Orbital, spin and valley contributions to Zeeman splitting of excitonic resonances in MoSe₂, WSe₂ and WS₂ Monolayers

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Abstract
We present a comprehensive optical study of the excitonic Zeeman effects in transition metal dichalcogenide monolayers, which are discussed comparatively for selected materials: MoSe₂, WSe₂ and WS₂. We introduce a simple semi-phenomenological description of the magnetic field evolution of individual electronic states in fundamental sub-bands by considering three additive components: valley, spin and orbital terms. We corroborate the validity of the proposed description by inspecting the Zeeman-like splitting of neutral and charged excitonic resonances in absorption-type spectra. The values of all three terms are estimated based on the experimental data, demonstrating the significance of the valley term for a consistent description of magnetic field evolution of optical resonances, particularly those corresponding to charged states. The established model is further exploited for discussion of magneto-luminescence data. We propose an interpretation of the observed large g-factor values of low energy emission lines, due to so-called bound/localized excitons in tungsten based compounds, based on the brightening mechanisms of dark excitonic states.

Magneo-optical response of semiconducting transition metal dichalcogenide (sc-TMD) monolayers is commonly investigated to probe the coupling strength of effective out-of-plane angular momentum of carriers in K-valleys with external magnetic field in the limit of 2D confinement. The direct band gap character of sc-TMD monolayers [1–5] allows for a comparative study of absorption-type (reflectance and transmission) and photoluminescence processes, both related to the K-valley states. The most obvious manifestation of magnetic coupling is revealed by Zeeman-like splitting of excitonic resonances observed when the magnetic field is applied perpendicularly to the surface of the structure [6–13]. The magnitude of the splitting is a quantitative measure of magnetic-field-induced energy shifts of conduction and valence states involved in the optical transitions, however the splitting of individual electron levels remains elusive and cannot be established from most of available magneto-optical data. The Zeeman-like effect for optical resonances may act as a validity test for theoretical predictions and basic understanding of magnetic field impact on the energy of electronic states in fundamental, K-point, sub-bands [14–23]. As for now, the accuracy of developed models is rather poor, so that the explanation of even the simplest observations remains disputable. Especially elusive is the role of so-called valley term, which is responsible for band-type effects sensitive to magnetic field. Here, we aim to deepen the understanding of magneto-optical properties of sc-TMD monolayers by introducing a phenomenological description of linear-with-magnetic-field evolution of conduction and valence states involved in experimentally identified optical transitions. This simple model includes valley, spin and orbital terms treated as additive components. Three parameters related to these contributions can be estimated by comparatively analyzing polarization-resolved magneto-reflectance spectra of different representatives of sc-TMD family (MoSe₂, WSe₂ and WS₂ are considered in this work). Particularly, the examination of the resonances due
to negatively charged excitons provides information on magnetic field splitting of an individual state in the conduction band, which unambiguously demonstrates the significance of the valley term in the interpretation of experimental data and yields an estimation of its value. Further consequences arising from the introduced model are revealed by the analysis of magneto-luminescence spectra, which unveil large g-factor values of lines corresponding to bound/localized excitons combined sometimes with peculiar polarization properties.

The band-edge reflectivity spectra of sc-TMD monolayers are dominated by two robust resonances, known as A and B, which arise due to large spin–orbit splitting [24] strongly pronounced in the valence band at the K-point. Both resonances are related to free neutral exciton states and are classified according to the valence sub-band involved in the optical transition [25–32]. The lower/higher energy excitons A/B are related to transitions involving a hole from the upper/lower valence band state, respectively. Representative reflectance spectra of MoSe2, WSe2 and WS2 monolayers, measured with circular polarization resolution as a function of the external out-of-plane magnetic field, are presented in figure 1. In sc-TMD monolayers, the $\sigma^+ / \sigma^-$ circular polarization of light is used to probe optical transition in $K+/K-$ valleys, providing a remarkably simple sensitivity to valley degree of freedom [33–35].

Upon application of an out-of-plane magnetic field, the splitting between $\sigma^+ / \sigma^-$ components (defined as $E_{\sigma^+} - E_{\sigma^-} = (\mu_B B)$) appears to be equal for A and B excitons for all three materials within the experimental accuracy and the resulting g-factor values are found to be close to $g \approx -4$. Assuming that Zeeman splitting of an excitonic transition reflects the relative Zeeman shifts of corresponding single-particle subbands, the experimental observation, $g_A = g_0(\approx -4)$, represents a perceptible condition to be fulfilled by Zeeman shifts of individual electronic states. When combined with symmetric evolution of $K+/K-$ states imposed by preservation of time-reversal symmetry, the $g_A = g_0$ condition leads to a 3-term parametrization of linear-with-field contributions to the energy of fundamental conduction and valence subbands. Although different possible sets of these 3 parameters can be formally introduced, we follow here a common wisdom and assume that Zeeman shifts of all electronic subbands in the following way:

where $E_{\sigma^+}^{\pm (\rightarrow)}$ is the energy of conduction ($c$) or valence ($v$), spin-up ($\uparrow$) or spin-down ($\downarrow$) subband in $K+$ or $K-$ valleys, $\mu_B$ is Bohr magneton, $B$ stands for the strength of the magnetic field, and $g_A$, $g_S$, $g_d$ are g-factors corresponding to $E_v$, $E_S$ and $E_d$ terms, respectively. A pictorial representation of how each term independently affects the energy states in the conduction band (CB) and valence band (VB) in $K+/K-$ valleys is illustrated in figure 2. It is important to note that there exist two possible alignments of spin in the conduction spin–orbit–split subbands.

The energy distance between A and B excitons is mostly defined by a large separation of spin–orbit–split subbands in the valence band whereas a considerable smaller spin–orbit effects in the conduction band cannot be directly inferred from simple absorption/reflectance spectra. Information whether the optically bright A exciton is associated with lower or upper conduction band subband has been however supplied by extensive studies of the photoluminescence response of different sc-TMD monolayers and under various conditions (such as analysis of the spectral response to the in-plane magnetic field and including studies involving unusual configuration of the emitted light with respect to the monolayer plane). It is now rather clear that MoSe2 monolayer is a material with bright ground exciton state [36, 37], contrary to WSe2 and WS2 for which the ground exciton state is dark [37–40]. The relevant consequence of the existence of two types of materials, tentatively named as ‘bright’ and ‘darkish’, is a significant difference in g-factor value for the lower energy conduction band state. The spin and valley terms add up in ‘bright’ materials and compensate each other in ‘darkish’ materials, leading to larger magnetic-field-induced splitting of lower conduction state for ‘bright’ than ‘darkish’ materials.

In order to investigate the validity of this prediction, we will analyze the magneto-reflectance spectra focusing on charged exciton resonance (CX) (assuming it is a negatively charged state7), which appears as a weaker feature below the energy of a free neutral exciton A [42]. Typical reflectivity spectra showing CX resonance for MoSe2, WSe2 and WS2 monolayers are presented in figure 3.

We will focus on the interpretation of data for MoSe2 and WS2 materials, considering them as representatives of ‘bright’ and ‘darkish’ family. The CX resonance in WSe2 monolayer is very weak and broad in our samples, making it difficult to analyze and interpret the data unambiguously. In the absorption process leading to creation of CX, there is a single electron in...
The initial state, which at low temperature occupies the lower energy conduction band state. In such case, thermal redistribution of the occupation of this individual electronic state leads to polarization of the CX absorption resonance at higher magnetic fields. The rate of the polarization degree increase is directly indicative of the g-factor value corresponding to this individual state. In Boltzmann approximation to Fermi–Dirac statistics, which is valid if the thermal energy is larger than Fermi energy ($kT > E_F$), i.e. when the electron concentration is sufficiently small and effective mass is large, what we expect in our remotely doped monolayers, the polarization degree in external magnetic field is given by a formula:

\[
\frac{|I_{\sigma^+} - I_{\sigma^-}|}{I_{\sigma^+} + I_{\sigma^-}} = \tanh \left( \frac{g \mu_B B}{kT} \right) = \tanh \left( \frac{g_S \pm g_V}{kT} \right) \mu_B B
\]

where $I_{\sigma^+}/I_{\sigma^-}$ is the absorption strength of CX resonance detected in $\sigma^+ / \sigma^-$ polarization, respectively under excitation with linearly polarised laser light (514 nm), are shown in the energy range of free neutral exciton resonances $A$ and $B$ for (a) and (b) MoSe$_2$, (c) and (f) WSe$_2$ and (d) and (i) WS$_2$ monolayers. The energies of resonances are obtained by fitting the spectra with curves derived by transfer matrix method including Lorentzian contributions to account for excitonic resonances. The magnetic field evolution of the energy of $\sigma^+$ (red dots) and $\sigma^-$ (blue dots) components are presented for (c) and (d) MoSe$_2$, (g) and (h) WSe$_2$ and (k) and (l) WS$_2$ monolayers. The open circles represent a mean value of the energy of both components ($E_{\sigma^+} + E_{\sigma^-}$) / 2, to demonstrate that no detectable diamagnetic shift (term $\propto B^2$) is seen. The values of the g-factors for each transition, obtained by fitting the field–dependent energy $E_{\sigma^+} - E_{\sigma^-}$ with linear function $g \mu_B B$, are presented in tables.
singlet and triplet configurations of conduction electrons in ‘bright’ and ‘darkish’ materials are presented in figure 4.

The magnetic field evolution of the CX state in ‘darkish’ WS$_2$ may be accounted for if two transitions exhibiting the same g-factor value ($g_{\text{CX}} = -3.8$; same as for the neutral exciton) value and zero-field splitting of 5 meV are considered [47], in combination with polarization effects imposed by the thermal redistribution of population of the excess electron state. For the singlet state of the charged exciton, the higher energy $\sigma^-$ component accumulates the majority of oscillator strength at higher fields, contrary to the triplet state, for which the lower energy $\sigma^+$ component gets enhanced. Overall, due to small zero field splitting with respect to the linewidths of transitions (~20 meV) the CX features in ‘darkish’ WS$_2$ give impression of a single resonance, but upon closer inspection it becomes clear that both singlet and triplet CX states are involved and careful analysis allows estimation of the oscillator strength of $\sigma^+ / \sigma^-$ components (see figure 3(g)) and eventually establish g-factor of the lower energy con-

Figure 2. Scheme of the valley, spin and orbital contributions to the energies of electronic levels is presented for fundamental sub-bands relevant for the optical transitions at K point of the Brillouin zone, which are observed in absorption-type (and emission) spectra. (a) The upper panel shows the evolution of states in the conduction and valence bands, (b) the bottom panel shows the total energy variation (when all contributions are taken into account) for all states involved in optical transition, which are marked with red/blue arrows for $\sigma^+ / \sigma^-$ active optical excitations, respectively.
duction electron by describing the increase of polarization degree with aforementioned Boltzmann-type formula (see figure 3(h)). As a result, continuing the assumption of 10 K temperature of electron gas, we obtain the value of the lower conduction state $g$-factor $g = 1.08$.

In order to translate the parameters extracted from experiments into the spin and valley terms appearing in our model, we will need to make certain assumptions. One can assume, for instance, that the spin and valley $g$-factors are equal for MoSe$_2$ and WS$_2$ monolayers, which will lead to a simple linear equation:

\[
g_S - g_V = 1.08 \Rightarrow g_S = 0.38, \quad g_V = 1.46.
\]

An alternative method is to assume that the value of the spin term is the same as for a free electron in vacuum.
Experimentally estimated values of the three terms used to describe the magnetic field impact on the energy of individual states in fundamental sub-bands of sc-TMD monolayers are presented. Two approaches are used, based on different assumptions. In the first case, it is assumed that valley and spin terms are the same for MoSe₂ and WS₂ materials. In the second case, the spin term is fixed to the value of the free electron in vacuum \((g_S = 1)\). Independently of the approach, the valley term is found to provide a significant contribution to the energy of individual states and its value can be estimated to be \(g_V = 1.5 \pm 0.5\).

| Nr | Material | \(g_V\) (MoSe₂) | \(g_V\) (WS₂) | \(g_S\) (MoSe₂) | \(g_S\) (WS₂) | \(g_S + g_V\) | \(g_S - g_V\) |
|----|----------|-----------------|----------------|-----------------|----------------|---------------|---------------|
| 1  | MoSe₂   | 2.1 (exp)       | 1.9 (exp)      | 1.84 (exp)      | 1.08 (exp)     | 1.46          | 1.46          |
|    | WS₂     | 1 (assump.)     | 1.9 (exp)      | 1.84 (exp)      | 0.84           | 2.08          |

The results of both treatments of experimental data are summarized in Table 1. Although these estimations are very rough, they quite certainly indicate that the valley term is a substantial part of a cohesive description of the magneto-optical properties of TMDC monolayers and cannot be neglected.

Our description of the magnetic field evolution of the electronic states may be further exploited to shed more light onto the magneto-luminescence spectra. As demonstrated in Figure 5, the PL spectra of MoSe₂ monolayers are rather simple, showing neutral and charged exciton lines (X and CX), which split with g-factors values mimicking those observed in absorption-type spectra.

Both resonances are polarized in higher fields so that the lower energy \((\sigma^-)\) component gains in intensity, most likely due to thermal distributions of excitons between field-split states. The ‘darkish’ WS₂ and WSe₂ monolayers exhibit much more complicated PL response. The neutral and charged exciton lines (X and CX) are accompanied by a lower energy multi-peak PL band. It has been argued that the lines forming this band originate, perhaps partially, from recombination of dark exciton states via different brightening mechanisms \([37, 49, 50]\).

Table 2 presents the g-factor values for all distinguishable lines in PL spectra of MoSe₂, WSe₂ and WS₂ monolayers. Notably, the lines forming low energy band in WSe₂ and WS₂ exhibit g-factors from 4
up to 13.5 in absolute value, in most cases significantly larger than g-factors of free excitonic resonances. The origin of enhanced magnetic field splitting of lower energy PL lines in ‘darkish’ materials remains unclear.

However, our description of magnetic effects indicates that it is plausible that larger g-factors are related to recombination of dark exciton states. Conceptually, dark excitons may be brightened due to mechanisms mixing states from $K^+/K^-$ valleys hence allowing intra-valley recombination or one could consider inter-valley recombination mediated e.g. by phonons to preserve carrier momentum or defect states which are known to be particularly pronounced in ‘darkish’ TMDc mono- and multilayers [51–55]. Both types of processes are illustrated in figure 6.

Employing our estimation of parameters, we can estimate the g-factor values of such optical transitions in a following way:

$$\begin{align*}
g_{\text{inter}} &= 2 \left( g_d^2 + 2g_V \right) \approx 10 \\
g_{\text{intra}} &= 2 \left( g_d + 2g_S \right) \approx 8
\end{align*}$$

assuming the following values of our parameters: $g_d \approx 2, g_V \approx 1.5, g_S \approx 1$. Notably large g-factors (about 8) have been recently reported for intra valley dark excitons in WSe$_2$ monolayer encapsulated in hBN [56]. Our simple consideration takes into account recombination of neutral complexes. More complicated transitions could be realised with charged excitons, involving for instance shake-up process with elevation of an excess electron from lower to upper conduction band state. That could potentially lead to peculiar polarisation properties, when higher energy line gains in intensity at higher fields, as is observed, e.g. for lines A1 in WSe$_2$ monolayer and A2 in WS$_2$ monolayer (see figure 5).

In summary, we have presented a collection of magneto-optical spectra, based on reflectance and PL measurements, of three sc-TMD compounds: MoSe$_2$, WSe$_2$, and WS$_2$. This data helped us to develop a simple model of three additive terms (valley, spin and orbital contributions), which we used to describe the linear-with-magnetic-field (Zeeman) energy shifts of electronic states in fundamental conduction and valence sub-bands. We have demonstrated the significance of the valley term by analysing the magnetic-field-induced increase of polarisation degree of CX state in absorption-type spectra. Particularly, we have observed a clear signature of singlet and triplet CX states in ‘darkish’ WS$_2$ monolayers. The values of the g-factors of lower energy conduction band state obtained for MoSe$_2$ and WS$_2$ materials allowed us to estimate the value of the valley term and therefore have a tentative description of the evolution of all the electronic states involved in fundamental optical transitions. As a result of this analysis, we have proposed a reasoning, which sheds light onto the expatiation of large g-factor values for lower energy PL lines in ‘darkish’ monolayers by attribution them to dark states, which become partially allowed through various brightening mechanisms.
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Notes

The authors declare no competing financial interest.

Appendix. Materials and methods

Sample preparation by mechanical exfoliation

Monolayer MoSe2, WSe2 and WS2 flakes were obtained by mechanical exfoliation (polydimethylsiloxane-based technique [57]) of bulk crystals in 2H phase. Crystals from different sources were used including commercial suppliers (HQ Graphene). Exfoliated flakes were deposited on Si/SiO2 substrates and initially inspected under an optical microscope to determine the thickness of flakes based on their optical contrast. Eventually, the characteristic PL response from measured flakes unambiguously confirms their monolayer thickness.

Experimental setup and methods

The magneto-optical experiments were done in high magnetic field facility in Grenoble. Specially designed probes were used with resistive magnets (supplying magnetic field up to 30 T with 50 mm diameter bore) at low temperatures (via helium exchange gas) to measure reflected or emitted light from the samples. The fiber based set-up allowed focalization of the incoming light to a spot of a about ten micrometers in size. Piezo-positioners were used for x-y-z movement of the sample. A halogen lamp provided illumination for reflectance measurements and 514.5 nm Ar+ laser line for photoluminescence investigations. A quarter-waveplate followed by a polarizer was mounted in a fixed position before the detection fiber entrance to determine the detection fiber entrance helicity. The reflectivity contrast was obtained by measuring the spectra on two locations: on the flake and on the nearby Si/SiO2 substrate region, then calculated as:

\[ R(E) = \frac{R_{\text{flake}}(E) - R_{\text{substrate}}(E)}{R_{\text{flake}}(E) + R_{\text{substrate}}(E)}. \]

The reflectivity spectra were reproduced by using a transfer matrix method including Lorentzian contributions to account for resonances observed in the experimental spectra. The data were fitted with such phenomenological curves to establish the energy and oscillator strength of transitions separately in spectra measured in \( \sigma^+ / \sigma^- \) polarizations.

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References

[1] 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
[2] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim C Y, Galli G and Wang F 2010 Emerging photoluminescence in monolayer MoS2 Nano. Lett. 10 1271–5
[3] Zhao W, Ghorannevis Z, Chu L, Toh M, Kloc C, Tan P H and Eda G 2013 Evolution of electronic structure in atomically thin sheets of WS2 and WSe2 ACS Nano 7 791–7
[4] Zhang Y et al 2014 Direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial MoSe2 Nat. Nanotechnol. 9 111–5
[5] Lezama I G, Arora A, Ubaldini A, Barreteau C, Giannini E, Potekhin M and Morpurgo A F 2015 Indirect-direct band gap crossover in few-layer MoTe2 Nano. Lett. 15 2336–42
[6] Li Y et al 2014 Valley splitting and polarization by the zeeman effect in monolayer MoSe2 Phys. Rev. Lett. 113 266804
[7] Srivastava A, Sidler M, Allain A V, Lembke D S, Kis A and Imamoglu A 2015 Valley Zeeman effect in elementary optical excitations of monolayer WSe2 Nat. Phys. 11 141–7
[8] Wang G, Bouet L, Glazov M M, Ambard T, Ichenko E L, Palleau E, Marie X and Urbaszek B 2015 Magneto-optics in transition metal diselenide monolayers 2D Mater. 2 034002
[9] 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
[10] MacNeil D, Heikes C, Mak K F, Anderson Z, Kormányos A, Zólyomi V, Park J and Ralph D C 2015 Breaking of valley degeneracy by magnetic field in monolayer MoSe2 Phys. Rev. Lett. 114 037401
[11] Mitioglou A A, Plochocka P, Granados del Aguila A, Christianen P C M, Deligeorgis G, Angeli S, Kulyuk I and Maude D K 2015 Optical investigation of monolayer and bulk tungsten diselenide (WSe2) in high magnetic fields Nano. Lett. 15 4387–92
[12] 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
[13] Stier A V, McCreary K M, Jonker B T, Konjo 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
[14] Liu G-B, Xiao D, Yao Y, Xu X and Yao W 2015 Electronic structures and theoretical modelling of two-dimensional group-VIB transition metal dichalcogenides Chem. Soc. Rev. 44 2643–63
[15] Zhu Z Y, Cheng Y C and Schwinghamer D 2011 Giant spin-orbit-induced spin splitting in two-dimensional transition metal dichalcogenide semiconductors Phys. Rev. B 84 153402
[16] Ramasubramaniam A 2012 Large excitonic effects in monolayers of molybdenum and tungsten Dichalcogenides Phys. Rev. B 86 115409
[17] Xiao D, Liu G-B, Feng W, Xu Y and Yao W 2012 Coupled spin and valley physics in monolayers of MoS2, and other group-VI dichalcogenides Phys. Rev. Lett. 108 196802
2D Mater. 6 (2019) 015001

[18] Kumar A and Ahluwalia P K 2012 Electronic structure of transition metal dichalcogenides monolayers (M – MX2 (M = Mo, W; X = S, Se, Te)) from ab initio theory: new direct band gap semiconductors Eur. Phys. J. B 85 186

[19] Cheiwchanchamnanjitt T and Lambrecht W R L 2012 Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS2 Phys. Rev. B 85 205302

[20] 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 85433

[21] Kösimer K, González J W and Fernández-Rossier J 2013 Large spin splitting in the conduction band of transition metal dichalcogenide monolayers Phys. Rev. B 88 245436

[22] 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 MoS2 Phys. Rev. B 88 45412

[23] Kormányos A, Burkard G, Gmitra M, Fabian J, Zolyomy V, Drummond N D and Fal’ko V I 2015 k · p theory for two-dimensional transition metal dichalcogenide semiconductors 2D Mater. 2 22001

[24] Riley J M et al 2014 Direct observation of spin-polarized bulk bands in an inversion-symmetric semiconductor Nat. Phys. 10 835–9

[25] Wilson J A and Yoffe A D 1969 The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties Adv. Phys. 18 193–335

[26] Koperski M, Molas M R, Arora A, Nogajewski K, Slobodeniuk A O, Faugeras C and Potemski M 2017 Optical properties of atomically thin transition metal dichalcogenides: observations and puzzles Nanophotonic 6 1289

[27] Ugeda M M et al 2014 Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor Nat. Mater. 13 1091–5

[28] Chernikov A, Berkelbach T C, Hill H M, Rigosi A, Li Y, Aslan O B, Reichman D R, Hybertsen M S and Heinze T F 2014 Exciton binding energy and nonhydrogenic rydberg series in monolayer WS2 Phys. Rev. Lett. 113 076802

[29] He K, Kumar N, Zhao L, Wang Z, Mak K F, Zhao H and Shan J 2014 Tightly bound excitons in monolayer WS2 Phys. Rev. Lett. 113 026803

[30] Zhu B, Chen X and Cui X 2015 Exciton binding energy of monolayer WS2 Sci. Rep. 5 9218

[31] Hill H M, Rigosi A F, Rosquelet C, Chernikov A, Berkelbach T C, Reichman D R, Hybertsen M S, Brus L S and Heinze T F 2015 Observation of excitonic rydberg states in monolayer MoS2 and WS2 by photoluminescence excitation spectroscopy Nano Lett. 15 2992–7

[32] Chernikov A, van der Zande A M, Hill H M, Rigosi A F, Velauchapillai A, Hone J and Heinze T F 2015 Electrical tuning of exciton binding energies in monolayer WS2 Phys. Rev. Lett. 115 126802

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

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

[35] Smolenski T, Goryca M, Koperski M, Faugeras C, Kazimierczuk T, Bogucki A, Nogajewski K, Kossacki P and Potemski M 2016 Tuning valley polarization in a WSe2 monolayer with a tiny magnetic field Phys. Rev. X 6 021024

[36] Arora A, Nogajewski K, Molas M, Koperski M and Potemski M 2015 Exciton band structure in layered MoSe2 from a monolayer to the bulk limit Nanoscale 7 20769–75

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

[38] Ye Z, Cao T O, Brien K, Zhu H, Yin X, Wang Y, Louie S G and Zhang X 2014 Probing excitonic dark states in single-layer tungsten disulphide Nature 513 214–8

[39] Zhang X-X, You Y, Zhao SY F and Heinz T F 2015 Experimental evidence for dark excitons in monolayer WSe2 Phys. Rev. Lett. 115 257403

[40] Arora A, Koperski M, Nogajewski K, Marcus J, Faugeras C and Potemski M 2015 Excitonic resonances in thin films of WSe2: from monolayer to bulk material Nanoscale 7 10421–9

[41] Jones A M et al 2013 Optical generation of excitonic valley coherence in monolayer WSe2 Nat. Nanotechnol. 8 634–8

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

[43] Boulesbaa A et al 2015 Observation of two distinct negative triions in tungsten disulphide monolayers Phys. Rev. B 92 115443

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

[45] Plechinger G, Nagler P, Arora A, Schmidt R, Chernikov A, Granados del Águila A, Christianen P C M, Bratschitsch R, Schüller C and Korn T 2016 Trion fine structure and coupled spin–valley dynamics in monolayer tungsten disulphide Nat. Commun. 7 12271

[46] Courtade E et al 2017 Charged excitons in monolayer WSe2: experiment and theory Phys. Rev. B 96 085302

[47] Vlačivkova D, Wyzula J, Nogajewski K, Bartos M, Slobodeniuk A O, Faugeras C, Potemski M and Molas M R 2018 Singlet and triplet triions in WS2, monolayer encapsulated in hexagonal boron nitride Nanotechnology 29 325705

[48] Molas M R, Nogajewski K, Slobodeniuk A O, Binder J, Bartos M and Potemski M 2017 The optical response of monolayer, few-layer and bulk tungsten disulphide Nanoscale 9 13128–41

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

[50] Slobodeniuk A O and Basko D M 2016 Spin–flip processes and radiative decay of dark intravalley excitons in transition metal dichalcogenide monolayers 2D Mater. 3 035009

[51] 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

[52] Srivastava A, Siddur M, Allain A V, Lemke D S, Kis A and Imamoglu A 2015 Optically active quantum dots in monolayer WSe2 Nat. Nanotechnol. 10 491–6

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

[54] Chakraaborty C, Kinnschitzke L, Goodfellow K M, Beams R and Vamvakas A N 2015 Voltage-controlled quantum light from an atomically thin semiconductor Nat. Nanotechnol. 10 507–11

[55] Lindlau J et al 2018 Identifying optical signatures of momentum–dark excitons in transition metal dichalcogenide monolayers (arXiv:1710.00988)

[56] Robert C, Amand T, Cadiz F, Lagarde D, Courtade E, Manca M, Taniguchi T, Watanabe K, Urbaszek B and Marie X 2017 Fine structure and lifetime of dark excitons in transition metal dichalcogenide monolayers Phys. Rev. B 96 155423

[57] Castellanos-Gomez A, Buscema M, Molenar R, Singh V, Janssen L, van der Zant H S J and Steele G A 2014 Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping 2D Mater. 1 011002