Topical Review

Valley degree of freedom in two-dimensional van der Waals materials

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Abstract
Layered materials can possess valleys that are indistinguishable from one another except for their momentum. These valleys are individually addressable in momentum space at the K and K' points in the first Brillouin zone. Such valley addressability opens up the possibility of utilizing the momentum states of quasi-particles as a completely new paradigm in both quantum and classical information processing. This review focuses on the physics behind valley polarization and discusses carriers of valley degree of freedom (VDF) in layered materials. We then provide a detailed survey of simple spectroscopic techniques commonly utilized to identify and manipulate valley polarization in van der Waals layered materials. Finally, we conclude with recent developments in the manipulation of VDF for device applications and associated challenges.

Keywords: valley polarization, 2D materials, valley degree of freedom, exciton, valley lifetime

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

1. Introduction

Two-dimensional materials are members of a family of layered crystal structures whose atoms are connected through strong intra-layer bonds but have weak interlayer van der Waals (vdW) coupling. Graphene, an atomically thin carbon layer, was the first well-known 2D material \cite{1, 2}. It exhibits interesting 2D Dirac fermion-like features (e.g. integer and fractional quantum Hall effects) \cite{3, 4} and ballistic conduction of charge carriers \cite{1, 5}. Graphene is not ideal for electronic applications because of its zero-bandgap semi-metallic nature. However, the bandgap of graphene can be opened up by applying a magnetic field \cite{6}, creating a heterostructure \cite{7–9}, or preparing a bilayer \cite{10}. Inspired by the fascinating properties and applications of graphene, researchers have developed a plethora of 2D materials. The 2D materials that emerged after the discovery of graphene include transition-metal dichalcogenides (TMDs) \cite{11}, transition-metal monochalcogenides (TMMCs) \cite{12}, hexagonal boron nitride (h-BN) \cite{13}, black phosphorous (BP) \cite{14}, and graphitic carbon nitride \cite{15}. The extraordinary electronic properties of these novel 2D materials make them interesting for applications in diverse technologies (e.g. sensors, LEDs, field effect transistors (FETs), catalysis, biomedicine, and environmental science) \cite{16–21}.

In a crystalline solid, a local energy minimum in the conduction band (CB) or a local energy maximum in the valence band (VB) in the momentum space is known as a valley.
In addition to charge and spin, a carrier is assigned a valley degree of freedom, indicating the valley that the carrier occupies. Electrons, holes, or excitons can populate the valleys to store and carry information and form the basis of the so-called valleytronics [22–24]. While electronics utilizes the charges of carriers and spintronics exploits carrier spin, in valleytronics, the valley pseudospin of a quasi-particle forms the basis of a possible new technology.

Few conventional semiconductors (e.g. silicon, aluminum arsenide, and bismuth) have multiple valleys in the CB (figure 1(a)) [25]. In silicon (Si), six equivalent valleys lie along the $\Delta$-direction and near the zone boundary ($X$). Recently, efforts have been made to manipulate the VDF in traditional semiconductors [23]. Valley-polarized current has been generated and detected in bulk diamond [26]. The charge conductivity of bismuth can be controlled by manipulating the polarization of Dirac valleys using a magnetic field [27]. The valley degeneracy in Si-based systems is increased by introducing valley splitting, which can be tuned by controlling the applied electrostatic potential [28, 29]. Despite a few encouraging results, the difficulty with these materials is to maintain the VDF using simple external agents such as an electric field, a magnetic field, light, strain, etc.

Two-dimensional materials may intrinsically possess or be tailored to produce contrasting valley properties that can be exploited in valleytronics. In 2D-dimensional materials with hexagonal honeycomb structures (e.g. graphene and TMDCs), two valleys are present at the $+K$ and $-K$ points at the edges of the Brillouin zone (figure 1(b)) [30]. Among the 2D materials, valley-contrasting physics was first detected and manipulated in graphene [2, 31, 32]. Graphene exhibits contrasting circular dichroism in different $k$-space regions due to inversion symmetry breaking [33, 34]. Therefore, it obeys a valley-contrast optical selection rule, which can be exploited for optoelectronics applications in which light polarization information can be converted into electronic information [31, 35, 36]. In 2010, Mak et al proposed a new direct bandgap semiconductor, 2D MoS$_2$, that exhibits very high luminescence quantum efficiency compared to that of the bulk material [37, 38]. Polarization can be achieved and manipulated in monolayer MoS$_2$ through the optical pumping of circularly polarized light [39–41]. Valley-selective photoluminescence (PL) has been detected in many other TMDCs (e.g. MoSe$_2$, WS$_2$, and WSe$_2$) [42, 43]. Both graphene and 2D TMDCs have non-centrosymmetric hexagonal crystal structures, which cause inversion symmetry breaking and result in valley-contrast properties. Graphene does not naturally possess valley-selective circular dichroism, but it can exhibit valley polarization under the influence of an external magnetic or electric field. The valleys of these vdWs layered materials can be coupled with circularly polarized photons, leading to valley-selective circular dichroism [44, 45]. Although 2D TMMCs and BP exhibit VDF, the nature of the valleys in such materials is quite different from those of graphene and TMDCs, and valley polarization can be created in them using linear polarized light [46–48]. The main advantage of 2D materials over traditional semiconducting materials is that 2D materials host inequivalent valleys and valley polarization can easily be generated (e.g. by applying polarized light).

The practical realization of valleytronics devices is highly dependent on our understanding of VDF in 2D materials, including the manipulation of valley pseudospin. Graphene and TMDCs which have hexagonal crystal structures possess inequivalent valleys at the $K$ and $K'$ points. Moreover, both of them show valley-selective circular dichroism due to coupling with circularly polarized photons that follows similar optical selection rules. Here, we present the necessary valley physics to understand the origin of valley-contrast properties in such 2D vdW materials. The details of the carriers of valley pseudospin in layered materials will be discussed here. This review will attempt to summarize the techniques currently used to investigate the VDF in 2D vdW systems. Finally, we will explore the available ways of manipulating valley polarization and valley coherence in 2D hexagonal materials.

2. Valley physics

The valleys in crystalline solids can be equivalent or inequivalent, depending on the nature of the unit cell. When there is some asymmetry in the unit cell, valleys exhibit different characteristics. For example, in the hexagonal graphene lattice, which can be considered as a superposition of two identical sub-lattices offset by the carbon–carbon bond length (figure 1(c)), two inequivalent (since the two sublattices are distinct) but otherwise identical valleys are present at the $K$ and $K'$ points in the Brillouin zone. The $K$ and $K'$ points in graphene are related to inversion and time-reversal symmetry [51]. Due to the broken sublattice symmetry in 2D TMDCs, the valleys located at $K$ and $K'$ are degenerate but have opposite momentum [25]. To differentiate these valleys, a new index, known as valley pseudospin ($\tau_z$), has been introduced [31]. It is called pseudospin because it carries information, i.e. up-down or valley one or two, in the same way as spin. The values of $\tau_z$ for TMDCs are $\pm 1$, which describe the position of a particle: in the $K$ valley or the $K'$ valley [31]. In 2D materials, there are two physical quantities—orbital angular momentum and Berry curvature, which are different in the $K$ and $K'$ valleys.

2.1. Orbital magnetic moment ($m$)

The orbital magnetic moment is one of the valley-contrast parameters in 2D materials [52, 53]. It can be regarded as the self-rotation of the electron wave packet clockwise in one valley (at $K$) and anticlockwise in the other valley (at $K'$), which gives rise to an opposite value of $m$ (figure 1(d)). The spin magnetic moment is different for the spin-up and -down states; in the same way, the orbital angular moment discriminates between different valley states. The valley-contrast magnetic moment can be defined as [31]

$$m(k) = \tau_z \frac{3e\alpha^2 \Delta^2}{4\hbar(\Delta^2 + 3q^2\alpha^2\tau^2)}$$

(1)
where $\tau_z = \pm 1$ labels the two valleys, $m(k)$ is the orbital magnetic momentum, $q$ is the canonical momentum taken from the valley centre, $a$ is the lattice constant, $t$ is the nearest-neighbour hopping energy, and $\Delta$ is the energy difference between sublattices. The orbital magnetic moment in a crystal is related to some fundamental symmetries (time-reversal symmetry and inversion symmetry). Time reversal is the name of a particular symmetry transformation that stands for an inversion of the direction of time [54], while spatial inversion symmetry refers to symmetry under a reversal of the directions of all the coordinate axes [55]. The signs of both $m$ and $\tau_z$ are changed by a time-reversal symmetry operation. On the contrary, only $\tau_z$ (not $m$) changes sign under spatial inversion. This implies that $m$ can only be zero when the system remains invariant under both time-reversal and inversion symmetries. The value of the orbital magnetic moment can be nonzero only in systems with broken inversion symmetry. Although the $K$ and $K'$ points are time-reversed images of one another, the orbital angular momenta are inequivalent at these points in hexagonal 2D materials due to the violation of spatial inversion symmetry.
The Berry curvature of the energy bands of crystalline solids is defined as
\[ \frac{\partial^2}{\partial k^2} + V(r) \]
where \( V(r) \) is the periodic potential. According to Bloch's theorem, the energy eigenstates of a periodic Hamiltonian can be written in the form [60]:
\[ \psi_{nk}(r + a) = e^{iak} \psi_{nk}(r) \]
where \( a \) is the Bravais lattice vector, \( n \) is the band index, and \( \hbar k \) is the crystal momentum. Although the Hamiltonian of the system is \( k \)-independent, the boundary condition depends on \( k \). The Hamiltonian can be made \( k \)-dependent through a unitary transformation of the form
\[ H(k) = e^{-ikr}He^{ikr} = \frac{\hbar^2 k^2}{2m} + V(r). \]
The function \( u_{nk}(r) = e^{-ikr}\psi_{nk}(r) \), satisfies the periodic boundary condition
\[ u_{nk}(r + a) = u_{nk}(r). \]
All such eigenfunctions belong to the same Hilbert space. Therefore, the Brillouin zone can be the parameter space of the transformed Hamiltonian \( H(k) \) with \( |u_{nk}(k)| \) as the basis function.

Since the \( k \) dependence of the basis function is inherent to the Bloch problem, various Berry phase effects can be expected in crystals. For example, in crystals, if \( k \) is considered to be in the momentum space, then a Berry phase will be associated with the Bloch state:
\[ \Phi_{B} = \oint Cdk \cdot \left( u_{nk}(k) |i\Delta k| u_{nk}(k) \right) = \oint Cdk \cdot \Omega_{n}(k). \]
The Berry curvature of the energy bands of crystalline solids is defined as
\[ \Omega_{n}(k) = \Delta_{k} \times \left( u_{nk}(k) |i\Delta k| u_{nk}(k) \right). \]
It depends on the wave function and is hence an intrinsic property of the crystal. It plays a vital role in the accurate description of the dynamics of Bloch electrons.

In the Aharonov–Bohm effect, which is a purely quantum mechanical phenomenon, an electromagnetic potential \( (\varphi, A) \) affects an electrically charged particle, even if both the magnetic \( (B) \) and electric \( (\varepsilon) \) fields are zero in that region [61]. A beam of electrons is split into two and sent past a solenoid on different sides of it (figure 1(e)). Suppose the solenoid contains a magnetic field (a non-zero vector potential outside the solenoid). In this case, the electronic state will acquire an additional phase \( (\Phi) \), which is proportional to the magnetic flux \( (\phi_m) \) inside the solenoid
\[ \Phi = \frac{e}{\hbar} \int A(r) = \frac{e}{\hbar} \phi_m. \]
where \( da \) and \( B \) are the cross-sectional areas of the solenoid and the magnetic field, respectively. This effect is known as the magnetic Aharonov–Bohm effect. Making an analogy between the Berry-phase effect and the magnetic Aharonov–Bohm effect, the Berry phase and Berry curvature can be considered as a magnetic flux and a magnetic field in the momentum space, respectively [62].

The value of the Berry curvature is nonzero for crystals with broken time-reversal or inversion symmetry. Two-dimensional TMDCs have non-zero Berry curvature due to the absence of an inversion center in the structure. In these materials, maximum Berry curvatures are observed at the \( K \) and \( K' \) points (figure 1(f)) [50]. The Berry curvature introduces energy splitting between exciton states with opposite angular momentums by modifying the effective Hamiltonian for excitons [63]. Another example of a system in which both symmetries are not simultaneously present is monolayer graphene with a staggered sublattice potential, in which inversion symmetry is broken [64]. The Berry curvature of this system possesses opposite signs at the valleys \( K \) and \( K' \) due to time-reversal symmetry [31, 65]. As the energy gap approaches zero, the Berry phase of an electron after completing one cycle around the valley becomes \( \pm \pi \). The intrinsic graphene sheet exhibits a Berry phase of \( \pi \) [4, 34].

2.3. Valley-selection rule

When a Bloch electron travels adiabatically in a non-degenerate energy band, in general, the real-space dimension of the associated wave packet is much larger than the lattice constant, but much smaller than the length scale of the external perturbation [66, 67]. Therefore, the wave packet and the wave vector of the electron can be considered independently. In this case, we can describe the motion of electrons in the crystal lattice by the semi-classical equation in which the wave function is a Bloch function and the mean velocity is related to the electronic energy gradient of the band [68, 69]. When the periodicity, as well as the applied magnetic field, are taken into consideration, an anomalous velocity exists due to the Berry curvature of the electronic band. The Berry curvature of the Bloch states exists in the absence of external fields and...
manifests itself in a quasi-particle velocity when the crystal momentum is changed by external forces [70, 71].

The semi-classical dynamics of a Bloch electron under applied electric and magnetic fields can be expressed as

$$\frac{dr}{dt} = \frac{1}{\hbar} \frac{\partial E_n(k)}{\partial k} - \frac{dk}{dt} \times \Omega_n(k) \quad (10)$$

and

$$\hbar \frac{dk}{dt} = -e \varepsilon - e \frac{dk}{dt} \times \vec{B} \quad (11)$$

where $E_n(k)$ is the energy dispersion of the $n$th band, $r$ is the crystal momentum and the position of the electron wave packet, and $\varepsilon$ and $\vec{B}$ represent the applied electric and magnetic fields, respectively. The Berry curvature can be defined in terms of the Berry phase relation

$$A_n(k) = \langle u_n(k) | i \nabla_k | u_n(k) \rangle \quad (12)$$

as

$$\Omega_n(k) = \nabla_k \times A_n(k). \quad (13)$$

According to the Kubo formula [68, 72, 73], the Berry curvature of the Bloch states can also be written as

$$\Omega_n(k) = i \frac{\hbar^2}{m^2} \sum_{\alpha' \neq \alpha \pm m} \frac{\langle u_{n\alpha'} | v | u_{n\alpha} \rangle \times \langle u_{n\alpha} | v | u_{n\alpha'} \rangle}{[E_n^{(0)} - E_{n\alpha'}^{(0)}]^2} \quad (14)$$

where $E_n^{(0)}$ is the energy dispersion of the $n$th band, and $v$ is the velocity operator. Since the equations of motion remain invariant under symmetry operations, $\Omega_n(k) = -\Omega_n(-k)$ under time-reversal symmetry, and $\Omega_n(k) = \Omega_n(-k)$ under inversion symmetry. Therefore, valley-contrast properties appear when one of the symmetries is broken.

Berry curvature gives rise to an anomalous transverse velocity (Hall velocity) in a 2D crystal in the presence of an electric field [59]:

$$v_{\perp} = \frac{dk}{dt} \times \Omega_n(k). \quad (15)$$

As the directions of the electron velocity are opposite in opposite valleys, the electron motion in a particular valley can be selected by changing the direction of the applied electric field.

The electron energy dispersion can be written in terms of the orbital angular momentum as

$$E_n(k) = E_n^{(0)}(k) - m_n(k) \vec{B} \quad (16)$$

where

$$m(k) = i \frac{e \hbar}{m^2} \sum_{\alpha' \neq \alpha \pm m} \frac{\langle u_{n\alpha'} | v | u_{n\alpha} \rangle \times \langle u_{n\alpha} | v | u_{n\alpha'} \rangle}{[E_n^{(0)} - E_{n\alpha'}^{(0)}]^2}. \quad (17)$$

The valley magnetic moment of a valley carrier interacts with an external magnetic field, giving rise to a valley Zeeman effect similar to the spin Zeeman effect. Therefore, an external magnetic field can be an additional way of controlling the VDF. Nonetheless, due to the finite orbital magnetic moment, the valley carriers interact differently with left and right circularly polarized light [40, 41, 74]. Such optical circular dichroism due to the orbital magnetic moment provides an optical selection rule for valley carriers [25].

In monolayer TMDCs, contrasting $\Omega$ and $m$ values in the $\pm K$ valley gives rise to valley selection rules. In the tight-binding approximation, the Hamiltonian of a single TMDC sheet depends on nearest-neighbour hopping energy (hopping integral) $t$ and the energy difference between sublattices $\Delta$. The low-energy description of the Hamiltonian near the Dirac points is given by [42, 75]

$$\hat{H} = at(\tau.k_{\parallel} \sigma_z + k_{\parallel} \sigma_\gamma + \frac{\Delta}{2} \sigma_z) \quad (18)$$

where $\sigma$ is the Pauli matrix, accounting for the sublattice index and the lattice constant. According to this model, the valley-contrast Berry curvature takes the form

$$\Omega_\gamma(k) = -\frac{\hbar^2}{2} \frac{2a^2t^2 \Delta}{(2a^2t^2k^2 + \Delta^2)^{3/2}} \tau_z. \quad (19)$$

As the values of $\tau_z = \pm 1$, $\Omega_\gamma$ assumes equal but opposite values in the $K$ or $K'$ valleys of monolayer TMDCs. The valley-contrast $\Omega_\gamma$ gives rise to a current of the carriers, whose sign depends on the valley index ($\tau_z$) when exposed to an in-plane electric field. The photoexcited electrons and holes move to the two opposite edges of the TMDC sheet, developing a transverse bias (figure 2(a)) [42, 76]. This phenomenon is known as the valley Hall effect.

According to the massive Dirac fermion model, the orbital angular momentum can be expressed as

$$m(k) = -\frac{\hbar^2}{4a^2t^2k^2 + \Delta^2/2h} \tau_z. \quad (20)$$

In the low-energy limit ($k \rightarrow 0$), the orbital magnetic moment is [31]

$$m(m_{1,2}) = \tau_{\gamma} \mu_{\parallel}^a \text{ with } \mu_{\parallel}^a = \frac{e \hbar}{2m^*_{\parallel}} \quad (21)$$

where $m^*_{\parallel} = (2\Delta/h^2)/(3a^2t^2)$ is the effective mass of the electron at the bottom of the band. As a result, monolayer TMDCs exhibit valley-contrast magnetic moments, which can be detected through an applied magnetic field (figure 2(a)) [42].

The optical circular dichroism in 2D TMDCs is given by

$$\eta(k) = -\frac{m(k) \tilde{\Omega}}{\mu_{\parallel}^a} = -\frac{\Omega(k) \tilde{\tau}_z}{\mu_{\parallel}^a(k)} \frac{e}{2h} \Delta(k). \quad (22)$$

In the Brillouin zone, at high symmetry points, the Bloch states are invariant under a $q$-fold discrete rotation about the direction of light propagation: $R\left(\frac{2\pi}{q} \tilde{\tau}_z \right) | \psi_{\gamma}(k) \rangle = e^{-i\frac{2\pi q}{q}} | \psi_{\gamma}(\tilde{\tau}_z) \rangle$. The azimuthal selection rule for interband transitions due to circularly polarized light is $l_s \pm 1 = l_c + qN$ [33], where $l_s$ and $l_c$ are azimuthal quantum numbers. In TMDCs, the right and left circularly polarized lights couple
to interband transitions in the $K$ and $K'$ valleys, respectively \[66\].

The lattice of 2D TMDC crystals has no inversion symmetry, and therefore its six energy valleys in momentum space constitute two inequivalent sets ($K$ and $K'$) (figure 2(b)). The strong spin-orbital coupling between the $d$ orbitals of the chalcogenide atoms introduces large splits in the valence bands $[78, 79]$. The spin splitting in different valleys is opposite, due to time-reversal symmetry and the lack of inversion symmetry in space. The spins of the holes in the $V_A$ band are $-3/2$ and $+3/2$, respectively, while the spins in the $V_B$ band assume the values $+1/2$ and $-1/2$ in the respective valleys \[77\]. Because of this unique spin feature, the spin and valley degrees of freedom of holes are inherently coupled in the valence bands \[25, 80\]. However, the degeneracy of the CBs near the band minima in TMDCs (figure 2(c)) \[77\] provides interesting spin and valley structures, which gives rise to spin- and valley-selective optical coupling \[81\]. The holes in the $V_A$ and $V_B$ bands are combined with the electrons in the CB to form $A$ and $B$ excitons, respectively (figure 2(d)) \[77\].

In the $K$ valley, a spin-down hole ($-3/2$) and either a spin-up ($+1/2$) or a spin-down ($-1/2$) electron constitute an $A$-exciton. The spin of the exciton in the first case is $-1$ (down) and hence it couples to right circularly polarized photons (figure 2(d)). The second exciton is a dark exciton with a spin of $-2$, which does not couple to photons. Conversely, a bright $A$-exciton in the $K'$ valley is formed from a spin-up hole ($+3/2$) and a spin-down electron ($-1/2$); this exciton has a spin of $+1$ (a spin-up exciton), and hence couples to left circularly polarized photons (figure 2(d)). Hence, both spin- and valley-polarized excitons can be created in 2D TMDC crystals using circularly polarized lights of different kinds \[41, 81\].

2.4. Valley coherence

Valley coherence is a coherent superposition of two valley states with a fixed phase relationship. The valley indexes of 2D vdW materials can constitute a quantum two-level system, and the excited carriers in the $K$ and $K'$ valleys form excitons with pseudospins of $+1$ and $-1$ (the corresponding states are $|+1\rangle$ and $|-1\rangle$). The valley pseudospin of excitons, electrons, or holes can be used to perform quantum gate operations. A quantum state does not have to be composed of just a single particle (e.g. an exciton) in the state $|+1\rangle$ or $|-1\rangle$, but can also be formed by a coherent superposition of two states of two particles as $|X\rangle = 1/\sqrt{2}(|+1\rangle + |−1\rangle)$ \[82\]. In TMDCs, quantum coherence can be realized in well-separated band extrema in momentum space. Valley coherence allows the manipulation of the VDF and can be generated by linearly polarized light \[83, 84\]. Basically, linearly polarized light is a superposition of right and left circularly polarized photons, which simultaneously excite both valleys. The degree of valley
Figure 3. (a), (b) Measured local ($R_L$) and non-local ($R_{NL}$) resistances. Dependence of $R_L$ and $R_{NL}$ on the gate voltage, respectively. Back and top gate displacements are defined as $D_{BG} = \varepsilon_{BG} (V_{BG} - V_{BG}^0) / d_{BG}$ and $D_{TG} = -\varepsilon_{TG} (V_{TG} - V_{TG}^0) / d_{TG}$, respectively. (c) Comparison of the experimentally measured $R_{NL}$ and a calculation of the ohmic contribution. (a)–(c) Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Springer Nature] [Nature Physics] [93], copyright (2015). (d)–(g) Variation of $R_L$ and $R_{NL}$ with $V_t$ (voltage applied to the top gates) at fixed $V_b$ (voltage at bottom gates) at varying voltages. The sample dimensions were $5 \mu m \times 1.5 \mu m$. The dashed lines represent the expected ohmic non-local contributions. Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Springer Nature] [Nature Physics] [36], copyright (2015).

coherence (DOVC) or linear polarization is expressed by the following relation

$$\theta = \frac{I(\parallel) - I(\perp)}{I(\parallel) + I(\perp)}$$  \hspace{1cm} (23)$$

where $I(\parallel)$ and $I(\perp)$ are the parallelly and perpendicularly polarized emission intensities with respect to the polarization state of excitation, respectively. The coherence between the different valleys was first demonstrated in monolayer WSe$_2$ by monitoring the linearly polarized emission [85, 86]. The DOVC in a WSe$_2$ monolayer has been reported to be $\sim 40\%$ at 30 K [85]. Zhu et al observed DOVCs of around 4% and 80% for monolayer and bilayer WS$_2$, respectively at 10 K [87]. Valley coherence has also been detected in CVD-grown monolayer MoS$_2$ at cryogenic temperatures (20 K) under nearly resonant excitation [82]. Giant exciton valley coherence (DOVC $\sim 74\%$) has been reported in multilayer WS$_2$ large single crystals at room temperature [88]. In addition, perfect valley coherence (100% DOVC) has been achieved in monolayer MoS$_2$ sandwiched between two graphene layers [89].

3. Valley carriers

Like charge and spin, valley information can also be transported through materials. There are many carriers of valley pseudospin, such as free electrons and holes, doped electrons and holes, and quasi-particles such as neutral, charged, and bound excitons. Due to the availability of various valley information carriers, several different methods can be used to control the transport of valley polarization.

3.1. Electrons and holes

Hall currents flow transversely to the applied electric field in graphene placed on top of h-BN, even without a magnetic field [90]. Opposing Hall currents arise due to carriers located in opposite valleys [25, 31]. The inversion symmetry broken by the superlattice potential induced by the h-BN substrate gives rise to the Hall currents [91, 92]. Pure valley current flows through dual-gated bilayer graphene (BG) and produces a large non-local resistance that scales cubically with the local resistivity (figure 3) [93]. A pronounced non-local response in the resistance has also been observed as a result of the topological transport of valley pseudospin in BG.
The binding energy of excitons is predominantly due to the exchange interactions between charges are of two types: direct and exchange. While electrons and holes remain in the same valley, bright excitons have a binary valley pseudospin similar to those of free holes. For excitons, the Coulomb interactions are expected to be weak due to large Coulomb screening and wavefunction overlap [36, 105–108]. In a doped semiconductor, the neutral exciton can be combined with an extra electron or hole to form a charged exciton or trion [109, 110]. The enhanced Coulomb interaction in 2D materials (e.g., TMDCs) leads to the formation of biexcitons [111, 112].

3.2. Intralayer excitons

In low-dimensional materials, quasi-states (excitons, trions, and biexcitons) are formed due to weak electrostatic screening and large Coulomb interactions [102–104]. An exciton is the combined state of an electron in the CB and a hole in the VB [105–108]. In a doped semiconductor, the neutral exciton can be combined with an extra electron or hole to form a charged exciton or trion [109, 110]. The enhanced Coulomb interaction in 2D materials (e.g., TMDCs) leads to the formation of biexcitons [111, 112].

Monolayer TMDCs have a direct bandgap and exhibit a great resonance in their optical responses, such as absorption and PL due to the formation of neutral \( (X^0) \) and charged \( (X^\pm) \) excitons (figure 4(a)). The typical absorption spectra of monolayer TMDCs consist of several characteristic peaks due to exciton resonance and interband transitions [113]. Theoretical studies of such systems have reported unusual features in the density of states, i.e., ‘band nesting’ (figure 4(b)) [114]. According to these studies, the location of the band nesting region is near the midway point between \( \Gamma \) and \( K' \), where the CB and the VB are parallel to each other. The conduction band minima and valence band maxima are both located at the \( K/K' \) point of the Brillouin zone. Hence, the optical response of monolayer TMDCs is dominated by valley excitons (bound electron–hole pairs in the valleys).

Figure 4(c) shows the PL and differential reflectance spectra of monolayer MoS\(_2\), MoSe\(_2\), WSe\(_2\), and WS\(_2\) on a quartz substrate [115]. The peaks A and B are associated with the excitons that reside at the \( K \) and \( K' \) points. A strong absorption peak (similar to the C peak in figure 4(c)) is observed when the conduction and VBs are nested. As a consequence of the strong quantum confinement, the exciton binding energy in TMDCs is exceptionally high, about 0.5 eV [113, 116]. These excitons are bright excitons in which electrons and holes remain in the same valley. Therefore, bright excitons have a binary valley pseudospin similar to those of free electrons and holes. For excitons, the Coulomb interactions between charges are of two types: direct and exchange. While the binding energy of excitons is predominantly due to the direct part, the exchange Coulomb interaction results in a diagonal energy shift and off-diagonal coupling in the valley configurations [117]. The electron–hole exchange interaction between the excitons in the two valleys is equivalent to an in-plane effective magnetic field at the valley pseudospin [66, 118]. This effective magnetic field gives rise to the valley–orbit coupling, and the bright exciton dispersion is split into two branches that have in-plane valley pseudospins (figure 4(d)) [117].

Due to the substantial resonant excitonic absorption [37] of monolayer TMDCs, valley excitons can play an essential role in TMDC-based valleytronics devices [117]. These devices are expected to be easily initialized using light [39, 120], and readout can be performed using photon polarization [40, 120]. Valley excitons can be controlled by both magnetic [121–123] and optical fields [124, 125]. The major issue with this kind of valley carrier is the short (few nanoseconds) exciton lifetime [126, 127] and very short (few picoseconds) valley lifetimes [128, 129].

Nonetheless, recent theoretical and experimental reports suggest that dark excitons can play an important role in...
determining the valley degree of polarization in 2D materials [116, 130, 131]. The dark exciton ground state is a huge reservoir for valley polarization. Intravalley bright and dark exciton scatterings help to maintain a Boltzmann distribution of the bright exciton states in the same valley [130]. In TMDCs, the degree of circular polarization is directly related to the alignment of bright and dark exciton states. The PL quantum yield of tungsten-based TMDCs was found to increase at higher temperatures. This observation can be explained by the presence of dark exciton states whose energy is lower than those of the bright state.

Dark excitons can be classified as spin-forbidden and momentum-forbidden dark excitons (figure 5(a)). The spin–orbit interaction removes the spin degeneracy of the CB of TMDCs, leading to different spins for CB electrons. The signs of spin for CB electrons are different for tungsten- and molybdenum-based TMDCs [132]. As a result, spin-forbidden dark excitons can be formed in such systems (figure 5(a)). The energy of the spin-forbidden dark exciton is less than that of the bright exciton in molybdenum-based TMDCs, whereas its energy is lower than that of the bright exciton in tungsten-based TMDCs. These dark states can be brightened by applying strong in-plane magnetic fields, which mix the spin-split bands through the Zeeman effect [133, 134]. The result is the relaxation of the spin-selection rule and the brightening of dark excitons. The PL of dark excitons has been demonstrated in low-temperature magneto-PL experiments. In the presence of a magnetic field, the PL spectra of WS2 monolayers exhibit a doublet structure due to the splitting of the spin-forbidden states [133]. Moreover, spin-forbidden dark excitons in WSe2 have been activated on silver surfaces through coupling to surface plasmon modes [135].

The excitons that are formed due to Coulomb interactions between electrons and holes located in different valleys are momentum-forbidden dark excitons. In tungsten-based TMDCs, dark excitons are formed from an electron in the Λ valley and a hole in the K (figure 5(a)) [136]. These excitons can emit PL through phonon-assisted radiative recombination [137]. Another way of achieving PL in these dark excitons could be exciton–molecule coupling [138]. In the presence of high-dipole molecules, the translational symmetry of the TMDCs becomes disturbed, which can enable the K → Λ transition by supplying the required momentum. Theoretical studies suggest that dark excitons can be created in the monolayer of TMDC ternary alloys (Mo1−xWxX2) [131, 139].

### 3.3. Interlayer excitons

The long valley polarization lifetime that is required in valleytronic devices can be achieved by creating interlayer excitons. In vertically stacked 2D heterostructures, even when the electrons and holes are located in different TMDC layers, interlayer excitons are formed due to the strong Coulomb interaction (figure 5(b)) [140–146]. A type-II band alignment can be seen in a certain combination of TMDCs when they are vertically stacked [146–150]. In such vertical heterostructures, interlayer charge transfer occurs because of the staggered band alignment and large band offsets [140, 141, 151]. As a result of
the absence of a depletion region in such p-n junctions, electrons and holes are primarily localized in different layers [152–154]. These excitons are stable at room temperature and do not dissociate, even in the presence of external fields, due to the high binding energies (∼100 meV) [146, 155, 156]. Interlayer excitons have been identified in several TMDC heterostructures through their PL signatures [141–143, 157, 158]. The mechanical stacking of one 2D layer on top of another causes a mismatch in the lattice constants, and a twist between the two layers of a heterostructure leads to a Moiré pattern in real space (figure 5(c)) [159, 160]. The pattern depends on the twist angle between the two layers; therefore, the optical response of the heterostructures can be controlled by tuning the relative orientation of the layers [161–163].

The CBs and VBs of the two layers of a heterostructure are different, which makes interlayer excitons momentum-space indirect. These excitons are also spatially indirect, since their constituent electrons and holes reside in different 2D layers. The result is a much longer interlayer exciton lifetime than those of the intralayer excitons in monolayers [141, 142]. The interlayer exciton lifetime in WS2-MoS2 heterostructures is an order of magnitude longer than that of intralayer excitons [141, 142]. A valley lifetime of 40 nanoseconds has been achieved by creating interlayer exciton spin-valley polarization using circularly polarized light in WS2-MoS2 heterostructures [164]. The lifetime of interlayer excitons can be increased further by making a strongly confining trap array using a WS2/WSe2 heterostructure on a patterned substrate [165]. Interlayer excitons can be generated and controlled by applying an electric field. One of the most prominent examples of this is the optical and electrical generation of long-lived neutral and charged interlayer excitons in h-BN–encapsulated vdW heterostructures of MoSe2 and WSe2 [157, 166].

Two kinds of interlayer exciton (direct and indirect) have been observed in vdW heterostructures [158]. These excitons exhibit PL lifetimes of several tens of nanoseconds. In heterostructures of monolayers of MoSe2 and WSe2, the low-energy interlayer exciton is direct both in real and reciprocal space. In contrast, the high-energy interlayer exciton is only indirect in real space [158]. The interlayer dark excitons in 2D heterostructures can survive for a very long time (∼microsecond) [167]. Such long-lived excitons are produced by magnetic-field-suppressed valley mixing and hence can be controlled by the magnetic field.

3.4. Bound excitons

Bound excitons are formed in 2D TMDCs when electrons and holes are trapped in defects that are formed due to impurities and/or strain in samples. Such defects can affect the momentum-space valley properties by localizing excitons in real space, and hence valley polarization can be controlled by manipulating defects in 2D vdW materials. PL produced by bound excitons is observed at low temperatures [168]. These emission lines are spectrally narrow and are observed below the broad PL peak corresponding to the bright excitons [169–171]. In fact, the strong single-photon emission from TMDC monolayers appears due to the existence of bound excitons [172, 173]. The narrow emission lines emitted from both CVD-grown and exfoliated samples exhibit a fine-structure doublet [169, 170, 173]. In the absence of a magnetic field, the doublet is cross-linearly polarized [170].

A large Zeeman split (much more extensive than that of intrinsic excitons) is observed in WSe2 in the presence of a transverse magnetic field (applied in the Faraday geometry) [170]. The increase of the spectral splitting of the doublet with the strength of the applied magnetic field suggests a shift of the selection rule from linearly polarized to circularly polarized [169, 173, 174]. Under a high magnetic field (>5 T), the selection rule becomes similar to that for the recombinination of excitons in a regular WSe2 lattice. In the absence of a magnetic field, the mixing of circularly polarized transitions occurs at the two valleys (K and K’), which results in two linearly polarized transitions with an energy split. The linearly polarized doublet basically originates as a result of the asymmetry of the confining potential [170]. Due to the dominance of Zeeman splitting over the exchange energy, circularly polarized selection rules become relevant for strong magnetic fields. This means that bound exciton states are probably superpositions of intrinsic valley exciton states, and hence single localized valley excitons can be exploited as a basis for valleytronics. Although bound excitons exhibit a long lifetime (∼ns) [170, 172, 173] and can be controlled by magnetic [170, 173] and optical [170, 175] fields, it may be a real challenge to manipulate valley properties by tuning defects.

3.5. Trions

Charged excitons (trions), which are three-body bound states of electrons and holes, could potentially function as carriers in valleytronics [176–178] due to their much longer valley lifetime than that of excitons [176, 178], robust valley polarization, and coupling to the additional charge [179]. There are two types of trion: bright and dark [180]. Bright trions can have an intravalley singlet state in which carriers are located within one valley, and an intervalley triplet state with an exciton is located in one valley, and a charge carrier (electron/hole) is located in another valley. The fine structure of trions appears due to the exchange interaction, which splits the energy levels of singlet and triplet trions [181]. The energy of the singlet trion state is lower than that of the triplet state [119, 182–184]. In doped semiconductors, after the recombination of the electrons and holes of negatively charged trions, the background electron gas becomes spin-polarized [185–187]. In TMDCs, the residual charge can exhibit a definitive valley index and spin orientation, and, therefore, trions can be exploited to manipulate the VDF [188, 189]. The spin and valley lifetimes of trions are generally long because the intervalley scattering of the extra charge present in trions requires the simultaneous transfer of large momentum and a spin flip. Trions in 2D TMDCs exhibit a relaxation time of tens of picoseconds, which is much longer than the ultrafast exciton relaxation time [128, 190, 191]. The chemical doping of monolayer MoS2 leads to a large increase of the trion nonradiative lifetime [192]. A recent study demonstrated that chemical doping causes the conversion of excitons into trions in WS2 monolayers, where the emission becomes
dominated by trions with a strong valley polarization [193]. As a result of chemical doping, exciton emission is strongly quenched but highly valley polarized.

The excitation caused by a linearly polarized light creates a coherent superposition state of two trion valley configurations [194]. In the first trion configuration a σ+ photon and a spin-down electron are present, whereas the second configuration consists of a σ− photon and a spin-up electron. The superposition of these trion states leads to a spin-photon entangled state, |σ+⟩|↓⟩ + |σ−⟩|↑⟩. Trion valley polarization cannot be detected through linearly polarized emission due to the orthogonal spin states. Trion valley coherence has been resonantly generated and detected in monolayer MoSe2 using 2D coherent spectroscopy (three-pulse four-wave mixing technique) [194, 195]. When an in-plane electric field is applied, an anomalous transverse motion is induced, which gives rise to the trion Hall effect [117, 196]. The intense polarization of the trion complexes in a WS2 monolayer encapsulated in hBN under an applied magnetic field suggests that magnetic fields could be used to control trion valley polarization [197]. Valley polarization in 2D TMDCs can be manipulated by modulating the electron–hole exchange interaction experienced by the exciton and trion by applying an electric field [198].

4. Some ways to detect the valley polarization

4.1. Polarization-resolved PL

The valley properties of 2D materials can be investigated by monitoring the contrast between valley pseudospins in the K and K′ valleys. Because the two valleys absorb left and right circularly polarized light differently, the basic mechanism generally used in this context is circularly polarized optical excitation [31, 33]. The valley polarization of materials that exhibit PL can be measured via the circular dichroism of their PL [199]. When this approach is used, polarization-sensitive PL measurements are carried out following the selective excitation of electrons in one of the valleys by circularly polarized light. The main aim here is to assess the k-resolved degree of optical polarization or the degree of circular polarization, which can be defined as

$$\rho = \frac{I(\sigma^+) - I(\sigma^-)}{I(\sigma^+) + I(\sigma^-)}$$

where $I(\sigma^+)$ and $I(\sigma^-)$ are the PL intensities of the right- and left-handed circular components, respectively. The intensities of the PL for the σ+ (left-handed) and σ− (right-handed) polarizations of monolayer MoS2 at a low temperature (83 K) are very different (figure 6(a)). Upon excitation by a σ+ light at 1.96 eV, monolayer MoS2 exhibits a circular polarization of ∼50% [41]. However, the reported experimental values of polarization are inconsistent [39–41, 200]. The value of ρ varies from 100% to 32% [39, 40, 200]. The helicity parameter (ρ) is intimately linked to the A-exciton PL energy. It is found to be 100% for PL energies in the range 1.90–1.95 eV and decreases to 5% for PL energies below 1.8 eV (figure 6(b)) [40]. Nonetheless, the degree of circular polarization of MoS2 decreases as a function of the photo-excitation energy and possesses a very high value for resonant excitation near the bandgap. In fact, it decreases following a power law as the excitation energy increases (figure 6(c)) [201]. Kioseoglou et al [201] proposed a phonon-assisted intervalley scattering-based model to explain the variation in the reported values of the degree of circular polarization for MoS2.

The valley polarization of monolayer WS2 has been explored through polarization-dependent PL [87, 97]. Under near-resonance conditions, the monolayer exhibits a degree of circular polarization of 40% at 10 K (figure 6(d)) [87]. The degree of circular polarization is insensitive to PL energy, but decays with increasing temperature and drops to 10% at room temperature. However, it decreases as the excitation energy changes from near-resonance to off-resonance. Interestingly, robust PL circular dichroism was observed for bilayer WS2 under both resonance and off-resonance excitations [87]. The degree of circular polarization of bilayer WS2 under near-resonant excitation is 95% at 10 K and decreases to 60% at room temperature. The robustness of the valley polarization in bilayer WS2 is the result of the coupling of spin, layer, and valley degrees of freedom. According to Nayak et al [97], the effects of shorter exciton lifetime, smaller exciton-binding energy, extra spin-conserving channels, local spin polarization, and selective valley excitation can also contribute to the robustness of circular polarization in bilayers. Moreover, high valley polarization in other monolayer TMDCs has been detected through PL measurements [85, 202].

4.2. Valley Hall effect

As discussed in the previous sections, there could be a valley-dependent Berry phase effect that leads to a valley contrasting Hall transport. The charge carriers in the K and K′ valleys turn in opposite directions perpendicular to an in-plane electric field, giving rise to the valley Hall Effect. This effect can be used to identify the valley polarization in 2D materials [36]. In the case of net valley polarization, a transverse Hall current can be generated upon the application of an in-plane electric field in a valley filter device [22]. This Hall current causes a measurable transverse voltage, which can give a local mapping of the valley polarization of the sample (figure 7(a)) [31]. The valley Hall effect (VHE) can create an electrical response in remote regions, which can be exploited to experimentally identify the presence of Hall currents [90].

Graphene has Berry curvature due to the presence of a nonzero Berry phase [203]. When the crystallographic axes of graphene and hBN are aligned, the inversion symmetry is broken, and a finite Berry curvature is developed [92, 204]. The Hall current in such a system has been detected through non-local measurements (figure 7(b)). The origin of the non-local signal in a graphene/hBN device can be considered to be a combination of the VHE and a reverse VHE. A current applied (J) between any two contacts (figure 7(b)) induces a valley current $J_{v}$ in the direction perpendicular to J. The valley current creates an imbalance in valley populations, $\delta_{v} = \mu_{K} - \mu_{K'}$ between two distant contacts ($\mu_{K}, K'$ are the chemical potentials in the valleys K and K'). As a result, a voltage
(E) response is generated due to the reverse VHE. In this scenario,
\[ J_x = \sigma_{xy}^v E, \quad E = \frac{\sigma_{xy}^v \rho_{xx}}{2e} \nabla \delta \mu, \quad (25) \]
where \( \sigma_{xy}^v \) is the valley Hall conductivity and \( \rho_{xx} \) is the longitudinal resistivity. The charge-neutral valley current can persist over extended distances in the absence of intervalley scattering and generate non-local electrical signals [205–208]. The VHE-induced non-local resistance \( R_{NL} \) can be expressed in terms of the relation [90],
\[ R_{NL} = \left( \frac{\omega}{2\xi} \right) (\sigma_{xy}^v)^2 \rho_{xx}^3 \exp(-L/\xi), \quad (26) \]
where \( L \) is the distance between the current path and the voltage probes, \( \omega \) is the device width, and \( \xi \) is a constant. Sui et al. described a method for artifact-free measurement of \( R_{NL} \) [36].

A non-zero value of \( R_{NL} \) is observed if there is valley polarization. Graphene/hBN aligned devices exhibit prominent sharp peaks of \( R_{NL} \) at the main and hole-side non-local points. However, no non-local signal has been detected in (graphene/hBN) nonaligned devices from which valley polarization is absent (figure 7(c)) or in gapless bilayer graphene (BLG) in which inversion symmetry is present (figure 7(d)). Under a transverse electric field, BLG exhibits a giant nonlocal response due to the topological transport of valley pseudospin (figures 3(d)–(g)) [36]. In BLG, the intrinsic inversion symmetry is broken by the perpendicular electric field, which results in valley polarization [76, 96, 101].

The valley polarization in TMDCs can be monitored by measuring the photoinduced anomalous Hall effect (AHE) [76]. A Hall bar device of TMDC with a long Hall probe and a short conduction channel (figure 8(a)) is used to measure the Hall effect. The reasons for this device structure are (i) to produce a photocurrent near the centre of the device, so that the Hall probe can efficiently pick up any Hall voltage and (ii) to reduce the background photovoltage generated at the metal–semiconductor contacts of the Hall probe. Circularly polarized light is shone on the Hall bar device to produce valley polarization in TMDCs through the breaking of time-reversal symmetry (figure 8(a)). The Hall voltage is measured between the A and B contacts of the Hall probe (figure 8(a)) by applying a source–drain voltage (\( V_x \)) across the short channel. A positive Hall voltage is observed for a monolayer MoS\(_2\) device for a positive bias when the polarization of the incident light is modulated from right- to left (R-L)-handed (figure 8(b)) [76]. The sign of the Hall voltage is reversed in the case of left- to right (L-R)-handed modulation of the polarization of the incident light. However, no Hall voltage is developed for linear (\( s-p \)) polarization. The photoinduced AHE in monolayer MoS\(_2\) bears the signature of net valley
polarization under polarized light. On the contrary, the AHE is completely absent from bilayer MoS$_2$ (figure 8(b)) suggesting an absence of valley polarization in bilayers due to the unbroken inversion symmetry [76]. Wavelength-dependent mapping of the VHE in a transistor (made out of TMDCs) suggests that the VHE in TMDCs arises upon illumination by light that has an energy equal to the energy of excitons or trions (figure 8(c)) [209]. The VHE in TMDCs is directly generated by trions. However, excitons break down at the interface between a metal and a semiconductor, generating free electrons and holes that result in a VHE. An intrinsic VHE has been observed without any extrinsic symmetry breaking in both monolayer and trilayer MoS$_2$, even at room temperature [210]. A very similar non-local signal due to VHE suggests that the valence band carriers mainly contribute to the VHE in monolayer and trilayer MoS$_2$. The VDF has even been identified in multilayer WSe$_2$ by probing the valley Hall effect [211]. A current is generated in the presence of a drain–source voltage as a consequence of photoinduced VHE (figure 8(d)). Valley polarization in multilayer WSe$_2$ is induced by breaking the spatial-inversion symmetry, which is achieved by applying a transverse electric field through an ionic liquid gate.

4.3. Valley Zeeman effect

Investigation of the resonance of excitons and other pseudostates in the presence of an external magnetic field is an excellent way to study the immeasurable properties of semiconductor materials. In recent years, several experiments have been developed using TMDCs in the magneto-optical domain [121, 122, 155, 212, 213]. One such experiment investigated the valley Zeeman effect, which is used to identify valley polarization in TMDCs. In the conventional Zeeman effect, a spin-dependent energy shift of the electronic energy levels takes place in the presence of an external magnetic field, thereby increasing the degeneracy. Similarly, the valley pseudospin of electrons in TMDCs can interact with an external magnetic field, producing the valley Zeeman effect.

Helicity-resolved PL in an external magnetic field has been observed in the perpendicular plane of a mechanically exfoliated TMD layer [213]. To resolve the splitting between two valley excitons, the sample was both excited and detected with the same polarized light. The splitting can be determined by
addressing one valley at a time and comparing the peak positions of the PL for different polarizations. Representative PL spectra corresponding to different values of the magnetic field, B, are shown in figure 9(a). In the case of a zero magnetic field, the PL peaks associated with both valleys, i.e. $K^+$ (blue, $\sigma^+$) and $K^-$ (red, $\sigma^-$) are identical (middle). On the other hand, under a high magnetic field ($\sim 7$ T, top), both components’ spectra are split, and $\sigma^+$ has a slightly lower energy than $\sigma^-$. In contrast, under a low magnetic field ($\sim 7$ T, bottom), the $\sigma^+$ spectral component is shifted to a higher energy than that of the $\sigma^-$ component (figure 9(c)). The observed splitting is a consequence of the d-orbital magnetic moment of tungsten and the valley magnetic moment, which is the lattice contribution to the Berry curvature [25]. Figure 9(b) shows the Zeeman splitting of the bands due to each of these two contributions. The conduction and valence bands under a zero (positive) magnetic field are denoted by dashed (solid) lines. Due to the spin splitting of $\sim 0.4$ eV in the valence band, the $K^+$ ($K^-$) valley has only the spin-up (down) state. For the CB, the splitting is small, with opposite signs in the two valleys ($\sigma^+$) and $\sigma^-$). The observed splitting is a consequence of the d-orbital magnetic moment of tungsten and the valley magnetic moment, which is the lattice contribution to the Berry curvature [25]. The g-factor is given by $\Delta_v = 2\alpha_i \tau_z \mu_B B$ (green arrow), where $\alpha_i$ is the valley g-factor.

Polarization-resolved magneto-PL and magneto-reflectance contrast measurements for the MLs of semiconducting MoTe$_2$ in magnetic fields of up to 29 T were carried out by Arora et al [214]. The $\sigma^+$ (orange) and $\sigma^-$ (blue) components of the micro-reflectance contrast ($\mu$RC) spectra were measured for monolayer MoTe$_2$ exfoliated on Si/SiO$_2$ (figure 10(a)) and sapphire substrates (figure 10(b)) under different applied magnetic fields. The $\mu$RC spectrum can be obtained from the relation [214]

$$C(\lambda) = \frac{[R(\lambda) - R_0(\lambda)]}{[R(\lambda) + R_0(\lambda)]}, \quad (27)$$

where $R(\lambda)$ and $R_0(\lambda)$ are the wavelength-dependent reflectance spectra of the TMDC layer and the bare substrate, respectively. Zeeman splitting is clearly visible in the $X_{A}^{0}$ resonance, but the line shape of the resonance remains unchanged with the variation of the magnetic field. The value of Zeeman splitting for the A and B excitons can be used to find the g-factors. For ML MoTe$_2$ on a sapphire substrate, the value of g is $-4.7 \pm 0.4$ and $-3.8 \pm 0.6$ for the A and B excitons, respectively. Polarization-resolved micro-PL spectra for monolayer MoTe$_2$ at various applied magnetic fields can be seen in figure 10(c). Zeeman splitting is clearly visible in the $X^\pm$ and $X_{A}^{0}$ transitions. The transition energies for both...
the $\sigma^+$ and $\sigma^-$ polarizations vary as a function of the magnetic field (figure 10(c)). Zeeman splitting decreases with an increase in the magnetic field (figure 10(e)). The average value of the g-factor estimated from PL measurements for neutral excitons ($A$ and $B$) are $g_{X_A} = -4.7 \pm 0.4$ and $g_{X_B} = -3.8 \pm 0.6$ for ML on sapphire substrate [214]. Valley polarization is induced in TMDCs under an external magnetic field. Although the degree of circular polarization is zero in the absence of a magnetic field, it increases to 78% and 36% for neutral and charged excitons, respectively, under a magnetic field of 29 T (figure 10(f)). Many groups have demonstrated valley polarization in TMDCs through the valley Zeeman effect [214, 217–219].

5. Achieving and controlling the valley degree of freedom in optoelectronic devices

The main challenge in developing valleytronic devices is to achieve the ability to generate and manipulate permanent valley polarization. In TMDCs, optical excitonic transitions are dependent not only on the spin DOF, but they are also associated with the valley DOF [67]. Therefore, it is possible to interconvert valley polarization with the optical polarization of emitted and absorbed photons in 2D TMDCs. This means that valley polarization can be carried from one system to another by photons. Such valleytronics devices can be realized by developing a valley-polarized optoelectronic emitter and absorber (a valley optical interconnect).

In a recent report, Zhang et al demonstrated electrically switchable multilayer and monolayer WSe$_2$ p-n junctions, which emitted circularly polarized electroluminescence (EL) based on the VDF of the material [220]. They formed the junction using electrical double-layer (EDL) gating with multilayer WSe$_2$. EDL gating provides a very large gate field due to accumulation of carriers inside the 2D channel. There are two major difficulties with multilayer TMDCs: first, they have an indirect bandgap, which is undesirable for optoelectronic device applications, and second, restored inversion symmetry decreases the circular polarization. EDL gating overcomes these difficulties, as the large gate field produces higher carrier densities in the direct gap $K$ and $K'$ valleys and breaks
inversion symmetry. Hence, the multilayer EDL transistor operates in a similar way to the monolayer TMDC transistor [221]. The EL spectra of the EDL transistor are circularly polarized and the EL intensity increases with increasing gate voltage (figure 11(a)). The degree of polarization of the EL is comparable with that of the PL in monolayer TMDCs [39, 85]. The EL polarization is affected by changes in the bias of the source and drain, i.e. when the device is operated in p–n mode (current flows from right to left), the left circularly polarized emission dominates. In contrast, it decreases in n–p mode (figure 11(a)). This behaviour can be understood in the light of the variation of the electron–hole overlap distribution in the $K$ and $K'$ valleys as the bias is reversed (figure 11(b)).

Jae Dong Lee’s research team discovered the formation of the valley magnetic domain (VMD) in TMDCs (MoS$_2$) [222]. As a result of the VMD, TMDCs can be used as semiconducting devices that differ from existing devices that only allow current to flow in one direction under the influence of an external voltage. Control of the electric current can be achieved through VMD manipulation. Reversal of the electric field direction leads to VMD switching, which can be exploited in monolayer TMDCs to realize transverse diodes. Single-bit dynamic random-access memory (DRAM) has been demonstrated using two transverse diodes (two strained MoS$_2$ ribbons) (figure 11(c)) [222]. In the write process, a far-infrared wave (FIR) falls on the ‘WRITE’ channel (the MoS$_2$ ribbon on the left), producing a transverse current that charges the capacitor, recording a ‘one’ bit (figure 11(c) left). FIR light is applied to the ‘READ’ channel (the MoS$_2$ ribbon on the right), producing a transverse current flow out of the capacitor to discharge the capacitor during the read process (figure 11(c), right). In this type of memory device, read and write processes can be performed with THz speed.

Chiral valley Hall states have been generated in between layers of oppositely gated 2D graphene [224, 225]. Such states are called kink states, and enable several in situ transmission control mechanisms. The kink states of BG can be exploited for applications in waveguides, valves, and electron beam splitters.

Optical manipulation of valley behaviours has been successfully achieved at cryogenic temperatures. Phonon-assisted intervalley scattering increases at high temperatures, resulting in volatile valley states, which reduce the handedness of PL at room temperature. Valley-optical cavity hybrid systems can be used to maintain the handedness of PL at room temperature [226]. However, control of valley properties at room temperature is still limited due to imperfect spatial and spectral overlap between excitons and optical cavities. Recently, near-unity spin polarization has been realized in 2D vdW heterostructures by reducing their carrier lifetimes [227]. Li et al demonstrated room-temperature valleytronic building blocks that play a role similar to that of transistors in electronics [228]. They generated long-lived valley-polarized carriers in MoS$_2$ under linearly polarized infrared excitation using chiral nanocrescent plasmonic antennae. The field enhancement and near-field coupling properties of surface plasmon resonance have been widely exploited to modulate the valley polarization of TMDCs. A recent review discussed the mechanisms of plasmonic modulation of valleytronic emission in TMDCs using surface plasmon polaritons and localized surface plasmons (LSPs) [229]. Wu et al reported a delicate way to manipulate quantum-information carriers—i.e. pairs of positive and negative charges confined to momentum valleys at room temperature in a monolayer WSe$_2$ [223]. The new manipulation strategy is based on the strong light–matter interactions between the valley excitons and a plasmonic chiral
metamaterial consisting of two layers of periodic Au nanohole arrays with a controllable interlayer in-plane rotation angle (θ) (figures 11(d) and (e)). Photoinduced nonreciprocity in monolayer WS₂ has been achieved by circularly polarized light, which exploited the valley-selective response of TMDCs [230]. This approach can be used to develop all-optical isolators and circulators integrated into photonic systems. Substitutional doping has also proved to be a useful approach to manipulating and improving valley polarization in 2D materials [231, 232]. The valley polarization of a MoS₂ monolayer has been improved by Re substitution, even at room temperature [231].

6. Manipulation of valley coherence

Like valley polarization, valley coherence is critically important for useful information processing applications. Manipulation of valley coherence forms the basis for controlling a single qubit in valley-based quantum information technology. Manipulation of valley coherence in 2D materials has been demonstrated in a number of previous reports [83, 84, 233, 234]. Using linearly polarized light, a coherent superposition of two states, $1/\sqrt{2}(|K\rangle + e^{-i\omega t}|K'\rangle)$ can be created at the equator of a Bloch sphere, in which ω is proportional to the energy difference between the $K$ and $K'$ valleys. Valley coherence in the Bloch sphere can be tracked by measuring the linear polarization of the PL as it is parallel to the excitation polarization. If the valley pseudospin is rotated by an angle of $\theta$ then the polarization of PL rotates by an angle $\theta/2$. The application of an electric or magnetic field can break the degeneracy between the $K$ and $K'$ states (figures 12(a) and (b)). The induced change in the transition energy of the two valleys due to external fields gives rise to a dynamic phase difference, which can cause rotation of the valley pseudospin in the equatorial plane of the Bloch sphere. Demonstrating the rotation of valley pseudospin and developing techniques to control arbitrary valley states are crucial steps towards the development of valleytronic devices. Wang et al reported that the direction of the linear polarization of PL can be rotated by applying an external magnetic field [83]. They reported a change of $27° \pm 4°$ in the phase angle under a magnetic field of 9 T. A very strong magnetic field is required to obtain stable rotation. Nonetheless, valley coherence in 2D materials can be improved by combining the effect of suppression in the exchange interaction due to enhanced dielectric screening and a reduction in the exciton lifetime due to fast interlayer transfer [89].
7. Summary and future scope

In this review, we have presented a detailed account of the origin of VDF in 2D materials with hexagonal lattices. A significant amount of experimental work has investigated valley polarization by creating charge carriers, excitons, and other quasi-particles in graphene and TMDCs. Unfortunately, these carriers of valley pseudospin are short-lived and rapidly jump between the valleys, which hinders the storage of information for a longer time. Although interlayer and defect-bound excitons have shown promise in realizing long-lived valley-selective excitons, a concerted effort will be required to identify valley carriers with long lifetimes.

Dark excitons and trions could be excellent valley carriers, as they possess long lifetimes and better valley stability than the bright excitons and trions. A dark exciton or trion can decay into a phonon–photon pair with a particular handedness, depending on the direction of the decay process. The handedness of the emitted photon can be used to read the valley indices of the dark states, but research in this direction is still in its early stages.

Despite the rapid progress in the field of generation and modulation of valley polarization and coherence, there remain significant challenges to the practical development of valleytronic devices. One critical challenge is that almost all of the valley-dependent properties discovered to date have been observed at cryogenic temperatures. Further effort will be required to generate stable valley signatures at room temperatures and to develop methods for reading the valley indices for eventual applications of valleytronic technology.

Data availability statement

No new data were created or analysed in this study.

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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 Electric field effect in atomically thin carbon films Science 306 666
[2] Lee C, Wei X, Kysar J W and Hone J 2008 Measurement of the elastic properties and intrinsic strength of monolayer graphene Science 321 385
[3] Du X, Skachko I, Duerr F, Luican A and Andrei E Y 2009 Fractional quantum Hall effect and insulating phase of Dirac electrons in graphene Nature 462 192–5
[4] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Two-dimensional gas of massless Dirac fermions in graphene Nature 438 197–200
[5] Pal S K 2015 Versatile photoluminescence from graphene and its derivatives Carbon 88 86–112
[6] Lu J-D and Chen X-S 2021 Strain-controlled valley polarization in a graphene under the modulation of a realistic magnetic field J. Supercond. Nov. Magn. 34 2545–50
[7] Avetisyan A A, Partoens B and Peeters F M 2010 Stacking order dependent electric field tuning of the band gap in graphene multilayers Phys. Rev. B 81 115432

[8] Kumar P, Herath T M and Apalkov V 2021 Ultrafast valley polarization in bilayer graphene J. Appl. Phys. 130 164301

[9] Paradisanos I et al 2020 Prominent room temperature valley polarization in WS2/graphene heterostructures grown by chemical vapor deposition Appl. Phys. Lett. 116 203102

[10] Friedlan A and Dignam M M 2021 Valley polarization in biased bilayer graphene using circularly polarized light Phys. Rev. B 103 075414

[11] Manzeli S, Ovchinnikov D, Pasquier D, Yazey O V and Kis A 2017 2D transition metal dichalcogenides Nat. Rev. Mater. 2 17033

[12] Wang H and Qian X 2017 Two-dimensional multiferroics in monolayer Si monochalcogenides 2D Mater. 4 015042

[13] Liu L, Park J, Siegel D A, McCarty K F, Clark K W, Deng W, Basile L, Idrrobo J C, Li A-P and Gu G 2014 Heteroepitaxial growth of two-dimensional hexagonal boron nitride templated by graphene edges Science 343 163

[14] Asahina H and Morita A 1984 Band structure and optical properties of black phosphorus J. Phys. C: Solid State Phys. 17 1839–52

[15] Wei K, Liu Y, Yang H, Cheng X and Jiang T 2016 Large range modification of exciton species in monolayer WS2 Appl. Opt. 55 6251–5

[16] Khan K, Tareen A K, Aslam M, Zhang Y, Wang R, Ouyang Z, Gou Z and Zhang H 2019 Recent advances in two-dimensional materials and their nanocomposites in sustainable energy conversion applications Nanoscale 11 21622–78

[17] Wang Q, Rogers E T F, Gholioup B, Wang C-M, Yuan G, Teng J and Zheludev N I 2016 Optically reconfigurable metasurfaces and photonic devices based on phase change materials Nat. Photon. 10 60–65

[18] Wu Q and Song Y J 2018 The environmental stability of large-size and single-crystalline antimony flakes grown by chemical vapor deposition on SiO2 substrates Chem. Commun. 54 9671–4

[19] Nourbaksh A, Yu L, Lin Y, Hempel M, Shiue F J, Englund D and Palacios T 2019 Beyond-CMOS Technologies for Next Generation Computer Design ed R O Topaloglu and H S P Wong (Cham: Springer International Publishing) pp 43–84

[20] Cao W, Kang J, Sarkar D, Liu W and Banerjee K 2015 2D semiconductor FETs—projections and design for Sub-10 nm VLSI IEEE Trans. Electron Devices 62 3459–69

[21] Sarkar D, Xie X, Liu W, Cao W, Kang J, Gong Y, Kraemer S, Ajayan P M and Banerjee K 2015 A subthermionic tunnel field-effect transistor with an atomically thin channel Nature 526 91–95

[22] Rycerz A, Tworzydło J and Beenakker C W J 2007 Valley filter and valley valve in graphene Phys. Rev. Lett. 98 196802

[23] Xia H, Liu G-B, Feng W, Xu X and Yao W 2012 Coupled spin and valley physics in monolayers of MoS2 and other group-VI dichalcogenides Phys. Rev. Lett. 108 196802

[24] Isberg J, Gabrys M, Hammersberg J, Majdi S, Kovi K K and Twitchen D J 2013 Generation, transport and detection of valley-polarized electrons in diamond Nat. Mater. 12 760–4

[25] Zhu Z, Collaudin A, Fauquè B, Kang W and Behnia K 2012 Field-induced polarization of Dirac valleys in bismuth Nat. Phys. 8 89–94

[26] Hao X, Ruskov R, Xiao M, Tahan C and Jiang H 2014 Electron spin resonance and spin–valley physics in a silicon double quantum dot Nat. Commun. 5 3860

[27] Sakli J, Mol J A, Rahman R, Klimicke G, Simmons M Y, Hollenberg L C L and Rogge S 2014 Spatially resolving valley quantum interference of a donor in silicon Nat. Mater. 13 605–10

[28] Orlita M and Potemski M 2010 Dirac electronic states in graphene systems: optical spectroscopy studies Semicond. Sci. Technol. 25 063001

[29] Xiao D, Yao W and Niu Q 2007 Valley-contrast physics in graphene: magnetic moment and topological transport Phys. Rev. Lett. 99 236809

[30] Gorbachev R V, Tikhonenko F V, Mayorov A S, Horsell D W and Savchenko A K 2007 Weak localization in bilayer graphene Phys. Rev. Lett. 98 176805

[31] Yao W, Xiao D and Niu Q 2008 Valley-dependent optoelectronics from inversion symmetry breaking Phys. Rev. B 77 235406

[32] Zhang Y, Tan Y-W, Stormer H L and Kim P 2005 Experimental observation of the quantum Hall effect and Berry’s phase in graphene Nature 438 201–4

[33] Grote H, Danzmann K, Dooley K L, Schnabl R, Slutsky J and Vahlbruch H 2013 First long-term application of squeezed states of light in a gravitational-wave observatory Phys. Rev. Lett. 110 181101

[34] Sui M et al 2015 Gate-tunable topological valley transport in bilayer graphene Nat. Phys. 11 1027–31

[35] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Atomically thin MoS2: a new direct-gap semiconductor Phys. Rev. Lett. 105 136805

[36] Xu K, Wang Z, Du X, Safdar M, Jiang C and He J 2013 Atomic-layer triangular WS2 sheets: synthesis and layer-dependent photoluminescence property Nanolett. 13 3459–69

[37] Zeng H, Dai J, Yao W, Xiao D and Cui X 2012 Valley polarization in MoS2 monolayers by optical pumping Nat. Nanotechnol. 7 490–3

[38] Mak K F, He K, Shan J and Heinz T F 2012 Control of valley polarization in monolayer MoS2 by optical helicity Nat. Nanotechnol. 7 494–8

[39] Cao T et al 2012 Valley-selective circular dichroism of monolayer molybdenum disulphide Nat. Commun. 3 887

[40] Vitale S A, Nezich D, Varghese J O, Kim P, Gedik N, Jarillo-Herrero P, Xiao D and Rothschild M 2018 Valleytronics: opportunities, challenges, and paths forward Small 14 1801483

[41] Feng S et al 2019 Engineering valley polarization of monolayer WS2: a physical doping approach Small 15 1805503

[42] Wu Y-C, Taniguchi T, Watanabe K and Yan J 2021 Enhancement of exciton valley polarization in monolayer MoS2 induced by scattering Phys. Rev. B 104 L121408

[43] Zhao X W, Li Y, Liang R D, Hu G C, Yuan X B and Ren J F 2020 Enhanced valley polarization at valence/conduction band in transition-metal-doped WTe2 under strain force Appl. Surf. Sci. 504 144367

[44] Bao C and Zhou S 2020 Black phosphorous for pseudospintronics Nat. Mater. 19 263–4

[45] Oliveira C, Wozniak T, Dybala F, Tolloczko A, Kopaczek J, Scharoch P and Kudrawiec R 2020 Valley polarization investigation of GeS under high pressure Phys. Rev. B 101 235205
[48] Gomes L C and Carvalho A 2020 Electronic and optical properties of low-dimensional group-IV monochalcogenides J. Appl. Phys. 128 121101

[49] Contributors W C 2020 “File: Band structure Si schematic.svg” Wikimedia Commons, the free media repository (available at: https://commons.wikimedia.org/w/index.php?title=File:Band_structure_Si_schematic.svg%26oldid=468018240Online) (Accessed 29 January 2022)

[50] Feng W, Yao Y, Zhu W, Zhou J, Yao W and Xiao D 2012 Intrinsic spin Hall effect in monolayers of group-VI dichalcogenides: a first-principles study Phys. Rev. B 86 165108

[51] Fuchs J-N 2013 Dirac fermions in graphene and analogues: magnetic field and topological properties (arXiv: 1306.0380)

[52] Li W-F, Fang C and van Huis M A 2016 Strong spin-orbit splitting and magnetism of point defect states in monolayer WSe$_2$ Phys. Rev. B 94 195425

[53] Plechinger G et al 2016 Excitonic valley effects in monolayer WSe$_2$ under high magnetic fields Nat. Lett. 16 7899–904

[54] Cong C, Shang J, Wang Y and Yu T 2018 Optical properties of 2D semiconductor WS$_2$ Adv. Opt. Mater. 6 1700767

[55] Chen S-Y, Zheng C, Fuhrer M S and Yan J 2015 Helicity-resolved Raman scattering of MoS$_2$, MoS$_2$E, WS$_2$, and WSe$_2$: atomic layers Nat. Lett. 15 2526–32

[56] Berry M V 1984 Quantal phase factors accompanying adiabatic changes Proc. R. Soc. A 392 45–57

[57] Simon B 1983 Holonomy, the quantum adiabatic theorem, and Berry’s phase Phys. Rev. Lett. 51 2167–70

[58] Son D T and Yamamoto N 2012 Berry curvature, triangle anomalies, and the chiral magnetic effect in fermi liquids Phys. Rev. Lett. 109 181602

[59] Xiao D, Chang M-C and Niu Q 2010 Berry phase effects on electronic properties Rev. Mod. Phys. 82 1959–2007

[60] Arnold’l V I 2013 Mathematical Methods of Classical Mechanics vol 60 (Berlin: Springer)

[61] Aharony Y and Bohm D 1959 Significance of electromagnetic potentials in the quantum theory Phys. Rev. 115 485–91

[62] Wang S and Wang J 2015 Spin and valley half-metal state in MoS$_2$ monolayer Physica B 458 22–26

[63] Zhou J, Shan W-Y, Yao W and Xiao D 2015 Berry phase modification to the energy spectrum of excitons Phys. Rev. Lett. 115 166803

[64] Zhou X, Su Z, Anishkin A, Haynes W J, Friskee E M, Loukin S H, Kung C and Saimi Y 2007 Yeast screens show aromatic residues at the end of the sixth helix anchor transient receptor potential channel gate Proc. Natl Acad. Sci. USA 104 15555

[65] Xiao D, Yao Y, Fang Z and Niu Q 2006 Berry-phase effect in anomalous thermoelectric transport Phys. Rev. Lett. 97 026603

[66] Schaibley J R, Yu H, Clark G, Rivera P, Ross J S, Seyler K L, Yao W and Xu X 2016 Valleytronics in 2D materials Nat. Rev. Mater. 1 16055

[67] Xu X, Yao W, Xiao D and Heinz T F 2014 Spin and pseudospins in layered transition metal dichalcogenides Nat. Phys. 10 343–50

[68] Feng W, Liu C-C, Liu G-B, Zhou J-J and Yao Y 2016 First-principles investigations on the Berry phase effect in spin–orbit coupling materials Comput. Mater. Sci. 112 428–47

[69] Tahir M and Schwingenschlögl U 2014 Tunable thermoelectricity in monolayers of MoS$_2$, and other group-VI dichalcogenides New J. Phys. 16 115003

[70] Chang M-C and Niu Q 1996 Berry phase, hyperbortis, and the Hofstadter spectrum: semiclassical dynamics in magnetic Bloch bands Phys. Rev. B 53 7010–23

[71] Sundaram G and Niu Q 1999 Wave-packet dynamics in slowly perturbed crystals: gradient corrections and Berry-phase effects Phys. Rev. B 59 14915–25

[72] Thouless D J, Kohmoto M, Nightingale M P and den Nijs M 1982 Quantized Hall conductance in a two-dimensional periodic potential Phys. Rev. Lett. 49 405–8

[73] Yao Y, Kleinman L, MacDonald A H, Sinova J, Jungwirth T, Wang D-S, Wang E and Niu Q 2004 First principles calculation of anomalous Hall conductivity in ferromagnetic bcc Fe Phys. Rev. Lett. 92 037204

[74] Cha J J and Cui Y 2012 The surface interfaces Nat. Nanotechnol. 7 85–86

[75] Semenoff G W 1984 Condensed-matter simulation of a three-dimensional anomaly Phys. Rev. Lett. 53 2449–52

[76] Mak K F, McGill K L, Park J and McEuen P L 2014 The valley Hall effect in MoS$_2$ transistors Science 344 1489–92

[77] Kumar N, He J, He D, Wang Y and Zhao H 2014 Valley and spin dynamics in MoSe$_2$: two-dimensional crystals Nanoscale 6 12690–5

[78] Zhu Y, Cheng Y C and Schwingenschlögl U 2011 Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors Phys. Rev. B 84 153402

[79] Molina-Sánchez A, Sangalli D, Hummer K, Marini A and Wirtz L 2013 Effect of spin-orbit interaction on the optical spectra of single-layer, double-layer, and bulk MoS$_2$ Phys. Rev. B 88 045412

[80] Cheiwchanchamnangij T and Lambrecht W R L 2012 Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS$_2$ Phys. Rev. B 85 205302

[81] Gong Z, Liu G-B, Yu H, Xiao D, Cui X, Xu X and Yao W 2013 Magnetoelectric effects and valley-controlled spin quantum gates in transition metal dichalcogenide bilayers Nat. Commun. 4 2053

[82] Asakura E, Suzuki M, Karube S, Nitta J, Nagashio K and Kohda M 2019 Detection of both optical polarization and coherence transfers to excitonic valley states in CVD-grown monolayer MoS$_2$ Appl. Phys. Express 12 063005

[83] Wang G, Marie X, Liu B L, Amand T, Robert C, Cadiz F, Renucci P and Urbaszek B 2016 Control of exciton valley coherence in transition metal dichalcogenide monolayers Phys. Rev. Lett. 117 187401

[84] Ye Z, Sun D and Heinz T F 2017 Optical manipulation of valley pseudospin Nat. Phys. 13 26–29

[85] Jones A M et al 2013 Optical generation of excitonic valley coherence in monolayer WSe$_2$: Nat. Nanotechnol. 8 634–8

[86] Wang G, Glazov M M, Robert C, Amand T, Marie X and Urbaszek B 2015 Double resonant Raman scattering and valley coherence generation in monolayer WSe$_2$ Phys. Rev. Lett. 115 117401

[87] Zhu B, Zeng H, Dai J, Gong Z and Cui X 2014 Anomalously robust valley polarization and valley coherence in bilayer WS$_2$: Proc. Natl Acad. Sci. USA 111 11606–11

[88] Du L et al 2019 Giant valley coherence at room temperature in 3R WS$_2$: with broken inversion symmetry Research 2019 6494565

[89] Gupta G, Watanabe K, Taniguchi T and Majumdar K 2021 Observation of perfect valley coherence in monolayer MoS$_2$ through giant enhancement of exciton coherence time (arXiv:2106.03359)

[90] Gorbachev R V et al 2014 Detecting topological currents in graphene superlattices Science 346 448–51

[91] Yankowitz M, Xue J, Cormode D, Sanchez-Yamagishi J D, Watanabe K, Taniguchi T, Jarillo-Herrero P, Jacquod P and LeRoy B J 2012 Emergence of superlattice Dirac points in graphene on hexagonal boron nitride Nat. Phys. 8 382–6
[92] Hunt B et al 2013 Massive Dirac fermions and hořfstader butterfly in a van der Waals heterostructure Science 340 1427–30

[93] Shimazaki Y, Yamamoto M, Borzenets I V, Watanabe K, Taniguchi T and Tarucha S 2015 Generation and detection of pure valley current by electrically induced Berry curvature in bilayer graphene Nat. Phys. 11 1032–6

[94] Leutenantsmeyer J C, Inglá-Aynés J, Fabian J and van Wees B J 2018 Observation of spin-valley-coupling-induced large spin-lifetime anisotropy in bilayer graphene Phys. Rev. Lett. 121 127702

[95] Barman P K, Sarma P V, Shajumon M M and Kini R N 2019 High degree of circular polarization in WS₂ spiral nanostuctures induced by broken symmetry Sci. Rep. 9 2784

[96] Lee J, Mak K F and Shan J 2016 Electrical control of the valley Hall effect in bilayer MoS₂ transistors Nat. Nanotechnol. 11 421–5

[97] Nayak P K, Lin F-C, Yeh C-H, Huang J-S and Chiu P-W 2018 Exciton physics and device applications in two-dimensional semiconductors Nat. Sci. Rev. 5 545–6

[98] Hsu W-T, Chen Y-L, Chen C-H, Liu P-S, Hou T-H, Li L-J and Chang W-H 2015 Optically initialized robust valley-polarized holes in monolayer WSe₂Nat. Commun. 6 8963

[99] Erbstedt M et al 2020 Unveiling valley lifetimes of free charge carriers in monolayer WSe₂ Nano Lett. 20 3147–54

[100] McCormick E J, Newburger M J, Luo Y K, McCreary K M, Singh S, Martin I B, Cichewicz E J, Jonker B T and Kawakami R K 2017 Imaging spin dynamics in monolayer WSe₂ by time-resolved Kerr rotation microscopy 2D Mater. 5 011010

[101] Wu S et al 2013 Electrical tuning of valley magnetic moment through symmetry control in bilayer MoS₂ Nat. Phys. 9 149–53

[102] Raja A et al 2019 Dielectric disorder in two-dimensional materials Nat. Nanotechnol. 14 832–7

[103] Qiu D Y, da Jornada F H and Louie S G 2013 Optical spectrum of MoS₂: many-body effects and diversity of exciton states Phys. Rev. Lett. 111 216805

[104] Wu F, Qu F and MacDonald A H 2015 Exciton band structure of monolayer MoS₂ Phys. Rev. B 91 075310

[105] Mahan G D 1967 Excitons in degenerate semiconductors Phys. Rev. 153 882–9

[106] Hill H M, Rigosi A F, Roquelet C, Chernikov A, Berkelbach T C, Reichman D R, Hybertsen M S, Brus L E and Heinz T F 2015 Observation of excitonic rydberg states in monolayer MoS₂ and WSe₂ by photoluminescence excitation spectroscopy Nano Lett. 15 2992–7

[107] Shi H, Yan R, Bertolazzi S, Brivio J, Gao B, Kis A, Jena D, Xing H G and Huang L 2013 Exciton dynamics in suspended monolayer and few-layer MoS₂ 2D crystals ACS Nano 7 1072–80

[108] Zhang J Z and Ma J Z 2019 Two-dimensional excitons in monolayer transition metal dichalcogenides from radial equation and variational calculations J. Phys.: Condens. Matter 31 105702

[109] Pei J et al 2015 Exciton and trion dynamics in bilayer MoS₂ Small 11 6384–90

[110] Patton B, Langebin W and Woggon U 2003 Trion, biexciton, and exciton dynamics in single self-assembled CdSe quantum dots Phys. Rev. B 68 125310

[111] Kezherashvili R Y and Tsiklauri S M 2016 Trion and biexciton in monolayer transition metal dichalcogenides Few-Body Syst. 58 18

[112] Li Z et al 2018 Revealing the biexciton and trion-exciton complexes in BN encapsulated WSe₂ Nat. Commun. 9 3719

[113] Kaviraj B and Sahoo D 2019 Physics of excitons and their transport in two dimensional transition metal dichalcogenide semiconductors RSC Adv. 9 25439–61

[114] Carvalho A, Ribeiro R M and Castro Neto A H 2013 Band nesting and the optical response of two-dimensional semiconducting transition metal dichalcogenides Phys. Rev. B 88 115206

[115] Kozawa D et al 2014 Photocarrier relaxation pathway in two-dimensional semiconducting transition metal dichalcogenides Nat. Commun. 5 4543

[116] Mueller T and Malic E 2018 Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors npj 2D Mater. Appl. 2 29

[117] Yu H, Cui X, Xu X and Yao W 2015 Valley excitons in two-dimensional semiconductors Nat. Sci. Rev. 2 57–70

[118] Yu H, Liu G-B, Gong P, Xu X and Yao W 2014 Dirac cones and Dirac saddle points of bright excitons in monolayer transition metal dichalcogenides Nat. Commun. 5 3876

[119] Ross J S et al 2013 Electrical control of neutral and charged excitons in a monolayer semiconductor Nat. Commun. 4 1474

[120] de Vivo L, Landi S, Pannilio M, Barconcilli L, Chierzi S, Marotti L, Spolidero M, Pizzorusso T, Maffei L and Ratto G M 2013 Extracellular matrix inhibits structural and functional plasticity of dendritic spines in the adult visual cortex Nat. Commun. 4 1484

[121] Srivastava A, Sidler M, Allain A V, Lembke D S, Kis A and Imanoglu A 2015 Valley Zeeman effect in elementary optical excitations of monolayer WSe₂ Nat. Phys. 11 141–7

[122] Wang G, Bouset L, Glazov M M, Amand T, Ivchenko E L, Palleau E, Marie X and Urbaszek B 2015 Magnetooptics in transition metal diselenide monolayers 2D Mater. 2 034002

[123] Stier A V, McCreary K M, Jonker B T, Kono J and Crooker S A 2016 Exciton diamagnetic shifts and valley Zeeman effects in monolayer WS₂ and MoS₂ to 65 Tesla Nat. Commun. 7 10643

[124] Sie E J, McIver J W, Lee Y-H, Fu L, Kong J and Gedik N 2015 Valley-selective optical Stark effect in monolayer WS₂ Nat. Mater. 14 290–4

[125] Kim J, Hong X, Jin C, Shi S-F, Chang C-Y S, Chiu M-H, Li L-J and Wang F 2014 Ultrafast generation of pseudo-magnetic field for valley excitons in WSe₂ monolayers Science 346 1205–8

[126] Palumbo M, Bernardi M and Grossman J C 2015 Exciton radiative lifetimes in two-dimensional transition metal dichalcogenides Nat. Phys. 11 73–7

[127] Mohamed N B, Lim H E, Wang F, Koizala S, Mouri S, Shinozaki K, Miyauchi Y and Matsuda K 2017 Long radiative lifetimes of excitons in monolayer transition-metal dichalcogenides MX₂(M = Mo, W; X = S, Se) Appl. Phys. Express 11 015201

[128] Mai C, Barrette A, Yu Y, Semenov Y G, Kim K W, Cao L and Gundogdu K 2014 Many-body effects in valleytronics: direct measurement of valley lifetimes in single-layer MoS₂ Nano Lett. 14 202–6

[129] Dal Conte S et al 2015 Ultrafast valley relaxation dynamics in monolayer MoS₂ probed by nonequilibrium optical techniques Phys. Rev. B 92 235425

[130] Baranowski M, Surrante A, Maude D K, Ballottin M, Mitoglu A A, Christianen P C M, Kung Y C, Dumcenco D, Kis A and Plochocka P 2017 Dark excitons and the elusive valley polarization in transition metal dichalcogenides 2D Mater. 4 025016

[131] Bragança H, Riche F, Qu F, Lopez-Richard V and Marques G E 2019 Dark-exciton valley dynamics in transition metal dichalcogenide alloy monolayers Sci. Rep. 9 4575
[132] Kormányos A, Burkard G, Gmitra M, Fabian J, Zólyomi V, Drummond N D and Fal’ko V 2015 k · p theory for two-dimensional transition metal dichalcogenide semiconductors 2D Mater. 2 022001

[133] Molas M R, Faugeras C, Slobodeniuk A O, Nogajewski K, Barts M, Basko D M and Potemski M 2017 Brightening of dark excitons in monolayers of semiconducting transition metal dichalcogenides 2D Mater. 4 021003

[134] Zhang X-X et al 2017 Magnetic brightening and control of dark excitons in monolayer WSe₂ Nat. Nanotechnol. 12 883–8

[135] Zhou Y et al 2017 Probing dark excitons in atomically thin semiconductors via near-field coupling to surface plasmon polaritons Nat. Nanotechnol. 12 856–60

[136] Zhang C, Chen Y, Johnson A, Li M-Y, Li L-J, Mende P C, Feenstra R M and Shih C-K 2017 Probing critical point energies of transition metal dichalcogenides: surprising indirect gap of single layer WSe₂ Nano Lett. 15 6494–500

[137] Lindlau J, Robert C, Funk V, Förste J, Förg M, Colombier L, Neumann A, Courtade E, Shree S and Taniguchi T 2017 Identifying optical signatures of momentum-dark excitons in transition metal dichalcogenide monolayers (arXiv:1710.00988) (https://doi.org/10.1038/nnano.2016.282)

[138] Feierabend M, Berghäuser G, Knorr A and Malic E 2017 Proposal for dark exciton based chemical sensors Nat. Commun. 8 14776

[139] Wang G et al 2017 Spin-orbit engineering in transition metal dichalcogenide alloy monolayers Nat. Commun. 6 10110

[140] Fang H et al 2014 Strong interlayer coupling in van der Waals heterostructures built from single-layer dichalcogenides Proc. Natl Acad. Sci. USA 111 6198–202

[141] Rivera P et al 2015 Observation of long-lived interlayer excitons in monolayer MoSe₂–WSe₂ heterostructures Nat. Commun. 6 6242

[142] Nagler P et al 2017 Interlayer exciton dynamics in a dichalcogenide monolayer heterostructure 2D Mater. 4 025112

[143] Fogler M M, Butov L V and Novoselov K S 2014 High-temperature superfluidity with indirect excitons in van der Waals heterostructures Nat. Commun. 5 4555

[144] Gao S, Yang L and Spataru C D 2017 Interlayer coupling and gate-tunable excitons in transition metal dichalcogenide heterostructures Nano Lett. 17 7809–13

[145] Hanbicki A T, Chuang H-J, Rosenberger M R, Hellberg C S, Sivaram S V, McCreary K M, Mazin I I and Jonker B T 2018 Double indirect interlayer exciton in a MoSe₂/WSe₂ van der Waals heterostructure ACS Nano 12 4719–26

[146] Kamban H C and Pedersen T G 2020 Interlayer excitons in van der Waals heterostructures: binding energy, Stark shift, and field-induced dissociation Sci. Rep. 10 5537

[147] Zheng S, Sun L, Yin T, Dubrovkin A M, Liu F, Liu Z, Shen Z X and Fan H J 2015 Monolayers of W_xMo_1-xS_2 alloy heterostructures with in-plane composition variations Appl. Phys. Lett. 106 063113

[148] Kösmider K and Fernández-Rossier J 2013 Electronic properties of the MoS₂–WSe₂ heterojunction Phys. Rev. B 87 075451

[149] Chiu M-H, Zhang C, Shiu H-W, Chou C-P, Chen C-H, Chang C-Y S, Chen C-H, Chou M-Y, Shih C-K and Li L-J 2015 Determination of band alignment in the single-layer MoSe₂/WSe₂ heterojunction Nat. Commun. 6 7606

[150] Ovseen S, Brem S, Linderälv C, Li M-Y, Mende P C, Korn T, Erhart P, Selig M and Malic E 2019 Interlayer exciton dynamics in van der Waals heterostructures Phys. Rev. Lett. 123

[151] Hong X, Kim J, Shi S-F, Zhang Y, Jin C, Sun Y, Tongay S, Wu J, Zhang Y and Wang F 2014 Ultrafast charge transfer in atomically thin MoS₂/WSe₂ heterostructures Nat. Nanotechnol. 9 682–6

[152] Ceballos F, Bellus M Z, Chiu H-Y and Zhao H 2014 Ultrafast charge separation and indirect exciton formation in a MoS₂–MoSe₂ van der Waals heterostructure ACS Nano 8 12717–24

[153] Gong Y et al 2014 Vertical and in-plane heterostructures from WSe₂/MoSe₂ monolayers Nat. Mater. 13 1135–42

[154] Ho et al 2015 Interlayer orientation-dependent light absorption and emission in monolayer semiconductor stacks Nat. Commun. 6 7372

[155] Li et al 2014 Valley splitting and polarization by the Zeeman effect in monolayer MoSe₂ Phys. Rev. Lett. 113 266804

[156] van der Donck M and Peeters F M 2018 Interlayer excitons in transition metal dichalcogenide heterostructures Phys. Rev. B 98 115104

[157] Jauregui I A et al 2019 Electrical control of interlayer exciton dynamics in atomically thin heterostructures Science 366 870–5

[158] Miller B, Steinhoff A, Pano B, Klein J, Jahnke F, Holleitner A and Wurstbauer U J et al 2017 Long-lived direct and indirect interlayer excitons in van der Waals heterostructures Nano Lett. 17 5229–37

[159] Yu H, Liu G-B, Tang J, Xu X and Yao W 2017 Moiré excitons: from programmable quantum emitter arrays to spin–orbit–coupled artificial lattices Sci. Adv. 3 e1701696

[160] Brem S, Linderälv C, Erhart P and Malic E 2020 Tunable phases of moiré excitons in van der Waals heterostructures Nano Lett. 20 8534–40

[161] Patel H, Huang L, Kim C-J, Park J and Graham M W 2019 Stacking angle-tunable photoluminescence from interlayer exciton states in twisted bilayer graphene Nat. Commun. 10 1445

[162] Wu F, Lovorn T and MacDonald A H 2018 Theory of optical absorption by interlayer excitons in transition metal dichalcogenide heterobilayers Phys. Rev. B 97 035306

[163] Zuo L et al 2017 Polymer-modified halide perovskite films for efficient and stable planar heterojunction solar cells Sci. Adv. 3 e1700106

[164] Rivera P, Seyler K L, Yu H, Schaibley J R, Yan J, Mandrus D G, Yao W and Xu X 2016 Valley-polarized exciton dynamics in a 2D semiconductor heterostructure Science 351 688–91

[165] Montblanch A R-P, Kara D M, Paradisanos I, Purser C M, Feuer M S, Alexeev E M, Stefan L, Qin Y, Biehl M and Wang G 2020 Confinement of long-lived interlayer excitons in WSe₂/WSe₂ heterostructures Commun. Phys. 4 1–8

[166] Unuchek D, Ciarrocchi A, Avsar A, Watanabe K, Taniguchi T and Kis A 2018 Room-temperature electrical control of exciton flux in a van der Waals heterostructure Nature 560 340–4

[167] Jiang C, Xue W, Rasmita A, Huang Z, Li K, Xiong Q and Gao W-B 2018 Microwave dark-exciton valley polarization memory in two-dimensional heterostructures Nat. Commun. 9 753

[168] Cadiz F et al 2017 Excitonic linewidth approaching the homogeneous limit in MoS₂-based van der Waals heterostructures Phys. Rev. X 7 021026

[169] Srivastava A, Siddler M, Allain A V, Lembke D S, Kis A and Imamoglu A 2015 Optically active quantum dots in monolayer MoS₂ ACS Nano 9 12152–6

[170] He Y-M et al 2015 Single quantum emitters in monolayer semiconductors Nat. Nanotechnol. 10 497–502

[171] Chow P K, Jacobs-Gedrim R B, Gao J, Lu T-M, Yu B, Terrones H and Koratkar N 2015 Defect-induced
photoluminescence in monolayer semiconducting transition metal dichalcogenides ACS Nano 9 1520–7

[172] Tonndorf P, Schmidt R, Schneider R, Kern J, Buscema M, Steele G A, Castellanos-Gomez A, van der Zant H S J, Michaelis de Vasconcellos S and Bratschitsch R 2015 Single-photon emission from localized excitons in an atomically thin semiconductor Optica 2 347–52

[173] Chakraborty C, Kinnischtzke L, Goodfellow K M, Beams R and Vamivakas A N 2015 Voltage-controlled quantum light from an atomically thin semiconductor Nat. Nanotechnol. 10 507–11

[174] Koperski M, Nogajewski K, Arora A, Cherkez V, Mallet P, Veuillen J Y, Marcus J, Kossacki P and Potemski M 2015 Single photon emitters in exfoliated WSe2 structures Nat. Nanotechnol. 10 503–6

[175] Kumar S, Kaczmarczyk A and Gerardot B D 2015 Strain-induced spatial and spectral isolation of quantum emitters in mono- and bilayer WSe2 Nat. Lett. 15 7567–73

[176] Singh A et al 2016 Long-lived valley polarization of intravalley trions in monolayer WSe2 Phys. Rev. Lett. 117 257402

[177] Hoshi Y, Kuroda T, Okada M, Moriya R, Masubuchi S, Watanabe K, Taniguchi T, Kitaara R and Machida T 2017 Suppression of exciton-creation annihilation in tungsten disulfide monolayers encapsulated by hexagonal boron nitrides Phys. Rev. B 95 241403

[178] Zhang X et al 2019 Defect-controlled nucleation and orientation of WSe2 on hBN: a route to single-crystal epitaxial monolayers ACS Nano 13 3341–52

[179] Wang G, Bouet L, Lagarde D, Vidal M, Balocchi A, Amand T, Marc X and Ursaszek B 2014 Valley dynamics probed through charged and neutral exciton emission in monolayer WSe2 Phys. Rev. B 90 075413

[180] Fu J, Cruz J M R and Qu F 2019 Valley dynamics of different trion species in monolayer WSe2 Appl. Phys. Lett. 115 082101

[181] Plechinger G, Nagler P, Arora A, Schmidt R, Chernikov A, Del Aguila A G, Christianen P C M, Bratschitsch R, Schüller C and Korn T 2016 Trion fine structure and coupled spin–valley dynamics in monolayer tungsten disulfide Nat. Commun. 7 12715

[182] Mak K F, He K, Lee C, Lee G H, Hone J, Heinz T F and Shan J 2013 Tightly bound trions in monolayer MoS2 Nat. Mater. 12 207–11

[183] Lui C H, Frenzel A J, Pilon D V, Lee Y H, Ling X, Akseirod G M, Kong J and Gedik N 2014 Trion-induced negative photoconductivity in monolayer MoS2 Phys. Rev. Lett. 113 166801

[184] Singh A et al 2016 Trion formation dynamics in monolayer transition metal dichalcogenides Phys. Rev. B 93 041401

[185] Dutt M V G et al 2005 Stimulated and spontaneous optical generation of electron spin coherence in charged GaAs quantum dots Phys. Rev. Lett. 94 227403

[186] Anghel S, Singh A, Fassmann F, Iwata H, Moore J N, Yusa G, Li X and Betz M 2016 Enhanced spin-polarization lifetimes in a two-dimensional electron gas in a gate-controlled GaAs quantum well Phys. Rev. B 94 035303

[187] Vanelle E, Paillard M, Marie X, Amand T, Gilliot P, Brinkmann D, Lévy R, Cibert J and Tataronko S 2000 Spin coherence and formation dynamics of charged excitons in CdTeCd1−xMgxZnxTe quantum wells Phys. Rev. B 62 2696–701

[188] Yang L, Singh S N A, Chen W, Yuan J, Zhang J, Lou J and Crooker Scott A 2015 Long-lived nanosecond spin relaxation and spin coherence of electrons in monolayer MoS2 and WSe2 Nat. Phys. 11 830–4

[189] Song X, Xie S, Kang K, Park J and Sih V 2016 Long-lived hole spin/valley polarization probed by kerr rotation in monolayer WSe2 Nano Lett. 16 5010–4

[190] Poellmann C, Steinleitner P, Leierseder U, Nagler P, Plechinger G, Poer R, Bratschitsch R, Schüller C, Korn T and Huber R 2015 Resonant internal quantum transitions and femtosecond radiative decay of excitons in monolayer WSe2 Nat. Mater. 14 889–93

[191] Zhu C R, Zhang K, Glazov M, Ursaszek B, Amand T, Ji Z W, Liu B L and Marie X 2014 Exciton valley dynamics probed by Kerr rotation in WSe2 monolayers Phys. Rev. B 90 161302

[192] Zhang W, Tanaka K, Hasegawa Y, Shinokita K, Matsuda K and Miyauuchi Y 2020 Bright and highly valley polarized trions in chemically doped monolayer MoS2 Appl. Phys. Express 13 035002

[193] Carmiggelet J J, Borst M and van der Sar T 2020 Exciton-to-trion conversion as a control mechanism for valley polarization in room-temperature monolayer WS2 Sci. Rep. 10 17389

[194] Hao K et al 2017 Trion valley coherence in monolayer semiconductors 2D Mater. 4 025105

[195] Cundiff S T, Bristow A D, Siemons Li H, Moody G, Karaiskaj D, Dai X and Zhang T 2012 Optical 2D fourier transform spectroscopy of excitons in semiconductor nanostructures IEEE J. Sel. Top. Quantum Electron. 18 318–28

[196] Ichiri A and Jaziri S 2020 Trion fine structure and anomalous Hall effect in monolayer transition metal dichalcogenides Phys. Rev. B 102 085407

[197] Kapuscinski et al 2020 Valley polarization of singlet and triplet trions in a WS2 monolayer in magnetic fields Phys. Chem. Chem. Phys. 22 19155–61

[198] Chakraborty C, Mukherjee A, Qin L and Vamivakas A N 2019 Electrically tunable valley polarization and valley coherence in monolayer WSe2: embedded in a van der Waals heterostructure Opt. Mater. Express 9 1479–87

[199] Liu S et al 2020 Room-temperature valley polarization in atomically thin semiconductors via chalcogoniode alloying ACS Nano 14 9873–83

[200] Sallen G et al 2012 Robust optical emission polarization in MoS2 monolayers through selective valley excitation Phys. Rev. B 86 081301

[201] Kioseoglou G, Hanibicki A T, Currie M, Friedman A L, Gunlycke D and Jonker B T 2012 Valley polarization and intervalley scattering in monolayer MoS2 Appl. Phys. Lett. 101 221907

[202] Tornatzky H, Kulaizt A-M and Maultzsch J 2018 Resonance profiles of valley polarization in single-layer MoS2 and MoSe2 Phys. Rev. Lett. 121 167401

[203] Ando T, Nakanishi T and Saito R 1998 Berry’s phase and absence of back scattering in carbon nanotubes J. Phys. Soc. Japan 67 2857–62

[204] Woods C R et al 2014 Commensurate–incommensurate transition in graphene on hexagonal boron nitride Nat. Phys. 10 451–6

[205] Abanin D A et al 2011 Giant nonlocality near the Dirac point in graphene Science 332 328–30

[206] Renard J, Studer M and Folk J A 2014 Origins of nonlocality near the neutrality point in graphene Phys. Rev. Lett. 112 116601

[207] Titov M et al 2013 Giant magnetodrag in graphene at charge neutrality Phys. Rev. Lett. 111 166601

[208] Abanin D A, Shytov A V, Levitov L S and Halperin B I 2009 Nonlocal charge transport mediated by spin diffusion in the spin Hall effect regime Phys. Rev. B 79 035304

[209] Ubrig N, Jo S, Philippi M, Costanzo D, Berger H, Kuzmenko A B and Morpurgo A F 2017 Microscopic...
origin of the valley Hall effect in transition metal dichalcogenides revealed by wavelength-dependent mapping Nano Lett. 17 5719–25
[210] Wu Z et al 2019 Intrinsic valley Hall transport in atomically thin MoS2 Nat. Commun. 10 611
[211] Guan H, Tang N, Huang H, Zhang X, Su M, Liu X, Liao L, Ge W and Shen B 2019 Inversion symmetry breaking induced valley Hall effect in multilayer WS2 ACS Nano 13 9325–31
[212] Zou C et al 2018 Probing magnetic-proximity-effect enlarged valley splitting in monolayer WS2 by photoluminescence Nano Res. 11 6252–9
[213] Aivazian G, Gong Z, Jones A M, Chu R-L, Yan J, Mandrus D G, Zhang C, Cobden D, Yao W and Xu X 2015 Magnetic control of valley pseudospin in monolayer WS2 Nat. Phys. 11 148–52
[214] Arora A, Schmidt R, Schneider R, Molas M R, Breslavetz I, Potemski M and Bratschitsch R 2016 Valley Zeeman splitting and valley polarization of neutral and charged excitons in monolayer MoTe2 at high magnetic fields Nano Lett. 16 3624–9
[215] Kormányos A, Zólyomi V, Drummond N D, Raktya P, Burkard G and Fal’ko V I 2013 Monolayer MoS2: trigonal warping, the Γ valley, and spin-orbit coupling effects Phys. Rev. B 88 045416
[216] Liu G-B, Shan W-Y, Yao Y, Yao W and Xiao D 2013 Three-band tight-binding model for monolayers of group-VIB transition metal dichalcogenides Phys. Rev. B 88 085433
[217] Klein J et al 2021 Controlling exciton many-body states by the electric-field effect in monolayer MoS2 Phys. Rev. Res. 3 1022009
[218] Wang T et al 2020 Giant valley-Zeeman splitting from spin-singlet and spin-triplet interlayer excitons in WS2/MoS2 heterostructure Nano Lett. 20 694–700
[219] Zühlmann S, Cummings A W, Garcia J H, Kedves M, Watanabe K, Taniguchi T, Schönnerberger C and Mak K P 2018 Large spin relaxation anisotropy and valley-Zeeman spin-orbit coupling in WS2/graphene/h-BN heterostructures Phys. Rev. B 97 075434
[220] Zhang Y J, Oka T, Suzuki R, Ye J T and Iwasa Y 2014 Electrically switchable chiral light-emitting transistor Science 344 725–8
[221] Yuan H et al 2013 Zeeman-type spin splitting controlled by an electric field Nat. Phys. 9 563–9
[222] Kim Y and Lee J D 2019 Anomalous electron dynamics induced through the valley magnetic domain: a pathway to valleytronic current processing Nano Lett. 19 4166–73
[223] Wu Z, Li J, Zhang X, Redwing J M and Zheng Y 2019 Room-temperature active modulation of valley dynamics in a monolayer semiconductor through chiral Purcell effects Adv. Mater. 31 1904132
[224] Li J, Zhang R-X, Yin Z, Zhang J, Watanabe K, Taniguchi T, Liu C and Zhu J 2018 A valley valve and electron beam splitter Science 362 1149–52
[225] Jung J, Zhang F, Qiao Z and MacDonald A H 2011 Valley-Hall kink and edge states in multilayer graphene Phys. Rev. B 84 075418
[226] Lundt N et al 2019 Optical valley Hall effect for highly valley-coherent exciton-polaritons in an atomically thin semiconductor Nat. Nanotechnol. 14 770–5
[227] Zhang D et al 2020 Room temperature near unity spin polarization in 2D Van der Waals heterostructures Nat. Commun. 11 4442
[228] Fang Y, Verre R, Shao L, Nordlander P and Käll M 2016 Hot electron generation and cathodoluminescence nanoscopy of chiral split ring resonators Nano Lett. 16 5183–90
[229] Deng M, Wang X, Chen J, Li Z, Xue M, Zhou Z, Lin F, Zhu X and Fang Z 2021 Plasmonic modulation of valleytronic emission in two-dimensional transition metal dichalcogenides Adv. Funct. Mater. 31 2010234
[230] Gudella S, Kauguschi Y, Komissarenko F, Kiriushechkina S, Vakulenko A, Chen K, Ali A, Menon V M and Khaniakae A B 2021 All-optical nonreciprocity due to valley polarization pumping in transition metal dichalcogenides Nat. Commun. 12 3746
[231] Zhu X et al 2021 Revealing the many-body interactions and valley-polarization behavior in Re-doped MoS2 monolayers Appl. Phys. Lett. 118 113101
[232] Wei X, Zhang J, Zhao B and Yang Z 2020 Coexistence of valley polarization and Chern insulating states in MoS2 monolayers with n-p coding Sci. Rep. 10 9851
[233] Molas M R et al 2019 Probing and manipulating valley coherence of dark excitons in monolayer WS2 Phys. Rev. Lett. 123 096803
[234] Rupprecht C et al 2020 Manipulation of room-temperature valley-coherent exciton-polaritons in atomically thin crystals by real and artificial magnetic fields 2D Mater. 7 035025