Valley-optical properties in layered 2D transition metal dichalcogenides

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SINGAPORE

**VALLEY-OPTICAL PROPERTIES IN LAYERED 2D
TRANSITION METAL DICHALCOGENIDES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

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HUANG ZUMENG

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 or 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.

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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 is published as Chongyun, Jiang, Fucai Liu, Jorge Cuadra, Zumeng Huang, Ke Li, Abdullah Rasmita, Ajit Srivastava, Zheng Liu, and Wei-Bo Gao. "Zeeman splitting via spin-valley-layer coupling in bilayer MoTe₂." Nature communications 8, no. 1 (2017): 1-6. DOI: 10.1038/s41467-017-00927-4.

The contributions of the co-authors are as follows:

- The project is supervised by Prof. Weibo Gao, Prof Zheng Liu and Prof. Ajit Srivastava.
- The initial idea is provided by Chongyun Jiang and Prof. Weibo Gao.
- The sample is provided by Fucai Liu.
- The measurement is conducted by Chongyun Jiang and me.
- Ke Li helped with the design of setup.
- Abdullah Rasmita and Prof. Ajit Srivastava helped on the theoretical model.

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The contributions of the co-authors are as follows:

- The Project is supervised by Prof. Weibo Gao, Prof. Timonthy Liew and Prof. Jin Liu.
- The idea, experimental design, measurement, and data analysis are provided by me.
- Yuanda Liu, Qinghai Tan, Zhuojun Liu and Hanlin Fang fabricated the device.
- Kvin Dini provided the numerical simulation.

Chapter 4 is published as Qinghai Tan, Abdullah Rasmita, Zumeng Huang, Sheng Liu, Qihua Xiong, and Weibo Gao. "Interlayer exciton in multilayer-monolayer van der Waals heterostructures." arXiv preprint arXiv:1911.11967 (2019).

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- The Project is supervised by Prof. Weibo Gao and Prof Qihua Xiong.
- The idea is provided by Qinghai Tan.
- Abdullah Rasmita provided the rate equation model.
- Sheng Liu Helped on the Raman measurements.

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Abstract

Two-dimensional Transition Metal Dichalcogenides (TMDs) are a group of materials that draws intensive research interests because of their unique valley contrasting physics, in the application of next generation spintronics and valleytronics. Recently, the stacking of 2D TMDs to form heterostructures of layered TMDs have shown enhanced spin-valley phenomenon including longer exciton lifetime and valley lifetime. They also feature strong electron-electron correlation in the vicinity of Mott transition density for heterostructures with a moiré potential. All these properties provide opportunities for deeper understanding of TMDs valley physics. Here in this thesis, three aspects of the valley-optical physics in layered TMDs heterostructures is presented.

Firstly, the Zeeman splitting for σ_+ and σ_- emission for bilayer MoTe_2 in strong magnetic field is shown. In such inversion symmetry persevering system, because of spin-valley-layer locking effect the valley Zeeman splitting would be significant different from the monolayer counterpart. This enables the possibility for magnetic field control bilayer-based valley electro-optical devices.

Secondly, the interlayer exciton valley Hall effect (VHE) is investigated and presented. Comparing with the monolayer version of VHE which remains to be a low temperature phenomenon, interlayer exciton VHE can be observed for even room temperature, which paves the way for practical TMDs-based topological information devices.

Thirdly, the heterostructure formed by putting a TMDs monolayer on top of another multilayer is stated. As exploited with the band structure modification under different layer numbers, the PL emission under such configuration of TMDs heterostructure reflects band edge energy in semiconducting materials, which would otherwise experimentally detected by much more sophisticated methods like ARPES.

Lastly, some future perspectives related with the strong correlation and moiré excitons is presented.

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Chapter 1

Introduction

Ever since the invention of Field-effect transistor(FET) by John Bardeen and Walter Hauser Brattain in 1947[1], information technology has become the core of world economic growth and leads humankind's civilization to the 4th industrial revolution, which drastically changed everyone's live. At year 1965, Moore predicted the rapid advances of the integrated circuits that a single processor doubles its transistor number in about 2 years, which are later known as Moore's Law[2]. After over 70 years of the fast technology progression, people now have devices with computational power that are about 100,000 times stronger than the Apollo 11 on board computer (Apollo Guidance Computer) inside their pockets.

Figure 1.1: The revolution of energy cost in a single FET when switching its logic state. Dotted line indicates the minimum energy cost in a classical transistor at its thermodynamic limit ($k_B T$ where $T = 300\text{K}$, the thermal fluctuation energy level). The dark blue diamond represents data collected by Rolf Landauer in 1988 that spans of about 40 years[3]. He predicted that around year 2010 the dissipation energy for switching a logic device will reach its physical limit, which is clearly not achieved. Triangles and crosses are data for IBM and Intel devices during that periods. Along with a rapid voltage reduction led by IBM, the energy cost to drive a logic gate has been rapidly reduced, which also decreases the size of a logic device and increase its computational power. However the speed to reduce driving voltage is slowed, and is represented by the Slower V reduction arrow. Around year 2004 the clock frequency for each CPU reached its limit, which is pointed by the Clock freq. plateaus in map. Red squares are data predicted by International Technology Roadmap for Semiconductors(ITRS) at year 2013. Figure adapted from ref[4].

However, such accelerated achievements are about to end[4]. The silicon-based transistors are reaching its physical limit and the quantum effect are not negligible anymore. The superposition of electrons at source and drain, as well as tunneling effect from different electrodes fundamentally conflict with classical high and low voltage based "0 and 1" bits. And this is not even the first stumbling block. At around 2004 when the size of transistors are reducing to sub-100 nanometers, due

to the fact that dimensions are reduced so much, the heat generated by electrons passing through the transistors are too much and preventing a single "core" to have higher clock rate[5]. Having multiple cores means to run the task simultaneously, and despite the fact that lots of tasks are not able to be executed this way, the total energy consumed and heat generated are already a tremendous amount. When The consumer devices like cell phones and computers are likely to work more and more efficiently, the energy cost by data centers of big companies are estimated to increases to 8 percent of the global energy consumption by 2030. What's more, the research funding needed for new generations of silicon chip have also increased exponentially, leading to less players than ever for 3 nm process with only TSMC and Samsung. People could run out of money before run out of physics in silicon-based chips.

Figure 1.2: The energy consumption forecast for the information and communication technology(ICT). Prediction shows at "expected case", the total energy cost of ICT will goes to about 21 percent, and within which about one third is consumed by data centers. Figure adapted from ref[6].

1.1 Graphene

To overcome the disadvantages stated above, scientists are pursuing for new materials and new physics to increase the computation power and reduce the dissipation heat. Since the discovery of graphene in 2004[7], 2D materials have gained intensive interest and have been the hot spot in condensed matter physics due to their novel characteristics. Graphene itself holds many intriguing physics. As carbon based materials, each atom in the graphene have 6 electrons, where there are 2 electrons in each 1s, 2s and 2p orbitals. The electrons in 1s orbital are strongly bound to the carbon nucleus, and have very little influence in graphene's electrical properties. However the 2s and 2p orbitals are different, which is also the reason that carbon atoms have countless chemical compound and are the building blocks of all the organic substance. These electrons can mix with each other and hold sp^n ($n=1,2,3$) hybridization, whose energy is lower than the free $2s^2 2p^2$ electron and are thus stable. In diamond the 4 electrons form sp^3 hybridization, which holds 4 covalent bonds in the directions of a tetrahedron. In graphene the carbons hold sp^2 hybridization, where 3 covalent bonds are formed with carbon atoms in the equilateral triangle direction. Such bonds connecting the neighboring atoms are called a σ bond, and is responsible for the inertness of graphene and consequently makes it conduct better. Being a monolayer of carbon atoms, it could be the softest material; while it is also the strongest regarding their Young's modulus as a membrane of semimetal, because of the similarity it shared with diamond.

Figure 1.3: Illustration of a graphene sheet and its chemical bonds. Every carbon atom inside the sheet is connected to 3 neighboring atoms through a σ bond, and leaving a vertical π bond half filled. Figure adapted from ref[8].

Graphene behaves differently when conducting electrons comparing with normal metals. At K and K' valleys of graphene's first Brillouin zone, the conduction and valence band connect each other through a single point which is called Dirac point. Above and below the Dirac point the dispersion is linear for small k away from it[9]. Electrons inside these valleys are thus massless Dirac fermions[9, 10]. This makes graphene highly conductive, if the Fermi level is away from Dirac point[11]. It also provides the possibility to tune the conductivity based on the position of Fermi level, by tuning the chemical potential of graphene layer[11]. In 2018, Cao with colleagues find out the strong correlation effect[12] and unconventional superconductivity[13] inside bilayer of graphenes that are twisted 1.1 degree from the other layer. So it is no doubt that countries and companies are pursuing graphene based the next generation nanotechnology[14, 15].

Figure 1.4: Band structure of graphene. Energy are in units of nearest hopping energy $t = 2.7\text{eV}$. The second nearest hopping parameter is set to $t' = -0.2t$. Right figure is the zoom in of the energy dispersion in one of the valleys which features linear dispersion relation. Figure adapted from ref[9].

1.2 Transition Metal Dichalcogenides

The great success of graphene has stimulated a vast research on other two dimensional materials. Transition metal dichalcogenides(TMDs) is one kind of two dimensional materials that draws people's attention because of its extraordinary electrical and optical properties. It can generally be represented by MX_2 , which consist of one transition metal atom (M) such as Molybdenum and Tungsten, and two chalcogen atom such as Sulfur, Selenium and Tellurium. Similar with graphite, bulk crystal of TMDs are composed of countless single layers that stack on each other by a weak interlayer van der Waals force comparing with the strong intralayer chemical bonds, which makes it possible to get single layers by mechanical exfoliation.

1.2.1 Crystal structure

A single layer of TMDs consists 3 planes of atoms: one layer of transition metal at middle that are sandwiched by the top and bottom layer of chalcogen atoms. The

actual crystal structure of the 3 layers depends on the substances and environment (such as temperature and pressure), which can be generally divided into 3 phases: 2H, 1T and other phases.

Figure 1.5: Crystal structure of TMDs. Figure adapted from ref[16].

In the trigonal prismatic 2H stacking order, chalcogen atoms at top and bottom plane occupy the same in-plane position with each other, which is generally referred to as an ABA stacking order, and is the most stable phase for a wide variety of Molybdenum and Tungsten based TMDs. Trigonal symmetry breaks the inversion symmetry inside the system, which opens a possibility for spin and valley depended physics and will be the heart of this thesis. Meanwhile for 1T phase, one chalcogen item is at the opposite position if take metal atoms as the center. The inversion symmetry for 1T is reserved and the Berry phase disappears, which will be talked about later in this thesis. Their structure is generally called as ABC stacking. For some materials like WTe_2 , the crystal structure is not stable in either 2H and 1T phase, and is switching between a inversion symmetric 1T' phase and mirror symmetric $1T_d$

phase.

1.2.2 band structure

The vast varieties of TMDs with different elemental components and crystal structures give rise to a huge collection of diverse band structures. We will now be viewing on the dispersion relation of TMDs that are composed of transition metal Molybdenum and Tungsten, with chalcogen Sulfur and Selenium. Similar to graphene, they also feature excellent mobility that could be used for post-silicon electronics. These monolayers of MoS₂, MoSe₂, WS₂ and WSe₂ are semiconductors with a direct band-gap about 2eV, whose optical emission lying around the visible range and attracted researcher's interest in the realization of next generation optoelectronic devices.

As mentioned above, the thermodynamically stable trigonal prismatic structure (2H) give rise to the momentum extreme K and K' point at the edges of their hexagonal Brillouin zone. The conduction band minimum(CBM) and valance band maximum(VBM) are located at these edges for the monolayer of these 4 materials. However for nanosheets thicker than monolayer the position of CBM and VBM could change a lot based on the thickness of the sample.

The band structure calculated by the first principle density functional theory(DFT) has shown that by reducing the sample thickness from bulk crystal to monolayers, the sample will change from indirect band-gap semiconductor to a direct band-gap semiconductor. We can see that the energy at the K point in Brillouin zone of all thickness are nearly constant, and the transition is mainly due to the indirect band gap changing. This is primarily because of the spatial distribution of the orbitals in the metal and chalcogen atoms. The *d* orbitals in metal atoms composite the band structure at K point, which will have less interlayer coupling as compare to the *p* orbitals in chalcogen atoms that composite the Γ point and the CBM between Γ and K point.

Figure 1.6: Band structure of MoS₂ calculated by DFT for (a) bulk crystal, (b) 4-layers MoS₂, (c) 2-layers MoS₂ and (d) monolayer MoS₂. Figure adapted from ref[17].

Here we take the widely studied MoS₂ as the example of the group-VI TMDs. The band structure of MoS₂ was first studied by Mattheiss back in 1973[18]. Heavy metal and chalcogen atoms are bonded together by $s - p$ orbitals, and leaving the d orbital in metal unfilled. There are five kinds of d orbitals: d_{z^2} , d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_{yz} . Among which the strong hybridization only take place between the d_{z^2} to d_{xy} and $d_{x^2-y^2}$ bands when we taking the mirror symmetry into consideration. This hybridization is the reason for the 2eV band gap in group VI chalcogenides around the K and K' points in momentum space. The orbitals for conduction and valance bands are:

$$|\psi_c\rangle = |d_{z^2}\rangle \quad (1.1)$$

and

$$|\psi_v\rangle = \frac{1}{\sqrt{2}}(|d_{x^2-y^2}\rangle + i\tau|d_{xy}\rangle) \quad (1.2)$$

where $|\psi_c\rangle$ and $|\psi_v\rangle$ denote the wave function for conduction and valance band at K and K' points, and τ is the valley index ($\tau = 1$ for K point and $\tau = -1$ for K' point).

With the knowledge of the basis we now move to the Hamiltonian. By utilizing $k \cdot p$ method around K and K' points and consider the 2H symmetry of TMDs materials, we can write the Hamiltonian as:

$$\hat{\mathcal{H}} = at(\tau k_x \sigma_x + k_y \sigma_y) + \frac{\Delta}{2} \sigma_z - \lambda \tau \frac{\sigma_z - 1}{2} s_z \quad (1.3)$$

where a represents MoS₂ lattice constant, t is the hopping integral of the nearest neighboring metals atoms, k_x and k_y are the momentum space distance from K and K' point, σ_x, σ_y and σ_z are the Pauli matrices for the $(|\psi_c\rangle, |\psi_v\rangle)$ basis, Δ is the band gap, Λ is the strength for spin-orbit coupling and s_z is the Pauli z matrix for spin.

Comparing with graphene, there are some difference inside their $k \cdot p$ Hamiltonian. The second term in equation 1.3 shows the band gap opened by orbital hybridization of the d orbitals. It gives TMDs possibility to utilize the two states as an information carrier for next generation electronics. Meanwhile the third term indicates the spin-orbit coupling, which is a result of the inversion symmetry breaking in 2H TMDs and lifted the spin degeneracy at K and K' points. Also because of time reversal symmetry, the spin splitting in K and K' points are reversed. This makes it possible to fabricate spintronics and valleytronics devices with potentially much superior statistics than the silicon based ones.

We can also write it in the matrix form:

$$\hat{\mathcal{H}} = \begin{pmatrix} \frac{\Delta}{2} & at(\tau k_x - ik_y) \\ at(\tau k_x - ik_y) & -\frac{\Delta}{2} + \lambda \tau s_z \end{pmatrix} \quad (1.4)$$

with basis $(|\psi_c\rangle, |\psi_v\rangle)$, or write as:

$$\hat{\mathcal{H}} = \begin{pmatrix} \frac{\Delta}{2} & 0 & at(\tau k_x - ik_y) & 0 \\ 0 & \frac{\Delta}{2} & 0 & at(\tau k_x - ik_y) \\ at(\tau k_x - ik_y) & 0 & -\frac{\Delta}{2} + \lambda\tau & 0 \\ 0 & at(\tau k_x - ik_y) & 0 & -\frac{\Delta}{2} - \lambda\tau \end{pmatrix} \quad (1.5)$$

with basis($|\psi_c, \uparrow\rangle, |\psi_c, \downarrow\rangle, |\psi_v, \uparrow\rangle, |\psi_v, \downarrow\rangle$) where $\uparrow$ and $\downarrow$ denote the spin state for electrons in conduction and valance band.

We can calculate the dispersion relation at K and K' point based on equation 1.5. A typical result is plotted in figure 1.7. What shown here is the band structure of a small region around K and K' point in zero magnetic field. Under such circumstance, K and K' point are time reversal of each other. We can also see that the spin splitting in conduction band is very small, typically only several tens of meV (not shown here), while the valance band splitting is significant.

Figure 1.7: A schematic illustration of the band structure for 2H TMDs around K and K' point. Spin splitting in K and K' points are reversed because of time reversal symmetry. Here in this plot the spin splitting in conduction band is omitted.

1.2.3 Excitonic effect in TMDs

Excitons are hydrogen like bonded pairs consist of electrons and holes that normally live in the conduction and valance band of a semiconductor by their coulomb inter-

action. Generally excitons in semiconductors are created by photo absorption. A electron gains energy and jumps to the conduction band, which also leaves a hole in the valance band edge. If the coulomb force is strong enough to form a pair between them, then an exciton is created. The type of excitons can be defined based on their coulomb interaction. Typically when they are tightly bonded, with the Bohr radius in the order of unit cell and the binding energy is as strong as several hundreds of meV (0.1 to 1 eV), they are regarded as Frenkel exciton named after Yakov Frenkel who proposed the idea of exciton[19], as shown in Figure 1.8, left. As the binding energy is much stronger than room temperature thermal fluctuation ($k_B \cdot 298K = 25.7meV$), they can exist at higher temperature and are easier for future application. The other one is weakly bonded Wannier–Mott exciton. Their binding energy is generally low and require low temperature to observe, as shown in Figure 1.8, right. This is the typical kinds of excitons in GaAs-AlGaAs quantum wells[20]. In semiconducting 2D materials, the wavefunction are still Wannier-Mott type but their binding are as strong as the Frenkel type.

Figure 1.8: Two kinds of excitons. Left: Frenkel excitons with strong coulomb interactions. Right: Wannier-Mott exciton with weak binding. Figures are adapted form [21].

The isolation of monolayers of TMDs leads to the dramatic changes in their properties, primarily due to the confinement of charge carriers in two dimensions (x-and y-directions) due to the absence of interactions in the z-direction[22]. As the thickness of 2D materials is reduced to the monolayer limit, it confines exciton to move within one single plane and increase their binding. What's more, the interaction

between charge carrier with their surrounding electrostatic environment is also decreases, which reduces the screening effect and thus excitons can have smaller Bohr radius and stronger coulomb interaction like a Frankel exciton. Such effect is shown in the left side of Figure 1.9. Thus, single layered nanosheets are two-dimensional materials that possess dramatically different excitonic properties than the conventional two-dimensional GaAs-AlGaAs quantum wells.

Figure 1.9: Excitons in the 3D limit and 2D limit, respectively. For 3D limit, coulomb interaction for electrons and holes is reduced because of screening effect from the surrounding dielectric materials.

In an excitonic picture, attractive Coulomb interactions between photon-generated electrons and holes bond the electron-hole pairs to excitons, and consequently reduce the threshold of the optical interband transition because of the large binding energy. A direct consequence of strong Coulomb interactions is the giant excitonic features dominating the optical properties, which can be seen in Fig.1.9, that a strong and isolated exciton peak is located at the low energy side of the continuum absorption in the photo-absorption spectrum.

1.3 Berry phase effect in TMDs

As people understand deeper on the condensed matter physics, the dispersion relation, which only provides information on the energy eigenstates, is insufficient to fully describe the physical picture of modern condensed matter physics. Geometric and topological phases are usually required in such field, and researchers have developed a set of new theories to understand them. Berry phase effect is one of the most important theory developed in late 20th century[23] that has been both theoretically and experimentally investigated in the field of anomalous Hall effect[24] and spin Hall effect[25]. It describes an extra phase shift when a quantum system adiabatically changes one of its parameter and makes a closed loop in the parameter space. This phase is later named as Berry's phase and are responsible for all the interesting valley physics in TMDs.

1.3.1 Berry curvature

From now on we will mathematically derive the Berry curvature and understand why it is so important in TMDs physics. We start from the concept of adiabatic approximation. For a physical system, the eigenstates and eigenenergies are a function of a set of physical parameters. Consider the change of eigenstates and eigenenergies when one of the parameter is changing. If the parameter is changing slowly enough, we can say that the eigenstates and eigenenergies will change according to the change of that parameter. An example would be when slowly changing the magnetic field exerted on a free flying electron: its cyclotron frequency would change in pace with the change of magnetic field. Here we have the Schrödinger equation:

$$H|n\rangle = E_n|n\rangle \tag{1.6}$$

Where H is the system's Hamiltonian, $|n\rangle$ is the n th eigenstate, and E_n is the n th eigenenergy. Note that all these three values are time dependent. We can also

write the equation in the time-dependent form:

$$H|\alpha\rangle = i\hbar \frac{\partial}{\partial t} |\alpha\rangle \quad (1.7)$$

where

$$|\alpha\rangle = \sum_n c_n e^{i\theta_n} |n\rangle \quad (1.8)$$

and

$$\frac{d\theta_n}{dt} = -\frac{1}{\hbar} E_n \quad (1.9)$$

We deliberately write the system's state as a linear combination of its eigenstate, with an extra separation of the coefficient into c_n and $e^{i\theta_n}$ terms. Put equation 1.8 into equation 1.7 and using equation 1.9:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\alpha\rangle &= i\hbar \frac{\partial}{\partial t} \sum_n c_n e^{i\theta_n} |n\rangle \\ &= i\hbar \sum_n [\dot{c}_n e^{i\theta_n} |n\rangle + c_n e^{i\theta_n} |n\rangle i\dot{\theta}_n + c_n e^{i\theta_n} |\dot{n}\rangle] \\ &= i\hbar \sum_n [\dot{c}_n e^{i\theta_n} |n\rangle + c_n e^{i\theta_n} |\dot{n}\rangle] + \sum_n c_n e^{i\theta_n} |n\rangle E_n \\ H|\alpha\rangle &= H \sum_n c_n e^{i\theta_n} |n\rangle \\ &= \sum_n c_n e^{i\theta_n} E_n |n\rangle \end{aligned}$$

so:

$$\sum_n e^{i\theta_n} (\dot{c}_n |n\rangle + |\dot{n}\rangle c_n) = 0 \quad (1.10)$$

Take the product of $\langle m|$ on both sides of equation 1.10, we have:

$$\dot{c}_m = - \sum_{n \neq m} e^{i[\theta_n - \theta_m]} \langle m | \frac{\partial}{\partial t} | n \rangle \quad (1.11)$$

We now take time derivative on both side of equation 1.6:

$$\begin{aligned} \dot{H}|n\rangle + H|\dot{n}\rangle &= \dot{E}_n|n\rangle + E_n|\dot{n}\rangle \\ \langle m|\dot{H}|n\rangle + \langle m|H|\dot{n}\rangle &= \langle m|n\rangle\dot{E}_n + E_n\langle m|\dot{n}\rangle \end{aligned}$$

thus for all $m \neq n$,

$$\langle m|\dot{H}|n\rangle = (E_n - E_m)\langle m|\dot{n}\rangle \quad (1.12)$$

and this would give the general solution to the time dependent Schrödinger equation:

$$\dot{c}_m = -c_m\langle m|\dot{n}\rangle - \sum_{n \neq m} c_n e^{i(\theta_n - \theta_m)} \frac{\langle m|\dot{H}|n\rangle}{E_n - E_m} \quad (1.13)$$

Now is the time for us to use the adiabatic approximation. Because we are changing the system with an infinitely slow rate, the $\dot{H}$ inside the second term of equation 1.13 is zero compare with the first term. We thus write the solution to c_n as:

$$c_n(t) = e^{i\gamma_n(t)} c_n(t=0) \quad (1.14)$$

$$\gamma_n(t) = i \int_0^t \langle n|\dot{n}\rangle dt' \quad (1.15)$$

which is the phase shift accumulated form $t' = 0$ to t .

We now break the time dependence into a parameter space vector $\mathbf{R}$, which itself is time dependent:

$$\mathbf{R} = \mathbf{R}(t)$$

So we have:

$$\gamma_n(t) = i \int_0^t \langle n | \dot{n} \rangle dt' = i \int_0^t \langle n | \nabla n \rangle \frac{d\mathbf{R}}{dt'} dt' = i \int_{\mathbf{R}(0)}^{\mathbf{R}(t)} \langle n | \nabla n \rangle d\mathbf{R}$$

If the $\mathbf{R}(0)$ and $\mathbf{R}(t)$ are actually same point in space which means that the changing $\mathbf{R}$ forms a connected loop in the parameter space, we have:

$$\begin{aligned} \gamma_n(t) &= i \oint_{\mathbf{R}(0)}^{\mathbf{R}(t)} \langle n | \nabla n \rangle d\mathbf{R} \\ &= \oint_{\mathbf{R}(0)}^{\mathbf{R}(t)} \mathbf{A}_n(\mathbf{R}) d\mathbf{R} \end{aligned}$$

where

$$\mathbf{A}_n(\mathbf{R}) = i \langle n | \nabla n \rangle$$

. We can rewrite this using Stokes' theorem as:

$$\gamma_n(t) = \iint_S [\nabla \times \mathbf{A}_n(\mathbf{R})] \cdot d\mathbf{a} \quad (1.16)$$

$$= \iint_S \boldsymbol{\Omega}_n(\mathbf{R}) \cdot d\mathbf{a} \quad (1.17)$$

The $\boldsymbol{\Omega}_n(\mathbf{R})$ here is the Berry curvature. Notice that this is very similar to the vector potential of a electromagnetic field, and is gauge invariant. The total phase shift is thus only affected by the path itself but not by the start and end position. This is why Berry's Phase is sometimes called geometric phase.

We now going for the general solution to the Berry's phase[26]:

$$\begin{aligned}
\Omega_n(\mathbf{R}) &= \nabla \times \mathbf{A}_n(\mathbf{R}) \\
&= i\nabla \times \langle n | \nabla n \rangle \\
&= i(\nabla \langle n |) \times (\nabla |n \rangle) + i\langle n | (\nabla \times \nabla |n \rangle) \\
&= i(\nabla \langle n |) \times (\nabla |n \rangle) \\
&= i \sum_m (\nabla \langle n |) |m \rangle \times \langle m | (\nabla |n \rangle) \\
&= i \sum_{m \neq n} (\nabla \langle n |) |m \rangle \times \langle m | (\nabla |n \rangle)
\end{aligned}$$

We also calculate the gradient for both side of equation 1.6 and multiply $\langle m |$ to both sides:

$$\begin{aligned}
H|n \rangle &= E_n |n \rangle \\
(\nabla H)|n \rangle + H\nabla |n \rangle &= (\nabla E_n)|n \rangle + E_n \nabla |n \rangle \\
\langle m | \nabla H |n \rangle + \langle m | H \nabla |n \rangle &= \langle m | n \rangle \nabla E_n + E_n \langle m | \nabla |n \rangle \\
\langle m | \nabla H |n \rangle + E_m \langle m | \nabla |n \rangle &= E_n \langle m | \nabla |n \rangle \\
\langle m | \nabla |n \rangle &= \frac{\langle m | \nabla H |n \rangle}{E_n - E_m}
\end{aligned}$$

With functions above we can finally calculate Berry's phase and Berry curvature as:

$$\gamma_n = \iint_S \Omega_n(\mathbf{R}) \cdot d\mathbf{a} \quad (1.18)$$

$$\Omega_n(\mathbf{R}) = i \sum_{m \neq n} \frac{\langle n | \nabla H |m \rangle \times \langle m | \nabla H |n \rangle}{(E_n - E_m)^2} \quad (1.19)$$

1.3.2 Optical selection rules

We now look back to the TMDs case. As shown by $k \cdot p$ method [27], the orbital magnetic moment is contributed by collective motion of self-rotating wave packet, which is a similar effect comparing with the Berry curvature:

$$\mathbf{m}(\mathbf{k}) = -i \frac{e\hbar}{2m_e^2} \sum_{m \neq n} \frac{\mathcal{P}^{mn}(\mathbf{k}) \times \mathcal{P}^{nm}(\mathbf{k})}{E_{\mathcal{P}^{nm}}(\mathbf{k}) - E_m(\mathbf{k})} \quad (1.20)$$

where $\mathcal{P}_{x,y}^{mn} = m_e \langle u_m(\mathbf{k}) | \frac{\partial H}{\hbar \partial k_{x,y}} | u_n(\mathbf{k}) \rangle$ is the interband matrix element (Berry connection). In this system the coupling strength for light with σ_+ and σ_- polarization is $|\mathcal{P}_{\pm}|^2$ where $\mathcal{P}_{\pm} = \mathcal{P}_x^{mn} \pm i\mathcal{P}_y^{mn}$. The degree of circular polarization is thus:

$$\eta(\mathbf{k}) = \frac{|\mathcal{P}_+|^2 - |\mathcal{P}_-|^2}{|\mathcal{P}_+|^2 + |\mathcal{P}_-|^2} = \frac{\mathbf{m}(\mathbf{k}) \cdot \hat{\mathbf{z}}}{e\hbar/2m_e} \quad (1.21)$$

Taking equation 1.19 into consideration, equation 1.21 can be written as:

$$\eta(\mathbf{k}) = -\frac{\mathbf{\Omega}(\mathbf{k}) \cdot \hat{\mathbf{z}}}{e\hbar/2m_e} (E_m(\mathbf{k}) - E_n(\mathbf{k})) \frac{e}{2\hbar} \quad (1.22)$$

This directly links the valley selective optical absorption to their Berry curvature around K and K' point. In this simple system the Berry curvature is expressed as [28]:

$$\mathbf{\Omega}_c(\mathbf{k}) = -\tau \frac{2a^2 t^2 \Delta'}{(\Delta'^2 + 4a^2 t^2 k^2)^{3/2}} \quad (1.23)$$

where $\Delta' = \Delta - \tau s_z \lambda$ is the valley dependent band gap.

Figure 1.10: The optical selection rules for group VI 2H TMDs at K and K' valley. The spin splitting is omitted in the conduction band.

1.3.3 anomalous velocity and valley Hall effect

There is always an extra motion related to a spinning object. When playing ball games like ping-pong and basketball, the spin of the ball is vital for controlling their motion, which utilizes the Magnus effect. Similarly, the spin of wave packet in TMDs around K and K' valleys also features one kind of transverse motion, because the existence of Berry curvature[24].

$$\mathbf{v}(\mathbf{k}) = \frac{\partial E_n(\mathbf{k})}{\hbar \partial \mathbf{k}} - \frac{e}{\hbar} \mathbf{E} \times \mathbf{\Omega}_n(\mathbf{k}) \quad (1.24)$$

The first term in equation 1.24 is the normal group velocity for Bloch electrons, which is normally enough to describe the carrier velocity. However for system with strong Berry curvature around the quasi-momentum position of the carrier, there is a second anomalous velocity term, governed by the Berry curvature (and electric field and/or other kinds of potential field). So for TMDs if there is a carrier density difference in the two valleys and the carriers are moving by a driven field, carrier with

different valley index will go to different side edges of the device because of reversed Berry curvature for the two valleys, and eventually results in a valley version of Hall effect called valley Hall effect.

free carrier valley Hall effect

The predicted valley Hall effect is observed by Mak and colleges[29] in a MoS₂ transistor. The data shows that free carriers are moving to specific transverse edges based on their valley index and charge polarity. This study experimentally confirms the existence of Berry curvature inside group VI 2H TMDs, which is shown in 1.11.

Figure 1.11: Valley hall effect for free carriers in MoS₂ transistor. Left: schematic illustration. Laser excited free charge carriers is driven by a external electric field and move to the source and drain contacts. Meanwhile because the existence of Berry curvature, carriers also move towards the transverse edges based on their carrier type. Right: valley Hall effect data. Hall voltage is linear with driven electric field. By reversing the excitation polarity, the hall voltage also reverses accordingly (solid and dashed lines). For linear excitation and bilayer samples, there is no effect (blue and dotted lines).

exciton valley Hall effect

Besides free charge carriers, excitons are also found to carry the valley selective Berry curvature. Because excitons are charge neutral particles, they cannot be driven in a electric field; if the electric field is too large they may even deform to electrons and a holes. Because of this, the experimental driven force is the thermodynamic electrochemical potential gradient created by a density and temperature gradient between the excitation spot to the surrendering region. Polarization resolved PL

mapping shows the reversed transverse motion for excitons in different valleys, as shown in 1.12.

Figure 1.12: Exciton Hall effect in Monolayer MoS₂. Left: schematic shows that excitons are driven by an electrochemical potential gradient. Right: exciton Hall effect data. The σ_+ (red) and σ_- (blue) PL is mapped and split in the transverse direction of the driving field.

1.4 TMDs heterostructure

The 2D nature of monolayer TMDs makes it possible to stack different thin layers together, which opens a huge playground for new physics and device design. There are 3 types of possible alignment in TMDs heterostructure[30]:

Type I: the conduction band of one layer is higher, as well as the valance band in this layer is lower; Type II: the conduction band of one layer is in the band gap of the second layer, while the valance band is within the band gap of the first layer; Type III: the valance band of one layer is higher than the conduction band of second layer.

Figure 1.13: Band alignment of group VI TMDs. The conduction band minimum and valance band maximum are calculated based on two kinds of DFT calculation. Dotted lines are water reduction(up) and oxidation(down) levels.

A theoretical calculation[31] of the band alignment in several kinds of typical TMDs is presented in figure 1.13. Typically by putting a p-type tungsten based TMD with a n-type molybdenum one together we can get a Type II band alignment: through which the electrons are traveled to MoX₂ and holes are transferred to WX₂ through a ultra fast interlayer charge transfer process in the order of tens of femtoseconds.

Compare with monolayers, interlayer excitons in heterostructures have much longer lifetime and valley lifetime. As the carriers are already distributed to their lowest energy state where electrons and holes are separated into two layers, their wavefunction overlaps are much smaller than that in monolayers. The lattice constant mismatch and twist angle variation further reduces the exciton direct recombination process. Because of this, people are using TMDs heterostructures for the promising quantum information storage and manipulation application.

Bibliography

1. Bardeen, J. & Brattain, W. H. Transistor, a semiconductor triode. *Proceedings of the IEEE* **86**, 29–30. ISSN: 00189219 (1998).
2. Moore, G. M. Moore’s Law ,Electronics. *Electronics* **38**, 114. <https://newsroom.intel.com/wp-content/uploads/sites/11/2018/05/moores-law-electronics.pdf> (1965).
3. Landauer, R. and communication. *Nature* **335**, 779–784 (1988).
4. Theis, T. N. & Philip Wong, H. S. The End of Moore’s Law: A New Beginning for Information Technology. *Computing in Science and Engineering* **19**, 41–50. ISSN: 15219615 (2017).
5. Kobayashi, M. More than moore. *Kyokai Joho Imoji Zasshi/Journal of the Institute of Image Information and Television Engineers* **70**, 324–327. ISSN: 13426907 (2016).
6. Jones, N. How to stop data centres from gobbling up the world’s electricity. *Nature* **561**, 163–166. ISSN: 14764687 (2018).
7. Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *science* **306**, 666–669 (2004).
8. in. *Raman Spectroscopy in Graphene Related Systems* 1–15 (John Wiley & Sons, Ltd, 2011). ISBN: 9783527632695. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/9783527632695.ch1>. <https://onlinelibrary.wiley.com/doi/abs/10.1002/9783527632695.ch1>.

9. Castro Neto, A. H., Guinea, F., Peres, N. M., Novoselov, K. S. & Geim, A. K. The electronic properties of graphene. *Reviews of Modern Physics* **81**, 109–162. ISSN: 00346861. arXiv: 0709.1163 (2009).
10. Castro Neto, A. Pauling’s dreams for graphene. *Physics* **2**. ISSN: 1943-2879 (2009).
11. Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nature Materials* **6**, 183–191. ISSN: 14761122 (2007).
12. Cao, Y. *et al.* Correlated insulator behaviour at half-filling in magic-angle graphene superlattices. *Nature* **556**, 80–84. ISSN: 14764687 (2018).
13. Cao, Y. *et al.* Unconventional superconductivity in magic-angle graphene superlattices. *Nature* **556**, 43–50. ISSN: 14764687 (2018).
14. Schwierz, F. Graphene transistors. *Nature Nanotechnology* **5**, 487–496. ISSN: 17483395 (2010).
15. Lin, Y. M. *et al.* Operation of graphene transistors at gigahertz frequencies. *Nano Letters* **9**, 422–426. ISSN: 15306984 (2009).
16. Manzeli, S., Ovchinnikov, D., Pasquier, D., Yazyev, O. V. & Kis, A. 2D transition metal dichalcogenides. *Nature Reviews Materials* **2**, 17033 (2017).
17. Splendiani, A. *et al.* Emerging photoluminescence in monolayer MoS₂. *Nano letters* **10**, 1271–1275 (2010).
18. Mattheiss, L. F. Band structures of transition-metal-dichalcogenide layer compounds. *Physical Review B* **8**, 3719–3740. ISSN: 01631829 (1973).
19. Fenkel, Y. Excitons. *Phys. Rev.* **37**, 17 (1931).
20. Miller, R. & Kleinman, D. Excitons in GaAs quantum wells. *Journal of Luminescence* **30**, 520–540 (1985).
21. Fox, M. *Optical properties of solids* 2002.

22. Chernikov, A. *et al.* Exciton binding energy and nonhydrogenic Rydberg series in monolayer WS₂. *Physical Review Letters* **113**, 1–5. ISSN: 10797114. arXiv: 1403.4270 (2014).
23. Berry, M. V. Quantal phase factors accompanying adiabatic changes. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences* **392**, 45–57 (1984).
24. Xiao, D., Chang, M. C. & Niu, Q. Berry phase effects on electronic properties. *Reviews of Modern Physics* **82**, 1959–2007. ISSN: 00346861. arXiv: 0907.2021 (2010).
25. Nagaosa, N., Sinova, J., Onoda, S., MacDonald, A. H. & Ong, N. P. Anomalous hall effect. *Reviews of modern physics* **82**, 1539 (2010).
26. Sakurai, J. J. & Commins, E. D. *Modern quantum mechanics, revised edition* 1995.
27. Yao, W., Xiao, D. & Niu, Q. Valley-dependent optoelectronics from inversion symmetry breaking. *Physical Review B - Condensed Matter and Materials Physics* **77**, 1–7. ISSN: 10980121. arXiv: 0705.4683 (2008).
28. Xiao, D., Liu, G. B., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides. *Physical Review Letters* **108**, 1–5. ISSN: 00319007. arXiv: 1112.3144 (2012).
29. Mak, K. F., McGill, K. L., Park, J. & McEuen, P. L. The valley Hall effect in MoS₂ transistors. *Science* **344**, 1489–1492. ISSN: 0036-8075. arXiv: 1403.5039. <http://www.sciencemag.org/cgi/doi/10.1126/science.1250140> (2014).
30. Ihn, T. *Semiconductor Nanostructures: Quantum states and electronic transport* (Oxford University Press, 2010).
31. Kang, J., Tongay, S., Zhou, J., Li, J. & Wu, J. Band offsets and heterostructures of two-dimensional semiconductors. *Applied Physics Letters* **102**. ISSN: 00036951 (2013).

Chapter 2

Zeeman splitting in bilayer MoTe_2

Atomically thin TMDs possess coupling of spin and valley degrees of freedom, making them promising for spin-valleytronics[1–3]. In monolayer TMDs, the emission helicity is locked to the valleys as a consequence of spin-orbit coupling and inversion symmetry breaking, leading to a valley analog of Zeeman effect in the presence of an out-of-plane magnetic field [4–9]. As inversion symmetry is recovered in bilayers, the emission helicity should no longer be locked to the valleys. Here we show that Zeeman splitting, however, still persists in bilayers, as a result of an additional degree of freedom, namely the layer pseudospin and spin-valley-layer locking [2]. In contrast to monolayer, Zeeman splitting here exists without lifting valley degeneracy. The degree of circularly polarized photoluminescence can be tuned with magnetic field from -37% to 37% . Our results demonstrate the control of spin degree of freedom in bilayer with magnetic field, which, together with previous electric field control, makes bilayer a promising platform for spin-valley quantum gates based on magnetoelectric effects [10].

2.1 Introduction

In monolayer group VI TMDs such as MoS_2 and WSe_2 , spatial inversion symmetry is broken, leading to finite but opposite Berry curvature and magnetic moment in

the two valleys [11]. Due to strong spin-orbit coupling, spin and valley degrees of freedom are locked which results in a series of exotic valley effects, such as valley Hall effect [12, 13], valley optical selection rule [14–17] and valley Zeeman splitting [4–9]. In bilayer TMDs, the layers are rotated by 180° with respect to each other, resulting in the recovery of spatial inversion symmetry. It is then natural to ask whether the above-mentioned valley phenomena still exist in bilayer TMDs. Interestingly, when the interlayer coupling is much smaller than the spin-orbit interaction, bilayer TMDs can be regarded as two decoupled monolayers with the layer pseudospin leading to a spin-valley-layer coupling. This forms a potential platform for spin-valley quantum gates with magnetic and electric control [10]. To this end, spin-layer locking induced valley Hall effect [18], spin-polarized bulk bands [19], valley optical selection rule [20] and electric control [21] have been experimentally demonstrated. In this chapter, we demonstrate that magnetic field can be another addition in the toolbox to explore the rich interplay between real spin, valley and layer pseudospins in bilayer TMDs. Specifically, the Zeeman splitting of the two circularly polarized components of optical emission persists in bilayer TMDs regardless of the recovery of inversion symmetry due to spin-valley-layer locking. The magnetic field control, together with electric control as demonstrated previously, paves the ways for quantum manipulation of spin, valley, and layer degrees of freedom in bilayer TMDs [10].

We perform our experiments on 2H-MoTe₂, which is a layered semiconductor with hexagonal lattice. MoTe₂ acts as an ideal platform for bilayer physics since the emission in MoTe₂ bilayers are in the same order of monolayer, as compared to rapid decreasing of the emission intensity with increased layer number in other TMDs such as MoS₂, WSe₂. With decreasing number of layers, the indirect bandgap of bulk MoTe₂ turns into direct bandgap [22, 23]. Berry curvature and orbital magnetic moments can be studied through the polarization-selective emission of photoluminescence. Monolayer and bilayer 2H-MoTe₂ have a relatively smaller bandgap among the TMDs and their photoluminescence emission lies in the near infrared

range around ~ 1.1 eV. A reversible structural phase transition between hexagonal and stable monoclinic has been reported in bulk single-crystalline MoTe₂ [24] and a semiconductor-to-metal electronic phase transition has been demonstrated by thinning down bulk MoTe₂ or straining the MoTe₂ thin films [25]. These features make MoTe₂ a flexible material suitable for valley-based optoelectronic applications.

2.2 Results

An optical image of the studied sample is illustrated in Figure 2.1a, where the monolayer (1L) and bilayer (2L) can be easily identified by their optical contrasts. The flakes are mechanically exfoliated using adhesive tapes and then transferred onto a silicon wafer with a 300 nm thick thermally grown SiO₂. The as-prepared samples are kept under vacuum to prevent oxidation and deliquesce. The crystal structure of a bilayer AB-stacked MoTe₂ is shown in Figure 2.1b. The bilayer has inversion symmetry as compared to monolayers. Monolayer and bilayer MoTe₂ have exciton energy of ~ 1.1 eV, which can be experimentally extracted by the photoluminescence (PL) spectroscopy. We utilize a home-made fiber-based confocal microscope setup for the micro-PL experiments (see Figure 2.1(c)). We show the details of our experimental setup in the *Methods* section. The excitation and collection polarizations are controlled by a series of polarizers, half-wave plates and quarter-wave plates. Below, we refer to co-polarization (cross-polarization) when the quarter-wave plates are configured for the same (opposite) handedness.

To further confirm the number of layers in our sample, we perform Raman spectroscopy of the monolayer, bilayer and multilayers at room temperature as shown in Figure 2.1d. The B_{2g}^1 mode of the 2L is strong with a Raman shift of 292.4 cm⁻¹ while that of the 1L and multilayer is very weak. The in-plane mode E_{2g}^1 (out-of-plane mode A_{1g}) exhibits downshift (upshift) in energy as the number of layer increases. The results agree well with the previous report [26, 27], confirming the number of layers of the investigated sample. Temperature dependent exciton and trion peaks in

Figure 2.1: Sample characterization. (a) Optical microscope image of the MoTe₂ monolayer and bilayer. (b) Crystal structure of a bilayer MoTe₂. The two layers are rotated in plane by 180° relative to each other. (c) Optical setup for the polarization-resolved PL spectroscopy. The optical components are: achromatic lenses (AL1-3), polarizers (P1 and P2), half wave plates (HWP1 and HWP2), quarter wave plates (QWP1 and QWP2), a short pass filter (SPF), a long pass filter (LPF) and a beam splitter (BS). The sample is placed in a helium bath cryostat with an out-of-plane magnetic field in a Faraday geometry. The green arrow shows a negative magnetic field. (d) Raman spectroscopy of the MoTe₂ monolayer, bilayer and multilayer. A_{1g} , B_{2g}^1 and E_{2g}^1 represent different modes in Raman spectroscopy.

PL measurements (See Figure 2.5) also show results consistent with previous reports [22, 23].

After sample characterization, we demonstrate the Zeeman splitting in PL spectroscopy and PL polarization controlled by magnetic field. Following these, we will discuss the origin of our observations. Figure 2.2a and Figure 2.2b show the polarization-resolved PL spectra of monolayer and bilayer MoTe₂ under external magnetic field of -7 T, 0 T and +7 T perpendicular to the sample plane at 2 K.

Monolayer PL shows peak A_1 (B_1) with an energy of 1.187 eV (1.164 eV). The bilayer shows emissions at 1.154 eV and 1.136 eV (Peak A_2 and B_2 in Figure 2.2b). Peak A_2 (A_1) is attributed to the optical transition of the neutral exciton state in the 2L (1L) MoTe₂. Peak B_2 (B_1) corresponds to the transition of charged exciton (trion) state in the 2L (1L) [28]. From the figure, we can make two main observations: First, at zero magnetic field the wavelengths of PL emission are at the same position for σ_+ and σ_- detection. At -7 T (+7 T), however, the position of the peaks blueshifts (redshift) for σ_+ (σ_-) detection, which indicates an energy splitting. Second, the

Figure 2.2: Zeeman splitting and PL polarization in bilayer MoTe₂. **(a-b)** Off-resonant polarization-resolved PL spectra taken at -7 T, 0 T and +7 T at 2 K with an excitation energy of 1.560 eV (795 nm) in monolayer MoTe₂ (a) for reference and bilayer MoTe₂ (b). The excitation is set to σ_+ circular polarization. The detection polarization is configured to σ_+ (black solid lines) and σ_- (red solid lines) circular polarization. The PL intensity of the bilayer is one order of magnitude smaller than that in the monolayer due to higher symmetry of the bilayer. Here the PL spectra is normalized by emission maximum for each particular magnetic field and offset for better visualization. **(c-d)** Zeeman splitting (c) and PL polarization (d) of the neutral exciton (Peak A_2) in bilayer MoTe₂ (red symbols and lines) versus magnetic field at 2 K. The inset shows the PL polarization at different temperature at +7 T. The black symbols and lines are results of the monolayer (Peak A_1) for reference.

magnitudes of the peaks for σ_+ and σ_- detection under magnetic field also differ, which manifests itself as shown in magnetic field dependent PL polarization. Here the degree of the PL polarization can be defined as $\eta_{PL} = \frac{I_{\sigma_+} - I_{\sigma_-}}{I_{\sigma_+} + I_{\sigma_-}}$, where I_{σ_+} (I_{σ_-}) is the intensity of the PL emission in σ_+ (σ_-) configurations.

To further illustrate these results, spectrum splitting and PL polarization for the neutral excitons are quantitatively depicted in Figure 2.2c and Figure 2.2d, respectively. The Zeeman splitting of an optical transition is fit with $\Delta E = g\mu_B B$, where g is the g -factor associated with the magnetic moment in the system, μ_B is the Bohr magneton and B is the magnetic field. The energy splitting of the exciton state (Peak A_1 of 1L and A_2 of 2L) depends linearly on the magnetic field, with slopes of $-243 \pm 3 \mu\text{eV/T}$ and $-274 \pm 6 \mu\text{eV/T}$, corresponding to $g(A_1) = 4.21 \pm 0.06$ and $g(A_2) = 4.73 \pm 0.11$. The PL polarization of the 1L and 2L also depends linearly on

the magnetic field. Here we focus on the emission polarization only and the averaged PL polarization of σ_+ and σ_- excitation is shown. We fit the relationship of the PL polarization η_{PL} and the magnetic field B with $\eta_{PL} = \beta B$, where β is a coefficient with $(3.82 \pm 0.04) \times 10^{-2} \text{ T}^{-1}$ for Peak A_1 of the 1L and $(5.25 \pm 0.28) \times 10^{-2} \text{ T}^{-1}$ for Peak A_2 of the 2L. The fit result of the trion (Peak B_2) are shown in the Discussion section. In addition, we have measured the temperature dependence of the g factor and PL polarization for both monolayer and bilayer MoTe₂. As shown in the inset of Figure 2.2c and 2.2d, while g factor of monolayer exciton stays around 4, the g factor of bilayer varies from 4.73 to 2.54 when the temperature changes from 2K to 70K. When the temperature increases, PL polarization has a trend to decrease for both monolayer and bilayer as shown in the insert of Figure 2.2d.

The Zeeman splitting in MoTe₂ monolayers was already reported, which is attributed to the lifting of the valley degeneracy in the band structure due to the breaking of the time reversal symmetry in the presence of a magnetic field, so called valley Zeeman splitting, or valley splitting for short [4–7]. The main observation here is that such Zeeman splitting still persists in bilayer, which can not be simply considered as valley Zeeman splitting anymore. Below, we focus on the physical origin of such splittings, as well as the magnetic field dependent PL polarization.

In monolayer TMDs, the spin and the valley pseudospin are effectively coupled by spin-orbital coupling and broken inversion symmetry [1]. Bilayer TMDs possess another degree of freedom, viz., layer pseudospin [10]. In a bilayer, the Hamiltonian at $\pm K$ points can be expressed in a two-band approximation as $H_c = \Delta + \lambda_c \tau_z s_z \sigma_z^c$ for the conduction band and $H_v = -\lambda_v \tau_z s_z \sigma_z^v + t_\perp \sigma_x^v$ for the valence band, where Δ is the bandgap, λ_c (λ_v) denotes the spin-orbit coupling of conduction (valence) band and $t_\perp$ is the interlayer coupling of the layers. The strong coupling between the valley (τ_z) and layer ($\sigma_z^{c,v}$) pseudospin, and the real spin (s_z) is a distinguishing feature of bilayers. The layer Pauli operators σ_z^c (σ_z^v) are expressed in the basis of d_{z^2} ($d_{x^2-y^2} \pm id_{xy}$). The interlayer hopping, $t_\perp$, vanishes for conduction band due to the

Figure 2.3: **Origin for Zeeman splitting in bilayer.** **a**, Single particle energy states at $\pm K$ -points of bilayer TMDs at zero magnetic field and in presence of inter-layer hopping $t_\perp$. The spin-valley-layer locking results in optical selection rules such that in both valleys, the spin degree of freedom is locked to the emission helicity. **b**, Schematic diagram of the Zeeman splitting in bilayer MoTe_2 under positive magnetic field at $\pm K$ -points. Red (blue) transition indicates the PL emission with photon energy E_+ (E_-) and circular polarization σ_+ (σ_-). The upper and the lower layer in the same valley have opposite spin. Green and gray arrows show the magnetic moment contributions of the spin and atomic orbital to the Zeeman splitting, respectively. In the presence of a positive magnetic field, the spin contributions cancel while the intracellular or atomic orbital contribution leads to $E_+ < E_-$ in both the valleys.

symmetry of d_{z^2} orbitals. When the spin-orbit coupling strength λ_v is much larger than the interlayer hopping amplitude, holes are primarily confined to either upper or lower layer, which can be labeled with layer pseudospin up $|u\rangle$ or down $|l\rangle$.

Figure 2.3a depicts the energy level diagram at zero magnetic field emphasizing the spin-valley-layer locking in bilayer. At a given energy in a given valley, different layers carry opposite spins. The lowest energy single-particle optical transitions giving rise to excitonic resonance for different valley, layer and spins are also shown in Figure 2.3a. As the spin is conserved in the optical transition (singlet exciton), spin-valley-layer locking leads to emission helicity being locked with the spin degree of freedom in both valleys. Upon diagonalizing H_v , the hole energies shift from $\pm\lambda_v$ to $\pm\sqrt{\lambda_v^2 + t_\perp^2}$ and the new eigenstates are admixtures of $d_{x^2-y^2}^u \pm id_{xy}^u$ and $d_{x^2-y^2}^l \mp id_{xy}^l$ orbitals. Unlike the case of monolayer where helicity of emission is tied to the valley degree of freedom, optical transitions of either helicity are present in both valleys for bilayers. In the absence of magnetic field, all four optical transition depicted in Figure 2.3a are degenerate.

When an out-of-plane B field is applied, conduction and valence band energy will be shifted, in accordance with the respective magnetic moments as shown in Figure

2.3b. The conduction band states have contribution only from the spin as d_z^2 orbitals do not carry any magnetic moment whereas the valence band states have orbital magnetic moment (intracellular contribution) stemming from $d_{x^2-y^2} \pm id_{xy}$ orbitals in addition to the spin contribution. In the ideal case without substrate effect, spatial inversion symmetry is restored for bilayers [29], which makes intercellular contribution vanish. With possible substrate effect, there can still be asymmetry in bilayer, which might still introduce the intercellular term. The spin Zeeman shift can be written as $\Delta_s = 2s_z\mu_B B$. Since Δ_s has the same value for conduction and valence band, it thus does not contribute to the net energy shift. Thus, intracellular contribution which, differs for the two bands, causes a measurable shift in the optical transition energies.

In the limit of negligible interlayer coupling, the valence band is mainly comprised of $d_{x^2-y^2} \pm id_{xy}$ orbitals with $m = \pm 2$ while the conduction band has $m = 0$. This intracellular contribution leads to a valley Zeeman splitting with a g -factor of 4 in monolayer TMDs. The bilayer case is in stark contrast with this as can be seen from Figure 2.3b - although the valley degeneracy is not lifted, each valley experiences a splitting of emission helicity (σ_+/σ_-) due to intracellular contribution. In other words, while there is a lifting of degeneracy of σ_+/σ_- emission in bilayers in the presence of B field, it does not imply a valley Zeeman splitting as the emission helicity is no longer tied to the valley degree of freedom. Instead, the helicity of emission is tied to the spin degree of freedom. A g -factor of 4 is thus expected for bilayer Zeeman splitting as well, however, due to finite interlayer hopping, the valence band states are no longer purely $d_{x^2-y^2}^l + id_{xy}^l$ or $d_{x^2-y^2}^l - id_{xy}^l$ but an admixture of the two.

The exact eigenstates of H_v at K-valley ($\tau_z = 1$) and spin up ($s_z = 1$) are given by $u_+ = (\cos \theta/2, \sin \theta/2)^T$ and $u_- = (\sin \theta/2, \cos \theta/2)^T$ in the basis of where $\cos \theta = \frac{\lambda}{\sqrt{\lambda^2 + t_\perp^2}}$. Thus, the magnetic moment of valence band states reduces from $m = \pm 2$ to $sim m = (\pm 2)\cos^2\theta/2 + (\mp 2)\sin^2\theta/2 = \pm 2\cos \theta = \pm 2\frac{\lambda}{\sqrt{\lambda^2 + t_\perp^2}}$. This

would imply a Zeeman splitting g -factor of $\frac{4\lambda}{\sqrt{\lambda^2 + t_\perp^2}}$. From recent report of $A - B$ splitting of monolayers, we get λ of ~ 135 meV[30, 31]. Assuming B exciton has the same energy for monolayer and bilayers [31], and the difference of exciton peak position is $2\sqrt{\lambda^2 + t_\perp^2} - 2\lambda = 33$ meV, we get interlayer coupling of $t_\perp = 69$ meV and g factor of 3.56. We attribute the difference between the predicted value and experimental value to intercellular components which comes from inversion symmetry breaking. We have measured Second harmonic generation (SHG) for bilayers, which shows similar intensity with SHG for monolayers, confirming the existence of inversion symmetry breaking in bilayers due to substrate effect. We note that change of g factor for bilayer is much larger than the case of monolayer. A systematic understanding of the temperature dependence of g -factor is very interesting in its own right and is left for future investigations. We speculate that this temperature dependence arises due to the change in the interlayer distance with temperature, just as lattice constant changes with temperature [32–34]. This interlayer distance change could lead to possible stronger interlayer hopping integral and therefore lead to a strong mixing of bands in the same valley for two different layers. This mixing of bands with different spins would decrease the g factor. In addition, the intracellular contribution from other orbitals (e.g., p-orbitals for the conduction band) will need to be considered to calculate the value of precise g -factor [35].

Finally, we discuss the magnetic field dependence of η_{PL} shown in Figure 2.2d. As the PL polarization is primarily independent of the excitation polarization, we can conclude that there is fast spin relaxation which leads to creation of both σ_+ and σ_- excitons upon excitation. At zero field, conversion of σ_+ to σ_- and vice versa is equally likely leading to emission from both helicities, as dictated by time-reversal symmetry. At finite B -field, the emission intensity of the lower energy peak is always larger. This is true even when the polarity of the B -field is reversed implying that the higher energy exciton is transformed into the lower energy exciton with the opposite emission helicity on a timescale which is comparable to exciton lifetime.

Figure 2.4: **Origin for PL polarization in bilayer.** **a**, The requirement for the switching of light helicity can be thought of as interconversion between circularly polarized excitons, σ_+^{ex} and σ_-^{ex} . The emission helicity is tied to the spin of the electron in the exciton which is formed out of electron-hole pairs in both valleys/layers. The hole spin is labeled by thick vertical arrows and in our convention have spin which is opposite to that of the electron. Due to spin-valley-layer locking, both spin and valley need to be flipped for the switching of helicity, in the absence of interlayer hopping. **b**, At positive magnetic field, the selective conversion of σ_-^{ex} to σ_+^{ex} is energetically favorable due to Zeeman splitting (see main text for details).

If we assume that the interlayer coupling is suppressed due to large spin-orbit coupling, the conversion of a σ_+ -exciton to a σ_- -exciton and vice versa requires flipping of both spin and valley degrees of freedom, as shown in Figure 2.4a. The spin angular momentum required for such a process is possibly provided during scattering with residual charge carriers present in the sample due to accidental doping. While at zero B -field, such a spin flip induced conversion of exciton helicity can occur in both directions, at finite B -field, conversion to the lower energy exciton is energetically favorable. To explain the dependence of η_{PL} with B -field, we assume that the spin flip process is energy conserving while the energy relaxation via phonons primarily conserves spin. Although spin flip via phonon is possible in presence of spin-orbit coupling, it is usually slower than spin-conserving processes [36]. As shown in Figure 2.4b, at finite field, spin flip can happen from the higher energy exciton to the excited states of lower energy exciton band at the same energy, which then relax to the lowest energy states by phonons. The reverse process must first involve phonon absorption followed by spin flip due to the absence of opposite spin states for the lowest energy exciton. As the phonon absorption is suppressed by the Boltzmann factor,

$\exp(-\Delta_B/k_B T)$ for a Zeeman splitting of Δ_B , the intensity of PL from the lowest energy exciton is dominant. The quantitative dependence of η_{PL} on B depends on the spin-flip rate γ_s , exciton lifetime γ_l and the phonon relaxation rate γ_{ph} which appear to be comparable to each other in bilayer TMDs (see the discussion section below).

In summary, we have experimentally demonstrated the Zeeman splitting in bilayer TMDs and discussed their origin from spin-valley-layer coupling. Electrical control of orbital magnetic momentum as demonstrated previously [2, 21], together with magnetic control here will form a complete toolbox set for controlling valley and layer pseudospins. Magnetoelectric effect by the interference between electrical and magnetic field will be naturally the next step towards quantum gates or quantum entanglement between spin, valley and layer degree of freedom in bilayer platforms [10]. Optical stark effect by means of pseudomagnetic field has been demonstrated to control the coherence of valley pseudospins [37–39]. Real magnetic control of bilayer as demonstrated here, combined with pseudomagnetic method provides access to manipulate the coherence in the bilayer system.

2.3 Discussion

2.3.1 Sample characterization and Zeeman splitting for Trions in bilayer MoTe_2

Normalized temperature-dependent PL for both monolayer and bilayer MoTe_2 is shown in Figure 2.5. Power dependence for the A_2 peak (Figure 2.7) shows a linear power dependence, which shows its exciton character. Peak B_2 with an energy lower than peak A_2 is attributed to bilayer Trion peak. Zeeman splitting and PL polarization for bilayer trion peaks are shown in Figure 2.6

Figure 2.5: Normalized temperature-dependent PL spectra. (a) 1L MoTe₂. (b) 2L MoTe₂. The PL spectra are taken with 1.560 eV (795 nm) excitation energy. The exciton and trion state emission are labeled as A_1 (A_2) and B_1 (B_2) for 1L (2L) MoTe₂. The curves are offset for clarity. At 70K, the emission of the trion state vanishes.

2.3.2 Valley polarization for bilayer MoTe₂

The photoluminescence (PL) spectra with different circular polarization excitation are shown in Figure 2.8 for the bilayer. Although the emission polarization is predominantly independent of excitation polarization, there is indeed a finite correlation between the excitation and emission polarization, which we show in Figure 2.8. Such valley correlation has also been observed in bilayer WS₂[20]. Also to be mentioned, when we use a near resonant excitation, we don't see the A_1 peak in monolayer MoTe₂ as it is within the excitation laser spectrum. We also see a set of sharp peaks in the bilayer case which are the bilayer Raman peaks.

Figure 2.6: Trion emission of 1L and 2L MoTe₂ in magnetic field. (a) valley Zeeman splitting. (b) PL polarization, in 2L (red symbols and line) MoTe₂. The inset shows the temperature dependence of the PL polarization in 2L (red symbols and line). The symbols are experimental data. The solid lines are the linear regression of the experimental data. The black symbols and lines are data of the 1L MoTe₂ for reference.

2.3.3 Model to explain the magnetic field dependence of PL polarization

As discussed in the main text, we assume that interlayer coupling is suppressed due to large spin-orbit coupling. Below we use a rate equation model to estimate the decay rates. We put the rate of optical pumping to both σ_+ and σ_- excitons to be the same, Γ_{pump} . Let the energy conserving spin flip rate be γ_s , the phonon emission rate be γ_e while the phonon absorption rate be γ_a . Assuming a lattice temperature of T , we have $\gamma_a = \gamma_e e^{-\Delta_B/k_B T}$. Furthermore, we assume γ_l , the total lifetime of

Figure 2.7: PL intensity of exciton and trion emission as a function of the excitation power in 2L MoTe₂. The exciton (Peak A₂, black) exhibits a linear power dependence, whilst the trion (Peak B₂, red) shows a sublinear dependence with $I_{PL} \propto I_{ex}^{0.8}$, where I_{PL} and I_{ex} are the intensity of the excitation and photoluminescence, respectively.

both σ_+ and σ_- excitons to be the same. As the spin-flip process is assumed to be energy conserving, we can work with three levels to describe the conversion process between σ_+ and σ_- exciton. Let n_1 (n_3) be the population in the higher (lower) energy exciton and n_2 be population in the state obtained after elastic spin-flip from the higher energy exciton.

The following set of rate equations relate the steady populations:

$$\Gamma_{pump} - (\gamma_s + \gamma_l)n_1 + \gamma_s n_2 = 0$$

$$\gamma_s n_1 - (\gamma_e + \gamma_s)n_2 + \gamma_a n_3 = 0$$

$$\Gamma_{pump} + \gamma_e n_2 - (\gamma_l + \gamma_a)n_3 = 0$$

Figure 2.9 shows a fit of η_{PL} to data in Figure 2.2d, for similar values of all rates and lattice temperature of $T = 6.5$ K which is slightly higher than the assumed

Figure 2.8: Near-resonant magneto-photoluminescence. **(a-b)** Polarization-resolved PL spectra of 1L MoTe₂ (a) and 2L MoTe₂ (b) taken at -8 T, 0 T and +8 T at 4.2 K with an excitation energy of 1.192 eV (1040 nm). The excitation is set to σ_+ circular polarization. The detection polarization is configured to σ_+ (black solid lines) and σ_- (red solid lines) circular polarization. The PL intensity of the 2L is one order of magnitude smaller than that in the 1L due to higher symmetry of the bilayer. Here the PL spectra are normalized for each particular magnetic field and offset for clarity. Sharp peaks in the bilayer PL spectra are Raman scattering. **(c-d)** Exciton emission (Peak A_2) in 2L MoTe₂. Valley Zeeman splitting (c) and PL polarization (d) are illustrated with red symbols and lines. **(e-f)** Trion emission (Peak B_2) in 2L MoTe₂. Valley Zeeman splitting (e) and PL polarization (f) are illustrated with red symbols and lines. The black symbols and lines are the results (Peak B_1) of the 1L MoTe₂ for reference.

temperature of the sample (4.2 K), possibly due to optical excitation. Our simple model qualitatively captures the magnetic field dependence of PL polarization data reasonably well. It can be concluded that all rates in the model are comparable on the scale of picoseconds.

2.4 Methods

Spectroscopy experiment setup

The Raman spectra are taken at room temperature with an excitation wavelength of 532 nm using a commercial WITech confocal Raman spectrometer. We use a home-made fiber-based confocal microscope for polarization-resolved PL spectroscopy. The wavelength of the excitation is 795 nm (1.560 eV) for off-resonant excitation and 1040

Figure 2.9: Fit to the PL polarization of Figure 2.2d using the model described in the text.

nm (1.192 eV) for near-resonant excitation. The excitation power is $\sim 400 \mu\text{W}$ for 1040 nm excitation. Polarizers and quarter wave plates are installed on the excitation and detection arm of the confocal microscope for polarization-selective excitation and PL detection. The PL emission is directed by an multi-mode optical fiber into a spectrometer (Princeton Instruments) with a liquid nitrogen cooled infrared camera for spectroscopy recording. The sample is loaded into a magneto-cryostat (Cryomagnetics close-cycle cryostat for off-resonant experiment and Quantum Design Physical Properties Measurement System (PPMS) for near-resonant experiment) and cooled down to 2~4 Kelvin. The magnetic field is applied perpendicular to the sample plane ranging from -7 T to +7 T.

Preparation of MoTe_2 thin flakes

The MoTe_2 single crystals are synthesized through chemical vapor transport using iodine as the transport agent. A scotch tape-based mechanical exfoliation method is used to peel thin flakes from bulk crystal onto degenerately doped silicon wafer covered with a layer of 285 nm thermally grown silicon dioxide. Optical microscopy

(Olympus BX-51) is used to identify thin flake samples with different thickness via optical contrast.

Bibliography

1. Xiao, D., Liu, G.-B., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides. *Physical review letters* **108**, 196802 (2012).
2. Xu, X., Yao, W., Xiao, D. & Heinz, T. F. Spin and pseudospins in layered transition metal dichalcogenides. *Nature Physics* **10**, 343–350 (2014).
3. Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. *Nature* **499**, 419–425 (2013).
4. MacNeill, D. *et al.* Breaking of valley degeneracy by magnetic field in monolayer MoSe₂. *Physical review letters* **114**, 037401 (2015).
5. Srivastava, A. *et al.* Valley Zeeman effect in elementary optical excitations of monolayer WSe₂. *Nature Physics* **11**, 141–147 (2015).
6. Aivazian, G. *et al.* Magnetic control of valley pseudospin in monolayer WSe₂. *Nature Physics* **11**, 148–152 (2015).
7. Li, Y. *et al.* Valley splitting and polarization by the Zeeman effect in monolayer MoSe₂. *Physical review letters* **113**, 266804 (2014).
8. Stier, A. V., McCreary, K. M., Jonker, B. T., Kono, J. & Crooker, S. A. Exciton diamagnetic shifts and valley Zeeman effects in monolayer WS₂ and MoS₂ to 65 Tesla. *Nature communications* **7**, 1–8 (2016).

9. Arora, A. *et al.* Valley Zeeman splitting and valley polarization of neutral and charged excitons in monolayer MoTe₂ at high magnetic fields. *Nano letters* **16**, 3624–3629 (2016).
10. Gong, Z. *et al.* Magnetoelectric effects and valley-controlled spin quantum gates in transition metal dichalcogenide bilayers. *Nature communications* **4**, 1–6 (2013).
11. Xiao, D., Liu, G. B., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides. *Physical Review Letters* **108**, 1–5. ISSN: 00319007. arXiv: 1112.3144 (2012).
12. Li, X., Zhang, F. & Niu, Q. Unconventional quantum Hall effect and tunable spin Hall effect in Dirac materials: application to an isolated MoS₂ trilayer. *Physical Review Letters* **110**, 066803 (2013).
13. Mak, K. F., McGill, K. L., Park, J. & McEuen, P. L. The valley Hall effect in MoS₂ transistors. *Science* **344**, 1489–1492 (2014).
14. Mak, K. F., He, K., Shan, J. & Heinz, T. F. Control of valley polarization in monolayer MoS₂ by optical helicity. *Nature nanotechnology* **7**, 494–498 (2012).
15. Zeng, H., Dai, J., Yao, W., Xiao, D. & Cui, X. Valley polarization in MoS₂ monolayers by optical pumping. *Nature nanotechnology* **7**, 490–493 (2012).
16. Cao, T. *et al.* Valley-selective circular dichroism of monolayer molybdenum disulphide. *Nature communications* **3**, 1–5 (2012).
17. Jones, A. M. *et al.* Optical generation of excitonic valley coherence in monolayer WSe₂. *Nature nanotechnology* **8**, 634–638 (2013).
18. Lee, J., Mak, K. F. & Shan, J. Electrical control of the valley Hall effect in bilayer MoS₂ transistors. *Nature nanotechnology* **11**, 421–425 (2016).
19. Riley, J. M. *et al.* Direct observation of spin-polarized bulk bands in an inversion-symmetric semiconductor. *Nature Physics* **10**, 835–839 (2014).

20. Zhu, B., Zeng, H., Dai, J., Gong, Z. & Cui, X. Anomalous robust valley polarization and valley coherence in bilayer WS₂. *Proceedings of the National Academy of Sciences* **111**, 11606–11611 (2014).
21. Jones, A. M. *et al.* Spin-layer locking effects in optical orientation of exciton spin in bilayer WSe₂. *Nature Physics* **10**, 130–134 (2014).
22. Lezama, I. G. *et al.* Indirect-to-direct band gap crossover in few-layer MoTe₂. *Nano letters* **15**, 2336–2342 (2015).
23. Froehlicher, G., Lorchat, E. & Berciaud, S. Direct versus indirect band gap emission and exciton-exciton annihilation in atomically thin molybdenum ditelluride (MoTe₂). *Physical Review B* **94**, 085429 (2016).
24. Keum, D. H. *et al.* Bandgap opening in few-layered monoclinic MoTe₂. *Nature Physics* **11**, 482–486 (2015).
25. Song, S. *et al.* Room temperature semiconductor–metal transition of MoTe₂ thin films engineered by strain. *Nano letters* **16**, 188–193 (2016).
26. Pradhan, N. R. *et al.* Field-effect transistors based on few-layered α -MoTe₂. *ACS nano* **8**, 5911–5920 (2014).
27. Yamamoto, M. *et al.* Strong enhancement of Raman scattering from a bulk-inactive vibrational mode in few-layer MoTe₂. *Acs Nano* **8**, 3895–3903 (2014).
28. Yang, J. *et al.* Robust excitons and trions in monolayer MoTe₂. *ACS nano* **9**, 6603–6609 (2015).
29. Xiao, D., Yao, W. & Niu, Q. Valley-contrasting physics in graphene: magnetic moment and topological transport. *Physical Review Letters* **99**, 236809 (2007).
30. Ruppert, C., Aslan, O. B. & Heinz, T. F. Optical properties and band gap of single-and few-layer MoTe₂ crystals. *Nano letters* **14**, 6231–6236 (2014).
31. Robert, C. *et al.* Excitonic properties of semiconducting monolayer and bilayer MoTe₂. *Physical Review B* **94**, 155425 (2016).

32. Oestreich, M. & Rühle, W. Temperature dependence of the electron Landé g factor in GaAs. *Physical review letters* **74**, 2315 (1995).
33. Zawadzki, W. *et al.* Temperature dependence of the electron spin g factor in GaAs. *Physical Review B* **78**, 245203 (2008).
34. Zhao, H. *et al.* Electron spin quantum beats and room temperature g factor in GaAsN. *Applied Physics Letters* **95**, 041911 (2009).
35. Wang, G. *et al.* Magneto-optics in transition metal diselenide monolayers. *2D Materials* **2**, 034002 (2015).
36. Wang, Z.-W., Liu, L. & Li, S.-S. Spin-flip relaxation via optical phonon scattering in quantum dots. *Journal of Applied Physics* **114**, 224305 (2013).
37. Ye, Z., Sun, D. & Heinz, T. F. Optical manipulation of valley pseudospin. *Nature physics* **13**, 26–29 (2017).
38. Schmidt, R. *et al.* Magnetic-field-induced rotation of polarized light emission from monolayer WS₂. *Physical review letters* **117**, 077402 (2016).
39. Wang, G. *et al.* Control of exciton valley coherence in transition metal dichalcogenide monolayers. *Physical review letters* **117**, 187401 (2016).

Chapter 3

Interlayer exciton valley hall effect in TMDs heterostructure

The Berry curvature in the band structure of transition metal dichalcogenides introduces a valley-dependent effective magnetic field, which induces the valley Hall effect (VHE). Similar to the ordinary Hall effect, the VHE spatially separates carriers or excitons, depending on their valley index, and accumulates them at opposite sample edges. The VHE can play a key role in valleytronic devices, but previous observations of the VHE have been limited to cryogenic temperatures. In this chapter, we demonstrate the VHE of interlayer excitons in a $\text{MoS}_2/\text{WSe}_2$ heterostructure at room temperature. We monitored the in-plane propagation of interlayer excitons through photoluminescence mapping and observed their spatial separation into two opposite transverse directions that depended on the valley index of the excitons. Our theoretical simulations reproduced the salient features of these observations. Our demonstration of the robust interlayer exciton VHE at room temperature, enabled by their intrinsically long lifetimes, will open up realistic possibilities for the development of opto-valleytronic devices based on TMDs heterostructures.

3.1 Introduction

In monolayer transition metal dichalcogenides materials, two valleys, located at inequivalent corners of the hexagonal first Brillouin zone, have the same energy but opposite Berry curvatures[1–4]. These Berry curvatures serve as effective magnetic fields[5], which exert an effective force on accelerating carriers to deflect their transport current[6]. The direction of this force, however, is valley dependent because of the opposite signs of the Berry curvatures, resulting in valley-dependent spatial separation of carriers. This so-called valley Hall effect, analogous to the spin-dependent spatial separation in the spin Hall effect[7], has been observed for electrons in a MoS₂ transistor[8]. Furthermore, the excitonic version of the VHE has been theoretically proposed[9–13] and experimentally demonstrated in monolayer MoS₂[14] with a larger Hall angle. The observation of the excitonic VHE is particularly important for developing novel valley-dependent optoelectronic devices utilizing TMDs materials.

However, as has been shown in time- and polarization-dependent photoluminescence (PL) measurements, excitons in monolayer TMDs possess short valley lifetimes, typically in the picosecond range. In addition, the valley depolarization process gets even faster with increasing temperature, and the VHE has remained to be a low-temperature phenomenon. The strong electron-hole exchange interactions are believed to be responsible for the rapid valley depolarization of excitons. The valley lifetime of excitons can be significantly extended by using TMDs van der Waals heterostructures[15, 16]. In a TMDs heterostructure with type-II band alignment, electrons and holes stay in different layers. The formation time of such interlayer (or indirect) excitons is very short, typically on the order of 50 fs[17, 18], and the binding energies are still considerable despite the charge separation[19]. The electron-hole wavefunction overlap is heavily reduced, which not only leads to a long exciton lifetime due to the reduced recombination probability but also a long valley lifetime due to the reduced electron-hole exchange interaction[1, 16]. Because of this 3-orders longer exciton lifetime for interlayer excitons, they can thus travel significantly longer

compare with the intralayer counterpart, and experimentally we have seen the travel distance to be at least 5 μm . Therefore, interlayer excitons are ideal candidates for serving as robust carriers of valley information[20, 21].

Here, we report on the first observation of the VHE of interlayer excitons in $\text{MoS}_2/\text{WSe}_2$ heterostructures. Due to the type-II band alignment, electrons and holes reside in MoS_2 and WSe_2 , respectively, forming robust interlayer excitons[17, 22, 23]. We used spatially resolved polarization-dependent PL spectroscopy to map the intensity and polarization of PL emission from interlayer excitons and observed that they are spatially separated into two opposite transverse directions, depending on the valley index. We directly demonstrated a long (~ 1 ns) valley lifetime through time-resolved PL measurements, and finite valley polarization persisted up to room temperature. Consequently, the interlayer exciton VHE was robust, observed in different samples under various conditions of temperature, excitation wavelength, and excitation polarization. To enhance the VHE we use a unique suspended slab geometry where strain and consequently a strong potential gradient are expected. These observations demonstrate that interlayer excitons in TMDs heterostructures are promising for implementing valley-dependent properties in optoelectronic devices.

3.2 Results

Figure 1a shows a schematic energy-level diagram for interlayer excitons in a $\text{MoS}_2/\text{WSe}_2$ heterostructure with a stacking angle near zero degree. An interlayer exciton consists of an electron in the MoS_2 layer and a hole in the WSe_2 layer; It can radiatively recombine and emit a photon. Because of the lacking of inversion symmetry, the K and K' points are nonequivalent in momentum space although their energies are degenerate. Due to spin-orbit coupling, different valleys have opposite circular polarization selection rules[1, 24, 25] (Figure 3.1a), which allows us to detect excitons in different valleys with their exclusive optical helicity ($\sigma+$ and $\sigma-$). We characterized the MoS_2 -

WSe₂ monolayers and heterostructures using PL measurements. Their spectrum is shown in Figure 3.1b. Intralayer excitons in MoS₂ (WSe₂) show a peak at ~ 675 nm (~ 750 nm), while interlayer excitons in the heterostructure area show a peak at ~ 1130 nm. We fabricated several samples, and they all corroborate this result (see discussion section). Note that the peak wavelength (1130 nm) is consistent with the previous reports for interlayer excitons associated with the K-K transition measured through scanning tunneling microscopy[23] but is different from those reports for interlayer excitons associated with the K- Γ transition[26, 27], which have emission around 800 nm.

We also investigated the lifetime and valley polarization of the interlayer exciton emission peak at both cryogenic and room temperatures (Figure 3.1 c and d). An ultralong lifetime (~ 1 ns) was observed, confirming its interlayer exciton origin. Furthermore, by exciting with a CW laser at 726 nm and only detecting emission from interlayer exciton recombination using long pass filters, we collect the $\sigma+$ and $\sigma-$ polarized PL intensity data, and calculated the degree of polarization (DOP) as $(I_{\sigma+} - I_{\sigma-})/(I_{\sigma+} + I_{\sigma-})$, where $I_{\sigma+}$ and $I_{\sigma-}$ are the average PL intensity for $\sigma+$ and $\sigma-$ emission. The absolute value of DOP for both valleys were about 30% at the lowest temperature, gradually decreased with increasing temperature, and became $\sim 6\%$ at room temperature.

Figure 3.2a shows an optical microscope image of a representative device. The WSe₂ and MoS₂ monolayers were mechanically exfoliated from bulk single crystals onto polydimethylsiloxane stamps. Then they were stacked onto a silicon-on-insulator wafer with a 220 nm thick silicon film on a 2 μ m sacrificial silicon dioxide layer (see the Methods section for more details). Etching chemicals are then injected through the holes of the silicon layer to create an empty etched area below the system. As shown in Figure 3.2b, the silicon and the heterobilayer are therefore suspended which results in the appearance of strain at the edges of the slab. This strain, as described below, induces a potential required for the appearance of the VHE. Furthermore, excitons

Figure 3.1: Valley polarization of the interlayer exciton. (a) Interlayer exciton in different valleys. Electrons (grey dots) will hop to MoS₂ with a lower energy in the conduction band. Holes (empty dots) will hop to the valence band of WSe₂. The combination of electrons and holes emits photons with optical helicity. σ^+ (σ^-) circularly polarized light couples to the K (K') valley. (b) PL from intralayer and interlayer excitons. The wavelength of interlayer exciton emission is well separated from that in monolayer MoS₂ and WSe₂, making sure that we can detect interlayer exciton emission exclusively by using a long pass filter. (c) Time-resolved PL measurement for co-polarized and cross-polarized situation in low temperature (up) and room temperature (down). (d) DOP as a function of temperature for σ^+ and σ^- excitation. The valley polarization starts from around 30% and reduces to about 6% as the temperature goes higher from cryogenic temperature to room temperature. The error bar is smaller than the size of the dot.

in different valleys are expected to exhibit valley-contrasting transverse motion due to the opposite signs of their Berry curvatures, which were illustrated in Figure 3.2c.

The experimental setup used for polarization-dependent PL mapping is schematically shown in Figure 3.3a, and a detailed description can be found in the Methods

Figure 3.2: Concept of interlayer exciton valley hall effect. (a) Microscope image for our sample. The red dashed line represents monolayer WSe₂. The blue dashed line represents monolayer MoS₂. WSe₂ and MoS₂ are stacked on a silicon-on-insulator (SOI) substrate by dry transfer. In the middle of the substrate, a silicon suspended slab is fabricated in rectangular shape. (b) Schematic illustration of the silicon suspended slab. The suspended silicon layer is made of SOI material with a nominal 220 nm thick silicon layer on 2 μm buried oxide. It will bend due to gravity and create strain where the maximum is at the edge. Blue layer, silicon; gray layer, SiO₂; top transparent layer: 2D materials. (c) Side view of heterostructures with MoS₂ and WSe₂ monolayers. Under their Berry curvature and the external strain, interlayer excitons formed by electrons (e) and holes (h) will traverse to different directions according to their valleys (K and K').

section. In order to measure exciton transport, we fixed the excitation laser spot on the sample and then scanned the detection spot. Note that this scheme is different from normal PL mapping methods as used in Figures 3.7 and 3.3, for which the excitation and emission spot always overlapped with each other in a confocal microscope.

To characterize our setup, we first scan the emission pattern for the silicon PL from a heavily doped SiO₂-Si wafer, for which the shape should be centrosymmetric. As expected, the intensity distribution shows a Gaussian shape around the center of the excitation beam (Figure 3.3b). Next, we scan the emission pattern for interlayer exciton PL. Figure 3.3c shows a measured diagram which significantly distorts from the Gaussian shape. Clear peaks appear, and through comparison with sample images, we determined that the sidebands appeared at suspended slab edges. Similar patterns were observed in different samples that did not have the periodic holes but had strain at the edges (shown in Figure 3.14b).

Given the clearly detectable exciton transport, we then performed polarization-dependent PL mapping experiments. We used a linearly polarized excitation beam to

Figure 3.3: Experimental setup and detection of exciton transport. (a) Experimental setup. The sample is in a closed-cycle cryostat with variable temperature. A laser with controllable polarization is sent to the sample through a scanning galvo mirror set. PL is sent to the superconducting single photon detector (SSPD). The Galvo in the PL collection arm is used to implement PL mappings (See detail in the Method). BS, beam splitter; OBJ, objective lens; CPL, coupler; LP, long pass filter; SP, short pass filter; POL, polarizer; HWP, half wave plate; QWP, quarter wave plate. (b) The emission pattern for silicon PL. By scanning the Galvo 2 mirror set, we are able to detect the emission spatial profiles. As expected, the emission spot shows a Gaussian shape. The intensity as a function of position is shown on top for the horizontal linecut. The one for the vertical linecut is shown on the left. (c) Emission pattern for interlayer exciton PL. In stark contrast, here the emission shows a non-Gaussian profile. To see the profile more clearly, here we set the maximum intensity as one percent of the observed peak intensity. From the linecuts, we can see photon sidebands in both the horizontal and vertical directions. These sidebands come from the exciton transport over a sizable distance. The edges of the heterostructures and suspended rectangle substrate are shown with the red dashed line (the same for all other figures).

make sure that both valleys are equally populated and monitored $\sigma+$ and $\sigma-$ circularly polarized PL. With these data, we calculated the DOP map as shown in Figure 3.4a. After exciton propagating toward the sample edges (in directions indicated by the arrows), separation occurs between negative (blue) and positive (red) DOP regions.

To see it more clearly, Figures 3.4b and c show line cuts of the PL intensity and DOP along the green dashed line in Figure 3.4a. The $\sigma+$ and $\sigma-$ emission components are separated along the transverse (y) direction, with the corresponding DOP showing different signs. The PL intensity and DOP in another direction (yellow line) are shown in Figures 3.4d and e, which have similar behavior. From Figures 3.4b and d, we determined the distance between the separated intensity peaks ($\sigma+$ and $\sigma-$) to be $0.41 \pm 0.02 \mu\text{m}$ and $0.33 \pm 0.07 \mu\text{m}$ for the green and yellow line cuts, respectively.

Figure 3.4: Experimental demonstration of exciton valley Hall effect at cryo-temperature. (a) Degree of polarization. The origin of the x and y axes is at the excitation spot. (b) PL intensity with different polarization following the green linecut in (a). A separation of the intensity peak can be seen in the y direction, perpendicular to the exciton transport in the x direction. (c) Degree of polarization (DOP) as calculated from (b). (d) PL intensity with different polarization following the yellow linecut in (a). Separation of emission intensity peak and therefore different exciton movement in the transverse direction can be seen as well. (e) DOP as calculated from (d).

While the previous observation of the exciton VHE in monolayer MoS_2 was possible only at low temperatures, we can observe the interlayer exciton VHE even at room temperature, as shown in Figure 3.5. The first reason for that as described previously is the robustness of the interlayer excitons, giving them a long exciton and valley lifetime even at room temperature. The second one is that in previous experiments the gradient of potential was due to a gradient of temperature[14]. Here we design the system such that the existence of the gradient of potential is not temperature dependent. Clear separation between the $\sigma+$ and $\sigma-$ components, similar

to the low-temperature data in Figure 3.4, can be seen even though the contrast is smaller. The separation between the peaks is $0.30 \pm 0.02 \mu\text{m}$. We also moved the excitation spot to a different location on the samples (shown in Figure 3.5d-f). The results observed are similar to what is observed when the spot is not moved.

Figure 3.5: Room-temperature valley Hall effect. (a) Degree of polarization at room temperature. The green arrow represents the exciton transport direction from the excitation spot. Intensity (b) and DOP (c) following the dashed green linecut in (a). (d) Degree of polarization for another excitation spot. Intensity (e) and DOP (f) following the dashed green linecut in (d). The intensity peak separation is reversed in (b) and (e), due to the reversal of the dominant exciton transport direction.

In order to understand the observed polarization-dependent emission patterns, we developed a theoretical model and performed simulations. As the excitons in different valleys carry opposite Berry curvatures, when encountering a potential gradient, they will gain a valley-dependent transverse velocity. A way to describe such an effect is to introduce the following term in the exciton velocity[6], as mentioned in Chapter

1:

$$\mathbf{v}(\mathbf{\Omega}) = \nabla V(\mathbf{r}) \times \mathbf{\Omega}$$

where $\mathbf{\Omega}$ is the Berry curvature and V is the potential.

Figure 3.6: Degree of polarization and intensity distribution in the simulation. (a) Simulated total emission from a square shaped edge potential area. (b) Simulated DOP distribution. The $\sigma+$ and $\sigma-$ emission will split along the edge because of VHE and build up a DOP difference. The scale bar is $5 \mu\text{m}$.

For simulating the dynamics of interlayer excitons, we iteratively solved the equation of motion associated with the exciton ballistic motion and then calculated the average trajectory of many excitons, which are all assumed to originate from the pump spot center with uniformly distributed initial propagation directions and a Bose-Einstein distribution of initial energies (corresponding to different initial speeds).

Since the distance between the center of the pump spot and the edge depends on the direction, the intensity of the exciton will be larger for four particular directions. Therefore, for a centered pump we expect to obtain five high intensity spots: the central pump and four recombination spots on the edge. When reaching an edge of the system, the excitons encounter a potential barrier due to strain induced by bending of the silicon suspended layer. The localized pump laser can induce a temperature gradient from the center of the sample to the edge[14]. However, this gradient seems to be very small and therefore we choose to not include it in the simulations.

Introducing the edge potential in the equation of motion along with the Berry induced velocity, we obtain the DOP in the vicinity of the edges of the sample; see Figure 3.6. The DOP strongly depends on the value of the Berry curvature as well as the intensity and shape of the potential. We assumed the potential to be half a Gaussian near the edge with a maximum amplitude of 200 meV and a half width of 0.5 μm . Similar to TMDs monolayers, here we have taken the Berry curvature to be 15 $\text{\AA}^2$. With these parameters, we obtained the DOP and intensity distributions shown in Figure 3.6, which exhibit reasonable qualitative agreement with the experimental patterns. The quantitative difference between the intensity distributions in the model and the experiment can be attributed to extra energy relaxation processes omitted in the model.

To further explore the robustness of the observed interlayer-exciton VHE, we examined the PL emission patterns under different conditions. First, we used different excitation polarizations (Figures 3.11 and 3.12). After rotating the polarization direction of the linearly polarized excitation beam by 90 degrees, we obtained essentially the same results. Next, we demonstrated the VHE by using different excitation laser wavelengths (see Figure 3.13). Finally, in order to confirm that the origin of the potential is strain, we construct new samples, i.e., we stack directly the heterobilayer/h-BN on the SOI with rectangular holes at surface, which creates the aforementioned strain. As expected, the VHE is still present (Figure 3.14).

In summary, we report the first observation of the room temperature valley Hall effect using interlayer excitons in $\text{MoS}_2/\text{WSe}_2$ heterostructures. The robustness of exciton transport at room temperature comes from the much longer exciton and valley lifetimes as compared to that of intralayer excitons. Future work may include using electric field to control the transport of interlayer excitons since they possess an out of plane dipole with electron and hole separated in different layers[28–30]. Other fundamental questions include how the exciton repulsive interaction induced valley-polarized exciton gas and valley Hall effect affect each other; and how the VHE plays

a role in exciton superfluidics in TMDs heterostructures[31]. We note that valley separation has been achieved with the assistance of well-designed metasurfaces[32] and subwavelength asymmetric groove arrays[33]. Our demonstration of the control of valley information open new possibilities of opto-electronics and valleytronics applications for interlayer excitons.

3.3 Discussion

3.3.1 $\text{MoS}_2/\text{WSe}_2$ interlayer excitons

For the $\text{MoS}_2/\text{WSe}_2$ interlayer excitons, we observe the photoluminescence peak at ~ 1.05 eV. As mentioned previously, this peak is attributed to K-K transitions, consistent with previous STM measurement[23] but different from the previous observation for the K- Γ transition[26, 27] around 1.6 eV. Figure 3.7 shows a typical heterostructure sample and PL mapping. The PL mapping shows that the emission peak at 1150 nm is only in the heterostructure region. This excludes the possibility of such emission coming from defect emission. The above observation has been repeated for multiple samples.

Figure 3.7: Optical image of one heterostructure sample and spatial distribution of PL with wavelength above 1064nm. (a) The optical image of a MoS_2 - WSe_2 heterostructure sample. (b) PL mapping for the black square region shown in (a). This shows the PL emission above 1064 nm is only from a corner of the heterostructure region.

3.3.2 The influence of the SOI slab

Beside the strain created by the SOI slab, another important help is that PL is significantly enhanced at the part on the slab with periodic holes. The lattice constant of this structure is $a = 296.2$ nm and the radius of the air holes is $r = 83.4$ nm. This combination of geometries leads to a relative thickness of $d/a = 0.74$ and relative hole size of $r/a = 0.282$. We adopt 3D FDTD solutions to calculate the bandgap of this structure. In simulation, a group of dipoles with various orientations is used to excite the possible modes in this structure. The calculated bandgap structure of transverse electric modes is shown in Figure 3.8. As can be seen, it has a photonic bandgap ~ 240 nm and therefore serves as a mirror for the PL range around 1150 nm. Indeed, an enhancement of PL emission is observed as shown in Figure 3.9.

Figure 3.8: Band structure of the SOI slab for the TE modes. The blue dots represent TE bands and the dashed black lines represent the photonic bandgap of this structure is around 0.266 eV.

Figure 3.9: Color plot of interlayer exciton PL intensity mapping. The linear (a) and log (b) plot of PL from MoS₂/WSe₂ heterostructure, respectively. Here the excitation and detection spot (same spot) is scanned across the sample. The dotted red lines show the outline of the photonic crystal and heterostructure.

3.3.3 Setup characterization

To measure the polarization-dependent PL mapping, our two collection arms need to be precisely aligned. For PL signals without the Hall effect, the PL mapping should be the same for $\sigma+$ and $\sigma-$ detection. Instead of using the laser reflection signal, whose wavelength is different with the interlayer exciton emission, we choose the Silicon PL as a reference. It has a wavelength centered around 1100 nm, which is close to our interlayer exciton emission. Even though its intensity is ~ 100 times smaller than that of the interlayer excitons, it is enough to calibrate our setup.

We moved out of the heterostructure area and focused on a substrate without heterostructure. Subsequently, by focusing the excitation arm on the sample and then scanning the detection map of the silicon PL, the data shows a Gaussian shape for both $\sigma+$ and $\sigma-$ detection (Figure 3.10 a and b). Ideally the DOP calculated using these two sets of data should be exactly zero. For our experimental setup, the DOP for silicon PL is within $\pm 3\%$. We note that this is much smaller than the measured interlayer exciton DOP, which is around 30 %. In conclusion, our setup is aligned precisely enough to measure the interlayer exciton VHE.

Figure 3.10: Spatial distribution of Silicon PL signal in SiO₂-Si substrate. Spatial profile of emitting silicon PL signal under linear excitation, and σ^+ (a) and σ^- (b) detection. The signal is taken at the blank part of another heavily doped SiO₂-Si substrate. (c) Degree of polarization calculated for silicon signal using data from (a) and (b). For DOP, we use the same color bar as Figure 3.10a and Figure 3.5 a and d. A nearly white image shows that the experimental setup is well aligned with negligible DOP for silicon PL.

3.3.4 Excitation polarization dependence

We rotated the polarization direction of the linearly polarized excitation beam by 90 degrees and examined exciton VHE again at both cryogenic and room temperature. What our result shows is that, no matter what excitation polarization is used, all the excitons transported to the edges follow the same rule: K valley excitons turn to the right and K' valley excitons turn to the left. For cryo-temperature (Figure 3.11), two directions (right as green and down as yellow) show a clear splitting of the excitons with different polarizations, which is almost the same as the case of unrotated linearly polarized excitation (Figure 3.4). At room temperature (Figure 3.12), even the intervalley scattering is significantly enhanced and valley polarization is compressed, and the excitons are still separating along the direction perpendicular to their transport direction (Figure 3.12 b and e), showing strong robustness of VHE against excitation polarization and temperature changes.

3.3.5 Excitation wavelength dependence

Besides a 726nm CW laser, we also tested the performance of the interlayer exciton VHE using 532 nm and 690 nm diode laser excitation. Excitons that move in the x

Figure 3.11: The interlayer exciton VHE at cryogenic temperature. (a) Color plot of the exciton valley Hall effect after rotating the linearly polarized excitation direction by 90 degrees. $\sigma+$, $\sigma-$ PL (b) and DOP (c) at green linecut. $\sigma+$, $\sigma-$ PL (d) and DOP (e) at yellow linecut.

Figure 3.12: The interlayer exciton VHE at room temperature. (a) Color plot of the exciton valley Hall effect after rotating the linearly polarized excitation direction by 90 degrees. $\sigma+$, $\sigma-$ PL (b) and DOP (c) linecut at the green line. (d-f) Same as (a - c) but for another excitation spot, where interlayer excitons move left. Excitons move right (a - c) and left (d - f) showing a clear splitting in their trajectories with different polarization.

direction (right) are convincing evidence to show the interlayer exciton VHE robustness with different excitation wavelengths. The results are shown in 3.13. We can see that the valley polarization pattern closely resembles of that in near-resonance case (726 nm), especially in the vicinity of the right side denoted by the arrow. All the three wavelength excitation patterns show the separation of $\sigma+$ and $\sigma-$ to the right and left, respectively.

Figure 3.13: Interlayer exciton VHE excited with different wavelength. (a) DOP profile when pumped with a 532 nm laser with linear polarization. $\sigma+$, $\sigma-$ PL (b) and DOP (c) linecut at the edge (green line in (a)). (d-f) Same measurement with (a - c) but pumped with 690 nm laser with linear polarization.

3.3.6 VHE experiment on sample II with etched structure on substrate

In order to validate the potential trapping effect caused by the strain and exclude the possible effect of the periodic holes in the suspended silicon layer, we fabricated

a new batch of samples without periodic holes structure but only rectangular holes at the edge of the SOI substrate. Sample images after fabricating MoS₂/WSe₂ heterostructure are shown in Figure 3.14a. We focused light in the center of the sample and scanned the detection area. As can be seen from Figure 3.14b, even though only the sample center is excited, emission can come from the sample edge in the strained area. This clearly shows the funneling effect[34], which agrees with experimental demonstration of the strain effect as shown in previous work[12]. Under linearly polarized excitation and with polarization-resolved emission, the DOP can be calculated in Figure 3.14c. Excitons in one valley turn to the transverse direction perpendicular to the exciton propagation direction, causing DOP_y0 at the left side and DOP_x0 at the right side following the propagation directions. The PL intensity and DOP along two cutting lines in Figure 3.14 are shown in Figure 3.14 d-g.

3.4 Method

3.4.1 Sample fabrication.

The monolayers of WSe₂ and MoS₂ were mechanically exfoliated using viscoelastic polymer (polydimethylsiloxane), and then deposited consecutively onto a boron nitride flake on the silicon photonic crystal slab in a dry procedure, with their stacking angle was near zero degrees. The sample was then transferred to a chamber and annealed with Ar/H₂ (95%/5%) gas blowing at 473K for 3 hours, to improve the contact. The monolayers were optically selected with a microscope and confirmed by PL and Raman signal.

3.4.2 Polarization resolved double Galvo laser scanning system

The polarization and spatial resolved PL measurement was carried out by a home-made confocal microscope, as shown in Figure 3.3. Our sample is positioned by a

Figure 3.14: Interlayer exciton VHE on another sample. (a) optical image of samples after fabrication of TMDs on the substrate with etched rectangle-shaped holes. (b) The diffusion of excitons. (c) Color plot of the exciton valley Hall effect. The center point represents the excitation points and the green arrow represents the exciton diffusion direction. σ^+ and σ^- PL intensity (d) separation along the y direction as the excitons are moving in the $-x$ direction, and the DOP (e) calculated from (d). σ^+ and σ^- PL intensity (f) separation along the x direction as the excitons are moving in the $-y$ direction, and the DOP (g) calculated from (f).

three-dimensional piezoelectric stepper, which is mounted on a closed-cycle optical cryostat. The 726 nm diode laser is focused onto the sample with beam diameter around 1 μm, using a 50x infrared objective lens. The PL emission from the interlayer excitons was selected using a 1050 nm long pass filter. By rotating the polarizers and wave plates, we can reach any specific polarization state. To get Figure 3.7 and 3.9, we first tune Galvo 2 to let the detection spot meets the excitation spot. Then we use Galvo 1 to perform the PL mapping by moving that shared spot across the sample. For all other mappings, we fix Galvo 1 and therefore the excitation spot on the sample, while at the same time scan Galvo 2 placed at the detection arm. The detection fiber core will be imaged onto different locations on the sample by moving

Galvo 2, therefore a PL emission profile can be obtained. With the beam splitter and a multi-channel SSPD, the $\sigma+$ and $\sigma-$ components of the PL signal from each spot were measured simultaneously. The systematic efficiency difference of these two channels is canceled by combining the data before and after tuning the half wave plate at 45 degrees on the detection arm, and therefore switches the $\sigma+$ and $\sigma-$ for the two detection channels.

Bibliography

1. Xiao, D., Liu, G.-B., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides. *Physical review letters* **108**, 196802 (2012).
2. Cao, T. *et al.* Valley-selective circular dichroism of monolayer molybdenum disulphide. *Nature communications* **3**, 1–5 (2012).
3. Zeng, H., Dai, J., Yao, W., Xiao, D. & Cui, X. Valley polarization in MoS₂ monolayers by optical pumping. *Nature nanotechnology* **7**, 490–493 (2012).
4. Jones, A. M. *et al.* Optical generation of excitonic valley coherence in monolayer WSe₂. *Nature nanotechnology* **8**, 634–638 (2013).
5. Srivastava, A. *et al.* Valley Zeeman effect in elementary optical excitations of monolayer WSe₂. *Nature Physics* **11**, 141–147 (2015).
6. Xiao, D., Chang, M.-C. & Niu, Q. Berry phase effects on electronic properties. *Reviews of modern physics* **82**, 1959 (2010).
7. Sinova, J., Valenzuela, S. O., Wunderlich, J., Back, C. & Jungwirth, T. Spin hall effects. *Reviews of Modern Physics* **87**, 1213 (2015).
8. Mak, K. F., McGill, K. L., Park, J. & McEuen, P. L. The valley Hall effect in MoS₂ transistors. *Science* **344**, 1489–1492 (2014).
9. Yao, W. & Niu, Q. Berry phase effect on the exciton transport and on the exciton Bose-Einstein condensate. *Physical review letters* **101**, 106401 (2008).

10. Kuga, S.-i., Murakami, S. & Nagaosa, N. Spin Hall effect of excitons. *Physical Review B* **78**, 205201 (2008).
11. Yu, H., Liu, G.-B., Gong, P., Xu, X. & Yao, W. Dirac cones and Dirac saddle points of bright excitons in monolayer transition metal dichalcogenides. *Nature communications* **5**, 1–7 (2014).
12. Li, H. *et al.* Optoelectronic crystal of artificial atoms in strain-textured molybdenum disulphide. *Nature communications* **6**, 1–7 (2015).
13. Yu, T. & Wu, M. Valley depolarization dynamics and valley hall effect of excitons in monolayer and bilayer mos 2. *Physical Review B* **93**, 045414 (2016).
14. Onga, M., Zhang, Y., Ideue, T. & Iwasa, Y. Exciton Hall effect in monolayer MoS 2. *Nature materials* **16**, 1193–1197 (2017).
15. Rivera, P. *et al.* Valley-polarized exciton dynamics in a 2D semiconductor heterostructure. *Science* **351**, 688–691 (2016).
16. Jiang, C. *et al.* Microsecond dark-exciton valley polarization memory in two-dimensional heterostructures. *Nature communications* **9**, 1–8 (2018).
17. Hong, X. *et al.* Ultrafast charge transfer in atomically thin MoS 2/WS 2 heterostructures. *Nature nanotechnology* **9**, 682–686 (2014).
18. Zheng, W. *et al.* Probing and Manipulating Carrier Interlayer Diffusion in van der Waals Multilayer by Constructing Type-I Heterostructure. *Nano letters* **19**, 7217–7225 (2019).
19. Rivera, P. *et al.* Observation of long-lived interlayer excitons in monolayer MoSe 2–WSe 2 heterostructures. *Nature communications* **6**, 1–6 (2015).
20. Jin, C. *et al.* Imaging of pure spin-valley diffusion current in WS2-WSe2 heterostructures. *Science* **360**, 893–896 (2018).
21. Cheng, R. *et al.* High-performance, multifunctional devices based on asymmetric van der Waals heterostructures. *Nature Electronics* **1**, 356–361 (2018).

22. Pant, A. *et al.* Fundamentals of lateral and vertical heterojunctions of atomically thin materials. *Nanoscale* **8**, 3870–3887 (2016).
23. Chiu, M.-H. *et al.* Determination of band alignment in the single-layer MoS₂/WSe₂ heterojunction. *Nature communications* **6**, 1–6 (2015).
24. Schaibley, J. R. *et al.* Valleytronics in 2D materials. *Nature Reviews Materials* **1**, 1–15 (2016).
25. Mak, K. F., Xiao, D. & Shan, J. Light–valley interactions in 2D semiconductors. *Nature Photonics* **12**, 451–460 (2018).
26. Kunstmann, J. *et al.* Momentum-space indirect interlayer excitons in transition-metal dichalcogenide van der Waals heterostructures. *Nature Physics* **14**, 801–805 (2018).
27. Fang, H. *et al.* Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides. *Proceedings of the National Academy of Sciences* **111**, 6198–6202 (2014).
28. Unuchek, D. *et al.* Room-temperature electrical control of exciton flux in a van der Waals heterostructure. *Nature* **560**, 340–344 (2018).
29. High, A. A., Novitskaya, E. E., Butov, L. V., Hanson, M. & Gossard, A. C. Control of exciton fluxes in an excitonic integrated circuit. *Science* **321**, 229–231 (2008).
30. Grosso, G. *et al.* Excitonic switches operating at around 100 K. *Nature Photonics* **3**, 577–580 (2009).
31. Fogler, M., Butov, L. & Novoselov, K. High-temperature superfluidity with indirect excitons in van der Waals heterostructures. *Nature communications* **5**, 1–5 (2014).
32. Hu, G. *et al.* Coherent steering of nonlinear chiral valley photons with a synthetic Au–WS₂ metasurface. *Nature Photonics* **13**, 467–472 (2019).

- 33. Sun, L. *et al.* Separation of valley excitons in a MoS₂ monolayer using a sub-wavelength asymmetric groove array. *Nature Photonics* **13**, 180–184 (2019).
- 34. Feng, J., Qian, X., Huang, C.-W. & Li, J. Strain-engineered artificial atom as a broad-spectrum solar energy funnel. *Nature Photonics* **6**, 866 (2012).

Chapter 4

Bandgap modification in TMDs monolayer-multilayer heterostructure

Interlayer excitons are tightly bounded electron and hole pairs in heterostructures with electrons and holes residing in different layers. They have a long lifetime, making them a promising platform for exploiting many-body interactions. However, the current research is mostly focused on monolayer-monolayer heterostructures, which missed a huge playground for TMDs heterostructure physics. Here, we observed the photoluminescence from multilayer WSe₂/monolayer MoS₂ heterostructures. We found that the temperature dependence of the interlayer exciton photoluminescence intensity, lifetime, and peak energy depends on the number of the WSe₂ layers. By comparing the optical transition energies in monolayer-monolayer and multilayer-monolayer heterostructures, we can extract the valence band shift of multilayer WSe₂, which is otherwise only possible with sophisticated methods such as angle-resolved photoemission spectroscopy (ARPES). These findings expand our understanding of the interlayer excitons and bandgap engineering with the layer degree of freedom.

4.1 Introduction

Layered transition metal dichalcogenides (TMDs) exhibit many novel physical properties, such as the layer-dependent electronic band structure[1–3], valley polarization [4–6], and nonlinear optical response [8, 7, 8]. The flexibility of stacking two different layered TMDs together to form the van der Waals heterostructures (HS) opens up new degrees of freedom to further expand its fascinating properties [9]. One of the most interesting aspects of the HS is the existence of the interlayer excitons (IXs), where the electrons and holes are separated into different layers. Because of the spatially indirect nature and the suppressed electron-hole exchange interaction, the IXs have a long lifetime [10–12], a high valley polarization degree [14], and a long exciton diffusion length even at room temperature [13]. Moreover, the Moiré IXs formed in a HS with a small stacking angle provides another degree of freedom to tune the optical and electronic properties of HS [14–17]. However, up to now, most reports on the IXs concerns only bilayer HS system [11, 18–20] and, based on our knowledge, a detailed study of the effect of layers number has not been done. The question arises whether the number of TMDs layers can be an independent degree of freedom to tune the properties of IXs in multilayer HS.

On the other hand, the evolution of valance band maximum (VBM) and conduction band minimum (CBM) of TMDs with the number of layers plays fundamental importance in determining the properties of TMDs and the HS. However, each of the existing theoretical results is different due to the different choices in the approximation method, the lattice constant, and the interlayer distance [21–24]. Moreover, due to the atomic thickness and the small size of few-layer TMDs, only limited experimental methods can be directly used to determine the evolution of the band with layers [2, 21]. Some of these methods, such as the angle-resolved photoemission spectroscopy (ARPES), while can be used to obtain the overall band structure, requires sophisticated experimental condition such as ultrahigh vacuum and very clean sample surface[2, 21]. An alternative is to use the IXs in the HS. In the HS with type-II

band alignment, the IXs consists of conduction band electrons and valence band holes residing in different layers[11, 24]. This layer separation makes it an excellent system to investigate the band shifts by monitoring the energy shift of the IXs while keeping one layer the same and changing the other layers. This method is simpler than ARPES since it does not require an ultrahigh vacuum and can be applied to sample with lower surface quality.

4.2 Results

In this chapter, we studied the photoluminescence (PL) of the IXs from multilayer (mL) WSe₂/monolayer (1L) MoS₂ HS. We found that the temperature dependence of the IXs PL is sensitive to the relative energy level between K and Γ point of WSe₂. Based on the fitting result of the data to the theoretical model, we obtain the value of the energy difference between K and Γ point of multilayer WSe₂. More importantly, we show that these IXs can be used to extract the energy shift of the valence band at the K point and the evolution of the VBM of WSe₂ with the number of layers. Our study opens a new way to control IXs by layer engineering and provides an effective way to determine the band shift of TMDs. Figure 4.1a shows a schematic of multilayer HS formed by a monolayer (1L) MoS₂ and 1L to 4L WSe₂. The electrons and holes are separated into the MoS₂ layer and the WSe₂ layers, respectively, forming the IXs. Figure 4.1b shows a typical optical image for mL (here m=1 to 4) WSe₂/1L MoS₂ HS (mL/1L HS). The monolayer MoS₂ and the few-layer WSe₂ are first exfoliated mechanically from bulk crystals on polydimethylsiloxane (PDMS) stamps, and then transferred to form the HS by a dry transfer method. The sample preparation, optical setup detail, and the characterization of the number of layers using the Raman spectroscopy can be found in the discussion section.

Figure 4.1c shows the PL intensity map ($\lambda = 1064$ nm) in these HS at room temperature. The bright area matches well with the HS area, suggesting that the IXs are formed in these HS samples. As a comparison, we measured the intralayer

Figure 4.1: (a) A schematic of the IXs in 1L MoS₂ and 1L-4L WSe₂ HS. The electrons and holes reside in MoS₂ and WSe₂ layers, respectively. (b) The optical microscope image of mL (m=1 to 4) WSe₂/1L MoS₂ HS (mL/1L HS) of the sample S1, the scale bar is 5 μm. (c) PL intensity map of the IXs in HS shown in (b) at room temperature. A 1064 nm long pass (LP1064) is used. (d-e) The PL spectra of 1L/1L and 2L/1L HS at 4.6 K. (f-g) A schematic of the transition of the intralayer excitons (X⁰), the indirect intralayer excitons (IDX⁰), and the interlayer exciton (IX).

exciton PL spectra in the visible range in the area of 1L MoS₂, 1L WSe₂, 2L WSe₂, and HS at room temperature, as well as the IXs in 1L/1L HS (see Figure 4.7a-c). The PL intensity of the intralayer exciton in the HS region shows a significant attenuation, implying that an efficient charge transfer across layers leads to the quenching of the intralayer exciton emission [25]. More HS sample images and similar Raman and PL spectra characterizations are presented in Figure 4.8 and 4.9 in the discussion section. Figure 4.1d and e show the PL spectra of IX of 1L/1L and 2L/1L HS region at low temperature, respectively. We should note that the near-infrared region emission wavelength of IX in 1L/1L HS is far away from the emission of intralayer exciton [25], which can help us to avoid the influences of intralayer excitons by using a 1064 nm long pass.

Figure 4.1f and g show the schematic of IX transitions in 1L/1L and 2L/1L HS. In both cases, due to the type II band alignment and the large band offset between MoS₂ and WSe₂ [26, 27], the IXs consist of electrons located in CBM of MoS₂ and

holes located in VBM of WSe₂. Since both MoS₂ CBM and WSe₂ VBM are located at K valley, the lowest energy IX is a momentum direct (K-K) exciton. Moreover, considering the spin-orbit coupling induced conduction band splitting of MoS₂ [28, 29], the bright IX has lower energy than the dark one. This statement is true for both 1L/1L HS and 2L/1L HS. In contrast, while the lowest energy intralayer exciton in 1L WSe₂ is a momentum-direct exciton, it is a momentum-indirect exciton in bilayer WSe₂. This is because, for bilayer WSe₂, the CBM is located at Q valley while VBM is at K point[2]. Hence, in contrast to the bilayer WSe₂, the bilayer WSe₂/1L MoS₂ HS has a direct bandgap. More data on the intralayer exciton in 1L/1L and 2L/1L HS is presented in discussion sections.

Temperature-dependent PL measurement is used to confirm the transition nature of IXs in mL/1L HS further. The HS sample image and PL mapping at different temperatures are shown in Figure 4.2a-d. The PL intensity of the IXs in 1L/1L HS decreases as the temperature is increased (Figure 4.2e), which is consistent with the case of monolayer MoS₂ intralayer exciton [28, 30]. This observation can be understood by considering that the bright IX is the lowest exciton energy level in 1L/1L HS. As the temperature is increased, the bright IXs population will decrease since there is a higher probability that phonon can scatter the bright IXs to dark states with higher energy levels. Interestingly, the temperature dependence for IXs in 2L/1L HS shows similar behavior to the 1L/1L case, as shown in Figure 4.2f. This further confirms that the IXs in 2L/1L HS is from the K-K transition. In contrast to the 1L/1L and 2L/1L case, when the number of WSe₂ layers is more than two in mL/1L HS (e.g. m=3), the PL intensity of the IXs tends to increase with increasing temperature (Figure 4.2g). Since electrons are located in K valley of MoS₂ in all cases, this indicates that the VBM from multilayer WSe₂ changes from K to Γ point when the number of layers is increased to three. We note that these results are consistent with the recent direct measurement of the valance band of 1L-3L WSe₂ by the micrometer-scale angle-resolved photoemission spectroscopy (microARPES) [2].

Figure 4.2: (a) The optical microscope image of mL-WSe₂/1L-MoS₂ ($m=1$ to 3) HS of the sample S2. The scale bar is 10 μm . (b-d) The PL intensity map of the IXs at 4.6 K, 200 K, and 295 K, respectively. (e-f) The PL intensity of IXs of mL/1L HS as a function of temperature. The solid lines are the fitting results. The data point chosen for each region in e-f is the position where the PL emission is strongest at low temperature.

Figure 4.3a illustrates the IXs transitions and the energy levels in 1L/1L HS and 3L/1L HS. The fact that the WSe₂ VBM is in Γ means that the hole prefers to be in Γ instead of K point. This implies that the indirect IXs have lower energy than the direct ones. As a consequence, the exciton population at low temperatures is dominated by indirect IXs. The radiative emission of the indirect IXs is largely suppressed due to the mismatch between electron and hole momentum. As the temperature increases, more phonons lead to an increase in the scattering of the hole from Γ to K point, which results in the increased IXs PL intensity. Considering both the bright-dark and K- Γ transition, the rate equation model for both ($m=1,2$))L/1L and ($m>2$))L/1L can be derived (see Figure 4.3). As shown in Figure 4.2e-g the model can fit the data well. Based on the fitting result, we obtain the dark-bright energy separation, 20.8 meV, and the energy difference between WSe₂ K and Γ point, $\Delta E_{K-\Gamma} = 19 \pm 4 \text{ meV}$. These values are consistent with previously reported results[2, 29]. More experimental results (Figure 4.12) and detail about the model are presented in discussion section.

Additionally, we also measured the layer dependence of the IXs PL lifetime both at

Figure 4.3: (a) Illustration of the IX in 1L-MoS₂/1L-WSe₂ and 3L-WSe₂/1L-MoS₂ HS. (b, c) Rate equation model for (m=1,2)L/1L HS and (m>2)L/1L HS, respectively. The dashed brown lines show non-radiative dark transition. The solid brown lines are the optically active transition. The total population is conserved.

low (4.6 K) and room temperature (Figure 4.4). The lifetime in 1L/1L HS is in the ns regime, which is consistent with previously reported IXs results[11, 20]. Three main results can be observed here, (1) the lifetime decreases as the number of WSe₂ layers is increased. (2) In mL/1L HS (m>2), the lifetime is longer at room temperature as compared to 4.6K. (3) In 1L/1L case, the lifetime is shorter at room temperature as compared to 4.6K. This observation is consistent with our model. First, for mL/1L HS (m>2), K- Γ IX has a lower energy level than K-K IX. It provides additional efficient decay channel. With layer number increasing, this decay channel becomes more efficient and thus the lifetime is decreased. Second, for mL/1L HS (m>2), as the temperature is increased, due to a higher number of phonons, the decay channel from K-K IX to K- Γ IX is getting less efficient. This results in a longer lifetime as the temperature is increased. Third, for 1L/1L case, K- Γ IX is far above K-K IX energy level and will not affect the IX lifetime. Instead, it is affected by the dark state above K-K IX energy level. Therefore, it shows a reversed temperature dependence as compared to mL/1L HS case (m>2).

So intuitively, the whole picture for mL/1L HS (m>2) looks like this: As the

K- Γ excitons have lower energy than the K-K exciton, when temperature going high, the interchange rate for K- Γ exciton scattering to K-K state increase, and for K-K exciton scattering to K- Γ state decrease. So for excitons in K-K state it either radiatively decay and emit or scatter to the K-K to K- Γ then to vacuum through the non-radiative channel. As PL is proportional to the radiative rate over the total rate, it increases with increasing temperature. For lifetime, as it is inversely proportional to the sum of radiative rate and non-radiative rate, it also increases with temperature.

Figure 4.4: (a, b) Time-resolved PL of mL/1L HS (sampleS3) at room temperature and low temperature, respectively.

Our results also show that IX peak energy depends on the number of WSe₂ layers. As illustrated in Figure 4.5a, on a single HS sample with monolayer MoS₂ combined with either monolayer WSe₂ or multilayer WSe₂, the electron locates at the same energy, i.e., the CBM of MoS₂. Hence, in contrast with the WSe₂ intralayer exciton which is affected by both VBM and CBM of WSe₂, the IX energy in mL/1L HS is only affected by the change in VBM of WSe₂. Therefore, we can monitor the WSe₂ VBM shifts by measuring the optical energy shifts from IXs in 1L/1L HS and mL/1L HS. As shown in Figure 4.5b, the valence band K point energy shift from monolayer WSe₂ to bilayer WSe₂ is determined to be ~ 22 meV. A similar shift ~ 19 meV is observed in

sample S2, as shown in Figure 4.14. In contrast, the VBM shift in trilayer WSe₂ with respect to monolayer WSe₂ is ~ 40 meV (Figure 4.5c). These values are consistent with previously reported results obtained using microARPES[2]. We should note that the optical transition can have a slight energy difference for different samples due to the difference in stacking angles[14] and sample quality. Therefore, the monolayer-monolayer HS and monolayer-multilayer HS have to be from the same sample in the method above and they have to be measured in the same situation to get the best estimation for the layer dependence of the valence band shift.

Figure 4.5: (a) Illustration of the scheme to determine the VBM shift of mL WSe₂ by monitoring the IXs emission energy peak. (b, c) Comparison between the PL spectra of 1L/1L HS vs. 2L/1L HS, and 1L/1L HS vs. 3L/1L HS, respectively, showing the energy difference of the IXs emission in these HS. S1 and S3 represent two different samples.

In conclusion, we observed the IXs in multilayer WSe₂/monolayer MoS₂ heterostructures. We found that, as the number of the WSe₂ layers is increased, the temperature dependence of the IXs PL changes dramatically, indicating the WSe₂ VBM location transition from K to Γ point. Furthermore, we show that the band shift of the WSe₂ VBM at K point in the few-layer WSe₂ can be determined from the change in the IXs PL spectra in multilayer HS. Our study opens an opportunity

for layer engineering of the IXs and provides a convenient method to determine the energy shift of CBM and VBM in multilayer TMD materials.

4.3 Methods

Heterostructures fabrication and experiment setup

The monolayer MoS₂ and few-layer WSe₂ are first exfoliated mechanically from bulk crystals onto polydimethylsiloxane (PDMS) stamps, and then transferred to ultralow doping Si substrate that are covered by 285nm SiO₂, to form the heterostructures (HS) by a dry transfer method. Then the HS samples were annealed under ultrahigh vacuum (around 10⁻⁶ mbar) at 200°C for 3 hours. The photoluminescence (PL) intensity map was acquired using an infrared superconducting single-photon detector. The PL spectra were obtained by a spectrometer with a CCD detector (Andor). Unless otherwise stated, a laser with 726 nm was used as the excitation. A 50x objective lens (NA=0.65) is used to collect the signal. The sample is loaded to a cryostation (Montana Instruments). For all PL measurements of the interlayer exciton, a 1064 nm long-pass filter is used to cutout the laser and intralayer exciton signals. The Raman spectra were measured at room temperature using the T64000 Raman system equipped with a liquid nitrogen cooled CCD. The excitation wavelength for Raman spectra measurement is 532 nm. In all of the optical measurements, the laser power is below 100 μ W.

4.4 Discussion

4.4.1 Raman and PL of WSe₂, MoS₂ and mL-WSe₂/1L-MoS₂ HS

To understand the role of interlayer coupling between HS interface, we measured the ultralow to high-frequency Raman spectra of 1 L to 4L WSe₂ and the heterostructures

region (Figure 4.6a). In the high-frequency range (above 100 cm^{-1}), in addition to the E_{2g}^1 and A_g^1 modes from WSe_2 and MoS_2 , two more feature modes are observed in 1L- WSe_2 /1L- MoS_2 HS region. These two modes are the Raman-inactive E_{2g}^2 mode ($\sim 285 \text{ cm}^{-1}$) in monolayer MoS_2 and the B_{2g}^1 ($\sim 310 \text{ cm}^{-1}$) mode in monolayer WSe_2 . Both are activated in 1L/1L HS, owing to the reduced symmetry of the HS[31, 32]. For the same reason, more feature modes are observed in mL/1L HS than in multilayer WSe_2 . In the ultralow frequency range (below 50 cm^{-1}), we found a series of shear (S) and layer breathing (LB) modes. Their mode frequencies are layer dependent for 2D materials [33, 34]. We note that the S modes in mL /1L HS are almost the same with mL WSe_2 , suggesting that these modes are originated from mL WSe_2 . On the other hand, the LB modes in mL/1L HS behaves like $(1+m)\text{L}$ WSe_2 . For example, in the 1L/1L HS region, a new LB mode is observed with a frequency slightly larger than that in bilayer WSe_2 . Similar case has also been found in the twisted multilayer graphene[35].

The interlayer coupling strength can be represented by the coupling force constant per unit area, α . The value of α can be obtained directly from the frequency of the LB mode in the bilayer 2D MX_2 ($\text{M}=\text{Mo}, \text{W}; \text{X}=\text{S}, \text{Se}$) materials by the formula $\alpha = 2\mu(\pi c\omega_{LB})^2$, where c is speed of light, α is the force constant per unit area between the adjacent layers, and $\mu = m_M + 2m_X$ with m_M and m_X are the mass of the M and X component, respectively[31, 33]. The frequencies of LB modes are around 41 cm^{-1} , 27.6 cm^{-1} , and 31 cm^{-1} in bilayer MoS_2 , WSe_2 , and HS, respectively. Therefore, the interlayer coupling strength in multilayer WSe_2 is around 96.8% of that in multilayer MoS_2 , while in the HS, it is approximately 94.5% of the strength for multilayer WSe_2 .

Given the force constant, we can calculate the frequencies of the LB modes in multilayer WSe_2 by using the linear chain model [33, 34]. Figure 4.1b shows the calculated frequencies of LB modes in 1L to 5L WSe_2 as well as the experimental results of LB modes in 1L to 4L WSe_2 and its HS region. As can be seen from this

figure, the theoretical results agree well with the experimental results. Moreover, we also measured the PL map and Raman spectra of three more multilayer HS samples, including 1L-WSe₂/mL-MoS₂ (m=2,3) HS sample, as shown in Figure 4.8-4.9, and got similar results.

Figure 4.7 (a-b) show the intralayer exciton spectrum of 1L-MoS₂, 1L-WSe₂, 2L-WSe₂, 1L/1L HS, and 2L/1L HS at room temperature with 532 nm excitation. Because of the interlayer coupling and charge transfer between MoS₂ and WSe₂ layers, we have not only PL intensity attenuation but also a redshift of the X⁰ peak of WSe₂ in 1L/1L HS and 2L/1L HS, that moves from around 748 nm to 756 nm and 762 nm to 770 nm, respectively. The X⁰ peak of MoS₂ in 1L/1L HS and 2L/1L HS has similar small redshift from around 656 nm to 661 nm. Furthermore, we didn't observe any new peaks in the range of 600 nm to 950 nm besides the direct and indirect intralayer exciton (X⁰, IDX⁰). Figure 4.7c shows the PL spectrum of interlayer exciton in the 1L/1L HS region at room temperature. The emission wavelength is around 1220 nm, which is far away from that of the intralayer exciton in WSe₂ and MoS₂.

4.4.2 Temperature-dependent PL mapping measurement of IXs in mL of IXs in mL-WSe₂/1L-MoS₂

Here, we give a simple rate equation model to explain the temperature dependence of the IXs emission in mL/1L HS. We consider two different cases:

Case 1: WSe₂ VBM located at K point

As described in the results section, Case 1 is relevant for 1L/1L HS and 2L/1L HS. In this case, the K (MoS₂)-K (WSe₂) bright IX is the IX state with the lowest energy. Due to coupling with phonon, it to coupling with phonon, it can be scattered to a higher dark state (i.e., its emission is non-radiative or cannot be collected). Hence, the intensity decrease as the temperature is increased.

The rate equation of the model is shown in Figure 4.11a. The IXs emission

Figure 4.6: Raman spectrum measurement results. (a) Spectrum of sample S1 with mL WSe₂ and mL-WSe₂/1L-MoS₂ (m=1 to 4) HS. (b) The calculated layer breathing (LB) modes results of mL WSe₂ and mL/1L (m=1 to 4) HS and the experiment results, which fits well with each other.

Figure 4.7: (a, b) The PL spectrum of 1L-MoS₂, 1L, 1L-WSe₂, 2L, 2L-WSe₂, 1L, 1L/1L HS, and 2L/1L HS regions at room temperature with 532 nm excitation. X⁰ represents direct intralayer exciton, and IDX⁰ represents indirect intralayer exciton. (c) The PL spectrum of IXs at 1L/1L HS region at room temperature with 726 nm excitation.

intensity can be expressed as

$$I(T) = \frac{I_L}{1 + Ae^{-\frac{\Delta E_c}{k_B T}}} \quad (4.1)$$

Figure 4.8: (a) The microscope image of sample S3 which features mL/1L ($m=1, 3, 6$) HS. (b) PL intensity map of IXs at room temperature. A 1064 nm long pass 1064 nm long-pass filter and 726 nm excitation are used. (c) Raman spectra of mL WSe₂ and mL/1LmL/1L HS.

Figure 4.9: (a) The microscope image of sample S4, which has mL /1L ($m=1$ to 4) HS. (b) The PL mapping of IXs at room temperature. A 1064 nm long pass 1064 nm long-pass filter and 726 nm excitation are used. (c) Raman spectra of mL WSe₂ and mL/1LmL/1L HS.

Figure 4.10: (a) The optical microscope image of sample S1, which has mL/1L HS. similar to Figure 4.1b in the Result section. (b) PL mapping of IXs at room temperature.

where T is the sample temperature, k_B is Boltzmann constant, I_L is the intensity of the IXs emission at low temperature, ΔE_c is the energy difference between dark state and bright K-K IX state, and A is the fitting parameters described in Figure 4.11. We used I_L , A and ΔE_c as the fitting parameters. The fitting results for sample S2 and S3 are shown in Figure 4.2e-f and Figure 4.12e, respectively. As can be seen from these figures, the model fits the data quite well.

Case 2: WSe₂ VBM located at Γ point

Case 2 is relevant for mL ($m > 2$)/1L HS. In this case, the K(MoS₂)-K(WSe₂) bright IX is not the IX state with the lowest energy. Instead, the momentum indirect K- Γ IX state is the lowest. Due to its indirect nature, the K- Γ IXs radiative emission is largely suppressed as temperature goes down, when most of the IX population is in K- Γ state and result in weak IXs emission. Due to coupling with phonon, K- Γ IXs state can be scattered to the bright K-K IXs state at a higher temperature. This increases the IXs emission intensity as the temperature is increased. The rate equation of the model is shown in Figure 4.11b. The IXs emission intensity can be expressed as

$$I(T) = \frac{I_L(P + Qe^{-\frac{\Delta E_{K-\Gamma}}{k_B T}})}{1 + Ae^{-\frac{\Delta E_c}{k_B T}} + (P + Qe^{-\frac{\Delta E_{K-\Gamma}}{k_B T}})} \quad (4.2)$$

where $(I_L, T, k_B, A, \Delta E_c)$ is the same as in 1L/1L case, $\Delta E_{K-\Gamma}$ is the energy difference between K-K and K- Γ IXs state, and $[P, Q]$ are fitting parameters described in Figure 4.11. We used $[P, Q, \Delta E_{K-\Gamma}]$ as the fitting parameters while $[I_L, A, \Delta E_c]$ are obtained from the fitting result of IXs emission in 1L/1L HS. The fitting results for sample S2 and S3 are shown in Figure 4.2g and Figure 4.12f, respectively. We found the fitted value for $\Delta E_{K-\Gamma}$ is consistent with recent experimental results [2]. Figure 4.12f shows that, as the temperature is increased, the IXs emission in 6L/1L HS increases faster than the IXs emission in 3L/1L. This can be attributed to the larger energy difference between K and Γ valence band ($\Delta E_{K-\Gamma}$) in 6L/1L HS.

Figure 4.11: (a, b) Rate equation model for Case 1 and Case 2, respectively. The solid brown lines are the optically active transition. The dashed brown lines show dark transitions (either non-radiative or the optical emission cannot be collected). The total population is conserved. $\gamma_{DB}, \gamma_{B\Gamma} \gg$ other rates. The following relations are used: $\gamma_{BD} = \gamma_{DB}e^{-\frac{\Delta E_c}{k_B T}}$, $\gamma_{\Gamma B} = \gamma_{B\Gamma}e^{-\frac{\Delta E_{K-\Gamma}}{k_B T}}$. The derived fitting parameters used in equation 4.1 and 4.2 are: $A = \frac{R + \gamma_D}{R + \gamma_B}$, $P = \frac{R + \gamma_B}{\gamma_{B\Gamma}}$, and $Q = \frac{R + \gamma_B}{\gamma_{\Gamma}}$.

Figure 4.12: (a) The microscope image of sample S3, the scale bar is 10 μm . (b-d) PL intensity map of IXs at 4.6 K, 180 K, and 295 K, respectively. (e-f) The PL intensities of mL/1L HS as a function of temperature. The solid lines are the fitting results. The $E_{K-\Gamma}$ is 15 ± 5 meV in 3L WSe₂ and 27 ± 6 meV in 6L WSe₂.

4.4.3 Additional time-resolved PL measurement

Figure 4.13 shows time-resolved PL measurement data of sample S1. It shows similar trends with those observed in sample S3 (Figure 4.4), i.e.: 1. The lifetime getting shorter as the number of WSe₂ layers is increased. 2. As the temperature is increased, the IXs emission in 1L/1L and 2L/1L decays faster while it decays slower in the case of (m>3)L/1L HS. In particular, the lifetime of the IXs emission in (m>3)L/1L HS approaches that in 1L/1L HS as the temperature is increased.

Figure 4.14 shows the PL spectra of 1L/1L HS and 2L/1L HS in sample S2. Here the band shift is determined to be around 19 meV, which is determined to be around 19 meV, which is very close to the energy difference in sample 1. This shows the repeatability of our results.

4.4.4 Valley polarization for IXs

We found that the DOP for mL-WSe₂/1L-MoS₂ ($m > 1$) heterostructure is negligible (See Figure 4.15). Upon resonant excitation with σ_- (σ_+) circularly polarized

Figure 4.13: (a-b) The time-resolved PL spectra of resolved PL spectra of mL/1L ($m=1,3$ and 6) HS (S1) at room temperature and 4.6 K, respectively.

light (726 nm), the WSe₂ excitons are selectively created. Then an ultrafast charge transfer process takes the electrons from the multilayer WSe₂ layers to the K (K') valley of monolayer MoS₂ layer, leaving only the holes in the multilayer WSe₂ layers. Therefore, the vanishing valley polarization in the 2L-WSe₂/1L-MoS₂ case can only be attributed to the hole interlayer hopping between the WSe₂ layers. Additionally, in the 3L-WSe₂/1L-MoS₂ case, the VBM locates at Γ valley can couple to both polarizations equally. Consequently, the valley polarization of IX vanishes in mL-WSe₂/1L-MoS₂ ($m > 1$) and 2L-WSe₂/3L-MoS₂ heterostructures.

Figure 4.14: Comparison between the PL spectra of 1L/1L HS and 2L/1L HS, showing the energy difference of the IXs emission in sample S2.

Figure 4.15: The circularly polarized PL spectra of IXs from the mWSe₂/1L-MoS₂ heterostructures. (a)-(c) The circularly polarized PL spectra of IXs from the 1L-WSe₂/1L-MoS₂, 2L-WSe₂/1L-MoS₂ and 1L-WSe₂/3L-MoS₂ HS under different circular polarization configurations, respectively. (d) The calculated charge density distribution of holes in 2L-WSe₂/1L MoS₂ HS.

Bibliography

1. Splendiani, A. *et al.* Emerging photoluminescence in monolayer MoS₂. *Nano letters* **10**, 1271–1275 (2010).
2. Nguyen, P. V. *et al.* Visualizing electrostatic gating effects in two-dimensional heterostructures. *Nature* **572**, 220–223 (2019).
3. Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically thin MoS₂: a new direct-gap semiconductor. *Physical review letters* **105**, 136805 (2010).
4. Xu, X., Yao, W., Xiao, D. & Heinz, T. F. Spin and pseudospins in layered transition metal dichalcogenides. *Nature Physics* **10**, 343–350 (2014).
5. Tornatzky, H., Kaulitz, A.-M. & Maultzsch, J. Resonance profiles of valley polarization in single-layer MoS₂ and MoSe₂. *Physical review letters* **121**, 167401 (2018).
6. Xiao, D., Liu, G.-B., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides. *Physical review letters* **108**, 196802 (2012).
7. Autere, A. *et al.* Nonlinear optics with 2D layered materials. *Advanced Materials* **30**, 1705963 (2018).
8. Yin, X. *et al.* Edge nonlinear optics on a MoS₂ atomic monolayer. *Science* **344**, 488–490 (2014).
9. Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. *Nature* **499**, 419–425 (2013).

10. Jiang, C. *et al.* Microsecond dark-exciton valley polarization memory in two-dimensional heterostructures. *Nature communications* **9**, 1–8 (2018).
11. Rivera, P. *et al.* Observation of long-lived interlayer excitons in monolayer MoSe₂/WSe₂ heterostructures. *Nature communications* **6**, 1–6 (2015).
12. Kim, J. *et al.* Observation of ultralong valley lifetime in WSe₂/MoS₂ heterostructures. *Science advances* **3**, e1700518 (2017).
13. Unuchek, D. *et al.* Room-temperature electrical control of exciton flux in a van der Waals heterostructure. *Nature* **560**, 340–344 (2018).
14. Alexeev, E. M. *et al.* Resonantly hybridized excitons in moiré superlattices in van der Waals heterostructures. *Nature* **567**, 81–86 (2019).
15. Jin, C. *et al.* Observation of moiré excitons in WSe₂/WS₂ heterostructure superlattices. *Nature* **567**, 76–80 (2019).
16. Seyler, K. L. *et al.* Signatures of moiré-trapped valley excitons in MoSe₂/WSe₂ heterobilayers. *Nature* **567**, 66–70 (2019).
17. Tran, K. *et al.* Evidence for moiré excitons in van der Waals heterostructures. *Nature* **567**, 71–75 (2019).
18. Rivera, P. *et al.* Interlayer valley excitons in heterobilayers of transition metal dichalcogenides. *Nature nanotechnology* **13**, 1004–1015 (2018).
19. Kunstmann, J. *et al.* Momentum-space indirect interlayer excitons in transition-metal dichalcogenide van der Waals heterostructures. *Nature Physics* **14**, 801–805 (2018).
20. Rivera, P. *et al.* Valley-polarized exciton dynamics in a 2D semiconductor heterostructure. *Science* **351**, 688–691 (2016).
21. Bussolotti, F. *et al.* Roadmap on finding chiral valleys: screening 2D materials for valleytronics. *Nano Futures* **2**, 032001 (2018).

22. Kuc, A., Zibouche, N. & Heine, T. Influence of quantum confinement on the electronic structure of the transition metal sulfide T S 2. *Physical Review B* **83**, 245213 (2011).
23. Naik, M. H. & Jain, M. Origin of layer dependence in band structures of two-dimensional materials. *Physical Review B* **95**, 165125 (2017).
24. Jin, C. *et al.* Ultrafast dynamics in van der Waals heterostructures. *Nature nanotechnology* **13**, 994–1003 (2018).
25. Liu, Y. *et al.* Room temperature nanocavity laser with interlayer excitons in 2D heterostructures. *Science advances* **5**, eaav4506 (2019).
26. Kang, J., Tongay, S., Zhou, J., Li, J. & Wu, J. Band offsets and heterostructures of two-dimensional semiconductors. *Applied Physics Letters* **102**, 012111 (2013).
27. Chiu, M.-H. *et al.* Determination of band alignment in the single-layer MoS 2/WSe 2 heterojunction. *Nature communications* **6**, 1–6 (2015).
28. Zhang, X.-X., You, Y., Zhao, S. Y. F. & Heinz, T. F. Experimental evidence for dark excitons in monolayer WSe 2. *Physical review letters* **115**, 257403 (2015).
29. Echeverry, J., Urbaszek, B., Amand, T., Marie, X. & Gerber, I. Splitting between bright and dark excitons in transition metal dichalcogenide monolayers. *Physical Review B* **93**, 121107 (2016).
30. Tongay, S. *et al.* Thermally driven crossover from indirect toward direct bandgap in 2D semiconductors: MoSe2 versus MoS2. *Nano letters* **12**, 5576–5580 (2012).
31. Zhang, X. *et al.* Phonon and Raman scattering of two-dimensional transition metal dichalcogenides from monolayer, multilayer to bulk material. *Chemical Society Reviews* **44**, 2757–2785 (2015).
32. Luo, X. *et al.* Effects of lower symmetry and dimensionality on Raman spectra in two-dimensional WSe 2. *Physical Review B* **88**, 195313 (2013).

- 33. Liang, L. *et al.* Low-frequency shear and layer-breathing modes in Raman scattering of two-dimensional materials. *ACS nano* **11**, 11777–11802 (2017).
- 34. Zhang, X. *et al.* Raman spectroscopy of shear and layer breathing modes in multilayer MoS₂. *Physical Review B* **87**, 115413 (2013).
- 35. Wu, J.-B., Wang, H., Li, X.-L., Peng, H. & Tan, P.-H. Raman spectroscopic characterization of stacking configuration and interlayer coupling of twisted multilayer graphene grown by chemical vapor deposition. *Carbon* **110**, 225–231 (2016).

Chapter 5

Perspectives

Recently the investigation on strongly correlated electrons have gained a lot research interest because of the possibilities of superconductivity and Mott insulating state, stimulated by the magic-angle graphene. Here I present several possible directions in the related field.

5.0.1 Exciton condensation of interlayer excitons

Excitons, as spin 1 Bosons, are composite quasiparticals with two spin 1/2 particles: a electron and a hole. So a very straight forward question is whether they can form Bose-Einstein Condensation, which is called exciton condensation here, can be realized in a sufficient low temperature that are accessible in laboratories. If it is possible there would be vast interplay of valley physics with the macroscopic quantum phenomena that would open a huge playground for next generation quantum information application and post-silicon electronics.

The traditional GaAs/AlGaAs quantum wells have shown promising results[1–3]. When cooling to cryogenic temperature, because of the small effective mass in the system, exciton condensation emerges with a exciton density of about 10^{10} cm^{-2} . In TMDs electrons and holes have effective mass several times larger than that of traditional quantum wells, and recent paper[4] have shown evidence of the existence

of exciton condensate in a TMDs heterostructure. However, the macroscopic coherence have not been observed. The problems for TMDs now is that the monolayer are easily inhomogeneously doped to about 10^{10} cm^{-2} in the fabrication process of heterostructure, which might be a obstacle in its realization. As we already find out that the excitons could have profound long lifetime, comparing with the short lifetime ones, they could live long enough to be cooled to temperature cold enough for a condensate to emerge.

Figure 5.1: Exciton condensate in coupled quantum well. (a) The PL intensity distribution. (b) The first order correlation mapping of the PL emission suggest long range phase coherence in the emission pattern. The center spot is out of phase because of laser heating. Figures adapted from [3].

5.0.2 Strong coulomb drag in TMDs heterostructures

Compared with free carriers, excitons are charge neutral particles. It is possible for excitons to form a trion with the access of a free electron or hole and be a charge carrier, but generally it is not applicable to make excitons carry charges. So how can we exploits it potential to form a Bose-Einstein Condensation and utilize the superfluidity once it is evidently confirmed? A possible solution is to apply a "counter-flow" picture and utilize the carrier in two layers simultaneously. the electron passway and hole passway are physically brought close enough to let electrons and holes see

each other and form an excitonic pair.

Experimentally this has been investigated in bilayer graphene separated by a thin h-BN layer in between as an insulator[5]. However such scheme depends on Landau levels formed by strong magnetic field. Is it possible to use the massive and energy-favorable TMDs excitons to form strongly coupled interlayer excitons with a buffer h-BN layer? The possibility for people to detect the Hall drag flow current is a direct confirmation of the interlayer exciton valley Hall effect we observed. This could be an interesting topic to study.

Figure 5.2: Exciton drag in spatially separated graphene layers in the quantum Hall limit. (a) The schematic for quantum Hall drag. Doping levels are tuned by top and bottom gates. A drive current in one layer will induce a drag voltage drop in both the longitudinal and transverse directions. (b) Optical image of the sample. (c) When drive and drag layer both have filling factor equal to 0.5, the quantum Hall drag would emerge, which has the same magnitude as the drive layer. Figures adapted from [5].

5.0.3 Strong correlation effects in twisted bilayer TMDs

For moiré electrons in magic-angle twisted bilayer graphene, electrons show some interesting phenomena like correlated superconducting[6], Mott insulating[7] and ferromagnetism[8, 9]. For TMDs with broken inversion symmetry, it would be poten-

tially interesting if the valley physics can couple with strong correlation. The moiré potential created by the moiré periodicity shows strong excitonic effect, especially in their spectrum that have already been studied in the Zeeman splitting in hetero-bilayer $\text{MoSe}_2/\text{WSe}_2$ heterostructure. We can extend this idea to multi-monolayer heterostructures and homo-bilayer ones.

It is recently reported that in around 4° - 5° twisted bilayer WSe_2 there is Mott insulating state and evidence of superconducting state besides the Mott transition density[10]. So it leaves us the possibility to study the spontaneously broken time reversal symmetry induced ferromagnetism in TMDs system.

Figure 5.3: (a) Superconductivity and Mott insulating state in twisted bilayer WSe_2 as the temperature is reaching to 1.5K. (b) only in the vicinity of 0.5 filling factor there exist the zero resistance. Figures adapted from [10].

Bibliography

1. Butov, L., Gossard, A. & Chemla, D. Macroscopically ordered state in an exciton system. *Nature* **418**, 751–754 (2002).
2. High, A. A., Novitskaya, E. E., Butov, L. V., Hanson, M. & Gossard, A. C. Control of exciton fluxes in an excitonic integrated circuit. *Science* **321**, 229–231 (2008).
3. High, A. A. *et al.* Spontaneous coherence in a cold exciton gas. *Nature* **483**, 584–588 (2012).
4. Wang, Z. *et al.* Evidence of high-temperature exciton condensation in two-dimensional atomic double layers. *Nature* **574**, 76–80 (2019).
5. Liu, X., Watanabe, K., Taniguchi, T., Halperin, B. I. & Kim, P. Quantum Hall drag of exciton condensate in graphene. *Nature Physics* **13**, 746–750 (2017).
6. Cao, Y. *et al.* Unconventional superconductivity in magic-angle graphene superlattices. *Nature* **556**, 43–50 (2018).
7. Cao, Y. *et al.* Correlated insulator behaviour at half-filling in magic-angle graphene superlattices. *Nature* **556**, 80–84 (2018).
8. Sharpe, A. L. *et al.* Emergent ferromagnetism near three-quarters filling in twisted bilayer graphene. *Science* **365**, 605–608 (2019).
9. Serlin, M. *et al.* Intrinsic quantized anomalous Hall effect in a moiré heterostructure. *Science* **367**, 900–903 (2020).

10. Wang, L. *et al.* Correlated electronic phases in twisted bilayer transition metal dichalcogenides. *Nature Materials*, 1–6 (2020).