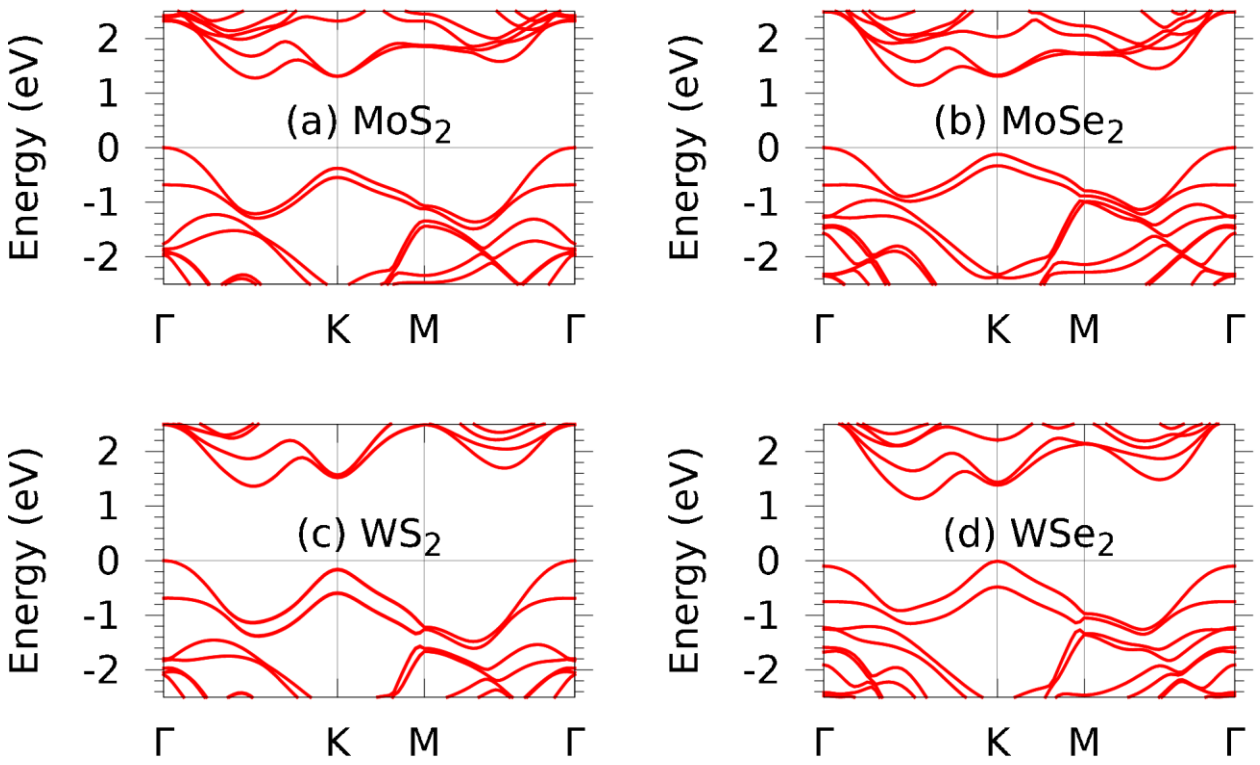
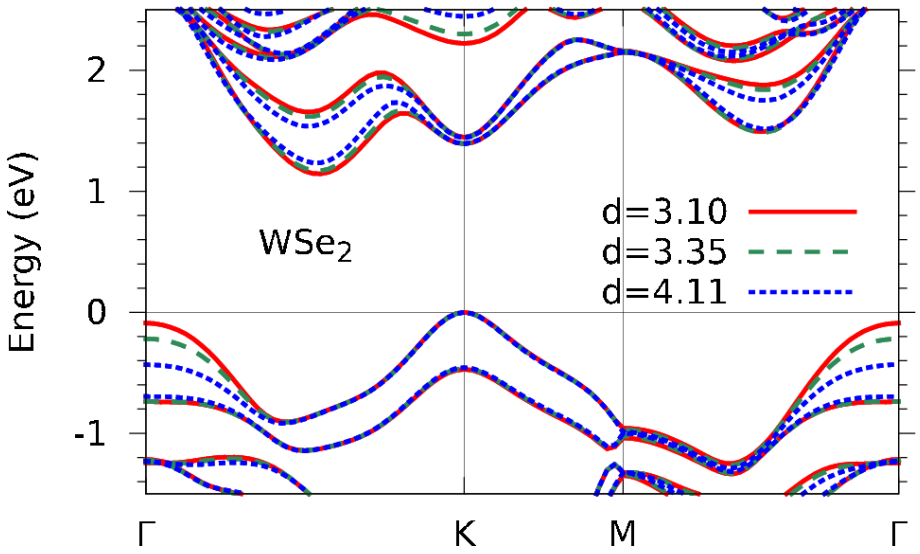
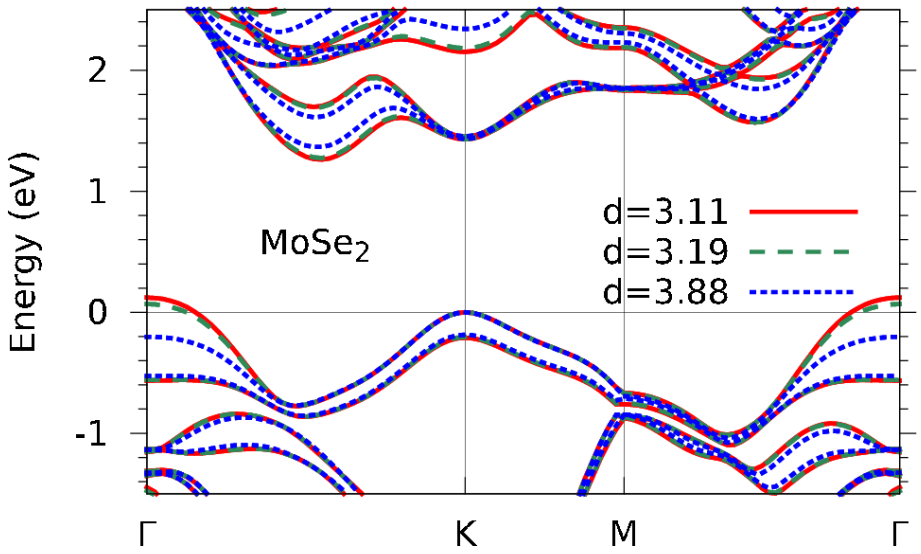
Supplementary Information



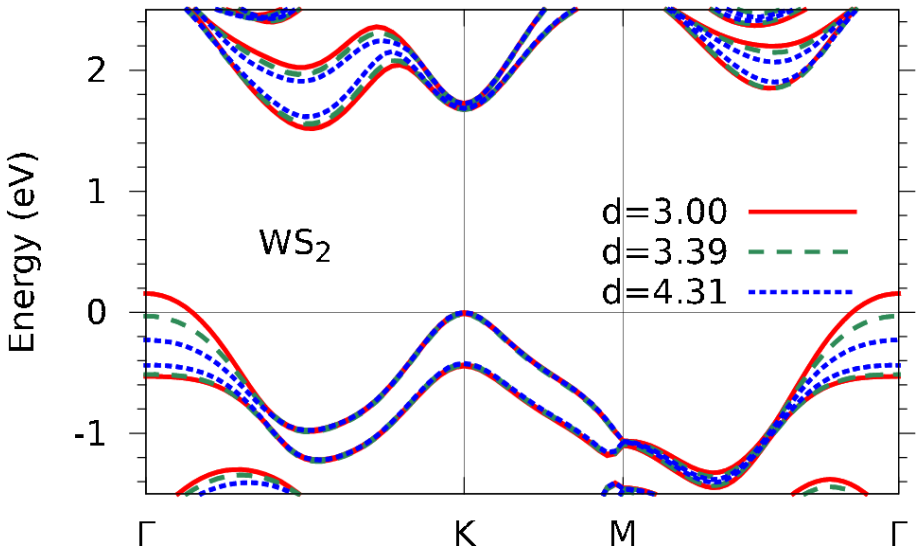
Supplementary Figure S1: *Ab initio* band structures in presence of spin-orbit coupling. Energy bands for (a) MoS_2, (b) $MoSe_2$, (c) WS_2, and (d) WSe_2 bilayers. It is worth noting that valence band maxima locate at *K* for WSe_2 bilayer. The structural parameters use the bulk values [37, 38].



Supplementary Figure S2: Band structures of WSe_2 bilayer. Band structures of WSe_2 bilayer with spin orbit coupling where interlayer separation d uses bulk value (d = 3.10 Å, red solid curve), relaxed values with vdW correction (d = 3.35 Å, green dashed curve), and without vdW correction (d = 4.11 Å, blue dotted curve).



Supplementary Figure S3: Band structures of $MoSe_2$ bilayer. Band structures of $MoSe_2$ bilayer with spin orbit coupling where interlayer separation d uses bulk value (d = 3.11 Å, red solid curve), relaxed values with vdW correction (d = 3.19 Å, green dashed curve), and without vdW correction (d = 3.88 Å, blue dotted curve).



Supplementary Figure S4: Band structures of WS_2 bilayer. Band structures of WS_2 bilayer with spin orbit coupling where interlayer separation d uses bulk value (d = 3.00 Å, red solid curve), relaxed values with vdW correction (d = 3.39 Å, green dashed curve), and without vdW correction (d = 4.31 Å, blue dotted curve).

Supplementary Note 1: Valence band maxima in WSe_2, $MoSe_2$, and WS_2 bilayers.

Our *ab initio* calculations show that valence band maxima in WSe_2 bilayer locate at *K* points, thus band edge holes have the valley degrees of freedom. This conclusion is independent of whether the structural parameters take the bulk value or the calculated value with structural relaxation. In $MoSe_2$ and WS_2 bilayers, the energy difference between the valence states at *K* points and Γ point is found to be small. Whether the valence band maxima locate at Γ or *K* points depends sensitively on the value of interlayer separation in the experimentally realized $MoSe_2$ and WS_2 bilayers. Nevertheless, hole pockets are expected to appear at *K* points in these bilayers at a much lower doping level compared to MoS_2 bilayer.

Supplementary Fig. S1 shows the band structures of MoX_2 and WX_2 (X = S or Se) bilayers from *ab initio* calculations. All four bilayers have indirect band gaps. However, for WSe_2 bilayer, the valence band maxima locate at *K* points. Structural parameters have not been measured for monolayers or bilayers. In the above calculations, the structural parameters use the bulk values [7, 38]. Alternatively, the *ab initio* calculations can also incorporate direct structure relaxation for bilayers, which will lead to a larger interlayer separation *d*. For example, for WSe_2 bilayer, the bulk value of the interlayer separation is d = 3.10 Å, while structure relaxation with (without) van der Waals (vdW) correction gives d = 3.35 Å (d = 4.11 Å) [39]. We note that, in these bilayers, the valence band splitting at Γ point is determined by the interlayer hopping, while the valence band splitting at *K* points is dominated by the spin-orbit coupling [25, 40]. Thus, with a larger *d*, the valence band energy at Γ will be further lowered compared to the *K* points, since larger layer separation results in a small interlayer hopping. This is clearly shown in Supplementary Fig. S2 where we compare the band structures of WSe_2 bilayer when the interlayer separation takes bulk value, relaxed values with and without vdW correction. In all three cases, the valence band maxima of WSe_2 bilayer locate at *K* points.

In Supplementary Fig. S3 (Supplementary Fig. S4), we also compare the band structures of $MoSe_2$ (WS_2) bilayer when the interlayer separation takes bulk value, relaxed values with and without vdW correction [39]. It is interesting to note that for these two materials, when the relaxed value without vdW correction is used for *d*, the valence band maxima locate at *K* points. If relaxed value with vdW correction is used for *d*, then the valence band maxima locate at Γ point for $MoSe_2$ and at *K* points for WS_2 while the energy difference between Γ and *K* points is small.

Supplementary References

37. R. A. Bromley, R. B. Murray & A. D. Yoffe, The band structures of some transition metal dichalcogenides. III. Group VIA: trigonal prism materials. J. Phys. C: Solid State Phys. **5**, 759-778 (1972).

38. R. Coehoorn, C. Haas, J. Dijkstra, C. J. F. Flipse, R. A. de Groot, & A. Wold, Electronic structure of $MoSe_2$, MoS_2, and WSe_2. I. Band-structure calculations and photoelectron spectroscopy. *Phys. Rev. B* **35**, 6195-6202 (1987).

39. S. Bhattacharyya & A. K. Singh, Semiconductor-metal transition in semiconducting bilayer sheets of transition-metal dichalcogenides. *Phys. Rev. B* **86**, 075454 (2012).

40. Z. Y. Zhu, Y. C. Cheng, & U. Schwingenschlögl, Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors. *Phys. Rev. B* **84**, 153402 (2011).