Topical Review

Light–matter interaction in van der Waals hetero-structures

Thorsten Deilmann¹, Michael Rohlfing¹ and Ursula Wurstbauer²,³

¹ Institut für Festkörertheorie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str.10, 48149 Münster, Germany
² Institute of Physics, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str.10, 48149 Münster, Germany
E-mail: wurstbauer@wwu.de

Received 14 January 2020, revised 28 February 2020
Accepted for publication 3 April 2020
Published 15 May 2020

Abstract

Even if individual two-dimensional materials own various interesting and unexpected properties, the stacking of such layers leads to van der Waals solids which unite the characteristics of two dimensions with novel features originating from the interlayer interactions. In this topical review, we cover fabrication and characterization of van der Waals hetero-structures with a focus on hetero-bilayers made of monolayers of semiconducting transition metal dichalcogenides. Experimental and theoretical techniques to investigate those hetero-bilayers are introduced. Most recent findings focusing on different transition metal dichalcogenides hetero-structures are presented and possible optical transitions between different valleys, appearance of moiré patterns and signatures of moiré excitons are discussed. The fascinating and fast growing research on van der Waals hetero-bilayers provide promising insights required for their application as emerging quantum-nano materials.

Keywords: van der Waals heterostructure, indirect exciton, two-dimensional material, light matter interaction

(Some figures may appear in colour only in the online journal)

1. Introduction

Two-dimensional (2D) crystals are highly ordered covalently or ionically bonded crystals with a sheet thickness of only one or few atoms resulting in a thickness of typically less than 1 nm. Their parental materials are layered crystals in which the individual layers are coupled by weak van der Waals (vdW) forces. Only 16 years ago, the cleavage of graphite into single atomic layers, called graphene [1] started a new research area on 2D materials, also called vdW materials. After the discovery of graphene, the most prominent representative of this class of materials, many other 2D crystals have been identified, often with intriguing properties that have no counterparts in three-dimensional solids. 2D materials cover a wealth of physical, mechanical and chemical properties. The real advantage of those materials is that they can be arbitrarily combined by mechanical stacking without the constraints of the out-of-plane registry as for conventional 3D solids [2, 3] facilitating new device architectures. Due to proximity and hybridization effects, the assembly in such new ‘artificial vdW solids’ can result in the emergence of new states of matter with novel functionalities [4] that not only depend on the combination of different 2D crystal but also on their rotational alignment opening the avenue for a new field called twistronics [5–14] as indicated in figures 1(c)–(e).

Since the first experimental evidence of a direct band gap in monolayer MoS₂ in 2010 [15, 16], a vivid and divers research area has evolved around transition metal dichalco-
ties up to room temperature \([31–35]\). The all-2D surface nature induced superconductivity, fascinating spin and valley properties \([25–27]\), catalytic activity and stability \([28–30]\) doping exciton dominated optical response even at room temperature electronic \([19, 23]\) and electronic \([24]\) properties including conducting TMDCs such as MoS\(_2\), WS\(_2\), MoSe\(_2\), and WSe\(_2\) strain or defects \([36–44]\).

Van der Waals hetero-bilayers (HBs) prepared from optically active semiconducting TMDC monolayers, such as MoS\(_2\) or WS\(_2\), combine the excellent properties of the individual layers with the potential for novel functionalities provided by the full control of vDW architecture \([45, 46]\). Stacking of two different TMDC monolayers on top of each other, the staggered electronic bands create an atomically sharp p–n heterojunction, effectively separating photo-generated electron-hole pairs as sketched in figures 1(a) and (b). This charge transfer \([34, 46–49]\) allows for the formation of so-called interlayer excitons (IXs) a.k.a. composite bosons with electrons and holes residing in different layers \([34, 46, 50, 51]\). The IX share the high binding energies, intriguing spin and valley properties and a reduced but still significant light-matter coupling strength with direct excitons in TMDC monolayers \([52, 53, 165]\). The separation creates a permanent out-of-plane dipolar moment facilitating the manipulation of IX with electric fields in gated structures \([54, 55]\). The reduced overlap of the electron and hole wave functions results in long exciton lifetimes of more than 100 ns \([50, 56]\) greatly exceeding the lifetime of intralayer excitons \([57, 58]\). Long lifetimes allow the thermalization of IX to lattice temperature. Diffusion of thermalized IX over several micrometers \([59, 60]\) and manipulation by electric fields allows the generation of dense exciton ensembles \([61]\) as well as the operation of functional excitonic devices \([59, 62]\). This synergy of fascinating physical properties makes the TMDC HBs not only a promising platform for application in the area of solid state lighting \([63]\), energy conversion \([23]\), as well as opto- and valleytronics \([64, 65]\), but also in exciton based information technologies \([54, 59]\), and in the design of novel designer quantum nano materials. Moreover, vDW structures exhibit potential to access collective excitonic phenomena like high-temperature superfluidity and Bose–Einstein condensation \([66–68]\) as well as excitons in moiré-super lattices \([11, 14, 69–71]\).

Here, we review the fascinating light-matter interaction properties with a focus on IX in semiconducting TMDC hetero-bilayers. We start with selected fabrication and characterization methods with a focus on the determination of the interlayer coupling strength and the precise measurement rotation angle between the individual layers using second harmonic generation (SHG) and Raman spectroscopy. Next we review theoretical approaches to the optical properties of TMDC hetero-structures. In the next section we discuss the impact of multi-valley properties and hybridization on the formation resulting in rich IX multiplet emission with interesting properties. From these considerations we will see that the picture of a formation of an atomically sharp p–n junction is oversimplified for the explanation of the optical properties of TMDC hetero-bilayers. These vDW structures behaves more like newly created vDW solid than a lose hetero-structure from two individual layers. These is even more evident in the next chapter, where the influence of moiré potentials given by small lattice mismatch and/or twist between the two adjacent layers results in the formation of so called moiré excitons. This topical review is closed by a summary and a brief outlook on the potential of van der Waals hetero-structures not only for electronic, optoelectronic, sensing and (solar) energy conversion applications, but also as promising quantum-nano materials supporting future key technologies.

![Figure 1.](image)
Figure 2. (a) Sketch of the most important steps during fabrication of vdW hetero-structures by micromechanical exfoliation and vdW assembly. A thin bulk crystal on adhesive tape is mechanically exfoliated on a viscoelastic PDMS stamp, monolayer flakes are identified via optical microscopy aligned and transferred onto the target substrate. Same approach for the next layer. (b) Optical micrograph of a MoSe2/WSe2 hetero-structures consisting of a hetero-bilayer region (marked region in the center) [56]. (c) Low-temperature (3K) PL measurement on the MoSe2/WSe2 hetero-bilayer shown in (b). Quenching of the direct excitons and a clear red-shifted signal from IX transition proofs strong interlayer coupling. The asymmetric IX peak indicates emission from an IX multiplet [56]. (b), (c) Reprinted with permission from [56]. Copyright (2017) American Chemical Society. (d) SHG intensity of isolated monolayers of MoSe2 (orange triangles) and WSe2 (blue squares) and the hetero-bilayer region (green circles). The intensity of the SHG signal is plotted versus the rotation angle $\theta$ of the parallel polarizers for incident and detected light. (e) Energy of the layer breathing phonon modes (LBM) from low-energy Raman spectroscopy in dependence of the twist angle $\theta$ for MoS2/MoSe2 hetero-bilayers [82]. (e) Reprinted figure with permission from [82]. Copyright (2015) by the American Physical Society.

2. Fabrication and characterization

To exploit the exciting properties of vdW hetero-structures, the synthesis of high-quality vdW crystals is essential. There are three routes for the synthesis of vdW structures [72]: (a) direct vdW growth on flat inert substrates by powder based or gas source chemical vapor deposition (CVD) or molecular beam epitaxy (MBE). Direct growth of vdW hetero-structure is challenging due to issues with nucleation sites resulting in small lateral domains, due to challenges in the precise control of the number of layers over large lateral dimensions and difficulties with intermixing and alloying hampering the formation of atomically sharp interfaces [73]. (b) Liquid exfoliation using either an intercalation approach or just application of mechanical forces by sonication with subsequent centrifugation to select crystallites of a certain thickness and size in solution [74, 75]. This ‘ink’ containing 2D crystallites with a typical size of a few micrometers can then be used for ink-printing spray or dip coating of a thin network of 2D crystals resulting in 2D networks, a method that is inapplicable to prepare at least several 10 micrometer large mono-crystalline TMDC hetero-bilayers with high quality and atomically sharp interfaces. (c) Micromechanical exfoliation from bulk crystal or pick-up of CVD grown monolayers using adhesive tapes and the subsequent vdW assembly into hetero stacks by various deterministic transfer processes [76–79] as schematically illustrated in figures 2(a). With help of mechanical translations- and rotations-stages for precise alignment, high quality samples with various combination of different materials and arbitrary number of layers can be assembled (figure 2(b)) e.g. combining different TMDC monolayers, graphene and hexagonal boron nitride (hBN) into field-effect structures [55]. The vdW
assembly can even be performed in inert-gas atmosphere in a glove-box. This might be of importance for several applications since the properties of the hetero-stacks sensitively rely on the quality of the atomic interfaces [80]. Intriguingly, the vdW force between adjacent layers is for a variety of 2D material combination sufficient to accumulate contaminants into isolated bubbles, leaving large lateral regions with atomically clean interfaces in between [81], enabling very good interface quality even when doing the whole vdW assembly process in ambient.

The vertical distance between adjacent layers and their rotational alignment determines the strength of the interlayer interaction that in turn quantifies the extent to which the properties of the hetero-structure deviate from the combined properties of individual isolated layers. The effect of interlayer interaction is reflected in the electronic band structure of TMDC hetero-bilayers and a sufficient degree of interlayer interaction is required for efficient charge transfer between the adjacent layers essential for the formation of IX. Under optical excitation above the band gap of the constituent TMDC monolayers, electron hole pairs are preferably generated within one layer due to the small oscillator strength of the inter band absorption at the IX transition [83] as illustrated in figure 1(b). Ultrafast separation of electrons and holes across the hetero junction [47, 53, 84, 85] results in accumulation of electrons in one layer and holes in the other layer, respectively. Strong delocalization [86] and hybridized Γ and Λ valleys (cf figure 1(d)) in the hetero-bilayers [87] are discussed as possible reason for efficient charge separation. A clear signature for strong interlayer coupling of a TMDC hetero bilayer is therefore a significantly quenched photoluminescence (PL) signal of the direct excitons compared to the corresponding isolated monolayers (cf figure 2(c)) [56, 84, 88, 89]. As shown in figure 2(c) on the example of a MoSe2/WSe2 hetero-bilayer, quenching of the intralayer exciton PL [90, 91] and the appearance of a red shifted IX PL signal absent for the individual monolayers are commonly used as a measure for sufficiently strong interlayer coupling. The homogeneous broadening of line width of intraand interlayer exciton PL can be greatly suppressed by hBN encapsulation of the TMDC mono- and hetero-bilayers [54, 55, 92–95] enabling the observation of fine-structures in the (IX) emission energy as a result of e.g. formation of charged excitons (trions) [96], spin-split bands [50, 54, 97], formation of momentum direct and indirect multi-valley excitons [55, 56, 95, 98, 99] or moiré excitons [11, 14, 69, 71, 100]. Moreover, exciton diffusion over micrometers has been demonstrated for IX hosted in a MoSe2/WSe2 hetero-bilayer [62] making those systems promising candidates for the realization of excitonic devices [59] and to study many-body of thermalized excitonic ensembles.

Control of the twist angle between the stacked TMDC monolayers is essential since interlayer coupling, hybridization and moiré physics crucially depend on their rotational alignment. The alignment of the crystal axes during the transfer process with an accuracy of better than \( \pm 1^\circ \) to \( 2^\circ \) can be achieved by determining and orienting the crystal axes by optical microscopy. This is possible since the crystal axes of the micromechanically exfoliated flakes breaks preferably under modulo 60\(^\circ\). With this method, it is not possible to distinguish between AA (0°) and AB (60°) stacking order and it would be desired to know the actual twist angle with better precision.

An accurate measurement of the stacking order and twist angle between adjacent layers is facilitated by polarization resolved second harmonic generation (SHG) experiments. Non linear terms of the electric susceptibility \( \chi \) can cause the generation of higher harmonics of a strong incident light field [101]. The electric susceptibility \( \chi \) is a tensor and reflects the crystal symmetry and in particular, the polarization induced by the second order of the susceptibility \( \chi^{(2)} \) is non-zero only for non-centro symmetric crystals as are TMDC monolayers and in more general TMDCs with an odd number of layers [102–104]. The crystal symmetry of TMDC monolayers dictates the intensity of the SHG \( I(\chi^{(2)}) \) to follow a 60\(^\circ\) oscillation \( I(\chi^{2}) \propto \sin^2(3\theta) \) with the angle \( \theta \) between polarization vector of light and crystal axis [102, 105]. Determination of the SHG intensity \( I(\theta) \) in dependence of the twist \( \theta \) of the individual layers provides a precise measurement of the twist between the two layers disregarding AA or AB stacking. The SHG signal taken on a coupled TMDC hetero-bilayer results as for natural TMDC bilayers from interference of the second harmonic fields of the two constituent layers [106]. The second harmonic fields of the hetero-bilayer interfere constructively for AA stacking and destructively for AB stacking order. Figure 2(d) displays SHG intensities in a polar representation of a MoSe2/WSe2 hetero-bilayer indicating a twist between the two layers of about \( \pm 2^\circ \). The vanishing signal from the hetero-structure region indicates AB stacking order [56].

Another fingerprint for strong interlayer coupling is the observation of layer breathing phonon modes in TMDC hetero-bilayers by means of ultra-low frequency Raman spectroscopy [82]. The mode energies are between 30 cm\(^{-1}\) and 40 cm\(^{-1}\) and evolve systematically with the twist angle as shown in figure 2(e) on example of MoS2/MoSe2 hetero-bilayers [82].

### 3. Theoretical description of intra- and inter valley excitons

In this chapter, we will discuss the theoretical description of electronic and optical properties from first principles. In the last years it has become clear that monolayer as well as homogeneous and lattice-matched heterogeneous multilayer can be described well by the commonly used GW-BSE methodology and its extension to trions which we will recapitulate in the following-up section. Thereafter, we will briefly discuss the ‘universal’ properties of intralayer excitons and, finally, we highlight the possibilities of excitons which are (partially) located on neighbouring layer and are thus called interlayer states.

#### 3.1. Theoretical methodology: ab initio GW-BSE calculations

A precise description of the optical and, in particular, of the excitonic properties requires reliable structural and electronic properties as a starting point. Geometric structures, especially chemical bonds (i.e. intralayer properties), are
often well described in the parameter-free density functional theory (DFT). On the other hand, DFT is not sufficient for a quantitative description of the electronic properties, e.g. the band gap, and more accurate methods are required. In recent years many-body perturbation theory [107–110] (i.e. the GW approximation for electronic properties, the Bethe–Salpeter equation (BSE) for optical properties of neutral excitations, and its extension for trions, i.e. charged excitations) has turned out as promising ab initio description. The (quasi-particle) energies \( E_{v \mathbf{k}} \) and wave functions \( \psi_{v \mathbf{k}} \) can be calculated by evaluating the Dyson equation

\[
[H_{\text{DFT}} - V_{\text{xc}} + \Sigma(E_{v \mathbf{k}})] \psi_{v \mathbf{k}} = E_{v \mathbf{k}} \psi_{v \mathbf{k}},
\]

in which \( \Sigma \) is the self-energy [111] that supersedes the exchange correlation potential \( V_{\text{xc}} \) obtained in DFT. Based on this, the BSE can be setup as

\[
(E_{v \mathbf{k}} - E_{v \mathbf{k}}' - \Sigma^v_{v \mathbf{k}, v' \mathbf{k}'} + \sum_{v' \mathbf{k'}} K^{\text{eh}}_{v \mathbf{k}, v' \mathbf{k'}} \Sigma^v_{v' \mathbf{k'}}) \psi_{v' \mathbf{k'}} = \Omega^v_{v \mathbf{k}} \Sigma^v_{v \mathbf{k}},
\]

where \( K^{\text{eh}} \) is the direct and exchange electron-hole interaction and \( \Omega^v_{v \mathbf{k}} \) is the quasi-particle energy of a third particle and its additional electron-hole attraction as well as electron-electron repulsion [110].

We underline that all three methods allow for system-independent and parameter-free descriptions. In contrast to DFT which is able to describe the interactions mediated by the wave-function overlap very well, the self-energy also incorporates long range non-local electrodynamical effects. Thus, in particular, the influence of neighboring layers is well described and both intra- and interlayer excitations can be compared on equal footing.

In addition, several parameter-driven models have been proposed to model two-dimensional materials [25, 112–116]. Most of them rely on an effective mass picture for electrons and holes and the Rytova–Keldysh potential for the interaction between the particles. While these models have been employed frequently for monolayers, their usage for hetero-structures is much more challenging. The number of parameters for the atom- and distance-depending interlayer couplings often prohibits simple and realistic models. For the sake of brevity, we will focus on the description from first principles in this review.

### 3.2. Intra layer excitons

The optical properties of monolayers, such as hBN, black phosphorus, and especially of TMDCs have been widely discussed in literature, see e.g. references [117, 118] and references therein. Besides the four main representative TMDCs MoS\(_2\), MoSe\(_2\), WS\(_2\), and WSe\(_2\) many further materials have been identified theoretically owning various interesting optical properties [119].

In Figure 3 the prototypical calculated absorption spectrum of MoS\(_2\) is shown. The two most prominent A and B excitons stem from transitions close to the direct gap at K [121] and their splitting results from the spin–orbit splitting of the involved valence bands. Interestingly, in TMDCs valleys and spins are coupled [31, 122] which allows for specific excitations using circular polarized light.

The reduced and anisotropic screening of two-dimensional monolayers have several interesting consequences. Typical exciton binding energies of about 0.8 eV (for MoS\(_2\)) and up to about 2.0 eV for wide band-gap materials like hBN have been calculated [123, 124]. At the same time the higher excited state experience spatially different dielectric screening which results in strong deviations from a Rydberg-like series [125]. A further consequence of the two-dimensionality is the vulnerability to environmental screening [120]. Figure 3 shows the modification of the absorption spectrum of MoS\(_2\) placed on a gold substrate. While the band gap is reduced significantly by 0.6 eV the electron-hole interaction is lowered by nearly the same amount and results in a red-shift of 0.05 eV (for the A exciton) only. Consequently, in hetero-structures the neighbouring layer can be utilized to fine-tune the properties of intralayer excitons.

### 3.3. Inter layer excitons

In stacked two-dimensional materials, like bilayers, trilayers, etc. up to bulk, the neighbouring layers interact with each other. This interaction, even if it is typically weak, results in a hybridization and leads to excitons which are localized on different layers. This concept of interlayer excitons (IX) has been utilized previously for double-well systems, and similarly for charge transfer excitations (CT) in molecular systems [126, 127].

As soon as two subsystems (i.e. layers) start to interact, interlayer excitons can and will form. However, due to the spatial separation of electron and hole on different layers the exciton binding energy of these states are typically smaller, e.g. in a hetero-bilayer of TMDCs the interlayer exciton binding energy has been calculated to about 0.35 eV compared to about
oscillator strength. States can hybridize and lead to mixed excitons with large oscillator strength if the energy is close to those of an intralayer exciton. These excitons can become the energetically lowest state and thus high-lyed especially in photoluminescence. On the other hand, these states as lowest energy state, in homo-bilayers and bulk inter-hetero-structures (type-II) interlayer excitons have been identified as lowest energy state, in homo-bilayers and bulk inter-layer states with strong oscillator strength [99, 124–129]. ARPES measurements indicate that the top-most valence band states of a MoSe2/WSe2 hetero-structure is still located at the K point [52]. In photoluminescence experiments, signatures for the formation of IX in TMDC hetero-bilayers have been observed for all possible combination of the four most prominent semiconducting TMDCs, MoS2, WS2, MoSe2, and WSe2 [50, 69, 85, 89, 146, 147].

The lowest conduction bands and topmost valence bands of a MoS2/WS2 hetero-bilayer from ab initio calculation based on density functional theory and many-body perturbation theory including the contributions of the atomic orbitals of the individual layers to the hybridized bands are shown in figure 1(d). The mixing of orbital states is particularly strong at the Γ point of the valence band and the Σ point (also referred to as Q or Λ point) of the conduction band. The hybridization shifts the global maximum of the valence band from the K point to the Γ point and the global minimum of the conduction band from the K point to the Σ point [55, 128, 133, 135, 141]. In general, the existence of multiple valleys that are very close in energy demands for a careful determination of the excitonic states contributing to IX formation in TMDC hetero-bilayers. Different degrees of hybridization of the electronic states of the constituent layers can cause the charge carriers to be delocalized across the hetero-bilayer at specific points in the Brillouin zone, while the carriers at other points remain nearly completely localized in one of the layers [95, 128, 133, 135, 148]. In this regard, such structures have to be thought in terms of ‘novel artificial vdW solids’, more than just a sum of two 2D materials. Exact energies of the valley specific electronic states as well as hybridization of bands have been reported to depend crucially on the material combination, their rotational alignment and their dielectric environment [56, 99, 134]. The crystal alignment not only determines the energy of the electronic bands, but also the location of the different valleys in momentum space [149].

In photoluminescence experiments, multiplet emission lines from IX recombination are reported from different combinations of TMDC hetero-structures, pointing towards a complex interplay between multi-valley physics and hybridization of electronic states [54–56, 96–99]. Doublet structures have been observed in the photoluminescence from MoSe2/WSe2
hetero-bilayer by several groups [35, 54, 96, 97]. From temperature and excitation power dependent experiments together with DFT calculations of the band structure, Miller et al interpret the emission doublet as a momentum indirect transition between Σ and K valley and a momentum direct interlayer transition between the K valley that are separated by about 40 meV [56] as sketched in figure 5(a). This combination of MoSe2 and WSe2 TMDC monolayers results in a momentum indirect lowest energy transition between $\Sigma^{MoSe_2}$ and $K^{WSe_2}$ that is activated by a phonon for momentum conservation. This indirect optical interband transition is most likely mediated by the longitudinal acoustic mode at the M point LA(M) featuring a high electron-phonon coupling strength [150].

The energetically slightly higher lying transition between the conduction band state $K^{MoSe_2}$ and the valence band state $K^{WSe_2}$ is slightly indirect in momentum space due to residual rotational and lattice mismatch. Radiative decay for IX located at the K point is possible for nearly aligned crystal axes as long as the IX kinematic momentum is sufficiently large to meet the light cone [50, 56, 149]. Photo excitation introduces long as the IX kinematic momentum is sufficiently large to compensate for the displacement vector between $K^{MoSe_2}$ and $K^{WSe_2}$. This interpretation holds for MoSe2/WSe2 hetero-structures with nearly AB (60 degrees) of nearly AA (0 degree) stacking order [56]. Baranowski et al used a very similar interpretation to explain the experimentally observed doublet structure in the photoluminescence from IX hosted by MoS2/MoSe2/MoS2 tri-layer structure [98]. A reduced splitting of the IX emission lines of about 25 meV for MoSe2/WSe2 hetero-bilayers is reported by Calman et al [96], by Hanbicki et al [97], and Ciarrocchi et al [54], respectively, with contrary interpretations. Calman et al explain the observed splitting due to neutral and charged interlayer excitons [96] in agreement with the interpretation for a IX doublet in a WSe2/MoSe2/WSe2 structure [151]. Whereas Hanbicki et al interpret the IX doublet in terms of momentum indirect interlayer transitions between electron states hosted in the spin split conduction band at the Σ valley with hole states localized at the K' valley (see figure 5(b)) [97]. The energy difference of 25 meV fits to the splitting due to spin–orbit coupling [97]. The authors point out that the transitions are not purely interlayer in character since the wave function of the electronic state at the Σ point have significant weight in both layers, while the hole state is localized in WSe2 [97]. Similarly, Ciarrocchi et al attribute the doublet structure to a momentum direct transition from the spin orbit split conduction bands at $K^{MoSe_2}$ to the topmost valence band state at $K^{WSe_2}$ as depicted in figure 5(c). Another group reports momentum direct (K – K) and momentum indirect (K – Γ) IXs in a MoS2/WSe2 hetero-bilayer with the emission energy and intensity strongly dependent on the twist angle of the adjacent layers [99]. Also this groups points towards the effect of hybridized electronic states since the momentum indirect IX are interpreted to be formed by an electron state localized in MoS2 at the $K^{MoS_2}$ point and delocalized holes in the hybridized Γ' point [99]. As demonstrated in figure 5(d), even triplet IX emission has been reported for hBN encapsulated MoS2/WS2 hetero-bilayers and interpreted as momentum direct and indirect IX transitions involving electron states at K and the hybridized Σ valley and hole states at K and the hybridized Γ' valley indicated in figure 5(e) [55, 95, 128, 133, 135]. Finite coupling of electronic states and valley selective hybridization together with the finite dipole moment of IX allows to tune and engineer the properties of the bound exciton states by application of an electric field normal to the hetero-bilayers utilized by gate electrodes [55, 133, 152]. Electric field control of layer index, orbital character, lifetime and emission energy of indirect excitons in MoS2/WSe2 hetero-bilayers embedded in a vdW field effected structure allows for the design of novel vdW based quantum-nano architectures as e.g. the suggested realization of charge qubits in a vdW hetero-bilayer [152].

5. Crystal alignment and moiré excitons

Because of the weak van der Waals forces between adjacent layers in a hetero-structure, the TMDC monolayers keep their individual in-plane lattice constants a [6], which vary by 0.15%–4% between MoS2 (a = 3.160 Å), WS2 (a = 3.155 Å), MoSe2 (a = 3.288 Å), and WSe2 (a = 3.280 Å) [153, 154]. Strain-free vdW assembly of hetero-stacks implies a spatial alternation of the atomic registry, i.e. the formation of a moiré pattern [6]. As depicted in figure 1(e) an additional twist angle between the crystal axes of the individual layers can further tune the moiré structure.

Most real structures exhibit a finite mismatch of the crystal axes. Deviation from the atomic registry of the 2H stacking (AB stacking) of natural homo-bilayers changes the interlayer distance due to steric effects [6, 155, 156]. The interlayer distance is smallest, but not equal, for the AA and AB stacking corresponding to a twist angle between adjacent layers of 0° and 60°, respectively [156]. The interlayer distance sensitively influences the electronic bands [6, 155, 156]. The most pronounced changes occur, where hybridization between the two layers is strong, that is in particular at the Γ valley of the valence band [6, 155]. An increase of the absolute energy of the valence band at the Γ point of up to 120 meV for twist angles that deviate significantly from 0° or 60° in artificially stacked MoS2 homo-bilayers has been determined from ARPES [157]. This trend is reflected in the twist angle dependence of the transition energy, the intensity and the decay time of interlayer excitons in hetero-bilayers [99, 134, 155, 158]. In addition, slightly modified IX transition energies for AA and AB stacking order in hetero-bilayers have been reported theoretically [156] and experimentally [159].

The charge transfer rate of photo-excited electron hole pairs is determined to be independent of the twist angle [143, 160]. This is explained by a much larger band offsets compared to dependence of the band energies on the twist angle [142]. In contrast, the formation and cooling dynamics of IX is dependent on the twist angle between adjacent TMDC monolayers [53].

For stacked TMDC homo- and hetero-bilayers, the atomic registry depends on the lateral arrangement of the two layers. For AA and AB stacking order the hollow sites of the two
hexagonal lattices of the individual monolayers are aligned to each other. For this configuration, the interlayer distance is highest compared to an alignment of the hollow site to the metal or the chalcogen site [5, 161]. The combined mismatch of the lattice constants and/or the rotational alignment (twist) between adjacent monolayers results in a periodic variation of the local atomic registry forming an hexagonal moiré superlattice pattern with a length scale in the order of 10 nm. The size of the moiré super-cell (figure 1(e)) depends on the lattice mismatch and rotational alignment and gets smaller with increasing twist, as a general tendency. The threefold rotation symmetry of the local atomic registry is restored at three points within the super-cell highlighted with circles in figure 1(e) and explicitly shown in figures 6(a)–(c). These high symmetry points are local energy extremes within the moiré supercell (figures 6(a) and (d)). The result is a periodic modulation of the energy landscape in real space with a magnitude in the order of up to 0.15 eV [5, 11]. The periodically modulated energy landscape in suitable TMDC hetero-bilayers enables the formation of spatially localized IX states trapped at different super-lattice sites [11, 14, 69] with moiré quasi angular momentum periodically switching the optical selection rules [71] as demonstrated in figures 6(b), (d)–(g).

The experimental signatures of those trapped moiré IX appearing just below the direct exciton emission are an ultra-narrow line-width in the order of 100 μeV, varying optical selection rule and a peculiar dependence on rotational alignment of the hetero-bilayer [11, 14, 69]. In particular, Tran et al observed multiple IX resonances with alternating circularly polarized emission in a hBN encapsulated MoSe2/WS2 hetero-bilayer with small twist [11]. The resonances are interpreted as ground state, excited states and phonon replica of IX confined within potential minima of the moiré potential [11] as demonstrated in figure 5. Similarly, Seyler et al report experimental evidence for ultra narrow (line width of about 100 μeV) photoluminescence from interlayer valley excitons that are trapped in the moiré potential of a MoSe2/WS2 with low twist angle [14]. Most significantly, in magneto-photoluminescence experiments the authors find that the $g$-factor only takes two values across a sample that matches those of interlayer excitons with -15.9 and 6.7, respectively [14]. From the $g$-factor results together with the circularly polarized emission strongly suggesting three-fold rotation symmetry of the emission sites, the author conclude the existence of trapped moiré excitons even in the presence of inhomogeneities and sample non-uniformity resulting in multiple emission line with similar characteristics [14]. Also for a different hetero-structure, hBN encapsulated closely aligned WSe2/WS2 hetero-bilayer, Jin et al report the observation of moiré super-lattice exciton states emerging as multiple emission peaks slightly red-shifted from the neutral WSe2 intralayer exciton [69]. Interestingly, the authors observe strong resonances that show a clear doping

\[ \Sigma \text{ and } K \text{ valleys}[56]. \]

\[ \text{(b) Momentum indirect IX formed between spin–orbit split conduction band states at the } K \text{ valley}[97]. \]

\[ \text{(c) Momentum direct IX formed between spin–orbit split conduction band states at } K \text{ valley with valence band states at the } K \text{ valley}[54]. \]

\[ \text{(d) Room temperature IX photoluminescence spectrum of a hBN encapsulated MoS2/WS2 hetero-bilayer clearly indicating a triplet structure. The individual contributions } I_1, I_2, I_3 \text{ are included from Voigt fits to the spectrum [95] (similar spectra shown in [55]).} \]

\[ \text{(e) DFT band structure of MoS2/WS2 hetero-bilayer with projections of bands onto individual layers are shown with a color gradient showing high degree of hybridization at the } \Gamma \text{ and } Q/\Sigma \text{ point [95].} \]

\[ \text{(d), (e) Reprinted with permission from [95]. Copyright (2018) American Chemical Society.} \]
Moiré super-lattice potential and localized moiré excitons in a MoSe₂/WSe₂ hetero-bilayer [11]. (a) Moiré potential of the interlayer exciton transition showing a local minimum at the $h$–$h$ site (1) and local maxima at the $h$–$X$ (2) and the $h$–$M$ (3). (b) Spatial map of the optical selection rules for $K$-valley excitons. The high-symmetry points of the moiré potential are circularly polarized and the regions in between are elliptically polarized. (c) Sketch of the atomic registry for the stacked layers at high symmetry points (1), (2) and (3) of the moiré potential as indicated in (a). (d) Spatial variation of the moiré potential and the confined multiple interlayer exciton resonances. (e) Photoluminescence spectra from for samples with twist angles of 1° (bottom) and 2° (top). The spectra are fitted with four (1°) and five (2°) Gaussian functions, respectively. (f) Degree of circular polarization for the spectra from (f). (a), (b), (d)–(g) Reprinted by permission from Macmillan Publishers Ltd: Nature [11], Copyright (2019).

6. Conclusion and future perspectives

The interaction of two-dimensional materials and their van der Waals hetero-structures with light is a versatile and fast-growing field. Due to their unique properties the class of transition metal dichalcogenides is still mostly used, even though further novel materials are proposed repeatedly. A central step is the synthesis (direct growth by chemical vapor deposition or molecular beam epitaxy, liquid exfoliation, or micromechanical exfoliation) and the reproducible stacking of the high-quality vdW materials. The rotational alignment of the crystal axes during the transfer process is possible by optical microscopy because of their preferable breaking points and can be effectively checked by polarization resolved second harmonic generation. The atomically resolved structure of heterostructures results in moiré patterns with a curvature as well as spatially varying distances of the individual layers. An accurate theoretical description from first principles requires many-body perturbation theory (most often in the GW/BSE approximation). However, its applicability is limited to a few atoms only and for the description of huge moiré patterns simplified models have to be employed.

Even though the properties of the individual layers mostly govern the interaction with light, the interlayer mixing is able to fine-tune these properties, but may also lead to completely new phenomena. Therefore, such van der Waals solids crucially depend on the spatially varying coupling which leads to two prominent effects: The hybridization of different valleys in the band structure changes and interlayer excitons, i.e. electron-hole pairs with different amounts of electrons and holes on different layers. Due to the effective charge separation in such interlayer excitons several interesting properties can be designed which may be interesting for instance for quantum-technology devices. Interlayer excitons own long lifetimes which allows for thermalization and diffusion over several micrometers. Furthermore, the out of plane dipole can be easily manipulated by electric fields and promotes van der Waals solids as light-emitting diodes, energy conversion, opto- and valleytronics, as well as for exciton based information technologies.

Moreover, vdW structures are also interesting candidates to study fundamental science. As recently demonstrated,
particular designed WSe$_2$/MoSe$_2$-heterostructures have the potential to investigate collective excitonic phenomena like high-temperature superfluidity and Bose–Einstein condensation [67, 68]. Very recently several works have started to investigate novel properties of moiré structures and their interaction with light. Tang et al [162] have proposed the WSe$_2$/WS$_2$ hetero-structure to probe the Hubbard model. Also in WSe$_2$/WS$_2$ Regan et al [163] have observed several unexpected insulating states. Wang et al [164] have investigated twisted bilayer WSe$_2$. For twist angles spanning from 4° to 5.1° the authors observe a flat band which has been put into context of superconductivity in graphene. Considering the quite rapid developments in this area in the last years, it is very likely that many extremely exciting developments will continue in near future.

Acknowledgments

We thank Bastian Miller, Florian Sigger, Jonas Kiemle and Fabian Kronowetter for support with the figure preparation. We acknowledge financial support from the German Research Foundation (Germany’s Excellence Strategy—EXC 2089/1—390776260, excellence cluster ‘Nanosystems Initiative Munich’ (NIM) and DFG Projects No. DE 2749/2-1 and WU 637/4-1).

ORCID iDs

Thorsten Deilmann https://orcid.org/0000-0003-4165-2446

Ursula Wurstbauer https://orcid.org/0000-0002-1764-5409

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Science 306 666–9
[2] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2005 Proc. Natl Acad. Sci. USA 102 15368–71
[3] Ajayan P, Kim P and Banerjee K 2016 Phys. Today 69 38
[4] Novoselov K S, Mishchenko A, Carvalho A and Castro Neto A H 2016 Science 353 47–51
[5] Zhang C, Chiu C-P, Ren X, Li M-Y, Li L-J, Jin C, Chou M-Y and Shih C-K 2017 Sci. Adv. 3 e1601459
[6] Kang J, Li J, Li S-S, Xia J-B and Wang L-W 2013 Nano Lett. 13 5485
[7] Ribeiro-Palau R, Zhang C, Watanabe K, Taniguchi T, Hone J and Dean C R 2018 Science 361 690
[8] Cao Y, Fatemi V, Fang S, Watanabe K, Taniguchi T, Kaxiras E and Jarillo-Herrero P 2018 Nature 556 43
[9] Hunt B et al 2013 Science 340 1427
[10] Dean C R et al 2013 Nature 497 598
[11] Tran K et al 2019 Nature 567 71
[12] Wu F, Lovorn T and MacDonald A H 2017 Phys. Rev. Lett. 118 147401
[13] Wu F, Lovorn T, Tutuc E and MacDonald A H 2018 Phys. Rev. Lett. 121 026402
[14] Seyler K L, Rivera P, Yu H, Wilson N P, Ray E L, Mandrus D G, Yan J, Yao W and Xu X 2019 Nature 567 66
[15] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Phys. Rev. Lett. 105 136805
[16] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim C-Y, Galli G and Wang F 2010 Nano Lett. 10 1271
[17] Wilson J A and Yoffe A D 1969 Adv. Phys. 18 193
[18] Mak K F and Shan J 2016 Nat. Photon. 10 216
[19] Mueller T and Malic E 2018 npj 2D Mater. Appl. 2 246
[20] Miró P, Audiffred M and Heine T 2014 Chem. Soc. Rev. 43 6537
[21] Koperski M, Molas M R, Arora A, Nogajewski K, Slobodeniuk A O, Faugeras C and Potemski M 2017 Nanophotonics 6 459
[22] Schneider C, Glazov M M, Korn T, Höfling S and Urbaszek B 2018 Nat. Commun. 9 026803
[23] Parzinger E, Mitterreiter E, Stelzer M, Kreufl F, Ager J W, Holleitner A W and Wurstbauer U 2017 Appl. Mater. Today 8 132
[24] Radisavljevic B, Radenovic A, Brivio J, Giacometti V and Kis A 2011 Nat. Nanotechnol. 6 147
[25] Chernikov A, Berkelbach T C, Hill H M, Rigosi A, Li Y, Aslan O B, Reichman D R, Hybertsen M S and Heinz T F 2014 Phys. Rev. Lett. 113 076802
[26] He K, Kumar N, Zhao L, Wang Z, Mak K F, Zhao H and Shan J 2014 Phys. Rev. Lett. 113 026803
[27] Wurstbauer U, Miller B, Parzinger E and Holleitner A W 2017 J. Phys. D: Appl. Phys. 50 173001
[28] Parzinger E, Miller B, Blaschke B, Garrido J A, Ager J W, Holleitner A and Wurstbauer U 2015 ACS Nano 9 11302
[29] He Z and Que W 2016 Appl. Mater. Today 3 23
[30] Mitterreiter E, Liang Y, Golibrzuch M, McLaughlin D, Csoklóczy L, Bartl J D, Holleitner A, Wurstbauer A and Bandarenka A S 2019 npj 2D Mater. Appl. 3 25
[31] Xiao D, Liu G-B, Feng W, Xu X and Yao W 2012 Phys. Rev. Lett. 108 196802
[32] Kormányos A, Zólomyi V, Drummond N D and Burkard G 2014 Phys. Rev. X 4 78
[33] Xu X, Yao W, Xiao D and Heinz T F 2014 Nat. Phys. 10 343
[34] Mak K F and Shan J 2018 Nat. Nanotechnol. 13 974
[35] Miller B, Lindlau J, Bommert M, Neumann A, Yamaguchi H, Holleitner A, Högele A and Wurstbauer U 2019 Nat. Commun. 10 807
[36] Blaauw M, Harms J, Prechtl M, Finley J J and Kaniber M 2017 2D Mater. 4 021011
[37] Tomandor P, Schmidt R, Schneider R, Kern J, Buscema M, Steele G A, Castellanos-Gomez A, van der Zant , Herre S J, Michaelis de Vasconcellos S and Bratschitsch R 2015 Optica 2 347
[38] Srivastava A, Sidler M, Allain A V, Lembke D S, Kis A and Imamoglu A 2015 Nat. Nanotechnol. 10 491
[39] Koperski M, Nogajewski K, Arora A, Cherkez V, Mallet P, Veuillen J-Y, Marcus J, Kossacki P and Potemski M 2015 Nat. Nanotechnol. 10 503
[40] Chakraborty C, Kinnischtzke L, Goodfellow K M, Beams R and Vamivakas A N 2015 Nat. Nanotechnol. 10 507
[41] Kern J, Niehues I, Tomandor P, Schmidt R, Wigner D, Schneider R, Stiehm T, de Vasconcellos M, Steffen D E R, Kuhn T and Bratschitsch R 2016 Adv. Mater. 28 7101
[42] Palacios-Berraquero C, Kara D M, Montblanch A R-P, Barbone M, Latawiec P, Yoon D, Ott A K, Loncar M, Ferrari A C and Atatüre M 2017 Nat. Commun. 8 15093
[43] Braazin A, Kumar S, Proux R and Gerardot B D 2017 Nat. Commun. 8 15053
[44] Klein J et al 2019 Nat. Commun. 10 2755
[45] Geim A K and Grigorieva I V 2013 Nature 499 419
[46] Rivera P, Yu H, Seyerl K L, Wilson N P, Yao W and Xu X 2018 Nat. Nanotechnol. 13 1004
[47] Rigosi A F, Hill H M, Li Y, Chernikov A and Heinz T F 2015 Nano Lett. 15 5033
