

PHOTOPHYSICS OF INTERLAYER EXCITONS IN TMDC HETEROBILAYERS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
OF BILKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
MASTER OF SCIENCE
IN
MATERIALS SCIENCE AND NANOTECHNOLOGY

By
Mehmet Atif Durmuş
May 2024

PHOTOPHYSICS OF INTERLAYER EXCITONS IN TMDC HET-
EROBILAYERS

By Mehmet Atıf Durmuş

May 2024

We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

İbrahim Sarpkaya(Advisor)

Hilmi Volkan Demir

Feridun Ay

Approved for the Graduate School of Engineering and Science:

Orhan Arıkan
Director of the Graduate School

ABSTRACT

PHOTOPHYSICS OF INTERLAYER EXCITONS IN TMDC HETEROBILAYERS

Mehmet Atif Durmuş

M.S. in MATERIALS SCIENCE AND NANOTECHNOLOGY

Advisor: İbrahim Sarpkaya

May 2024

Since the first isolation of graphene (a single sheet of graphite) in 2004 and the remarkable discoveries achieved in the following years, there has been an ongoing growth in studies and interest in two-dimensional (2D) materials and their heterostructures. With the constant discovery of new 2D materials over time, their range of material properties has expanded significantly as well, opening up a greater variety of applications and corresponding theoretical and experimental research inquiries for their implementation. The majority of them are classified as layered van der Waals (vdW) materials, and the development of different transfer techniques has made it possible to fabricate vdW heterostructures, which introduced exciting possibilities for the development of quantum technologies. The unique characteristics of the constituent layers, in conjunction with the high carrier mobility characteristic of 2D materials, provide a wealth of opportunities for the development of devices with remarkable properties for various applications. Interest in semiconducting transition metal dichalcogenides (TMDCs) among other 2D materials has grown significantly owing to their exceptional optical, mechanical, and electrical properties, particularly as they exhibit direct bandgaps in atomic layer thicknesses (i.e., monolayers). The vdW heterostructures of monolayer TMDCs have been growing in popularity among researchers over the last decade since they typically exhibit staggered type-II band alignment, which promotes ultra-fast charge transfer between the constituent layers, in turn, leading to the formation of strongly Coulomb-bound electron-hole pairs (i.e., interlayer excitons, IXs) located in different layers. The emission characteristics of the IXs can be regulated by varying the twist angle between the constituent layers of the heterostructures, and a superlattice of single-photon quantum emitters of IXs through their localization to periodic quantum dot-like Moiré potentials can be achieved. The main focus of this dissertation is investigating and understanding the photophysics of IXs of hBN-encapsulated WSe₂-MoSe₂ heterobilayers, which

will allow one to grasp the importance and capabilities they hold for the development of quantum applications. The heterobilayer samples used in this study were fabricated by first isolating the 2D layers using the micromechanical exfoliation method and then vertically stacking them via the dry transfer technique. Low-temperature photoluminescence (PL) spectroscopy methods have been performed on the IX species of the fabricated heterobilayers, including magneto-PL, excitation pump power-dependent PL, temperature-dependent PL, and time-resolved PL (TRPL). Finally, first-order correlation $g^{(1)}(\tau)$ measurements in the time domain were performed using a home-built free-space Michelson interferometer. Our results on the effect of Moiré-localization of IXs demonstrate that the well-protection of the localized emitters can lead to prolonged dephasing times ($T_2 \sim 730$ fs). Remarkably, we have also successfully shown the presence of coherent coupling for the first time between the two spin states (spin-singlet and spin-triplet) of IXs of hBN-encapsulated WSe_2 - MoSe_2 heterobilayers by utilizing the quantum beat interferometry in the time domain with resulting dephasing times up to $T_2 \sim 400$ fs. Our results on the dephasing characteristics of IXs can provide important insights into the future of exciton-based device development in quantum photonic and valleytronic applications.

Keywords: Transition metal dichalcogenides, TMDCs, vdW heterobilayers, Moiré superlattice, interlayer exciton, spin-singlet, spin-triplet, coherence time, quantum beating, coherent coupling, Michelson interferometer.

ÖZET

TMDC HETEROYAPILARINDAKİ KATMANLAR ARASI EKSİTONLARIN FOTOFİZİĞİ

Mehmet Atıf Durmuş

Malzeme Bilimi ve Nanoteknoloji, Yüksek Lisans

Tez Danışmanı: İbrahim Sarpkaya

Mayıs 2024

2004 yılında grafenin (tek katmanlı grafit tabakasının) ilk kez izole edilmesinden ve takip eden yıllarda elde edilen kayda değer keşiflerden bu yana, iki boyutlu (2D) malzemelere ve heteroyapılarına yönelik çalışmalara olan ilgi devamlı olarak artmıştır. Yeni 2D malzemelerin süregelen keşifleriyle birlikte bilinen malzeme özelliklerinin yelpazesi de önemli ölçüde genişlemiş, çeşitli uygulamalara yönelik hem teorik hem deneysel araştırma alanlarına dahil edilmelerine yol açmıştır. Birçoğu katmanlı van der Waals (vdW) malzemeleri sınıfına girmekte ve transfer tekniklerinde olan çeşitli gelişmeler ile vdW heteroyapılarının oluşturulabilmesinin önünün açılmasıyla birlikte kuantum teknolojilerinde ilerleme kaydedilmesi için heyecan verici olanaklar oluşmuştur. Bileşen katmanların benzersiz özellikleri, 2D malzemelerin yüksek taşıyıcı hareketliliği karakteristiği ile birlikte, çeşitli uygulamalar için çarpıcı özelliklere sahip cihazların geliştirilmesi açısından kapsamlı imkanlar sunmaktadır. Yarıiletken geçiş metali dikalkojenitlere (TMDC'lere) olan ilgi, atomik katman kalınlıklarında (yani tek katmanlarda) doğrudan bant aralıkları sergiledikleri ve olağanüstü optik, mekanik ve elektriksel özelliklere sahip oldukları için diğer 2D malzemelere göre önemli ölçüde artmıştır. Katman arası eksitonların emisyon özellikleri, bileşen katmanlar arasındaki açılı ile kontrol edilebilir ve periyodik kuantum nokta benzeri Moiré potansiyellerine hapsolmaları sonucunda tek foton kuantum yayıcılarından oluşan bir süperörgü elde edilebilir. Bu tez çalışmasının ana odak noktası, kuantum uygulamalarının geliştirilmesi için sahip oldukları önem ve kapasitelerin kavranmasını sağlamak adına hBN ile kapsüllenmiş $\text{WSe}_2\text{-MoSe}_2$ heteroyapılarının katmanlar arası eksitonlarının fotofiziğini araştırmak ve anlamaktır. Bu çalışmada kullanılan heteroyapı numuneleri, önce 2D malzemelerin mikromekanik eksfoliyasyon yöntemi kullanılarak izole edilmesi ve ardından kuru transfer tekniği ile dikey olarak istiflenmesi ile üretilmiştir. Hazırlanan heteroyapıların katmanlar

arası eksitonları üzerinde manyeto-PL, uyarma gücüne bağlı-PL, sıcaklığa bağlı-PL ve zamana bağlı-PL (TRPL) dahil olmak üzere çeşitli düşük sıcaklık optik spektroskopi yöntemleri kullanılmıştır. Son olarak, ev yapımı bir serbest-uzay Michelson interferometresi kullanılarak zaman düzleminde birinci dereceden korelasyon $g^{(1)}(\tau)$ ölçümleri gerçekleştirilmiştir. Katmanlar arası eksitonların Moiré yapılarında hapsolmasının etkilerine ilişkin sonuçlarımız, hapsolan yayıcıların sahip olduğu güçlü korunmanın uzun süreli faz bozunum sürelerine ($T_2 \sim 730$ fs) yol açabileceğini göstermektedir. Çarpıcı bir şekilde, hBN ile kapsüllenmiş WSe₂-MoSe₂ heteroyapılarının katmanlar arası eksitonlarının iki spin hali (spin-tekli ve spin-üçlü) üzerinde uyguladığımız kuantum vuru interferometresi ölçümlerimiz, bu spinler arasında zaman düzleminde $T_2 \sim 400$ fs kadar sürebilen faz bozunum süreleriyle eşvreli kuplajın oluştuğunu da ilk kez göstermiştir. Katmanlar arası eksitonların faz bozunum özelliklerine ilişkin sonuçlarımız, kuantum fotonik ve vaditronik uygulamalarda eksiton tabanlı cihazların geliştirilmesinin geleceğine yönelik önemli katkılar sağlayabilir.

Anahtar sözcükler: Geçiş metali dikalkojenitler, TMDCs, vdW heteroyapıları, Moiré süperörgüsü, katmanlar arası eksiton, spin-tekli, spin-üçlü, faz bozunum süresi, kuantum vuruş, eşvreli kuplaj, Michelson interferometresi.

Acknowledgement

I want to start by expressing my gratitude to my advisor, Asst. Prof. İbrahim Sarpkaya, for his guidance, support, and endless help. I am very grateful for this opportunity to work as a research assistant in the Quantum Photonics research group during my master's studies. He helped bring my motivation back when I had my most challenging times and always believed in me. He was always available for my research questions and assisted me in the construction of the free-space Michelson interferometer. He helped and supported me in every way possible during the writing and publishing processes of both of my research papers. I will always be grateful for the way that he has treated me, both as a peer and a friend. It inspired me to design and carry out experiments that I would never have the nerve to attempt on my own. I truly appreciate him for the waves of laughter, the novel experiences, and the difficult but significant scientific accomplishments during my time at the National Nanotechnology Research Center (UNAM).

I would like to thank my thesis committee, Prof. Hilmi Volkan Demir and Prof. Feridun Ay, for their comments and questions. Additionally, I would like to express my gratitude to Asst. Prof. Serkan Kasırğa and the Strongly Correlated Materials group members, especially my friend Uğur Başçı for teaching me the basics of the dry transfer method. I also want to thank the members Engin Can Sürmeli and Onuralp Ömürbek for their assistance with the specifics of laboratory equipment. Furthermore, I would like to thank the research engineers of UNAM for teaching me the theoretical and experimental practices of the laboratory instruments. Especially, Zeynep Tunalı for her assistance with the coating process of our substrates

For allowing me to be the teaching assistant in their courses and providing further guidance in the academic environment, I sincerely thank Asst. Prof. Seymur Jahangirov and Asst. Prof. Hasan Yılmaz.

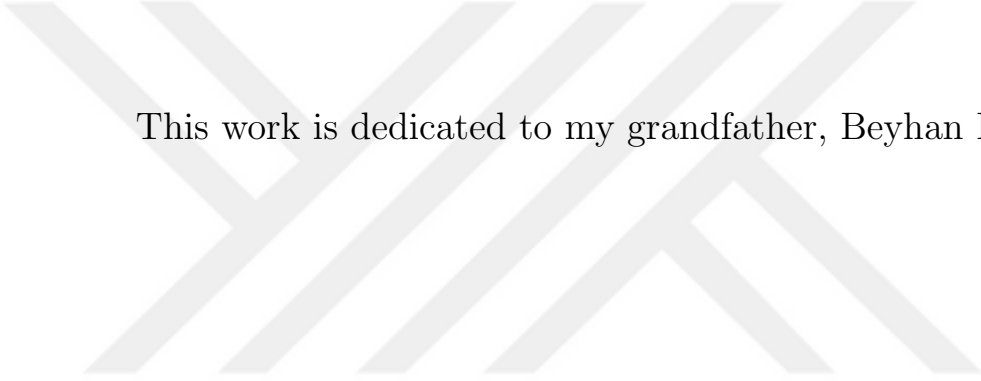
I want to acknowledge the support from İhsan Doğramacı Bilkent University, UNAM, TUBITAK-ARDEB 1001, and TUBITAK-BIDEB 2232 International Fellowship for Outstanding Researchers Program for providing financial support for this work.

I thank my fellow Quantum Photonics Group lab members and my friends at UNAM. I would especially like to thank Kaan Demiralay for his assistance and hard work in the LabVIEW programming of the Michelson interferometer. Also, I would like to thank Hilal Korkut for her diligent work in constructing the hole arrays on my sample substrates for the strain-localized quantum emitter research, and Şeyma Esra Atalay for her support with the fabrication of monolayer TMDCs. To my beloved friends Reyhan Kutan, Uğur Başçı, Koray Yavuz, Amna Amnar, Kaan Demiralay, Arda Kurucu, Emre Ece, Naz Bardakcı, Enise Kartal, Ece Karabey, Ahmet Osman Ölçer, Hilal Korkut, Ekin Bircan Boşdurmaz, Ata Utku Özkan, Şeyma Esra Atalay, Dilşad Taydaş, and Gizem Sunar Çetin I will always remember our talks and waves of laughter.

I want to thank and acknowledge my best friends Kutay Boyacıoğlu and İrem Akin for their fantastic companionship and ongoing emotional support since our undergrad years. Love you both.

Even though it may sound odd, I want to express my gratitude to Lana Del Rey and Ludwig Göransson for their music. Those tracks ended up being the soundtrack of my life while I was working on my thesis and doing my research.

Last but not least, the individuals who have the most to be grateful for are always at the end of the line. The final and most significant thing I want to do is to thank my wonderful parents, Nurhan and Zeki Durmuş. You were always there whenever I needed almost anything, and I am very thankful for that support.



This work is dedicated to my grandfather, Beyhan Boz

Let us start with some of my favorite quotes that define my outlook on life.

“Study hard what interests you the most in the most undisciplined, irreverent, and original manner possible.”

R. P. Feynman

“It is necessary to fall in love with a theory like falling in love with a woman. It is only possible if one does not completely understand her.”

R. P. Feynman

“Doing what you love is freedom; loving what you do is happiness.”

Lana Del Rey

“You need to know what to do when the sun is not shining.”

Robert Downey Jr.

“Failure is simply the opportunity to begin again, this time more intelligently.”

Henry Ford

“Whatever you do in this life, it’s not legendary unless your friends are there to see it.”

Barney Stinson, HIMYM

“Follow your passion and life will reward you.”

Uncle Iroh, ATLA

Contents

1	Introduction	1
2	Transition Metal Dichalcogenide Monolayers	7
2.1	Crystal Structure and Material Properties	8
2.2	Valley Magnetic Moment & Optical Selection Rules	11
2.3	Excitons in Monolayer TMDCs	13
2.4	Quantum Emitters in Monolayer TMDCs	15
3	van der Waals Heterostructures	18
3.1	Mechanical Exfoliation of 2D Materials	18
3.2	Fabricating the WSe ₂ -MoSe ₂ Heterobilayers	20
4	Interlayer Excitons in TMDC Heterobilayers	24
4.1	Band Alignment of the WSe ₂ -MoSe ₂ Heterobilayer	25
4.2	Interlayer Excitons in WSe ₂ -MoSe ₂ Heterobilayers	26

4.3	Moiré Interlayer Excitons in WSe ₂ -MoSe ₂ Heterobilayers	28
4.4	Magneto-PL Studies of IXs in WSe ₂ -MoSe ₂ Heterobilayers	31
4.5	Temperature and Pump Power Dependence of Spin-Singlet and Spin-Triplet IXs in WSe ₂ -MoSe ₂ Heterobilayers	35
4.6	Time-Resolved PL studies of IXs in WSe ₂ -MoSe ₂ Heterobilayers	38
4.7	Methods	42
4.7.1	Photoluminescence Spectroscopy	42
4.7.2	Magneto-PL Spectroscopy	47
4.7.3	Temperature-Dependent PL Spectroscopy	48
4.7.4	Time-Resolved PL Spectroscopy	49
5	Dephasing Time Studies of Interlayer Excitons in TMDC Heterobilayers	51
5.1	Coherence & First-Order Correlation Function	52
5.2	Michelson Interferometer	55
5.3	Dephasing Time Studies of Exciton Species in Monolayer MoSe ₂	56
5.4	Prolonged Dephasing Time of Ensemble of Moiré-trapped Interlayer Excitons in WSe ₂ -MoSe ₂ Heterobilayers	58
5.5	Quantum Beats Between Spin-singlet and Spin-triplet Interlayer Exciton Transitions in WSe ₂ -MoSe ₂ Heterobilayers	63
6	Conclusion & Outlook	76

List of Figures

- 2.1 **MX₂ crystal structure of monolayer TMDCs.** **a.** A single unit cell of the MX₂ crystal. Chalcogen and transition metal atoms are represented by the letters X and M, respectively. **b,c.** In-plane (**b**) and out-of-plane (**c**) views of a monolayer MX₂ crystal. Drawings are made by using the VESTA software. 8
- 2.2 **Indirect-to-direct band gap transition of MoS₂.** The valence band experiences an extensive phase shift upon thinning down from bulk crystal to monolayer, leading to a direct bandgap. Graphic from Ellis et al. *The indirect to direct band gap transition in multilayered MoS₂ as predicted by screened hybrid density functional theory*. Applied Physics Letters (2011). 9
- 2.3 **Electronic band structure of monolayer MoSe₂.** **a.** The real space in-plane hexagonal lattice structure of monolayer MoSe₂. Each sublattice is occupied with one Mo (blue circles) and two Se (yellow circles) atoms, where the red lines (**a**₁ and **a**₂) represent the two in-plane primitive lattice vectors. **b.** The first hexagonal Brillouin zone in the reciprocal lattice with corners at $\pm K$ valleys. Orange lines (**b**₁ and **b**₂) represent the reciprocal lattice vectors. 10

2.4	Valley optical selection rules for MX_2 type crystals. a. Berry curvature valley-contrasting resulting in a circular polarization of the coupled light for $\pm K$ valleys. b. Optical selection rules for the top (X_A) and bottom (X_B) excitons in the $\pm K$ valleys of the MX_2 crystals. Straight and dashed lines indicate the up and down spins, respectively.	12
2.5	Neutral and charged excitons in TMDC monolayers. a. Low-temperature PL spectrum of a MoSe_2 monolayer crystal under 532 nm CW laser excitation with 40 μW pump power at 3.5 K. Neutral exciton and charged exciton (trion) are labeled as X_0 and T, respectively. b. Band diagram schematic of the X_0 (purple colored) and T (orange colored) of the MoSe_2 monolayer. The spin states of the electron and holes in the conduction and valence bands are indicated by the red and blue arrows.	14
2.6	Bright and dark excitons in TMDC monolayers. a. Schematic of the ground state intravalley excitons in MoSe_2 and WSe_2 monolayers. The spin orientations of the band's electrons are indicated on their right side with the same color. The shown transitions are bright (spin-allowed) and dark (spin-forbidden) in MoSe_2 and WSe_2 monolayers, respectively. b. Illustration of the spin-allowed momentum-forbidden intervalley exciton in WSe_2 monolayer.	15

2.7 Strain-induced quantum emitters in TMDC monolayers.	
a. SEM image of an array of holes fabricated on an Au-coated substrate using focusing ion beam lithography. The red-lined upper right part indicates a magnified view of one of the holes. Illustration (b) and the optical image (c) of the dry transferred MoSe ₂ monolayers on the hole arrays. d. Low-temperature PL spectrum of the MoSe ₂ monolayer with T, X ₀ , and QE emission appearing at ~ 1.62 eV, ~ 1.66 eV, and ~ 1.59 eV, respectively, under 532 nm laser excitation with an incident power of $P = 10 \mu\text{W}$. Zoomed-in PL spectrum of the strain-induced QE with a linewidth of ~ 0.9 meV is displayed in the right panel.	16
3.1 Mechanical exfoliation steps of fabricating monolayer TMDCs.	
a. Initial step from one side of the scotch tape with a bulk TMDC crystal. b. Creating less layered crystals in certain parts of the tape as shown in (c) by folding the Scotch tape according to the specified steps I-II-III-IV. Stamping of the region left with possible monolayers to the PDMS to fabricate the desired TMDC monolayers (d)	19
3.2 Zigzag edge identification of the TMDC monolayers.	
Optical microscope images and the zigzag edge determination angles of the WSe ₂ and MoSe ₂ flakes before dry transfer. Yellow and red dashed lines show the monolayer part of the crystal flakes. The edge angles used for zigzag edge identification and the zigzag edges are shown with black lines.	20

3.3 Dry transfer and vertical stacking of TMDC monolayers.	
a. Alignment template of the two monolayers according to a specific twist angle $\theta \sim 57^\circ$. These templates can be opened semi-transparently on the real-time image by loading them into the camera software of the optical microscope. b. Schematic illustration of the dry transfer setup used to stack the crystal layers vertically to fabricate the heterostructures. The figure includes a label for every item utilized in the process.	21
3.4 Fabricated WSe₂-MoSe₂ heterobilayer. a,b. Schematic (a) and optical (b) images of an hBN-encapsulated WSe ₂ -MoSe ₂ heterobilayer sample on top of an ~ 100 nm thick Au-coated substrate, the steps of which are described above. Colored dashed lines highlight specific crystal areas. Black lines show the zigzag edges of the two monolayers and the 57° twist angle between them.	23
4.1 Band alignment of the WSe₂-MoSe₂ heterobilayer. a. Schematic of the type-II band alignment, showing intralayer and interlayer (IX) excitonic states of the heterobilayer. b. Illustration of the interlayer charge transfer at the heterojunction between the two monolayers. The offsets of the conduction and valence bands are denoted by Δ_c and Δ_v , respectively.	25

- 4.2 PL Characterization of the WSe₂-MoSe₂ heterobilayer. a.** Room-temperature PL spectrum of an hBN-encapsulated WSe₂-MoSe₂ heterobilayer sample with intralayer exciton emissions of MoSe₂ and WSe₂ monolayers appearing around ~ 1.57 eV and ~ 1.65 eV, respectively, under 532 nm CW laser excitation with an incident power of $P = 100 \mu\text{W}$. **b.** Low-temperature PL spectrum of an hBN-encapsulated WSe₂-MoSe₂ heterobilayer with the IX emission appearing at ~ 1.4 eV with a linewidth of 8.89 meV under 532 nm CW laser excitation with an incident power of $P = 50 \mu\text{W}$. The intralayer exciton emissions of the individual monolayers are quenched and their emission regions are indicated with green and purple boxes for MoSe₂ and WSe₂, respectively. 27
- 4.3 PL Characterization of Moiré-localized IXs of WSe₂-MoSe₂ heterobilayers. a.** Low-temperature PL spectra of an hBN-encapsulated WSe₂-MoSe₂ heterobilayer with the Moiré-localized IX emissions appearing at ~ 1.4 eV with the most intense one having a linewidth of 0.313 meV under 532 nm CW laser excitation with an incident power of $P = 3 \mu\text{W}$. The intralayer exciton emission regions of the individual monolayers are indicated with green and purple boxes for MoSe₂ and WSe₂, respectively. **b.** Low-temperature pump power-dependent PL spectra of the Moiré-localized IX emission showing the evaluation of the ensemble band of the Moiré-localized IXs. **c.** Low-temperature pump power-dependent PL spectra of a delocalized IX emission from another WSe₂-MoSe₂ heterobilayer sample. The PL evolution of this sample demonstrates no signs of narrow, sharp PL emission peaks at low pump power regimes, indicating that such kinds of samples do not exhibit 0D confinement. At the high pump power regime, the high energy spin-singlet emission can also be observed with the energy separation of ~ 25 meV from spin-triplet emission. Data are recorded at 3.5 K under 532 nm CW laser excitation for both pump power-dependence experiments. 30

- 4.4 **Valley-Zeeman splitting of spin-triplet and spin-singlet interlayer exciton emissions in a WSe₂-MoSe₂ heterobilayer sample with $\theta \sim 60^\circ$ stacking angle.** **a.** The PL spectra of spin states of the IXs as a function of the strength of an applied out-of-plane magnetic field under 532 nm CW laser excitation. The Zeeman splitting measured for spin-triplet (**b**) and spin-singlet (**c**) IXs with effective g factors of 15.42 ± 0.49 and 12.39 ± 0.37 , respectively. Data are recorded at 80 K. 33
- 4.5 **Zeeman Splitting of interlayer exciton emissions in WSe₂-MoSe₂ heterobilayers.** The PL spectra of the delocalized (**a**) and Moiré-trapped (**b**) IXs as a function of the strength of an applied out-of-plane magnetic field under 532 nm CW laser excitation. **c.** The PL peak energies of free and Moiré-localized IXs as a function of the applied magnetic field. **d.** The Zeeman splitting measured for free and Moiré-localized IXs with effective g factors of 16.29 ± 0.07 and 15.91 ± 0.33 , respectively. Data are recorded at 3.5 K. 34
- 4.6 **Temperature dependence of spin-singlet and spin-triplet interlayer excitons in WSe₂-MoSe₂ heterobilayers.** **a.** Temperature-dependent PL spectra of the spin states of IXs. **b.** The PL intensity ratio of spin-singlet to spin-triplet states of the IXs as a function of temperature. Data are recorded under a 532 nm CW laser with 400 μ W pump power. 36
- 4.7 **Pump power dependence of spin-singlet and spin-triplet interlayer excitons in WSe₂-MoSe₂ heterobilayers.** Pump power-dependent PL spectra of IXs at 3.5 K (**a**) and 90 K (**b**) under 532 nm laser excitation. 37

- 4.8 **Time-resolved PL of interlayer excitons in WSe₂-MoSe₂ heterobilayers.** TRPL intensity as a function of delay time of the ensemble of delocalized (a) and the ensemble of Moiré-localized (b) IXs under pulsed excitation at 532 nm with 6 μ W and 10 μ W pump powers, respectively. The red line in the plots indicates a bi-exponential fit featuring fast and slow lifetime components. The fits yield a fast decay of 2.58 ± 0.05 ns and 2.60 ± 0.02 ns, and a slow decay of 26.05 ± 0.55 ns and 21.07 ± 0.21 ns for delocalized and Moiré-localized IXs, respectively. **c.** Overview plot of the IX lifetimes of our WSe₂-MoSe₂ heterobilayer samples, where red squares represent the slow decay components and black triangles represent the fast decay components of the recombination lifetimes. The samples with Moiré-localized IXs are indicated in the plot as HS5, HS6, and HS7. Data are recorded at 3.5 K. 40
- 4.9 **Time-resolved PL spectroscopy of spin-singlet and spin-triplet interlayer excitons of WSe₂-MoSe₂ heterobilayers.** **a,b.** PL spectra of IX_T and IX_S at 90 K under 80-MHz pulsed laser excitation at 532 nm with an incident power of $P = 230$ μ W. The filtered regions of the PL spectra are indicated with blue-colored regions. Hard-coated band-pass filters with wavelengths of 880 nm and 905 nm are used for filtering IX_S and IX_T, respectively. **c,d.** The TRPL intensity of IX_S and IX_T emissions as a function of delay time after pulsed excitation at 532 nm. A mono-exponential decay of the lifetime is indicated by the red-lined fit, yielding $T_1 = 612.5 \pm 0.2$ ps for IX_S and $T_1 = 662.3 \pm 0.3$ ps for IX_T. 41
- 4.10 **Room temperature near-field scanning optical and confocal Raman microscope.** Schematic illustration of the Raman/PL setup that is used for the room temperature measurements. A 532 nm continuous wave laser is used as the excitation source. The PL/Raman spectra are collected with a cooled down (~ 213 K) CCD camera that is attached to the spectrograph. Obtained raw data are analyzed using a computer software. 43

- 4.11 **μ -PL setup and equipment details for cryogenic measurements.** **a.** Image of the optical breadboard mounted on the close-cycle cryostat system. Through the use of flip mirrors, we can practically switch between two modes, which are the imaging and the measurement modes. **b.** PDL 800-D laser diode controller is used to adjust the lasing modes and pump powers of the lasers used for excitation. **c.** Picosecond laser diodes that can operate at 730 nm and 532 nm wavelengths under both CW and pulsed modes. The laser light was sent through the window (**e**) of the microscope stick to the samples mounted on the piezo nanopositioners (**f**). Following the excitation, the PL signals were collected through the low-temperature compatible microscope objective (0.82 NA), as indicated by the yellow-colored dashed lines. Using a single-mode fiber, the collected emission is sent to the spectrograph once it has been filtered using the proper optical filters based on the desired wavelength of the PL spectrum to be viewed. **d** The spectrograph with 750 mm focal length (Princeton Instrument SpectraPro HRS-750) along with a liquid nitrogen-cooled silicon CCD camera (PyLoN) that is used to record the emitted PL signals. 44
- 4.12 **Imaging mode configuration of the μ -PL setup.** **a.** Schematic illustration of the imaging mode of the setup showing the path of the laser and white light. **b.** Real-life picture of the imaging mode configuration of the μ -PL setup. 45
- 4.13 **Measurement mode configuration of the μ -PL setup.** **a.** Schematic illustration of the measurement mode of the setup showing the path of the laser and the emitted PL from the sample (red colored line). Before sending the light to the spectrograph through a single-mode fiber, the emission was filtered using optical filters. **b.** Schematic of the 750 mm focal length spectrograph (Princeton Instrument SpectraPro HRS-750) and the mounted liquid nitrogen-cooled silicon CCD camera (PyLoN). **c.** Real-life picture of the measurement mode configuration of the μ -PL setup. 46

- 4.14 **Magneto-PL spectroscopy setup.** Schematic illustration of the magneto-PL measurement setup showing the applied magnetic field in Faraday geometry (i.e., applied field perpendicular to heterobilayer samples). Using the magnet power supply (Cryomagnetics APS 100), the applied field strength of the superconducting magnet can be controlled from 0 T up to 9 T. Data are recorded using the measurement mode shown in **Fig. 4.13**. 47
- 4.15 **Temperature-dependent PL spectroscopy setup.** Schematic illustration of the temperature-dependent PL measurement setup. Without requiring a change in pressure, the temperature of the sample can be regulated up to about 100 K using the temperature controller. Data are recorded using the measurement mode shown in **Fig. 4.13**. 48
- 4.16 **Time-resolved PL spectroscopy.** Schematic illustration of the time-correlated single photon counting (TCSPC) method. Green lines represent the laser pulses hitting the sample. The emitted light from the sample in each pulse is depicted with red circles, whereas $\Delta\tau_n$ spacings indicate the relaxation time after each pulsed excitation. The emissions are sent to an avalanche photodiode (APD) that is coupled to the TCSPC system (PicoQuant HydraHarp 400) with a timer resolution of 50 ps. After recording the data, the photon counts are plotted as a function of relaxation time, which can be fitted with an exponential decay function. . . . 49
- 5.1 **Types of coherence.** Schematic illustration of spatial and temporal coherence. Differences in length and time are denoted as Δr and $\Delta\tau$, respectively. 52

- 5.2 Home-built free-space Michelson interferometer. a,b.** Schematic (a) and real-life (b) images of the Michelson interferometer setup. The path of the light that is sent into the interferometer is depicted by the solid red line. Yellow lines show the course of the light after hitting the 50:50 BS, and orange lines show the path after it gets reflected off the retro mirror arms. Following the interference, the light is directed to a fiber-coupler and sent through a silicon APD via a single-mode fiber. Data are recorded using a PicoQuant Hydrharp 400 together with a LabVIEW program. 55
- 5.3 Dephasing time measurements of exciton species of a MoSe₂ monolayer using a Michelson interferometer. a,b.** Filtered PL spectra of the neutral exciton (a) and trion (b) of the MoSe₂ monolayer recorded with a 532 nm CW laser excitation under 50 μ W pump power at 3.5 K. The filtered part of the spectrum that was sent to the Michelson interferometer is shown with green boxes in both figures. **c,d.** Corresponding PL interferogram of the first-order correlation function $g^{(1)}(\tau)$ of the neutral exciton (c) and trion (d) of the MoSe₂ monolayer. **e,f.** The fringe visibilities as a function of the delay time in a semilog plot for neutral exciton (e) and trion (f). They both show a mono-exponential decay, which is fitted with Eq. 5.2, resulting in dephasing time values of $T_2 = 0.51$ ps and $T_2 = 0.42$ ps for neutral exciton and trion, respectively. 57

- 5.4 Dephasing time studies on interlayer excitons of WSe₂-MoSe₂ heterobilayers using a Michelson interferometer.** **a.** Interferogram of the first-order correlation function $g^{(1)}(\tau)$ of the IXs of HS1, where the right panel displays the pronounced fringe contrast near zero delay time. **b,c.** Plots of the fringe visibilities as a function of delay time for the delocalized (**b**) and Moiré-localized (**c**) IX emissions of the WSe₂-MoSe₂ heterobilayers (HS1 and HS6). **d.** Overview plot showing the comparison between the dephasing time values of the ensemble of delocalized and the ensemble of Moiré-localized IXs. The longest dephasing time is recorded as $T_2 = 0.73$ ps (HS7). Data are recorded at 3.5 K. 59
- 5.5 Pump power-dependent dephasing time studies on Moiré-localized interlayer excitons of WSe₂-MoSe₂ heterobilayers.** **a.** PL spectra of the ensemble of Moiré-localized IXs under various pump powers. Blue regions indicate the spectrally filtered parts of the PL spectra. **b.** Corresponding PL interferogram of the first-order correlation functions $g^{(1)}(\tau)$ obtained by sending the filtered emissions to the Michelson interferometer. **c.** Plots of the fringe visibilities as a function of delay time for the Moiré-localized IXs under each pump power. The red lines in each plot indicate the fit that yields the values of T_2 , and they display a mono-exponential decay. **d.** Overview plot of the dephasing time of the Moiré-localized IXs of our WSe₂-MoSe₂ heterobilayer sample (HS7) as a function of pump power. Data are recorded at 3.5 K. 60
- 5.6 Spectral linewidth investigations of interlayer excitons of WSe₂-MoSe₂ heterobilayers.** The energy difference (ΔE) between the spectral linewidth obtained from PL spectra and calculated from the measured recombination lifetime (T_1) and dephasing time (T_2) data shown in **Figs. 4.8** and **5.5**, respectively. Blue and green diamonds represent delocalized and Moiré-localized IXs, respectively. 62

- 5.7 Spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers.** **a.** Schematic illustration of the staggered type-II band alignment of the WSe₂-MoSe₂ heterobilayer, displaying the formation of spin-singlet (blue region) and spin-triplet (green region) IXs. Spin-up and spin-down configurations are represented with orange- and blue-colored arrows, respectively. **b.** The four-level diamond system showing the coherent coupling between the two spin states of the IXs. 65
- 5.8 Dephasing time studies of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers.** **a,b.** Spectrally filtered PL spectra of spin-singlet (**a**) and spin-triplet (**b**) IXs taken with a 532 nm CW laser excitation under 400 μ W pump power at 90 K. Blue-colored areas within the whole spectrum indicate the filtered PL that is sent to the Michelson interferometer. **c,d.** The corresponding PL interferograms of the first-order correlation functions $g^{(1)}(\tau)$ of the filtered PL spectra of spin-singlet (**c**) and spin-triplet (**d**) IXs. **e,f.** The fringe visibilities as a function of delay time for spin-singlet (**e**) and spin-triplet (**f**) IXs, which strongly deviates from a monoexponential decay, showing an inhomogeneous decay that corresponds to a Gaussian fit of $g^{(1)}(\tau) = \exp(-\tau^2/(\frac{T_2}{\sqrt{\pi/2}})^2)$. 66
- 5.9 Quantum beat interferometry of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers.** **a.** PL spectra of the spin-singlet and spin-triplet IXs recorded with 532 nm CW laser excitation under 400 μ W pump power at 90 K. **b.** Quantum beat interferogram produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the quantum beat decay that corresponds to $T_2 = 0.29 \pm 0.05$ ps. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval (± 0.05 ps) when fitting the beat interferogram via the above expression. 67

- 5.10 Linewidth and energy separation analysis of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers.** **a.** PL spectrum with Gaussian fits of the spin-singlet (blue-lined) and spin-triplet (red-lined) IXs yielding peak fits of 9.97 meV and 11.64 meV, respectively. **b.** The quantum beat period ($T_{\text{IXS-T}}$) of the corresponding PL interferogram, which is determined through the difference between two beat maxima points. **c.** The experimental energy separation ($\Delta E_{\text{IXS-T}}$) of the IX spin states. Data are recorded under 532 nm CW laser excitation with an incident power of 400 μW at 90 K. 69
- 5.11 Temperature-dependent quantum beat interferometry of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers under 532 nm laser excitation.** **a.** Temperature-dependent PL spectra of the spin-singlet and spin-triplet IXs recorded under 400 μW pump power. **b.** Temperature-dependent quantum beating interferograms of the spin-singlet and spin-triplet IXs, produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the decay that corresponds to the dephasing time for the spin-singlet and spin-triplet IX coherence. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval when fitting the beat interferogram via the above expression, which is given by ± 0.05 ps, ± 0.04 ps, ± 0.03 ps, ± 0.03 ps, and ± 0.03 ps, from 90 K to 3.5 K, respectively. 70

- 5.12 **Temperature-dependent quantum beat interferometry of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers under 730 nm laser excitation.** **a.** Temperature-dependent PL spectra of the spin-singlet and spin-triplet IXs recorded under 100 μ W pump power. **b.** Temperature-dependent quantum beating interferograms of the spin-singlet and spin-triplet IXs, produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the decay that corresponds to the dephasing time for the spin-singlet and spin-triplet IX coherence. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval when fitting the beat interferogram via the above expression, which is given by ± 0.03 ps, ± 0.03 ps, ± 0.04 ps, ± 0.03 ps, and ± 0.03 ps, from 90 K to 3.5 K, respectively. 71
- 5.13 **Pump power-dependent quantum beat interferometry of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers under 532 nm laser excitation.** **a.** Power-dependent PL spectra of the spin-singlet and spin-triplet IXs recorded at 90 K. **b.** Power-dependent quantum beating interferograms of the spin-singlet and spin-triplet IXs, produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the decay that corresponds to the dephasing time for the spin-singlet and spin-triplet IX coherence. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval when fitting the beat interferogram via the above expression, which is given by ± 0.05 ps, ± 0.04 ps, ± 0.05 ps, and ± 0.05 ps from 100 μ W to 600 μ W, respectively. 72

- 5.14 **Pump power-dependent quantum beat interferometry of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers under 730 nm laser excitation.** **a.** Power-dependent PL spectra of the spin-singlet and spin-triplet IXs recorded at 90 K. **b.** Power-dependent quantum beating interferograms of the spin-singlet and spin-triplet IXs, produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the decay that corresponds to the dephasing time for the spin-singlet and spin-triplet IX coherence. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval when fitting the beat interferogram via the above expression, which is given by ± 0.03 ps, ± 0.03 ps, and ± 0.04 ps from 50 μ W to 150 μ W, respectively. 73
- 5.15 **Overview plot of the temperature- and pump power-dependent quantum beat dephasing times of the interlayer excitons of WSe₂-MoSe₂ heterobilayers.** **a.** Temperature dependence of the quantum beat dephasing under 532 nm (green circles) and 730 nm (red circles) laser excitations with 400 μ W and 100 μ W pump powers, respectively. **b,c.** Pump power dependence of the quantum beat dephasing under 532 nm (**b**) and 730 nm (**c**) laser excitations, recorded at 90 K. 74

Chapter 1

Introduction

The lecture "There's Plenty of Room at the Bottom" by the famous physicist Richard P. Feynman in 1959 served as a trailblazer for scientific studies into nanotechnology, ultimately guiding researchers into exploring the field of two-dimensional (2D) materials. Studies and interest in 2D materials have grown steadily since the first isolation of graphene (i.e., a single layer of graphite) in 2004[1]. Its high degree of crystallinity and unique properties have led to groundbreaking discoveries in the fields of solid-state physics and materials science[2], including the discovery of the existence of massless Dirac fermions[3]. Scientific interest in other 2D materials and their heterostructures has developed significantly over the past years due to the extensive research and fascinating discoveries made through graphene. Their optical, thermal, and electrical properties have been the focus of numerous investigations, and given their extraordinary material characteristics, they have gained prominence in a wide range of research fields.

As novel 2D materials are continuously discovered through the years, their range of material properties has grown drastically as well, leading to a wider range of applications and related theoretical and experimental research investigations for their utilization. Along with graphene, which shows conductive behavior, other 2D materials that can exhibit semiconducting[4], insulating [5, 6],

superconducting[7], and ferromagnetic[8, 9] characteristics have also been identified as a result of this intensive ongoing research. The realization of layer-controllable fabrication methods of 2D materials is crucial to further understand and shine a light on their layer-dependent physical properties. Many techniques have been reported through the past years for this realization, including top-down approaches such as micromechanical[10] and chemical exfoliation[11], and bottom-up approaches such as chemical vapor deposition (CVD)[12] and hydrothermal synthesis[13]. Most of the 2D materials in research fall under the category of layered van der Waals (vdW) materials since their bulk crystal forms have 2D-oriented chemical bonds. Therefore, the top-down method of micromechanical exfoliation becomes appealing since, in comparison to the other approaches, it is easier and less expensive to create high-quality crystals. In this dissertation, the process of micromechanical exfoliation has also been utilized to fabricate our 2D materials (hBN, MoSe₂, and WSe₂). Details about the fabrication process of our 2D crystals will be discussed in Chapter 3.

Through the development of various transfer methods, vertical stacking of exfoliated 2D materials on top of one another to create vdW heterostructures became feasible, opening up further areas to explore in the field. The exceptional qualities of the constituent layers, along with the high carrier mobility feature of 2D materials[14], offer an abundant platform for the investigation and development of novel and intriguing physics. The physical properties of the vdW heterostructures are determined by their band alignment, which varies according to the constituent layers that form the heterojunction. Over the last decade, the vdW heterostructures of transition metal dichalcogenide (TMDC) monolayers have gained popularity among researchers due to their typically featured staggered type-II band alignment[15, 16]. By virtue of this band alignment, ultra-fast charge transfer between the constituent layers becomes facilitated, leading to the formation of strongly Coulomb-bound electron-hole pairs located in different layers (i.e., interlayer excitons)[17, 18]. Details of the interlayer excitons (IXs) formed in our WSe₂-MoSe₂ heterobilayers will be discussed in Chapter 4. Overall, comprehending the physical properties and future aspects of vdW heterostructures opens up new avenues for devices with exceptional qualities for various applications.

Despite having similar hexagonal lattice structures to graphene, monolayer TMDCs such as molybdenum disulfide (MoS_2), molybdenum diselenide (MoSe_2), tungsten disulfide (WS_2), and tungsten diselenide (WSe_2) are direct bandgap semiconductors[19]. They have been extensively studied in different research fields over the past years due to their intriguing thermal, mechanical, electronic, and optical properties[20]. The distinctive features of semiconducting TMDCs, which have the chemical formula MX_2 (M: Mo, W, etc., and X: S, Se, and Te), can be controlled by tuning the layer thicknesses during their fabrication process. By varying the thickness of their layers, their band gap can be tuned, which fundamentally modifies their physical properties and makes them suitable for a range of applications. More specifically, by reducing the layer thicknesses, it is possible to cause a shift in the band gap from indirect to direct, ultimately reaching the atomic layer thicknesses. Overall, TMDCs have demonstrated promising features for a variety of applications, including spintronics[21, 22], valleytronics[22, 23], optoelectronics[24], solar cells[25], transistors[26], photodetectors[27, 28], and hydrogen energy[29].

Monolayer TMDCs, which can be thought of as the puckered state of the material, can easily be obtained by using the micromechanical exfoliation method. The earliest report of monolayer TMDCs dates back to the 1980s, even though the scientific community did not investigate it in great detail at the time[30]. The discovery of graphene inspired researchers to reexamine the monolayer TMDCs in greater depth. Theoretical studies from the early 2000s predicted the direct bandgap feature of monolayer TMDCs[31], which was proven in the early 2010s when an exfoliated monolayer MoS_2 revealed its direct bandgap[32], making them promising candidates to be utilized in device applications. One can conceptualize the structure of monolayer TMDCs as a sandwich-like structure composed of two chalcogen atoms (X) planes with a hexagonally packed transition metal (M) in between. Similar to graphene, semiconducting monolayer TMDCs typically feature the 2H phase with hexagonal symmetry in both real and reciprocal spaces[20, 33]. Taken together, the distinct qualities of monolayer TMDCs present them as attractive candidates for a variety of emerging device applications. More details about monolayer TMDCs and their properties will be discussed in Chapter 2.

By employing the dry transfer technique, one can vertically stack monolayer TMDCs and fabricate vdW heterostructures. The most crucial factor to consider during the fabrication of the heterostructures is the twist angle between the TMDC monolayers. According to the stacking angle, the emission characteristics of the IXs can be controlled, and single-photon quantum emitters can be obtained through Moiré superlattices (i.e., Moiré-localized IXs)[34–43]. One of the most crucial elements affecting the physical characteristics of TMDC heterostructures, and ultimately their potential device applications, is the band alignment[44]. Earlier theoretical investigations have demonstrated that the staggered type-II band alignment, where the valence band maxima (VBM) and conduction band minima (CBM) are located in opposing monolayers, is present in the majority of heterostructures composed of monolayer TMDCs[15, 45–47]. The staggered type-II band alignment interface in the TMDC heterostructures acts as a formation layer for the IXs, facilitating the electron-hole charge transfer and separation within the heterojunction. Theoretical investigations have revealed that, although the monolayers are in contact through vdW forces, IXs have a Bohr radius larger than the layer separation, which favors the formation of bound exciton states by Coulomb interactions[44, 48, 49]. Although the binding energy of these IXs is comparable to the Frenkel exciton type, their wavefunction indicates that they are Wannier-Mott type excitons, which are formed through interlayer charge transfer[17, 18, 50].

The heterostructures of various 2D materials are promising candidates for the future of quantum technologies such as quantum computing[51, 52], quantum sensing[53–56], quantum communication[57, 58], quantum internet[59], quantum imaging[56, 60, 61], and quantum key distribution[62–64]. One can ascertain whether or not a 2D material is appropriate for such quantum applications by investigating its photophysics. The coherence (dephasing) time, which indicates the time interval of light to coherently influence quasiparticles, is one particular physical element to consider as it directly impacts quantum operations. Any loss of coherence can lead to errors in computation or communication; hence, it has a direct bearing on the dependability of quantum systems[65]. Therefore, it is important to consider it while developing devices for quantum applications.

The main focus of this dissertation will be on the photophysics studies of the IXs of hBN-encapsulated WSe₂-MoSe₂ heterobilayers. The encapsulating layers of hBN, along with WSe₂ and MoSe₂ monolayers, were fabricated using the micromechanical exfoliation technique, and photoluminescence (PL) spectroscopy was utilized to confirm the monolayer nature of the TMDC layers. Following their characterization, the zigzag edges were roughly defined using the edge identification method[66]. During the fabrication of the heterobilayers via the dry transfer technique, the desired twist angles between the WSe₂ and MoSe₂ monolayers were given based on these zigzag edges. After the fabrication of hBN-encapsulated WSe₂-MoSe₂ heterobilayers, room temperature PL spectroscopy was employed to observe the two intralayer exciton peaks originating from the constituent layers and confirm the formation of the heterojunction. Low-temperature (3.5 K) PL studies, magneto-PL, excitation pump power-dependent PL, temperature dependent-PL, and time-resolved PL (TRPL) were carried out on the IXs of our heterobilayer samples using a home-built μ -PL setup mounted on a close-cycle cryostat.

Finally, first-order correlation function $g^{(1)}(\tau)$ measurements in the time domain were performed on the IX species using a home-built free-space Michelson interferometer. The findings in our publication titled *“Prolonged Dephasing Time of Ensemble of Moiré-Trapped Interlayer Excitons in WSe₂-MoSe₂ Heterobilayers”* demonstrate that Moiré-localization of IXs could lead to prolonger dephasing times up to $T_2 \sim 730$ fs[43]. Furthermore, in our following publication titled *“Quantum Beats Between Spin-Singlet and Spin-Triplet Interlayer Exciton Transitions in WSe₂-MoSe₂ Heterobilayers”*, we have shown the existence of coherent coupling between spin-singlet and spin-triplet IXs of hBN-encapsulated WSe₂-MoSe₂ heterobilayers by recording the quantum beating signal between them for the first time in the time domain with dephasing times up to $T_2 \sim 400$ fs[67]. Overall, our findings regarding the influence of Moiré-localization on the dephasing characteristics of IXs can offer valuable perspectives on the future course of 2D material-based nanolasers[68]. Meanwhile, the significance of coupled quantum states of IXs can shed light on quantum photonic and exciton-based valleytronic

applications, including electromagnetically induced transparency[69, 70] and lasing without inversion[71, 72]. Details about the first-order correlation function $g^{(1)}(\tau)$ measurements of the IXs in our WSe₂-MoSe₂ heterobilayers will be covered in Chapter 5.



Chapter 2

Transition Metal Dichalcogenide Monolayers

With the isolation of graphene in 2004[1], the topic of 2D materials gained significant attention, opening the door for fundamental research as well as the development of future technologies. Numerous discoveries in materials science and fundamental physics research have been made possible through its remarkable electrical characteristics[2]. The finding won the 2010 Nobel Prize in Physics since it pioneered new developments in the disciplines of solid-state and condensed-matter physics. After this finding, researchers began seeking more 2D materials, which has led to a significant rise in the class of materials throughout the last decade.

Semiconducting TMDCs, which this thesis will focus on, are extensively investigated across a variety of areas of research due to their intriguing electronic, mechanical, and optical properties[20]. Their exceptional optical properties (i.e., direct band gap in monolayer form[32, 73], large exciton-binding energies[74, 75], strong light-matter interactions[24, 76–78], and valley-contrasting physics[79, 80]) made them attractive candidates for the development of various ultrathin optoelectronic, valleytronic, and quantum photonic applications. A variety of transfer

methods have also been developed in the past years that allow TMDC monolayers to be stacked vertically on top of one another without experiencing a lattice mismatching difficulty[81, 82]. The fabrication details of monolayer TMDCs and their heterobilayers will be discussed in Chapter 3. Moreover, due to the ultra-fast charge transfer between the two monolayers[17, 18], the staggered type-II band alignment of the aforementioned TMDC heterobilayers[46] promotes the creation of IXs[44, 48, 83–86]. The details of hBN-encapsulated WSe₂-MoSe₂ heterobilayers and their IXs will be discussed in Chapter 4. For the time being, the general characteristics of excitons and TMDC monolayers will be covered in this chapter.

2.1 Crystal Structure and Material Properties

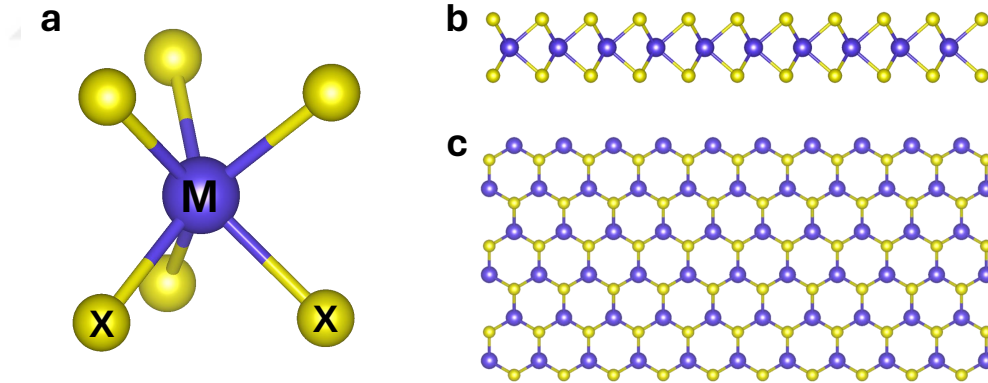


Figure 2.1: MX₂ crystal structure of monolayer TMDCs. **a.** A single unit cell of the MX₂ crystal. Chalcogen and transition metal atoms are represented by the letters X and M, respectively. **b,c.** In-plane (**b**) and out-of-plane (**c**) views of a monolayer MX₂ crystal. Drawings are made by using the VESTA software.

TMDCs have the chemical formula MX₂ (M: transition metal atom, X: chalcogen atoms), where the transition metals are sandwiched between two planes of chalcogen atoms[20]. As **Fig. 2.1a** displays, the unit cell of this covalently bonded transition metal with chalcogen atoms can have octahedral or trigonal prismatic coordination. **Figs. 2.1b** and **2.1c** show the side (in-plane) and top (out-of-plane) perspectives of the MX₂ crystal structure of a TMDC monolayer, with thicknesses of about angstrom levels. The bulk form of these materials

consists of repeating layers held together by weak van der Waals (vdW) forces. Because of their 2H stacking, these layers alternate between M and X atoms along their vertical axis, each of which has been separately rotated 180 degrees. The ability to peel off each layer without harming the crystals is made possible by the fact that the vdW forces are significantly weaker than the in-plane covalent bonds. The peeling technique that is generally referred to as the micromechanical exfoliation method or scotch-tape method, which is used to obtain graphene for the first time in 2004[1].

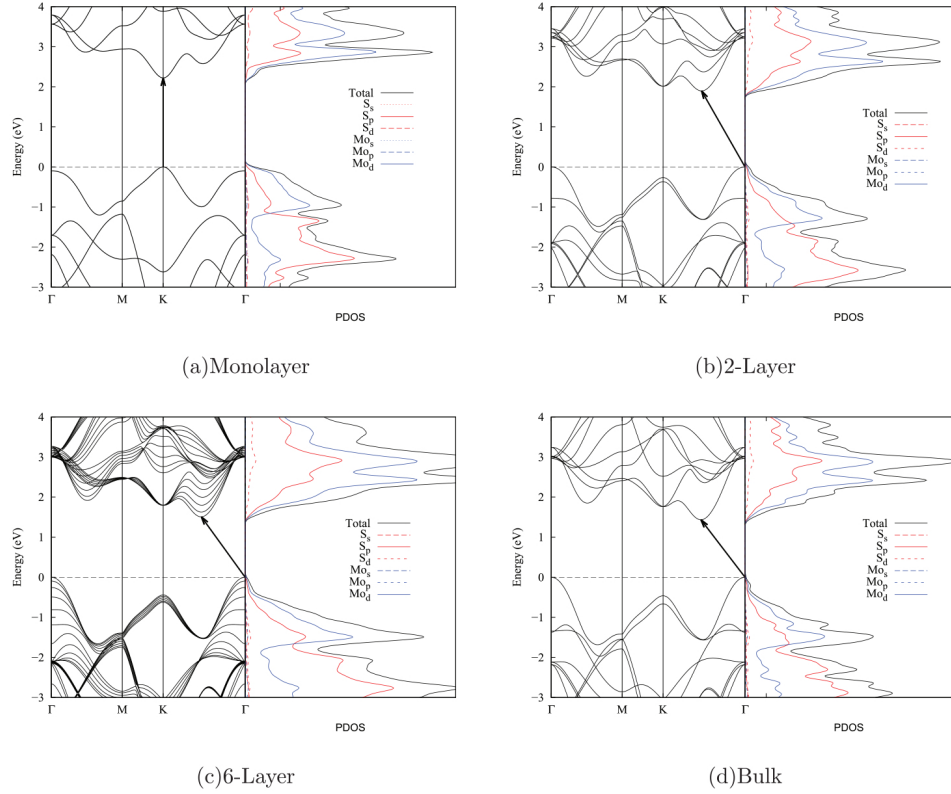


Figure 2.2: Indirect-to-direct band gap transition of MoS_2 . The valence band experiences an extensive phase shift upon thinning down from bulk crystal to monolayer, leading to a direct bandgap. Graphic from Ellis et al. *The indirect to direct band gap transition in multilayered MoS_2 as predicted by screened hybrid density functional theory*. Applied Physics Letters (2011).

While bulk TMDC crystals have long been understood to exhibit an indirect band gap[87, 88], their monolayers show a direct band gap, which is significantly different from the behavior in their bulk form[89]. The indirect-to-direct band gap

transition (**Fig. 2.2**) while thinning down the crystal flakes from bulk to single monolayer TMDCs makes them desirable candidates for future optoelectronic and photonic-related technologies due to their exciting optical, mechanical, and electronic properties[20].

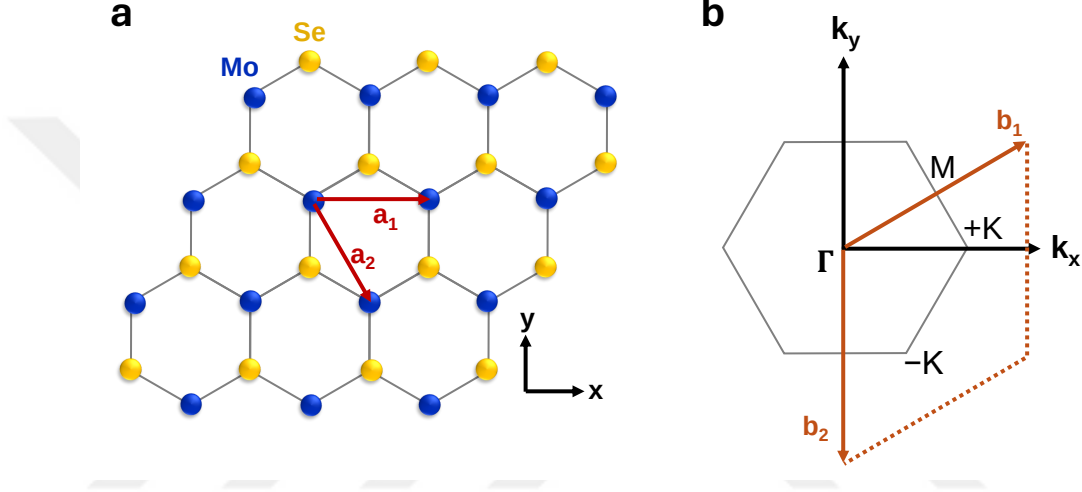


Figure 2.3: Electronic band structure of monolayer MoSe₂. **a.** The real space in-plane hexagonal lattice structure of monolayer MoSe₂. Each sublattice is occupied with one Mo (blue circles) and two Se (yellow circles) atoms, where the red lines (a_1 and a_2) represent the two in-plane primitive lattice vectors. **b.** The first hexagonal Brillouin zone in the reciprocal lattice with corners at $\pm K$ valleys. Orange lines (b_1 and b_2) represent the reciprocal lattice vectors.

The 2D hexagonal lattice of a TMDC monolayer is shown in **Fig. 2.3a**, where its reciprocal lattice vectors form the 2D hexagonal Brillouin zone that is shown in **Fig. 2.3b**. In a periodic lattice (e.g., the hexagonal lattice of TMDC monolayers), one can portray a single electron with continuous bands of Bloch waves in the momentum space, where the energy minima in this space correspond to the valleys in the electronic spectrum[90] and the valleys at the opposite corners of the Brillouin zone are termed as the $+K$ and $-K$ valleys. Furthermore, due to the distinct neighboring atoms (**Fig. 2.1c**) in their hexagonal lattice, the MX_2 structure of the TMDC monolayers exhibits broken sublattice symmetry. In this case, the minimum energy points are still present at the position of Dirac points of the hexagonal Brillouin zone (similar to graphene), yet they now have bandgaps (**Fig. 2.2**) in the visible and near-infrared ranges[20, 24, 91, 92], which can be useful in the development of exciton-based photonic applications.

Through spin-orbit coupling (i.e., coupling between the orbital angular momentum of an outer electron with the spin angular momentum of an excited electron)[79], the band structure of the MX_2 monolayer TMDCs can be manipulated, leading to exceptional material properties. In detail, an electron in a MX_2 type crystal must undergo a significant shift in momentum and energy (a spin flip) to move from one valley to another, resulting in the emergence of the spin-valley locking effect, which is the locking of the spin degree of freedom of $\pm K$ electrons with respect to their valley index[93].

2.2 Valley Magnetic Moment & Optical Selection Rules

The presence of an orbital magnetic moment μ_v and the light-coupling of electronic transitions in the bands of a material are both significantly impacted by inversion symmetry (i.e., invariance under a point reflection)[94, 95]. TMDCs exhibit significantly influenced interband electronic transitions at their $+K$ and $-K$ valleys due to having the MX_2 structure, which has a broken inversion symmetry. Since the motion in these monolayers is in a 2D plane, the originating orbital magnetic moment resulting from the self-rotation of the electron packet can therefore be regarded as out of plane[96]. Along with the orbital magnetic moment, Berry curvature Ω can also affect the valley degree of freedom (i.e., carrier-occupied valley). Ω can be considered as the corresponding magnetic field of the Berry phase, which is the magnetic flux in the momentum space[97]. The lack of inversion symmetry in TMDC monolayers causes Ω to be finite at $+K$ and $-K$ valleys, and have opposite signs for the conduction and the valence bands of the crystal in contrast to μ_v [95]. The spin magnetic moment-like behavior of μ_v leads to the conduction and the valence bands at $\pm K$ points to have a valley orbital angular momentum of $\pm\hbar/2$. Through the Zeeman effect (i.e., spectral line splitting in the presence of an applied magnetic field), the valley degeneracy, and ultimately the valley degree of freedom of the monolayer TMDCs can be controlled by coupling this moment with an applied magnetic field, which is

important for the future of valleytronics and spintronics applications[98, 99].

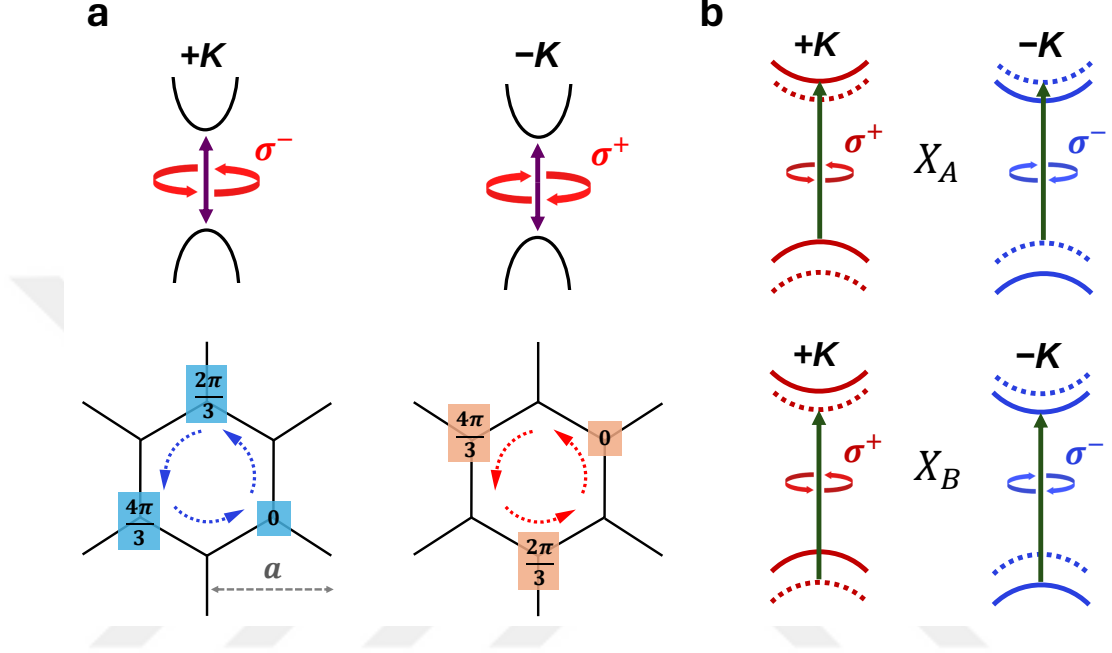


Figure 2.4: Valley optical selection rules for MX_2 type crystals. **a.** Berry curvature valley-contrasting resulting in a circular polarization of the coupled light for $\pm K$ valleys. **b.** Optical selection rules for the top (X_A) and bottom (X_B) excitons in the $\pm K$ valleys of the MX_2 crystals. Straight and dashed lines indicate the up and down spins, respectively.

It is possible to determine the allowed (i.e., bright excitons) and forbidden transitions (i.e., dark excitons) in an atom based on the energy eigenstates of the electrons by considering this momentum. However, in solid crystals, the Bloch electrons become involved, and because of the bands' Ω , their intracellular rotations might take on their orbital magnetic moment[79], which affects the optical dipole light coupling to the $\pm K$ valleys as shown in **Fig. 2.4a**. Interband transitions of the $\pm K$ valleys allow one to establish a set of optical selection rules by manipulating the polarization of light (**Fig. 2.4b**), as the two valleys have opposite helicity due to time reversal symmetry[100]. Furthermore, a linearly polarized light excitation, which is an equal superposition of light with positive (σ^+) and negative (σ^-) helicities, can also be used to populate the two exciton states, X_A and X_B , simultaneously. The emission of light along the excitation axis in this configuration confirms the coherence of valley excitons[101], indicating a preserved phase relation between valley populations, and underscores the robust

protection of the valley degree of freedom in monolayer TMDCs through the spin-valley locking effect and circular dichroism[80, 102]. All in all, the optical coupling of MX_2 crystal structure, the spin-valley locking effect, and the opportunity to study these uniquely coupled exciton states provided an excellent platform for optics and photonics researchers.

2.3 Excitons in Monolayer TMDCs

The bound state that results from the Coulomb attraction between an electron and a hole is known as an exciton, an electrically neutral quasiparticle. They can be formed through adequate stimulation (e.g., absorption of photons) that has enough energy to excite the electrons from the valence band to the conduction band, leaving a positively charged hole in the valence band. Through this creation, the Coulomb force results in the formation of the bound-stated excitons, which are considered to be composite bosons (i.e., the pairing of two fermions)[103]. Moreover, excitons are primarily found in condensed matter, and we are primarily interested in the excitons of semiconducting TMDCs. In monolayer TMDCs, intralayer excitons can be classified as charged or neutral type. To provide a clear and example-based explanation of these excitons, the PL spectrum and band diagram of the MoSe_2 monolayer taken at 3.5 K, as presented in **Fig. 2.5**, will be reviewed.

Intraband valley excitons with a single electron-hole pair and no electrical charge are known as neutral excitons. Considering the direct band gap transition in TMDC monolayers[89], the neutral excitons are created in a way that the momentum of the resulting pair is very close to zero as shown in the purple transition in **Fig 2.5b**. The creation of the free charge carriers from the resulting exciton pairs gives rise to the formation of other stable charged excitonic states at lower energies[104]. In the high carrier density regime, the free excitons can capture and bind an electron (X^-) or a hole (X^+), and form three particle charged states (i.e., trions)[75] as shown in the orange pairing in **Fig 2.5b**. Through the band structure of the TMDC monolayers, a possibility of different trion states

becomes possible[105], and their large binding energies[106, 107] can be related to the strong Coulomb interactions within the monolayers.

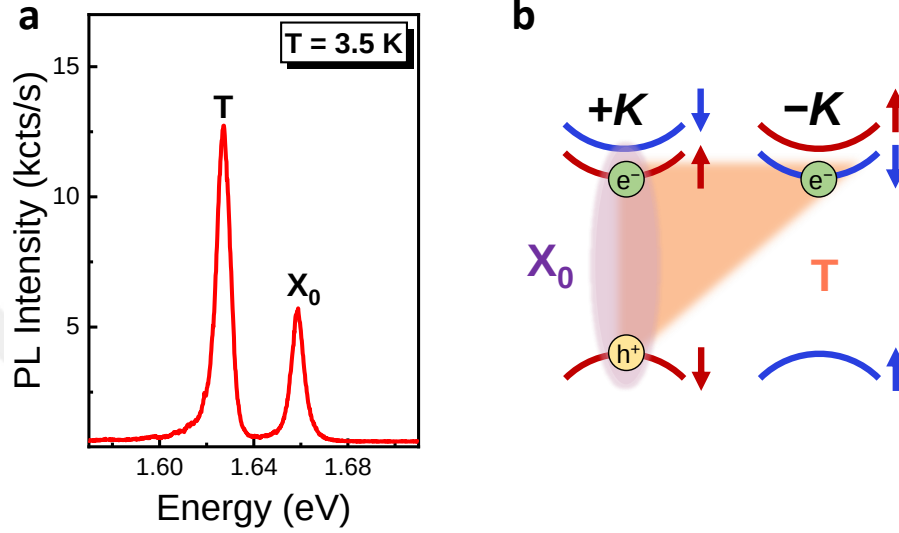


Figure 2.5: Neutral and charged excitons in TMDC monolayers. a. Low-temperature PL spectrum of a MoSe₂ monolayer crystal under 532 nm CW laser excitation with 40 μ W pump power at 3.5 K. Neutral exciton and charged exciton (trion) are labeled as X₀ and T, respectively. **b.** Band diagram schematic of the X₀ (purple colored) and T (orange colored) of the MoSe₂ monolayer. The spin states of the electron and holes in the conduction and valence bands are indicated by the red and blue arrows.

As mentioned, the allowed and forbidden excitons can be referred to as bright and dark excitons, respectively. Optically bright excitons occur when the conduction and valence band electrons of the material have the same spin while dark excitons have the opposite. In our monolayer TMDCs, the conduction and valance bands are split through the strong spin-orbit interaction due to the effect of transition metal states on the formation of the bands[86]. This splitting results in the conduction and valence band electrons to have the same spin for the MoSe₂ monolayer while it is the opposite for the WSe₂ monolayer[108]. Therefore, as shown in **Fig. 2.6a**, the ground state excitons are bright (spin-allowed) and dark (spin-forbidden) for the MoSe₂ and the WSe₂ monolayers, respectively. The optical brightness of the ground state excitons affects their radiative lifetime, and the difference in the population dynamics between these bright and dark states can cause a difference in the optical response (e.g., the temperature dependence

of the PL efficiency) of these two monolayers[109–111]. Furthermore, as shown in **Fig. 2.6b**, spin-allowed but momentum-forbidden dark excitons can also form in between separate valleys[112], such as in WSe₂ monolayers, in addition to the spin-forbidden intravalley dark excitons.

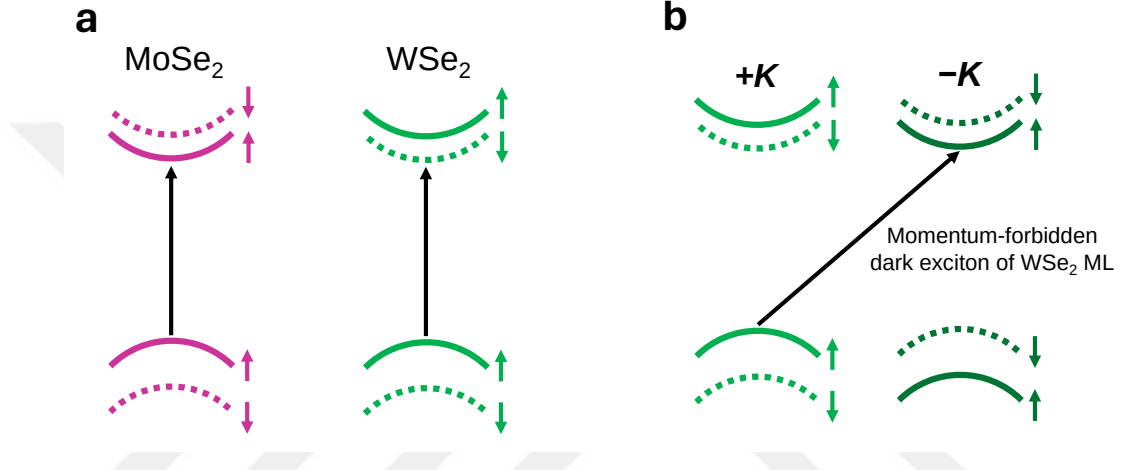


Figure 2.6: Bright and dark excitons in TMDC monolayers. **a.** Schematic of the ground state intravalley excitons in MoSe₂ and WSe₂ monolayers. The spin orientations of the band’s electrons are indicated on their right side with the same color. The shown transitions are bright (spin-allowed) and dark (spin-forbidden) in MoSe₂ and WSe₂ monolayers, respectively. **b.** Illustration of the spin-allowed momentum-forbidden intervalley exciton in WSe₂ monolayer.

2.4 Quantum Emitters in Monolayer TMDCs

Another feature of excitonic light emission in TMDC monolayers may result from localized crystal imperfections or impurities. Through these crystal imperfections, discrete energy levels can be created that can lead to quantized light emissions (i.e., quantum emitters), which are highly desirable and crucial for quantum photonic applications due to their ability to emit single photons[58, 113, 114].

Strong anti-bunching has been observed in previous investigations on second-order correlation function $g^{(2)}(\tau)$ measurements of these emitters, confirming that

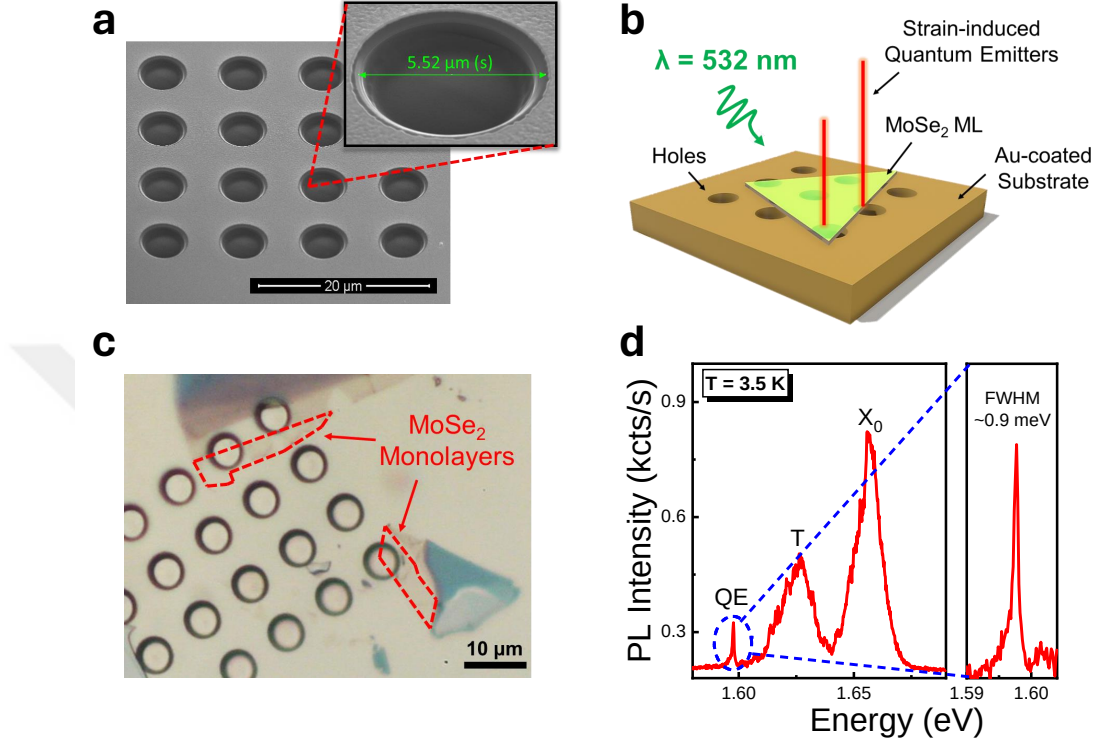


Figure 2.7: Strain-induced quantum emitters in TMDC monolayers. **a.** SEM image of an array of holes fabricated on an Au-coated substrate using focusing ion beam lithography. The red-lined upper right part indicates a magnified view of one of the holes. Illustration **(b)** and the optical image **(c)** of the dry transferred MoSe₂ monolayers on the hole arrays. **d.** Low-temperature PL spectrum of the MoSe₂ monolayer with T, X₀, and QE emission appearing at ~ 1.62 eV, ~ 1.66 eV, and ~ 1.59 eV, respectively, under 532 nm laser excitation with an incident power of $P = 10 \mu\text{W}$. Zoomed-in PL spectrum of the strain-induced QE with a linewidth of ~ 0.9 meV is displayed in the right panel.

they are indeed single-photon quantum emitters[115–117]. Using strain engineering, one can create and control strain-localized quantum emitters in TMDC monolayers[118, 119]. Through this idea, as shown in **Fig. 2.7**, TMDC monolayers can be deposited on a hole-array substrate to create a localized strain that can lead to the formation of quantum emitters. The MoSe₂ quantum emitters, depicted in **Fig. 2.7d**, exhibit linewidth values that correlate with earlier studies[117], implying their single-photon emission nature. Although we were able to obtain these quantum emitters from MoSe₂, they did not exhibit sufficient emission intensity for the first-order correlation function $g^{(1)}(\tau)$ measurements.

It is possible to argue that these restrictions limit their potential. Therefore, understanding and manipulating these quantum emitters in TMDC monolayers can contribute significantly to the advancement of cutting-edge technology for quantum information applications[120].



Chapter 3

van der Waals Heterostructures

The ability to stack TMDC monolayers vertically to create advanced vdW heterostructures has sparked a new movement in materials science and engineering. The extraordinary electrical and optical properties of these materials, together with the potential to further design and engineer them through the fabrication of heterostructures, have brought about a significant development in fundamental and solid-state physics research. In this dissertation, the heterostructures consisting of MoSe₂ and WSe₂ monolayer TMDCs were studied. The next sections provide a detailed explanation of the steps involved in fabricating the exfoliated monolayers and constructing the heterostructures using the dry transfer approach.

3.1 Mechanical Exfoliation of 2D Materials

As previously stated, the mechanical exfoliation approach gained prominence following the isolation of graphene in 2004[1]. It is a straightforward process with additional benefits, including the ability to create high-quality crystals with excellent optical and electrical properties. Along with these advantages, TMDC monolayers can be mechanically exfoliated as well due to the weak van der Waals forces between the stacked layers of their bulk crystal. The procedures shown in

Fig. 3.1 are followed for the fabrication of the required TMDC monolayers (i.e., MoSe_2 and WSe_2) in this research.

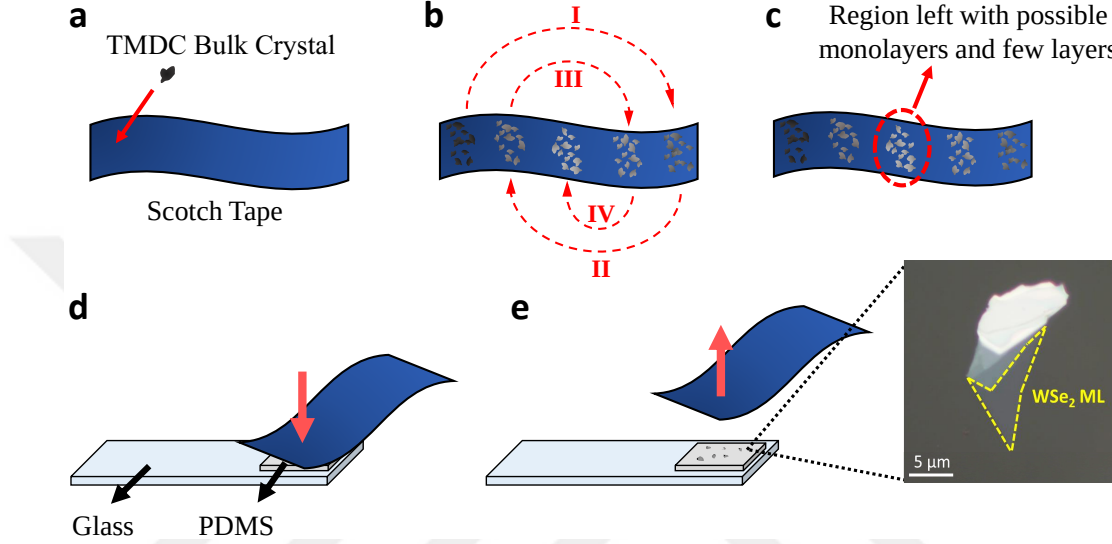


Figure 3.1: Mechanical exfoliation steps of fabricating monolayer TMDCs. **a.** Initial step from one side of the scotch tape with a bulk TMDC crystal. **b.** Creating less layered crystals in certain parts of the tape as shown in **(c)** by folding the Scotch tape according to the specified steps I-II-III-IV. Stamping of the region left with possible monolayers to the PDMS to fabricate the desired TMDC monolayers **(d)**.

As shown in **Fig. 3.1a**, the initial stage in the production process involves placing a small portion of the bulk TMDC crystal (obtained from 2D Semiconductors) on the scotch tape and performing mechanical exfoliation by applying the appropriate steps (**Fig. 3.1b**). This enhances the probability of finding monolayers in a particular area of the tape (**Fig. 3.1c**) and prevents the section where the crystals have already been exfoliated from being transferred on top of one another again. As shown in **Fig. 3.1d**, the part shown in **Fig. 3.1c** of the tape is pressed on PDMS, and then TMDC crystals were examined with an optical microscope. Using the color contrast between the bulk and monolayer parts of the crystals, monolayers can be identified (**Fig. 3.1e**), and can further be confirmed by using PL spectroscopy at room temperature (i.e., MoSe_2 peak ~ 1.57 eV and WSe_2 peak ~ 1.65 eV[121]). After confirmation, the ones that are satisfying and big enough are used in the fabrication process of the heterostructure. It is significant to note that finding the monolayer flakes during the dry transfer process is

substantially aided by taking plenty of images of them at different magnifications, such as 5X, 20X, and 100X.

3.2 Fabricating the WSe_2 - MoSe_2 Heterobilayers

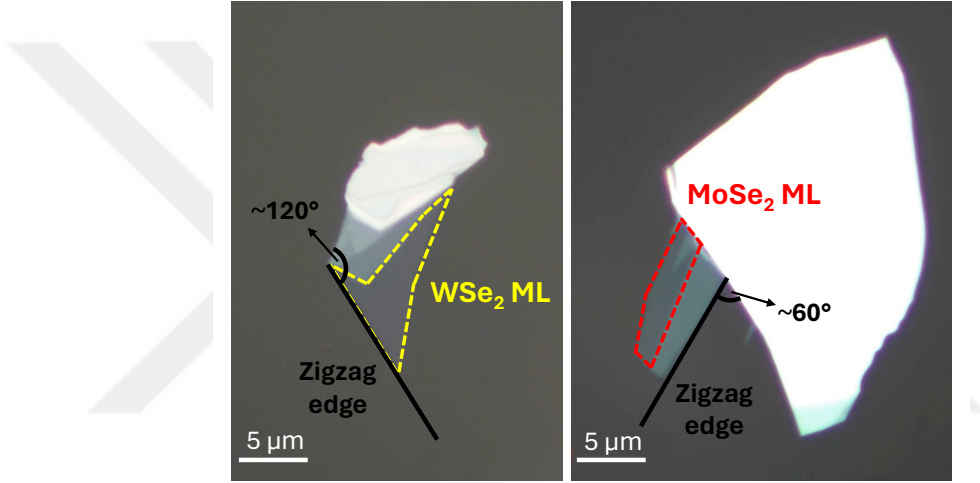


Figure 3.2: Zigzag edge identification of the TMDC monolayers. Optical microscope images and the zigzag edge determination angles of the WSe_2 and MoSe_2 flakes before dry transfer. Yellow and red dashed lines show the monolayer part of the crystal flakes. The edge angles used for zigzag edge identification and the zigzag edges are shown with black lines.

Before beginning the fabrication of TMDC heterostructures, it is necessary to identify the lattice orientations of the monolayers to be used, particularly the zigzag edges. The lattice direction of 2D layered materials can be determined using a variety of methods, including Transmission Electron Microscopy (TEM)[122–124], second harmonic generation (SHG)[83, 125–127], polarized infrared absorption[128], Raman spectroscopy[129, 130], and a recently developed optical microscopy technique called the edge identification method[66]. To determine the lattice direction of our exfoliated WSe_2 and MoSe_2 monolayers, we have utilized a non-invasive and relatively fast edge identification technique. Prior research has demonstrated that TMDC crystal flakes frequently cleave along a zigzag direction[34, 66, 131]. Therefore, as seen in **Fig. 3.2**, the zigzag and arm-chair crystal directions can simply be determined by utilizing the straight edges

of the exfoliated monolayer TMDC crystals with edge angles of 60° or 120° .

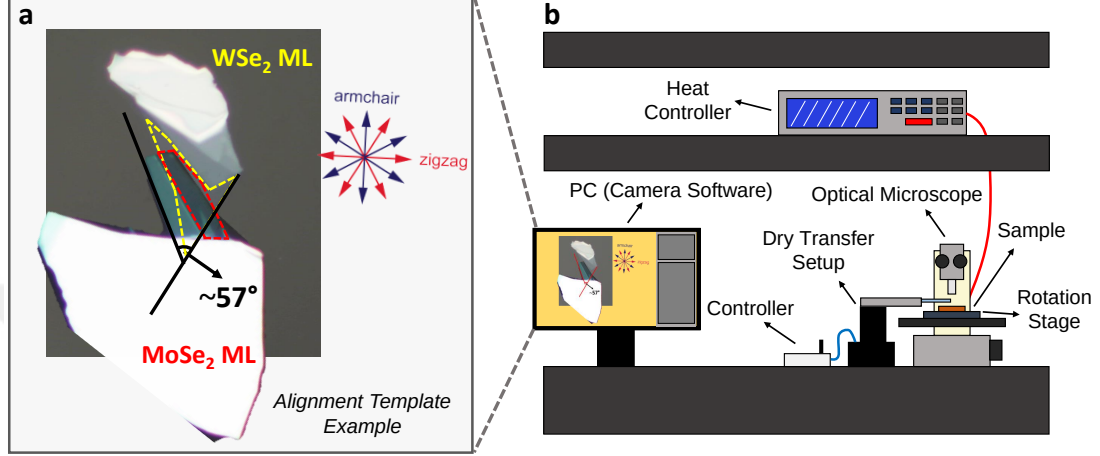


Figure 3.3: Dry transfer and vertical stacking of TMDC monolayers. **a.** Alignment template of the two monolayers according to a specific twist angle $\theta \sim 57^\circ$. These templates can be opened semi-transparently on the real-time image by loading them into the camera software of the optical microscope. **b.** Schematic illustration of the dry transfer setup used to stack the crystal layers vertically to fabricate the heterostructures. The figure includes a label for every item utilized in the process.

The vertical stacking procedure starts once all of the crystal layers needed to fabricate the desired heterostructure have been obtained and characterized. Importantly, one should remember that each layer needs to have a backup sample on hand in case something goes wrong during the transfer process. Furthermore, based on my experiences, it may be more advantageous to find at least a couple of TMDC monolayers of both materials and match them with each other based on their sizes and shapes rather than proceeding straight to the transfer process with each monolayer crystal found. Using a computer software (e.g., MS PowerPoint), alignment templates can be prepared with the paired flakes as shown in **Fig. 3.3a** to be used in the camera software of the optical microscope setup. It is possible to almost align the two monolayers to the desired twist angle by using these templates. In addition, it should be noted that both of the monolayer images should be inversed when creating these alignment templates, as they will remain that way following the transfer. This could lead to confusion while stacking if it is ignored.

Fig. 3.3b shows an illustration of the dry transfer setup used in the vertical stacking process of the crystal layers. Initially, hBN layers from PDMS that have the proper thickness to act as the bottom encapsulation layer are transferred onto the substrate that has been ~ 100 nm Au-coated. Followingly, the first TMDC monolayer is transferred onto these bottom-hBN layers. The sample stage must be heated to at least 80°C after the monolayer and hBN make their first contact, and the PDMS glass must be further stamped during the heating process. The heating should then be turned off and using the controller at temperatures around 65°C , the glass should be pulled up very slowly while the stage cools down. In contrast to the first one, the second monolayer must be transferred according to a twist angle, which means a few extra steps must be considered. As a start, one should upload the alignment template to the PC software, then adjust the picture according to the real-time image of the second monolayer on the PDMS that is mounted on the transfer setup. The bottom layer should then be aligned using the rotation stage in accordance with the adjusted alignment template picture. Therefore, by applying the template and these steps, the monolayer on the substrate mounted on the rotation stage becomes aligned with the monolayer on the PDMS that is mounted on the transfer setup. Once more, the stage should be heated to 80°C when the two monolayers come into contact during transfer, and the PDMS should be raised very slowly as the platform cools. The last step here is to encapsulate the heterostructure by transferring a very thin hBN layer on top of it by using the same steps. For these vertical stacking fabrication process, I often use an objective lens with a 40X magnification (ZEISS LD Plan-Neofluar 40x/0.60 Corr), and to properly observe both monolayers while transferring, I had to operate in extremely dim lighting. According to my experience, if these steps are followed, monolayer transfers and heterobilayer fabrications can be completed smoothly and without any crystal shattering.

Fig. 3.4a displays the schematic representation of the heterobilayer that will be obtained following the vertical stacking process, each of which steps is described in detail above. Furthermore, **Fig. 3.4b** displays the optical microscope image of the heterobilayer sample that was fabricated after the monolayers were stacked according to the alignment template in **Fig. 3.3a**. As observed after

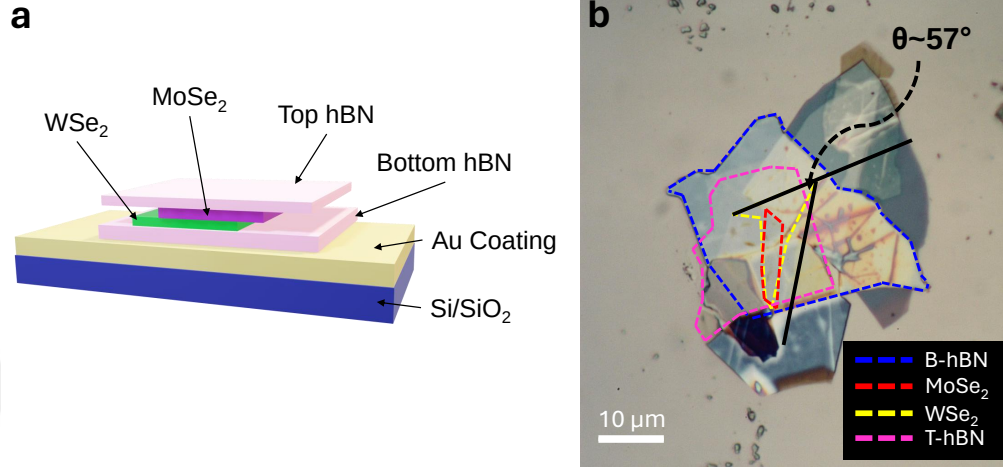


Figure 3.4: Fabricated WSe₂-MoSe₂ heterobilayer. **a,b.** Schematic (**a**) and optical (**b**) images of an hBN-encapsulated WSe₂-MoSe₂ heterobilayer sample on top of an ~ 100 nm thick Au-coated substrate, the steps of which are described above. Colored dashed lines highlight specific crystal areas. Black lines show the zigzag edges of the two monolayers and the 57° twist angle between them.

numerous tries, there can be around 1° inaccuracy in the twist angle between the two monolayers using the above-explained dry transfer steps. It is important to note that the twist angles between the two monolayers were selected in accordance with the findings of earlier research to obtain the Moiré-localized IXs[34–40].

Chapter 4

Interlayer Excitons in TMDC Heterobilayers

This chapter will include details on the hBN-encapsulated WSe₂-MoSe₂ heterobilayers (fabrication details were mentioned in the previous chapter) along with the formation of interlayer excitons and Moiré superlattices. The explanations, discussions, and figures shown in this chapter are from the findings of our publications:

1. **Durmuş, M. A.**, Demiralay, K., Khan, M. M., Atalay, Ş. E. & Sarpkaya, I. Prolonged Dephasing Time of Ensemble of Moiré-Trapped Interlayer Excitons in WSe₂-MoSe₂ Heterobilayers. *Npj 2D Mater. Appl.* 7, 65 (2023).
2. **Durmuş, M. A.** & Sarpkaya, I. Quantum Beats Between Spin-Singlet and Spin-Triplet Interlayer Exciton Transitions in WSe₂-MoSe₂ Heterobilayers. *Nano Letters*. 24, 5767–5773 (2024).

The details about the dephasing time results of these studies will be discussed in Chapter 5.

4.1 Band Alignment of the WSe₂-MoSe₂ Heterobilayer

Determining the band alignment of semiconductor vdW heterostructures is crucial for understanding their possible applications and physical characteristics. The majority of TMDC heterostructures, as well as our heterobilayer, have the staggered type-II band alignment, according to the results of theoretical[15, 45–47] and experimental research[16, 132]. **Fig. 4.1a** displays the electronic band diagram of the WSe₂-MoSe₂ heterobilayer, illustrating the type-II alignment. The band alignment in these heterobilayers indicates that the VBM and CBM are located in distinct monolayers, meaning that the electrons find their energy minima in the MoSe₂ layer while holes find it in WSe₂ layer as shown in **Fig. 4.1b**.

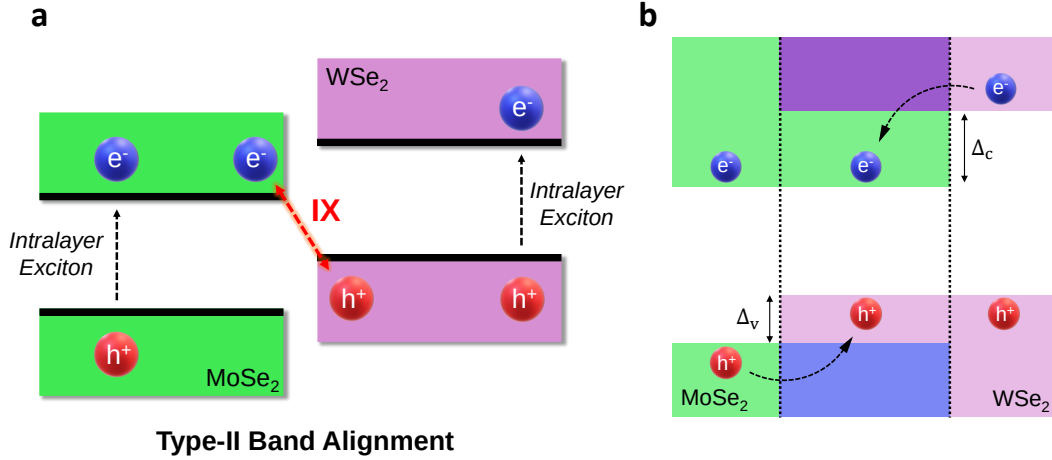


Figure 4.1: Band alignment of the WSe₂-MoSe₂ heterobilayer. a. Schematic of the type-II band alignment, showing intralayer and interlayer (IX) excitonic states of the heterobilayer. **b.** Illustration of the interlayer charge transfer at the heterojunction between the two monolayers. The offsets of the conduction and valence bands are denoted by Δ_c and Δ_v , respectively.

Through this heterojunction, a natural ultra-fast charge transfer happens between the two monolayers within the time scale of femtoseconds[17, 18]. Despite the weak vdW forces between the monolayers, the charge carriers in the opposing layers have a strong Coulomb interaction[48, 83–85] due to the ultra-fast charge transfer and the small (>1 nm) layer separation between the TMDC monolayers,

which leads to the formation of a bound excitonic state (i.e., interlayer excitons). It should be noted that the interlayer coupling, which is influenced by the momentum mismatch and interlayer distance between the layers, plays a major role in the formation or observation of these IXs[44]. Prior research on WSe₂-MoSe₂ heterostructures demonstrates that the stacking angle between the layers significantly impacts the PL intensity and energy of the IXs, with enhancements occurring particularly around 0° and 60° twist angles[35, 38, 98, 133]. In particular, the coupling of IXs to the light cone is highly dependent on the twist angle between the monolayers, which modifies the displacement of the constituent $\pm K$ valleys[134]. The heterobilayers in this study were therefore constructed in compliance with the findings of the twist angles ($\theta \sim 0^\circ$ or 60°) of these earlier investigations.

4.2 Interlayer Excitons in WSe₂-MoSe₂ Heterobilayers

As previously stated, the strong Coulomb interaction between the electrons and holes in the opposing monolayers forms the IXs. Through their spatially indirect nature, the ability to control their optical and transport properties[83, 105, 135] makes them highly desirable for developing potential excitonic circuits. Their valley-contrasting physical properties make them desirable candidates for valleytronics applications as well[48, 79, 80, 133]. Furthermore, small twist angles and lattice mismatching between the monolayers can result in the appearance of in-plane Moiré superlattices in heterostructures, which may serve as potential traps to localize the IXs (i.e., Moiré-localized IXs)[136]. Their ability to be programmed and their unique optical selection rules provide new opportunities in the development of quantum applications[137]. All in all, this unique excitonic system creates a variety of intriguing features not available to traditional direct excitons, opening up new avenues for research and facilitating the development of promising solid-state excitonic devices.

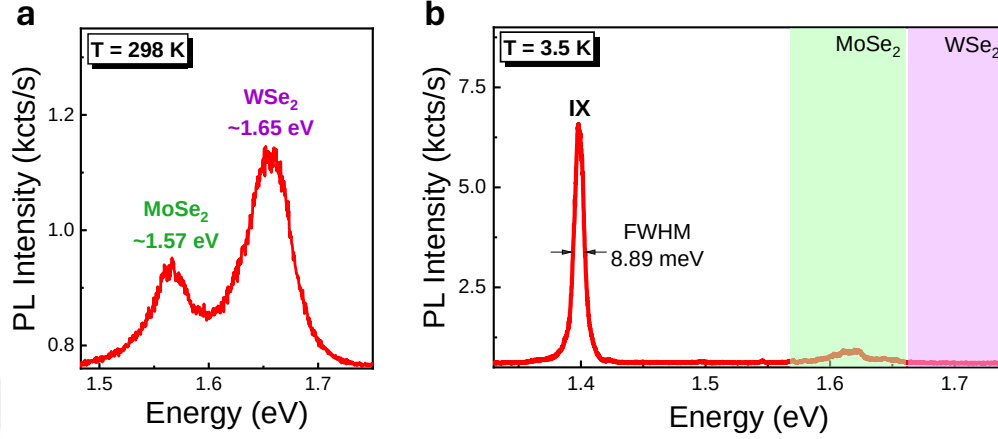


Figure 4.2: PL Characterization of the WSe₂-MoSe₂ heterobilayer. a. Room-temperature PL spectrum of an hBN-encapsulated WSe₂-MoSe₂ heterobilayer sample with intralayer exciton emissions of MoSe₂ and WSe₂ monolayers appearing around ~ 1.57 eV and ~ 1.65 eV, respectively, under 532 nm CW laser excitation with an incident power of $P = 100 \mu\text{W}$. **b.** Low-temperature PL spectrum of an hBN-encapsulated WSe₂-MoSe₂ heterobilayer with the IX emission appearing at ~ 1.4 eV with a linewidth of 8.89 meV under 532 nm CW laser excitation with an incident power of $P = 50 \mu\text{W}$. The intralayer exciton emissions of the individual monolayers are quenched and their emission regions are indicated with green and purple boxes for MoSe₂ and WSe₂, respectively.

Experimentally, at low temperatures, the extra PL peaks that arise at lower energies than the intralayer excitons are one of the most significant features of IXs. Additionally, as has also been seen in previous studies, the PLs of intralayer excitons of monolayers quenches in addition to this extra peak[48, 83–85, 132, 133, 138]. At room temperature, the intralayer exciton peaks from the constituent monolayers are observable with the emissions occurring at around 1.57 eV for MoSe₂ and 1.65 eV for WSe₂ as shown in **Fig. 4.2a**. On the contrary, as displayed in **Fig. 4.2b**, the intralayer exciton peaks emitted from monolayers become quenched (1.6 and 1.7 eV regions for MoSe₂ and WSe₂, respectively) at low temperatures, and a highly observable IX peak emerges at around 1.4 eV, which is very consistent with the characteristics mentioned above. According to my experience, one should not infer low-temperature PL emission from the PL spectra recorded at room temperature. Furthermore, the PL characteristic varies mostly depending on the twist angle, and if a clean interface is created during the fabrication of the heterobilayer, both highly visible IXs and Moiré-localized

IXs can be obtained at low temperatures. Additionally, consistent with earlier research[35, 38, 98], at high pump powers, the spin-singlet (IX_S) emission peak arises with extremely low intensity at around 25 meV lower energy than the spin-triplet (IX_T), which will be addressed later on.

4.3 Moiré Interlayer Excitons in $\text{WSe}_2\text{-MoSe}_2$ Heterobilayers

Moiré superlattices in vdW heterostructures of monolayer TMDCs have drawn significant amounts of attention since the discovery of unusual superconductivity and insulating states in twist angle-given graphene lattices[139, 140], giving rise to a new field of research called twistronics. A Moiré pattern with periodic variations in the interlayer atomic registry, with a period ranging from a few to tens of nanometers, can naturally emerge in TMDC heterobilayers fabricated using vertical the dry transfer technique[137]. Only when the TMDC layers are completely aligned and stacked, which is nearly impossible in dry stacking, can the Moiré superlattice show up to be absent. In other words, to avoid observing any Moiré superlattice, there should not be a lattice mismatch between the layers of the heterobilayer, and earlier research demonstrates that it is achievable in the case of rotationally aligned CVD-grown heterobilayers[36]. Furthermore, these superlattices of vdW heterostructures offer an array of possibilities for quantum photonic researchers, which certainly will contribute to the advancement of related applications.

While there is a continual variation in the interlayer atomic registry across the superlattice, the three-fold rotational symmetry $\hat{C}_3$ remains maintained[141]. The local band gap and interlayer distance could be modulated laterally due to this registry variation, creating position-dependent potentials (i.e., Moiré potentials), which can confine and trap the excitons. Depending on the twist angle of the stacked monolayers (i.e., $\sim 0^\circ$ and $\sim 60^\circ$ for R-type and H-type, respectively), the heterobilayers can have either R-type (R_h^h, R_h^X, R_h^M) or H-type (H_h^h, H_h^X ,

H_h^M) symmetry. Here, the letters X , M , and h stand for the chalcogen site, metal site, and hollow center of the hexagon, respectively. The indication of writing subscript and superscript letters in the R- or H-type stacking shows which site of the electron and hole layers are vertically overlapping. For instance, the representation of H_h^X denotes an overlap between the hexagon center of the hole layer and the chalcogen site of the electron layer. It should be noted that in the H-type stacking, the valley indexes of the conduction and valence bands have opposing signs ($+K$, $-K'$ or $-K$, $+K'$), whereas the ones in R-type stacking have the same signs ($+K$, $+K'$ or $-K$, $-K'$), leading to larger Landé g factor values of IXs in H-type stacked heterobilayers[44]. Furthermore, as the name implies, IXs are highly influenced by the interlayer registry and configurations. These periodic patterns on these Moiré superlattices allow one to manipulate the physical properties of the IXs, and it would be conceivable to realize 2D quantum dot arrays at the nanoscale[137, 142]. A superlattice of excitons can be formed by trapping and localizing the IXs through these quantum dot-like Moiré potentials. Using strain-modulation[143–145], the twist angle variations between the monolayers[34, 40], or an external electric field[137, 146], one can adjust the Moiré patterns within the heterobilayer to form the intended superlattice for the desired IX properties.

In contrast to the delocalized IX peaks observed in earlier research[83, 84, 133, 147] and the PL spectrum presented in **Fig. 4.2b**, IXs localized in Moiré potentials exhibit PL emissions with linewidths nearly two orders of magnitude narrower, and they are comparable to the single photon quantum emitters in hBN[148] and WSe₂[149]. Recently done photon antibunching studies have verified the quantum nature (i.e., single-photon characteristics) of the emitted light from the Moiré-localized IXs[34]. Experimentally, a clear signature of the Moiré-trapped IXs is the previously described extremely narrow PL emission lines in the PL spectrum, showing the formation of the 0D Moiré superlattice within the heterostructure. **Fig. 4.3a** shows a low pump power ($P = 3 \mu\text{W}$) PL spectrum of one of the samples with the 0D Moiré potentials that are fabricated in this research, which has a very intense Moiré-localized IX emission with a linewidth of 0.313 meV. To observe the evolution of these localized emissions and see how

they vary from the delocalized ones, we performed pump power-dependent PL spectroscopy measurements at low temperatures. The PL evolutions of Moiré-localized and delocalized IXs are shown in **Figs. 4.3b** and **4.3c**, respectively, and it is evident that the delocalized ones lack the signature of narrow and sharp PL lines at low pump powers.

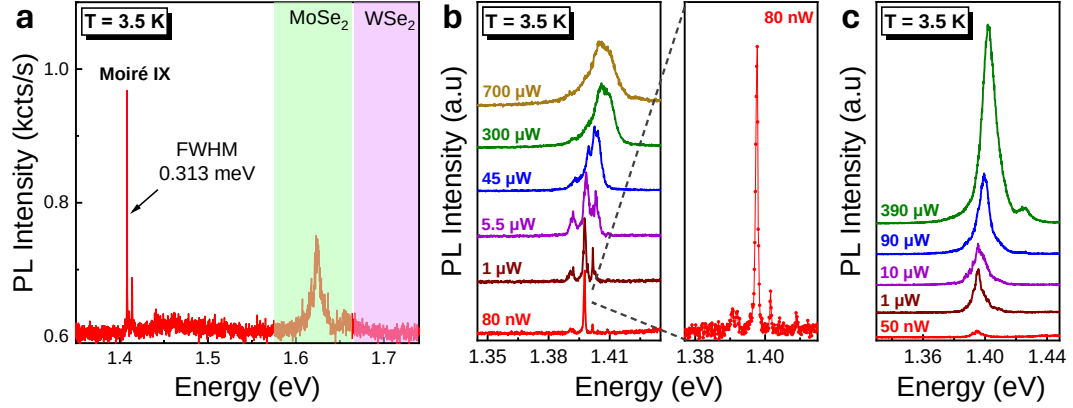


Figure 4.3: PL Characterization of Moiré-localized IXs of WSe₂-MoSe₂ heterobilayers. **a.** Low-temperature PL spectra of an hBN-encapsulated WSe₂-MoSe₂ heterobilayer with the Moiré-localized IX emissions appearing at ~ 1.4 eV with the most intense one having a linewidth of 0.313 meV under 532 nm CW laser excitation with an incident power of $P = 3 \mu\text{W}$. The intralayer exciton emission regions of the individual monolayers are indicated with green and purple boxes for MoSe₂ and WSe₂, respectively. **b.** Low-temperature pump power-dependent PL spectra of the Moiré-localized IX emission showing the evaluation of the ensemble band of the Moiré-localized IXs. **c.** Low-temperature pump power-dependent PL spectra of a delocalized IX emission from another WSe₂-MoSe₂ heterobilayer sample. The PL evolution of this sample demonstrates no signs of narrow, sharp PL emission peaks at low pump power regimes, indicating that such kinds of samples do not exhibit 0D confinement. At the high pump power regime, the high energy spin-singlet emission can also be observed with the energy separation of ~ 25 meV from spin-triplet emission. Data are recorded at 3.5 K under 532 nm CW laser excitation for both pump power-dependence experiments.

As previously stated, the delocalization cannot result from the Moiré superlattice being absent from the heterobilayer. Nevertheless, it is possible that the Moiré superlattice might be affected by an unintended strain that occurred during the layer stacking part of the heterostructure fabrication process. Previous studies showed that the primary cause of Moiré superlattice distortion is a strain

within the crystal[144, 145]. Through this distortion, 0D, 1D, and 2D trap domains in various regions of the heterostructure can be formed, which have different confinement characteristics. According to the proposals of the study (i.e., 2D harmonic trap model)[144], 1D Moiré localization potentials can have a high density of states. Radiative recombination can occur from many different levels through these densely packed excitonic levels, leading to a broadening of the PL spectrum even at low pump powers (**Fig 4.3c**). In contrast to the 1D trapping characteristics, in 0D confinement potentials, the lowest exciton state dominates the PL spectrum. Thus, one can see the Moiré-localized sharp PL peaks at low pump power at 3.5 K as shown in **Fig 4.3b**. In the light of this, it can be deduced that for the heterobilayer samples without narrow PL emissions, the 0D confinement potentials could be distorted due to accidental strain within the samples during the vertical stacking process. From this discussion, it can be concluded that extreme caution and sensitivity are required throughout the vertical stacking process of the monolayers during the fabrication of the heterobilayer samples to form the Moiré superlattices and localization potentials.

4.4 Magneto-PL Studies of IXs in WSe₂-MoSe₂ Heterobilayers

The valley polarization of IXs can be manipulated through their valley-contrasting physical properties. Experimental investigations confirmed the validity of the valley-dependent optical selection rules of the IXs of TMDC heterostructures[150–154], which were theoretically predicted with opposed valleys having opposite helicities[134, 155]. Earlier research has demonstrated that the valley polarization of the IXs can be controlled by externally applied fields[98, 133, 147, 151, 152] and that they exhibit observable behavior of both Zeeman[98, 133] and valley Hall[156] phenomena. Furthermore, the spin-orbit splitting of the conduction band (i.e., MoSe₂ layer) results in observable spin state (IX_S and IX_T) emissions with opposing helicities in the same valley configuration and atomic registry[44], illuminating the complex excitonic physics

underlying the TMDC heterostructures. These two distinct IX spin states have been predicted theoretically[155] and have been shown to exist in WSe₂-MoSe₂ heterobilayers in recent experimental investigations[38, 43, 98, 154, 157]. Notably, they represent interesting possibilities for future valleytronic applications due to their experimentally reported long spontaneous emission lifetime[98], near-unity valley polarization[98, 133, 154], and the ability to tune their PL emission through external optical[158] and electrical[98, 147, 157] fields. Moreover, the distinct polarization patterns exhibited between these spin states[98, 147, 154] could render them valuable for enabling the development of exciton-based valley polarization switch devices. It is also necessary to determine whether there is a correlation or interaction between these states to effectively use them in possible valleytronics applications. Even though this topic has not been investigated before, our quantum beating investigations, which will be covered in more detail in the Chapter 5, have revealed the presence of this interaction[67].

To learn about the assignment of spin states of IXs and the nature of Moiré-localized ones in WSe₂-MoSe₂ heterobilayers, one can employ magneto-PL spectroscopy. Through the Zeeman splitting effect, the effective Landé g factors of these emissions can be calculated and used for their identification. According to earlier research, the effective g factors of the intralayer excitons in TMDC monolayers are around 4[99, 159]. Conversely, the effective g factors of IXs of their heterostructures are much larger than them due to the non-vanishing valley contribution to the Zeeman splitting, creating a giant valley splitting with near-unity valley polarization[98, 133]. Based on the theoretical studies, the g factor of spin-singlet IXs of WSe₂-MoSe₂ heterobilayers was predicted to be ~ 6 for R-type and ~ 12 for H-type stackings, while the g factor of spin-triplet IXs predicted to be ~ 10 for R-type and ~ 16 for H-type stackings[157, 160]. The experimentally obtained g factors are in very well agreement with these predictions for both R-type and H-type stackings, particularly for the stacking $\sim 60^\circ$ twist angle[35, 38, 40, 98, 133].

In order to confirm the spin states of our IXs and the H-type stacking of our WSe₂-MoSe₂ heterobilayer samples, we also performed magneto-PL measurements as shown in **Fig. 4.4**. The experiment was carried out at 80 K, where

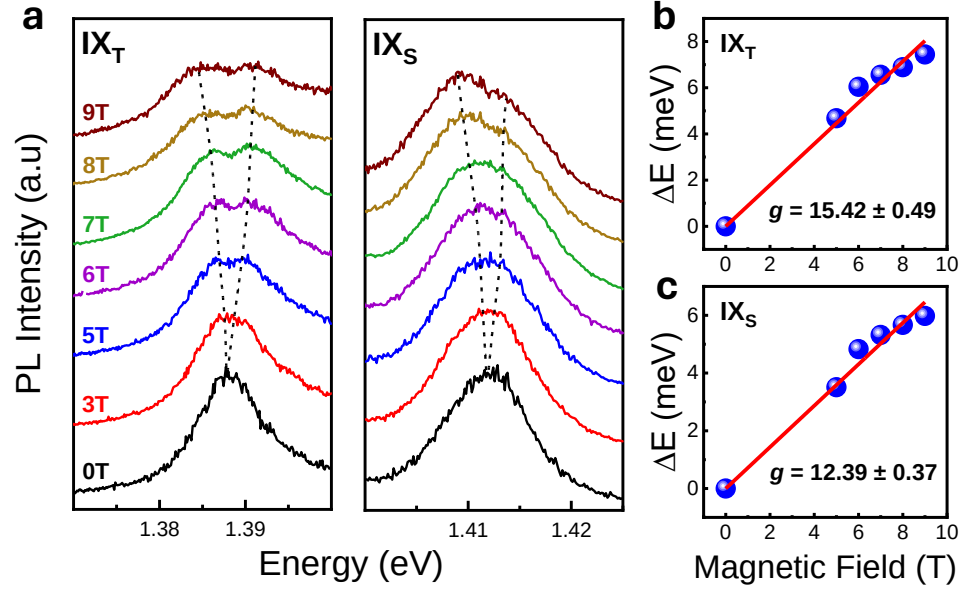


Figure 4.4: Valley-Zeeman splitting of spin-triplet and spin-singlet interlayer exciton emissions in a WSe₂-MoSe₂ heterobilayer sample with $\theta \sim 60^\circ$ stacking angle. a. The PL spectra of spin states of the IXs as a function of the strength of an applied out-of-plane magnetic field under 532 nm CW laser excitation. The Zeeman splitting measured for spin-triplet (b) and spin-singlet (c) IXs with effective g factors of 15.42 ± 0.49 and 12.39 ± 0.37 , respectively. Data are recorded at 80 K.

the intensities of the spin-state emissions were almost equal, allowing us a clear observation of both. The PL emissions were collected as a function of the applied magnetic field in a Faraday geometry (i.e., applied field perpendicular to the heterobilayer sample) and a linearly polarized 532 nm CW laser was used as the excitation source. The Zeeman shift of the corners (K and K' valleys) of the hexagonal Brillouin zone of the heterobilayer causes both of the PL peaks of the IX_S and IX_T emissions to split into two with an increase in magnetic field, as **Fig. 4.4a** displays. The Zeeman splitting energy can be defined with the expression of $|\Delta E| = g\mu_{\text{B}}B$, where g is the effective Landé g factor, μ_{B} is the Bohr magneton ($\sim 58 \mu\text{eV/T}$), and B is the strength of the applied magnetic field. As shown in **Figs. 4.4b** and **4.4c**, the energy splitting values over applied field points can be fitted with this expression, resulting in g factor values of 15.42 ± 0.49 for IX_T and 12.39 ± 0.37 for IX_S emissions, which are in excellent agreement with previous studies[35, 38, 98, 133, 144, 160].

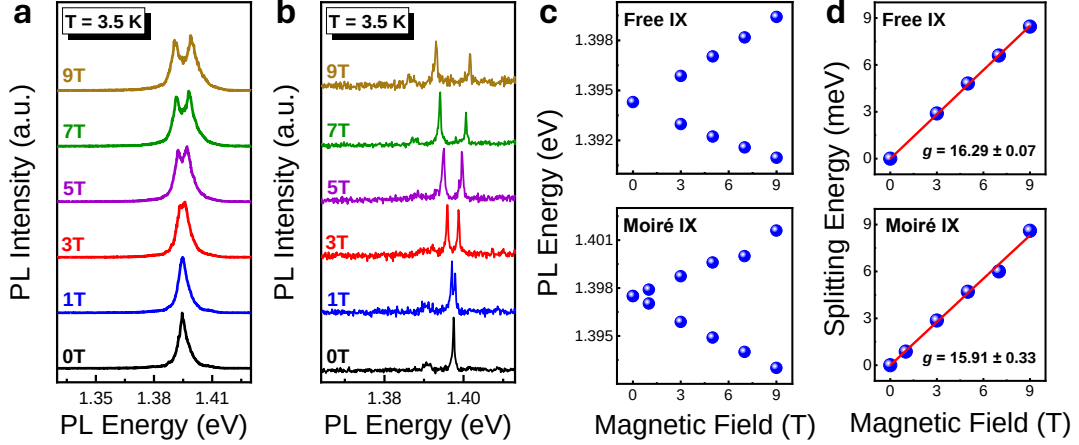


Figure 4.5: Zeeman Splitting of interlayer exciton emissions in WSe₂-MoSe₂ heterobilayers. The PL spectra of the delocalized (a) and Moiré-trapped (b) IXs as a function of the strength of an applied out-of-plane magnetic field under 532 nm CW laser excitation. **c.** The PL peak energies of free and Moiré-localized IXs as a function of the applied magnetic field. **d.** The Zeeman splitting measured for free and Moiré-localized IXs with effective g factors of 16.29 ± 0.07 and 15.91 ± 0.33 , respectively. Data are recorded at 3.5 K.

As mentioned, one can also learn about the nature of the Moiré-localized IXs via their Landé g factors. Examining the degree to which the g factors of the ensemble of delocalized IXs and the g factors of Moiré-localized IXs match is one approach to do this. Earlier magneto-PL investigations have demonstrated that the formation of Moiré quantum emitters in WSe₂-MoSe₂ heterobilayers results from the confinement of free (delocalized) IXs to Moiré potentials[34, 35]. It is observed in both studies that the effective g factor of a single Moiré IX quantum emitter (~ 16 [34, 35]) is remarkably similar to the g factor of spin-triplet IXs. Therefore, it can be deduced that Moiré-localized IXs also have a spin-triplet nature. To see the same behavior, we also conducted magneto-PL experiments for samples exhibiting Moiré-localized IXs and delocalized IXs as shown in **Fig. 4.5**. Both the PL spectra of delocalized (**Fig. 4.5a**) and Moiré-localized (**Fig. 4.5b**) IXs exhibit a distinct Zeeman splitting with the increasing magnetic field. **Fig. 4.5d** illustrates the plotting of energy separation values as a function of the applied field, which can be obtained by extracting the energy splitting points of these peaks (**Fig. 4.5c**). For delocalized and Moiré-localized IXs, the Zeeman energy splitting fits show remarkably similar Landé g factors of 16.29 ± 0.07

and 15.91 ± 0.33 , respectively. Consequently, our results also support the idea presented by earlier research that the confinement of delocalized spin-triplet IXs to the Moiré potentials can explain the nature of the formation of Moiré-localized IXs.

4.5 Temperature and Pump Power Dependence of Spin-Singlet and Spin-Triplet IXs in WSe₂-MoSe₂ Heterobilayers

To study the emission nature of the IX_S and IX_T emissions, one can perform temperature-dependent and pump power-dependent PL spectroscopy. As mentioned, the IX_T emission is in a lower energy band, meaning that it will be more intense than the IX_S emission in 3.5 K under moderate pump powers. Several control knobs can be used to observe how they operate, such as electrostatic gating[98, 147, 157], temperature[38, 147, 153, 154], and pump power of the excitation laser[157]. It is crucial that these IX spin states have almost comparable PL intensities for the purposes of quantum beat spectroscopy. The forthcoming chapter will cover the specifics of this experiment as well as the rationale behind the comparable PL intensities. For the time being, only the behavior of the PL emissions of these IX spin states with the change in temperature and excitation pump power will be discussed.

The previously done temperature-dependent PL studies show that the intensity of IX_T emission decreases while it increases for IX_S emission. In agreement with these previous results, our temperature-dependent PL measurements (**Fig. 4.6a**) also demonstrate a pronounced IX_S emission since it gets thermally populated at higher temperatures. Each of the emission peaks exhibits a redshift with increasing temperature, in agreement with the previous research[38, 147, 153, 154]. Moreover, the extracted PL intensity ratio of the IX_S and IX_T emissions at different temperatures is displayed in **Fig. 4.6b**. As the figure illustrates, this ratio increases along with the temperature and takes the value of ~ 1 at 90 K.

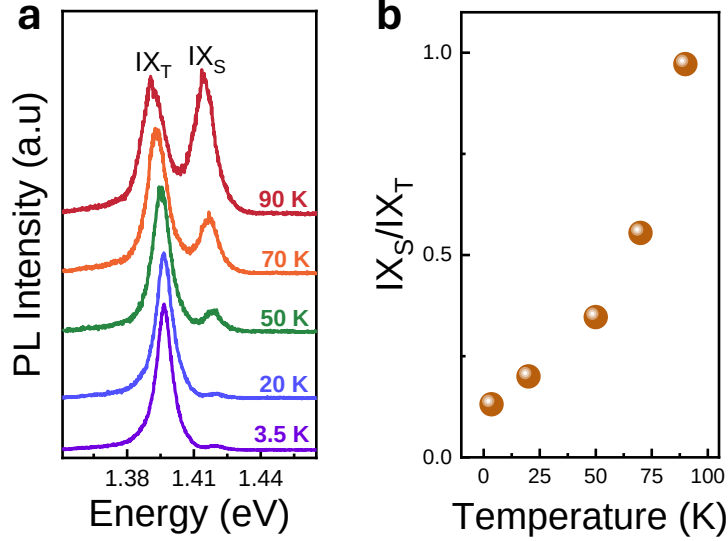


Figure 4.6: Temperature dependence of spin-singlet and spin-triplet interlayer excitons in WSe₂-MoSe₂ heterobilayers. **a.** Temperature-dependent PL spectra of the spin states of IXs. **b.** The PL intensity ratio of spin-singlet to spin-triplet states of the IXs as a function of temperature. Data are recorded under a 532 nm CW laser with 400 μ W pump power.

Excitation pump power can also be used to control the PL intensities of the spin states of IXs. Prior research indicates that there is a point at which the intensities of IX_T and IX_S emissions increase simultaneously[161]. However, the IX_T intensity eventually saturates while the IX_S intensity continues to rise. This phenomenon can generally be explained by the spin-orbit coupling-induced conduction band splitting of the MoSe₂[162]. In detail, a rise in the excitation pump power causes the low-energy spin-triplet band to fill up first, and when it is further increased, the high-energy spin-singlet band also starts to fill out due to the phase space-filling effect[163]. At a certain point, the PL intensity of the IX_T state starts to saturate, whereas the IX_S intensity continues to increase with the power[85].

These findings are further supported by our low-temperature pump power-dependent PL studies as shown in **Fig. 4.7a**. As a signature of the repulsive dipolar interactions[43, 84], the PL emission lines of both IX spin states show a blueshift with the increasing pump power. Moreover, it can be observed that the PL spectrum is dominated by the Moiré-localized IXs in the low pump power

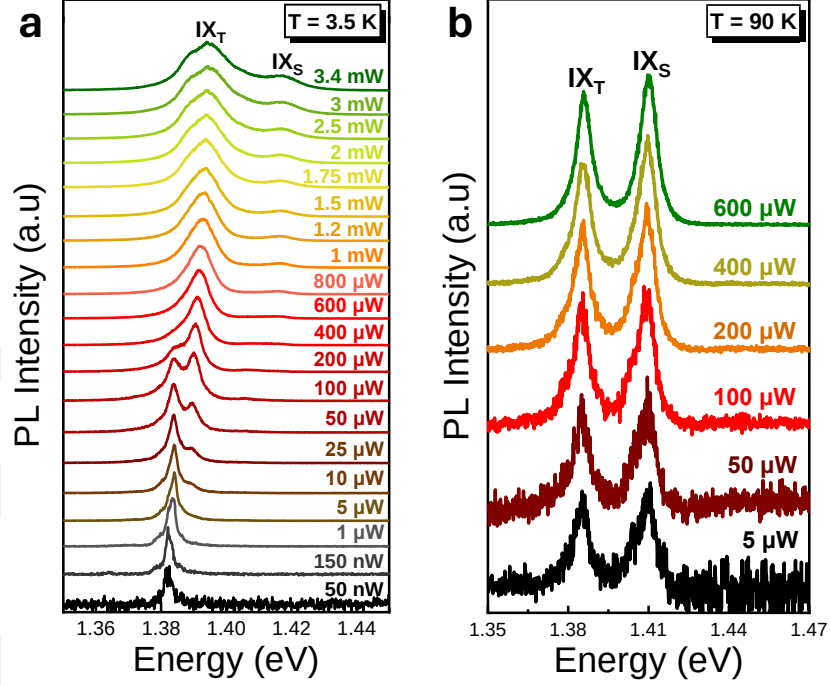


Figure 4.7: Pump power dependence of spin-singlet and spin-triplet interlayer excitons in WSe₂-MoSe₂ heterobilayers. Pump power-dependent PL spectra of IXs at 3.5 K (a) and 90 K (b) under 532 nm laser excitation.

regime, which eventually develops into an ensemble band of the IX_T configuration. Around $P = 400 \mu\text{W}$ excitation powers, the IX_S state also starts to show up with an energy separation of ~ 24 meV from the IX_T emission. As previously mentioned, their PL intensity increases with the pump power until the IX_T one ultimately saturates while the IX_S continues to increase. Here, it is important to highlight that the concept of using pump power as a control knob to even out the PL intensities (for the quantum beat spectroscopy) is a bit problematic because the desired PL spectra can only be obtained at very high pump powers, which can harm the heterobilayer sample and inhomogeneously broaden the PL spectra. Furthermore, both spin states respond quite similarly to an increase in pump power at 90 K, where they consistently have comparable PL intensities, as seen in **Fig. 4.7b**.

4.6 Time-Resolved PL studies of IXs in WSe₂-MoSe₂ Heterobilayers

Interlayer excitons of TMDC heterobilayers have a reduced wavefunction overlap of their charge carriers (electrons and holes) since they have a spatially indirect nature (**Fig. 4.1**). This reduced overlap of IXs results in them having lower oscillator strengths than the intralayer excitons of individual TMDC monolayers[134, 142]. On the other side, the reduced oscillator strength denotes a significantly longer recombination lifetime (in the range of ns to μ s), as demonstrated by previously done theoretical and experimental studies[48, 83–85, 133, 150–152, 164–169]. These earlier investigations also revealed that the lifetime of the IXs is strongly influenced by external factors such as temperature[84, 85, 150, 169], electric field[152, 170], interlayer distance[168], and stack angle between the monolayers[165].

Time-resolved PL (TRPL) spectroscopy and femtosecond pump-probe spectroscopy are two ultrafast optical spectroscopy techniques that can be used to measure the lifetime (T_1) of IXs. In our instance, we measured the recombination lifetime of our IXs using the TRPL spectroscopy method (**Fig. 4.16**). Previous studies have shown that IXs formed in WSe₂-MoSe₂ heterobilayers typically have two lifetime components (i.e., bi-exponential decay)[44]. In particular, the lifetime of the slow component can reach hundreds of nanoseconds, whereas the fast component lasts about tens of nanoseconds. Remarkably, a study found that dark excitons generated in WSe₂-MoSe₂ heterobilayers can have recombination lifetimes of up to microseconds[151]. These findings represent a major step forward in the development of next-generation exciton-based devices with long-range exciton transport capabilities.

To further investigate and explore the dynamics of the recombination lifetimes, we have also performed TRPL measurements on the ensemble of delocalized and the ensemble of Moiré-localized IXs of WSe₂-MoSe₂ heterobilayers as shown in **Fig. 4.8**. The TRPL intensity as a function of delay time plots for the ensemble of delocalized and Moiré-localized IXs are shown in **Figs. 4.8a** and **4.8**,

respectively. The red line in the plots shows the bi-exponential fits that yield a fast and slow recombination lifetime component of 2.58 ± 0.05 ns and 26.05 ± 0.55 ns for the delocalized, and 2.60 ± 0.02 ns and 21.07 ± 0.21 ns for the Moiré-localized IXs, respectively. An overview plot displaying the fast and slow components of the lifetime values of IXs obtained from our TRPL measurements is shown in **Fig. 4.8c**. The lifetimes of delocalized IXs (HS1-HS4) that we experimentally obtained accord extremely well with the values that have been reported earlier[34, 48, 83–85]. Given the TRPL results, one might anticipate the Moiré-localized IXs to have longer recombination lifetimes than the delocalized ones. However, in contrast to the findings of previous studies involving the localization of IXs[119, 171–173], the findings of a recent study demonstrate that the localization of IXs dramatically shortens their lifetimes[174]. Nevertheless, it is also important to remember that extrinsic inhomogeneous effects, such as defects, impurities, and adsorbates, which could be introduced to the heterobilayer during the fabrication process, also have an impact on the observed lifetimes of excitons (both intra- and inter-layer). The aforementioned inhomogeneous effects can lead to an increase in the prevalence of long-lived, highly effective non-radiative recombination decay channels, which in turn can extend the lifetime. This idea motivates the prolonged lifetimes of our IXs from the heterobilayers HS1-HS4, which can be explained by the fact that they are delocalized, highly mobile IXs with longer diffusion lengths. Since they can explore these long-lived recombination centers freely, the domination by radiative recombination from those long-lived energy levels to the ground state results in longer lifetimes. In the localization case, either in an extrinsically strain-induced potential well[174] or intrinsic Moiré potential (as in our case), the diffusion lengths of the IXs become constrained, causing them to rarely encounter those centers. Therefore, the observed lifetime of our Moiré-localized IXs (HS5-HS7) is rather shorter or similar to the delocalized IXs (HS1-HS4). When it comes to intralayer excitons, one can see the direct influence of homogeneous effects on their lifetime in contrast to IXs since their shorter lifetimes and diffusion lengths will cause the influence of the localization on the suppression of non-radiative decay channels to be relatively small.

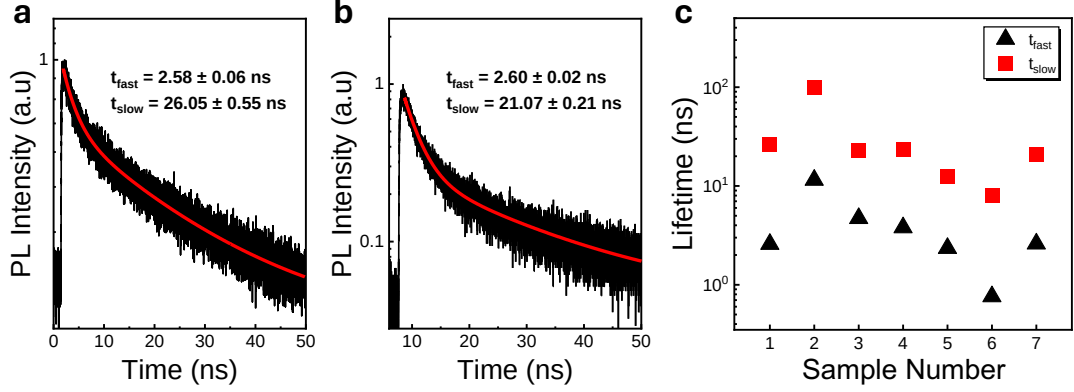


Figure 4.8: Time-resolved PL of interlayer excitons in WSe₂-MoSe₂ heterobilayers. TRPL intensity as a function of delay time of the ensemble of delocalized (a) and the ensemble of Moiré-localized (b) IXs under pulsed excitation at 532 nm with 6 μ W and 10 μ W pump powers, respectively. The red line in the plots indicates a bi-exponential fit featuring fast and slow lifetime components. The fits yield a fast decay of 2.58 ± 0.05 ns and 2.60 ± 0.02 ns, and a slow decay of 26.05 ± 0.55 ns and 21.07 ± 0.21 ns for delocalized and Moiré-localized IXs, respectively. c. Overview plot of the IX lifetimes of our WSe₂-MoSe₂ heterobilayer samples, where red squares represent the slow decay components and black triangles represent the fast decay components of the recombination lifetimes. The samples with Moiré-localized IXs are indicated in the plot as HS5, HS6, and HS7. Data are recorded at 3.5 K.

We have also conducted TRPL studies on IX_S and IX_T spin states of interlayer excitons at 90 K (where their intensities were equal) to further explore the nature of their recombination lifetime dynamics. **Fig. 4.9** displays the filtered PL spectra and their corresponding lifetime plots of the spin states of the IXs of one of our WSe₂-MoSe₂ heterobilayer samples. In contrast to our 3.5 K results, our 90 K data showed a mono-exponential decay as shown in **Figs. 4.9c** and **4.9d**. The red-lined fits in the TRPL intensity as a function of delay time plots, yield recombination lifetimes of $T_1 = 612.5 \pm 0.2$ ps and $T_1 = 662.3 \pm 0.3$ ps for IX_S and IX_T emissions under 532 nm pulsed excitation with an incident power of $P = 230$ μ W, respectively. Additionally, we performed the same experiment using lower pump power as well ($P = 50$ μ W), which yielded $T_1 = 660.0 \pm 2.0$ ps and $T_1 = 710.0 \pm 0.5$ ps for IX_S and IX_T emissions, respectively. These obtained radiative lifetimes of spin states of interlayer excitons at 90 K are almost three orders of magnitude larger than their dephasing times, indicating that radiative lifetime

contributions to the spectral linewidth are negligible, which will be covered in the next chapter[67]. Furthermore, TRPL measurements at 90 K yielded three orders of magnitude shorter recombination lifetime values than those obtained at 3.5 K. The observed trend can be explained by the potential suppression of non-radiative recombination channels at low temperatures[44], which results in prolonged lifetimes than those recorded at higher temperatures.

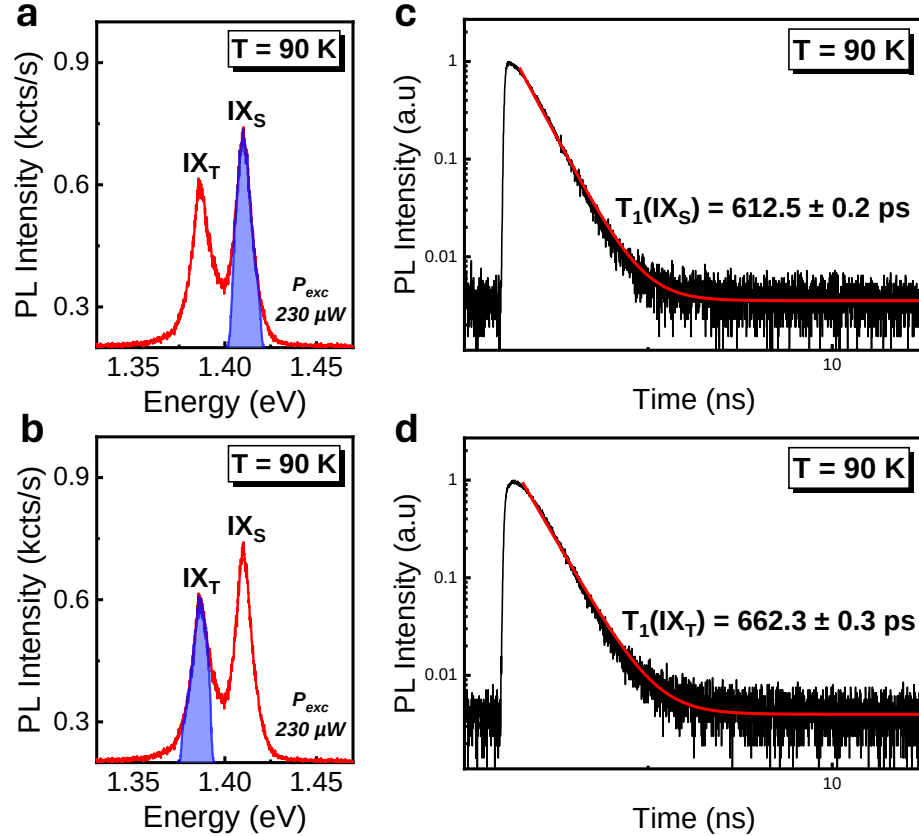


Figure 4.9: Time-resolved PL spectroscopy of spin-singlet and spin-triplet interlayer excitons of WSe₂-MoSe₂ heterobilayers. **a,b.** PL spectra of IX_T and IX_S at 90 K under 80-MHz pulsed laser excitation at 532 nm with an incident power of $P = 230 \mu\text{W}$. The filtered regions of the PL spectra are indicated with blue-colored regions. Hard-coated band-pass filters with wavelengths of 880 nm and 905 nm are used for filtering IX_S and IX_T, respectively. **c,d.** The TRPL intensity of IX_S and IX_T emissions as a function of delay time after pulsed excitation at 532 nm. A mono-exponential decay of the lifetime is indicated by the red-lined fit, yielding $T_1 = 612.5 \pm 0.2 \text{ ps}$ for IX_S and $T_1 = 662.3 \pm 0.3 \text{ ps}$ for IX_T.

4.7 Methods

The methodology of the experiments mentioned in this chapter will be explained in sub-sections as follows.

4.7.1 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a highly valuable technique for determining the properties of semiconductors, thus, an important tool in quantum photonics research[175]. One can employ it to determine the characteristic band gap of the material, together with information regarding impurities and defects within the crystal. Additionally, by utilizing the full-width half maximum (FWHM) of the collected PL spectrum, one can learn about the quality of the semiconducting crystal[176]. In our case, it can also provide details regarding the IX emissions and the quality of the heterostructures that were fabricated.

The general working principle of PL spectroscopy is simply stimulating and exciting the electrons in the valence band (i.e., the ground state) of the semiconducting material to its conduction band through photon absorption using a light source with satisfying energy (i.e., equal, or higher energy than its band gap or the excited state). The excited electrons leave holes in the valence band, resulting in the creation of electron-hole bound states, which are the excitons. Even while these electrons stay in the excited state for a time (the relaxation lifetime), they eventually revert to the ground state and emit photons that have an energy equivalent to the band gap or the energy difference between the excited and ground states of the material.

PL spectroscopy at room temperature is initially employed to analyze the TMDC monolayers and their heterostructures. After confirming the monolayer nature of the TMDC crystals through their PL emission wavelengths, they were vertically stacked to fabricate the heterostructures (details in Chapter 3). The

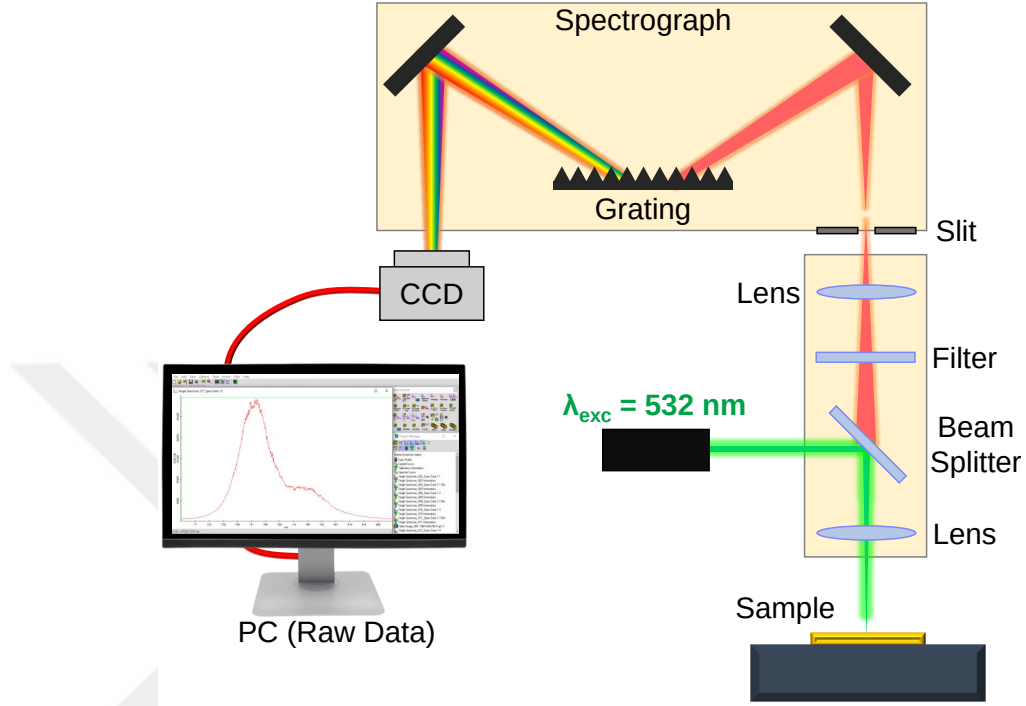


Figure 4.10: Room temperature near-field scanning optical and confocal Raman microscope. Schematic illustration of the Raman/PL setup that is used for the room temperature measurements. A 532 nm continuous wave laser is used as the excitation source. The PL/Raman spectra are collected with a cooled down (~ 213 K) CCD camera that is attached to the spectrograph. Obtained raw data are analyzed using a computer software.

room temperature characterizations were performed using the configuration depicted in **Fig. 4.10**. Using the optical microscope configuration of the setup, one can locate the sample to be studied before the characterization step begins. The PL measurements can be carried out once the sample area to be characterized has been located. In detail, a 532 nm CW laser was utilized as the excitation source, and the emission from the sample was collected using a spectrograph coupled to a CCD camera. The intralayer exciton emissions of the $\text{WSe}_2\text{-MoSe}_2$ heterobilayers were collected using 770 nm as the center wavelength of the PL spectrum and an integration time of 1 s was used (**Fig. 4.2a**). On the other hand, characterizations of IX emissions were carried out using 920 nm as the center wavelength and an integration time of 60 s. Based on my experiences, it should be mentioned that the PL spectrum at room temperature does not accurately predict the PL spectrum that will be observed at cryogenic temperatures.

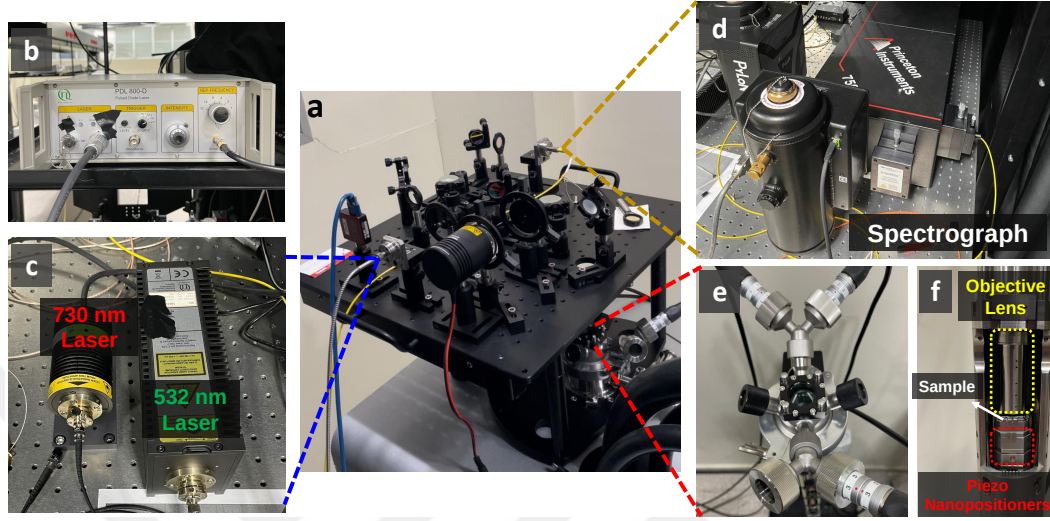


Figure 4.11: μ -PL setup and equipment details for cryogenic measurements. **a.** Image of the optical breadboard mounted on the close-cycle cryostat system. Through the use of flip mirrors, we can practically switch between two modes, which are the imaging and the measurement modes. **b.** PDL 800-D laser diode controller is used to adjust the lasing modes and pump powers of the lasers used for excitation. **c.** Picosecond laser diodes that can operate at 730 nm and 532 nm wavelengths under both CW and pulsed modes. The laser light was sent through the window (**e**) of the microscope stick to the samples mounted on the piezo nanopositioners (**f**). Following the excitation, the PL signals were collected through the low-temperature compatible microscope objective (0.82 NA), as indicated by the yellow-colored dashed lines. Using a single-mode fiber, the collected emission is sent to the spectrograph once it has been filtered using the proper optical filters based on the desired wavelength of the PL spectrum to be viewed. **d** The spectrograph with 750 mm focal length (Princeton Instrument SpectraPro HRS-750) along with a liquid nitrogen-cooled silicon CCD camera (PyLoN) that is used to record the emitted PL signals.

Following the room temperature PL studies, a close-cycle cryostat (attoDRY 1000) and a home-built μ -PL system (**Fig. 4.11**) were used for the low-temperature PL measurements. For the excitation, two distinct picosecond pulsed laser diodes operating at 532 nm and 730 nm (**Fig. 4.11c**), which can function in both CW and pulsed modes, were employed. The samples to be investigated were mounted on the piezo nanopositioners (**Fig. 4.11f**) of the microscope stick. Following a successful sample placement, the microscope stick was reinserted into the vacuum tube. To attain 3.5 K when we place the tube inside the cryostat,

there are a few steps we must perform before sealing the tube. Initially, the microscope stick has to be evacuated, and any water vapor or residual gas has to be removed from the vacuum tube. To meet this requirement, the internal pressure of the tube has to be regulated around $\sim 10^{-4}$ mbar, which can be done by using a turbo vacuum pump. Following this step, the tube should be purged and filled with liquid helium up to ~ 20 mbar, which ensures good thermal contact. Therefore, a base temperature of around 3.5 K can be achieved after inserting the tube into the cryostat. The cooling down duration of the base temperature of the tube takes around a few hours. Once it reaches around 3.5 K, one can begin their experiments. Using the nanopositioners, the samples and the heterostructure regions can be located in the imaging mode of the setup (**Fig 4.12**). After adjusting the laser pump power using the diode controller (**Fig. 4.11b**), it can be sent through the optical window (**Fig. 4.11e**) to the desired region of the sample. To collect the emitted light and record it, the configuration of the optical breadboard setup should be switched to the measurement mode (**Fig. 4.13**). The part that follows will provide an explanation of the details of these configurations.

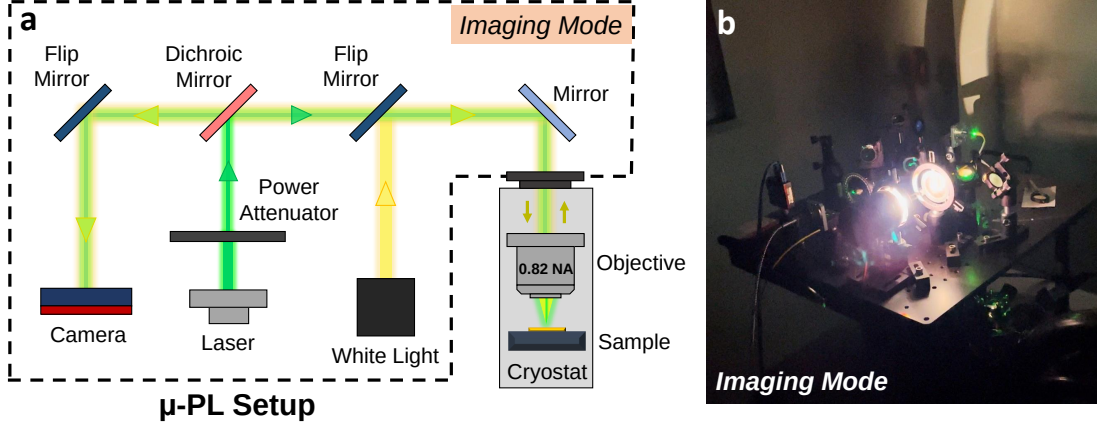


Figure 4.12: Imaging mode configuration of the μ -PL setup. **a.** Schematic illustration of the imaging mode of the setup showing the path of the laser and white light. **b.** Real-life picture of the imaging mode configuration of the μ -PL setup.

To locate the samples, and the heterobilayer regions, we first use the imaging mode configuration of the μ -PL setup, which is shown in **Fig 4.12**. The heterobilayers on the samples can be located using the piezo nanopositioners. The

reflected light from the sample surface is coupled to a CCD camera to image and target the desired region where the laser light would excite. In my experience, it is simpler to locate the heterobilayer regions by having a picture of the entire sample surface taken with 5X magnification on one hand while searching the samples with the nanopositioners. Furthermore, the laser light can be made to appear as a very tiny spot in the CCD camera image by reducing its power with the power attenuator. This makes it easier and more accurate to determine the part of the heterobilayer region that is intended to be stimulated. After everything is set, one can flip the flip mirrors and switch to the measurement mode configuration of the setup.

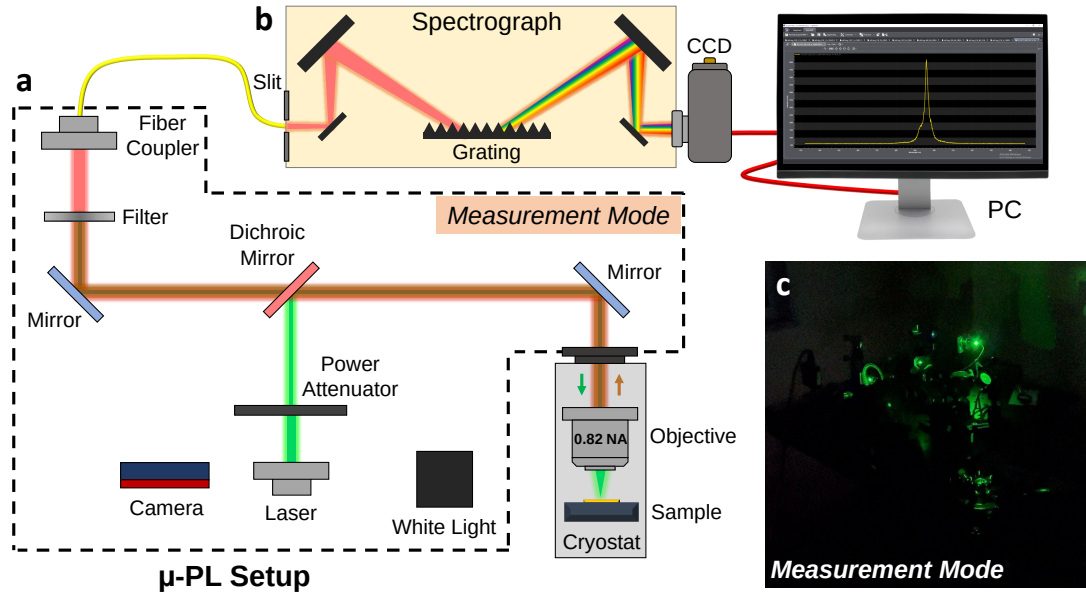


Figure 4.13: Measurement mode configuration of the μ -PL setup. **a.** Schematic illustration of the measurement mode of the setup showing the path of the laser and the emitted PL from the sample (red colored line). Before sending the light to the spectrograph through a single-mode fiber, the emission was filtered using optical filters. **b.** Schematic of the 750 mm focal length spectrograph (Princeton Instrument SpectraPro HRS-750) and the mounted liquid nitrogen-cooled silicon CCD camera (PyLoN). **c.** Real-life picture of the measurement mode configuration of the μ -PL setup.

The measurement mode configuration of the μ -PL setup is shown in **Fig. 4.13**. Initially, the samples were excited with a laser light. As mentioned, both the laser and emitted light go through the optic window (**Fig. 4.11e**) and a

low-temperature compatible microscope objective (**Fig. 4.11f**). Through mirrors, the collected PL signal was directed toward the fiber coupler. It should be noted that optical filters based on the intended wavelength for observation should be used to filter the PL emission before it enters the fiber. For the whole spectrum, a 550 nm long-pass filter (Thorlabs FEL0550) was used. Depending on the PL characteristics, 850 nm long-pass (Thorlabs FELH0850), 880 nm (Thorlabs FBH880), or 905 nm hard-coated (Thorlabs FBH905) band-pass filters were used to further filter the IXs and their spin states separately. After filtering, the emitted PL light can be sent to the spectrograph (**Fig. 4.11d** and **Fig. 4.13b**) through a single-mode fiber, and data can be recorded with the liquid nitrogen-cooled silicon CCD camera.

4.7.2 Magneto-PL Spectroscopy

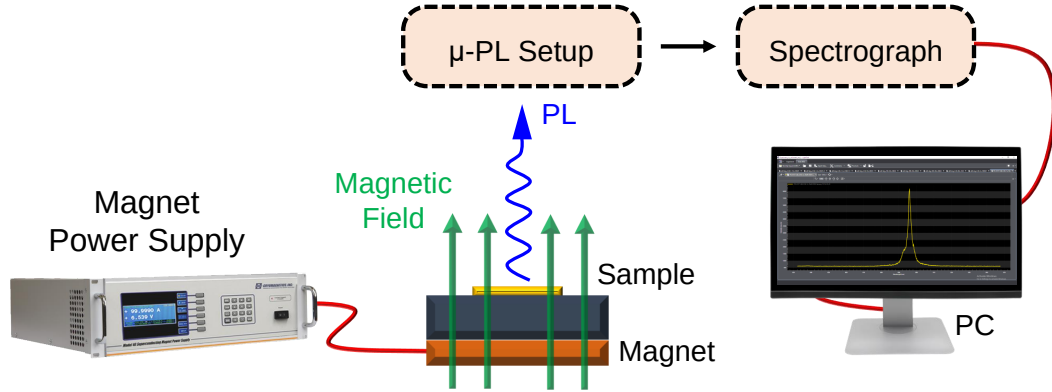


Figure 4.14: Magneto-PL spectroscopy setup. Schematic illustration of the magneto-PL measurement setup showing the applied magnetic field in Faraday geometry (i.e., applied field perpendicular to heterobilayer samples). Using the magnet power supply (Cryomagnetics APS 100), the applied field strength of the superconducting magnet can be controlled from 0 T up to 9 T. Data are recorded using the measurement mode shown in **Fig. 4.13**.

As mentioned in section 4.4, magneto-PL spectroscopy can be employed to observe the Zeeman splitting and extract the Landé g factors of the excitons. In our experiments, a built-in superconducting magnet (Cryomagnetics, 090-275-010-LCF) inside the close-cycle cryostat was used to apply the out-of-plane directed magnetic fields (i.e., Faraday geometry) from 0 T up to 9 T at 3.5

K. **Fig. 4.14** shows a schematic representation of the magneto-PL experimental setup. When employing the superconducting magnet, it is first necessary to switch on the hot plate and wait for a few minutes. Then, using the software of the cryostat equipment, the desired magnetic fields can be applied to the samples, and PL spectra in each can be recorded using the μ -PL setup (**Fig. 4.13**). Furthermore, controlling the pressures in the inner and outer vacuum chambers is necessary for the magneto-PL studies conducted at elevated sample temperatures. The turbo vacuum pump can be used to raise the chamber pressures to the necessary levels. The purpose of controlling the pressure in these chambers is to thermally decouple the magnet from the sample space. Thus, it is possible to prevent the superconducting magnet from being unintentionally quenched.

4.7.3 Temperature-Dependent PL Spectroscopy

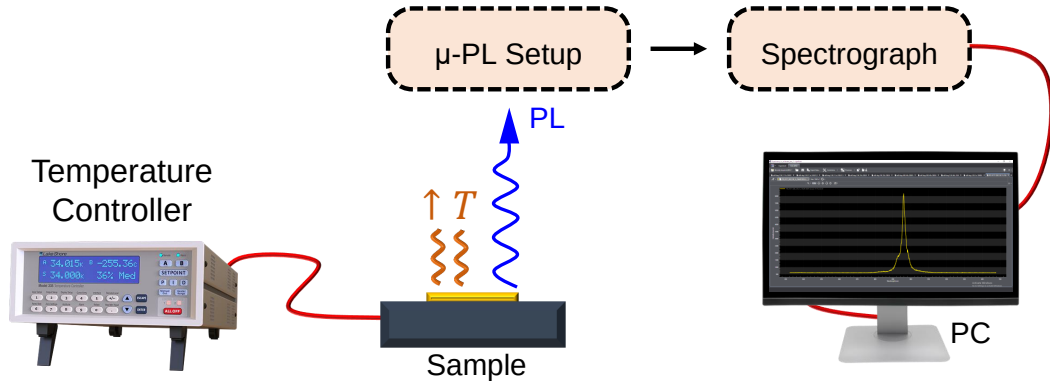


Figure 4.15: Temperature-dependent PL spectroscopy setup. Schematic illustration of the temperature-dependent PL measurement setup. Without requiring a change in pressure, the temperature of the sample can be regulated up to about 100 K using the temperature controller. Data are recorded using the measurement mode shown in **Fig. 4.13**.

The temperature-dependent PL measurements were done by using the μ -PL setup along with a cryogenic temperature controller (LakeShore 335). A schematic illustration of the setup is shown in **Fig. 4.15**. The controller was used to reach the predetermined temperature values, and PL data was recorded, similar to the magneto-PL studies. Up to around 100 K, the temperature of

the samples can be adjusted without requiring any adjustments to the internal pressure of the vacuum tube. However, higher temperatures require vacuuming the tube to an internal pressure of around 10^{-4} mbar, which can be done using the turbo vacuum pump. Following the adjustment, the samples can be heated to room temperature; however, it is crucial to remember that a further helium purge is required to bring the temperature back to 3.5 K.

4.7.4 Time-Resolved PL Spectroscopy

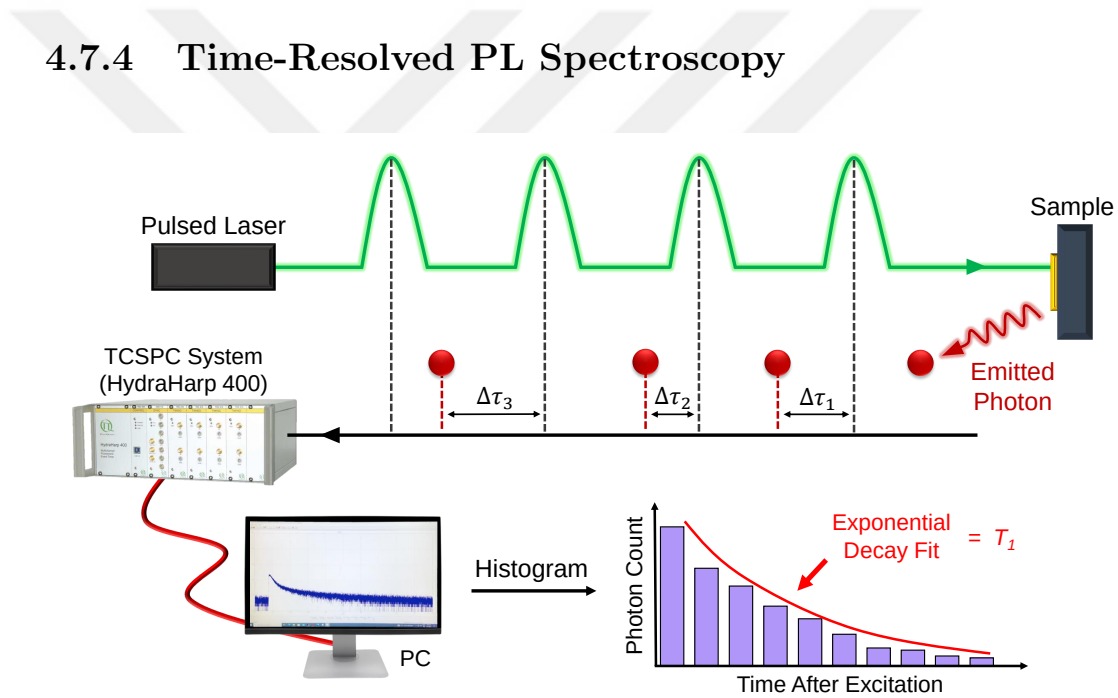


Figure 4.16: Time-resolved PL spectroscopy. Schematic illustration of the time-correlated single photon counting (TCSPC) method. Green lines represent the laser pulses hitting the sample. The emitted light from the sample in each pulse is depicted with red circles, whereas $\Delta\tau_n$ spacings indicate the relaxation time after each pulsed excitation. The emissions are sent to an avalanche photodiode (APD) that is coupled to the TCSPC system (PicoQuant HydraHarp 400) with a timer resolution of 50 ps. After recording the data, the photon counts are plotted as a function of relaxation time, which can be fitted with an exponential decay function.

Time-resolved PL (TRPL) spectroscopy can be used to directly measure the recombination lifetime of the IXs. Performing it can be divided into two parts. **Fig. 4.16** depicts a schematic of the concept of a lifetime measurement. Initially, the μ -PL setup has to be utilized with a laser diode that operates in the pulsed

mode to collect the IX emission in light pulses. Then, using the time-correlated single photon counting (TCSPC) method the time interval between the excitation pulse and the emitted light can be measured. In detail, a timer initiates when the sample is exposed to pulsed laser stimulation, which produces the emission. The emission is then directly delivered to a silicon avalanche photodiode (APD) via a single-mode fiber, and the timer stops when the light emission is detected. Using the TCSPC instrument HydraHarp 400 with a time resolution of 50 ps, these time intervals after each pulse hit can be recorded, and this process is repeated numerous times. From there, a histogram plot displaying the photon count as a function of time interval can be generated. Keep in mind that the duration of the experiment may vary depending on the quantity of photons that the APD detects. The lifetime (T_1) of the emitted light (IX emissions in our case) could be determined by fitting the histogram plot using an exponential decay function as shown in the figure.

Chapter 5

Dephasing Time Studies of Interlayer Excitons in TMDC Heterobilayers

This chapter will focus on the dephasing time studies of the interlayer excitons formed in hBN-encapsulated WSe₂-MoSe₂ heterobilayers. The explanations, discussions, and figures shown in this chapter are from the results of our publications:

1. **Durmuş, M. A.**, Demiralay, K., Khan, M. M., Atalay, Ş. E. & Sarpkaya, I. Prolonged Dephasing Time of Ensemble of Moiré-Trapped Interlayer Excitons in WSe₂-MoSe₂ Heterobilayers. *Npj 2D Mater. Appl.* 7, 65 (2023).
2. **Durmuş, M. A.** & Sarpkaya, I. Quantum Beats Between Spin-Singlet and Spin-Triplet Interlayer Exciton Transitions in WSe₂-MoSe₂ Heterobilayers. *Nano Letters*. 24, 5767–5773 (2024).

5.1 Coherence & First-Order Correlation Function

Coherence can simply be defined as the physical phenomenon that describes the stability of light. Given that it directly affects quantum operations, it is an essential characteristic aspect to be considered. For optoelectronic devices, decoherence (dephasing) time is a crucial parameter since it defines the time interval in which light can coherently influence electrons or quasiparticles. The significance of decoherence time for quantum applications can be elaborated upon by identifying the specific effects that impact different applications. In detail, it directly influences the stability of the qubits[177] (quantum computing), establishes the dependable transmission range and efficiency of the quantum information[178] (quantum communication & network), and has an impact on the accuracy and sensitivity of quantum measurements[179, 180] (quantum metrology). In a nutshell, it can be stated that comprehending and increasing coherence time has a direct impact on quantum research to fully realize the potential of quantum technologies in a variety of applications.

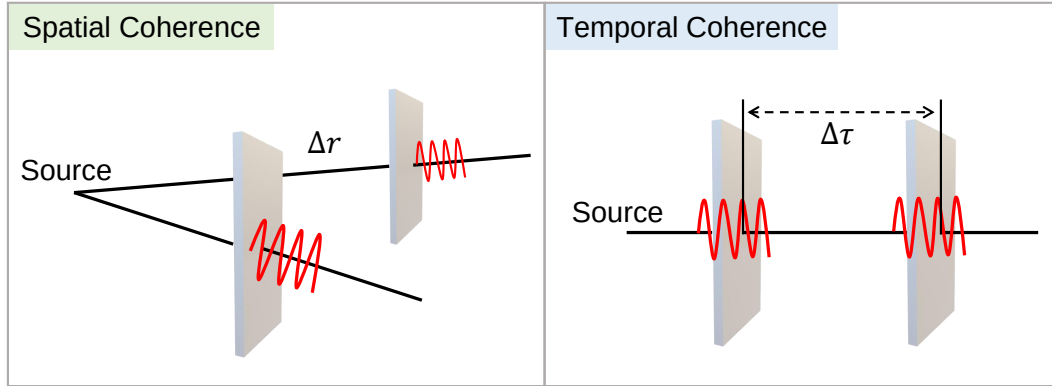


Figure 5.1: Types of coherence. Schematic illustration of spatial and temporal coherence. Differences in length and time are denoted as Δr and $\Delta \tau$, respectively.

Coherence can be broadly classified as spatial (transverse) and temporal (longitudinal) coherence. The main distinction between the two is that the former refers to the correlation between waves at different points in space, while the

latter describes the correlation between waves that are observed at different moments in time[181], as illustrated in **Fig. 5.1**. The discussion that follows will center on the temporal coherence, which is the main emphasis of this chapter.

The coherence (dephasing) time T_2 , or the amount of time over which the phase of a wave train is steady, can be used for determining the temporal coherence of a light beam. In other words, it displays the time duration at which the phase of an excitonic transition is conserved. The first-order correlation function (or degree of first-order coherence) $g^{(1)}(\tau)$, which can be defined as follows, provides a more precise quantification of temporal coherence.

$$g^{(1)}(\tau) = \frac{\langle \varepsilon^*(t)\varepsilon(t+\tau) \rangle}{\langle |\varepsilon(t)|^2 \rangle} \quad (5.1)$$

Here, $\varepsilon(t)$ denotes the input field, $\langle \dots \rangle$ denotes taking the average, t denotes time, and τ denotes delayed time. In the case of a quasi-monochromatic input wave with a center frequency of ω_0 , one can see that the real part of $g^{(1)}(\tau)$ is an oscillatory function of τ with a period of $2\pi/\omega_0$ [181]. Through these rapid oscillations, one can obtain fringe patterns in interference experiments. Furthermore, a light can be considered to be perfectly coherent if it exhibits $|g^{(1)}(\tau)| = 1$ for every value of the delayed time τ , which implies infinite coherence time and length[181]. The monochromatic light produced by a laser operating in a single longitudinal mode is the most authentic real-world example of perfectly coherent light. In the case of a partially coherent light with a Lorentzian shape the real part of $g^{(1)}(\tau)$ takes the form of:

$$g^{(1)}(\tau) = \exp(-\frac{|\tau|}{T_2}) \quad (5.2)$$

Whereas the corresponding expression for a Gaussian-shaped one can be written as:

$$g^{(1)}(\tau) = \exp(-\tau^2 / (\frac{T_2}{\sqrt{\pi/2}})^2) \quad (5.3)$$

Using a Michelson interferometer, one can experimentally record the oscillations of the real part of the first-order correlation function $g^{(1)}(\tau)$, producing an interferogram with visible fringes that decay in accordance with the light's dephasing time. The visibility of the obtained fringes from an interference experiment can be calculated with the relation:

$$V(\tau) = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} \quad (5.4)$$

where I_{max} and I_{min} are the fringe maxima and minima extracted from distinct fringe patterns at varying delay times. Through the expression, one can easily see that the visibility of a light is determined by its coherence time. Therefore, it is possible to establish a relationship between visibility and the first-order correlation function, which can be expressed as:

$$V(\tau) = \exp\left(-\frac{|\tau|}{T_2}\right) = g^{(1)}(\tau) \quad (5.5)$$

To derive an expression for the relationship between delay time (τ) and path length difference (ΔL), one can assume that the beam-splitter (BS) in the Michelson interferometer has a direct 50:50 power splitting ratio with no errors and a phase shift ($\Delta\phi$) that is equal to π (i.e., energy conversion at BS). Therefore, a direct relation between τ and ΔL can be written as:

$$\tau = \frac{2\Delta L}{c} \quad (5.6)$$

Here, ΔL is multiplied by two because the light travels a doubled path length due to its back-and-forth motion between the retro mirrors and the beam-splitter. We have calculated the x-axis delay time values in the interferometric measurements in our studies utilizing this relation.

5.2 Michelson Interferometer

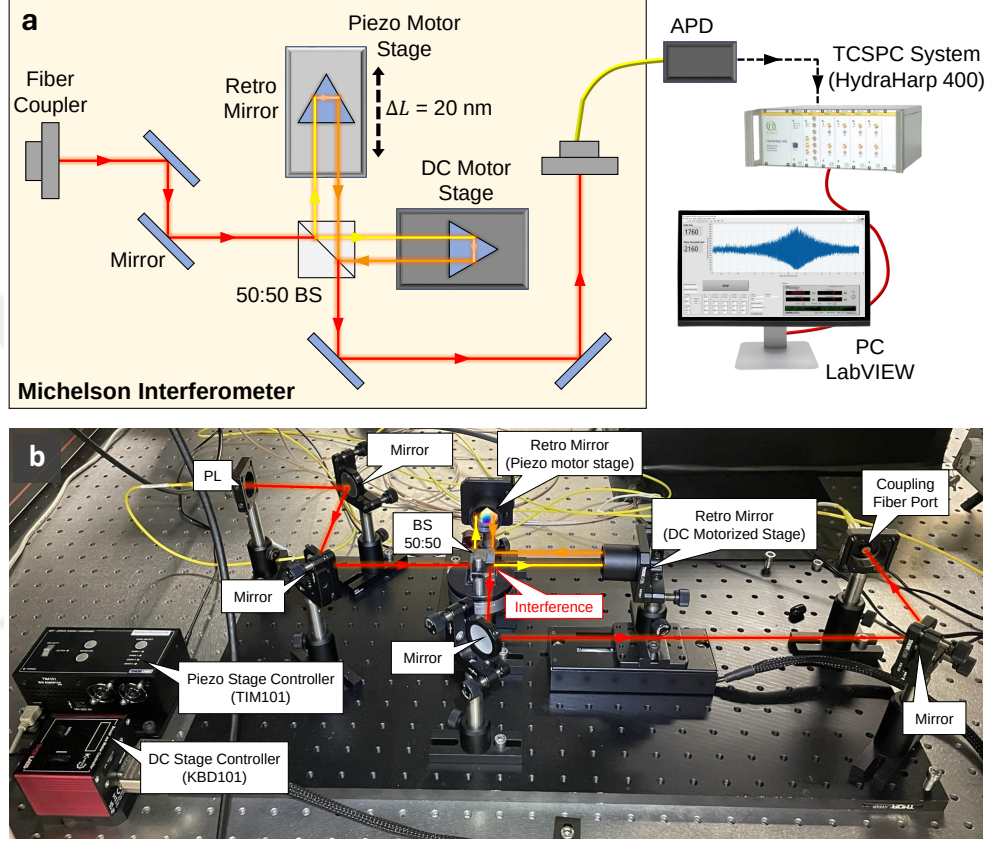


Figure 5.2: Home-built free-space Michelson interferometer. a,b. Schematic (a) and real-life (b) images of the Michelson interferometer setup. The path of the light that is sent into the interferometer is depicted by the solid red line. Yellow lines show the course of the light after hitting the 50:50 BS, and orange lines show the path after it gets reflected off the retro mirror arms. Following the interference, the light is directed to a fiber-coupler and sent through a silicon APD via a single-mode fiber. Data are recorded using a PicoQuant Hydraharp 400 together with a LabVIEW program.

To measure the exciton dephasing times (T_2) in the time domain, we have conducted a home-built free-space Michelson interferometer that consists of a 50:50 BS and two movable retroreflector arms. Each arm consisted of different motorized stages with mounted retro mirrors, which could be controlled with a LabVIEW program through appropriate control boxes (Thorlabs KBD101 and TIM101). More specifically, the interferometer consisted of one retro mirror mounted on a DC motorized stage (Thorlabs DDS050) with a step size of $5 \mu\text{m}$

and another one on the piezo motor stage (Thorlabs PIA13) with a step size of 20 mm. Due to its capability of resolving the fringes, first-order correlation function $g^{(1)}(\tau)$ measurements were performed using the piezo stage. In each step, the corresponding PL intensity was recorded using the PicoQuant HydraHarp 400 together with a silicon avalanche photodiode (APD) through a photon time resolution of 50 ps. The schematic and real-life images of our home-built free-space Michelson interferometer are shown in **Figs. 5.2a** and **5.2b**, respectively.

Note that improper alignment of the interferometer setup could lead to a decay in the visibility of the fringes of the interferogram, which can lead to misleading results in the experiments. To properly align the retro mirrors, one can use laser light, and check to see if there is any decay in the visibility of the fringes. The extremely coherent laser light produces an almost decay-free interferogram (with coherence lengths up to meters), allowing the alignment of the setup to be examined. Stated differently, an alignment issue can be identified if there is a decay in the PL interferogram that was acquired during the laser-based interferometric experiments. By employing laser light, we successfully aligned our setup and attained a fringe contrast of around 95% at time zero (i.e., the point where the distances of the retro mirrors to the beam splitter are equal). The next step was to check the accuracy of the interferograms in the measurements taken. An easy way to accomplish this was to compare our interferometric measurement results of the excitons from our own MoSe₂ monolayers with those from earlier studies. Through this approach, we were able to confirm the accuracy of the LabVIEW program and setup alignment. The upcoming section will include specifics regarding these experiments on monolayer MoSe₂.

5.3 Dephasing Time Studies of Exciton Species in Monolayer MoSe₂

Both the Michelson interferometer[182] and the four-wave mixing method[183–185] have been used in earlier research on the dephasing time studies of monolayer

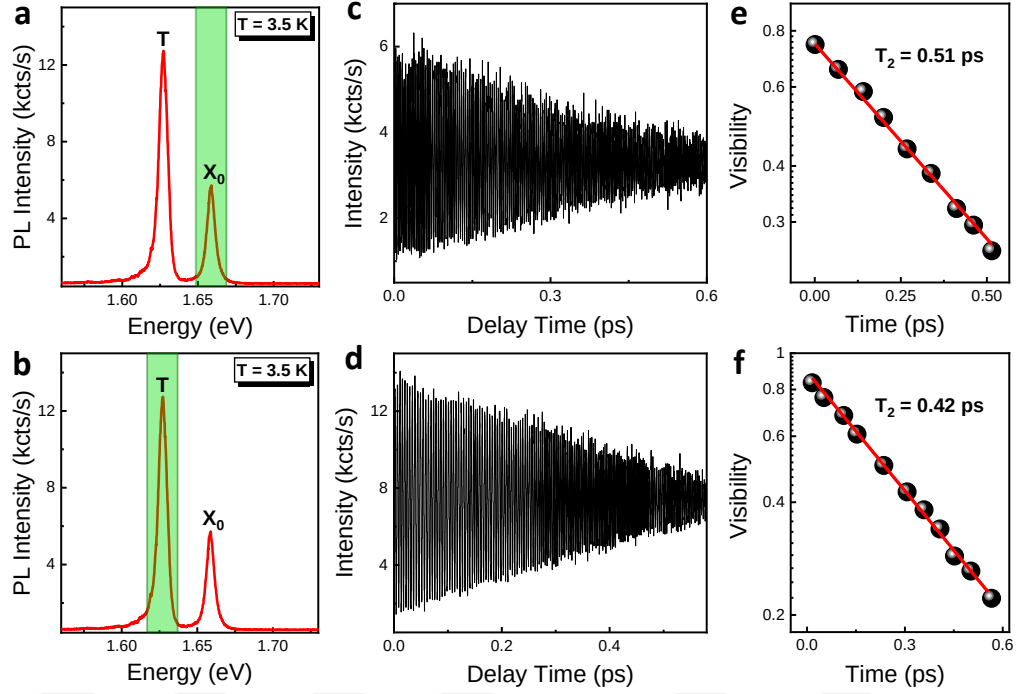


Figure 5.3: Dephasing time measurements of exciton species of a MoSe₂ monolayer using a Michelson interferometer. **a,b.** Filtered PL spectra of the neutral exciton (**a**) and trion (**b**) of the MoSe₂ monolayer recorded with a 532 nm CW laser excitation under 50 μ W pump power at 3.5 K. The filtered part of the spectrum that was sent to the Michelson interferometer is shown with green boxes in both figures. **c,d.** Corresponding PL interferogram of the first-order correlation function $g^{(1)}(\tau)$ of the neutral exciton (**c**) and trion (**d**) of the MoSe₂ monolayer. **e,f.** The fringe visibilities as a function of the delay time in a semilog plot for neutral exciton (**e**) and trion (**f**). They both show a mono-exponential decay, which is fitted with Eq. 5.2, resulting in dephasing time values of $T_2 = 0.51$ ps and $T_2 = 0.42$ ps for neutral exciton and trion, respectively.

MoSe₂. Considering the findings of these investigations, particularly those conducted with the Michelson interferometer, we performed both fine-tuning of the LabVIEW software program and verification of the data that we acquired from our interferometer setup. **Fig. 5.3** displays our findings for the trion (T) and neutral exciton (X₀) dephasing times from our MoSe₂ monolayer at 3.5 K. The spectrally filtered (green-colored boxes) PL spectra of the neutral exciton and trion at 3.5 K are displayed in **Figs. 5.3a** and **5.3b**, respectively. The corresponding PL interferograms of the first-order correlation function $g^{(1)}(\tau)$ function and the resulting visibility decay of them are shown in **Figs. 5.3c** and **5.3d**. The

resulting visibility decays that are shown in a semilog plot in **Figs. 5.3e** and **5.3f**, were fitted using the Lorentzian $g^{(1)}(\tau)$ (Eq. 5.2), yielding dephasing times of $T_2 = 0.51$ ps and $T_2 = 0.42$ ps for X_0 and T, respectively.

5.4 Prolonged Dephasing Time of Ensemble of Moiré-trapped Interlayer Excitons in WSe₂-MoSe₂ Heterobilayers

As discussed in Chapter 4, the photophysics of IXs are significantly impacted by Moiré superlattices formed in TMDC heterostructures. Recent transport studies have demonstrated that Moiré potentials have a significant impact on the diffusion properties of IXs of TMDC heterostructures[36, 42]. Nevertheless, the impact of such intrinsic localization mechanisms on the IX dephasing characteristics of WSe₂-MoSe₂ heterobilayers has remained unclear up to this point.

To study the coherence properties of IXs in the time domain, we have fabricated hBN-encapsulated WSe₂-MoSe₂ heterobilayers with a nearly 0° or 60° twist angle (details in Chapter 3). Upon determining the localization features and performing PL characterizations of the IXs (details in Chapter 4), we sent their PL emissions to our Michelson interferometer. It is noteworthy to mention here that interferometric measurements require the maximum number of photons possible to acquire a clear PL interferogram of the emission. Therefore, in both the delocalized and Moiré-localized scenarios, we conducted our measurements with their ensemble band at moderate pump powers (**Fig. 4.3**) with the objective of obtaining clear interferograms.

Fig. 5.4 displays the outcomes of the dephasing time measurements for the ensemble of delocalized and the ensemble of Moiré-localized IXs[43]. **Fig. 5.4a** shows a well-defined interferogram of a light example obtained from the IXs of a WSe₂-MoSe₂ heterobilayer (HS1), together with a right panel that highlights the strong fringe contrast around time zero. Using the visibility relation (Eq.

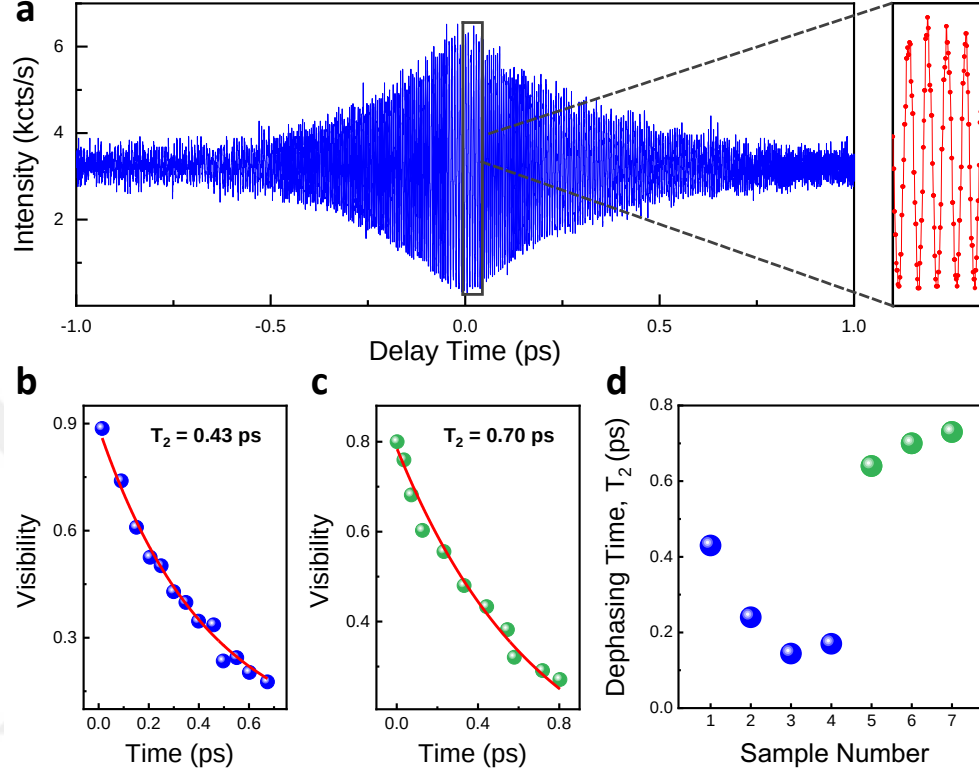


Figure 5.4: Dephasing time studies on interlayer excitons of WSe₂-MoSe₂ heterobilayers using a Michelson interferometer. **a.** Interferogram of the first-order correlation function $g^{(1)}(\tau)$ of the IXs of HS1, where the right panel displays the pronounced fringe contrast near zero delay time. **b,c.** Plots of the fringe visibilities as a function of delay time for the delocalized (**b**) and Moiré-localized (**c**) IX emissions of the WSe₂-MoSe₂ heterobilayers (HS1 and HS6). **d.** Overview plot showing the comparison between the dephasing time values of the ensemble of delocalized and the ensemble of Moiré-localized IXs. The longest dephasing time is recorded as $T_2 = 0.73$ ps (HS7). Data are recorded at 3.5 K.

5.4), one can estimate the visibility of fringes at various times, which can be fit mono-exponentially with the expression Eq. 5.5 as shown in **Figs. 5.4b** and **5.4c**. Our results from the ensemble band of both scenarios are displayed as an overview graph shown in **Fig. 5.4d**, where blue and green circles represent the dephasing time values of the ensemble of delocalized and the ensemble of Moiré-localized IXs, respectively. The dephasing time results (160 fs to 430 fs) for the ensemble of delocalized IXs (HS1-HS4) are in excellent agreement with those that were previously measured[186]. As can be seen in **Fig. 5.4d**, our dephasing time values in the ensemble of Moiré-localized IXs case (HS5-HS7)

are nearly two to almost five times longer than the values we obtained from the delocalized ones. Meanwhile, they are more than two times prolonged compared to the previously reported T_2 values of ~ 300 fs[186]. The results of the prolonged dephasing times strongly indicate that the IX-IX[187] and IX-low energy acoustic phonon scattering[186] dephasing mechanisms are suppressed by the presence of Moiré localization potentials within the WSe₂-MoSe₂ heterobilayer samples (HS5-HS7). Prior research on the impact of spatial localization on exciton dephasing characteristics also found a comparable outcome for the positively charged trion (X^+) of monolayer MoSe₂[182].

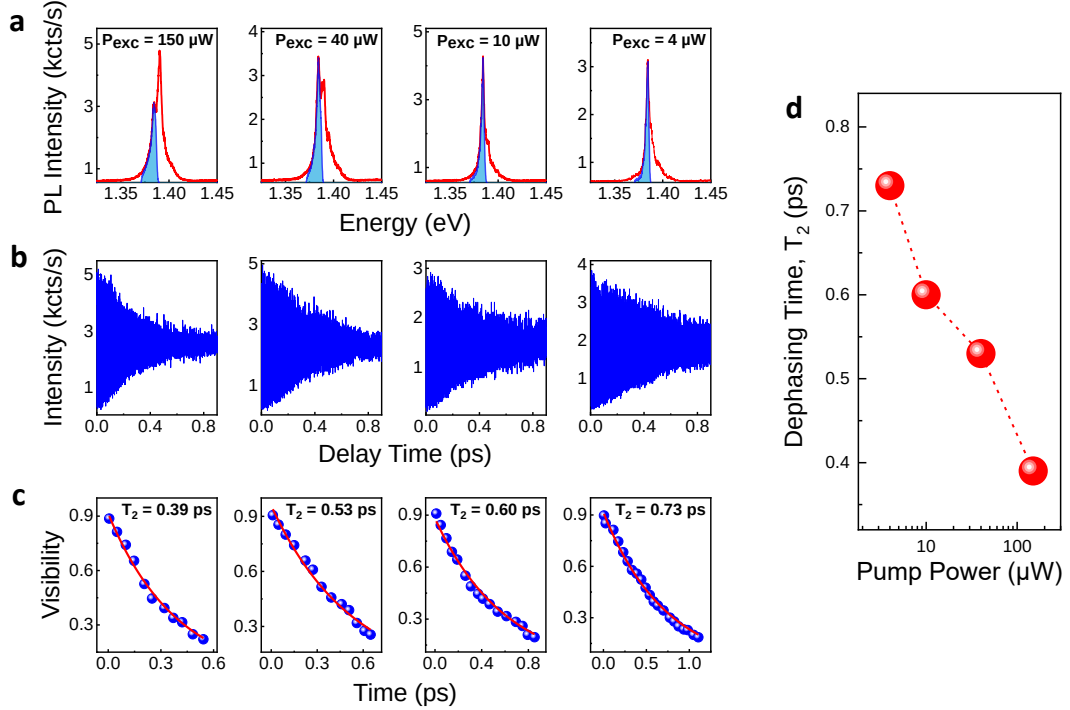


Figure 5.5: Pump power-dependent dephasing time studies on Moiré-localized interlayer excitons of WSe₂-MoSe₂ heterobilayers. **a.** PL spectra of the ensemble of Moiré-localized IXs under various pump powers. Blue regions indicate the spectrally filtered parts of the PL spectra. **b.** Corresponding PL interferogram of the first-order correlation functions $g^{(1)}(\tau)$ obtained by sending the filtered emissions to the Michelson interferometer. **c.** Plots of the fringe visibilities as a function of delay time for the Moiré-localized IXs under each pump power. The red lines in each plot indicate the fit that yields the values of T_2 , and they display a mono-exponential decay. **d.** Overview plot of the dephasing time of the Moiré-localized IXs of our WSe₂-MoSe₂ heterobilayer sample (HS7) as a function of pump power. Data are recorded at 3.5 K.

To further understand the dephasing mechanism of Moiré-localized IXs in our WSe₂-MoSe₂ heterobilayers, we conducted pump power-dependent interferometric measurements as displayed in **Fig. 5.5**. We tried to obtain reliable PL interferograms by working our way down from the high pump powers to lowest pump power as possible. However, because of the weak PL signal of the single or few Moiré-localized IXs, definitive T₂ measurements could not be performed below 1 μW pump power. The findings presented in **Fig. 5.5d** demonstrate that the dephasing time increases as the excitation pump power decreases, suggesting that ultra-long dephasing times could be expected if the measurements are performed in the very low pump power regime with the narrow PL emission line of a single Moiré-localized IX. Additionally, these results indicate that the primary dephasing mechanism for the studied IXs in our WSe₂-MoSe₂ heterobilayers is the pump power-induced IX-IX scattering.

One can gain a deeper understanding of the impact of localization on the dephasing time of IXs by calculating the energy difference (ΔE) between the experimental and theoretical spectral linewidth values. Fitting the PL emissions with a Gaussian or Lorentzian (in our case) fit will yield the experimental linewidth values. Theoretical spectral linewidth values, on the other hand, can be calculated (for the Lorentzian PL case) using the recombination lifetime (T₁) and dephasing time (T₂) using the well-known relation[188]:

$$\Gamma = \frac{\hbar}{T_1} + \frac{2\hbar}{T_2} \quad (5.7)$$

Theoretical values of the spectral linewidth of each IX emission from different samples (HS1-HS7) were calculated by applying the recombination lifetime (**Fig. 4.8**) and dephasing time (**Fig. 5.4**) values to this expression. One can see from the indicated figures that the recombination lifetime values (~ns) are almost three orders of magnitude higher than the dephasing time values (~ps). The influence of T₂ on the spectral linewidth would predominate over the effect of T₁ if both were applied to the expression. Consequently, by ignoring the impact of a lifetime on spectral linewidth, Eq. 5.7 can be made simpler as follows:

$$\Gamma \sim \frac{2\hbar}{T_2} \quad (5.8)$$

Ultimately, by using the theoretical and experimental spectral linewidth values, the energy difference between them can be calculated. **Fig. 5.6** shows ΔE values of the IXs of our WSe₂-MoSe₂ heterobilayers. As it shows, the Moiré-localized IXs (green diamonds) have substantially smaller ΔE values than the delocalized ones (blue diamonds). In detail, the Moiré-localized ones yielded a minimum ΔE value of 0.9 meV, while the delocalized ones yielded a maximum ΔE value of 17 meV. The smaller ΔE values observed when the IXs are intrinsically localized indicate a significant suppression of the inhomogeneous linewidth broadening contribution resulting from both the strong repulsive IX-IX scattering and the charge fluctuations near the emitter[187].

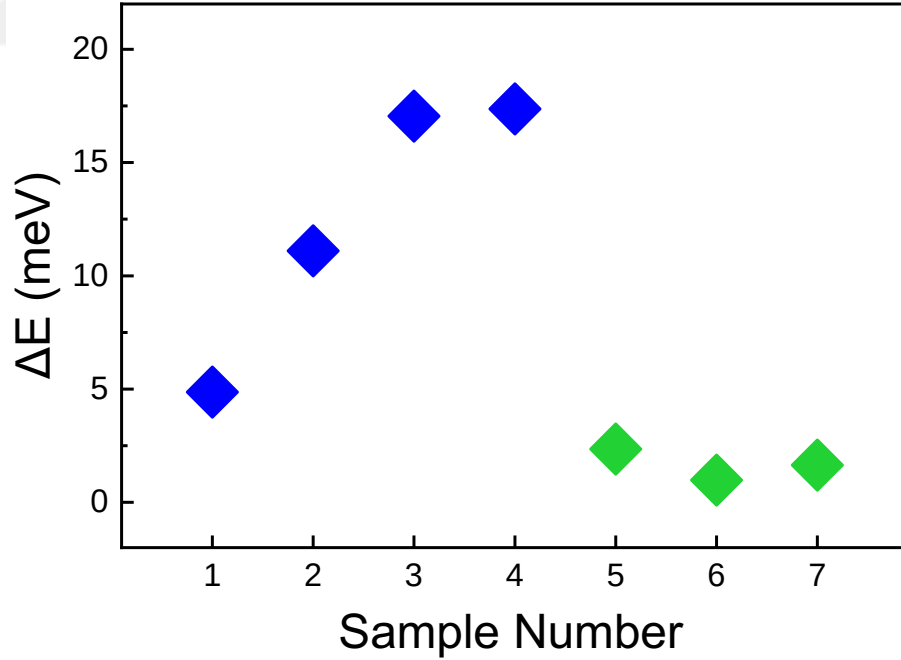


Figure 5.6: Spectral linewidth investigations of interlayer excitons of WSe₂-MoSe₂ heterobilayers. The energy difference (ΔE) between the spectral linewidth obtained from PL spectra and calculated from the measured recombination lifetime (T_1) and dephasing time (T_2) data shown in **Figs. 4.8** and **5.5**, respectively. Blue and green diamonds represent delocalized and Moiré-localized IXs, respectively.

In summary, we demonstrated in this paper[43] that intrinsic localization of IXs to the Moiré potentials could lead to prolonger dephasing times. The dephasing time values of our Moiré-localized IXs are two to almost fivefold longer than our delocalized ones (**Fig. 5.6**), and they are more than twofold longer than the T_2 values of ~ 300 fs that have been previously reported[186]. We attribute this enhancement to the suppression of the dephasing mechanisms (i.e., IX-IX and low-energy IX-acoustic photon interactions) discussed earlier, and based on this, one can highlight the fact that an interferometric measurement from a single Moiré-localized IX can yield ultra-long dephasing times. Overall, our investigation on the impact of Moiré superlattices on the IX dephasing times can provide insights into the future directions of 2D material-based nanolasers[68] and quantum information science applications.

5.5 Quantum Beats Between Spin-singlet and Spin-triplet Interlayer Exciton Transitions in WSe₂-MoSe₂ Heterobilayers

The PL characterizations of the spin states of the IXs of WSe₂-MoSe₂ heterobilayers were discussed in Chapter 4. This part of the thesis will be devoted to our research on quantum beating that results from the interaction between IX_S and IX_T emissions, as well as their dephasing times.

The Quantum beating phenomenon can be explained as the behavior of intensity oscillations of a light that is emitted from a system with the coherent superposition of two excited states[189]. The presence and the nature of the interaction between these excited states, if there is one, can be revealed by employing quantum beat spectroscopy[190]. Previous studies have been conducted using this method for the closely spaced different transitions of various material platforms, such as quantum dots[191], quantum wells[192–196], monolayers of 2D TMDCs[182, 183, 185], and ReS₂[197]. Moreover, the coherent coupling between the intralayer excitons of the MoSe₂ and WSe₂ monolayers in a WSe₂-MoSe₂

heterobilayer has also been shown in a recent work[198]. Up to our study, the interaction between the spin states of IXs of TMDC heterobilayers has remained unknown. In this study, we studied and showed the coherent coupling between IX_S and IX_T emissions of WSe_2 - $MoSe_2$ heterobilayers by employing quantum beat spectroscopy using a home-built free-space Michelson interferometer. In our case, these mentioned excited superposition states are the spin states of IXs, and their coupled state is denoted by the symbol IX_{S-T} in the following discussions.

It should be remembered that if two separate (uncoupled) two-level systems with almost equal transition energies are coupled in interferometric measurements, one can also observe a beat pattern in the time domain as well. In this scenario, the oscillations (beats) are created due to the interfering polarizations of the two-level systems, which is referred to as polarization interference. In our case, the coupling between the spin states of the IXs of WSe_2 - $MoSe_2$ heterobilayers can be explained with the four-level diamond system (i.e., an extension of the V-type three-level system)[190]. Here, the quantum beating interference is created through the quantum mechanical coupling between the closely separated transitions. Moreover, it is important to note that distinguishing between quantum beat and polarization interference is almost impossible by using linear optical techniques if the nature of the system of the emitted light is unknown.

As previously stated, the conduction band splitting of the $MoSe_2$ layer is the primary cause of the formation of the two spin states of the IXs of WSe_2 - $MoSe_2$ heterobilayers. **Fig. 5.7a** depicts a typical type-II band alignment of the heterobilayer along with the formation of the IX_S and IX_T states. Since both spin states derive their holes from the same valance band, it is evident that they share a single ground state. The diamond system that explains the coupling between our spin states contains two excited states (IX_T and IX_S), a coupled state (IX_{S-T}), and one common ground state (G), as schematically illustrated in **Fig. 5.7b**. Furthermore, for the best resolution and interference contrast of the quantum beats in the interferometric measurements, the PL intensities of the excited states should be nearly equal. If not, there will be a resolution drop where the beats become less visible. Therefore, we conducted our experiments at 90 K, where the IX_S and IX_T emissions have nearly equal intensities (**Fig. 4.6**).

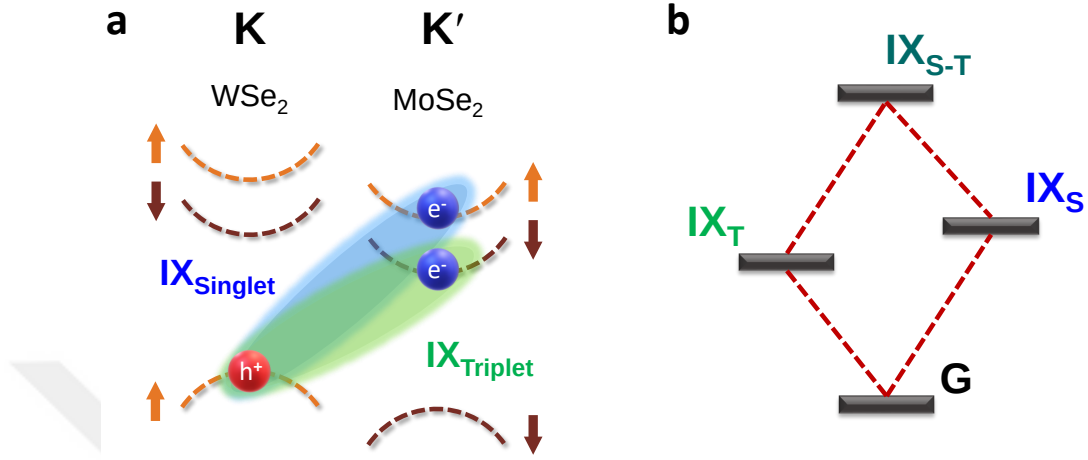


Figure 5.7: Spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers. **a.** Schematic illustration of the staggered type-II band alignment of the WSe₂-MoSe₂ heterobilayer, displaying the formation of spin-singlet (blue region) and spin-triplet (green region) IXs. Spin-up and spin-down configurations are represented with orange- and blue-colored arrows, respectively. **b.** The four-level diamond system showing the coherent coupling between the two spin states of the IXs.

Before studying the coherent coupling between the IXs' spin states, we examined each one of their dephasing properties separately. They were spectrally filtered with 10 nm bandpass filters before being introduced into the interferometer. The filtered PL spectra (blue-colored regions) of the spin states at 90 K are displayed in **Figs. 5.8a** and **5.8b**, respectively. They exhibit inhomogeneous broadening and a deviation from a Lorentzian fit towards a Gaussian fit. Moreover, their corresponding PL interferograms are shown in **Figs. 5.8c** and **5.8d**, which were gathered using our home-built Michelson interferometer. As explained in the last section, one can calculate the fringe visibilities at various delay times using Eq. 5.4 and plot the results in a semilog plot as a function of delay time as shown in **Figs. 5.8e** and **5.8f**. In contrast to our previous work[43], one can easily observe through the initial kicks in both figures (around 150 fs) that they deviate from a mono-exponential decay. Thus, a Gaussian first-order correlation function $g^{(1)}(\tau)$ as expressed in Eq. 5.3 can be used to describe the decay dynamics of IX_S and IX_T emissions. Fitting the fringe visibilities with this expression results in dephasing times of $T_2 = 0.535$ ps and $T_2 = 0.575$ ps for IX_S and IX_T, respectively.

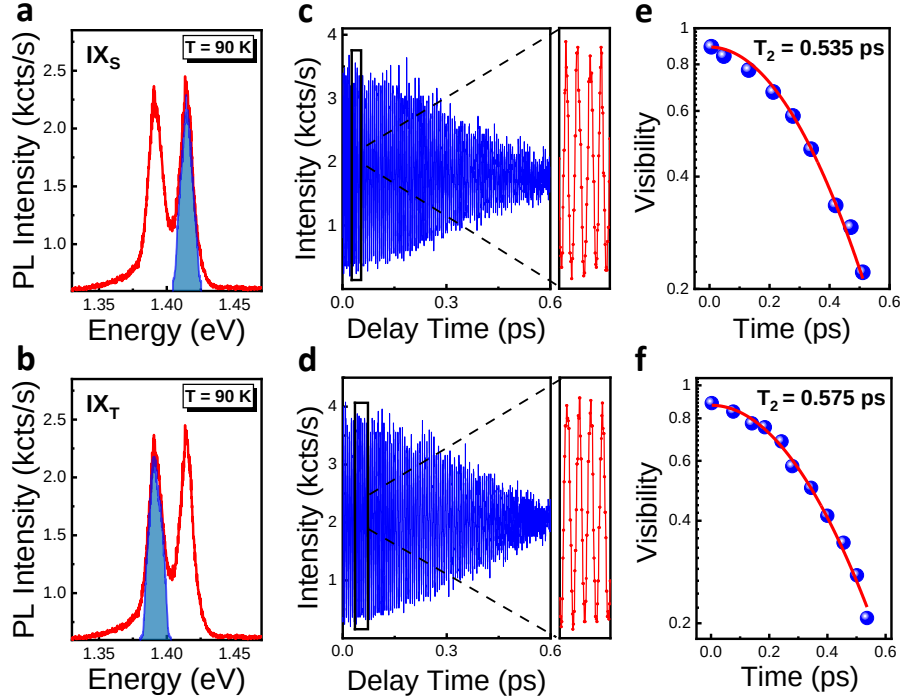


Figure 5.8: Dephasing time studies of the spin states of interlayer excitons of $\text{WSe}_2\text{-MoSe}_2$ heterobilayers. **a,b.** Spectrally filtered PL spectra of spin-singlet (**a**) and spin-triplet (**b**) IXs taken with a 532 nm CW laser excitation under $400\ \mu\text{W}$ pump power at 90 K. Blue-colored areas within the whole spectrum indicate the filtered PL that is sent to the Michelson interferometer. **c,d.** The corresponding PL interferograms of the first-order correlation functions $g^{(1)}(\tau)$ of the filtered PL spectra of spin-singlet (**c**) and spin-triplet (**d**) IXs. **e,f.** The fringe visibilities as a function of delay time for spin-singlet (**e**) and spin-triplet (**f**) IXs, which strongly deviates from a monoexponential decay, showing an inhomogeneous decay that corresponds to a Gaussian fit of $g^{(1)}(\tau) = \exp(-\tau^2/(\frac{T_2}{\sqrt{\pi/2}})^2)$.

After studying the dephasing characteristics of IX spin states individually, we next studied the coherent interaction between them by sending both emissions to the interferometer simultaneously. The PL spectrum of the two spin states of the IXs of a $\text{WSe}_2\text{-MoSe}_2$ heterobilayer sample is shown in **Fig. 5.9a**. With three visible beats before going out of phase, the resultant PL interferogram in **Fig. 5.9b** displays the quantum beat pattern, a hallmark of coherent coupling. One can fit the beat envelope using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$ to determine the dephasing time of the coupled state $\text{IX}_{\text{S,T}}$, which yields $T_2 = 0.29 \pm 0.05$ ps.

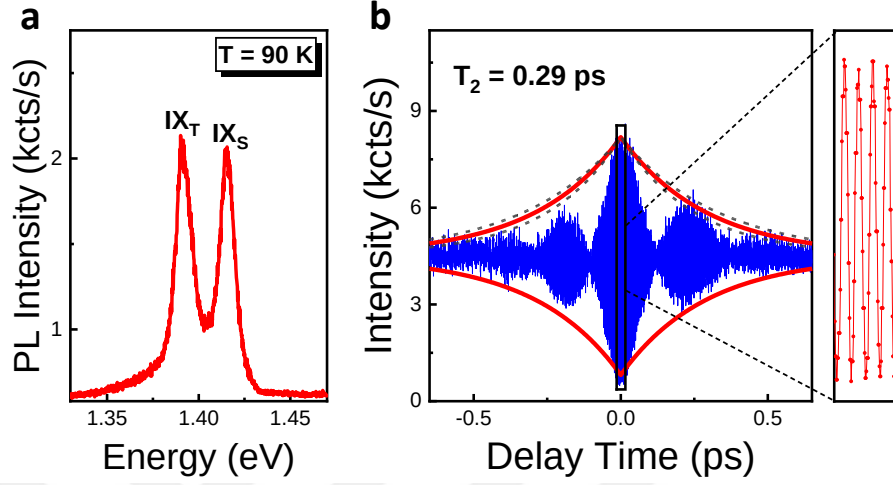


Figure 5.9: Quantum beat interferometry of the spin states of inter-layer excitons of WSe₂-MoSe₂ heterobilayers. **a.** PL spectra of the spin-singlet and spin-triplet IXs recorded with 532 nm CW laser excitation under 400 μ W pump power at 90 K. **b.** Quantum beat interferogram produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the quantum beat decay that corresponds to $T_2 = 0.29 \pm 0.05$ ps. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval (± 0.05 ps) when fitting the beat interferogram via the above expression.

Moreover, a comparative analysis of the theoretical linewidth values can provide light on the nature of the strong damping of the quantum beats. Since PL interferograms of the filtered emissions show a Gaussian type of decay, a Gaussian expression must be used for linewidth calculation, which can be written as:

$$\Gamma = \frac{\hbar\sqrt{8\pi\ln 2}}{T_2} \quad (5.9)$$

The dephasing time (T_2) here can be expressed with the relation:

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*} \quad (5.10)$$

where T_2^* is the pure dephasing time and T_1 is the radiative lifetime of the IXs. One can see from their measured lifetime values (**Fig. 4.9**) that they are almost three orders of magnitude higher than their dephasing time values (**Fig. 5.8**),

indicating that contributions from the radiative lifetimes to the spectral linewidth would have a very small effect. Therefore, it is possible to approximate $T_2^* \sim T_2$ and apply it in the spectral linewidth calculation. Using the individual T_2 values (0.535 ps and 0.575 ps) and the T_2 of the coupled state (0.29 ps) in Eq. 5.9, the linewidth values are determined as 5.13 meV, 4.77 meV, and 9.47 meV for IX_S and IX_T , and coupled-state (IX_{S-T}), respectively. As can be seen from **Fig. 5.10a**, the experimental spectral linewidths of IX_S (9.97 meV) and IX_T (11.64 meV) emissions are inhomogeneously broadened and can be attributed to the charge fluctuations. Moreover, the corresponding homogeneous linewidth of 9.47 meV is almost equal to the sum of the homogeneous (calculated) linewidths of individual spin states (9.89 meV), indicating there is no correlation between the spectral fluctuations that cause inhomogeneous broadening in each linewidth[199]. Similar to the earlier observations of inhomogeneously broadened neutral exciton and trion spectra of $MoSe_2$ [183], the strong damping of our quantum beats (**Fig. 5.9b**) can be attributed to these uncorrelated fluctuations.

The coherent nature of the coupling between the two spin states of IXs can be further confirmed through a comparison study between the experimental and the calculated energy separation ($\Delta E_{IX_{S-T}}$) values. As shown in **Fig. 5.10b**, the average quantum beat period ($T_{IX_{S-T}}$) can be obtained by the difference in minima or maxima between two beats, resulting in $T_{IX_{S-T}} = 195 \pm 17$ fs, and it can be used to calculate the $\Delta E_{IX_{S-T}}$ with the expression:

$$\Delta E_{IX_{S-T}} = \frac{2\pi\hbar}{T_{IX_{S-T}}} \quad (5.11)$$

According to Eq. 5.11, the obtained average beat period corresponds to a theoretical energy separation of $\Delta E_{IX_{S-T}} = 21.3 \pm 1.9$ meV. Furthermore, as the time-integrated PL spectrum displays in **Fig. 5.10c**, the interval between the IX peaks can be used to determine the experimental value of the energy separation, which yields $\Delta E_{IX_{S-T}} \sim 23.13$ meV. The close agreement between the spin states of IXs indicates the coherent nature of the coupling between the spin states of IXs. Overall, it can be concluded that the dephasing of IXs itself is the primary cause of the fast dephasing of the coherent coupling.

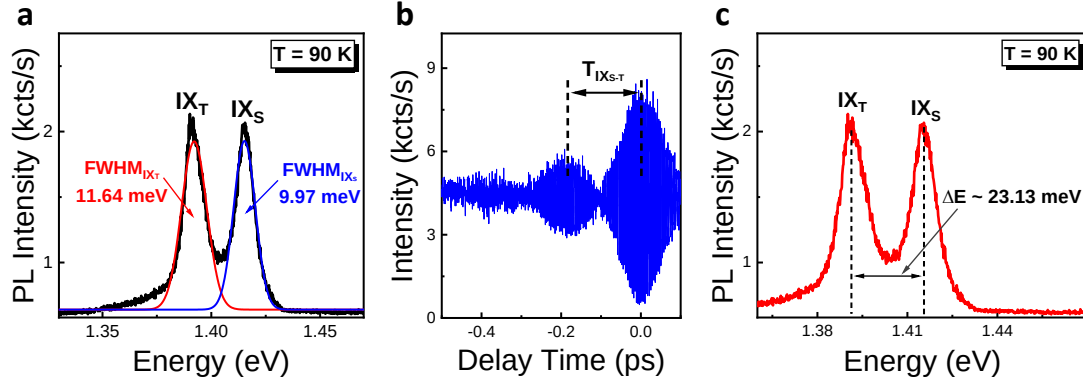


Figure 5.10: Linewidth and energy separation analysis of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers. **a.** PL spectrum with Gaussian fits of the spin-singlet (blue-lined) and spin-triplet (red-lined) IXs yielding peak fits of 9.97 meV and 11.64 meV, respectively. **b.** The quantum beat period ($T_{\text{IX}_{\text{S-T}}}$) of the corresponding PL interferogram, which is determined through the difference between two beat maxima points. **c.** The experimental energy separation ($\Delta E_{\text{IX}_{\text{S-T}}}$) of the IX spin states. Data are recorded under 532 nm CW laser excitation with an incident power of 400 μW at 90 K.

To gain further insight into the dephasing mechanism of the quantum beating between the spin states of IXs, one can perform temperature- and pump power-dependent interferometric measurements. Following this path, we performed both types of interferometric measurements using two different excitation photon energies (532 nm and 730 nm). Similar to the earlier research[83, 84, 98], the PL emission intensities of the IX spin states (**Figs. 5.11a, 5.12a, 5.13a, and 5.14a**) are resonantly increased in both dependence experiments in the case of near-resonant 730 nm excitation when compared to the off-resonant 532 nm excitation. The maximal absorption in the WSe₂ layer is primarily responsible for these resonantly enhanced PL intensities in the low pump power regime when near-resonant laser excitation is utilized. More specifically, the higher intralayer exciton content in the WSe₂ layer enhances the charge transfer, which in turn raises the quantity of excited IXs. As a result, it would result in a higher radiative recombination rate and more intense light emission.

Figs. 5.11 and 5.12 display the results of our temperature-dependent quantum beat interferometry experiments. For these measurements, the pump power of the excitation laser was kept fixed at 400 μW for off-resonant excitation (532

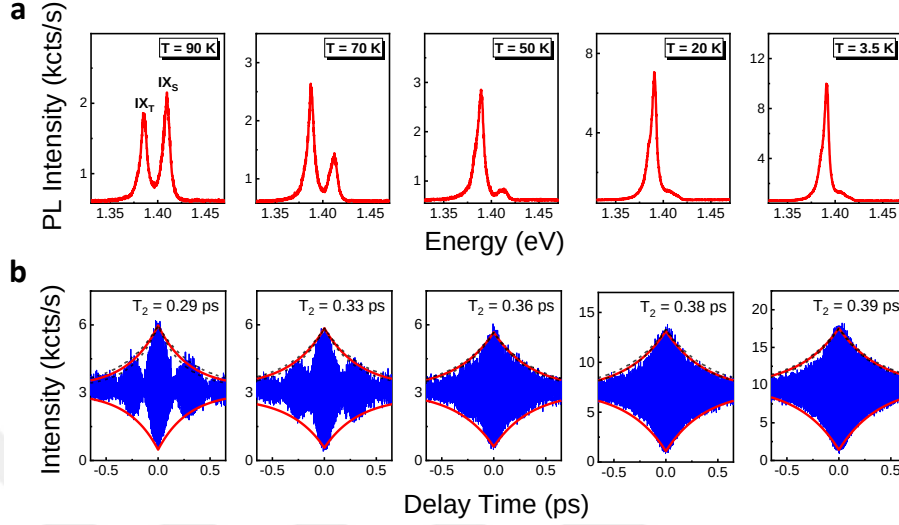


Figure 5.11: Temperature-dependent quantum beat interferometry of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers under 532 nm laser excitation. **a.** Temperature-dependent PL spectra of the spin-singlet and spin-triplet IXs recorded under 400 μ W pump power. **b.** Temperature-dependent quantum beating interferograms of the spin-singlet and spin-triplet IXs, produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the decay that corresponds to the dephasing time for the spin-singlet and spin-triplet IX coherence. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval when fitting the beat interferogram via the above expression, which is given by ± 0.05 ps, ± 0.04 ps, ± 0.03 ps, ± 0.03 ps, and ± 0.03 ps, from 90 K to 3.5 K, respectively.

nm) and 100 μ W for near-resonant (of WSe₂ layer) excitation of 730 nm. As observed in both figures, the beat resolution improves with temperature since the PL intensities of the spin states get closer together, yet the dephasing time drops. Here, as in our previous work, two different mechanisms (i.e., excitation-induced IX-IX scattering and IX-low energy acoustic phonon interaction) can contribute to the dephasing of IXs. According to a recent study, the low-energy acoustic phonon interaction is the primary dephasing mechanism for both spin states of the IXs below 150 K, with corresponding Huang-Rhys factors of 1.70 for IX_T and 1.85 for IX_S emissions[186]. Furthermore, a $T^{-\frac{1}{2}}$ temperature dependence for excitation-induced dephasing for IXs is also predicted by a different recent work[187]. Together with the findings from these two investigations, our results

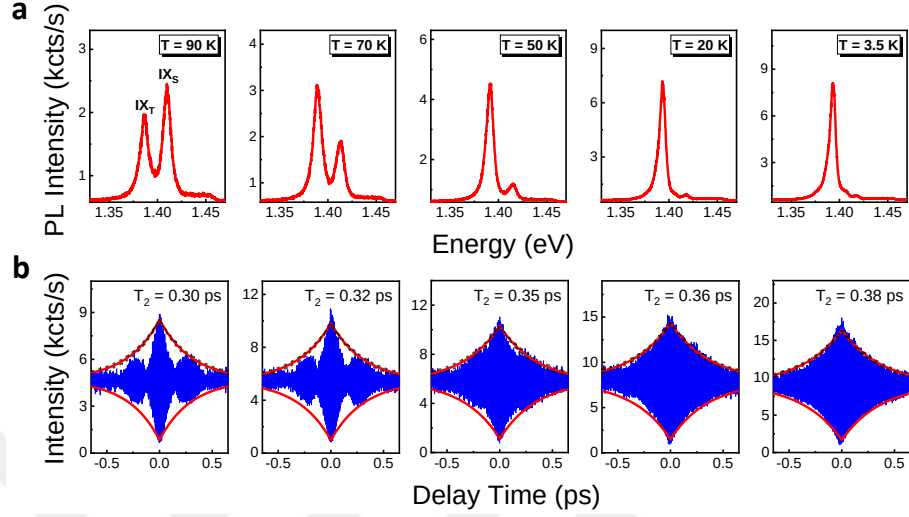


Figure 5.12: Temperature-dependent quantum beat interferometry of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers under 730 nm laser excitation. **a.** Temperature-dependent PL spectra of the spin-singlet and spin-triplet IXs recorded under 100 μ W pump power. **b.** Temperature-dependent quantum beating interferograms of the spin-singlet and spin-triplet IXs, produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the decay that corresponds to the dephasing time for the spin-singlet and spin-triplet IX coherence. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval when fitting the beat interferogram via the above expression, which is given by ± 0.03 ps, ± 0.03 ps, ± 0.04 ps, ± 0.03 ps, and ± 0.03 ps, from 90 K to 3.5 K, respectively.

(**Figs. 5.11** and **5.12**) indicate that the strong low-energy acoustic phonon interaction is the primary cause of the rapid decay of coherent coupling at 90 K, whereas it is driven by the IX-IX interaction at 3.5 K. Moreover, it appears that starting from 20 K, the IX_T emission dominates the PL emission, and quantum beating patterns start to fade away because of the nearly zero interference contrast between the spin states of the excitons. In the light of this, it can be anticipated that the dephasing time of IX_T dominates and/or determines the dephasing time of residual coupling between the spin states at these low temperatures. For future studies, electrostatic gating can be used to equate the intensities of the IX spin states at low temperatures[147], and further information about the nature of the coherent coupling and the dephasing mechanism can be obtained.

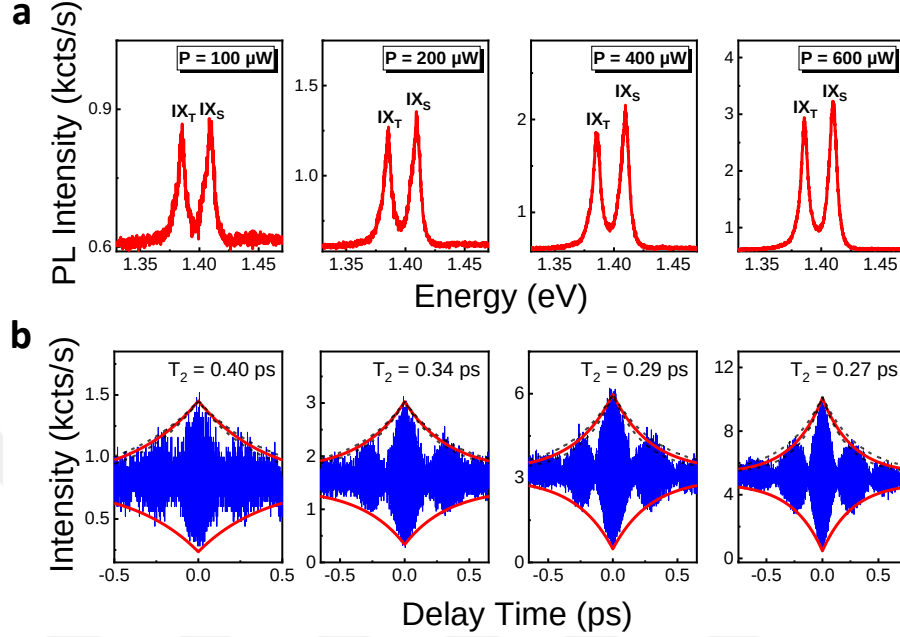


Figure 5.13: Pump power-dependent quantum beat interferometry of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers under 532 nm laser excitation. a. Power-dependent PL spectra of the spin-singlet and spin-triplet IXs recorded at 90 K. **b.** Power-dependent quantum beating interferograms of the spin-singlet and spin-triplet IXs, produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the decay that corresponds to the dephasing time for the spin-singlet and spin-triplet IX coherence. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval when fitting the beat interferogram via the above expression, which is given by ± 0.05 ps, ± 0.04 ps, ± 0.05 ps, and ± 0.05 ps from 100 μ W to 600 μ W, respectively.

We also carried out pump power-dependent interferometric experiments at 90 K using two different excitation photon energies to investigate the influence of excitation laser power on the dephasing times of quantum beats between the spin states of IXs. In the near-resonant (730 nm) and off-resonant (532 nm) cases, the beating experiments were conducted in the pump power ranges of 50-100 μ W and 100-600 μ W, respectively. The PL spectra and the corresponding quantum beating PL interferograms of spin states of our IXs for the pump power-dependent experiments are displayed in **Figs. 5.13** and **5.14**. The PL interferograms that are obtained at the highest pump powers (**Figs. 5.13b** and **5.14b**) demonstrate

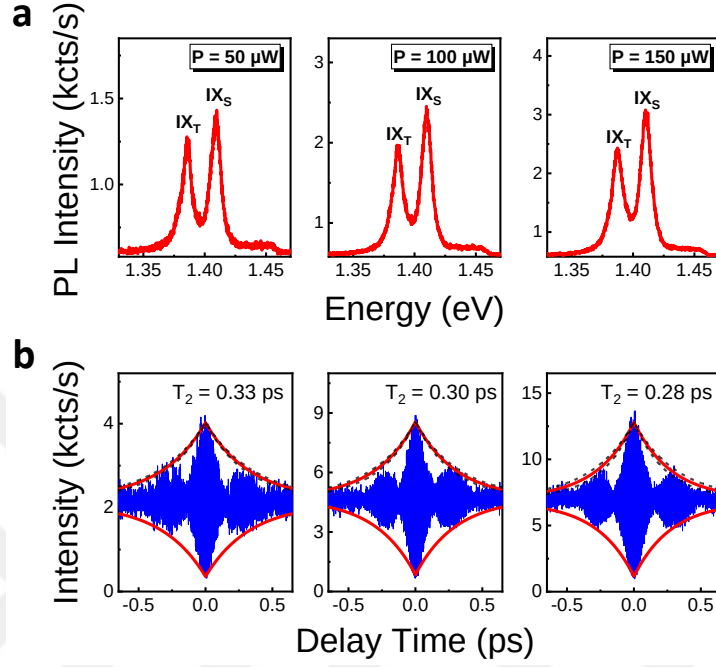


Figure 5.14: Pump power-dependent quantum beat interferometry of the spin states of interlayer excitons of WSe₂-MoSe₂ heterobilayers under 730 nm laser excitation. a. Power-dependent PL spectra of the spin-singlet and spin-triplet IXs recorded at 90 K. **b.** Power-dependent quantum beating interferograms of the spin-singlet and spin-triplet IXs, produced by sending both emissions simultaneously into the Michelson interferometer. The red-lined beat envelope shows the best fit of the decay that corresponds to the dephasing time for the spin-singlet and spin-triplet IX coherence. The fit is obtained by using the expression $g^{(1)}(\tau) = I_0(1 + A \exp(-|\tau|/T_2))$. The dashed lines show the error interval when fitting the beat interferogram via the above expression, which is given by ± 0.03 ps, ± 0.03 ps, and ± 0.04 ps from 50 μ W to 150 μ W, respectively.

a clear quantum beat pattern with up to five visible beats. As the figures show, the dephasing time of the resulting quantum beat signal shows an increasing trend while the pump power decreases. Here, the fast decay of the quantum beats with increasing pump power can be attributed to the IX-IX scattering caused by the increase in the excitation pump power[187].

An overall comparison study, displaying the findings of both dependence experiments that are conducted with two different excitation photon energies is shown in **Fig. 5.15**. Interestingly, T_2 values achieved for the quantum beating

are almost the same whenever the peak intensities of these two PL emissions were nearly equal, even though the near-resonant excitation pump powers are relatively lower than those used in the off-resonant excitation (e.g., PL spectra taken under 532 nm excitation with 400 μW and 730 nm excitation with 100 μW). Our findings suggest that a comparable number of IXs might have been created in the heterobilayer through two distinct mechanisms (i.e., strong pumping and resonant enhancement), leading to matching dephasing times caused by the IX-IX scattering.

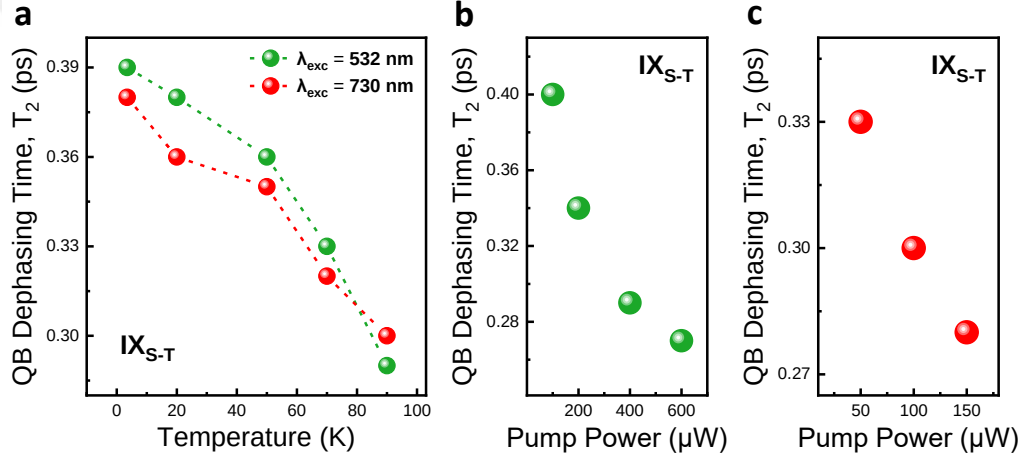


Figure 5.15: Overview plot of the temperature- and pump power-dependent quantum beat dephasing times of the interlayer excitons of WSe₂-MoSe₂ heterobilayers. **a.** Temperature dependence of the quantum beat dephasing under 532 nm (green circles) and 730 nm (red circles) laser excitations with 400 μW and 100 μW pump powers, respectively. **b,c.** Pump power dependence of the quantum beat dephasing under 532 nm (**b**) and 730 nm (**c**) laser excitations, recorded at 90 K.

To sum this paper up[67], we have used the Michelson interferometer to perform quantum beat spectroscopy and demonstrate for the first time the existence of coherent coupling between the IX_S and IX_T emissions of hBN-encapsulated WSe₂-MoSe₂ heterobilayers. As a clear indicator of coherent coupling, the quantum beating signal has been observed for the first time between the two spin states of the IXs in the time domain with dephasing times up to $T_2 \sim 400$ fs (**Fig. 5.15**). The calculated energy difference obtained by the measured beating

period of $T_{\text{IX}_{\text{S-T}}} = 195 \pm 17$ fs is in close agreement with the energy separation between the PL emission peaks of IX_{S} and IX_{T} (**Fig. 5.10c**) in the time-integrated PL spectrum, further confirming the coherent nature of the coupling between these states. Moreover, quantum beat spectroscopy offers a practical and appropriate method to examine the fine structure of IXs not only in our WSe_2 - MoSe_2 heterobilayer but also for other TMDC heterobilayers, such as WS_2 - WSe_2 [158]. Our findings further emphasize the significance of coupled quantum states for potential applications in quantum photonics and exciton-based valleytronics, including electromagnetically induced transparency[69, 70] and lasing without inversion[71, 72].

Chapter 6

Conclusion & Outlook

This dissertation demonstrates the unique photophysics of interlayer excitons formed in TMDC heterobilayers. The ability to manipulate the band structure of the heterobilayers, ultimately the physical properties of interlayer excitons, by controlling the twist angle between the constituent layers opened up intriguing possibilities in the field of twistronics and for the development of exciton-based devices. Through the Moiré superlattices formed within the heterobilayers, interlayer excitons can be intrinsically localized (trapped) to the Moiré potentials, which leads to an enhancement in their optical properties. The impact of Moiré-localization has been thoroughly investigated in many condensed-matter and solid-state studies over the past years. However, their influence on the temporal coherence properties of interlayer excitons has remained elusive.

The primary objective of this work was to investigate the coherence properties of the interlayer excitons of hBN-encapsulated WSe₂-MoSe₂ heterobilayers in conjunction with other photophysics studies. To achieve our goal, we have constructed a home-built free-space Michelson interferometer to perform first-order correlation $g^{(1)}(\tau)$ measurements in the time domain. The findings of our study *“Prolonged Dephasing Time of Ensemble of Moiré-Trapped Interlayer Excitons in WSe₂-MoSe₂ Heterobilayers”* sheds light on the impact of Moiré potentials on the coherence properties of interlayer excitons. In this work, we have shown the

possibility of reaching longer dephasing times ($T_2 \sim 730$ fs) of interlayer excitons through their intrinsic localization to the 0D Moiré potentials. Subsequently, we investigated the dephasing mechanism and the interaction between the two spin states (spin-singlet and spin-triplet) of interlayer excitons in our following investigation “*Quantum Beats Between Spin-Singlet and Spin-Triplet Interlayer Exciton Transitions in WSe_2 - $MoSe_2$ Heterobilayers*”. Utilizing the quantum beat interferometry, we have successfully shown the presence of coherent coupling between IX_S and IX_T for the first time with beating dephasing times up to $T_2 \sim 400$ fs. Our findings on both publications provide valuable insights regarding the future course of the implementation of monolayer TMDCs and their heterostructures to exciton-based photonic device applications.

Even though this dissertation addressed several open questions regarding interlayer exciton photophysics and their temporal coherence characteristics, there are still a few topics that require further investigation for future work. For instance, the dephasing time measurement of a single Moiré-localized interlayer exciton. Our findings on the prolonging effect of Moiré-localization on the interlayer excitons highly suggest that if interferometric measurements can be performed with a single Moiré-localized interlayer exciton, ultra-long dephasing times can be achieved. Although single Moiré-localized interlayer excitons exhibiting relatively high PL intensities were obtained, their PL counts were not sufficient enough to ensure the reliability of interferometric measurements. For this reason, we were unable to perform first-order correlation $g^{(1)}(\tau)$ measurements with the individual single Moiré-localized interlayer exciton. To overcome this problem, photonic structure engineering can be performed on the substrate on which the heterobilayer is fabricated, to create structures that can enhance the luminescence properties such as distributed Bragg reflectors (DBRs), metasurfaces, nanopillars, and micro-concaves. With an appropriate substrate design, suspended heterobilayers with proper twist angles can be fabricated as well, which can also lead to an enhancement in the Moiré-localized emission. Furthermore, by using proper photonics engineering, interlayer excitons can also be coupled with plasmonics to boost the interlayer coupling and, ultimately, their light intensity.

Overall, the unique physical properties and the controllability of interlayer excitons in TMDC vdW heterostructures make them promising candidates for both fundamental and potential photonic applications. The formation of Moiré superlattices within these heterostructures and their enhancing impact on optical characteristics have attracted the interest of numerous disciplines, which could lead to a rise in the development of quantum photonic applications. I foresee that through the engineering of vdW materials and solving the current challenges, significant discoveries will be achieved in the near future. Future quantum technologies will benefit greatly from the research, discoveries, and the ever-expanding infrastructure of 2D materials and their vdW heterostructures.

Bibliography

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, “Electric field effect in atomically thin carbon films,” *Science*, vol. 306, no. 5696, pp. 666–669, 2004.
- [2] A. K. Geim and K. S. Novoselov, “The rise of graphene,” *Nature Materials*, vol. 6, no. 3, pp. 183–191, 2007.
- [3] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, “Two-dimensional gas of massless dirac fermions in graphene,” *Nature*, vol. 438, no. 7065, pp. 197–200, 2005.
- [4] A. Chaves, J. G. Azadani, H. Alsalman, D. R. da Costa, R. Frisenda, A. J. Chaves, S. H. Song, Y. D. Kim, D. He, J. Zhou, A. Castellanos-Gomez, F. M. Peeters, Z. Liu, C. L. Hinkle, S.-H. Oh, P. D. Ye, S. J. Koester, Y. H. Lee, P. Avouris, X. Wang, and T. Low, “Bandgap engineering of two-dimensional semiconductor materials,” *npj 2D Materials and Applications*, vol. 4, no. 1, pp. 1–21, 2020.
- [5] K. Zhang, Y. Feng, F. Wang, Z. Yang, and J. Wang, “Two dimensional hexagonal boron nitride (2d-hbn): synthesis, properties and applications,” *Journal of Materials Chemistry C*, vol. 5, no. 46, pp. 11 992–12 022, 2017.
- [6] T. Knobloch, Y. Y. Illarionov, F. Ducry, C. Schleich, S. Wachter, K. Watanabe, T. Taniguchi, T. Mueller, M. Waltl, M. Lanza, M. I. Vexler, M. Luisier, and T. Grasser, “The performance limits of hexagonal boron nitride as an

- insulator for scaled cmos devices based on two-dimensional materials,” *Nature Electronics*, vol. 4, no. 2, pp. 98–108, 2021.
- [7] Y. Saito, T. Nojima, and Y. Iwasa, “Highly crystalline 2d superconductors,” *Nature Reviews Materials*, vol. 2, no. 1, pp. 1–18, 2016.
 - [8] W. Xing, Y. Chen, P. M. Odenthal, X. Zhang, W. Yuan, T. Su, Q. Song, T. Wang, J. Zhong, S. Jia, X. C. Xie, Y. Li, and W. Han, “Electric field effect in multilayer cr₂ge₂te₆: a ferromagnetic 2d material,” *2D Materials*, vol. 4, no. 2, p. 024009, 2017.
 - [9] M. Gibertini, M. Koperski, A. F. Morpurgo, and K. S. Novoselov, “Magnetic 2d materials and heterostructures,” *Nature Nanotechnology*, vol. 14, no. 5, pp. 408–419, 2019.
 - [10] H. Li, J. Wu, Z. Yin, and H. Zhang, “Preparation and applications of mechanically exfoliated single-layer and multilayer mos₂ and wse₂ nanosheets,” *Accounts of Chemical Research*, vol. 47, no. 4, pp. 1067–1075, 2014.
 - [11] L. Zhang, J. Liang, Y. Huang, Y. Ma, Y. Wang, and Y. Chen, “Size-controlled synthesis of graphene oxide sheets on a large scale using chemical exfoliation,” *Carbon*, vol. 47, no. 14, pp. 3365–3368, 2009.
 - [12] X. Wang, Y. Gong, G. Shi, W. L. Chow, K. Keyshar, G. Ye, R. Vajtai, J. Lou, Z. Liu, E. Ringe, B. K. Tay, and P. M. Ajayan, “Chemical vapor deposition growth of crystalline monolayer mose₂,” *ACS Nano*, vol. 8, no. 5, pp. 5125–5131, 2014.
 - [13] X. Zhang, G. Ma, and J. Wang, “Hydrothermal synthesis of two-dimensional mos₂ and its applications,” *Tungsten*, vol. 1, no. 1, pp. 59–79, 2019.
 - [14] R. Mas-Ballesté, C. Gómez-Navarro, J. Gómez-Herrero, and F. Zamora, “2d materials: to graphene and beyond,” *Nanoscale*, vol. 3, no. 1, pp. 20–30, 2011.

- [15] C. Gong, H. Zhang, W. Wang, L. Colombo, R. M. Wallace, and K. Cho, “Band alignment of two-dimensional transition metal dichalcogenides: Application in tunnel field effect transistors,” *Applied Physics Letters*, vol. 103, no. 5, p. 053513, 2013.
- [16] M.-H. Chiu, C. Zhang, H.-W. Shiu, C.-P. Chuu, C.-H. Chen, C.-Y. S. Chang, C.-H. Chen, M.-Y. Chou, C.-K. Shih, and L.-J. Li, “Determination of band alignment in the single-layer mos2/wse2 heterojunction,” *Nature Communications*, vol. 6, no. 1, p. 7666, 2015.
- [17] X. Hong, J. Kim, S.-F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, and F. Wang, “Ultrafast charge transfer in atomically thin mos2/ws2 heterostructures,” *Nature Nanotechnology*, vol. 9, no. 9, pp. 682–686, 2014.
- [18] F. Ceballos, M. Z. Bellus, H.-Y. Chiu, and H. Zhao, “Ultrafast charge separation and indirect exciton formation in a mos2–mose2 van der waals heterostructure,” *ACS Nano*, vol. 8, no. 12, pp. 12 717–12 724, 2014.
- [19] A. Kumar and P. K. Ahluwalia, “Electronic structure of transition metal dichalcogenides monolayers 1h-mx2 ($m = \text{mo}, \text{w}$; $x = \text{s}, \text{se}, \text{te}$) from ab-initio theory: new direct band gap semiconductors,” *The European Physical Journal B*, vol. 85, no. 6, p. 186, 2012.
- [20] E.-H. Yang, D. Datta, J. Ding, and G. Hader, Eds., *Synthesis, modelling, and characterization of 2D materials, and their heterostructures*, ser. Micro nano technologies series. Amsterdam Kidlington Cambridge: Elsevier, 2020.
- [21] R. Bertoni, C. Nicholson, L. Waldecker, H. Hübener, C. Monney, U. De Giovannini, M. Puppin, M. Hoesch, E. Springate, R. Chapman, C. Cacho, M. Wolf, A. Rubio, and R. Ernstorfer, “Generation and evolution of spin-, valley-, and layer-polarized excited carriers in inversion-symmetric wse2,” *Physical Review Letters*, vol. 117, no. 27, p. 277201, 2016.
- [22] N. Zibouche, P. Philipsen, A. Kuc, and T. Heine, “Transition-metal

- dichalcogenide bilayers: Switching materials for spintronic and valleytronic applications,” *Physical Review B*, vol. 90, no. 12, p. 125440, 2014.
- [23] M. Deng, X. Wang, J. Chen, Z. Li, M. Xue, Z. Zhou, F. Lin, X. Zhu, and Z. Fang, “Plasmonic modulation of valleytronic emission in two-dimensional transition metal dichalcogenides,” *Advanced Functional Materials*, vol. 31, no. 20, p. 2010234, 2021.
- [24] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides,” *Nature Nanotechnology*, vol. 7, no. 11, pp. 699–712, 2012.
- [25] M. K. Agarwal and V. V. Rao, “Growth, characterization and fabrication of n-wse2 pec solar cells,” *Crystal Research and Technology*, vol. 24, no. 12, pp. 1215–1222, 1989.
- [26] J. Wang, D. Rhodes, S. Feng, M. A. T. Nguyen, K. Watanabe, T. Taniguchi, T. E. Mallouk, M. Terrones, L. Balicas, and J. Zhu, “Gate-modulated conductance of few-layer wse2 field-effect transistors in the subgap regime: Schottky barrier transistor and subgap impurity states,” *Applied Physics Letters*, vol. 106, no. 15, p. 152104, 2015.
- [27] W. Gao, F. Zhang, Z. Zheng, and J. Li, “Unique and tunable photodetecting performance for two-dimensional layered mose2/wse2 p–n junction on the 4h-sic substrate,” *ACS Applied Materials Interfaces*, vol. 11, no. 21, pp. 19 277–19 285, 2019.
- [28] P. Pataniya, C. K. Zankat, M. Tannarana, C. K. Sumesh, S. Narayan, G. K. Solanki, K. D. Patel, V. M. Pathak, and P. K. Jha, “Paper-based flexible photodetector functionalized by wse2 nanodots,” *ACS Applied Nano Materials*, vol. 2, no. 5, pp. 2758–2766, 2019.
- [29] S. Hussain, D. Vikraman, M. T. Mehran, M. Hussain, G. Nazir, S. A. Patil, H.-S. Kim, and J. Jung, “Ultrasonically derived wse2 nanostructure embedded mxene hybrid composites for supercapacitors and hydrogen evolution reactions,” *Renewable Energy*, vol. 185, pp. 585–597, 2022.

- [30] P. Joensen, R. F. Frindt, and S. R. Morrison, “Single-layer mos₂,” *Materials Research Bulletin*, vol. 21, no. 4, pp. 457–461, 1986.
- [31] G. Seifert, H. Terrones, M. Terrones, G. Jungnickel, and T. Frauenheim, “Structure and electronic properties of mos₂ nanotubes,” *Physical Review Letters*, vol. 85, no. 1, pp. 146–149, 2000.
- [32] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, “Atomically thin mos₂: A new direct-gap semiconductor,” *Physical Review Letters*, vol. 105, no. 13, p. 136805, 2010.
- [33] A. V. Kolobov and J. Tominaga, *Two-Dimensional Transition-Metal Dichalcogenides*, ser. Springer Series in Materials Science. Springer International Publishing, Cham, 2016, vol. 239.
- [34] H. Baek, M. Brotons-Gisbert, Z. X. Koong, A. Campbell, M. Rambach, K. Watanabe, T. Taniguchi, and B. D. Gerardot, “Highly energy-tunable quantum light from moiré-trapped excitons,” *Science Advances*, vol. 6, no. 37, p. eaba8526, 2020.
- [35] M. Brotons-Gisbert, H. Baek, A. Campbell, K. Watanabe, T. Taniguchi, and B. D. Gerardot, “Moiré-trapped interlayer trions in a charge-tunable wse₂ / mos₂ heterobilayer,” *Physical Review X*, vol. 11, no. 3, p. 031033, 2021.
- [36] J. Choi, W.-T. Hsu, L.-S. Lu, L. Sun, H.-Y. Cheng, M.-H. Lee, J. Quan, K. Tran, C.-Y. Wang, M. Staab, K. Jones, T. Taniguchi, K. Watanabe, M.-W. Chu, S. Gwo, S. Kim, C.-K. Shih, X. Li, and W.-H. Chang, “Moiré potential impedes interlayer exciton diffusion in van der waals heterostructures,” *Science Advances*, vol. 6, no. 39, p. eaba8866, 2020.
- [37] M. Förg, A. S. Baimuratov, S. Y. Kruchinin, I. A. Vovk, J. Scherzer, J. Förste, V. Funk, K. Watanabe, T. Taniguchi, and A. Högele, “Moiré excitons in mos₂-wse₂ heterobilayers and heterotrilayers,” *Nature Communications*, vol. 12, no. 1, p. 1656, 2021.

- [38] E. Liu, E. Barré, J. van Baren, M. Wilson, T. Taniguchi, K. Watanabe, Y.-T. Cui, N. M. Gabor, T. F. Heinz, Y.-C. Chang, and C. H. Lui, “Signatures of moiré trions in wse2/mose2 heterobilayers,” *Nature*, vol. 594, no. 7861, pp. 46–50, 2021.
- [39] F. MahdikhanySarvejahany, D. N. Shanks, C. Muccianti, B. H. Badada, I. Idi, A. Alfrey, S. Raglow, M. R. Koehler, D. G. Mandrus, T. Taniguchi, K. Watanabe, O. L. A. Monti, H. Yu, B. J. LeRoy, and J. R. Schaibley, “Temperature dependent moiré trapping of interlayer excitons in mose2-wse2 heterostructures,” *npj 2D Materials and Applications*, vol. 5, no. 1, p. 67, 2021.
- [40] K. L. Seyler, P. Rivera, H. Yu, N. P. Wilson, E. L. Ray, D. G. Mandrus, J. Yan, W. Yao, and X. Xu, “Signatures of moiré-trapped valley excitons in mose2/wse2 heterobilayers,” *Nature*, vol. 567, no. 7746, pp. 66–70, 2019.
- [41] X. Wang, J. Zhu, K. L. Seyler, P. Rivera, H. Zheng, Y. Wang, M. He, T. Taniguchi, K. Watanabe, J. Yan, D. G. Mandrus, D. R. Gamelin, W. Yao, and X. Xu, “Moiré trions in mose2/wse2 heterobilayers,” *Nature Nanotechnology*, vol. 16, no. 11, pp. 1208–1213, 2021.
- [42] L. Yuan, B. Zheng, J. Kunstmann, T. Brumme, A. B. Kuc, C. Ma, S. Deng, D. Blach, A. Pan, and L. Huang, “Twist-angle-dependent interlayer exciton diffusion in ws2-wse2 heterobilayers,” *Nature Materials*, vol. 19, no. 6, pp. 617–623, 2020.
- [43] M. A. Durmuş, K. Demiralay, M. M. Khan, E. Atalay, and I. Sarpkaya, “Prolonged dephasing time of ensemble of moiré-trapped interlayer excitons in wse2-mose2 heterobilayers,” *npj 2D Materials and Applications*, vol. 7, no. 1, p. 65, 2023.
- [44] Y. Jiang, S. Chen, W. Zheng, B. Zheng, and A. Pan, “Interlayer exciton formation, relaxation, and transport in tmd van der waals heterostructures,” *Light: Science Applications*, vol. 10, no. 1, p. 72, 2021.
- [45] Y. Guo and J. Robertson, “Band engineering in transition metal dichalcogenides: Stacked versus lateral heterostructures,” 2016.

- [46] J. Kang, S. Tongay, J. Zhou, J. Li, and J. Wu, “Band offsets and heterostructures of two-dimensional semiconductors,” *Applied Physics Letters*, vol. 102, no. 1, p. 012111, 2013.
- [47] V. O. Özçelik, J. G. Azadani, C. Yang, S. J. Koester, and T. Low, “Band alignment of two-dimensional semiconductors for designing heterostructures with momentum space matching,” *Physical Review B*, vol. 94, no. 3, p. 035125, 2016.
- [48] P. Rivera, H. Yu, K. L. Seyler, N. P. Wilson, W. Yao, and X. Xu, “Inter-layer valley excitons in heterobilayers of transition metal dichalcogenides,” *Nature Nanotechnology*, vol. 13, no. 11, pp. 1004–1015, 2018.
- [49] H. Yu, X. Cui, X. Xu, and W. Yao, “Valley excitons in two-dimensional semiconductors,” *National Science Review*, vol. 2, no. 1, pp. 57–70, 2015.
- [50] A. Ramasubramaniam, “Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides,” *Physical Review B*, vol. 86, no. 11, p. 115409, 2012.
- [51] A. Kavokin, T. C. H. Liew, C. Schneider, P. G. Lagoudakis, S. Klemmt, and S. Hoefling, “Polariton condensates for classical and quantum computing,” *Nature Reviews Physics*, vol. 4, no. 7, pp. 435–451, 2022.
- [52] H.-S. Zhong, H. Wang, Y.-H. Deng, M.-C. Chen, L.-C. Peng, Y.-H. Luo, J. Qin, D. Wu, X. Ding, Y. Hu, P. Hu, X.-Y. Yang, W.-J. Zhang, H. Li, Y. Li, X. Jiang, L. Gan, G. Yang, L. You, Z. Wang, L. Li, N.-L. Liu, C.-Y. Lu, and J.-W. Pan, “Quantum computational advantage using photons,” *Science*, vol. 370, no. 6523, pp. 1460–1463, 2020.
- [53] C. Degen, F. Reinhard, and P. Cappellaro, “Quantum sensing,” *Reviews of Modern Physics*, vol. 89, no. 3, p. 035002, 2017.
- [54] B. J. Lawrie, C. E. Marvinney, Y.-Y. Pai, M. A. Feldman, J. Zhang, A. J. Miller, C. Hua, E. Dumitrescu, and G. B. Halász, “Multifunctional superconducting nanowire quantum sensors,” *Physical Review Applied*, vol. 16, no. 6, p. 064059, 2021.

- [55] A. Karnieli, S. Tsesses, R. Yu, N. Rivera, Z. Zhao, A. Arie, S. Fan, and I. Kaminer, “Quantum sensing of strongly coupled light-matter systems using free electrons,” *Science Advances*, vol. 9, no. 1, p. eadd2349, 2023.
- [56] S. Vaidya, X. Gao, S. Dikshit, I. Aharonovich, and T. Li, “Quantum sensing and imaging with spin defects in hexagonal boron nitride,” *Advances in Physics: X*, vol. 8, no. 1, 2023.
- [57] T. Gao, M. Von Helversen, C. Antón-Solanas, C. Schneider, and T. Heindel, “Atomically-thin single-photon sources for quantum communication,” *npj 2D Materials and Applications*, vol. 7, no. 1, p. 4, 2023.
- [58] H. Zhao, M. T. Pettes, Y. Zheng, and H. Htoon, “Site-controlled telecom-wavelength single-photon emitters in atomically-thin mote2,” *Nature Communications*, vol. 12, no. 1, p. 6753, 2021.
- [59] C.-Y. Lu and J.-W. Pan, “Quantum-dot single-photon sources for the quantum internet,” *Nature Nanotechnology*, vol. 16, no. 12, pp. 1294–1296, 2021.
- [60] V. Vidyapin, Y. Zhang, D. England, and B. Sussman, “Characterisation of a single photon event camera for quantum imaging,” *Scientific Reports*, vol. 13, no. 1, p. 1009, 2023.
- [61] A. J. Healey, S. C. Scholten, T. Yang, J. A. Scott, G. J. Abrahams, I. O. Robertson, X. F. Hou, Y. F. Guo, S. Rahman, Y. Lu, M. Kianinia, I. Aharonovich, and J.-P. Tetienne, “Quantum microscopy with van der waals heterostructures,” *Nature Physics*, vol. 19, no. 1, pp. 87–91, 2023.
- [62] V. Scarani, H. Bechmann-Pasquinucci, N. J. Cerf, M. Dušek, N. Lütkenhaus, and M. Peev, “The security of practical quantum key distribution,” *Reviews of Modern Physics*, vol. 81, no. 3, pp. 1301–1350, 2009.
- [63] F. Grünenfelder, A. Boaron, G. V. Resta, M. Perrenoud, D. Rusca, C. Barreiro, R. Houlmann, R. Sax, L. Stasi, S. El-Khoury, E. Hänggi, N. Bosshard, F. Bussi eres, and H. Zbinden, “Fast single-photon detectors and real-time key distillation enable high secret-key-rate quantum key distribution systems,” *Nature Photonics*, pp. 1–5, 2023.

- [64] Samaner, S. Paçal, G. Mutlu, K. Uyanık, and S. Ateş, “Free-space quantum key distribution with single photons from defects in hexagonal boron nitride,” *Advanced Quantum Technologies*, vol. 5, no. 9, p. 2200059, 2022.
- [65] E. Joos, H. D. Zeh, C. Kiefer, D. Giulini, J. Kupsch, and I.-O. Stamatescu, *Decoherence and the Appearance of a Classical World in Quantum Theory*. Berlin, Heidelberg: Springer, 2003.
- [66] Y. Guo, C. Liu, Q. Yin, C. Wei, S. Lin, T. B. Hoffman, Y. Zhao, J. H. Edgar, Q. Chen, S. P. Lau, J. Dai, H. Yao, H.-S. P. Wong, and Y. Chai, “Distinctive in-plane cleavage behaviors of two-dimensional layered materials,” *ACS Nano*, vol. 10, no. 9, pp. 8980–8988, 2016.
- [67] M. A. Durmuş and I. Sarpkaya, “Quantum beats between spin-singlet and spin-triplet interlayer exciton transitions in wse2–mose2 heterobilayers,” *Nano Letters*, vol. 24, no. 19, p. 5767–5773, 2024.
- [68] C. Qian, M. Troue, J. Figueiredo, P. Soubelet, V. Villafañe, J. Beierlein, S. Klemmt, A. V. Stier, S. Höfling, A. W. Holleitner, and J. J. Finley, “Lasing of moiré trapped mose2/wse2 interlayer excitons coupled to a nanocavity,” *Science Advances*, vol. 10, no. 2, p. eadk6359, 2024.
- [69] J. E. Field, K. H. Hahn, and S. E. Harris, “Observation of electromagnetically induced transparency in collisionally broadened lead vapor,” *Physical Review Letters*, vol. 67, no. 22, pp. 3062–3065, 1991.
- [70] K.-J. Boller, A. Imamoglu, and S. E. Harris, “Observation of electromagnetically induced transparency,” *Physical Review Letters*, vol. 66, no. 20, pp. 2593–2596, 1991.
- [71] M. O. Scully, S.-Y. Zhu, and A. Gavrielides, “Degenerate quantum-beat laser: Lasing without inversion and inversion without lasing,” *Physical Review Letters*, vol. 62, no. 24, pp. 2813–2816, 1989.
- [72] S. E. Harris, “Lasers without inversion: Interference of lifetime-broadened resonances,” *Physical Review Letters*, vol. 62, no. 9, pp. 1033–1036, 1989.

- [73] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, “Emerging photoluminescence in monolayer mos₂,” *Nano Letters*, vol. 10, no. 4, pp. 1271–1275, 2010.
- [74] A. Chernikov, T. C. Berkelbach, H. M. Hill, A. Rigosi, Y. Li, B. Aslan, D. R. Reichman, M. S. Hybertsen, and T. F. Heinz, “Exciton binding energy and nonhydrogenic rydberg series in monolayer $\{nm\mathrm{athrm}\{ws\}\}_{2}$,” *Physical Review Letters*, vol. 113, no. 7, p. 076802, 2014.
- [75] K. He, N. Kumar, L. Zhao, Z. Wang, K. F. Mak, H. Zhao, and J. Shan, “Tightly bound excitons in monolayer wse₂,” *Physical Review Letters*, vol. 113, no. 2, p. 026803, 2014.
- [76] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, and M. C. Hersam, “Emerging device applications for semiconducting two-dimensional transition metal dichalcogenides,” *ACS Nano*, vol. 8, no. 2, pp. 1102–1120, 2014.
- [77] H. Wang, H. Feng, and J. Li, “Graphene and graphene-like layered transition metal dichalcogenides in energy conversion and storage,” *Small*, vol. 10, no. 11, pp. 2165–2181, 2014.
- [78] M. Bernardi, M. Palummo, and J. C. Grossman, “Extraordinary sunlight absorption and one nanometer thick photovoltaics using two-dimensional monolayer materials,” *Nano Letters*, vol. 13, no. 8, pp. 3664–3670, 2013.
- [79] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, “Coupled spin and valley physics in monolayers of mos₂ and other group-vi dichalcogenides,” *Physical Review Letters*, vol. 108, no. 19, p. 196802, 2012.
- [80] T. Cao, G. Wang, W. Han, H. Ye, C. Zhu, J. Shi, Q. Niu, P. Tan, E. Wang, B. Liu, and J. Feng, “Valley-selective circular dichroism of monolayer molybdenum disulphide,” *Nature Communications*, vol. 3, no. 1, p. 887, 2012.
- [81] P. Ajayan, P. Kim, and K. Banerjee, “Two-dimensional van der waals materials,” *Physics Today*, vol. 69, no. 9, pp. 38–44, 2016.

- [82] A. K. Geim and I. V. Grigorieva, “Van der waals heterostructures,” *Nature*, vol. 499, no. 7459, pp. 419–425, 2013.
- [83] P. Rivera, J. R. Schaibley, A. M. Jones, J. S. Ross, S. Wu, G. Aivazian, P. Klement, K. Seyler, G. Clark, N. J. Ghimire, J. Yan, D. G. Mandrus, W. Yao, and X. Xu, “Observation of long-lived interlayer excitons in monolayer mose2–wse2 heterostructures,” *Nature Communications*, vol. 6, no. 1, p. 6242, 2015.
- [84] P. Nagler, G. Plechinger, M. V. Ballottin, A. Mitiglu, S. Meier, N. Paradiso, C. Strunk, A. Chernikov, P. C. M. Christianen, C. Schüller, and T. Korn, “Interlayer exciton dynamics in a dichalcogenide monolayer heterostructure,” *2D Materials*, vol. 4, no. 2, p. 025112, 2017.
- [85] B. Miller, A. Steinhoff, B. Pano, J. Klein, F. Jahnke, A. Holleitner, and U. Wurstbauer, “Long-lived direct and indirect interlayer excitons in van der waals heterostructures,” *Nano Letters*, vol. 17, no. 9, pp. 5229–5237, 2017.
- [86] I. Sarpkaya, “4 - optical properties of semiconducting transition metal dichalcogenide materials,” in *Synthesis, Modeling, and Characterization of 2D Materials, and Their Heterostructures*, ser. Micro and Nano Technologies, E.-H. Yang, D. Datta, J. Ding, and G. Hader, Eds. Elsevier, 2020, pp. 57–75.
- [87] J. Wilson and A. Yoffe, “The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties,” *Advances in Physics*, vol. 18, no. 73, pp. 193–335, 1969.
- [88] L. F. Mattheiss, “Band structures of transition-metal-dichalcogenide layer compounds,” *Physical Review B*, vol. 8, no. 8, pp. 3719–3740, 1973.
- [89] J. K. Ellis, M. J. Lucero, and G. E. Scuseria, “The indirect to direct band gap transition in multilayered mos2 as predicted by screened hybrid density functional theory,” *Applied Physics Letters*, vol. 99, no. 26, p. 261908, 2011.
- [90] N. W. Ashcroft, N. D. Mermin, and S. Rodriguez, “Solidstatephysics,” *American Journal of Physics*, vol. 46, no. 1, pp. 116–117, 1978.

- [91] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, *Nature Chemistry*, vol. 5, no. 4, pp. 263–275, 2013.
- [92] A. O. A. Tanoh, N. Gauriot, G. Delport, J. Xiao, R. Pandya, J. Sung, J. Allardice, Z. Li, C. A. Williams, A. Baldwin, S. D. Stranks, and A. Rao, “Directed energy transfer from monolayer ws₂ to near-infrared emitting pbs-cds quantum dots,” *ACS Nano*, vol. 14, no. 11, pp. 15 374–15 384, 2020.
- [93] X. Xu, W. Yao, D. Xiao, and T. F. Heinz, “Spin and pseudospins in layered transition metal dichalcogenides,” *Nature Physics*, vol. 10, no. 5, pp. 343–350, 2014.
- [94] M. Guimarães and B. Koopmans, “Spin accumulation and dynamics in inversion-symmetric van der waals crystals,” *Physical Review Letters*, vol. 120, no. 26, p. 266801, 2018.
- [95] K. F. Mak, D. Xiao, and J. Shan, “Light–valley interactions in 2d semiconductors,” *Nature Photonics*, vol. 12, no. 8, pp. 451–460, 2018.
- [96] D. Xiao, W. Yao, and Q. Niu, “Valley-contrasting physics in graphene: Magnetic moment and topological transport,” *Physical Review Letters*, vol. 99, no. 23, p. 236809, 2007.
- [97] D. Xiao, M.-C. Chang, and Q. Niu, “Berry phase effects on electronic properties,” *Reviews of Modern Physics*, vol. 82, no. 3, pp. 1959–2007, 2010.
- [98] T. Wang, S. Miao, Z. Li, Y. Meng, Z. Lu, Z. Lian, M. Blei, T. Taniguchi, K. Watanabe, S. Tongay, D. Smirnov, and S.-F. Shi, “Giant valley-zeeman splitting from spin-singlet and spin-triplet interlayer excitons in wse₂ / mose₂ heterostructure,” *Nano Letters*, vol. 20, no. 1, pp. 694–700, 2020.
- [99] A. Srivastava, M. Sidler, A. V. Allain, D. S. Lembke, A. Kis, and A. Imamoglu, “Valley zeeman effect in elementary optical excitations of monolayer wse₂,” *Nature Physics*, vol. 11, no. 2, pp. 141–147, 2015.

- [100] B. Fallahazad, H. C. Movva, K. Kim, S. Larentis, T. Taniguchi, K. Watanabe, S. K. Banerjee, and E. Tutuc, “Shubnikov–de haas oscillations of high-mobility holes in monolayer and bilayer wse₂ landau level degeneracy, effective mass, and negative compressibility,” *Physical Review Letters*, vol. 116, no. 8, p. 086601, 2016.
- [101] A. M. Jones, H. Yu, N. J. Ghimire, S. Wu, G. Aivazian, J. S. Ross, B. Zhao, J. Yan, D. G. Mandrus, D. Xiao, W. Yao, and X. Xu, “Optical generation of excitonic valley coherence in monolayer wse₂,” *Nature Nanotechnology*, vol. 8, no. 9, pp. 634–638, 2013.
- [102] X. Chen, T. Yan, B. Zhu, S. Yang, and X. Cui, *ACS Nano*, vol. 11, no. 2, pp. 1581–1587, 2017.
- [103] M. Combescot, O. Betbedermatibet, and F. Dubin, “The many-body physics of composite bosons,” *Physics Reports*, vol. 463, no. 5-6, pp. 215–320, 2008.
- [104] A. Singh, G. Moody, K. Tran, M. E. Scott, V. Overbeck, G. Berghäuser, J. Schaibley, E. J. Seifert, D. Pleskot, N. M. Gabor, J. Yan, D. G. Mandrus, M. Richter, E. Malic, X. Xu, and X. Li, *Physical Review B*, vol. 93, no. 4, p. 041401, 2016.
- [105] L. A. Jauregui, A. Y. Joe, K. Pistunova, D. S. Wild, A. A. High, Y. Zhou, G. Scuri, K. De Greve, A. Sushko, C.-H. Yu, T. Taniguchi, K. Watanabe, D. J. Needleman, M. D. Lukin, H. Park, and P. Kim, “Electrical control of interlayer exciton dynamics in atomically thin heterostructures,” *Science*, vol. 366, no. 6467, pp. 870–875, 2019.
- [106] J. S. Ross, S. Wu, H. Yu, N. J. Ghimire, A. M. Jones, G. Aivazian, J. Yan, D. G. Mandrus, D. Xiao, W. Yao, and X. Xu, “Electrical control of neutral and charged excitons in a monolayer semiconductor,” *Nature Communications*, vol. 4, no. 1, p. 1474, 2013.
- [107] K. Kheng, R. T. Cox, M. Y. d’ Aubigné, F. Bassani, K. Saminadayar, and

- S. Tatarenko, “Observation of negatively charged excitons x^- in semiconductor quantum wells,” *Physical Review Letters*, vol. 71, no. 11, pp. 1752–1755, 1993.
- [108] A. Kormányos, G. Burkard, M. Gmitra, J. Fabian, V. Zólyomi, N. D. Drummond, and V. Fal’ko, “ k - p theory for two-dimensional transition metal dichalcogenide semiconductors,” *2D Materials*, vol. 2, no. 2, p. 022001, 2015.
- [109] X.-X. Zhang, Y. You, S. Y. F. Zhao, and T. F. Heinz, “Experimental evidence for dark excitons in monolayer WSe_2 ,” *Physical Review Letters*, vol. 115, no. 25, p. 257403, 2015.
- [110] J. P. Echeverry, B. Urbaszek, T. Amand, X. Marie, and I. C. Gerber, “Splitting between bright and dark excitons in transition metal dichalcogenide monolayers,” *Physical Review B*, vol. 93, no. 12, p. 121107, 2016.
- [111] C. Robert, B. Han, P. Kapuscinski, A. Delhomme, C. Faugeras, T. Amand, M. R. Molas, M. Bartos, K. Watanabe, T. Taniguchi, B. Urbaszek, M. Potemski, and X. Marie, “Measurement of the spin-forbidden dark excitons in MoS_2 and WSe_2 monolayers,” *Nature Communications*, vol. 11, no. 1, p. 4037, 2020.
- [112] G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, “Colloquium: Excitons in atomically thin transition metal dichalcogenides,” *Reviews of Modern Physics*, vol. 90, no. 2, p. 021001, 2018.
- [113] X. Zhou, Z. Zhang, and W. Guo, “Dislocations as single photon sources in two-dimensional semiconductors,” *Nano Letters*, vol. 20, no. 6, pp. 4136–4143, 2020.
- [114] O. Iff, D. Tedeschi, J. Martín-Sánchez, M. Moczala-Dusanowska, S. Tongay, K. Yumigeta, J. Taboada-Gutiérrez, M. Savaresi, A. Rastelli, P. Alonso-González, S. Höfling, R. Trotta, and C. Schneider, “Strain-tunable single photon sources in WSe_2 monolayers,” *Nano Letters*, vol. 19, no. 10, pp. 6931–6936, 2019.

- [115] Y.-M. He, G. Clark, J. R. Schaibley, Y. He, M.-C. Chen, Y.-J. Wei, X. Ding, Q. Zhang, W. Yao, X. Xu, C.-Y. Lu, and J.-W. Pan, “Single quantum emitters in monolayer semiconductors,” *Nature Nanotechnology*, vol. 10, no. 6, pp. 497–502, 2015.
- [116] P. Tonndorf, R. Schmidt, R. Schneider, J. Kern, M. Buscema, G. A. Steele, A. Castellanos-Gomez, v. d. H. S. J. Zant, d. S. M. Vasconcellos, and R. Bratschitsch, “Single-photon emission from localized excitons in an atomically thin semiconductor,” *Optica*, vol. 2, no. 4, pp. 347–352, 2015.
- [117] L. Yu, M. Deng, J. L. Zhang, S. Borghardt, B. Kardynal, J. Vučković, and T. F. Heinz, “Site-controlled quantum emitters in monolayer mose2,” *Nano Letters*, vol. 21, no. 6, pp. 2376–2381, 2021.
- [118] S. Kumar, A. Kaczmarczyk, and B. D. Gerardot, “Strain-induced spatial and spectral isolation of quantum emitters in mono- and bilayer wse2,” *Nano Letters*, vol. 15, no. 11, pp. 7567–7573, 2015.
- [119] A. Branny, S. Kumar, R. Proux, and B. D. Gerardot, “Deterministic strain-induced arrays of quantum emitters in a two-dimensional semiconductor,” *Nature Communications*, vol. 8, no. 1, p. 15053, 2017.
- [120] I. Aharonovich, D. Englund, and M. Toth, “Solid-state single-photon emitters,” *Nature Photonics*, vol. 10, no. 10, pp. 631–641, 2016.
- [121] J. Jadcak, J. Kutrowska-Girzycka, P. Kapuściński, Y. S. Huang, A. Wójs, and L. Bryja, “Probing of free and localized excitons and trions in atomically thin wse2, ws2, mose2 and mos2 in photoluminescence and reflectivity experiments,” *Nanotechnology*, vol. 28, no. 39, p. 395702, 2017.
- [122] A. M. van der Zande, P. Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G.-H. Lee, T. F. Heinz, D. R. Reichman, D. A. Muller, and J. C. Hone, “Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide,” *Nature Materials*, vol. 12, no. 6, pp. 554–561, 2013.
- [123] Q. Feng, N. Mao, J. Wu, H. Xu, C. Wang, J. Zhang, and L. Xie, “Growth of $\text{mos}_{2(1-x)}\text{se}_{2x}$ ($x = 0.41\text{--}1.00$) monolayer alloys with controlled morphology

- by physical vapor deposition,” *ACS Nano*, vol. 9, no. 7, pp. 7450–7455, 2015.
- [124] J. Brivio, D. T. L. Alexander, and A. Kis, “Ripples and layers in ultrathin mos2 membranes,” *Nano Letters*, vol. 11, no. 12, pp. 5148–5153, 2011.
- [125] K.-I. Lin, Y.-H. Ho, S.-B. Liu, J.-J. Ciou, B.-T. Huang, C. Chen, H.-C. Chang, C.-L. Tu, and C.-H. Chen, “Atom-dependent edge-enhanced second-harmonic generation on mos2 monolayers,” *Nano Letters*, vol. 18, no. 2, pp. 793–797, 2018.
- [126] S. Psilodimitrakopoulos, L. Mouchliadis, I. Paradisanos, A. Lemonis, G. Kioseoglou, and E. Stratakis, “Ultrahigh-resolution nonlinear optical imaging of the armchair orientation in 2d transition metal dichalcogenides,” *Light: Science Applications*, vol. 7, no. 5, pp. 18 005–18 005, 2018.
- [127] N. Kumar, S. Najmaei, Q. Cui, F. Ceballos, P. M. Ajayan, J. Lou, and H. Zhao, “Second harmonic microscopy of monolayer mos₂,” *Physical Review B*, vol. 87, no. 16, p. 161403, 2013.
- [128] F. Xia, H. Wang, and Y. Jia, “Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics,” *Nature Communications*, vol. 5, no. 1, p. 4458, 2014.
- [129] D. Wolverson, S. Crampin, A. S. Kazemi, A. Ilie, and S. J. Bending, “Raman spectra of monolayer, few-layer, and bulk res₂: An anisotropic layered semiconductor,” *ACS Nano*, vol. 8, no. 11, pp. 11 154–11 164, 2014.
- [130] Y.-C. Lin, H.-P. Komsa, C.-H. Yeh, T. Björkman, Z.-Y. Liang, C.-H. Ho, Y.-S. Huang, P.-W. Chiu, A. V. Krashenninnikov, and K. Suenaga, “Single-layer res₂: Two-dimensional semiconductor with tunable in-plane anisotropy,” *ACS Nano*, vol. 9, no. 11, pp. 11 249–11 257, 2015.
- [131] M. Brotons-Gisbert, H. Baek, A. Molina-Sánchez, A. Campbell, E. Scerri, D. White, K. Watanabe, T. Taniguchi, C. Bonato, and B. D. Gerardot, “Spin–layer locking of interlayer excitons trapped in moiré potentials,” *Nature Materials*, vol. 19, no. 6, pp. 630–636, 2020.

- [132] N. R. Wilson, P. V. Nguyen, K. Seyler, P. Rivera, A. J. Marsden, Z. P. L. Laker, G. C. Constantinescu, V. Kandyba, A. Barinov, N. D. M. Hine, X. Xu, and D. H. Cobden, “Determination of band offsets, hybridization, and exciton binding in 2d semiconductor heterostructures,” *Science Advances*, vol. 3, no. 2, p. e1601832, 2017.
- [133] P. Nagler, M. V. Ballottin, A. A. Mitioğlu, F. Mooshammer, N. Paradiso, C. Strunk, R. Huber, A. Chernikov, P. C. M. Christianen, C. Schüller, and T. Korn, “Giant magnetic splitting inducing near-unity valley polarization in van der waals heterostructures,” *Nature Communications*, vol. 8, no. 1, p. 1551, 2017.
- [134] H. Yu, Y. Wang, Q. Tong, X. Xu, and W. Yao, “Anomalous light cones and valley optical selection rules of interlayer excitons in twisted heterobilayers,” *Physical Review Letters*, vol. 115, no. 18, p. 187002, 2015.
- [135] D. Unuchek, A. Ciarrocchi, A. Avsar, K. Watanabe, T. Taniguchi, and A. Kis, “Room-temperature electrical control of exciton flux in a van der waals heterostructure,” *Nature*, vol. 560, no. 7718, pp. 340–344, 2018.
- [136] C. Zhang, C.-P. Chuu, X. Ren, M.-Y. Li, L.-J. Li, C. Jin, M.-Y. Chou, and C.-K. Shih, “Interlayer couplings, moiré patterns, and 2d electronic superlattices in mos₂/wse₂ hetero-bilayers,” *Science Advances*, vol. 3, no. 1, p. e1601459, 2017.
- [137] H. Yu, G.-B. Liu, J. Tang, X. Xu, and W. Yao, “Moiré excitons: From programmable quantum emitter arrays to spin-orbit-coupled artificial lattices,” *Science Advances*, vol. 3, no. 11, p. e1701696, 2017.
- [138] P. K. Nayak, Y. Horbatenko, S. Ahn, G. Kim, J.-U. Lee, K. Y. Ma, A.-R. Jang, H. Lim, D. Kim, S. Ryu, H. Cheong, N. Park, and H. S. Shin, “Probing evolution of twist-angle-dependent interlayer excitons in mose₂/wse₂ van der waals heterostructures,” *ACS Nano*, vol. 11, no. 4, pp. 4041–4050, 2017.
- [139] Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras,

- and P. Jarillo-Herrero, “Unconventional superconductivity in magic-angle graphene superlattices,” *Nature*, vol. 556, no. 7699, pp. 43–50, 2018.
- [140] Y. Cao, V. Fatemi, A. Demir, S. Fang, S. L. Tomarken, J. Y. Luo, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, E. Kaxiras, R. C. Ashoori, and P. Jarillo-Herrero, “Correlated insulator behaviour at half-filling in magic-angle graphene superlattices,” *Nature*, vol. 556, no. 7699, pp. 80–84, 2018.
- [141] K. Tran, G. Moody, F. Wu, X. Lu, J. Choi, K. Kim, A. Rai, D. A. Sanchez, J. Quan, A. Singh, J. Embley, A. Zepeda, M. Campbell, T. Autry, T. Taniguchi, K. Watanabe, N. Lu, S. K. Banerjee, K. L. Silverman, S. Kim, E. Tutuc, L. Yang, A. H. MacDonald, and X. Li, “Evidence for moiré excitons in van der waals heterostructures,” *Nature*, vol. 567, no. 7746, pp. 71–75, 2019.
- [142] F. Wu, T. Lovorn, and A. H. MacDonald, “Theory of optical absorption by interlayer excitons in transition metal dichalcogenide heterobilayers,” *Physical Review B*, vol. 97, no. 3, p. 035306, 2018.
- [143] D. Waters, Y. Nie, F. Lüpke, Y. Pan, S. Fölsch, Y.-C. Lin, B. Jariwala, K. Zhang, C. Wang, H. Lv, K. Cho, D. Xiao, J. A. Robinson, and R. M. Feenstra, “Flat bands and mechanical deformation effects in the moiré superlattice of mos₂-wse₂ heterobilayers,” *ACS Nano*, vol. 14, no. 6, pp. 7564–7573, 2020.
- [144] S. Zhao, Z. Li, X. Huang, A. Rupp, J. Göser, I. A. Vovk, S. Y. Kruchinin, K. Watanabe, T. Taniguchi, I. Bilgin, A. S. Baimuratov, and A. Högele, “Excitons in mesoscopically reconstructed moiré heterostructures,” *Nature Nanotechnology*, vol. 18, no. 6, pp. 572–579, 2023.
- [145] Y. Bai, L. Zhou, J. Wang, W. Wu, L. J. McGilly, D. Halbertal, C. F. B. Lo, F. Liu, J. Ardelean, P. Rivera, N. R. Finney, X.-C. Yang, D. N. Basov, W. Yao, X. Xu, J. Hone, A. N. Pasupathy, and X.-Y. Zhu, “Excitons in strain-induced one-dimensional moiré potentials at transition metal dichalcogenide heterojunctions,” *Nature Materials*, vol. 19, no. 10, pp. 1068–1073, 2020.

- [146] B. Amin, N. Singh, and U. Schwingenschlögl, “Heterostructures of transition metal dichalcogenides,” *Physical Review B*, vol. 92, no. 7, p. 075439, 2015.
- [147] A. Ciarrocchi, D. Unuchek, A. Avsar, K. Watanabe, T. Taniguchi, and A. Kis, “Polarization switching and electrical control of interlayer excitons in two-dimensional van der waals heterostructures,” *Nature Photonics*, vol. 13, no. 2, pp. 131–136, 2019.
- [148] H. Korkut and Sarpkaya, “Controlling the photoluminescence of quantum emitters in hexagonal boron nitride by external magnetic fields,” *2D Materials*, vol. 10, no. 1, p. 015004, 2022.
- [149] A. Srivastava, M. Sidler, A. V. Allain, D. S. Lembke, A. Kis, and A. Imamoglu, “Optically active quantum dots in monolayer wse2,” *Nature Nanotechnology*, vol. 10, no. 6, p. 491–496, 2015.
- [150] M. Baranowski, A. Surrente, L. Klotkowski, J. M. Urban, N. Zhang, D. K. Maude, K. Wiwatowski, S. Mackowski, Y. C. Kung, D. Dumcenco, A. Kis, and P. Plochocka, “Probing the interlayer exciton physics in a mos2/mose2/mos2 van der waals heterostructure,” *Nano Letters*, vol. 17, no. 10, pp. 6360–6365, 2017.
- [151] C. Jiang, W. Xu, A. Rasmita, Z. Huang, K. Li, Q. Xiong, and W.-b. Gao, “Microsecond dark-exciton valley polarization memory in two-dimensional heterostructures,” *Nature Communications*, vol. 9, no. 1, p. 753, 2018.
- [152] P. Rivera, K. L. Seyler, H. Yu, J. R. Schaibley, J. Yan, D. G. Mandrus, W. Yao, and X. Xu, “Valley-polarized exciton dynamics in a 2d semiconductor heterostructure,” *Science*, vol. 351, no. 6274, pp. 688–691, 2016.
- [153] A. T. Hanbicki, H.-J. Chuang, M. R. Rosenberger, C. S. Hellberg, S. V. Sivaram, K. M. McCreary, I. I. Mazin, and B. T. Jonker, “Double indirect interlayer exciton in a mose2/wse2 van der waals heterostructure,” *ACS Nano*, vol. 12, no. 5, pp. 4719–4726, 2018.

- [154] L. Zhang, R. Gogna, G. W. Burg, J. Horng, E. Paik, Y.-H. Chou, K. Kim, E. Tutuc, and H. Deng, “Highly valley-polarized singlet and triplet interlayer excitons in van der waals heterostructure,” *Physical Review B*, vol. 100, no. 4, p. 041402, 2019.
- [155] H. Yu, G.-B. Liu, and W. Yao, “Brightened spin-triplet interlayer excitons and optical selection rules in van der waals heterobilayers,” *2D Materials*, vol. 5, no. 3, p. 035021, 2018.
- [156] Z. Huang, Y. Liu, K. Dini, Q. Tan, Z. Liu, H. Fang, J. Liu, T. Liew, and W. Gao, “Robust room temperature valley hall effect of interlayer excitons,” *Nano Letters*, vol. 20, no. 2, pp. 1345–1351, 2020.
- [157] A. Y. Joe, L. A. Jauregui, K. Pistunova, A. M. Mier Valdivia, Z. Lu, D. S. Wild, G. Scuri, K. De Greve, R. J. Gelly, Y. Zhou, J. Sung, A. Sushko, T. Taniguchi, K. Watanabe, D. Smirnov, M. D. Lukin, H. Park, and P. Kim, “Electrically controlled emission from singlet and triplet exciton species in atomically thin light-emitting diodes,” *Physical Review B*, vol. 103, no. 16, p. L161411, 2021.
- [158] Y. Hu, X. Wen, J. Lin, W. Yao, Y. Chen, J. Li, S. Chen, L. Wang, W. Xu, and D. Li, “All-optical valley polarization switch via controlling spin-triplet and spin-singlet interlayer exciton emission in ws_2/wse_2 heterostructure,” *Nano Letters*, vol. 23, no. 14, pp. 6581–6587, 2023.
- [159] D. MacNeill, C. Heikes, K. F. Mak, Z. Anderson, A. Kormányos, V. Zólyomi, J. Park, and D. C. Ralph, “Breaking of valley degeneracy by magnetic field in monolayer mose_2 ,” *Physical Review Letters*, vol. 114, no. 3, p. 037401, 2015.
- [160] T. Woźniak, P. E. Faria Junior, G. Seifert, A. Chaves, and J. Kunstmann, “Exciton g factors of van der waals heterostructures from first-principles calculations,” *Physical Review B*, vol. 101, no. 23, p. 235408, 2020.
- [161] H. Fang, Q. Lin, Y. Zhang, J. Thompson, S. Xiao, Z. Sun, E. Malic, S. P.

- Dash, and W. Wieczorek, “Localization and interaction of interlayer excitons in mose2/wse2 heterobilayers,” *Nature Communications*, vol. 14, no. 1, p. 6910, 2023.
- [162] A. Kormányos, V. Zólyomi, N. D. Drummond, and G. Burkard, “Spin-orbit coupling, quantum dots, and qubits in monolayer transition metal dichalcogenides,” *Physical Review X*, vol. 4, no. 1, p. 011034, 2014.
- [163] D. Huang, J.-I. Chyi, and H. Morkoç, “Carrier effects on the excitonic absorption in gaas quantum-well structures: Phase-space filling,” *Physical Review B*, vol. 42, no. 8, pp. 5147–5153, 1990.
- [164] H. Heo, J. H. Sung, S. Cha, B.-G. Jang, J.-Y. Kim, G. Jin, D. Lee, J.-H. Ahn, M.-J. Lee, J. H. Shim, H. Choi, and M.-H. Jo, “Interlayer orientation-dependent light absorption and emission in monolayer semiconductor stacks,” *Nature Communications*, vol. 6, no. 1, p. 7372, 2015.
- [165] H. Zhu, J. Wang, Z. Gong, Y. D. Kim, J. Hone, and X.-Y. Zhu, “Interfacial charge transfer circumventing momentum mismatch at two-dimensional van der waals heterojunctions,” *Nano Letters*, vol. 17, no. 6, pp. 3591–3598, 2017.
- [166] M. Palummo, M. Bernardi, and J. C. Grossman, “Exciton radiative lifetimes in two-dimensional transition metal dichalcogenides,” *Nano Letters*, vol. 15, no. 5, pp. 2794–2800, 2015.
- [167] S. Ovesen, S. Brem, C. Linderälv, M. Kuisma, T. Korn, P. Erhart, M. Selig, and E. Malic, “Interlayer exciton dynamics in van der waals heterostructures,” *Communications Physics*, vol. 2, no. 1, p. 23, 2019.
- [168] H. Zhou, Y. Zhao, W. Tao, Y. Li, Q. Zhou, and H. Zhu, “Controlling exciton and valley dynamics in two-dimensional heterostructures with atomically precise interlayer proximity,” *ACS Nano*, vol. 14, no. 4, pp. 4618–4625, 2020.
- [169] C. Choi, J. Huang, H.-C. Cheng, H. Kim, A. K. Vinod, S.-H. Bae, V. O. Özçelik, R. Grassi, J. Chae, S.-W. Huang, X. Duan, K. Kaasbjerg, T. Low,

- and C. W. Wong, “Enhanced interlayer neutral excitons and trions in tri-layer van der Waals heterostructures,” *npj 2D Materials and Applications*, vol. 2, no. 1, pp. 1–9, 2018.
- [170] J. Kiemle, F. Sigger, M. Lorke, B. Miller, K. Watanabe, T. Taniguchi, A. Holleitner, and U. Wurstbauer, “Control of the orbital character of indirect excitons in MoS_2/WS_2 heterobilayers,” *Physical Review B*, vol. 101, no. 12, p. 121404, 2020.
- [171] C. Palacios-Berraquero, D. M. Kara, A. R.-P. Montblanch, M. Barbone, P. Latawiec, D. Yoon, A. K. Ott, M. Loncar, A. C. Ferrari, and M. Atatüre, “Large-scale quantum-emitter arrays in atomically thin semiconductors,” *Nature Communications*, vol. 8, no. 1, p. 15093, 2017.
- [172] V. Perebeinos, “Two dimensions and one photon,” *Nature Nanotechnology*, vol. 10, no. 6, pp. 485–486, 2015.
- [173] X. Ma, N. F. Hartmann, J. K. S. Baldwin, S. K. Doorn, and H. Htoon, “Room-temperature single-photon generation from solitary dopants of carbon nanotubes,” *Nature Nanotechnology*, vol. 10, no. 8, pp. 671–675, 2015.
- [174] W. Wang and X. Ma, “Strain-induced trapping of indirect excitons in $\text{MoS}_2/\text{WSe}_2$ heterostructures,” *ACS Photonics*, vol. 7, no. 9, pp. 2460–2467, 2020.
- [175] W. Lu and Y. Fu, *Spectroscopy of semiconductors: numerical analysis bridging quantum mechanics and experiments*, ser. Springer series in optical sciences. Cham, Switzerland: Springer, 2018.
- [176] S. Perkowitz, *Optical characterization of semiconductors: infrared, Raman, and photoluminescence spectroscopy*, ser. Techniques of physics. London ; San Diego: Academic Press, 1993.
- [177] H. Bluhm, S. Foletti, I. Neder, M. Rudner, D. Mahalu, V. Umansky, and A. Yacoby, “Dephasing time of GaAs electron-spin qubits coupled to a nuclear bath exceeding 200 ns,” *Nature Physics*, vol. 7, no. 2, pp. 109–113, 2011.

- [178] M. Rančić, M. P. Hedges, R. L. Ahlefeldt, and M. J. Sellars, “Coherence time of over a second in a telecom-compatible quantum memory storage material,” *Nature Physics*, vol. 14, no. 1, pp. 50–54, 2018.
- [179] S. Zaiser, T. Rendler, I. Jakobi, T. Wolf, S.-Y. Lee, S. Wagner, V. Bergholm, T. Schulte-Herbrüggen, P. Neumann, and J. Wrachtrup, “Enhancing quantum sensing sensitivity by a quantum memory,” *Nature Communications*, vol. 7, no. 1, p. 12279, 2016.
- [180] D. P. Pires, I. A. Silva, E. R. deAzevedo, D. O. Soares-Pinto, and J. G. Filgueiras, “Coherence orders, decoherence, and quantum metrology,” *Physical Review A*, vol. 98, no. 3, p. 032101, 2018.
- [181] M. Fox, *Quantum optics: an introduction*, ser. Oxford master series in physics. Oxford ; New York: Oxford University Press, 2006.
- [182] G. D. Shepard, J. V. Ardelean, O. A. Ajayi, D. Rhodes, X. Zhu, J. C. Hone, and S. Strauf, “Trion-species-resolved quantum beats in mose2,” *ACS Nano*, vol. 11, no. 11, pp. 11 550–11 558, 2017.
- [183] K. Hao, L. Xu, P. Nagler, A. Singh, K. Tran, C. K. Dass, C. Schüller, T. Korn, X. Li, and G. Moody, “Coherent and incoherent coupling dynamics between neutral and charged excitons in monolayer mose2,” *Nano Letters*, vol. 16, no. 8, pp. 5109–5113, 2016.
- [184] M. Titze, B. Li, X. Zhang, P. M. Ajayan, and H. Li, “Intrinsic coherence time of trions in monolayer mose₂ measured via two-dimensional coherent spectroscopy,” *Physical Review Materials*, vol. 2, no. 5, p. 054001, 2018.
- [185] T. Jakubczyk, V. Delmonte, M. Koperski, K. Nogajewski, C. Faugeras, W. Langbein, M. Potemski, and J. Kasprzak, “Radiatively limited dephasing and exciton dynamics in mose2 monolayers revealed with four-wave mixing microscopy,” *Nano Letters*, vol. 16, no. 9, pp. 5333–5339, 2016.
- [186] L. Sigl, F. Sigger, F. Kronowetter, J. Kiemle, J. Klein, K. Watanabe, T. Taniguchi, J. J. Finley, U. Wurstbauer, and A. W. Holleitner, “Signatures of a degenerate many-body state of interlayer excitons in a van der waals heterostack,” *Physical Review Research*, vol. 2, no. 4, p. 042044, 2020.

- [187] D. Erkensten, S. Brem, and E. Malic, “Exciton-exciton interaction in transition metal dichalcogenide monolayers and van der waals heterostructures,” *Physical Review B*, vol. 103, no. 4, p. 045426, 2021.
- [188] I. Sarpkaya, Z. Zhang, W. Walden-Newman, X. Wang, J. Hone, C. W. Wong, and S. Strauf, “Prolonged spontaneous emission and dephasing of localized excitons in air-bridged carbon nanotubes,” *Nature Communications*, vol. 4, no. 1, 2013.
- [189] W. W. Chow, M. O. Scully, and J. O. Stoner, “Quantum-beat phenomena described by quantum electrodynamics and neoclassical theory,” *Physical Review A*, vol. 11, no. 4, pp. 1380–1388, 1975.
- [190] J. Erland and I. Balslev, “Theory of quantum beat and polarization interference in four-wave mixing,” *Physical Review A*, vol. 48, no. 3, pp. R1765–R1768, 1993.
- [191] G. Moody, R. Singh, H. Li, I. A. Akimov, M. Bayer, D. Reuter, A. D. Wieck, and S. T. Cundiff, “Correlation and dephasing effects on the non-radiative coherence between bright excitons in an inas qd ensemble measured with 2d spectroscopy,” *Solid State Communications*, vol. 163, pp. 65–69, 2013.
- [192] K. Leo, T. C. Damen, J. Shah, and K. Köhler, “Quantum beats of free and bound excitons in $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ quantum wells,” *Physical Review B*, vol. 42, no. 17, pp. 11 359–11 361, 1990.
- [193] B. F. Feuerbacher, J. Kuhl, R. Eccleston, and K. Ploog, “Quantum beats between the light and heavy hole excitons in a quantum well,” *Solid State Communications*, vol. 74, no. 12, pp. 1279–1283, 1990.
- [194] P. Gilliot, D. Brinkmann, J. Kudrna, O. Crégut, R. Lévy, A. Arnoult, J. Cibert, and S. Tatarenko, “Quantum beats between trion and exciton transitions in modulation-doped CdTe quantum wells,” *Physical Review B*, vol. 60, no. 8, pp. 5797–5801, 1999.
- [195] K.-H. Pantke, D. Oberhauser, V. G. Lyssenko, J. M. Hvam, and

- G. Weimann, “Coherent generation and interference of excitons and biexcitons in $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ quantum wells,” *Physical Review B*, vol. 47, no. 4, pp. 2413–2416, 1993.
- [196] G. Moody, I. Akimov, H. Li, R. Singh, D. Yakovlev, G. Karczewski, M. Wiaterski, T. Wojtowicz, M. Bayer, and S. Cundiff, “Coherent coupling of excitons and trions in a photoexcited $\text{CdTe}/\text{CdMgTe}$ quantum well,” *Physical Review Letters*, vol. 112, no. 9, p. 097401, 2014.
- [197] S. Sim, D. Lee, A. V. Trifonov, T. Kim, S. Cha, J. H. Sung, S. Cho, W. Shim, M.-H. Jo, and H. Choi, “Ultrafast quantum beats of anisotropic excitons in atomically thin res_2 ,” *Nature Communications*, vol. 9, no. 1, p. 351, 2018.
- [198] T. L. Purz, E. W. Martin, P. Rivera, W. G. Holtzmann, X. Xu, and S. T. Cundiff, “Coherent exciton-exciton interactions and exciton dynamics in a $\text{MoSe}_2/\text{WSe}_2$ heterostructure,” *Physical Review B*, vol. 104, no. 24, p. L241302, 2021.
- [199] S. T. Cundiff, “Effects of correlation between inhomogeneously broadened transitions on quantum beats in transient four-wave mixing,” *Physical Review A*, vol. 49, no. 4, pp. 3114–3118, 1994.