Light-matter interaction in 2D transition metal dichalcogenide heterostructure : magneto photoluminescence, lasing, and photocurrent

Rasmita, Abdullah

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**LIGHT-MATTER INTERACTION IN 2D TRANSITION
METAL DICHALCOGENIDE HETEROSTRUCTURE:
MAGNETO PHOTOLUMINESCENCE, LASING, AND
PHOTOCURRENT**

ABDULLAH RASMITA

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

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MAGNETO PHOTOLUMINESCENCE, LASING, AND
PHOTOCURRENT**

ABDULLAH RASMITA

SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree of professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

07 January 2020

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I have reviewed the content and presentation style of this thesis and declare it of sufficient grammatical clarity to be examined. To the best of my knowledge, the thesis is free of plagiarism and the research and writing are those of the candidate's except as acknowledged in the Author Attribution statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Weibo Gao

Authorship Attribution Statement

This thesis contains material from 3 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 2.1 contains material from C. Jiang, W. Xu, A. Rasmita, Z. Huang, K. Li, Q. Xiong, and W.B. Gao. Microsecond dark-exciton valley polarization memory in two-dimensional heterostructures. *Nature communications* **9(1)**, 753 (2018). DOI: 10.1038/s41467-018-03174-3.

The contributions of the co-authors are as follows:

- The overall project is supervised by Prof. W.B. Gao and Prof Q. Xiong.
- The initial idea and the experiment design are done by C. Jiang and Prof. W.B. Gao.
- The samples are prepared by W. Xu.
- The SHG experiment is done by W. Xu.
- The time-resolved and steady state magneto PL are performed by C. Jiang and Z. Huang.
- The data analysis is done by me and C. Jiang.
- The numerical modeling and theoretical works are contributed by me.
- K. Li gave support for the PL experiment.
- The manuscript is written by me, C. Jiang, W. Xu, Prof. W.B. Gao, Prof. Q. Xiong, and Z. Huang. It is reviewed and modified by all authors.

Chapter 2.2 contains material from C. Jiang, A. Rasmita, W. Xu, A. Imamoğlu, Q. Xiong, and W.B. Gao, Optical spin pumping induced pseudomagnetic field in two-dimensional heterostructures. *Physical Review B* **98(24)**, 241410 (2018). DOI: 10.1103/PhysRevB.98.241410.

The contributions of the co-authors are as follows:

- The overall project is supervised by Prof. W.B. Gao and Prof Q. Xiong.
- The experiments are designed by me, C. Jiang, and Prof. W.B. Gao.
- The samples are prepared by W. Xu.

- The experiments and the analysis of the data are done by me and C. Jiang.
- The theoretical works are contributed by me and Prof. A. Imamoğlu.
- The numerical simulation is done by me.
- The manuscript is written by me, C. Jiang, Prof. W.B. Gao, and Prof. A. Imamoğlu. It is reviewed and modified by all authors.

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The contributions of the co-authors are as follows:

- The project is supervised and conceived by Prof. W.B. Gao, Prof. J. Liu, and Prof. N. Zheludev.
- The personnel doing the experiments are Y. Liu and Y. Zhou.
- The cavity fabrication is done by H. Fang, Prof. J. Li, and Prof. J. Liu.
- The theoretical works are carried out and conceived by me.
- The results are analyzed and discussed by Prof. W.B. Gao, Prof. T. Yu, and Prof. Q. Xiong along with other authors.
- The manuscript is written by Prof. W.B. Gao, Prof. T. Yu, and Prof. Q. Xiong, along with other authors.

Chapter 4 contains material from A. Rasmita, C. Jiang, H. Ma, Z. Ji, R. Agarwal, and W.B. Gao. Circular photogalvanic effect in 2D van der Waals heterostructure. (Remark: not published in peer-reviewed journal/conference yet. The preprint version can be found at <https://arxiv.org/abs/1910.13118>.)

The contributions of the co-authors are as follows:

- The work is supervised by Prof. W.B. Gao.
- The initial idea and the experiment design are done by C. Jiang
- The heterostructure samples are prepared by H. Ma.
- The experiments are done by C. Jiang.
- The data analysis is done by me and C. Jiang.

- The theoretical works including the numerical simulations are done by me.
- The manuscript is written by me along with other authors.

07 January 2020

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Date

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Abdullah Rasmita

Abstract

The two-dimensional (2D) transition metal dichalcogenide (TMD) features many properties that are desirable for applications in spintronics and valleytronics, as well as in excitonic devices, all of which aims for more energy-efficient devices. Moreover, even richer physical phenomena involving interlayer interaction can be observed when two TMD monolayers are stacked together creating, the 2D TMD heterostructure.

This thesis presents the study of several aspects of the interaction between matter and light in the two-dimensional TMD heterostructure. First, the study regarding the $\text{MoSe}_2/\text{WSe}_2$ interlayer exciton dynamics under circularly polarized excitation and magnetic field influence is presented. We show that the interlayer exciton dynamic is affected by the dark WSe_2 exciton. Moreover, we found that the interlayer exciton transition energy corresponding to maximum transition strength depends on the excitation polarization indicating a large optically induced pseudomagnetic field.

Next, the study of the interaction between the $\text{MoS}_2/\text{WSe}_2$ interlayer exciton with light inside a cavity is presented. We show that the long interlayer exciton lifetime enables an excitonic laser with ultralow threshold power even with a low Q-factor cavity.

Lastly, we show that the circular photogalvanic effect (CPGE) can be generated at the boundary between the 2D $\text{MoS}_2/\text{WSe}_2$ heterostructure and a metal electrode. The observed CPGE is due to the valley-dependent shift of the valence band induced by the combination of the built-in electric field and the optical selection rule of the valley as well as the different effective relaxation times between electron and hole in the 2D heterostructure.

The findings presented in this thesis may be useful for realizing opto-valleytronics, opto-spintronics, as well as excitonic device applications which is based on 2D TMD heterostructure as a platform. We discuss several possible future research directions based on these findings.

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Chapter 1. Introduction

1.1. Background and motivation

Since the graphene discovery, many other classes of 2D material has been found. This includes other single-element 2D material such as 2D black phosphorous¹ and silicene² and compound 2D material such as 2D transition metal dichalcogenide (TMD)³ and 2D hexagonal boron nitride (hBN)⁴. Moreover, due to the absence of dangling bonds, 2D materials can be put on top of each other and weakly bonded by utilizing the van der Waals forces creating the 2D layered material⁵, which offer even richer physics. For example, it is found that by stacking two graphene layers on top of each other at a certain angle, a high-temperature superconducting state can be created⁶. Another example of the rich physics in the 2D layered material is the creation of the Moiré superlattice by stacking two 2D TMD material^{7,8} with the possible application includes the creation of Moiré-based quantum emitter array⁹. Additionally, the proximity effect between the 2D materials in the 2D heterostructure can result in the modification of the property of each constituent layer¹⁰. For example, stacking 2D TMD with graphene enables the induction of more spin-orbit coupling into the layer of graphene¹¹, which is desirable in realizing the graphene spintronics device.

Regarding the 2D TMD material class, it has been well-known for its remarkable properties. Unlike graphene and the 3D TMD, the 2H-phase 2D TMD material with formula MX_2 (X: Se or S and M: W or Mo) is a direct bandgap semiconductor³. This enables its utilization in studying the interaction between matter and light in the two-dimensional regime. Compared to the 3D regime, the dielectric screening at the 2D regime is significantly reduced. This enables the creation of electron-hole pair (exciton) with a large binding energy of several hundred meV, which is much bigger than the room temperature thermal energy¹². Such property is highly sought for the creation of room temperature excitonic devices.

Additionally, unlike in the conventional GaAs semiconductor, the bandgap of the 2D TMD material is located at the $\text{K}(\text{K}')$ valley¹³. The heavy transition metal element has a strong spin-orbit coupling. Because of this, at the $\text{K}(\text{K}')$ valley, the valley and spin are locked, i.e., one valley couple strongly to one specific spin species¹⁴. Moreover, only

light with certain circular polarization couples to each valley, enabling the control of both valley and spin degrees of freedom by manipulating the optical excitation polarization¹⁵⁻¹⁸. This shows that the 2D TMD material is a promising platform for realizing not only the excitonic devices but also the spintronics and valleytronics devices. The development of these devices can result in more energy-efficient information processing devices.

Significant works have been done on understanding the interaction between matter and light in 2D TMD monolayer as well as making use of the unique properties of 2D TMD monolayer to create useful devices. Previous works related to the light-matter interaction in 2D TMD heterostructure have shown that the control of the exciton energy can be performed using an external magnetic field^{19,20}. Moreover, when an ultrafast laser is used, the optical excitation can induce a significant pseudomagnetic field, which also affects the energy of the exciton²¹. Related to the valleytronics and spintronics application, optical valley Hall effect²² and the circular photogalvanic effect (CPGE)^{23,24} have been demonstrated. Regarding photonic devices, light-emitting diode²⁵, photon detectors²⁶, and excitonic laser²⁷⁻³⁰ based on the 2D TMD have been demonstrated.

The 2D TMD heterostructure is created by putting one 2D TMD monolayer on top of another monolayer consisting of different TMD. Depending on the band alignment between the layers, it is possible that the holes and electrons prefer to be in different layers, creating the so-called interlayer exciton that has lower energy compared to the exciton in the individual monolayer³¹. Hence, it is possible to modify the optical emission by layer engineering. Moreover, the hole-electron layer separation causes this interlayer exciton to have a longer lifetime (~ 100 ns³²) compared to the intralayer exciton (in the order of picosecond³³). A long exciton lifetime is important in many applications, including excitonic devices³⁴. This carrier layer separation can also result in enhanced electron-electron interaction as well as phenomena associated with the asymmetry between electron and hole dynamics.

1.2. Objective

Despite the many theoretical and experimental studies on the 2D TMD heterostructure, there are still many questions to be answered, especially related to the exciton and carrier

dynamics in this system. This thesis' main goal is to study both the exciton and carrier dynamic when the 2D TMD heterostructure is optically excited. In particular, the following outstanding problems are considered:

1. A long valley (polarization) lifetime is necessary for valleytronics. Even for the bright interlayer exciton, the valley polarization lifetime is still limited to few ns.
2. The ultrafast manipulation of the valley information is possible by using optical signal to break the valley degeneracy. However, this optically induced valley splitting mechanism for interlayer exciton has not been demonstrated.
3. Coherent interaction between the interlayer exciton and light has not been demonstrated.
4. Although the conversion between the charge and the valley information has been demonstrated in the 2D TMD monolayer, it has not been demonstrated in the 2D TMD heterostructure.

1.3. Organization

There are five chapters in this thesis. In Chapter 1 (this chapter), the motivation and objective of the project, the organization of the thesis, as well as some theoretical background which is used in the subsequent experimental and theoretical studies are presented. These studies are presented in Chapter 2, 3, and 4.

In Chapter 2, the study of the interlayer exciton dynamics under circularly polarized excitation and under magnetic field influence is presented. We show that the interlayer exciton valley lifetime can be prolonged by applying a magnetic field. This is explained by considering the role of the intralayer dark exciton in the interlayer exciton dynamics. Moreover, we reported the experimental demonstration of the interlayer exciton valley splitting induced by the circularly polarized light. In Chapter 3, the study of the coherent light-exciton interaction inside a cavity is presented. In this regard, we show that the long lifetime of the interlayer exciton relaxes the cavity requirement needed to achieve excitonic lasing. In Chapter 4, we show that circular photocurrent can be generated when the heterostructure-electrode interface is optically excited. Theoretically, we show that this is due to the valence band shifting caused by the interface built-in electric field. Combined with the valley circular optical selection rule, this demonstrates the

conversion between the valley and charge information. Finally, in Chapter 5, several possible future research directions based on these findings are discussed.

1.4.Theoretical background

The selection of the content in this review chapter is mainly based on the theory used in the experimental and theoretical study presented in Chapter 2, 3, and 4. Along the way, we mentioned several notable relevant experimental and theoretical results.

We start by discussing the molecular and the band structure of the 2D TMD monolayer and heterostructure. We then introduce different types of excitons. Next, we discuss the effect of a perturbation on the carrier and exciton dynamics. We start with the perturbation that does not mix the band index, including static and magnetic field perturbation, and how this type of perturbation can be handled using the wave packet formulation of semiclassical transport theory.

Afterwards, we discuss the effect of the perturbation that causes the optical interband transition. We briefly discuss the monolayer valley optical selection rule and how this selection rule change for the case of 2D TMD heterostructure. The semiconductor Hamiltonian and cluster expansion method are then introduced as a method to handle the carrier-carrier and carrier-photon interaction. Lastly, we discuss the circularly polarized PL measurement setup and how the Jones calculus can be used in the experiment to calculate the effect of the wave plate and polarizer angle.

1.4.1. TMD Molecular and electronic band structure

The general molecular structure of 2D TMD heterostructure is shown in Fig. 1.1(a) using MoS₂/WSe₂ as an example. The monolayer MoS₂ (WSe₂) consists of two S (Se) atomic layers with one Mo (W) atomic layer located between these two layers. As a result, a hexagonal lattice with a lattice constant around 3.1 to 3.4 Å¹⁴ is created. The van Der Waals force weakly binds the two layers. Each monolayer does not have a center of inversion and belongs to the C_{3v} symmetry group. In general, there will be a nonzero twist angle between the layers. Hence, the 2D heterostructure does not have vertical mirror symmetry and belongs to the C_3 symmetry group.

Fig. 1.1. a. The 2D TMD heterostructure molecular structure. Here the MoS₂/WSe₂ is used as an example. **b.** The 2D TMD heterostructure band structure. The band alignment is of type II. The holes relax to the WSe₂ layer while the electrons relax to the other layer. This results in a reduced electron-hole exchange interaction. The two different colors (red and blue) indicate different spin species.

We first discuss the band structure of the monolayer, which has been discussed extensively in the literature. The calculation utilizing the density functional theory (DFT) shows that the MX₂ (X = S, Se and M = Mo, W) has a direct bandgap of around 1.4 to 1.8 eV located at K(K') point in the Brillouin zone. Further studies using the DFT, *k.p* method, and tight binding approach shows that the spin-orbit coupling at K (K') points (valleys) splits both the valence band (VB) and the conduction band (CB) with the sign of the conduction band splitting is different for Mo-based and W-based TMD^{14,35,36}. Also, the sign of the band splitting in K valley is opposite to that in K' valley due to the time-reversal symmetry.

When the two materials are put together, it is important to consider the band alignment between these two materials. In general, there are three possible band alignments for heterostructure³⁷: (1) type I: the CB and VB edges of one material are between the CB and VB edges of the other material,

(2) type II: only the CB edge of one material is between the CB and VB edged of the other material, and

(3) type III: the CB and VB edges of one material are below the VB edge of the other material.

For 2D heterostructure consisting of MoX₂ and WX₂, it is found that the band alignment is type II³⁸. Based on the description in this paragraph and the previous paragraph, the band structure at K and K' valley of 2D MoX₂/WX₂ heterostructure can be illustrated

as in Fig. 1.1(b). Moreover, due to this band alignment of type II, the electron tends to go to the MoX₂ layer while the hole tends to go to the WX₂ layer³¹.

We next discuss the wavefunction properties of the TMD monolayer near K (K') valley. The Bloch state near the K (K') valley can be built by mainly using the d_{z^2} and $\frac{1}{\sqrt{2}}(d_{x^2-y^2} + i\tau d_{xy})$ orbital with the value of the valley index $\tau = 1(-1)$ for K (K') valley^{14,35}. The Bloch state corresponding to these two orbitals can be written as

$$|\Phi_1(\vec{k}, \vec{r})\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} |d_{z^2}(\vec{r} - \vec{R})\rangle, \quad (1.1)$$

$$|\Phi_2^\tau(\vec{k}, \vec{r})\rangle = \frac{1}{\sqrt{2N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left\{ |d_{x^2-y^2}(\vec{r} - \vec{R})\rangle + i\tau |d_{xy}(\vec{r} - \vec{R})\rangle \right\}, \quad (1.2)$$

with $\vec{R}$ is summed over all lattice vectors, N is the lattice sites number, and $\vec{k}$ (with respect to K(K') point) is the momentum. A suitable basis for the $\vec{k}$ -dependent Hamiltonian matrix can consists of $\{|\Phi_1(\vec{k}, \vec{r})\rangle, |\Phi_2^\tau(\vec{k}, \vec{r})\rangle\}$. In $\{|\Phi_1(\vec{k}, \vec{r})\rangle, |\Phi_2^\tau(\vec{k}, \vec{r})\rangle\}$ basis, H_0 can be expressed as^{14,35}

$$H_0(\vec{k}) = \begin{bmatrix} \Delta/2 & a_0 t (\tau k_x - i k_y) \\ a_0 t (\tau k_x + i k_y) & -\Delta/2 \end{bmatrix}, \quad (1.3)$$

where the Hamiltonian is expressed up to first order in $\vec{k}$, a_0 is the lattice constant, Δ is the bandgap at K(K') point ($\vec{k} = 0$), and t is the effective hopping integral (~ 0.9 to 1.4 eV). To keep the discussion simple, here the spin-orbit coupling term is neglected.

Table 1.1. Energy eigenvalue and eigenstate of monolayer TMD. Here the basis is $\{|\Phi_1(\vec{k}, \vec{r})\rangle, |\Phi_2^\tau(\vec{k}, \vec{r})\rangle\}$. The k parameter is defined as $k = \sqrt{k_x^2 + k_y^2}$.

Eigenvalue	Eigenstate
$\varepsilon_{VB} = -\frac{1}{2}\sqrt{\Delta^2 + (2a_0 t k)^2}$	$ VB^\tau\rangle = \frac{2a_0 t k}{\sqrt{(2a_0 t k)^2 + (\Delta - \sqrt{\Delta^2 + (2a_0 t k)^2})}} \begin{bmatrix} \Delta - \sqrt{\Delta^2 + (2a_0 t k)^2} \\ 2a_0 t (\tau k_x + i k_y) \\ 1 \end{bmatrix}$
$\varepsilon_{CB} = \frac{1}{2}\sqrt{\Delta^2 + (2a_0 t k)^2}$	$ CB^\tau\rangle = \frac{2a_0 t k}{\sqrt{(2a_0 t k)^2 + (\Delta + \sqrt{\Delta^2 + (2a_0 t k)^2})}} \begin{bmatrix} \Delta + \sqrt{\Delta^2 + (2a_0 t k)^2} \\ 2a_0 t (\tau k_x + i k_y) \\ 1 \end{bmatrix}$

We can then obtain the energy eigenstate and eigenvalue by solving the eigenproblem associated with the Hamiltonian in Eq. (1.3). The results are shown in Table 1.1. Near the K and K' valley, the band is parabolic. Moreover, as the wave number gets further from the K and K' valley, the two orbitals start to mix.

Another important parameter related to the energy eigenstate is the Berry curvature. The n^{th} band Berry curvature for a multi-band system can be expressed as³⁹

$$\overrightarrow{\Omega}_n(\vec{k}) = \sum_{m \neq n} \frac{-2}{(\varepsilon_n - \varepsilon_m)^2} \text{Im} \left\{ \langle u_n | \frac{\partial H}{\partial k_x} | u_m \rangle \langle u_m | \frac{\partial H}{\partial k_y} | u_n \rangle \right\} \hat{z}, \quad (1.4)$$

where $|u_n\rangle$ and ε_n are the $\vec{k}$ -dependent eigenstate and energy of the n^{th} band, respectively. For a 2-band system, the CB and VB Berry curvature can be expressed as

$$\overrightarrow{\Omega}_{CB}(\vec{k}) = \frac{-2}{\varepsilon_g^2} \text{Im} \left\{ \langle u_C | \frac{\partial H}{\partial k_x} | u_V \rangle \langle u_V | \frac{\partial H}{\partial k_y} | u_C \rangle \right\} \hat{z}, \quad (1.5)$$

$$\overrightarrow{\Omega}_{VB} = -\overrightarrow{\Omega}_{CB}, \quad (1.6)$$

where $|u_{V(C)}\rangle$ is the VB(CB) $\vec{k}$ -dependent electron eigenstate and $\varepsilon_g = \varepsilon_{CB} - \varepsilon_{VB}$ is the bandgap. In our case, the $|u_{V(C)}\rangle = |VB^{\tau}(CB^{\tau})\rangle$ and $H = H_0(\vec{k})$. Hence, by using Eq. (1.3)-(1.5), and Table 1.1, we obtain

$$\Omega_{CB}^{\tau} = -\frac{2\tau a_0^2 t^2 \Delta}{(\Delta^2 + (2a_0 t k)^2)^{3/2}} \hat{z}. \quad (1.7)$$

As can be seen from Eq. (1.7), the Berry curvature is nonzero at K and K' valleys (due to the center of inversion absence) with its polarity is opposite between these two valleys. We will see later that this Berry curvature plays an important role in the optical selection rule of the valley as well as the monolayer TMD valley Hall effect.

1.4.2. Exciton in 2D TMD heterostructure

When an electron is excited from the VB to the CB, it leaves a positive quasiparticle in the VB called hole. Beyond the single particle model, the Coulombic attraction between the hole and electron in an electron-hole pair (exciton) must be considered when solving the energy band structure. This interaction results in the excitonic energy level below the conduction band. The binding energy is the difference between the exciton energy and the CB minimum. In 3D material, due to the dielectric screening, the binding energy

is quite small and, hence, the excitonic energy level is only important at low temperatures. However, in 2D TMD, because of the reduced dielectric screening, the value of this energy is several hundred meV. Hence, the Coulombic attraction in the electron-hole pair (exciton) has to be considered even at room temperature.

Fig. 1.2. Exciton types in the 2D heterostructure. (a) Bright intralayer A exciton. (b) Bright intralayer B exciton. (c) Dark intralayer exciton. (d) Momentum-indirect exciton. (e) Interlayer exciton. In all the figures, the yellow circles are electrons and the purple circles are holes. Red and blue lines indicate different spin species, while black lines represent the electron-hole Coulomb interactions.

There are many different types of excitons in the 2D TMD. These are illustrated in Fig. 1.2. Considering only one layer and one valley, there are A (hole in higher energy VB, Fig. 1.2(a)) and B exciton (hole in lower VB, Fig. 1.2(b)). The A exciton dominates the optical response. This is due to the large valence band splitting of several hundred meV (~ 150 meV for MoX₂ and ~ 450 meV for WX₂)¹³. When the electron and hole have different spins, the optical transition between the band is forbidden resulted in the dark exciton⁴⁰ (Fig. 1.2(c)). Considering different valleys, it is possible to have momentum-indirect exciton (Fig. 1.2(d)). Due to the momentum conservation, the optical transition

involving this type of exciton must involve phonon and hence, it is unlikely to happen at low temperature. Finally, we have interlayer exciton (hole in one layer and electron in the other layer, Fig. 1.2(e)). Due to the larger electron-hole separation distance in the interlayer exciton, its lifetime (~ 100 ns³²) is longer than the intralayer one (in the order of picosecond³³).

In addition to the hole-electron Coulomb interaction, there are several aspects internal to the material itself that must be considered in analyzing the exciton and carrier dynamics^{41,42}:

1. The fermionic nature of the many-body electron wavefunction results in electron-electron and hole-electron exchange interaction terms in the Hamiltonian. These terms affect both the free carrier energy and the exciton binding energy. It also contributes to spin depolarization and intervalley scattering⁴³.
2. The electron spin dynamics are also affected by the electron orbital dynamics because of spin-orbit coupling. The electron orbital dynamics are affected by interaction with phonon, impurities, and defects. Hence, not only that this interaction affects the intervalley scattering, but it also affects the spin depolarization. It has also been suggested that the intralayer-to-interlayer conversion involves the phonon-assisted electron scattering from K to Q point and the hole scattering from K to Γ valley⁴⁴.
3. The electron spins can also couple to the nuclear spins. This results in further splitting in electron energy level (hyperfine splitting) and affects the electron spin dynamics.

The spin depolarization mechanism can be treated as the mixing of the spin states by an equivalent in-plane magnetic field acting within certain depolarization time period⁴². Similarly, the valley index is like a pseudospin, and the valley mixing mechanism can also be treated as the effect of an equivalent in-plane magnetic field⁴³. Both the spin depolarization and intervalley scattering will result in the inter-conversion between different excitonic states. Compared to the intralayer exciton and the carrier in monolayer TMD, these two processes are greatly suppressed for the interlayer exciton and carrier in the 2D TMD heterostructure because the hole-electron wavefunction overlap is much smaller in the heterostructure^{43,45}.

As a first approximation, it is sufficient to treat the conversion rate between the excitonic states as a constant. However, we must impose that when two excitonic state P and Q have different energies, the conversion rate from P to Q has to be different than from Q to P. In particular, usually we can impose that $k_{P \rightarrow Q} = k_{Q \rightarrow P} \exp\left(-\frac{E_Q - E_P}{k_B T}\right)$ where $k_{P \rightarrow Q}$ ($k_{Q \rightarrow P}$) is the conversation rate from P to Q (Q to P), k_B is the Boltzmann constant, the energy of P state (E_P) is less than the energy of Q state (E_Q), and T is the material temperature. By imposing this, the population in different excitonic states will asymptotically reach the Boltzmann distribution.

1.4.3. Wave packet dynamic under electric and magnetic field perturbation

An external field can be used to change the quantum state of a material. The perturbation approach can be used when the external field is small. Generally, the perturbation will result in a new quantum state, which can be expanded using the quantum states without perturbation as the basis. For a crystal, the unperturbed quantum states are Bloch states. In this section, the case where the perturbation mixes the quantum states within one energy band only is discussed. In this case, the wave packet formulation has been found to be quite successful in describing the carrier dynamics in a crystal^{39,46,47}. Moreover, we limit our discussion when the external field is a static electric and magnetic field.

The 2D wave packet can be expressed as^{39,46,47}

$$|\Psi\rangle = \int d^2k w(\vec{k}, t) \Phi_n(\vec{k}), \quad (1.8)$$

where $\Phi_n(\vec{k})$ is the Bloch states for the n^{th} band and $w(\vec{k}, t)$ is chosen such that

$$\int d^2k \left| w(\vec{k}, t) \right|^2 = 1, \quad (1.9)$$

$$\int d^2k \vec{k} \left| w(\vec{k}, t) \right|^2 = \vec{k}_c, \quad (1.10)$$

$$\langle \Psi | \vec{r} | \Psi \rangle = \vec{r}_c, \quad (1.11)$$

where $\vec{r}_c$ and $\vec{k}_c$ is the wave packet center position and mean wave packet, respectively.

To first order, $\left| w(\vec{k}, t) \right| \approx \delta(\vec{k} - \vec{k}_c)$. The equation of motion for the wave packet can

then be obtained from the Lagrangian $L = \langle \Psi | i\hbar \frac{d}{dt} - H | \Psi \rangle$.

Considering the static electric and magnetic field effect, the Hamiltonian can be expressed as

$H(\vec{k}, \vec{r}_c) = H_0(\vec{k} + e\vec{A}(\vec{r}_c)) - eV(\vec{r}_c)$, where $\vec{A}(\vec{r}_c)$ and $V(\vec{r}_c)$ are the vector and scalar

potential, respectively, and they are related to the electric and magnetic field by

$\vec{E} = -\vec{\nabla}V(\vec{r}_c)$ and $\vec{B} = \vec{\nabla} \times \vec{A}(\vec{r}_c)$ ⁴⁶. Treating both potentials as perturbations, the equation

of motion of the wave packet can be expressed as

$$\frac{d\vec{r}_c}{dt} = \frac{1}{\hbar} \frac{\partial(\varepsilon_n + \Delta\varepsilon_n)}{\partial \vec{k}_c} - \frac{d\vec{k}_c}{dt} \times \vec{\Omega}_n(\vec{k}_c), \quad (1.12)$$

$$\hbar \frac{d\vec{k}_c}{dt} = -e\vec{E} - e \frac{d\vec{r}_c}{dt} \times \vec{B}, \quad (1.13)$$

where ε_n is the unperturbed n^{th} band energy and $\Delta\varepsilon_n = -\vec{m}(\vec{k}) \cdot \vec{B}$ with $\vec{m}(\vec{k})$ is the

intercellular orbital magnetic moment of the n^{th} band defined as

$$\begin{aligned} \vec{m}(\vec{k}) &= -i \frac{e}{2\hbar} \left\langle \frac{\partial u_n}{\partial \vec{k}} \right| \times (H - \varepsilon_n) \left| \frac{\partial u_n}{\partial \vec{k}} \right\rangle \\ &= -\frac{e}{\hbar} \sum_{m \neq n} \frac{1}{(\varepsilon_n - \varepsilon_m)} \text{Im} \left\{ \left\langle u_n \left| \frac{\partial H}{\partial k_x} \right| u_m \right\rangle \left\langle u_m \left| \frac{\partial H}{\partial k_y} \right| u_n \right\rangle \right\} \hat{z}. \end{aligned} \quad (1.14)$$

First, we note that the magnetic field changes the energy of the carrier (the energy band)

when $\vec{m}(\vec{k})$ is not zero. Considering the two-band system explained in section 1.4.1,

this orbital magnetic moment and Berry curvature is proportional to each other:

$$\overrightarrow{m}_{CB}^{\tau}(\vec{k}) = \overrightarrow{m}_{VB}^{\tau}(\vec{k}) = -\frac{\tau a_0^2 t^2 \Delta e}{\hbar (\Delta^2 + (2a_0 t k)^2)} \hat{z}. \quad (1.15)$$

Since $\overrightarrow{m}(\vec{k})$ is the same for both VB and CB, it will not contribute to the exciton energy magnetic field dependence. However, due to the asymmetry between electron and hole caused by other bands, there is a slight difference between the value of $\overrightarrow{m}(\vec{k})$ in the conduction and valence band. This difference will contribute to the dependence of the exciton energy on the magnetic field^{19,20}. For the valence band, there are three contributions to the carrier magnetic moment: the intracellular orbital due to the $\frac{1}{\sqrt{2}}(d_{x^2-y^2} + i\tau d_{xy})$ orbital (exciton g-factor = 2 in K valley and -2 in K' valley), the spin, and the intercellular contribution (as in Eq. (1.15)). Due to the interaction between orbital and spin, the spin magnetic moment will not be the same as in the free electron case where the g-factor is equal to one³⁶. For the conduction band, there intracellular orbital magnetic moment is negligible compared to the intercellular one because it mainly consists of the d_{z^2} orbital. Since the optical response is dominated by the bright exciton, the magnetic field dependence of the photoluminescence (PL) signal is not affected by the spin magnetic moment^{19,20}. Hence, only the orbital magnetic moment contributes to the difference in K and K' valley emission peak energy. This energy difference is found to be $\sim 4.3\mu_B B$ where μ_B is the Bohr magneton¹⁹. The value of 4 is due to the intracellular contribution, while the 0.3 is due to the intercellular contribution.

Next, considering the special case where there is only the electric field, Eq. (1.13) and (1.14) can be combined to give the total velocity of the wave packet:

$$\frac{d\vec{r}_c}{dt} = \frac{1}{\hbar} \frac{\partial \varepsilon_n}{\partial \vec{k}_c} + \frac{e}{\hbar} \vec{E} \times \overrightarrow{\Omega}_n(\vec{k}_c), \quad (1.16)$$

The $\frac{1}{\hbar} \frac{\partial \varepsilon_n}{\partial \vec{k}_c}$ is called the normal velocity, while the $\frac{e}{\hbar} \vec{E} \times \overrightarrow{\Omega}_n(\vec{k}_c)$ term is the intrinsic contribution to the anomalous velocity^{39,46,47}. The normal velocity results in the current along the electric field direction, while the Berry curvature-induced anomalous velocity results in current orthogonal to the total electric field. The latter phenomenon is called the Hall effect. Usually, it can only happen if the magnetic field is present. However, in

the material where inversion symmetry is broken, it can happen without the magnetic field.

We note that the theory presented here does not consider the many-body interaction between the carriers. This interaction can also affect the exciton energy. We explore this topic more in Chapter 2. Moreover, the theory here only considers the first-order correction due to the field. When considering second-order correction, not only the magnetic field but also the electric field can change the energy of the wave packet. We elaborate more on this in Chapter 4.

1.4.4. Interband transition and optical selection rule

We now shift our attention to the harmonic perturbation, i.e., the perturbation is varying in time. In this case, the mixing between states in different bands (the interband transition) is possible depending on the so-called selection rule. For optical perturbation, due to the small momentum of the light, the usual assumption used is that an optical perturbation does not change the carrier momentum. In this case, within the rotating wave approximation, the selection rule can be derived from the Fermi golden rule⁴⁸. For a multiband system, the Fermi golden rule can be stated as

$$\Gamma_{m \rightarrow n} = \frac{2\pi e^2}{\hbar m_e^2} \int_{BZ} \frac{d^2 k}{(2\pi)^2} \left| \langle \Psi_n | \vec{A}_0 \cdot \vec{p} | \Psi_m \rangle \right|^2 \delta(\varepsilon_n - \varepsilon_m - \hbar\omega), \quad (1.17)$$

where $\Gamma_{m \rightarrow n}$ is the transition rate from m^{th} band to n^{th} band, Ψ_n is the $\vec{k}$ -dependent quantum state at n^{th} band, $\vec{p} = \frac{m_e}{\hbar} \nabla_k H$ is the momentum operator, the integration is over the whole Brillouin zone, and $\vec{A}_0 = \frac{E_\omega \hat{e}}{\omega}$ with E_ω is amplitude of the optical excitation, $\hat{e}$ is the light polarization direction, and the optical excitation has energy $\hbar\omega$. When the dipole matrix element $\langle \Psi_n | \vec{A} \cdot \vec{p} | \Psi_m \rangle$ is zero, the transition is forbidden. Hence, the optical selection rule depends on this dipole matrix element.

We note here that this transition rate is the radiation induced transition rate. Hence, it corresponds to both the absorption rate and the stimulated emission rate. The remaining interband transition type is the spontaneous emission, where the carrier spontaneously decays to lower energy state. This type of transition can only be described by the

quantization of both the material and the electromagnetic field. Such a transition can be radiative or non-radiative with the radiative spontaneous emission rate is proportional to the stimulated emission rate. Hence, the selection rule is applicable to all types of optical transitions.

We can now derive the circular polarization selection rule for the simple two-band model of TMD monolayer at K and K' points. This is done by calculating the dipole matrix element¹⁴

$$P_{\pm} = \frac{m_e^2}{\hbar^2} \left| \langle u_c | \left(\frac{\partial H}{\partial k_x} \pm i \frac{\partial H}{\partial k_y} \right) | u_v \rangle \right|^2$$

$$= \frac{m_e^2 a_0^2 t^2}{\hbar^2} \left(1 \pm \tau \frac{\Delta}{(\Delta^2 + (2a_0 t k)^2)^{1/2}} \right)^2, \quad (1.18)$$

where $P_{+(-)}$ is proportional to the absorption rate for the left (right) circularly polarized excitation. As can be seen from Eq. (1.18), at K valley, only the left circularly polarized (σ_+) excitation can be absorbed and, at K' valley, only the right circularly polarized (σ_-) excitation can be absorbed. Here, the handedness is defined as if the light comes from the sample. If we defined as if the light comes from the excitation source K valley coupled to the right circularly polarized (σ_-) excitation while K' valley coupled to the left circularly polarized (σ_+) excitation. A similar result can be obtained for the sample emission: K valley coupled to the right circularly polarized (σ_-) emission while K' valley coupled to the left circularly polarized (σ_+) emission where the handedness is defined as if the light comes from the sample. This valley optical selection rule is the mechanism behind the observed valley polarization in monolayer TMD¹⁴⁻¹⁸. Moreover, when combined with the Berry curvature-induced anomalous velocity mechanism explained in the previous section, it results in the optical valley Hall effect²².

In the case of the interlayer exciton in 2D TMD heterostructure, the case is more complicated since the hole and electron reside in different layers^{9,49}. The nonzero twist angle between the layer and the difference in the lattice constant cause the bright interlayer exciton to have a nonzero center of mass momentum. Moreover, these will

also result in a superlattice on top of monolayer TMD lattice. This superlattice is called Moiré superlattice, and it introduces an additional modulation on crystal potential. As a result, both the interlayer exciton optical selection rule and energy has a dependence on the excitation location. In contrast, only the intralayer exciton energy is modulated by the Moiré superlattice, while the optical selection rule is the same as in the monolayer TMD case.

Similar to the way the effect of the perturbation on the carrier dynamics is handled in the previous section, the exciton dynamic under a general perturbation can be studied in terms of the exciton wave packet. For a small twist angle, the Moiré superlattice period will be much bigger than the exciton wave packet size. Hence, at each point in the sample, the wave packet can be seen to encounter different periodic crystal potential. This way, the band theory and the Fermi golden rule can still be used to derive the position-dependent interlayer exciton energy and optical selection rule, respectively⁹.

Alternatively, the symmetry argument can be employed to obtain the optical selection rule at high symmetry points (see Fig. 1.3). It is found that, at the three symmetry points, the following optical selection rule is applicable to the interlayer exciton⁹:

- 1) At point A, the hexagon center in the WX_2 layer has the same in-plane position as the hexagon center in the MoX_2 layer. Here, the interlayer exciton optical selection rule is the same as the one for MoX_2 intralayer exciton.
- 2) At point B, the hexagon center in the WX_2 layer has the same in-plane position as the chalcogen position in the MoX_2 layer. Here, the interlayer exciton has opposite optical selection rule (K coupled to σ_+ , while K' coupled to σ_-) compared to the MoX_2 intralayer exciton (K coupled to σ_- , while K' coupled to σ_+).
- 3) At point C, the hexagon center in the WX_2 layer has the same in-plane position as the transition metal position in the MoX_2 layer. At this position, there is no interlayer exciton emission.

Fig. 1.3. Moiré superlattice. The red dots represent the W atoms, the blue dots represent the Mo atoms, while the nodes without dots represent the chalcogen (S or Se) position. The three high symmetry locations are indicated as A, B, and C.

1.4.5. Semiconductor Hamiltonian and cluster expansion method

In the previous sections, we have discussed the carrier and exciton dynamic under static and harmonic electromagnetic perturbation. However, our discussion mainly focused on the semiclassical treatment, where the state of the matter is quantized, but the electromagnetic field itself is treated classically. Moreover, our discussion mostly focuses on the single particle picture instead of the many-body wavefunction.

To treat both the light and the matter quantum mechanically and to include the many-body interactions, we can use the second quantization to build the semiconductor Hamiltonian and try to solve it. In order to simplify the description, we do not consider nuclear-electron interaction, phonon contribution, electric quadrupole contribution, and intraband photon-assisted carrier transition. In this case, the semiconductor Hamiltonian is given by^{50,51}

$$H = H_{el}^{free} + H_{em}^{free} + H_{em-el} + V_c, \quad (1.19)$$

where H_{el}^{free} is the contribution from the electron in crystal potential, H_{em}^{free} is the photon contribution, H_{em-el} is the light-matter interaction contribution, and V_c is the contribution from the electron-electron Coulomb interaction. The form of each of these Hamiltonian is given by

$$H_{el}^{free} = \sum_{\lambda, \vec{k}} \varepsilon_{\lambda, \vec{k}} a_{\lambda, \vec{k}}^\dagger a_{\lambda, \vec{k}}, \quad (1.20)$$

$$H_{em}^{free} = \sum_{\alpha, \vec{q}} \hbar \omega_{\vec{q}, \alpha} \left(b_{\vec{q}, \alpha}^\dagger b_{\vec{q}, \alpha} + \frac{1}{2} \right), \quad (1.21)$$

$$H_{em-el} = - \sum_{\alpha, \vec{q}, \vec{k}, \lambda \neq \lambda'} \left(g_{\vec{q}, \alpha}^* b_{\vec{q}, \alpha}^\dagger a_{\lambda, \vec{k}}^\dagger a_{\lambda', \vec{k}+\vec{q}} + g_{\vec{q}, \alpha} b_{\vec{q}, \alpha} a_{\lambda', \vec{k}+\vec{q}}^\dagger a_{\lambda, \vec{k}} \right), \quad (1.22)$$

$$V_c = \frac{1}{2} \sum_{\vec{k}, \vec{k}', \vec{q} \neq 0, \lambda, \lambda'} V_{\vec{k}, \vec{k}', \vec{q}}^{\lambda, \lambda'} a_{\lambda, \vec{k}}^\dagger a_{\lambda', \vec{k}'}^\dagger a_{\lambda', \vec{k}'+\vec{q}} a_{\lambda, \vec{k}-\vec{q}}, \quad (1.23)$$

where $\varepsilon_{\lambda, \vec{k}}$ is the electron energy, $a_{\lambda, \vec{k}}$ ($a_{\lambda, \vec{k}}^\dagger$) is the electron annihilation (creation) operator, $\omega_{\vec{q}, \alpha}$ is the photon mode frequency, $b_{\vec{q}, \alpha}^\dagger$ ($b_{\vec{q}, \alpha}$) is the photon creation (annihilation) operator, $g_{\vec{q}, \alpha}$ is the light-matter coupling element, $V_{\vec{k}, \vec{k}', \vec{q}}^{\lambda, \lambda'}$ is the Coulomb matrix element, $\lambda(\lambda')$ is the band index, $\vec{k}(\vec{k}')$ is the electron wave vector, $\vec{q}$ is either in-plane photon wave vector or in-plane electron wave vector, and the photon polarization state is represented by α . The electron creation and annihilation operators follow the Fermionic commutation relation while the photon creation and annihilation operators follow the Bosonic commutation relation. Due to the involvement of a large number of quantum states, the application of the approximation technique is necessary in order to get the expectation values of the observables. Here, a brief review of one of the methods called the cluster expansion method is presented.

The dynamic of the observable operator O can be expressed using the Heisenberg equation of motion

$$i\hbar \frac{\partial}{\partial t} O = [O, H], \quad (1.24)$$

where $[O, H] = OH - HO$. Using Eq. (1.19)-(1.24), we can get the equation of motion for each operator that appears in the semiconductor Hamiltonian. However, this will result in an infinite number of coupled differential equations. This is called the operator hierarchy problem. This problem can be easily illustrated if we neglect H_{el}^{free} and V_c . Using Eq. (1.19), (1.21), (1.22), and (1.24), it can be shown that

$$i\hbar \frac{\partial}{\partial t} b_{\bar{q},\alpha} = \hbar \omega_{\bar{q},\alpha} b_{\bar{q},\alpha} - g_{\bar{q},\alpha}^* P_q, \quad (1.25)$$

$$i\hbar \frac{\partial}{\partial t} b_{\bar{q},\alpha}^\dagger = -\hbar \omega_{\bar{q},\alpha} b_{\bar{q},\alpha}^\dagger + g_{\bar{q},\alpha} P_q^\dagger, \quad (1.26)$$

$$i\hbar \frac{\partial}{\partial t} P_{\bar{q}} = -\sum_{\alpha, \bar{q}'} \left(g_{\bar{q}',\alpha}^* b_{\bar{q}',\alpha}^\dagger \left[P_{\bar{q}}, P_{\bar{q}'} \right] + g_{\bar{q},\alpha} b_{\bar{q},\alpha} \left[P_{\bar{q}}, P_{\bar{q}'}^\dagger \right] \right), \quad (1.27)$$

where $P_{\bar{q}} = \sum_{\vec{k}, \vec{\lambda} \neq \vec{\lambda}'} a_{\vec{\lambda}, \vec{k}}^\dagger a_{\vec{\lambda}', \vec{k} + \vec{q}}$ is the polarization operator. As can be seen from Eq. (1.27),

there are new higher order operator terms ($b_{\bar{q},\alpha}^\dagger P_{\bar{q}}, b_{\bar{q},\alpha}^\dagger P_{\bar{q}'}^\dagger, b_{\bar{q},\alpha} P_{\bar{q}}, b_{\bar{q},\alpha} P_{\bar{q}'}^\dagger$) appear. Hence, a set of equations of motion of these operators also needs to be derived. However, in the case of H_{el}^{free} is included, these new set of equations will contain operators with order higher than these operators. This increase in the order of operator happens for an indefinite number of times resulted in an infinite number of coupled differential equations.

To solve this, we notice that what we need is the equation of motion for the expectation value instead of the operator itself. We can then assume that the operator expectation value terms with an order higher than a certain limit is zero. Operators with the same order belong to a cluster and, hence, this method is called the cluster expansion method. Also, it should be noted that the operator expectation value is calculated using the many-body wavefunction. At first approximation, we can assume that the many-body wavefunction consists of non-interacting particles fulfilling the canonical commutation relation (the Hartree-Fock approximation). We then can include the correlation term corresponding to doublet (two-particles interaction is considered), triplet (three-particles correlation), up to N^{th} order correlation where N is the limit of the cluster size.

Another thing to consider is that the Heisenberg equation gives the rate of change of the operator. Hence, if the rate is very fast for a certain operator term, this term can be neglected in the steady state case (for example, when continuous optical excitation is used). These terms are called coherent terms, while the terms that change slowly are called the incoherent terms. For photoluminescence under CW condition, only the incoherent terms need to be considered.

1.4.6. Polarization-resolved PL measurement setup and Jones calculus

In some experiments described in this thesis, we modulate the polarization state of the optical excitation and collect polarization-resolved photoluminescence (PL), in particular, the circularly polarized PL. Due to the circular polarization selection rule of the TMD, this type of setup can be used to study the valley polarization and valley degeneracy breaking mechanism. In this section, we describe this experimental setup and how Jones calculus can be used to analyze the setup.

Fig. 1.4. Polarization-resolved photoluminescence (PL) measurement setup. A combination of a polarizer, a half wave plate, and a quarter waveplate is used to control the polarization state. A dichroic mirror or beam splitter used to separate the excitation and detection arm. Additionally, an optical filter can also be used. The PL signal is sent to a spectrometer or to avalanche photodiode (APD) for further analysis.

The experimental setup of the polarization-resolved PL measurement setup is shown in Fig. 1.4. The optical excitation polarization state and detected PL signal is controlled using a polarizer, half wave plate, and quarter waveplate combination. A dichroic mirror is used to separate the excitation laser from the PL spectrum. This dichroic mirror can also be replaced with a beam splitter. Additionally, an optical filter can be used to filter out the unwanted part of the spectrum. The PL signal is sent to a spectrometer or to avalanche photodiode (APD) for further analysis.

To analyze the effect of the optical component to the polarization state, Jones calculus can be used. In the Jones calculus, the polarization state of light is represented by 2×1

matrix with the basis are two orthogonal polarization states of light (for example, horizontal linear polarization (H) and vertical linear polarization (V)). This matrix is called the Jones vector. The optical components are represented by 2x2 matrices called Jones matrices. The output Jones vector after passing through the optical component is given by matrix multiplication of the input Jones vector and the optical component Jones matrix. The Jones matrices for the polarizer, the beam splitter, the half wave plate, and the quarter wave plate in the H/V basis are given in Table 1.2. It should be noted that the Jones calculus only applied to light with a well-defined polarization state, which is the case for the polarization-resolved PL measurement. In the case of partially polarized light, the more general Mueller calculus has to be used.

Table 1.2. Jones matrix. The Jones matrix for optical components used in the experiment. The angle θ is the angle between the fast axis (polarization axis) of the wave plate (polarizer) and the horizontal polarization direction.

Optical component	Jones matrix
Polarizer	$\begin{bmatrix} \cos^2(\theta) & \cos(\theta)\sin(\theta) \\ \cos(\theta)\sin(\theta) & \sin^2(\theta) \end{bmatrix}$
Beam splitter (note: the value of α in our case is found by calibration)	$\begin{bmatrix} 1 & 0 \\ 0 & \exp(i\alpha) \end{bmatrix}$ when the light is reflected $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ when the light is transmitted
Quarter wave plate	$\begin{bmatrix} \cos^2(\theta) + i\sin^2(\theta) & (1-i)\cos(\theta)\sin(\theta) \\ (1-i)\cos(\theta)\sin(\theta) & \sin^2(\theta) + i\cos^2(\theta) \end{bmatrix}$
Half wave plate	$\begin{bmatrix} \cos^2(\theta) - \sin^2(\theta) & 2\cos(\theta)\sin(\theta) \\ 2\cos(\theta)\sin(\theta) & \sin^2(\theta) - \cos^2(\theta) \end{bmatrix}$

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Chapter 2. Interlayer exciton dynamics in 2D heterostructure

In this chapter, we discuss the interlayer exciton dynamics in 2D MoSe₂/WSe₂ heterostructure. There are two findings regarding this topic. The first one is related to the role of the intralayer dark exciton in interlayer exciton emission, and the second one is related to a novel mechanism to generate a pseudomagnetic field that breaks the valley degeneracy. This chapter is divided into two sections related to each finding.

2.1. Microsecond dark exciton valley polarization memory in 2D heterostructure

As stated in Chapter 1, due to the electron-hole layer separation, the interlayer exciton has a longer lifetime (~ 100 ns^{1,2}) compared to the intralayer exciton (in the order of picosecond³⁻⁵). A long exciton lifetime is crucial for the generation of high-temperature macroscopically ordered exciton state, which forms the basis of a series of fundamental physics phenomena such as superfluidity⁶ and Bose-Einstein condensation⁷⁻⁹. Moreover, longer survival of excitons means a longer distance of exciton transport, which is useful for excitonic devices^{10,11}.

Another important parameter is the valley polarization lifetime, i.e., the measure of how long the exciton stays in one valley. This is important in valleytronics as it determines how long an operation can be performed before the valley information is lost. The interlayer exciton has been measured to have around tens of nanosecond valley polarization lifetime¹². A method to extend both lifetime and valley polarization lifetime is then highly sought-after.

Here, we show that both the lifetime and valley polarization lifetime of the interlayer exciton can be extended by applying a perpendicular magnetic field (Faraday geometry). We first provide the spectroscopic evidence of the interlayer exciton existence in our sample. We then show that the valley polarization under continuous wave (CW) excitation is affected by the magnetic field. Finally, by using time-resolved photoluminescence (PL) measurement, we show that the magnetic field under Faraday geometry can extend both the lifetime and valley polarization lifetime of the interlayer exciton. Theoretically, we attribute this to the role of the WSe₂ dark excitons, which act

as a reservoir for the interlayer exciton on a long time scale. With magnetic field suppressed valley mixing, the dark exciton can serve as a microsecond valley polarization memory for interlayer excitons. This is two orders longer than the case without an applied magnetic field.

2.1.1. Sample characterization and interlayer exciton spectrum

The optical microscope image of the MoSe₂/WSe₂ sample used in this study is shown in Fig. 2.1(a). The sample consists of a MoSe₂ monolayer on top of a WSe₂ monolayer, which is supported by SiO₂/Si substrate. The heterostructure region is separated into two regions, H1 and H2. The armchair axes of both layers are aligned within $\pm 2^\circ$, and the stacking sequence is determined to be AA stacking (i.e., stacking angle $0^\circ (\pm 2^\circ)$).

The photoluminescence (PL) spectrum of the H1, H2, and MoSe₂ region under 633 nm continuous wave (CW) excitation at temperature 2.3 K is shown in Fig. 2.1(b). Comparing the PL spectrum from H2 and MoSe₂ regions, it can be concluded that there is an interlayer exciton state with energy ~ 1.34 eV. Moreover, there is no interlayer exciton in the H1 region. This can be attributed to the weaker interlayer coupling in this region.

Fig. 2.1. Sample characterization and interlayer exciton spectrum. **(a)** The optical microscope image of the MoSe₂/WSe₂ heterostructure. The MoSe₂ monolayer is on top of the WSe₂ monolayer. The heterostructure consists of H1 and H2 regions. **(b)** The PL spectrum at temperature 2.3 K from the heterostructure H1 and H2 region, as well as from the MoSe₂ region. The excitation wavelength is 633 nm. The interlayer exciton emission is observed from the H2 region. The label X_{Mo(W)} and T_{Mo(W)} correspond to the MoSe₂ (WSe₂) neutral and charged exciton, respectively, while the interlayer exciton emission is labeled as Int.

2.1.2. Valley polarization with CW laser

Fig. 2.2. Valley polarization with CW laser excitation. **(a, b)** Valley polarization at 0 T. Left and right circularly polarized light are labeled as σ_+ and σ_- . Under σ_+ laser excitation, σ_+ PL output component is more than σ_- and vice versa for σ_- excitation. This shows evidence of valley polarization. **(c, d)** Valley polarization at -7 T. Valley polarization is enhanced by applying a magnetic field perpendicular to the sample surface. **(e)** The valley polarization degree as a function of the applied magnetic field in the z direction. The solid line is the fitting result following equation $P^j = P_0^j \pm P_1^j \left(1 - \frac{1}{r^2 + r\sqrt{1+r^2} + 1} \right)$, $r = |B|/\alpha$ where j indicates the excitation polarization, P_0^j is the residual degree of polarization at 0 T, P_1^j is the saturation level of degree of polarization, and α represents the intervalley scattering term. **(f)** The valley polarization degree as a function of the applied magnetic field in the y direction with $B_z = 0$ T.

We firstly carried out the measurement of valley polarization with a CW pump laser. The results are shown in Fig. 2.2. In order to increase the count of the interlayer exciton, an excitation laser with a wavelength of 1.708 eV is used. This corresponds to the resonant excitation of the WSe₂ charged exciton. The polarization states of the excitation and detection are set to the left circular polarization (σ_+ : Jones vector, $|\sigma_+\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix}$

looking from the source) or right circular polarization (σ_- : Jones vector, $|\sigma_-\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix}$

looking from the source), and the degree of circular polarization is extracted from these four polarization combinations. The emission polarization will have a small distortion away from circular polarization due to the existence of the Moiré pattern¹³⁻¹⁶. However, circular polarization still acts as a good approximation for studying the dynamics of valley polarization here. The PL emissions of different configurations at 0 T are shown in Fig. 2.2(a, b). It is observed that the PL intensity of the co-polarization is always larger than that of the cross-polarization, corresponding to valley polarization. Next, we apply a magnetic field of -7 T perpendicular to the sample surface (out-of-plane direction, B_z). The results are shown in Fig. 2.2(c, d). As can be seen from these figures, the emission difference between the case with co-polarization and cross-polarization excitation gets larger at $B_z = -7$ T compared to 0 T.

To quantify this difference, we measured the degree of polarization as a function of the magnetic field in both B_z (Faraday geometry) and B_y directions (parallel to sample surface, Voigt geometry). Here, we define the degree of polarization as $P^j = \frac{I_{\sigma_+}^j - I_{\sigma_-}^j}{I_{\sigma_+}^j + I_{\sigma_-}^j}$,

where $I_{\sigma_+}^j$ ($I_{\sigma_-}^j$) is the σ_+ (σ_-) polarized PL intensity when excited with j polarization.

The degree of polarization pumped by σ_+ and σ_- excitation versus the magnetic field in the Faraday and Voigt geometry are shown in Fig. 2.2(e, f). We can observe a dip of the degree of polarization at a low magnetic field around 0 T in Faraday geometry. The valley polarization is around 17% at 0 T and quickly increases to $\sim 35\%$ at ~ 1 T. For Voigt geometry, the degree of polarization does not show any dependence on the magnetic field.

Regarding the Faraday geometry, our observation of increased valley polarization near 0 T is in line with the report in ref. 17 where it is attributed to the suppression of the intervalley electron-hole exchange interaction. Similar to the traditional semiconductor quantum wells and quantum dots, the valley depolarization in the 2D material is affected by the electron-hole exchange interaction¹⁸⁻²⁰. The larger binding energy of excitons in monolayer TMDs further enhances such interaction, leading to valley depolarization and short valley polarization lifetime. The intervalley scattering can be understood in terms

of the in-plane depolarizing field^{20,21}. Hence, by increasing the magnitude of the out-of-plane magnetic field, the valley depolarization can be suppressed^{19,22}. This model can also explain why the degree of polarization saturates at the high magnetic field regime. Drawing an analogy with the quantum dot case with symmetry lower than D_{2d} ¹⁹, we fit the degree of polarization with equation $P^j = P_0^j \pm P_1^j \left(1 - \frac{1}{r^2 + r\sqrt{1+r^2} + 1} \right)$, $r = \frac{|B|}{\alpha}$ where j indicates the excitation polarization, P_0^j is the residual degree of polarization at 0 T, P_1^j is the saturation level of degree of polarization, and α represents the intervalley scattering term. The experimental data fit very well with this model within the magnetic field range of our experiment.

The exchange interaction-based argument can also be used to explain why the degree of polarization does not show any magnetic field dependence under the Voigt geometry. In order to discuss this, it should be noted that the 2D material can be seen as an atomic-thin quantum well. It is known that the effect of an in-plane magnetic field to the exchange interaction is proportional to the quantum well thickness²³. Hence, for the in-plane magnetic field magnitude consider here (≤ 0.7 T), the exchange interaction is practically independent of the magnetic field under the Voigt geometry, which results in the magnetic field-independent degree of polarization.

2.1.3. Time-resolved experiment with pulsed laser excitation.

Fig. 2.3. Time-resolved PL. (a) The three panels represent the time-resolved PL under σ_+ excitation at out-of-plane magnetic field $B_z = +3$ T, 0 T and -3 T. (b) similar as a but under σ_- excitation.

To understand the dynamics of the interlayer exciton emission, we carried out the time-resolved PL experiment with pulsed laser excitation. The laser has a pulse width of ~ 100 ps with a repetition period of $8 \mu\text{s}$ and has the same wavelength as the one used in the CW experiment. The time-resolved interlayer PL emission for $B_z = +3 \text{ T}$, 0 T and -3 T for σ_+ and σ_- excitation are shown in Fig. 2.3(a) and (b) respectively. Based on this measurement, the time-resolved degree of polarization can be determined. Moreover, we can also use the measured data in Fig. 2.3(a, b) to do sanity check of the measurement setup. The red and black curve should interchange each other when time reversal operator is applied to both the magnetic field and the optical excitation, i.e., if both the polarity of the magnetic field and spin angular momentum of the excitation change sign. For example, the $\sigma_+\sigma_+$ and $\sigma_+\sigma_-$ at $B_z = +3 \text{ T}$ should be the same as the $\sigma_-\sigma_-$ and $\sigma_-\sigma_+$ at $B_z = -3 \text{ T}$, respectively. This is what is observed in Fig. 2.3 with the small difference at the tail of the graph can be attributed to the experimental uncertainty related to the polarization state of the optical excitation.

The time-resolved degree of polarization is shown in Fig. 2.4(a). We can see that the degree of polarization P^{σ_+} decays quickly to zero at 0 T , while it has an extra slow decay component and remains above 0.2 for up to $2.5 \mu\text{s}$ at -3 T and 3 T . To quantify it, here we address two different types of degree of polarization: valley polarization and PL polarization. The former depends on the polarization state of the excitation, i.e., co-polarization and cross-polarization give different PL intensity. It can be calculated as

$$P_{val} = \frac{P^{\sigma_+} - P^{\sigma_-}}{2}. \text{ The latter one solely depends on the polarization of the PL emission,}$$

and it does not depend on the excitation. It can be calculated as the average of the

$$\text{individual degree of polarization pumped by } \sigma_+ \text{ or } \sigma_- \text{ excitation: } P_{PL} = \frac{P^{\sigma_+} + P^{\sigma_-}}{2}.$$

Fig. 2.4. Time-resolved degree of polarization. (a) The degree of polarization for σ_+ and σ_- excitation calculated from the time-resolved PL (Fig. 2.3). (b,c) Corresponding valley and PL polarization. The inset in the middle panel shows the zoom-in of the data at the early time. (d) The CW-equivalent degree of polarization as a function of the out-of-plane magnetic field B_z derived from time-resolved PL data. This is calculated using $P^j = \frac{I_{\sigma_+}^j - I_{\sigma_-}^j}{I_{\sigma_+}^j + I_{\sigma_-}^j}$, where $I_{\sigma_+}^j$ ($I_{\sigma_-}^j$) is the integration from 21 ns to 7 μ s of σ_+ (σ_-) polarized time-resolved PL intensity when excited with j polarization.

The time-resolved valley polarization is shown in Fig. 2.4(b). As can be seen from this figure, the lifetime of the valley polarization at 3 T and -3 T are similar to each other. In both cases, the valley polarization lifetime is much bigger than the 0 T case. By using single exponential decay fitting, we obtain a valley polarization lifetime of 1.745 ± 0.007

μs at -3 T while it is $15 \pm 0.3\text{ ns}$ at 0 T . Hence, by applying an out-of-plane magnetic field, a two-order enhancement on the valley polarization lifetime can be achieved. In addition to the CW data (Fig. 2.2(e)), The magnetic field dependence of the valley polarization lifetime further shows that the intervalley scattering rate can be suppressed by applying an out-of-plane magnetic field.

Regarding the PL polarization (Fig. 2.4(c)), its value at -3 T differs from the one at 3 T . In particular it saturates (time $> 6\text{ }\mu\text{s}$) to different values at different magnetic field: ~ 0.2 at -3 T , and ~ -0.2 at 3 T . Since interlayer exciton itself has $\sim\text{ns}$ lifetime, this indicates that the interlayer exciton emission is affected by the population of another exciton population which has a lifetime in the microsecond order.

Additionally, we can integrate the PL signal to get the total emission from each valley and plot the degree of polarization of this total emission as a function of the out-of-plane magnetic field. This is shown in Fig. 2.4(d). As shown in this figure, until around 0.8 T , the magnitude of both P^{σ_+} and P^{σ_-} becomes larger as the magnetic field increased for both excitation polarization cases. This is similar to the CW excitation case. However, differ from CW excitation case, the value of P^{σ_+} and P^{σ_-} approaching the same value as the magnetic field magnitude becomes larger than 0.8 T . This can be understood by considering that there are two competing mechanisms which affect the degree of polarization as the magnetic field is increased: **(1)** the smaller intervalley scattering tends to make P^{σ_+} differ from P^{σ_-} (increase in valley polarization), and **(2)** the valley degeneracy breaking by magnetic field tends to make P^{σ_+} to be the same as P^{σ_-} (decrease in valley polarization). At a small magnetic field up to $\sim 0.8\text{ T}$, the first mechanism is dominant and hence, the valley polarization is increased. However, at a bigger magnetic field, the second mechanism becomes more dominant and, as a result, valley polarization is decreased. Note that for the CW excitation case, the constant optical excitation in one valley prevents the valley polarization from decreasing. In the next subsection, the theoretical model to explain the magnetic field dependence of the time-resolved PL is presented.

2.1.4. Theoretical model and data analysis of the time-resolved PL

Fig. 2.5. Sample of the experimental data (temperature, $T = 2.3$ K) and the fitting to the theoretical model. The data is obtained using σ_- polarized pulsed excitation and σ_- polarized PL detection.

We first analyze the time-resolved PL for three particular cases: $B_z = -7, 0, 7$ T at low temperature ($T = 2.3$ K). The time-resolved PL in these three cases for σ_- polarized excitation and σ_- polarized detection is shown in Fig. 2.5. First, we consider the high magnetic field case ($B_z = -7$ T and $B_z = 7$ T). In this case, we found that the time-resolved PL can be fitted using

$$I = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + \frac{B}{t + t_0}, \quad (2.1)$$

where τ_1 and τ_2 are related to the lifetimes of the slow and fast decay, respectively while A_1 , A_2 , B , and t_0 are other fitting parameters related to the initial population and rate constants. The value of τ_1 is ~ 1 μ s while τ_2 has a value of ~ 10 ns. However, for the small magnetic field case ($B_z = 0$ T), Eq. (2.1) cannot fit the data. This can be explained by the fact that at the small magnetic field case, there are more dynamics involved since the intervalley scattering is not suppressed while in the high magnetic field case, this scattering is suppressed.

The next questions are which type of intervalley scattering is suppressed by the out-of-plane magnetic field. The fact that, at a high magnetic field, the long decay is observed indicates that the suppressed scattering involves exciton with a weak oscillation strength. We argue that the suppressed scattering is the intervalley scattering of the dark WSe₂ exciton. Some physical considerations supporting this assignment are:

1. Due to the observed long (μs) interlayer exciton lifetime, the excitonic species involved in the magnetically suppressed scattering must have a long lifetime. Hence, it is either the dark intralayer exciton or the dark interlayer exciton.
2. It cannot be attributed to the interlayer exciton intervalley scattering since the interlayer exciton exchange interaction is too weak to be affected by the applied magnetic field. Hence, it should be the dark interlayer exciton. Since only the WSe_2 exciton is optically excited and the hole does not undergo the interlayer charge transfer, this exciton must be the dark WSe_2 exciton.

We can now present a more thorough model to come up with a better fitting. In this model, each valley has one WSe_2 dark exciton state and two types of interlayer exciton states. The first type of the interlayer exciton decays following the power law while the second type undergoes a normal exponential decay. The dark exciton can scatter to the interlayer exciton of the second type. Additionally, a dark exciton in one valley can scatter to become a dark exciton in the other valley.

Fig. 2.6. Theoretical model and fitting parameters. The terms N_d (N'_d) and N_x (N'_x), are the population of K (K') valley's dark exciton and interlayer exciton. The term N_{xx} (N'_{xx}) corresponds to the population of the additional exciton level at K (K') valley to account for the power decay with decay rate equal to $k_0 N_{xx}$ for K valley and $k'_0 N'_{xx}$ for K' valley. The parameter k_3 is the intervalley scattering rate, k_1 (k'_1) is the dark-to-interlayer scattering rate and k_2 (k'_2) is the interlayer exciton decay rate. The interlayer exciton emission is taken to be proportional to its population: $I_{\sigma^+} \propto N'_{xx} + N'_x$ and $I_{\sigma^-} \propto N_{xx} + N_x$.

The diagram illustrating this theoretical model showing all the parameters involved in the data fitting is shown in Fig. 2.6. Here, the terms $N_d(N'_d)$ and $N_x(N'_x)$, are the population of K (K') valley's dark exciton and interlayer exciton. The term $N_{xx}(N'_{xx})$ corresponds to the population of the additional exciton level at K (K') valley to account for the power decay with decay rate equal to $k_0 N_{xx}$ for K valley and $k'_0 N'_{xx}$ for K' valley. The parameter k_3 is the intervalley scattering rate, $k_1(k'_1)$ is the dark-to-interlayer scattering rate, and $k_2(k'_2)$ is the interlayer exciton decay rate. Assuming that the interlayer exciton decay rate is not affected by the magnetic field, the interlayer exciton emission is proportional to the sum of the two interlayer exciton populations. That is $I_{\sigma_+} \propto N'_{xx} + N'_x$ and $I_{\sigma_-} \propto N_{xx} + N_x$.

Due to the decoupling of the N'_{xx} and N_{xx} from the rest of the system, this rate equation model can be solved analytically. The closed-form solutions are

$$N_d = c_1 e^{-tk_-} + c_2 e^{-tk_+}, \quad (2.2)$$

$$N_x = c_3 e^{-tk_2} + c_1 \frac{k_1}{k_2 - k_-} e^{-tk_-} - c_2 \frac{k_1}{k_+ - k_2} e^{-tk_+}, \quad (2.3)$$

$$N_{xx} = \frac{1/k_0}{t + c_4}, \quad (2.4)$$

$$N'_d = c_1 \frac{k_3}{\sqrt{\Delta^2 + k_3^2} - \Delta} e^{-tk_-} - c_2 \frac{k_3}{\sqrt{\Delta^2 + k_3^2} + \Delta} e^{-tk_+}, \quad (2.5)$$

$$N'_x = c_5 e^{-tk'_2} + c_1 \frac{k_3}{\sqrt{\Delta^2 + k_3^2} - \Delta} \frac{k'_1}{k'_2 - k_-} e^{-tk_-} + c_2 \frac{k_3}{\sqrt{\Delta^2 + k_3^2} + \Delta} \frac{k'_1}{k_+ - k'_2} e^{-tk_+}, \quad (2.6)$$

$$N'_{xx} = \frac{1/k'_0}{t + c_6}, \quad (2.7)$$

where $k_{\pm} = \frac{k_1 + k'_1}{2} + k_3 \pm \sqrt{\Delta^2 + k_3^2}$, $\Delta = \frac{k_1 - k'_1}{2}$, and c_i terms are constants that depend on the initial condition.

It is possible to fit these equations straight away to the experimental data. However, since there are many independent variables, there is a possibility that multiple local optimum solutions exist where some of the solutions are not physically reliable. A different strategy can be employed by using the fact that for a magnetic field with big

enough magnitude, the value of k_3 is negligible. We can assume $k_3 \approx 0$ MHz for $|B_z| > 0.8$ T since the saturation of the valley polarization in the case of CW excitation happens around 0.8 T (see Fig. 2.2(e)). In this case, the N_{xx} and N'_{xx} are still given by (2.4) and (2.7), respectively, while N_x , N'_x , N_d , and N'_d can be approximated as

$$N_d = c_2 e^{-tk_1}, \quad (2.8)$$

$$N_x = c_3 e^{-tk_2} + c_2 \frac{k_1}{k_2 - k_1} e^{-tk_1}, \quad (2.9)$$

$$N'_d = c_7 e^{-tk'_1}, \quad (2.10)$$

$$N'_x = c_5 e^{-tk'_2} + c_7 \frac{k'_1}{k'_2 - k'_1} e^{-tk'_1}. \quad (2.11)$$

As can be seen from Eq. (2.4), (2.7), (2.8)-(2.11), and by considering that $I_{\sigma_+} \propto N'_{xx} + N'_x$ and $I_{\sigma_-} \propto N_{xx} + N_x$, for the big magnetic field case, the model is equivalent to Eq. (2.1). In this case, each experimental PL data can be fitted separately.

From the fitting results at big magnetic fields, we extract the magnetic field dependence of $k_1, k'_1, k_2, k'_2, \frac{N_d}{N_x + N_{xx}}, \frac{N'_d}{N'_x + N'_{xx}}$, and $\frac{N_d + N_x + N_{xx}}{N'_d + N'_x + N'_{xx}}$. From these data, the values of these parameters at small magnetic fields are interpolated by using linear interpolation. The value of k_0, k'_0, N_{xx} , and N'_{xx} are obtained by doing the fitting using Eq. (2.4), (2.7), (2.8)-(2.11) for both small and big magnetic field. The intervalley scattering rate (k_3) is used as a fitting parameter in Eq. (2.2)-(2.7) for the small magnetic field case.

The fitting result at big magnetic fields can be used to check the sanity of the model. The model predicts that the value of various decay rates ($k_1, k'_1, k_2, k'_2, k_0, k'_0$) should be independent of excitation polarization. We found that this is the case with a small difference for the power decay rate (k_0, k'_0). Moreover, the model also assumes that the interlayer exciton decay rate (k_2, k'_2) should be independent of the magnetic field. We found that this is indeed the case.

The fitting results for the three special cases mentioned before are shown in Fig. 2.5 (red line). As can be seen from these figures, the model can fit the experimental data very well. The dark-to-interlayer exciton scattering rate is found to be in the MHz regime. This suggests that the dark exciton lifetime should be in the order of μs , which is exceptionally long compared to the lifetime of other exciton types. The maximum value of the dark exciton intervalley scattering rate is found to be ~ 100 MHz at $B_z = 0$ T. It decreases quickly with increasing magnetic field. Note that this scattering rate is much lower than the intralayer bright exciton intervalley scattering rate, which can be attributed to the fact that the exchange interaction between dark excitons is much smaller compared to that between bright excitons. However, here we need to consider the microsecond time scale. For this time scale, the valley depolarization of dark exciton needs to be taken into account.

Fig. 2.7. The dark-to-interlayer exciton conversion process. (a, b) The two conversion pathways from the WSe₂ dark exciton to the interlayer exciton. In the first pathway (A-B-D), the spin-flip happens before the interlayer charge transfer, while in the second one (A-C-D), the interlayer charge transfer occurs before the spin-flip. The conversion rate in the first path has an exponential magnetic field dependence while it is constant for the second path. (c) Scattering rate from dark exciton to interlayer exciton versus magnetic field. The dark-to-interlayer scattering rates in K valley (σ_- polarized PL) and K' valley (σ_+ polarized PL) are plotted against the magnetic field and fitted using an exponential function.

The dark-to-interlayer scattering rate (k_1, k'_1) has an exponential dependence on the magnetic field (Fig. 2.7(c)). This can be understood by analyzing the scattering mechanism from the dark exciton to the interlayer exciton. The dark exciton can scatter to become an interlayer exciton by following two different paths. These two paths are illustrated in Fig. 2.7(a, b). In the first path (A-B-D path in Fig. 2.7(a, b)), the conduction band electron undergoes spin-flipping before the charge transfer happens while in the second path (A-C-D path in Fig. 2.7(a, b)) the charge transfer occurs before the spin-flipping. Following the first path, the dark exciton will transform into an intermediate bright exciton before transforming into an interlayer exciton. According to the previous measurement results, the charge transfer from the bright monolayer exciton to the interlayer exciton is very fast ~ 100 fs²⁴. Therefore, we can safely neglect the charge transfer time. This means that the contribution of the first path to the dark-to-interlayer scattering rate will be approximately the same as the dark-to-bright exciton scattering rate. As can be seen from Fig. 2.7(b), this scattering rate at temperature T can be written as $r_0 e^{-\frac{(\Delta E_0 + g \mu_B B)}{k_B T}}$, where ΔE_0 is the energy difference between the dark exciton and bright exciton at 0 T and r_0 is the bright-to-dark exciton scattering rate. This shows that this contribution from the first path has an exponential dependence on the magnetic field. On the contrary, the second path does not have strong magnetic field dependence because the transition only happens from a higher energy level to a lower energy level. Hence, its contribution to the dark-to-interlayer scattering rate is constant.

Based on our explanation above, the g-factor of the conduction band electron can be obtained from the magnetic dependence of the dark-to-interlayer exciton scattering rate at a fixed temperature. This can be used to check the sanity of our model. For K valley, the value 1.07 ± 0.079 is found while it is equal to -1.11 ± 0.095 for K' valley. These g-factor values agree well with the theoretical prediction of the conduction band g-factor for WSe₂ when the out-of-plane effective spin g-factor has negative sign²⁵. From the fitting in Fig. 2.7(c), it can also be seen that the dark-to-interlayer exciton scattering rate saturates to a finite value of ~ 1 MHz at a big magnetic field as predicted by the model.

Fig. 2.8. Temperature dependence of the interlayer exciton PL. (a,c) The σ_- polarized PL at $B_z = 0$ T and $B_z = 7$ T. In both case, σ_- polarized pulsed excitation were used. (b,d) The temperature dependence of the corresponding dark-to-interlayer exciton scattering rate (k_1).

Additionally, the value of the energy level difference between the bright and dark excitons at a zero magnetic field (ΔE_0) can also be calculated from the temperature dependence of k_1 . The time-resolved PL measurement results at various temperatures for the case where σ_- polarized pulsed excitation and σ_- polarized PL detection are used can be seen in Fig. 2.8(a) (for $B_z = 0$ T) and (c) (for $B_z = 7$ T). The corresponding temperature dependence of k_1 together with the fitting result at these two different magnetic fields is shown in Fig. 2.8(b) (for $B_z = 0$ T) and (d) (for $B_z = 7$ T). Based on the fitting results, we obtain $\Delta E_0 = 58.2 \pm 20$ meV. Considering the experimental uncertainty, this result is comparable to the reported values of this parameter^{26,27}.

It can also be observed from Fig. 2.8(a,c) that, while the PL intensity has a monotonic temperature dependence at $B_z = 7$ T, it has a non-monotonic temperature dependence at $B_z = 0$ T. The reason behind this phenomenon will need further investigation beyond the scope of the presented work. One possible reason is related to the exciton-to-trion decay. Since the probability of the formation of the trion decreases with increasing

temperature, we only need to consider this decay channel at low temperature. Given a longer lifetime of the trion compared to the exciton, this decay channel results in a lower PL intensity at 2.3 K compared to at 30 K. This is the case for the $B_z = 0$ T case. On the other hand, for the $B_z = 7$ T case, the suppression of the intervalley scattering may result in a much smaller exciton-to-trion decay rate since the formation of the trion species consisting of carriers in different valleys (e.g. two electrons (holes) in K and K' valley and one hole (electron) in K valley) is suppressed. Hence, while the temperature dependence of the PL intensity is non-monotonic at $B_z = 0$ T, it is monotonic at $B_z = 7$ T.

The fact that there are two types of interlayer exciton and that the time-resolved PL signal follows a multi-exponential decay has been reported before^{1,2,28}. The component with slow exponential decay of this PL signal has been attributed to the extrinsic defect² and also to a transition that is indirect in both real space and momentum space¹. However, these two possible explanations cannot be used to explain the magnetic dependence of the slow decay rate that is observed in our data. Instead, we attribute this slow decay component to the slow conversion rate from the dark exciton to the bright exciton. By doing so, the magnetic field dependence of this decay rate can be explained.

2.1.5. Summary and conclusion

In summary, we have experimentally demonstrated the long valley polarization lifetime in the order of microsecond in 2D heterostructures. This is primarily induced by magnetic field suppressed valley mixing for dark excitons. The long lifetime of the dark exciton put the dark exciton as a reservoir for the interlayer exciton on a long time scale. The long lifetime of exciton in 2D heterostructures makes 2D heterostructure to be a promising candidate for the realization of the ultralong distance exciton transport and exciton devices^{10,11}. The possibility to realize superfluidity⁶ in 2D heterostructures with a long exciton lifetime may provide a future platform towards low-energy dissipation valleytronic devices.

2.2. Optical spin pumping induced pseudomagnetic field in 2D heterostructures

In this section, while still using the same MoSe₂/WSe₂ sample described in the previous section, we shift our attention to the effect of the excitation polarization on the exciton energy. The primary finding is that the energy of the emission from the K or the K' valley depends on the excitation light polarization. Analogous with the role of the magnetic field in shifting the energy of the exciton, the circularly polarized excitation generates an optically induced pseudomagnetic field which also shifts the energy of the exciton. As stated in Chapter 1, regarding previous pioneer works on the optically induced pseudomagnetic field, all of the reported approaches require ultrafast lasers with high peak power for realizing inverse Faraday effect²⁹⁻³¹, AC stark shift^{32,33} or recently Bloch-Siegert shift³⁴.

Here, we demonstrate a new way to generate an optically induced pseudomagnetic field by optical spin pumping mechanism in 2D TMD heterostructures. The method does not need an ultrafast laser with high power and only utilizes a low power CW excitation. The introduction of the pseudomagnetic field relies on the ultrafast charge transfer^{24,35} and the optical spin pumping. The coupling between this field and the interlayer exciton results in optically detectable valley degeneracy breaking.

We first observe a spectrum splitting between different valley transitions of more than 10 meV, which corresponds to ~30 T pseudomagnetic field. This shows that the degeneracy between the valleys can be lifted by using a continuous-wave (CW) optical excitation. We then present a theoretical model to explain this valley splitting. The valley splitting dependence on excitation power, excitation wavelength, and temperature dependence are then described. Lastly, we show that the valley splitting magnitude can be controlled by changing the excitation laser degree of circular polarization.

2.2.1. Interlayer exciton spectrum and magnetic field dependent valley splitting

Fig. 2.9. (a) Interlayer exciton spectrum at 2 K and magnetic field $B = 2$ T for σ_+ and σ_- excitation. The red (blue) solid and dashed lines indicate the spectrum and main peak position (obtained using multiple peak Gaussian fitting (as shown in (c))) of σ_+ (σ_-) collection respectively. The difference in the peak position for the same collection polarization indicates optically induced valley degeneracy breaking. (b) Interlayer exciton spectrum at 2 K and magnetic field $B = 0$ T. (c) Multiple peaks fitting of interlayer exciton at $B = 2$ T and temperature 2 K. The two-peaks Gaussian fitting result (light-blue solid lines) shows a good agreement with the raw data (solid red lines). The parts of the spectrum corresponded to the first and the second peak are shown as dotted and solid black lines, respectively. (d) Magnetic field dependence of the valley splitting. The valley splitting is defined as the difference between σ_- and σ_+ collection peak position. Three different cases are shown: the σ_- excitation, σ_+ excitation, and copolarized (collection state = excitation state) cases. The excitation state dependence of the valley splitting is attributed to the optically induced pseudomagnetic field. The copolarized case shows Zeeman-like linear behavior while the other two show a non-linear trend (a dip) near $B = 0$ T, which is attributed to the suppression of intervalley scattering by the out-of-plane magnetic field.

Fig. 2.9(a) shows the interlayer exciton spectrum and peak position under different excitation polarization at out-of-plane magnetic field $B = 2$ T and temperature 2 K. Here, we use multiple peaks Gaussian fitting (Fig. 2.9(c)) to obtain the main peak position. As shown in Fig. 2.9(a), with the σ_+ light excitation, light emission with the σ_+ polarization has lower energy than the light emission with the σ_- polarization. More interestingly, the σ_+ emission energy becomes higher than the σ_- emission energy if we use the σ_- light excitation, as shown in the lower spectrums in Fig. 2.9(a). A similar behavior is observed for $B = 0$ T (Fig. 2.9(b)). We emphasize that we monitor the energy splitting of the σ_+ and σ_- emission but not their intensity.

To know more about the spectrum splitting, we further measured this splitting at several out-of-plane magnetic field values. From Fig. 2.9(d) (red and blue dots), one can see that such spectrum splitting exists in all magnetic field strength. Even in the absence of a magnetic field, such energy splitting exists even though with a smaller value. The splitting here is much larger than the normal valley Zeeman splitting in an external magnetic field as measured in the copolarized cases^{17,36}, as denoted with purple triangles in Fig. 2.9(d). The result of the same experiment on another MoSe₂/WSe₂ sample (Fig. 2.10) shows the repeatability of the observed phenomenon.

Fig. 2.10. Excitation polarization and magnetic field dependence of the interlayer exciton valley splitting for the second MoSe₂/WSe₂ sample. A similar dependence is observed for the second sample, which shows the repeatability of the observed optically induced pseudomagnetic field.

2.2.2. Valley splitting mechanism

Fig. 2.11. (a) Carrier spin dynamics in the 2D heterostructure. (i), initial heterostructures. (ii), the heterostructure is excited with circularly polarized laser creating the electron and hole in the WSe₂ layer. (iii), due to the ultrafast charge (electron) transfer from WSe₂ to MoSe₂, most of the created conduction band electron migrates to the MoSe₂ layer. (iv), both carriers (i.e., hole and electron) undergo depolarization mainly due to the intervalley scattering with the electron scattering rate in MoSe₂ (k_e) is much faster than the hole scattering rate in WSe₂ (k_h). This reduces both the total valley pseudospin and the total net spin of the carriers (electrons and holes). The total net spin is proportional to the pseudomagnetic field that affects the exciton emission energy. **(b)** Rate equation model for the process described in (a). In this model, N_e (N'_e) and N_h (N'_h) are the electron and hole population in K (K') valley respectively, N_R is non-excited population density, Γ (Γ') is the electron-hole injection rate in K(K') valley, γ is the electron-hole recombination rate, and σ_K (σ'_K) is the optical state that is coupled to K(K') valley.

Next, we analyze the mechanism of this optically controlled spectrum splitting and compare it with previous pseudomagnetic field generation schemes. Unlike phenomena observed in TMD monolayer^{32,33}, the observed optically induced valley degeneracy breaking cannot be attributed to the valley-selective optical Stark effect. The optical excitation energy (1.707 eV) is too far blue-detuned from the interlayer exciton energy level range (1.3 - 1.4 eV) and its intensity is too small ($< 100 \text{ kW/cm}^2$). For comparison, the detuning and the intensity of the optical pump used to generate the valley degeneracy breaking of more than 2 meV is around 0.2 eV red-detuned and 1 GW/cm^2 respectively³³. Hence, the contribution of the valley-selective optical Stark effect can be

neglected. Moreover, unlike in the case of the excitation-induced exciton energy splitting in semiconductor quantum well³⁷⁻⁴⁰ where the cross-polarized component (i.e., the emission polarization is orthogonal to the excitation polarization) has lower energy than the co-polarized component (i.e., the emission polarization is the same as the excitation polarization), we observed that the cross-polarized component has higher energy than the co-polarized one.

The emergence of the effective net carrier spin due to the strong spin-orbit coupling of valence band states in WSe₂ is sketched in Fig. 2.11(a). When we resonantly excite the exciton transition of WSe₂ with the σ_- light, electrons and holes with spin up are generated in WSe₂. Due to the energy band alignment, electrons will tunnel to the conduction band of MoSe₂ in a short time while spin up holes remain in WSe₂, which provides the lowest energy states available for holes. In this way, the electrons and holes are separated, ensuring that electron-hole exchange is ineffective in effecting a joint electron-hole valley flip. Although both electrons and holes experience spin flipping/valley scattering, the strong spin-orbit coupling in the valence band ensures that holes have a long spin/valley lifetime exceeding microsecond⁴¹. This results in the net carrier spin in the system.

Due to the Coulomb exchange interaction, the presence of optically injected spin-polarized holes implies that in the presence of a large hole population in the K-valley, the net Coulomb repulsion experienced by a K-valley (spin up) hole is reduced as compared to that of a K'-valley hole. As a consequence, the energy of a K-valley interlayer exciton is reduced as compared to that of K'-valley, leading to the observed splitting in the emission spectrum. Note also that the spin polarization of the electron will also contribute additively to the splitting. However, the spin/valley lifetime of the electron is much shorter compared to that of the hole, which resulted in much smaller net polarization of the electron.

The fast change of valley splitting between $B = 0$ T to $B = \pm 2$ T (Fig. 2.9(d)) is observed for the case of σ_- and σ_+ excitation but not observed for the copolarized case. To explain this rapid increase, we note that the carrier net polarization is also affected by the intralayer exciton valley polarization since what the optical pump does is to create the

intralayer exciton which then undergoes conversion into the free carrier or other excitonic species. The rapid increase of the valley splitting at the small magnetic field regime can then be explained as the result of the suppression of the intralayer exciton intervalley scattering by magnetic field (see previous section). For a magnetic field magnitude bigger than 2 T the expected linear behavior of valley splitting^{17,36} is observed since the intralayer exciton intervalley scattering has been largely suppressed. This nonlinear behavior is not observed in copolarized case because the pseudomagnetic field due to two orthogonal optical excitations will have an opposite sign. Hence, the valley splitting is only affected by the external magnetic field for the copolarized case. In the next subsection, we give the microscopic description of the valley splitting mechanism.

2.2.3. Microscopic description of the valley splitting mechanism

We can describe how the emission peak depends on the carrier density using the microscopic equation of motion framework utilizing cluster expansion method⁴² (see also a brief overview of this method in Chapter 1). In our case, we are using a low intensity CW laser excitation. If we neglect the contribution from the B interlayer exciton, we can just treat the interlayer exciton emission using a 4-band model. Hence, we can write

$$I_{PL}(\omega_{q,\alpha}) = \frac{\partial}{\partial t} \Delta \langle b_{q,\alpha}^\dagger b_{q,\alpha} \rangle = 2 \text{Re} \left[\sum_{k,\xi'} g_{q,\xi',\alpha} \Pi_{k,\xi',\alpha,q} \right], \quad (2.12)$$

where $I_{PL}(\omega_q)$ is the interlayer exciton emission spectrum, $b_{q,\alpha}$ is the annihilation operator of photon with wave vector q and polarization α , $\Pi_{k,\xi,\alpha,q}$ is the photon-assisted polarization and can be expressed as $\Pi_{k,\xi,\alpha,q} = \Delta \langle b_{q,\alpha}^\dagger a_{v,k-q,\xi}^\dagger a_{c,k,\xi} \rangle = \langle b_{q,\alpha}^\dagger a_{v,k-q,\xi}^\dagger a_{c,k,\xi} \rangle - \langle b_{q,\alpha}^\dagger \rangle \langle a_{v,k-q,\xi}^\dagger a_{c,k,\xi} \rangle$ with $a_{c(v),k,\xi}$ is the annihilation operator of the MoSe₂ conduction band electron (WSe₂ valence band electron) with momentum k with respect to the valley ξ , and $g_{q,\xi,\alpha}$ is the strength of light-matter interaction. Note that the term $\Delta \langle O \rangle$ is called the correlation term and defined as $\Delta \langle O \rangle = \langle O \rangle - \langle O \rangle_s$ where $\langle O \rangle_s$ is the expectation value under singlet factorization (Hartree-Fock approximation)⁴². Note that the wave vector q has two

components: the in-plane component $q_{\parallel}$ and the out-of-plane component q_z such that $q \equiv (q_{\parallel}, q_z)$.

In order to derive the expression of the photon assisted polarization, we use the following rules:

1. The K(K') valley only couples to $\sigma_{-(+)}$ polarized light. The coupling strength can be expressed as $g_{q,\xi,\alpha} = g_q (\delta(\xi, K)\delta(\alpha, \sigma_-) + \delta(\xi, K')\delta(\alpha, \sigma_+))$.
2. We are in the weak excitation regime. Hence, stimulated emission (absorption) is negligible.
3. At each valley, only 4 band needs to be considered: WSe₂ upper conduction and valence band, MoSe₂ upper valence band, and MoSe₂ lower conduction band.
4. The only excitonic intervalley coupling that is not negligible is only between intralayer excitons, for example, through the Maialle-Silva-Sham mechanism^{18,20}. Hence, the intervalley coupling can be neglected from the photon-assisted dynamics of the interlayer excitonic transition. However, it has to be included in the dynamics of the carrier.
5. The interlayer exciton emission only involves photons and carriers with almost zero in-plane momentum ($q_{\parallel}, k \approx 0$).

In this case, we can express the dynamic of the system as

$$I_{PL}(\omega_{q,\sigma^+(\sigma^-)}) = 2\text{Re}\left[g_q \Pi_{0,\mathbf{K}'(\mathbf{K}),\sigma^+(\sigma^-),q}\right], \quad (2.13)$$

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Pi_{0,\mathbf{K}'(\mathbf{K}),\sigma^+(\sigma^-),q} = & \left(E_{g,0}^{\mathbf{K}'(\mathbf{K})} - \hbar\omega_q - \left(V_{0,0,0}^{c,c,\mathbf{K}'(\mathbf{K})} f_{0,\mathbf{K}'(\mathbf{K})}^e + V_{0,0,0}^{v,v,\mathbf{K}'(\mathbf{K})} f_{0,\mathbf{K}'(\mathbf{K})}^h\right) - i\gamma\right) \Pi_{0,\mathbf{K}'(\mathbf{K}),\sigma^+(\sigma^-),q} \\ & - \left(\left(1 - f_{0,\mathbf{K}'(\mathbf{K})}^h\right) V_{0,0,0}^{c,v,\mathbf{K}'(\mathbf{K})} - f_{0,\mathbf{K}'(\mathbf{K})}^e V_{0,0,0}^{v,c,\mathbf{K}'(\mathbf{K})}\right) \Pi_{0,\mathbf{K}'(\mathbf{K}),\sigma^+(\sigma^-),q} \\ & + ig_q \left(f_{0,\mathbf{K}'(\mathbf{K})}^e f_{0,\mathbf{K}'(\mathbf{K})}^h + c_x^{0,0,0,\mathbf{K}'(\mathbf{K})}\right), \end{aligned} \quad (2.14)$$

Here, $E_{g,0}^{\xi}$ is the bandgap at zero carrier density at valley ξ without Coulomb contribution, $f_{k,\xi}^e = \langle a_{c,k,\xi}^\dagger a_{c,k,\xi} \rangle$ and $f_{k,\xi}^h = 1 - \langle a_{v,k,\xi}^\dagger a_{v,k,\xi} \rangle$ are the occupation number of electron and hole with momentum k at valley ξ , respectively, $c_x^{q,k',k,\xi} = \Delta \langle a_{c,k}^\dagger a_{v,k'}^\dagger a_{c,k'+q} a_{v,k-q} \rangle$ is the incoherent exciton correlation. The term $V_{k,k',q}^{\lambda,\lambda',\xi}$ is the

Coulomb matrix element with $\lambda(\lambda')$ is the band index, $k(k')$ is the momentum, and ξ is the valley index. The form of the Coulomb matrix is determined by the form of Coulomb potential and the wavefunction overlap. More discussion about this can be found, for example, in the paper by Berghäuser et al⁴³. We also note that the proper way is to use the total occupation around $k = 0$ (i.e., $N_{\mathbf{K}(\mathbf{K}')}^{e(h)} = \sum_{k \approx 0} f_{k, \mathbf{K}(\mathbf{K}')}^{e(h)}$) instead of occupation number at $k = 0$. However, we argue that due to the long lifetime of the interlayer exciton, these two quantities will be similar as long as the excitation power is low enough (much below the one required for Mott transition).

Under the CW excitation, the system will reach a steady state where the change in the carrier, exciton, and polarization is zero. Hence, from Eq. (2.13) and (2.14), we obtain

$$I_{PL}(\omega_{q, \sigma^+ (\sigma^-)}) = \frac{2\gamma g_q (f_{\mathbf{K}'(\mathbf{K})}^e f_{\mathbf{K}(\mathbf{K}')}^h + c_x^{\mathbf{K}'(\mathbf{K})})}{\left(\omega_q - \left(E_g^{\mathbf{K}'(\mathbf{K})} - \left((V^{c,c, \mathbf{K}'(\mathbf{K})} - V^{v,c, \mathbf{K}'(\mathbf{K})}) f_{\mathbf{K}'(\mathbf{K})}^e + (V^{v,v, \mathbf{K}'(\mathbf{K})} - V^{c,v, \mathbf{K}'(\mathbf{K})}) f_{\mathbf{K}(\mathbf{K}')}^h \right) \right) \right)^2 + \gamma^2}, \quad (2.15)$$

where $E_g^{\mathbf{K}'(\mathbf{K})}$ is the bandgap at zero carrier density and the subscripts related to momentum has been removed. For interlayer exciton, $V^{(v,v)(c,c), \xi} \gg V^{(v,c)(c,v), \xi}$. Hence, Eq. (2.15) shows that the peak of the interlayer exciton emission will be red-shifted at higher carrier density.

The valley splitting then can be expressed as:

$$\begin{aligned} VS &= (\sigma^- \text{ emission peak}) - (\sigma^+ \text{ emission peak}) \\ &= (E_g^{\mathbf{K}} - E_g^{\mathbf{K}'}) + \left((N_{\mathbf{K}'}^e + N_{\mathbf{K}'}^h) - (N_{\mathbf{K}}^e + N_{\mathbf{K}}^h) \right) V^{x,x}, \end{aligned} \quad (2.16)$$

where we have neglected $V^{(v,c)(c,v), \xi}$. Due to symmetry, the absolute value of the interband Coulomb matrix will be the same for different valleys. Hence, the valley index has been dropped for the Coulomb interaction term. Moreover, we assume that the Coulomb matrix is the same for the valence band and the conduction band electron. The change in the zero density bandgap is caused by the magnetic field due to the valley Zeeman effect¹⁷, which is independent of the carrier density.

Using the rate equation model of the carrier dynamic (Fig. 2.11(a)) and Eq. (2.16), the valley splitting can be expressed as

$$VS = (E_g^K - E_g^{K'}) - \frac{2(\gamma + k_e + k_h)}{(\gamma + 2k_e)(\gamma + 2k_h)} V^{x,x} (\Gamma_K - \Gamma_{K'}), \quad (2.17)$$

where k_e (k_h) is the depolarization rate of the electron (hole), Γ_K ($\Gamma_{K'}$) is the electron-hole injection rate in K (K') valley and γ is the electron-hole recombination rate. The second term on the right hand side can be treated as proportional to a pseudomagnetic field

$$B_{pseudo} \propto -\frac{2(\gamma + k_e + k_h)}{(\gamma + 2k_e)(\gamma + 2k_h)} V^{x,x} (\Gamma_K - \Gamma_{K'}). \quad (2.18)$$

Note that the same carrier dynamic model can be used to calculate the degree of

polarization which is defined as $DoP^j = \frac{I_{\sigma_-}^j - I_{\sigma_+}^j}{I_{\sigma_-}^j + I_{\sigma_+}^j}$, where $I_{\sigma_+}^j$ ($I_{\sigma_-}^j$) is the σ_+ (σ_-)

polarized PL intensity when excited with j polarization (note: the degree of polarization defined here is the negative of the degree of polarization defined for section 2.1).

However, for valley polarization calculation, we should impose that $N_{K(K')}^{e,exc} = N_{K(K')}^{h,exc} = N_{K(K')}^{exc}$ and $k_e^{exc} = k_h^{exc} = k_{exc}$ where the superscript (subscript) “exc” means that the electron and hole are from exciton contribution. The degree of polarization can then be expressed as

$$\begin{aligned} DoP &= \frac{(\sigma^- \text{ Intensity}) - (\sigma^+ \text{ Intensity})}{(\sigma^- \text{ Intensity}) + (\sigma^+ \text{ Intensity})} = \frac{N_K^{exc} - N_{K'}^{exc}}{N_K^{exc} + N_{K'}^{exc}} \\ &= \frac{\gamma}{\Gamma_{total}(\gamma + 2k_{exc})} (\Gamma_K - \Gamma_{K'}), \end{aligned} \quad (2.19)$$

Here, we assume that $\Gamma_{total} = \Gamma_K + \Gamma_{K'}$ is roughly constant. Comparing the pseudomagnetic term in Eq. (2.17) and the DoP expression in Eq. (2.19), we can see that the increase in valley splitting is proportional to the decrease in the degree of polarization. In the next section, we show this experimentally by studying the excitation power and excitation wavelength dependence of both the valley splitting and the degree of polarization.

2.2.4. Temperature, excitation power, and excitation wavelength dependence

The temperature dependence of the valley splitting at $B = 2$ T is shown in Fig. 2.12. The effect of the excitation polarization to the valley splitting can be observed at a temperature as high as 90 K. Its effect decreases with increasing temperature. This can be understood as the valley depolarization rate is higher at higher temperature⁴¹ and, hence, the optically induced pseudomagnetic field will also decrease with increasing temperature.

Fig. 2.12. Temperature dependence. Temperature dependence of valley splitting under $B = 2$ T with excitation power 510 μ W and excitation wavelength 726 nm.

Fig. 2.13. Power and excitation wavelength dependence. (a,b) Power dependence of valley splitting and degree of polarization (DoP) under $B = 2$ T with excitation wavelength 726 nm and temperature 2 K. The

degree of polarization is defined as $DoP^j = \frac{I_{\sigma_-}^j - I_{\sigma_+}^j}{I_{\sigma_-}^j + I_{\sigma_+}^j}$, where $I_{\sigma_+}^j$ ($I_{\sigma_-}^j$) is the σ_+ (σ_-) polarized PL

intensity when excited with j polarization. (c,d) Excitation wavelength dependence of the valley splitting and DoP at $B = 2$ T and temperature 2 K. The powers at each wavelength are 260 μ W for 532 nm, 140 μ W for 589 nm, 455 μ W for 633 nm, 385 μ W for 685 nm, and 460 μ W for 726-796 nm.

The power and excitation wavelength dependence of the valley splitting and degree of polarization at $B = 2$ T are shown in Fig. 2.13. Comparing Fig. 2.13(a,b) and (c,d), it can be seen that there is a close relationship between the degree of polarization and valley splitting. In particular, the degree of polarization decreases when the valley splitting increases which is in line with the result from the theoretical model.

Unlike in the case of valley splitting due to the optical Stark effect or Bloch-Siegert shift, the observed valley splitting does not increase with increasing excitation power (Fig. 2.13(a)). Other than the apparent decreasing trend that can be attributed to optical excitation-induced heating, the valley splitting tends to be a constant of power. This can be understood as the pseudomagnetic field only depends on the population density difference between spin up and spin down holes. As the hole population density reaches a saturation point, the valley splitting dependence on power gets weaker.

The effect of the optically induced valley splitting is maximum near 726 nm (Fig. 2.13(c)), which corresponds to the WSe₂ charged exciton energy level. At 532 nm, there is virtually no valley splitting and the *DoP* is very close to zero. This can be understood as the pseudomagnetic field depends on the polarized hole population generation in the WSe₂ layer. As the excitation wavelength gets smaller, the intervalley scattering of intralayer exciton becomes more prominent, which results in reduced polarized carrier population.

2.2.5. Polarization control of valley splitting

Fig. 2.14. (a, b) Illustration of the trajectory of the optical state on the surface of the Poincaré sphere. The polarization state of the optical excitation is swept through two different trajectories. The state for those trajectories can be expressed as $|\Psi_1\rangle = \frac{1}{\sqrt{2}}(|H\rangle + e^{i\alpha}|V\rangle)$ and $|\Psi_2\rangle = \cos(\frac{\alpha}{2})|H\rangle + ie^{i\phi}\sin(\frac{\alpha}{2})|V\rangle$ with $\phi = -136 \pm 5^\circ$ for trajectory in (a) and (b), respectively. (c, d) Valley splitting as a function of the excitation polarization state. Here the dots represent the experimental data while the lines are the theoretical fitting result. The result in (c) corresponds to the trajectory in (a), while (d) corresponds to (b).

Based on Eq. (2.17), it is possible to tune the valley splitting by changing the proportion of σ_+ and σ_- part of the optical excitation. In order to prove this, we measure the valley splitting as a function of the excitation polarization state $|\Psi_1\rangle = (|H\rangle + e^{i\alpha}|V\rangle)/\sqrt{2}$ and the excitation polarization state $|\Psi_2\rangle = \cos(\alpha/2)|H\rangle + ie^{i\phi}\sin(\alpha/2)|V\rangle$ with $\phi = -136 \pm 5^\circ$ and various values of α (see parameter definition in Fig. 2.14(a, b)). The data is collected for two different values of the magnetic field ($B = -2$ T and 2 T). The result is shown in Fig. 2.14(c, d). As shown in these figures, we have successfully controlled the valley degeneracy by excitation polarization manipulation.

In order to fit the data to the theoretical model, we have to consider that, due to the effect of the Moiré pattern, the optical selection rule and the oscillator strength become position-dependent with periodicity around a few nm¹⁴. Since our excitation beam has

a diameter in μm scale, the optical polarization state that has the largest coupling strength to the K valley will, in general, have elliptical polarization.

We denote this optical polarization state as σ_K . Due to the time-reversal symmetry, the optical polarization state orthogonal to σ_K (denoted as σ'_K) will have the largest

coupling strength to the K' valley. For $|\sigma_K\rangle = \begin{bmatrix} \cos(\frac{\theta}{2}) \\ e^{i\varphi} \sin(\frac{\theta}{2}) \end{bmatrix}$, the valley splitting VS caused

by the optical excitation with polarization state $|\Psi\rangle = \begin{bmatrix} \cos(\frac{\theta'}{2}) \\ e^{i\alpha} \sin(\frac{\theta'}{2}) \end{bmatrix}$ can be expressed as

$$VS(|\Psi\rangle) \propto \left| \langle \sigma'_K | \Psi \rangle \right|^2 - \left| \langle \sigma_K | \Psi \rangle \right|^2 \\ \propto -\cos(\theta)\cos(\theta') - \sin(\theta)\sin(\theta')\cos(\alpha - \varphi). \quad (2.20)$$

The $|\sigma_K\rangle$ state can be obtained by fitting the valley splitting expression above to the valley splitting data for the two circular trajectories in the Poincaré sphere (Fig. 2.14(a, b)) with a constant term is added to represents the valley splitting due to the external magnetic field. The fitting function is

$$VS(|\Psi(\alpha, \theta')\rangle; \theta, \varphi) = VS_{\text{max}} (-\cos(\theta)\cos(\theta') - \sin(\theta)\sin(\theta')\cos(\alpha - \varphi)) + VS_0(B), \quad (2.21)$$

where the fitting parameters are: VS_{max} , $VS_0(B)$, θ , and φ . The term VS_{max} is the maximum optically induced valley splitting. The term $VS_0(B)$ is the valley splitting due to the magnetic field dependent valley Zeeman effect. It does not depend on the excitation polarization. Based on the fitting result (Fig. 2.14(c, d)), we obtained $\theta = 68 \pm 6^\circ$ and $\varphi = -84 \pm 6^\circ$ where the uncertainty is derived from the uncertainty in the orientation of the optical components. From this data, we can also estimate the pseudomagnetic field value by comparing the amplitude of the oscillation with the constant difference between the valley splitting at $B = -2$ T and 2 T, as shown by the difference of two oscillation curves in Fig. 2.14(c)-(d). We estimated that the pseudomagnetic field induced by circularly polarized light is $\sim \pm 31$ T.

2.2.6. Summary and conclusion

In summary, we show that the degeneracy between the valleys can be lifted by using optical excitation even for vanishing external magnetic fields. This valley degeneracy breaking can be explained using the optically induced spin pumping mechanism. Furthermore, we show that the valley splitting can be well controlled by manipulating the optical excitation state. The realization of optically induced pseudomagnetic field can pave the way for optical control of valleytronics devices, which is considerably faster than controlling the external magnetic field.

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Chapter 3. Light-exciton interaction in a 2D heterostructure cavity

Interaction between the light and the matter can be enhanced by confining both the light and the matter within an optical cavity. When sufficient light-matter interaction strength is achieved, the nonlinear regime can be reached where the interaction changes the photon distribution function. Such is what happens when lasing occurs.

In this chapter, we report the demonstration of the first nanocavity laser based on Van der Waals heterostructures. We start by introducing the device structure and the spectrum of the nanolaser. Next, the characterization of the interlayer excitonic laser is presented. This includes its operation in both low and room temperature. By using the cluster expansion method, we theoretically show that due to the long lifetime of the interlayer exciton, the requirement for cavity Q-factor can be relaxed.

3.1. Device structure and optical spectrum

The optical microscope image of the real device is shown in Fig. 3.1(a). Van der Waals MoS₂/WSe₂ heterostructure plays the role of the gain medium on a vertically coupled, free-standing photonic crystal cavity (PhCC). The cavity structure is designed such that the field maximum is in excellent spatial overlap with the gain medium.

As shown in Fig. 3.1(b), the intralayer exciton recombination in MoS₂ and WSe₂ monolayers results in PL peaks at about 668 nm and 750 nm, respectively. For MoS₂/WSe₂ heterostructures with AA stacking, a new PL peak centering at 1128.6 nm has been observed (Fig. 3.1(b)), which we attribute to the interlayer excitonic emission. As shown in Fig. 3.1(c), when the interlayer exciton is coupled to the cavity, a sharp cavity mode in the emission spectrum was observed with wavelength located at ~ 1122 nm, corresponding to the designed cavity mode of the PhCC. Here, the single-mode fiber is used.

Fig. 3.1. MoS₂/WSe₂ heterobilayer-PhCC nanolaser. **(a)** First panel: Optical microscope image of the MoS₂/WSe₂ heterobilayer on silicon PhCC. The MoS₂, WSe₂ monolayers, and PhCC are indicated by the red, blue and black dashed lines, respectively. Second panel: Top-view scanning electron micrograph around the defect region of the L3-type defect silicon photonic crystal cavity. The arrows show the displacement of the two end-holes by 48.4 nm. The radius of the other gray holes are shrunk to ~62.4 nm to enhance the far-field vertical coupling. **(b)** Interlayer excitonic emission in the MoS₂/WSe₂ heterobilayer compared to the intralayer emission in the two constituents. The spectra of monolayers were measured at room temperature with 532 nm excitation, and the spectrum of heterobilayer was measured at 5 K with 740 nm excitation. **(c)** Cavity lasing mode emission spectrum taken at a CW pump power of 190 μW, T = 5 K. Lasing action occurs at 1122.5 nm with a measured linewidth of ~2.7 nm.

3.2. Lasing characterization

Next, we proceed to prove the lasing behavior of our device. One of the laser properties is that emission intensity in the cavity mode will increase faster when the pump power is above the lasing threshold. First, we investigate the lasing behavior at cryo-temperature ~ 5K. An example of the Lorentzian fitting used to extract both the heterostructure background emission and the cavity mode part of the emission is shown in Fig. 3.2(a). In order to see the spontaneous emission more clearly, here we collect with a multimode fiber in contrast to single-mode fiber. The broad emission spectrum corresponds to the spontaneous emission of the interlayer excitons (background emission). Fig. 3.2(b) exhibits the log-log plot of the cavity mode component intensity as a function of excitation power at low temperature (5 K). When the excitation intensity exceeds a certain value (threshold), we can observe the change in the slope, indicating that stimulated emission starts taking place in our device. The rather soft turn-on shoulder near the threshold implies a large β factor, which is defined as the ratio of the spontaneous emission coupled into the laser cavity mode over the total spontaneous emission from the material. Therefore, the β factor is a measure of the optical efficiency of a laser. Its theoretical limit is unity, corresponding to the case of thresholdless lasing.

Fig. 3.2. Lasing characterization. **(a)** Cavity lasing emission as compared to the heterobilayer photoluminescence background. The green line represents the Lorentzian fit to the experimental data (black line), while red and blue lines represent cavity mode component and the background component, respectively. **(b)** Log-Log plot of the cavity mode emission intensity as a function of the pump power at low temperature (5 K). Solid lines are the simulated results of a rate-equation calculation with different β factors. The red line shows the best fit to the experimental data (red circles) corresponding to $\beta = 0.17$. The corresponding fitting using $\beta = 0.1, 0.4$, and 1 are also shown for comparison. **(c)** Similar to (b) but at room temperature. The best fit to the experimental data (red circles) is given by $\beta = 0.27$. The corresponding fitting using $\beta = 0.1, 0.5$, and 1 are also shown.

We estimated the β value by fitting the log-log plot of the L-L curve to the theoretical model based on classical atomic laser rate equations¹. The cavity mode intensity can be expressed as

$$P = \frac{a\Gamma_c R_{ex} - \frac{1}{\beta} + \sqrt{\left(a\Gamma_c R_{ex} - \frac{1}{\beta}\right)^2 + 4a\Gamma_c R_{ex}}}{2a}, \quad (3.1)$$

where a is stimulated emission coefficient, Γ_c is equal to the cavity confinement factor divided by the cavity photon decay rate, and R_{ex} is the optical pumping rate. The solid red curve in Fig. 3.2(b, c) is the best fit to the experimental data, yielding $\beta = 0.17$ at low temperature and $\beta = 0.27$ at room temperature. The lasing threshold can be obtained by setting $aP = 1$ in Eq. (3.1) which results in the lasing threshold,

$$R_{\text{th}} = \frac{1 + 1/\beta}{2a\Gamma_c} \quad (3.2)$$

Using Eq. (3.2), we extract a lasing threshold of $\sim 33 \mu\text{W}$ at low temperature and a lasing threshold of $\sim 54 \mu\text{W}$ at room temperature. In the next section, we discuss the cavity Q-factor requirement for the lasing to happen and argue that the long exciton lifetime of the interlayer exciton is advantageous in relaxing this requirement.

3.3. Effect of exciton lifetime on lasing threshold

The quality (Q) factor was estimated to be ~ 423 from $Q = \lambda/\Delta\lambda$, where $\Delta\lambda$ is the FWHM ($\sim 2.65 \text{ nm}$) of the spectral cavity emission peak just above the threshold. This Q factor is much lower than the Q-factor of the cavity used in previously reported intralayer exciton lasers¹⁻⁴. Here, we will show that the more relax cavity Q-factor requirement is due to the interlayer excitons having a much longer lifetime ($\sim \text{ns}$) compared to the intralayer exciton ($\sim \text{ps}$). In particular, it can be shown that for the same cavity quality, a longer carrier lifetime will result in a lower lasing threshold.

We first note that the lasing threshold expression in Eq. (3.2) gives the impression that the lasing threshold is independent of the interlayer exciton lifetime. However, this is only strictly true for an atomic system which is not our case. In order to obtain a better description of the effect of the lifetime to the lasing threshold, we perform the following tasks:

1. Analysis of lifetime dependence of β factor
2. Modeling the lasing emission using microscopic equation of motion theory based on semiconductor Hamiltonian⁵ together with the cluster expansion method.

The β factor is defined as the ratio between the spontaneous emission that is coupled to the lasing mode and the total spontaneous emission. It depends on the cavity parameter, the emitter lifetime, and the dephasing mechanism. In our case, the exciton spectrum broadening is mainly due to the dephasing caused by inhomogeneous broadening⁶. In this case, the β factor can be treated to be independent of lifetime⁷. Hence, we can use a constant value for β in our microscopic equation.

The microscopic theory is obtained by deriving the Heisenberg equation of motion from the semiconductor Hamiltonian⁵. As discussed in Chapter 1, the resulting equations are generally not solvable because of the time dependence of the lower order operator is coupled to higher order operator, the so-called operator hierarchy problem⁸. To handle this problem, the cluster expansion method can be used to truncate the problem to correlations of finite order^{5,8}.

Fig. 3.3. Rate equation of the carrier dynamics. Here, f_e (f_h) is the electron (hole) occupation number of the on-resonance energy levels while f_{e2} (f_{h2}) is the carrier occupation of the off-resonance energy level, ηP is carrier generation rate, t_{SE2}^{-1} is the spontaneous emission rate of the off-resonance level, t_R^{-1} is the relaxation rate to resonance level, and t_{SE}^{-1} is the interlayer exciton spontaneous emission rate. The cavity-enhanced photon-carrier interaction will contribute to the stimulated emission and absorption.

Next, we need to model the carrier dynamics. If we consider the case of an off-resonance excitation, the carrier dynamic can be illustrated as in Fig. 3.3. Here, f_e (f_h) is the electron (hole) occupation number of the lasing transition energy levels and f_{e2} (f_{h2}) is the electron (hole) occupation of the off-resonance energy level. The carrier (in our case, the intralayer exciton) is generated with the carrier generation rate ηP where P is the input power. After it is generated, it can recombine with the spontaneous emission rate t_{SE2}^{-1} or relax to the lower energy level with the relaxation rate t_R^{-1} . The carrier can then recombine with a recombination rate equal to t_{SE}^{-1} which results in the interlayer exciton spontaneous emission. Additionally, the cavity-enhanced photon-carrier interaction will contribute to the stimulated emission and absorption.

If we neglect the Coulomb interaction between the carriers and the exciton-exciton interaction, we will get the following set of differential equations^{5,8}:

$$\hbar \frac{d}{dt} \langle b^\dagger b \rangle = -2\kappa \langle b^\dagger b \rangle + N \frac{\hbar\beta(\kappa + \Gamma)}{t_{SE}} \langle b^\dagger v^\dagger c \rangle, \quad (3.3)$$

$$\hbar \frac{d}{dt} \langle b^\dagger v^\dagger c \rangle = -(\kappa + \Gamma) \langle b^\dagger v^\dagger c \rangle + f_e f_h - (1 - f_e - f_h) \langle b^\dagger b \rangle + \delta \langle b^\dagger b c^\dagger c \rangle - \delta \langle b^\dagger b v^\dagger v \rangle, \quad (3.4)$$

$$\hbar \frac{d}{dt} \delta \langle b^\dagger b c^\dagger c \rangle = -\frac{\hbar\beta(\kappa + \Gamma)}{t_{SE}} \left(\delta \langle b^\dagger b^\dagger b v^\dagger c \rangle + (\langle b^\dagger b \rangle + f_e) \langle b^\dagger v^\dagger c \rangle \right) - 2\kappa \delta \langle b^\dagger b c^\dagger c \rangle, \quad (3.5)$$

$$\hbar \frac{d}{dt} \delta \langle b^\dagger b v^\dagger v \rangle = -\frac{\hbar\beta(\kappa + \Gamma)}{t_{SE}} \left(\delta \langle b^\dagger b^\dagger b v^\dagger c \rangle + (\langle b^\dagger b \rangle + f_h) \langle b^\dagger v^\dagger c \rangle \right) - 2\kappa \delta \langle b^\dagger b v^\dagger v \rangle, \quad (3.6)$$

$$\hbar \frac{d}{dt} \delta \langle b^\dagger b^\dagger b b \rangle = -4\kappa \delta \langle b^\dagger b^\dagger b b \rangle + 2N \frac{\hbar\beta(\kappa + \Gamma)}{t_{SE}} \delta \langle b^\dagger b^\dagger b v^\dagger c \rangle, \quad (3.7)$$

$$\begin{aligned} \hbar \frac{d}{dt} \delta \langle b^\dagger b^\dagger b v^\dagger c \rangle = & -(3\kappa + \Gamma) \delta \langle b^\dagger b^\dagger b v^\dagger c \rangle - \frac{\hbar\beta(\kappa + \Gamma)}{t_{SE}} \langle b^\dagger v^\dagger c \rangle^2 \\ & - (1 - f_e - f_h) \langle b^\dagger b^\dagger b b \rangle + 2 \left(f_h \delta \langle b^\dagger b c^\dagger c \rangle - f_e \delta \langle b^\dagger b v^\dagger v \rangle \right), \end{aligned} \quad (3.8)$$

$$\frac{d}{dt} f_e = -\frac{\hbar\beta(\kappa + \Gamma)}{t_{SE}} \langle b^\dagger v^\dagger c \rangle - \frac{(1 - \beta) f_e f_h}{t_{SE}} + \frac{(1 - f_e) f_{e2}}{t_R}, \quad (3.9)$$

$$\frac{d}{dt} f_h = -\frac{\hbar\beta(\kappa + \Gamma)}{t_{SE}} \langle b^\dagger v^\dagger c \rangle - \frac{(1 - \beta) f_e f_h}{t_{SE}} + \frac{(1 - f_h) f_{h2}}{t_R}, \quad (3.10)$$

$$\frac{d}{dt} f_{e2} = \eta P (1 - f_{e2} - f_{h2}) - \frac{f_{e2} f_{h2}}{t_{SE2}} - \frac{(1 - f_e) f_{e2}}{t_R}, \quad (3.11)$$

$$\frac{d}{dt} f_{h2} = \eta P (1 - f_{e2} - f_{h2}) - \frac{f_{e2} f_{h2}}{t_{SE2}} - \frac{(1 - f_h) f_{h2}}{t_R}, \quad (3.12)$$

where the b , v , c ($b^\dagger$, $v^\dagger$, $c^\dagger$) are the annihilation (creation) operators for cavity mode photon, the hole of the interlayer exciton, and the electron of the interlayer exciton, respectively. The equations are then solved for steady state condition. The constant parameters used are shown in Table 3.1.

The system reaches the lasing threshold when the stimulated emission has the same contribution as the spontaneous emission. Using Eq. (3.4), this happens when $f_e f_h = - (1 - f_e - f_h) \langle b^\dagger b \rangle$. Based on this condition, we can get the lasing threshold as a function of the exciton lifetime. The value of the lasing threshold as the lifetime is varied from 0.1 to 1 ns is shown in Fig. 3.4. As can be seen, the lasing threshold is

reduced from 180 μW to 33 μW as the exciton lifetime is increased from 0.1 ns to 1 ns. As the inset of Fig. 3.4 shows, the lasing threshold is proportional to the spontaneous emission rate, i.e., it is inversely proportional to the exciton lifetime.

Table 3.1. Definition and values of the parameters used in the theoretical model

Symbol	Description	Value
η	Pumping efficiency: [pump rate] = η [pump power]	0.00016 THz/ μW
κ	Cavity loss rate. The value is calculated from the lasing emission linewidth.	0.55 THz
N	Maximum number of carriers. The value is obtained by fitting the L-L curve.	1400
β	β factor. The value is obtained by fitting the L-L curve.	0.16863
Γ	Linewidth broadening. The value is calculated from the spontaneous emission linewidth.	20 THz
t_R	Relaxation rate (including the interlayer tunneling) of the carrier	1 fs
t_{SE2}	Spontaneous emission rate of the intralayer exciton into the cavity mode.	1 ps

Fig. 3.4. Lasing threshold vs exciton lifetime. The inset shows a linear fitting of the lasing threshold as a function of spontaneous emission rate.

3.4. Summary and conclusion

In summary, for the first time, we have realized a room temperature near-infrared laser based on the interlayer excitons in $\text{MoS}_2/\text{WSe}_2$ van der Waals heterostructures. The long interlayer exciton lifetime allows relaxation on the cavity Q-factor requirement for lasing to happen. The flexibility of heterostructures brings more possibilities in future⁹.

Ternary phase layered material such as MoS_xSe_y or WS_xSe_y has been demonstrated to have tunable wavelength^{10,11}. Vertical stacking of these materials could engineer more possible bandgap. The wide range of the 2D materials, combined with stacking orientations, different layer numbers, allows for the controlled material response and shows a great promise for their nanophotonic applications. Future full integration of coherent light sources, waveguides, modulators, and detectors on single chips may eventually lead to on-chip 2D material integrated photonics^{12,13}.

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Chapter 4. Circular photogalvanic effect in 2D heterostructure

Due to the possibility to engineer the interlayer interaction¹⁻⁶ and to tailor the properties of different materials through proximity effect⁷⁻¹³, the two-dimensional van der Waals heterostructure has emerged as a potential material class for realizing future spintronics/valleytronics devices¹³⁻¹⁷ which can result in practical information processing devices that are more energy-efficient compared to the currently utilized charge-based approach^{18,19}. However, an efficient method of generating spin/valley current in 2D heterostructure is still lacking. Since 2D heterostructure consists of monolayers, it is natural to try to extend the technique of spin/valley current generation in the monolayer to the 2D heterostructure. This includes utilizing the circular photogalvanic effect (CPGE) to create the spin photocurrent.

Here, we report an observation of the CPGE when the MoS₂/WSe₂ heterostructure-electrode boundary is optically excited under a normal incidence. This phenomenon has been observed in some 2D Weyl semimetals such as WTe₂²⁰, MoTe₂, and Mo_{0.9}W_{0.1}Te₂²¹. In the monolayer WTe₂ case, the low order symmetry is intrinsically inherent and the CPGE is closely related to the topological properties in this material through the Berry curvature dipole²² while in the MoTe₂ and Mo_{0.9}W_{0.1}Te₂ case it is related to the asymmetric carrier generation due to the Gaussian profile of the optical excitation²¹. In contrast, for the MX₂ (M = Mo, W, and X = S, Se) materials, only CPGE under oblique incidence has been observed²³⁻²⁶.

The observation of CPGE under normal incidence shows that the symmetry near the electrode-sample boundary is reduced from three-fold rotational symmetry (C_3) to C_s or lower order. In particular, in this region, there is a built-in in-plane electric field due to the laterally extending Schottky depletion region^{27,28}, which contributes to the overall system symmetry reduction. Following this reasoning, it should be possible to modulate the circular photocurrent (CPGE current) by applying an external electric field. Indeed, we show that the source-drain bias can modulate both the magnitude and the polarity of

the CPGE current. Moreover, we show that the back gating can be used to control the magnitude of the CPGE current.

We also propose a theoretical explanation for the observed CPGE. Specifically, we show that the in-plane electric field shifts the valence band of WSe₂ near the electrode-sample boundary with the K and K' valley shift in the opposite direction. As the electron and hole have different effective relaxation time in the heterostructure, this will result in a sizable nonzero valley-dependent photocurrent that has opposite direction in the K and K' valleys. Combined with the valley optical selection rules, this results in the observed CPGE. Our theoretical simulation results show a good agreement with the experimental results. To the best of our knowledge, our finding is the first demonstration of CPGE induced by an in-plane electric field in 2D TMD heterostructure.

4.1. Device description, experimental setup, and CPGE map

Fig. 4.1(a) shows a microscopic image of the fabricated device. It consists of gold electrodes patterned on top of MoS₂/WSe₂ heterostructure with SiO₂/Si as the substrate. As discussed in Chapter 1, due to the absence of the inversion symmetry, the Berry curvature becomes nonzero at K and K' valleys with its polarity is opposite between these two valleys. As a result, different circular polarization couples to different valleys²⁹⁻³⁴. Moreover, the type-II band alignment of MoS₂/WSe₂ causes electrons to relax to the MoS₂ layer while holes relax to the WSe₂ layer suppressing the electron-hole exchange interaction. Such suppression reduced the intervalley scattering³⁵⁻³⁷, which results in a significant valley polarization of the carrier even at room temperature^{38,39}. Additionally, the suppression of the intervalley scattering could increase the carrier relaxation time. Both the high carrier valley polarization and the long carrier relaxation time in MoS₂/WSe₂ can contribute to a sizable CPGE current.

Fig. 4.1. Device and experimental setup. **(a)** Optical image of the device. The device consists of gold electrodes patterned on top of MoS₂/WSe₂ heterostructure with SiO₂/Si as the substrate. The numbers shown are for easy reference to the electrodes. **(b)** Experimental setup. The chopper used in tandem with the use of the quarter-wave plate and the galvo mirror system used to control the excitation location are not shown.

The setup for detecting and characterizing the CPGE is shown in Fig. 4.1(b). The polarization state of the light is controlled either by changing the phase retardation of the liquid crystal modulator or by changing the quarter-wave plate (QWP) axis orientation. The excitation can be scanned over the sample area by using a galvo mirror system (not shown in the schematic) before the polarizer. In the case that liquid crystal is used to modulate the circular polarization, the current is passed into a lock-in amplifier to get the CPGE current. In the case the QWP is used, the dark current is subtracted by using a chopper and a lock-in amplifier. Here, the CPGE current is defined as the difference between the source-drain current under left-circularly (σ_+) and right-circularly (σ_-) polarized excitation: $I_{CPGE} = I_{SD}(\sigma_+) - I_{SD}(\sigma_-)$. The source-drain voltage, V_{SD} , and the back gate voltage, V_G , can be varied independently. All of the experiments were done under a normal incidence optical excitation, which rules out any contribution from the circular photon drag effect²⁶. The excitation wavelength is 720 nm, which is near the WSe₂ exciton transition⁴⁰ with the excitation power is around 100 to 115 μ W.

Fig. 4.2. (a) CPGE map with source: electrode 3 and drain: electrode 2. (b) CPGE map with source: electrode 6 and drain: electrode 5. Both CPGE map is obtained using 720 nm 115 μW excitation at room temperature (295 K). (c,d) Similar as (a,b) but at low temperature and with 720 nm 100 μW excitation.

We obtained the CPGE map (i.e. I_{CPGE} , vs. excitation location) under zero bias ($V_{SD} = V_G = 0\text{V}$) with the circular polarization is modulated by using a liquid crystal modulator. The CPGE map for two different electrode configurations at room temperature are shown in Fig. 4.2(a, b), respectively, while the ones obtained at low temperature (140 K) are shown in Fig. 4.2(c, d), respectively. The reproducibility of the phenomenon is confirmed by testing a different sample using the same setup (Fig. 4.3(b)). In particular, the CPGE is much more apparent for excitation near the edge of the metal electrodes compared to the other parts of the sample. This shows that the CPGE depends on parameters that are large only near the electrode edges. One candidate for such parameters is the built-in in-plane electric field, which is caused by the band bending near the electrode-sample interface.

Fig. 4.3. CPGE map at room temperature for another $\text{MoS}_2/\text{WSe}_2$ heterostructure device. (a) The layout of the device. The two electrodes numbered 4 are shorted to each other. The dashed line shows the boundary of the heterostructure. (b) CPGE map with source: electrode 3 and drain: electrode 4. There is no source-drain bias apply to the sample. The gate voltage of 5V is used. The unit of the CPGE current is nA.

4.2. Effect of the external electric field effect on the CPGE current

We then study how the CPGE is affected by the external electric field, starting with the effect of the in-plane electric field. This is done by modulating the source-drain voltage. For this experiment, we use a quarter-wave plate to modulate the excitation polarization. In Fig. 4.4(a), the photocurrent at various source-drain voltage is plotted as a function of quarter-wave plate fast axis angle with respect to the polarizer axis. The data is fitted using the fitting function

$$I_{SD} = I_0 + I_1 \sin(4\theta) + I_2 \cos(4\theta) + I_{CPGE} \sin(2\theta), \quad (4.1)$$

where I_0 is the polarization-independent photocurrent while I_1 and I_2 are related to the linear photocurrent (i.e., photocurrent caused by linearly polarized optical excitation). In Fig. 4.4(b), I_{CPGE} obtained from the fitting is plotted as a function of source-drain voltage. From this figure, it can be concluded that the in-plane electric field modulates both the magnitude and the polarity of the CPGE current.

Fig. 4.4. CPGE characterization against source-drain voltage at 140 K. **(a)** Excitation polarization effect on the source-drain current at various source-drain voltage. The source-drain current is plotted as a function of the quarter-wave plate fast axis angle with respect to the polarizer axis. Only the photocurrent is measured. The dark current is subtracted by using a chopper and a lock-in amplifier. **(b)** CPGE current as a function of source-drain voltage. The results are obtained by fitting the data in (a) using Eq. (4.1). All of the data is collected using 720 nm 100 μ W excitation.

Next, we study the back gate voltage dependence of the photocurrent, which mainly affects the out-of-plane electric field. First, we use the liquid crystal modulator to modulate the excitation polarization. The plot of I_{CPGE} as a function of the back gate voltage V_G is shown in Fig. 4.5(a) upper panel. Additionally, we also study the polarization-independent part (including the dark current) defined as $\overline{I_{SD}} = \frac{I_{SD}(\sigma_+) + I_{SD}(\sigma_-)}{2}$. The plot of $\overline{I_{SD}}$ as a function of source-drain voltage is shown in Fig. 4.5 (a) lower panel. By comparing Fig. 4.5(a) upper and lower panels, we can see that both I_{CPGE} and $\overline{I_{SD}}$ goes to zero as the back gate voltage goes to a more negative value. We then replace the liquid crystal modulator with a quarter-wave plate. The plot of photocurrent as a function of the quarter-wave plate fast axis angle at various back gate voltage is shown in Fig. 4.5(b). The plot of the three types of photocurrent extracted using Eq. (4.1) as a function of the back gate voltage is given in Fig. 4.5(c). As can be seen from this figure, regardless of the type (polarization-independent, linear, and circular), all photocurrents show the same trend of going to zero as the back gate voltage becomes more negative.

Fig. 4.5. CPGE characterization against gate voltage at 295 K. **(a)** CPGE current as a function of gate voltage. A liquid crystal modulator is used to modulate between σ_+ and σ_- excitation. The data is obtained using a 720 nm 115 μ W laser. **(b)** Excitation polarization effect on the source-drain current at various gate voltage. The source-drain current is plotted as a function of the quarter-wave plate fast axis angle with respect to the polarizer axis. Only the photocurrent is measured. The dark current is subtracted by using a chopper and a lock-in amplifier. **(c)** CPGE, LPGE, and polarization-independent current as a function of the source-drain voltage. The results are obtained by fitting the data in (b) using Eq. (4.1) with $I_{LPGE} = \sqrt{I_1^2 + I_2^2} \approx I_1$. The data is collected using a 720 nm 115 μ W laser excitation.

Based on the experiments above, we can conclude three things: (1) the in-plane electric field affects both the CPGE current magnitude and polarity, (2) the out-of-plane electric field does not change the CPGE current polarity, and (3) out-of-plane electric field affects the CPGE current magnitude the same way as it affects the magnitude of other types of current. These indicate that the CPGE generation mechanism depends on the in-plane electric field, while the out-of-plane electric field affects overall conductivity. In the next part, we discuss the theoretical explanation of these experimental results.

4.3. Theoretical model

We start by analyzing the effect of the in-plane electric field on the circular photocurrent. As discussed in Chapter 1, under the influence of the in-plane electric field, the electron wave packet velocity will have two components: **(1)** a component proportional to the

slope of the energy band, and **(2)** the anomalous velocity perpendicular to the in-plane electric field⁴¹⁻⁴⁴. Since the observed circular photocurrent has a direction parallel to the electric field, it cannot be attributed to the anomalous velocity. Hence, the observed CPGE must be attributed to the modification of the energy band due to the electric field.

The energy band modification by the electric field can be obtained from the second-order semi-classical transport theory⁴¹. In the second-order theory, in addition to the unperturbed local Hamiltonian, the band is also affected by the local first-order perturbation. Hence the band energy can be obtained by solving

$$H|u_n\rangle = (H_0 + \Delta H)|u_n\rangle = \varepsilon_n|u_n\rangle, \quad (4.2)$$

where H_0 is the unperturbed local Hamiltonian, ΔH is the first-order perturbation, $|u_n\rangle$ is the energy eigenstate, and ε_n is the band energy.

Fig. 4.6. Space coordinate definition used in the report.

Our interest is to solve Eq. (4.2) near K (K') valley for the case of a uniform electric field. For a perturbation by a uniform electric field, $\Delta H = V(\vec{r}) = V(x, y) = eA(x \cos \alpha + y \sin \alpha)$, where e is the electron charge, (A, α) represents electric field amplitude and direction, and (x, y) represents a position in space with respect to the wave packet center (see Fig. 4.6). Next, we need to choose a suitable basis for the $\vec{k}$ -dependent Hamiltonian matrix.

The electronic Bloch states near the K (K') valley have been discussed in Chapter 1 ($\{|\Phi_1(\vec{k}, \vec{r})\rangle, |\Phi_2^\tau(\vec{k}, \vec{r})\rangle\}$ in Eq. (1.1) and (1.2)) with the H_0 in this Bloch state basis is

given by Eq. (1.3). Similarly, the element of the ΔH matrix can be obtained from $\Delta H_{ij}(\vec{k}) = \langle \Phi_i(\vec{k}, \vec{r}) | V(\vec{r}) | \Phi_j^\tau(\vec{k}, \vec{r}) \rangle$ by utilizing the nearest neighbor approximation and just keeping the terms up to first order in $\vec{k}$. We can then solve Eq. (4.2) to get the band energy. Doing so up to first order in the electric field and second order in $\vec{k}$, we obtain

$$\varepsilon_{CB}(\vec{k}) = \frac{\Delta}{2} + \frac{a_0^2 t^2 k^2}{\Delta}, \quad (4.3)$$

$$\varepsilon_{VB}(\vec{k}) = -\frac{\Delta}{2} - \frac{a_0^2 t^2 k^2}{\Delta} + \tau A [C_1 k_x \sin(\alpha) + C_2 k_y \cos(\alpha)], \quad (4.4)$$

with $C_1 = 2ea_0(Y_0 - Y_1)$,

$$C_2 = 2ea_0(\sqrt{3}X_1),$$

$$X(Y)_m = \langle d_{xy}(\vec{r}) | x(y) | d_{x^2-y^2}(\vec{r} - \vec{R}_m) \rangle, \text{ and}$$

$$\vec{R}_m = a_0 \left(\cos\left(m\frac{2\pi}{3}\right) \hat{x} + \sin\left(m\frac{2\pi}{3}\right) \hat{y} \right),$$

where a_0 is the lattice constant, Δ is the bandgap at $\vec{k} = 0$, and t is the effective hopping integral.

Hence, there is no band modification due to the electric field for the conduction band, while the valence band has a modification linear to the applied electric field amplitude with the slope sign is opposite for K and K' valley (i.e., the band shift in the opposite direction at K and K' valley). It is reasonable to assume that a_0 is big enough such that, at the neighbor lattice site, the value of the radial part of the orbital function is constant: $d_\alpha(\vec{r} - \vec{R}_m) \approx CL_\alpha(\vec{r} - \vec{R}_m)$ where C is a constant and $L_\alpha(\vec{r})$ is the angular part of the orbital function. It is then possible to show that, when the lattice has three-fold rotational symmetry, $(Y_0 - Y_1) \approx -\sqrt{3}X_1$. This has a consequence that $C_1 + C_2 = 0$. However, near the electrode-sample boundary, it is expected that the lattice rotational symmetry is broken due to the residual strain. In the simplest case of a uniform strain along the electrode-sample boundary, the $C_{1(2)}$ is a constant with the value of $C_1 + C_2 \neq 0$. Given this valence band shift, we can then explain the CPGE mechanism.

Fig. 4.7. Microscopic model of the CPGE generation and the simulation result. **(a)** Near the electrode-sample boundary, the in-plane electric field shifts the valence band at K and K' valley in two opposite directions. Resonant optical excitation creates electron and hole in the WSe₂ layer with the same nonzero velocity. Electrons then transfer to the MoS₂ layer via an ultrafast charge transfer process. Due to the difference in the carrier relaxation time in MoS₂ and WSe₂, the hole and electron will have different effective relaxation time. Hence, a nonzero valley-dependent photocurrent is generated. The photocurrent has an opposite direction between K and K' valley. Combined with the valley optical selection rule, this results in electrically tunable CPGE current density. **(b, c)** COMSOL simulation of the I_{CPGE} for (source, drain): (electrode 3, 2) and (electrode 6, 5) respectively. The unit for I_{CPGE} is the same in both figures. The simulation results agree well with the experimental results.

The proposed mechanism is illustrated in Fig. 4.7(a) for the case of resonant excitation (i.e., the excitation energy is resonant with the energy gap at $\vec{k}=0$). The optical excitation creates the non-equilibrium electron and hole population with their velocity proportional to the conduction and valence band slope, respectively. Due to the valley optical selection rule in WSe₂, the light with σ_+ (σ_-) polarization can only generate carrier around K (K') valley. Considering only one valley, there are two transitions with the same energy. One of the transitions generates nonzero electron current while the other generates nonzero hole current, both in the same direction. Due to the opposite charge between electron and hole, the two contributions tend to eliminate each other. However, in MoS₂/WSe₂ heterostructure, the electron will undergo ultrafast charge transfer to the MoS₂ layer. Since both the electron relaxation time and the conduction band curvature of MoS₂ are different than those in WSe₂, the current generated by the electrons and holes will not cancel each other, and a nonzero photocurrent is generated in K/K' valley. Due to the opposite shift between the valence band in the K and K' valley, the photocurrent will have an opposite direction for these two valleys, which results in

a nonzero CPGE current. Furthermore, since the shift is linearly proportional to the in-plane electric field, the CPGE current will also be linearly proportional to this field.

Following this model, we can then derive the expression of the CPGE current density, $\overrightarrow{J_{CPGE}}$. Since the anomalous velocity contribution can be ignored, the general expression of the photocurrent in a two-band system is given by^{20,26,45}

$$\overrightarrow{J_{ph}} = -\frac{2\pi e^3}{\hbar m_e^2} \int \frac{d^2k}{(2\pi)^2} (f_v - f_c) (\tau_c \overrightarrow{v_c} - \tau_v \overrightarrow{v_v}) \left| \langle \Phi_c | \overrightarrow{A} \cdot \overrightarrow{p} | \Phi_v \rangle \right|^2 \delta(\varepsilon_g - \hbar\omega), \quad (4.5)$$

where m_e is the bare electron mass, $f_{v(c)}$ is the electron occupation number in valence (conduction) band, $\tau_{v(c)}$ is the relaxation time of the valence(conduction) band, $\overrightarrow{v_{v(c)}} = \nabla_k \mathcal{E}_{VB(CB)} / \hbar$ is the electron velocity in valence(conduction) band, $\overrightarrow{A}$ is the vector potential of the optical excitation, $\overrightarrow{p} = (m_e / \hbar) \nabla_k H$ is the momentum operator, ε_g is the energy gap, and $\hbar\omega$ is the excitation energy.

For circularly polarized excitation, $\overrightarrow{A} \cdot \overrightarrow{p} = \frac{E_\omega m_e}{i\hbar\omega\sqrt{2}} \left(\frac{\partial H}{\partial k_x} \pm i \frac{\partial H}{\partial k_y} \right)$ with E_ω is the electric

field amplitude of the optical excitation and the $\pm$ depends on the handedness of the circularly polarized excitation. For the case where an undoped wide bandgap material is weakly excited, the valence band can be treated as fully occupied, and the conduction band is empty. Hence, $f_v - f_c$ can be taken to be equal to 1. The CPGE current density can be obtained from $\overrightarrow{J_{CPGE}} = \overrightarrow{J_{ph}^+} - \overrightarrow{J_{ph}^-}$ where the superscript indicates if it's left-handed (+) or right-handed (-) excitation. Using the description above and Eq. (4.5), we obtain

$$\overrightarrow{J_{CPGE}} = \frac{e^3 E_\omega^2}{2\pi \hbar^3 \omega^2} \int d^2k (\tau_c \overrightarrow{v_c} - \tau_v \overrightarrow{v_v}) \varepsilon_g^2 \Omega_{CB} \delta(\varepsilon_g - \hbar\omega), \quad (4.6)$$

where $\Omega_{CB} \hat{z}$ is the Berry curvature of the conduction band (see Chapter 1):

$$\Omega_{CB} = \frac{-2}{\varepsilon_g^2} \text{Im} \left\{ \langle u_c | \frac{\partial H}{\partial k_x} | u_v \rangle \langle u_v | \frac{\partial H}{\partial k_y} | u_c \rangle \right\}, \quad (4.7)$$

with $|u_{v(c)}\rangle$ is the $\vec{k}$ -dependent quantum state of the valence(conduction) band electron obtained by solving Eq. (4.2) in $\left\{ |\Phi_1(\vec{k}, \vec{r})\rangle, |\Phi_2^\tau(\vec{k}, \vec{r})\rangle \right\}$ basis. For the case of a uniform electric field, the Berry curvature near the K (K') valley can be expressed as

$$\Omega_{CB}^{\tau}(\vec{k}) \approx \frac{2\tau a_0^2 t^2}{\Delta^2} \left(\begin{aligned} &\left(-1 + \frac{6a_0^2 t^2 k^2}{\Delta^2} \right) + \sqrt{2} e A a_0 \sin(\alpha) \left((Y_0^A - Y_1^A) + \sqrt{3} Y_1^B \right) \\ &-\frac{3\tau A}{\Delta} [C_1 k_x \sin(\alpha) + C_2 k_y \cos(\alpha)] \end{aligned} \right), \quad (4.8)$$

with $X(Y)_m^A = \langle d_{xy}(\vec{r}) | x(y) | d_{z^2}(\vec{r} - \vec{R}_m) \rangle$, and $X(Y)_m^B = \langle d_{x^2-y^2}(\vec{r}) | x(y) | d_{z^2}(\vec{r} - \vec{R}_m) \rangle$.

For the 2D heterostructure, both the effective mass and relaxation time is different for electron and hole. Hence, it should be model as two-band with different effective mass and relaxation time. However, it is quite straight forward to show that the effect of the difference in the effective mass can be incorporated into an effective relaxation time since the only relevant term is the multiplication between velocity (which is affected by the mass) and relaxation time. Furthermore, due to the three-fold rotational symmetry, the charge transfer does not change the velocity direction of the electron. Hence, we can model the 2D heterostructure as a two-band system with the electron and hole have the same effective mass but different relaxation time.

To analyze the effect of the relaxation time difference, we rewrite Eq. (4.6) to

$$\overrightarrow{J_{CPGE}} = \frac{e^3 E_{\omega}^2}{2\pi \hbar^3 \omega^2} \left(\begin{aligned} &\int d^2 k \tau_v (\vec{v}_C - \vec{v}_V) E_g^2 \Omega_{CB} \delta(E_g - \hbar \omega) \\ &+ \int d^2 k (\tau_C - \tau_v) \vec{v}_C E_g^2 \Omega_{CB} \delta(E_g - \hbar \omega) \end{aligned} \right). \quad (4.9)$$

By using Eq. (4.3), (4.4), and (4.8) the first term in Eq. (4.9), which is related to the Berry curvature dipole^{20,22}, can be proven to be zero in our case. This left us only with the second term:

$$\begin{aligned} \overrightarrow{J_{CPGE}} &= \frac{e^3 E_{\omega}^2 (\tau_C - \tau_v)}{2\pi \hbar^3 \omega^2} \int d^2 k \vec{v}_C E_g^2 \Omega_{CB} \delta(E_g - \hbar \omega) \\ &= \frac{e^3 E_{\omega}^2 (\tau_C - \tau_v)}{2\pi \hbar^4 \omega^2} \int d^2 k E_g^2 \Omega_{CB} \delta(E_g - \hbar \omega) \left(\frac{\partial E_{CB}}{\partial k_x} \hat{x} + \frac{\partial E_{CB}}{\partial k_y} \hat{y} \right) \\ &= \frac{e^3 E_{\omega}^2 (\tau_C - \tau_v)}{2\pi \hbar^2} \oint_{E_g = \hbar \omega} dl \frac{\Omega_{CB} \left(\frac{\partial E_{CB}}{\partial k_x} \hat{x} + \frac{\partial E_{CB}}{\partial k_y} \hat{y} \right)}{\sqrt{\left(\frac{\partial E_g}{\partial k_x} \right)^2 + \left(\frac{\partial E_g}{\partial k_y} \right)^2}} \end{aligned} \quad (4.10)$$

Here, $dl = \sqrt{(dk_x)^2 + (dk_y)^2}$ and the relation $\int_{\mathbf{R}^n} d\vec{r} f(\vec{r}) \delta(g(\vec{r})) = \int_{g^{-1}(0)} d\sigma(\vec{r}) \frac{f(\vec{r})}{|\nabla_r g|}$,

where the $\sigma(\vec{r})$ indicates a path where $g(\vec{r}) = 0$ holds, has been used. Using Eq. (4.3), (4.4), (4.8) and (4.10) we obtain, up to first order in the electric field

$$\overrightarrow{J_{CPGE}} = M \{ C_1 \sin(\alpha) \hat{x} + C_2 \cos(\alpha) \hat{y} \}, \quad (4.11)$$

$$\text{with } M = \left(\frac{3e^3}{2\hbar^2 \Delta} \left(\frac{\hbar\omega}{\Delta} - \frac{4}{3} \right) \right) E_\omega^2 A (\tau_c - \tau_v).$$

Given the expression of $\overrightarrow{J_{CPGE}}$, we can obtain the CPGE current as⁴⁶

$$I_{CPGE} = \int \overrightarrow{J_{CPGE}}(\vec{r}) \cdot \nabla_r \psi(\vec{r}) d^2r, \quad (4.12)$$

with $\psi(\vec{r})$ is the solution of $\nabla \cdot (\nabla(\sigma^T \psi)) = 0$ and σ is the in-plane conductivity tensor. In our case, due to the three-fold rotational symmetry, the in-plane conductivity can be taken to be isotropic. In this case, $-\nabla_r \psi(\vec{r})$ can be treated as a virtual electric field going from the (+) electrode to (-) electrode. For the rest of the discussion, we will ignore the negative sign as it is only a multiplication constant. The value of I_{CPGE} can then be obtained by taking the scalar product between $\overrightarrow{J_{CPGE}}$ and the virtual electric field and integrating it over the sample. By repeating this procedure for all excitation locations, we can obtain the CPGE map.

To give a qualitative picture of the CPGE map, we first neglect the effect of the floating electrodes (i.e., electrodes that do not draw any current). Near the current collecting electrode, the virtual electric field will have the same direction as the built-in electric field: $\nabla_r \psi(\vec{r}) \propto \beta (\hat{x} \cos \alpha + \hat{y} \sin \alpha)$ where $\beta = 1$ for (+) electrode and $\beta = -1$ for the (-) electrode. Using this expression and Eq. (4.11) in Eq. (4.12) we obtain

$$\begin{aligned} I_{CPGE} &\propto \int_{\text{Excitation location}} E_\omega^2 A \beta (C_1 \sin(\alpha) \hat{x} + C_2 \cos(\alpha) \hat{y}) \cdot (\hat{x} \cos \alpha + \hat{y} \sin \alpha) d^2r \\ &\propto \frac{(C_1 + C_2)}{2} E_\omega^2 A \beta \sin(2\alpha). \end{aligned} \quad (4.13)$$

As discussed before, $(C_1 + C_2) \neq 0$ only for the region near electrodes where the three-fold symmetry is broken. Also, since the built-in electric field is only significant near

the electrode edge, I_{CPGE} is reduced significantly for the optical excitation far away from the edge. Moreover, at the two sides of the same electrode, α differs by 180° , which results in the same sign for the CPGE current, while between the two perpendicular sides of the electrode, α differs by 90° , which results in the opposite sign for the CPGE current. This is in line with the conclusions obtained from the experimental results (Fig. 4.2).

Equation (4.12) can be used to get the CPGE map for a general case that includes the floating electrode. We obtain the virtual electric field by using COMSOL. The optical beam is modeled as a Gaussian beam with the full width at half maximum (FWHM) taken to be 400 nm. Given that the excitation wavelength is 720 nm, this beam width is still above the diffraction limit. The built-in electric field is modeled as an exponentially decaying negative value electric field with the direction normal to the electrode edge with a decay constant of 10 nm. Referring to Fig. 4.1 (a) and Fig. 4.6, the x-direction is taken to be 10° from the direction from electrode 4 to electrode 1. The values of $C_1 = 1$ and $C_2 = -0.6$ are used. Since the magnitude of the built-in electric field is highly dependent on the contact, each electrode can have a different maximum built-in electric field. These weighting factors are chosen to match the CPGE maps (Fig. 4.2). The CPGE current simulation results, including the effect of both current-collecting and floating electrodes, is shown in Fig. 4.7(b, c). They show a good agreement with the experimental results.

We now discuss the effect of the back-gate voltage (the out-of-plane electric field). Applying a back-gate voltage is equivalent to the carrier doping, which will change the Fermi level. There are two effects of changing the Fermi level. The first one is that it will change the built-in electric field since it affects the band bending between the $\text{MoS}_2(\text{WSe}_2)$ and the Cr/Au electrode. This will affect I_{CPGE} in the same way as the in-plane electric field does. The second effect is that it can change the conduction band electron mobility. When the Fermi level is higher than the energy of some defect states, the defects will be fully occupied and cannot act as a scattering center²³. This results in a higher conduction band electron mobility. Unlike the first mechanism, the second one will affect all types of current. The interplay between these two mechanisms depends

on the energy level of the traps. However, based on the fact that all type of currents shows similar behavior as the gate voltage is changed, we conclude that the second mechanism is more dominant in our case.

4.4.Theoretical estimation of the CPGE current magnitude

In this section, we estimate the CPGE current based on the proposed theory above and compare it with the observed CPGE current. To do this estimation, we consider the case where:

1. The electric field is constant within the depletion region and zero outside the depletion region. Let the depletion length is symbolized as l_d , then the electric field can be expressed as $A = \frac{\varepsilon_\Delta}{el_d}$ with ε_Δ is the difference between the work function of the region covered and not covered by the electrodes.
2. The value of $\nabla_{\vec{r}}\psi(\vec{r})$ can be approximated as $\frac{K}{d}$ where d is the distance between the electrode and $K > 1$ is a constant proportional to the focusing of electric field line near the electrode: i.e., the value of K will be bigger at the sharp corner of the electrode than at the straight edge.
3. The light intensity is uniform within an area of $D \times D$ where D is the diameter of the optical beam. For $l_d \ll D$, the integration area needs to be considered is $l_d \times D$.
4. The excitation energy, $\hbar\omega$, has the same value as Δ .
5. The relaxation time of the valence band hole is negligible compared to that of the conduction band (CB) electron: $(\tau_c - \tau_v) \approx \tau_c$.
6. The value of $(C_1 + C_2)$ is taken to be $\sim 2ea_0^2$.
7. The value of E_ω^2 can be obtained from the optical excitation power through $E_\omega^2 \approx \frac{2P}{c\varepsilon_0 D^2}$ where P is the optical excitation power. Here, we take that the effective refractive index in the out-of-plane direction is equal to one⁴⁷.

Applying those points above in Eq. (4.11) and (4.12), we obtain

$$I_{CPGE} = \left(\frac{e^3 \varepsilon_\Delta a_0^2 \tau_c}{2\hbar^2 \Delta c \varepsilon_0} \right) \left(\frac{KP}{dD} \right) \beta \sin(2\alpha). \quad (4.14)$$

Considering the work function of Au and MoS₂⁴⁸, we take $\varepsilon_A \approx 1.5$ eV. The value of $a_0^2 \approx 0.1$ nm² and $\Delta \approx 1.7$ eV are used. The relaxation time of the CB electron (τ_c) is taken to be ~ 200 fs⁴⁹. The electrode and optical beam parameter used are: $d \approx 1$ μ m, $D \approx 0.4$ μ m, and $P \approx 100$ μ W. The value of $K \approx 2$ is used to account for the electrode corner influence. Using these values, we obtain

$$I_{CPGE} \approx 1.2\beta \sin(2\alpha) \text{ [nA]}, \quad (4.15)$$

for the optical excitation near the current-collecting electrode. This is agreeable with the order of magnitude of the experimentally observed I_{CPGE} (Fig. 4.2). Moreover, based on the COMSOL simulation, we found that the CPGE map can be reproduced (Fig. 4.7(b, c)) by using $l_d \approx 30$ nm. This value of l_d is comparable to the depletion width at TMD/metal interface reported in other studies⁵⁰. Using this value of l_d , the built-in electric field can be estimated as $A \approx 50$ V/ μ m.

4.5. Summary and conclusion

In summary, we have experimentally demonstrated the CPGE under normal incidence optical excitation near MoS₂/WSe₂ heterostructure-electrode interface. The CPGE can be controlled by the source-drain bias and the electrical back gating. The source-drain dependence can be explained by the valence band shift due to the in-plane electric field, valley-specific optical selection rules, and the asymmetry in electron and hole effective relaxation time. The simulation results of the CPGE maps fits well with the experimental results. The back gate dependence is attributed to the modulation of the doping level, which affects the charge trap occupation and, hence, the carrier mobility. Combined with the long carrier and spin polarization lifetime in 2D heterostructure^{40,51}, this finding may be utilized to realize a practical valleytronics and spintronics semiconductor devices.

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Chapter 5. Summary and possible future works

5.1. Summary

In conclusion, we have discussed several aspects of the light-matter interaction in the 2D TMD heterostructure. Most of the unique properties of this type of material stem from the layer separation between electron and hole and the interlayer coupling. Moreover, the twist angle and lattice mismatch create a superlattice called Moiré superlattice, which modulates the monolayer crystal potential.

There are four findings related to the light-matter interaction in 2D TMD heterostructure that have been discussed both experimentally and theoretically:

1. The dark intralayer exciton acts as an interlayer exciton valley polarization reservoir. When the dark intralayer exciton intervalley scattering is suppressed, the interlayer exciton valley polarization lifetime can reach the microsecond regime.
2. The hole-electron layer separation results in the reduced electron-hole Coulomb interaction. As a result, the interaction between electrons (holes) can affect the exciton energy through optical spin pumping. Utilizing the optical spin-pumping in the optically addressed valley, the optically induced valley splitting of the interlayer exciton is demonstrated.
3. The interlayer exciton long lifetime relaxes the cavity Q-factor requirement to create the ultralow threshold excitonic laser. By realizing the interlayer exciton laser, we demonstrated the coherent interaction between interlayer exciton and light.
4. At the boundary between 2D TMD heterostructure and electrode, there is a Schottky barrier, which results in the laterally extending built-in electric field. This built-in electric field is responsible for the circular photocurrent observed when the boundary is optically excited. The circular photogalvanic effect mechanism involves the in-plane electric field induced valence band shifting. Combined with the valley circular optical selection rule, this demonstrates the conversion between the valley and charge information in the 2D TMD heterostructure.

In the next section, we discuss several possible future works based on these findings.

5.2. Possible future works

5.2.1. Dark exciton Bose-Einstein condensate (BEC)

The Bose-Einstein condensate (BEC) has been observed in electrically pumped interlayer exciton¹. The long lifetime of the interlayer exciton makes it possible to observe BEC at a high temperature (above 100 K). Dark exciton has an even longer lifetime than the interlayer exciton². Hence, it is expected that the dark exciton BEC can be observed even at a higher temperature, possibly at room temperature. The problem with this type of dark BEC is that it is difficult to be observed³. The coupling between the dark exciton and the interlayer exciton in 2D TMD heterostructure can enable the observation of dark exciton BEC signature in the interlayer exciton emission.

5.2.2. Optically defined excitonic circuit

As we have shown in Chapter 2, it is possible to control the exciton energy at the excitation location by controlling the optical excitation polarization. Controlling the exciton energy landscape using external stimuli is the basic working mechanism of an excitonic circuit. Currently, this has been achieved by using electrical gating⁴. Since it is possible to control the position-dependent exciton energy using CW light, it is then possible to control the exciton energy landscape using CW light, thus resulting in an optically defined excitonic circuit. In this type of excitonic circuit, the excitonic circuit is drawn by controlling the position-dependent light polarization, for example, using a spatial light modulator (SLM). The exciton that is traveling through the circuit can be either optically generated using another optical source or electrically generated. Since the circuit is optically defined, this can result in a higher modulation rate than in electrically defined excitonic circuit. One of the challenges is that currently, the phenomenon is only observed at a low temperature (< 100 K). In order to make a practical device, the working temperature must be close to the room temperature.

5.2.3. Multilayer TMD heterostructure

In this thesis, we have discussed only the hetero bilayer system. Adding more layers consisting of 2D TMD or other materials can result in other interesting phenomena. For example, due to the proximity effect, it has been shown that TMD can induce a large

spin-orbit coupling in graphene⁵. Similarly, the reverse will also be true: graphene or other material can affect the exciton in the 2D TMD. Stacking more TMD layers on top of the hetero bilayer will result in the change of the valence band maxima or conduction band minima from K (K') point to other high symmetry points⁶. This can result in more population of the momentum-indirect exciton population, which can convert to momentum-direct exciton by electron-phonon coupling at a high temperature. The change in the interlayer electron-hole separation distance will also affect both valley polarization and the exciton lifetime, which may be useful in realizing TMD-based valleytronics devices.

5.2.4. Strain and electric field engineering of circular photocurrent

As has been discussed in chapter 4, external stimuli can be used to control the symmetry of the 2D material. Other than the electric field, the use of strain to break the symmetry of monolayer TMD has been experimentally demonstrated through the observation of valley magnetoelectricity⁷. Theoretically, it has been suggested that strain can also induce valley magnetization⁸ and anomalous transverse current similar to nonlinear valley Hall effect⁹. However, such studies have not been done on the 2D TMD heterostructure. Due to the Moiré pattern, 2D TMD heterostructure has a built-in periodic strain and large strain gradient^{10,11}. A localized strain can be induced using an atomic force microscope (AFM) tip to break this periodicity. The presence of the large strain gradient can greatly enhance the effect of the locally strain-induced symmetry breaking. Hence, the application of both the strain and electric field may result in a larger circular photocurrent.

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