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PAPER

Brightening of spin- and momentum-dark excitons in transition metal dichalcogenides

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Abstract

Monolayer transition metal dichalcogenides (TMDs) have been in focus of current research, among others due to their remarkable exciton landscape consisting of bright and dark excitonic states. Although dark excitons are not directly visible in optical spectra, they have a large impact on exciton dynamics and hence their understanding is crucial for potential TMD-based applications. Here, we study brightening mechanisms of dark excitons via interaction with phonons and in-plane magnetic fields. We show clear signatures of momentum- and spin-dark excitons in WS₂, WSe₂ and MoS₂, while the photoluminescence of MoSe₂ is only determined by the bright exciton. In particular, we reveal the mechanism behind the brightening of states that are both spin- and momentum-dark in MoS₂. Our results are in good agreement with recent experiments and contribute to a better microscopic understanding of the exciton landscape in TMDs.

Transition metal dichalcogenides (TMDs) exhibit a number of fundamentally interesting and technologically promising properties [1–3]. Their electronic band structure consists of multiple minima and maxima in the valence and conduction band, which—combined with the strong Coulomb interaction—leads to a variety of exciton states, cf. figure 1(a) [1, 4, 5]. Intervallley excitons consisting of electrons and holes located in different valleys (K, L, Γ), are momentum-dark since photons cannot provide the required momentum necessary for an indirect recombination [6]. Furthermore, the spin–orbit coupling gives rise to pronounced spin-splitting in both conduction and valence bands [7–10] leading to spin-allowed (same spin for valence and conduction band) and spin-dark (different spin) states. While bright excitons, consisting of Coulomb-bound electrons and holes in the same valley with the same spin, can be directly activated by light and have been extensively investigated in literature [2, 4, 5, 11, 12], spin- and/or momentum-dark excitons need an additional brightening mechanism to be visible in optical spectra [13, 14]. Recently, signatures of spin-dark excitons have been observed in experiments with large aperture even in the absence of a magnetic field [15] and hence spin-dark excitons are rather darkish, since they exhibit an out of plane dipole.

Dark excitons are highly interesting for TMD research, as they can lie energetically below bright excitons [16–18] (figure 1(b)) and hence have a significant impact on non-equilibrium dynamics as well as optical response of these materials. Different mechanisms can principally brighten up dark exciton states. This includes in-plane magnetic fields, which mix the spin states making spin-dark excitons visible [14, 19]. Phonons, disorder or molecules provide an additional center-of-mass momentum to activate momentum-dark excitons [20–25]. In this work, we present a microscopic approach allowing us to investigate the possibility to brighten up states that are both spin- and momentum-dark. Our work is motivated by an experimental study observing a yet unidentified low-energy peak in MoS₂ monolayers in presence of an in-plane magnetic field. While brightening of spin-dark excitons in tungsten-based TMDs has been well understood [26–30], only little is known about spin- and momentum-dark excitons in MoS₂. Including a magnetic field in our equation-of-motion approach, we find a field-induced mixing of spin-up and spin-down states, which activates the originally spin-dark exciton resulting in an additional peak in optical spectra, cf. figure 1(c). Including phonon-assisted optical transitions on the same microscopic footing, we investigate the possibility to even brighten up states that are both spin- and momentum-dark.
1. Theoretical approach

To obtain a microscopic access to the optical response of TMDs after an optical excitation, we apply the density matrix formalism with semiconductor Bloch equations in its core [31–34]. The particular goal of this work is to describe many-particle mechanisms brightening up momentum- and spin-dark states. The intensity of photoluminescence (PL) can be expressed as [24, 25, 35]

\[ I(\omega_q) \propto \hbar \omega_q \Omega_{q}(\langle \epsilon_q^x \epsilon_q^y \rangle) \propto \Im \langle \epsilon_q^x \epsilon_q^y \rangle. \]  

The PL is given by the time derivative of the photon density \( \langle \epsilon_q^x \epsilon_q^y \rangle \) that is determined by the photon-assisted polarization \( \langle \epsilon_q^x \epsilon_q^y \rangle \) corresponding to the recombination of an exciton \( \langle X_q^0 \rangle \) under emission of a photon \( \langle \epsilon_q^x \epsilon_q^y \rangle \). Here, we have introduced the photon creation and annihilation operators \( \epsilon_q^x, \epsilon_q^y \) and the exciton annihilation operator \( X_q^0 \) that will be defined below. The introduced PL equation only describes direct radiative recombination processes and thus contains only signatures from the bright exciton. To include also possible features stemming from dark excitons via higher order processes, we have to extend the PL equation by implementing phonon-assisted radiative recombination processes and the impact of a magnetic field.

To account for excitonic effects, which are dominant in TMD monolayers [2, 5, 11, 12, 36], it is convenient to project the many-particle system into an excitonic basis. Following Katsch et al [37], we introduce the exciton operator

\[ X_Q = \sum_q \varphi_q^{\alpha^\dagger} \varphi_q^{\beta Q}. \]  

which includes the electron (hole) operator \( a^{(v)} \), relative \( q \) and center of mass \( Q \) momenta. They can be translated into electron and hole momenta via \( q = \alpha k_e + \beta k_h \) and \( Q = k_e - k_h \) with \( \alpha(\beta) = m_e/m_h \). Moreover, (2) contains the exciton wavefunction \( \varphi_q \) obtained by solving the Wannier equation [5, 17, 25, 31, 32]

\[ \frac{\hbar^2 q^2}{2\mu} \varphi_q - \sum_k V_{\text{exc}}(k) \varphi_q - \epsilon \varphi_q = 0. \]

with the reduced mass \( \mu = (m_e m_h)/(m_e + m_h) \) the excitonic energy \( \epsilon \) and the Keldysh potential \( V_{\text{exc}} \). By introducing the exciton operator in the pair-space, we can define an excitonic Hamilton operator including the interaction with phonons and a magnetic field.

The Hamiltonian reads \( H = H_0 + H_{\text{photon}} + H_{\text{magn}} \), where

\[ H_0 = \sum_{Q,s} \epsilon(s) X_Q^0 X_Q^s + \sum_{Q,s} \hbar \omega_{Q,s}^x \varphi_q^{\dagger} \varphi^s_q + \sum_{Q,s} M_0 \Omega_{Q,s}^x B_{Q,s}^x \]

is the interaction-free part for excitons, photons and phonons with the excitonic energy \( \epsilon(s) \) in the state \( s = (s, \eta) \) with the spin \( s = \uparrow, \downarrow \) and the valley \( \eta = (\text{KK}, \text{KK}', \text{KA}, \text{FK}) \) as solutions from the Wannier equation, cf. (3). The photon energy \( \hbar \omega_{Q,s}^x \) with the polarization mode \( s \), and the phonon energy \( \hbar \Omega_{Q,s}^x \) with the phonon mode \( \zeta \). The exciton-phonon interaction reads

\[ H_{\text{photon}} = \sum_{Q,s} M_0 \Omega_{Q,s}^x \varphi_q^{\dagger} X_Q^s + \text{h.c.} \]

with the excitonic optical matrix element \( M_0^x = \sum_q \varphi_q^{\dagger} M_0^x q \delta_{Q,0} \) and the coupling element \( M_0^x \) for interband transitions [5].

Finally, the interaction between excitonic spin states \( i, j \) and an in-plane magnetic field \( B \) is described by the Hamiltonian

\[ H_{\text{magn}} = \sum_{Q,i,j} G_{ij} \frac{\mu_B}{2} B X_Q^i X_Q^j. \]

The matrix element \( G_{ij} \) reads in excitonic basis

\[ G_{ij} = \langle \varphi_q^{\alpha^\dagger} \varphi_q^{\beta} \rangle \sum_q \varphi_q^{\dagger} \varphi_q^{\beta} \text{ with the electrons (holes) keeping their spins, while mixing of spins in the valence (conduction) band of one valley takes place, i.e., } \varphi_q^{(v)} = \varphi_q^{(v)} \delta_{\eta, \eta_0} (1 - \delta_{\eta, \eta_0} \delta_{\delta \delta}(x)). \] Here, \( \delta_{\eta, \eta_0} \) is the experimentally accessible g-factor for the conduction (valence) band in the valley \( \eta \) and \( \mu_B \) is the Bohr magneton. The g-factors in 2D materials are an ongoing topic of research [39–42] and still under debate as they can differ significantly for bright, dark and charged states in in-plane and out-of-plane magnetic fields.
Since we are investigating in-plane magnetic fields, it is the in-plane component of the magnetic moment ($\mu_{\text{spin}} = \pm 1$ [43, 44]) that determines the g-factor resulting in $g_{\text{eff}} = 2$, which is in agreement to earlier work [14, 28, 45, 46]. Note that the g-factor plays a crucial role for the brightening process of the spin-dark excitons. The larger the g-factor, the more efficient is the mixing of spin-allowed and spin-dark excitons. The larger the g-factor, the more efficient is the mixing of spin-allowed and spin-dark states determining the gained oscillator strength of the latter in a magnetic field.

Now, we have all ingredients at hand to derive the equation of motion for our key quantity, the photon-assisted polarization $\langle \epsilon_i^X X_i^\dagger \rangle$ providing access to the PL, cf (1). However, the equation can be simplified resulting in an intuitive Elliott-like formula including both phonon- and magnetic field-induced PL.

To get there, we perform a unitary transformation to include the magnetic field into $H_0$ and subsequently apply a cluster expansion approach to account for phonon-assisted radiative recombinations. We start by modifying the system with an unitary transformation, such that $H_{x=\text{mag}}$ becomes included in $H_0$. To illustrate the idea, we simplify our system for the moment the interaction with photons and phonons)

$$ H = \sum_\eta q_i^{\eta} X_i^{\eta\dagger} X_i^{\eta} + \sum_{\eta,\eta'} G_{\eta,\eta'}^{\hbar B} B X_i^{\eta\dagger} X_j^{\eta'} $$

$$ = \sum_i q_i^{\eta} X_i^{\eta\dagger} X_i^{\eta} $$

with the new quantum number $i$, and new energy $\tilde{\varepsilon}_i^\eta$ and state operator $\tilde{X}_i^\eta$, i.e.

$$ \tilde{\varepsilon}_i^\eta = \varepsilon_i^\eta \pm \sqrt{\frac{\Delta^\eta}{2} + \left(\frac{\tilde{g}}{2\mu B}\right)^2} $$

$$ \tilde{X}_i^{\eta(1)} = U_{\eta}^{\eta\dagger} X_i^{\eta(1)} + U_{\eta}^{\eta\dagger} X_i^{\eta(1)} = \frac{h_{\eta}^{\eta} X_i^{\eta(1)} + X_i^{\eta(2)}}{\sqrt{1 + h_{\eta}^{\eta^2}}} $$

We introduced the abbreviations $h_{\eta}^{\eta} = \Delta^\eta / (\mu B) + \lambda \sqrt{1 + \Delta^2 / (\mu B^2)}$, $\Delta^\eta = \varepsilon_i^\eta - \varepsilon_i^\eta$ and $\lambda = \pm$. The latter can be positive or negative depending on the energetic ordering in the investigated TMD material. Note that for the definition of the transformation matrix $U_\eta$, we exploited $X_i^{\eta(1)} = U_\eta X_i^{\eta(1)} = \sum_j U_{\eta}^{\eta\dagger} X_j^{\eta(1)}$ and $U_\eta U_\eta^\dagger = 1$, i.e. a uniform transformation.

We can now transform the rest of the Hamilton operator into this basis, yielding for the exciton-photon coupling $H_{\text{exc-phot}} = \sum \epsilon_i M_i \tilde{X}_i^{\eta\dagger} + \text{h.c.}$ with the new matrix elements $\tilde{M}_i = MU_i$. Neglecting for the moment the interaction with phonons (as we put $Q \approx 0$), we derive the equation of motions for the photon-assisted polarization $\tilde{S}_i^{\eta} = \langle \epsilon_i^X X_i^\dagger \rangle$ appearing in (1):

$$ i\hbar \partial_t \langle \epsilon_i^X X_i^\dagger \rangle = (\varepsilon_i^\eta - \hbar \omega) \langle \epsilon_i^X X_i^\dagger \rangle - \tilde{M}_i^{\eta} \langle \epsilon_i^X X_i^\dagger \rangle $$

with occupations $\tilde{N}_i^{\eta} = \langle \tilde{X}_i^{\eta} \tilde{X}_i^{\eta\dagger} \rangle$. To calculate the PL intensity in presence of a magnetic field we solve this equation in the adiabatic limit, i.e. assuming slowly varying exciton occupations compared to the photon-assisted polarization [25, 31, 32], yielding

$$ I(\omega) \propto \hbar \omega \sum_{\eta,\eta'} \langle \tilde{M}_i^{\eta\dagger} \rangle^2 N_i^{\eta\dagger} $$

with the exciton occupations $N_i^{\eta}$, excitonic energy $\tilde{\varepsilon}_i^{\eta\dagger}$ and dephasing $\gamma_i^{\eta}$, where $\eta$ and $i$ are the exciton and spin index.

### 2. Brightening of spin-dark excitons

For a better understanding of the influence of the magnetic field, we disregard for the moment the impact of momentum-dark excitons and consider only the bright state $\eta = \text{KK}$, $i = \uparrow \uparrow$ (denoted by B) and the spin-dark state $\eta = \text{KK}$, $i = \uparrow \downarrow$ (denoted by D). Furthermore we consider the situation $\mu B \ll \Delta^\eta$, where the energy difference between spin-allowed and spin-dark state is large compared to the Zeeman splitting. Here, the Zeeman term gives only a small correction to the energy, which is the case in tungsten-based TMDs for experimentally available magnetic field strengths. Then, we split up the sum over $\eta$ in (11) into dark and bright state and enter the solutions $\tilde{M}_i^B = MU_i^B$. Moreover, we set $U_\eta^D = \text{const}$ for the bright states and perform a Taylor expansion of $U_\eta^D$ for the dark states. This results in a more intuitive expression for the PL

$$ I(\omega) \propto \hbar \omega \sum \left[ \frac{M_i^2 N_i^{B\dagger}}{\tilde{\varepsilon}_B - \hbar \omega - i\gamma_B} + \frac{M_i^2 (\frac{\mu B}{2\hbar})^2 N_i^{D\dagger}}{\tilde{\varepsilon}_D - \hbar \omega - i\gamma_D} \right] $$

The first term describes the direct PL contribution stemming from the bright KK↑↑ exciton and resulting in a resonance at the energy $\tilde{\varepsilon}_B$. In addition, the magnetic field appearing in the second term gives rise to a new resonance at the position $\tilde{\varepsilon}_D$ due to the activation of spin-dark excitons. Previous microscopic studies [16, 25] have shown that excitons thermalize on a femtosecond timescale. Since the focus of our work lies on the stationary PL after exciton thermalization, we can approximate the exciton densities with equilibrium Boltzmann distributions.

Now, we numerically evaluate (12) to calculate the PL spectrum of WSe₂ as an exemplary TMD material.
is TMD-specific and depends specifically on the (i) relative energetic position of dark and bright excitons ($\frac{\Delta}{\epsilon} \approx 1$), (ii) the TMD-specific g-factor and dark-bright energy splitting $\Delta$, and (iii) the relative temperature-dependent exciton densities ($\frac{N_D}{N_B} = e^{-\frac{\Delta}{k_B T}}$). In materials with $\epsilon_D > \epsilon_B$ (e.g. MoSe$_2$) this factor will quickly approach 0 at low temperatures and hence we do not expect the dark state to brighten up, since its occupation is very low. On the other side, for tungsten-based materials with $\epsilon_D < \epsilon_B$ the factor will instead approach infinity at low temperatures and enables pronounced brightening of dark states. However, as the temperature increases the factor $\frac{N_D}{N_B}$ becomes smaller and hence the intensity of the peaks decreases as dark excitons thermalize and recombine via phonons. This is why spin-dark states are observed mainly at low temperatures [14, 19]. For the curvature we can extract $\xi(WSe_2, 35 K) = 0.0099 T^{-2}$ and $\xi(WSe_2, 35 K) = 0.0019 T^{-2}$. This means that WSe$_2$ is by a factor of two more responsive to an external magnetic field, which is in good agreement with experimentally observed values [14]. Note that slight differences in the g-factor of the two materials are expected to slightly change the difference in the curvature.

3. Brightening of spin- and momentum-dark excitons

So far, we have only included the effect of phonons in the linewidth of the exciton resonances [6, 25, 38]. However, under certain circumstances phonons can drive indirect radiative transitions from momentum-dark states [21, 25]. Hence, to fully understand the influence of the magnetic field on PL spectra, we now include exciton-phonon scattering and consider both momentum- and spin-dark exciton states.

We extend the exciton Hamiltonian by the exciton-phonon coupling

$$ H_{x-\text{phon}} = \sum_{Q, Q', \eta_1, \eta_2, j, \zeta} D_{Q, Q'}^{\eta_2, \eta_1} \phi_{\eta_1}^{\eta_2} \phi_{\eta_2}^{\eta_1} + \text{h.c.} $$

(14)

which creates an exciton with the momentum $Q + Q'$ in the state $\eta_1, j$ and annihilates an exciton with the momentum $Q$ in the state $\eta_2, j$ under creation of a phonon with the momentum $-Q'$ and the mode $\zeta = (LA, TA, LO, TO)$. In other words, it describes scattering of excitons by emitting or absorbing phonons in the mode $\zeta$. The exciton-phonon matrix element in the magnetic field basis reads $D_{Q, Q'}^{\eta_2, \eta_1} = \sum_{k, \lambda, \eta, \eta'} U_{\eta, \eta'}^{\eta_1, \eta_2} \phi_{\eta}^{\eta_1} \phi_{\eta'}^{\eta_2} U_{\eta_1}^{\eta_2} + \text{h.c.}$ with transformation matrices $\tau_\alpha = \phi_{\eta}^{\eta_1} \phi_{\eta_2}^{\eta_1}$. For the carrier-phonon coupling $d_{Q, \lambda, \eta_1, \eta_2}^{\eta_1, \eta_2}$ in the band $\lambda = (c, v)$ we use the deformation potential approximations [25] for acoustic...
and optical phonons from density functional perturbation theory (DFPT) [47]. Furthermore, we introduced \( \xi^\pm = \alpha, \beta \) with excitonic mass factors \( \alpha(\beta) = m_0 \left( m_{\pm} / m_0 \right) \) for the valence(conduction) band. We can see that the phonon introduces a momentum \( Q' \) into the system, which is transferred to the exciton. Depending on the efficiency of the exciton-phonon coupling, this can lead to the activation of momentum-dark excitons [25].

The transformation into the magnetic field basis enables us to exploit the TMD Bloch equations for phonon-assisted PL derived in our previous work [25] with the modified optical matrix element \( \hat{M}^0 \rightarrow \hat{M}^p \) and exciton energies \( \tilde{\epsilon}^\mu_{Q'0} \). We obtain a new expression for direct PL

\[
I(\omega)^p \propto \sum_{\mu} \frac{|\tilde{\Delta}^\mu_{Q'|Q} \rho_{\eta_i}^\mu|^2}{(\tilde{\epsilon}^\mu_{Q'|Q} - \hbar \omega)^2 + \gamma^\mu_{Q'|Q} / 4},
\]

which is analogue to (11) but now not only includes the radiative dephasing \( \gamma^{\eta_0}_{Q0} \) but also phonon-induced dephasing \( \Gamma_{Q0}^\mu \). For the indirect phonon-assisted PL allowing us to reach momentum-dark excitons we obtain the expression

\[
I(\omega)^p \propto \sum_{\mu \in Q, \pm} \Omega^\mu(\omega) \frac{|\tilde{\Delta}^\mu_{Q'|Q} \rho_{\eta_i}^\mu|^2}{(\tilde{\epsilon}^\mu_{Q'|Q} - \hbar \omega)^2 + \gamma^\mu_{Q'|Q} / 4},
\]

where we have introduced the abbreviation \( \Omega^\mu(\omega) = \tilde{\Delta}^\mu_{Q'|Q} \rho_{\eta_i}^\mu / (\tilde{\epsilon}^\mu_{Q'|Q} - \hbar \omega)^2 + \gamma^\mu_{Q'|Q} / 4 \), determining i.a. the oscillator strength. The position of the new phonon-induced signatures in the PL is determined by the energy of the exciton \( \tilde{\epsilon}^\mu_{Q'0} \) and the energy of the involved phonon \( \pm \Omega_0 \). The sign describes either the absorption (+) or emission (−) of phonons. We take into account all in-plane optical and acoustic phonon-modes. Moreover, the appearing phonon occupation \( n_{\eta_0}^\mu_Q = \left( \frac{1}{2} \pm \frac{n_{\eta_0}^\mu_Q}{2} \right) \) is assumed to correspond to the Bose equilibrium distribution according to the bath approximation [48]. Since dark states can not decay radiatively, the peak width is only given by non-radiative dephasing processes \( \Gamma^\mu_{Q0} \).

The total PL in presence of phonons and magnetic fields is obtained by adding (15) and (16), which now includes mixing of spin and momenta by the appearing sums \( \mu = KK'^{\uparrow \downarrow}, KK'^{\downarrow \uparrow} \) and \( \nu = KK'^{\uparrow \uparrow}, KK'^{\downarrow \downarrow}, KA'^{\uparrow \downarrow}, \Gamma K'^{\downarrow \uparrow}, \Gamma K'^{\downarrow \downarrow} \).

Now, we investigate the PL spectra at an exemplary low temperature of 35 K for both tungsten- and molybdenum-based TMDs, cf figure 3. We chose a temperature of 35 K, since at very low temperatures below 10 K, pumping, phonon-induced relaxations as well as radiative and non-radiative recombination take place on comparable time scales resulting in deviations from the equilibrium Boltzmann distributions. We directly compare the spectrum with and without the presence of a magnetic field. The lower panel of each picture shows the differential PL directly illustrating the impact of the field. The first observation is that even without the magnetic field additional low-energy signatures are observed in most TMD materials. They stem from momentum-dark states (black vertical lines) and are activated via phonon-assisted radiative recombination [25]. In the case of WS\(_2\), the peaks between 1.65 and 1.70 eV stem from phonon emission and absorption from energetically lower lying KK'^{\uparrow \uparrow} and KA'^{\uparrow \downarrow} excitons, respectively, cf the red line in figure 3(a). Those phonon-sidebands appear since phonons add an additional center-of-mass momentum allowing excitons to recombine. The features are not observed directly at the position of these excitons, but are shifted by the energy of the involved phonon, i.e. \( \tilde{\epsilon}^\mu_{Q'|Q} \pm \Omega_0 \). The latter state appearing in MoS\(_2\) is both spin- and momentum-dark and requires brightening via both phonons and an in-plane magnetic field.
combination with overlapping phonon replica, to broader low energy peaks between 1.86 and 1.91 eV, cf figure 3(d). Moreover, the lower energy shoulder of the bright peak can be explained by phonon replica of the KK$^{↑↑}$ exciton. Note that the linewidths of the peaks are calculated on a microscopic level (for more details see our previous work [6, 38, 49]) and are in agreement with experiments [14]. Since the phonon replica and linewidths are very sensitive to the exact position and contributions of the valleys [49], the appearance of phonon sidebands can be signatures of lower lying ΓK excitons in MoS$_2$
.

Note that the excitonic landscape in MoS$_2$ including the relative position of momentum- and spin-dark excitons is still under debate in literature [18, 46, 50]. Furthermore, the energetic ordering and hence the nature of the energetically lowest state might vary from sample to sample due to strain/surface roughness or defects [49].

Now, we investigate the changes of PL signatures in presence of a magnetic field, cf blue lines in figure 3 and for a better illustration the differential PL spectra $\Delta PL = I_{45T} - I_{045}$ in the lower panels of the figure. We observe for both tungsten-based TMDs and MoS$_2$ an upcoming peak around 50–70 meV below the bright KK$^{↑↑}$. We can trace back this new peaks to the activation of (i) spin-dark KK$^{↑↓}$ excitons in WSe$_2$ and WS$_2$, and (ii) spin- and momentum-dark ΓK$^{↑↑}$ and ΓK$^{↑↓}$ states in MoS$_2$. Moreover, MoS$_2$ exhibits an additional peak just below the bright KK exciton which can be assigned to the spin-dark KK$^{↑↓}$ exciton. In contrast, MoSe$_2$ does not exhibit any additional field- or phonon-induced peaks. This reflects the excitonic landscape in this material with the bright KK$^{↑↑}$ as the energetically lowest state [17, 18]. Note that very recent experiments by Lu et al [45] and Robert et al [46] observed an upcoming peak 1–2 meV above the bright peak in MoSe$_2$ in very high magnetic field ($B \approx 30–60$ T), suggesting a possible brightening of KK$^{↑↑}$ excitons in these materials. We find small shifts at the position of the KK$^{↑↑}$ exciton reflecting the Zeeman shift. It is in the range of $10^{-1}$ meV and only visible in the differential PL spectra.

The field-induced difference in the PL between tungsten- and molybdenum-based TMDs stems from different underlying brightening mechanisms: While in WSe$_2$ and WS$_2$ the magnetic field induces a mixing of spin-allowed and spin-forbidden KK excitons, resulting in a peak at the position of the spin forbidden KK$^{↑↓}$ exciton, in MoS$_2$ it additionally couples spin-allowed and momentum-dark ΓK$^{↑↑}$ states with spin- and momentum-dark ΓK$^{↑↓}$ excitons, resulting in phonon replica energetically below these ΓK$^{↑↓}$ states. The strong mixing of spin- and momentum-dark states in MoS$_2$ can be traced back to the degeneracy of the states and the strong electron-phonon matrix elements [47, 51]. Since there is no splitting of spin-states in the valence band of the Γ valley and since the splitting is small in the conduction band (in the range of 3 meV) [9], ΓK excitons are energetically very close enhancing the interaction and mixing of these states. Note that the splitting in the Γ states is more pronounced in the excitonic picture, i.e. $\varepsilon_{nK}^{↑↑} - \varepsilon_{nK}^{↑↓} \approx 8$ meV due to the influence of different exciton masses. In tungsten-based TMDs, the spin- and momentum-dark KK$^{↑↑}$ and KK$^{↑↓}$ states are energetically more close to the bright state [9, 17, 18] and hence do not contribute to the PL due to the very low occupation.

To understand the qualitative differences between different TMD materials, we have to outline the crucial importance of the spectral distance $\Delta$ between KK$^{↑↑}$ and KK$^{↑↓}$ excitons for the brightening of spin-dark excitons. This quantity enters in (13) both directly and indirectly via exciton occupations $N_{DB}(T)$. Comparing WSe$_2$ and WS$_2$ we find that the effect of a magnetic field is clearly stronger in the first, since KK$^{↑↑}$ and KK$^{↑↓}$ excitons are further apart (55 vs 50 meV) and hence the differences in occupations are larger and thus $\xi(WSe_2, T) > \xi(WS_2, T)$. For spin-and momentum-dark states in MoS$_2$, (i) this factor is smaller since $\Gamma K^{↑↓} - \Gamma K^{↑↑} \approx 30–40$ meV, and (ii) the process is phonon-assisted as $\Gamma K^{↑↑} + \Gamma K^{↑↓}$ is a momentum- and spin-dark state and hence the brightening process also depends on the strength of exciton-phonon coupling.

Comparing our results with experimental observations [14], we find a very good qualitative agreement of the field-dependent PL in all four TMDs. Both theory and experiment find an additional narrow peak in tungsten-based TMDs, a broad low-energy peak in MoS$_2$ and no field-induced signatures in MoSe$_2$ in the investigated magnetic fields of up to 15 T. Note that in the experiment a peak splitting of the spin-dark resonance appears in the presence of a magnetic field, which can be ascribed to the Coulomb exchange interaction [14] that has not been taken into account in our model. Since the exchange interaction only affects momentum-allowed states [52], the splitting does not occur for MoS$_2$, where spin and momentum-dark ΓK$^{↑↑}$ excitons play the crucial role.

So far we have discussed PL signatures of dark states at one exemplary temperature. Now, we vary the temperature and investigate how the impact of the magnetic field and phonons changes, cf figure 4. We assume a constant magnetic field of 14 T for all investigated TMDs. We find for tungsten-based TMDs that at low temperatures, the lowest resonances stemming from KK$^{↑↑}$ and KK$^{↑↓}$ excitons dominate the PL spectrum, while at temperature above 60 K the bright peak becomes crucial—in agreement with experimental results [26]. Note that the intensity dependence on the temperature is a result of an interplay between phonon and exciton occupations in the corresponding exciton state on the one side and the exciton-phonon scattering determining the linewidth of the resonance on the other side [6, 25, 38].
For molybdenum-based materials, we find that MoS\(_2\) is dominated by the bright KK\(^{\uparrow\downarrow}\) exciton at all temperatures, however exhibiting an increased peak broadening at higher temperatures due to the enhanced exciton-phonon interaction. In contrast, MoS\(_2\) shows even at low temperatures two broad peaks stemming from (i) phonon sidebands of the spin- and momentum-dark \(\Gamma K \Gamma^{-1} \Gamma \uparrow \downarrow\) excitons and (ii) direct emission from the momentum-allowed KK\(^{\uparrow\uparrow}\) exciton around 1.95 eV. With increasing temperature, the indirect peaks become broader and increase in intensity due to enhanced exciton-phonon scattering.

### 4. Conclusions

We have investigated the impact of an in-plane magnetic field on the optical properties of TMDs. Exploiting a fully quantum-mechanical and microscopic approach, we provide insights into signatures of momentum- and spin-dark excitons in PL spectra. We find that the field-induced mixing of spin-up and spin-down states results in a brightening of spin-dark excitons leading to new resonances. We show that the origin of the new peak is the direct emission of the KK\(^{\uparrow\downarrow}\) exciton in tungsten-based materials, whereas for MoS\(_2\) it is the indirect, phonon-induced transition from the spin- and momentum-dark \(\Gamma K^{\uparrow \downarrow \uparrow \downarrow}\) excitons. Our work provides microscopic insights into experimentally observed PL spectra in presence of magnetic fields and overall sheds light on the excitonic landscape in 2D materials.

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