Engineering Interlayer Hybridization in Energy Space via Dipolar Overlayers

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The interlayer hybridization (IH) of van der Waals (vdW) materials is thought to be mostly associated with the unignorable interlayer overlaps of wavefunctions (t) in real space. Here, we develop a more fundamental understanding of IH by introducing a new physical quantity, the IH admixture ratio \( \alpha \). Consequently, an exotic strategy of IH engineering in energy space can be proposed, i.e., instead of changing t as commonly used, one can be effectively tuned in energy space by changing the on-site energy difference (2\( \Delta \)) between neighboring-layer states. In practice, this is feasible via reshaping the electrostatic potential of the surface by depositing a dipolar overlayer, e.g., crystalline ice. Our first-principles calculations unveil that IH can be adjusted 2\( \Delta \) can greatly tune interlayer optical transitions in transition-metal dichalcogenide bilayers, switch different types of Dirac surface states in Bi\(_2\)Se\(_3\) thin films, and control magnetic phase transition of charge density waves in 1H/1T-TaS\(_2\) bilayers, opening new opportunities to govern the fundamental optoelectronic, topological, and magnetic properties of vdW systems beyond the traditional interlayer distance or twisting engineering.

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The interlayer hybridization (IH) of stacked two-dimensional (2D) van der Waals (vdW) materials manifests itself as a unique tuning knob for their overall physical properties.\([1-6]\) Compared with conventional bulk materials, this hybridization arises from the relatively weak vdW interaction, whose strength is comparable to that of external stimuli. Therefore, (i) it can be lifted by mechanical exfoliation,\([7]\) opening the door for atomically thin 2D materials; (ii) it can also be utilized to manipulate the electronic properties of vdW homo/hetero structures, not only to engineer their band structures,\([3,4,8]\) but also to drive a variety of many-body phenomena such as magnetic phase transitions,\([9,10]\) superconductivity,\([11]\) interlayer excitons,\([5,12,13]\) and charge density waves (CDWs);\([14,15]\) (iii) it can even be applied to realize twist engineering, bringing the studies of superconducting\([16]\) or strongly correlated phases\([17]\) in the 2D limit to a new level. Thus, searching an efficient way of tuning the IH always plays a central role for both fundamental studies and practical applications of stacked vdW materials.

In general, the electronic states of each monolayer component in vdW-stacked systems can be considered as states confined in a vertical finite-depth quantum well. As demonstrated in Fig. 1(a) (upper panel), the states in each well cannot be fully confined, leading to unignorable overlap of their wavefunctions in real space, referred to as t, between the quantum wells of different layers. Usually, the IH is tacitly accepted to be mostly associated with t, whose value can be effectively tuned in real space by mechanical exfoliation,\([7]\) stacking modulation,\([14,15]\) and twisting,\([16,17]\) resulting in scientific (i)–(iii) discoveries stated above. A fundamental question is raised here: Besides tuning t being commonly used, is there an alternative way to tune the IH? The answer to this question relies on a more fundamental understanding of the IH.

In addition to t in real space, as shown in Fig. 1(a) (lower panel), there can be an offset energy, referring to 2\( \Delta \), in the on-site energy of neighboring-layer states in energy space. Similar to real-space t, this 2\( \Delta \) can be understood as the energy-space “overlap” of the coupled states. Considering these two overlaps and summarizing all the k-dependence of the initial energy dispersion in \( \varepsilon_0(k) \), the IH can be illustrated in a minimal two-band model involving states |\( \alpha \rangle \rangle = (10) \) and |\( \beta \rangle \rangle = (0,1) \) belonging to the A and B layers, respectively. The resulting Hamiltonian reads \( \hat{H}(k) = \varepsilon_0(k)\mathbb{1} + t\sigma_1 + \Delta\sigma_3 \), where the \( \sigma_i \) refer to the Pauli matrices. The eigenstates of the Hamiltonian are |\( + \rangle \rangle = \cos(\phi)|\( \beta \rangle \rangle + \sin(\phi)|\( \alpha \rangle \rangle \) and |\( - \rangle \rangle = \cos(\phi)|\( \alpha \rangle \rangle - \sin(\phi)|\( \beta \rangle \rangle \), respectively, with tan(2\( \phi \)) = t/2\( \Delta \) and corresponding energies \( \varepsilon_\pm(k) = \varepsilon_0(k) \pm \sqrt{\Delta^2 + t^2} \). The IH yields an admixture of the wavefunctions of |\( \alpha \rangle \rangle \) and |\( \beta \rangle \rangle \). To describe the degree of this admixture, we define a key physical quan-

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tivity, the IH admixture ratio $\alpha$, as the difference of the eigenstates’ weights on $|a\rangle$ and $|b\rangle$, which reads

$$\alpha = 1 - \frac{[(|+\rangle a |\pm\rangle) - (|\pm\rangle b |b\rangle) + (|\pm\rangle b |b\rangle) + (|\pm\rangle b |b\rangle) - (|\pm\rangle b |\pm\rangle)]}{(|\pm\rangle a |\pm\rangle) + (|\pm\rangle b |b\rangle) + (|\pm\rangle b |b\rangle) + (|\pm\rangle b |b\rangle) + (|\pm\rangle b |\pm\rangle)} = 1 - \frac{1}{\sqrt{1 + 4(\Delta/2\Delta)^2}},$$

with $t/2\Delta \in [0, +\infty]$. Importantly, the $\alpha$ unveils a more fundamental understanding of the IH, i.e., the IH is instead prone to the ratio of the two overlaps $t/2\Delta$, not merely related to $t$ as generally accepted.

The phase diagram of $\alpha$ as a function of $t$ and $2\Delta$ is depicted in Fig. 1(b), where the two parameters of several commonly used homo/hetero-structures are also shown.

Crystalline ice, exhibiting the hexagonal Ih phase (Ih-ice) under a normal pressure,\cite{18} is one of the most common dipole layers existing in nature. Here, we propose to engineer $\alpha$ via modulating $2\Delta$ instead of $t$, which can be achieved by depositing an Ih-ice overlayer on the upper surface of 2D vdW systems. Using first-principles calculations, we demonstrate that IH engineering via tuning $2\Delta$ can realize greatly tunable interlayer optical transitions in transition-metal dichalcogenide (TMD) bilayers, switchable different types of Dirac surface states in Bi$_2$Se$_3$ thin films, and controllable magnetic phase transition of CDW in 1H/1T-TaS$_2$ hetero-bilayers, which potentially open a new door to engineer the optoelectronic, topological, and magnetic properties of 2D vdW systems.

**Case I: Tunable Interlayer Optical Transitions in TMD Bilayers.** Band-edge optical transitions (BOTs) play a central role in determining the fundamental optoelectronic properties of semiconductors. In general, there are two types of BOTs in layered materials, i.e., interlayer BOTs and intralayer BOTs. In practice, it is interesting to realize a highly tunable interlayer BOT, which is fundamentally related to the magnitude of interlayer optical transition probabilities ($r^2$, squares of transition dipole moments) between the band-edge states, for controllable interlayer exciton and lighting.\cite{19,22} Usually, the interlayer $r^2$ denotes the intrinsic properties of a system, which strongly depends on $\alpha$. Taking TMD bilayers as examples, as shown in Fig. 2(a), the smaller (larger) $\alpha$ in the hetero-bilayer (homo-bilayer) indicates a weaker (stronger) IH admixture between different layers, which may consequently result in a weaker (stronger) interlayer $r^2$. Here, we propose that via $2\Delta$ engineering, i.e., tuning IH by changing $2\Delta$, we may greatly tune $r^2(\alpha)$ in TMD bilayers.

To verify this idea, we construct a supercell with a $\sqrt{3} \times \sqrt{3}$ Ih-ice overlayer on a $\sqrt{7} \times \sqrt{7}$ TMD bilayer (see Figs. S1 and S2 in the Supplementary Material) to minimize the lattice mismatch between them. First, we consider the hetero-bilayer WS$_2$/MoS$_2$. The calculated $2\Delta = 169$ meV gives rise to a small $\alpha = 12.5\%$ in WS$_2$/MoS$_2$. Figure 2(b) shows the calculated unfolded orbital-resolved effective band structure of AB-stacked WS$_2$/MoS$_2$. Overall, the band-edge states in WS$_2$/MoS$_2$ exhibit a type-II band alignment. Interestingly, depositing a double-layer (2L) Ih-ice on top of WS$_2$/MoS$_2$ [Fig. 2(c)] effectively reduces $2\Delta$ from 169 to 57 meV, leading to a large enhancement of $\alpha$ from 12.5% to 47.9%. More importantly, although the band structures before and after Ih-ice deposition are very similar, the interlayer $r^2$ is significantly enhanced [Fig. 2(g)] with respect to the ice-free (0L) case [Fig. 2(f)], consistent with the mechanism proposed in Fig. 2(a).

**Fig. 1.** Interlayer hybridization (IH) engineering in stacked vdW systems. (a) Schematic diagram of the IH in real space (upper panel) and energy space (lower panel). Reshaping the electrostatic potential, denoted by dashed lines, leads to the variation of the on-site energy of layer B, along with the change of on-site energy difference $2\Delta$ between neighboring layers. (b) Phase diagram of the IH admixture ratio $\alpha$ as a function of $t$ and $2\Delta$, where the calculated $\alpha$ of several commonly used 2D systems are also indicated.
Second, we consider the homo-bilayer \( \text{MoS}_2/\text{MoS}_2 \). Since \( 2\Delta = 0 \) in \( \text{MoS}_2/\text{MoS}_2 \) [Fig. 2(d)], \( \alpha = 100\% \), leading to the electronic states from different MoS layers being energetically degenerated. The \( \alpha = 100\% \) in \( \text{MoS}_2/\text{MoS}_2 \) induces large band splittings around the \( \Gamma \) point in the top of the valence band and along the paths \( \Gamma - K/\Gamma - M \) at the bottom of the conduction band, which are absent in monolayer MoS\(_2\) (see Fig. S3). The situation is dramatically changed when a 2L Ih-ice is deposited on top of \( \text{MoS}_2/\text{MoS}_2 \). As shown in Fig. 2(e), the bands from different layers are rigidly shifted with respect to each other, forming an ideal type-II band alignment. The calculated \( 2\Delta = 222 \text{ meV} \) gives rise to a dramatic reduction of \( \alpha \) from 100\% to 7.6\%. This rather small \( \alpha \) can not only effectively eliminate the original band splitting in the ice-free (0L) case [Fig. 2(d)], but also convert the band structure of the top \( \text{MoS}_2 \) layer in \( \text{MoS}_2/\text{MoS}_2 \) from indirect bandgap to direct bandgap, similar to that of monolayer MoS\(_2\). More importantly, compared with the 0L case [Fig. 2(h)], the interlayer \( r^2 \) in the 2L case is greatly suppressed to almost zero due to the largely reduced \( \alpha \) [Fig. 2(i)], consistent with the mechanism proposed in Fig. 2(a). Therefore, via \( 2\Delta \) engineering, we may strongly enhance (suppress) the interlayer BOTs for hetero-bilayer (homo-bilayer) TMDs, yielding the corresponding enhancement (suppression) in its low energy adsorption spectroscopy (see Fig. S4).

![Fig. 2. Optoelectronic engineering in TMD bilayers. (a) Schematic diagram of tuning interlayer optical transition probabilities \( r^2 \) in TMD bilayers. Interlayer \( r^2 \) in TMD hetero- and homo-bilayers are weak and strong, respectively. Via \( 2\Delta \) engineering, the interlayer \( r^2(\alpha) \) of hetero- and homo-bilayers can be greatly enhanced and weakened, respectively. Orbital-resolved effective band structures of WS\(_2/\text{MoS}_2 \) covered by (b) 0L and (c) 2L Ih-ice. Electronic states of top WS\(_2 \) and bottom MoS\(_2 \) layers are highlighted by red and blue colors, respectively. (d)–(e) The same as (b)–(c) but for the cases of MoS\(_2/\text{MoS}_2 \). Electronic states of top and bottom MoS\(_2 \) layers are highlighted by blue and red colors, respectively. (f)–(i) Calculated interlayer \( r^2 \) among four band-edge states in the band structures of WS\(_2/\text{MoS}_2 \) shown in (b)–(c), respectively. (h)–(i) The same as (f)–(g) but for the case of MoS\(_2/\text{MoS}_2 \).](image)

Case II: Switchable Different Types of Dirac Fermions in Bi\(_2\)Se\(_3\) Thin Films. Topological materials, starting from topological insulators (TIs), are standing in the cutting edge of quantum materials.\(^{[20–22]}\) An ideal TI, e.g., Bi\(_2\)Se\(_3\), is a quantum material with a bulk gap and an odd number of relativistic Dirac fermions on the surface, in which the bulk is insulating but the surface can conduct electric current with helical spin texture.\(^{[23,24]}\) However, it is known that Dirac surface states can only be realized in a thick Bi\(_2\)Se\(_3\) slab, i.e., more than six quintuple layers (QLs). Once the thickness of Bi\(_2\)Se\(_3\) is less than six QLs, the III between the top and bottom Dirac surface states can induce a hybridization gap [Fig. 3(a), left and middle panels], destroying the massless feature of Dirac surface states.\(^{[25,26]}\) As shown in Fig. 1(b), via 2\( \Delta \) engineering, we may reduce the \( \alpha \) in Bi\(_2\)Se\(_3\) ultrathin films, which may lift the coupling between top and bottom surface states [Fig. 3(a), right panel] and result in a transition from massive to massless Dirac fermions.

To verify this idea, as shown in Fig. 3(b), we have selected 3QL-Bi\(_2\)Se\(_3\) ultrathin films as an example, in which the top surface of 3QL-Bi\(_2\)Se\(_3\) is covered by an Ih-ice overlayer. In the ice-free case (0L), \( 2\Delta = 0 \), therefore, \( \alpha = 100\% \). The hybridization between the top and bottom Dirac surface states in 3QL-Bi\(_2\)Se\(_3\) can induce a large hybridization gap of about 50 meV between them, transforming the original massless Dirac fermions to massive ones.\(^{[25]}\) Moreover, because of the effective surface-state coupling, the spin texture of massive Dirac surface states, which are completely degenerate in energy space, is far away from the ideal helical one [inset of Fig. 3(c)], i.e., the directions of the spin moments are not perpendicular to those of the crystal momenta.

When a 2L Ih-ice overlayer is deposited on the top of 3QL-Bi\(_2\)Se\(_3\) slab (see Fig. S5), it can result in a 2\( \Delta = 239 \text{ meV} \), which can consequently reduce \( \alpha \) from 087303-3
100% to almost 0%. As a result, the surface states from top and bottom layers are no longer degenerate in energy space. The Dirac fermions on the top and bottom surfaces are restored to be massless. Interestingly, the spin textures of the Dirac surface states, which are fully separated in the energy space, are also restored to the ideally helical

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Fig. 3. Dirac surface states engineering in Bi$_2$Se$_3$ thin films. (a) Schematic diagram of switchable massive-massless Dirac fermions in 3QL-Bi$_2$Se$_3$. Because of the strong orbital hybridization, the surface states of 3QL-Bi$_2$Se$_3$ open a gap and Dirac fermions are massive (left panel to middle panel). By depositing the Ih-ice overlayer, this hybridization is expected to be effectively reduced, thus, the surface Dirac fermions will be recovered to be massless (middle panel to right panel). (b) Side view of atomic structure of 3QL-Bi$_2$Se$_3$ covered by 2L Ih-ice. Orbital-resolved effective band structure of 3QL-Bi$_2$Se$_3$ with (c) 0L and (d) 2L Ih-ice overlayer. Weights of the surface states from the top and bottom sides are highlighted by red and blue colors, respectively. Insets: spin textures of the surface states from top (red arrow) and bottom (blue arrow) sides with the corresponding constant energies. Shift of the surface states to lower energies in (d) results from the charge transfer from the Ih-ice overlayer to the Bi$_2$Se$_3$ (see Fig. S6 in the Supplementary Material).

**Case III: Controllable Magnetic Phase Transition of CDW in 1T/1H-TaS$_2$.** Magnetism is one of the central phenomena in condensed matter physics, which is mainly determined by the spin exchange interaction $J$ in the system. The realization of controllable $J$ is the key to realize controllable magnetic phase transition. A 1T/1H-TaS$_2$ heterostructure has recently been proposed to be a promising platform to simulate a Kondo lattice, [27,28]. The 1T-TaS$_2$ in the Star-of-David (SoD) charge-density wave (CDW) phase naturally forms a large unit cell with a single localized spin moment. Because of the large spatial separation, the magnetic exchange interaction between the localized spin moments is extremely weak, i.e., these localized spin moments directly interact with each other. By stacking the 1T-TaS$_2$ on top of the 1H-TaS$_2$ layer, the conduction electrons in the 1H-TaS$_2$ interact with the localized spin moments in the 1T-TaS$_2$ due to IH denoting as $J$. Thus, the $J$ between localized spin moments and conduction electrons highly depends on $\alpha$, i.e., $J$ is a function of $\alpha$ [Fig. 4(a)]. The conduction electrons can travel around in the 1H-TaS$_2$ layer and have interactions with each localized spin moments in the 1T-TaS$_2$. As a result, the localized spin moments establish indirect magnetic exchange interaction between them via the conduction electrons, i.e., the directions of the spin moments are rigorously perpendicular to those of the crystal momenta. Therefore, an interesting transition from massive to massless Dirac fermions can be well achieved by 2$\Delta$ engineering, along with the modulation of its spin texture.

When the conduction electrons have strong interaction with the localized spin moments, the localized spin moment would be completely screened by conduction electrons, i.e., the localized spin moment cannot be seen from “outside”, which is called the Kondo effect. However, if the interaction between the conduction electron and localized spin moments becomes weak, the localized spin moments are not completely screened by the conduction electrons. In this scenario, the magnetic exchange interaction between the localized spin moment belongs to the so-called RKKY type. In short, the key factor of determining the system entering the magnetically ordered state or the Kondo screened state is the interaction strength $J(\alpha)$ between the localized spin moment in the 1T-TaS$_2$ layer and the conduction electrons in the 1H-TaS$_2$ layer. Thus, by 2$\Delta$ engineering, we may effectively control $J(\alpha)$ in 1T/1H-TaS$_2$, which can consequently control the magnetic phase transition of CDW in 1T/1H-TaS$_2$.

To verify this idea and to model the 1T/1H-TaS$_2$ heterostructure with the SoD-CDW phase, we combine a $\sqrt{39} \times \sqrt{39}$ 1T-TaS$_2$ structure with a $6 \times 6$ 1H-TaS$_2$ struc-
ture (see Fig. S7). The calculated local spin moment on the Ta atom in the center each SoD cluster is about 0.2µ₀, and its direction can be flipped freely (there is an energy barrier of about 0.02 meV per SoD cluster), which results in a paramagnetic phase. As shown in Fig. 4(b), the calculated density of states (DOS) indicates that the half-occupied state contributed by the Ta-d₃ in the center of SoD in 1T-TaS₂ is pushed upwards to higher energies, while the states derived from the Ta-d in 1H-TaS₂ are pushed downwards to lower energies. This noticeable level repulsion between 1T and 1H layers around the Fermi level manifests the existence of an unignorable IH, as also indicated by the calculated α = 13.9%. Considering both the spin-polarization and DOS calculations, it can be concluded that the 1T/1H-TaS₂ heterostructure probably falls into the Kondo screened regime in the phase diagram in Fig. 4(c), consistent with the experimental observations.[28]

![Fig. 4](image)

**Fig. 4.** Engineering magnetic phase transition in 1T/1H-TaS₂ heterostructure. (a) Side view of atomic structure of 1T/1H-TaS₂, where the top of the 1T layer is covered by Ih-ice. J is a function of α. (b) Projected DOS of 1T/1H-TaS₂ with 0 L (dashed line) and 2 L (solid line) Ih-ice overlayer. The projection on dₓ²−ᵧ² orbital of the central Ta in the SoD of the 1T-TaS₂ layer is highlighted by green color, while the projection on the dₓ, dᵧ, and dₓ±ᵧ orbitals of Ta in the 1H layer is highlighted by orange color. (c) Schematic diagram of the magnetic phase transition between a magnetically ordered phase induced by RKKY interaction and a paramagnetic phase resulting from the Kondo screening. Left and right panels show the calculated spin density maps of the 1T/1H-TaS₂ heterostructure with 2 L and 0 L Ih-ice overlayer, respectively.

If 2 L Ih-ice is deposited on top of the 1T-TaS₂ layer, the increased 2α can weaken α. Interestingly, as shown in Fig. 4(b), although α is slightly reduced from 13.9% to 10.2%, it can strongly suppress the level repulsion between the 1T- and 1H-TaS₂ layers. Instead, the Kondo spin screening of the local moments will be dominated by the RKKY interaction,[29] leading to a magnetic order. Indeed, with the assistance of Ih-ice overlayer, the freely flipped localized spin moment in the 1T-TaS₂ layer becomes magnetically ordered with the local magnetic moment of the center Ta in each SoD cluster being of about 0.3µ₀ [left in Fig. 4(c)]. During the self-consistent iterations, all the different initial magnetic configurations will eventually converge to a collective order [left in Fig. 4(c)], indicating a (strong) local energy minimum. Thus, a novel magnetic phase transition of CDW in the 1T/1H-TaS₂ heterostructure can be well controlled by 2Δ engineering.

**Discussion.** The critical factor of the IH engineering in energy space proposed here is to find a feasible approach to strongly reshape the local electrostatic potential of a surface layer. In principle, candidates for the dipole overlayers can generally be any materials with a net dipole moment perpendicular to the surface. The choice of an Ih-ice overlayer in this work is based on two concerns. First, the water molecules possess a large dipole moment (1.8–3.0 Debye),[30] being capable of sharply tailoring the surface electrostatic potential. Second, water molecules can be frozen into a crystalline phase with its polarization controlled by external fields.[31–33] Although there are reports on polar molecules as adsorbates influencing the electronic structures of solid surfaces,[34–37] the adsorbate-induced variations in the IH admixture ratio is barely explored and poorly understood.

In summary, beyond the common belief that IH is mostly associated with the wavefunction overlap in real space t, we propose that IH can also be dramatically engineered in energy space by tuning the energy separation 2Δ. Via the proposed 2Δ engineering, we demonstrate that the optoelectronic, topological, and magnetic properties of different 2D vdW homo/hetero-junctions can be well modulated. Our concept and material demonstrations may open the way for new ideas for the IH engineering in vdW systems beyond the conventional ways.

**Computational Details.** For the density-functional theory calculations, we use the Vienna _ab initio_ simulation package (VASP)[38] with the projector-augmented-wave basis sets[39,40] and the generalized gradient approximation to the exchange-correlation potential.[41] While the lattice constants of 1H-MoS₂, 1H-WS₂, 1T-TaS₂, and 1H-TaS₂ are fully optimized, the crystal structure of Bi₂Se₃ is taken from Ref. [42]. To obtain a commensurate structure, we construct slabs of a $\sqrt{3} \times \sqrt{3}$ supercell of Ih-ice overlayer on a $\sqrt{7} \times \sqrt{7}$ supercell of MoS₂/MoS₂ (MoS₂/WS₂), a $1 \times 1$ Ih-ice overlayer on a $1 \times 1$ 3QL-Bi₂Se₃, a $\sqrt{21} \times \sqrt{21}$ supercell of Ih-ice overlayer on a $\sqrt{39} \times \sqrt{39}$ supercell of bilayer 1T-TaS₂ on a $6 \times 6$ supercell of 1H-TaS₂, where the Ih-ice overlayers are laterally compressed or expanded to eliminate the lattice mismatch. The in-plane lattice constant of the 1T/1H-TaS₂ supercell is set to be the average value of the $\sqrt{39} \times \sqrt{39}$ supercell of 1T-TaS₂ and the $6 \times 6$ 1H-TaS₂. A vacuum separation of more than 15 Å is used in all the slabs. In all the cases, the structures are relaxed until the forces acting on them are below 0.01 eV/Å. In the evaluation of the electronic structures, we choose a plane-wave cut-off energy of 400 eV for all the cases and a $\Gamma$-centered 7×7×1, 15×15×1, and 5×5×1 k-mesh for the MoS₂/MoS₂ (MoS₂/WS₂), 3QL-Bi₂Se₃, and 1T/1H-TaS₂ cases, respec-
tively. The convergence criterion for the total energy is a change of less than $10^{-5}$ eV between self-consistency iterations. We have taken into account the vdW interaction via the D2 method of Grimme [43] in all the calculations, and we have applied a dipole correction [44] in the direction perpendicular to the slab in the cases with Ih-ice overlayer. The spin-orbit coupling is included in the calculations of the MoS$_2$/MoS$_2$ (MoS$_2$/WS$_2$) case, the surface state and the spin texture of 3QL-Bi$_2$Se$_3$. The $+U$ correction [45] with $U - J = 2.27$ eV [46,47] has been applied to the Ta-d orbital in the 1T layer.

**Effective Wannier Hamiltonian.** We construct an effective Hamiltonian in the basis of atomic projected Wannier functions in the MoS$_2$/MoS$_2$, MoS$_2$/WS$_2$, and 3QL-Bi$_2$Se$_3$ cases using the Wannier90 package, [48] see Figs. S8, S9, and S10 in the Supplementary Material. We choose the W-d, Mo-d, and S-p orbitals of MoS$_2$ and WS$_2$, O-p orbitals of the Ih-ice, and Bi-p and Se-p orbitals of Bi$_2$Se$_3$ as initial projections in the disentanglement process. In the case of the TMD bilayers, the effective Hamiltonian of the supercell is further mapped to the TMD primitive cell using our developed routines in the elphmod package. [49] Here, the exact choice of the primitive cell does not have a noticeable influence on the resulting band structure, showing that the change of the on-site energy differences $2\Delta$ due to the Ih-ice overlayer is homogeneous.

**Estimation of the Admixture Ratio.** For the case of MoS$_2$/MoS$_2$, MoS$_2$/WS$_2$, and 3QL-Bi$_2$Se$_3$, we estimate the corresponding admixture ratio $\alpha$ from the expression $\alpha = 1 - \sqrt{1 + 4(t/2\Delta)^2}$. We choose the parameter $t$ as the leading term of the nearest-neighbor hopping between the orbitals from different layers, which are $\{\text{Mo/W}, d_{2z}^{up}, d_{2z}^{down}\}$ and $\{\text{Bi/Se}, p_{z}\}$ in the case of MoS$_2$/MoS$_2$ (WS$_2$/MoS$_2$) and 3QL-Bi$_2$Se$_3$, respectively. The parameter $2\Delta$ is obtained as the difference of the on-site energies between the corresponding orbitals. Given the large number of atoms in the 1T/1H-TaS$_3$ system, we select an alternative way of estimating the admixture ratio $\alpha$ for computational feasibility. We integrate the density of states projected on the $d_{2z}$ orbital of the Ta atom in the center of SoD cluster ($T_{\text{SoD}}$-$d_{2z}$) and on the $d_{2z}$ orbital of its nearest-neighboring Ta atom in the 1H layer. The integration energy window is determined by the full width at half maximum of the $T_{\text{SoD}}$-$d_{2z}$ peak. The admixture ratio $\alpha$ is then calculated as $\alpha = 1 - |N_{1T}^\alpha - N_{1H}^\alpha|/(N_{1T}^\alpha + N_{1H}^\alpha)$, where $N_{1T}$ and $N_{1H}$ are the integrated projected densities of states.

**Calculation of the Optical Transition Dipole Moments (TDMs).** The effective Wannier Hamiltonians of the primitive cell of the TMD bilayers and their eigenfunctions are applied to calculate the band velocity $v_{nm}$ with $v_{nm} = \langle n, k | \partial_k H | m, k \rangle$, where $n$ and $m$ are electronic band indices. To identify the interlayer contributions to the band velocity, we introduce the project operator by following $v_{nm}^{\text{inter}} = \langle g, k | \partial_k H | g', k \rangle = \sum_{n,m} \langle g, k | n, k \rangle \langle n, k | \partial_k H | m, k \rangle \langle m, k | g', k \rangle$, where the local orbitals $|g, k\rangle$ and $|g', k\rangle$ belong to different layers. The TDMs $r_{nm}$ can be obtained with the relation $r_{nm} = v_{nm}/\omega_{nm}$ ($m \neq n$), with $\omega_{nm}$ being the eigenvalue difference between $|n, k\rangle$ and $|m, k\rangle$. Here, the estimated $r^2$ (squares of TDMs) are the sum of four optical transition processes between the top two valence bands and the bottom two conduction bands. These calculations are performed in our homemade NOPSS package. [50]

**Calculation of Orbital-Resolved Effective Band Structures.** Using the effective Wannier Hamiltonian, we calculate the interpolated band structure $\epsilon_n(k)$ and its Bloch state $|n,k\rangle$ in the cases of MoS$_2$/MoS$_2$, MoS$_2$/WS$_2$, and 3QL-Bi$_2$Se$_3$. Then, we estimate the orbital-resolved effective band structure via the spectral function $A(\omega, k)$ on a localized orbital $|g, k\rangle$ defined as

$$A^g(\omega, k) = -2\text{Im} \langle n, k | g, k \rangle \langle g, k | n, k \rangle / \omega - \epsilon_n(k) + i\delta^0,$$

where $\delta^0$ is an imaginary offset.

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