Controlling exciton many-body states by the electric-field effect in monolayer MoS$_2$

J. Klein,1, 2,∗ A. Hötger,1 M. Florian,3 A. Steinhoff,3 A. Delhomme,4 T. Taniguchi,5 K. Watanabe,5 F. Jahnke,3 A. W. Holleitner,1 M. Potemski,4 C. Faugeras,4 J. J. Finley,1, ‡ and A. V. Stier1, †

1Walter Schottky Institut and Physik Department, Technische Universität München, Am Coulombwall 4, 85748 Garching, Germany
2Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
3Institut für Theoretische Physik, Universität Bremen, P.O. Box 330 440, 28334 Bremen, Germany
4Université Grenoble Alpes, INSA Toulouse, Univ. Toulouse Paul Sabatier, EMFL, CNRS, LNCMI, 38000 Grenoble, France.
5Research Center for Functional Materials, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

(Dated: 2021-09-15)

We report magneto-optical spectroscopy of gated monolayer MoS$_2$ in high magnetic fields up to 28 T and obtain new insights on the many-body interaction of neutral and charged excitons with the resident charges of distinct spin and valley texture. For neutral excitons at low electron doping, we observe a nonlinear valley Zeeman shift due to dipolar spin-interactions that depends sensitively on the local carrier concentration. As the Fermi energy increases to dominate over the other relevant energy scales in the system, the magneto-optical response depends on the occupation of the fully spin-polarized Landau levels in both K/K’ valleys. This manifests itself in a many-body state.

Our experiments demonstrate that the exciton in monolayer semiconductors is only a single particle boson close to charge neutrality. We find that away from charge neutrality it smoothly transitions into polaronic states with a distinct spin-valley flavour that is defined by the Landau level quantization spin and valley texture.

A bosonic exciton immersed in a Fermi gas is an example of the im purity-model that can be understood in terms of a polaronic picture - dressing of the exciton by collective excitations of the many-body environment [1-8]. The role of electron-electron interactions on the properties of two-dimensional (2D) electron and hole gases has been extensively studied in GaAs [9-11], AlAs [12, 13] and recently also in graphene [14, 15]. Typically the spin- and valley susceptibility of the system is found to be enhanced by interactions. Signatures of collective phenomena are particularly pronounced in 2D materials [16-19] such as semiconducting transition metal dichalcogenide (TMDC) MoS$_2$ owing to strong Coulomb interaction [20, 21]. Elegant control knobs, such as static electric-field effects have been used for tuning many-body interactions for the study of Fermi-polarons [22-27]. Specifically in the very low density regime, valley dichroism in the presence of a magnetic field generates a unique local spin and valley texture of excess charge carriers. Here, only few spin-polarized Landau levels (LLs) with low filling factors are involved in shaping the many-body environment. Therefore, the interaction of excitons immersed in the fermionic bath depends on those LLs. Quantum transport studies are intrinsically restricted to the high density regime where LLs with high filling factors are typically probed [28-35] whereas optical measurements facilitate access to the entire density regime [25, 27]. The large variation of reported g-factors for excitons in MoS$_2$ [36-40] and other 2D materials [25, 27, 36, 39, 41-48] with arbitrary carrier concentration further highlights the necessity for studying valley Zeeman shifts with tunable and controlled carrier densities in 2D semiconductors.

In this Letter, we fully address the variation of g-factors in the literature which is a direct consequence of the many-body interaction with the fermionic bath. We control the carrier concentration n in a dual-gate field-effect device (Fig. 1(a)) and study the magneto-optical response in high magnetic fields up to B = 28 T. Simultaneous control of n and B allows us to prepare a unique global spin texture originating from the quantization of excess carriers in fully spin-polarized LLs. We study the magnetic field dependence of neutral and charged excitons (Fermi-polarons) which encode the evolution of the total magnetic energy including carrier spin, valley magnetic moment (Berry phase) and cyclotron phenomena arising from quantization of electrons and/or holes into discrete LLs [25, 27, 41-45, 48]. From our measurements, we directly observe that shape and magnitude of the valley Zeeman shift $\Delta E_{VZ}$ of excitons very sensitively depend on the spin and valley texture. Our results suggest that the interaction of the exciton with the Fermi-bath at low densities is driven by dipolar spin-interaction which markedly differs from previous observations that have not taken into account the unique LL quantization in 2D TMDCs [22-27].

We excite the sample with unpolarized light at $\lambda = 514$ nm and an excitation power of 30 µW and detect $\sigma^-$ polarized PL at $T = 5$ K. Due to the robust optical selection rules in monolayer TMDCs, we only probe the emission from excitonic recombination in the $K'$ valley for positive and negative polarities of the $B$-field [49]. Figure 1(b) shows a carrier concentration dependent false colour PL map recorded at $B = -28$ T. We symmet-
has recently been attributed to a Mahan-like exciton [54], or an exciton-plasmon-like excitation [56], but its precise origin is not yet fully understood. We repeated the measurement for various static magnetic fields ranging from $-28 \text{T}$ to $28 \text{T}$.

Figure 1(c) depicts the spin and valley band sequence of monolayer MoS$_2$ in an excitonic picture. Electron-hole exchange leads to an optically dark alignment of the spin-orbit split conduction bands $c_1$ and $c_2$ ($\Delta db \sim 14 \text{ meV}$), which has been theoretically proposed [57] and experimentally verified [28, 58]. Throughout this Letter, we describe all observed effects on the basis of this picture. For $B = 0$ and $E_F$ situated slightly above the lower conduction band minima ($e_1$), an equal number of spin-up ($\uparrow$) and spin-down ($\downarrow$) electrons occupy the bands at $K$ and $K'$ ($N_\uparrow = N_\downarrow$) resulting in zero net spin-polarization (Fig. 1(c)). However, an applied magnetic field breaks time-reversal symmetry, shifts the conduction band minima, and the resident electrons condense into LLs resulting in an occupation imbalance between the valleys. A direct consequence is the emergence of a spin-polarized Fermi sea ($N_\uparrow \neq N_\downarrow$) in either $K$ or $K'$ for positive and negative magnetic fields (Fig. 1(d)). Therefore, the resulting spin-valley texture of the electrons depends on the carrier concentration ($E_F$) and the direction and magnitude of the applied magnetic field as visualized for monolayer MoS$_2$ in Fig. 1(f). For other monolayer TMDCs, this depends on the details of the respective band structure. In general, the global degree of spin-polarization $\eta_s = (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$ enters different regimes ranging from $|\eta_s| = \pm 1$ at low carrier concentration and high magnetic fields (regime II), through intermediate densities with $|\eta_s| < 1$ (regime III) to the absence of $\eta_s$ at highest $n$ where $E_F$ resides well above the minimum of the upper conduction band $c_2$ (regime IV). For our consideration, we model only the relevant LLs in the conduction bands with a finite inhomogeneous broadening (4 meV) and determine the number of spin-$\uparrow$ and spin-$\downarrow$ electrons from integrating over the corresponding density of states (see Fig. 1(e) and further details in the Supplemental Material [59]).

An applied magnetic field lifts the $K/K'$ valley degeneracy by shifting time-reversed pairs of states in opposite directions in accord with the Zeeman energy $-\mu_B B$ [60]. This effect will shift the exciton energy when the magnetic moment of conduction and valence bands are not equal, $\Delta E_{VZ} = -\mu_e - \mu_v \cdot B = \frac{1}{2}g\mu_B B$. Figures 2(a) and (b) show the magnetic field dependent $X^0$ PL close to charge neutrality ($n \sim 0 \text{ cm}^{-2}$) and for low electron densities ($n \sim 1.45 \cdot 10^{12} \text{ cm}^{-2}$). While $\Delta E_{VZ}$ is completely linear at charge neutrality, strikingly it becomes nonlinear with electron doping. The observation is summarized in Fig. 2(c), where the $B$-field dependent peak positions for a sequence of charge concentrations are shown.

At charge neutrality, we measure a $g$-factor of $X^0$,
The nonlinear valley Zeeman shift in the n-charging regime directly correlates with $\eta_g$ and is a direct consequence of a dipolar spin-interaction of the exciton with the local spin-polarized fermionic bath. An enhancement in the context of conduction band filling has been observed in WSe$_2$ at high densities [24]. However, our reported results clearly show that the interaction is driven by few electrons occupying fully spin-polarized LLs. Similar physics can be found for electrons interacting with local magnetic moments in dilute magnetic semiconductors [65]. In our case, the effective magnetic moment originates from a magnetic field induced net spin-polarization of excess carriers as depicted schematically in Fig 1(d). Qualitatively, this can be pictured as a paramagnetic spin ordering effect of conduction band electrons where the MoS$_2$ effectively undergoes a ferrimagnetic-to-ferromagnetic phase transition [34]. When a sufficiently large magnetic field is applied, the valley degeneracy is lifted, which leads to a repopulation of electrons into the lowest conduction band LL. As such a net spin imbalance, $S_Z(B) = -1/2 \cdot B_j(x)$, between the valleys occurs at higher $B$. Here, the Brillouin function [65] is $B_j(x) = \frac{2x_j + 1}{2x_j} \coth \left( \frac{1}{2x_j} x \right)$ where $s_z = 1/2$ is the electron spin in $c_1$ and $x = gyBS_z/k_BT$. The net magnetization is then $M \sim \Delta N \cdot S_z(B)$ with the total number of polarized electron spins $\Delta N = |N_\uparrow - N_\downarrow|$. Therefore, the total valley Zeeman $g$-factor for the exciton in regime II can be expressed as the addition of spin and valley net magnetization effects as

$$g^n(n, B) = g_{X^0} + g_m(n) \cdot S_z(B)$$

such that the nonlinear valley Zeeman shift is $\Delta E_{VZ}^{n}(n, B) = 1/2g^n(n, B)\mu_B B$. As shown by the fits to the data in Fig. 2(c), this simple model captures the nonlinear valley Zeeman shift surprisingly well. Note that we do not observe a nonlinearity in the p-charging regime I. This may be expected as interaction effects are more prominent in the conduction band [28].

Finally, we summarize the valley susceptibility of all features in our accessible density range in Fig. 3(a).

Regime I.—The $X^0$ $g$-factor monotonically increases from $\sim -1.27$ at charge neutrality to $-2.1$ at the highest hole density while the $X^+$ $g$-factor exhibits a value of $-3.52 \pm 0.35$ suggesting that the extra hole adds lower lying bands resulting in a finite inter-cellular contribution. However, even the most sophisticated theoretical approaches to date ignore the many-body nature of the electron-hole pair which we demonstrate here. We further note that the exciton $g$-factor results from couplings of energetically remote bands [64], which may be perturbed by free carriers as well as impurities [51].

FIG. 2. (a) and (b) Normalized $\mu$-PL spectra of $X^0$ for applied magnetic fields at $n = 0$ cm$^{-2}$ ($n = 1.45 \cdot 10^{12}$ cm$^{-2}$) from $-28$ T to $28$ T. The solid lines are a guide to the eye. (c) Carrier density dependent valley Zeeman shift $\Delta E_{VZ}$ of the $X^0$ in the electron and hole charged regime.
\( \sim 1.5 \mu_B \) to the valley susceptibility of the exciton. Most strikingly, we find that \( g^* \) monotonically increases from the value observed close to charge neutrality to the trion \( g \)-factor, showing the direct dependence of the exciton \( g \)-factor on the carrier density and strongly pointing towards the exciton having the character of a spin-polarized magnetic polaron at finite electron density.

**Regime II.**—Introducing electrons to the system and using Eq. 1 to obtain \( g^*(n, B) \), the magnetic moment of \( X^0 \) (see Fig. 2(c)) increases monotonically with carrier concentration, peaking at \( g^* \sim -5.5 \) for a density of \( n_1 \sim 2 \cdot 10^{12} \text{cm}^{-2} \). This confirms our expectation that for \( n > n_1 \), the increased magnetic susceptibility of \( X^0 \) arises from the density of spin-polarized electrons in the lower \( K' \) valley (see Fig. 1(f)) and the magnitude of \( g^*(n, B) \) is highly sensitive to the local electron concentration. This conclusion may explain the large variation in the literature of reported \( g \)-factors for excitons in MoS\(_2\) [36–40]. Crucially, \( g^*(n, B) \) smoothly approaches the \( g \)-factor observed for \( X^- \) at higher electron concentrations, indicating that both states have a similar spin and valley structure. The \( X^0 \) interacts with the spin-polarized Fermi sea while the strength of the interaction is tuned by the Fermi energy, very similar to the Kondo problem of an isolated impurity spin interacting with a spin-polarized Fermi sea [66]. For high densities, the spin structure of \( X^0 \) increasingly resembles that of \( X^- \). Indeed, at the carrier density of \( n_1 \), \( X^0 \) sees on average \( \sim 0.1 \) electrons within its wave function.

**Regime III.**—Increasing the electron concentration from moderate (\( n_1 \)) to high (\( n_2 \)) densities, we find an asymmetry of the \( X^- \) valley Zeeman shift in positive (\( X^- (s^+) \)) and negative (\( X^- (s^-) \)) magnetic fields (see Fig. S5 in the Supplemental Material [59]). We attribute this to LL occupation differences in the \( K'/K \) valley in the lower conduction bands \( c_1 \) (see Fig. 1(e)). The \( g \)-factor for negative \( B \) increases to \( \sim -10 \). Similar to \( X^0 \), \( X^- \) also interacts with electrons in the Fermi sea. However, unlike \( X^0 \) the local spin valley texture admits electrons residing in both valleys since \( E_F \) is located in the lower conduction bands (regime III). This picture is also supported by the spin texture, shown in Fig. 3(c).

**Regime IV.**—For \( n > n_2 \), the PL is quickly dominated by the feature \( X'^- \) which emerges precisely at the carrier density when \( E_F \) shifts into the upper conduction bands \( c_2 \) (\( n_2 \sim 4 \cdot 10^{12} \text{cm}^{-2} \) in our device) [28]. We find that \( \Delta E_{VZ} \) of \( X^- \) is symmetric and linear in \( B \) for all accessible densities (see inset Fig. 3(a)). The \( g \)-factor of \( X'^- \) equals \( g_{X^- (s^-)} \) at \( n_2 \), which suggests a qualitatively similar magnetic moment. Indeed, a bound complex with
the excess electron occupying the $\nu = +0K\ LL$ in the $c_2$
is such a configuration (see inset Fig. 3(b)). This is fur-
ther substantiated by the very strong valley polarization
of this feature (see Fig. S6 and S7 in the Supplemental
Material [59]). Both, $\eta_s$ and the $g$-factor of $X'$ simulta-
neously diminish above $n_3$ with $\eta_s \sim 0$ and a minimum $g$
factor of $\sim -5$. Strikingly, at exactly this concentration,
a change in the dependence of the $X'$ binding energy
$E_B = E(X') - E(X''')$ occurs from a linear to a sub-
linear dependence on $E_F$ (see Fig. 3(b)). For $n > n_3$, all
valleys and electron spin species are available since $E_F$
is situated well within $c_2$. The electron concentration
approaches the Mott density [67] where strong many-body
effects start to dominate the interaction of $X'$ and elec-
trons of all spins forming a strongly dressed many-body
state (see inset Fig. 3(b)). Here the precise local spin
structure becomes less relevant, and mean field-like"theories become applicable. A detailed description of this
state would call for dedicated many-body calculations of
the spin susceptibility.

Our results show that all excitons in 2D materials are
many-body correlated states that have a magneto-optical
response that is sensitive to the local carrier density and
related spin and valley textures. We explain the large
variation of $g$-factors observed in the literature as arising
from lack of control of local doping. The findings of
our study represent an important step towards studying
and engineering many-body related phases and novel
interaction phenomena in atomically thin materials.

Supported by Deutsche Forschungsgemeinschaft
(DFG) through the TUM International Graduate
School of Science and Engineering (IGSSE) and the
German Excellence Cluster-MCQST and e-conversion.
We gratefully acknowledge financial support by the
PhD program ExQM of the Elite Network of Bavaria,
financial support from the European Union’s Horizon
2020 research and innovation programme under grant
agreement No. 820423 (S2QUIP) the German Federal
Ministry of Education and Research via the funding
program Photonics Research Germany (contracts num-
ber 13N14846) and the Bavarian Academy of Sciences
and Humanities. J.K. acknowledges support by the
Alexander von Humboldt foundation. M.F., A.S. and
F.J. were supported by the Deutsche Forschungsge-
meinschaft (DFG) within RTG 2247 and through a
grant for CPU time at the HLRN (Berlin/Göttingen).
J.J.F and A.H. acknowledge support from the Technical
University of Munich - Institute for Advanced Study,
funded by the German Excellence Initiative and the
European Union FP7 under grant agreement 291763 and
the German Excellence Strategy Munich Center for
Quantum Science and Technology (MCQST). K.W. and
T.T. acknowledge support from the Elemental Strategy
Initiative conducted by the MEXT, Japan, Grant
Number JPMXP0112101001, JSPS KAKENHI Grant
Number JP20H00354 and the CREST(JPMJCR15F3),
JST. The work has been partially supported by the EC
Graphene Flagship project (no. 604391), by the ANR
projects ANR-17-CE24-0030 and ANR-19-CE09-0026.
We further thank Scott Crooker and Mark Goerbig for
insightful and stimulating discussions.

* jpklein@mit.edu
† finley@wsi.tum.de
‡ andreas.stier@wsi.tum.de

[1] Massignan, P., Zaccanti, M. & Bruun, G. M. Polarons,
dressed molecules and itinerant ferromagnetism in ul-
tracold fermi gases. Reports on Progress in Physics
77, 034401 (2014). URL https://doi.org/10.1088/
0034-4885/77/3/034401.
[2] Bloch, I., Dalibard, J. & Zwerger, W. Many-body
physics with ultracold gases. Reviews of Modern Physics
80, 885–964 (2008). URL https://doi.org/10.1103/
revmodphys.80.885.
[3] Boll, M. et al. Spin- and density-resolved microscopy of
antiferromagnetic correlations in fermi-hubbard chains.
Science 353, 1257–1260 (2016). URL https://doi.org/
10.1126/science.aag1635.
[4] Mazurenko, A. et al. A cold-atom fermi–hubbard anti-
ferromagnet. Nature 545, 462–466 (2017). URL:
https://doi.org/10.1038/nature22362.
[5] Efimkin, D. K. & MacDonald, A. H. Many-body theory
of trion absorption features in two-dimensional semicon-
ductors. Physical Review B 95 (2017). URL
https://doi.org/10.1103/physrevb.95.035417.
[6] Koepsell, J. et al. Imaging magnetic polarons in the
doped fermi-hubbard model. Nature 572, 358–362
(2019). URL https://doi.org/10.1038/
s41586-019-1463-1.
[7] Fey, C., Schmelcher, P., Imamoglu, A. & Schmidt, R.
Theory of exciton-electron scattering in atomically thin
semiconductors. Physical Review B 101 (2020). URL
https://doi.org/10.1103/physrevb.101.195417.
[8] Glazov, M. M. Optical properties of charged excitons in
two-dimensional semiconductors. The Journal of Chemi-
cal Physics 153, 034703 (2020). URL https://doi.org/
10.1063/5.0012475.
[9] Chen, W. et al. Interaction of magnetoeectrons and two-
dimensional electron gas in the quantum hall regime.
Physical Review Letters 64, 2434–2437 (1990). URL
https://doi.org/10.1103/physrevlett.64.2434.
[10] Goldberg, B. B., Heiman, D., Pinczuk, A., Pfeiffer, L.
& West, K. Optical investigations of the integer and
fractional quantum hall effects: Energy plateaus, in-
term valley minima, and line splitting in band-gap emis-
ion. Physical Review Letters 65, 641–644 (1990). URL:
https://doi.org/10.1103/physrevlett.65.641.
[11] Zhu, J., Stormer, H. L., Pfeiffer, L. N., Baldwin, K. W.
& West, K. W. Spin susceptibility of an ultra-low-
density two-dimensional electron system. Physical Re-
view Letters 90 (2003). URL https://doi.org/10.
1103/physrevlett.90.056805.
[12] Gunawan, O. et al. Valley susceptibility of an interact-
ing two-dimensional electron system. Physical Review Letters 97 (2006). URL https://doi.org/10.1103/physrevlett.97.186404.

[13] Sarma, S. D., Hwang, E. H. & Li, Q. Valley-dependent many-body effects in two-dimensional semiconductors. Physical Review B 80 (2009). URL https://doi.org/10.1103/physrevb.80.121303.

[14] Nomura, K. & MacDonald, A. H. Quantum hall ferromagnetism in graphene. Physical Review Letters 96 (2006). URL https://doi.org/10.1103/physrevlett.96.256602.

[15] Young, A. F. et al. Spin and valley quantum hall ferromagnetism in graphene. Nature Physics 8, 550–556 (2012). URL https://doi.org/10.1038/nphys2307.

[16] Huang, B. et al. Layer-dependent ferromagnetism in a van der waals crystal down to the monolayer limit. Nature 546, 270–273 (2017). URL https://doi.org/10.1038/nature22391.

[17] Tang, Y. et al. Simulation of hubbard model physics in WSe$_2$/WS$_2$ moiré superlattices. Nature 579, 353–358 (2020). URL https://doi.org/10.1038/s41586-020-2085-3.

[18] Shimazaki, Y. et al. Strongly correlated electrons and hybrid excitons in a moiré heterostructure. Nature 580, 472–477 (2020). URL https://doi.org/10.1038/s41586-020-2092-4.

[19] Regan, E. C. et al. Mott and generalized wigner crystal states in WSe$_2$/WS$_2$ moiré superlattices. Nature 579, 359–363 (2020). URL https://doi.org/10.1038/s41586-020-2092-4.

[20] Chernukiv, A. et al. Exciton binding energy and non-hydrogenic rydberg series in monolayer WS$_2$. Physical Review Letters 113 (2014). URL https://doi.org/10.1103/physrevlett.113.076802.

[21] Stier, A. et al. Magnetooptics of exciton rydberg states in a monolayer semiconductor. Physical Review Letters 120 (2018). URL https://doi.org/10.1103/physrevlett.120.057405.

[22] Sidler, M. et al. Fermi polaron-polaritons in charge-tunable atomically thin semiconductors. Nature Physics 13, 255–261 (2016). URL https://doi.org/10.1038/nphys3949.

[23] Ravets, S. et al. Polaron polaritons in the integer and fractional quantum hall regimes. Physical Review Letters 120 (2018). URL https://doi.org/10.1103/physrevlett.120.057401.

[24] Wang, Z., Mak, K. F. & Shan, J. Strongly interaction-enhanced valley magnetic response in monolayer WSe$_2$. Physical Review Letters 120 (2018). URL https://doi.org/10.1103/physrevlett.120.066402.

[25] Smolenski, T. et al. Interaction-induced shubnikov–de haas oscillations in optical conductivity of monolayer MoS$_2$. Physical Review Letters 123 (2019). URL https://doi.org/10.1103/physrevlett.123.097403.

[26] Tan, L. B. et al. Interacting polaron-polaritons. Physical Review X 10 (2020). URL https://doi.org/10.1103/physrevx.10.021011.

[27] Liu, E. et al. Landau-quantized excitonic absorption and luminescence in a monolayer semiconductor. Physical Review Letters 124 (2020). URL https://doi.org/10.1103/physrevlett.124.097401.

[28] Pisoni, R. et al. Interactions and magnetotransport through spin-valley coupled landau levels in monolayer MoS$_2$. Physical Review Letters 121 (2018). URL https://doi.org/10.1103/physrevlett.121.247701.

[29] Movva, H. C. et al. Density-dependent quantum hall states and zeeman splitting in monolayer and bilayer WSe$_2$. Physical Review Letters 118 (2017). URL https://doi.org/10.1103/physrevlett.118.247701.

[30] Xu, S. et al. Odd-integer quantum hall states and giant spin susceptibility in p-type few-layer WSe$_2$. Physical Review Letters 118 (2017). URL https://doi.org/10.1103/physrevlett.118.067702.

[31] Gustafsson, M. V. et al. Ambipolar landau levels and strong band-selective carrier interactions in monolayer WSe$_2$. Nature Materials 17, 411–415 (2018). URL https://doi.org/10.1038/s41563-018-0036-2.

[32] Larentis, S. et al. Large effective mass and interaction-enhanced zeeman splitting of k-valley electrons in MoS$_2$. Physical Review B 97 (2018). URL https://doi.org/10.1103/physrevb.97.201407.

[33] Fallahazad, B. et al. Shubnikov–de haas oscillations of high-mobility holes in monolayer and bilayer WSe$_2$: Landau level degeneracy, effective mass, and negative compressibility. Physical Review Letters 116 (2016). URL https://doi.org/10.1103/physrevlett.116.086601.

[34] Lin, J. et al. Determining interaction enhanced valley susceptibility in spin-valley-locked MoS$_2$. Nano Letters 19, 1736–1742 (2019). URL https://doi.org/10.1021/acs.nanolett.8b04731.

[35] Li, J. et al. Spontaneous valley polarization of interacting carriers in a monolayer semiconductor. Physical Review Letters 125 (2020). URL https://doi.org/10.1103/physrevlett.125.147602.

[36] Stier, A. V., McCreary, K. M., Jonker, B. T., Kono, J. & Crooker, S. A. Exciton diamagnetic shifts and valley zeeman effects in monolayer WS$_2$ and MoS$_2$ to 65 tesla. Nature Communications 7 (2016). URL https://doi.org/10.1038/ncomms10643.

[37] Mitioglu, A. A. et al. Magnetoeexcitons in large area CVD-grown monolayer MoS$_2$ and MoSe$_2$ on sapphire. Physical Review B 93 (2016). URL https://doi.org/10.1103/physrevb.93.165412.

[38] Cadiz, F. et al. Exciton linewidth approaching the homogeneous limit in MoS$_2$-based van der waals heterostructures. Physical Review X 7 (2017). URL https://doi.org/10.1103/physrevx.7.021026.

[39] Goryca, M. et al. Revealing exciton masses and dielectric properties of monolayer semiconductors with high magnetic fields. Nature Communications 10 (2019). URL https://doi.org/10.1038/s41467-019-12180-y.

[40] Jadczak, J. et al. Fine structure of negatively charged neutral excitons in monolayer MoS$_2$. arXiv preprint arXiv:2001.07929 (2020). URL https://arxiv.org/abs/2001.07929v2.

[41] Aivazian, G. et al. Magnetic control of valley pseudospin in monolayer WSe$_2$. Nature Physics 11, 148–152 (2015). URL https://doi.org/10.1038/nphys3201.

[42] Srivastava, A. et al. Valley zeeman effect in elementary optical excitations of monolayer WSe$_2$. Nature Physics 11, 141–147 (2015). URL https://doi.org/10.1038/nphys3203.

[43] MacNeill, D. et al. Breaking of valley degeneracy by magnetic field in monolayer MoSe$_2$. Physical Review Letters 114 (2015). URL https://doi.org/10.1103/physrevlett.114.037401.

[44] Li, Y. et al. Valley splitting and polarization by the zeeman effect in monolayer MoSe$_2$. Physical Review
[45] Wang, Z., Shan, J. & Mak, K. F. Valley- and spin-polarized Landau levels in monolayer WS\textsubscript{2}. *Nature Nanotechnology* **12**, 144–149 (2016). URL https://doi.org/10.1038/nnano.2016.213.

[46] Stier, A. V., Wilson, N. P., Clark, G., Xu, X. & Crooker, S. A. Probing the influence of dielectric environment on excitons in monolayer WS\textsubscript{2}: Insight from high magnetic fields. *Nano Letters* **16**, 7054–7060 (2016). URL https://doi.org/10.1021/acs.nanolett.6b03276.

[47] Lyons, T. P. et al. The valley zeeman effect in inter- and intra-valley trions in monolayer WS\textsubscript{2}. *Nature Communications* **10** (2019). URL https://doi.org/10.1038/s41467-019-10228-7.

[48] Wang, T. et al. Observation of quantized exciton energies in monolayer WS\textsubscript{2} under a strong magnetic field. *Physical Review X* **10** (2020). URL https://doi.org/10.1038/physrevx.10.021024.

[49] Xiao, D., Liu, G.-B., Feng, W., Xu, X. & Yao, W. Coupled spin and valley physics in monolayers of MoS\textsubscript{2} and other group-VI dichalcogenides. *Physical Review Letters* **108** (2012). URL https://doi.org/10.1038/physrevlett.108.196802.

[50] Volmer, F. et al. How photoinduced gate screening and leakage currents dynamically change the fermi level in 2d materials. *physica status solidi (RRL) – Rapid Research Letters* **14**, 2000298 (2020). URL https://doi.org/10.1002/pssr.202000298.

[51] Klein, J. et al. Impact of substrate induced band tail states on the electronic and optical properties of MoS\textsubscript{2}. *Applied Physics Letters* **115**, 261603 (2019). URL https://doi.org/10.1063/1.5131270.

[52] Wierzchowski, J. et al. Direct exciton emission from atomically thin transition metal dichalcogenide heterostructures near the lifetime limit. *Scientific Reports* **7** (2017). URL https://doi.org/10.1038/s41598-017-09739-4.

[53] Florian, M. et al. The dielectric impact of layer distances on exciton and trion binding energies in van der waals heterostructures. *Nano Letters* **18**, 2725–2732 (2018). URL https://doi.org/10.1021/acs.nanolett.8b00840.

[54] Roch, J. G. et al. First-order magnetic phase transition of mobile electrons in monolayer MoS\textsubscript{2}. *Physical Review Letters* **124** (2020). URL https://doi.org/10.1038/physrevlett.124.187602.

[55] Barbone, M. et al. Charge-tuneable biexciton complexes in monolayer WS\textsubscript{2}. *Nature Communications* **9** (2018). URL https://doi.org/10.1038/s41467-018-05632-4.

[56] Tuan, D. V., Scharf, B., Žutić, I. & Dery, H. Marrying excitons and plasmons in monolayer transition-metal dichalcogenides. *Physical Review X* **7** (2017). URL https://doi.org/10.1103/physrevx.7.041040.

[57] Deilmann, T. & Thygesen, K. S. Dark excitations in monolayer transition metal dichalcogenides. *Physical Review B* **96** (2017). URL https://doi.org/10.1103/physrevb.96.201113.

[58] Robert, C. et al. Measurement of the spin-forbidden dark excitons in MoS\textsubscript{2} and MoSe\textsubscript{2} monolayers. *Nature Communications* **11** (2020). URL https://doi.org/10.1038/s41467-020-17608-4.

[59] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevResearch.X.XXXXX for device preparation and electrical device characterization, magnetic field and carrier density dependent PL data, carrier density dependent valley Zeeman shifts, calculation of the quantized spin-valley texture, theoretical considerations to the magnetic moment, as well as magnetic field and carrier density dependent valley polarization data.

[60] Xu, X., Yao, W., Xiao, D. & Heinz, T. F. Spin and pseudospins in layered transition metal dichalcogenides. *Nature Physics* **10** (2014). URL https://doi.org/10.1038/nphys2942.

[61] Wang, G. et al. Magneto-optics in transition metal diselenide monolayers. *2D Materials* **2**, 034002 (2015). URL https://doi.org/10.1088/2053-1583/2/3/034002.

[62] Deilmann, T., Krüger, P. & Rohlfing, M. Ab initio studies of exciton g factors: Monolayer transition metal dichalcogenides in magnetic fields. *Physical Review Letters* **124** (2020). URL https://doi.org/10.1038/physrevlett.124.226402.

[63] Woźniak, T., Junior, P. E. F., Seifert, G., Chaves, A. & Kunstmann, J. Exciton g factors of van der waals heterostructures from first-principles calculations. *Physical Review B* **101** (2020). URL https://doi.org/10.1103/physrevb.101.235408.

[64] Jovanov, V. et al. Observation and explanation of strong electrically tunable exciton factors in composition engineered In(Ga)As quantum dots. *Physical Review B* **83** (2011). URL https://doi.org/10.1103/physrevb.83.161303.

[65] Furdyna, J. K. Diluted magnetic semiconductors. *Journal of Applied Physics* **64**, R29–R64 (1988). URL https://doi.org/10.1063/1.341700.

[66] Latta, C. et al. Quantum quench of kondo correlations in optical absorption. *Nature* **474**, 627–630 (2011). URL https://doi.org/10.1038/nature10204.

[67] Steinhoff, A. et al. Exciton fission in monolayer transition metal dichalcogenide semiconductors. *Nature Communications* **8** (2017). URL https://doi.org/10.1038/s41467-017-01298-6.
Supplemental Material - Controlling exciton many-body states by the electric-field effect in monolayer MoS$_2$

J. Klein$^*$

Walter Schottky Institut and Physik Department, Technische Universität München,
Am Coulombwall 4, 85748 Garching, Germany and
Department of Materials Science and Engineering,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, USA

A. Hötger, A. W. Holleitner, J. J. Finley,$^†$ and A. V. Stier$^‡$

Walter Schottky Institut and Physik Department,
Technische Universität München, Am Coulombwall 4, 85748 Garching, Germany

M. Florian, A. Steinhoff, and F. Jahnke
Institut für Theoretische Physik, Universität Bremen,
P.O. Box 330 440, 28334 Bremen, Germany

A. Delhomme, M. Potemski, and C. Faugeras
Université Grenoble Alpes, INSA Toulouse,
Univ. Toulouse Paul Sabatier, EMFL,
CNRS, LNCMI, 38000 Grenoble, France.

T. Taniguchi and K. Watanabe
Research Center for Functional Materials,
National Institute for Materials Science,
1-1 Namiki, Tsukuba 305-0044, Japan

(Dated: 2021-09-15)
CONTENTS

I. Field-effect device for carrier density control in monolayer MoS$_2$ 4

II. Transfer characteristics in high magnetic fields 5

III. Carrier density dependent magneto-photoluminescence of monolayer MoS$_2$ 7

IV. Quantized spin-valley texture 8

V. Magnetic moment of Bloch electrons: lattice Hamiltonian vs. atomic contributions 10

VI. Valley Zeeman shift of $X^-$, $X^+$ and $X'-$ 15

VII. Magnetic field and density dependent valley dichroism 16

References 19
I. FIELD-EFFECT DEVICE FOR CARRIER DENSITY CONTROL IN MONOLAYER MoS$_2$

We make use of field-effect devices to control the carrier density in monolayer MoS$_2$. [1] Figure S1 shows the two device geometries used in this manuscript. In our device, monolayer MoS$_2$ is encapsulated in hBN. We use the hBN for two main reasons: (i) Encapsulation reduces inhomogeneous linewidth broadening of excitons [2] and (ii) as gate dielectric that withstands high breakdown fields, [3] thus preventing leakage currents. We use few-layer graphite as the gate-electrode and to directly contact the MoS$_2$. The heterstacks are assembled by the dry viscoelastic transfer technique iteratively stacking the individual layers using PDMS stamping. [1] The dual-gate device with top and bottom gates as shown in Fig. S1. We apply equal gate voltages with the same polarity to the gates $V_{bg} = V_{tg}$ with respect to the monolayer MoS$_2$ for controlling the carrier density. In this device, we are also able to tune from the n- into the p-doped regime. The observation that only the n-doped regime is accessible with a single-gate is common in the literature for monolayer MoS$_2$. [4, 5] It is likely that the dual-gate device allows to access the p-doped regime since it overcomes Fermi-level pinning effects by the symmetric device geometry. Furthermore, dual gates allow larger applied effective fields for tuning the carrier density. We determine the carrier density by using a simple plate capacitor model where the device capacitance is $C = \epsilon_0 \epsilon_{hBN}/d$ with the dielectric constant of multilayer hBN $\epsilon_{hBN} = 2.5$ [3, 6–8] and the hBN layer thickness $d = 14$ nm which is determined by atomic force microscopy (AFM). Since top and bottom hBN thickness are very similar for the dual-gate device we relate, the carrier density with the gate voltage through $n = C(V_{tg} + V_{bg})/e = 2CV/e$. 


Figure S 1. Schematic of the field-effect van der Waals device. Monolayer MoS$_2$ is encapsulated between hBN. The device is a dual-gate device where the carrier density is controlled with a top- and bottom-gate $V_{tg}$ and $V_{bg}$. The same voltage with same polarity is applied to both gates for enhancing the gating effect.

II. TRANSFER CHARACTERISTICS IN HIGH MAGNETIC FIELDS

Figure S 2. Transfer characteristics of the dual-gate device. Top panels: I-V curves for all magnetic fields applied. Bottom panels: Current density as a function of applied bias voltage ($V = V_{bg} = V_{tg}$). The monolayer MoS$_2$ is excited with 30 µW at 514 nm with a laser spot diameter at the sample of $\sim$ 4 µm.

For the gate-dependent magneto-photoluminescence measurements, we apply a magnetic field and vary the gate voltage in steps of 100 mV while collecting PL spectra for every gate voltage step. We perform the same gate biasing sequence for every magnetic field, thus...
ensuring that the voltage sweeps at different magnetic fields are directly comparable. We first apply a static magnetic field and then we tune the bias voltage from max. $V_+$ to max. $V_-$. Typical current voltage characteristics are presented in Fig. S2(a) and (b). We apply equal voltage to top- and bottom-gate ($V = V_{bg} = V_{tg}$). From the transfer characteristics of both devices, we find that our biasing scheme is highly reproducible for all magnetic fields applied in the experiment. The reproducibility is due to the graphite contacts to the MoS$_2$ which is known for low contact resistance and small Schottky barrier heights. [9, 10] The leakage currents are in the noise floor for most of the range and negligible leakage currents of < 1.5 nA, that correspond to current densities of < $10^{-2}$ A cm$^{-2}$, at the highest bias voltages. The data are collected for a laser excitation power of 30 µW with a laser excitation energy of 2.41 eV.
III. CARRIER DENSITY DEPENDENT MAGNETO-PHOTOLUMINESCENCE OF MONOLAYER MOS$_2$

The $\sigma^-$ circularly polarized, charge carrier density dependent magneto-photoluminescence is shown in Fig. S3. The above described biasing sequence is used to maintain sample stability throughout the individual voltage sweeps for static magnetic fields ranging from $B = -28$ T to $B = 28$ T.

Figure S 3. Carrier density dependent low-temperature ($T = 5$ K) $\mu$-PL for static magnetic fields ranging from $-28$ T to $28$ T. The $X^0$, $X^-$, $X^+$ and $X'^-$ PL features are marked.
IV. QUANTIZED SPIN-VALLEY TEXTURE

The Zeeman shift of electrons in the spin-orbit split conduction band valleys in monolayer MoS$_2$ manifests from spin, the Berry phase and due to quantization of electrons in Landau levels in each valley. The shift for the lower conduction band $c_1$ is given by

$$E_{c_1} = \tau_s s_z 2\mu_B B + \tau_i m_e \mu_B B + \nu \frac{\hbar e B}{m_e},$$

while the shift of the upper conduction band $c_2$ is

$$E_{c_2} = \Delta_{db} + \tau_s s_z 2\mu_B B + \tau_i m_e \mu_B B + \nu \frac{\hbar e B}{m_e}.$$  \hspace{1cm} (2)

Here, the valley and spin indices are $\tau_s = \pm 1 \ (K = +1 K \text{ and } K' = -1 K)$ and $\tau_i = \pm 1 \ (+1 \text{ spin-\textup{↑} and } -1 \text{ spin-\textup{↓}})$. We used an electron mass of $m_e = 0.44m_0$. Moreover, $\nu$ is the filling factor of the LL and $\Delta_{db}$ the energy splitting between $c_1$ and $c_2$ for no magnetic field applied. We model two LLs for each valley with $\nu = +0$ and $\nu = +1$ in $K'$. [11] After quantifying the energy shift of each LL of each spin in every valley, we can further calculate the density of states (DOS) as a function of the Fermi level $E_F$ (applied gate voltage). From this quantity, we can then infer the number of electrons populating the spin-\textup{↓} and spin-\textup{↑} LLs to deduce the degree of spin polarization for a given $E_F$. We model each LL by using a Gaussian function

$$DOS_{LL} = \frac{e|B|}{h} \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{(E - E_{LL})^2}{2\sigma^2} \right),$$

with $eB/h$ as the degeneracy per unit area and the energetic position of the LL $E_{LL}$ as defined in Eq. 1 and 2 and a FWHM of each LL of $\Gamma = 2\sqrt{2\ln(2)}\sigma = 4\text{ meV}$ accounting for the experimentally observed inhomogeneous broadening. The total DOS for all spin-\textup{↑} electrons is given through

$$DOS^\uparrow_{LL} = \sum_{i=0}^{\nu=1} DOS^{\uparrow,i}_K + \sum_{i=1}^{\nu=2} DOS^{\uparrow,i}_{K'},$$

and the DOS for all spin-\textup{↓} electrons are given by

$$DOS^\downarrow_{LL} = \sum_{i=1}^{\nu=2} DOS^{\downarrow,i}_K + \sum_{i=0}^{\nu=1} DOS^{\downarrow,i}_{K'}.$$  \hspace{1cm} (5)
By integrating the DOS to $E_F$ we obtain the number of electrons populating each LL with the total number of electrons with spin-$\uparrow$

$$N_\uparrow = \int_0^{E_F} \text{DOS}_{LL}^\uparrow dE$$

(6)

and spin-$\downarrow$

$$N_\downarrow = \int_0^{E_F} \text{DOS}_{LL}^\downarrow dE$$.

(7)

We can now compute the global degree of spin polarization all magnetic fields and $E_F$

$$\eta_s(B, E_F) = \frac{N_\downarrow - N_\uparrow}{N_\downarrow + N_\uparrow}.$$  

(8)
V. MAGNETIC MOMENT OF BLOCH ELECTRONS: LATTICE HAMILTONIAN VS. ATOMIC CONTRIBUTIONS

The magnetic moment is comprised of a contribution due to the orbital motion of a Bloch electron and a contribution due to the electron spin. The z-component of the orbital magnetic moment is given by:

\[ \mu_{\text{orb}}^{n,k} = -\frac{e}{2m_e} \langle \Phi^n_k | \hat{l}_z | \Phi^n_k \rangle = -\frac{e}{2m_e} \langle \Phi^n_k | \hat{x}\hat{p}_y - \hat{y}\hat{p}_x | \Phi^n_k \rangle. \]  

(9)

Consider the general expression \( \langle \Phi^n_k | \hat{x}_i\hat{p}_j | \Phi^n_k \rangle \) and insert a complete set of Bloch states:

\[ \langle \Phi^n_k | \hat{x}_i\hat{p}_j | \Phi^n_k \rangle = \sum_{n'k'} \langle \Phi^n_k | \hat{x}_i | \Phi^{n'}_{k'} \rangle \langle \Phi^{n'}_{k'} | \hat{p}_j | \Phi^n_k \rangle. \]  

(10)

The momentum matrix elements are diagonal in \( k \) due to translational invariance:

\[ \langle \Phi^{n'}_{k'} | \hat{p}_j | \Phi^n_k \rangle = \langle \Phi^{n'}_{k'} | \hat{p}_j | \Phi^n_k \rangle \delta_{k,k'}. \]  

(11)

The position matrix element can be transformed using the Schrödinger equation of Bloch states,

\[ H \Phi^n_k = \varepsilon^n_k \Phi^n_k, \]  

(12)

and the commutator relation [12]

\[ \frac{1}{m_e} \hat{p} = i \hbar [H, \hat{r}], \]  

(13)

which holds in case of a local one-electron potential. It is still valid in the presence of spin-orbit interaction, as long as the latter can be approximately treated as an on-site potential. Using Eqs. (11), (12) and (13), we find:

\[ \langle \Phi^n_k | \hat{x}_i\hat{p}_j | \Phi^n_k \rangle = \sum_{n'} \frac{\hbar}{im_e} \langle \Phi^n_k | \hat{p}_i | \Phi^{n'}_{k'} \rangle \frac{1}{\varepsilon^n_k - \varepsilon^{n'}_{k'}} \langle \Phi^{n'}_{k'} | \hat{p}_j | \Phi^n_k \rangle. \]  

(14)

The crystal wave functions can be constructed as a linear combination of localized orbitals in the following way such that they fulfill Bloch’s theorem:

\[ | \Phi^n_k \rangle = \sum_{\alpha} c^n_{\alpha}(k) | \kappa \alpha \rangle, \quad | \kappa \alpha \rangle = \frac{1}{\sqrt{N}} \sum_R e^{i k \cdot R} | R \alpha \rangle \]  

(15)

with the orthonormality relations

\[ \langle R \alpha | R' \alpha' \rangle = \delta_{RR'} \delta_{\alpha \alpha'}. \]  

(16)
and
\[ \langle k\alpha | k'\alpha' \rangle = \delta_{kk'} \delta_{\alpha \alpha'}, \quad (17) \]
where \( N \) is the number of lattice sites. We can formulate the crystal (lattice) Hamiltonian in terms of the localized orbitals:
\[
H = \sum_{RR',\alpha\alpha'} t_{RR'}^{\alpha\alpha'} \langle R\alpha | R'\alpha' \rangle.
\quad (18)
\]
Inserting the ansatz (15) into Eq. (14), we obtain:
\[
\langle \Phi_k^n | \hat{x}_i \hat{p}_j | \Phi_k^n \rangle = \sum_n \frac{\hbar}{im_e} \frac{1}{\varepsilon_k^n - \varepsilon_k^{n'}} \sum_{\alpha\alpha'} (c_{\alpha\alpha}^n(k))^* c_{\alpha\alpha'}^{n'}(k) \langle k\alpha | \hat{p}_i | k\alpha' \rangle \sum_{\alpha'\alpha} (c_{\alpha'\alpha}^n(k))^* c_{\alpha\alpha'}^n(k) \langle k\alpha' | \hat{p}_j | k\alpha \rangle.
\quad (19)
\]
Following [13], we analyze the momentum matrix element by using the commutator relation (13) again, transforming the momentum states according to (15) and inserting a complete set of position states:
\[
\langle k\alpha' | \hat{p}_j | k\alpha \rangle = -\frac{im_e}{\hbar} \frac{1}{N} \sum_{R,R'} e^{ik(R-R')} \int dr \left[ \langle R'\alpha' | \hat{r}_j | r \rangle \langle r | H | R\alpha \rangle - \langle R'\alpha' | H | r \rangle \langle r | \hat{r}_j | R\alpha \rangle \right].
\quad (20)
\]
One has to distinguish between the continuous space variable \( r \) and the discrete unit-cell label \( R \). The position operator acts as \( \hat{r}_j | r \rangle = r_j | r \rangle \). The momentum matrix element contains contributions that can be directly related to the discrete lattice as well as contributions that arise due to the spatial extension of orbitals. We separate these contributions by shifting \( r \to r + R' \) in the first term and \( r \to r + R \) in the second term:
\[
\langle k\alpha' | \hat{p}_j | k\alpha \rangle = -\frac{im_e}{\hbar} \frac{1}{N} \sum_{R,R'} e^{ik(R-R')} \int dr \bigg[ \langle R'\alpha' | r_j + R' | r + R' \rangle \langle r + R' | H | R\alpha \rangle

- \langle R'\alpha' | H | r + R \rangle \langle r + R | r_j + R_j | R\alpha \rangle \bigg]

= -\frac{im_e}{\hbar} \frac{1}{N} \sum_{R,R'} e^{ik(R-R')} (R_j' - R_j) \langle R'\alpha' | H | R\alpha \rangle

- \frac{im_e}{\hbar} \frac{1}{N} \sum_{R,R'} e^{ik(R-R')} \int dr' r_j \bigg[ \langle R'\alpha' | r + R' \rangle \langle r + R' | H | R\alpha \rangle

- \langle R'\alpha' | H | r + R \rangle \langle r + R | R\alpha \rangle \bigg],
\quad (21)
\]
where we made use of the completeness of position states again to derive the first term of the second line. This so-called Peierls contribution given by *inter*-site hopping can be written as a generalized Fermi velocity:

\[
-\frac{i e}{\hbar} \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}' \neq \mathbf{R}} e^{i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} (\mathbf{R}'_j - \mathbf{R}_j) \langle \mathbf{R}' \alpha' | \mathbf{H} | \mathbf{R} \alpha \rangle
\]

\[
= m_e \frac{\partial}{\partial k_j} \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}' \neq \mathbf{R}} e^{i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} \langle \mathbf{R}' \alpha' | \mathbf{H} | \mathbf{R} \alpha \rangle
\]

\[
= m_e \frac{\partial}{\partial k_j} \tilde{H}_{k}^{\alpha' \alpha}.
\]  

(22)

It follows from the Schrödinger equation (12) that the Hamiltonian \( \tilde{H}_{k}^{\alpha' \alpha} \) defines the tight-binding-like eigenvalue problem

\[
\sum_{\alpha'} \tilde{H}_{k}^{\alpha' \alpha} c_{n}^{\alpha'}(k) = \varepsilon_{k}^{n} c_{\alpha}^{n}(k).
\]  

(23)

The second term in Eq. (21) contains continuum contributions due to the finite extension of the electron wave functions. It can be written as

\[
-\frac{i e}{\hbar} \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}' \neq \mathbf{R}} e^{i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} \int d\mathbf{r} r_j \sum_{R'' \alpha''} \left[ \langle \mathbf{R}' \alpha' | \mathbf{r} + \mathbf{R}' \rangle \langle \mathbf{r} + \mathbf{R}' | R'' \alpha'' \rangle \langle R'' \alpha'' | \mathbf{H} | \mathbf{R} \alpha \rangle - \langle \mathbf{R}' \alpha' | \mathbf{H} | R'' \alpha'' \rangle \langle R'' \alpha'' | \mathbf{r} + \mathbf{R} \rangle \langle \mathbf{r} + \mathbf{R} | \mathbf{R} \alpha \rangle \right]
\]

\[
= -\frac{i e}{\hbar} \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}' \neq \mathbf{R}} e^{i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} \int d\mathbf{r} r_j \sum_{R'' \alpha''} \left[ (\chi_{\mathbf{R}' \alpha'}(\mathbf{r} + \mathbf{R}'))^{*} \chi_{\mathbf{R}'' \alpha''}(\mathbf{r} + \mathbf{R}') \langle \mathbf{R}' \alpha' | \mathbf{H} | R'' \alpha'' \rangle \langle \mathbf{R}' \alpha' | \mathbf{r} + \mathbf{R} \rangle \langle \mathbf{r} + \mathbf{R} | \mathbf{R} \alpha \rangle - \langle \mathbf{R}' \alpha' | \mathbf{H} | R'' \alpha'' \rangle \chi_{\mathbf{R}'' \alpha''}(\mathbf{r} + \mathbf{R}') \langle \mathbf{R}' \alpha' | \mathbf{r} + \mathbf{R} \rangle \langle \mathbf{r} + \mathbf{R} | \mathbf{R} \alpha \rangle \right]
\]  

(24)

with the wave functions \( \chi_{\mathbf{R} \alpha}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{R} \alpha \rangle \). This term accounts on the one hand for all atomic or *intra*-site (\( \mathbf{R} = \mathbf{R}' \)) processes and on the other hand for corrections to the *inter*-site processes contained in the Peierls term. Hence, we can split the momentum matrix element into three contributions:

\[
\langle \mathbf{k} \alpha' | \hat{p}_j | \mathbf{k} \alpha \rangle = \frac{m_e}{\hbar} \frac{\partial}{\partial k_j} \tilde{H}_{k}^{\alpha' \alpha} + [p_{k,j}^{\alpha' \alpha} |_{\text{inter-site corr.}} + p_{k,j}^{\alpha' \alpha} |_{\text{intra-site corr.}}].
\]  

(25)

In the limit of well-localized orbitals, the dominant correction is given by the *intra*-site term [13]. It is obtained by using the lattice periodicity, \( \chi_{\mathbf{R} \alpha}(\mathbf{r} + \mathbf{R}) = \chi_{\alpha \alpha}(\mathbf{r}) \), to shift the origins of all wave functions to the same unit cell, which is labeled 0. We then identify those terms
where the wave function arguments also lie within the same unit cell \((\mathbf{R}'' = \mathbf{R}'\) in the first term, \(\mathbf{R}'' = \mathbf{R}\) in the second term):

\[
\hat{P}_{k,j}^{\alpha^\prime|\alpha}_{\text{intra-site corr.}} = -\frac{\imath m_e}{\hbar} \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}'} e^{\imath k \cdot (\mathbf{R} - \mathbf{R}')} \int d\mathbf{r}_j \sum_{\alpha''} \left[ (\chi_{0\alpha'}(\mathbf{r}))^* \chi_{0\alpha''}(\mathbf{r}) \langle \mathbf{R}' \mathbf{0}^\prime | H \mathbf{R} \alpha \rangle - \langle \mathbf{R}' \mathbf{0}^\prime | H \mathbf{0}^\prime'' \alpha''(\mathbf{r})^* \chi_{0\alpha}(\mathbf{r}) \right]
\]

\[
= -\frac{\imath m_e}{\hbar} \int d\mathbf{r}_j \sum_{\alpha''} (r_j^{\alpha\alpha''} \tilde{H}_k^{\alpha''\alpha} - \tilde{H}_k^{\alpha'\alpha''} r_j^{\alpha''\alpha})
\]

with the atom-like dipole matrix elements

\[
r_j^{\alpha\alpha'} = \int d\mathbf{r} (\chi_{0\alpha}(\mathbf{r}))^* \chi_{0\alpha'}(\mathbf{r})
\]

forcing the usual optical selection rules \(\Delta l = \pm 1, \Delta m = 0, \pm 1\). Note that the \textit{intra}-site term (26) needs to take into account the same set of localized orbitals that is used to set up the lattice Hamiltonian (18). The fact that the coupling to the magnetic field via the vector potential has to be two-fold in a tight-binding or lattice approach has also been discussed in Ref. [14]. There are always contributions that can not be captured by the so-called Peierls substitution [13] in the lattice Hamiltonian leading to the first term in (25).

If we nevertheless use the Peierls contribution alone, we end up with the following lattice formulation of the orbital magnetic moment:

\[
\mu_{z,k}^{\text{orb,n}}|_{\text{lat}} = -\frac{e}{2 m_e} \frac{\hbar}{m_e} \left(\frac{\hbar}{m_e}\right)^2 \sum_{\alpha,\alpha'} \frac{1}{\varepsilon_{k}^\alpha - \varepsilon_{k}^{\alpha'}} \sum_{\alpha,\alpha'} (c_{\alpha}^n(\mathbf{k}))^* c_{\alpha'}^{n'}(\mathbf{k}) \frac{\partial}{\partial k_x} \tilde{H}_k^{\alpha'\alpha} \sum_{\alpha,\alpha'} (c_{\alpha}^{n'}(\mathbf{k}))^* c_{\alpha}^{n}(\mathbf{k}) \frac{\partial}{\partial k_y} \tilde{H}_k^{\alpha'\alpha}
\]

\[
= \frac{e}{2 \hbar} \sum_{\alpha,\alpha'} \frac{1}{\varepsilon_{k}^\alpha - \varepsilon_{k}^{\alpha'}} \left\{ \sum_{\alpha,\alpha'} (c_{\alpha}^n(\mathbf{k}))^* c_{\alpha'}^{n'}(\mathbf{k}) \frac{\partial}{\partial k_x} \tilde{H}_k^{\alpha'\alpha} \sum_{\alpha,\alpha'} (c_{\alpha}^{n'}(\mathbf{k}))^* c_{\alpha}^{n}(\mathbf{k}) \frac{\partial}{\partial k_y} \tilde{H}_k^{\alpha'\alpha} - \text{c.c.} \right\}
\]

\[
= -\frac{e}{\hbar} \sum_{\alpha,\alpha'} \frac{1}{\varepsilon_{k}^\alpha - \varepsilon_{k}^{\alpha'}} \text{Im} \left\{ \sum_{\alpha,\alpha'} (c_{\alpha}^n(\mathbf{k}))^* c_{\alpha'}^{n'}(\mathbf{k}) \frac{\partial}{\partial k_x} \tilde{H}_k^{\alpha'\alpha} \sum_{\alpha,\alpha'} (c_{\alpha}^{n'}(\mathbf{k}))^* c_{\alpha}^{n}(\mathbf{k}) \frac{\partial}{\partial k_y} \tilde{H}_k^{\alpha'\alpha} \right\}.
\]

In a simple two-band model, the structure of this expression leads to equal orbital magnetic moments for conduction and valence electrons. Corrections are expected due to transitions from each band, respectively, to energetically higher and lower bands. Moreover, if the two
fundamental bands are composed of localized orbitals that do not allow for atom-like dipole transitions (e.g., $d_{z^2}$- and $d_{x^2-y^2}/d_{xy}$-orbitals in transition metal dichalcogenide monolayers), the \textit{intra}-site correction will vanish. The exciton g-factor, calculated directly from the magnetic moments of conduction and valence bands at the $K$-point as $g_X = 2(\mu_{zK}^c - \mu_{zK}^v)/\mu_B$, will therefore be zero since the net spin of the exciton is zero. This is consistent with the $k \cdot p$-picture discussed in Ref. [14].
VI. VALLEY ZEEMAN SHIFT OF $X^-$, $X^+$ AND $X'^-$

![Figure S 4](image)

Figure S 4. (a) Carrier density dependent Zeeman shift of the positively charged exciton $X^+$. (b) Carrier density dependent Zeeman shift of the strongly dressed high density feature $X'^-$. 
Figure S 5. Valley Zeeman shift of the negatively charged exciton $X^-$ for positive (s+) and negative (s-) magnetic field direction for electron concentrations of $n = 1.45 \times 10^{12}$ cm$^{-2}$, $3.25 \times 10^{12}$ cm$^{-2}$ and $4.51 \times 10^{12}$ cm$^{-2}$.

VII. MAGNETIC FIELD AND DENSITY DEPENDENT VALLEY DICHROISM

Figure S 6. False color maps of the energy and carrier density dependent degree of valley polarization $\eta_v$ at $|B| = 5$ T, 10 T, 15 T, 20 T and 28 T. Charge neutrality is highlighted with the dashed black line. The $X^-$ and $X'-$ reveal enhanced degree of polarization for higher magnetic field.
Figure S 7. (a) Magnetic field dependence of the degree of valley polarization $\eta_v$ of the $X'^{-}$ for $n = 8.49 \cdot 10^{12}$ cm$^{-2}$. Solid line is a linear fit to the data. (b) Electron concentration dependence of $\eta_v$ at $|B| = 28$ T.
Figure S 8. Electron density dependent degree of valley polarization of the intravalley trion $X^-$ for magnetic fields ranging from $|B| = 5 \text{T}$ to $28 \text{T}$. For $|B| = 28 \text{T}$, LLs with filling factors of $\nu = +0K$ and $\nu = +1K$ are highlighted by the two arrows, respectively.
[1] A. Castellanos-Gomez, M. Buscema, R. Molenaar, V. Singh, L. Janssen, H. S. J. van der Zant, and G. A. Steele, 2D Materials 1, 011002 (2014), URL https://doi.org/10.1088/2053-1583/1/1/011002.

[2] J. Wierzbowski, J. Klein, F. Sigger, C. Straubinger, M. Kremser, T. Taniguchi, K. Watanabe, U. Wurstbauer, A. W. Holleitner, M. Kaniber, et al., Scientific Reports 7 (2017), URL https://doi.org/10.1038/s41598-017-09739-4.

[3] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, et al., Nature Nanotechnology 5, 722 (2010), URL https://doi.org/10.1038/nnano.2010.172.

[4] C. Robert, M. A. Semina, F. Cadiz, M. Manca, E. Courtade, T. Taniguchi, K. Watanabe, H. Cai, S. Tongay, B. Lassagne, et al., Physical Review Materials 2 (2018), URL https://doi.org/10.1103/physrevmaterials.2.011001.

[5] J. G. Roch, G. Froehlicher, N. Leisgang, P. Makk, K. Watanabe, T. Taniguchi, and R. J. Warburton, Nature Nanotechnology 14, 432 (2019), URL https://doi.org/10.1038/s41565-019-0397-y.

[6] K. K. Kim, A. Hsu, X. Jia, S. M. Kim, Y. Shi, M. Dresselhaus, T. Palacios, and J. Kong, ACS Nano 6, 8583 (2012), URL https://doi.org/10.1021/nn301675f.

[7] B. Hunt, J. D. Sanchez-Yamagishi, A. F. Young, M. Yankowitz, B. J. LeRoy, K. Watanabe, T. Taniguchi, P. Moon, M. Koshino, P. Jarillo-Herrero, et al., Science 340, 1427 (2013), URL https://doi.org/10.1126/science.1237240.

[8] A. Laturia, M. L. V. de Put, and W. G. Vandenbergh, npj 2D Materials and Applications 2 (2018), URL https://doi.org/10.1038/s41699-018-0050-x.

[9] X. Cui, G.-H. Lee, Y. D. Kim, G. Arefe, P. Y. Huang, C.-H. Lee, D. A. Chenet, X. Zhang, L. Wang, F. Ye, et al., Nature Nanotechnology 10, 534 (2015), URL https://doi.org/10.1038/nnano.2015.70.

[10] A. Allain, J. Kang, K. Banerjee, and A. Kis, Nature Materials 14, 1195 (2015), URL https://doi.org/10.1038/nmat4452.

[11] F. Rose, M. O. Goerbig, and F. Piéchon, Physical Review B 88 (2013), URL https://doi.org/10.1103/physrevb.88.125438.
[12] M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller, and F. Bechstedt, Physical Review B 73 (2006), URL https://doi.org/10.1103/physrevb.73.045112.

[13] J. M. Tomczak and S. Biermann, Physical Review B 80 (2009), URL https://doi.org/10.1103/physrevb.80.085117.

[14] G. Wang, L. Bouet, M. M. Glazov, T. Amand, E. L. Ivchenko, E. Palleau, X. Marie, and B. Urbaszek, 2D Materials 2, 034002 (2015), URL https://doi.org/10.1088/2053-1583/2/3/034002.