

Microscopic origin of Rashba coupling from first principles: Layer-resolved orbital asymmetry in transition metal dichalcogenides

Miguel Morales-Cócera^{1,2}, Marta Prada³, Franz Fischer^{1,2} and Gabriel Bester^{1,4}

¹*Institute of Physical Chemistry, University of Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany*

²*Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22761 Hamburg, Germany*

³*I. Institute of Theoretical Physics, Notkestraße 9-11, 22607 Hamburg, Germany*

⁴*The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany*



(Received 19 February 2026; revised 17 June 2026; accepted 10 August 2026; published 10 September 2026)

Spin-orbit coupling in two-dimensional materials gives rise to a Rashba spin splitting when inversion and mirror symmetries are broken, yet its microscopic origin and quantitative characterization in transition metal dichalcogenides remain incomplete. Using first-principles calculations, we investigate monolayer MX_2 transition metal dichalcogenides ($M = \text{Mo, W}; X = \text{S, Se, Te}$), and homobilayers lacking inversion and mirror symmetries, exhibiting zero-field Rashba splitting. We determine the field- and momentum-independent Rashba coefficients and intrinsic electric fields of these systems, establishing a direct connection to the Rashba Hamiltonian. Surprisingly, the Rashba effect on the topmost valence band is substantially smaller in bilayers than in monolayers at typical fields. This motivates an analytical microscopic model that identifies the orbital processes responsible for Rashba spin splitting. It confirms that, in bilayers, the effect is governed by the competition between layer-resolved charge deformation and interlayer coupling. To quantify this competition, we introduce the orbital polarization imbalance and orbital polarizability as order parameters and, by combining them with first-principles calculations, identify the dominant microscopic channel responsible for the Rashba splitting.

DOI: [10.1103/4hpr-dmmf](https://doi.org/10.1103/4hpr-dmmf)

I. INTRODUCTION

A novel class of quasi-two-dimensional (2D) materials—such as bilayers of transition metal dichalcogenides (TMDs) or Janus TMD monolayers—exhibits a built-in electric dipole that arises naturally when mirror symmetry (m_z) is broken [1–3]. When inversion symmetry ($\mathcal{I}$) is also broken, a zero-field Rashba spin splitting near the Γ point arises [4–8]. This feature offers a potential pathway toward low-power spintronic applications with nonvolatile spin control [9,10].

TMDs, in particular, have emerged at the forefront of spin-related applications due to their strong spin-orbit coupling (SOC) [11–13], and have been extensively studied as hosts of tightly bound charged and neutral excitons [14,15], making them ideal platforms for integrating spin, charge, and optical functionalities [16–21]. Additionally, recent studies indicate that the Γ -point neighborhood may play a central role in high-energy excitonic processes in few-layer systems [18], as this is the key region in the Brillouin zone where interlayer hybridization, valence band maximum, and electric field effects converge, giving rise to rich excitonic phenomena that were previously overlooked.

Despite the growing interest in Rashba SOC in TMDs [22–26], a quantitative and qualitative understanding of its

intrinsic origin remains incomplete. Previous studies have characterized Rashba splittings through energy-momentum extrema, providing limited insight into the fundamental coupling mechanisms [22–30]. Here, we introduce a framework that resolves the Rashba coefficient, λ_R^n , which quantifies the system's response to an applied external field, and the intrinsic orbital field, E_0^n , which captures the built-in asymmetry responsible for finite band-dependent spin splitting at zero bias. These quantities provide a physically transparent description of Rashba effects, bridging atomic-scale asymmetry and layer polarization. Our perspective clarifies why the topmost valence band (VB), despite their built-in dipole at zero field, exhibits a smaller reaction to the electric field than monolayers do, and establishes a unified foundation for comparing Rashba coupling across the TMD family.

We perform systematic *ab initio* calculations of monolayer (ML) and homobilayer (BL) MX_2 ($M = \text{Mo, W}; X = \text{S, Se, Te}$) systems, focusing on the top two valence bands near the Γ point. The observed Rashba spin splittings are elucidated in terms of a microscopic model that treats orbital hybridization and atomic SOC perturbatively, and reveals the relevant atomistic processes that yield Rashba splitting in TMDs. We introduce the orbital polarization imbalance, ξ^n , as a central descriptor of Rashba behavior, quantifying the (band-dependent) orbital asymmetry induced by the breaking of the mirror symmetry m_z . This quantity not only governs the spin ordering (sign of the spin gap), but also describes the intrinsic orbital field which impacts the magnitude of Rashba splitting. Finally, by performing a Wannierization of the density functional theory (DFT) Kohn-Sham states, we

Published by the American Physical Society under the terms of the Creative Commons Attribution 4.0 International license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

investigate the role of the in-plane orbitals as mediators in the first-order Rashba processes essential to the SOC mechanism. Our analysis reveals that the magnitude of the Rashba splitting arises from a nontrivial competition between the system's atomic SOC strengths, orbital polarization, and band composition.

II. METHODS

We performed *ab initio* DFT calculations using the generalized-gradient approximation for the exchange-correlation functional, as parametrized by Perdew, Burke and Ernzerhof [31], and utilize the DFT-D3-BJ implementation [32] to treat the van der Waals interaction.

To incorporate SOC we employ fully relativistic, norm-conserving pseudopotentials [33] with a plane-wave cutoff energy of 100 Ry using the QUANTUM ESPRESSO package [34,35]. An out-of-plane cell dimension of 50 bohr has been used to suppress the spurious interaction of periodic images. During structural optimization all atomic forces were converged below 10^{-4} Ry/bohr leading to lattice constants in close agreement with experimental values [36–39]. The Brillouin zone was sampled using a Γ -centered $15 \times 15 \times 1$ Monkhorst grid [40].

Additionally, we wannierized the DFT wave functions of the BL system to obtain an orbital-resolved Hamiltonian using the WANNIER90 package [41]. We incorporated chalcogen p and transition metal d orbitals, as these represent the leading orbital contributions in the close vicinity of the Fermi level [42,43], leading to a basis set size of 44 Wannier functions. Furthermore, a denser k grid ($21 \times 21 \times 1$) allowed reliable results [44,45].

III. RESULTS

A. From monolayer to bilayer: Symmetry and spin splitting in TMDs

We consider ML and BL MX_2 ($M = \text{Mo, W}$; $X = \text{S, Se, Te}$) TMDs in the $1H$ phase at the ML level. MLs lack inversion symmetry ($\mathcal{I}$) but preserve the mirror symmetry (m_z), which forbids any linear-in- k Rashba term; hence, only a small cubic splitting is allowed unless an external electric field breaks m_z . In BLs, $\mathcal{I}$ is restored in the H stacking, but it is broken in R -type stacking. Among them, only the R_X^M configuration [symmetry equivalent to the R_M^X in homobilayers; see Figs. 1(d) and 1(e)] breaks both $\mathcal{I}$ and m_z [46], enabling Rashba splitting in the absence of an external electric field. We therefore focus on BLs in the R_X^M stacking, also called R_{hm} , R_h^M , $B^{M/X}$, and AB in the literature [47], and compare them with the MLs through the (field-independent) Rashba coefficient λ_R^n developed in Sec. III B.

In Fig. 1(a) we show the band structure of MoSe₂ along k_x with an out-of-plane electric field $E_{\text{ext}} = 0.2 \text{ V/\AA}$. The bands are colored according to their spin expectation value $\langle \hat{S}_y \rangle$ to highlight the dominant spin component perpendicular to momentum, as expected from the Rashba spin texture [4,48]. The left inset shows a magnification of the Rashba spin splitting and the right inset illustrates the linearity of that spin splitting, ΔE , with respect to k for increasing values of external field (yellow to blue: 0.05, 0.1, and $0.2 \text{ V/\AA}$), which is a feature

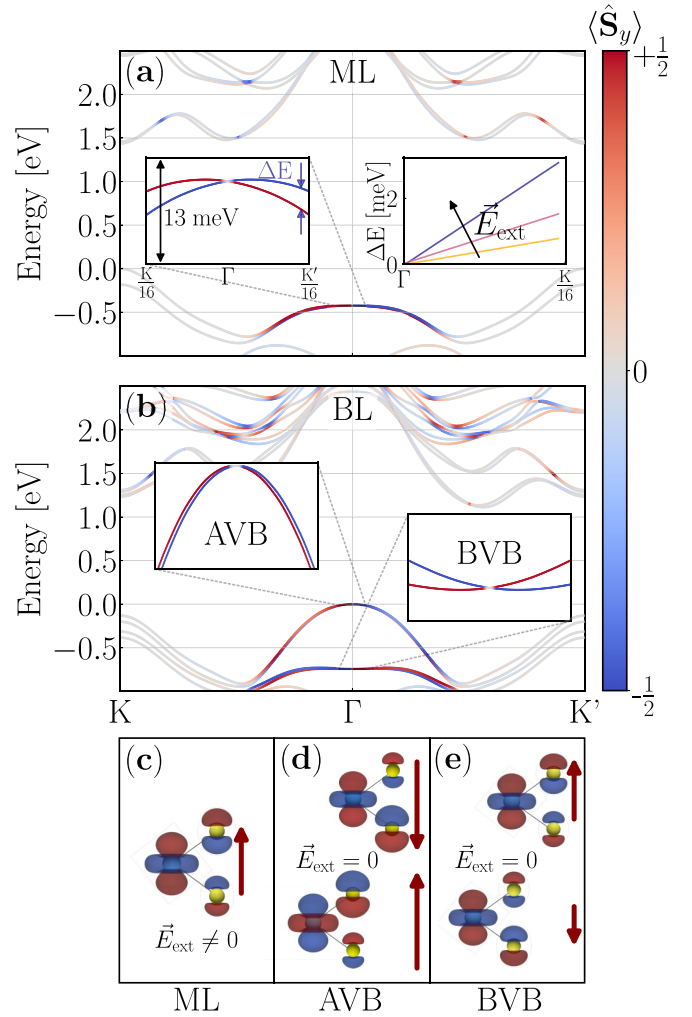


FIG. 1. Band structure of MoSe₂ with color-coded $\langle \hat{S}_y \rangle$ projections for ML (a) and BL (b) in the R_X^M stacking. The insets correspond to the zoom-ins of the target bands, with equal energy (13 meV) and momentum window (from $K/16$ to $K'/16$) for quantitative comparison between the states. The right inset in (a) shows the spin splitting ΔE for different electric fields (yellow to blue: 0.05, 0.1, and $0.2 \text{ V/\AA}$). Wave function representation of the top VB of a ML under an external electric field E_{ext} (c), and of AVB (d) and BVB (e) in the BL at zero field. The color of the orbitals schematically represents their phase. Red arrows represent the orbital polarization at the ML level.

of the Rashba effect. We stress that the spin splitting near Γ increases significantly along k_x towards the K point, where the spins become oriented out of plane [negligible in-plane spin expectation values in Fig. 1(a)]. This splitting is sometimes referred to as Zeeman type [49,50], and leads to the A and B exciton splitting in optics. In this work we focus in the Γ neighborhood where the Rashba effect occurs, and its linearity in k can be clearly disentangled from other SOC mechanisms.

Figure 1(b) shows the corresponding plot for the BL of MoSe₂ with R_X^M stacking in the absence of an external electric field. The insets show the nonzero spin splitting of the topmost two (four, including spin) Γ -point VBs. These bands result from layer hybridization, splitting the top VB of the two

MLs into a lower-energy bonding valence band (BVB) and a higher-energy antibonding valence band (AVB) [51].

In Figs. 1(c)–1(e) we schematically depict the wave functions at Γ for the ML VB and the AVB and BVB of the BL. Red arrows indicate the orbital polarization induced by either the external electric field E_{ext} in the case of the ML (c) or the stacking configuration of the BL (d), (e). The phase of the wave functions shows the antibonding character of the AVB and the bonding character of the BVB. Although we would not classify the AVB state as a genuine interface state, its charge distribution shows a certain interfacelike character: It shows enhanced weight on the inner chalcogen atoms and in the interlayer region, despite retaining the expected antibonding phase relation and nodal structure. This suggests that the state is not a simple two-orbital antibonding combination, but contains an appreciable admixture of out-of-plane orbital components with enhanced interface character.

B. Rashba coefficient λ_R^n and intrinsic orbital field E_0^n

ML TMDs belong to the point group D_{3h} , and the symmetry reduces to C_{3v} upon application of an out-of-plane electric field, which breaks in-plane mirror symmetry m_z . Similarly, the R_X^M stacked BLs lack inherently both $\mathcal{I}$ and m_z even in the absence of an external field; consequently, they also belong to the point group C_{3v} . As a result, both systems allow a linear-in- k Rashba spin splitting around the Γ point:

$$H_R = \alpha_R^n (k_x \sigma_y - k_y \sigma_x), \quad (1)$$

where $k_i = p_i/\hbar$ is the crystal momentum, σ_j are the Pauli matrices, and α_R^n is the state-dependent Rashba prefactor [52], which additionally depends on the strength of the applied electric field. Without loss of generality, we will focus on the k_x momentum direction.

There are two common methods to extract the field- and band-dependent Rashba prefactor α_R^n from DFT calculations. The first is to identify the valence band maximum, which shifts slightly away from Γ in the presence of Rashba splitting. α_R^n can be derived from the k -point offset and the corresponding energy difference between the maximum and the Γ point [22,28]. The second approach, used in this work, involves extracting the spin splitting within the linear regime, both in momentum and in electric field. From Eq. (1) and along the Γ - K direction, this is

$$\Delta E = \alpha_R^n k_x = \lambda_R^n (E_{\text{ext}} + E_0^n) k_x. \quad (2)$$

This method allows us to extract both the Rashba coefficient λ_R^n and the intrinsic orbital field E_0^n , which is a (band-dependent) field related to the internal orbital asymmetry that results from the atomic arrangement and the broken m_z . Note that only the z component of E_0^n is allowed, owing to the C_{3v} symmetry, while E_{ext} is the out-of-plane external field. By calculating ΔE for several k_x values within the linear regime, the prefactor $\lambda_R^n (E_{\text{ext}} + E_0^n)$ can be obtained directly from the linear dependence [see insets of Fig. 1(a)]. By varying E_{ext} , the Rashba coefficient λ_R^n and the field offset E_0^n can be extracted with a linear fit.

Figure 2(a) illustrates the specific spin textures—defined by the spin expectation value $\langle \hat{S}_y \rangle$ along k_x —relevant to the spin-split AVB and BVB in BLs. Here, the bands are colored

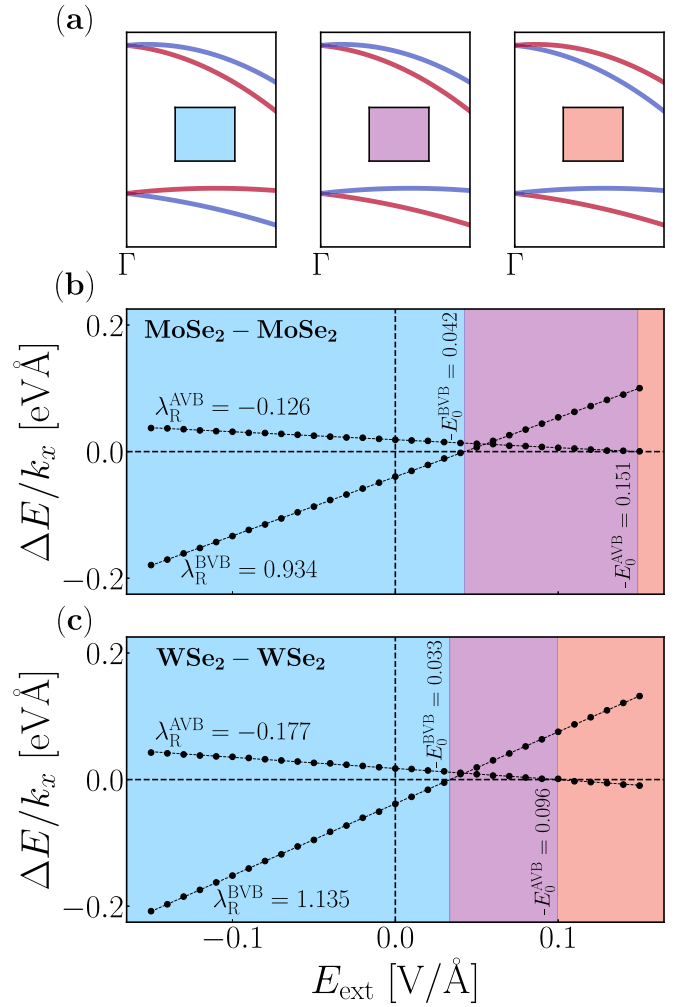


FIG. 2. (a) Schematic ($\hat{S}_y$) arrangement of the spin-split AVB and BVB. The color code defined in (a) is indicated by the background colors in (b) and (c). $\Delta E/k_x$ as a function of the external field E_{ext} for AVB and BVB in BL MoSe₂ (b) and BL WSe₂ (c). Band-dependent Rashba coefficients λ_R^n in units of $\text{eV}\text{\AA}^2/\text{V}$ are reported for the relevant states under investigation together with the intrinsic orbital field E_0^n in units of $\text{V}/\text{\AA}$.

red for spin up ($\uparrow$) and blue for spin down ($\downarrow$). Note that the fourth arrangement possibility is not depicted, since it is not observed for the respective BLs. The color codes established in the insets of Fig. 2(a) are subsequently used as background indicators in Figs. 2(b) and 2(c) for BL MoSe₂ (b) and BL WSe₂ (c), where $\Delta E/k_x$ is evaluated at $k_x = K/20$ along the Γ - K high-symmetry line as a function of the external field E_{ext} . We adopt the convention $\Delta E = E_{\downarrow} - E_{\uparrow}$, so that the spin-splitting sign is encoded in λ_R^n . Note that λ_R^n is the slope of the splitting with field (linear fit), while the field at which the splitting vanishes relates to the value of the intrinsic orbital field E_0^n : Namely, the splitting is canceled when the condition $E_{\text{ext}} = -E_0^n$ is met. The change in background color in Figs. 2(b) and 2(c) highlights the spin-control capability of the external field, with $-E_0^n$ marking a reversal of the spin character. The results for the other materials are given in the Supplemental Material [53].

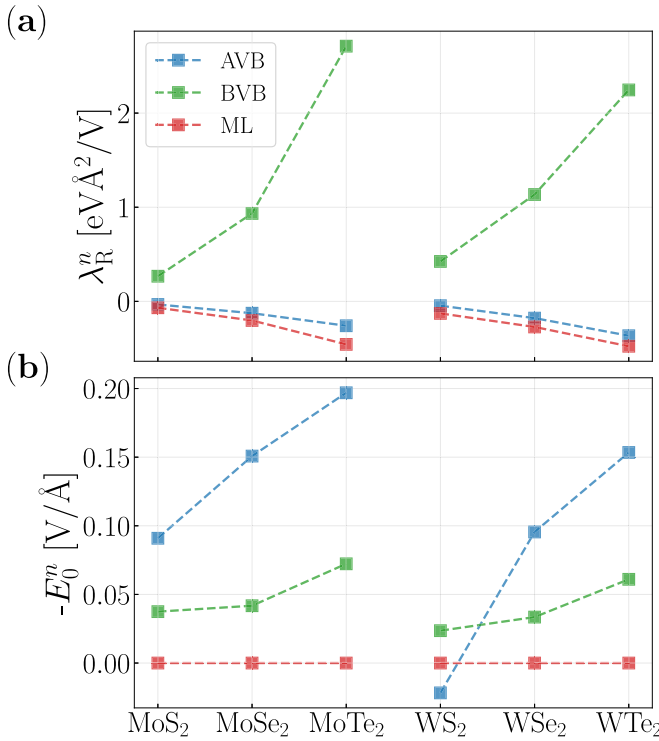


FIG. 3. Rashba coefficient λ_R^n (a) and intrinsic orbital field E_0^n (b) of the VB maximum for different TMD MLs, as well as for the AVB and BVB states in the corresponding TMD BLs.

In Fig. 3(a), we show the Rashba coefficients λ_R^n , for different TMDs resolved for the ML VB maximum and the AVB and BVB states of the BL. The values for the AVB are consistently smaller in magnitude than those for the BVB and, notably, also smaller than the corresponding ML values. Moving to heavier chalcogen atoms (left to right) significantly increases the magnitude of the Rashba coefficients, whereas the influence of the metal appears to be smaller. Figure 3(b) shows the intrinsic orbital field values of the different materials, showing also a monotonic increase with the chalcogen's mass, and strikingly, a decrease with the heavier metal, which will be physically interpreted in the next section. The resulting zero-field Rashba parameters [$\alpha_R^n(0) = \lambda_R^n E_0$] span approximately 1–200 meV Å across the materials studied (from WS₂ to MoTe₂; see Table 1 in the Supplemental Material [53]), comparable to the values reported for conventional Rashba systems such as Si-SiGe quantum wells ($\simeq 0.01$ meV Å) [54], oxide interfaces like LaAlO₃/SrTiO₃ (10–50 meV Å) [55], semiconductor heterostructures including InGaAs/InAlAs (40–70 meV Å) [56,57], or AlGaIn/GaN (81 meV Å) [58].

C. Orbital polarization imbalance: Order parameter

To connect the obtained numerical results to an intuitive charge-based quantity, we start with the simpler ML and follow a similar strategy as originally formulated for surfaces by Petersen and Hedegård [59] and later confirmed with DFT calculations [60,61]. Namely, we introduce a parameter ξ^n that quantifies the charge imbalance between the upper and lower parts of the monolayer. This quantity depends on the

chosen band n and the k point. We will choose a value of $k = K/40$ subsequently, but this choice has no consequences for the results, unless explicitly discussed. For a ML our order parameter takes the simple form

$$\xi_{\text{ML}}^n = \left(\int_{-z_{\infty}}^{z_M} \langle \rho_{nk} \rangle_{xy} dz - \int_{z_M}^{z_{\infty}} \langle \rho_{nk} \rangle_{xy} dz \right) C^{-1},$$

where $\langle \rho_{nk} \rangle_{xy}$ is the plane-averaged charge density of band n at k , z_M is the z coordinate of the metal plane, and $C = \int \langle \rho_{nk} \rangle_{xy} dz$ is a normalization constant. In other words, ξ_{ML}^n encodes the asymmetry in the charge distribution with respect to the plane of the transition metal. This quantity is zero in the absence of an external electric field, since the ML maintains m_z , and serves as an order parameter of the mirror symmetry breaking that enables the Rashba splitting.

The choice of order parameter for the BL is less trivial. One may think that since the AVB and BVB states are true bilayer states, the governing quantity for a Rashba-type spin splitting is the charge imbalance between both layers. However, this definition leads to poor results and even qualitative differences. For instance, a charge balanced bilayer, could have zero as order parameter, but not necessarily zero Rashba (not shown). The working alternative is to picture both layers as contributing individually to the Rashba state splitting. This leads to the definition of the orbital polarization imbalance, ξ^n , as a sum of both ML charge asymmetries encoded in ξ_{ML}^n :

$$\xi^n = (\xi_{L_1}^n + \xi_{L_2}^n) C^{-1},$$

with

$$\begin{aligned} \xi_{L_1}^n &= \int_{-z_{\infty}}^{-z_1} \langle \rho_{nk} \rangle_{xy} dz - \int_{-z_1}^0 \langle \rho_{nk} \rangle_{xy} dz, \\ \xi_{L_2}^n &= \int_0^{z_1} \langle \rho_{nk} \rangle_{xy} dz - \int_{z_1}^{z_{\infty}} \langle \rho_{nk} \rangle_{xy} dz, \end{aligned} \quad (3)$$

with $\pm z_1$ being the transition metal planes and $z = 0$ the middle point between these planes, as shown in Figs. 4(a) and 4(b). This term can be zero, even if both MLs within the BL have a nonvanishing asymmetry. These ML asymmetries can cancel each other, just as two dipoles can lead to a vanishing overall dipolar moment. In Fig. 4(c) we show the orbital polarization imbalance, ξ^n , for the AVB (blue) and BVB (green) as a function of electric field for MoSe₂. Remarkably, ξ^n exhibits a step at 0.042 and 0.151 V/Å for BVB and AVB, respectively. The step occurs precisely at the external fields where the spin splitting ΔE is zero, i.e., when $E_{\text{ext}} = -E_0^n$ [see Fig. 2(b)]. The height of the step is proportional to the value of k chosen for the calculation, while the field at which it occurs is independent of it (see Supplemental Material Fig. S1 [53], for different values of k). Additionally, the difference in slopes of Fig. 2(c) is qualitatively reproduced by the order parameter ξ^n : While the absolute values of the slopes of ξ^n depend on the chosen k , the qualitative behavior remains consistent. The arrows in Fig. 4(c) depict the expectation value of spin ($\hat{S}$) of the upper band in the z - y plane. The spin projections reveal a clear Rashba spin texture where S_y is a good quantum number, except at the neighborhood of $E_{\text{ext}} = -E_0^n$ [see zoom-in of the step in Fig. 4(c)]. The analysis of the orbital polarization imbalance ξ^n demonstrates its suitability as a reliable indicator of Rashba spin splitting across all examined systems

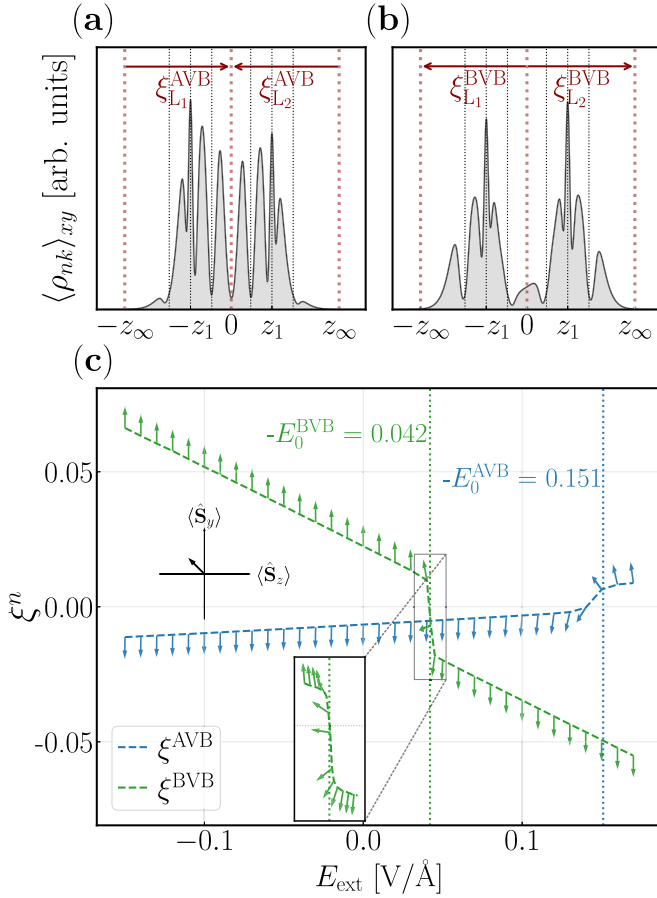


FIG. 4. Plane-averaged $\langle \rho_{nk} \rangle_{xy}$ as a function of the out-of-plane coordinate z at $k = K/40$ for the MoSe₂ BL states AVB (a) and BVB (b), respectively. The red arrows indicate the sign (not the magnitude) of the ML ξ_{ML}^n contribution to the BL ξ^n . (c) Order parameter ξ^n for AVB (blue arrows) and BVB (green arrows). The arrows depict the expectation value of the spin in the z - y plane (see coordinate system). The vertical dotted lines depict the electric field that closes the Rashba splitting in the AVB (blue) and BVB (green) in units of V/Å.

(see Supplemental Material Fig. S3 [53]). It shows that the Rashba effect in the BL case arises from the sum of the two ML-specific charge asymmetries.

D. Interpretation of the observed trends in λ_R^n and E_0^n

As shown in Fig. 3, both λ_R^n and the intrinsic field $-E_0^n$ increase from S to Te, consistent with the increasing polarizability across the series [62]. This trend is expected, since greater polarizability should lead to both a larger intrinsic field and a stronger response to an external field. Furthermore, the (heavier metal) W-based compounds display an overall reduction in the magnitude of $-E_0^n$, including a sign reversal in the AVB of WS₂.

We attempt to explain this behavior by an interpretation of the *ab initio* AVB charge density in the plane containing the six atoms in the unit cell shown in Fig. 5. The difference between the electronic densities of the two chalcogen within one layer, are shown as green arrows. The deformation of the transition metal (TM) density is encoded in the blue arrow.

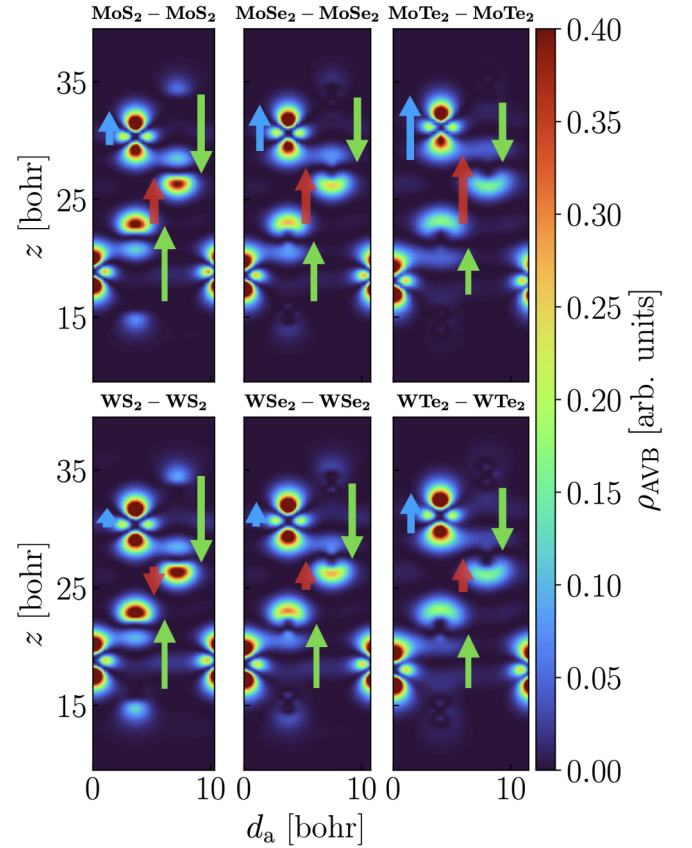


FIG. 5. ρ_{AVB} in the d_a - z plane cutting through the six atoms in the unit cell for all TMD bilayers at $k = K/40$ and $E_{\text{ext}} = 0$. The densities are normalized to their maximum value, and the color scale is truncated at 0.4 to enhance contrast. Blue arrows depict the direction and magnitude of the deformation of the metal density in the upper layer. For the lower layer TM we see no deformation and hence no arrow is shown. The green arrows show the orientation and the magnitude of the charge imbalance between both chalcogens within one layer. The red arrows are the sum of blue and green arrows and give the overall deformation, which is related to ξ^{AVB} , and thus, to $-E_0^{\text{AVB}}$ (see text).

Since the lower layer has no significant transition metal density deformation, we have omitted the lower layer blue arrow. The red arrows are the sum of the blue and green arrows. The green arrows are long since the upper and lower chalcogens of one layer have significantly different densities. This imbalance in the upper layer is almost entirely compensated by the imbalance of the lower layer where the arrow points upwards. However, the compensation is only partial because of the structural asymmetry: the lower layer interface chalcogen faces a TM in the z direction, while the upper layer faces a hollow site along $-z$. This interface effect leads to a somewhat longer green arrow in the top layer. The same interface effect explains the asymmetry in the upper TM shown as a blue arrow: the upper TM faces a chalcogen along $-z$. The lower TM faces a hollow site and is hence more symmetric.

The red arrow is therefore the result of a competition between the asymmetry of chalcogens and the TM atoms. The main difference between the Mo and the W compounds is that the asymmetry of the upper layer TM atom is less in the W

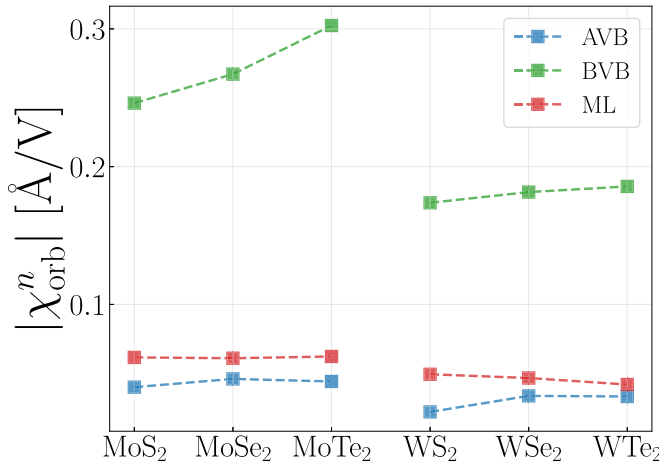


FIG. 6. Orbital polarizability χ_{orb}^n for the VB maximum of various TMD MLs, as well as the AVB and BVB states of the TMD homo-BLs.

compounds. We suggest that it can be rationalized by the lanthanide contraction, which leads to orbitals with similar extent in Mo and W, despite the large difference in the number of electrons. A more tight electron distribution in W may be less deformable, explaining the difference. Finally, the negative value of $-E_0^{\text{AVB}}$ in WS₂ corresponds to the situation where the chalcogen asymmetry wins over the TM asymmetry, while the situation is opposite for the other materials.

Figure S5 in the Supplemental Material [53] shows analogous trends for the BVB; however, the BVB, with in-phase character at the interface lobes [see Figs. 1(e) and 1(f)], allows more efficient charge redistribution and therefore exhibits a stronger field response than the AVB, where out-of-phase lobes result in enhanced rigidity for the charge redistribution.

E. Orbital polarizability

Since the dependence of the orbital polarization imbalance ξ^n on the external field is nearly linear [see Fig. 4(c)], we can define a meaningful derivative

$$\chi_{\text{orb}}^n = \frac{d\xi^n}{dE_{\text{ext}}}. \quad (4)$$

This quantity describes how the charge asymmetry, encoded in ξ^n , is affected by an external field. Conceptually, it is analogous to a polarizability, and we tentatively refer to χ_{orb}^n as orbital polarizability. Figure 6 displays χ_{orb}^n for various materials revealing that its magnitude is smallest in the AVB, intermediate at the VB maximum of the ML, and largest in the BVB, matching the hierarchy of λ_R^n , shown in Fig. 3(a). Interestingly, W-based systems (right) show reduced χ_{orb}^n , explaining the behavior of λ_R^n when replacing Mo with W: whereas heavier metal (W) has larger atomic SOC, the reduced polarizability limits the overall splitting.

We thus propose ξ^n and χ_{orb}^n as efficient, generalizable descriptors for Rashba spin splitting, readily applicable to more complex stacks and heterostructures of two-dimensional materials.

F. Microscopic model

The behaviors of the orbital polarization imbalance and orbital polarizability underscore the central role of orbital asymmetry—particularly involving chalcogen p_z orbitals—in determining both the magnitude and the sign of Rashba splitting. To further deepen this understanding, we develop a microscopic model that elucidates the underlying mechanisms at the orbital level. Specifically, we incorporate SOC perturbatively within a tight-binding framework and compute the resulting spin splitting. This splitting naturally incorporates the asymmetry described by ξ^n , thus providing a direct qualitative explanation for the DFT trends.

We start from the description of the ML. Near the Γ point, the top VB of the ML is primarily composed of orbitals with $m_l = 0$, namely, the $|d_{z^2}\rangle$, $|p_{z_1}\rangle$, and $|p_{z_2}\rangle$ orbitals from the metal, lower and upper chalcogens, respectively [46,63]. The sign of $|p_{z_2}\rangle$ is opposite to the sign of $|p_{z_1}\rangle$ according to the DFT results and a mirror symmetric system, so that we write an “unperturbed” state as

$$|\psi_{\text{ML}}^{(0)}\rangle \simeq \frac{1}{N} \left[\frac{1-\epsilon}{\sqrt{2}} |p_{z_1}\rangle - \frac{1+\epsilon}{\sqrt{2}} |p_{z_2}\rangle + b |d_{z^2}\rangle \right] \otimes |\sigma\rangle, \quad (5)$$

where b is the relative d_{z^2} contribution, $|\sigma\rangle$ denotes the spin degree of freedom, and $N = \sqrt{1+b^2} + O(\epsilon^2)$ is a normalization constant. The small quantity $|\epsilon| \ll 1$ captures the breaking of the mirror symmetry m_z . Note that for $\epsilon = 0$ the state is even under m_z . Our ϵ is conceptually very similar to the γ parameter defined in [59] that characterizes the structural asymmetry at surfaces. ϵ describes an asymmetry at the ML level that may be induced by an internal or external electric field. Defined in real space, ϵ has similar field dependence as the orbital polarization introduced above for Bloch states, ξ_{ML}^n . Since ξ_{ML}^n is linear in momentum, this suggests

$$|\xi_{\text{ML}}^n| = c_{\text{ML}}^n k \epsilon,$$

where c_{ML}^n is an irrelevant constant for this discussion. We assume in the following: (i) the long-wavelength approach, $k \ll a^{-1}$, where a is the lattice constant, (ii) the atomic SOC is small compared with other relevant energy scales (hopping, orbital energies, crystal field corrections, energy difference between orbitals or gap), and (iii) small orbital asymmetry due to an electric field, $|\epsilon| \ll 1$, as stated above.

Rashba splitting arises at lowest order by hybridization of the $m_l = 0$ states (p_z, d_{z^2}) with $m_l = \pm 1$ orbitals (p_x, p_y, d_{xz} , and d_{yz}), mediated by momentum-dependent hopping. Atomic SOC couples these admixtures back to the original valence states, producing a spin-dependent correction. Without losing generality, we consider momentum along k_x near Γ , $k_x \ll a^{-1}$, i.e., the mixing is limited to p_x and d_{xz} orbitals to lowest order. Two leading second-order processes contribute to spin splitting:

$$\begin{aligned} \text{(i)} \quad & |p_{z_i}\rangle \xrightarrow{\text{NN hopping} \propto k_x} |d_{xz}\rangle \xrightarrow{\text{SOC}} |d_{z^2}\rangle, \\ \text{(ii)} \quad & |d_{z^2}\rangle \xrightarrow{\text{NN hopping} \propto k_x} |p_{z_i}\rangle \xrightarrow{\text{SOC}} |p_{z_i}\rangle. \end{aligned}$$

We focus first on the nearest neighbor (NN) hopping within the two-center approach, introducing mixing with $m_l = \pm 1$ orbitals in reciprocal space (see Eq. (3) in Supplemental Material [53]). The first-order corrections to the $|p\rangle$ and $|d\rangle$

components of $|\psi_{\text{ML}}^{(0)}\rangle$ possess the k -linearity of Rashba splitting:

$$\begin{aligned} \text{(i)} \quad & |\psi_d^{(1)}\rangle = i\epsilon(k_x a) \frac{t_{z,xz}}{\epsilon_{pd}} |d_{xz}\rangle \otimes |\sigma\rangle, \\ \text{(ii)} \quad & |\psi_p^{(1)}\rangle = -i\epsilon(k_x a) b \frac{t_{x,z^2}}{\epsilon_{pd}} (|p_{x_1}\rangle + |p_{x_2}\rangle) \otimes |\sigma\rangle, \end{aligned}$$

where $t_{z,xz} = 3[\sqrt{3}n_z^2 V_{pd\sigma} + (1 - 2n_z^2) V_{pd\pi}]$ and $t_{x,z^2} = 3[\sqrt{3}n_z^2 V_{pd\pi} + (1 - 2n_z^2) V_{pd\sigma}]$ are effective hopping amplitudes determined from Slater-Koster integrals $V_{pd\sigma}, V_{pd\pi}$ [64], n_z is the directive cosine along z , and ϵ_{pd} the energy denominators of the intermediate virtual states.

SOC then connects the electron spin and orbital degrees of freedom, $\hat{V}_{\text{SOC}} = \lambda_l \hat{\mathbf{L}} \cdot \hat{\sigma}$, where $\hat{\sigma}$ is the Pauli matrices vector, $\hat{\mathbf{L}}$ is the angular momentum operator given in the basis of direct atomic orbitals, and λ_l is the angular momentum-resolved atomic SOC strength, with $l = \{s, p, d, \dots\}$. This yields a spin-dependent correction to the energy, $\epsilon_a^{(2)} = \langle \psi_{\text{ML}}^{(0)} | \hat{V}_{\text{SOC}} | \psi_a^{(1)} \rangle$:

$$\begin{aligned} \text{(i)} \quad & \epsilon_d^{(2)} = \frac{2\sqrt{3}b\epsilon}{N^2} k_x a \frac{t_{z,xz}}{\epsilon_{pd}} \lambda_d S_y, \\ \text{(ii)} \quad & \epsilon_p^{(2)} = -\frac{2b\epsilon}{N^2} k_x a \frac{t_{x,z^2}}{\epsilon_{pd}} \lambda_p S_y, \end{aligned}$$

where $S_y = \langle \sigma | \hat{\sigma}_y | \sigma \rangle$ is the spin component perpendicular to momentum, typical of a Rashba-type interaction. Adding both contributions (details of analytical calculations are given in the Supplemental Material, Eqs. (2)–(28) [53]), we obtain a linear-in- k and linear-in-field splitting (recall that ϵ scales linearly with E_{ext} , $\epsilon = \kappa E_{\text{ext}}$ with κ being material and state dependent),

$$\Delta E = \frac{2bk_x a}{N^2} \frac{(\sqrt{3}t_{z,xz}\lambda_d - t_{x,z^2}\lambda_p)}{\epsilon_{pd}} \epsilon = \lambda_R^{\text{VB}} E_{\text{ext}} k_x, \quad (6)$$

where we have used (2), and identified $\lambda_R^{\text{VB}} = 2bak(\sqrt{3}t_{z,xz}\lambda_d - t_{x,z^2}\lambda_p)/N^2\epsilon_{pd}$. Importantly, the Rashba splitting originates from two competing microscopic channels associated with chalcogen- p and metal- d SOC, which contribute with opposite sign. This can be generalized to a BL structure in the R_X^M/R_M^X stacking. By inspection of the symmetry and orbital composition of the obtained DFT results [see Figs. 1(d) and 1(e)], we have for the AVB at $E_{\text{ext}} = 0$,

$$\begin{aligned} \psi_A^{(0)} = \frac{1}{N_A} & \left[\frac{1 - \epsilon_{L_1}^A}{\sqrt{2}} |p_{z_1}\rangle - \frac{1 + \epsilon_{L_1}^A}{\sqrt{2}} |p_{z_2}\rangle + b_A |d_{z_1}^2\rangle \right. \\ & \left. - \frac{1 + \epsilon_{L_2}^A}{\sqrt{2}} |p_{z_3}\rangle + \frac{1 - \epsilon_{L_2}^A}{\sqrt{2}} |p_{z_4}\rangle - b_A |d_{z_2}^2\rangle \right], \end{aligned}$$

where $|p_{z_i}\rangle$ with $i = 1, 2, 3, 4$ are the $|p_z\rangle$ orbitals in ascending order along the stacking direction, $|d_{z_i}^2\rangle$ are the metal contributions of the bottom ($i = 1$) and top layers ($i = 2$), respectively, and $\epsilon_{L_i}^A \propto |\xi_{L_i}^A|/k_x$ describe the break of symmetry of the AVB at the ML level. Note that the signs of $\epsilon_{L_i}^A$ are adapted to the DFT results of Figs. 1(d) and 1(e). Treating again both layers

separately and repeating the calculations above, we obtain

$$\begin{aligned} \Delta E^{\text{AVB}} &= \frac{2b_A k_x a}{N_A^2} \frac{(\sqrt{3}t_{z,xz}\lambda_d - t_{x,z^2}\lambda_p)}{\epsilon_{pd}} (\epsilon_{L_1}^A - \epsilon_{L_2}^A) \\ &= \lambda_R^{\text{AVB}} (E_{\text{ext}} + E_0) k_x, \end{aligned} \quad (7)$$

where the individual Rashba corrections from each ML cancel partially, which aligns with the concept of orbital polarization imbalance [recall that each ML has a charge asymmetry of different sign, that is, $\xi^A \propto \epsilon_{L_2}^A - \epsilon_{L_1}^A = \kappa^A (E_{\text{ext}} + E_0)$]. Moreover, the mirror symmetry is broken at $E_{\text{ext}} = 0$, that is, $\epsilon_{L_2}^A - \epsilon_{L_1}^A$ is in general finite at zero field, yielding a Rashba splitting.

For the BVB, we have

$$\begin{aligned} \psi_B^{(0)} = \frac{1}{N_B} & \left[\frac{1 + \epsilon_{L_1}^B}{\sqrt{2}} |p_{z_1}\rangle - \frac{1 - \epsilon_{L_1}^B}{\sqrt{2}} |p_{z_2}\rangle + b_B |d_{z_1}^2\rangle \right. \\ & \left. + \frac{1 - \epsilon_{L_2}^B}{\sqrt{2}} |p_{z_3}\rangle - \frac{1 + \epsilon_{L_2}^B}{\sqrt{2}} |p_{z_4}\rangle + b_B |d_{z_2}^2\rangle \right], \end{aligned}$$

which differs from the AVB mainly by the relative signs between the layer contributions, reflecting the even symmetry of the bonding state. Repeating the perturbative analysis yields a Rashba splitting of the same form as in the AVB case, but with opposite sign owing to the different bonding symmetry and associated orbital polarization pattern:

$$\begin{aligned} \Delta E^{\text{BVB}} &= -\frac{2b_B k_x a}{N_B^2} \frac{(\sqrt{3}t_{z,xz}\lambda_d - t_{x,z^2}\lambda_p)}{\epsilon_{pd}} (\epsilon_{L_1}^B - \epsilon_{L_2}^B) \\ &= \lambda_R^{\text{BVB}} (E_{\text{ext}} + E_0) k_x. \end{aligned} \quad (8)$$

Comparing Eqs. (7) and (8), we find that λ_R^{BVB} has opposite sign to λ_R^{AVB} , consistent with the *ab initio* calculations (see Fig. 2 and Fig. S4 in the Supplemental Material [53]).

G. Role of mediator orbitals

To evaluate the role of orbitals involved in mechanisms (i) and (ii), Fig. 7 presents the Rashba spin splitting (shown in blue, left y axis) alongside the percentage contributions of $d_{xz/yz}$ and $p_{x/y}$ orbitals (depicted in red, right y axis) in the AVB (a), (b) and BVB (c), (d) as functions of in-plane biaxial strain. These values are obtained from Wannierization of the DFT Bloch functions in the vicinity of the Γ point, at $k = K/16$. We observe that both the spin splitting and the orbital weights of the in-plane orbitals ($d_{xz/yz}$ and $p_{x/y}$), show a similar strain dependence. This similarity points to the crucial role of these mediator orbitals, in agreement with our microscopic model.

A more detailed look at Fig. 7 shows that for the in-plane $d_{xz/yz}$ contribution the splitting and the weight follow each other more closely than for the $p_{x,y}$. Another indication that let us conclude on the importance of the d vs p orbitals is the difference in the weight of the orbitals in the AVB and BVB states. For the d states [Figs. 7(a) and 7(c)] the orbital weight changes by an order of magnitude between BVB and AVB. This is in line with the value of λ_R , that also differs by roughly an order of magnitude between both states [red and blue lines in Fig. 3(a)]. The weight of the $p_{x/y}$ states, however, is lower for the BVB in contradiction to the larger λ_R value.

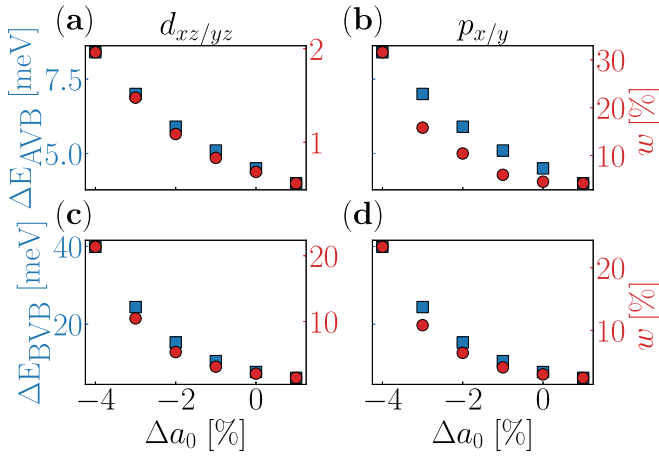


FIG. 7. Rashba splitting and orbital weight as a function of in-plane biaxial strain for BL MoSe₂ at $k = K/16$. The upper (lower) row shows the AVB (BVB) results, resolved for $d_{xz/yz}$ orbitals in the first column and $p_{x/y}$ orbitals in the second column.

We tentatively conclude from this observation, that from both mediator orbitals, the $d_{xz/yz}$ have a larger contribution, that is, $\sqrt{3}t_{z,xz}\lambda_d > t_{x,z^2}\lambda_p$ [see Eqs. (6)–(8)].

IV. CONCLUSION

In summary, we have carried out a systematic first-principles and microscopic analysis of Rashba spin splitting in monolayer and homobilayer (R_X^M stacking) MX_2 ($M = \text{Mo}, \text{W}; X = \text{S}, \text{Se}, \text{Te}$) TMDs, focusing on the top valence bands near the Γ point. For the monolayer and the bilayer systems, we show that the stronger atomic SOC of W compounds is largely compensated by a reduced orbital polarization, yielding Rashba coefficients surprisingly comparable to those of their Mo counterpart. Furthermore, we observe a pronounced increase in the magnitude of the Rashba coefficient upon progressing from S to Se to Te. We attribute this trend to the higher polarizability of the heavier chalcogens, which facilitates stronger symmetry breaking and, consequently, enhanced Rashba responses. We also find that the Rashba response is strongly band dependent in the bilayer system. In particular, the AVB (VBM) shows a substantially weaker

Rashba coefficient than the next valence band BVB. The monolayer coefficients lie in between.

To make these numerical results more intuitive, we use a density-based quantity and introduce the band (n)-resolved polarization imbalance ξ^n and the orbital polarizability χ_{orb}^n . We can show that they quantitatively predict both the Rashba coefficient and the critical field $-E_0^n$ at which the splitting vanishes. Especially E_0^n can be understood in further detail by an analysis of the real-space charge density. We show that the final overall asymmetry, giving rise to Rashba physics, is the result of a competition not only between layers, but also between a TM asymmetry and an asymmetry between the chalcogens. Both effects can compensate each other.

A central outcome of this work is a microscopic model based on perturbative orbital mixing and atomic SOC that faithfully reproduces the linearity in k and in E_{ext} . It identifies two competing Rashba pathways mediated by $p \leftrightarrow d$ hybridization, each of which acquires distinct layer-resolved contributions. The resulting Rashba coefficient λ_R^n in BLs emerges from an intricate competition both between the p and d channels and between their layer-resolved contributions, where the asymmetry plays a central role. The model and Wannier analysis confirms that $d_{xz/yz}$ orbitals dominate the leading Rashba process.

In short, our results establish internal orbital symmetry as the key descriptor governing Rashba coupling in TMDs. The concepts of orbital polarization imbalance and orbital polarizability provide predictive tools for understanding and engineering SOC effects through stacking, composition, and gating, and are extendable to more complex van der Waals systems, such as Janus structures or heterobilayers.

ACKNOWLEDGMENTS

The authors would like to thank Carl Emil Mørch Nielsen for fruitful discussions. The project is supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) within the Priority Program SPP2244 2DMP and by the Cluster of Excellence “Advanced Imaging of Matter” of the DFG–EXC 2056–project ID 390715994. Calculations were carried out on Hummel funded by the DFG–498394658.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

- [1] S. Picozzi, Ferroelectric Rashba semiconductors as a novel class of multifunctional materials, *Front. Phys.* **2**, 10 (2014).
- [2] X. Wang, K. Yasuda, Y. Zhang, S. Liu, K. Watanabe, T. Taniguchi, J. Hone, L. Fu, and P. Jarillo-Herrero, Interfacial ferroelectricity in rhombohedral-stacked bilayer transition metal dichalcogenides, *Nat. Nanotechnol.* **17**, 367 (2022).
- [3] S. Leiva-Montecinos, L. Vojáček, J. Li, M. Chshiev, L. Vila, I. Mertig, and A. Johansson, Current-induced spin and orbital polarization in the ferroelectric Rashba semiconductor GeTe, *Phys. Rev. Res.* **7**, 043329 (2025).

- [4] E. I. Rashba and V. I. Sheka, Symmetry of energy bands in crystals of Wurtzite type II. Symmetry of bands with spin-orbit interaction included, *New. J. Phys.* **17**, 050202 (2015); Originally published in *Fiz. Tverd. Tela: Collected Papers* **2**, 62 (1959).
- [5] K. Yasuda, X. Wang, K. Watanabe, T. Taniguchi, and P. Jarillo-Herrero, Stacking-engineered ferroelectricity in bilayer boron nitride, *Science* **372**, 1458 (2021).
- [6] L. Molino, L. Aggarwal, V. Enaldiev, R. Plumadore, V. I. Fal'ko, and A. Luican-Mayer, Ferroelectric switching at

- symmetry-broken interfaces by local control of dislocations networks, *Adv. Mater.* **35**, 2207816 (2023).
- [7] A. Weston *et al.*, Interfacial ferroelectricity in marginally twisted 2D semiconductors, *Nat. Nanotechnol.* **17**, 390 (2022).
- [8] J. Ji, G. Yu, C. Xu, and H. J. Xiang, General theory for bilayer stacking ferroelectricity, *Phys. Rev. Lett.* **130**, 146801 (2023).
- [9] T. S. Ghiasi, A. A. Kaverzin, P. J. Blah, and B. J. van Wees, Charge-to-spin conversion by the Rashba–Edelstein effect in two-dimensional van der Waals heterostructures up to room temperature, *Nano Lett.* **19**, 5959 (2019).
- [10] R. Kavkhani, B. A. Hanedar, K. Anar, A. I. Şahin, A. Johansson, and M. C. Onbasli, Ultrahigh mobility and Rashba spin splitting in Sb-substituted bismuth telluride and bismuth selenide, *Nanoscale* **18**, 3352 (2026).
- [11] G. Bihlmayer, P. Noël, D. V. Vyalikh, E. V. Chulkov, and A. Manchon, Rashba-like physics in condensed matter, *Nat. Rev. Phys.* **4**, 642 (2022).
- [12] M. J. Szary, Rashba effect: a chemical physicist’s approach, *Phys. Chem. Chem. Phys.* **25**, 30099 (2023).
- [13] A. Bordoloi, A. C. Garcia-Castro, Z. Romestan, A. H. Romero, and S. Singh, Promises and technological prospects of two-dimensional Rashba materials, *J. Appl. Phys.* **135**, 220901 (2024).
- [14] C. E. M. Nielsen, F. Fischer, and G. Bester, Beyond the K-valley: Exploring unique trion states in indirect band gap monolayer WSe₂, *npj 2D Mater. Appl.* **9**, 11 (2025).
- [15] C. E. M. Nielsen, F. Fischer, M. Prada, and G. Bester, From dark to bright: First-principles prediction of ground state excitons and trions in Janus transition metal dichalcogenide bilayers, *2D Mater.* **12**, 045015 (2025).
- [16] S. Kovalchuk, K. Greben, A. M. Kumar, S. Pessel, J. Soyka, Q. Cao, K. Watanabe, T. Taniguchi, D. Christiansen, M. Selig, A. Knorr, S. Eigler, and K. I. Bolotin, Revealing hidden interlayer excitons in 2D bilayers via hybrid molecular gating, *Nat. Commun.* **16**, 9893 (2025).
- [17] J. Huang, Z. Xiong, J. He, X. Wu, K. Watanabe, T. Taniguchi, S. Lai, T. Zhang, Z. V. Han, and S. Zhao, Electrically tunable Γ –Q interlayer excitons in twisted MoSe₂ bilayers, *J. Mater. Sci. Technol.* **207**, 70 (2025).
- [18] Y.-H. Chen, P.-Y. Lo, K. W. Boschen, C.-E. Hsu, Y.-N. Hsu, L. N. Holtzman, G.-H. Peng, C.-J. Huang, M. Holbrook, W.-H. Wang, K. Barmak, J. Hone, P. Hawrylak, H.-C. Hsueh, J. A. Davis, S.-J. Cheng, M. S. Fuhrer, and S.-Y. Chen, Efficient light upconversion via resonant exciton-exciton annihilation of dark excitons in few-layer transition metal dichalcogenides, *Nat. Commun.* **16**, 2935 (2025).
- [19] J. T. Gish, D. Lebedev, T. W. Song, V. K. Sangwan, and M. C. Hersam, Van der Waals opto-spintronics, *Nat. Electron.* **7**, 336 (2024).
- [20] J. D. Cao, G. Xu, B. Scharf, K. Denisov, and I. Žutić, Emergent bright excitons with Rashba spin-orbit coupling in atomic monolayers, *Phys. Rev. B* **109**, 085407 (2024).
- [21] H. Mittenzwey, A. M. Kumar, R. Dhirga, K. Watanabe, T. Taniguchi, C. Gahl, K. I. Bolotin, M. Selig, and A. Knorr, Ultrafast optical control of Rashba interactions in a TMDC heterostructure, *Phys. Rev. Lett.* **134**, 026901 (2025).
- [22] C. Cheng, J.-T. Sun, X.-R. Chen, H.-X. Fu, and S. Meng, Non-linear Rashba spin splitting in transition metal dichalcogenide monolayers, *Nanoscale* **8**, 17854 (2016).
- [23] Q.-F. Yao, J. Cai, W.-Y. Tong, S.-J. Gong, J.-Q. Wang, X. Wan, C.-G. Duan, and J. H. Chu, Manipulation of the large Rashba spin splitting in polar two-dimensional transition-metal dichalcogenides, *Phys. Rev. B* **95**, 165401 (2017).
- [24] L. Xiang, Y. Ke, and Q. Zhang, Tunable giant Rashba-type spin splitting in PtSe₂/MoSe₂ heterostructure, *Appl. Phys. Lett.* **115**, 1203501 (2019).
- [25] S. Gupta and B. I. Yakobson, What dictates Rashba splitting in 2D van der Waals heterobilayers, *J. Am. Chem. Soc.* **143**, 3503 (2021).
- [26] H. Mehdipour and P. Kratzer, First-principles calculations of MoSeTe/WSeTe bilayers: Stability, phonons, electronic band offsets, and Rashba splitting, *Phys. Rev. B* **109**, 085425 (2024).
- [27] M. N. Gjerding, A. Taghizadeh, A. Rasmussen, S. Ali, F. Bertoldo, T. Deilmann, N. R. Knøsgaard, M. Kruse, A. H. Larsen, S. Manti, T. G. Pedersen, U. Petralanda, T. Skovhus, M. K. Svendsen, J. J. Mortensen, T. Olsen, and K. S. Thygesen, Recent progress of the computational 2D materials database (C2DB), *2D Mater.* **8**, 044002 (2021).
- [28] Z. Lin, C. Si, S. Duan, C. Wang, and W. Duan, Rashba splitting in bilayer transition metal dichalcogenides controlled by electronic ferroelectricity, *Phys. Rev. B* **100**, 155408 (2019).
- [29] Q. Zhang and U. Schwingenschlögl, Rashba effect and enriched spin-valley coupling in GaX/MX₂ ($M = \text{Mo, W}$; $X = \text{S, Se, Te}$) heterostructures, *Phys. Rev. B* **97**, 155415 (2018).
- [30] A. Rezavand and N. Ghobadi, Stacking-dependent Rashba spin-splitting in Janus bilayer transition metal dichalcogenides: The role of in-plane strain and out-of-plane electric field, *Physica E* **132**, 114768 (2021).
- [31] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [32] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu, *J. Chem. Phys.* **132**, 154104 (2010).
- [33] M. van Setten, M. Giantomassi, E. Bousquet, M. Verstraete, D. Hamann, X. Gonze, and G.-M. Rignanese, The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table, *Comput. Phys. Commun.* **226**, 39 (2018).
- [34] P. Giannozzi *et al.*, QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [35] P. Giannozzi *et al.*, Advanced capabilities for materials modelling with QUANTUM ESPRESSO, *J. Phys.: Condens. Matter* **29**, 465901 (2017).
- [36] W. S. Yun, S. W. Han, S. C. Hong, I. G. Kim, and J. D. Lee, Thickness and strain effects on electronic structures of transition metal dichalcogenides: 2H-MX₂ semiconductors ($M = \text{Mo, W}$; $X = \text{S, Se, Te}$), *Phys. Rev. B* **85**, 033305 (2012).
- [37] J. Huang, L. Yang, D. Liu, J. Chen, Q. Fu, Y. Xiong, F. Lin, and B. Xiang, Large-area synthesis of monolayer WSe₂ on a SiO₂/Si substrate and its device applications, *Nanoscale* **7**, 4193 (2015).
- [38] J. Chen, X. Zhao, S. J. R. Tan, H. Xu, B. Wu, B. Liu, D. Fu, W. Fu, D. Geng, Y. Liu, W. Liu, W. Tang, L. Li, W. Zhou, T. C. Sum, and K. P. Loh, Chemical vapor deposition of large-size monolayer MoSe₂ crystals on molten glass, *J. Am. Chem. Soc.* **139**, 1073 (2017).

- [39] J. Gusakova, X. Wang, L. L. Shiao, A. Krivosheeva, V. Shaposhnikov, V. Borisenko, V. Gusakov, and B. K. Tay, Electronic properties of bulk and monolayer TMDs: Theoretical study within DFT framework (GVJ-2e method), *Phys. Status Solid* **214**, 1700218 (2017).
- [40] H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* **13**, 5188 (1976).
- [41] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, wannier90: A tool for obtaining maximally-localised Wannier functions, *Comput. Phys. Commun.* **178**, 685 (2008).
- [42] K. Kořmider, J. W. González, and J. Fernández-Rossier, Large spin splitting in the conduction band of transition metal dichalcogenide monolayers, *Phys. Rev. B* **88**, 245436 (2013).
- [43] W. Feng, Y. Yao, W. Zhu, J. Zhou, W. Yao, and D. Xiao, Intrinsic spin Hall effect in monolayers of group-VI dichalcogenides: A first-principles study, *Phys. Rev. B* **86**, 165108 (2012).
- [44] N. Marzari and D. Vanderbilt, Maximally localized generalized Wannier functions for composite energy bands, *Phys. Rev. B* **56**, 12847 (1997).
- [45] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Maximally localized Wannier functions: Theory and applications, *Rev. Mod. Phys.* **84**, 1419 (2012).
- [46] E. Cappelluti, R. Roldán, J. A. Silva-Guillén, P. Ordejón, and F. Guinea, Tight-binding model and direct-gap/indirect-gap transition in single-layer and multilayer MoS₂, *Phys. Rev. B* **88**, 075409 (2013).
- [47] D. Huang, J. Choi, C.-K. Shih, and X. Li, Excitons in semiconductor moiré superlattices, *Nat. Nanotechnol.* **17**, 227 (2022).
- [48] J. Ji, F. Lou, R. Yu, J. S. Feng, and H. J. Xiang, Symmetry-protected full-space persistent spin texture in two-dimensional materials, *Phys. Rev. B* **105**, L041404 (2022).
- [49] H. Yuan, M. S. Bahrany, K. Morimoto, S. Wu, K. Nomura, B.-J. Yang, H. Shimotani, R. Suzuki, M. Toh, C. Kloc, X. Xu, R. Arita, N. Nagaosa, and Y. Iwasa, Zeeman-type spin splitting controlled by an electric field, *Nat. Phys.* **9**, 563 (2013).
- [50] X. Wang, W. Yang, W. Yang, Y. Cao, X. Lin, G. Wei, H. Lu, P. Tang, and W. Zhao, Spin manipulation by giant valley-Zeeman spin-orbit field in atom-thick WSe₂, *Appl. Phys. Rev.* **9**, 031402 (2022).
- [51] T. Li and G. Galli, Electronic properties of MoS₂ nanoparticles, *J. Phys. Chem. C* **111**, 16192 (2007).
- [52] R. Winkler, *Spin-Orbit Coupling Effects in Two-Dimensional Electron and Hole Systems* (Springer, Berlin, Heidelberg, 2003).
- [53] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/4hpr-dmmf> for Tables of Rashba parameters in different structures and of structural symmetry arguments, figures of orbital polarization imbalance for different materials as a function of k and E , and charge density of pertinent eigenvalues, and analytical, perturbative derivation of spin splitting corrections.
- [54] M. Prada, G. Klimeck, and R. Joynt, Spin-orbit splittings in Si/SiGe quantum wells: From ideal Si membranes to realistic heterostructures, *New J. Phys.* **13**, 013009 (2011).
- [55] Z. Zhong, A. Tóth, and K. Held, Theory of spin-orbit coupling at LaAlO₃/SrTiO₃ interfaces and SrTiO₃ surfaces, *Phys. Rev. B* **87**, 161102(R) (2013).
- [56] B. Das, D. C. Miller, S. Datta, R. Reifenberger, W. P. Hong, P. K. Bhattacharya, J. Singh, and M. Jaffe, Evidence for spin splitting in In_xGa_{1-x}As/In_{0.52}Al_{0.48}As heterostructures as $B \rightarrow 0$, *Phys. Rev. B* **39**, 1411 (1989).
- [57] J. Nitta, T. Akazaki, H. Takayanagi, and T. Enoki, Gate control of spin-orbit interaction in an inverted In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As heterostructure, *Phys. Rev. Lett.* **78**, 1335 (1997).
- [58] K. S. Cho, T.-Y. Huang, H.-S. Wang, M.-G. Lin, T.-M. Chen, C.-T. Liang, Y. F. Chen, and I. Lo, Zero-field spin splitting in modulation-doped Al_xGa_{1-x}N/GaN two-dimensional electron systems, *Appl. Phys. Lett.* **86**, 222102 (2005).
- [59] L. Petersen and P. Hedegård, A simple tight-binding model of spin-orbit splitting of sp -derived surface states, *Surf. Sci.* **459**, 49 (2000).
- [60] G. Bihlmayer, Y. Koroteev, P. Echenique, E. Chulkov, and S. Blügel, The Rashba-effect at metallic surfaces, *Surf. Sci.* **600**, 3888 (2006).
- [61] M. Nagano, A. Kodama, T. Shishidou, and T. Oguchi, A first-principles study on the Rashba effect in surface systems, *J. Phys.: Condens. Matter* **21**, 064239 (2009).
- [62] T. Tian, D. Scullion, D. Hughes, L. H. Li, C.-J. Shih, J. Coleman, M. Chhowalla, and E. J. G. Santos, Electronic polarizability as the fundamental variable in the dielectric properties of two-dimensional materials, *Nano Lett.* **20**, 841 (2020).
- [63] R. Roldán, M. P. López-Sancho, F. Guinea, E. Cappelluti, J. A. Silva-Guillén, and P. Ordejón, Momentum dependence of spin-orbit interaction effects in single-layer and multilayer transition metal dichalcogenides, *2D Mater.* **1**, 034003 (2014).
- [64] J. C. Slater and G. F. Koster, Simplified LCAO method for the periodic potential problem, *Phys. Rev.* **94**, 1498 (1954).