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Emergent electronic and excitonic physics in WSe₂/WS₂ moiré superlattices

By

Emma Caitlin Regan

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

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in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Feng Wang, Chair
Professor Michael F. Crommie
Assistant Professor Michael Zaletel

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Emergent electronic and excitonic physics in WSe₂/WS₂ moiré superlattices

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Abstract

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In the fascinating family of two-dimensional (2D) materials, layers of atoms are bonded strongly into sheets that are held together by weak van der Waals bonds. Consequently, atomically-thin layers of various 2D materials can be isolated into monolayers and stacked together to form synthetic materials with emergent electronic and optical properties. The behavior of a 2D stack is determined by the behavior of electrons within each layer and interactions between the layers, which provides remarkable opportunities for creativity and control in electronic material design. In the past few years, a unique and exciting prospect for 2D stacks has emerged: the ability to tune the twist angle between atomic layers. With a small twist angle or lattice mismatch, the interference of two atomic lattices produces a large periodic pattern, called a moiré superlattice, where the alignment between atoms varies periodically across the system. Recently, it has become clear that moiré superlattices can dramatically modify the electronic properties of a 2D stack, resulting in novel states of matter, modified light-matter interactions, and more.

In this dissertation, I focus on moiré superlattices formed from WSe₂ and WS₂ monolayers, which are both members of the semiconducting transition metal dichalcogenide (TMD) family known for their strong light-matter interactions and promise for optoelectronic applications. I begin with an introduction to semiconducting TMDs, which guides our understanding of TMD stacks and, in particular, moiré superlattices. I then describe several experimental studies highlighting how a simple interference pattern can produce fascinating electronic and optical behavior. First, I consider how a moiré superlattice modifies the excitonic properties of TMDs, where our combined experimental and theoretical investigations reveal exciton states unique to superlattices. From there, I describe how moiré superlattices can lead to novel correlated states of matter by shifting the balance between the kinetic energy and interaction energy of electrons. Using a new experimental approach, we reveal the presence of generalized Wigner crystal states in TMD moiré superlattices thanks to the enhanced influence of electron-electron interactions. Finally, I demonstrate an optical technique for measuring spin transport in TMD moiré superlattices that provides insight into how spin behave in correlated 2D materials.

To my daughter, Rowan.

Table of contents

Abstract	i
Table of contents	ii
List of figures	iv
Acknowledgments	xii
1 Introduction	1
1.1 Background and Motivation	1
1.2 Outline of thesis	2
2 Introduction to transition metal dichalcogenide heterostructures	4
2.1 Transition metal dichalcogenide monolayers	4
2.2 Transition metal dichalcogenide heterostructures	5
2.3 Transition metal dichalcogenide moiré superlattices	7
2.4 Heterostructure fabrication	10
2.5 General experimental approaches	13
3 Excitons in WSe ₂ /WS ₂ moiré superlattices	17
3.1 Introduction	17
3.2 Observation of intralayer moiré exciton states in aligned WSe ₂ /WS ₂ heterostructures	18
3.2.1 Optical characterization	18
3.2.2 Modeling the moiré potential	24
3.3 Origin of intralayer moiré exciton states in aligned WSe ₂ /WS ₂ heterostructures	28
3.3.1 A more complete model of moiré excitons	29
3.3.2 Experimental evidence for character of moiré exciton states	32
3.4 Discussion	38
4 Correlated electronic states in WSe ₂ /WS ₂ moiré superlattices	40
4.1 Introduction	40
4.2 Optical detection of correlated electronic states	42
4.2.1 Optically detected resistance and capacitance (ODRC) technique	42
4.2.2 Circuit model	46
4.2.3 ODRC in large twist angle WSe ₂ /WS ₂ heterostructure	49
4.3 Observation of Mott and Wigner crystal states in a WSe ₂ /WS ₂ moiré superlattices	50

4.3.1	Spin lifetime in correlated electron system.....	53
4.4	Discussion	54
5	Spin transport in WSe ₂ /WS ₂ moiré superlattices.....	57
5.1	Introduction	57
5.2	Probing spin transport via spatially resolved pump probe experiments.....	59
5.2.1	Spatial-temporal imaging technique	59
5.2.2	Example spin transport data and fitting to diffusion model.....	61
5.3	Spin transport in WSe ₂ /WS ₂ moiré superlattices	64
5.4	Discussion	67
	References	69

List of figures

- Fig. 2.1 | TMD monolayers.** **a.** Structure of 2H TMD monolayer with chalcogen (S, Se) in green and transition metal (Mo, W) in purple. **b.** Schematic of the bright A excitons and the K and K' corners of the Brillouin zone (hexagon) of a TMD monolayer. Excitons at the K (K') valley couple to σ^+ (σ^-) light. Both spin split conduction bands are shown. Only the highest valence band is shown because the spin splitting is large. 4
- Fig. 2.2 | TMD heterostructures.** **a.** Schematic of a TMD heterobilayer. **b.** Schematic of a heterobilayer formed by two TMDs (light and dark green) in momentum space. The heterobilayer is characterized by the lattice mismatch, twist angle (θ), and band alignment between the two layers. **d.** | Schematic of intralayer and interlayer excitons at the K valley of two layers forming a heterostructure with type II band alignment..... 6
- Fig. 2.3 | TMD moiré superlattices.** **a.** Illustration of a moiré superlattice formed by two TMDs in real space. The superlattice vectors are labelled as a_1 and a_2 and form the superlattice unit cell. There are three high-symmetry positions in the superlattice where the local atomic configuration has three-fold rotational symmetry. The stacking is labelled at these positions (AA, AB, and BA). **b.** Schematic of the Brillouin zones of each monolayer (green and orange) and the mini Brillouin zone (mBZ) of the superlattice, where the mBZ wavevector corresponds to the difference between the two K points of the monolayers. **c.** Schematic of monolayer TMD bands (green) folded in the mBZ. The moiré potential opens a gap at the mBZ boundary, which produces flatter electronic bands (grey). **d.** Atomic-resolution high-angle annular dark-field STEM image of a near-zero twist angle WSe₂/WS₂ heterostructure showing a moiré superlattice with superlattice vectors a_1 and a_2 8
- Fig. 2.4 | Schematic of a WSe₂/WS₂ heterostructure.** Hexagonal boron nitride (hBN) layers are included for encapsulation and few-layer graphite (Gr) are used as gate and contact. A voltage V_g can be applied between the back gate and the contact to control the carrier concentration in the heterostructure. 10
- Fig. 2.5 | TMD heterostructure fabrication process.** **a.** Optical microscope images of sample WS₂ and WSe₂ flakes, chosen for their long, straight edges. **b.** Schematic of a TMD lattice, where x' lies along the armchair direction. θ denotes the angle between the armchair axis and the polarization of the incident beam (red). **c.** A sample heterostructure after PET transfer. From top to bottom, the device includes the following layers: top hBN, WS₂, WSe₂, few-layer graphite contact, bottom hBN, and few-layer graphite back gate. The WS₂ and WSe₂ are outlined in yellow and green, respectively. **d.** The same sample in c but with gold electrodes. **e.** Polarization-dependent SHG signal for WS₂ and WSe₂ monolayers after heterostructure assembly shows that the TMD flakes are well-aligned (< 0.5 degrees). **f.** SHG counts on the monolayer and heterostructure regions shows that the device has near-0-degree twist angle, rather than near-60-degree..... 11

Fig. 2.6 | Reflection contrast spectrum of an hBN-encapsulated WSe₂ monolayer at 10 K.

The main peaks correspond to the A exciton (~715 nm), 2s state (~667 nm), and B exciton (~575 nm). The asymmetry of the A exciton is due to the local field factor, which mixes the real and imaginary parts of the optical conductivity. 15

Fig. 3.1 | PL measurements of a WSe₂/WS₂ moiré superlattice. a. Schematic of PL

measurement in a WSe₂/WS₂ heterostructure. A laser is used to selectively excite excitons in WSe₂. Due to the type II band alignment, electrons transfer almost immediately to the WS₂ layer. Interlayer excitons form across the interface, and their recombination results in PL emission at a characteristic energy. **b.** PL spectrum of a near-zero-twist-angle device (blue) and reference monolayer WSe₂ sample (green). **c.** Same as c but on a logarithmic scale. The disappearance of the monolayer PL and the emergence of interlayer exciton PL in the heterostructure indicates efficient interlayer coupling in the device. 18

Fig. 3.2 | Absorption measurements of a WSe₂/WS₂ moiré superlattice. a. Reflection contrast

spectra of a near-zero-twist-angle heterostructure D1 (upper panel) and a large-twist-angle heterostructure (lower panel). The latter shows only a single resonance in the energy range of the WSe₂ A exciton. In contrast, the moiré superlattice formed in device D1 gives rise to three prominent peaks with comparable oscillator strength in this range (labeled I, II, and III), corresponding to different moiré exciton states. **b.** The interlayer exciton PL excitation spectrum (black dots), compared to the reflection contrast spectrum (blue curve). The interlayer exciton PL is strongly enhanced when the system is excited at all moiré exciton states. 19

Fig. 3.3 | Twist angle dependent absorption spectra. Reflection-contrast spectra from 18

WSe₂/WS₂ heterostructures spanning a large range of twist angles close to AA stacking (upper panel) and AB stacking (lower panel). Devices with twist angle < 1 degree from AA or AB stacking consistently show three peaks in the WSe₂ A exciton range. 21

Fig. 3.4 | Twist-angle-dependence of peak I position. Black and red symbols represent results

from near-AA stacked and near-AB stacked bilayers, respectively. Three large-twist-angle (>10 degree) devices are also included as reference (gray symbols). 22

Fig. 3.5 | Gate-dependent reflection contrast spectra. a. Gate-dependent reflection contrast

spectra of an aligned WSe₂/WS₂ heterostructure under both electron- (positive carrier concentration) and hole- (negative carrier concentration) doping. White dashed box encloses the photon energy range near the WSe₂ A exciton, where the three prominent moiré exciton states (labeled as I, II, and III) appear. **b.** Gate-dependent reflection contrast spectrum of a large twist angle device for reference. Figure adapted from reference ⁸⁸. **c.** Reflection contrast spectra in the WSe₂ A exciton range on the electron-doping side (electron concentration for each spectrum is noted in units of cm⁻²). Peak I shows a strong blueshift and transfers its oscillator strength to another emerging peak at lower energy (I'), and peak III shows a strong blueshift with diminished oscillator strength. On the other hand, peak II remains largely unchanged except for a small energy shift. 23

- Fig. 3.6 | Temperature-dependent reflection contrast in near-zero-twist-angle WSe₂/WS₂ heterostructure.**..... 24
- Fig. 3.7 | WSe₂ exciton dispersion in the mBZ with a moiré potential. a.** $V = 0$ meV (zero coupling), **b.** $V < Ek$ ($V = 5$ meV, weak coupling), and **c.** $V > Ek$ ($V = 25$ meV, strong coupling). Here Ek is the exciton kinetic energy in the first mBZ. The lower panel shows the corresponding absorption spectra (**d-f**). A broadening of 2 meV is used to calculate the absorption spectrum. The inset in **a** illustrates the mBZ in momentum space and the high-symmetry points. Horizontal arrows in **a-c** labels the optically active exciton states in each case that give rise to absorption peaks (vertical arrows in **d-f**). The exciton dispersion is strongly modified in the “strong coupling” regime due to the strong mixing between different exciton states **c**, which gives rise to multiple moiré exciton peaks with comparable oscillator strength in the absorption spectrum (peak I to III in **f**) from different moiré mini bands (state I to III in **c**). 26
- Fig. 3.8 | Real space moiré potential and exciton wavefunctions. a.** The simulated real space distribution of the moiré potential with $V = 25$ meV and $\psi = 15^\circ$. The potential minimum is labeled as α . **b-d** Real space distribution of exciton center-of-mass wavefunction in the “strong-coupling” regime. The strong moiré potential traps the lowest-energy exciton state I around its minimum point (**a**). Interestingly, state III is also centered at point α (**b**) but state II is centered at a different point β (**c**), which can account for the remarkably different gate dependence between the moiré exciton states. 27
- Fig. 3.9 | Reconstruction of the moiré superlattice. a.** Schematic of the WSe₂/WS₂ moiré superlattice with the superlattice unit cell outlined in black and the high symmetry positions labelled. **b.** Computed strain distribution in the WSe₂ layer, plotted as a percentage change in the local lattice parameter from equilibrium. **c.** The effective moiré potential, computed as the variation in the WSe₂ band gap due to the local strain shown in **b**. 29
- Fig. 3.10 | Electronic wavefunctions at conduction (a) and valence (b) band edges of the inhomogeneously strained WSe₂.** 30
- Fig. 3.11 | Absorption spectrum of intralayer excitons. a.** Experimental reflection contrast spectrum of near-zero-degree WSe₂/WS₂. **b.** Computed absorbance spectrum of the inhomogeneously strained WSe₂ computed with the ab initio GW-BSE approach. 31
- Fig. 3.12 | Exciton charge distribution.** Distribution of electron charge density of the computed exciton (**a.** peak I, **b.** peak III) for three fixed hole positions (red dot) in the moiré unit cell. Peak I is a Wannier-like exciton, where the electron and hole are both localized around the AA position. Peak III is a charge-transfer exciton, where the electron and hole occupy different positions in the superlattice unit cell. 31
- Fig. 3.13 | Behavior of WSe₂/WS₂ moiré excitons under charge doping. a.** Experimental doping-dependent reflection contrast spectrum of a WSe₂/WS₂ moiré superlattice shows distinct behavior for WSe₂ moiré excitons I, II, and III. Negative (positive) charge concentration refers to hole (electron) doping. The redshift (blueshift) of peak III under hole

(electron) doping is highlighted with dashed (dotted) white lines. **b.** Experimental doping-dependent reflection contrast spectrum of a reference misaligned WSe₂/WS₂ heterostructure. The WSe₂ exciton interacts strongly with doping doped holes in the WSe₂ layer, forming a trion state, but weakly with doped electrons in the WS₂ layer. 33

Fig. 3.14 | Fitting of peak energies in doping dependent reflection contrast. At each charge concentration, the spectrum was fit using three Lorentzian functions. The extracted peak energies are plotted only in doping ranges where the peaks can be easily distinguished. 33

Fig. 3.15 | Interaction of excitons and doped holes. Schematic of moiré exciton I (left) and III (right) under hole doping. from both top-down (top) and side (bottom) views. Exciton I is a tightly bound exciton at the AA position, while exciton III is a charge-transfer exciton with the hole at the B^{Se/W} position and electron density at the surrounding AA positions. Doped holes reside at the B^{Se/W} positions. In the case of exciton III, we consider two scenarios: in scenario A, the doped hole is at the same B^{Se/W} site as the constituent hole, and in scenario B, the doped hole is at the adjacent B^{Se/W} site. 34

Fig. 3.16 | Interaction of excitons and doped electrons. Schematic of moiré exciton I (left) and III (right) under hole doping. from both top-down (top) and side (bottom) views. Exciton I is a tightly bound exciton at the AA position, while exciton III is a charge-transfer exciton with the hole at the B^{Se/W} position and electron density at the surrounding AA positions. Doped electrons reside at the B^{Se/W} positions. In the case of exciton III, we consider two scenarios: in scenario A, the doped electron is at the same B^{Se/W} site as the constituent hole, and in scenario B, the doped electron is at the adjacent B^{Se/W} site. 35

Fig. 3.17 | Doping dependence of moiré excitons under magnetic field. Hole doping dependent reflection contrast spectra of WSe₂/WS₂ moiré superlattice (**a**) and WSe₂ monolayer (**b**) for both left and right circularly polarized light under a perpendicular magnetic field at $B = 6$ T. Hole density is labeled for each set of spectra. In the WSe₂/WS₂ moiré superlattice, exciton I and III show relatively weak dependence on the exciton valley due to the spatial separation between doped holes at the K' valley and the constituent holes. Exciton II shows a relatively strong difference in behavior between K and K' valley excitons due to the partial overlap between doped holes at the K' valley and the exciton. On the other hand, the monolayer WSe₂ A exciton is strongly modified by the doped holes at the K' valley due to the large exchange interaction. K' valley doped holes form trion states with the K valley exciton, resulting in an absorption peak at lower energy. 37

Fig. 4.1 | Flat bands and correlations in TMD moiré superlattices. **a.** Schematic of monolayer TMD bands (green) folded in the mBZ. The moiré potential opens a gap at the mBZ boundary, which produces flatter electronic bands (grey). **b.** Illustration of a Mott insulator state in a WSe₂/WS₂ moiré superlattice with one hole per superlattice unit cell. 40

Fig. 4.2 | Exciton as a probe of charge. The doping dependent reflection contrast spectrum of the WSe₂ moiré excitons in a WSe₂/WS₂ moiré superlattice. The white dashed box highlights a hole doping range where the change in the spectrum is large and linear with doping. 43

- Fig. 4.3 | Schematic of ODRC measurements.** Sketch of an ODRC measurement in a WSe_2/WS_2 heterostructure, which includes a local top gate and global back gate. A small AC bias ΔV leads to charge redistribution between region 1 and region 2 (Δn), which is detected via the change in optical reflectivity of the WSe_2 exciton in region 2. A DC bias V_{top} (not shown) is also applied to the local top gate to change the carrier concentration in region 1. 43
- Fig. 4.4 | ODRC device.** Side-view illustration (a) and optical microscope image (b) of near-zero twist angle heterostructure used for the ODRC measurements described in this chapter. The graphite top gate, WS_2 , and WSe_2 flakes are outlined in grey, yellow, and green, respectively. c. Optical absorption spectrum of the heterostructure showing splitting of the WSe_2 A exciton into three prominent peaks, which is characteristic of intralayer moiré excitons in an aligned heterostructure. The ODRC measurements use a laser probe in resonance with the lowest energy exciton peak (red arrow). 44
- Fig. 4.5 | Experimental setup for an ODRC measurement.** 45
- Fig. 4.6 | ODRC experiment checks.** a. Reflection contrast spectra for the lowest-energy WSe_2 A exciton resonance in region 2 when the local top gate voltage V_{top} is tuned from 0.5 V to -3.5 V. Region 2 is not affected when the hole concentration is tuned in region 1 by V_{top} . b. Reflection contrast spectra for the WSe_2 A exciton in region 2 when the global back gate is tuned from -0.95 V to -1.05 V. Inset shows zoomed-in view of the exciton peak. The spectral change is monotonic and approximately linear with carrier concentration. c. ODRC signal measured at very low frequency for a range of modulation voltages, showing that the contact freezes around 1 Hz..... 46
- Fig. 4.7 | Circuit model of ODRC measurement.** a. Device schematic for an ODRC measurement in a WSe_2/WS_2 heterostructure, which includes a local top gate and global back gate. A small AC bias ΔV leads to charge redistribution between region 1 and region 2 (Δn), which is detected via the change in optical reflectivity of the WSe_2 exciton in region 2. This AC measurement can be modeled as an effective RC circuit, where the elements are shown schematically in b. C_1 , C_B , and C_2 are the illustrated geometric capacitances in the system, and R and C_Q are the doping-dependent resistance and quantum capacitance of region 1 that we measure. 47
- Fig. 4.8 | ODRC signal for large twist angle WSe_2/WS_2 heterostructure.** ODRC signal, ΔOC , for a large twist angle heterostructure. When holes are injected into the sample, charge redistribution begins and ΔOC rapidly increases. For increasing hole concentration, the charge redistribution is relatively constant. The signal falls off with increasing frequency, characteristic of an RC circuit. 49
- Fig. 4.9 | Raw ODRC signal in WSe_2/WS_2 moiré superlattice.** ODRC signal, ΔOC , signal at 1 kHz (grey) and 30 kHz (black) from charge neutral to moderate hole doping. Strong gap-like features are observed at hole doping levels of $n = n_0/3$ (orange dashed line), $n = 2n_0/3$ (green dashed line), and $n = n_0$ (blue dashed line). The purple dashed line corresponds to $n = 0$ 50

- Fig. 4.10 | Extracted resistance and capacitance from circuit model.** **a.** Frequency-dependent ODRC signal at representative doping levels. Dots are data, curves are fits to the RC circuit model for a given doping level. **b.** and **c.** Extracted capacitance C_{eff} (**a**) and resistance (**b**) of region 1 from the data in Fig. 4.9 (grey curves) and from the frequency dependent ODRC signal in **a** (black dots). The decreased capacitance and increased resistance indicate emerging insulating states at $n = n_0/3$, $n = 2n_0/3$, and $n = n_0$ 51
- Fig. 4.11 | Illustrations of generalized Wigner crystal ($n = n_0/3$, $n = 2n_0/3$) and Mott insulator states ($n = n_0$) in a WSe_2/WS_2 moiré superlattice.** 52
- Fig. 4.12 | Temperature dependence of Mott and generalized Wigner crystal states.** **a.** Extracted resistance from ODRC measurements taken from 3 K to 70 K. The Mott insulator at $n = n_0$ is observable up to 45 K, and the generalized Wigner crystal states at $n = n_0/3$ and $n = 2n_0/3$ persist until 10 K. (**b**) Plot of $\ln(R)$ versus $1/kBT$ for Mott (blue) and generalized Wigner crystal states (orange and green). Error bars correspond to the estimated uncertainty in the extracted resistance values. 53
- Fig. 4.13 | Optical investigation of low-energy spin excitation dynamics of a WSe_2/WS_2 Mott insulator.** **a.** Schematic of an optically-generated low energy spin excitation in the lower Hubbard band of a WSe_2/WS_2 superlattice. **b.** Doping dependent decay dynamics of the optically generated pure spin excitations. **c.** Summary of the spin (blue) and charge (black) lifetimes as a function of hole doping. The spin relaxation slows down markedly near $n = n_0$, with a lifetime as long as 8 μs . On the other hand, the total charge population decays quickly for all doping levels. 54
- Fig. 4.14 | Nanoscale conductivity imaging of a WSe_2/WS_2 moiré superlattice.** Topography (**a**) and MIM-Im images (**b**) of the WSe_2 and heterostructure regions. **c.** MIM-Im signals at three different locations labeled in (**a**) as a function of the back-gate voltage (i.e. carrier concentration). The positions of $n/n_0 = 1$ are indicated by arrows for each curve. 55
- Fig. 4.15 | Imaging Mott and Wigner crystal states with STM.** From left to right: dI/dV map of the Mott insulator and Wigner crystal states in the WSe_2/WS_2 moiré superlattice. The triangular lattice formed by the AB stacking sites is labelled with red dots. 56
- Fig. 5.1 | Spin transport in a correlated electronic state.** Schematic of an optically generated spin excitation moving in a Mott insulator of holes (red circles) in a WSe_2/WS_2 moiré superlattice. A second probe beam can monitor the spin population in space and time. 57
- Fig. 5.2 | Generating pure spin excitations in a WSe_2/WS_2 heterostructure.** **a.** With left-handed circularly polarized photons, K valley excitons in WSe_2 are selectively excited and efficiently converted into excess holes within 100 fs through the ultrafast interlayer charge transfer process. **b.** In 100 ns, electrons in WS_2 recombine with K and K' holes in WSe_2 with almost equal probabilities, resulting in an excess of K valley holes and a deficiency of K valley holes in WSe_2 . **c.** The valley-polarized hole population has ultralong lifetime of many microseconds. The dashed line denotes the Fermi level before optical excitation. Adapted from reference ⁸⁸. 58

- Fig. 5.3 | Schematic of a spatial-temporal imaging experiment in WSe₂/WS₂ moiré superlattice.** A circularly polarized pump beam generated a 1D pure spin excitation in the superlattice. A circularly polarized probe beam monitors the dynamics of the spin population. To obtain spatial information, the pump beam is scanned across the sample and the delay-dependent circular dichroic signal is measured for each Δx . The carrier concentration is tuned via the graphite gate. 59
- Fig. 5.4 | Spatial-temporal imaging experiment. a.** Microscope image of a WSe₂/WS₂ sample (heterostructure region outlined in black) with a schematic of the pump (orange) and probe (red) beams overlayed. The pump beam is scanned across the sample using a piezo-controlled mirror, following the black dashed line. **b.** Experimental setup for spatial-temporal imaging measurement. Two laser diodes are driven by a function generator to create pulse trains. A piezo controlled mirror is used to move the pump across the sample. The circular dichroic signal is measured with an APD and sent to a lockin detector. 60
- Fig. 5.5 | Sample spatially resolved circular dichroism data from a 5° twist angle WSe₂/WS₂ heterostructure.** Plot of the pump-induced circular dichroism of the probe beam for various delays and pump-probe separations (Δx). Squares are data, lines are guides to the eye connecting the data points for each Δx . When the pump and probe are overlapped (purple data), simple decay behavior is observed. When the pump and probe are spatially separated, the spins diffuse from the pump location to the probe location, resulting in an increase in signal after t_0 . This data is taken at moderate hole doping. 62
- Fig. 5.6 | Sample spatially resolved circular dichroism showing spin transport in a doped 5° twist angle WSe₂/WS₂ heterostructure.** The hole concentration, labelled for each plot, increases from left to right. This figure includes only a subset of the hole concentrations measured. 62
- Fig. 5.7 | Extracted doping-dependent spin diffusion constant (a) and lifetime (b) for a 5° twist angle WSe₂/WS₂ heterostructure.** Values are obtained by fitting spatial-temporal circular dichroism maps to a diffusion model. Error bars show 95% confidence intervals. . 63
- Fig. 5.8 | Spatial-temporal imaging of spin transport in doped WSe₂/WS₂ superlattice.** The hole concentration, labelled for each plot, increases from left to right. This figure includes only a subset of the hole concentrations measured. 64
- Fig. 5.9 | Diffusive spin transport in WSe₂/WS₂ moiré superlattice.** Spatial-temporal circular dichroism at (a) $n/n_0 = 1/2$ and (b) $n/n_0 = 1$. Dots of a given color are experimental data for each pump probe separation, and lines are corresponding fits to the diffusion model. **c.** Extracted diffusion constant from fitting spatial-temporal circular dichroism maps to diffusion model at each hole concentration. Error bars represent 95% confidence intervals of the fit. 65
- Fig. 5.10 | Spin diffusion in doped near-zero and large twist angle WSe₂/WS₂ heterostructures.** Extracted spin diffusion constant from spatially dependent circular dichroism maps taken in two near-zero-degree heterostructures (black and blue dots) and a

large twist angle heterostructure (green circles, from ref ⁸⁸). The superlattice samples show strongly reduced spin diffusion at all hole concentrations. 66

Fig. 5.11 | Temperature dependent spin diffusion in doped WSe₂/WS₂ superlattice.
Extracted spin diffusion constant from spatially dependent circular dichroism maps taken at three temperatures: 11 K (base temperature), 22 K, and 45 K. We observe weak temperature dependence around the $n/n_0 = 1$, the Mott state, highlighted with the black dashed line..... 66

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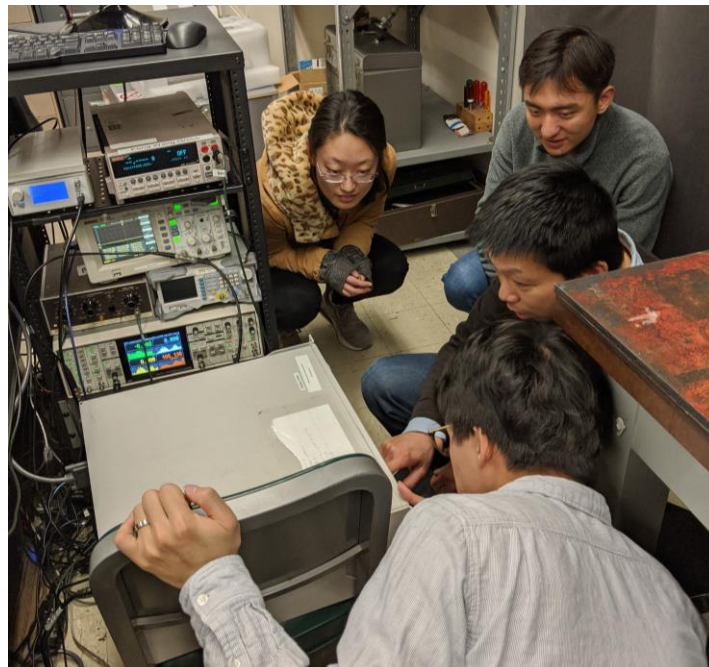


Fig. 0.1 | Wang Lab. Danqing Wang, Zheyu Lu, Feng Wang, Yoseob Yoon, and me (not pictured) working together in B145.

I am thankful for everyone who has come through the Wang lab during my time here. I am especially grateful for many years of productive collaborations with Iqbal Utama, Sihan Zhao, Wenyu Zhao, Zuocheng Zhang, and Zheyu Lu. I have learned so much from sharing space and conversations with many graduate students, postdocs, and visitors, including Yoseob Yoon, Sudi Chen, Seok Jae Yoo, Shaowei Li, Guorui Chen, Sasha Zibrov, Lili Jiang, Chan-Shan Yang, Patrick Gallagher, Tairu Lyu, Shaoxin Wang, Hongyuan Li, Sheng Wang, Qi Liu, and Shilong Zhao. Two graduate students in particular, Halleh Balch and Steve Drapcho, have been wonderful mentors, always up for a coffee and a conversation about managing graduate school and the future. In the past couple of years, many new students and postdocs have given the lab renewed energy. The lab is in good hands with Collin Sanborn, Ziyu Xiang, Can Uzundal, Ruichi Qi, Jingxu Xie, Qixin Feng, Haleem Kim, and Andy Joe around. We are all lucky to have Ron Shen down the hall. We benefit enormously from his scientific expertise and experience during group meetings and from his thoughtfulness during group lunches. I am also indebted to the professors outside of our lab who have mentored me and served on my committees throughout my PhD.

So many others at Berkeley have supported my growth over the past six years: the AS&T community, the Berkeley Science Review, and the Physics department staff, to name a few. I am especially grateful for daily interactions with Carlos Bustamante whose kindness is a true gift to the Physics department. Many of my friendships in graduate school began through interactions on campus, and I feel so lucky to have met such interesting, kind, and thoughtful people at this stage in my life. I am also grateful for many friends outside of the Berkeley community, especially Jenny Luppino and Cecilia Nowell.

My husband, Conrad, and I started our PhDs together at Berkeley after living apart for too long. Sharing this journey in science with him has been so special. He has listened to hours of practice talks before conferences and group meetings, helped me with problem sets, and most importantly, been my source of strength, laughter, and love. I am so grateful for the home we have built together and the family that we are growing—our goofy cats, Smudge and Moose, and our sweet baby, Rowan, who was born during our last semester at Berkeley and who slept in my lap while I wrote most of this dissertation.

Finally, to my family—Mom, Dad, and Anna—who supported me through every step of my academic journey. I wouldn't be here without you. I am lucky to be surrounded by so much love.

1 Introduction

1.1 Background and Motivation

Before I motivate my thesis research, I must introduce the main characters. This dissertation is centered around a family of materials known as the transition metal dichalcogenides (TMDs). They are part of a larger family of two dimensional (2D) materials that have strong covalent bonds between the atoms in plane and weak van der Waals bonds holding the sheets together in the third dimension. Because of these weak out-of-plane bonds, single atomic layers—known as monolayers—can be physically peeled from the bulk and studied as independent or combined systems.

Here I focus on semiconducting TMDs, whose monolayers efficiently absorb and emit visible light. Considering their atomic thickness, TMD monolayers interact remarkably strongly with light, absorbing nearly 100% of incoming light under ideal conditions. The strong light-matter interactions led scientists and engineers to study TMDs as potential active materials in optoelectronic devices, like light emitters and solar cells, and integrated silicon-based photonic devices. Driven by these possible applications, enormous improvements in TMD material quality—for example, reduced defect densities—were achieved in the past decade. At the same time, researchers discovered how to (somewhat) effectively add electrical contacts to TMDs, how to inject excess charge carriers to tune the electrical conductivity, and why exactly TMDs interact so strongly with light.

As the material quality and device techniques improved, another set of researchers—condensed matter physicists—became increasingly interested in TMDs and other 2D materials for a different reason: unprecedented levels of tunability and creativity in materials design. In particular, different 2D materials can be isolated and stacked together into heterostructures with completely different electronic properties than any single material. Since the layers are held together with weak van der Waals bonds, any 2D material can be stacked on top of any other 2D material without concern for lattice matching or growth dynamics. In fact, these layers can be stacked together at any twist angle, an idea that is central to this dissertation. Scientists can then control the symmetry and electronic properties of the stack by carefully considering the electronic states within each layer and their interlayer coupling. And once the layers are together, electrical contacts and gates can efficiently and reversibly inject extra electrons into the systems, which is not possible in bulk materials. These levels of control—from the individual materials to the electronic doping—allow us to think about 2D heterostructures as highly tunable condensed matter simulators.

In this dissertation, the common thread that connects each project is the twist angle degree of freedom in 2D heterostructures. When two layers with similar lattices are stacked together at small twist angle, a larger periodic pattern emerges known as a moiré superlattice. Anyone who has tried to take a picture of a computer or TV screen with a cellphone camera is familiar with a moiré superlattice, which is nothing more than the interference of two periodic patterns. In 2D

moiré superlattices, the interference of two similar atomic lattices—for example, two TMD monolayers, as I focus on here—creates a periodic variation in the alignment of the atoms in the two layers, which in turn creates a periodic potential in the stack. During the past few years, I and other scientists have discovered that a moiré superlattice can have wild and unexpected implications for a 2D heterostructure, leading to new electronic states, modified interactions with light, and unusual quantum states of matter. In particular, by choosing the constituent layers and their relative angle, we can reproduce strange and fascinating electronic behavior typically only seen in more complex materials that are difficult to study theoretically.

In my dissertation research, I focus on experimental investigations of a moiré superlattice formed by two specific semiconducting TMD monolayers: WSe_2 and WS_2 . I discuss the implications for the optical (excitonic) and electronic properties of the TMD stack, where again and again the twist angle proved to be more powerful and interesting tool than we ever expected.

1.2 Outline of thesis

This dissertation is organized as follows.

Chapter 2 is a deeper discussion about TMD monolayers and their heterostructures, both to provide a general background about this fascinating family of materials and to motivate the predictions and experimental approaches that I describe throughout the dissertation.

In Chapter 3, I consider how a moiré superlattice impacts the exciton states in a heterostructure, a question that bookends my PhD. First, I describe our initial experimental investigation of intralayer exciton states in WSe_2/WS_2 moiré superlattices, which demonstrated that a moiré superlattice leads to dramatic modification of the exciton states. Then I turn to a second project, a combined theory-experiment collaboration, where we used more sophisticated approaches to uncover the precise nature of the moiré exciton states in WSe_2/WS_2 superlattices.

References: C. Jin*, E. C. Regan*, A. Yan, M. I. B. Utama, D. Wang, S. Zhao, Y. Qin, S. Yang, Z. Zheng, S. Shi, K. Watanabe, T. Taniguchi, S. Tongay, A. Zettl, F. Wang. “Observation of moiré excitons in WSe_2/WS_2 heterostructure superlattices,” *Nature* 567, 76-80 (2019).

M. H. Naik*, E. C. Regan*, Z. Zhang*, Y. Chan, Z. Li, D. Wang, Y. Yoon, C. S. Ong, W. Zhao, S. Zhao, M. I. B. Utama, B. Gao, X. Wei, M. Sayyad, K. Yumigeta, K. Watanabe, T. Taniguchi, S. Tongay, F. H. da Jornada, F. Wang, S. G. Louie. “Nature of moiré exciton states in WSe_2/WS_2 heterobilayers,” Submitted (2021).

In Chapter 4, I turn to the electronic states in a WSe_2/WS_2 superlattice. I demonstrate how we can take advantage of the strong light–matter interactions in TMDs to optically probe correlated electronic states, where interactions between electrons dominate their properties. This new technique leads us to discover Mott and generalized Wigner crystal states in WSe_2/WS_2 moiré superlattices, confirming that correlations are very strong in TMD moiré superlattices.

Reference: E. C. Regan*, D. Wang*, C. Jin*, M. I. B. Utama, B. Gao, X. Wei, S. Zhao, W. Zhao, Z. Zhang, K. Yumigeta, M. Blei, J. Carlstroem, K. Watanabe, T. Taniguchi, S. Tongay, M. Crommie, A. Zettl, F. Wang. “Mott and generalized Wigner crystal states in WSe₂/WS₂ moiré superlattices,” *Nature* 579, 359-363 (2020).

Chapter 5 focuses on the spin degree of freedom in WSe₂/WS₂ moiré superlattices. Thanks to the optical selection rules of TMDs, we have an exciting opportunity to optically generate and monitor spin populations in the correlated electronic states. Using a spatially resolved pump probe experiment, we create a spin polarization and track its evolution in time and space. We demonstrate that spin and charge are decoupled in the correlated states and that spin transport is overall suppressed in a moiré superlattice.

Reference: Manuscript in preparation.

At the end of each experimental chapter, I comment briefly on other projects that I have been involved with that are thematically connected to the work discussed in detail here.

Note: * indicates equal author contribution. I am deeply grateful to have had productive, supportive, and kind close collaborators during my PhD. None of this would be possible without them.

2 Introduction to transition metal dichalcogenide heterostructures

2.1 Transition metal dichalcogenide monolayers

TMDs are a diverse family of materials with rich electronic and optical properties. In their bulk form, TMDs are layered materials with weak interlayer van der Waals interactions. Consequently, TMDs can be mechanically and chemically isolated into few-layer and monolayer crystals. My work focuses on a subset of the TMDs: 2H phase MX_2 compounds (Fig. 2.1a) with $M = (\text{Mo}, \text{W})$ and $X = (\text{S}, \text{Se})$, which are stable under ambient conditions and have been the emphasis of much recent work in both monolayers and heterostructures^{1,2}. As the TMDs are thinned to the monolayer limit, the bandgap transitions from indirect to direct, with the band extrema at the K and K' corners of the hexagonal Brillouin zone^{3,4} (Fig. 2.1b). Monolayer TMDs have broken inversion symmetry, so spin-orbit coupling is strong and the K and K' valleys exhibit valley-contrasting Berry curvature and orbital magnetic moments^{5,6}.

In a 2D environment, dielectric screening of the Coulomb interactions between electrons and holes is reduced, leading to a large family of tightly-bound exciton states, including momentum-direct excitons composed of an electron and a hole at the K (K') valley (Fig. 2.1b). The exciton binding energies can be hundreds of millielectronvolts, an order of magnitude larger than in typical bulk semiconductors like GaAs^{7,8}. The corresponding exciton Bohr radius is a few nanometers and extends over several lattice periods. Due to their large binding energies, excitons can have large oscillator strengths and dominate the optical properties of monolayer TMDs at cryogenic and room temperatures⁹. The optical selection rules for excitons at the K and K' valleys

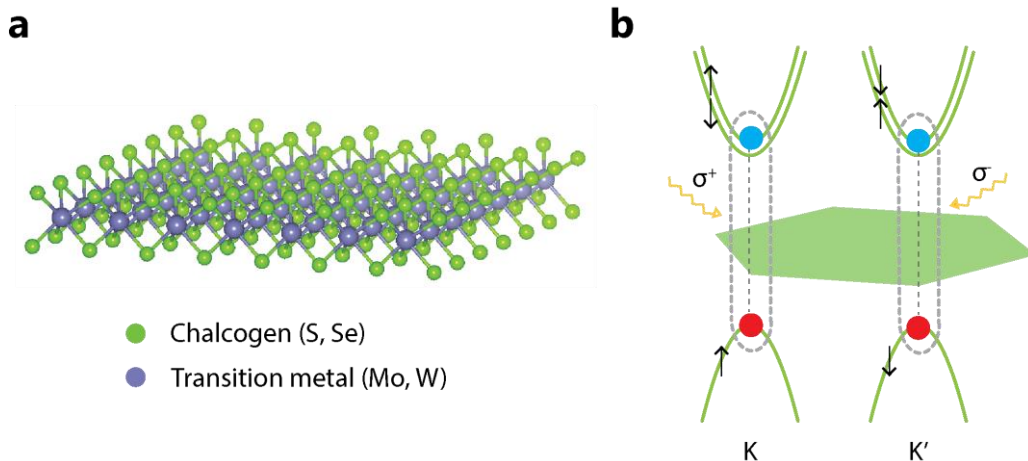


Fig. 2.1 | TMD monolayers. **a.** Structure of 2H TMD monolayer with chalcogen (S, Se) in green and transition metal (Mo, W) in purple. **b.** Schematic of the bright A excitons and the K and K' corners of the Brillouin zone (hexagon) of a TMD monolayer. Excitons at the K (K') valley couple to σ^+ (σ^-) light. Both spin split conduction bands are shown. Only the highest valence band is shown because the spin splitting is large.

are determined by the angular momentum of the exciton. Contributions to the angular momentum from the conduction and valence band wavefunctions, as well as the valley pseudospin, require that direct interband transitions at the K and K' valleys couple exclusively to left and right circularly polarized light^{10–15}. This optical selection rule provides valuable access to the valley degree of freedom, where circularly polarized light can be used to create valley-polarized exciton populations and probe their behavior.

The conduction and valence bands at K and K' are largely composed of transition metal *d* orbitals, allowing spin-orbit coupling to be strong, unlike in graphene^{16–18}. At the valence band maximum, the spin splitting is large: around 0.2 eV for Mo-based TMDs^{3,4} and 0.4 eV for W-based TMDs^{19,20}. A smaller spin splitting occurs in the conduction band^{21,22}. Transitions between valence and conduction band of the same spin result in two bright exciton states, typically referred to as the A and B excitons (Fig. 2.1b). It has been experimentally demonstrated that the lowest energy exciton is optically bright (electron and hole of same spin) in MoSe₂ and dark (opposite spin) in WS₂, WSe₂, and MoS₂^{23–25}. This detail has important consequences for light emission since a lower-energy dark state dramatically reduces emission at low temperatures²⁶. Additionally, the spin splitting has opposite signs in the K and K' valleys because of time reversal symmetry, which effectively locks the spin and valley degrees of freedom: the bright exciton is spin up in one valley and spin down in the other¹⁷. Therefore, the valley optical selection rule also gives direct access to spin in monolayer TMDs.

Additional electron and hole states are distributed throughout the Brillouin zone, which form a family of momentum-dark exciton states with non-zero center-of-mass momentum. After optical excitation of a zero-momentum state, phonon scattering can populate finite momentum exciton states^{27,28}. Momentum-dark states have important consequences for exciton emission, dynamics, and transport, especially when they are degenerate with or at lower energy than the bright exciton states.

In practice, TMD monolayers contain high defect densities, which inevitably affect the exciton properties. Indeed, even the cleanest WSe₂ crystals obtained via self-flux growth contain defect densities of $\sim 10^{11} \text{ cm}^{-2}$ (Ref. ²⁹). Defect-bound excitons have been exploited for realizing single photon emitters in TMDs^{30,31}, but they also limit the optoelectronic performance of TMD-based devices and can complicate the interpretation of exciton behavior in monolayers and heterostructures².

2.2 Transition metal dichalcogenide heterostructures

Stacks of TMDs (Fig. 2.2a), along with other 2D materials such as few-layer graphite (fLG) and hexagonal boron nitride (hBN), have become a fruitful material platform for realizing emergent excitonic states, including states in which correlations and topology play a major role. In addition to exciton states localized in each TMD monolayer, heterostructures may also support new emergent exciton states.

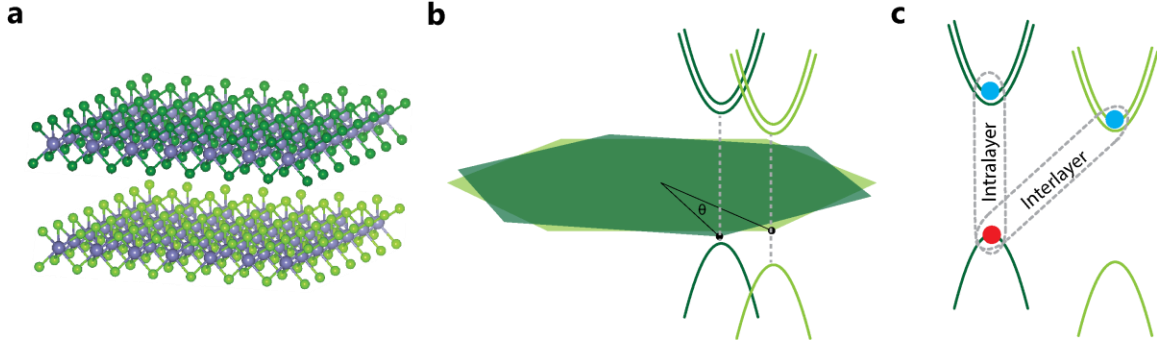


Fig. 2.2 | TMD heterostructures. **a.** Schematic of a TMD heterobilayer. **b.** Schematic of a heterobilayer formed by two TMDs (light and dark green) in momentum space. The heterobilayer is characterized by the lattice mismatch, twist angle (θ), and band alignment between the two layers. **c.** Schematic of intralayer and interlayer excitons at the K valley of two layers forming a heterostructure with type II band alignment.

In general, several factors are important in determining the properties of excitons in a TMD heterostructure: the electronic structure of each monolayer, the relative band alignment between layers, and the twist angle (θ) and lattice mismatch between the layers (δ) (Fig. 2.2b). In TMDs, interlayer coupling at the K and K' points is relatively weak, so it is commonly assumed that the K-point monolayer electronic states are largely localized within individual layers^{32,33}. This assumption is particularly reasonable in heterostructures with large twist angles or lattice mismatches since the Brillouin zones of each layer are shifted, suppressing interlayer coupling. When the twist angle is small and the bands are close in energy, interlayer hybridization can occur, as one might expect considering the change from direct to indirect bandgaps in bilayer TMDs.

Bilayers formed from two of the common semiconducting TMDs—MoS₂, MoSe₂, WS₂, and WSe₂—are type II heterostructures, where the lowest conduction band and highest valence band are in different materials^{34,35} (Fig. 2.2c). In this case, the excitons at the K and K' valleys within each layer (intralayer excitons) are similar to their monolayer counterparts but with additional screening from the neighboring material^{36,37}. Lower-energy interlayer exciton states, where the electron and hole reside in different layers^{38,39}, also exist. The spatial separation of the electron and hole gives interlayer excitons fascinating properties: they have long valley lifetimes due to reduced exchange interactions^{40,41}, their energies can be tuned with electric fields because of their permanent electric dipole moment³⁹, and they show promise for Bose-Einstein condensation^{42,43}.

Interlayer excitons can be optically bright or dark depending on the stacking configuration of the layers^{44–46}. Although the oscillator strength of interlayer excitons is relatively small due to the spatial separation between electrons and holes, interlayer excitons can dominate the emission of heterostructures because they are the lowest energy states. In bilayers with small twist angle (close to 0 degrees or 60 degrees) and small lattice mismatch, the Brillouin zones of the monolayers are nearly aligned, so electrons and holes can recombine and emit photons efficiently. When the conduction band and valence band are misaligned in k-space, the bilayer has poor emission characteristics: intralayer exciton emission is quenched because the excitons separate faster than their radiative recombination time³⁹, and the interlayer excitons do not recombine radiatively. Interlayer excitons in homobilayers can have strong absorption due to mixing with intralayer

exciton states that are close in energy^{47–49}. Recently, bright interlayer excitons have gained attention for their potential optoelectronic applications.

Interlayer excitons can be formed by optical and electrical methods and are often created by first exciting intralayer excitons. In type II heterobilayers, optically excited intralayer excitons quickly separate into electrons in one layer and holes in the other via an ultrafast charge transfer process, occurring in less than 50 fs⁵⁰. The Coulomb interaction between the spatially separated electrons and holes can then lead to the formation of bound interlayer excitons^{28,51}. It is also possible to directly create interlayer exciton states via resonant optical excitation in aligned heterostructures, but the efficiency is low due to the small absorption of interlayer excitons⁵². Additionally, interlayer excitons can be formed via electrical injection of electrons and holes into the constituent layers^{53,54}.

Heterostructures formed from two layers of the same material, often called homobilayers, can also support interesting exciton states. Homobilayers can be naturally found bilayer TMDs or artificially stacked TMD monolayers. Due to interlayer hybridization, the lowest energy exciton state can become momentum indirect, where the gap size depends on the twist angle between the layers^{55,56}. Interestingly, electron and hole states at the K and K' valleys remain largely localized within each layer, manifested as the co-existence of both intralayer and interlayer exciton states at the K and K' points in homobilayers^{57–59}. Without the type II band alignment, homobilayers have degenerate exciton states in both layers. With an applied electric field, electrons and holes preferentially occupy different layers, and the interlayer exciton dipole orientation is determined by the direction of the applied field⁶⁰.

2.3 Transition metal dichalcogenide moiré superlattices

The superposition of atomic lattices in a heterostructure can produce a larger-scale periodicity (Fig. 2.3a), called a moiré pattern, which arises from a small difference in the lattice constants of the materials (δ) or a twist angle between their lattices (θ). When $\delta \ll 1$ and $\theta \ll 1$, the superlattice periodicity l varies continuously with twist angle as $l = a_0 / \sqrt{\delta^2 + \theta^2}$, where $\delta = |a'_0 - a_0|/a_0$, and a_0, a'_0 are the lattice constants of the two layers. The superlattice periodicity introduces a new length and energy scale that can dramatically modify the electronic and excitonic behavior of the system. On the atomic scale, the alignment between the atoms in each layer varies across the moiré unit cell, creating a periodic potential for electrons and excitons that can be as large as hundreds of millielectronvolts^{61–70}. The potential minima and maxima are usually centered at one of the high symmetry positions in the lattice. The stacking is labelled at these positions in Fig. 2.3a. Hybridization of the electronic states in the two layers can further modify the electronic structure of the superlattice.

To zeroth order, the low-energy exciton bandstructure in the moiré superlattice can be considered as a modification of the original TMD bands around the K and K' valleys. The large real-space periodicity generates a small reciprocal space periodicity, referred to as the moiré mini-Brillouin zone (mBZ) (Fig. 2.3b). The moiré potential folds the original bands into the mBZ and

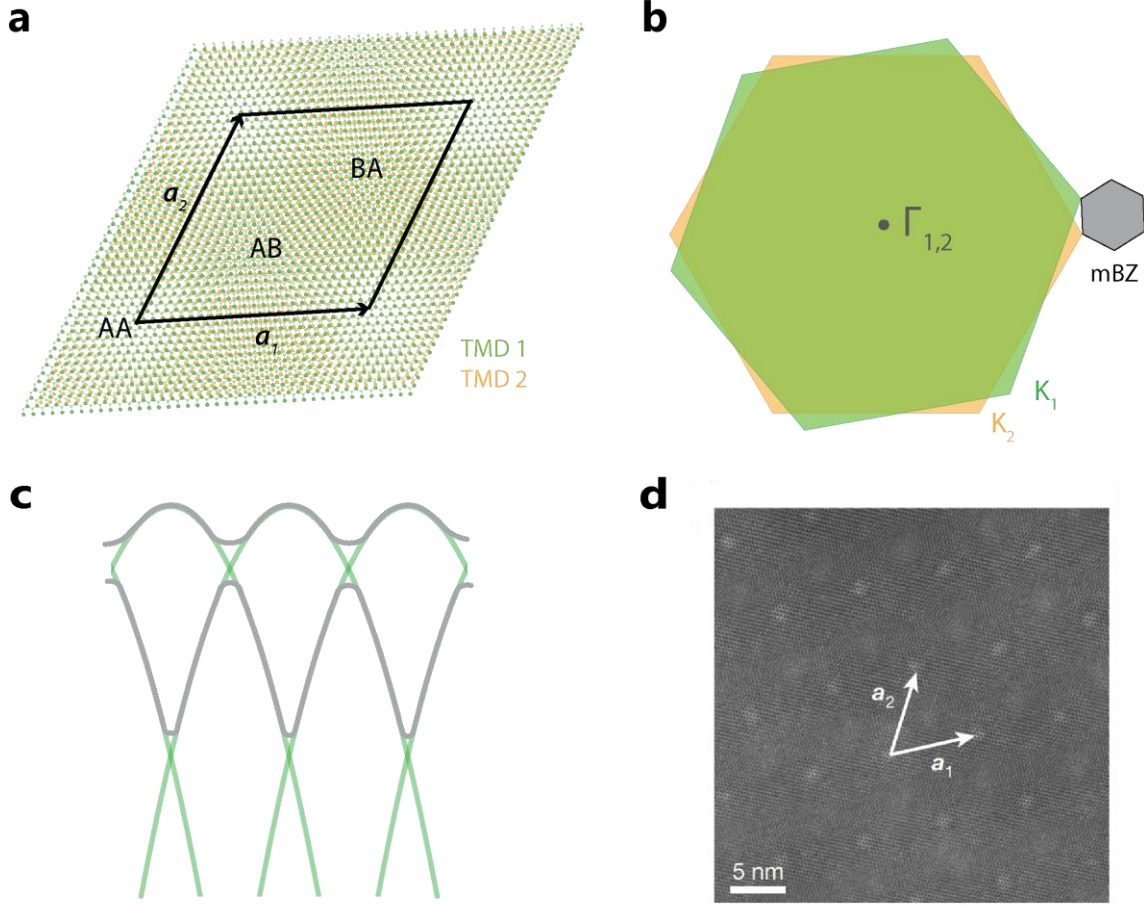


Fig. 2.3 | TMD moiré superlattices. **a.** Illustration of a moiré superlattice formed by two TMDs in real space. The superlattice vectors are labelled as a_1 and a_2 and form the superlattice unit cell. There are three high-symmetry positions in the superlattice where the local atomic configuration has three-fold rotational symmetry. The stacking is labelled at these positions (AA, AB, and BA). **b.** Schematic of the Brillouin zones of each monolayer (green and orange) and the mini Brillouin zone (mBZ) of the superlattice, where the mBZ wavevector corresponds to the difference between the two K points of the monolayers. **c.** Schematic of monolayer TMD bands (green) folded in the mBZ. The moiré potential opens a gap at the mBZ boundary, which produces flatter electronic bands (grey). **d.** Atomic-resolution high-angle annular dark-field STEM image of a near-zero twist angle WSe_2/WS_2 heterostructure showing a moiré superlattice with superlattice vectors a_1 and a_2 .

opens a gap at the mBZ boundary (Fig. 2.3c). For large moiré superlattices, the width of the low energy bands can be very small because of the small mBZ and the gap opening. These relatively flat bands can lead to interesting strong correlation effects, as will be discussed later in this dissertation.

In reality, lattice relaxation and strain determine the final three-dimensional structure of the superlattice and the precise potential landscape. The variation in atomic stacking across the moiré unit cell leads to a position-dependent interlayer stacking energy^{65,68,69,71} and charge redistribution⁷². To reduce the overall energy, the superlattice can relax and expand the regions of lowest energy. In a relaxed superlattice, domains of the energetically preferred stacking

configuration form and are separated by a network of domain walls that accommodate lattice constant differences and twists. For homobilayers and same-chalcogen heterobilayers (which have negligible lattice mismatch) at small twist angle (< 2 deg), the moiré superlattice periodicity can be tens of nanometers^{73–75}, exceeding domain wall widths and therefore allowing domains to fully form. At larger twist angles, homobilayer and same-chalcogen heterobilayers form more ideal moiré superlattice structures without large domains⁷⁶. Similarly, heterobilayers formed by TMDs with different chalcogen atoms (large lattice mismatch), which I focus on in this dissertation, have a smaller moiré periodicity and tend to form more ideal moiré superlattices^{63,77,78}.

In addition to the final superlattice geometry after relaxation, in- and out-of-plane strain play important roles in determining the strength of the moiré potential. For example, scanning tunneling microscopy (STM) of a $\text{WSe}_2/\text{MoSe}_2$ heterobilayer indicates that the moiré potential is hundreds of meV for both electrons and holes, which is much larger than expected based on stacking alone but can be explained by in and out of plane distortions⁷⁰.

Hybridization of the electronic states from the two layers can also influence the electronic structure in a moiré superlattice, particularly in homobilayer superlattices, where the electronic states in each layer are degenerate. In general, states at Γ hybridize strongly because the electron and hole wavefunctions extend out of the layer, while states at K hybridize less due to their confined wavefunctions and large spin-orbit coupling^{18,79}.

Together, these effects introduce a periodic potential landscape to the heterostructure that modifies the single particle (i.e. electron and hole) and many-body (i.e. exciton) bandstructures. As we will see, the periodic potential can be quite large and lead to localization of electrons, holes, and excitons at specific positions in the superlattice unit cell. This localization leads to fascinating new behavior in a heterostructure, from novel exciton states to exotic correlation effects to enhanced exciton-charge interactions.

In this dissertation, I focus on a specific moiré superlattice formed by a layer of WSe_2 and a layer of WS_2 . In this case, a $\sim 4\%$ lattice mismatch between the layers leads to a triangular superlattice with lattice constant of ~ 8 nm when the lattices are aligned to zero degrees. Hybridization effects are weak due to the band offsets. During our initial investigation of this system, we collaborated with Aiming Yan of Alex Zettl’s group to collect atomic-resolution scanning transmission electron microscope (STEM) images of a WSe_2/WS_2 heterostructure using STEM high-angle-annular-dark field imaging at the National Center for Electron Microscopy of Lawrence Berkeley National Lab (TEAM 1)⁷⁷. In a near-zero twist angle sample transferred to a TEM grid, we observe a nearly ideal triangular superlattice with a well-defined periodicity of ~ 8 nm (Fig. 2.3d). The superlattice is robust across the sample and returns only tens of nanometers from bubbles. A later STM study of a WSe_2/WS_2 superlattice from our group⁸⁰ demonstrated that the layers are buckled out of plane, and this strain results in a particularly large moiré potential.

In the following chapters, I will walk through our evolving understanding of exciton and correlated physics in this surprisingly fascinating stack of materials.

2.4 Heterostructure fabrication

To experimentally study TMD heterostructures, my colleagues and I designed and fabricated more than one hundred high-quality, gate-tunable samples with various twist angles. A heterostructure device includes the relevant TMD layers, along with hexagonal boron nitride (hBN) layers for encapsulation and few-layer graphite flakes to control the carrier concentration in the TMD layers (Fig. 2.4). One graphite flake is used as a contact to the TMD layer, and additional larger flakes form electrostatic gates, either above or below the hBN-TMD-hBN stack, or both. Here, the hBN layers also serve as gate dielectrics. 2D heterostructure fabrication generally involves exfoliating bulk material to obtain thin flakes and then stacking the flakes together using a polymer stamp.

Fabricating van der Waals heterostructures is a bit of an art. We follow established recipes and protocols, but we also have our own superstitions and preferences for exactly how steps are completed. My detailed fabrication procedure for an aligned WSe_2/WS_2 device structure is summarized below. For context, this is a rather simple procedure compared to many device protocols that involve complex etching steps, ultrahigh vacuum annealing, multiple transfers, and more.

First, monolayer WSe_2 , monolayer WS_2 , few-layer graphite, and thin hBN flakes are exfoliated onto silicon substrates with a 90 nm SiO_2 layer using the commonly used Scotch-tape method. The precise recipe (including exfoliation speed and temperature) is different for each material family, but the idea is the same: transfer a relatively thin piece of bulk crystal onto a piece

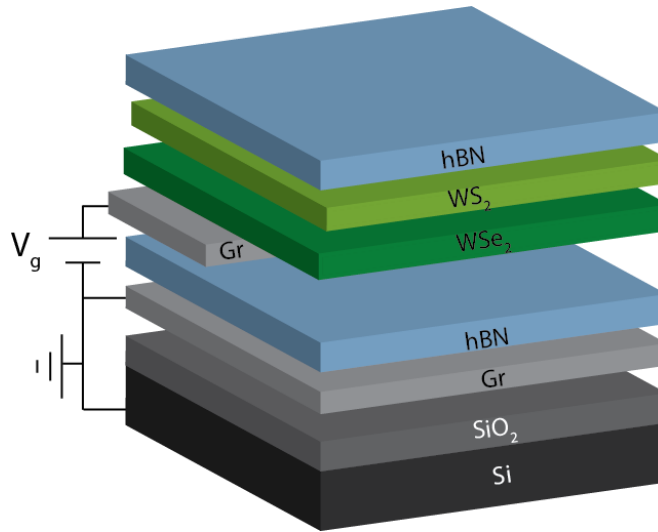


Fig. 2.4 | Schematic of a WSe_2/WS_2 heterostructure. Hexagonal boron nitride (hBN) layers are included for encapsulation and few-layer graphite (Gr) are used as gate and contact. A voltage V_g can be applied between the back gate and the contact to control the carrier concentration in the heterostructure.

of tape, thin the crystal down until it is as uniform and beautiful as possible, place the tape onto the Si/SiO₂ substrate and make sure the crystal and substrate are in good contact, and slowly peel the tape off. We create libraries of materials and then choose flakes of similar sizes and shapes to stack together.

To create heterostructures with well-defined twist angles, we must determine the crystal orientation of the WS₂ and WSe₂ monolayers and align the crystal axes precisely during the transfer process. This alignment is easiest if an edge corresponds to a high-symmetry crystal axis in each flake. In this case, we can simply align the edges of the flakes. For this reason, we choose monolayer WSe₂ and WS₂ flakes with long, straight edges that likely correspond to breaks along high symmetry directions (Fig. 2.5a). To confirm this assumption, we use polarization-dependent second harmonic generation (SHG) to determine the relative angles between the flake edges and the crystal axes (Fig. 2.5b).

SHG is a nonlinear optical process that depends sensitively on the orientation of the crystal

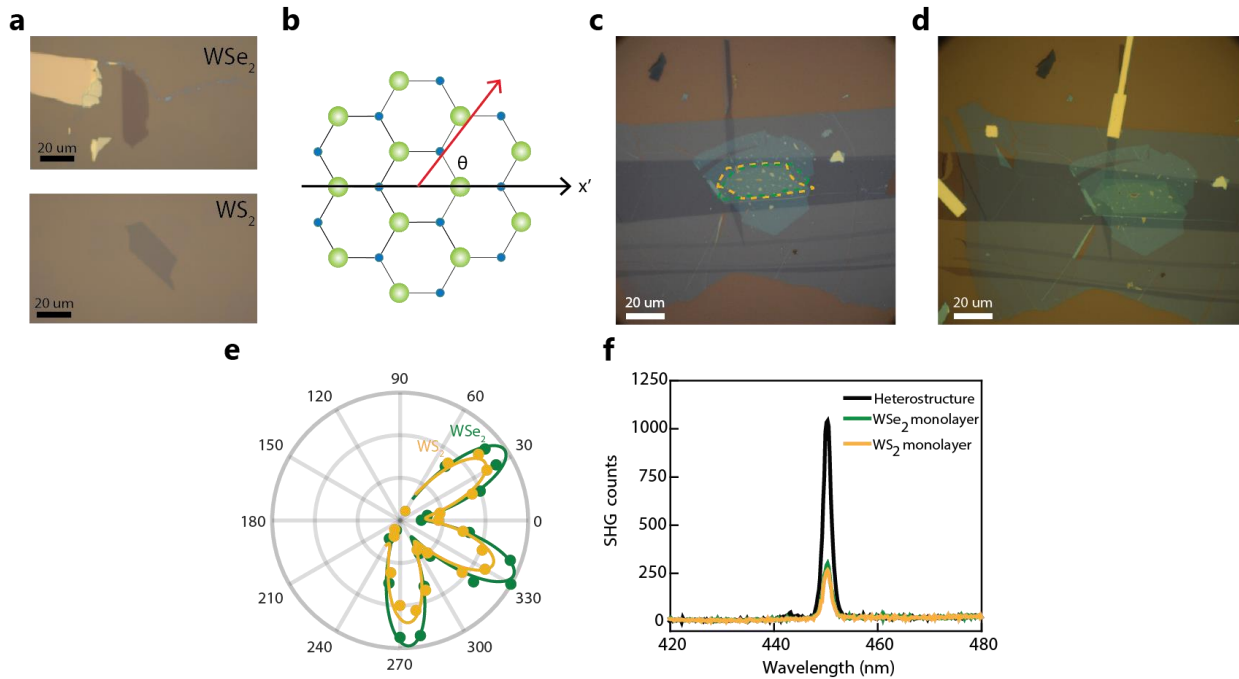


Fig. 2.5 | TMD heterostructure fabrication process. **a.** Optical microscope images of sample WS₂ and WSe₂ flakes, chosen for their long, straight edges. **b.** Schematic of a TMD lattice, where x' lies along the armchair direction. θ denotes the angle between the armchair axis and the polarization of the incident beam (red). **c.** A sample heterostructure after PET transfer. From top to bottom, the device includes the following layers: top hBN, WS₂, WSe₂, few-layer graphite contact, bottom hBN, and few-layer graphite back gate. The WS₂ and WSe₂ are outlined in yellow and green, respectively. **d.** The same sample in c but with gold electrodes. **e.** Polarization-dependent SHG signal for WS₂ and WSe₂ monolayers after heterostructure assembly shows that the TMD flakes are well-aligned (< 0.5 degrees). **f.** SHG counts on the monolayer and heterostructure regions shows that the device has near-0-degree twist angle, rather than near-60-degree.

axes relative to the incident polarization. TMD monolayers have D_{3h} symmetry, so the second order nonlinear susceptibility tensor has nonzero elements

$$\chi_{y'y'y'}^{(2)} = -\chi_{y'x'x'}^{(2)} = -\chi_{x'x'y'}^{(2)} = -\chi_{x'y'x'}^{(2)},$$

where x', y', z' are the crystal coordinates, and x' is along the armchair direction^{81,82}. This symmetry information can be used to show that the parallel component of the second harmonic intensity is proportional to $\sin^2 3\theta$, where θ is the angle between the armchair axis and the incident polarization.

During this measurement, we expose the flake to a below-gap laser beam and record the SHG signal as a function of incident polarization angle. A regenerative amplifier (Light Conversion PHAROS) produces femtosecond pulses that are used to pump an optical parametric amplifier to generate pulses at 800 nm. A polarizer is used to set the linear polarization of the 800 nm beam, and a half wave plate (after the beamsplitter) is used to rotate the plane of polarization relative to the sample. This beam is focused onto the sample using an objective lens, and the SHG signal (400 nm) that is parallel to the incident polarization is collected by placing a second polarizer in front of a spectrometer. By noting the angle of the flake edge relative to the polarization, we can determine if the zigzag or armchair edge lies along the flake edge. Experimentally, we find that long, straight edges correspond to high symmetry axes about 90% of the time, so this step is not strictly necessary.

Once we confirm the crystal orientations, we stack the flakes together using a polymer-based dry transfer method^{83–85} (Fig. 2.5c). For a simple heterostructure with a back gate, like the one shown in Fig. 2.4, we use a polymer stamp to pick up the top hBN, the WS_2 monolayer, the WSe_2 monolayer, a few-layer graphite electrode, the top hBN flake, and the few-layer graphite back in sequence. The angle of the stamp is adjusted between picking up the WS_2 and WSe_2 monolayers to ensure a near-zero twist angle between the flakes. The polymer with the heterostructure is then stamped onto a clean silicon substrate with 90 nm SiO_2 , and the polymer is dissolved with a solvent. For more complex heterostructures, the process is generally the same but with more pick-up steps.

Several different polymers can be used in this process. We initially used polyethylene terephthalate (PET) stamps because they are robust and have low failure rates. However, we switched to propylene carbonate (PC) on polydimethylsiloxane (PDMS) stamps, which typically lead to cleaner samples with fewer bubbles between layers. When using a PET stamp, the flakes and PET are heated to 60°C to facilitate pick up and to 130°C for the final stamp process. When using a PC stamp, the pickup process can be done at lower temperatures (room temperatures), which can also help reduce twist-angle relaxation during transfer. Other polymers, including polypropylene carbonate (PPC), are also commonly used.

Once the flakes are stacked together, we use electron-beam or photo lithography and electron-beam evaporation to deposit electrodes (~ 75 nm gold with ~ 5 nm chromium adhesion layer) that form electrical contacts to the few-layer graphite gate and contact (Fig. 2.5d). The entire

sample is then mounted in a chip carrier and wire-bonded, so we can apply voltages to control the carrier concentration and electric fields using additional hardware.

As a last characterization step, we do a second round of polarization-dependent SHG on the WS_2 and WSe_2 monolayer regions in the device to measure the twist angle between the two TMD flakes: if the flakes are well-aligned, the sinusoidal SHG signal will show aligned peaks and dips (Fig. 2.5e). However, since the SHG patterns for both materials have six-fold rotational symmetry, near-zero degree (AA stacking) and near-60 degree (AB stacking) cannot be distinguished from the monolayer SHG. We can directly measure the SHG from the heterostructure itself to gain this information: in the AA (AB) stacking case, the second harmonic fields of the two layers constructively (destructively) interfere, giving SHG signal that is stronger (weaker) than the individual monolayers. Fig. 2.5f shows the SHG intensity for the WSe_2 , WSe_2 , and heterostructure regions of a device. The WSe_2 and WS_2 regions show similar SHG intensity, while the heterostructure shows approximately four times larger SHG signal, indicating that the device has near-zero-degree twist angle. A near-60-degree sample shows negligible SHG from the heterostructure region. A moiré superlattice to form in both cases, but it is important to be able to distinguish them.

2.5 General experimental approaches

A complete description of all experimental techniques used during my PhD would be exhausting to read (and to write). However, there are several guiding themes and approaches that are worth mentioning here.

Throughout my PhD, optics has been the tool of choice for understanding emergent physics in TMD moiré superlattices because excitons interact so strongly with light. We can study excitons themselves by monitoring their absorption and emission. We can also use excitons to probe the local charge environment, which is a powerful approach for studying correlations in TMD heterostructures.

By controlling characteristics of our light sources, we can access different information about a physical system. In this dissertation, we take advantage of five main degrees of freedom: energy, bandwidth, polarization, temporal profile, and spatial beam profile.

- Energy: The photon energy can be used to selectively excite and probe specific populations, such as A excitons in one layer of the heterostructure but not the other. Additionally, we can probe below or above the bandgap of a material to intentionally create free carriers or not.
- Bandwidth: Using narrow band lasers, we can generate and monitor specific populations. We can also use narrow band lasers to selectively probe energy regions that give us the highest sensitivity to a given process, as described in Chapter 4. Using a broadband light source, like a tungsten lamp or supercontinuum source, we can

monitor many populations at once. Broadband and narrow band reflection contrast measurements (see below) using a tungsten lamp is my bread and butter.

- Polarization: Thanks to the optical selection rules in TMDs, we can generate and monitor specific spin/valley populations using circularly polarized light. Using polarizers, half wave plates, and quarter wave plates, we can control the polarization of the excitation and probe beams.
- Temporal profile: We use pulsed light sources to obtain temporal information about processes in our sample via optical pump-probe experiments. Using ultrafast sources, we can monitor processes on a timescale of a few hundred femtoseconds to a few hundred picoseconds. Using electronically-pulsed diode lasers, we can access the nanosecond to microsecond regime. Ultrafast sources also give us access to large peak electric fields, which are important for nonlinear generation (for example, white light generation and second harmonic generation).
- Spatial profile: The shape of the optical beam on the sample allows us to selectively excite and probe specific regions of the heterostructure. Typically, we use round, nearly-diffraction-limited beams to probe specific regions. We also use cylindrical beams to create one-dimensional excitations, as discussed in Chapter 5.

With these tuning knobs, we still need to decide what optical experiment is best to answer a given physical question. Throughout my PhD, I have learned to prefer absorption-based (rather than emission-based) optical measurements because absorption directly measures the oscillator strength of a state and is not complicated by relaxation processes. Photoluminescence spectroscopy (PL, an emission-based measurement) is widely used for materials characterization, but the interpretation of the spectrum is more complicated because the measured PL intensity depends on the lifetime of the emitting states. Higher energy states can quickly relax into lower energy states that dominate the emission spectrum. This can be very useful when studying low energy states that do not have strong absorption—defect states and interlayer excitons, for example. However, for monitoring intralayer exciton states at low temperature, as we do throughout the dissertation, absorption measurements are much more direct. Here, absorption measurements come in two flavors: broadband reflection contrast spectroscopy and narrowband reflectivity.

To measure the broadband absorption of a 2D heterostructure on Si/SiO₂, we measure the reflection contrast of the sample under illumination by a supercontinuum source or tungsten lamp. Reflection contrast is the differential reflectivity of the sample and a reference, typically a region of the sample without the active layers (i.e. TMDs) but with all other materials (i.e. hBN, graphene, etc.). When the reflectivity of the sample is much weaker than that of the substrate, the reflection contrast can be interpreted as the imaginary part of the optical conductivity σ , modified by a local field factor η that depends on the thin film interference⁸⁶:

$$\frac{\delta R}{R} = \frac{R_{\text{sample}} - R_{\text{reference}}}{R_{\text{reference}}} \propto \text{Im}(\sigma \cdot \eta).$$

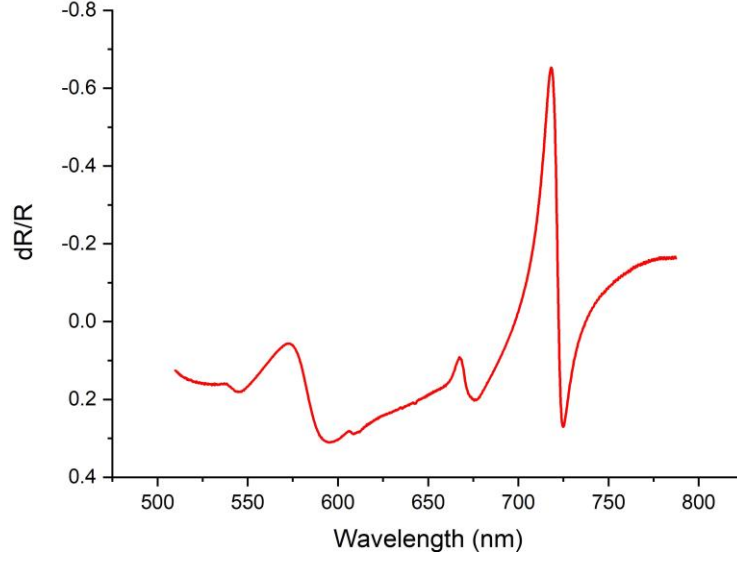


Fig. 2.6 | Reflection contrast spectrum of an hBN-encapsulated WSe₂ monolayer at 10 K. The main peaks correspond to the A exciton (~715 nm), 2s state (~667 nm), and B exciton (~575 nm). The asymmetry of the A exciton is due to the local field factor, which mixes the real and imaginary parts of the optical conductivity.

Note that the assumption that the reflectivity of the TMD is a perturbation is not always true at the exciton resonances, particularly in high quality samples at low temperature where the exciton linewidth can be very narrow. In general, we can model the reflection as a multilayer thin film interference process, which allows us to directly extract the complex dielectric function of the TMD. In most cases, this analysis is not critical, and we simply monitor the reflection contrast directly. The reflection contrast spectrum of an hBN-encapsulated WSe₂ monolayer taken with a tungsten lamp is shown in Fig. 2.6.

Using narrow band lasers, such as a diode laser or a broadband source with a bandpass filter, we can monitor the absorption of a chosen state via the reflection at or near the resonant wavelength. We use this approach in circular dichroism and optically-detected resistance and capacitance measurements, as discussed in later chapters.

In addition to optical approaches, the gates and contacts to the sample provide electrical control. Applying gate voltages allows us to carefully control the charge doping and the electric fields in the TMD heterostructures. We model the charge density n and electric field using a parallel plate capacitor model. For a sample with two gates, the charge density is

$$n = \pm \frac{1}{e} \left[\frac{\epsilon_{hBN} \epsilon_0}{d_t} (V_t - V_{t0}) + \frac{\epsilon_{hBN} \epsilon_0}{d_b} (V_b - V_{b0}) \right],$$

where ϵ_{hBN} is the dielectric constant of hBN (we measured $\epsilon_{hBN} = 4.2 \pm 0.2$ in Ref. ⁸⁷), ϵ_0 is the permittivity of free space, d_t (d_b) is the thickness of the top (bottom) hBN layer, and V_t (V_b) is

the voltage applied to the top (bottom) gate. We can account for the quantum capacitance, voltage range where charges are not injected as the Fermi level moves through the bandgap, using offset voltages V_{t0} and V_{b0} . Using DC voltages, we can create equilibrium charge populations, and using AC voltages, we can modulate charge populations and induce charge motion. Together with our optical tools, we can define experiments with electrical pumps and optical probes, and visa versa.

To effectively combine optical and electrical techniques at low temperatures, most of our experiments take place in a closed-loop optical cryostat from Montana Instruments (Cryostation) with base temperature of ~ 10 K. When magnetic fields are also required, we use a second optical cryostat from Quantum Designs (OptiCool) with a built-in 7 T magnet and a base temperature of 1.7 K. I will discuss our choice of experimental tools in detail in each chapter.

3 Excitons in WSe₂/WS₂ moiré superlattices

3.1 Introduction

As described in Chapter 2, moiré superlattices offer a method for engineering the bandstructure of collective excitations, such as excitons, in TMD heterostructures. Depending on the strength and structure of the moiré potential, the superlattice can perturb the exciton states or dramatically modify the exciton bandstructure. In this chapter, I will show that the WSe₂/WS₂ superlattice is definitively in the latter case.

I began my adventures with TMD moiré superlattices by accident. When studying WSe₂/WS₂ heterostructures for another project (spin transport in heterostructures, which we will return to in Chapter 5), we were startled to find that one sample behaved quite differently than the others. We measured the twist angle between the WS₂ and WSe₂ monolayers and found that I had accidentally aligned the two flakes to approximately zero degrees. Using our simplest experimental tools—absorption and photoluminescence spectroscopy—we began to systematically investigate the exciton states in WSe₂/WS₂ moiré superlattices. These experiments indicated that something significant was happening here; in other words, the moiré superlattice in WSe₂/WS₂ is not a small perturbation on the electronic states. However, it took us several years and more sophisticated theoretical tools to truly understand the origin and nature of what we saw. This chapter describes two studies that bookend my PhD: first, our initial observation of multiple moiré exciton states in a superlattice, and second, extended optical measurements paired with a fruitful theory collaboration that finally explained the origin of the split moiré excitons.

In section 3.2, I describe our initial optical characterization⁷⁷ of intralayer excitons in WSe₂/WS₂ moiré superlattices. Using absorption spectroscopy, we showed that the moiré superlattice splits the WSe₂ A exciton resonance into multiple peaks with comparable oscillator strengths. We refer to these emergent states as moiré excitons. The emergent exciton states show distinct doping dependences that are different from that of the A exciton in WSe₂ monolayers and in large-twist-angle WSe₂/WS₂ heterostructures. We explain this behavior using a simple continuum model for moiré excitons with a peak-to-peak potential energy of 250 meV. The periodic potential energy is much larger than the exciton kinetic energy of 8 meV within the first mini-Brillouin zone, and it dramatically modifies the exciton dispersion in the moiré superlattice, leading to flat low-energy exciton bands with localized exciton density of states.

In section 3.3, I describe the results⁸⁸ from a collaboration with Steve Louie’s group, where we combined a new theoretical approach with more sophisticated experiments to identify the nature of the moiré exciton states described in section 3.2. We use large-scale first-principles calculations to demonstrate that the moiré exciton states have distinct characters, including modulated Wannier excitons and previously unidentified intralayer charge-transfer excitons. Notably, these excitons cannot be explained using the continuum models used thus far. Using micro-reflection spectroscopy, we find signatures of these distinct excitonic characters

experimentally via the unique carrier-density and magnetic-field dependences of different moiré exciton resonances. Ultimately, this study highlights the highly non-trivial exciton states that can emerge in TMD moiré superlattices and bring some closure to our investigation of moiré excitons in WSe₂/WS₂ superlattices.

Finally, in section 3.4, I briefly describe outstanding questions and additional experimental studies of moiré excitons that I have been involved with.

3.2 Observation of intralayer moiré exciton states in aligned WSe₂/WS₂ heterostructures

3.2.1 Optical characterization

We used several optical techniques to probe the influence of a moiré superlattice on excitons in the WSe₂/WS₂ heterostructure. Unless otherwise noted, the following data is from one device, D1, which serves as a representative sample. Using polarization resolved SHG measurements, we determined the twist angle of D1 to be 0.5 ± 0.3 degrees. Measurements were taken at 10 K in the Montana optical cryostat.

Although we will rely on absorption measurements to directly probe the intralayer exciton states in the superlattice, emission measurements provide important information about the sample quality, in particular the coupling between the WSe₂ and WS₂ layers. The WSe₂/WS₂

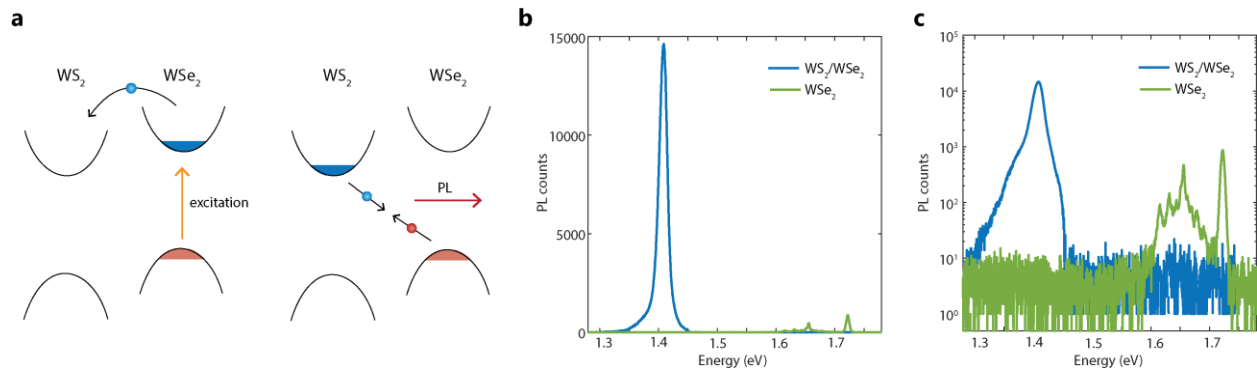


Fig. 3.1 | PL measurements of a WSe₂/WS₂ moiré superlattice. **a.** Schematic of PL measurement in a WSe₂/WS₂ heterostructure. A laser is used to selectively excite excitons in WSe₂. Due to the type II band alignment, electrons transfer almost immediately to the WS₂ layer. Interlayer excitons form across the interface, and their recombination results in PL emission at a characteristic energy. **b.** PL spectrum of a near-zero-twist-angle device (blue) and reference monolayer WSe₂ sample (green). **c.** Same as c but on a logarithmic scale. The disappearance of the monolayer PL and the emergence of interlayer exciton PL in the heterostructure indicates efficient interlayer coupling in the device.

heterostructure has type II band alignment, where the conduction band minimum and the valence band maximum reside in WS_2 and WSe_2 , respectively^{34,35}. When excitons are photoexcited in WSe_2 , electrons rapidly transfer to WS_2 , and the holes remain in WSe_2 (Fig. 3.1a)⁵⁰. This ultrafast charge transfer process quenches intralayer exciton emission (PL) from WSe_2 , so it is a poor tool for studying the WSe_2 excitons directly. After the charge transfer, the transferred electrons in WS_2 and the remaining holes in WSe_2 can form low energy interlayer excitons^{38,39}, which dominate the emission spectrum. Fig. 3.1 shows the photoluminescence (PL) spectrum of the device D1, shown in linear and log scales. The heterostructure PL shows a single peak at 1.41 eV and shows no emission from intralayer excitons in the WSe_2 or WS_2 layers, indicating that the device has efficient interlayer coupling across the whole measured region.

Next, we turn to reflection contrast spectroscopy to study the intralayer excitons in the WSe_2/WS_2 heterostructure: we measured the reflection contrast between the sample and the substrate, which is directly related to the absorption of the sample. Fig. 3.2a shows the reflection contrast spectrum for D1 (upper panel) and a reference large-twist-angle WSe_2/WS_2 heterostructure (lower panel) measured under illumination by a tungsten lamp. A slowly varying background due to the local field has been subtracted to better resolve the resonances.

The absorption spectrum of device D1 is strikingly different from that of a large-twist-angle device. The large-twist-angle device shows a resonant absorption peak corresponding to the WSe_2 A exciton (1.715 eV) and B exciton (2.15 eV), the WS_2 A exciton (2.035 eV), and the

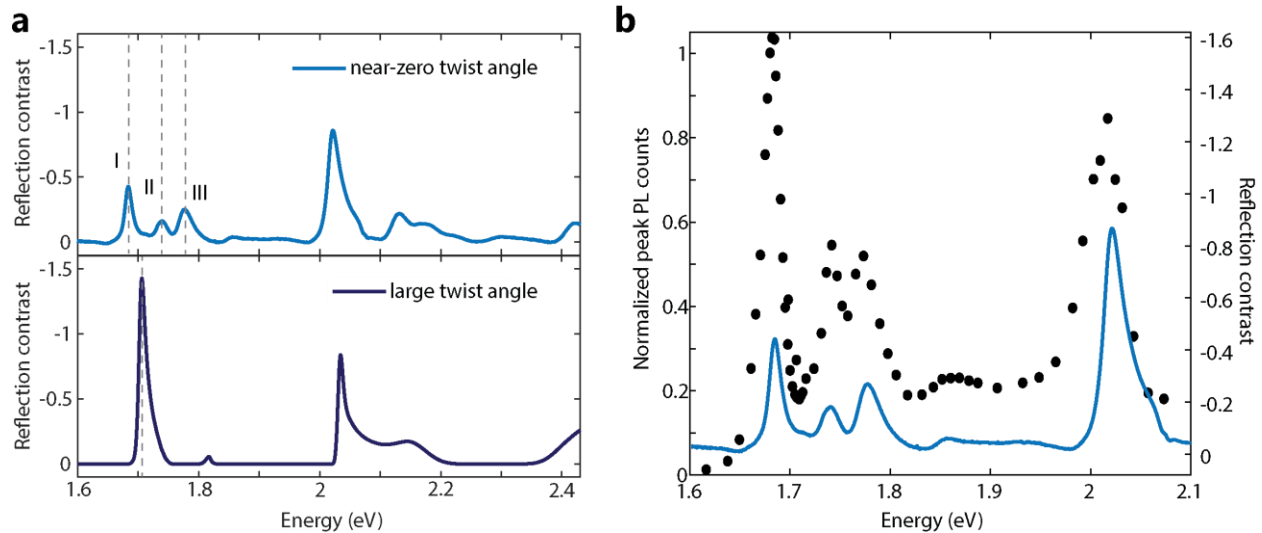


Fig. 3.2 | Absorption measurements of a WSe_2/WS_2 moiré superlattice. a. Reflection contrast spectra of a near-zero-twist-angle heterostructure D1 (upper panel) and a large-twist-angle heterostructure (lower panel). The latter shows only a single resonance in the energy range of the WSe_2 A exciton. In contrast, the moiré superlattice formed in device D1 gives rise to three prominent peaks with comparable oscillator strength in this range (labeled I, II, and III), corresponding to different moiré exciton states. **b.** The interlayer exciton PL excitation spectrum (black dots), compared to the reflection contrast spectrum (blue curve). The interlayer exciton PL is strongly enhanced when the system is excited at all moiré exciton states.

WSe₂ 2s excited state exciton (1.816 eV). These features are all commonly observed in hBN-encapsulated heterostructures. In comparison, the near-zero-twist-angle sample shows many emergent features. We focus on the spectral range between 1.6 to 1.8 eV (near the WSe₂ A exciton), since it is well separated from all WS₂ resonances. While the large-twist angle heterostructure only shows a WSe₂ A exciton peak at 1.715 eV, three prominent peaks emerge in device D1 at 1.683, 1.739, and 1.776 eV, labeled as resonance I, II, and III, respectively. All three resonances show strong absorption, with peak II and peak III having oscillator strengths of 20% and 50% of the peak I value.

To better understand the origin of the new exciton peaks, we measured the photoluminescence excitation (PLE) spectrum of device D1 by monitoring the interlayer exciton emission intensity while sweeping the excitation energy from 1.6 to 2.1 eV. If the new peaks correspond to states in the coupled heterostructure, we expect increased interlayer exciton PL emission when the excitation beam is resonant with these states. In Fig. 3.2b, the black dots correspond to the interlayer exciton PL intensity, and the blue curve shows the result from absorption spectroscopy. The emergent exciton peaks between 1.6 to 1.8 eV all enhance the interlayer exciton emission, indicating that they all arise from the strongly coupled WSe₂/WS₂ heterostructure, instead of several separated domains or defects.

If the emergent peaks are related to the moiré superlattice, then they should only exist in aligned samples. Therefore, we systematically investigated 18 heterostructures spanning a large range of twist angles, as determined by polarization-dependent SHG measurements. The 10 K absorption measurements for the 18 devices are summarized in Fig. 3.3, where the top panel shows devices with near AA stacking (0 degrees) and the bottom panel shows devices with near AB stacking (60 degrees). Note that the spectra have varied background due to the different local field factor between devices. Overall, the spectra can be classified into three groups. WSe₂/WS₂ heterostructures with twist angle < 1 degree consistently show three prominent absorption peaks. When the twist angle is larger than ~ 3 degrees, the spectra largely recover to the response of weakly-coupled bilayers, where only a single prominent peak is present in the WSe₂ A exciton range. For twist angles between 1 and 3 degrees, the spectra show intermediate behaviors: the higher energy side peaks are very weak, and the lowest energy (most prominent) exciton peak has a resonance between the near-zero-twist-angle and large-twist-angle cases.

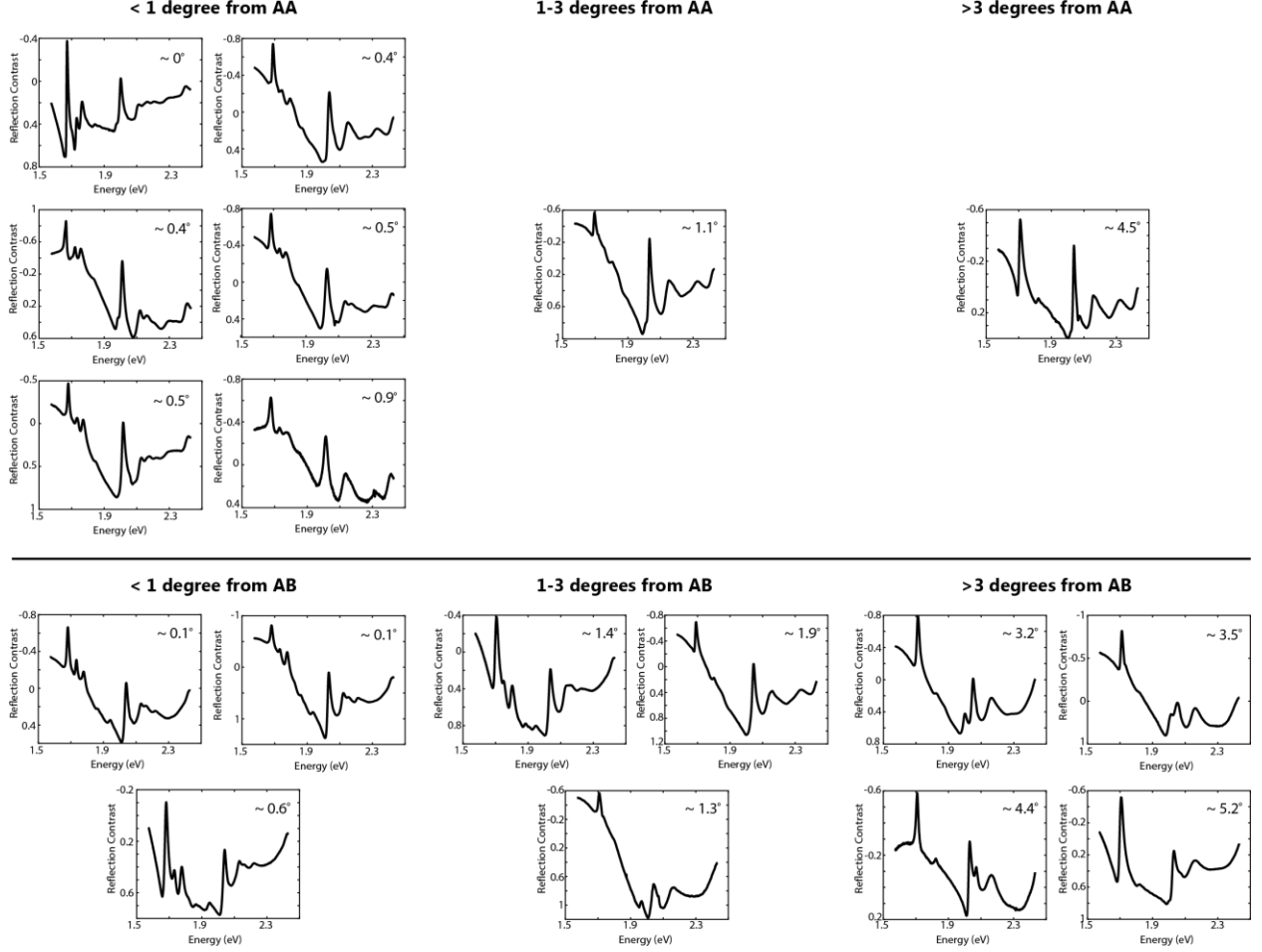


Fig. 3.3 | Twist angle dependent absorption spectra. Reflection-contrast spectra from 18 WSe₂/WS₂ heterostructures spanning a large range of twist angles close to AA stacking (upper panel) and AB stacking (lower panel). Devices with twist angle < 1 degree from AA or AB stacking consistently show three peaks in the WSe₂ A exciton range.

Although the high-energy emergent peaks become broad and weak for devices with twist angle > 1 degree, we can easily track the lowest energy peak for all devices. Fig. 3.4 shows the twist-angle dependence of the lowest-energy exciton peak position: black and red symbols represent results from near-AA stacked and near-AB stacked bilayers, and gray symbols represent large-twist-angle devices for reference. At small twist angle (< 1 degree), the lowest-energy exciton peak shows a systematic redshift of ~ 40 meV. As the twist angle increases, the redshift goes away quickly and disappears at > 3 degrees, which is consistent with the range in which the emergent peaks vanish. The abrupt disappearance of the emergent exciton peaks, as well as the energy redshift, can be potentially understood if a large lattice corrugation is formed at near-zero twist angle, which becomes increasingly unstable at larger twist angle and undergoes a sudden relaxation at some critical angle. Because the amplitude of the moiré potential depends sensitively on the strain landscape, a sudden change of structure can cause a large change in the moiré potential and its effect on the excitons.

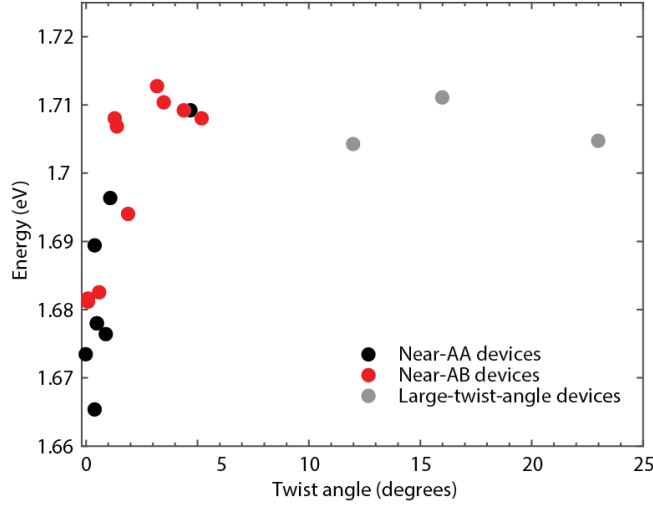


Fig. 3.4 | Twist-angle-dependence of peak I position. Black and red symbols represent results from near-AA stacked and near-AB stacked bilayers, respectively. Three large-twist-angle (>10 degree) devices are also included as reference (gray symbols).

From the PLE and twist-angle dependence, we determine that the emergent peaks come from the strongly-coupled heterostructure and only exist for small twist angles. Therefore, we conclude that additional exciton states emerge due to the moiré superlattice, and we call these states moiré excitons.

The interactions of the moiré excitons with doped electrons and holes can provide further information about the exciton states. We used the few-layer-graphite back gate and contact to change the carrier concentration in the sample, and we measured the effect on the sample with absorption spectroscopy, as shown in Fig. 3.5a. The three main peaks in the WSe_2 A exciton range show rich spectral changes upon both electron and hole doping. The strong gate-dependence upon electron doping is particularly interesting, since the type II band alignment in WSe_2/WS_2 heterostructures dictates that doped electrons reside mostly in the WS_2 layer and should have a relatively weak effect on the interlayer excitons in WSe_2 . The large-twist-angle case, shown in Fig. 3.5b for reference, follows the expected doping behavior for a type II heterostructure: upon electron doping, the WSe_2 A exciton does not change (except for slight redshift), while WS_2 shows a dramatic decrease and blueshift of the exciton, along with an emerging trion. The opposite is true in for hole doping. The large change of the WSe_2 exciton peaks with electron doping in the near-aligned heterostructure is therefore quite surprising and indicates that the interlayer electron-exciton interaction is strongly enhanced through the moiré superlattice.

A closer look at the absorption spectra for electron doping (Fig. 3.5c) also indicates that the doping dependence varies for different exciton peaks. Peak I shows a strong blueshift and transfers its oscillator strength to another emergent peak at lower energy (I'). Peak III also shows a strong blueshift with diminished oscillator strength. On the other hand, peak II remains largely unchanged except for a slight blueshift. The different gating behavior of the exciton peaks cannot

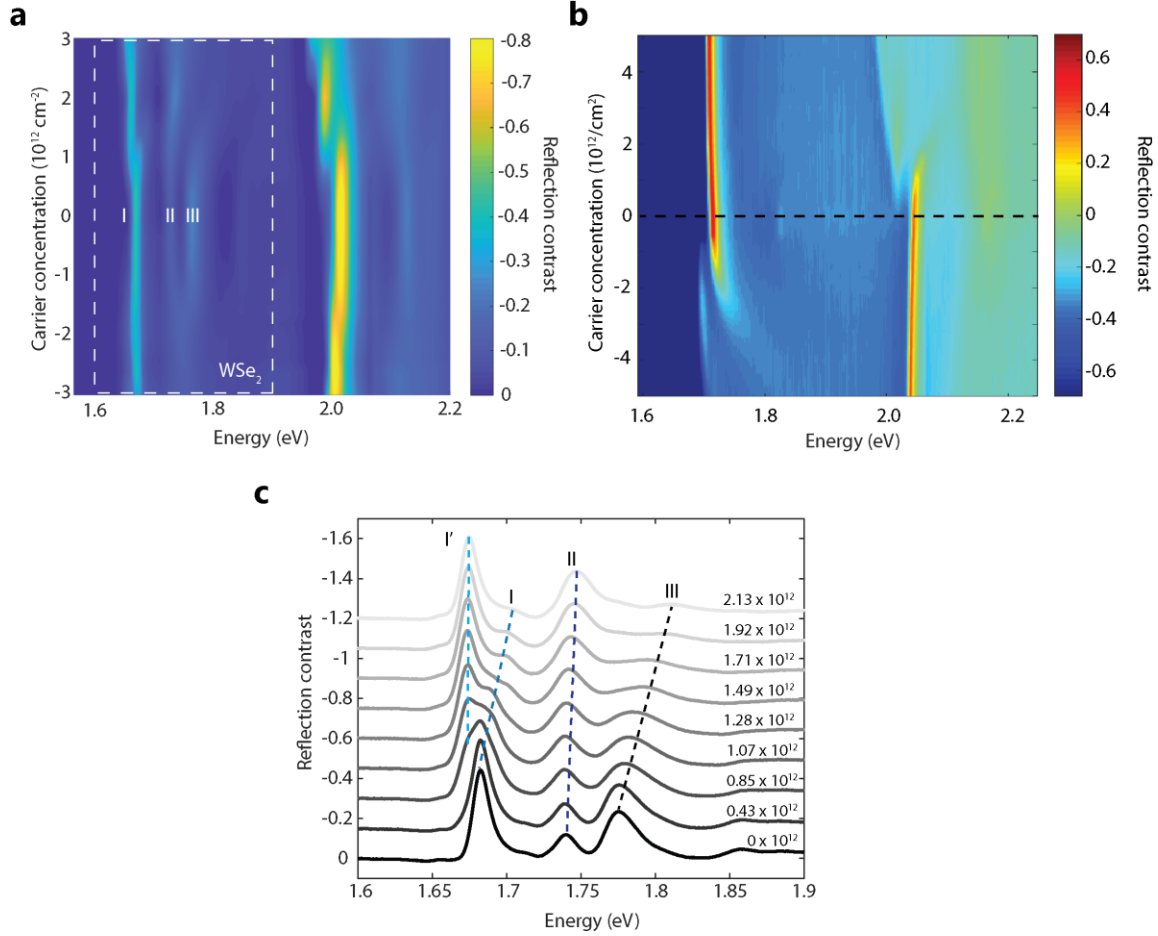


Fig. 3.5 | Gate-dependent reflection contrast spectra. **a.** Gate-dependent reflection contrast spectra of an aligned WSe_2/WS_2 heterostructure under both electron- (positive carrier concentration) and hole- (negative carrier concentration) doping. White dashed box encloses the photon energy range near the WSe_2 A exciton, where the three prominent moiré exciton states (labeled as I, II, and III) appear. **b.** Gate-dependent reflection contrast spectrum of a large twist angle device for reference. Figure adapted from reference⁸⁹. **c.** Reflection contrast spectra in the WSe_2 A exciton range on the electron-doping side (electron concentration for each spectrum is noted in units of cm^{-2}). Peak I shows a strong blueshift and transfers its oscillator strength to another emerging peak at lower energy (I'), and peak III shows a strong blueshift with diminished oscillator strength. On the other hand, peak II remains largely unchanged except for a small energy shift.

be explained by any established electron-exciton interactions in monolayers, such as dielectric screening effects³⁶ or trion formation⁹⁰, which affect all exciton peaks similarly. Instead, our observation suggests that exciton peaks I, II, and III correspond to different exciton states within the moiré superlattice.

Finally, to demonstrate that the emergent exciton peaks are visible at more easily-achievable temperatures, we measured the absorption spectrum of another representative device above liquid nitrogen temperature (80 K and 100 K), as shown in Figure 10. We find that the moiré exciton peaks largely remain the same from 10 to 100 K, except for slight redshift and

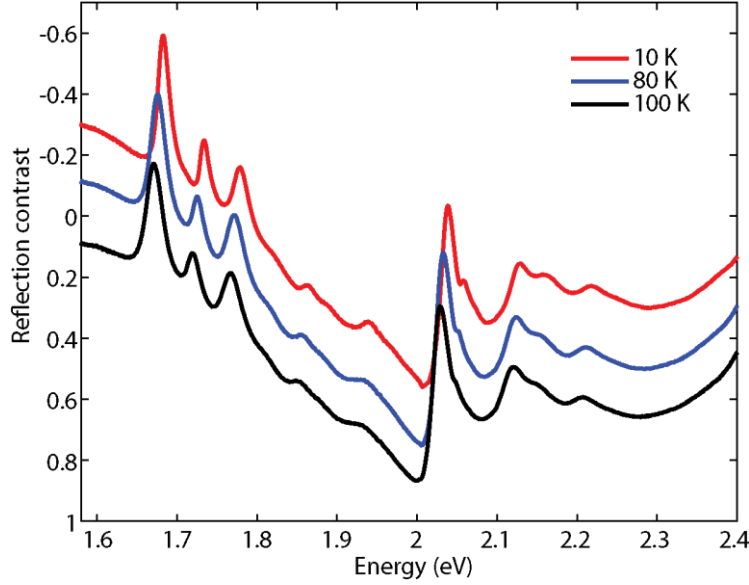


Fig. 3.6 | Temperature-dependent reflection contrast in near-zero-twist-angle WSe_2/WS_2 heterostructure.

broadening, which is expected at higher temperatures. This result is consistent with a large moiré potential that is much larger than the thermal energy in this temperature range ($100 \text{ K} = 8 \text{ meV}$).

3.2.2 Modeling the moiré potential

Based on our initial optical characterization of the moiré excitons described in the previous section, we turned to an empirical continuum model to extract the strength of the moiré potential. As we later discovered, this model is overly simplistic because it assumes that the nature of the exciton does not change in the moiré superlattice; in other words, the exciton remains a tightly bound Wannier exciton with electron and hole sitting at the same position in the superlattice unit cell. In reality, this assumption is poor because the electron and hole can experience different moiré potentials and therefore different spatially modulated densities. We will return to this idea later in this chapter. For now, we consider a continuum model.

The emergence of multiple exciton peaks and their doping dependence can be understood within an empirical continuum model in which a strong, periodic moiré exciton potential is introduced. Due to the periodic variation in the stacking arrangement, the moiré superlattice leads to a spatial modulation of the exciton potential energy across the unit cell. Following the model introduced in reference ⁶², we model the effect of the moiré superlattice on the WSe_2 A exciton. The variation in the exciton potential energy as a function of position $\mathbf{r}$ can be adequately approximated by the lowest harmonic term:

$$V_m(\mathbf{r}) = \sum_{n=1}^6 V_j \exp(i\mathbf{b}_j \cdot \mathbf{r}),$$

where V_j describe the effective potential on the exciton by the moiré pattern, and $\mathbf{b}_j$ are the reciprocal lattice vectors of the moiré superlattice. The three-fold rotational symmetry of the lattice constrains

$$V_1 = V_3 = V_5 \quad V_2 = V_4 = V_6,$$

and since V_m must be real, we also require $V_1 = V_4^*$ and so on. Therefore, we can describe all six V_j by a single term $V_1 = V \exp(i\psi)$. The peak-to-peak amplitude of the moiré potential is much larger than V after summing the contributions from the six components.

To model the WSe₂ A exciton, we use the Hamiltonian

$$H = H_0 + V_m = H_0 + \sum_{j=1}^6 V_j \exp(i\mathbf{b}_j \cdot \mathbf{r}),$$

where H_0 is the low-energy effective Hamiltonian of the WSe₂ A exciton described by

$$H_0 = \left(E_0 + \frac{\hbar^2 \mathbf{Q}^2}{2M} \right) \tau_0 + J|\mathbf{Q}| \tau_0 + J|\mathbf{Q}| [\cos(2\phi_Q) \tau_x + \sin(2\phi_Q) \tau_y].$$

Here, $\mathbf{Q}$ is the exciton total momentum, ϕ_Q is the polar angle of $\mathbf{Q}$ in the momentum space, $M \approx m_0$ is the total mass of the electron and the hole, $J = 0.04 \text{ eV} \cdot \text{nm}$ describes the intra- and intervalley exchange interaction, and τ_j ($j = 0, x, y, z$) is the Pauli matrices for valley pseudospin. E_0 is the $Q = 0$ energy, $\hbar^2 Q^2 / 2M$ is the exciton's center-of-mass kinetic energy, and the second and third terms describe the intravalley and intervalley electron-hole exchange interactions.

The exciton dispersion in the mini-Brillouin zone (mBZ) for various potentials can be directly calculated from the described model, as shown in Fig. 3.7a-c. Chenhao Jin, a postdoc in our lab and close collaborator, implemented this model. Without the moiré potential, the exciton shows two continuous bands at low energy that are degenerate at the γ point (Fig. 3.7a): the higher band has linear dispersion and the lower band is quadratic due to the intervalley exchange interaction⁹¹. Because photons have negligible momentum, only the lowest energy exciton interacts with light, giving a single strong peak at $E = E_0$ in the absorption spectrum (Fig. 3.7d). The moiré potential can mix exciton states with momenta that differ by $\mathbf{b}_j$, which leads to additional absorption features from the γ point of higher-energy minibands.

Now we consider the case when the moiré potential is finite but weak relative to the exciton kinetic energy in the first mBZ, E_k . In Fig. 3.7b,e shows the exciton dispersion and absorption spectrum for $V = 5 \text{ meV}$. We find that the dispersion remains largely unchanged and only a small side peak emerges in the absorption spectrum. This can be understood intuitively from perturbation theory: the first order correction to the wavefunction requires that states at $\mathbf{Q} = \mathbf{b}_j$ is mixed with the $\mathbf{Q} = 0$ state as follows.

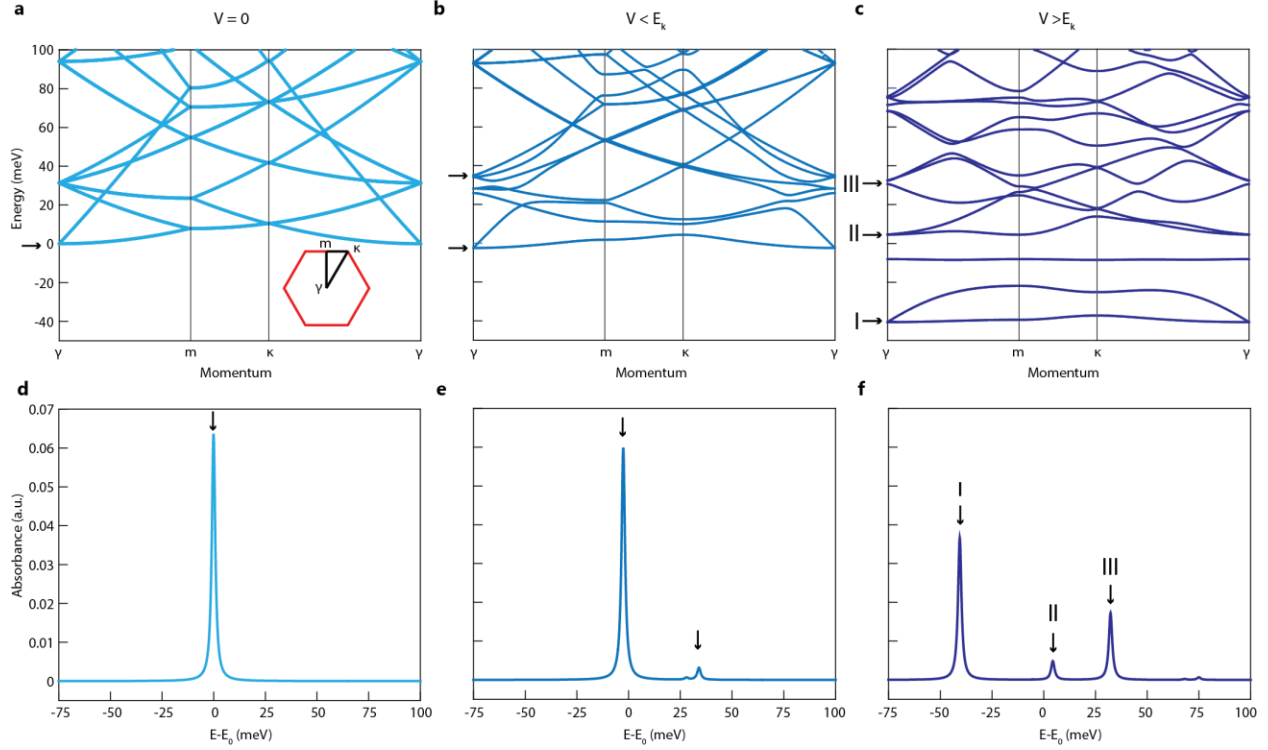


Fig. 3.7 | WSe₂ exciton dispersion in the mBZ with a moiré potential. **a.** $V = 0$ meV (zero coupling), **b.** $V < E_k$ ($V = 5$ meV, weak coupling), and **c.** $V > E_k$ ($V = 25$ meV, strong coupling). Here E_k is the exciton kinetic energy in the first mBZ. The lower panel shows the corresponding absorption spectra (**d-f**). A broadening of 2 meV is used to calculate the absorption spectrum. The inset in **a** illustrates the mBZ in momentum space and the high-symmetry points. Horizontal arrows in **a-c** labels the optically active exciton states in each case that give rise to absorption peaks (vertical arrows in **d-f**). The exciton dispersion is strongly modified in the “strong coupling” regime due to the strong mixing between different exciton states **c**, which gives rise to multiple moiré exciton peaks with comparable oscillator strength in the absorption spectrum (peak I to III in **f**) from different moiré mini bands (state I to III in **c**).

$$\Phi(\mathbf{b}_j)^1 - \Phi(\mathbf{b}_j)^0 = \frac{\langle \Phi(\mathbf{b}_j)^0 | V_m | \Phi(0)^0 \rangle}{E(\mathbf{b}_j) - E_0} \Phi(0)^0 \sim \frac{V_j}{4E_m} \Phi(0)^0,$$

where $\Phi(\mathbf{Q})$ is the exciton center-of-mass wavefunction at momentum $\mathbf{Q}$ and $E_m = \hbar^2 b_j^2 / (8M) \approx 8$ meV in a WSe₂/WS₂ moiré superlattice. The wavefunction of excitons at $\mathbf{Q} = \mathbf{b}_j$ now contain part of the bright exciton wavefunction, so their transition from the ground state is no longer forbidden and has oscillator strength of roughly $|V_j / (4E_k)|^2$. This results in an absorption side peak at $4Ek \approx 30$ meV above the main peak, regardless of the exact form of the moiré potential. The amplitude of the side peak is much smaller than the main peak due to weak mixing between states. This small moiré potential cannot explain the dramatic modification of the absorption spectrum that we see experimentally.

On the other hand, when the moiré potential is large ($V > E_k$), it strongly modifies the exciton dispersion (Fig. 3.7c,f). We refer to this as the “strong coupling” regime. Strong mixing between different excitons makes their oscillator strengths comparable to each other, resulting in several peaks of similar amplitude in the absorption spectrum. By taking $V = 25$ meV and $\psi = 15$, the simulated absorption spectrum can reproduce our experimental observations. The phase ψ is only important when the moiré potential is large, where higher order mixing between exciton states becomes relevant and different mixing paths can interfere. The exact determination of ψ is difficult, but changing the value of ψ will not qualitatively change the system. We can therefore settle on $\psi = 15$ for further discussion. With this parameter set, the moiré potential has a peak-to-peak amplitude V_{pp} of 250 meV, and its real-space distribution is shown in Fig. 3.8a.

Using this model, we can also calculate the real space distribution of the exciton states. The flattening in the exciton dispersion in momentum space implies that the exciton center-of mass wavefunctions are now localized in real space. Fig. 3.8c-d shows the calculated distribution of the exciton probability density for states I, II, and III in the moiré unit cell. The originally homogeneous WSe₂ A exciton wavefunction distribution is now dramatically different: state I and III are concentrated around the moiré potential minimum (labeled as point α), while state II is centered around a different point β .

The real space positions of the moiré exciton states may explain their distinctive doping dependence. The doped electrons also have a localized density of states in real space, so if the gate-induced electrons in WS₂ are also localized at point α , they will predominantly change the exciton peaks I and III but leave peak II little affected, as observed in experiment.

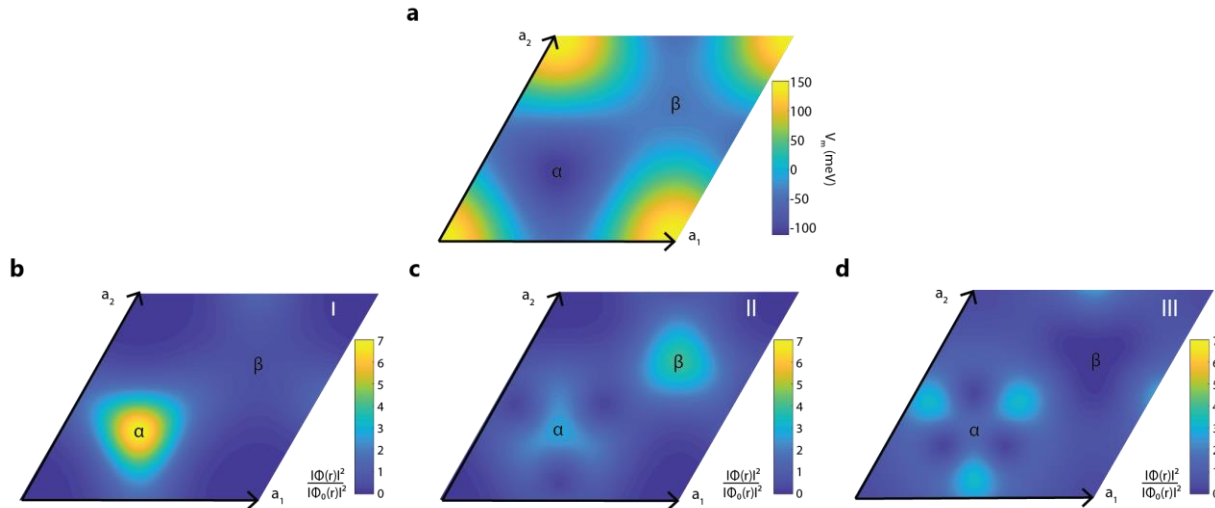


Fig. 3.8 | Real space moiré potential and exciton wavefunctions. **a.** The simulated real space distribution of the moiré potential with $V = 25$ meV and $\psi = 15^\circ$. The potential minimum is labeled as α . **b-d** Real space distribution of exciton center-of-mass wavefunction in the “strong-coupling” regime. The strong moiré potential traps the lowest-energy exciton state I around its minimum point (a). Interestingly, state III is also centered at point α (b) but state II is centered at a different point β (c), which can account for the remarkably different gate dependence between the moiré exciton states.

At the time of this work, our extracted peak-to-peak amplitude of the moiré potential was much larger than that predicted by density functional theory calculations for similar heterostructures⁶². The value of the moiré potential at a given point in space can be approximately understood from the modulation of the local bandstructure by the interlayer interaction with local atom registry. Therefore, its exact form will depend sensitively on the atomic configuration of the system. For example, one would expect the moiré potential to have a large amplitude if lattice corrugation or large strain field exists. Initial STM studies suggested that a significant lattice corrugation exists in $\text{WSe}_2/\text{MoS}_2$ heterostructures⁶³, which hinted at why the extracted moiré potential amplitude could be orders of magnitude larger than the predicted values. However, it is difficult to extrapolate between different heterostructures, as the interactions between layers with common/different chalcogens and transition metals may be quite different. Nevertheless, our simple moiré exciton model captures most of the salient features observed experimentally, and it shows that WSe_2/WS_2 heterostructures exhibit sufficiently strong interlayer interaction to enter the “strong coupling” regime for excitons, where the moiré excitons become spatially concentrated at well-separated points and form a quantum array in an extended moiré superlattice^{62,92}.

During the two years following the publication of this study, many details about the physical and electronic structure of the WSe_2/WS_2 superlattice were unearthed. In particular, a team of Berkeley researchers from the Wang and Louie groups imaged the moiré flat bands in WSe_2/WS_2 superlattice using STM and found that the system is buckled out of plane, resulting in a large in-plane strain that is responsible for the large moiré potential⁸⁰. Using ab initio simulations that include this 3D reconstruction, they can reproduce their experimental results. In the following section, I describe the results from a collaboration with the Louie group where we make use of this new information to truly understand the nature of these new exciton states.

In summary, we observed moiré superlattice exciton states in aligned WSe_2/WS_2 heterostructures. The moiré exciton states manifest as multiple emergent peaks around the original WSe_2 A exciton resonance in the absorption spectra with distinct and interesting gate dependences. The observed phenomena can be described by a simple theoretical model with a periodic potential that is much larger than the exciton kinetic energy, suggesting that the moiré superlattice dramatically modifies the bandstructure. In this “strong coupling” regime, flat low-energy exciton bands appear, which suggests that near-aligned WSe_2/WS_2 heterostructures may support strongly correlated exciton states^{93,94}.

3.3 Origin of intralayer moiré exciton states in aligned WSe_2/WS_2 heterostructures

This work⁸⁸ is the result of a close collaboration between Feng Wang’s group and Steve Louie’s group. Mit Niak, a postdoc in the Louie group, led the theoretical modeling and deserves credit for much of the results in section 3.3.1. Here, I briefly describe the approach and main results of the theoretical modeling in section 3.3.1 and focus on our contributions, the experimental data and interpretation, in 3.3.2.

3.3.1 A more complete model of moiré excitons

As discussed in the previous section, continuum models have been the primary approach for predicting exciton states in TMD moiré superlattices. This model hypothesizes an effective moiré potential that modifies the monolayer exciton states. It assumes that the intrinsic nature of the exciton does not change in the moiré superlattice—i.e., the internal spatial electron-hole correlations are unchanged from those of pristine single layers. However, this assumption is likely to fail in real moiré systems, where the electrons and holes can experience different moiré potentials and exhibit very different spatially modulated moiré flat bands^{65,69,73,76,78,80}. Continuum model calculations have explained some experimental findings in the WSe₂/WS₂ superlattice, such as the existence of split absorption peaks, but provides few answers about the nature of the states or their complex doping dependences. On the other hand, parameter-free *GW* plus Bethe-Salpeter equation (*GW*-BSE) calculations^{95,96} can handle the electron and hole states and their intricate interactions but are computationally intractable due to the large number of atoms in the moiré unit cell. In this section, I describe an approach developed by the Louie group to avoid this computational challenge.

Before diving into the theoretical treatment of the exciton states, we must first discuss the treatment of electron and hole states in the superlattice. As described previously, the WSe₂/WS₂ superlattice (Fig. 3.9a) undergoes a structural relaxation due to the energetics of various stacking arrangements^{68,69} that leads to a 3D buckling and large in-plane strain⁸⁰. Fig. 3.9 shows the computed strain distribution in the WSe₂ layer (b) and the resulting modification of the WSe₂ band gap (c) that can be used as an effective potential in a continuum model. The WSe₂ band states around the K point, which make up the low energy intralayer exciton states, are dominated

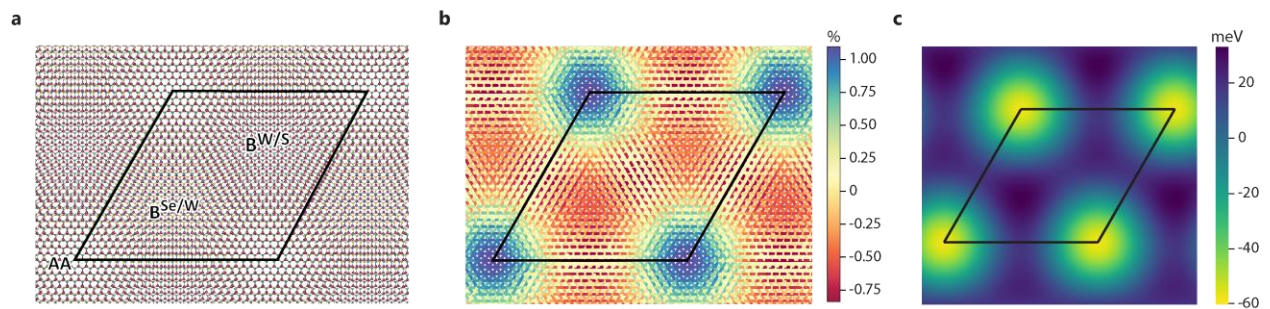


Fig. 3.9 | Reconstruction of the moiré superlattice. **a.** Schematic of the WSe₂/WS₂ moiré superlattice with the superlattice unit cell outlined in black and the high symmetry positions labelled. **b.** Computed strain distribution in the WSe₂ layer, plotted as a percentage change in the local lattice parameter from equilibrium. **c.** The effective moiré potential, computed as the variation in the WSe₂ band gap due to the local strain shown in b.

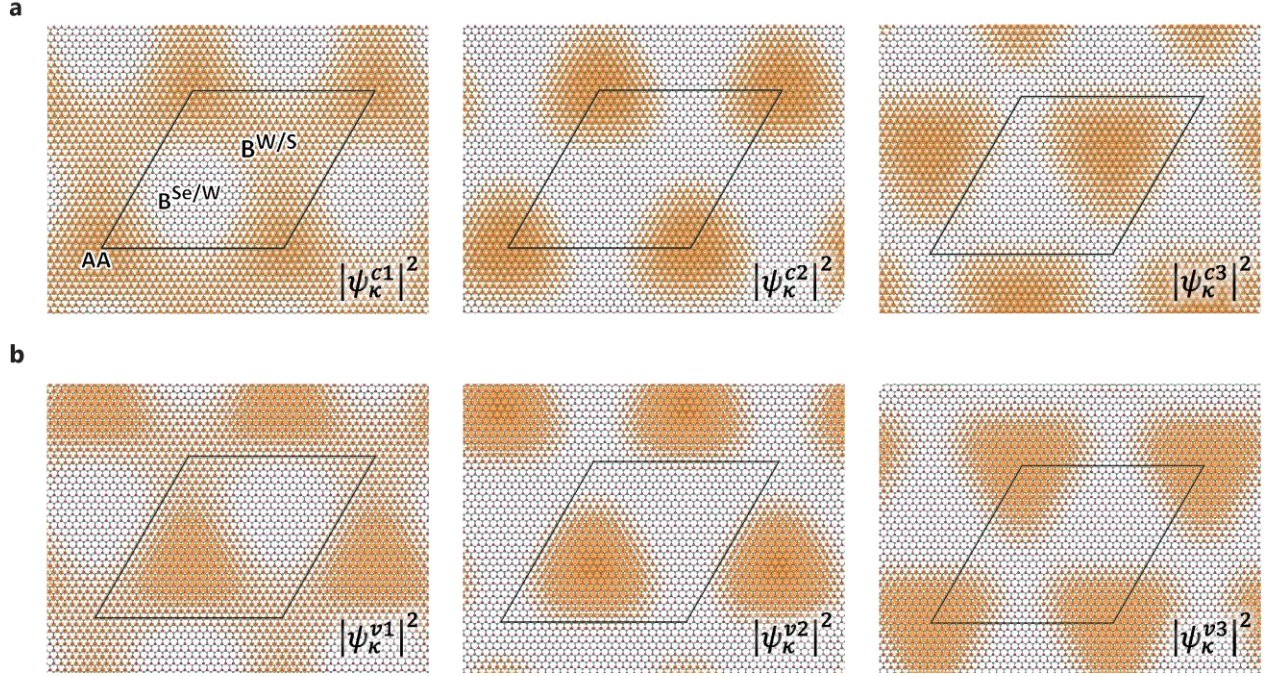


Fig. 3.10 | Electronic wavefunctions at conduction (a) and valence (b) band edges of the inhomogeneously strained WSe₂.

by this strain redistribution⁸⁰, rather than interlayer coupling, so we can consider the electron and hole states in a strained WSe₂ layer as the starting point for predicting intralayer exciton states in the superlattice. Fig. 3.10 shows the spatial modulation of the WSe₂ states at the valence and conduction band edges due to the inhomogeneous strains. Interestingly, the lowest energy electron and hole states are localized around different high symmetry positions in the superlattice unit cell, which reaffirms the importance of moving away from continuum models.

Computing the exciton states in the strained WSe₂ layer is computationally challenging because the interaction kernel, which considers the attractive and exchange-like repulsive interactions between the electron and hole that lead to the formation of excitons, involves an integral over the entire superlattice unit cell. To get around this problem, we can expand the wavefunctions of the strained WSe₂ in a basis of pristine WSe₂ states. Then the electron-hole interactions can be computed in the pristine basis, speeding up the calculation by six orders of magnitude. The absorption spectrum computed using this approach gives three moiré exciton peaks (Fig. 3.11b), similar to the experimental spectrum (Fig. 3.11a). On the other hand, the continuum model using an effective potential of ~90 meV (plotted in Fig. 3.9c) gives only two exciton states.

We then consider the spatial distribution of the exciton states computed with the GW-BSE approach. Fig. 3.12 shows the electron charge density for fixed hole coordinate of peaks I and III. For the case of the A exciton of a pristine WSe₂ layer, the electron density always centers around the hole, forming a Wannier exciton, with no preference for specific sites. On the other hand,

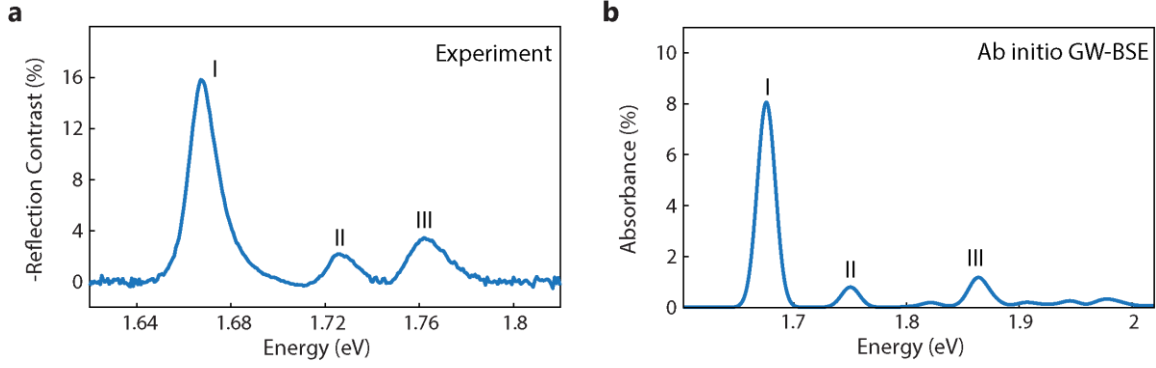


Fig. 3.11 | Absorption spectrum of intralayer excitons. **a.** Experimental reflection contrast spectrum of near-zero-degree WSe₂/WS₂. **b.** Computed absorbance spectrum of the inhomogeneously strained WSe₂ computed with the ab initio GW-BSE approach.

the modulation of the electron and hole states (Fig. 3.10) in the strained superlattice leads to a dramatic change in the moiré exciton states. For exciton I from *ab initio* GW-BSE, the electron density is maximum at the AA stacking site when the hole position is also at the same stacking site (Fig. 3.12a). This exciton has a modulated Wannier character with the electron and hole centered around the same position. The exciton III, in contrast, has maximum electron density at the nearby AA stacking sites when the hole coordinates are at the B^{Se/W} site region (Fig. 3.12b). Since the electron and hole densities are separated, exciton III is a charge transfer exciton with electron-hole separation of ~ 5 nm. The continuum model is unable to predict such a state because the separate electron and hole degrees of freedom are not explicitly included. Exciton II has mixed character, so we focus on states I and III for the remainder of this chapter.

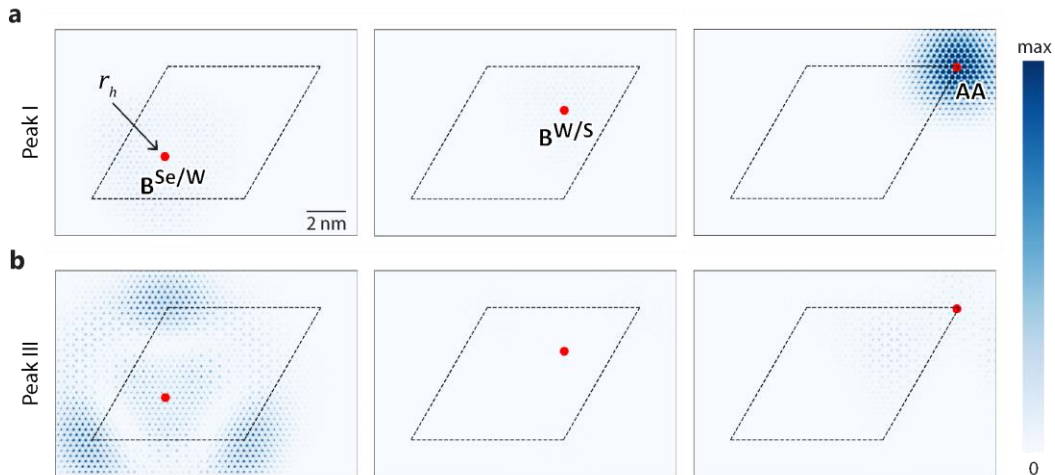


Fig. 3.12 | Exciton charge distribution. Distribution of electron charge density of the computed exciton (**a.** peak I, **b.** peak III) for three fixed hole positions (red dot) in the moiré unit cell. Peak I is a Wannier-like exciton, where the electron and hole are both localized around the AA position. Peak III is a charge-transfer exciton, where the electron and hole occupy different positions in the superlattice unit cell.

In the following section, I describe experimental signatures of such exciton states in the evolution of the states under charge doping and applied magnetic field.

3.3.2 Experimental evidence for character of moiré exciton states

The distinct nature of these moiré excitons can be experimentally probed through their carrier doping dependence, with and without a magnetic field, in a WSe_2/WS_2 moiré superlattice. For many years, the doping dependence of the moiré exciton states puzzled us. We discovered that some features were related to correlated states, as described in Chapter 4, but much of the behavior was still unexplained, including seemingly straightforward behavior like the direction of the peak shifts. Our new understanding of the nature of these states—thanks to the theoretical advances described above—allowed us to both validate the theory and answer our longstanding questions. Here, we will focus on the moiré peaks I and III, which have well-defined Wannier and charge-transfer characteristics, respectively. The data shown here are from a representative near-zero-twist-angle sample that was fabricated and measured by Zuocheng Zhang, a postdoc in our lab. Data from other samples that I fabricated and measured show similar results.

We measure the reflection contrast using a laser diode that is driven below the lasing threshold, producing a relatively broadband beam centered around 730 nm. This approach allows us to measure the reflection contrast of the three moiré exciton peaks using a stable, focused beam, rather than using full white-light illumination. Both approaches are fine for this purpose. The spectra include a slowly varying background due to multi-layer interference, so a polynomial background is fitted to the data and subtracted to observe the exciton states more easily.

Fig. 3.13a shows the evolution of the WSe_2 intralayer moiré exciton resonances as a function of electron and hole doping in a near-zero-twist-angle WSe_2/WS_2 heterostructure, which reveals different behavior compared with the exciton transitions in a large-twist-angle heterostructure (Fig. 3.13b). In both twist-angle cases, the doped electrons reside in the WS_2 layer and the doped holes reside in the WSe_2 layer due to the type II band alignment. We focus on a relatively low doping range, so there is no more than one electron or hole per moiré unit cell (see right y-axis in Fig. 3.13a).

The doping-dependent absorption of the WSe_2 excitons in the large-twist-angle WSe_2/WS_2 heterostructure can be understood straightforwardly⁸⁹. Hole doping in the WSe_2 layer leads to the formation of a positively charged trion resonance, which appears as a new peak at lower energy than the A exciton. At the same time, the A exciton transition is suppressed and blueshifts due to Pauli blocking. On the other hand, electron doping in the WS_2 layer leads to a slight redshift in the A exciton peak due to screening from the free carriers in the adjacent layer⁹⁷.

Meanwhile, the doping-dependence of the moiré exciton absorption spectra in aligned WSe_2/WS_2 heterobilayer is highly counterintuitive at first sight (Fig. 3.13a and Fig. 3.14). First, moiré exciton peak I shows negligible energy shift when holes are doped into the same WSe_2

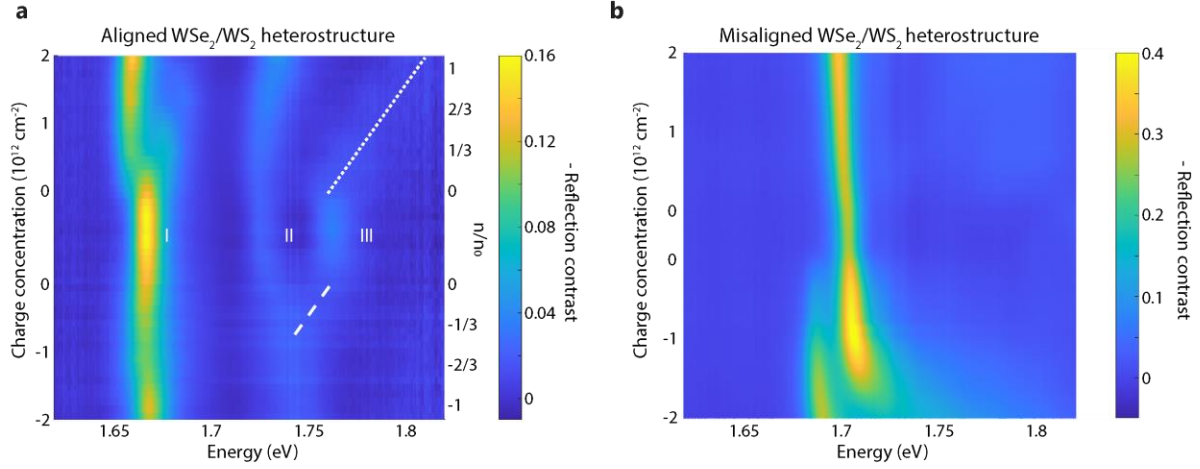


Fig. 3.13 | Behavior of WSe₂/WS₂ moiré excitons under charge doping. **a.** Experimental doping-dependent reflection contrast spectrum of a WSe₂/WS₂ moiré superlattice shows distinct behavior for WSe₂ moiré excitons I, II, and III. Negative (positive) charge concentration refers to hole (electron) doping. The redshift (blueshift) of peak III under hole (electron) doping is highlighted with dashed (dotted) white lines. **b.** Experimental doping-dependent reflection contrast spectrum of a reference misaligned WSe₂/WS₂ heterostructure. The WSe₂ exciton interacts strongly with doping doped holes in the WSe₂ layer, forming a trion state, but weakly with doped electrons in the WS₂ layer.

layer with no apparent trion formation. On the other hand, peak III is strongly affected by doped holes. Second, moiré peaks I and III both exhibit strong apparent changes when electrons are doped into the WS₂ layer. These large shifts cannot be explained solely by considering screening effects from the doping carriers and instead are due to the unique character of the moiré exciton states.

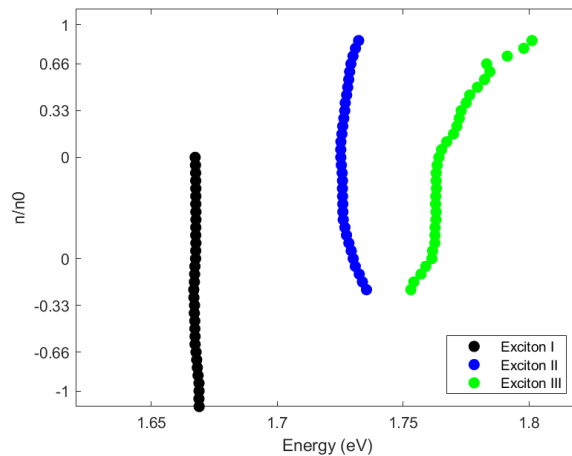


Fig. 3.14 | Fitting of peak energies in doping dependent reflection contrast. At each charge concentration, the spectrum was fit using three Lorentzian functions. The extracted peak energies are plotted only in doping ranges where the peaks can be easily distinguished.

interaction between the doping hole and the moiré exciton dipole decreases the total energy and leads to a redshift in peak III (dashed line in Fig. 3.13a). The combination of scenario A and B accounts for the observed overall redshift of peak III upon hole doping.

Next, we consider electron doping using the schematic shown in Fig. 3.16. STM measurements of the WSe_2/WS_2 superlattice have shown that the doped electrons have the maximum density at the $\text{B}^{\text{Se/W}}$ site in the WS_2 layer⁸⁰. The electrons are not in the WSe_2 layer, consistent with the type II band alignment. If electron doping in the WS_2 layer only has minimum effect on the tightly bound 1s exciton in the WSe_2 layer in a large twist angle heterostructure (Fig. 3.13b), how can it exert strong effect on intralayer moiré excitons in an aligned sample?

The doped electrons at the WS_2 $\text{B}^{\text{Se/W}}$ site should have negligible effect on the moiré peak I, where the constituent electrons and holes occupy the AA site in WSe_2 (Fig. 3.12a). However, the spectrum changes dramatically in the energy range around peak I. To explain this behavior, we must turn to exciton III.

In moiré peak III, the constituent hole is at the $\text{B}^{\text{Se/W}}$ site and the constituent electron is at the AA site (Fig. 3.12b). The extremely large dipole of charge-transfer exciton in moiré peak III allows for strong Coulomb coupling to the doped electrons in the WS_2 layer. Again, we

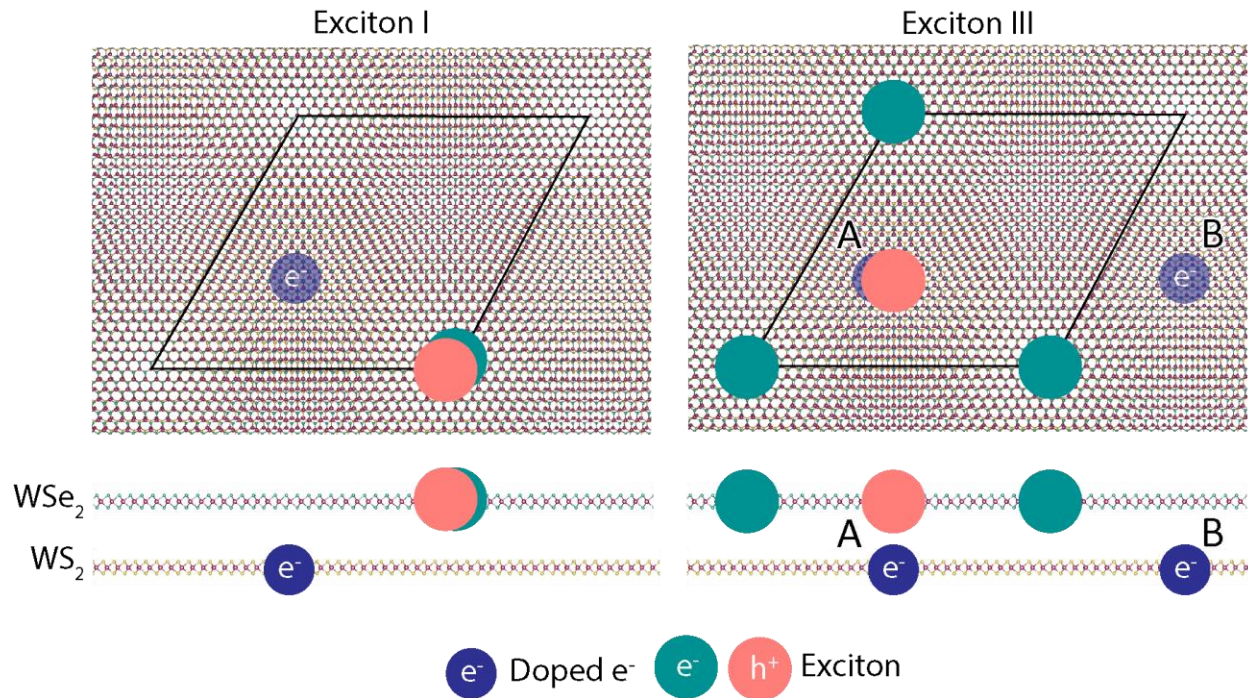


Fig. 3.16 | Interaction of excitons and doped electrons. Schematic of moiré exciton I (left) and III (right) under hole doping, from both top-down (top) and side (bottom) views. Exciton I is a tightly bound exciton at the AA position, while exciton III is a charge-transfer exciton with the hole at the $\text{B}^{\text{Se/W}}$ position and electron density at the surrounding AA positions. Doped electrons reside at the $\text{B}^{\text{Se/W}}$ positions. In the case of exciton III, we consider two scenarios: in scenario A, the doped electron is at the same $\text{B}^{\text{Se/W}}$ site as the constituent hole, and in scenario B, the doped electron is at the adjacent $\text{B}^{\text{Se/W}}$ site.

distinguish two scenarios when doped electrons are present only in a fraction of the moiré lattice sites. In scenario A, the doped electron and the constituent hole occupy the same $B^{\text{Se/W}}$ site. The attractive electron-hole interaction dramatically reduces the exciton energy, creating a new peak very close to moiré peak I that can partially hybridize with the moiré peak I through near-resonant coupling. This effect explains the large change in the spectrum around peak I. The Louie group estimated this redshift by computing the electrostatic interaction of the doped electron density in the WS_2 layer with the charge-transfer exciton in the WSe_2 layer. Using the computed charge densities of the electrons and holes, they estimate a redshift of ~ 120 meV, in good agreement with the experimental observation.

In scenario B, the doped electron and constituent hole occupy adjacent $B^{\text{Se/W}}$ sites. In this case, the Coulomb interaction between the doped electron and the moiré exciton dipole increases the total energy and leads to a blueshift in peak III, as observed experimentally (dotted line in Fig. 3.13a). Therefore, the shifts of peaks I and III under electron and hole doping can all be explained by the modulated electron, hole, and exciton densities due to the superlattice.

Next, we add a perpendicular magnetic field and consider the response of each exciton state. A strong perpendicular magnetic field completely valley polarizes the doped carriers. Here we will focus on doped holes. By monitoring the difference in absorption (reflection contrast) for K valley and K' valley excitons in this situation, we gain information about the exchange interaction between the valley polarized doped holes and the constituent holes in each exciton state. Since the exchange interaction depends on the wavefunction overlap, this tells us about the spatial separation between excitons and charges. We use circularly polarized light to monitor excitons in the two valleys. To generate circularly polarized light, a quarter-wave plate is placed before the objective. The reflected light, collected by the same objective, goes through the same quarter-wave plate before reaching the camera. A half wave plate is used to switch between right ($\sigma+$) and left ($\sigma-$) circularly polarized light to probe excitons in the K and K' valleys, respectively.

Fig. 3.17 shows the reflection contrast spectra of WSe_2/WS_2 moiré superlattice (Fig. 3.17a) and a WSe_2 monolayer (Fig. 3.17b) for both left and right circular light with $B = 6$ T. At charge neutral, the monolayer WSe_2 A exciton and the three moiré excitons in the aligned heterostructure shows a weak Zeeman splitting of the exciton transitions. Upon hole doping, each exciton feature exhibits a distinct evolution depending on its interaction with the K' valley doped holes.

First let's consider the monolayer case for comparison. The exchange interaction is strong in monolayer WSe_2 , where there is no wavefunction modulation, leading to very different spectra for K and K' valley excitons upon hole doping (Fig. 3.17b). The K'-valley doped holes and K valley exciton can form bound trion state at a lower energy⁹⁰. A similar trion state is not present for K'-valley exciton due to the exchange interaction between the valley-polarized holes.

In contrast, the moiré excitons in the aligned heterostructure exhibit different behavior from the monolayer A exciton and from each other. Moiré peak I shows a much smaller difference between the K and K' valley excitons upon hole doping at K' valley compared with that in

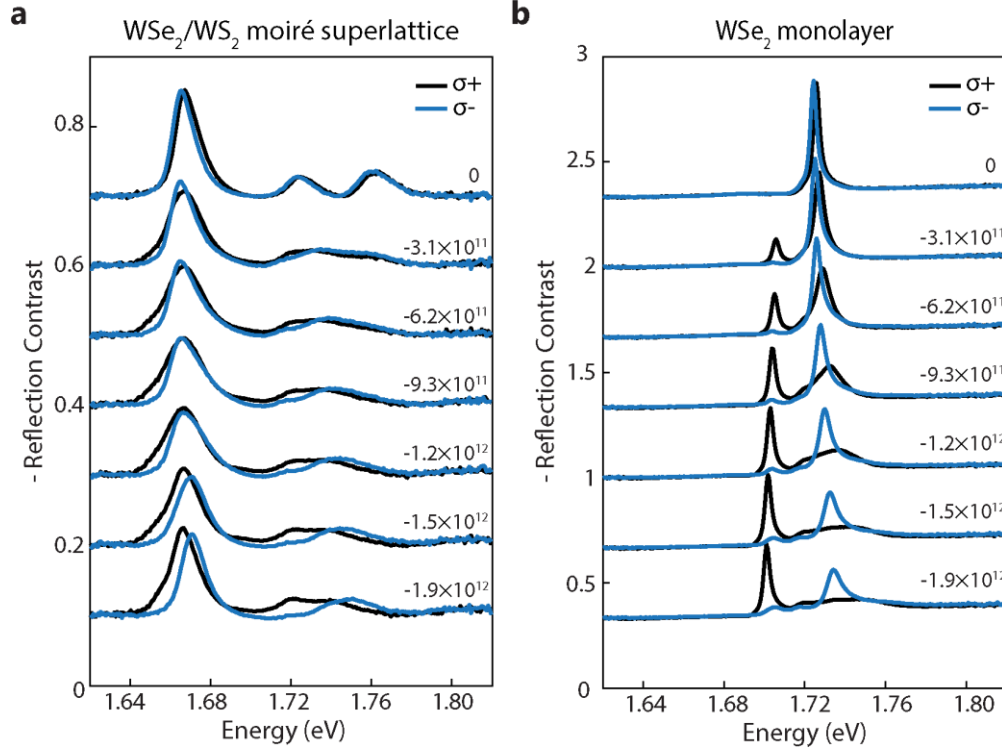


Fig. 3.17 | Doping dependence of moiré excitons under magnetic field. Hole doping dependent reflection contrast spectra of WSe₂/WS₂ moiré superlattice (a) and WSe₂ monolayer (b) for both left and right circularly polarized light under a perpendicular magnetic field at $B = 6$ T. Hole density is labeled for each set of spectra. In the WSe₂/WS₂ moiré superlattice, exciton I and III show relatively weak dependence on the exciton valley due to the spatial separation between doped holes at the K' valley and the constituent holes. Exciton II shows a relatively strong difference in behavior between K and K' valley excitons due to the partial overlap between doped holes at the K' valley and the exciton. On the other hand, the monolayer WSe₂ A exciton is strongly modified by the doped holes at the K' valley due to the large exchange interaction. K' valley doped holes form trion states with the K valley exciton, resulting in an absorption peak at lower energy.

monolayer WSe₂, indicating a very weak exchange interaction between the exciton I and the doped holes. This behavior is a manifestation of the hole and exciton separation: the doped holes have largest charge density at the B^{Se/W} site of the WSe₂ layer (Fig. 3.10b), while both the electron and hole of moiré exciton I are at the AA stacking site (Fig. 3.12b). Moiré peak II shows relatively strong difference in the K and K' exciton absorption with doped holes at K' valley. This observation is consistent with the partial spatial overlap of the constituent hole in moiré exciton II and the doped hole at the B^{Se/W} site, which results in significant exchange interaction. Moiré peak III shows a strongly diminished peak upon hole doping with no valley polarization dependence (beyond the Zeeman effect). The residue moiré peak III comes from scenario B in Fig. 3.15, where the doped hole and constituent hole of exciton III occupy adjacent B^{Se/W} sites. Because the doped holes have no spatial overlap with the exciton, the exchange interaction is negligible in this case.

Overall, the interactions between the doped charges and each exciton state, with and without a magnetic field, are consistent with the predicted spatial distribution of the moiré excitons. Therefore, we have shown that novel exciton states with unusual electron-hole correlations, such as intralayer charge transfer excitons, can exist in a TMD moiré superlattice. These states can have dramatically enhanced electron-exciton interactions, as demonstrated by the strong coupling of an electron in one layer with the charge-transfer exciton in the other layer. We expect similar states to exist in other moiré superlattices that also have strong spatial modulation of the electronic wavefunctions, where the details depend on the exact charge distribution. For example, near-60-degree WSe₂/WS₂ moiré superlattices also show three moiré exciton peaks in the absorption spectra, but the evolution of the peaks with electron doping is somewhat different. This observation may be consistent with a slightly different wavefunction modulation in the 60-degree sample and is worth further investigation.

3.4 Discussion

In summary, we observed multiple intralayer exciton states in a WSe₂/WS₂ moiré superlattice and determined their character using combined theoretical and experimental tools. At this point, it is clear that the moiré superlattice is not a simple perturbation on the individual layers. Instead, it creates a large potential due to structural relaxation that can dramatically modify the electronic states in each layer, leading to flatter bands and more localized charge densities. In the following chapters, we will consider other consequences of the strong moiré potential and the resulting bandstructure modifications.

Many questions remain about how moiré exciton states may be used in optoelectronic applications. Because the moiré potential can be very large, as is the case in WSe₂/WS₂ heterostructures, moiré exciton states are robust at room temperature. The enhanced charge-exciton interactions may lead to novel optical sensors and efficient electro-optic modulation devices based on moiré superlattices. Additionally, the choice of TMDs and twist angle provides a way for engineering exciton states with specific spatial characters and resulting charge interactions.

Our understanding of the moiré exciton states in aligned WSe₂/WS₂ heterostructures evolved in fits and starts. In mid-2017, we first observed three absorption peaks and determined that they were related to the superlattice. In mid-2021, we finally understood the nature of each exciton state and their interactions with doped charge. In between, we focused on other scientific questions related to exciton states in the superlattice. I briefly describe two studies that I was involved with below.

In collaboration with Chenhao Jin and Danqing Wang, I investigated the effect of a moiré superlattice on interlayer exciton states⁵². Due to the type II band alignment in WSe₂/WS₂ heterostructures, interlayer exciton states exist where the electrons and holes reside in different layers. Using a novel resonant optical pump-probe spectroscopy and PL excitation spectroscopy,

we demonstrated that the moiré superlattice localizes interlayer exciton states at different superlattice positions and modifies their optical selection rules due to a spatially varying moiré quasi-angular momentum.

Wenyu Zhao, also of the Wang lab, led a project⁹⁸ to dynamically tune the moiré excitons by mechanically deforming the WSe₂/WS₂ superlattice and modifying the potential. Using a fiber tip of a cryogenic scanning near-field optical microscope, we locally deformed the heterostructure while measuring the change in the intralayer and interlayer excitons. This study showed that it is possible to reversibly modify the strength of the moiré potential.

4 Correlated electronic states in WSe₂/WS₂ moiré superlattices

4.1 Introduction

Like excitons, single particle electronic states are also strongly modified by a moiré superlattice. The periodic potential leads to the formation of a set of minibands in the electron bandstructure with reduced bandwidth (Fig. 4.1a) and therefore reduced kinetic energy. In this case, the interaction between electrons can become important, leading to mysterious physical phenomena not described by simple band theory.

To better understand how a superlattice can lead to correlated electronic phenomena, let's consider a simplified but highly informative toy model: a 2D electron gas in a periodic potential of periodicity L . Since the electrons are localized on the length-scale of the superlattice, the on-site electron-electron interaction U can be estimated as the Coulomb repulsion between two charges at neighboring superlattice sites:

$$U \sim \frac{e^2}{4\pi\epsilon L}.$$

Note that this is a rough lower bound on the on-site interaction energy. Here ϵ is the effective dielectric constant. The electronic bandwidth W of the lowest electronic miniband can be estimated as the kinetic energy evaluated at the mBZ corner:

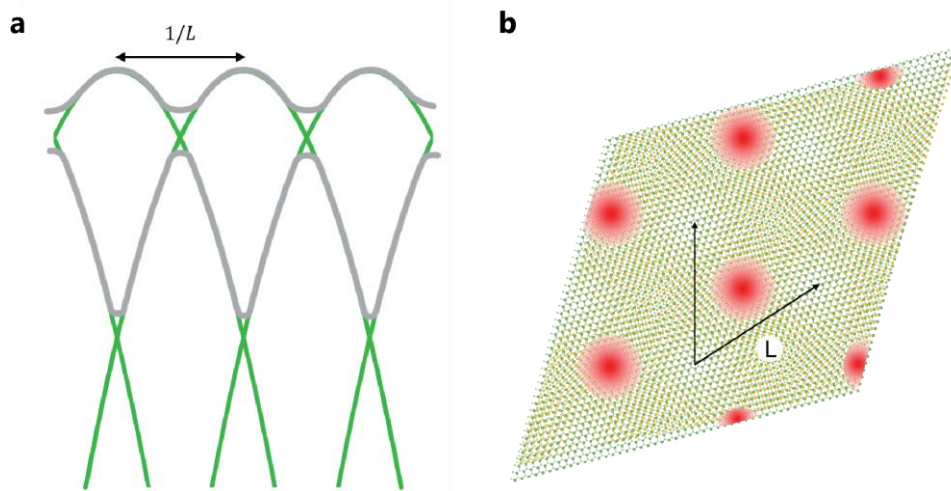


Fig. 4.1 | Flat bands and correlations in TMD moiré superlattices. **a.** Schematic of monolayer TMD bands (green) folded in the mBZ. The moiré potential opens a gap at the mBZ boundary, which produces flatter electronic bands (grey). **b.** Illustration of a Mott insulator state in a WSe₂/WS₂ moiré superlattice with one hole per superlattice unit cell.

$$W \sim \frac{\hbar^2 k^2}{2m_e^*} \sim \frac{\hbar^2 \pi^2}{2m_e^* L^2}.$$

Here m_e^* is the electron effective mass. The ratio U/W scales linearly with $m_e^* L$. Strong correlation, when $U/W > 1$, can be readily achieved with sufficiently large $m_e^* L$: for example, with a moiré superlattice ($L \sim 10$ nm) and an effective mass $m_e^* > 0.1m_0$ for $\epsilon \sim 4\epsilon_0$, all achievable values in practice. If the periodic moiré potential is very strong, the electron bandwidth W will be additionally suppressed, further enhancing the correlation effects.

Many fascinating states can arise when a physical system is dominated by interactions. A prominent example of a strongly correlated electronic system is the Mott insulator at one hole per superlattice site ($n = n_0$)^{99,100}, as illustrated in Fig. 4.1b. Here, when the superlattice is filled to precisely the right carrier density, the repulsive Coulomb interaction suppresses hopping between superlattice sites, leading to electrically insulating behavior. In fact, the isolated hole band in a WSe₂/WS₂ superlattice, which we focus on in this chapter, can be mapped to the single-band Hubbard model of the form⁶⁴

$$H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

where $\langle ij \rangle$ are nearest neighbors on the triangular lattice formed by the moiré potential, σ is the spin/valley index, and U is an on-site repulsive interaction. Hubbard model systems are expected to host a large range of exotic electronic states, from correlated insulating states at half filling^{99,100} to quantum spin liquid behavior¹⁰¹. Here, the superlattice serves as a quantum simulator: a physical realization of the Hubbard model in 2D, which has proved difficult to solve theoretically.

Correlated physics in moiré superlattices was first observed in twisted bilayer graphene^{102,103} and trilayer graphene/hBN^{104–106} samples, where observations of correlated insulating states and superconductivity delighted the field. However, TMD moiré superlattices have several distinctions and advantages. First, TMDs are predicted to exhibit very strong correlation effects because of their moderate effective masses ($m_e^* \sim 0.3\text{--}0.8 m_0$)^{107–109} relative to single and few-layer graphene. With larger effective mass, the bands of the constituent layers are already much flatter, leading to even flatter bands in the superlattice. Therefore, we can expect even stronger correlated behavior. Second, the spin/valley optical selection rules give direct access to the spin degrees of freedom in TMDs, providing an opportunity to investigate spin structures in the correlated states.

Although correlated insulating states are commonly probed via transport measurements, the prohibitively large contact resistance in TMD devices¹¹⁰ shifted our attention towards optical approaches. Excitons are extremely sensitive to the local charge density^{90,111} and dielectric environment³⁶, which makes it possible to probe electronic states using excitons. Using a novel optical technique that I describe in section 4.2, we optically detect both the quantum capacitance (proportional to the density of states) and electrical resistance of a WSe₂/WS₂ moiré heterostructure while avoiding complications from contact resistances. In section 4.3, I discuss our observation of a Mott insulator state at one hole per superlattice site ($n = n_0$) and surprising insulating phases at fractional filling $n = 1/3n_0$ and $n = 2/3n_0$, which we assign to generalized Wigner crystallization on an underlying lattice. The emergence of the generalized Wigner crystal

states necessitates an extended Hubbard model with not only on-site (short-range) but also inter-site (long-range) interactions^{112,113}.

In addition, the strong light-matter interaction and unique spin-valley selection rules allow us to optically create and detect different elementary excitations associated with the strongly correlated ground states in TMD moiré heterostructures. I briefly discuss how we use circularly polarized light to generate a low-energy pure spin excitation and our observation of an increased spin lifetime at the Mott insulating state. In Chapter 5, I build on this result and discuss the spin diffusion in a moiré superlattice.

4.2 Optical detection of correlated electronic states

To look for correlated electronic behavior in the WSe_2/WS_2 superlattice, we developed a new optical technique⁸⁷ for detecting charge transport characteristics. Typically, transport measurements are used to directly probe correlated insulating states, but the large contact resistance in TMD heterostructures makes direct transport measurements difficult, especially at low temperatures and low doping. The large contact resistance can be explained by two phenomena¹¹⁰: first, the large semiconductor bandgap in TMDs leads to the formation of Schottky barriers at metal-TMD junctions, and second, the TMDs have no interfacial bonds to facilitate contact formation. In our samples, the charge injection occurs with a time constant of ~ 1 s, much too slow for high quality transport measurements. Our optical approach, which we call optically detected resistance and capacitance (ODRC), avoids the challenges associated with the large contact resistance. Instead, it takes advantage of it!

4.2.1 Optically detected resistance and capacitance (ODRC) technique

The ODRC technique takes advantage of the fact that excitons are very sensitive probes of charge. One might wonder why we do not simply monitor the absorption of the excitons as we tune the doping to look for evidence of interactions with correlated states. Fig. 4.2 shows the reflection contrast spectrum of a WSe_2/WS_2 moiré superlattice when the sample is doped in a range of about $n = \pm n_0$. In addition to the smooth shifts with charge doping that I describe in the previous chapter, we see clear jumps and enhancements in the peaks at discrete doping levels. For example, we find that peak I is enhanced when there is one electron or hole per moiré unit cell, suggesting some connection to a Mott insulator state. So, in principle, we can directly use the absorption data to look for correlated states. However, we do not have good predictions for exactly how the exciton states interact with correlated electronic states, so it is difficult to interpret this information rigorously.

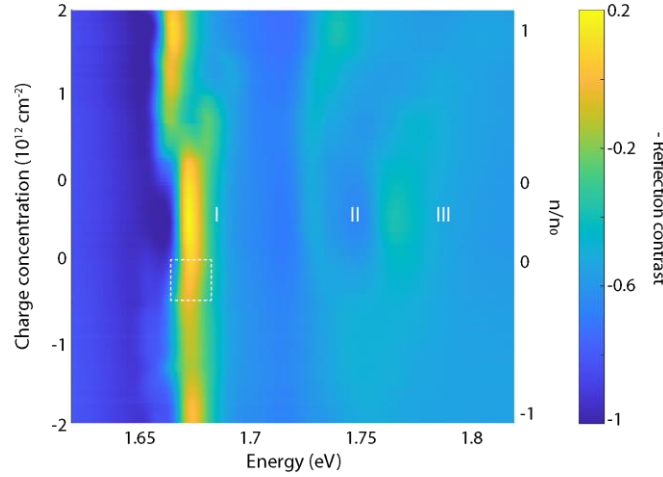


Fig. 4.2 | Exciton as a probe of charge. The doping dependent reflection contrast spectrum of the WSe₂ moiré excitons in a WSe₂/WS₂ moiré superlattice. The white dashed box highlights a hole doping range where the change in the spectrum is large and linear with doping.

Instead, we would like to use the exciton as a probe of the charge order, while keeping it a stable, sensitive, and simple probe. We find that for some doping ranges—for example at moderate hole doping, as highlighted in the white box in Fig. 4.2—the exciton absorption changes approximately linearly with doping. Under these conditions, the exciton is an ideal probe of charge. Therefore, we will use a two-region device structure, where one region is tuned through correlated electronic states, while the second region remains in this stable, sensitive configuration to probe charge transport characteristics.

For the ODRC measurements, we make use of a special device (Fig. 4.3) configuration

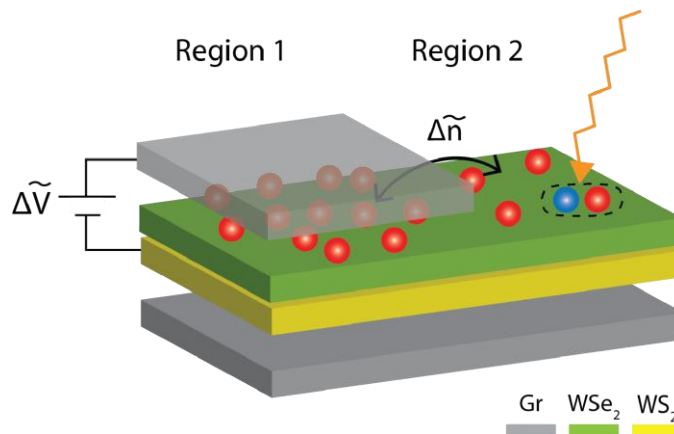


Fig. 4.3 | Schematic of ODRC measurements. Sketch of an ODRC measurement in a WSe₂/WS₂ heterostructure, which includes a local top gate and global back gate. A small AC bias $\Delta\tilde{V}$ leads to charge redistribution between region 1 and region 2 ($\Delta\tilde{n}$), which is detected via the change in optical reflectivity of the WSe₂ exciton in region 2. A DC bias V_{top} (not shown) is also applied to the local top gate to change the carrier concentration in region 1.

with two regions: one half of the device has a local graphite top gate (region 1), and the other half does not (region 2). An AC excitation voltage ($\Delta\tilde{V}$) is applied to the local top gate. For excitation frequencies higher than 10 Hz, the electrical contact is effectively frozen and the TMD heterostructure is floated electrically. In this case, the AC excitation voltage only leads to charge redistribution between region 1 and region 2 with no total charge change. The charge redistribution dynamics depends on the quantum capacitance and resistance in the moiré system, providing us with the charge transport characteristics that we are interested in.

We detect the resulting change of carrier concentration in region 2 ($\Delta\tilde{n}$) optically through the induced change in absorption (or optical contrast, ΔOC) at the intralayer exciton resonance. Here, we probe the lowest-energy moiré exciton peak (Fig. 4.4c), since it is the most sensitive to changes in charge (Fig. 4.2).

The global graphite back gate is used to set the DC doping level of region 2 to optimize the exciton optical response to change in doping. Typically, the DC doping level of region 2 is set to moderate p-doping, where the change in the exciton absorption is large and linear with changes in doping (Fig. 4.2).

We are interested in measuring the sample resistance and capacitance as we change the carrier concentration in the moiré superlattice. Therefore, we also add a DC voltage on the local top gate (V_{top}) to tune the carrier doping in region 1. Since charge injection occurs with a time constant of ~ 1 s, the DC voltage is able to change the carrier concentration. Therefore, the combination of DC and AC bias allows us to independently change the carrier concentration and induce charge motion, which we then probe optically. A full device schematic and microscope image of a ODRC sample are shown in Fig. 4.4a and b, respectively.

Implementing the ODRC measurement is fairly straightforward (Fig. 4.5). A function generator (Rigol 1022Z) is used to generate the top gate voltage consisting of a DC offset, V_{top} , with small AC modulation, $\Delta\tilde{V}$. A voltage source (Keithley 2400) is used for the back gate

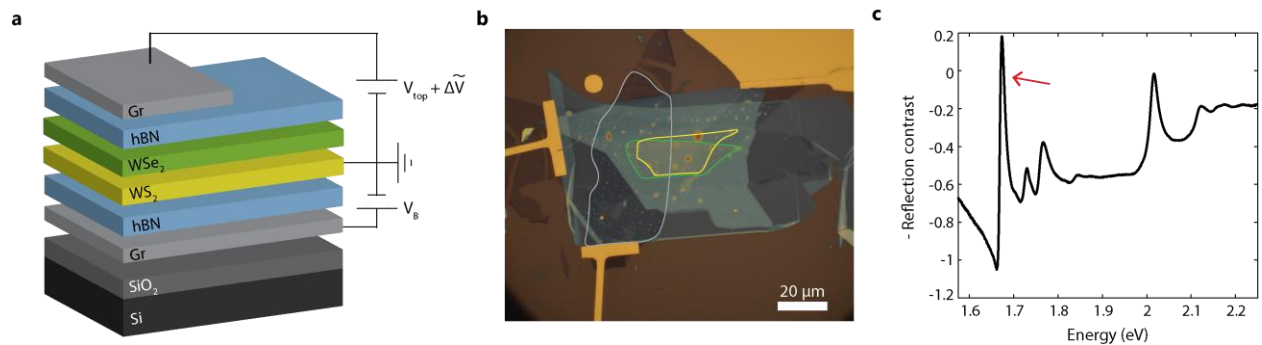


Fig. 4.4 | ODRC device. Side-view illustration (a) and optical microscope image (b) of near-zero twist angle heterostructure used for the ODRC measurements described in this chapter. The graphite top gate, WS_2 , and WSe_2 flakes are outlined in grey, yellow, and green, respectively. c. Optical absorption spectrum of the heterostructure showing splitting of the WSe_2 A exciton into three prominent peaks, which is characteristic of intralayer moiré excitons in an aligned heterostructure. The ODRC measurements use a laser probe in resonance with the lowest energy exciton peak (red arrow).

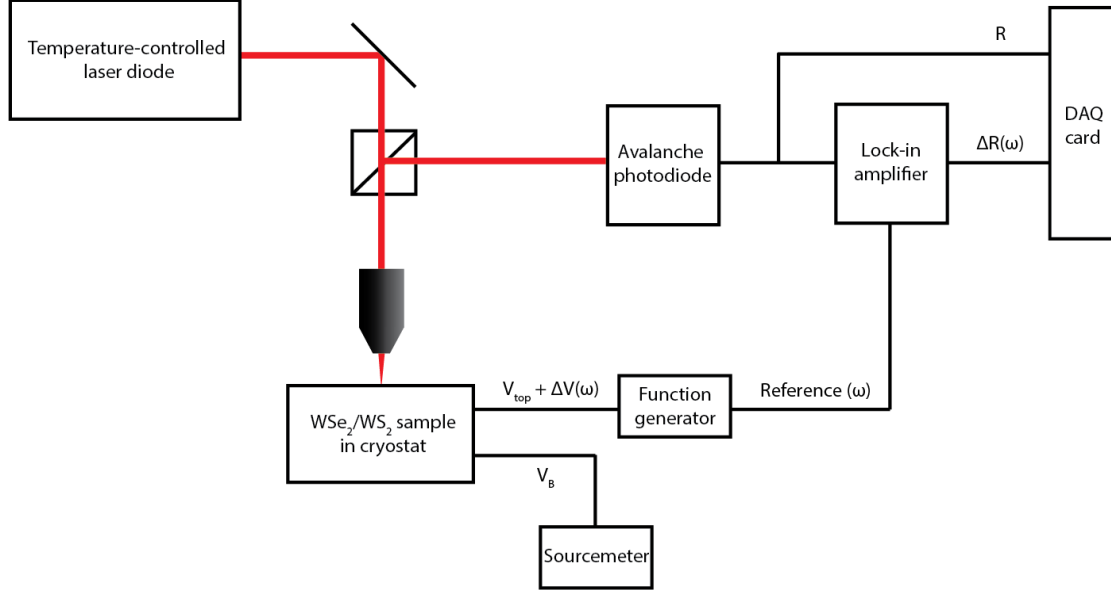


Fig. 4.5 | Experimental setup for an ODRC measurement.

voltage. A laser diode with center energy of 1.66 eV serves as the probe light. The diode energy is fine-tuned using a thermoelectric cooler, so that the probe energy is resonant with the lowest energy WSe₂ A exciton absorption peak in region 2 (Fig. 4.4c). The reflected probe light is collected with an avalanche photo diode (Thorlabs APD 410A) and then analyzed using a lock-in amplifier that is locked to the function generator output.

Before we consider any data taken with this technique, we must confirm that real devices will support such a measurement. The tests described below were conducted in the same WSe₂/WS₂ moiré superlattice sample used in the rest of the chapter. The exact voltages and frequencies are specific to this sample, but the conclusions hold generally.

The lowest-energy WSe₂ A exciton in region 2 is used to measure the electrical properties of region 1 as the local top gate DC bias is tuned. To be a reliable probe, the exciton in region 2 should only respond to charge redistribution due to the modulation voltage $\Delta\tilde{V}$, but not to the DC bias applied to the local top gate, V_{top} . We measure the optical spectrum of the lowest-energy WSe₂ A exciton (between 1.6 to 1.74 eV) while sweeping V_{top} from 0.5 V to -3.5 V (Fig. 4.6a). We record the spectrum 15 s after changing V_{top} to ensure the contact injects charge. We observe almost no change in the spectrum. Therefore, the static local top gate does not influence the hole concentration in region 2, and it remains a stable probe for all V_{top} used.

Next, we measure the absorption spectrum as a function of the carrier density in region 2 by varying the global back gate voltage. Fig. 4.6b shows the absorption spectra when the back gate voltage is tuned in a small range around -1 V. For the ODRC measurement, the modulation voltage $\Delta\tilde{V}$ is typically set to 10-25 mV, so the redistributed charges correspond to a small back gate voltage change of <25 mV. Within this range, the exciton resonance (1.673 eV) shows monotonic and linear change with carrier concentration. Therefore, the responsivity is a

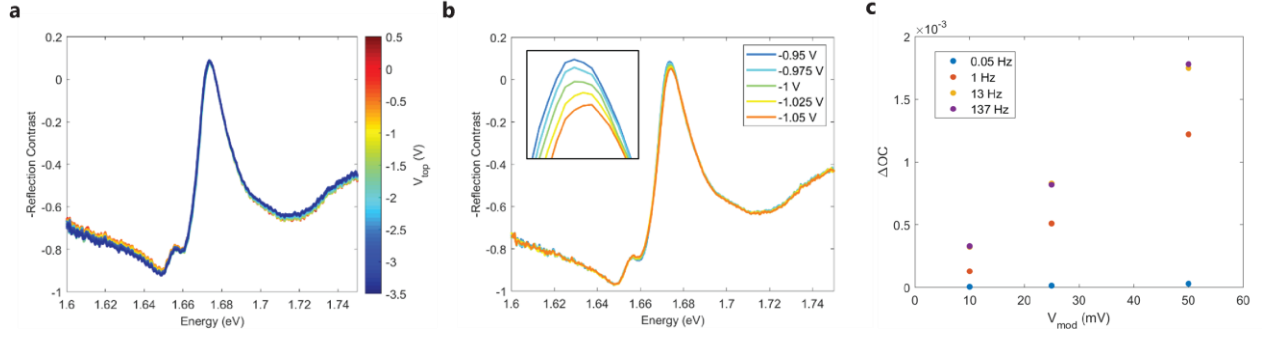


Fig. 4.6 | ODRC experiment checks. **a.** Reflection contrast spectra for the lowest-energy WSe₂ A exciton resonance in region 2 when the local top gate voltage V_{top} is tuned from 0.5 V to -3.5 V. Region 2 is not affected when the hole concentration is tuned in region 1 by V_{top} . **b.** Reflection contrast spectra for the WSe₂ A exciton in region 2 when the global back gate is tuned from -0.95 V to -1.05 V. Inset shows zoomed-in view of the exciton peak. The spectral change is monotonic and approximately linear with carrier concentration. **c.** ODRC signal measured at very low frequency for a range of modulation voltages, showing that the contact freezes around 1 Hz.

constant for our choice of back gate voltage. We estimate an optical detection responsivity α of $\sim 1.4 \times 10^{-12} \text{ cm}^2$. The noise of the ODRC signal is at $\sim 2 \times 10^{-6}$ level in our lock-in measurement for 3 s average time. We can detect a carrier density change in region 2 as small as 10^6 cm^{-2} with optical detection. This sensitivity surprised us initially—the lowest energy moiré exciton is truly an exquisite probe of charge!

Finally, we must confirm that the contact is frozen at high frequencies. Fig. 4.6c shows the frequency-dependent ODRC for modulation frequencies between 0.05 Hz to 137 Hz. The carrier injection through the graphite contact has a characteristic time constant of $\sim 1 \text{ s}$. At the lowest modulation frequency (0.05 Hz), the graphite contact can efficiently inject charge in response to $\Delta\tilde{V}$. As a result, the carrier density in region 2 remains a constant and the overall ODRC signal is negligible. At 1 Hz, the ODRC signal is partially reduced compared with higher frequency responses because the contact can inject some charge in response to $\Delta\tilde{V}$. For frequencies higher than $\sim 10 \text{ Hz}$, the contact becomes frozen. As a result, the heterostructure is effectively floated and the ODRC signal reaches its typical low-frequency value. For samples with better electrical contacts, this technique should also work, but one would need to use higher modulation frequency to ensure that the contact is frozen, which can be experimentally challenging. Additionally, as we describe below, the frequency range of interest is set by the resistance and capacitance of the sample, so the contact must be frozen at these frequencies.

We have demonstrated that the exciton in region 2 is a sensitive and stable probe of induced charge movement in the sample. Now let's consider how to interpret the ODRC signal.

4.2.2 Circuit model

The AC electrical transport in the TMD heterostructure can be modeled by an effective

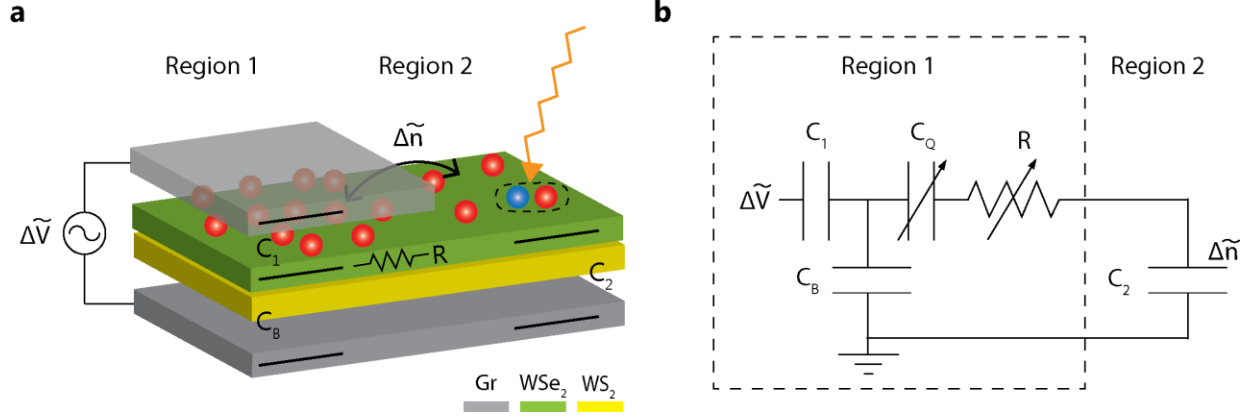


Fig. 4.7 | Circuit model of ODRC measurement. **a.** Device schematic for an ODRC measurement in a WSe₂/WS₂ heterostructure, which includes a local top gate and global back gate. A small AC bias $\Delta\tilde{V}$ leads to charge redistribution between region 1 and region 2 ($\Delta\tilde{n}$), which is detected via the change in optical reflectivity of the WSe₂ exciton in region 2. This AC measurement can be modeled as an effective RC circuit, where the elements are shown schematically in **b**. C_1 , C_B , and C_2 are the illustrated geometric capacitances in the system, and R and C_Q are the doping-dependent resistance and quantum capacitance of region 1 that we measure.

RC circuit shown in Fig. 4.7. C_1 and C_B are the geometric capacitances between the TMD and the top and bottom gates in region 1, respectively, and C_2 is the geometric capacitance between the TMD and the bottom gate in region 2. The geometric capacitances are defined by $C_i = \epsilon_0 \epsilon_r A_i / d_i$, where ϵ_r is the dielectric constant of the gate dielectric, and A_i and d_i denote the relevant capacitor area and separation. C_Q and R are the quantum capacitance and resistance of region 1, respectively. The ODCR signal measures the modulation induced optical contrast change in region 2, which can be understood as the optical response to an effective voltage change on region 2 (ΔV_2) due to the AC capacitive excitation in region 1 ($\Delta\tilde{V}$):

$$\Delta V_2 = \Delta\tilde{V} \left(1 - \frac{\frac{1}{i\omega C_1}}{\frac{1}{i\omega C_1} + \frac{1}{i\omega C_B + \frac{1}{\frac{1}{i\omega C_Q} + \frac{1}{i\omega C_2} + R}}} \right) \frac{\frac{1}{i\omega C_2}}{\frac{1}{i\omega C_Q} + R + \frac{1}{i\omega C_2}},$$

which can be simplified to:

$$\Delta V_2 = \Delta\tilde{V} \left(\frac{C_1}{C_1 + C_B} \right) \frac{\frac{1}{C_2}}{\frac{1}{(C_1 + C_B)} + \frac{1}{C_Q} + \frac{1}{C_2} + i\omega R}.$$

For simplicity, we define an effective capacitance as

$$\frac{1}{C_{eff}} = \frac{1}{(C_1 + C_B)} + \frac{1}{C_2} + \frac{1}{C_Q},$$

so

$$\Delta V_2 = \Delta \tilde{V} \left(\frac{C_1}{C_1 + C_B} \right) \frac{\frac{1}{C_2}}{\frac{1}{C_{eff}} + i\omega R}.$$

The effective voltage change leads to a total charge change $\Delta \tilde{Q}$ in region 2:

$$\Delta \tilde{Q} = \Delta V_2 C_2 = \Delta \tilde{V} \left(\frac{C_1}{C_1 + C_B} \right) \frac{1}{\frac{1}{C_{eff}} + i\omega R},$$

and corresponding change in hole density:

$$\Delta \tilde{n} = \frac{\Delta \tilde{Q}}{A_2 e} = \frac{1}{A_2 e} \Delta \tilde{V} \left(\frac{C_1}{C_1 + C_B} \right) \frac{1}{\frac{1}{C_{eff}} + i\omega R}$$

where e is the electron charge. The ODCR signal, ΔOC , is related to $\Delta \tilde{n}$ by the optical detection responsivity α , which describes the change in the optical absorption for a given change in doping:

$$\Delta OC = \alpha \Delta \tilde{n} = \frac{\alpha}{A_2 e} \Delta \tilde{V} \left(\frac{C_1}{C_1 + C_B} \right) \frac{1}{\frac{1}{C_{eff}} + i\omega R}.$$

The responsivity α is set to $1.4 \times 10^{-12} \text{ cm}^2$, so that $\frac{1}{C_{eff}} = \frac{1}{(C_1 + C_B)} + \frac{1}{C_2}$ at high doping, where the quantum capacitance is much larger than the geometry capacitances and has negligible contribution. This value of α also is also consistent with the value determined by the doping-dependent optical absorption of region 2.

Measuring the frequency-dependent optical signal $\Delta OC(\omega)$ allows us to extract the values of both C_Q and R : At low excitation frequencies the resistance is negligible, so the optical signal probes the quantum capacitance C_Q , which is proportional to the density of states of the moiré heterostructure. At high modulation frequencies, both C_Q and R contribute to the optical signal.

In summary, we developed an optical technique for measuring the resistance and capacitance of a sample in situations where the contact resistance is prohibitively large. This method takes advantage of the poor contact resistance to independently tune the carrier concentration and induce charge motion. Furthermore, we achieve remarkably high sensitivity thanks to the excellent sensitivity of the lowest energy moiré exciton to changes in charge. The method is not specific to the TMD heterostructures, but TMDs do fulfill the requirements: relatively poor contacts and excellent optical response.

4.2.3 ODRC in large twist angle WSe₂/WS₂ heterostructure

To get a sense of what ODRC data looks like for a TMD heterostructure, let's consider the ODRC signal in a large twist angle WSe₂/WS₂ heterostructure, where there is no large-scale moiré superlattice or strong moiré potential. Here, we probe the WSe₂ A exciton. As we increase the carrier concentration, the ODRC signal should reflect the decrease in resistance and increase in quantum capacitance as the Fermi level leaves the bandgap and enters the band. The circuit model tells us that this should result in a large increase in the ODRC signal at this point.

Fig. 4.8 shows the doping dependent ODRC signal at three frequencies for a large twist angle heterostructure. As expected, the signal shows a sharp increase when holes are doped into the system, indicating that charges are present and can redistribution occurs. For increased hole density, the signal increases with hole density without any features that might suggest unexpected insulating behavior, a sharp contrast to what I describe in the next section. The frequency dependence of the signal shows a characteristic RC circuit fall-off with increasing frequency, consistent with our model.

Next, we consider the same measurement in a WSe₂/WS₂ moiré superlattice.

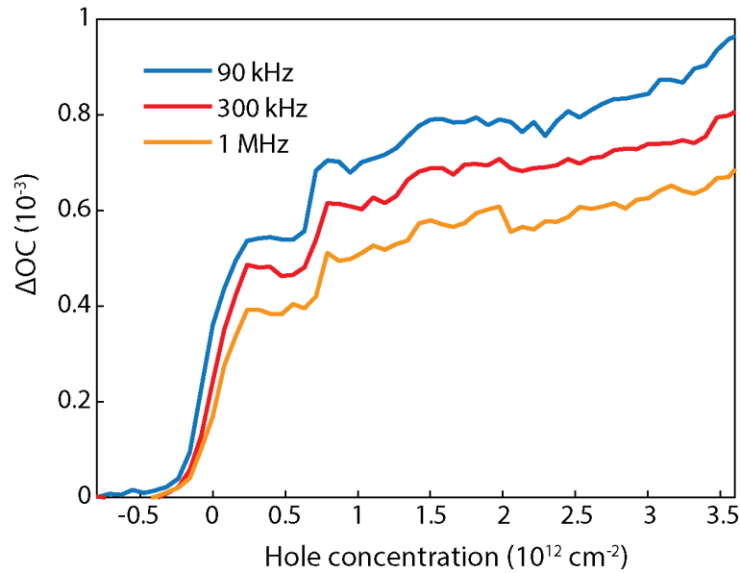


Fig. 4.8 | ODRC signal for large twist angle WSe₂/WS₂ heterostructure. ODRC signal, ΔOC , for a large twist angle heterostructure. When holes are injected into the sample, charge redistribution begins and ΔOC rapidly increases. For increasing hole concentration, the charge redistribution is relatively constant. The signal falls off with increasing frequency, characteristic of an RC circuit.

4.3 Observation of Mott and Wigner crystal states in a WSe₂/WS₂ moiré superlattices

Fig. 4.9 shows the ODRC signals as a function of the hole doping of the WSe₂/WS₂ moiré superlattice in region 1. We use an AC excitation voltage with the peak-to-peak amplitude of 10 mV at 1 kHz and 30 kHz. When region 1 is near charge neutral ($V_{\text{top}} > 0.2$ V), the ΔOC signal is small because no carriers are available to redistribute in the bandgap of WSe₂. When region 1 is hole doped ($V_{\text{top}} < 0.2$ V), charge redistribution occurs, leading to a large increase in signal. Interestingly, we observe a strong gap-like feature at -1 V (blue dashed line in Fig. 4.9). This voltage corresponds to a hole concentration of $1.86 \times 10^{12} \text{ cm}^{-2}$, which matches well with the density of one hole per moiré unit cell ($n_0 = 1.88 \times 10^{12} \text{ cm}^{-2}$). We also observe two sharp dips at -0.2 V and -0.6 V (orange and green dashed lines in Fig. 3.8), which correspond to hole concentrations of $n = n_0/3$ and $n = 2n_0/3$, respectively. Additionally, a broad, weaker feature is observed at -2.25 V, corresponding to $n = 2n_0$. These features become stronger at higher excitation frequency of 30 kHz.

To quantitatively test our effective circuit model, we measured the frequency dependence of the ODRC signal at several representative hole-doping densities (Fig. 4.10a). For all hole

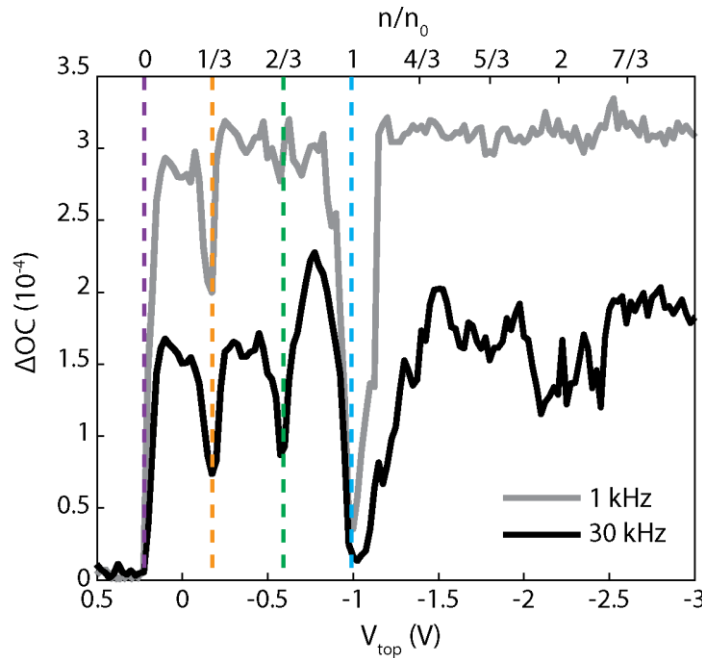


Fig. 4.9 | Raw ODRC signal in WSe₂/WS₂ moiré superlattice. ODRC signal, ΔOC , signal at 1 kHz (grey) and 30 kHz (black) from charge neutral to moderate hole doping. Strong gap-like features are observed at hole doping levels of $n = n_0/3$ (orange dashed line), $n = 2n_0/3$ (green dashed line), and $n = n_0$ (blue dashed line). The purple dashed line corresponds to $n = 0$.

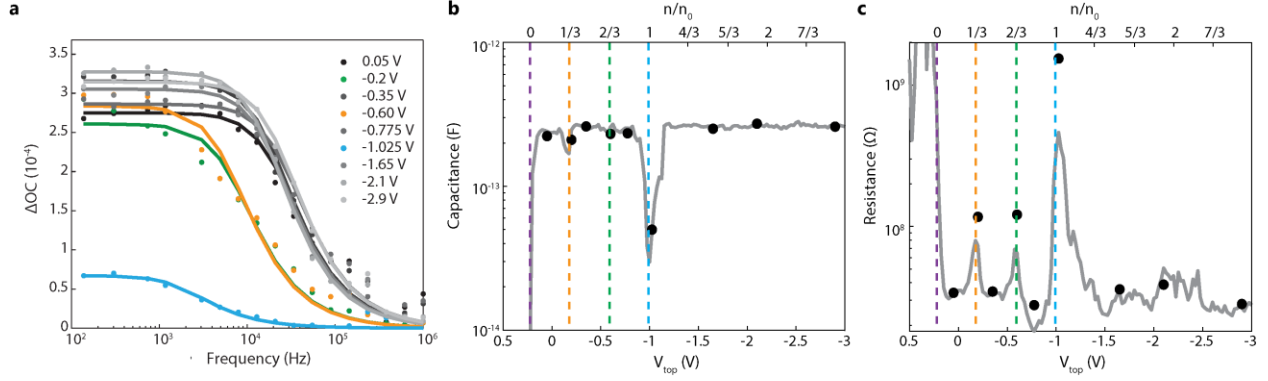


Fig. 4.10 | Extracted resistance and capacitance from circuit model. **a.** Frequency-dependent ODRC signal at representative doping levels. Dots are data, curves are fits to the RC circuit model for a given doping level. **b.** and **c.** Extracted capacitance C_{eff} (a) and resistance (b) of region 1 from the data in Fig. 4.9 (grey curves) and from the frequency dependent ODRC signal in a (black dots). The decreased capacitance and increased resistance indicate emerging insulating states at $n = n_0/3$, $n = 2n_0/3$, and $n = n_0$.

concentrations, we observe a clear signal fall-off with increasing frequency, and data can be reproduced by the circuit model prediction (solid lines). Next, we extract numerical values for the doping-dependent C_{eff} and R of the moiré heterostructure based on the effective circuit model. We plot C_{eff} and R as a function of carrier doping in Fig. 4.10b and Fig. 4.10c, respectively. The grey lines are the extracted values from the ODRC data in Fig. 4.9, and the dots are extracted values from the frequency dependence at select doping levels in Fig. 4.10a.

At $n = n_0$, $n = n_0/3$, and $n = 2n_0/3$, C_{eff} decreases while the geometric capacitances remain unchanged (Fig. 4.10b). This decrease of C_{eff} is due to a much smaller quantum capacitance C_Q , which results from significantly reduced density of states at these fillings. At the same time, the electrical resistance shows marked increases at $n = n_0$, $n = n_0/3$, and $n = 2n_0/3$ (Fig. 4.10c). The simultaneous reduction of the density of state and large increase of the resistance indicate the emergence of insulating states at these fillings.

Our results show that the WSe_2/WS_2 moiré heterostructure hosts insulating states with reduced density of states and increased resistance at $n = n_0$, $n = n_0/3$, and $n = 2n_0/3$. These features are completely absent in large twist angle WSe_2/WS_2 heterostructures (Fig. 4.8) and only emerge in the moiré superlattices. The insulating state at $n = n_0$ corresponds to half filling of the moiré miniband because TMDC heterostructure has a degeneracy of 2 from spin-valley locking¹⁷ (Fig. 4.11). This state is typically assigned to a Mott insulator^{99,100}, but it may also be described by an interaction-driven Wigner crystal state^{112–117} or a charge transfer insulator¹¹⁸. Similar correlated insulating states have also been observed at $n = n_0$ in twisted bilayer graphene and ABC trilayer graphene/hBN moiré superlattices^{102–105}.

On the other hand, the observation of insulating states at $n = n_0/3$ and $n = 2n_0/3$ is quite surprising. Insulating states at fractional filling of the lattice sites have not been observed in other moiré superlattice systems and cannot be described as a Mott insulator or by a Hubbard model with only on-site repulsive interactions. We hypothesize that these insulating states at $n = n_0/3$

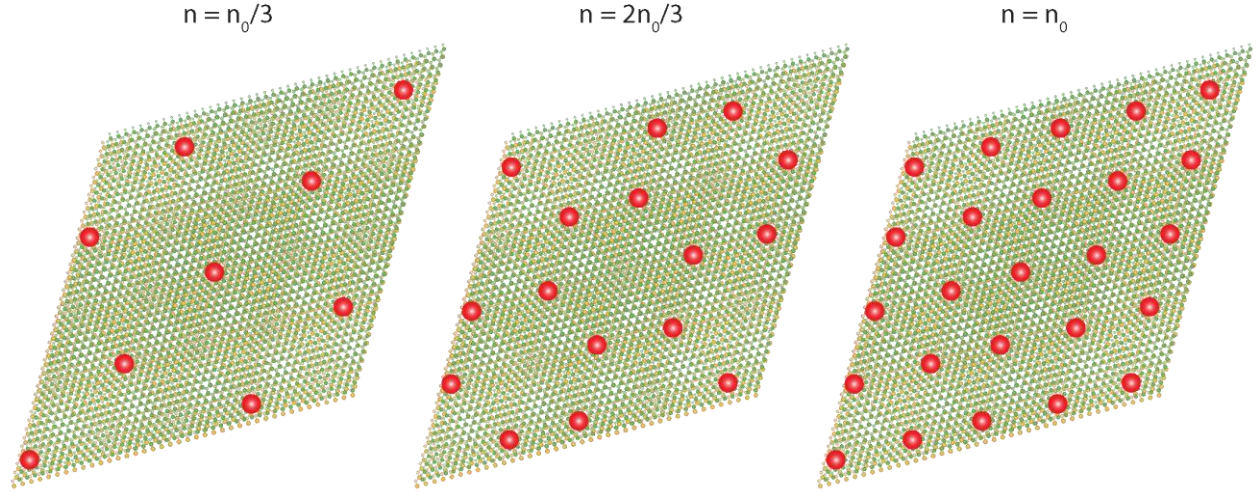


Fig. 4.11 | Illustrations of generalized Wigner crystal ($n = n_0/3$, $n = 2n_0/3$) and Mott insulator states ($n = n_0$) in a WSe_2/WS_2 moiré superlattice.

and $n = 2n_0/3$ correspond to generalized Wigner crystallization^{112–117} of holes in the TMD moiré superlattice. Fig. 4.11 illustrates the real-space configurations of the generalized Wigner crystal states, where holes try to avoid not only double-occupation in one site, but also simultaneous occupation of adjacent sites. The emergence of these generalized Wigner crystal states suggests that even the inter-site (long-range) interaction energy is larger than the moiré miniband bandwidth, confirming the very strong correlation in the TMD moiré heterostructure.

To estimate the size of the insulating gaps, we performed the ODRC measurements at different temperatures. Fig. 4.12a shows the extracted resistance for temperatures from 3 K to 70 K. The resistance peaks of the Mott insulator and generalized Wigner crystal states are observable up to temperatures of 45 K and 10 K, respectively. We estimate the Mott-Hubbard gap to be $\Delta \sim 10$ meV by fitting the resistance to a thermal activation function $\exp[-\Delta/(2k_B T)]$ for the Mott insulator state at $n = n_0$ (black dashed line in Fig. 3b). Due to the limited range exhibiting thermal activation behavior, the estimated Mott gap has relatively large uncertainty. It is difficult to estimate the size of the insulating gaps of the generalized Wigner crystal states from the experimental data, but they are likely to be 5-10 times smaller than the Mott insulator gap based on the temperature at which the generalized Wigner crystal signatures disappear.

In summary, the ODRC technique allows us to measure the doping and temperature dependent resistance and capacitance in a WSe_2/WS_2 moiré superlattice. Importantly, we can monitor the behavior at low doping, typically not possible due to contact resistance, to observe Wigner crystallization in a moiré superlattice for the first time.

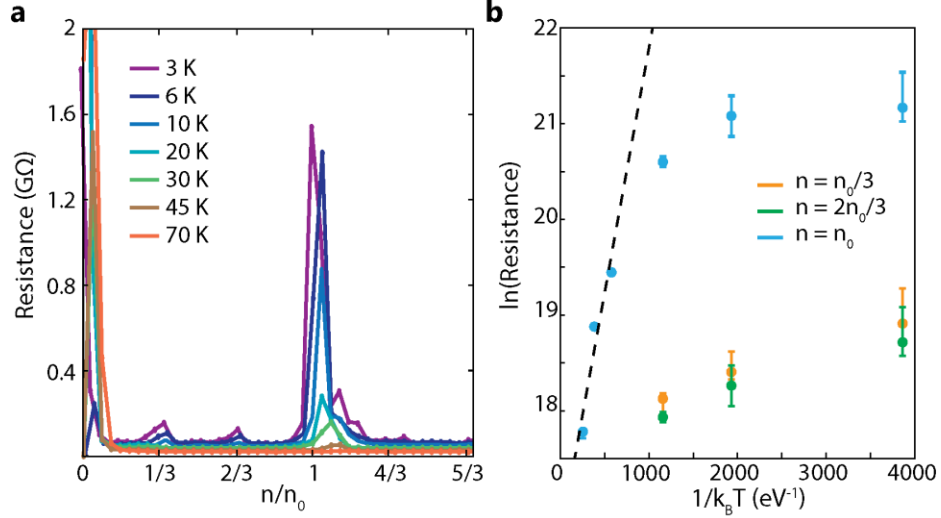


Fig. 4.12 | Temperature dependence of Mott and generalized Wigner crystal states. **a.** Extracted resistance from ODRC measurements taken from 3 K to 70 K. The Mott insulator at $n = n_0$ is observable up to 45 K, and the generalized Wigner crystal states at $n = n_0/3$ and $n = 2n_0/3$ persist until 10 K. **(b)** Plot of $\ln(R)$ versus $1/k_B T$ for Mott (blue) and generalized Wigner crystal states (orange and green). Error bars correspond to the estimated uncertainty in the extracted resistance values.

4.3.1 Spin lifetime in correlated electron system

The strong electron-correlation and light-matter-interaction in the heterostructure provides unique opportunities to optically investigate excited states from the correlated phases, such as low-energy charge and spin excitations. Charge excitations in Mott insulator systems have been intensively studied, featuring ultrafast decay dynamics (typically few picoseconds) from the holon-doublon recombination process^{119–121}. On the other hand, the dynamics of pure spin-excitations (Fig. 4.13) have been difficult to explore. In this system, we directly measure the doping-dependent decay of a pure spin excitation by taking advantage of the unique spin-valley selection rules in the TMD heterostructure^{10,11,17}.

We use the pump-probe scheme described in Ref. ¹²² to generate and probe the spin excitation in the moiré superlattice. This technique is described in detail in Chapter 5. To summarize, a circularly polarized pump excitation is employed to selectively excite K-valley excitons composed of spin-up holes and electrons. The relaxation of the spin-polarized electrons and holes within about 100 ns results in a residual spin polarization in the Mott insulator lower Hubbard band, as illustrated in Fig. 4.13a. We probe the evolution of the residual spin polarization through the pump-induced circular dichroism signal and the charge population through the pump-induced change in total absorption of a probe beam.

Fig. 4.13b shows the time evolution of the spin population at different hole densities measured at 20 K. We choose this temperature to simplify the interpretation: the Wigner crystal states are melted, so we can just consider the Mott state. The doping-dependent spin

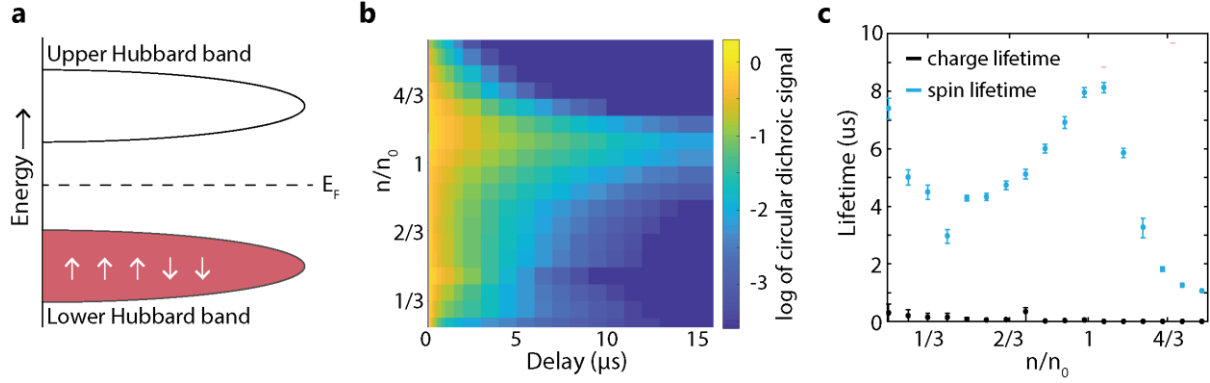


Fig. 4.13 | Optical investigation of low-energy spin excitation dynamics of a WSe₂/WS₂ Mott insulator. **a.** Schematic of an optically-generated low energy spin excitation in the lower Hubbard band of a WSe₂/WS₂ superlattice. **b.** Doping dependent decay dynamics of the optically generated pure spin excitations. **c.** Summary of the spin (blue) and charge (black) lifetimes as a function of hole doping. The spin relaxation slows down markedly near $n = n_0$, with a lifetime as long as 8 μ s. On the other hand, the total charge population decays quickly for all doping levels.

lifetime, summarized as blue symbols in Fig. 4.13c, shows a prominent increase at the Mott insulator state ($n = n_0$) and reaches more than 8 μ s. In contrast, lived spin excitations from the Mott insulator state can provide important information about its spin configuration. It has been proposed that the Mott insulator state in the WSe₂/WS₂ moiré superlattice can host intriguing spin states such as quantum spin liquid^{101,123}. Further theoretical studies will be required to understand the experimentally observed spin dynamics in the Mott insulating state.

In Chapter 5, we will return to the question of spin behavior in a WSe₂/WS₂ moiré superlattice and consider the spin diffusion.

4.4 Discussion

In summary, we developed an optical technique for measuring resistance and capacitance in TMD heterostructures, which we used to probe correlated electronic states in a WSe₂/WS₂ moiré superlattice. We observed a Mott insulator state at one hole per superlattice site ($n = n_0$) and surprising insulating phases at fractional filling $n = 1/3n_0$ and $n = 2/3n_0$, which we assigned to generalized Wigner crystallization on an underlying lattice. Further, we optically generated a spin population in the Mott state and demonstrated an increased spin lifetime. Our results demonstrate the TMD moiré heterostructures can host novel quantum correlated phases and offer an attractive platform for probing excited state and non-equilibrium dynamics of the correlated phases due to a unique combination of highly correlated electrons, strong light-matter interactions, and large spin-orbital effect in the system.

Our detection of correlated electronic states in the WSe₂/WS₂ moiré superlattice opens up many additional questions in the field of moiré physics. For example, our system exists in the limit

where the interaction energy is much larger than the kinetic energy. Fascinating physics can emerge when these two energy scales are comparable, which may be achieved using intermediate twist angle samples. Another interesting direction involves studying moiré superlattices made of other TMDs, both heterobilayers and homobilayers, where the superlattice can have different spatial symmetries and moiré potentials. Since we can think of moiré superlattices as quantum simulators, creating simple material systems with a given symmetry on demand is a very powerful capability. Additionally, the exact nature of the correlated states is still open. For example, one proposal suggests that the insulating state at $n = n_0$ is actually a charge transfer insulator, rather than a Mott insulator¹¹⁸. Finding experimental signatures to differentiate between these possibilities is important.

Since this study, I have been involved in two other projects that aim to answer another outstanding question: can we visualize the correlated states in WSe_2/WS_2 moiré superlattices? Using far-field optical techniques, the diffraction limit restricts our spatial resolution to $\sim 1 \mu\text{m}$. Imaging correlated states with higher spatial resolution provides complementary and useful information.

First, I worked with Zhaodong Chu, a graduate student the University of Texas at Austin, to image correlated states with $\sim 100 \text{ nm}$ spatial resolution across an aligned WSe_2/WS_2 sample¹²⁴. Using microwave impedance microscopy (MIM), we observed significant inhomogeneity of the Mott state across the sample (Fig. 4.14), suggesting that there is local disorder in the moiré potential or the electrostatic doping. This work suggests that improvements in sample uniformity, such as reduced surface impurities and better gating schemes, will be important for in-depth understanding of correlation physics in 2D moiré superlattices devices.

Second, I played a small role in an STM study of correlated states in WSe_2/WS_2 superlattices¹²⁵. Hongyuan Li and Shaowei Li, a graduate student and postdoc in our group, developed a non-invasive STM technique to directly visualize the Mott and Wigner crystal

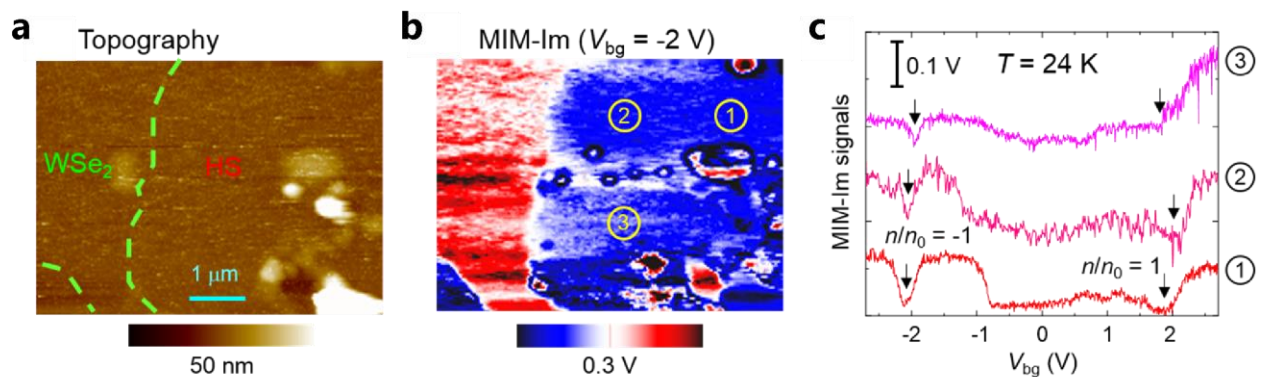


Fig. 4.14 | Nanoscale conductivity imaging of a WSe_2/WS_2 moiré superlattice. Topography (a) and MIM-Im images (b) of the WSe_2 and heterostructure regions. c. MIM-Im signals at three different locations labeled in (a) as a function of the back-gate voltage (i.e. carrier concentration). The positions of $n/n_0 = 1$ are indicated by arrows for each curve.

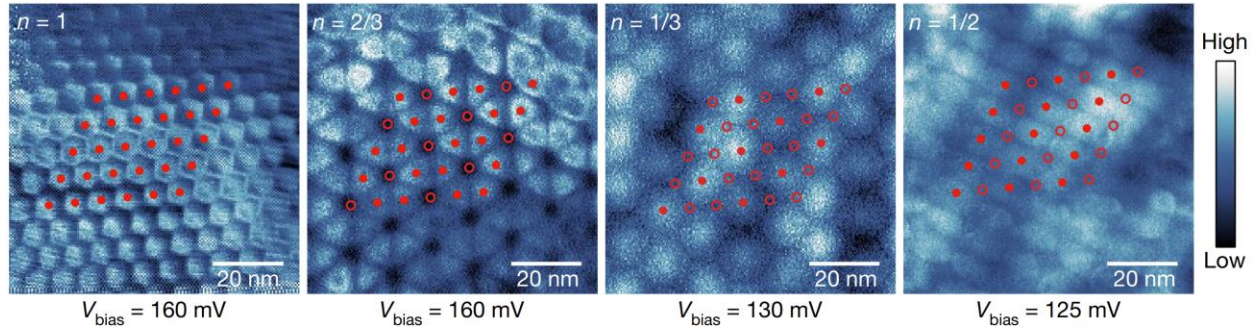


Fig. 4.15 | Imaging Mott and Wigner crystal states with STM. From left to right: dI/dV map of the Mott insulator and Wigner crystal states in the WSe₂/WS₂ moiré superlattice. The triangular lattice formed by the AB stacking sites is labelled with red dots.

states with nanometer resolution (Fig. 4.15). In addition to the $n = 1/3n_0$ and $n = 2/3n_0$ states, they find an additional crystallization $n = 1/2n_0$ that spontaneously breaks the C3 symmetry of the system. These stunning images provide a foundation for seeing correlated electron states in 2D materials.

5 Spin transport in WSe₂/WS₂ moiré superlattices

5.1 Introduction

In correlated materials, the spin and charge degrees of freedom often do not behave in the same way. This spin-charge separation naturally emerges in a Hubbard model at half filling, where charges are localized but spins can still move via super-exchange. Therefore, although charge dynamics have been studied extensively in strongly correlated systems, including in many moiré superlattices, we cannot infer the behavior of the spins from this knowledge in most cases. In the WSe₂/WS₂ moiré superlattice, we have a unique opportunity to optically generate and probe spin excitations with relative ease, allowing us to study spin transport in a strongly correlated system (Fig. 5.1).

In general, the optical selection rules in TMDs allow us to conveniently create and probe spin excitations using circularly polarized light^{10–15}. Typically, a circularly polarized pump beam generates an exciton population in one valley, which is also spin-polarized due to the spin-valley locking in TMDs¹⁷. However, this spin polarization is short lived due to the electron-hole exchange interaction, and therefore the spin lifetime is only picoseconds long in monolayers^{126,127}. In a hole doped WSe₂/WS₂ heterostructure, however, we have a much more exciting prospect: we can optically create a pure spin excitation, with no associated charge excitation, that has a lifetime of 10s of microseconds⁸⁹.

The generation of a long-lived pure spin population in a hole doped WSe₂/WS₂ heterostructure was described in Ref. ⁸⁹ and is summarized in Fig. 5.2. A circularly polarized beam selectively excites excitons in the K valley of WSe₂. Due to the type II band alignment, the

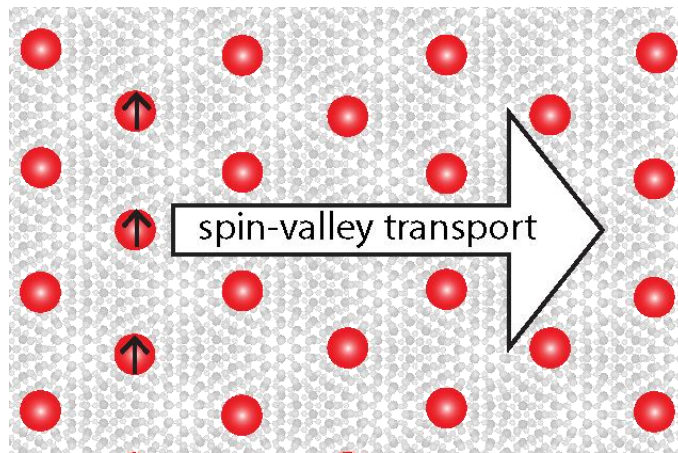


Fig. 5.1 | Spin transport in a correlated electronic state. Schematic of an optically generated spin excitation moving in a Mott insulator of holes (red circles) in a WSe₂/WS₂ moiré superlattice. A second probe beam can monitor the spin population in space and time.

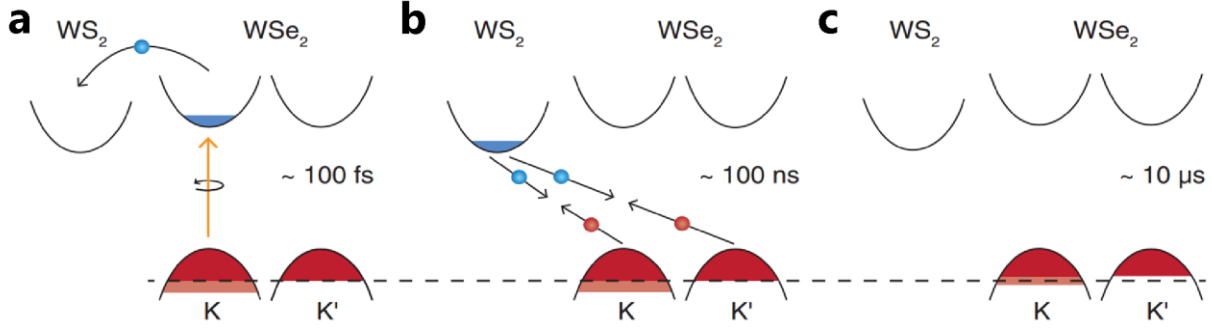


Fig. 5.2 | Generating pure spin excitations in a WSe₂/WS₂ heterostructure. **a.** With left-handed circularly polarized photons, K valley excitons in WSe₂ are selectively excited and efficiently converted into excess holes within 100 fs through the ultrafast interlayer charge transfer process. **b.** In 100 ns, electrons in WS₂ recombine with K and K' holes in WSe₂ with almost equal probabilities, resulting in an excess of K valley holes and a deficiency of K valley holes in WSe₂. **c.** The valley-polarized hole population has ultralong lifetime of many microseconds. The dashed line denotes the Fermi level before optical excitation. Adapted from reference ⁸⁹.

constituent electrons quickly transfer to the WS₂ layer, suppressing the exchange interaction between the electron and the hole. The electrons then recombine with the holes in WSe₂: both the electrostatically injected holes (in both valleys) and the optically generated holes (in one valley). After ~100 ns, all electrons have recombined, leaving behind a valley—and therefore spin—imbalance with no extra charge. The lifetime of this spin polarization is not limited by the charge lifetime or the exchange interaction and can be tens of microseconds.

Using this process, we can create a pure spin excitation in the WSe₂/WS₂ moiré superlattice, and then monitor its dynamics in space and time via the circular dichroism (difference in absorption of left and right circularly polarized light) of a second probe beam⁸⁹. Further, we can tune the hole doping and monitor spin excitations in and out of correlated electronic states. In this study, we focus on the spin behavior around the Mott state at a hole concentration of $n/n_0 = 1$ because it is more experimentally robust and more easily addressed theoretically than the Wigner crystal states at fractional filling, which require considering long range interactions^{87,112}. We can model the spin transport at and around the Mott state by consider a t - J model^{128,129} on a triangular lattice. Here spins conduction occurs via nearest neighbor hopping of spin-polarized free carriers (t) and via exchange interactions (J). This model predicts diffusive spin transport with specific doping and temperature trends depending on the relative scale of t and J . Additional theoretical proposals have suggested that the correlated state at one hole per moiré unit cell may support other interesting spin transport, such as spin superfluidity¹³⁰ and quantum spin liquid behavior^{64,131}.

In this chapter, I describe a spatially resolved pump probe measurement of the doping- and temperature-dependent spin transport in WSe₂/WS₂ moiré superlattices. We observe diffusive spin transport at all hole concentrations measured with a reduced spin diffusion constant compared to large twist angle samples. The doping-dependent diffusion constant shows a peculiar temperature dependence, with nearly no change in the diffusion constant at the Mott state over the temperature range measured. Initial analysis suggests that some of our observations can be explained using the

t - J model. I will explain the experimental technique in section 5.2. Then, in section 5.3, I will describe our spin transport data and preliminary analysis. Note: the manuscript describing this work is in preparation, and the analysis is ongoing.

5.2 Probing spin transport via spatially resolved pump probe experiments

5.2.1 Spatial-temporal imaging technique

To study spin transport in a WSe_2/WS_2 moiré superlattice, we use a spatial-temporal imaging technique (Fig. 5.3). We focus a circularly polarized pump beam at 1.80 eV (above gap for WSe_2 , below gap for WS_2) into a line to generate a 1D pure spin excitation. A second probe beam measures the circular dichroism at moiré exciton I (~ 1.68 eV) to monitor the spin-polarized hole population. By varying the temporal delay and the distance between the pump and probe beams (Δx), we measure the evolution of the spin excitation in time and in space. In practice, we keep the probe beam fixed on the sample and move the pump beam since the off-resonant pump is much less sensitive to local shifts in the exciton energy than the on-resonant probe. At the same time, we can tune the hole concentration in the sample via graphite gates. Therefore, this technique allows us to image spin propagation in and out of the correlated electronic states in a TMD moiré superlattice.

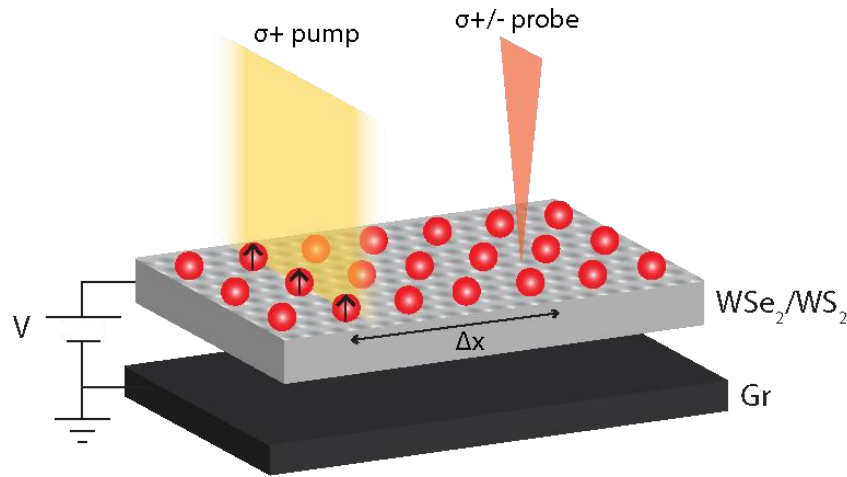


Fig. 5.3 | Schematic of a spatial-temporal imaging experiment in WSe_2/WS_2 moiré superlattice. A circularly polarized pump beam generated a 1D pure spin excitation in the superlattice. A circularly polarized probe beam monitors the dynamics of the spin population. To obtain spatial information, the pump beam is scanned across the sample and the delay-dependent circular dichroic signal is measured for each Δx . The carrier concentration is tuned via the graphite gate.

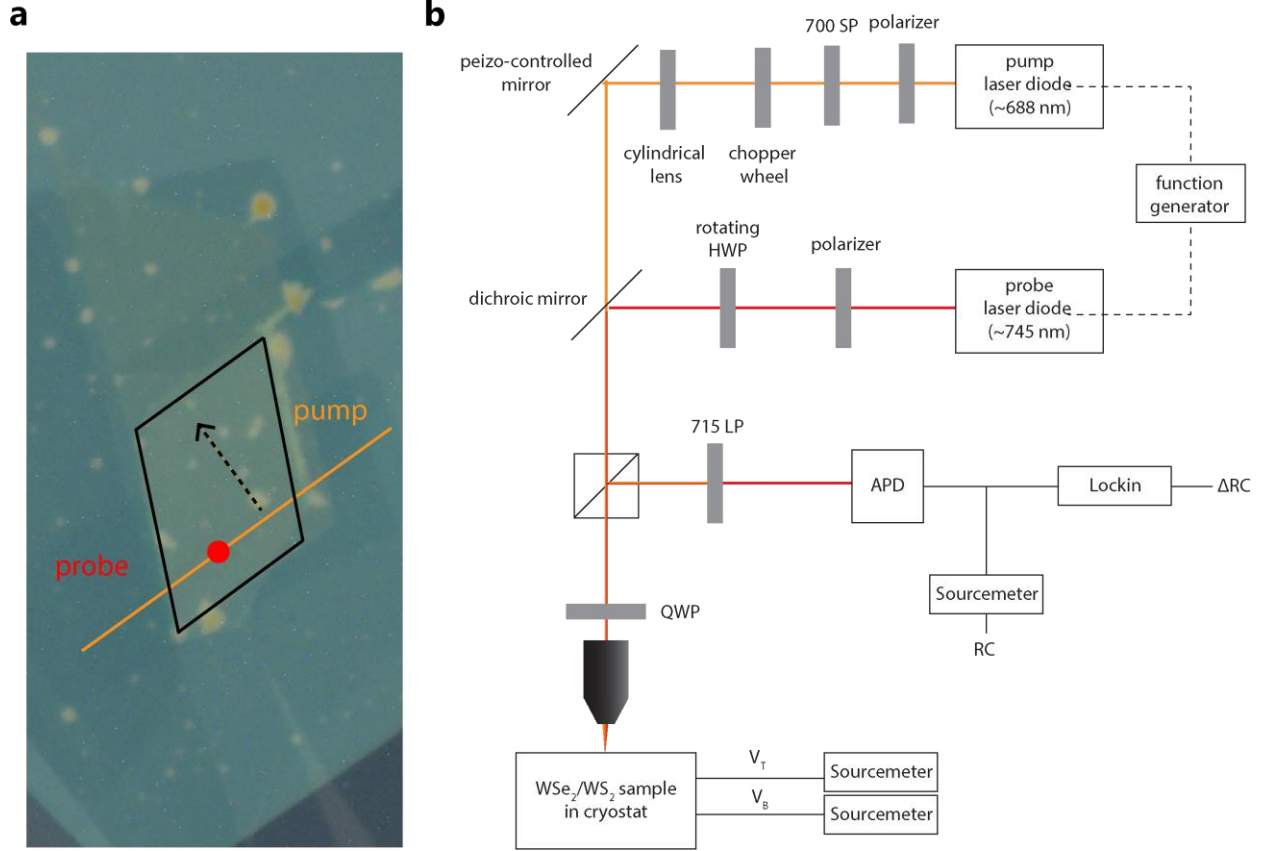


Fig. 5.4 | Spatial-temporal imaging experiment. **a.** Microscope image of a WSe_2/WS_2 sample (heterostructure region outlined in black) with a schematic of the pump (orange) and probe (red) beams overlaid. The pump beam is scanned across the sample using a piezo-controlled mirror, following the black dashed line. **b.** Experimental setup for spatial-temporal imaging measurement. Two laser diodes are driven by a function generator to create pulse trains. A piezo controlled mirror is used to move the pump across the sample. The circular dichroic signal is measured with an APD and sent to a lock-in detector.

Fig. 5.4b shows a schematic of the experimental setup used to measure spin transport. Two laser diodes are driven by a function generator to create pulsed pump and probe beams with $\sim 5\text{-}10$ ns pulse width and $5\text{-}10$ μs period. The pump pulse train is modulated by an optical chopper for lock-in detection at ~ 1 kHz. The polarization of the pump and probe beams are set with independent linear polarizers and a shared quarter wave plate. An electronically-controlled half wave plate in the probe path switches the probe polarization for the circular dichroism measurement. A cylindrical lens is used to focus the pump beam into an ellipse, with the length of the beam much larger than the sample size (Fig. 5.4a), to create a quasi-1D excitation with full width at half maximum of ~ 1 μm . A piezo-controlled mirror is used to electronically tune the position of the pump beam on the sample. The pump and probe beams are combined with a dichroic mirror and focused onto the sample with an objective. The reflected probe beam is collected and sent to an avalanche photodiode (APD). The pump-induced circular dichroic signal is detected with an SRS lock-in detector, and the static reflectivity is monitored with a Keithley source meter.

This technique was first developed by Chenhao Jin, then a postdoc in our group. Since his implementation, we made several modifications to improve the speed and reproducibility of the measurement, which were critical for conducting spin transport measurements over a large range of carrier concentrations. Before settling on the final experimental configuration described above, we made a detour into another (seeming better) approach. The initial measurements used parallel, elliptical pump and probe beams. To collect spin transport data more efficiently, we rotated the probe to be perpendicular to the pump beam. Then we imaged the probe beam onto a linear array camera and implemented lock-in detection scheme with software. In this case, the pump creates a 1D excitation, and the perpendicular probe beam simultaneously measures the circular dichroism at many points across the sample, and there is no need to scan Δx . I implemented this modification with Danqing Wang, another graduate student, but we ran into a fundamental challenge: because we probe many different positions, the experiment is extremely sensitive to spatial inhomogeneity in the exciton energy across the sample. On top of this, artifacts in the linear array camera added additional complexity. These challenges are described in detail in Danqing’s dissertation.

Ultimately, we returned to an approach similar to the initial technique, but with some modifications to improve the data acquisition speed. On the collection side, we swapped the photomultiplier tube for an APD and switched to a sourcemeter for faster, lower-noise measurements. We also added a piezo-controlled mirror to automate sweeping Δx . Finally, we switched to a focused, circular probe to maximize the reflected light that we collect. In this configuration, the experiment is fully automated, fast enough to collect spin transport at many hole concentrations, and less sensitive to sample inhomogeneity because we probe a single position.

5.2.2 Example spin transport data and fitting to diffusion model

A sample data set collected with our updated spatial-temporal pump probe technique is shown in Fig. 5.5 for a 5° twist angle WSe_2/WS_2 heterostructure. I will use data from this sample to explain our technique and then turn to a near-zero-degree sample to discuss spin transport in correlated states. In this plot, each color corresponds to a different pump-probe spatial separation Δx . At zero time delay, t_0 , the pump-generated spin excitation is localized at the pump position, and the circular dichroism is negligible away from the pump. After a finite time delay, valley polarized holes begin to diffuse out of the excitation region, leading to a decrease in signal close to the excitation (purple data in Fig. 5.5) and an increase in signal at large pump probe separations. This data is characteristic of a diffusive spin current in a misaligned WSe_2/WS_2 heterostructure, as described in Ref. ⁸⁹.

We can then change the hole concentration in the sample and measure the spatial-temporal circular dichroism at each doping level, as shown in Fig. 5.6. Here, and for the rest of this chapter, I plot this data in 2D color maps to better visualize the spin transport. At low doping,

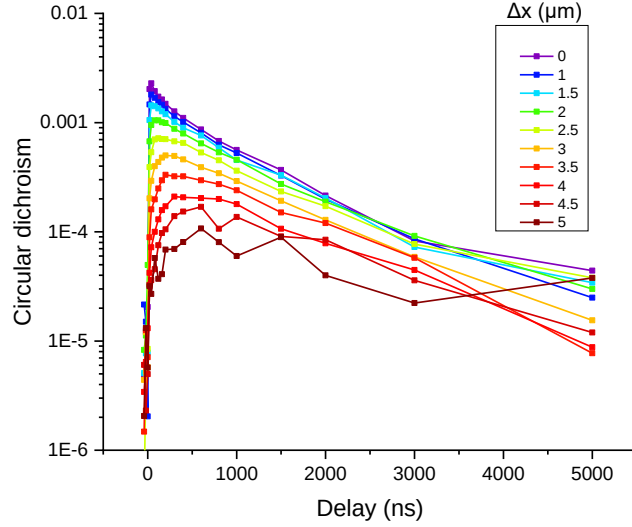


Fig. 5.5 | Sample spatially resolved circular dichroism data from a 5° twist angle WSe₂/WS₂ heterostructure. Plot of the pump-induced circular dichroism of the probe beam for various delays and pump-probe separations (Δx). Squares are data, lines are guides to the eye connecting the data points for each Δx . When the pump and probe are overlapped (purple data), simple decay behavior is observed. When the pump and probe are spatially separated, the spins diffuse from the pump location to the probe location, resulting in an increase in signal after t_0 . This data is taken at moderate hole doping.

the spin-polarized holes are largely localized, and the spin lifetime is short. With increasing hole doping, the lifetime increases significantly, and spins begin to move. Finally, at high doping, the lifetime again becomes short, but the spins remain mobile. These observations are consistent with the data presented in Ref. ⁸⁹, though with many more hole concentrations measured thanks to the speed up in data acquisition (three hole concentrations in Ref. ⁸⁹ vs. 16 hole concentrations measured here, with only a subset shown in Fig. 5.6 for simplicity). The increased lifetime at moderate doping is due to the decoupling of spin and charge lifetimes, as described in the previous section. Notably, we are able to measure the spin dynamics at low temperatures and low

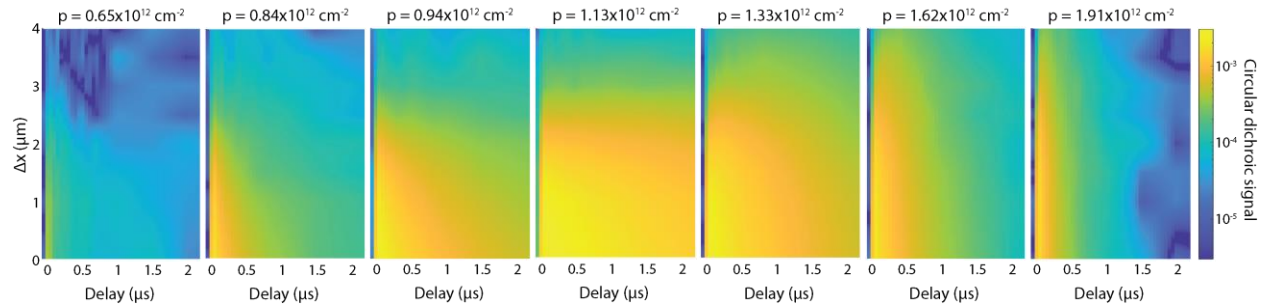


Fig. 5.6 | Sample spatially resolved circular dichroism showing spin transport in a doped 5° twist angle WSe₂/WS₂ heterostructure. The hole concentration, labelled for each plot, increases from left to right. This figure includes only a subset of the hole concentrations measured.

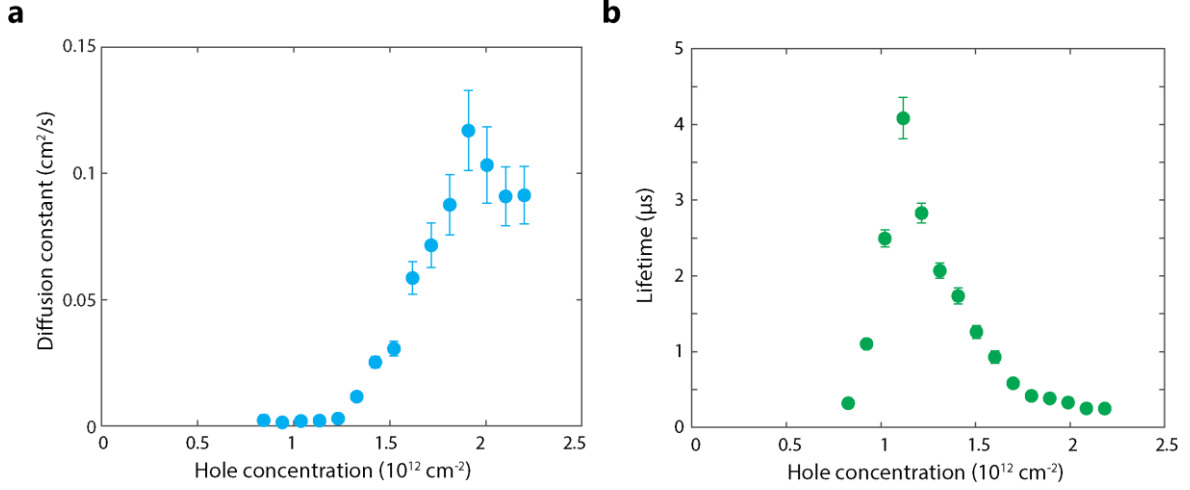


Fig. 5.7 | Extracted doping-dependent spin diffusion constant (a) and lifetime (b) for a 5° twist angle WSe₂/WS₂ heterostructure. Values are obtained by fitting spatial-temporal circular dichroism maps to a diffusion model. Error bars show 95% confidence intervals.

carrier concentration, where typical contacts to 2D materials fail. This pump-probe measurement provides a contact-free approach to measuring spin and charge transport in a TMD.

The spin transport in a large-twist-angle WSe₂/WS₂ heterostructure is diffusive, so we can extract the spin diffusion constant D and lifetime τ using a diffusion-decay model⁸⁹:

$$\Delta n_v(x, t) = \frac{\Delta n_0}{\sqrt{\pi(\sigma_0^2 + 4Dt)}} e^{-\frac{x^2}{\sigma_0^2 + 4Dt}} e^{-\frac{t}{\tau}}.$$

Here Δn_0 is the total number of pump-induced spin-polarized holes, and σ_0 is the full width at half maximum of the pump beam. x and t are the space and time coordinates. The fitting procedure was initially implemented by Danqing. The spatial-temporal map for each hole concentration is fit to the diffusion model, providing a doping dependent spin lifetime and diffusion constant. We also allow for a smaller, slowly-decaying signal in the fitting, which represents a non-zero background for all pump-probe separations. Fig. 5.7 shows the extracted spin diffusion constant and lifetime for the data set shown in Fig. 5.6, providing quantitative information to complement the trends observed directly from the 2D maps.

We reserve the 5° data set for technique demonstration because although there is no large moiré potential at this twist angle, it is possible that some superlattice effects still play a role at this moderate twist angle regime. Notably, the spin diffusion constant is about 5x smaller than in a 23° sample studied in Ref ⁸⁹. Therefore, we will not use this sample as an ideal large twist angle reference. In general, intermediate twist angle samples are very interesting because of the opportunity to consider different balances of bandwidth and interaction energies.

5.3 Spin transport in WSe₂/WS₂ moiré superlattices

We now turn to a near-zero-degree WSe₂/WS₂ superlattice and consider how the spin transport is modified due to the strong correlations. The experiments were conducted in close collaboration with Danqing Wang and Zheyu Lu. Our analysis has benefitted from ongoing discussions with Liang Fu, Yang Zhang, and Trithep Devakul at MIT.

Using the technique described above, we generate and monitor a pure spin population in a WSe₂/WS₂ moiré superlattice as we tune the hole concentration from near charge neutral to past the Mott state at $n/n_0 = 1$ at 11 K (a subset of the data is shown in Fig. 5.8). At this temperature, many correlated states exist at fractional fillings below the Mott state^{87,132}. In our analysis, we focus on the Mott state because it is the most robust and most straightforward to address theoretically. The doping-dependent spin lifetime was discussed in the previous chapter⁸⁷, so here we concentrate on the spin transport characteristics. From a quick glance at Fig. 5.8, we can see that spins are mobile at all doping levels shown, even though the sample is electrically insulating in the correlated states, particularly at $n/n_0 = 1$. Therefore, the spin transport is decoupled from the charge transport. Further, we do not observe any spin-wave-like behavior or dramatic deviations from diffusive spin transport.

In fact, we find that the spin transport is diffusive in the moiré superlattice, like it is in the large twist angle samples. Fig. 5.9a and b show the spatial-temporal circular dichroism data (points) with fits to the diffusion model (lines) for $n/n_0 = 1/2$ and $n/n_0 = 1$, respectively. In both cases, and for all hole concentrations measured, the data is fit well with a diffusion model. Therefore, we can extract a spin diffusion constant at each hole concentration and quantitatively compare the spin transport (Fig. 5.9c). We find that the spin diffusion is small below the Mott state and increases quickly with additional hole doping.

Next, we compare the spin diffusion constant of the WSe₂/WS₂ moiré superlattice to that of a large twist angle heterostructure (23°), which was studied in Ref. ⁸⁹. Fig. 5.10 shows the doping-dependent spin diffusion constant for the sample described above, a second near-zero-

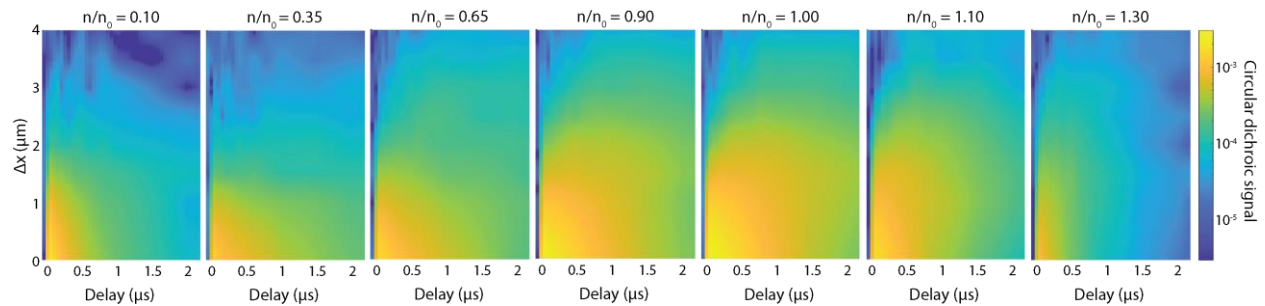


Fig. 5.8 | Spatial-temporal imaging of spin transport in doped WSe₂/WS₂ superlattice. The hole concentration, labelled for each plot, increases from left to right. This figure includes only a subset of the hole concentrations measured.

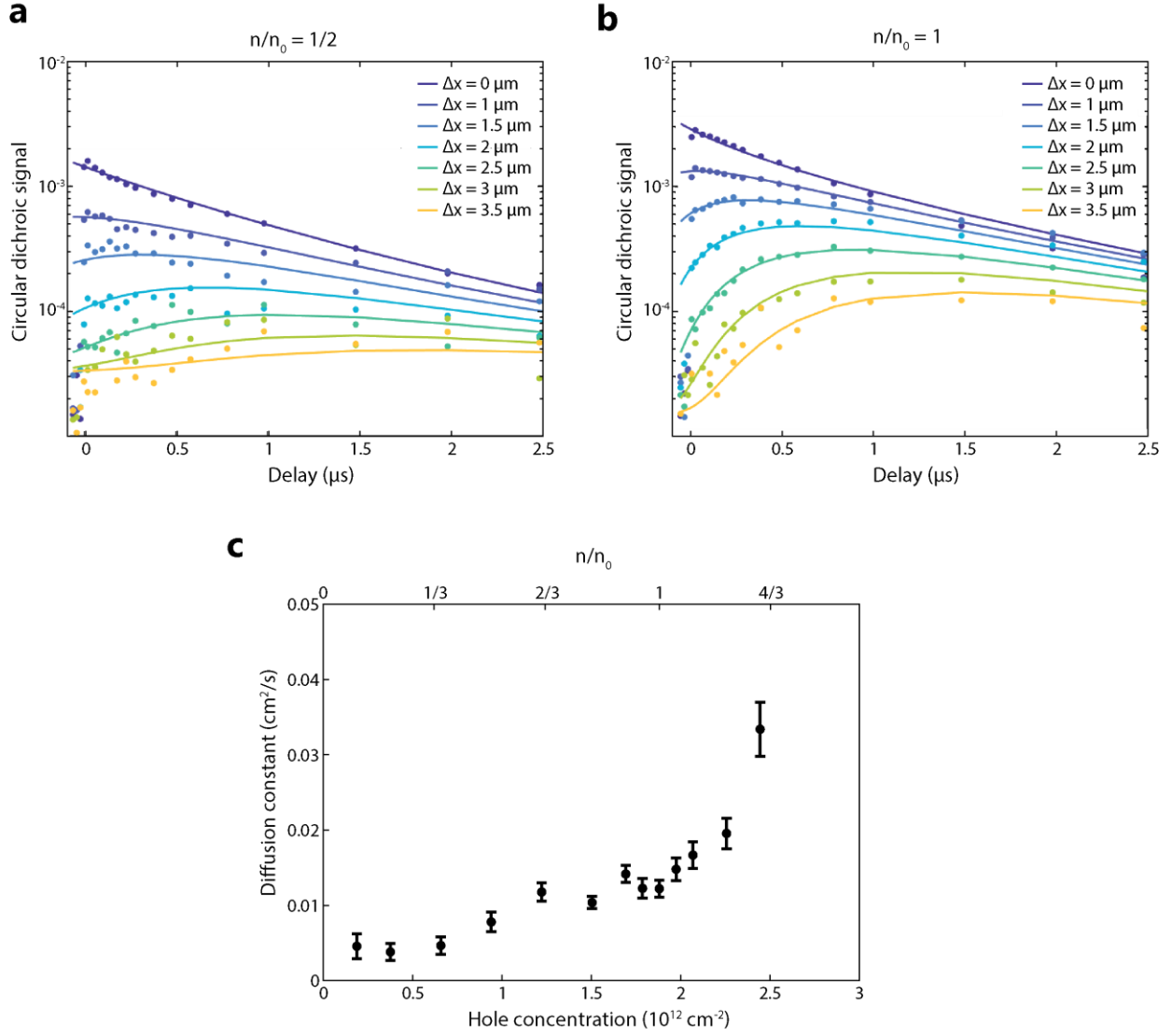


Fig. 5.9 | Diffusive spin transport in WSe₂/WS₂ moiré superlattice. Spatial-temporal circular dichroism at (a) $n/n_0 = 1/2$ and (b) $n/n_0 = 1$. Dots of a given color are experimental data for each pump probe separation, and lines are corresponding fits to the diffusion model. c. Extracted diffusion constant from fitting spatial-temporal circular dichroism maps to diffusion model at each hole concentration. Error bars represent 95% confidence intervals of the fit.

degree WSe₂/WS₂ superlattice, and the large twist angle heterostructure. The two superlattice samples show similar spin diffusion constants for a given hole concentration. On the other hand, in the large twist angle sample, spins move with more than 10 times larger diffusion constant for the same doping. The reduction in spin diffusion in the superlattice is not a property of a specific correlated state, but rather appears at all doping levels.

To look for signatures of interesting spin transport near the Mott state, we measure the doping-dependent spin transport at three temperatures: 11 K, 22 K, and 45 K. The extracted diffusion constants are shown in Fig. 5.11. Below $n/n_0 = 1$, the spin transport has a relatively

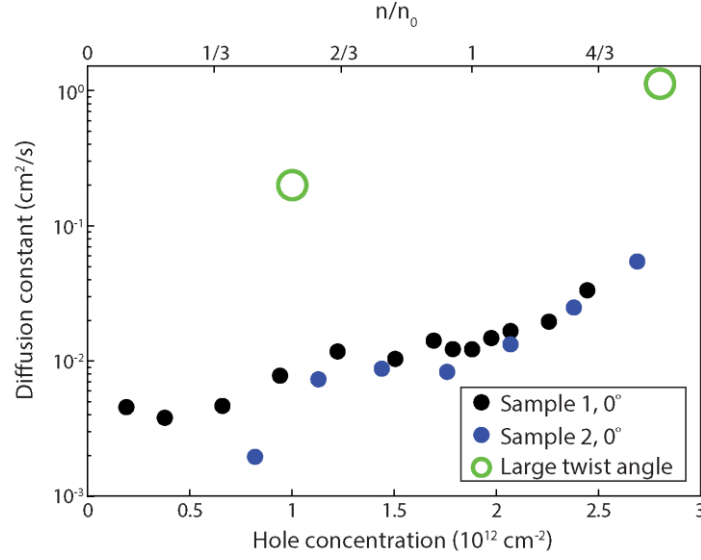


Fig. 5.10 | Spin diffusion in doped near-zero and large twist angle WSe₂/WS₂ heterostructures. Extracted spin diffusion constant from spatially dependent circular dichroism maps taken in two near-zero-degree heterostructures (black and blue dots) and a large twist angle heterostructure (green circles, from ref⁸⁹). The superlattice samples show strongly reduced spin diffusion at all hole concentrations.

weak temperature dependence. Interestingly, around $n/n_0 = 1$, we observe almost no change in the spin diffusion constant over this temperature range. For larger hole doping, the spin diffusion increases quickly with temperature. We note that at 45 K, all fractional states below $n/n_0 = 1$ are melted^{87,132}, yet the relatively small diffusion constant remains.

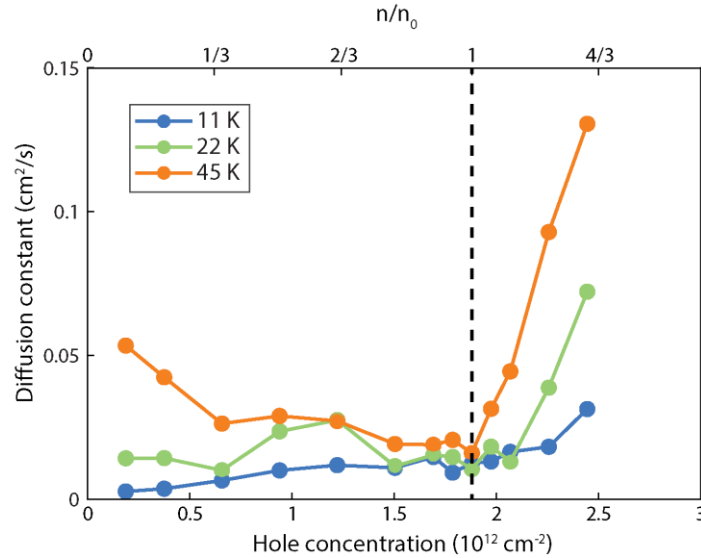


Fig. 5.11 | Temperature dependent spin diffusion in doped WSe₂/WS₂ superlattice. Extracted spin diffusion constant from spatial-temporal circular dichroism maps taken at 11 K, 22 K, and 45 K. We observe weak temperature dependence around the Mott state, highlighted with the black dashed line.

To explain some of our observations, we turn back to the t - J model, which can be used to describe the temperature and doping dependence of the spin diffusion near the Mott state. Our analysis is ongoing, so I focus on conclusions from our initial discussions with Liang Fu and his team and leave the numerical analysis for a later date.

The doping- and temperature-dependent spin transport is highly non-trivial in correlated states, even for a simple t - J model. Therefore, we consider certain limits based on the relevant energy scales in our system. In the WSe_2/WS_2 moiré superlattice, the nearest neighbor hopping $t \sim 1$ meV, and is much smaller than the onsite interaction term U . The exchange coupling J goes as t^2/U , and is therefore very small. In our measurements, the temperature T is ~ 1 -4 meV (from 11 K to 45 K), so the temperature scale is large than J and sometimes larger than t .

For this discussion, we focus on the high temperature limit (45 K data), where the t - J model is solvable. In this limit, theoretical analysis¹²⁸ suggests that the spin diffusion constant should increase linearly with doping (for small doping) away from the Mott state because the spin-current carriers are mobile holes. At 45 K, we observe a minimum in the spin diffusion around the Mott state. Here, the spin diffusion constant is asymmetric around $n/n_0 = 1$: it increases faster when holes are added to the Mott state than when they are removed. This suggests different hopping parameters for holes and doublons in the superlattice. Interestingly, at low temperature (11 K), the spin diffusion increases monotonically through the entire doping range we consider. In this case, many correlated states exist at fractional filling of the superlattice below $n/n_0 = 1$, so long-range interactions must be considered, and this theory does not directly apply.

The peculiar temperature dependence of the spin diffusion at the Mott state is consistent with the predicted behavior of the t - J model^{128,129} in the regime of large interactions (U) and at temperatures on the scale of the kinetic energy ($T \sim t$). Here, the model predicts that the spin diffusion depends very weakly on temperature at the Mott state and then increases with temperature when the system is hole doped away from the Mott state, as we observe. This model predicts an increase in the spin diffusion constant at higher temperatures, potentially due to the increase in empty and doubly occupied sites that allow for new spin conduction mechanisms¹²⁹. Unfortunately, it is difficult to probe these higher temperature regimes (>45 K) because the spin lifetime becomes very short. At lower temperatures, spin-charge separation is strong and spin waves may dominate the spin transport.

5.4 Discussion

In summary, we used a spatial-temporal pump probe technique to optically generate and probe a pure spin excitation in a WSe_2/WS_2 moiré superlattice. We find that the spin transport is diffusive for all hole concentrations and temperatures measured, and that the spin diffusion is much reduced compared to a large twist angle heterostructure. The t - J model provides some understanding of the peculiar doping and temperature dependent spin transport, demonstrating that the WSe_2/WS_2 moiré superlattice can be a quantum simulator for spin, in addition to charge.

Overall, this experiment contributes to the understanding of spin dynamics in a strongly correlated material, a complex and fascinating problem in condensed matter physics.

There are several unexplored experimental regimes that may provide even more interesting spin transport. At lower temperatures, the coherence length is increased, and spin waves are predicted to dominate the spin transport in the Mott state, leading to a diverging spin diffusion constant¹²⁹. We can potentially probe this regime by implementing the spatial-temporal circular dichroism measurement in a dilution fridge. Additionally, a controllable displacement field may also be required for realizing spin wave behavior¹³⁰. Luckily this degree of freedom is relatively easy to implement using two gates in a heterostructure.

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