Valley Contrasting Magnetoluminescence in Monolayer MoS$_2$ Quantum Hall Systems

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The valley dependent optical selection rules in recently discovered monolayer group-VI transition metal dichalcogenides (TMDs) make possible optical control of valley polarization, a crucial step towards valleytronics applications. However, in presence of Landau level(LL) quantization such selection rules are taken over by selection rules between the LLs, which are not necessarily valley contrasting. Using MoS$_2$ as an example we show that the spatial inversion-symmetry breaking results in unusual valley dependent inter-LL selection rules, which directly locks polarization to valley. We find a systematic valley splitting for all Landau levels (LLs) in the quantum Hall regime, whose magnitude is linearly proportional to the magnetic field and in comparable with the LL spacing. Consequently, unique plateau structures are found in the optical Hall conductivity, which can be measured by the magneto-optical Faraday rotations.

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Monolayers of MoS$_2$ and other group-VI transition-metal dichalcogenides (TMDs) represent a family of two-dimensional (2D) materials beyond graphene that are promising for the next generation nanoelectronics [1, 2]. Because of their coupled spin and valley physics, they have become exciting platforms for exploring novel valleytronics applications [2–8]. A significant challenge for valleytronics is to achieve the valley polarization or lift the valley degeneracy in a controllable way [9–11]. One unique property for monolayer MoS$_2$ is that the two valleys K and K' feature opposite orbital helicity and direct band gaps, which allows one to selectively pump electrons from the valence band to the conduction band in a single valley with circular polarized lights [3–6]. The valley polarization is then detected from circular polarization of the photoluminescence from the recombination of electrons and holes, as demonstrated in recent experiments [3–6, 12–13].

However, in the presence of a magnetic field $B_\perp$ perpendicular to the sample plane, which causes the energy spectrum to collapse into discrete Landau levels (LLs), optical excitations and magnetoluminescence involving conduction and valence bands will occur only between appropriate LLs. The low energy band structure of monolayer MoS$_2$ can be described by a two-band Dirac model [5]. But unlike graphene, because of the large gap terms, the band edges are parabolic instead of linear, resulting in a LL spectrum that is linear instead of square root dependent on $B_\perp$, as well as LL index $n$ [14]. Nevertheless, it is well known for both parabolic bands (e.g. GaAs) [15–17] and linear Dirac cones (e.g. graphene) [18–21] that the optical transitions between the LLs are governed by the selection rules: $\pm n \leftrightarrow \pm |n \pm 1|$ [22]. Even when considering a single valley such selection rules will allow interband excitations and magnetoluminescence in both $\sigma_{+/\pm}$ polarizations, which is different from the valley-polarization locking at zero magnetic field for TMDs. It is thus unclear for monolayer MoS$_2$ how the valley degree of freedom relates to circular polarizations in presence of the LL quantization. Another motivation of this work is to see how the valley degree of freedom plays a role in the optical Hall conductivity in the ac regime. For graphene the ac quantum Hall physics has been well explored [19, 20, 23–27], in which the two valleys can be treated equally due to valley degeneracy.

In this work, we study the monolayer MoS$_2$ quantum Hall systems based on an atomic tight-binding model. We show that (i) A systematic valley splitting exists for all LLs, which is not revealed by the simplified two-band Dirac model [14]. The splitting magnitude is linear against $B_\perp$ and is comparable with the LL spacing. This valley splitting is manifested in spin-valley polarized interband optical transitions due to valley imbalanced Pauli blocking. (ii) The interband optical transitions follow a valley dependent selection rule: only $-(n+1) \leftrightarrow n$ is allowed in one valley and $-n \leftrightarrow n+1$ in the other. (iii) The polarization($\sigma_{+/\pm}$) of the optical transitions are locked to the valley degree of freedom due to such selection rules. Consequently a series of spin-valley polarized transitions can be addressed in circular dichroism and magnetoluminescence under resonant excitations. (iv) The optical Hall conductivity shows plateau structures and features valley-contrasting components, which hallmark the fully degeneracy-lifted LLs. Our predictions also apply to other group-VI TMDs.

LLs and valley splitting. The monolayers of MoS$_2$ consist of a Mo layer sandwiched between two S layers in a trigonal prismatic arrangement. Although similar to graphene in many aspects, some of its properties are more favorable than graphene. It features a direct band
FIG. 1: (color online) (a) schematic of the spin-valley coupled band structure of TMDs. Red(blue) represents spin up(down), respectively. (b) and (c): Conduction and valence band LLs for MoS$_2$ under $B_{\perp} = 20$ T. K(K') valley is on the left(right). The crossing-LL states in the conduction band are from the dangling bonds on the zigzag edges$^31$, which do not affect the LLs. Dash line is a guide to eye for valley splitting and also marks filling level $n$.

The Zeeman splitting is first neglected here and will be discussed later. We label the LLs and assign the $n = 0$ LLs according to the analytic solutions from the two-band Dirac model$^{12}$. When $B_{\perp} > 0$ they appear only in conduction band of K valley and valence band of K' valley. Therefore the valley degeneracy for them is already lifted. Note that the $n = 0$ in K valley’s conduction band is still spin degenerate in the TB model although the first-principle calculations suggest the spin degeneracy is slightly lifted$^{[3, 33]}$. Here our focus is on the more general $n \neq 0$ LLs.

We notice a systematic valley splitting exists for all $n \neq 0$ LLs with the magnitude comparable to the LL spacing, as shown in Fig.1. A linear relation with $B_{\perp}$ is found. Here we let $B_{\perp} > 5$T to ensure $E_y >> l_B$. The linearity should extend to the low field situation in this single-particle calculation. In the case of graphene, the valley degeneracy is known to be lifted in high magnetic fields via electron-electron or electron-phonon interactions$^{[32–36]}$. Similar linear relations between the valley splitting and $B_{\perp}$ have also been experimentally observed in silicon and AlAs 2D electron systems$^{[36, 37]}$. Their physical origin, however, remains controversial.

The valley splitting here has a few direct consequences:

(i) The $n = 0, 1$ LLs in conduction band are always valley polarized and $n = 0, -1$ in valence band spin-valley polarized.

(ii) The total filling factor follows a sequence $\nu = 2, 3, 4, \ldots$ in the electron doped regime and $\nu = -1, -2, -3, \ldots$ in the hole doped regime. The lifting of valley degeneracy in $n = 0$ LLs can be attributed to the broken spatial-inversion symmetry in the monolayer. Such symmetry is known to guarantee the valley degeneracy rigorously on graphene, regardless of the time-reversal symmetry$^{[38]}$. However, it does not explain the splitting in $n \neq 0$ LLs$^{[39]}$. Instead, using graphene lattice as a toy model (see appendix), we find the splitting in $n \neq 0$ LLs can be induced by the next-nearest-neighbour (NNN) electron hopping, which breaks the electron-hole symmetry. Therefore the valley-splitting in $n \neq 0$ LLs stems from spontaneous breaking of spatial-inversion, electron-hole and time-reversal symmetry. In fact, the low energy physics in MoS$_2$ is dominated by electron hopping between Mo atoms, which is indeed the NNN hopping on the honeycomb lattice$^{[3, 6]}$.

Valley dependent selection rules: We now turn to the optical properties of these valley-degeneracy-lifted LLs. Because $\hbar \omega_c \ll \Delta$, the intraband and interband optical transitions in this system belongs to two completely different regimes: intraband in the microwave to terahertz and interband in the visible frequency range. We will set our focus on the latter because for MoS$_2$ the valley contrasting interband optical transitions have been the most intriguing property in experiments for valleytronics$^{33, 12}$.

When considering the transitions between levels $n'$ and $n$, the well-known selection rule for 2D electron systems and graphene requires $|n| = |n'| \pm 1$.$^{[19, 21, 23, 24, 40]}$. At first glance, since the LL spacing is comparable in the conduction and valence bands, four transitions would occur at very close but non-degenerate photon energies:
As the filling level goes up, the number of spin-valley polarization peaks has an alternating $2 - 1 - 2 - 1$ pattern, which can be attributed to the valley-imbalanced Pauli blocking caused by the $n = 0$ LLs and the valley splitting as illustrated in Fig. 2(g-h).

To further understand the role played by the valley degree of freedom in the optical Hall effect, we calculate the optical Hall conductivity using the Kubo formula [23, 24, 40],

$$
\sigma_{ij}(\omega) = \frac{i}{L_x L_y} \sum_{\epsilon_n, \epsilon_{n'}, \mu, \mu'} \frac{1}{\epsilon_{n'} - \epsilon_n - \omega - i\Gamma} \left( \frac{\mathbf{J}^{n'n'}_{ij} \mathbf{J}^{n'n'}_{ij}}{\epsilon_{n'} - \epsilon_n - \omega - i\Gamma} - \frac{\mathbf{J}^{n'n'}_{ij} \mathbf{J}^{n'n'}_{ij}}{\epsilon_{n'} - \epsilon_n + \omega + i\Gamma} \right),
$$

where $i,j = x, y$. Following Ref. [23], here we retain 40 LLs and impose periodic boundary conditions along the $x$ and $y$ directions. $B_\perp$ is kept at 20.8 T, as close as possible to that used in Fig. 1 and 2, since in such calculations $B_\perp$ can only take discrete levels. The two valleys cannot be distinguished in the momentum space. However, since the valley index is associated with spin, we can distinguish valleys by spins. The result is shown in Fig. 3, where $\sigma_{\pm}(\omega) = \sigma_{xx}(\omega) \pm i\sigma_{xy}(\omega)$ is the optical conductivity for the right and left circular polarized light. Spin-valley polarized resonance structures for $\sigma_{xy}$ is found, similar to Fig. 2. In this set-up, for the electron(hole) doped regime the spin-valley polarization is achieved for the spin up (down) and K’(K) valley, respectively. Upon switching the sign of $B_\perp$ the valley and spin polarization also flips. At resonance photon frequencies $\sigma_{xy}$ from the

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**FIG. 2:** (color online) Optical absorption spectrum in the quantum Hall regime. The solid(dash) lines represent K(K’) valley, respectively. Red(blue) represents spin up(down), respectively. Spin-valley polarized transitions between $(n,n')$ are labeled. (a) & (d): $\nu(K) = 4$, $\nu(K') = 0$. (b) & (e): $\nu(K) = 4$, $\nu(K') = 2$. (c) & (f): $\nu(K) = 6$, $\nu(K') = 2$. $\Gamma = 0.1\hbar\omega_c$. (g-h) Schematic of the inter-LL transitions corresponding to (b,e) and (c,f). Red(solid) crosses indicate Pauli blocking. Green(dash) crosses indicate vanishing probability.

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**FIG. 3:** (color online) Optical Hall conductivity in unit of $e^2/h$ with filling factors $\nu(K) = 6$, $\nu(K') = 2$, corresponding to Fig. 2(c). (a): optical conductivity $\sigma_{xy}$ and $\sigma_{xx}$ for spin up, K’ valley. (b): spin down, K valley. (c) total $\sigma_{xy}$, the dash line schematically shows the cancelling out situation when $\Delta_c = \Delta_{01}$. (d): total $\sigma_{+/-}$. Only the real part is plotted.
two valleys actually have the opposite signs. This is another distinctive feature from graphene, in which both valleys contribute equally to the total $\sigma_{xy}$ [21,22]. But due to the difference in $\Delta_0^1$ and $\Delta_0^0$ (Fig. 1d), the resonance frequencies in the two valleys are slightly mismatched, leading to spin-valley mixed resonance peaks in $\sigma_{xy}$ (starting from the third resonance in Fig. 3c) instead of cancelling out.

A more important message from Fig. 3 when compared with Fig. 2 is that the allowed interband transitions in $K$ and $K'$ valleys are solely attributed to the left and right circular polarized light separately

$$K : - (n+1) \leftrightarrow n, \sigma_-$$

$$K' : - n \leftrightarrow n+1, \sigma_+$$

where $n \geq 0$. Consequently the circular polarization is directly locked with the valley degree of freedom in optical transitions in the quantum Hall regime. Upon flipping the direction of $B_\perp$, the valley index will switch, i.e. $K(\sigma_-)$ and $K'(\sigma_+)$.  

**Optical Hall plateaus.** The optical conductivity as a function of the chemical potential $\mu$ is shown in Fig. 4, where $\omega$ is slightly away from resonance. The static quantum Hall conductivity is also presented, showing fully valley-degeneracy-lifted and well quantized plateaus. We notice that in the optical conductivity each spin or valley component also develops its own and contrasting plateaus, although like the net $\sigma_{xy}(\omega)$ they are not quantized either. The $n=0$ LLs and the valley splitting are manifested in the alternating sequence of the step structures in these two components, which also leads to a unique sequence of filling factors in the net $\sigma_{xy}(\omega)$ plateaus, as labelled in Fig. 4. To be specific, 2,3 spans $n=0$ to $n=1$ in $K$ valley and $4,5$ $n=1$ in $K$ to the $n=1$ in $K'$ valley, and so on. Interestingly, the valley contrasting plateaus persist even when $\mu$ is in the band gap, as is seen for the $0$ plateau that extends all the way to the valence band top.

**Circular dichroism, magnetoluminescence and Faraday rotation.** Valley resolved interband optical transitions shown in Fig. 2 are readily detectable by the circular dichroism spectroscopy due to the polarization-valley locking. Given the already excellent photoluminescence of monolayer TMDs in zero-field, magnetoluminescence would be an ideal test of the valley dependent selection rules, in which luminescence between individual LLs in a selected valley can be driven by resonant circular polarized excitations in the Faraday geometry [12,17]. The optical Hall conductivity $\sigma_{xy}(\omega)$ can be measured from the Faraday rotation angle $\theta(\omega)$ [23,24]. A spin-valley polarized excitation would be indicated by a single maximum absolute slope $|d\theta/d\omega|$ at resonant frequencies as shown in Fig. 3c.

**Interplay of valley and spin splitting.** The Zeeman splitting is estimated to be much smaller than the valley splitting when we assume an ordinary g-factor for electrons ($g=2$). For the LLs close to the valence band top the valley splitting is enlarged by the Zeeman splitting while for the split-off valence bands the valley splitting is reduced. The LLs in the conduction band follows correspondingly. However, since the optical transitions only happen between LLs with the same spins, the optical Hall conductivity as functions of $\omega$ in each valley is unaffected by the spin splitting (i.e. Fig. 2 and Fig. 3). Fig. 4 will be affected by the spin splitting where the red(blue) plateaus slightly shift right(left), respectively.

To conclude, we have shown that valley splitting exists for all the LLs in monolayer MoS$_2$ and other TMDs even without considering the interaction effects. Optical transitions in the quantum Hall regime follow valley dependent selection rules, which locks the circular polarization and valley degree of freedom together. Finally we propose circular dichroism spectroscopy, magnetoluminescence and Faraday rotation measurements as potential tests for the selection rules as well as the valley splitting. An interesting extension of current study would be the disorder and localization effect in the optical Hall effect, since in this system the mixing of valleys inevitably involves spin flipping, which is distinct from graphene [23,24].

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