Fine structure of negatively charged and neutral excitons in monolayer MoS$_2$

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Abstract. We present experimental and theoretical results on the high-quality single-layer MoS$_2$ which reveal the fine structure of charged excitons, i.e., trions. In the emission spectra we resolve and identify two trion peaks, $T_1$ and $T_2$, resembling the pair of singlet and triplet trion peaks ($T_S$ and $T_T$) in tungsten-based materials. However, in polarization-dependent photoluminescence measurements we identify these peaks as novel intra- and inter-valley singlet trions, constituting the trion fine structure distinct from that already known in bright and dark 2D materials with large conduction-band splitting induced by the spin-orbit coupling. We show that the trion energy splitting in MoS$_2$ is a sensitive probe of inter- and intra-valley carrier interaction. With additional support from theory we claim that the existence of these singlet trions combined with an anomalous excitonic g-factor and the characteristic temperature dependence of the emission spectra together suggest that monolayer MoS$_2$ has a dark excitonic ground state, despite having ”bright” single-particle arrangement of spin-polarized conduction bands.

Keywords: transition metal dichalcogenides monolayers, molybdenum disulfide, exciton, trion, Zeeman g-factor
1. Introduction

Monolayer transition metal dichalcogenides (TMDs) have attracted considerable scientific interest due to their unique physical properties [1, 2, 3], such as direct optical bandgaps located at $K^\pm$ valleys of two dimensional (2D) hexagonal Brillouin zone [4] and coupling of spin and valley degrees of freedom [5]. Their 2D nature and reduced dielectric screening enable formation of excitons with binding energies of few hundreds of meV [6], orders of magnitude larger than those in typical quasi-2D quantum wells [7, 8]. In addition to neutral excitons, in the presence of excess carriers, also trions can be formed [9, 10, 11, 12, 13, 14] with binding energies ($E_b$) of tens of meV, resulting in their stability even at room temperatures [15, 16, 17]. Consequently, the monolayer TMDs constitute a novel platform to optically probe many-body effects in the presence of strong Coulomb interactions [11, 18, 19, 20, 21, 22], particularly when Fermi level in conduction band for n-doped samples is lower or of the same order as the trion binding energy [23, 24, 25].

Monolayer MoS$_2$ is probably the best-known member of semiconducting TMDs [26], due to its natural abundance in almost chemically pure mineral molybdenite [27]. Compared to other materials from the MX$_2$ (M = Mo, W; X = S, Se, Te) family, MoS$_2$ is unique in that the spin splitting of the conduction band is small, $\sim$ 3 meV [28], in comparison to typical Fermi energies in n-type exfoliated TMDs monolayers (ML) transferred onto standard SiO$_2$/Si substrate [3, 29]. Until recently, the optical quality of monolayer MoS$_2$ was inferior in quality to the related materials, such as MoSe$_2$, WS$_2$, and WSe$_2$. This allowed to observe in photoluminescence only broad peaks, dominated by trions [15]. However, progress was made by encapsulation of a MoS$_2$ monolayer with hexagonal boron nitride (hBN) layers, resulting in observation of narrow neutral exciton lines, with bandwidth approaching 2 meV at low temperatures (4 K) [30]. The high-quality MoS$_2$/hBN van der Waals heterostructures hence enabled the observation of subtle optical and spin-valley properties of monolayer MoS$_2$ [30, 31, 25].

Recent works reported splitting of trion in the presence of carriers in gated nanostructures [25], similar to other "dark" TMDs [32]. Within a trion model, inter- and intra-valley singlet and triplet trion nature of these split lines was suggested [23], with splitting energy $\sim$ 5 meV. Contrary to those calculations, triplet trion in MoS$_2$ was shown to be unbound in reference [33], predicting intra-/inter-valley singlet-singlet splitting $\sim$ 4 meV. Interestingly, small values of an effective exciton g-factor in hBN encapsulated MoS$_2$ monolayers, $g = -1.7$ in magneto-photoluminescence experiments [30] and $g = -3.0$ in magneto-transmission measurements [31] have also been observed. Furthermore, the detailed magneto-transmission experiments have revealed that reduced mass of exciton in monolayer MoS$_2$ is heavier than predicted by density functional theories [28, 34], suggesting large electron mass consistent with recent values determined from transport studies of n-type MoS$_2$ monolayers [35]. Complicated interplay of band structure [28, 36], electron-electron interactions [11, 24, 37, 38], enhanced spin-splitting [39], dynamical effects [40] and inter-/ intra-valley phonon [41] and plasmon [20]
contributions makes MoS$_2$ one of the most challenging systems to understand.

![Figure 1](image)

**Figure 1.** The comparative PL and RC spectra for (a) MoS$_2$/hBN, (b) MoSe$_2$/hBN, (c) WS$_2$/hBN, (d) WSe$_2$/hBN structures measured at 7 K.

2. PL and RC measurements of MX$_2$

As a first step toward this understanding we present results of photoluminescence (PL) and reflectance contrast (RC) measurements of Mo- and W-based monolayer TMDs. Figure 1a-d compares low temperature (7 K) PL and RC spectra of molybdenum and tungsten based TMDs monolayers deposited on hBN/SiO$_2$/Si substrate. The PL spectra are excited non-resonantly at energy of 2.33 eV. For all monolayers, the optical transitions are associated with the nearly free states of the neutral exciton (X) [16] and different types of trions (T$_1$, T$_2$, T$_S$, T$_T$) [42, 43]. In all spectra the energies are measured from exciton energy. In figure 1a we show PL and RC spectra for MoS$_2$ while figure 1b shows the same spectra for MoSe$_2$. Interestingly, in the PL spectrum of MoS$_2$ we see an exciton peak and two, T$_1$ and T$_2$, peaks at lower energy. As seen in figure 1a) the energy separation between these optical transitions is $\Delta \approx 10$ meV. We attribute them tentatively to recombination from trion states. The MoS$_2$ spectra are to
be contrasted with an exciton and a single trion \( T_1 \) line in the spectra of MoSe\(_2\), shown in figure 1(b). However, the doublet structure of the trion emission line positioned below the neutral exciton in MoS\(_2\) is similar to trion emission spectra in tungsten based monolayers, shown in figure 1(c-d). In the PL and RC spectra of WS\(_2\) (figure 1(c)) and WSe\(_2\) (figure 1(d)), the \( T_S \) and \( T_T \) optical transitions are identified at low doping level \((E_F << E_B)\). The energy difference between \( T_S \) and \( T_T \) is equal to \( \sim 6 \) meV, and is in good agreement with the recently reported values \([43]\). As seen in figures 1(c) and 1(d), the \( T_T \) emission line in the PL spectra of WSe\(_2\) is relatively more prominent than the corresponding optical transition observed in the PL spectra of WS\(_2\). This feature likely depends on the different two-dimensional electron gas (2DEG) concentration in studied monolayers, which in sulfides is typically two orders of magnitude higher than in selenides \([29, 44]\). In contrast, in the PL and RC spectra of MoSe\(_2\) (figure 1(b)) the double trion structure is not detected, with only single line \( T_1 \) visible.

**Figure 2.** Summary of optically bright trion possibilities in MX\(_2\). (a) Inter- and (b) intra- valley singlet-singlet trions in material with small CB spin splitting and dark exciton ground state. (c) Inter- and (d) intra- valley triplet-singlet trions in material with dark bands and dark exciton ground state. (e) Trion in compounds with bright bands arrangement and bright exciton ground state.

### 3. Theoretical considerations

Our interpretation of two emission lines resolved in the spectra of MoS\(_2\), shown in figure 1(a), as originating from two trion states, \( T_1 \) and \( T_2 \), is summarized in figures 2(a-b). Figure 2(a) shows schematically an electronic configuration for inter-valley singlet trion \( T_2 \), with one spin up electron in valley +\( K \), second electron with spin down and a spin down missing valence band electron (valence hole) in valley −\( K \). The left column, single particle states in valley +\( K \), correspond to positive spin-orbit splitting of the conduction band spin states and optically active single particle transitions. The right column shows electron configurations including electron-electron interactions. It is important to observe that in this picture the energy of the spin down −\( K \) valley electron is above the spin up empty electron state, there is an inversion of the order of electron states and the lowest energy state is dark. We now explain \([45]\) this bright-dark
Fine structure of negatively charged and neutral excitons in monolayer MoS$_2$

ground excitonic state inversion shown in figure 2(a). The first mechanism is related to different masses of spin up and down electrons in the conduction band. The higher energy spin up conduction band in the $-K$ valley is heavier, hence the higher electron mass combined with electron-hole attraction results in more strongly bound dark state, pushing the electron-hole bright configuration up in energy. The second contribution adding to the blue shift of the energy of the bright configuration is the repulsive electron-hole exchange interaction. The two effects combine, resulting in splitting of bright-dark 1s excitons up to 9 meV. Figure 2(b) shows the configuration of intra-valley trion where two electrons in the CB are in the same $-K$ valley and hence necessarily in the singlet state. Hence both trions T$_1$ and T$_2$ are bright singlet trions and the lowest energy trion is also dark.

The unusual arrangement of trion states in material with positive and small spin-orbit induced splitting of the conduction band is to be contrasted with trion states in materials with negative and large spin-orbit induced splitting of the conduction band such as WS$_2$ and WSe$_2$, shown in figure 2(c,d). Note that in figure 2(c,d) the single particle arrangement of levels (left panel, valley +$K$) is opposite to level arrangement in figure 1(a,b). There is no inversion of electronic levels for electron in the presence of valence hole in valley $-K$. Hence the T$_T$ trion is a triplet and the lowest energy inter-valley trion is dark. The T$_S$ trion is a singlet trion, as T$_1$ in MoS$_2$. The observation of the doublet structure of bright higher energy trions (T$_S$, T$_T$) in WSe$_2$ and WS$_2$ monolayers results from the fact that in tungsten based monolayers the optically active exciton (X) is associated with the top spin-split valence band (VB) sub-band and the upper spin-split conduction band (CB) sub-band. Hence, for low two-dimensional electron gas concentration, as the electron Fermi level is positioned between spin-split conduction bands, the triplet trion (figure 2(c)) comprises two electrons from different valleys [16], whereas singlet trion must involve two electrons from the same valley (figure 2(d)). Additionally, in the simplest case of only one charged complex, the T$_1$ trion in MoSe$_2$ (figure 1(b)) is formed from the optically active exciton (X) associated with the top spin-split valence band (VB) subband and the lower spin-split conduction band (CB) subband, see figure 2(e). Accordingly, for the low 2DEG concentration and Fermi level positioned close to the lower spin split conduction band, the singlet trion should involve two electrons from the different valley forming the inter-valley spin singlet trion (T$_S$) with two electrons located in the lower conduction bands.

Hence attribution of T$_2$ (figure 2(a)) and T$_1$ (figure 2(b)) emission features in MoS$_2$ to the inter-valley and intra-valley bright singlet trions instead of singlet-triplet trions is related to the relatively smaller, compared with WS$_2$ or WSe$_2$ monolayers, spin-splitting and Fermi level in the conduction band. We note that inter-valley triplet trion in such band arrangement is not only less probable due to Fermi level position, but was also predicted to be unbound due to exchange interaction [33].
Fine structure of negatively charged and neutral excitons in monolayer MoS$_2$

4. Polarization-resolved PL excitation of trions in monolayer MoS$_2$

To firmly establish the singlet nature of the T$_1$ and T$_2$ transitions observed in the PL spectra of monolayer MoS$_2$, we perform polarization-resolved and excitation energy-dependant PL measurements at $T = 7$ K. Figure 3 shows the examples of polarization-resolved PL spectra excited strictly-resonantly at the neutral exciton energy of 1.9514 eV (figure 3(a)) and near-resonantly at the energy of 1.9730 eV (figure 3(b)). We observe also the Raman features, which shift as function of the excitation energy and are attributed to the first- and second-order scattering processes, such as $A'_1$, $E'$ modes and $b$, 2LA ($M$) or LA ($M$) bands, respectively [47, 48]. The presence of the LA($M$) band in the Raman scattering spectrum is likely due to defects or disorder in the sample which localizes phonons [47]. Next we analyze the optical orientation of trions, i.e. the helicity of the outgoing light with respect to the helicity of the excitation light. Based on the fitting of trion contributions to the PL spectrum excited at neutral exciton energy X (figure 3(a)) with a combination of two Lorenz curves, we determine the degree of helicity preservation of the emitted light with respect to exciting light defined as $P = (I_{\sigma+\sigma} - I_{\sigma-\sigma})/(I_{\sigma+\sigma} + I_{\sigma-\sigma})$ for each trion component, where $\sigma^+\sigma^+$ and $\sigma^+\sigma^-$ indicate the co-circular and cross-circular configurations, respectively. The T$_1$ line displays the $P_{T_1}$ value of almost 66%, while the T$_2$ line has a slightly higher $P_{T_2}$, of about 72%. For the excitation energy equal to 1.9730 eV (slightly higher than the energy of X) we obtain P values of 44%, 46% and 49% for T$_1$, T$_2$ and X, respectively (figure 3(b)). In monolayer TMDs, the large exciton valley polarization obtained in the steady-state PL experiments results from the competition between the valley depolarization time ($\sim 1$ ps) and the ultra-fast exciton population relaxation time ($\sim 100 - 200$ fs) [49, 50]. However, the trions exhibit an extended population relaxation time of tens of
picoseconds. It has been established in recent work [51], that the most efficient scattering mechanism responsible for the trion valley depolarization in WSe₂ is due to scattering of an electron-hole pair between valleys. This process is mediated by the electron-hole exchange interaction towards an energetically favorable trion state. In contrast to tungsten based TMDs, where the preservation of helicity of the excitation light in the emission spectrum of T₁ and T₂ trions is significantly different, e.g. about 16% and 50% in steady-state PL measurements of monolayer WS₂ [43], in monolayer MoS₂ both values are comparable, supporting interpretation of both trion lines as originating from trion singlets.

5. Trion in MoS₂ in magnetic field

To further emphasize different character of T₁ and T₂ lines in MoS₂ compared to WX₂, let us discuss magneto-optical response observed in the PL spectra measured at T = 5 K. Using non-resonant (2.331 eV) and linearly polarized laser excitation we find that at zero magnetic field the trion lines are equally strong for both σ⁺ and σ⁻ polarization detections, and hence they are not well resolved (figure 4(a)). However, upon applying the external magnetic field to 10 T, the T₁ and T₂ lines shift spectrally away from one another, which is emphasized in figure 4(b). This energy shift is consistent with the valley Zeeman effect. As seen in figure 4(b), the T₁ resonance is much more prominent for σ⁺ configuration in B = 10 T (correspondingly σ⁻ in B = −10 T). Even though trion features are broad and hence difficult to analyze, we fit the trion fine structure at
\[ B = +10 \text{ T} \] using Lorentz functions, as shown on figure 4(b). For this purpose, we take into account two assumptions: (1) at \( B = 10 \text{ T} \) the \( T_1 \) and \( T_2 \) lines are separated by at least 12−13 meV, which is consistent with the energy difference of \( \Delta = 10 \text{ meV} \) at zero magnetic field, (2) the linewidths of \( T_1 \) and \( T_2 \) are 20 meV and for both \( \sigma^+ \) and \( \sigma^- \) polarizations remain the same.

From the extracted Zeeman splitting \( (E_{\sigma^+} - E_{\sigma^-}) \) of \( T_1 \) and \( T_2 \) transitions equal to 2.8 meV and 2.1 meV, respectively, we calculate effective \( g \)-factors of \( g_1 = -4.8 \) and \( g_2 = -3.6 \), accordingly. We can therefore attribute \( T_1 \) and \( T_2 \) emission lines to the inter-valley and intra-valley bright singlet trions, respectively, due to nearly similar \( g \)-factors, which should be much different if \( T_1 \), \( T_2 \) were singlet-triplet, as discussed in reference [32].

6. Trion splitting as a measure of correlations

Having established singlet nature of \( T_1 \) and \( T_2 \) trions, we comment on processes determining their energy splitting. The difference of total energy of \( T_1 \) and \( T_2 \) configurations \( E_{T_1} - E_{T_2} = \Delta_{SOC} + V^* \), can be written as a sum of conduction band spin splitting \( \Delta_{SOC} \) and electron-electron interactions, \( V^* \). \( V^* \) reflects subtle imbalance between electron-hole and electron-electron interactions inside and between valleys. Simple analysis leads to expression

\[
V^* = \left[ V^D(e_1, +K; e_2, +K) - V^D(h_1, +K; e_2, +K) \right] + \left[ V^D(e_1, +K; e_2, -K) - V^D(h_1, +K; e_2, -K) \right],
\]

where \( e_{1,2} (h_1) \) describe electrons (hole) forming trion (see figure 2(a)) and \( V^D \) is the total direct interaction energy between particles. We see that \( V^* \) is the sum of two contributions, a difference between the electron-electron repulsion and electron-hole attraction in the same valley and between valleys. Interestingly, similar analysis of singlet-triplet trion splitting in tungsten-based materials leads to \( E_{T_3} - E_{T_T} = V^X(e_1, +K; e_2, -K) + V^* \), suggesting energy of singlet-singlet splitting is a new measure for electronic correlations in 2D crystals with small spin-orbit splitting in conduction bands.

7. Zeeman g-factor and temperature dependencies supporting dark X ground state

In figure 4(c) we extracted Zeeman splitting \( \Delta_Z \) of the neutral exciton X, defined as the shift between the \( \sigma^+ \) and \( \sigma^- \) polarized components of the PL \( \Delta_Z = E_{\sigma^+} - E_{\sigma^-} = g\mu_B B \).

This quantity depends linearly on the magnetic field and our measurement suggest exciton g-factor of \( g_X = -1.39 \pm 0.01 \). Furthermore, we probed temperature dependence of a exciton effective g-factor in the reference high quality hBN-encapsulated MoS\(_2\) sample, which emission spectra were dominated only by a sharp X line. Figure 5(a) compares typical PL spectra of hBN-encapsulated monolayer MoS\(_2\) measured at different temperatures (5 K, 20 K, 40 K, 60 K) and magnetic field of \( B = 10 \text{ T} \). The exciton
Zeeman splitting at four different temperatures is shown in figure 5(b). As seen in figure 3(c), the absolute value of the exciton g-factor increases from 1.15 to 1.74 for increasing temperature from 5 K to 60 K. This increase of exciton g-factor by about 34% is related to the temperature broadening of the X emission line (see figure 5(a)). However, it also can result from different thermal distributions of electrons in spin split sub-bands. Our results are consistent with previously reported studies of high quality hBN-encapsulated MoS₂ monolayers with very narrow exciton linewidths (2-4 meV), showing exciton g-factor of \( g_X = -1.7 \) [30]. It is worth noting that the Zeeman splitting, and hence g-factors, appear to depend on the overall optical quality of the sample (doping level), which in turn can be reflected by the linewidth of the PL or RC transitions. However, in comparison to other monolayer TMDs [31, 52], the small exciton Zeeman splitting in monolayer MoS₂ may arise from the interaction with close, spin- and valley-forbidden, dark excitons.

8. Temperature dependence of PL spectra in monolayer MoS₂

To establish arrangement of those excitonic bright and dark states, we analyze the temperature evolution of PL spectra for two MoS₂ flakes exhibiting different doping level. Different 2DEG concentration in the studied samples was estimated qualitatively on the basis of a shape of the PL spectra, i.e. the presence of the trion emission. Figures 6(a) and 6(b) show typical PL spectra of MoS₂/hBN structure (without the hBN cap) and hBN-encapsulated one layer MoS₂, respectively, measured in temperature range \( T = 7 - 300 \) K. The comparative analysis of the integrated emission intensities of excitons (X) and trions (T) as a function of the temperature is shown in figure 6(c). Interestingly, in the MoS₂/hBN structure the PL intensity of X line (orange triangles)
decreases 50 times at temperatures from 7 K to 240 K, whereas the average PL intensity of trions T (orange stars) shows an initial and subtle increase up to 60 K and a further decrease at high temperatures. This is in contrast to recent report [53], where emission intensity of trion decreases with rising temperature. It is likely due to different 2DEG concentration in the studied sample, also revealed by prominent trion emission which exceeds that of neutral exciton [53]. However, it is worth to note that the total PL intensity in our MoS$_2$/hBN structure decreases only 4 times. In the hBN-encapsulated sample, for which we observe only X line reflecting the total PL intensity, it decreases 6 times in temperature range from 7 K to 300 K. Even though, e.g., the total PL intensity of X line decreases (4 and 6 times for MoS$_2$/hBN and hBN/MoS$_2$/hBN structures, respectively) with increasing temperature, suggesting bright excitonic ground state [54], we conclude that general trend is more consistent with similar measurements in tungsten based materials [16], again supporting our interpretation that MoS$_2$ has excitonic dark ground state despite ”bright” conduction bands arrangement.

9. Conclusions

In summary, we present experimental and theoretical results on the high-quality single-layer MoS$_2$ which reveal the fine structure of charged excitons, i.e., trions. In the emission spectra we resolve and identify two trion peaks, T$_1$ and T$_2$, resembling the
pair of singlet and triplet trion peaks ($T_S$ and $T_T$) in tungsten-based materials. In polarization-dependent photoluminescence measurements we identify these peaks as novel intra- and inter-valley singlet trions, constituting the trion fine structure distinct from that already known in bright and dark 2D materials with large conduction-band splitting induced by the spin-orbit coupling. With additional support from theory we claim that the existence of these singlet trions combined with an anomalous excitonic g-factor and the characteristic temperature dependence of the emission spectra together suggest that monolayer MoS$_2$ has a dark excitonic ground state, despite having "bright" single-particle arrangement of spin-polarized conduction bands.

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References

[1] Andre K Geim and Irina V Grigorieva. Van der Waals heterostructures. *Nature*, 499(7459):419, 2013.
[2] Kin Fai Mak, DI Xiao, and Jie Shan. Lightvalley interactions in 2D semiconductors. *Nature Photonics*, 12:451, AUG 2018.
[3] Gang Wang, Alexey Chernikov, Mikhail M. Glazov, Tony F. Heinz, Xavier Marie, Thierry Amand, and Bernhard Urbaszek. Colloquium: Excitons in atomically thin transition metal dichalcogenides. *Rev. Mod. Phys.*, 90:021001, Apr 2018.
[4] Kin Fai Mak, Changgu Lee, James Hone, Jie Shan, and Tony F. Heinz. Atomically thin MoS$_2$: A new direct-gap semiconductor. *Phys. Rev. Lett.*, 105:136805, Sep 2010.
[5] Di Xiao, Gui-Bin Liu, Wanxiang Feng, Xiaodong Xu, and Wang Yao. Coupled spin and valley physics in monolayers of MoS$_2$ and other group-VI dichalcogenides. *Phys. Rev. Lett.*, 108:196802, May 2012.
[6] Diana Y. Qiu, Felipe H. da Jornada, and Steven G. Louie. Optical spectrum of MoS$_2$: Many-body effects and diversity of exciton states. *Phys. Rev. Lett.*, 111:216805, Nov 2013.
[7] R. Dingle, W. Wiegmann, and C. H. Henry. Quantum states of confined carriers in very thin Al$_x$Ga$_{1-x}$As-GaAs-Al$_x$Ga$_{1-x}$As heterostructures. *Phys. Rev. Lett.*, 33:827–830, Sep 1974.
[8] J. Jadczak, L. Bryja, A. Wójs, and M. Potemski. Optically induced charge conversion of coexistent free and bound excitonic complexes in two-beam magnetophotoluminescence of two-dimensional quantum structures. *Phys. Rev. B*, 85:195108, May 2012.
Fine structure of negatively charged and neutral excitons in monolayer MoS$_2$

[9] Murray A. Lampert. Mobile and immobile effective-mass-particle complexes in nonmetallic solids. *Phys. Rev. Lett.*, 1:450–453, Dec 1958.

[10] K. Kheng, R. T. Cox, Merle Y. d’Aubigné, Franck Bassani, K. Saminadayar, and S. Tatarenko. Observation of negatively charged excitons X$^-$ in semiconductor quantum wells. *Phys. Rev. Lett.*, 71:1752–1755, Sep 1993.

[11] Pawel Hawrylak. Optical properties of a two-dimensional electron gas: Evolution of spectra from excitons to Fermi-edge singularities. *Phys. Rev. B*, 44:3821–3828, Aug 1991.

[12] J. Jadczak, A. Wójcik, G. Bartsch, D. R. Yakovlev, M. Bayer, P. Plochocka, M. Potemski, D. Reuter, and A. D. Wieck. Cyclotron-resonant exciton transfer between the nearly free and strongly localized radiative states of a two-dimensional hole gas in a high magnetic field. *Phys. Rev. B*, 85:165308, Apr 2012.

[13] L. Bryja, J. Jadczak, A. Wójcik, G. Bartsch, D. R. Yakovlev, M. Bayer, P. Plochocka, M. Potemski, D. Reuter, and A. D. Wieck. Cyclotron-resonant exciton transfer between the nearly free and strongly localized radiative states of a two-dimensional hole gas in a high magnetic field. *Phys. Rev. B*, 85:165308, Apr 2012.

[14] J. Jadczak, J. Kutrowska-Girzycka, P. Kapuściński, Y S Huang, A Wójcik, and L Bryja. Probing of free and localized excitons and trions in atomically thin WSe$_2$, WS$_2$, MoSe$_2$ and MoS$_2$ in photoluminescence and reflectivity experiments. *Nanotechnology*, 28(39):395702, sep 2017.

[15] J. Jadczak, A. Delgado, L. Bryja, Y. S. Huang, and P. Hawrylak. Robust high-temperature trion emission in monolayers of Mo(SySe$_{1-y}$)$_2$ alloys. *Physical Review B*, 95(19):195427, May 2017.

[16] J. Jadczak, A. Delgado, L. Bryja, Y. S. Huang, and P. Hawrylak. Robust high-temperature trion emission in monolayers of Mo(SySe$_{1-y}$)$_2$ alloys. *Physical Review B*, 95(19):195427, May 2017.

[17] J. Jadczak, L. Bryja, J. Kutrowska-Girzycka, P. Kapuściński, M. Bieniek, Y.-S. Huang, and P. Hawrylak. Room temperature multi-phonon upconversion photoluminescence in monolayer semiconductor WS$_2$. *Nature Communications*, 10(1):107, 2019.

[18] Matthias Drüppel, Thorsten Deilmann, Peter Krüger, and Michael Rohlfing. Diversity of trion states and substrate effects in the optical properties of an MoS$_2$ monolayer. *Nature Nanotechnology*, 14(5):432–436, 2019.

[19] J. Jadczak, L. Bryja, J. Kutrowska-Girzycka, P. Kapuściński, M. Bieniek, Y.-S. Huang, and P. Hawrylak. Room temperature multi-phonon upconversion photoluminescence in monolayer semiconductor WS$_2$. *Nature Communications*, 10(1):107, 2019.

[20] T. Scrace, Y. Tsai, B. Barman, L. Schweidenback, A. Petrou, G. Kioseoglou, I. Ozfidan, M. Korkusinski, and P. Hawrylak. Magnetoluminescence and valley polarized state of a two-dimensional electron gas in WS$_2$ monolayers. *Nature Nanotechnology*, 10(7):603–607, 2015.

[21] Jonas Gaël Roch, Guillaume Froehlicher, Nadine Leisgang, Peter Makk, Kenji Watanabe, Takashi Taniguchi, and Richard John Warburton. Spin-polarized electrons in monolayer MoS$_2$. *Nature Nanotechnology*, 14(5):432–436, 2019.

[22] Eugene S. Kadantsev and Pawel Hawrylak. Electronic structure of a single MoS$_2$ monolayer. *Solid...
Fine structure of negatively charged and neutral excitons in monolayer MoS$_2$

State Communications, 152(10):909, 2012.

[29] B Radisavljevic, A Radenovic, J Brivio, V Giaconetti, and A Kis. Single-layer MoS$_2$ transistors. Nat. Nano., page 14750, 2011.

[30] F. Cadiz, E. Courtade, C. Robert, G. Wang, Y. Shen, H. Cai, T. Taniguchi, K. Watanabe, H. Carrere, D. Lagarde, M. Manca, T. Amand, P. Renucci, S. Tongay, X. Marie, and B. Urbaszek. Excitonic linewidth approaching the homogeneous limit in MoS$_2$-based van der Waals heterostructures. Phys. Rev. X, 7:021026, May 2017.

[31] M. Goryca, J. Li, A. V. Stier, T. Taniguchi, K. Watanabe, E. Courtade, S. Shree, C. Robert, B. Urbaszek, X. Marie, and S. A. Crooker. Revealing exciton masses and dielectric properties of monolayer semiconductors with high magnetic fields. Nature Communications, 10(1):4172, 2019.

[32] T. P. Lyons, S. Dufferwiel, M. Brooks, F. Withers, T. Taniguchi, K. Watanabe, K. S. Novoselov, G. Burkard, and A. I. Tartakovskii. The valley Zeeman effect in inter- and intra-valley trions in monolayer WSe$_2$. Nature Communications, 10(1):2330, 2019.

[33] Roel Tempelaar and Timothy C. Berkelbach. Many-body simulation of two-dimensional electronic spectroscopy of excitons and trions in monolayer transition metal dichalcogenides. Nature Communications, 10(1):3419, 2019.

[34] Andor Kormánynos, Guido Burkard, Martin Gmitra, Jaroslav Fabian, Viktor Zólyomi, Neil D Drummond, and Vladimir Fal’ko. kp theory for two-dimensional transition metal dichalcogenide semiconductors. 2D Materials, 2(2):022001, 2015.

[35] Riccardo Pisoni, Andor Kormánynos, Matthew Brooks, Zijin Lei, Patrick Back, Marius Eich, Hiske Overweg, Yongjin Lee, Peter Rickhaus, Kenji Watanabe, Takashi Taniguchi, Atac Imamoglu, Guido Burkard, Thomas Ihn, and Klaus Ensslin. Interactions and magnetotransport through spin-valley coupled landau levels in monolayer MoS$_2$. Phys. Rev. Lett., 121:247701, Dec 2018.

[36] Maciej Bieniek, Marek Korkusiński, Ludmiła Szulakowska, Paweł Potasz, Işıl Özfidan, and Paweł Hawrylak. Band nesting, massive dirac fermions, and valley Landé and Zeeman effects in transition metal dichalcogenides: A tight-binding model. Phys. Rev. B, 97:085153, Feb 2018.

[37] Dmitry K. Efimkin and Allan H. MacDonald. Many-body theory of trion absorption features in two-dimensional semiconductors. Phys. Rev. B, 95:035417, Jan 2017.

[38] Shiyuan Gao and Li Yang. Renormalization of the quasiparticle band gap in doped two-dimensional materials from many-body calculations. Phys. Rev. B, 96:155410, Oct 2017.

[39] Yago Ferreiros and Alberto Cortijo. Large conduction band and Fermi velocity spin splitting due to Coulomb interactions in single-layer MoS$_2$. Phys. Rev. B, 90:195426, Nov 2014.

[40] Fang Liu, Mark E. Ziffer, Kameron R. Hansen, Jue Wang, and Xiaoyang Zhu. Direct determination of band-gap renormalization in the photoexcited monolayer MoS$_2$. Phys. Rev. Lett., 122:246803, Jun 2019.

[41] M. M. Glazov, M. A. Semina, C. Robert, B. Urbaszek, T. Amand, and X. Marie. Intervalley polaron in atomically thin transition metal dichalcogenides. Phys. Rev. B, 100:041301, Jul 2019.

[42] E. Courtade, M. Semina, M. Manca, M. M. Glazov, C. Robert, F. Cadiz, G. Wang, T. Taniguchi, K. Watanabe, M. Pierre, W. Escoffer, E. L. Ivchenko, P. Renucci, X. Marie, T. Amand, and B. Urbaszek. Charged excitons in monolayer WSe$_2$: Experiment and theory. Phys. Rev. B, 96:085302, Aug 2017.

[43] D Vlaclavkova, J Wyzula, K Nogajewski, M Bartos, A O Slobodeniuk, C Faugeras, M Potemski, and M R Molas. Singlet and triplet trions in WS$_2$ monolayer encapsulated in hexagonal boron nitride. Nanotechnology, 29(32):325705, Jun 2018.

[44] Jason S. Ross, Sanfeng Wu, Hongyi Yu, Nirmal J. Ghimire, Aaron M. Jones, Grant Aivazian, Jiaqiang Yan, David G. Mandrus, Di Xiao, Wang Yao, and Xiaodong Xu. Electrical control of neutral and charged excitons in a monolayer semiconductor. Nature Communications, 4(1):1474, 2013.

[45] Maciej Bieniek, Ludmiła Szulakowska, and Paweł Hawrylak. arXiv e-prints, 2020.
Fine structure of negatively charged and neutral excitons in monolayer MoS$_2$

[46] Hongyi Yu, Xiaodong Cui, Xiaodong Xu, and Wang Yao. Valley excitons in two-dimensional semiconductors. National Science Review, 2(1):57–70, 01 2015.

[47] Maciej R. Molas, Katarzyna Golasa, Łukasz Bala, Karol Nogajewski, Miroslav Bartos, Marek Potemski, and Adam Babinski. Tuning carrier concentration in a superacid treated MoS$_2$ monolayer. Scientific Reports, 9(1):1989, 2019.

[48] Joanna Kutrowska-Girzycka, Joanna Jadczak, and Leszek Bryja. The study of dispersive 'b'-mode in monolayer MoS$_2$ in temperature dependent resonant Raman scattering experiments. Solid State Communications, 275:25 – 28, 2018.

[49] Galan Moody, Chandriker Kavir Dass, Kai Hao, Chang-Hsiao Chen, Lain-Jong Li, Akshay Singh, Kha Tran, Genevieve Clark, Xiaodong Xu, Gunnar Berghäuser, Ermin Malic, Andreas Knorr, and Xiaojin Li. Intrinsic homogeneous linewidth and broadening mechanisms of excitons in monolayer transition metal dichalcogenides. Nature Communications, 6(1):8315, 2015.

[50] Galan Moody, John Schaibley, and Xiaodong Xu. Exciton dynamics in monolayer transition metal dichalcogenides. J. Opt. Soc. Am. B, 33(7):C39–C49, Jul 2016.

[51] Akshay Singh, Kha Tran, Mirco Kolarczik, Joe Seifert, Yiping Wang, Kai Hao, Dennis Pleskot, Nathaniel M. Gabor, Sophia Helmrich, Nina Owshimikow, Ulrike Woggon, and Xiaojin Li. Long-lived valley polarization of intravalley trions in monolayer WSe$_2$. Phys. Rev. Lett., 117:257402, Dec 2016.

[52] Maciej Koperski, Maciej R Molas, Ashish Arora, Karol Nogajewski, Miroslav Bartos, Jan Wyzula, Diana Vaclavkova, Piotr Kossacki, and Marek Potemski. Orbital, spin and valley contributions to Zeeman splitting of excitonic resonances in MoSe$_2$, WSe$_2$ and WS$_2$ monolayers. 2D Materials, 6(1):015001, oct 2018.

[53] Ashish Arora, Nils Kolja Wessling, Thorsten Deilmann, Till Reichenauer, Paul Steeger, Piotr Kossacki, Marek Potemski, Steffen Michaelis de Vasconcellos, Michael Rohlfing, and Rudolf Bratschitsch. arXiv e-prints, 2019.

[54] Xiao-Xiao Zhang, Yumeng You, Shu Yang Frank Zhao, and Tony F. Heinz. Experimental evidence for dark excitons in monolayer WSe$_2$. Phys. Rev. Lett., 115:257403, Dec 2015.