Theory of the Coherent Response of Magneto-Excitons and Magneto-Biexcitons in Monolayer Transition Metal Dichalcogenides

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The recent accessibility of high quality, charge neutral monolayer transition metal dichalcogenides with narrow exciton linewidths at the homogeneous limit provides an ideal platform to study excitonic many-body interactions. In particular, the possibility to manipulate coherent exciton-exciton interactions, which govern the ultrafast nonlinear optical response, by applying an external magnetic field has not been considered so far. We address this discrepancy by presenting a nonlinear microscopic theory in the coherent limit for optical excitations in the presence of out-of-plane, in-plane, and tilted magnetic fields. Specifically, we explore the magnetic-field-induced exciton and biexciton fine structure and calculate their oscillator strengths based on a Heisenberg equations of motion formalism. Our microscopic evaluations of pump-probe spectra allow to interpret and predict coherent signatures in future wave-mixing experiments.

I. INTRODUCTION

Monolayer transition metal dichalcogenides (TMDCs) exhibit outstanding electronic and optical properties [1, 2] including excitons (bound electron-hole pairs) with exceptionally large binding energies [3–6]. The TMDC band structure is characterized by direct band gaps with strong spin-orbit interaction leading to a spin-splitting of valence and conduction bands at the non-equivalent corners K and K' of the first Brillouin zone [7–12]. The spin-splitting together with the valley selective circular dichroism of monolayer TMDCs allows to separately access the valley and spin degree of freedom. The complex band structure introduces a variety of distinct exciton configurations [13–15] as well as related trion [16–21] and biexciton configurations [22–24]. Gates, barriers, or common accidental impurities, resulting in doped TMDC samples with pronounced trions besides neutral excitons, motivated numerous experimental investigations of the exciton and trion dynamics [25–37]. In contrast, experimental investigations of biexcitons are more involved because biexciton resonances are hard to resolve in spectroscopic experiments performed on monolayer TMDCs [22, 38] due to the small biexciton binding energy [39–47] compared to the large exciton linewidth [48–51]. However, recent advance in encapsulating monolayer TMDCs in hexagonal boron nitride (hBN) demonstrated to dramatically decrease the exciton linewidth down to the homogeneous limit resulting in spectrally sharp exciton resonances [52–58]. Therefore, the encapsulation of TMDCs in hBN together with an externally applied gate voltage can effectively suppress highly charge tunable features like trions and allows to accomplish intrinsic TMDC samples approaching the homogeneous limit at cryogenic temperatures where charge neutral biexcitons are significant [59–64].

Whereas the energetically highest valence and lowest conduction bands near the K and K' points are symmetric except for opposite spins, this symmetry is broken by external magnetic fields: Out-of-plane magnetic fields (oriented perpendicular to the monolayer plane in a Faraday geometry) introduce different valley and spin-dependent Zeeman shifts of the exciton energies at the K and K' points [65–87], cf. Fig. 1 (a). On the other hand, in-plane magnetic fields (oriented parallel to the monolayer plane in a Voigt geometry) soften the optical selection rules and lead to a brightening of spin-forbidden excitons with increasing magnetic fields [88–93]. Hence, exposing TMDCs to an external magnetic field is expected to represent an ideal platform to study Coulomb many-body interactions in coherent pump-probe experiments performed on high quality monolayer TMDCs at cryogenic temperatures. Here, exciton-exciton scattering and a rich biexciton fine structure are expected to govern the ultrafast nonlinear optical response. Whereas previous experimental studies concentrated on incoherent photoluminescence measurements [59–64], we propose to gain a new perspective of exciton-exciton interaction and the biexciton dynamics via our theoretical analysis in ultrafast pump-probe spectroscopy.

We demonstrate that the pump-probe spectra mirror the excitonic Zeeman shifts in the presence of an out-of-plane magnetic field. In particular, biexciton resonances inherit the g-factor of the probed exciton resonances. Moreover, we show pronounced nonlinear renormalizations of previously spin-forbidden dark excitons and a rich biexciton fine structure induced by an in-plane magnetic field. The combined influence of out-of-plane and in-plane magnetic field contributions for a tilted magnetic field allows to enhance or suppress the pump-probe response of dark excitons as well as corresponding biexciton resonances.

This paper is organized as follows: We first introduce
the observables including bright and dark excitons as well as biexcitons and exciton-exciton scattering continua required for a nonlinear coherent description in section II. Subsequently, in section III we develop a microscopic theory based on excitonic Heisenberg equations of motion for the coherent response of monolayer TMDCs in the presence of an externally applied magnetic field. In section IV we separately study out-of-plane, in-plane, and tilted magnetic fields. At first, we summarize the magnetic-field-dependent shifted exciton resonance energies and linear transmission. Afterwards, we focus on the rich magnetic-field-induced biexciton landscape and the magnetic-field-induced resonance energy shifts. On the basis of numerical evaluations of coherent pump-probe spectroscopy, we investigate the pump-dependent changes of the exciton resonances due to exciton-exciton scattering. Moreover, we identify biexcitons with sufficient oscillator strength to appear in the nonlinear optical response and how the oscillator strength can be manipulated in the presence of differently orientated magnetic fields. Our analysis shows that coherent spectroscopy performed on hBN encapsulated TMDCs at low temperatures significantly enhances the understanding and interpretation of many-body states in monolayer TMDCs. Finally, we conclude in section V.

II. OBSERVABLES

The optical response of monolayer TMDCs is determined by the polarization density $P^{\sigma_\pm(t)}(t)$:

$$
P^{\sigma_\pm(t)}(t) = (\delta_{+,\pm} \delta_{\xi,K} + \delta_{-,\pm} \delta_{\xi,K'}) \times \sum_{\nu,\xi,s} \varphi_{\nu}^* \xi,s \frac{d_{\nu}^*}{d_{\nu}} \xi,s \frac{P_{\nu}^*}{P_{\nu}} \xi,s + c.c.
$$

Due to the valley selective circular dichroism [94, 95], the polarization density $P^{\sigma_\pm(t)}(t)$ is associated with the $\xi = K$ valley and $P^{\sigma_\pm(t)}(t)$ with the $\xi = K'$ valley. $\varphi_{\nu}^* \xi,s$ is the exciton wave function obtained from solving the Wannier equation [96] for excitons at the $\xi = K, K'$ point with same electron and hole spin $s = \uparrow, \downarrow$ and exciton quantum number $\nu$. $P_\nu^\pm$ is defined in Eq. (B1). To work in a convenient basis set, interband transitions $\langle \psi_{\xi,s_1,k}^\dagger | \nu_k \psi_{\xi,s_2,k} \rangle$ were expanded in terms of exciton transitions $P_{\nu}^{\xi,s_1,s_2}$:

$$
\langle \psi_{\xi,s_1,k}^\dagger | \nu_k \psi_{\xi,s_2,k} \rangle = \sum_{\nu} \varphi_{\nu}^* \xi,s_1 \psi_{\nu,k} \xi,s_2 P_{\nu}^{\xi,s_1,s_2}.
$$

The energetically lowest exciton series associated with the $s_1 = s_2 = \uparrow (\downarrow)$ conduction and valence bands at the $\xi = K^{(i)}$ point are referred to as $A^{(i)}$ excitons $P_{\nu}^{K^{(i)}\uparrow \uparrow}$ ($P_{\nu}^{K^{(i)}\downarrow \downarrow}$), cf. Fig. 1. The spin-split energetically higher $B^{(i)}$ transitions $P_{\nu}^{K^{(i)}\uparrow \downarrow}$ ($P_{\nu}^{K^{(i)}\downarrow \uparrow}$) are associated with the $s_1 = s_2 = \downarrow (\uparrow)$ conduction and valence bands at the $\xi = K^{(i)}$ point. These $A^{(i)}$ and $B^{(i)}$ exciton states exhibit an in-plane dipole and are referred to as bright excitons since they can be optically excited with $\sigma_+ (-)$ circularly polarized light perpendicular to the monolayer plane [97–99]. In contrast, dark excitons with out-of-plane dipole are characterized by opposite electron and hole spins $s_1 \neq s_2$ and can not be optically excited with light perpendicular to the monolayer plane [97–99]. The energetically lower dark transitions are referred to as $A'^{(i)}$ excitons $P_{\nu}^{K^{(i)}\uparrow \downarrow}$ ($P_{\nu}^{K^{(i)}\downarrow \uparrow}$), whereas the higher states are called $B'^{(i)}$ excitons $P_{\nu}^{K^{(i)}\uparrow \downarrow}$ ($P_{\nu}^{K^{(i)}\downarrow \uparrow}$), cf. Fig. 1.

The dynamics of bright and dark exciton transitions $P_{\nu}^{\xi,s_1,s_2}$ is based on Heisenberg equations of motion truncated to the third order in the exciting electro-
magnetic field [100–104]. In this coherent limit valid on ultrashort timescales [105], the exciton transitions couple to two-electron and two-hole Coulomb correlations \( \langle \epsilon^{\xi_{1},s_{1},1} + P^{\xi_{1},s_{2},1} \rangle \) expressed in the coherent basis of transitions \( B_{\xi_{1},s_{1}}^{\pm,\pm} \) [106, 107]:

\[
\langle \epsilon^{\xi_{1},s_{1},1} + P^{\xi_{1},s_{2},1} \rangle = \sum_{\pm,\mp,\pm,\mp} \left( \mathcal{P}_{\xi_{1},s_{1},\xi_{2},s_{2},\pm,\mp,\pm,\mp} B_{\xi_{1},s_{1}}^{\pm,\pm} \right)
\]

Solving the two-electron and two-hole Wannier equation [106, 107] provides the wave functions \( \Phi_{\xi_{1},s_{1},\xi_{2},s_{2},\pm,\mp,\pm,\mp} \) where the quantum number \( \mu \) includes biexcitons (bound solutions \( \mu = b \)) and continuous states of the exciton-exciton scattering continuum (continuum of unbound solutions \( \mu \neq b \)) [108–110]. The index \( \pm,\mp \) states whether the two-electron and two-hole correlation in Eq. (3) is symmetric (+) or anti-symmetric (−) under electron exchange [106]. In particular, only the anti-symmetric (−) channel exhibits bound solutions indicated by \( \mu = b \) [107].

In case of a vanishing in-plane magnetic field, as investigated in Ref. [24], only two-electron and two-hole Coulomb correlations \( B_{\xi_{1},s_{1}}^{\pm,\pm} \) with pairwise identical electron and hole spins \( s_{1} = s_{2} \) and \( s_{3} = s_{4} \) need to be considered. However, nonzero in-plane magnetic fields break this symmetry and require to consider additional two-electron and two-hole transitions \( B_{\xi_{1},s_{1}}^{\pm,\pm} \) with \( s_{1} \neq s_{2} \) or \( s_{2} \neq s_{3} \). In the following, the correlations \( B_{\xi_{1},s_{1}}^{\pm,\pm} \) are referred to as \{\( \xi_{1},s_{1},s \}\} \{\( \xi_{2},s_{2},s \}\} Coulomb correlations. The denotation hints at the valleys and spins of the involved electrons and holes: For instance, \( B_{\xi_{1},s_{1}}^{\pm,\pm} \) corresponds to the A–B correlation (which is identical to the Ad–Bd correlations) and \( B_{\xi_{1},s_{1}}^{\pm,\pm} \) is called Ad–Ad’ correlation. Fig. 2 illustrates a selection of (a) intra-valley and (b–i) inter-valley \{\( \xi_{1},s_{1},s \}\} \{\( \xi_{2},s_{2},s \}\} Coulomb correlations. Note that the repulsive interaction of two electrons or holes in the same conduction or valence bands precludes the formation of intra-valley A–A, B–B, Ad–Ad, and A–Bd biexcitons.

### III. EXCITONIC EQUATIONS OF MOTION

The Heisenberg equation of motion for the exciton transition \( P_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} \) is given by:

\[
\begin{aligned}
\frac{\partial}{\partial t} + \gamma_{\nu_{1}} P_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} &= -i \hbar \left( \epsilon_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} + \epsilon_{B_{\nu_{1}}}^{\xi_{1},s_{1},s_{2}} \right) P_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} \\
&= -i \delta_{\nu_{1},s_{1}} \Omega^{\xi_{1},s_{1},s_{2}} + \frac{\partial}{\partial t} P_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} |_{HF} + \frac{\partial}{\partial t} P_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} |_{corr.}.
\end{aligned}
\]

The left-hand side of Eq. (4) describes excitonic oscillations with the exciton resonance energy at zero magnetic field \( \epsilon_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} \). An out-of-plane magnetic field \( B_{\nu_{1}} \) normalizes the exciton energy by \( \epsilon_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} \), cf. Fig. 1. The Zeeman shift \( \epsilon_{B_{\nu_{1}}}^{\xi_{1},s_{1},s_{2}} = \epsilon_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} - \epsilon_{\nu_{1},B_{\nu_{1}}}^{\xi_{1},s_{1},s_{2}} \) breaks the symmetry between the K and K’ points due to conduction \( \nu_{1},B_{\nu_{1}} \) and valence band shifts \( \epsilon_{\nu_{1},B_{\nu_{1}}}^{\xi_{1},s_{1},s_{2}} \) with different signs and magnitude depending on the valley \( \xi_{1} \) and spins \( s_{1} \) and \( s_{2} \):

\[
\begin{aligned}
\epsilon_{\nu_{1},B_{\nu_{1}}}^{\xi_{1},s_{1},s_{2}} &= \left( \delta_{\xi_{1}} \epsilon_{-K} - \delta_{\xi_{1}} \epsilon_{-K'} \right) \frac{m_{0}}{\bar{m}} + \left( \delta_{s_{1}} \gamma_{s_{1},s_{2}} \right) \mu_{B} B_{\nu_{1}}, \\
\epsilon_{\nu_{1},B_{\nu_{1}}}^{\xi_{1},s_{1},s_{2}} &= \left( \delta_{\xi_{1}} \epsilon_{-K} - \delta_{\xi_{1}} \epsilon_{-K'} \right) \frac{2 + \frac{m_{0}}{\bar{m}}}{\mu_{B} B_{\nu_{1}}},
\end{aligned}
\]

Here, \( \mu_{B} \) is the Bohr magneton, \( m_{0} \) is the free electron mass, and \( \bar{m} \) is the effective mass of the eight band model [111, 112]. The latter involves the effective mass \( m_{0}(s) \) of the \{\( \xi,\nu \)\} conduction (valence) band. A derivation based on the underlying different magnetic moments contributing in the presence of a magnetic field (atomic orbital, valley orbital, and spin magnetic moments) is given in Appendix A. Exciton-phonon interactions damp the excitonic oscillations described by Eq. (4) with the microscopically calculated dephasing constant \( \gamma_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} \) [49, 113]. On the other hand, the radiative dephasing \( \gamma_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} \), which dominates the exciton dephasing of hBN encapsulated high-quality monolayer TMDCs at cryogenic temperatures [52, 53, 55–57], does not appear explicitly in Eq. (4). Instead, the radiative dephasing \( \gamma_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} \) directly follows from the simultaneous solution of Maxwell’s wave equation together with the excitonic Bloch equations [114, 115].

The first contribution to the right-hand side of Eq. (4) describes the optical source term for bright excitons \( P_{\nu_{1}}^{\xi_{1},s_{1},s_{2}} \) with equal electron and hole spin \( s_{1} = s_{2} \). The excitonic Rabi frequency \( \Omega^{\xi_{1},s_{1}} \) depends on the dipole matrix element \( d_{\nu_{1}}^{\xi_{1},s_{1}} \) and the envelope of the light field at
the monolayer position $\tilde{E}\sigma_{\pm}(t)$:

$$
\Omega_{\nu_1}^{s_1,s_2} = (\delta_{+,-} \delta_{\xi_1,K} \pm \delta_{-} \delta_{\xi_1,K'})
\times \frac{1}{\hbar} \sum_q \varphi^{s_1,s_1,s_2}_{\nu_1,q} \left( d^{\nu_1}_{\xi_2,s_2} \right)^* \tilde{E}\sigma_{\pm}(t) e^{i\omega_0 t}.
$$

The valley selection rules \[95\] are represented by $(\delta_{+,-} \delta_{\xi_1,K} \pm \delta_{-} \delta_{\xi_1,K'})$, i.e., $\sigma_{+(-)}$ circularly polarized light generates interband transitions at the K(0) point. $\omega_0$ denotes the laser frequency.

The second term on the right-hand side of Eq. (4) couples bright excitons $P_{1}^{s_1,s_2}$ with $s_1 = s_2$ and dark excitons with $s_1 \neq s_2$ proportional to the in-plane magnetic field $B_{||}$, cf. Fig. 1:

$$
\partial_t P_{1}^{s_1,s_2} |_{PB}^{B_{||}} = -\frac{i\mu B_{||}}{\hbar} \sum_{q} \varphi^{s_1,s_1,s_2}_{1,q} \varphi^{s_1,s_1,s_2}_{1,q} P_{1}^{s_1,s_1,s_2} + \frac{i\mu B_{||}}{\hbar} \sum_{q} \varphi^{s_1,s_1,s_2}_{1,q} \varphi^{s_1,s_1,s_2}_{1,q} P_{1}^{s_1,s_1,s_2}.
$$

The first contribution to Eq. (8) couples $P_{1}^{s_1,s_2}$ to $P_{1}^{s_1,s_2}$ excitons in the same valley $\xi_1$ and with identical electron spin $s_1$ but with opposite hole spin $s_2 \neq s_2$, i.e., $\xi_2 = \downarrow$ for $s_2 = \uparrow$ and vice versa. The last line of Eq. (8) couples $P_{1}^{s_1,s_2}$ to $P_{1}^{s_1,s_2}$ excitons in the valley $\xi_1$ with opposite electron spin $s_1 \neq s_1$ and equal hole spin $s_2$. The mixing among excitons with electrons in different conduction bands and holes in the same valence band dominates (second contribution to Eq. (9)). This is due to the small energy splitting of spin-$\uparrow$ and spin-$\downarrow$ conduction bands of a few to tens of meV compared to the significantly larger valence band splitting of more than one hundred meV \[116\]. Nevertheless, we take account of both terms.

The third term on the right-hand side of Eq. (4) characterizes Pauli blocking:

$$
\partial_t P_{1}^{s_1,s_2} |_{PB} = i \sum_{s_3 \neq s_2 \neq s_2} \tilde{\Omega}_{s_2,s_3}^{s_1,s_3,s_1} P_{s_2}^{s_1,s_2} (P_{s_3}^{s_1,s_3})^* + i \sum_{s_3 \neq s_2 \neq s_2} \tilde{\Omega}_{s_2,s_3}^{s_1,s_2,s_3} P_{s_2}^{s_1,s_2} (P_{s_3}^{s_1,s_3})^*,
$$

with the Pauli blocking parameter:

$$
\tilde{\Omega}_{s_2,s_3}^{s_1,s_2,s_3} = (\delta_{+,-} \delta_{\xi_1,K} \pm \delta_{-} \delta_{\xi_1,K'}) \frac{1}{\hbar} \sum_{q} \varphi^{s_1,s_1,s_2}_{1,q} \varphi^{s_1,s_1,s_2}_{1,q} \tilde{E}\sigma_{\pm}(t) e^{i\omega_0 t}.
$$

The first contribution to Eq. (9) originates from a coherent exciton population $\sim P_{1}^{s_1,s_1,s_1} (P_{1}^{s_1,s_1,s_1})^*$ in the same valley $\xi_1$ as $P_{1}^{s_1,s_1,s_1}$, with identical electron spin $s_1$ and either equal $s_2 = s_1$ or opposite hole spins $s_3 \neq s_1$. The second term on the right-hand side of Eq. (9) induces a blocking due to excitons $\sim P_{1}^{s_1,s_1,s_2} (P_{1}^{s_1,s_1,s_2})^*$ with identical electron spin $s_1$ as $P_{1}^{s_1,s_1,s_2}$ and either same $s_3 = s_2$ or opposite hole spins $s_3 \neq s_2$. In particular, the contributions including spin-forbidden dark excitons only appear in the presence of a magnetic field.

The fourth term on the right-hand side of Eq. (4) represents instantaneous Coulomb scattering among excitons.
in the same valley $\xi_1$ on a Hartree–Fock level:

\begin{align}
\partial_t P_{v_1}^{\xi_1,s_1,s_2} |_{\text{HF}} &= \delta_{s_1,s_2} \frac{i}{\hbar} \sum_{v_2,s_3,s_4} W_{v_1,v_2,s_1,s_3,s_4} P_{v_2}^{\xi_1,s_3,s_4} \\
&\quad + \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_4} \left( P_{v_4}^{\xi_1,s_3,s_4} \right)^* \times P_{v_3}^{\xi_1,s_3,s_2} P_{v_4}^{\xi_1,s_4} \\
&\quad - \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_2} P_{v_4}^{\xi_1,s_3,s_1} \\
&\quad + \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_2} P_{v_3}^{\xi_1,s_3,s_4} \times P_{v_4}^{\xi_1,s_4,s_1} \\
&\quad + \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_2} P_{v_3}^{\xi_1,s_3,s_4} \times P_{v_4}^{\xi_1,s_4,s_1}. \tag{11} \end{align}

The first contribution to the right-hand side of Eq. (11) describes linear intravalley exchange Coulomb interactions. This term originates from a local field effect which only affects bright excitons with same electron and hole spin $s_1 = s_2$ [117, 118]. This term enhances the exciton resonance energies and mixes bright A and B excitons as well as A’ and B’ excitons. The matrix element $W_{v_1,v_2,s_1,s_3}$ is given in Eq. (B5). All following nonlinear exciton-exciton scattering contributions on the right-hand side of Eq. (11) include Coulomb scattering involving not only bright but also dark excitons: The second term on the right-hand side of Eq. (11) characterizes Coulomb scattering associated with the direct Coulomb potential $W_{v_1,v_2,s_1,s_3,s_4}$ defined in Eq. (B2). The third and fourth terms of Eq. (11) represent the nonlinear counterpart of the linear local field contribution (first term) with the coupling elements $W_{v_1,v_2,s_1,s_3,s_4}$ and $W_{v_1,v_2,s_1,s_3,s_4}$ defined in Eq. (B6). The last two contributions to Eq. (11) are associated with the exchange Coulomb matrix elements $W_{v_1,v_2,s_1,s_2,s_3,s_4}$ and $W_{v_1,v_2,s_1,s_2,s_3,s_4}$ defined in Eq. (B7). These terms originate from a $k\cdot p$ expansion which resembles a dipole–dipole interaction [122].

The last term on the right-hand side of Eq. (11) incorporates exciton-exciton scattering beyond a Hartree–Fock approximation and represents the coupling of the exciton transition $P_{v_1}^{\xi_1,s_1,s_2}$ to two-electron and two-hole transitions $B_{\xi_1,s_1,s_2,s_3,s_4}$ introduced in Eq. (3):

\begin{align}
\partial_t P_{v_1}^{\xi_1,s_1,s_2} |_{\text{corr.}} &= \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_4} \times \sum_{\mu} \phi_{R}^{\xi_1,s_2,s_4} \left( B_{\mu}^{\xi_1,s_1,s_2,s_3,s_4} \right) \\
&\quad - \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_4} \times \sum_{\mu} \phi_{R}^{\xi_1,s_2,s_4} \left( B_{\mu}^{\xi_1,s_1,s_2,s_3,s_4} \right) \\
&\quad - \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_4} \times \sum_{\mu} \phi_{R}^{\xi_1,s_2,s_4} \left( B_{\mu}^{\xi_1,s_1,s_2,s_3,s_4} \right). \tag{12} \end{align}

Direct Coulomb scattering, associated with the Coulomb matrix $W_{v_1,v_2,s_1,s_2,s_3,s_4}$ given in Eq. (B9), couples the exciton transition $P_{v_1}^{\xi_1,s_1,s_2}$ to the exciton transition and two-electron and two-hole Coulomb correlations $P_{v_4}^{\xi_1,s_3,s_4}$ as well as to $B_{\mu}^{\xi_1,s_1,s_2,s_3,s_4}$ accompanied by the Coulomb matrix $X_{v_1,v_2,v_3,v_4}$ defined in Eq. (B10). In contrast to nonlinear exciton-exciton interaction on a Hartree–Fock level, Eq. (12) includes not only intravalley scattering $\xi_2 = \xi_1$ but also intervalley scattering $\xi_2 \neq \xi_1$. The two-electron and two-hole Coulomb correlation dynamics for $B_{\mu}^{\xi_1,s_1,s_2,s_3,s_4}$ is described by:

\begin{align}
\left( \partial_t + \gamma_x^{\xi_1,s_1,s_2} + \gamma_x^{\xi_2,s_3,s_4} \right) P_{v_1}^{\xi_1,s_1,s_2} &= \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_4} \\
&\quad + \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_4} \\
&\quad - \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_4} \\
&\quad + \frac{i}{\hbar} \sum_{v_2,s_3,s_4} \left( W_{v_1,v_2,s_1,s_3,s_4} \right) P_{v_2}^{\xi_1,s_3,s_4}. \tag{13} \end{align}
The left-hand side of Eq. (14) describes oscillations with energy $\hat{\epsilon}_{\xi_1,\xi_2,\xi_3,\xi_4}$ damped by $\gamma_{\xi_1,\xi_2} + \gamma_{\xi_2,\xi_3,\xi_4}$. The resonance energy $\hat{\epsilon}_{\xi_1,\xi_2,\xi_3,\xi_4}$ involves the two-electron and two-hole correlation energy $\hat{\epsilon}_{\xi_1,\xi_2,\xi_3,\xi_4}$ obtained from solving the two-electron and two-hole Schrödinger equation which are renormalized by $\Delta_{\xi_1,\xi_2,\xi_3,\xi_4}$ and $\Delta_{\xi_2,\xi_3,\xi_4}$:

$$
\hat{\epsilon}_{\xi_1,\xi_2,\xi_3,\xi_4} = \hat{\epsilon}_{\xi_1,\xi_2,\xi_3,\xi_4} + \Delta_{\xi_1,\xi_2,\xi_3,\xi_4} + \Delta_{\xi_2,\xi_3,\xi_4}.
$$

The renormalization $\Delta_{\xi_1,\xi_2,\xi_3,\xi_4}$ is obtained by firstly, diagonalization of the eight-dimensional linear exciton Hamiltonian spanned by $P_{\xi_1,\xi_2,\xi_3,\xi_4}$ ($\xi_1 = K, K', \xi_2 = \uparrow, \downarrow, \xi_3 = \uparrow, \downarrow, \xi_4 = \uparrow, \downarrow$) including $B_{\uparrow}$ and $B_{\downarrow}$ dependent energy renormalizations (Eqs. (5), (6), and (8)) and linear local field exchange Coulomb scattering (first term of Eq. (11)), and secondly, subtracting the respective exciton binding energies $\hat{\epsilon}_{\xi_1,\xi_2}$ determined by the Wannier equation.

The first term on the right-hand side of Eq. (14) characterizes the mixing among two-electron and two-hole Coulomb correlations proportional to the in-plane magnetic field $B_{\uparrow}$: $B_{\xi_1,\xi_2,\xi_3,\xi_4}$ couples to correlations with opposite electron spin $s_1 \neq \bar{s}_1$ ($B_{\xi_1,\xi_2,\xi_3,\xi_4}$) and $s_3 \neq \bar{s}_3$ ($B_{\xi_1,\xi_2,\xi_3,\xi_4}$) as well as to correlations with different hole spin $s_2 \neq \bar{s}_2$ ($B_{\xi_1,\xi_2,\xi_3,\xi_4}$) or $s_4 \neq \bar{s}_4$ ($B_{\xi_1,\xi_2,\xi_3,\xi_4}$). The matrix $S_{\xi_1,\xi_2,\xi_3,\xi_4}$ directly follows from the definition of the two-electron and two-hole correlation function in Eq. (3) and is defined in Eq. (B11). Since $S_{\xi_1,\xi_2,\xi_3,\xi_4}$ is solely determined by the conduction and valence band curvatures, which are very similar for monolayer TMDCs [116], the coupling matrix is approximated by:

$$
\sum_{\nu_1,\nu_2,\nu_3,\nu_4} \Phi_{\xi_1,\xi_2,\xi_3,\xi_4}^{P_{\nu_1,\nu_2,\nu_3,\nu_4}} \left( \sum_{\nu_1,\nu_2} \Phi_{\xi_1,\xi_2,\xi_3,\xi_4}^{P_{\nu_1,\nu_2}} \right)^{-1} \sum_{\nu_1,\nu_2} S_{\xi_1,\xi_2,\xi_3,\xi_4}^{\nu_1,\nu_2} \Phi_{\xi_1,\xi_2,\xi_3,\xi_4}^{R_{\nu_1,\nu_2}} \Phi_{\xi_1,\xi_2,\xi_3,\xi_4}^{P_{\nu_1,\nu_2,\nu_3,\nu_4}} \approx \delta_{\nu_1,\nu_2'}.
$$

The second contribution to the right-hand side of Eq. (14) describes Coulomb-driven source terms of $B_{\xi_1,\xi_2,\xi_3,\xi_4}$. In particular, an in-plane magnetic field does not only account for source terms due to bright excitons ($s_1 = s_2$ and $s_3 = s_4$) but includes dark exciton source terms ($s_1 \neq s_2$ or $s_3 \neq s_4$) as well. The appearing direct $W_{\xi_1,\xi_2,\xi_3,\xi_4}$ and exchange Coulomb matrices $\hat{X}_{\xi_1,\xi_2,\xi_3,\xi_4}$ are defined in Eqs. (B9) and (B10), respectively.

IV. RESULTS

A careful investigation of our equations of motion in section III reveals that a multitude of new effects appear in the presence of magnetic fields, which have to be considered in the interpretation of experiments:

1. out-of-plane magnetic-field-dependent Zeeman shifts of the exciton energies,
2. in-plane magnetic-field-dependent brightening of dark excitons $P_{\xi_1,\xi_2}^{\xi_1,\xi_2}$ (opposite electron and hole spins $s_1 \neq s_2$) which couple to bright excitons $P_{\xi_1,\xi_2}^{\xi_1,\xi_2}$ (same electron and hole spins $s_1 = s_2$),
3. additional Pauli blocking contributions associated with coherent dark exciton densities,
4. new direct and exchange exciton-exciton scattering terms accounting for Coulomb interactions including dark excitons,
5. further two-electron and two-hole Coulomb correlations $B_{\xi_1,\xi_2,\xi_3,\xi_4}$ with $s_1 \neq s_2$ or $s_3 \neq s_4$ representing new Coulomb scattering channels,
6. out-of-plane magnetic-field-dependent Zeeman shifts of the two-electron and two-hole correlation energies,
7. in-plane magnetic-field-dependent coupling among two-electron and two-hole Coulomb correlations, and
8. additional source terms of the two-electron and two-hole Coulomb correlations due to dark excitons.

The coupled dynamics of exciton transitions and two-electron and two-hole Coulomb correlations described by
the excitonic Bloch equations, Eqs. (4) and (14), are numerically evaluated together with Maxwell’s wave equation [114, 115] for the energetically lowest $\nu = 1s, 2s,$ and $3s$ exciton transitions and the corresponding two-electron and two-hole correlations with s-symmetry of MoS$_2$ encapsulated in hBN at a temperature of 5 K. The required material parameters are summarized in Ref. [24].

In the following, the linear transmission and nonlinear differential transmission of monolayer MoS$_2$ encapsulated in hBN are separately discussed for different magnetic field orientations with respect to the monolayer plane: an out-of-plane magnetic field $B_\perp$ (subsection IV A), an in-plane magnetic field $B_\parallel$ (subsection IV B), and a magnetic field $B_\perp$ oriented in a tilt angle of 45° (subsection IV C). For the nonlinear transmission we choose a $\sigma_+$ circularly polarized 50 fs Gaussian pump pulse (intensity FWHM). Its access energy is resonant to the respective magnetic-field-dependent A$_{1s}$ exciton energy. The differential transmission spectrum (DTS) $\delta T(\omega) = T_{p+t}(\omega) - T_t(\omega)$ of the probe pulse is defined as the transmission of the pumped system $T_{p+t}(\omega)$ minus the linear transmission of the probe pulse $T_t(\omega)$. In order to directly visualize the pump-induced changes of the transmission, we do not divide the DTS by the linear transmission of the test pulse $T_t(\omega)$. However, dividing by $T_t(\omega)$ would not qualitatively change the DTS but only enhance the signal directly at the exciton resonances while features which are further away from the exciton resonances are less pronounced. The energetically broadband 1 fs probe pulse is either $\sigma_+$ circularly polarized to investigate intravalley exciton-exciton interaction or $\sigma_-$ circularly polarized in order to study intervalley scattering, cf. optical selection rules as indicated in Fig. 1. Assuming zero time delay between pump and probe pulses allows to neglect contributions from incoherent exciton densities in the following [123–125].

### A. Out-of-plane Magnetic Field

**Linear response:** With increasing out-of-plane magnetic field $B_\perp > 0$ T, the A and B excitons associated with the K valley experience Zeeman shifts toward lower energies shown as solid lines in Fig. 3 (a). Simultaneously, the A’ and B’ transitions plotted as dotted lines in Fig. 3 (a) shift toward higher energies due to Zeeman shifts with opposite sign for the K valley. The linear transmission spectrum of monolayer MoS$_2$ at zero magnetic field $B_\perp = 0$ T is plotted as red lines in Fig. 3 (b,d) and shows two prominent exciton resonances which are referred to as A$_{1s}$ and B$_{1s}$ excitons with the exciton quantum number $\nu = 1s$. Additionally, the A$_{2s}$ exciton resonance associated with the quantum number $\nu = 2s$ of the A series can be observed energetically above the B$_{1s}$ exciton. As a benchmark to recent literature, for instance Ref. [90], the out-of-plane magnetic field $B_\perp$ dependent linear transmission is shown in Fig. 3 (b,d) for $\sigma_+$ and $\sigma_-$ circularly polarized light, respectively. The red curves in Fig. 3 (b,d) represent the linear transmission at $B_\perp = 0$ T which is identical for $\sigma_+$ and $\sigma_-$ circular excitations. In contrast, the spectra at $B_\perp = 15$ T and $B_\perp = 30$ T, plotted as purple and blue lines in Fig. 3 (b,d), mirror the opposite Zeeman shifts of A, B and A’, B’ excitons. Our microscopically calculated A$_{1s}$ exciton linewidth includes a phonon-mediated part of $2\gamma_{x_{1s}} = 0.4$ meV at 5 K and a radiative part of $2\gamma_{1s}^\rho = 1.4$ meV. The B$_{1s}$ exciton linewidth exhibits a much larger phonon-induced contribution of $2\gamma_{x_{1s}} = 11.6$ meV at 5 K which overshadows the radiative part of $2\gamma_{1s}^\rho = 1.6$ meV. The increased phonon-mediated $B_{1s}$ linewidth contribution $\gamma_{x_{1s}}$ stems from phonon emission of acoustic and optical K phonons which drive the relaxation of B$_{1s}$ excitons into exciton states including a hole at the $\Gamma$ point [113]. In contrast, the reduced A$_{2s}$ linewidth originates from a reduced radiative linewidth contribution of only $2\gamma_{1s}^\rho = 0.2$ meV due to the increased spatial extent of exciton wave functions with higher exciton quantum numbers [126, 127]. In particular, the low A$_{2s}$ linewidth for high quality TMDCs leads to a relatively large oscillator strength.

**DTS for $\sigma_+$ pump and $\sigma_+$ probe pulses:** At first, we recapitulate the expected DTS for a vanishing magnetic field $B_\perp = 0$ T plotted as red curve in Fig. 3 (c). Here, the A excitons shifts blue giving a dispersive DTS signal with a positive contribution followed by a negative one as schematically illustrated in Fig. 4 (a). Asymmetric sidebands on the high energy side of the A excitons, originating from the intravalley A–A exciton-exciton scattering continuum, further enhance the negative DTS contributions [128]. In contrast, the DTS near the B resonances is expected to first show a negative DTS signal below the B exciton energy as illustrated in Fig. 4 (b) which corresponds to the intravalley A–B exciton-exciton scattering (Fig. 2 (a)). Moreover, a blue shift of the B resonances together with exciton-scattering-induced sidebands (due to the A–B exciton-exciton scattering continuum) [128] induce a dispersive DTS signal with a positive feature followed by a negative contribution above the B$_{1s}$ exciton energy. The increased $B_{1s}$ exciton linewidth compared to A$_{1s}$ excitons results in weaker DTS signals since the oscillator strength is distributed over a larger energy range. Therefore, the energy range around the B$_{1s}$ exciton is shown ten times enhanced as indicated by the arrow in Fig. 3 (c). Additionally, the expected negative DTS feature above the B$_{1s}$ excitons is absent due to the positive DTS contribution of A$_{2s}$ excitons.

The DTS for an out-of-plane magnetic field of $B_\perp = 15$ T and $B_\perp = 30$ T are shown as purple and blue lines in Fig. 3 (c). With increasing $B_\perp$ the whole DTS shifts towards lower energies according to the Zeeman shifted A and B exciton resonances. Interestingly this holds also true for the intravalley A–B intravalley biexciton resonance, such that the energetic position of the biexciton resonance with respect to the B$_{1s}$ exciton is unchanged due to the same Zeeman shifts, cf. also dashed line in Fig. 3 (a). Even though a simple band analysis sug-
Figure 3. Out-of-plane magnetic-field-dependent transmission and differential transmission. (a) Exciton and biexciton resonance energies for different out-of-plane magnetic fields $B_\perp$, cf. Figs. 1 and 2. Solid (dotted) lines represent exciton resonances and dashed (dash-dotted) lines biexciton resonances for $\sigma_+$ ($\sigma_-$) circularly polarized excitation. Pale lines indicate vanishing oscillator strengths of the resonances. (b,d) Linear transmission spectra of monolayer MoS$_2$ encapsulated in hBN at 5 K for (b) $\sigma_+$ and (d) $\sigma_-$ circularly polarized light for different $B_\perp$. The $B_\perp$ dependent exciton energies are indicated as colored bars above. (c,e) Normalized differential transmission spectra for different magnetic fields $B_\perp$. The $A_{1s}$ exciton is resonantly pumped by $\sigma_+$ circularly polarized light and the energetically broadband probe pulse is either (c) $\sigma_+$ circularly polarized or (e) $\sigma_-$ circularly polarized. The differential transmission is partially enhanced as indicated while the original signal is plotted by dotted lines. The colored long bars above mark the exciton energies, whereas the shorter bars indicate the biexciton energies.
Differential transmission
Fig. 3 (e) shifts the A energies, cf. dotted lines in Fig. 3 (a). Accordingly, the
scattering continua. The resulting DTS is schematically

described by Eq. (14) indeed has a doubled
B
factor of the A
−factor of the A
b
factors of the A and B excitons exhibits first a negative feature from a biexciton resonance, followed by a positive and than negative contribution from the blue shifted exciton with an exciton-scattering-induced sideband on the high energy side.

suggests a doubled biexciton g-factor with respect to the B
exciton, this expectation is not mirrored in the differential transmission. While the biexciton B
A,B
\( \sigma_{a,B} \) described by Eq. (14) indeed has a doubled g-factor, only the exciton resonance B
1s
\( \sigma_{c,b} \) couples to the exciton resonance determined by Eq. (12). As the g-factors of the biexciton resonance B
1s
\( \sigma_{c,b} \) associated with the A
exciton cancel, the biexciton resonance inherits the g-factor of the B
exciton. Negative magnetic fields B
\( < 0 \) lead to DTS shifted in the opposite energetic direction, cf. Appendix C.

\textbf{DTS for \( \sigma_+ \) pump and \( \sigma_- \) probe pulses:} At first, we again discuss the expected DTS at zero magnetic fields B
\( = 0 \) plotted as a red curve in Fig. 3 (e). Here, the intervalley A–A' and A–B' biexciton resonances (Fig. 2 (b) and (f)) lead to negative signatures in the DTS below the A' and B' energies. These negative contributions follow first a positive and then a negative DTS signal accounting for the blue shifted A' and B' transitions with exciton-scattering-induced sidebands on the high energy side of the exciton resonances [128]. The latter originate from the A–A' and A–B' exciton-exciton scattering continua. The resulting DTS is schematically illustrated in Fig. 4 (b).

Applying an out-of-plane magnetic field B
\( = 15 \) T and B
\( = 30 \) T shown as purple and blue lines in Fig. 3 (e) shifts the A' and B' excitons towards higher energies, cf. dotted lines in Fig. 3 (a). Accordingly, the DTS also shift toward higher energies while the dispersive

\textbf{B. In-plane Magnetic Field}

\textbf{Linear response:} Next, we study the impact of an in-plane magnetic field B
\( \parallel \). In contrast to an out-of-plane magnetic field B
\( \perp \), an in-plane magnetic field B
\( \parallel \) leads to identical shifts of A and A' as well as B and B' excitons in the linear regime drawn as solid lines in Fig. 5 (a). This is due to a valley independent coupling among bright and dark excitons described by Eq. (8). Therefore, the linear response plotted in Fig. 5 (b) is identical for \( \sigma_+ \) and \( \sigma_- \) circularly polarized light. The linear transmission at B
\( = 0 \) T is plotted as a red line in Fig. 5 (b) and shows the A
excitons, respectively. This is in contrast to a simple band analysis which suggests that the Zeeman shift of the A
exciton is compensated by an opposite shift of the A'
excitons leading to an almost vanishing biexciton g-factor. While this compensation of g-factors applies to the A–A' and A–B' biexcitons B
A,A
1s
\( \sigma_{a,b} \) and B
A,B
1s
\( \sigma_{c,b} \) it does not hold true for the biexciton resonances B
A,A
1s
\( \sigma_{a,b} \) and B
A,B
1s
\( \sigma_{c,b} \). Therefore, the biexciton resonances B
A,A
1s
\( \sigma_{a,b} \) and B
A,B
1s
\( \sigma_{c,b} \) inherit the g-factors of the A
excitons, respectively. In contrast, we expect a twice as large Zeeman shift of A–Ad' and Ad–A' biexciton resonances, cf. pale dash-dotted line Fig. 3 (c). However, due to their negligible oscillator strengths in coherent pump-probe spectroscopy they appear not as resonances in Fig. 3 (c). Note that previous photoluminescence measurements [60–62] ascribed A–Ad' and Ad–A' biexciton resonances a smaller Zeeman shift which is similar to our expectations for the A–A' biexciton resonance.

We have shown that the differential transmission spectra in the presence of an out-of-plane magnetic field B
\( \perp \) mirror the Zeeman shifts. In particular, the g-factor of bright–bright biexciton resonances inherits the g-factor of the associated exciton resonance.
Figure 5. In-plane magnetic-field-dependent transmission and differential transmission. (a) Exciton and biexciton resonance energies for different in-plane magnetic fields $B_{\parallel}$, cf. Figs. 1 and 2. Solid (dotted) lines represent exciton resonances and dashed (dash-dotted) lines biexciton resonances for $\sigma_+$ ($\sigma_-$) circularly polarized excitation. (b) Linear transmission spectra of monolayer MoS$_2$ encapsulated in hBN at 5 K for different $B_{\parallel}$. (The transmission for $\sigma_+$ and $\sigma_-$ circularly polarized light is identical.) The $B_{\parallel}$ dependent exciton energies are indicated as colored bars above. (c,d) Normalized differential transmission spectra for different magnetic fields $B_{\parallel}$. The $A_{1s}$ exciton is resonantly pumped by $\sigma_+$ circularly polarized light and the energetically broadband probe pulse is either (c) $\sigma_+$ circularly polarized or (d) $\sigma_-$ circularly polarized. The differential transmission is partially enhanced as indicated while the original signal is plotted by dotted lines. The colored long bars above mark the exciton energies, whereas the shorter bars indicate the biexciton energies.

Contributions. This is in agreement with experimental observations [88, 98, 129]. The dark exciton linewidths are dominated by the phonon-mediated linewidth contributions $2\gamma_{A_{1s}} = 0.4$ meV at 5 K [130]. With increasing $B_{\parallel}$, the redistribution from bright to dark exciton oscillator strength increases the radiative $A_{1s}$ exciton linewidth contribution from $2\gamma_{A_{1s}} = 0$ meV at $B_{\parallel} = 0$ T to $2\gamma_{A_{1s}} = 0.1$ meV at $B_{\parallel} = 30$ T. Thus, the total $A_{1s}$ exciton linewidth slightly rises from 0.4 meV to 0.5 meV. Simultaneously, the radiative $A_{1s}$ exciton linewidth slightly decreases from $2\gamma_{A_{1s}} = 1.4$ meV at $B_{\parallel} = 0$ T to $2\gamma_{A_{1s}} = 1.3$ meV at $B_{\parallel} = 30$ T and the total $A_{1s}$ linewidth declines from 1.8 meV to 1.7 meV. Even though the dark $B_{1s}$ exciton with a phonon-mediated linewidth contribution of $2\gamma_{B_{1s}} = 11.4$ meV at 5 K is also excited, its appearance as a sharp resonance in
DTS for $\sigma_+$ pump and $\sigma_-$ probe pulses: Compared to a zero in-plane magnetic field $B_\parallel = 0$ T, shown as red line in Fig. 5 (c), an in-plane magnetic field of $B_\parallel = 15$ T or $B_\parallel = 30$ T plotted as purple and blue lines in Fig. 5 (c) leads to additional DTS features associated with dark Ad excitons. These DTS features describe dispersive profiles which – similar to the $A_{1s}$ and $A_{2s}$ response – account for blue shifted dark $A_{1s}$ and $A_{2s}$ exciton resonances with exciton-scattering-induced sidebands, cf. Fig. 4 (a). The level repulsion between bright and dark excitons, cf. solid lines in Fig. 5 (a), is also mirrored in the DTS shown by the purple and blue lines in Fig. 5 (c). In contrast, the large $B_{1s}$ and $B_{1s}$ exciton linewidths compared to their small energy separation obscure the identification of DTS features from $B_{1s}$ excitons.

DTS for $\sigma_+$ pump and $\sigma_-$ probe pulses: With rising $B_\parallel$ from $B_\parallel = 0$ T plotted as red line in Fig. 5 (d) to $B_\parallel = 15$ T and $B_\parallel = 30$ T shown as purple and blue lines in Fig. 5 (d), the pump-dependent renormalizations and redistributions of oscillator strengths of dark $A_{1s}$ excitons yield dips superimposed on the negative DTS signal from $A-\bar{A}$ intervalley biexcitons (Fig. 2 (b)). Similarly, the dispersive DTS profile at $A_{1s}$ accounts for a blue shifted $A_{1s}$ resonance with exciton-scattering-induced sidebands. The $B_\parallel$ dependent brightening of dark $A_{1s}$ and $B_{1s}$ excitons also results in additional intervalley biexciton resonances. In general, this includes $A-\bar{A}$, $A-\bar{A}$, $A-\bar{A}$, $B_{-ld}$–$B_{ld}$, $B_{ld}$–$B_{ld}$, $B_{ld}$–$B_{ld}$, $B_{ld}$–$B_{ld}$, $A-\bar{A}$, $B_{ld}$–$B_{ld}$, $B_{ld}$–$B_{ld}$, $B_{ld}$–$B_{ld}$, $A-\bar{A}$. In Fig. 5 (a), the $A-\bar{A}$ and $A-\bar{A}$ intervalley excitons are visible as superimposed weak negative DTS signals below the $A-\bar{A}$ biexcitons. In contrast, $A-\bar{A}$ and $A-\bar{A}$ intervalley biexcitons are obscured due to their large phonon-mediated linewidths. On the other hand, $A-\bar{A}$ and $A-\bar{A}$ intervalley biexcitons exhibit very low oscillator strengths since they are only Coulomb driven by dark Ad, Ad′, and Bd′ excitons with much lower oscillator strengths than their bright counterparts.

Applying an in-plane magnetic field $B_\parallel$ brightens not only previously spin-forbidden dark exciton resonances but also a multitude of bright–dark and dark–dark biexciton resonances. Furthermore, an in-plane magnetic field $B_\parallel$ leads to a pronounced differential transmission signatures due to the renormalization of $A_{1s}$ and $A_{2s}$ excitons.

C. Tilted Magnetic Field

Linear response: In the following, we study the influence of magnetic fields $B_\perp$ applied under a 45° tilt angle. This combines the previously discussed effects from out-of-plane $B_\perp$ and in-plane $B_\parallel$ fields. The $B_\perp$ dependent shifts of exciton resonances for monolayer MoS$_2$ are shown in Fig. 6 (a). Like the bright $A_{1s}$ transition, the dark $A_{1s}$ exciton shifts red but with approximately double magnitude increasing the bright-dark splitting $\Delta_{A_{1s}-A_{1s}}$ with rising $B_\perp > 0$ T. The increasing $\Delta_{A_{1s}-A_{1s}}$ yields weakly pronounced $A_{1s}$ excitons in the $\sigma_+$ circularly polarized linear transmission at $B_\perp = 15$ T and $B_\perp = 30$ T plotted as blue and purple lines in Fig. 6 (b). Simultaneously, the bright-dark splitting $\Delta_{A_{1s}-A_{1s}}$ decreases for increasing $B_\perp > 0$ T. This leads to strongly pronounced $A_{1s}$ excitons in the $\sigma_-$ circularly polarized linear transmission at $B_\perp = 15$ T and $B_\perp = 30$ T shown as purple and blue curves in Fig. 6 (d).
Figure 6. **Tilted magnetic-field-dependent transmission and differential transmission.** (a) Exciton and biexciton resonance energies for different tilted magnetic fields $B_\perp$, cf. Figs. 1 and 2. Solid (dotted) lines represent exciton resonances and dashed (dash-dotted) lines biexciton resonances for $\sigma_+$ ($\sigma_-$) circularly polarized excitation. (b,d) Linear transmission spectra of monolayer MoS$_2$ encapsulated in hBN at 5 K for (b) $\sigma_+$ and (d) $\sigma_-$ circularly polarized light for different $B_\perp$. The $B_\perp$ dependent exciton energies are indicated as colored bars above. (c,e) Normalized differential transmission spectra for different magnetic fields $B_\perp$. The $A_{1s}$ exciton is resonantly pumped by $\sigma_+$ circularly polarized light and the energetically broadband probe pulse is either (c) $\sigma_+$ circularly polarized or (e) $\sigma_-$ circularly polarized. The differential transmission is partially enhanced as indicated while the original signal is plotted by dotted lines. The colored long bars above mark the exciton energies, whereas the shorter bars indicate the biexciton energies.
In conclusion, we have presented a microscopic description to access the coherent exciton kinetics in monolayer TMDCs in the presence of differently oriented magnetic fields. We provide the magnetic-field-dependent exciton and biexciton resonance energies, transmission spectra, and differential transmission spectra. In particular, the latter reveals the manipulation of exciton-exciton scattering by magnetic fields. Here, we focused on the scattering induced changes of the exciton resonances, calculated the biexciton oscillator strengths, and predicted the possibility to detect the corresponding biexcitons in optical wave-mixing spectroscopy. Thus, our results provide a roadmap to interpret coherent pump-probe spectra in the presence of external magnetic fields.

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Appendix A: Magnetic Field

In this Appendix the different magnetic moments are individually discussed. Without loss of generality, the in-plane component of the magnetic field is assumed to be aligned along the x-direction \( B = (B_\parallel, 0, B_\perp)^T \) with the in-plane \( B_\parallel = B \sin \theta \) and out-of-plane contributions \( B_\perp = B \cos \theta \).

1. Atomic Orbital Magnetic Moment

The atomic orbital contribution of the Zeeman shift also referred to as intracellular orbital moment \( m_\lambda \mu_B B_\perp \) \([66, 69]\) is determined by the magnetic quantum number \( m_\lambda \), the Bohr magneton \( \mu_B \), and the magnetic field perpendicular to the monolayer sample \( B_\perp \). As the conduction bands are primarily constructed from hybridized \( d_z \) orbitals with \( l = m_l = 0 \) \([94, 95, 131]\) the associated atomic orbital magnetic moment is negligible. In contrast, the valence bands arise from hybridization of \( d_{x^2-y^2} \) and \( d_{xy} \) orbitals with magnetic quantum number \( m_l = 2 \) for the K valley and \( d_{x^2-y^2} - id_{xy} \) with \( m_l = -2 \) for the K’ valley \([8, 94, 95, 132]\). The resulting intracellular orbital magnetic moment is described by:

\[
H_{\text{atomic}} = \sum_{\xi,s,q} 2 (\delta_{\xi,K} - \delta_{\xi,K'}) \mu_B B_\perp v_{\xi,s,q}^\dagger v_{\xi,s,q} \quad (A1)
\]

2. Valley Orbital Magnetic Moment

The Zeeman shift associated with the valley magnetic moment is determined by \( (\delta_{\xi,K} - \delta_{\xi,K'}) \mu_B m_0 / (\bar{m}) B_\perp \) \([111, 112]\). \( m_0 \) denotes the free electron mass and \( \bar{m} = \frac{1}{2} \sum_{\xi,s} (m_{\xi,s}^e + m_{\xi,s}^h) \) is the mean effective mass of the eight-band model. The valley orbital magnetic moment leads to shifts of all conduction and valence bands with identical magnitudes but in opposite directions for the K and K’ valley described by the Hamiltonian:

\[
H_{\text{valley}} = \sum_{\lambda,\xi,s,q} (\delta_{\xi,K} - \delta_{\xi,K'}) \frac{\mu_B m_0}{\bar{m}} B_\perp \lambda_{\xi,s,q}^\dagger \lambda_{\xi,s,q} \\
\quad \times \left( c_{\xi,s,q}^\dagger c_{\xi,s,q} + v_{\xi,s,q}^\dagger v_{\xi,s,q} \right). \quad (A2)
\]

3. Spin Magnetic Moment

The spin magnetic moment is determined by \( \frac{1}{2} g \mu_B s \cdot B \) where \( s = (s_x, s_y, s_z)^T \) denotes the vector of spin Pauli matrices \( s_x, s_y, \) and \( s_z \). The spin magnetic moment leads to a contribution associated with the in-plane component of the magnetic field \( \frac{1}{2} g \mu_B s_z B_\parallel \) as well as a term connected with the out-of-plane magnetic field \( \frac{1}{2} g \mu_B s_z B_\perp \) \([90, 133]\). Here, the \( g \)-factor can be approximately described by the free electron \( g \)-factor \( g_e \approx 2 \) \([134]\) which is in excellent agreement with experimental measurements \([91]\). The associated Hamiltonian is given by:

\[
H_{\text{spin}} = \sum_{\lambda,\xi,s,q} (\delta_{s,\uparrow} - \delta_{s,\downarrow}) \mu_B B_\perp \lambda_{\xi,s,q}^\dagger \lambda_{\xi,s,q} \\
\quad + \sum_{\lambda,\xi,s,q} \mu_B B_\parallel \lambda_{\xi,s,q}^\dagger \lambda_{\xi,s,q}. \quad (A3)
\]

with \( \hat{s} \neq s \), i.e., \( \hat{s} = \downarrow \) for \( s = \uparrow \) and \( \hat{s} = \uparrow \) for \( s = \downarrow \). The first term on the right-hand side of Eq. (A3) describes a spin-dependent Zeeman shift of the conduction and valence bands in the presence of an out-of-plane magnetic field \( B_\perp \). The second line of Eq. (A3) describes a spin-mixing of electrons in the presence of an in-plane magnetic field \( B_\parallel \).

4. Total Hamiltonian

The electronic Hamiltonian involving the atomic orbital, valley orbital, and spin magnetic moment is repre-
sent by:
\[
H_B = H_{\text{atomic}} + H_{\text{valley}} + H_{\text{spin}} = \sum_{\xi,s,q} \varepsilon_{\xi,s,B\perp} c_{\xi,s,q}^\dagger c_{\xi,s,q} + \sum_{\xi,s,q} \varepsilon_{\xi,v,B\parallel} v_{\xi,s,q}^\dagger v_{\xi,s,q} + \sum_{\xi,q,s} \mu_B B_{\parallel} c_{\xi,s,q}^\dagger c_{\xi,s,q} + \sum_{\xi,s,q} \mu_B B_{\parallel} v_{\xi,s,q}^\dagger v_{\xi,s,q},
\]  
(A4)

with the conduction \(\varepsilon_{\xi,s,B\perp}\) and valence \(\varepsilon_{\xi,v,B\parallel}\) band Zeeman shifts defined in Eqs. (5) and (6) which linearly increase with the out-of-plane magnetic field \(B_{\parallel}\). The individual contributions due to the atomic orbital, valley orbital, and spin magnetic moment are illustrated in Fig. 7.

**Appendix B: Coulomb Matrices**

The dipole matrix element \(d_{\xi,s}^{c,v}\) projected on normalized Jones vectors are defined by [94]:
\[
d_{\xi,s}^{c,v} = -i \frac{\sqrt{2} e_0 a_0 t_0}{\varepsilon_{g,s}^{\xi}}. \tag{B1}
\]

Here, \(a_0\) is the lattice constant, \(t_0\) is the effective hopping integral, and \(\varepsilon_{g,s}^{\xi}\) is the energy gap between conduction and valence bands at the \(\xi\) point with spin \(s\).

The matrix element associated with direct Coulomb scattering on a Hartree–Fock level is given by:
\[
W_{\xi_1,s_1,s_2,s_3,s_4}^{\xi_2,s_2,s_3,s_4} = \sum_{k_1,k_2} V_{k_1-k_2} \varphi_{\xi_1,s_1}^{*} \varphi_{\xi_2,s_2} \varphi_{\xi_3,s_3}^{*} \varphi_{\xi_4,s_4}
\times \left( \varphi_{\nu_1,k_1}^{*} - \varphi_{\nu_1,k_2} \right)
\times \left( \varphi_{\nu_1,k_1}^{*} - \varphi_{\nu_1,k_2} \right). \tag{B2}
\]

The screened Coulomb potential \(V_{k_1-k_2}\) is defined by an analytical model [135] which agrees with results obtained from \(ab\) \(initio\) calculations [136–139].

Exchange Coulomb interactions originating from a local field effect [13, 117, 118] are described by [24]:
\[
X_{\xi_1,s_1,s_2,s_3}^{\xi_2,s_2,s_3} = V_{c,v,c,v} \varphi_{\xi_1,s_1,s_2,s_3}^{*} \varphi_{\xi_2,s_2,s_3} \varphi_{\nu_1,s_3}^{*} \varphi_{\nu_2,s_2} \varphi_{\nu_1,s_1}^{*} \varphi_{\nu_2,s_2}. \tag{B3}
\]

The electron-hole exchange Coulomb potential on the right-hand side of Eq. (B3) is adjusted to density function theory which calculate the constant value \(C\) for the \(\{K,\uparrow\}\) excitons [117]. Therefore, we renormalize the value for \(C\) by the \(\{K,\uparrow\}\) exciton corresponding wave function \(\varphi_{1s,q}^{K,\uparrow}\):
\[
V_{c,v,c,v}^{\xi_1,s_1,s_2,s_1,s_2,s_3} \approx \frac{C_{\xi_1,s_1,s_2}}{\sum_{q} \varphi_{1s,q}^{K,\uparrow}}, \tag{B4}
\]

The matrix element for linear and nonlinear exchange Coulomb scattering including the local-field exchange po-
tential defined in Eq. (B3) is given by:

$$W^{ξ_1,s_1,ξ_3}_{q_1,q_2} = \sum_{q_1,q_2} X^{ξ_1,s_1,ξ_3}_{q_1,q_2},$$  \hspace{1cm} (B5)$$

$$W^{ξ_1,s_1,ξ_2,ξ_4}_{q_1,q_2} = \sum_{q_1,q_2} X^{ξ_1,s_1,ξ_2,ξ_4}_{q_1,q_2} \varphi^{*}_{ν_4,q_1},$$  \hspace{1cm} (B6)$$

Nonlinear exchange Coulomb interactions due to a nonlocal-field effect are described by:

$$W^{ξ_1,s_1,ξ_2,ξ_4}_{q_1,q_2} = \sum_{q_1,q_2} V^{ξ_1,s_1,ξ_2,ξ_4}_{q_1,q_2} \varphi^{*}_{ν_4,q_1} \varphi^{*}_{ν_2,q_2} \varphi^{*}_{ν_3,q_3} \varphi^{*}_{ν_4,q_4}.$$  \hspace{1cm} (B7)$$

The involved exchange Coulomb matrix element $V^{ξ_1,s_1,ξ_2,ξ_4}_{q_1,q_2}$ is defined according to:

$$V^{ξ_1,s_1,ξ_2,ξ_4}_{q_1,q_2} = \frac{C}{ε(ξ)} \frac{d^{ξ_1,s_1}}{k_{ξ_1,s_1}} \left( d^{ξ_2,s_2}_{ν_1,s_1} \right) \varphi^{*}_{ν_1,s_1} \varphi^{*}_{ν_2,s_2} \varphi^{*}_{ν_3,s_3} \varphi^{*}_{ν_4,s_4},$$  \hspace{1cm} (B8)$$

where $C > 0$ denotes the elementary charge. The two wave vectors $q^{ξ_1}, q^{ξ_2}$ are defined by $q^{ξ} = q + i(δ^{ξ}_x − δ^{ξ}_y)$ $q_y$, and the dipole matrix elements $d^{ξ_1,s_1}_{ν_1,s_1}, d^{ξ_s}_{ν_2,s_2}$ were defined in Eq. (B1).

The two-electron and two-hole Coulomb interaction kernel for the two-electron and two-hole Schrödinger equation is defined by:

$$W^{ξ_1,s_1,ξ_2,s_2}_{±ν_1,ν_2,ν_3,ν_4} \cdot P \cdot K = V^{ξ_1,s_1,ξ_2,s_2}_{ν_1,ν_2} \left( \varphi^{*}_{ν_1,ν_2} \varphi^{*}_{ν_3,ν_4} \varphi^{*}_{ν_4,ν_3} \varphi^{*}_{ν_2,ν_1} \right) = \sum_{k_1,k_2} V_{ν_1,ν_2}^{k_1,k_2} \left( \varphi^{*}_{ν_1,ν_2} \varphi^{*}_{ν_3,ν_4} \varphi^{*}_{ν_4,ν_3} \varphi^{*}_{ν_2,ν_1} \right) \left( P + K \right)$$

Finally, the overlap matrix which directly appears due to the definition of the two-electron and two-hole correlation function in Eq. (3) reads:

$$S^{ξ_1,s_1,ξ_2,s_2}_{±ν_1,ν_2,ν_3,ν_4} \cdot P \cdot K = δ^{P,K} \sum_{k_1,k_2} \varphi^{*}_{ν_1,ν_2} \varphi^{*}_{ν_3,ν_4} \varphi^{*}_{ν_4,ν_3} \varphi^{*}_{ν_2,ν_1} \left( \varphi_{ν_1,ν_2} \varphi_{ν_3,ν_4} \varphi_{ν_4,ν_3} \varphi_{ν_2,ν_1} \right) \left( P + K \right)$$

### Appendix C: Negative Magnetic Fields

In the following, the results for negative magnetic fields are discussed. These results are equivalent to positive magnetic fields for pumping with $σ_-$ circularly polarized light and probing with same $σ_-$ or oppositely $σ_+$ circularly polarized light.

The DTS for negative out-of-plane fields $B_⊥ < 0$ T is shown in Fig. 8. In contrast to the response for positive magnetic fields $B_⊥ > 0$ T plotted in Fig. 3, the DTS signal in Fig. 8 mirrors the Zeeman shifts with opposite sign. Apart from this, the results closely resemble the positive magnetic fields and a corresponding interpretation holds true.

As the DTS for an in-plane magnetic field with opposite sign is identical to the results in Fig. 5, we directly move on to discuss the case of a titled magnetic field $B_⊥ < 0$ T as shown in Fig. 9. Compared to Fig. 6 (c), more pronounced $Ad_{1s}$ and less pronounced $Ad_{2s}$ features appear in Fig. 9 (b) for pumping and probing with $σ_-$ circularly polarized light. On the other hand, for a $σ_+$ circularly polarized pump pulse and a $σ_-$ circularly polarized probe pulse, the $A−A'$ intervalley biexciton and $Ad_{1s}$ resonance show an energy crossing which gives an interfering signal, cf. Fig. 9 (c). Additionally, Fig. 9 (c) shows less pronounced DTS from $A−Ad'$ biexcitons compared to Fig. 6 (e).
Figure 8. **Out-of-plane magnetic-field-dependent differential transmission.** Same as in Fig. 3 but for negative magnetic fields $B_\perp$ perpendicular to the monolayer sample.

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Figure 9. Tilted magnetic-field-dependent differential transmission. Same as in Fig. 6 but for negative tilted magnetic fields $B_z$. 

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