Supplementary Material

Effect of atomic configuration and spin-orbit coupling on thermodynamic stability and electronic band gap of monolayer 2H-$Mo_{1-x}W_xS_2$ solid solutions

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I. ATOMIC CONFIGURATIONS

1. Two-site clusters for ordered configurations in cluster expansion

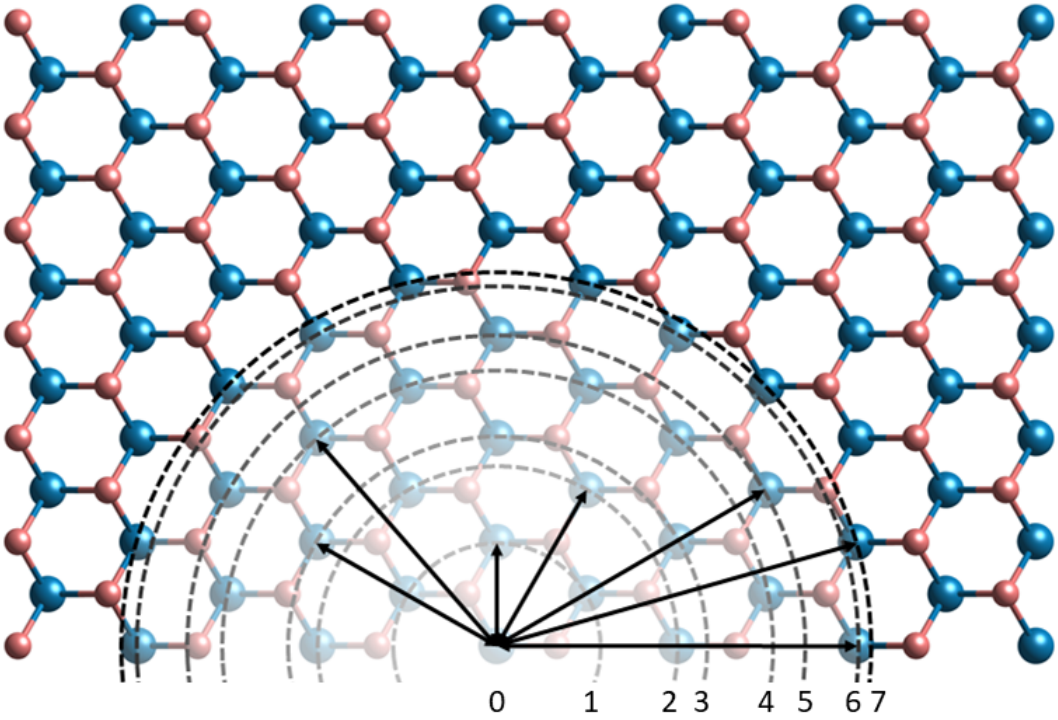


FIG. S1: Top view of the two-site clusters up to the seventh coordination shells (black dashed line) of monolayer 2H-$Mo_{1-x}W_xS_2$ solid solutions. The light blue and pink spheres represent atoms residing in the metal and chalcogen sublattices, respectively. The figure is visualized by the Visualization for Electronic and STructural Analysis (VESTA) program.

2. Predicted ordered ground-state (GS) configurations

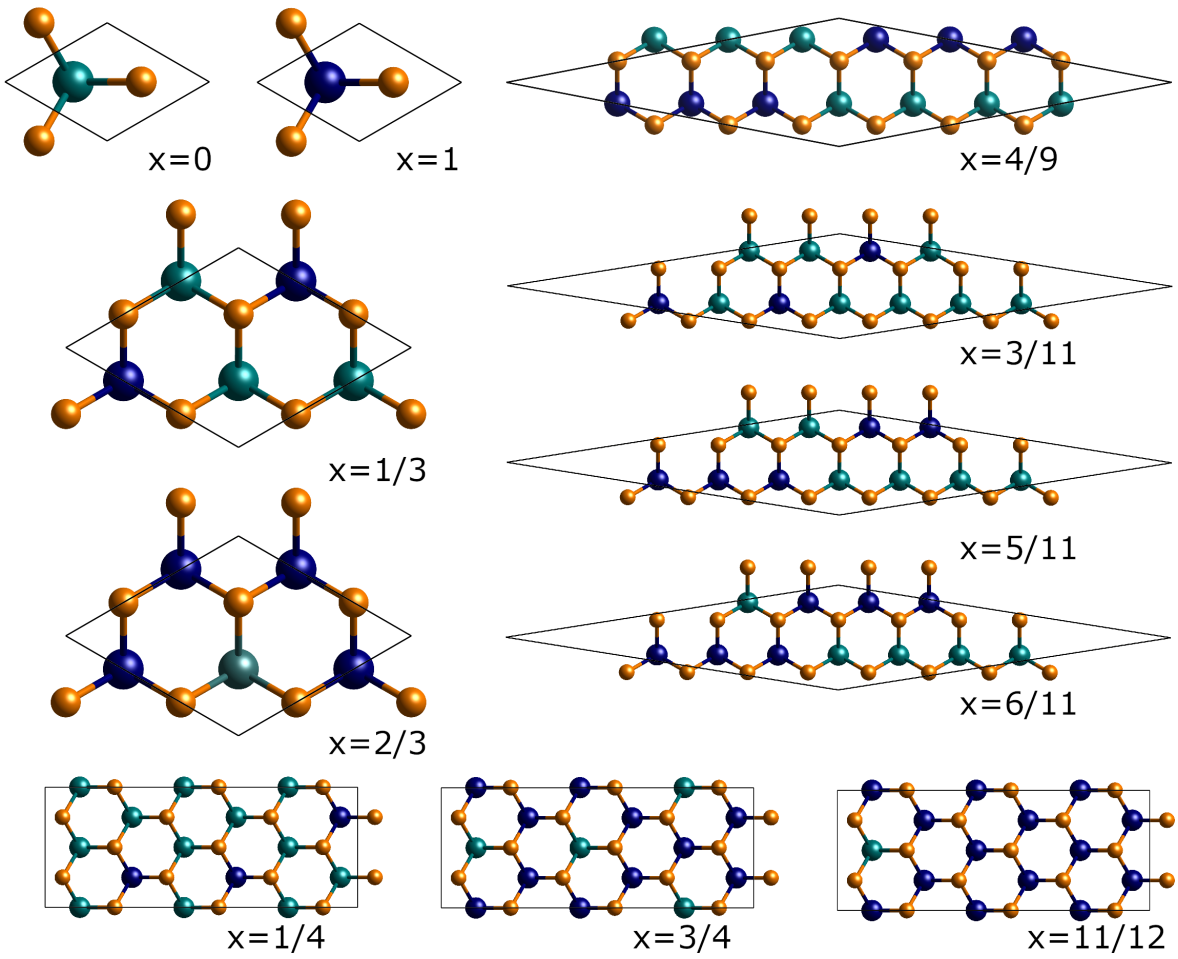


FIG. S2: Top views of the eleven ordered ground-state (GS) configurations of monolayer 2H-$Mo_{1-x}W_xS_2$ solid solutions at different composition x, which are predicted in the present work by cluster-expansion (CE) method. The teal, blue, and orange spheres represent Mo, W, and S atoms, respectively, and all figures are visualized by the Visualization for Electronic and STructural Analysis (VESTA) program.

3. Ideally random (SQS) configurations

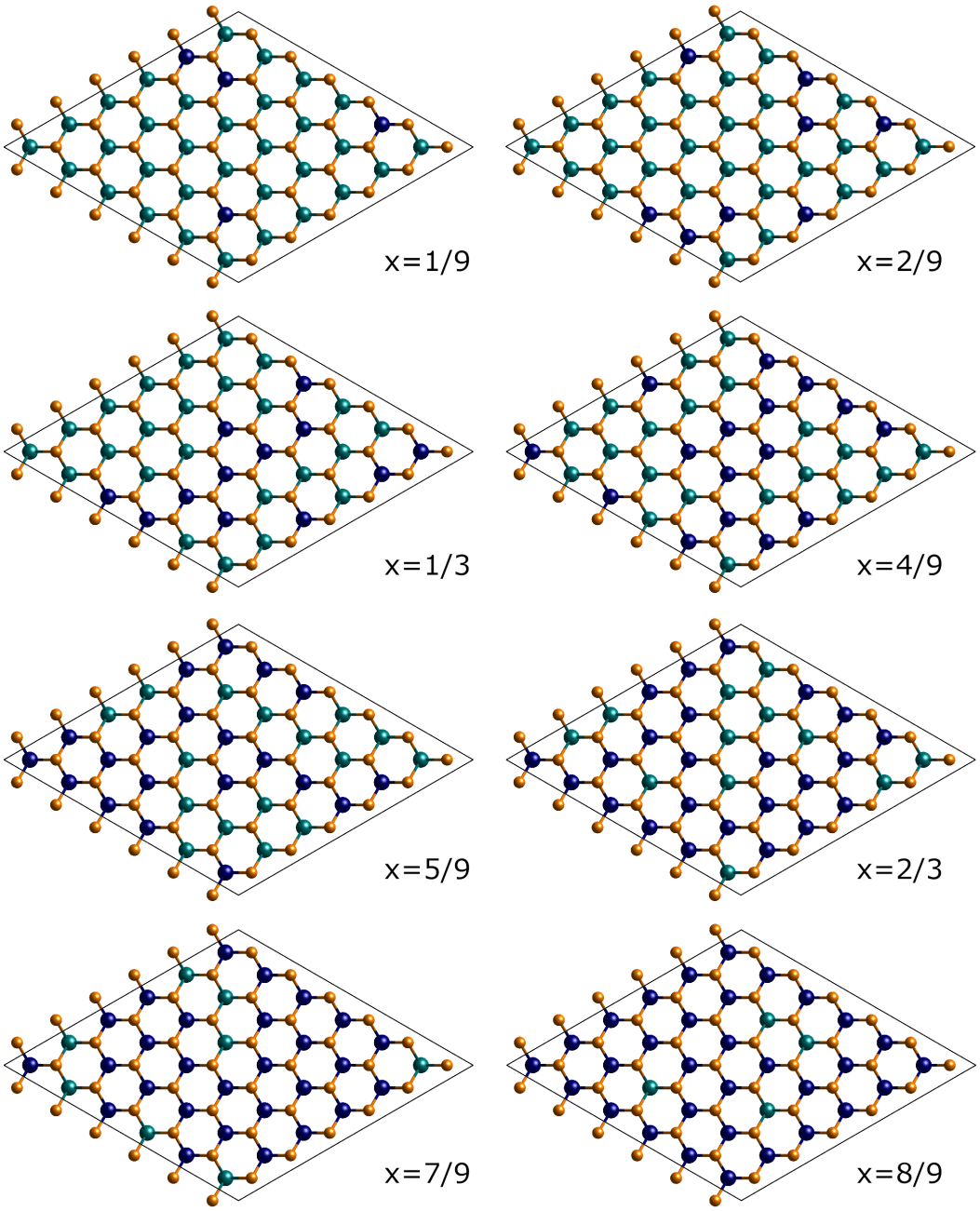


FIG. S3: Top views of the eight ideally random configurations of monolayer 2H-$Mo_{1-x}W_xS_2$ solid solutions at x = 1/9, 2/9, 1/3, 4/9, 5/9, 2/3, 7/9, and 8/9, which are all modeled within a 108-atom primitive supercell by the special quasirandom structure (SQS) method. The teal, blue, and orange spheres represent Mo, W, and S atoms, respectively, and all figures are visualized by the Visualization for Electronic and STructural Analysis (VESTA) program.

II. ELECTRONIC DENSITY OF STATES

4. Partial electronic density of states (PDOS) of ground-state (GS) configurations

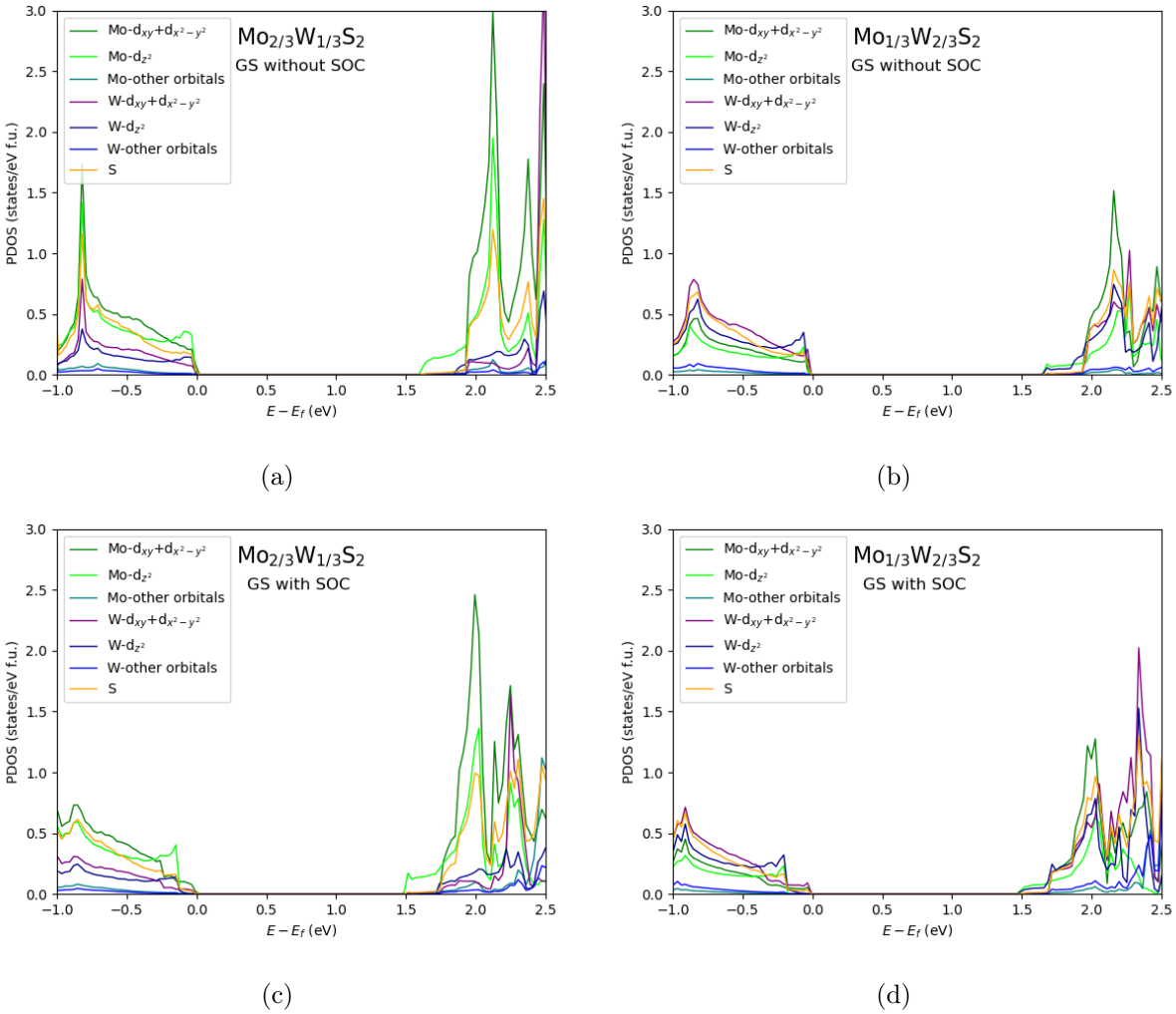


FIG. S4: Partial electronic density of states (PDOS) per formula unit (f.u.) of the ordered ground-state (GS) solid solutions of monolayer 2H-$Mo_{1-x}W_xS_2$ with $x = 1/3$ and $2/3$, evaluated with and without the effect of spin-orbit coupling (SOC).

5. Partial electronic density of states (PDOS) of random (SQS) configurations

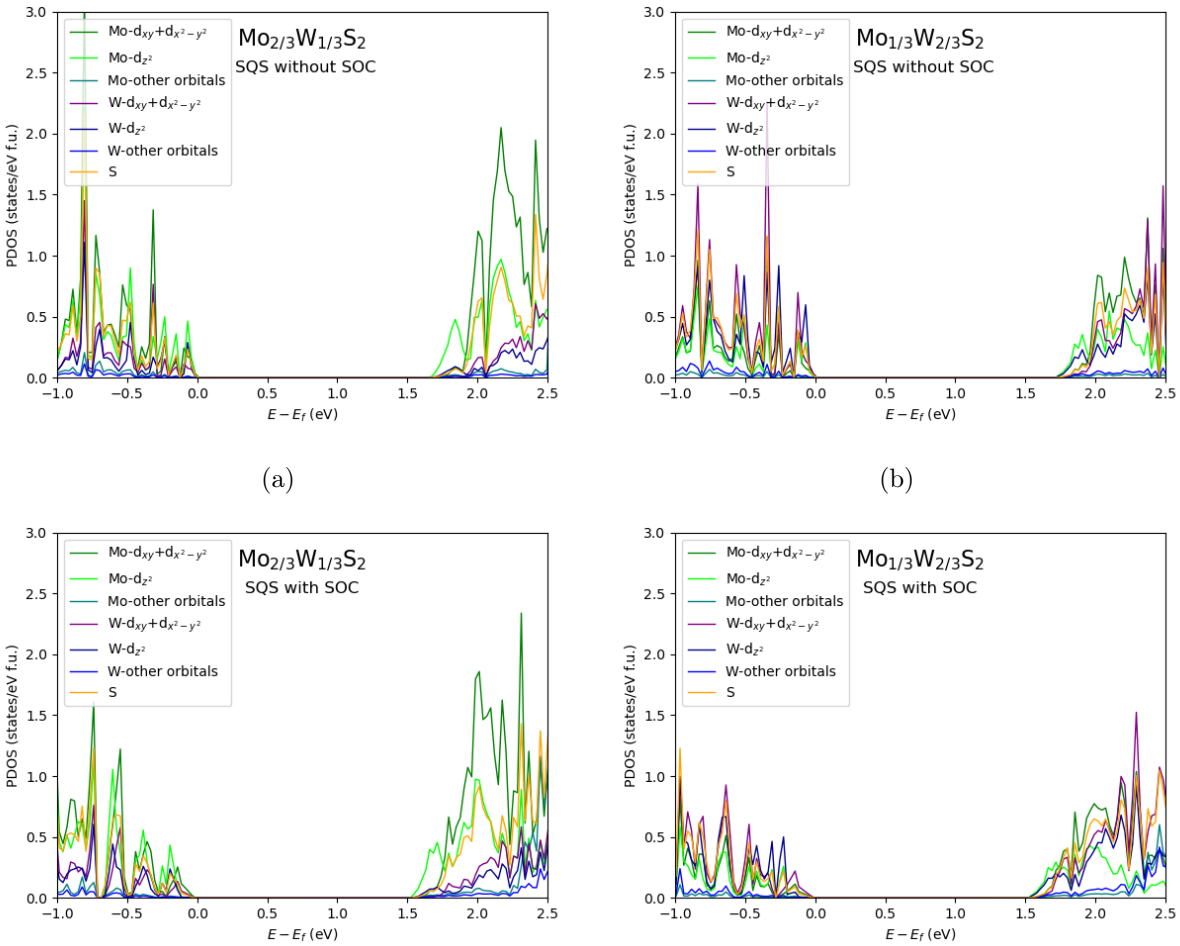
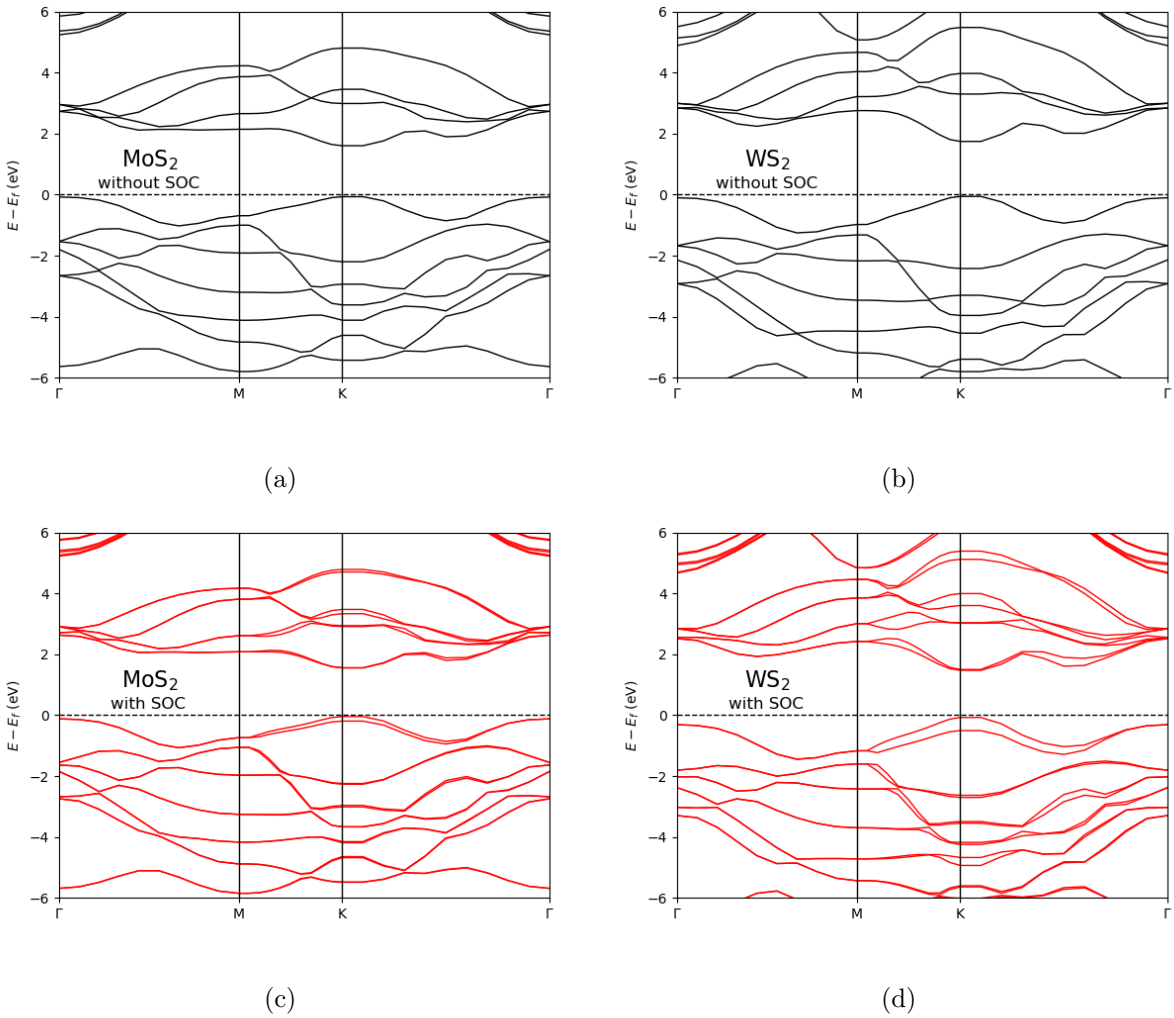


FIG. S5: Partial electronic density of states (PDOS) per formula unit (f.u.) of ideally random (SQS) solid solutions of monolayer 2H-$Mo_{1-x}W_xS_2$ with $x = 1/3$ and $2/3$, evaluated with and without the effect of spin-orbit coupling (SOC).

III. BAND STRUCTURES

6. Band Structures of monolayer 2H-MoS_2 and WS_2

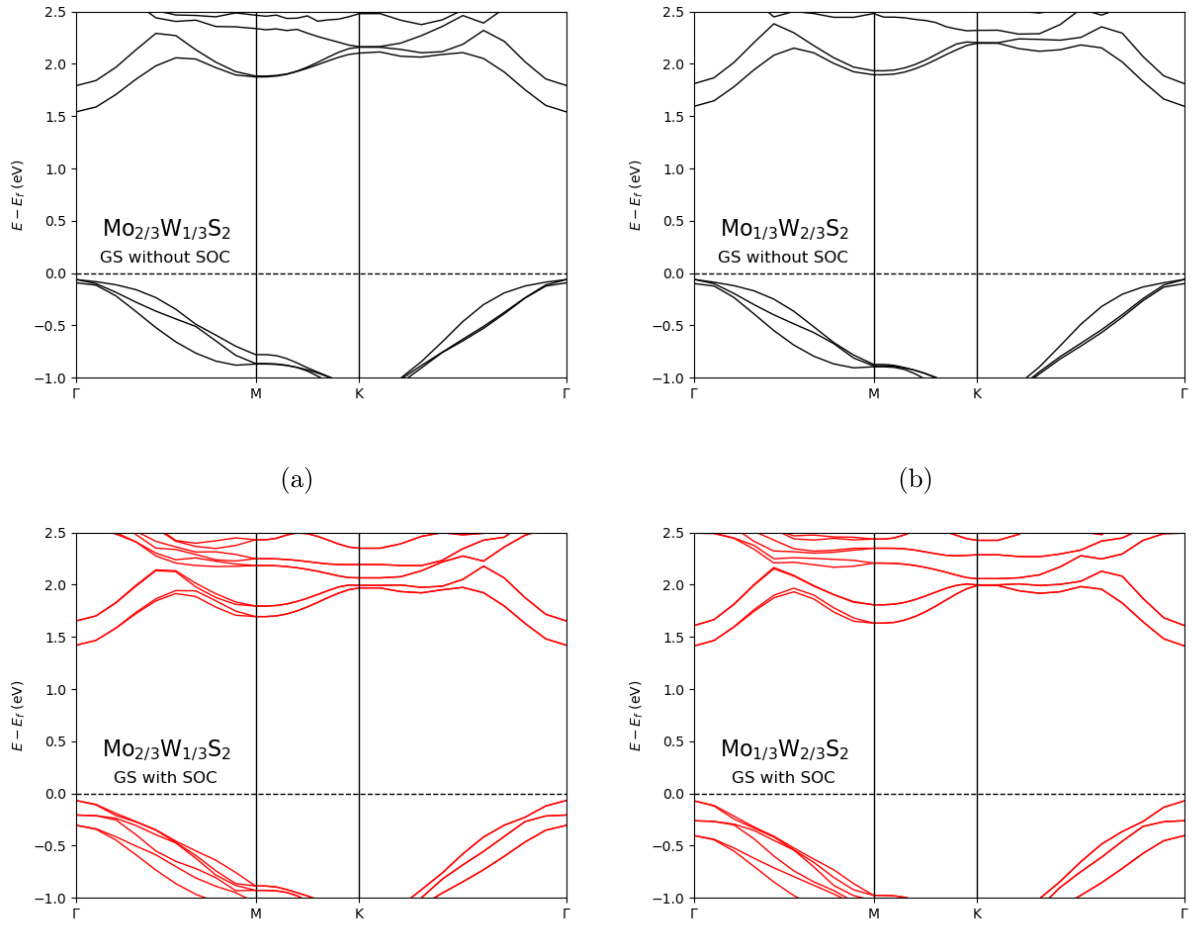


(a) (b)

(c) (d)

FIG. S6: Electronic band structures along high-symmetry paths for the two-dimensional hexagonal lattice of (a) monolayer 2H-MoS_2 and (b) 2H-WS_2, evaluated with and without the effect of spin-orbit coupling (SOC).

7. Band Structures of ground-state (GS) configurations

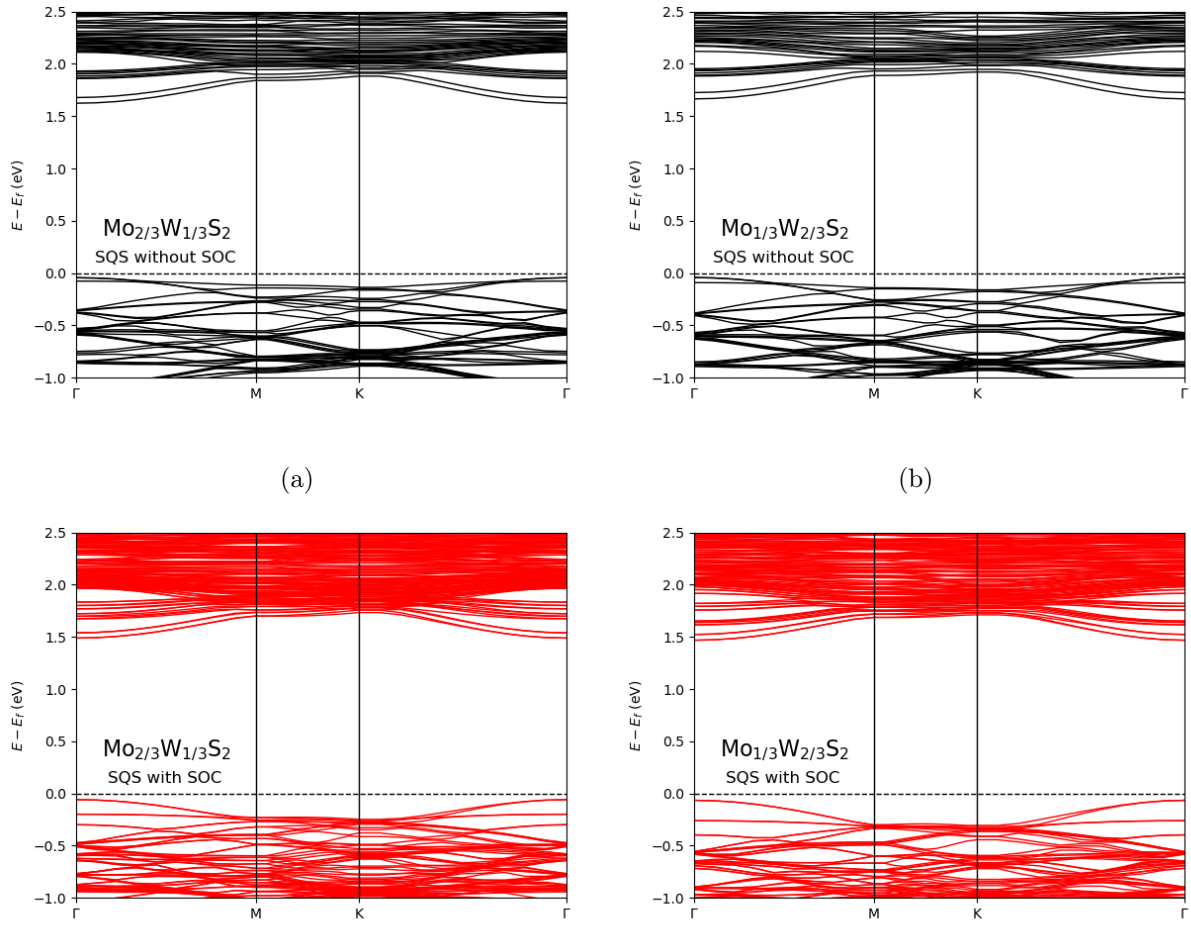


(a) (b)

(c) (d)

FIG. S7: Folded electronic band structures along high-symmetry path of the two-dimensional hexagonal lattice of the ordered ground-state (GS) solid solutions of monolayer 2H-$Mo_{1-x}W_xS_2$ with $x = 1/3$ and $2/3$, evaluated with and without the effect of spin-orbit coupling (SOC). Note that as the primitive supercells are used for modeling these GS configurations, their corresponding Brillouin zone shrinks, and as a result their direct-bandgap is shifted to the Γ point due to the band folding.

8. Band Structures of random (SQS) configurations

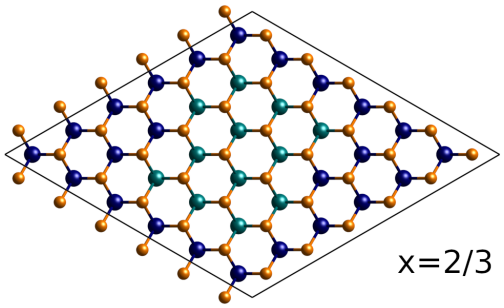


(a) (b)

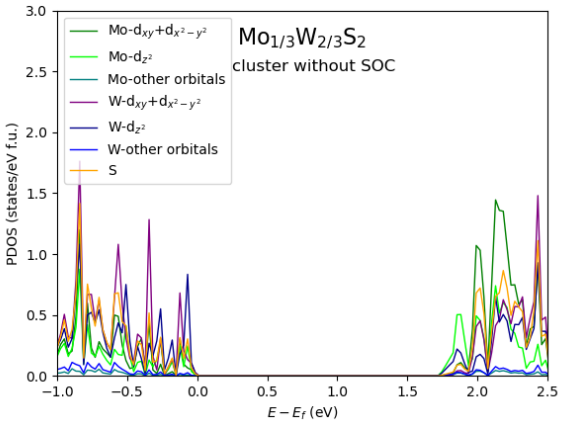
(c) (d)

FIG. S8: Folded electronic band structures along high-symmetry path of the two-dimensional hexagonal lattice of ideally random (SQS) solid solutions of monolayer 2H-$Mo_{1-x}W_xS_2$ with $x = 1/3$ and $2/3$, evaluated with and without the effect of spin-orbit coupling (SOC). Note that as the $6 \times 6 \times 1$ hexagonal supercells are used for modeling these random configurations, their corresponding Brillouin zone shrinks, and as a result their direct-bandgap is shifted to the Γ point due to the band folding.

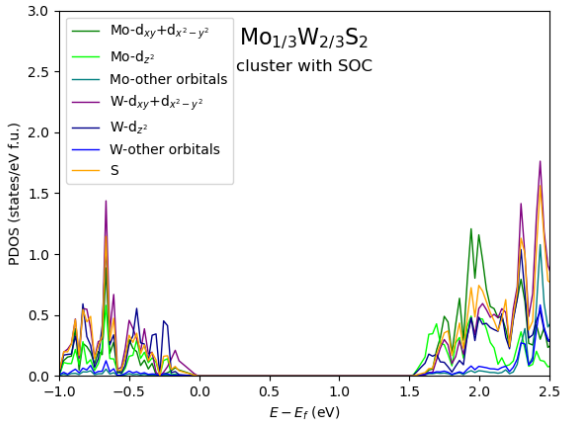
IV. CLUSTERED CONFIGURATION



(a)



(b)



(c)

FIG. S9: (a) Top view of the clustered configurations, where Mo and W atoms segregate resulting in Mo-rich and W-rich clusters/regions of monolayer 2H-$Mo_{1-x}W_xS_2$ with $x = 2/3$, which is modeled within a 108-atom supercell. The teal, blue, and orange spheres represent Mo, W, and S atoms, respectively. (b-c) Partial electronic density of states (PDOS) per formula unit (f.u.) of the clustered configurations of monolayer 2H-$Mo_{1-x}W_xS_2$ with $x = 2/3$, evaluated with and without the effect of spin-orbit coupling (SOC).

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