively. The first integral (w.r.t. \( t' \)) second integral (w.r.t. \( t'' \)) and third integral (w.r.t. \( t''' \)) correspond to the interaction of pulse \( A^*, B, \) and \( C \) with the system, respectively. The field is defined as \( E_i = \hat{E}_i(t) e^{-i\omega_i t} \) for \( i = A,B,C \) and * indicating the complex conjugate pulse. Equation A.1 can be simplified by making the substitution \( \mathbf{k}_S = -\mathbf{k}_A + \mathbf{k}_B + \mathbf{k}_C \), and using the fact that \( \omega = \omega_A = \omega_B = \omega_C \):

\[
\rho_{e\!g}^{(3)} = \rho_{gg}^{(0)} \frac{-i\mu_{eg}\mu_{ge}}{8\hbar^3} e^{i\mathbf{k}_S \cdot \mathbf{r}} e^{-i(\omega_{eg}-i\gamma_{eg})t} \\
\times \int_{-\infty}^{t} dt'' e^{-i(\omega-\omega_{ge}+\omega_{ge})t''} e^{(\gamma_{eg}-\gamma_{ge})t''} \hat{E}_C(t'') \\
\times \int_{-\infty}^{t''} dt'' e^{-i(\omega_{ge}+\omega_{ge})t''} e^{(\gamma_{ge}-\gamma_{ge})t''} \hat{E}_B(t'') \\
\times \int_{-\infty}^{t''} dt'' e^{-i(\omega_{ge}+\omega_{ge})t''} e^{(\gamma_{ge})t''} \hat{E}_A^{*}(t')
\]

(A.2)

In order to solve these integrals, the assumption that the pulse duration is much shorter than the system dynamics is made. In this case, the electric field can be approximated as \( \hat{E}_i = E_i \cdot \delta(t-t_i) \) where \( t_i \) is the arrival time of pulse \( i \). This simplifies the previous equation to:

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\[ \hat{\rho}^{(3)}_{eg} = \rho_{gg}^{(0)} \frac{-i \mu_{eg} \mu_{ge} \mu_{ge}}{8 \hbar^3} e^{i k S \cdot r} E_A^* E_B E_C \cdot \Theta(t) \Theta(T) \Theta(\tau) \]
\[ e^{-(\gamma_t - \gamma_{gg} - \gamma_{ge} - \omega_{gg}T)} e^{i (\omega_t - \omega_{eg})t} e^{-i (\omega_t - \omega_{ge})\tau} \] (A.3)

where \( t \equiv t - t_C \), \( T \equiv t_C - t_B \), and \( \tau \equiv t_B - t_A \), \( \Theta(T) \) is the Heaviside function, and \( \hat{\rho}^{(3)}_{eg} = \rho^{(3)}_{eg} e^{i \omega t} \). To obtain the third order polarization, \( \hat{P}^{(3)} \), the trace of the density matrix with the dipole operator \( \mu \) needs to be performed, according to equation 3.50. Additionally, to account for any inhomogeneity in the distribution of frequencies, the resulting density matrix element needs to integrated over a two-dimensional Gaussian:

\[ \hat{P}^{(3)}_{eg} = \frac{N \mu_{eg} \sqrt{a_{11}a_{22} - a_{12}^2}}{\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega_{eg} d\omega_{ge} \hat{\rho}^{(3)}_{eg} \cdot e^{[a_{11}(\omega_{eg} - \omega_{c,eg})^2 + 2a_{12}(\omega_{eg} - \omega_{c,eg})(\omega_{ge} - \omega_{c,ge}) + a_{22}(\omega_{ge} - \omega_{c,ge})^2]} \] (A.4)

where the Gaussian is centered at frequencies \( \omega_{c,eg} \) and \( \omega_{c,ge} \). Making the substitutions:

\[ R = \frac{a_{12}}{\sqrt{a_{11}a_{22}}} \]
\[ \delta \omega_{eg} = \sqrt{\ln(2) \frac{a_{22}}{a_{11}a_{22} - a_{12}^2}} \]
\[ \delta \omega_{ge} = \sqrt{\ln(2) \frac{a_{11}}{a_{11}a_{22} - a_{12}^2}} \] (A.5)

The variables \( R \) is the correlation between \( \omega_{eg} \) and \( \omega_{ge} \) and \( R = 1 \) for perfect correlation.
and $R = 0$ means there is no correlation. $\delta \omega_{eg}$ and $\delta \omega_{ge}$ are the half-width at half-maximum of the two-dimensional Gaussian. Finally, the integral in equation A.4 can be performed to yield:

$$
\hat{P}_{eg}^{(3)} = \rho_{gg}^{(0)} \frac{-i \mu_{eg} \mu_{ge} \mu_{ge}}{8 \hbar^3} e^{i k_S \cdot r} E_A^* E_B E_C \cdot \Theta(t) \Theta(T) \Theta(\tau) \\
\times e^{-i(\omega - \omega_{ge}^c) \tau} \cdot e^{i(\omega - \omega_{eg}^c) t} \cdot e^{-\gamma_{eg} t - \gamma_{gg} t - \gamma_{ge} \tau - i \omega_{gg} T} \\
\times e^{-1/4 \ln(2)[(\delta \omega_{ge} \tau)^2 - 2 R \delta \omega_{ge} \delta \omega_{eg} \tau t + (\delta \omega_{eg} t)^2]}
$$

(A.7)

The resulting expression is the third order polarization for the one double-side Feynman diagram shown at the beginning of this appendix. A similar calculation can be performed for each diagram to obtain the total third-order polarization. Or, the variables can be substituted in based on the different states in each Feynman diagram taking into account the correct sign.
Appendix B

Supporting Experimental Results for Absorption Measurements

B.1 AFM measurements for MoSe$_2$ and WSe$_2$ samples

The Atomic Force Microscopy measurements performed on all of the MoSe$_2$ and WSe$_2$ samples can be seen in figure B.1 and B.2 and were used to characterize the sample surfaces as well as thickness. For the monolayer samples, photoluminescence and Raman spectroscopy was also performed to confirm the AFM scans. The red circle in each scan shows the approximate size of the white light spot to further confirm that light did not leak around the sample. It additionally indicates the location the measurement was performed on the sample. The measurements were performed on the most uniform part of the sample and away from areas where different layer thicknesses were present. The number of layers was calculated using an interlayer spacing of 6.5 Å.
Figure B.1: AFM measurements performed on all MoSe$_2$ samples. The red circle indicates the approximate size of the white light spot and location the measurement was taken on the sample.
Figure B.2: AFM measurements performed on all WSe$_2$ samples. The red circle indicates the approximate size of the white light spot and location the measurement was taken on the sample.
B.2 Absolute Absorption Measurements Comparison

The experimental and theoretical absorption spectra comparison for all samples can be seen in figures B.3, B.4, B.5, and B.6. In each plot, the transmission (black line), the reflection (red line) and absorption (blue line) spectra are shown.

Figure B.3: Experimental and theoretical transmission, reflection and absorption spectra for MoSe$_2$ samples.
Figure B.4: Experimental and theoretical transmission, reflection and absorption spectra for MoSe$_2$ samples.
Figure B.5: Experimental and theoretical transmission, reflection and absorption spectra for WS\textsubscript{e}\textsubscript{2} samples.
Figure B.6: Experimental and theoretical transmission, reflection and absorption spectra for WSe$_2$ samples.
Appendix C

Microscopic Theory of Radiatively Coupled Excitons

In order to model the experimental results presented in chapter 4, a semi-classical theory of radiatively coupled two-dimensional excitons based on the semiconductor Maxwell-Bloch equations is used. Screening and radiative coupling is included dynamically for the bands under consideration (4 band model, top two valence and bottom two conduction), whereas all other bands, as well as the dielectric environment are contained in the background dielectric tensor \[134\]. Starting from the following approach for the dielectric displacement field:

\[
D = \epsilon_\parallel E_\parallel + \epsilon_\perp E_z e_z + 4\pi P, \tag{C.1}
\]

where \(\epsilon_\parallel\) and \(\epsilon_\perp\) is the in-plane and out-of-plane background dielectric constants and \(P\) is the non-local, time and frequency dependent resonant contributions of the bands under consideration.

Using the Coulomb gauge, \(\epsilon_\parallel \nabla_\parallel \cdot A_\parallel + \epsilon_\perp \partial_z A_z = 0\), and restricting the results to light propagating along the c-axis, the wave equation for the transverse optical field and the Poisson’s equation for the scalar potential are obtained:

\[
(-\partial^2_z - \epsilon_\parallel (z) \frac{\omega^2}{c^2}) E_T^\parallel (z, \omega) = 4\pi \frac{\omega^2}{c^2} P_T^\parallel (\omega) \tag{C.2}
\]

\[
(-\epsilon_\perp \partial^2_z + \epsilon_\parallel q^2_\parallel) \phi(q_\parallel, z) = 4\pi (\rho - \nabla \cdot P^L), \tag{C.3}
\]

where \(E_T = -\frac{1}{c} \dot{A}\), \(E^L = -\nabla \phi\), \(A\) and \(\phi\) are the vector and scalar potential, and the superscripts \(T\) and \(L\) are for the transverse and longitudinal contributions.

The resonant contribution from each layer is approximated as:

\[
P = \sum_n P_{n\parallel} \delta(z - z_n), \tag{C.4}
\]

where \(z_n = (n - 1/2)d\) and is the center position of layer \(n\), \(d\) is the layer to layer spacing, and \(P_{n\parallel}\) is the polarization contribution for layer \(n\). The radiative coupling effects is seen as the interaction of the emitted light from the individual layers with the light from all layers \[93\]. This can be seen in the following equation:

\[
E_T^\parallel (z_n, \omega) = E_m^\parallel (z_n, \omega) + 4\pi \frac{\omega^2}{c^2} \sum_m G_0(z_n, z_m, \omega) P_{m\parallel}^T(\omega) \tag{C.5}
\]

\(^1\)Contents of this appendix are published in “C. E. Stevens et al. Optica 5, 749-755 (2018)”
\(^2\)c.g.s units are used throughout this appendix
where $E_{\parallel}^n(z,\omega)$ is the incoming field and $G_0(z,z',w)$ is the radiation from the embedded local oscillator. The transverse polarization, $P_{n\parallel}^T$ is related to the transverse optical field, $E_{\parallel}^T$, by $P_{n\parallel}^T(\omega) = \chi_{\parallel}^T(\omega)E_{\parallel}^T$ where $\chi_{\parallel}^T(\omega)$ is the transverse susceptibility of the $n$th layer. In order to calculate the transverse susceptibility, the massive Dirac Fermion model is used [38] where the system is adjusted for the hexagonal lattice for these materials.

Due to the symmetry the A-B stacking provides, the Brillouin zone of the overall system can be easily related by the layer index, $n$, using $\tau_n = \pm(-1)^n$. Therefore, the individual layer susceptibility needs to be calculated. This is done microscopically using the coupled gap equations and the Dirac-Bloch equations, described in [134]. Using this, there is only one free parameter, which is related to the thickness of a monolayer. The other parameters are obtained from density functional theory calculations. Therefore, the model can easily be switched from the full geometry (setting the interlayer spacing to 6.5 Å) or the superradiant geometry (artificially setting the spacing to 0).

Furthermore, for a monolayer embedded between two dielectrics with top and bottom refractive indices $n_T = \sqrt{\epsilon_T^{\parallel}}$ and $n_B = \sqrt{\epsilon_B^{\parallel}}$, the transmission $t(\omega)$ and reflection $r(\omega)$ coefficients can be related to the incoming light by:

$$t(\omega) = \frac{n_T}{(n_T + n_B)/2 - 2\pi i c \omega \chi_{\parallel}^T(\omega)}, \quad (C.6)$$

$$r(\omega) = t(\omega) - 1 \quad (C.7)$$

This leads to the true absorption coefficient for a monolayer:

$$\alpha(\omega) = \frac{4\pi n_T \omega c \text{Im}[\chi_{\parallel}^T(\omega)]}{| (n_T + n_b)/2 - 2\pi i c \chi_{\parallel}^T(\omega) |^2} \quad (C.8)$$
Appendix D

Theoretical Calculations for TI-FWM signal in External Magnetic Field

D.1 DFT Method for Modeling MoSe$_2$ Electronic Structure

D.1.1 Ground State Calculation

The electronic band structure for an MoSe$_2$ monolayer was calculated using static Density Functional Theory (DFT) calculations where spin-orbit coupling (SOC) and Van der Waals corrections are added. The results are seen in figure D.1(a). It can be seen that the SOC is 187.3 meV and 20.7 meV for the valence and conduction band, respectively, and the spin ordering is flipped. These calculations result in a band gap energy, $E_g = 1.45$ eV. These results are in good agreement with experimental measurements of 1.58 eV, 180 meV, and 10 meV for the band gap energy and valence band SOC splitting, and conduction band SOC splitting, respectively [175,176]. In figure D.1(b), a graphical representation of the bands at zero magnetic field is shown.

D.1.2 Finite Field Case

For applied magnetic fields $B \leq 25$ T, the magnetic field effect can be added as a perturbation to the system. The reasoning for this is two-fold. First, the magnetic length

$$l_B = \sqrt{\frac{\hbar}{eB}} = \frac{25.6}{\sqrt{B(T)}} \text{nm} \quad (D.1)$$

is always much less than the zero-field exciton radius for a monolayer ($\sim 1$ nm). Secondly, the cyclotron energy,

$$\hbar \omega_c = \hbar \sqrt{\frac{2v}{l_B}} \approx 0.01 \sqrt{B(T)} \text{eV} \quad (D.2)$$

is much smaller than the exciton binding energy of $\sim 0.5$ eV, and the band splitting. In equation D.2, $v \approx 10^6 \text{m/s}$ and is the "Fermi velocity".

Therefore, to model the effects of the magnetic field, in its lowest approximation, only the excited charge density is significantly affected. Thus, the Landau level splitting of both the electron and hole need to be taken into account. This is done as follows:

For a low energy four band system, the minimal Hamiltonian is:

$$\hat{H} = at(\tau k_x \sigma_x + k_y \sigma_y) + \frac{\Delta}{2} \sigma_z - \lambda_c \tau \sigma_z - \frac{1}{2} \hat{s}_z - \lambda_c \tau \sigma_z + \frac{1}{2} \hat{s}_z \quad (D.3)$$

\[1\]Contents of this appendix are published in “C. E. Stevens et al. Nat. Commun. 9, 3720 (2018), suppl. mat.”
Figure D.1: (a) Calculated electronic band structure for a MoSe$_2$ monolayer showing the splitting due to spin-orbit coupling. (b) Pictorial representation of K and K’ valley for monolayer MoSe$_2$ at zero magnetic field. The band colors represent their spin selection.

where $\sigma_z$ is the Pauli matrix operator, $\hat{s}_z$ is the spin projection matrix, $\Delta$ is the bandgap, $2\lambda_v$ and $2\lambda_c$ are the valence and conduction band splittings. Diagonalization of this Hamiltonian yields:

$$E_{\tau S_z}(k) = \frac{1}{2}(\lambda_v - \lambda_c)\tau S_z \pm \sqrt{\frac{a^2 t^2 k^2}{4} + \frac{1}{4}(\Delta - (\lambda_v + \lambda_c)\tau S_z)^2} \approx \begin{cases} \frac{\Delta}{2} - \lambda_c\tau S_z + \frac{(\Delta k)^2}{\Delta} (\text{con.}) \\
-\frac{\Delta}{2} + \lambda_v\tau S_z - \frac{\Delta}{\Delta} (\text{val.}) \end{cases}$$

(D.4)

where the “+” is for the conduction band and the “-” is for the valence band. Using values $\lambda_v \sim 0.09eV$, $\lambda_c \sim 0.01eV$, $t \sim 0.94eV$, and that $ak$ is significantly smaller then $\pi$, $\Delta \sim 1.47eV$ dominates on the left hand side of equation D.4. Therefore, the band splitting in each valley is $2\lambda_v$ for the valence band and $2\lambda_c$ for the conduction band but with different spin orderings ($\tau = 1$ or $\tau = -1$) for the K and K’ valley.

When an external field is applied, $\mathbf{k} \rightarrow \pi = \mathbf{k} + \frac{e}{c} \mathbf{A}$, in the Hamiltonian in equation D.3. Here, the magnetic field satisfies the Landau gauge $\mathbf{A}(\mathbf{r}) = (0, Bx)$. Considering the field is not sufficiently strong, $\pi_x + i\pi_y$ can be replaced with the lowering operator. This changes the bands into Landau levels and changes the squared kinetic energy ($a^2 t^2 k^2$) to $\hbar^2 \omega_c^2 n$, using the cyclotron energy above. Therefore, equation D.4 becomes:

$$E_n = \frac{1}{2}(\lambda_v - \lambda_c)\tau S_z \pm \sqrt{\hbar^2 \omega_c^2 n + \frac{1}{4}(\Delta - (\lambda_v + \lambda_c)\tau S_z)^2} \approx \begin{cases} \frac{\Delta}{2} - \lambda_c\tau S_z + \frac{\hbar^2 \omega_c^2 n}{\Delta} (\text{con.}) \\
-\frac{\Delta}{2} + \lambda_v\tau S_z - \frac{\hbar^2 \omega_c^2 n}{\Delta} (\text{val.}) \end{cases}$$

(D.5)

using $\hbar \omega_c \ll \Delta$.

This result is used as a correction term in the zero field DFT results for when field is applied thus changing the exciton-exciton and exciton-biexciton interactions. One conclusion that can be drawn is that splitting between Landau levels is small ($\sim 2$ meV @ 25 T) when compared to the band splitting (conduction band splitting = 20 meV). This conclusion is important in explaining the experimental results as it significantly effects the number of
excited charges (i.e. scatterers) for a given pulse. This can be seen in figure D.2. In the next section, the derivation of the TI-FWM spectrum is discussed.

D.2 Third-order Polarization Equations and TI-FWM signal

To begin, the Time-Dependent Density Functional Theory (TD-DFT) Kohn-Sham equation is used, and is:

\[
i \frac{\partial \Psi^V_k(r, t)}{\partial t} = \left[ -\frac{\nabla^2}{2m} + V_H[n(r, t)] + V_{XC}[n(r, t)] + e \cdot \vec{r} \cdot \vec{E}(t) \right] \Psi^V_k(r, t)
\]  

(D.6)

where the terms of the Hamiltonian can be described as: the kinetic energy operator, the Hartree and exchange-correlation (XC) potentials, and the electric field pulse. The indices \( v \) and \( k \) on \( \Psi \), correspond to the valence band index and the wave vector, respectively.

Equation D.6 needs to be solved in conjunction with the equation for the electron density seen below:

\[
n(r, t) = \sum_{l,|k|<k_F} |\Psi^I_k(l, t)|^2
\]  

(D.7)

where \( l \) is the band index. This can be accomplished by using the density matrix formalism, where the time dependent wave function is separated in the basis of the static wave function and a time-dependent coefficient as seen in the following equation:

\[
\Psi^V_k(r, t) = \sum_l c^I_k(l)(t) \psi^I_k(r)
\]  

(D.8)

here, \( c^I_k(t) \) completely describes the dynamics of the system. To better understand the systems response, its easier to look at the bilinear combination of the coefficients in the density matrix:

\[
\rho^{lm}_{kq}(t) = c^I_k(t)c^m_q(t)
\]  

(D.9)

In the density matrix, the diagonal elements describes the occupation of states and the off diagonal terms describes the electron and hole transitions as well as excitonic effects. Additionally, the density matrix satisfies the Liouville equation:

\[
i \frac{\partial \rho^{lm}_{kq}(t)}{\partial t} = [H(t), \rho(t)]^{lm}_{kq}
\]  

(D.10)

with matrix elements of the Hamiltonian have the form:

\[
H^{lm}_{kq}(t) = \int \psi^*_k(r)H[n(r, t)]\psi^m_q(r)dr
\]  

(D.11)
For the case of two different excitons, the equations for the third-order polarization are:

\[
i \frac{\partial}{\partial t} P_{1k}(t) = [\epsilon_k^c - \epsilon_k^{\ast}] P_{1k}(t) + 2 \sum_q \int_{-\infty}^{t} dt' F_{11kq}(t, t') P_{1q}(t') + d_k^{c1} E(t)
\]

\[
+ \sum_{q, p, Q} P_1^*(t) \int_{-\infty}^{t} dt' H_{11kqpQ}(t, t') P_{1p}(t') P_{1Q}(t')
\]

\[
+ \sum_{q, p, Q} P_{22}(t) \int_{-\infty}^{t} dt' H_{12kqpQ}(t, t') P_{1p}(t') P_{2Q}(t')
\]

\[
+ \sum_{q, p, Q} P_{1q}^*(t) \int_{-\infty}^{t} dt' F_{21kqpQ}(t, t') B_{12pqpQ}(t')
\]

\[
+ \sum_{q, p, Q} P_{22}(t) \int_{-\infty}^{t} dt' F_{22kqpQ}(t, t') B_{12pqpQ}(t')
\]

(D.12)

\[
i \frac{\partial}{\partial t} P_{2k}(t) = [\epsilon_k^v - \epsilon_k^{\ast v}] P_{2k}(t) + 2 \sum_q \int_{-\infty}^{t} dt' F_{22kq}(t, t') P_{2q}(t') + d_k^{v2} E(t)
\]

\[
+ \sum_{q, p, Q} P_1^*(t) \int_{-\infty}^{t} dt' H_{22kqpQ}(t, t') P_{2p}(t') P_{2Q}(t')
\]

\[
+ \sum_{q, p, Q} P_{1q}^*(t) \int_{-\infty}^{t} dt' H_{21kqpQ}(t, t') P_{2p}(t') P_{1Q}(t')
\]

\[
+ \sum_{q, p, Q} P_{2q}^*(t) \int_{-\infty}^{t} dt' F_{12kqpQ}(t, t') B_{21pqpQ}(t')
\]

\[
+ \sum_{q, p, Q} P_{1q}^*(t) \int_{-\infty}^{t} dt' F_{11kqpQ}(t, t') B_{21pqpQ}(t')
\]

\[
(D.13)
\]

where:

\[
F_{ijkqk'q'}(t - t') = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^\ast_k(\mathbf{r}_1) \psi_j^\ast_q(\mathbf{r}_1) f_{XC}(\mathbf{r}_1, \mathbf{r}_2, t - t') \psi_k^\ast_{k'}(\mathbf{r}_2) \psi_{q'}^\ast(\mathbf{r}_2)
\]

(D.14)

Here, \(F_{ii}\) represent the strength of the electron-hole interaction, and \(F_{ij}\) is the exciton-biexciton interaction strength. Additionally, \(H_{ij}\) describes the exciton-exciton interactions. Assuming the excitation fields are not strong, the pair-pair correlation functions of the four-particle part can be ignored and just the biexciton term included [177]. The last lines in equations D.13D.14, represent the biexciton contributions to the third-order polarization.
The exciton-exciton interactions \( (H_{ij} \text{ matrix elements}) \) are:

\[
H_{i_k q p Q}(t, t') = \frac{1}{3!} \iiint dr dr' dr'' \phi_k^* (r) \phi_q^* (r') \phi_p^* (r'') h_{XYC} (r, t; r', t; r'', t') \phi_p (r'') \phi_q (r') \phi_{Q} (r'') \phi_{Q} (r')
\]

and

\[
H_{i_j k q p Q}(t, t') = \frac{1}{3!} \iiint dr dr' dr'' \phi_k^* (r) \phi_q^* (r') \phi_p^* (r'') h_{XYC} (r, t; r', t; r'', t') \phi_p (r'') \phi_q (r') \phi_{Q} (r'') \phi_{Q} (r')
\]

\[
[D.15]

For the biexciton, like with the exciton, the wave function can be expanded in terms of two static wave functions and a time-dependent coefficient as follows:

\[
\Psi_{k_1 k_2} (r_1, r_2, t) = \sum_{l=v,c} D^{l_{k_1 k_2}}_{k_1 k_2} (t) \Psi^l_{k_1} (r_1) \Psi^m_{k_2} (r_2)
\]

Using this expansion, the density matrix for the two-particle states can be written as:

\[
\Gamma^{|ablcm}_{k_1 k_2 k_3 k_4} (t) = D^{ab}_{k_1 k_2} (t) C^{c}_{k_3} (t) C^{d}_{k_4} (t)
\]

\[
[D.18]

The equations of motion can directly be written using the definitions of \( C^{c}_{k} (t), -i \frac{\partial C^{c}_{k} (t)}{\partial t} = \sum_{m=v,c} C^{m*}_{k} (t) H^{m}_{k k} (t), \) and \( D^{ab}_{k_1 k_2} (t). \) Additionally, the biexciton component, for \( \Gamma^{|ablcm}_{k_1 k_2 k_3 k_4} (t) \equiv B^{|ablcm}_{k_1 k_2 k_3 k_4} (t), \) is:

\[
i \frac{\partial B^{c_{i} c_{j} \nu_{i} \nu_{j}}_{k_1 k_2 k_3 k_4}}{\partial t} (t) = (\epsilon_{k_1} + \epsilon_{k_2} - \epsilon_{k_3} - \epsilon_{k_4} - \frac{i}{\tau_{XXij}}) B^{c_{i} c_{j} \nu_{i} \nu_{j}}_{k_1 k_2 k_3 k_4} (t) + \sum_{q} F_{k_1 k_2 q q} B^{c_{i} c_{j} \nu_{i} \nu_{j}}_{q k_3 k_4} (t) + \sum_{q} F_{k_2 k_3 q q} B^{c_{i} c_{j} \nu_{i} \nu_{j}}_{k_1 k_4 q} (t)
\]

\[
+ \sum_{p q} w^{c_{i} c_{j} \nu_{i} \nu_{j}}_{k_1 p k_2 q} B^{c_{i} c_{j} \nu_{i} \nu_{j}}_{k_3 k_4} (t) + \sum_{p q} w^{c_{i} c_{j} \nu_{i} \nu_{j}}_{k_2 p k_1 q} B^{c_{i} c_{j} \nu_{i} \nu_{j}}_{k_3 k_4} (t) + \sum_{p q} w^{c_{i} c_{j} \nu_{i} \nu_{j}}_{k_3 p k_1 q} B^{c_{i} c_{j} \nu_{i} \nu_{j}}_{k_2 k_4} (t)
\]

\[
+ 2 F_{k_1 k_2 k_1} P_{k_1} (t) P_{k_2} (t) + F_{k_1 k_2 k_2} P_{k_1} (t) P_{k_2} (t)
\]

\[
+ 2 F_{k_2 k_1 k_2} P_{k_1} (t) P_{k_1} (t)
\]

the last two lines in equation D.19 are source terms.
In order to solve equations D.12, D.13 and D.19, the following definitions were used:

\[ h_{XCij}(r; t', r''; t', r''; t''; r'') = \]
\[ \delta(r - r')\delta(r' - r'')\delta(t - t')\delta(t'' - t'') \times \frac{\delta^2 f_{XC}^{Slater}(rt; r't')}{\delta n(r't'')\delta n(r''t'')} j_{XCij}(t - t'') \quad (D.24) \]

where

\[ f_{XC}^{Slater}(rt; r't') = -\frac{2|\Sigma_{j,k} \psi_j^*(r) \psi_k^*(r')|^2}{\epsilon |r - r'| n_0(r) n_0(r') \delta(t - t')} \quad (D.25) \]

and

\[ j_{XCij}(\omega) = \frac{1}{\omega - E_{XXij} + \frac{i}{\tau_{XXij}}} \quad (D.26) \]

where the static dielectric function, \( \epsilon \), and the excitonic basis equations, D.12, D.13 and D.19 become:

\[ (i \frac{\partial}{\partial t} - E_{X1} + \frac{i}{\tau_{X1}})P_1(t) = \]
\[ = d_1 E(t) + 3P_1^*(t) \int_{-\infty}^{t} dt' H_{11}(t, t') P_1(t') P_1(t') \]
\[ + 9P_2^*(t) \int_{-\infty}^{t} dt' H_{12}(t, t') P_1(t') P_2(t') + 9(F_{11}^* P_1^*(t) + F_{12}^* P_2^*(t)) B_{12}(t) \quad (D.27) \]

\[ (i \frac{\partial}{\partial t} - E_{X2} + \frac{i}{\tau_{X2}})P_2(t) = \]
\[ = d_2 E(t) + 3P_2^*(t) \int_{-\infty}^{t} dt' H_{22}(t, t') P_2(t') P_2(t') \]
\[ + 9P_1^*(t) \int_{-\infty}^{t} dt' H_{21}(t, t') P_2(t') P_1(t') + 9(F_{12}^* P_2^*(t) + F_{11}^* P_1^*(t)) B_{21}(t) \quad (D.28) \]

\[ (i \frac{\partial}{\partial t} - E_{12}^{XX} + \frac{i}{\tau_{12}^{XX}})B_{12}(t) = \]
\[ 3F_{21} P_1(t) P_1(t) + 6F_{11} P_1(t) P_2(t) + 6F_{22} P_2(t) P_1(1) + 3F_{12} P_2(t) P_2(t) \quad (D.29) \]
\[
(i \frac{\partial}{\partial t} - E_{21}^{XX} + \frac{i}{\tau_{X21}})B_{21}(t) = 3F_{12}P_2(t)P_2(t) + 6F_{22}P_2(t)P_1(t) + 6F_{11}P_1(t)P_2(1) + 3F_{21}P_1(t)P_1(t)
\]  
(D.30)

where \(E_{Xi}\) and \(E_{XXij}\) are the energies for the \(i^{th}\) exciton and \(ij^{th}\) biexciton. Similarly, \(\tau_{Xi}\) and \(\tau_{XXij}\) are their lifetimes. \(d_i\) is the dipole moment of the transition in the i’s valley. Additionally,

\[
H_{ij}(t, t') = \frac{1}{3} \int dr |\psi_{K_i}^{ci}(r)\psi_{K_i}^{vi}(r)|^2 h_{XC}(r)|\psi_{K_j}^{cj}(r)\psi_{K_j}^{vj}(r)|^2 e^{-i(E_{XXij} - \frac{i}{\tau_{XXij}})(t-t')}
\]  
(D.31)

which uses the kernel

\[
h_{XC}(r) = \delta(r - r')\delta(r - r'')\delta(r - r''')\frac{\delta^2 f_{Slater}^{Slater}(r, r')}{\delta n(r')\delta n(r'')}
\]  
(D.32)

In the reproduction of the data, the excitonic decay times were chosen to be 170 fs (co-circular), 228 fs (cross-circular) in the zero field case. These values are in good agreement with other estimations and experimental results [180, 181]. For the 25 T case, 184 fs (co-circular) and 359 fs (cross-circular) were used. Additionally, the biexcitonic decay times used are twice as small as the exciton decay times. The longer times used in the applied field case is due to the reduction in excited carriers (see appendix D.1) which causes reduced screening and longer lifetimes. The difference in the values due to polarization is attributed to the excitons attracting stronger in the cross-circular case compared to the co-circular case.

To obtain the final TI-FWM spectrum, the equations of motion are solved yielding the third order polarization, \(P^3\), which in turn is used in the following equation:

\[
I(\tau, T = 0) = \int_0^\infty |P^3(\tau, T = 0)|^2 dt
\]  
(D.33)

which results in the final TI-FWM spectrum.
Figure D.2: Diagram of the magnetic field effect on the absorption spectra for a MoSe$_2$ monolayer. As the magnetic field increases, the spacing between levels increases linearly. This causes less carriers to be excited for a given excitation pulse. Therefore, less scatterers will be present, increasing the relaxation times.
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