Supporting Information

A Unified Understanding of the Thickness-Dependent Bandgap Transition in Hexagonal Two-Dimensional Semiconductors

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Figure S1. Evolution of the energy levels of MoS$_2$ as a function of the number of layers ($N$). Perturbation theory results first including (a) and then neglecting (b) the surface effect on the diagonal components of the $N \times N$ perturbation matrix (see text for details). The results in (b) were obtained by using $\varepsilon^{(0)}$(bulk) as the diagonal components of the perturbation matrix. It is interesting to note that if the surface effect is not taken into account, the monolayer MoS$_2$ phase becomes an indirect bandgap material.
Derivation of the selective p–d orbital couplings of TMD. Monolayer H-TMD consists of TM atoms on one sublattice and group-VI atoms on the other (Figure S2). For a pair of TM d- and group-VI p-orbitals, \((\varphi^d_m, \varphi^p_{m'})\), the orbital coupling is described by the electron-hopping amplitude \(t\) between the neighboring TM and group-VI sites. Because of the threefold rotational symmetry, there are three symmetry-related hopping amplitudes as denoted by \(t^{(1)}_{mm'}\), \(t^{(2)}_{mm'}\), and \(t^{(3)}_{mm'}\) in Figure S2b, which can differ only by a phase factor as follows: \(t^{(2)}_{mm'} = e^{i2\pi/3(-m+m')} t^{(1)}_{mm'}\) and \(t^{(3)}_{mm'} = e^{-i2\pi/3(-m+m')} t^{(1)}_{mm'}\).

For \(k = k_1b_1 + k_2b_2\), the hopping amplitude \(t_{mm'}(k)\) of the Bloch Hamiltonian \(H(k)\) is then written as

\[
t_{mm'}(k) = t^{(1)}_{mm'} \left[ 1 + e^{-i2\pi k_1 e^{i2\pi/3(-m+m')}} + e^{-i2\pi(k_1+k_2)} e^{-i2\pi/3(-m+m')} \right],
\]

where \(b_1\) and \(b_2\) are the reciprocal lattice vectors. Note that for high-symmetry \(k\) such as \(\Gamma\) and \(K\), the summation of the phase factors can be either zero or three. At the \(\Gamma\) point, the \(p–d\) orbital coupling is allowed only if \(-m + m' = 3n\) for an integer \(n\). At the \(K\) point (i.e., \(k_1 = k_2 = 1/3\)), the selection rule for the \(p–d\) orbital coupling is \(-m + m' = 3n + 1\), while it is \(-m + m' = 3n - 1\) at \(-K\). The symmetry-allowed orbital couplings are listed in Table 2 in the main text.

Figure S2. (a) Atomic arrangement of group-VI atoms around a central TM atom in H-TMD and (b) a top view of monolayer TMD. Three equivalent electron-hopping amplitudes, \(t^{(1)}\), \(t^{(2)}\) and \(t^{(3)}\), are shown.