

Exchange-enhanced spin-orbit splitting and its density dependence for electrons in monolayer transition metal dichalcogenides

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We show that spin-orbit splitting (SOS) in monolayers of semiconducting transition metal dichalcogenides (TMDs) is substantially enhanced by an electron-electron interaction. This effect, similar to the exchange enhancement of the electron g factor, is most pronounced for conduction band electrons (in particular, in MoS_2), and it has a nonmonotonic dependence on the carrier sheet density n . That is, the SOS enhancement is peaked at the onset of filling of the higher-energy spin-split band by electrons, n_* , which also separates the regimes of slow (at $n < n_*$) and fast (for $n > n_*$) spin and valley relaxation of charge carriers. Moreover, this density itself is determined by the enhanced SOS value, making the account of exchange renormalization important for the analysis of the spintronic performance of field-effect transistors based on two-dimensional TMDs.

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Among all two-dimensional (2D) materials, a special place is taken by monolayers of transition metal dichalcogenides semiconductors [1–9] (TMDs, MX_2 , where $M = \text{Mo}, \text{W}$ and $X = \text{S}, \text{Se}, \text{Te}$). These compounds have conduction and valence band edges at the K points (corner of the hexagonal Brillouin zone) with a strong light-matter interaction, ideal for optoelectronics applications [10–13]. They also feature a strong spin-orbit interaction, inherited from the constituent transition metal atoms. When combined with middle-plane mirror symmetry and inversion asymmetry, this results in a spin-valley locking [14,15], which can potentially lead to long spin and valley memories of the resulting Ising-type charge carriers [16–20]. This determines the interest in monolayer TMDs, implemented in field-effect transistors [21–28], as a promising platform for spintronic devices [4,6,29–31].

In this respect, the magnitude of spin-orbit splitting (SOS) in the TMD monolayer bands, Δ , is important for the spin and valley memory of charge carriers: It determines the carrier density range where only one spin-orbit-split band is populated in each valley. In this regime spin-valley locking suppresses spin relaxation [32] because the latter requires simultaneous spin-flip and intervalley scattering to happen in one quantum process. Due to the orbital composition of the K -point valence band states [33], SOS is very large for holes [26,34–36], which determines their long spin-valley memories. It is much less for conduction band electrons, so that at high carrier densities the electron Fermi level can reach the upper spin-orbit-split bands, thus opening independent channels for both intravalley spin flips (due to spin-orbit scattering by wrinkles [37,38]) and non-spin-flip intervalley scattering

(e.g., by vacancies or K -point phonons), leading to a faster spin and valley relaxation. By now, the magnitude of SOS for electrons in monolayer TMDs has been studied theoretically in numerous *ab initio* density-functional theory (DFT) simulations [33,39–41], reporting a relatively wide spread of SOS values for each MX_2 compound, as compared to only a

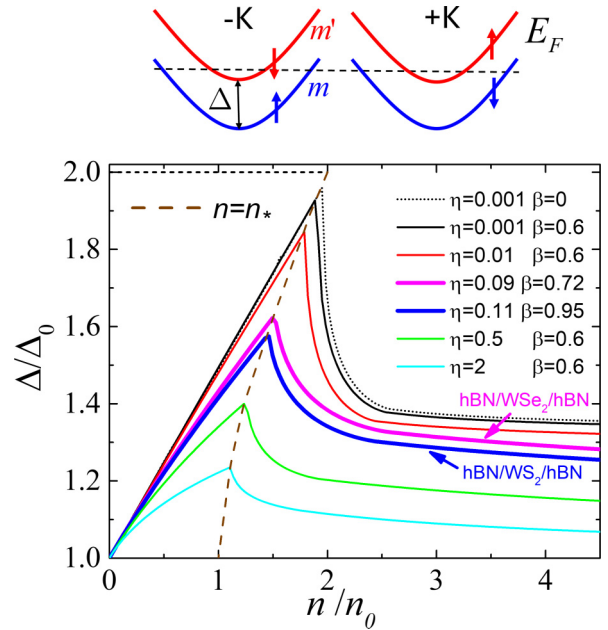


FIG. 1. Density-dependent renormalization of spin-orbit splitting Δ between two Kramers doublets in TMD monolayers. The data are shown for different values of bare Δ_0 , in-plane polarizabilities, effective band masses, and various dielectric environments, encoded in $\eta = \frac{|\Delta_0|}{e^2/r_s \epsilon}$, $n_0 = \frac{m|\Delta_0|}{\pi \hbar^2}$, $\beta = \frac{\hbar^2 \epsilon}{m^2 r_s} \sim 0.6$ (typical for the studied TMDs). The two highlighted curves correspond to WSe_2 and WS_2 monolayers with parameters determined for the interpretation of exciton spectroscopy data from Ref. [75]. The dashed line traces the threshold density n_* .

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handful of experimental results based on the interpretation of magnetospectroscopy data [42–50] and magnetotransport data [28,51–53]. Reported values for both conduction and valence band SOS are summarized in the Supplemental Material [54] (see also Refs. [13,36,46–50,51,55–67] therein).

Having in mind the above-discussed crossover in the electron spin-valley relaxation in highly doped TMD monolayers, it would be desirable to quantify the relevant threshold density more precisely. In this respect, we point out that SOS in 2D TMDs, $\Delta(n)$, may be sensitive to the carrier density n due to an exchange interaction between electrons [68]. This effect is analogous to the exchange enhancement of the electron's g factor established in various 2D systems (such as accumulation layers in semiconductor heterostructures) [69–72]. Due to such renormalization, the apparent absolute value of SOS, $\Delta(n_*)$, at the threshold density n_* would substantially differ from the single-particle value Δ_0 (provided by DFT computations [33,73,74]), as illustrated in Fig. 1 for electrons in the spin-split bands shown in the sketch. The dependence $\Delta(n)$ shown in Fig. 1 is obtained by analyzing the exchange contribution to the self-energy taking into account a specific feature of the electron-electron interaction in 2D semiconductors [76–78]: Their in-plane dielectric polarizability transforms the $1/r$ Coulomb potential into an approximately logarithmic “Keldysh-like” form [79,80] inside a finite radius r_* , which is longer than a nominal Bohr radius in the system, r_B . In Fig. 1, we show several exemplary curves for $\Delta(n)$, that we computed for a broad range of input parameters ($r_* > r_B$, the effective electron band mass m , Δ_0 defined as always a positive absolute value of SOS) and plotted in the axis for Δ normalized by Δ_0 and electron density by $n_0 = \frac{m\Delta_0}{\pi\hbar^2}$. Here, the initial rise of $\Delta(n)$ reflects the fact that the exchange energy increases with the number of interacting carriers. This increase is terminated at the density n_* , for which the Fermi level of carriers, E_F , reaches the higher spin-split bands, $E_F(n_*) = \Delta(n_*)$, and it is followed by a decline, caused by more efficient screening in systems with a twice-higher density of occupied states and reflecting the form factor of the Keldysh-like electron-electron interaction. In the set, displayed in Fig. 1, the two boldest curves show the results obtained with the input parameters attributed to WSe₂ (magenta) and WS₂ (blue), for which we obtain Δ_0 from experimentally measured dark-bright exciton splittings for hexagonal boron nitride (hBN)-encapsulated monolayers [75] following a procedure described in the Supplemental Material [54] and discussed at the end of this Letter.

To analyze the renormalization of SOS, we employ the Hartree-Fock theory for the Fermi sea of electrons filling in the conduction band of a TMD. In the description of the interaction between charge carriers we account for screening by 2D electrons in the random phase approximation (RPA), a relevant dielectric environment, as well as the specific feature introduced by the in-plane dielectric polarizability of the TMD crystal. At a single-particle level, electrons near the τK points ($\tau = \pm$) of the conduction band edges of a TMD monolayer are described by

$$H = \xi_{\mathbf{k}}^l + \frac{\Delta_0}{2}\tau s, \quad \xi_{\mathbf{k}}^l \equiv \frac{\hbar^2 \mathbf{k}^2}{2m_l}, \quad (1)$$

where $\mathbf{k} \equiv -i\nabla_{\mathbf{r}}$ is an in-plane wave vector, and the valley and spin states (the z component of spin is a good quantum number) are distinguished by $\tau = \pm 1$ and $s = \pm 1$, respectively. A bare SOS is described by the energy difference, $\Delta_0 > 0$, between two Kramers doublets in Fig. 1 (upper bands $l = 1$ for $\tau s = 1$ with $m_1 \equiv m'$; lower bands $l = 2$ for $\tau s = -1$ with $m_2 \equiv m$). For the interaction we use

$$V(|\mathbf{r} - \mathbf{r}'|) = \int V_{\mathbf{q}} e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} d^2\mathbf{q}/(2\pi)^2, \\ V_{\mathbf{q}} = \frac{2\pi e^2/\varepsilon}{q(1 + r_*q) + \Pi_{\mathbf{q}} 2\pi e^2/\varepsilon}, \quad r_* \equiv 2\pi\kappa/\varepsilon, \\ \Pi_{\mathbf{q}} = \sum_{\nu=\tau,s} \frac{m_l}{2\pi\hbar^2} \left[1 - \theta\left(1 - \frac{8\pi n_{\nu}}{q^2}\right) \sqrt{1 - \frac{8\pi n_{\nu}}{q^2}} \right], \quad (2)$$

as determined by the interplay between the dielectric environment with the effective dielectric constant ε , polarizability κ of the TMD crystal, and screening by the Fermi sea of the electrons/holes described by the polarization operator $\Pi_{\mathbf{q}}$ calculated in the random phase approximation [81] (which accounts for both spin-orbit-split bands of charge carriers—for details, see Supplemental Material [54]).

To describe the renormalization, $\Delta_0 \Rightarrow \Delta$, in the Hartree-Fock theory, we describe the ground state of electrons as a product of four Slater determinants, built from plane waves, of four spin-valley species. Then, we analyze the ground state energy and self-energy contributions to the spectra,

$$\mathcal{E} = \sum_{\tau,s} \int \frac{d^2\mathbf{k}}{(2\pi)^2} f_{\mathbf{k}\tau s} \left[\xi_{\mathbf{k}}^l + \frac{\Delta_0}{2}\tau s + \frac{1}{2}\Sigma_{\tau s} \right], \\ \Sigma_{\tau s}(\mathbf{k}) = - \int \frac{d^2\mathbf{q}}{(2\pi)^2} f_{(\mathbf{k}+\mathbf{q})\tau s} V_{\mathbf{q}}, \quad (3)$$

where $f_{\mathbf{k}\tau s}$ are the Fermi-step functions, corresponding to the densities $n_{\nu} = \int \frac{d^2\mathbf{k}}{(2\pi)^2} f_{\mathbf{k}\tau s}$ for each species of particles, $\nu = (\tau, s)$.

Then, we minimize $\mathcal{E}$ with respect to the densities n_{ν} , under a constraint that $\sum_{\nu} n_{\nu} = n$, determining the densities n_l of electrons in each Kramers doublet, $n_1 = n_{+,+} + n_{-,-}$ and $n_2 = n_{+,-} + n_{-,+}$ (n_2 denotes the charge density of the lowest-energy doublet, corresponding to the topmost valence bands or bottommost conduction bands in K and $-K$), which we further use for calculating the SOS renormalization,

$$\Delta(n) = \Delta_0 + \sum_{l=1,2} (-1)^l \int \frac{V_{\mathbf{q}} d^2\mathbf{q}}{(2\pi)^2} \theta\left(\frac{\pi\hbar^2 n_l}{m_l} - \xi_{\mathbf{q}}^l\right). \quad (4)$$

We perform these calculations for each of the TMDs across a broad carrier density range and combine all relevant material-specific parameters into the following factors,

$$n_0 = \frac{m\Delta_0}{\pi\hbar^2}, \quad \eta = \frac{\Delta_0}{e^2/r_*\varepsilon}, \quad \beta = \frac{\hbar^2\varepsilon}{me^2r_*} \equiv \frac{r_B}{r_*}. \quad (5)$$

The first of these three factors, n_0 , determines a characteristic scale for the crossover density, n_* , between the regimes where only the lower Kramers doublet (with mass $m_2 \equiv m$) is filled ($n_2 = n < n_*$ and $n_1 = 0$) and $n > n_*$, where both n_1 and n_2

TABLE I. Parameters for TMD monolayers sourced from DFT data [33,82]. Here, m (m') is the effective mass in the lower (upper) spin-split band, $r_* \cdot \varepsilon \equiv \frac{1}{2}(\varepsilon_{MX_2}^{\parallel} - 1)c_{MX_2}$, where $\varepsilon_{MX_2}^{\parallel}$ and c_{MX_2} are the in-plane dielectric constant and interlayer distance of the corresponding bulk TMD [83].

	$m' (m_e)$	$m (m_e)$	Δ_0 (meV)	$r_* \cdot \varepsilon$ (nm)	$n_0/10^{12} \text{ cm}^{-2}$	η	β
MoS ₂	0.46	0.43	3	3.9	0.6	0.008	0.75
MoSe ₂	0.56	0.49	22	4	4.6	0.05	0.83
MoTe ₂	0.62	0.53	34	7.3	7.4	0.17	0.33
WS ₂	0.26	0.35	32	3.8	4.7	0.08	0.95
WSe ₂	0.28	0.39	37	4.5	6.1	0.12	0.72
$\varepsilon = \sqrt{\varepsilon_{\text{hBN}}^{\parallel} \varepsilon_{\text{hBN}}^{\text{zz}}}$							4.9

are finite. The second, η , compares bare SOS to the Coulomb interaction at the Keldysh length, r_* . The third parameter is the ratio between the Bohr radius, $r_B = \frac{\hbar^2 \varepsilon}{m e^2}$, and r_* (in all studied TMD monolayers, $r_B < r_*$).

In Fig. 1 we use these parameters to represent the results of numerically computed SOS renormalization. At densities $n < n_0$, where all electrons are in the lower spin-split band and screening makes the e - e interaction essentially short ranged, hence nondispersive [in Eq. (2), $V_q \approx \text{const}$ if $\Pi_q 2\pi e^2/\varepsilon > q, r_* q^2$ for $q \sim k_F$], SOS increases with the density almost linearly, as more electrons are engaged in the exchange interaction. This agrees with the earlier discussed long-wavelength limit [68] of exchange renormalization of the band gap in 2D systems. We note that $\Delta/\Delta_0 \leq 2$ remains always finite, indicating that the system does not undergo any Stoner transition into an Ising ferromagnet. At densities $n \sim n_0$, we observe the strongest renormalization, followed by a decline of Δ/Δ_0 , caused by the enhanced screening upon filling the upper spin-split band and the q dispersion of V_q at $\Pi_q 2\pi e^2 \varepsilon < q, r_* q^2$.

We also note that for all TMD monolayers $\frac{r_B}{r_*} \equiv \beta < 1$ (see Table I), hence, we developed a semianalytical description based on the interaction approximated by

$$V_q \approx \frac{2\pi e^2/\varepsilon}{r_* q^2 + [1 + \theta(n_1)]4\pi e^2/\varepsilon}, \quad (6)$$

which corresponds to $\beta = 0$ and assumes that $m = m'$ as the effect of a 10%–30% mass difference in the two spin-orbit bands appears to be rather weak (see Supplemental Material [54]). At short distances, the inverse Fourier transform of such V_q corresponds to $V(r) \sim (e^2/\varepsilon r_*) \ln(r/r_*)$, characteristic for the Keldysh potential [79,80], while at long distances it is fully screened. In Fig. 1, we illustrate the validity of such an approximation by comparing the data obtained for $\beta = 0.6$ (solid line) and $\beta = 0$ (dotted line). This form of V_q enabled us to perform the integration in k space analytically (see Supplemental Material [54]), resulting in a closed analytical form for the renormalized SOS and densities,

$$n_1 = \frac{n - n_0}{2} - \frac{1}{4S} \ln \frac{\sqrt{4(n - n_1)S[\theta(n_1) + 1]^{-1} + 1} + 1}{\sqrt{4n_1S[\theta(n_1) + 1]^{-1} + 1} + 1} \quad \text{for } n > n_*, \quad n_1 = 0 \text{ for } n < n_*,$$

$$\Delta \approx \Delta_0 + \frac{e^2}{2r_* \varepsilon} \ln \frac{(n - n_1)S + [1 + \theta(n_1)]}{n_1 S + [1 + \theta(n_1)]}, \quad n_* = n_0 + \frac{\ln(\sqrt{S n_* + 1/4} + 1/2)}{2S}, \quad S = \pi r_B r_*. \quad (7)$$

We note that in the limit of metallic screening, $r_* \rightarrow 0$, for which the interaction is essentially δ functional in real space, $\Delta \approx \Delta_0 + E_F/2$, reproducing the result of Ref. [68] obtained for $V_q = V_{q \rightarrow 0}$.

We note that the initial rise of $\Delta(n)$ in Fig. 1 and in Eq. (7) can be used to describe the SOS renormalization for holes in p -doped TMDs (see Supplemental Material [54] for more details), where only densities $n \ll n_0$ can be achieved in realistic devices, due to the much larger values of bare SOS in the valence band.

In Fig. 2 we display the results of SOS renormalization for K -valley electrons for hBN-encapsulated monolayers. We note that the SOS renormalization factor is the largest in MoS₂, almost doubling the value of Δ at the density $n = n_* \approx 10^{12} \text{ cm}^{-2}$. Although relative changes of the SOS are smaller in other TMDs, nevertheless, their absolute increase across the density range up to 10^{13} cm^{-2} appears to be substantial,

and we note that for all of these materials $\Delta(n)$ features a nonmonotonic dependence with a maximum at n_* , $n_0 < n_* < 2n_0$ which determines the onset of filling of the upper spin-orbit-split band. In a wide range of material parameters the numerically calculated n_* using the full interaction potential (2) is well approximated by Eq. (7), as shown in Fig. 2(b). We note that at small densities one should expect a departure from the RPA approximation used to describe the metallic screening. The pink region shows the range of parameters where the Wigner radius $r_s = \frac{m e^2}{\varepsilon \hbar^2 \sqrt{\pi n}} > 10$ and the RPA calculation would underestimate SOS renormalization and n_* .

For a confident description of SOS dependence on carrier density and the threshold value n_* it would be wise to use the experimentally measured value of bare SOS, Δ_0 . In principle, the latter could be measured using the electron spin resonance (which probes zero-momentum collective excitations in the electronic liquid); however, such an experiment is yet to be

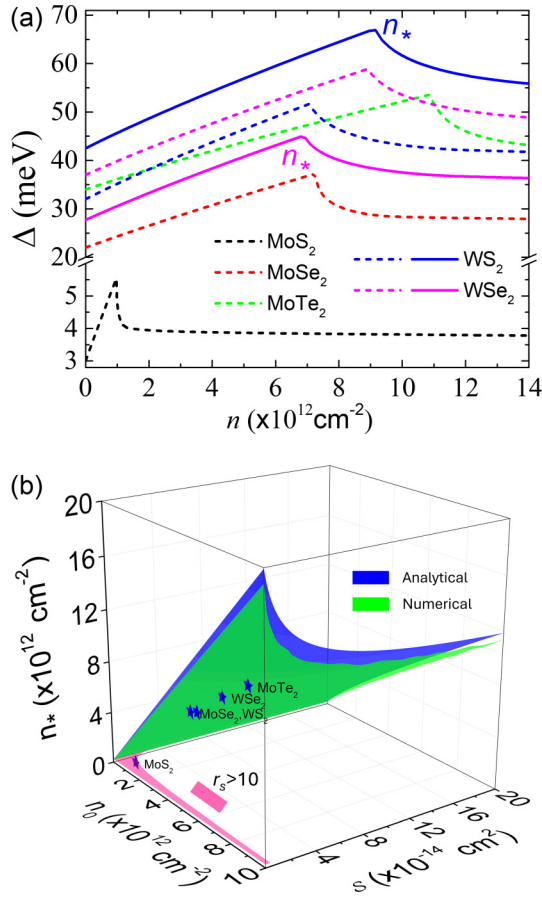


FIG. 2. Exchange-enhanced SOS for electrons in TMD monolayers. (a) Dashed lines correspond to material parameters listed in Table I. Solid lines show the calculation using single-particle SOS values Δ_0 calculated from exciton splittings in WX_2 compounds reported in Ref. [75]. The corresponding values of the threshold densities are $n_* = 6.8 \times 10^{12} \text{ cm}^{-2}$ for WSe_2 and $n_* = 9.0 \times 10^{12} \text{ cm}^{-2}$ for WS_2 . (b) Density n_* calculated analytically using Eq. (7) (blue surface) and numerically (green), with stars identifying n_* for the studied MX_2 compounds. The red region on the bottom plane shows where $r_s > 10$.

made. Fortunately, Δ_0 can also be extracted from the energy splitting between bright and dark excitons in monolayers, in particular, in WX_2 compounds, where the lowest-energy exciton is dark. Such experiments have been reported in Ref. [75] making use of unconventional geometries and peculiar selection rules enabling one to observe both dark and bright excitons with splitting $\delta_{BD} = 40 \text{ meV}$ for WSe_2 and $\delta_{BD} = 55 \text{ meV}$ for WS_2 , both encapsulated in hBN. Then, for

TABLE II. SOS parameters for hBN-encapsulated WSe_2 and WS_2 monolayers. Bare SOS was determined from bright-dark exciton splittings in Ref. [75]. The threshold density n_*^{th} was computed using Eq. (7) and masses given in Table I, in comparison with the only available experimental result, n_*^{expt} , from Ref. [66].

	Δ_0 (meV)	$n_0/10^{12}$ cm^{-2}	$n_*^{\text{th}}/10^{12}$ cm^{-2}	$n_*^{\text{expt}}/10^{12}$ cm^{-2}	$\Delta(n_*)$ (meV)
WSe_2	28	4.0	6.8	6.6 [66]	45
WS_2	43	6.3	9.0		67

determining Δ_0 from the exciton splitting, one has to take into account the difference in the electron masses m_1, m_2 in the spin-split bands ($m_2/m_1 = 1.39$ in WSe_2 , $m_2/m_1 = 1.35$ in WS_2 [33,84]): The heavier mass in the lower electron band increases the dark exciton binding energy, thus making the exciton splitting larger than Δ_0 [85]. Using the description of exciton binding energies in Ref. [86] and the open source code available in Ref. [82], we recalculate the exciton splittings into single-particle SOS [87] as $\Delta_0 = 28 \text{ meV}$ for WSe_2 and $\Delta_0 = 43 \text{ meV}$ for WS_2 . These values, gathered in Table II, are different from those computed using DFT for isolated monolayers, which may be attributed to the influence of hBN encapsulation [65].

For those values of Δ_0 , the computed $\Delta(n)$ is shown by two highlighted curves in Fig. 2. In particular, we note that for WSe_2 the enhancement of SOS determines the threshold density $n_* = 6.8 \times 10^{12} \text{ cm}^{-2}$ (as compared to $n_0 = 4.0 \times 10^{12} \text{ cm}^{-2}$ estimated from bare SOS), which is close to the threshold density $n_* = 6.6 \times 10^{12} \text{ cm}^{-2}$ observed in Ref. [66] based on the analysis of Shubnikov–de Haas oscillations. Such a threshold density plays an important role for spintronic characteristics of MX_2 -based field-effect transistors. This is because it separates the regime of the slow spin-valley relaxation of electrons at $n < n_*$ (because such relaxation requires simultaneous spin-flip and intervalley scattering, as prescribed by the spin-valley locking), from the fast spin-relaxation regime at $n > n_*$ (where both intravalley spin-flip and non-spin-flip intervalley processes are allowed) [32].

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