

Supplementary Information

Effects of p - d mixings on magnetocrystalline anisotropy for D_{3d} -symmetric ferromagnetic semiconducting monolayers

Chenhai Shen,^{*} Xueping Li, Tianxing Wang, Guangtao Wang, and Congxin Xia^{*}

Figures

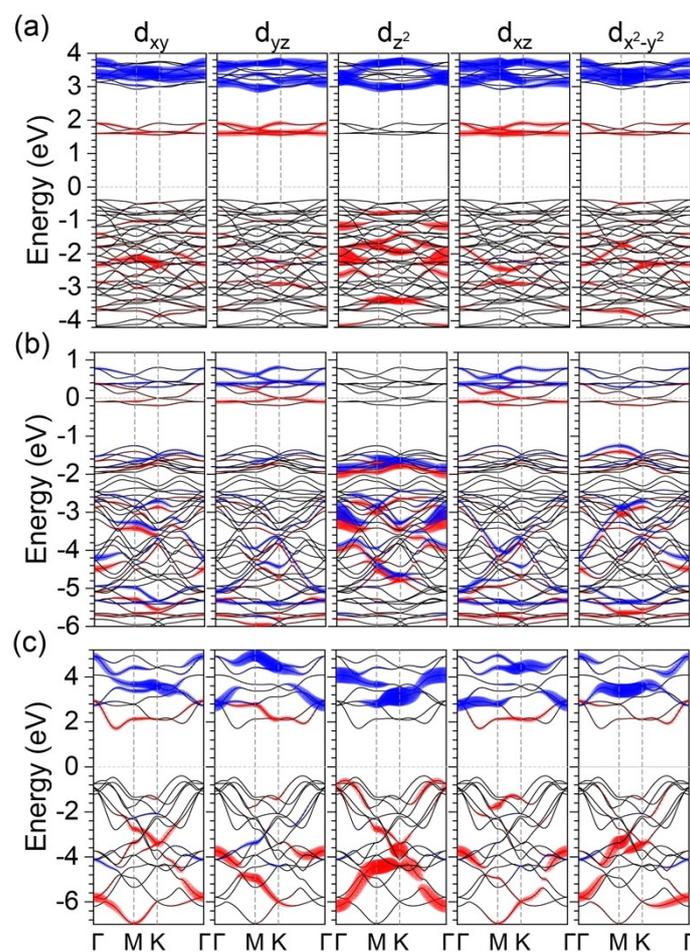


Fig. S1 Orbital-resolved electronic structures for d -electrons of transition metal atoms in the following ferromagnetic semiconducting monolayers: (a) CrBr₃, (b) PtBr₃ and (c) MnO₂ monolayers. Red (blue) color lines represent spin-up (-down) orbitals and their thickness represents the weight.

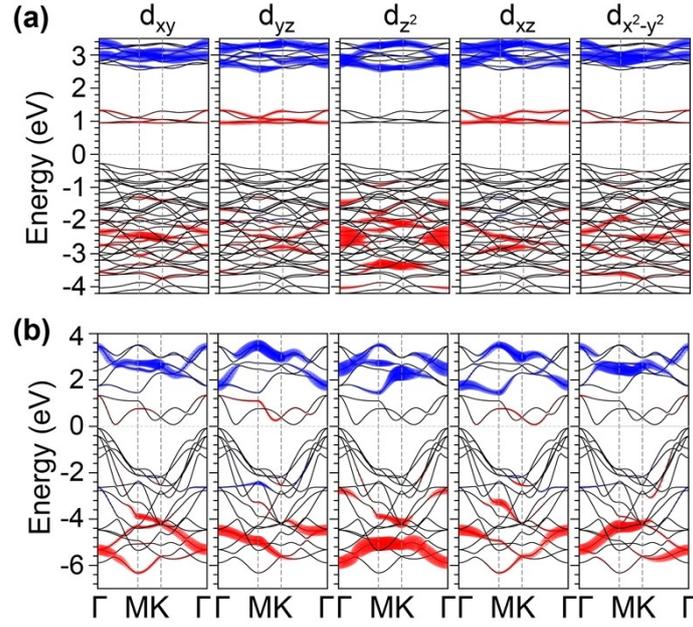


Fig. S2 Orbital-resolved electronic structures for d -electrons of transition metal atoms in the following ferromagnetic semiconducting monolayers: (a) CrI_3 and (b) MnS_2 monolayers. Red (blue) color lines represent spin-up (-down) orbitals and their thickness represents the weight.

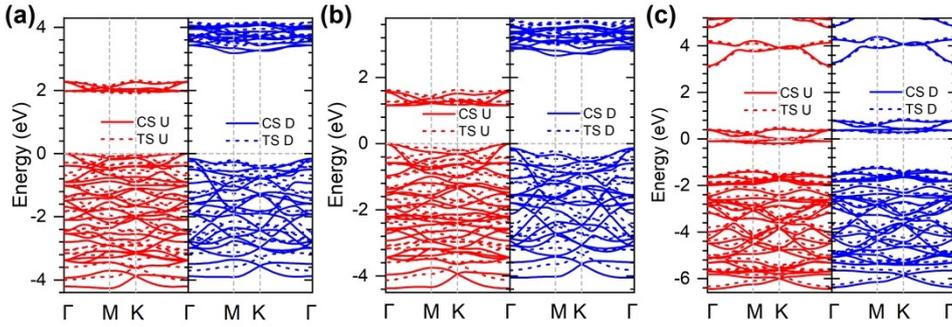


Fig. S3 Electronic structures of (a) CrBr_3 , (b) CrI_3 and (c) PtBr_3 monolayers under different strain. Solid (dotted) lines represent the electronic structure under compressive (tensile) strain and red (blue) colors denote the spin-up (-down) subbands.

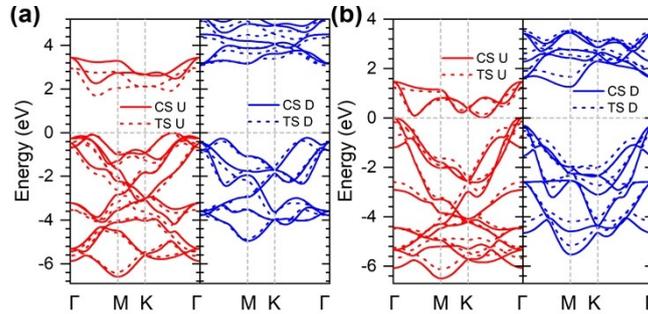


Fig. S4 Electronic structures of (a) MnO_2 and (b) MnS_2 monolayers under different strain. Solid (dotted) lines represent the electronic structure under compressive (tensile) strain and red (blue) colors denote the spin-up (-down) subbands.

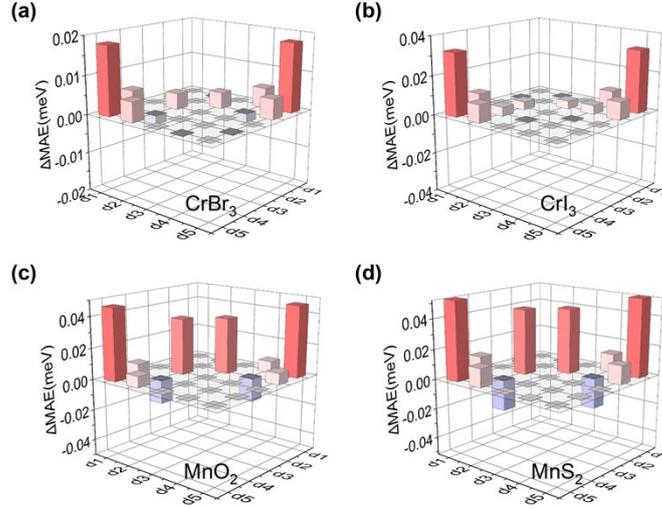


Fig. S5 Strain-induced changes in magnetocrystalline anisotropy energy (ΔMAE) for interorbital couplings between different d -orbitals of the transition metal in (a) CrBr_3 , (b) CrI_3 , (c) MnO_2 and (d) MnS_2 monolayers, which is obtained by another set U values: 3.0 eV for CrX_3 ($X = \text{Br}$ or I) and 1.2 eV for MnX_2 ($X = \text{O}$ or S).

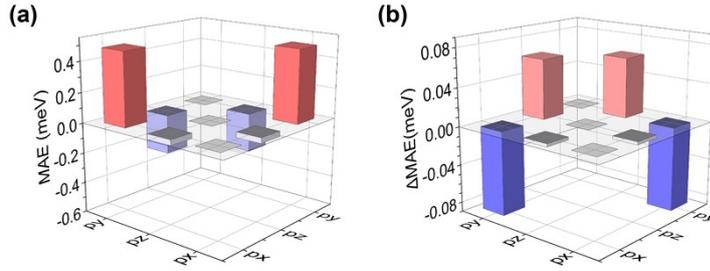


Fig. S6 (a) Magnetocrystalline anisotropy energy (MAE) and (b) strain-induced change in MAE (ΔMAE) for interorbital couplings between different I - p orbitals of CrI_3 .

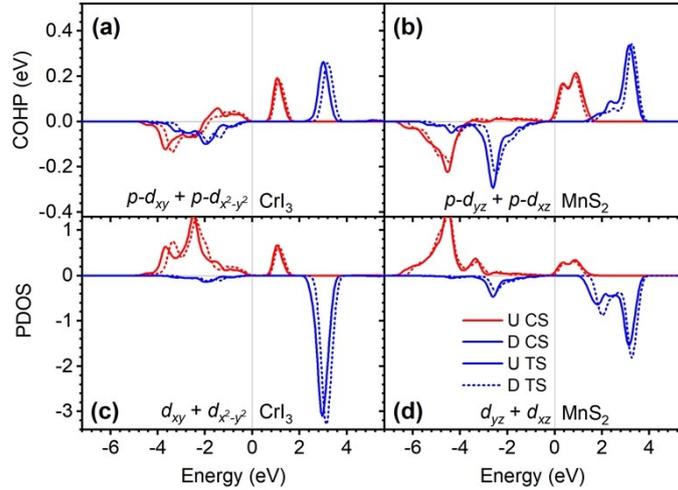


Fig. S7 Sum of the crystal orbital Hamilton populations (COHPs) of p - d_{xy} and p - $d_{x^2-y^2}$ mixings in (a) CrI_3 , the COHP sum of p - d_{yz} and p - d_{xz} for (b) MnS_2 monolayer, the sum of partials density of states (PDOSs) of d_{xy} and $d_{x^2-y^2}$ orbitals of (c) CrI_3 , and the PDOS sum of d_{yz} and d_{xz} of (d) MnS_2 monolayer, where the COHPs (DOSs) have the same scale. The lines and colors have the same meaning as those in Fig. 4 of the main text.

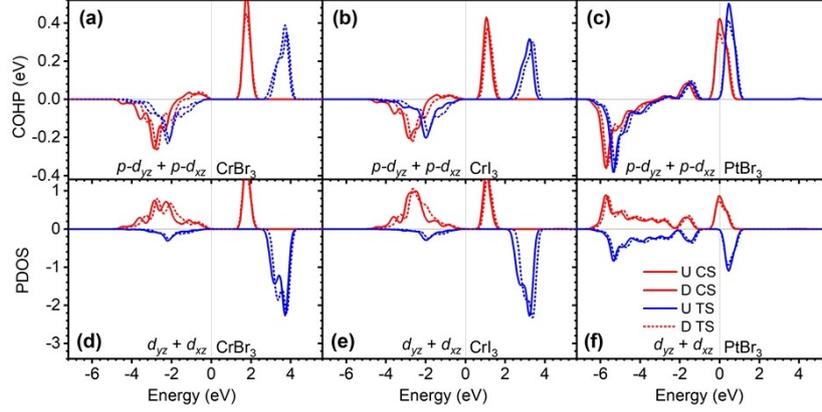


Fig. S8 Sum of the crystal orbital Hamilton populations (COHPs) of $p-d_{yz}$ and $p-d_{xz}$ mixings for (a) CrBr₃, (b) CrI₃ and (c) PtBr₃ monolayers, and the sum of the partial density of states (PDOSs) of d_{yz} and d_{xz} orbitals for (d) CrBr₃, (e) CrI₃ and (f) PtBr₃ monolayers. The COHPs (PDOSs) have the same scale. The lines and colors have the same meaning as those in Fig. 4 of the main text.

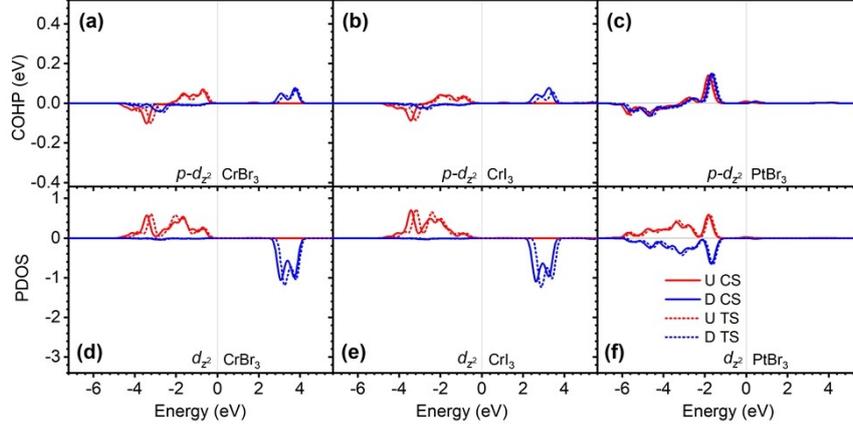


Fig. S9 Crystal orbital Hamilton populations (COHPs) of $p-d_{z^2}$ mixing for (a) CrBr₃, (b) CrI₃ and (c) PtBr₃ monolayers, and partial density of states (PDOSs) of d_{z^2} orbital for (d) CrBr₃, (e) CrI₃ and (f) PtBr₃ monolayers. The COHPs (PDOSs) have the same scale. The lines and colors have the same meaning as those in Fig. 4 of the main text.

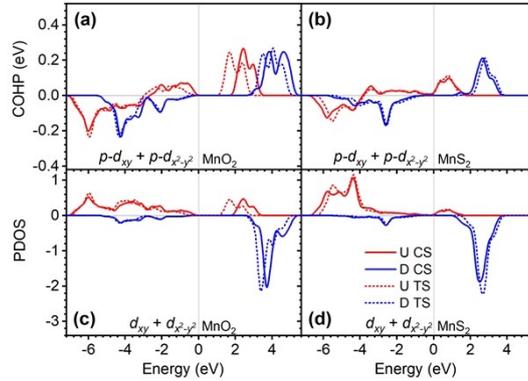


Fig. S10 Sum of crystal orbital Hamilton populations (COHP) of $p-d_{xy}$ and $p-d_{x^2-y^2}$ mixings in (a) MnO₂ and (b) MnS₂ monolayers, and the sum of the partials density of states (PDOS) of d_{xy} and $d_{x^2-y^2}$ orbitals of (c) MnO₂ and (d) MnS₂ monolayers, where the COHPs (DOSs) have the same scale. The lines and colors have the same meaning as those in Fig. 4 of the main text.

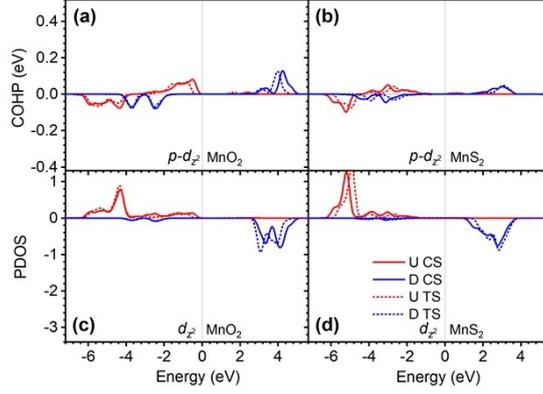


Fig. S11 Crystal orbital Hamilton populations (COHP) of $p-d_{z^2}$ mixing in (a) MnO₂ and (b) MnS₂ monolayers, and the sum of the partial density of states (PDOS) of d_{xy} and $d_{x^2-y^2}$ orbitals of (c) MnO₂ and (d) MnS₂ monolayers, where the COHPs (DOSs) have the same scale. The lines and colors have the same meaning as those in Fig. 4 of the main text.

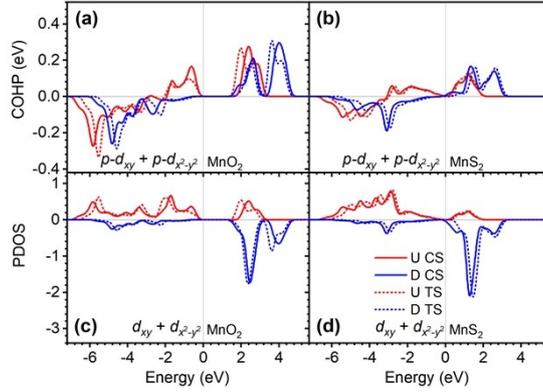


Fig. S12 Sum of crystal orbital Hamilton populations (COHP) of $p-d_{xy}$ and $p-d_{x^2-y^2}$ mixings for (a) MnO₂ and (b) MnS₂ monolayers, and partial density of states (PDOS) of d_{z^2} orbital of (c) MnO₂ and (d) MnS₂ monolayers, where the COHPs (DOSs) have the same scale and these values are calculated with a U_{eff} of 1.2 eV. The lines and colors have the same meaning as those in Fig. 4 of the main text.

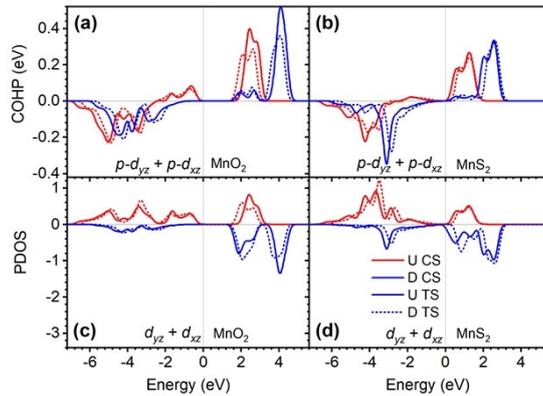


Fig. S13 Sum of the crystal orbital Hamilton populations (COHPs) of $p-d_{yz}$ and $p-d_{xz}$ mixings for (a) MnO₂ and (b) MnS₂ monolayers, and the sum of the partial density of states (PDOSs) of d_{yz} and d_{xz} orbitals for (a) MnO₂ and (b) MnS₂ monolayers, where these values are calculated with a U_{eff} of 1.2 eV. The COHPs (PDOSs) have the same scale. The lines and colors have the same meaning as those in Fig. 4 of the main text.

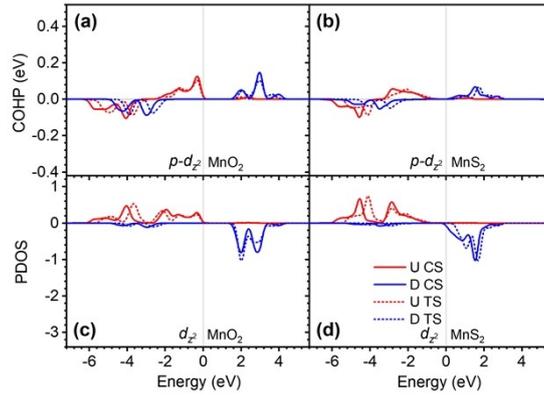


Fig. S14 Crystal orbital Hamilton populations (COHP) of p - d_{z^2} mixing in (a) MnO_2 and (b) MnS_2 monolayers, and the partials density of states (PDOS) of d_{z^2} orbitals of (c) MnO_2 and (d) MnS_2 monolayers, where the COHPs (DOSs) have the same scale and these values are calculated with a U_{eff} of 1.2 eV. The lines and colors have the same meaning as those in Fig. 4 of the main text.

II. TABLES

Table S1 Integral COHP (ICOHP) and DOS (IPDOS) for ferromagnetic semiconducting monolayers under the compressive strain (CS) and the tensile strain (TS). The u (d) in the second column stands for the spin-up (-down), the B (a -B) in the third column represent the bonding (antibonding) state and the occ (uno) denotes the occupied (unoccupied) state.

			CrBr ₃		CrI ₃		PtBr ₃		MnO ₂		MnS ₂		
			CS	TS	CS	TS	CS	TS	CS	TS	CS	TS	
p - d_{xy} + p - $d_{x^2-y^2}$	u	B (<i>occ</i>)	ICOHP	-0.191	-0.185	-0.149	-0.142	-0.265	-0.263	-0.339	-0.317	-0.183	-0.176
		IPDOS	1.151	1.193	1.342	1.391	1.090	1.065	1.209	1.259	1.514	1.553	
	d	a -B (<i>occ</i>)	ICOHP	0.079	0.073	0.057	0.050	0.175	0.174	0.116	0.089	0.082	0.074
		IPDOS	0.469	0.411	0.339	0.281	0.729	0.753	0.381	0.315	0.303	0.263	
	u	a -B (<i>uno</i>)	ICOHP	0.112	0.112	0.091	0.091	0.090	0.090	0.230	0.234	0.101	0.103
		IPDOS	0.367	0.383	0.315	0.315	0.161	0.162	0.376	0.394	0.155	0.155	
	d	B (<i>occ</i>)	ICOHP	-0.176	-0.169	-0.142	-0.137	-0.271	-0.270	-0.340	-0.315	-0.192	-0.184
		IPDOS	0.211	0.205	0.190	0.182	1.040	1.042	0.347	0.324	0.265	0.246	
	u	a -B (<i>occ</i>)					0.116	0.114					
		IPDOS					0.623	0.611					
	d	a -B (<i>uno</i>)	ICOHP	0.174	0.168	0.142	0.137	0.155	0.157	0.348	0.321	0.193	0.185
		IPDOS	1.776	1.781	1.796	1.811	0.318	0.328	1.628	1.653	1.723	1.743	
p - d_{yz} + p - d_{xz}	u	B (<i>occ</i>)	ICOHP	-0.267	-0.245	-0.219	-0.201	-0.330	-0.319	-0.372	-0.326	-0.233	-0.209
		IPDOS	0.989	1.054	1.138	1.216	1.120	1.111	1.110	1.191	1.386	1.425	
	d	a -B (<i>occ</i>)	ICOHP	0.033	0.027	0.021	0.017	0.157	0.150	0.053	0.058	0.022	0.030
		IPDOS	0.212	0.172	0.177	0.124	0.537	0.553	0.295	0.305	0.237	0.264	
	u	a -B (<i>uno</i>)	ICOHP	0.233	0.219	0.196	0.183	0.172	0.167	0.315	0.264	0.210	0.177
		IPDOS	0.775	0.752	0.663	0.640	0.309	0.305	0.557	0.473	0.336	0.276	
	d	B (<i>occ</i>)	ICOHP	-0.246	-0.228	-0.205	-0.190	-0.339	-0.326	-0.357	-0.308	-0.266	-0.232
		IPDOS	0.317	0.297	0.298	0.274	1.042	1.046	0.379	0.332	0.405	0.339	
	d	a -B (<i>occ</i>)					0.062	0.062					
		IPDOS					0.062	0.367					
	d	a -B (<i>uno</i>)	ICOHP	0.243	0.225	0.204	0.189	0.275	0.263	0.353	0.302	0.264	0.230
		IPDOS	1.661	1.683	1.685	1.712	0.573	0.557	1.590	1.644	1.575	1.645	

Table S2 Diagram of diagonal and off-diagonal coupling product terms. Numbers 1–5, in turn, represent d_{xy} , d_{yz} , d_{z^2} , d_{xz} and $d_{x^2-y^2}$ orbital. As an example, 15 denotes the interorbital coupling between occupied d_{xy} and unoccupied $d_{x^2-y^2}$ orbitals, i.e., $\langle x^2 - y^2 | L_z | xy \rangle$, and 15* is its transpose $\langle xy | L_z | x^2 - y^2 \rangle$. Triangles represent diagonal coupling product terms and numbers 1–15 in the table represent off-diagonal coupling product terms, and their corresponding occupation product are electron occupation product and cross-occupation product, respectively.

	15*	51*	24*	42*	14*	41*	25*	52*	23*	32*
15	Δ	1	2(5)	3(4)						
51		Δ	4(3)	5(2)						
24			Δ	6						
42				Δ						
14					Δ	7	8(13)	9(12)	10	11
41						Δ	12(9)	13(8)	14	15
25							Δ	16	17	18
52								Δ	19	20
23									Δ	21
32										Δ

Comments: For D_{3d} symmetry, d orbitals are split into a_{1g} (d_{z^2}) and two twofold degenerate $2e_g$ ($\{d_{x^2-y^2}, d_{xy}\}$, $\{d_{xz}, d_{yz}\}$), which determines that the a_{1g} is not allowed to hybridize with $2e_g$ ideally. Hence, these off-diagonal coupling product terms marked by dark gray color contribute to Λ and $\Delta\Lambda$ negligibly. Their values in our calculations are one to two orders of magnitude smaller than the total Λ and $\Delta\Lambda$.

Table S3 Values of Λ for ferromagnetic monolayers under unstrained state. The contributions from the diagonal and off-diagonal coupling product terms are listed, respectively. The $up-dn$ represents the interorbital coupling between the occupied spin-up and unoccupied spin-down orbitals.

Λ	CrBr ₃	CrI ₃	MnO ₂	MnS ₂	PtBr ₃	VS ₂
diagonal coupling (10^{-3} eV ⁻¹)	40.18	33.27	62.89	56.98	48.35	58.43
off-diagonal coupling (10^{-3} eV ⁻¹)						
$up-up$	2.84	0.76	-2.18	-1.91	36.81	-2.56
$dn-dn$	-0.35	-0.35	-0.89	-0.76	2.97	2.10
$up-dn$	-1.65	-1.05	-4.33	-1.85	-6.84	20.34
$dn-up$	0.36	-0.15	0.49	-0.74	-1.31	7.03
Sum (10^{-3} eV ⁻¹)	41.38	32.47	55.98	51.72	79.98	85.33

Calculation details

Second-order perturbation (SOP) calculations

Here, MAE is expressed as:

$$\begin{aligned} \text{MAE}^{\alpha\beta} &= E^{\alpha\beta}(x) - E^{\alpha\beta}(z) \\ &= (-1)^l \xi^2 \sum_{o^\alpha, u^\beta} \frac{|\langle \varphi_{o^\alpha} | \mathbf{L}_x | \varphi_{u^\beta} \rangle|^2 - |\langle \varphi_{o^\alpha} | \mathbf{L}_z | \varphi_{u^\beta} \rangle|^2}{\varepsilon_{u^\beta} - \varepsilon_{o^\alpha}} \quad \backslash * \\ &= (-1)^{l+m} \xi^2 \sum_{o^\alpha, u^\beta} \sum_{c \in (x,z)} \frac{|\langle \varphi_{o^\alpha} | \mathbf{L}_c | \varphi_{u^\beta} \rangle|^2}{\varepsilon_{u^\beta} - \varepsilon_{o^\alpha}}, \end{aligned}$$

MERGEFORMAT (S1)

where $E(x)$ [$E(z)$] is the total energy of a system with magnetization along x (z) direction, ξ is spin-orbit coupling (SOC) constant, ε_u (ε_o) is the energy eigenvalues of unoccupied (occupied) states, both α and β stand for spin-up (u) or -down (d), and $\langle \varphi_{o^\alpha} | \mathbf{L}_c | \varphi_{u^\beta} \rangle$ is angular momentum coupling matrix elements between occupied (o) and unoccupied (u) states for the spin combination $\alpha\beta$, both $l = 0$ ($l = 1$) for $\alpha \neq \beta$ ($\alpha = \beta$) and $m = 0$ ($m = 1$) for $c = x$ ($c = z$) make $(-1)^{l+m}$ include the positive and negative contribution of interstate couplings to MAE. Within the projected augmented-wave (PAW) method, $\varphi_{n,k} = \sum_{atom} \sum_i c_i \phi_i$, where ϕ_i is the i th partial wave (or orbital) of electrons and c_i is the complex coefficient. We thus get

$$|\langle \varphi_o | \mathbf{L}_c | \varphi_u \rangle|^2 = \sum_{i,i',j,j'} c_{oi}^* c_{oi'} c_{uj}^* c_{uj'} \langle \phi_{oi} | \mathbf{L}_c | \phi_{uj} \rangle \langle \phi_{uj'} | \mathbf{L}_c | \phi_{oi'} \rangle, \quad \backslash *$$

MERGEFORMAT (S2)

where $\langle \phi_{oi} | \mathbf{L}_c | \phi_{uj} \rangle$ is interorbital coupling matrix elements.

The MAE of a particular k -point is the sum over the contribution of all the nonvanishing interorbital couplings at this point and the MAE of a system is the average of the MAE of all the k -points in the first Brillouin zone. Because the eigenstate at a general k -point comprises the admixture of several symmetry-identical orbitals, we discuss Eq. * MERGEFORMAT (S2) in two cases.

The first case corresponds to both $i = i'$ and $j = j'$. Equation * MERGEFORMAT (S2) is further written as

$$\begin{aligned} |\langle \varphi_o | \mathbf{L}_c | \varphi_u \rangle|^2 &= \sum_{i,j} c_{oi}^* c_{oi} c_{uj}^* c_{uj} \langle \phi_{oi} | \mathbf{L}_c | \phi_{uj} \rangle \langle \phi_{uj} | \mathbf{L}_c | \phi_{oi} \rangle \quad \backslash * \\ &= \sum_{i,j} w_{oi} w_{uj} |\langle \phi_{oi} | \mathbf{L}_c | \phi_{uj} \rangle|^2, \end{aligned}$$

MERGEFORMAT (S3)

where w_{oi} (w_{uj}) is the electron occupation of the i th (j th) partial wave of an occupied (unoccupied) state. Hence, $w_{oi}w_{uj}$ is called electron occupation product.

The second case corresponds to $i \neq i'$ and/or $j \neq j'$. Equation * MERGEFORMAT (S2) cannot be simplified further. Here, the contribution of the interstate coupling to MAE includes the contributions from the matrix elements $\langle \phi_{oi} | \mathbf{L}_c | \phi_{uj} \rangle$ and $\langle \phi_{uj'} | \mathbf{L}_c | \phi_{oi'} \rangle$. Here, we call $c_{oi}^* c_{oi'} c_{uj'}^* c_{uj}$ the cross-occupation product (see Sec. B in this supplementary material for how it is calculated).

For the convenience of discussion, we can express the $\langle \phi_{oi} | \mathbf{L}_c | \phi_{uj} \rangle \langle \phi_{uj'} | \mathbf{L}_c | \phi_{oi'} \rangle$ in Eq. * MERGEFORMAT (S2) by a matrix-like form (see Table S2). The first case corresponds to the diagonal term in the matrix and the second case to the off-diagonal term. Hence, we call the first case the diagonal coupling product and call the second the off-diagonal coupling product.

Considering that the SOC constant of an element is virtually unchanged with strain, we further simplify Eq. * MERGEFORMAT (S1) as

$$\Lambda = \Lambda(x) - \Lambda(z) = (-1)^{l+m} \xi^2 \sum_{o^\alpha, u^\beta} \sum_{c \in (x,z)} \frac{|\langle \phi_{o^\alpha} | \mathbf{L}_c | \phi_{u^\beta} \rangle|^2}{\delta \mathcal{E}}. \quad \text{* MERGEFORMAT (S4)}$$

MERGEFORMAT (S4)

Thereafter, the analysis of MAE (Δ MAE) is replaced by the analysis of Λ ($\Delta\Lambda$). $\Delta\Lambda = \Lambda_{ts} - \Lambda_{cs}$, where Λ_{ts} (Λ_{cs}) denotes the Λ value of a material under tensile (compressive) strain.

Note: 1. For d -orbitals, the nonvanishing interorbital matrix elements include $\langle x^2 - y^2 | \mathbf{L}_z | xy \rangle$, $\langle xz | \mathbf{L}_z | yz \rangle$, $\langle z^2 | \mathbf{L}_x | yz \rangle$, $\langle x^2 - y^2 | \mathbf{L}_x | yz \rangle$, $\langle xz | \mathbf{L}_x | xy \rangle$ and their transposes. As an example, the $\langle xz | \mathbf{L}_z | yz \rangle$ is short for $\langle d_{xz} | \mathbf{L}_z | d_{yz} \rangle$, which denotes the coupling between occupied d_{xz} and unoccupied d_{yz} orbitals, while its transpose is $\langle yz | \mathbf{L}_z | xz \rangle$, which means the coupling between occupied d_{yz} and unoccupied d_{xz} orbitals.

2. An interorbital coupling and its transpose equally contribute to MAE. Therefore, the coupling-contributed value of $(xz, yz)_z$, as an example, represents the sum of the contributed values from the coupling and from its transpose.

In the matrix-like form (Table S2), numbers 1–5, in turn, represent the d_{xy} , d_{yz} , d_{z^2} , d_{xz} and $d_{x^2-y^2}$ orbitals. As an example, the transpose of the diagonal term 42-42* is 24-24*, where the 42-42* (24-24*) is $\langle xz | L_z | yz \rangle \langle yz | L_z | xz \rangle$ ($\langle yz | L_z | xz \rangle \langle xz | L_z | yz \rangle$); the transpose of the off-diagonal term 15-24* is 24-15*, where the 15-24* (24-15*) is $\langle xy | L_z | x^2 - y^2 \rangle \langle xz | L_z | yz \rangle$ ($\langle yz | L_z | xz \rangle \langle x^2 - y^2 | L_z | xy \rangle$).

Electron occupation product

In this section, we define a quantity to discuss whether the dominant factor of $\Delta\Lambda$ is electron occupation. The quantity is introduced by removing both the denominator and the coupling product in Eq. * MERGEFORMAT (S4) or by setting them to be one for all the nonvanishing interorbital couplings, such that the result only includes the contribution from the occupation product. We define the anisotropy occupation product Π for these nonvanishing couplings as

$$\begin{aligned} \Pi &= \Pi(x) - \Pi(z) \\ &= (-1)^{l+m} \sum_{i,i',j,j'} \sum_{o,u} c_{oi}^* c_{oi'} c_{uj}^* c_{uj}. \end{aligned} \quad \text{* MERGEFORMAT (S5)}$$

For the electron occupation product,

$$\begin{aligned} \Pi &= (-1)^{l+m} \sum_{i,j} \sum_{o,u} c_{oi}^* c_{oi} c_{uj}^* c_{uj} \\ &= (-1)^{l+m} \sum_{i,j} \sum_{o,u} w_{oi} w_{uj} \quad \text{* MERGEFORMAT (S6)} \\ &= (-1)^{l+m} \sum_{i,j} \left(\sum_o w_{oi} \sum_u w_{uj} \right) \end{aligned}$$

This equation shows that for the coupling between the i th and j th orbital at one k -point, the Π can be calculated easily by the product of the sum of the occupation number of the occupied i th orbital ($\sum_o w_{oi}$) and the sum of the occupation number of the unoccupied j th orbital ($\sum_u w_{uj}$).

For the cross-occupation product, although the calculation is slightly more cumbersome than that for the electron occupation product, it is still easily obtained from the electronic structures. The equation is expressed as:

$$\begin{aligned} \Pi &= (-1)^{l+m} \sum_{i,i',j,j'} \left\{ \sum_o (c_{oi}^{(r)} c_{oi'}^{(r)} + c_{oi}^{(i)} c_{oi'}^{(i)}) \sum_u (c_{ui}^{(r)} c_{ui'}^{(r)} + c_{ui}^{(i)} c_{ui'}^{(i)}) + \right. \\ &\quad \left. \sum_o (c_{oi}^{(r)} c_{oi'}^{(i)} - c_{oi}^{(i)} c_{oi'}^{(r)}) \sum_u (c_{ui}^{(r)} c_{ui'}^{(i)} - c_{ui}^{(i)} c_{ui'}^{(r)}) \right\}, \end{aligned} \quad \text{*}$$

MERGEFORMAT (S7)

where the superscript (r) [i] represents the real (imaginary) part of the complex coefficient of partial orbitals.

Discussion about the effect of Hubbard U on the interorbital coupling ($d_{xy}, d_{x^2-y^2}$) for MnX_2

The ΔMAE of the coupling ($d_{xy}, d_{x^2-y^2}$) increases with U changing from 1.2 eV to these values listed in Section Computational methods. As can be seen from Figs S12(c) and S12(d), the MAE of ($d_{xy}, d_{x^2-y^2}$) is dominated by two components: the positive MAE of ($d_{xy}, d_{x^2-y^2}$)^{uu} and the negative MAE of ($d_{xy}, d_{x^2-y^2}$)^{ud}. By comparing Figs S12(c) and S12(d) with Figs S10(c) and S10(d), we can find that the obvious different is the PDOS of the unoccupied spin-down states. An isolated higher peak appears in the case of $U = 3.9$ eV while two relative lower peaks can be observed in the case of $U = 1.2$ eV. For MnO_2 in the case of $U = 3.9$ eV, the strain-induced increase and left shift of the PDOS of the unoccupied spin-down states lead to the decrease in the ΔMAE of ($d_{xy}, d_{x^2-y^2}$)^{ud}, which is why the ΔMAE of ($d_{xy}, d_{x^2-y^2}$) is a small positive value. For the unoccupied spin-down states when $U = 1.2$ eV, the effect of the increase of the low-energy PDOS peak on MAE is counteracted by the effect of the more significant decrease and left shift of the high-energy PDOS peak. Hence, the ΔMAE of ($d_{xy}, d_{x^2-y^2}$) is larger than that in the case of $U = 3.9$ eV. For MnS_2 with $U = 3.9$ eV, the increase in the PDOS of the unoccupied spin-down states contributes a negative ΔMAE , which causes the positive ΔMAE of the ($d_{xy}, d_{x^2-y^2}$) is small. For MnS_2 with $U = 1.2$ eV, the large ΔMAE of ($d_{xy}, d_{x^2-y^2}$) is attributed to the significant increase in occupied spin-up PDOS peak. It is important to point out that the PDOS of the unoccupied spin-down state for $U = 1.2$ eV is significantly different from that for $U = 3.9$ eV. This implies that the value of U affects the ΔMAE of interorbital coupling by changing the p - d mixing. It is well known that the value of U has a reason range to reproduce the real electron structure. The $U = 1.2$ eV might be unreasonable, as be confirmed by Sun *et al.*¹

Discussion about the dominant interorbital coupling for PtBr₃

The SOP calculations indicate that the largest positive $\Delta\Lambda$ of PtBr₃ at the K point is contributed by the coupling $(d_{z^2}, d_{yz})^{uu}$. However, the conclusion contradicts the result shown in Fig. 2(h) of the main text, where the ΔMAE of $(d_{xy}, d_{x^2-y^2})$ is largest. This contradiction stems from a drawback of the second-order perturbation method to calculate the case that the energy difference between the occupied and unoccupied bands approaches zero electron volt. The unusually large (singular) values of the coupling $(d_{z^2}, d_{yz})^{uu}$ at and near the K points is just due to the bandgap of almost zero and thus are unreal. Finally, we find that the $\Delta\Lambda$ of PtBr₃ should be dominated by the off-diagonal terms $(d_{xy} + d_{yz}, d_{x^2-y^2} + d_{xz})^{uu}$ which includes the contribution of the interorbital coupling $(d_{xy}, d_{x^2-y^2})^{uu}$.

References

¹ C. Sun, Y. Wang, J. Zou and S. C. Smith, *Phys. Chem. Chem. Phys.*, 2011, **13**, 11325.